

Application of the Dynamic Mercury Cycling Model (D-MCM) to the South River, Virginia

Final Report

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Executive Summary

Mercury (Hg) was used between 1929 and 1950 at a former DuPont facility producing rayon acetate fiber in Waynesboro, VA. Fish sampling in the South River and South Fork Shenandoah River was conducted based on suspected releases, which led to a 1977 fish consumption advisory on sections of those rivers. Baseline studies carried out since 2001 have shown that Hg concentrations in some fish species in the South River have not declined as expected, compared to tissue levels observed in 1977-1978. Hg levels in adult smallmouth bass, for example, currently range from less than $1 \mu\text{g g}^{-1}$ up to roughly $4 \mu\text{g g}^{-1}$ along a 25-mile river section downstream of the facility. A conceptual model representing key processes affecting total Hg and methylmercury (MeHg) was assembled in 2011-2012 to help explain how Hg moves through the system to biota, and to help assess the potential benefits of remediation options. This report describes the subsequent application of a mass balance simulation model to further characterize Hg cycling and bioaccumulation in the South River and predict the efficacy of remedial options. The Dynamic Mercury Cycling Model (D-MCM) is a time-dependent model predicting concentrations and fluxes of inorganic Hg, MeHg and elemental Hg in water, sediments and biota. The model was applied to the South River from the facility site at Waynesboro downstream approximately 26 miles, just downstream of the confluence with the North River. The model was calibrated to data from 2006-2014, followed by a sensitivity analysis and remediation simulations.

The model analysis supports the conceptual model that the largest source of Hg to the river is bank erosion ($\sim 50 \text{ kg/yr}$, 80% of external inputs), while the greatest simulated source of MeHg to water is internal supply from the sediment bed. Bank leaching of inorganic Hg(II) was roughly $\frac{1}{4}$ of the load from bank erosion, but it had a strong influence on simulated THg concentrations in water, especially under low flow conditions. This was partly because bank leaching was assumed to be loaded at constant rate, an assumption that should be revisited.

The model calibration to 2006-2014 data reflected observed magnitudes and spatial trends of increases in total Hg and MeHg in water, sediments and biota. High rates of Hg loading from riverbanks and MeHg loads from the sediment bed in simulations resulted in large increases in Hg and MeHg concentrations as water flowed through the modeled river reach. Residual ongoing Hg loading at the site of the former DuPont facility was assigned a loading rate of 1 g/day . This is environmentally relevant, sufficient to increase concentrations of Hg in water by about 5 ng/L (using a median flow of 73 cfs at Waynesboro) and is being addressed through permitting. It is not sufficient however to explain observed increases in water column Hg concentrations to levels in the range of 100 ng/L . Most of the increase in water column Hg and MeHg concentrations in simulations was due to the remobilization and transformation (for MeHg) of legacy inputs that originally occurred decades ago.

Hydrodynamics and particle dynamics exerted strong influences on mercury cycling and concentrations in the contaminated river in simulations. Short term events were important in terms of the remobilization and downstream transport of solids and Hg from riverbanks and the sediment bed. Simulations assumed that the 25-mile river reach was nearly non-depositional in the long term, *i.e.* on a decadal or longer time scale. Most solids loaded from riverbanks were therefore eventually transported downstream in simulations, rather than buried locally. This had important implications for natural recovery and remediation.

Remediation scenarios involving bank stabilization were simulated, reducing bank erosion of Hg by roughly 90% for RRM 0-5. The model predicted that inorganic Hg and MeHg concentrations would decline over a period of years, and benefits were predicted to be greater in areas where remediation was carried out. MeHg concentrations in adult smallmouth bass were predicted by the food web component of the model to decline up to 60% locally near remediated areas, and to a lesser extent downstream. The response to remediation progressed over time and was not complete after 9 years in the simulations. Downstream areas lagged the response in upstream areas.

The timing and magnitude of natural recovery and the response to remediation were strongly influenced by particle dynamics, which are uncertain. Future efforts to better quantify particle loading rates and downstream transport, and the role of short-term events, would be valuable. A better understanding of pools of inorganic Hg that are available for methylation would also help clarify the relationship between a reduction in sediment Hg concentrations following remediation and the resulting response (linear or otherwise) of MeHg concentrations in the system.

1 INTRODUCTION

Mercury (Hg) was used between 1929 and 1950 at a former DuPont facility producing rayon acetate fiber in Waynesboro, VA, at a site located along the shoreline of the South River. In 1976, globules of elemental Hg were discovered in soils during on-site construction activities, and concentrations up to $7,000 \mu\text{g g}^{-1}$ were observed (Carter, 1977). Subsequent fish sampling in the South River and South Fork Shenandoah River led to a 1977 fish consumption advisory on sections of those rivers (Bolgiano, 1980).

A monitoring plan for the South River, South Fork Shenandoah River and the adjacent terrestrial floodplains was established in 1984 by the State of Virginia. In 1998, the U.S. EPA issued a Resource Conservation and Recovery Act (RCRA) permit to DuPont to investigate potential releases at the former DuPont plant and to remediate contamination sources, including residual Hg contamination. RCRA investigations of groundwater, stormwater, and soil testing at the former DuPont plant have been completed. Corrective actions are underway at the site.

In 2001, the State of Virginia and DuPont established an integrated, watershed-scale, risk-based program for Hg in the South River. This was an important step toward a comprehensive understanding of Hg cycling and bioaccumulation in the river. The group of participants in the program became known as the South River Science Team (SRST), and includes DuPont, the Virginia Department of Environmental Quality, U.S. EPA Region 3, academic institutions and environmental groups. SRST studies are designed to better understand the behavior of Hg in the river system and floodplain, particularly factors controlling the current levels and slow recovery of fish Hg concentrations in the system. Baseline studies of Hg and relevant site conditions carried out since 2001 have shown that Hg concentrations in some fish species in the South River have not declined as expected, compared to tissue levels observed in 1977-1978. Hg levels in adult smallmouth bass, for example, currently range from approximately 1 to $4 \mu\text{g g}^{-1}$ along a 25-mile river section downstream of the former DuPont plant. Fish consumption advisories due to mercury exist 156 mi downstream of the former DuPont plant, including sections of the South River and South Fork Shenandoah River (Virginia Department of Health, 2019).

In 2004, DuPont sold the manufacturing assets of the Waynesboro site to subsidiaries of Koch Industries, Inc., and the name of the facility was changed to Invista. In 2019, Koch Industries sold the manufacturing assets to Shandong Ruyi Investment Holding. DuPont continues to own the property and retains responsibility for environmental cleanup under the RCRA Corrective Action permit. The Lycra Company, LLC (a subsidiary of Shandong Ruyi Investment Holding) owns and operates the manufacturing assets, including the stormwater and wastewater outfalls permitted by the Virginia Department of Environmental Quality. DuPont has also investigated Hg contamination in the South River ecosystem as part of a settlement agreement with the Natural Resources Defense Council and the Sierra Club. This study began in 2006 and included a first phase that characterized Hg impacts in the South River ecosystem and a second phase completed in 2012 that focused on specific sources of Hg, and Hg methylation sites.

A remedial options team was established in 2008 to evaluate remediation alternatives with the goals of (1) reducing fish tissue Hg levels in smallmouth bass to less than the U.S. EPA's guidance concentration of $0.3 \mu\text{g g}^{-1}$ in connection with fish consumption by the general population (U.S. EPA 2001), and (2) ensuring the protection of aquatic and terrestrial ecology with respect to Hg exposure. A remediation

proposal was submitted by DuPont in 2013. Remediation from River Mile 0-2 is currently underway to reduce Hg inputs from eroding banks.

A conceptual model representing key processes affecting methylmercury (MeHg) levels in biota of concern in the system was assembled to help explain how Hg moves through the ecosystem to biota, and to help assess the potential benefits of remediation options (Harris *et al.*, 2012a; Dyer *et al.*, 2011). An Enhanced Adaptive Management (EAM) framework has been developed to help design, track, and assess the benefits of remedial actions. To assist with this framework, a quantitative mass balance simulation model was applied to help understand Hg cycling and predict the efficacy of remedial options in the South River. The Dynamic Mercury Cycling Model (D-MCM) (EPRI, 2013) is a time-dependent model predicting concentrations and fluxes of inorganic Hg(II), MeHg and elemental Hg in water, sediments and biota. This report describes the application of D-MCM to the South River from the Lycra Company site at Waynesboro downstream approximately 26 miles, just downstream of the confluence with the South Fork Shenandoah River.

2 OBJECTIVES

Study objectives included using D-MCM to:

- 1- Help understand Hg cycling and bioaccumulation in the South River, including processes controlling MeHg supply and the slow natural rate of recovery;
- 2- Help predict the benefits of remedial actions to reduce Hg concentrations in water, sediments and biota, as a function of location and time;
- 3- Help interpret monitoring carried out to assess the benefits of remedial actions; and
- 4- Provide input to the EAM framework.

3 STUDY APPROACH

Major steps in the application of D-MCM to the South River are shown in Figure 1. Hydrology and particle transport have major influences on the mobilization and fate of Hg in the river and were simulated prior to carrying out Hg simulations. Once these model components were developed, existing Hg conditions in the system were simulated in the following sequence:

- Inorganic Hg in water and sediments
- MeHg in water and sediments
- MeHg in the aquatic food web

The overall sequence is based on the assumption that each major step was a prerequisite to steps that followed, while not being strongly impacted by later steps. For example, Hg is affected by hydrodynamics, but not vice-versa.

Spatially, the model was applied to a 26-mile portion of the river from the site of the original facility that released Hg at Waynesboro, to approximately 2 miles past the junction of the South River with the North River.

D-MCM was first calibrated to existing conditions in the river from 2006-2014, when the best Hg data were available. A sensitivity analysis was carried out to examine the processes and model inputs that exerted the greatest influence on model outputs. The calibrated model was then used to predict the potential benefits of future remediation scenarios provided by DuPont. Predictions were made as a function of time and location. This was important because of the potential for response to remediation to depend on location and time (Figure 2).

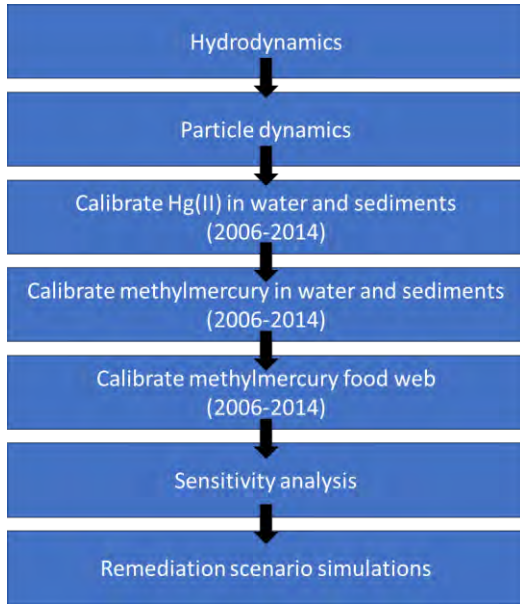


Figure 1. Major steps in application of D-MCM to the South River

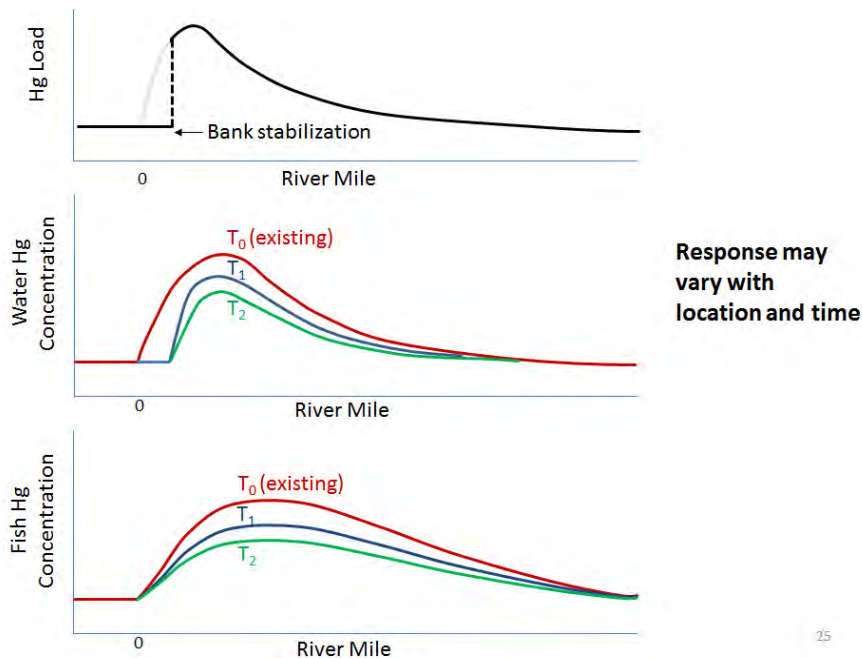


Figure 2. Conceptual illustration of model outputs for Hg concentrations at different locations and times. T_0 , T_1 and T_2 are times relative to when remediation is carried out.

4 MODEL DESCRIPTION

The Dynamic Mercury Cycling Model (D-MCM) was originally developed to simulate Hg cycling and bioaccumulation in water, sediments and biota in lakes, then extended for a broader range of aquatic systems. A mass balance approach is used to simulate time-dependent concentrations for three forms of Hg in water and sediments (dissolved and particulate phases) and a food web (Figure 3). Previous versions of D-MCM have been used in large multidisciplinary research projects in the Gulf of Mexico (Harris *et al.*, 2012b), Florida Everglades (Harris *et al.*, 2003a), METAALICUS (Harris *et al.*, 2007), and Wisconsin Lakes (Hudson *et al.*, 1994). It has also been used in pilot TMDL studies in Florida (Atkeson *et al.*, 2003) and Wisconsin (Harris *et al.*, 2003b) and a model analysis of the effects of climate change on Hg cycling and bioaccumulation in the Great Lakes Basin, funded by the US EPA (Harris *et al.*, 2015, 2012c).

The current version of the model (Version 4) has a generalized three-dimensional capability that makes simulations possible for rivers, lakes, estuaries, wetlands, and large freshwater and marine systems. It can be set up as a single cell or in multi-cell three dimensional configurations, and can simultaneously simulate open waters and wetlands, including aquatic vegetation. It considers the effects of key factors affecting Hg cycling and bioaccumulation (*e.g.* Hg loading, hydrology, water quality, trophic structure). External¹ Hg loads include atmospheric Hg deposition (wet and dry), upstream Hg loads, bank erosion and leaching, and point sources of Hg. D-MCM includes an integrated flexible food web with up to 30 lower trophic level compartments, and as many fish species as desired. Fish migration is included and is important if fish move among habitats with different MeHg exposures.

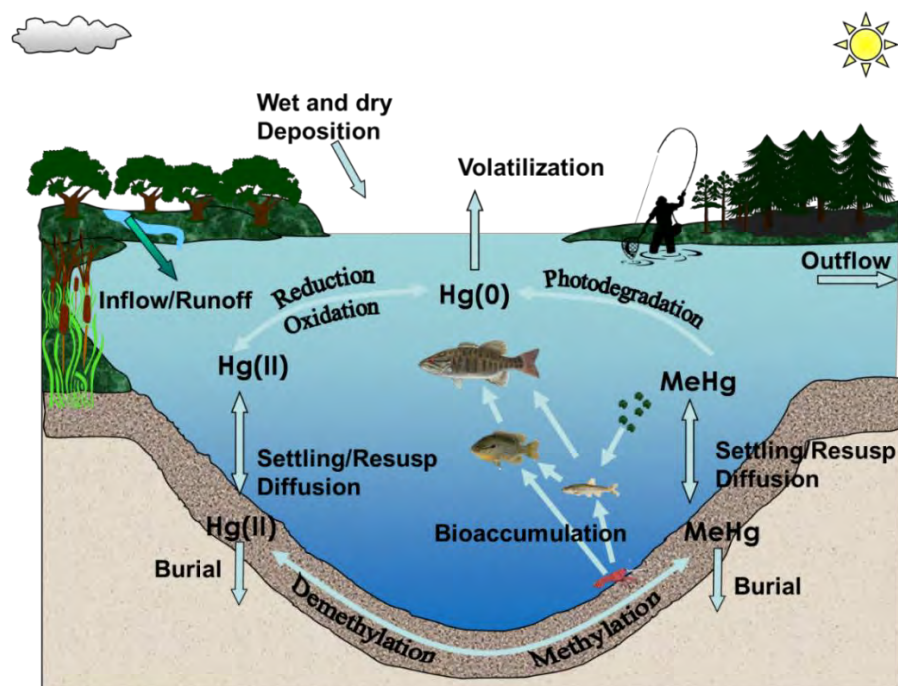


Figure 3. Conceptual diagram of mercury cycling and bioaccumulation in D-MCM Version 4

¹ External is defined as an external source to the combined water/sediment/biota system. Fluxes from sediments to water are not considered external in this analysis.

5 FORMER DUPONT WAYNESBORO FACILITY AND STUDY AREA

5.1 Former DuPont Facility

DuPont acquired 62 ha near the small town of Waynesboro, Va., in 1928 as a manufacturing site for acetate rayon fibers. In the acetate rayon process, elemental Hg was reacted with sulfuric acid to produce a mercuric sulfate catalyst for an intermediate reaction step. The spent mercuric sulfate catalyst was sent to a retort operation where elemental Hg was regenerated for reuse. Elemental and inorganic Hg(II) were both inadvertently released and transported into surface water, sediment, floodplain soil, and biota of the South River and part of the South Fork Shenandoah River. Bolgiano (1981) estimated that ~44 tons of Hg contamination were present in South River floodplain soil, and ~800 kg of Hg contamination were present in river sediment. The use of Hg at the site ceased in 1950 (Stahl *et al.*, 2014).

5.2 South River Hydrology

The South River is located in the Valley and Ridge geomorphic province of Virginia (Figure 4). The region has a humid temperate climate, with average January and July temperatures of 6 °C and 29 °C respectively (US Climate Data, 2019). Precipitation is highest from March - September, with an annual average of 94 cm (SERCC, 2012). The South River is 80 km in length, typically 20-30 m wide with bank-full depths ranging from 2-3 m. Flowing north through Waynesboro, VA, the South River joins the North River 39 km (24 miles) downstream near Port Republic to form the South Fork Shenandoah River. The South Fork Shenandoah River flows ~160 km (100 miles) to Front Royal, Virginia, where it joins the North Fork Shenandoah River and forms the Shenandoah River. The Shenandoah River drains to the Potomac River, and then into Chesapeake Bay. Land use in the South River watershed is typically agricultural, excluding municipalities that include Waynesboro (Figure 5). The river has also been influenced by a variety of engineering structures including river straightening, levees, stabilized banks, dams and other channel controls in Waynesboro and other municipalities.

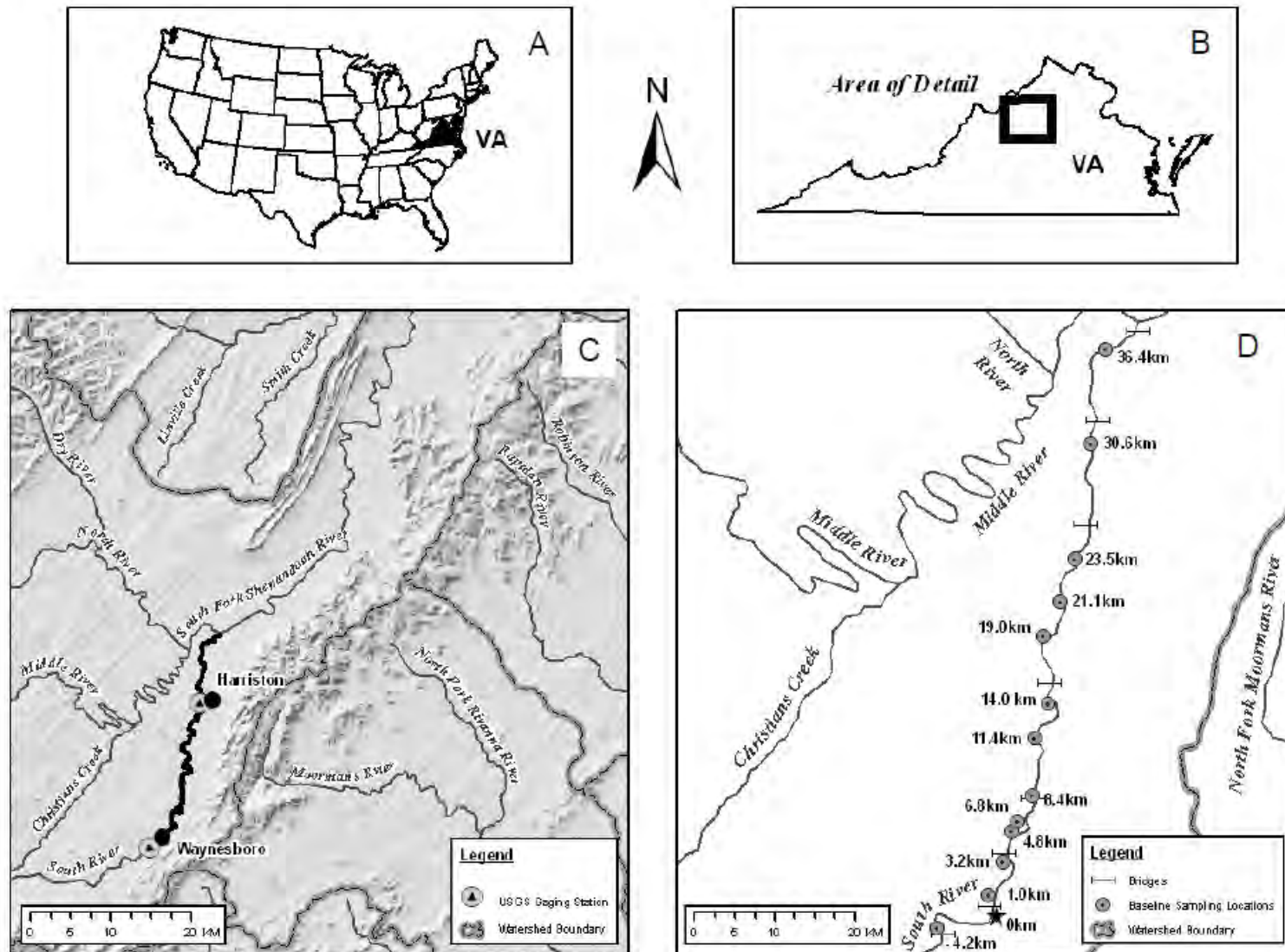


Figure 4. South River, VA study area. Panel C shows the study area (thick black line). Panel D shows the sample locations and the distance downstream of the former DuPont plant in Waynesboro, VA (located at RRM 0). From Flanders *et al.* (2010).

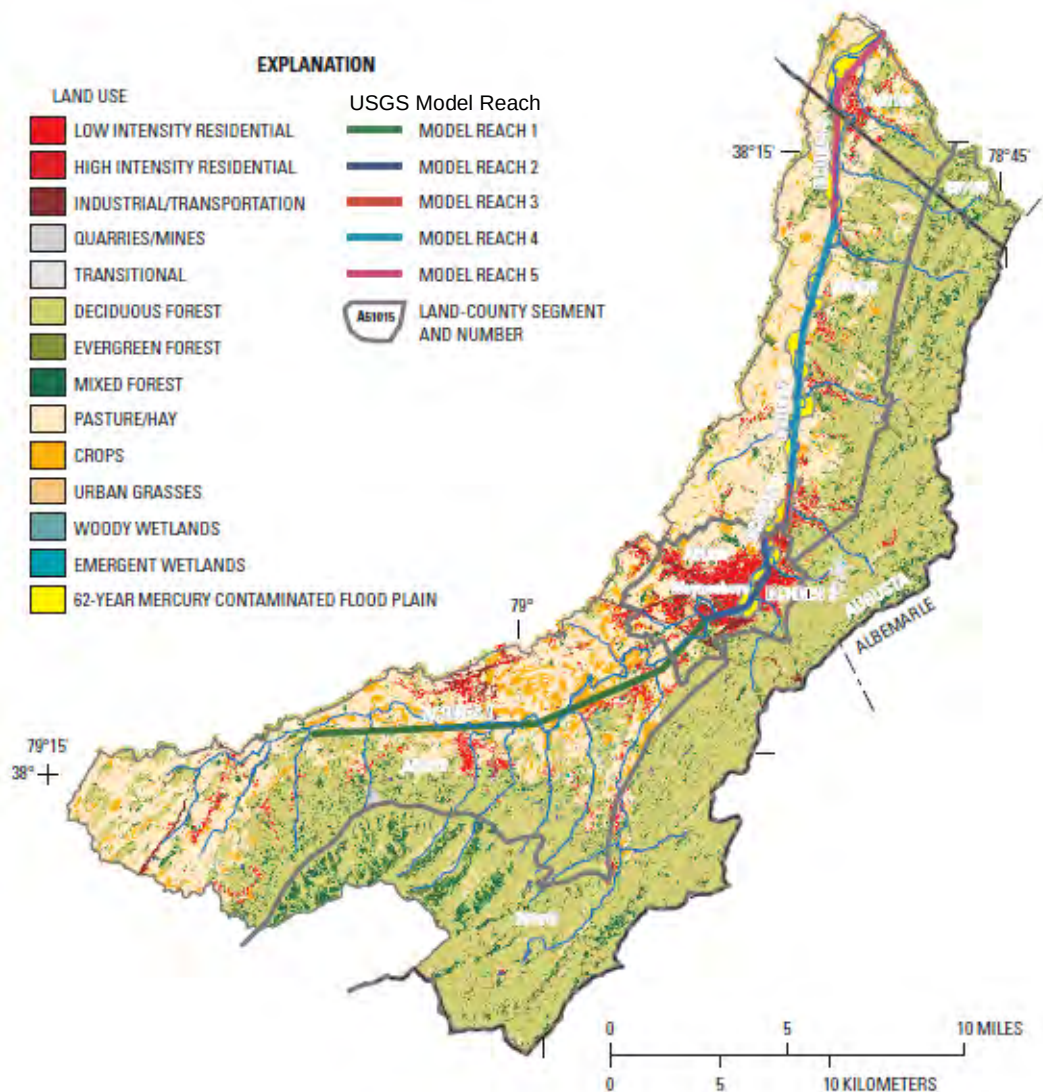


Figure 5. Land use for South River watershed from upstream of Waynesboro to Port Republic (from Eggleston, 2009). Model reaches refer to USGS model called HSPF, not the model applied in this study.

The South River is a single thread sinuous gravel bed river, and is bedrock controlled (Pizzuto *et al.*, 2006). The bed material consists predominantly of gravel-sized sedimentary particles. The section of the river from Waynesboro downstream to Port Republic can be divided into two reaches with different geomorphic characteristics (Figure 6). The upper reach is located between RRM 0 and ~RRM 13, with an average slope of 0.0013 and a wide floodplain composed of silty alluvium. The lower reach (RRM 13 to 24) has an average slope of 0.0024, a narrow floodplain composed of sandy or gravelly alluvium, and abundant forested islands. Several long reaches with very low slope (0.0005 to 0.0008) exist along the South River, ranging in length from approximately 0.4 – 1.3 mi, often controlled by bedrock outcrops. Floodplain deposits exposed on the banks vary from cohesive silt and clay to sand and gravel, but are typically cohesive sediments composed of mixtures of sand, silt, and clay.

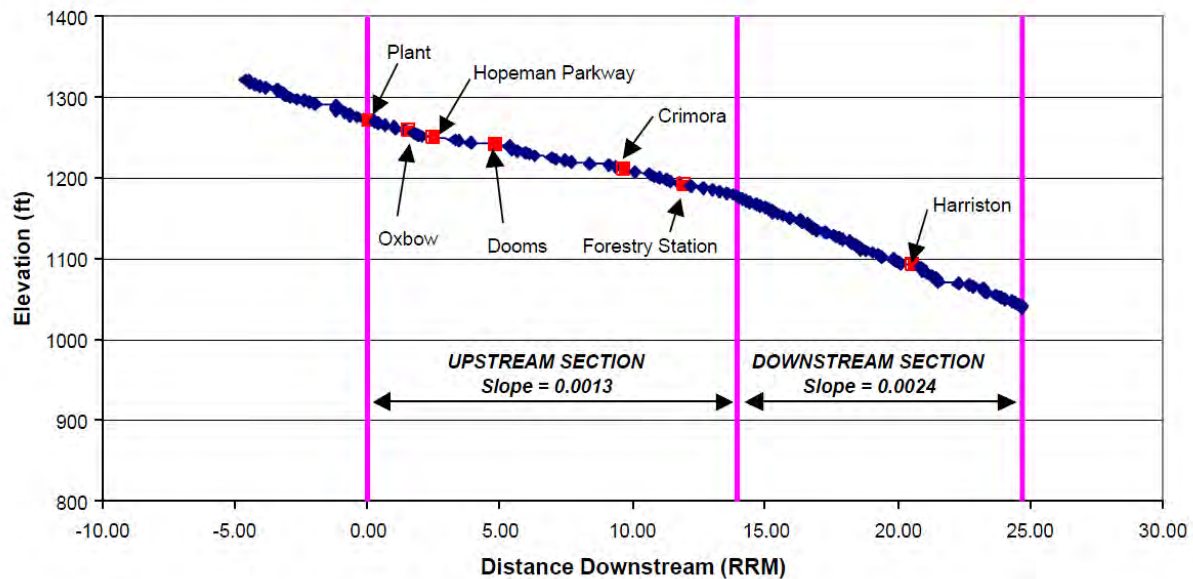


Figure 6. Longitudinal profile of South River from Waynesboro to Port Republic (from Pizzuto *et al.*, 2006).

The river bed is predominantly gravel sized ($\sim 85\%$ of the total bed area). There are areas with fine material (Figure 7), including pools caused by bedrock or old mill dams, channel margins, side channel backwaters where flow separates around islands, and bank obstructions usually caused by downed trees, which are common. Fine sediment accumulation also occurs within the interstices of the coarse material in the channel bed. Bank soils may slump into the river and temporarily reside at the base of the bank until river flow of sufficient energy suspends part or all of the slumped material.



Figure 7. Areas tending to collect fine-grained material in the South River. (a) Pools with low slopes (example looking upstream near Dooms) where mud storage occurs on both sides of the pool; (b) Just downstream of riffles in the channel margins where large woody debris exists; (c) Bank obstructions such as living trees; (d) Side channel backwaters, *e.g.*, downstream of channel bifurcations around islands (from Pizzuto *et al.*, 2006).

6 MERCURY CONCENTRATIONS IN THE SOUTH RIVER

6.1 Spatial Extent of Mercury Contamination

Elevated Hg concentrations persist downstream of the former DuPont plant in water, sediments, eroding banks, and fish (Figure 8 - Figure 10). At Port Republic, there is a decline in fish Hg levels where the South River converges with the North River, but fish Hg remains elevated and continues to decline downstream as far as Berryville, VA near the Route 7 bridge. The current fish consumption impairment listing for Hg extends ~150 mi downstream of the former DuPont plant, including a portion of the South River (~24 mi), the full length of the South Fork Shenandoah River from Port Republic to Front Royal, VA (~100 mi), a short section of the North Fork Shenandoah River upstream to the Riverton Dam (~0.6 mi), and the mainstem Shenandoah River to the West Virginia State Line (~30 mi) (Virginia Department of Health, 2019).

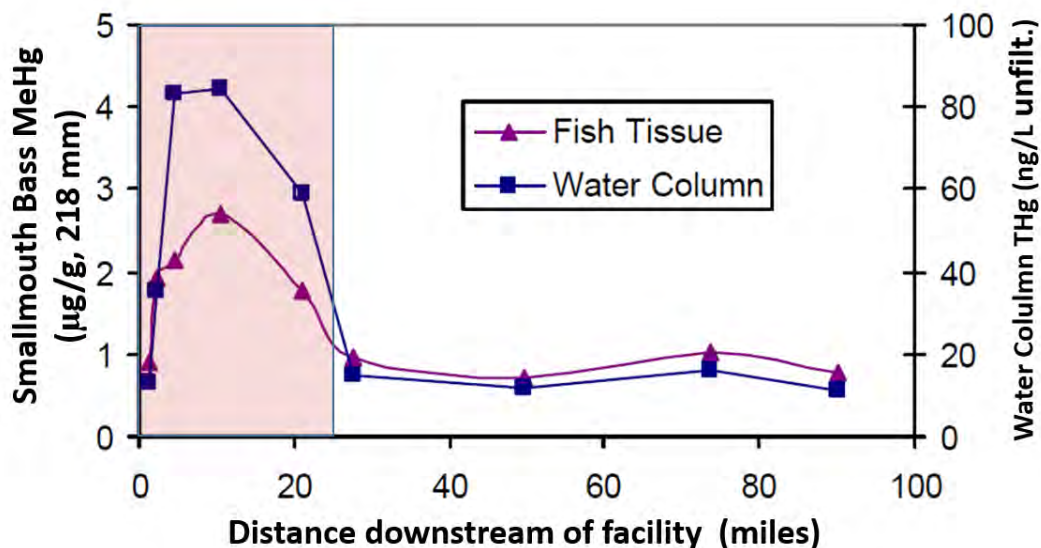


Figure 8. Size-normalized Smallmouth Bass tissue MeHg and water column Hg concentrations in the South River and South Fork Shenandoah River downstream from the former DuPont facility in Waynesboro, VA. Figure adapted from Virginia DEQ (2009). Red shading shows portion of river modeled in this study. Fish values are normalized to a 218 g fish, using data collected from 1999-2005. Water data are from 2002-2009.

Peak Hg concentrations in water (unfiltered) and biota do not occur in the immediate vicinity of the former DuPont plant facility, instead rising to peak levels in the vicinity of RRM 5-10 then declining downstream (Figure 8). This is also the pattern for Hg in sediments (Figure 9). Filtered inorganic Hg(II) and MeHg concentrations in water also rise from Waynesboro to roughly RRM 10 but do not show a clear decline for the remainder of the South River (Figure 10).

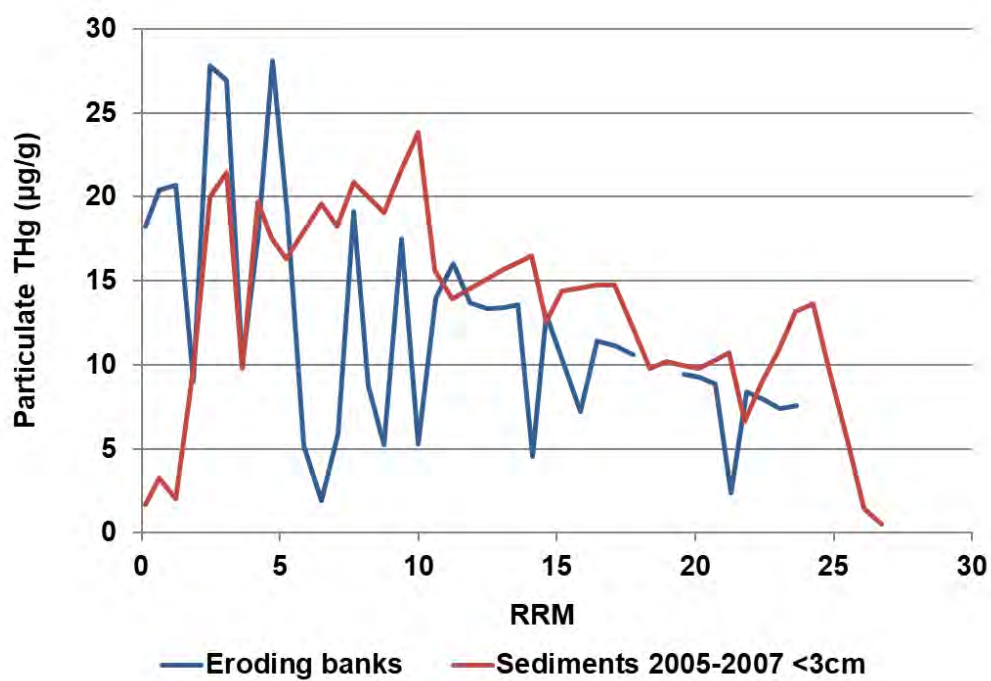


Figure 9. Average THg concentrations in eroding banks and sediment bed. Concentrations are averages for field samples within each model cell. Bank concentrations estimated as described in Section 7.4.1. Sediment values are averages based on 2005-2007 field data < 3 cm depth, derived from Collins (2018a).

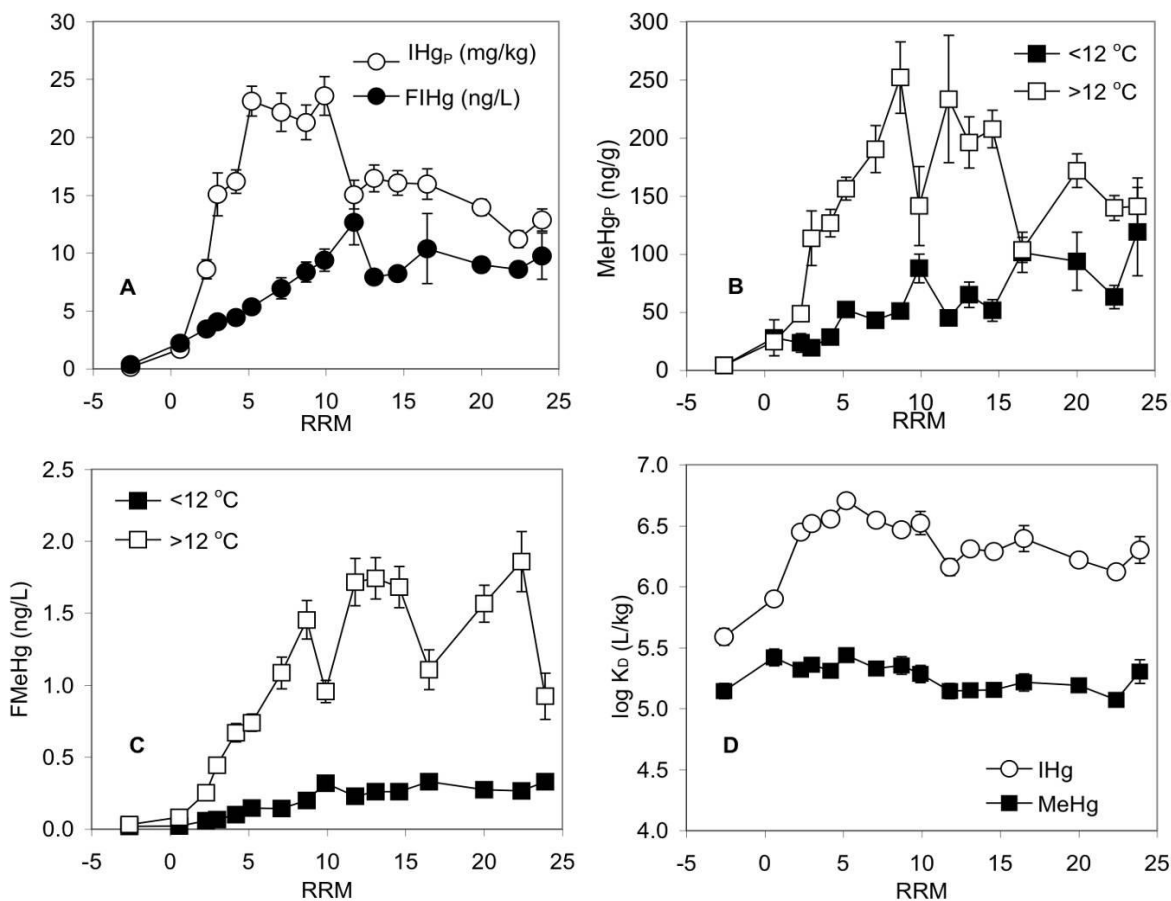


Figure 10. Inorganic Hg and MeHg concentrations and partitioning in South River waters downstream of the former DuPont plant from March 2006-May 2007: (a) Inorganic Hg(II) concentrations on suspended particulates and in filtered samples; (b) MeHg concentrations on suspended particulates when temperatures were greater and less than 12 °C; (c) MeHg concentrations in filtered samples when temperatures were greater and less than 12 °C; (d) Inorganic Hg(II) and MeHg particle-water distribution coefficient ($\log_{10} K_d$). Reprinted with permission from Flanders *et al.* (2010).

6.2 Temporal Trends for Mercury in the South River

The first measurements of fish Hg concentrations in the South River were made in 1977. In a settlement between DuPont and the State Water Control Board in 1984, DuPont established a trust fund to support a 100-year monitoring program for Hg. This fund is managed by the Virginia Department of Environmental Quality and has supported monitoring for fish, water, and sediments since that time. Data collected over the last 20 years indicate that fish tissue levels have remained stable. Mercury concentrations in surface waters of the South River fluctuate in response to local conditions, but show no consistent decreasing trend based on data collected from 2004 to 2018 (Figure 11, Figure 12).

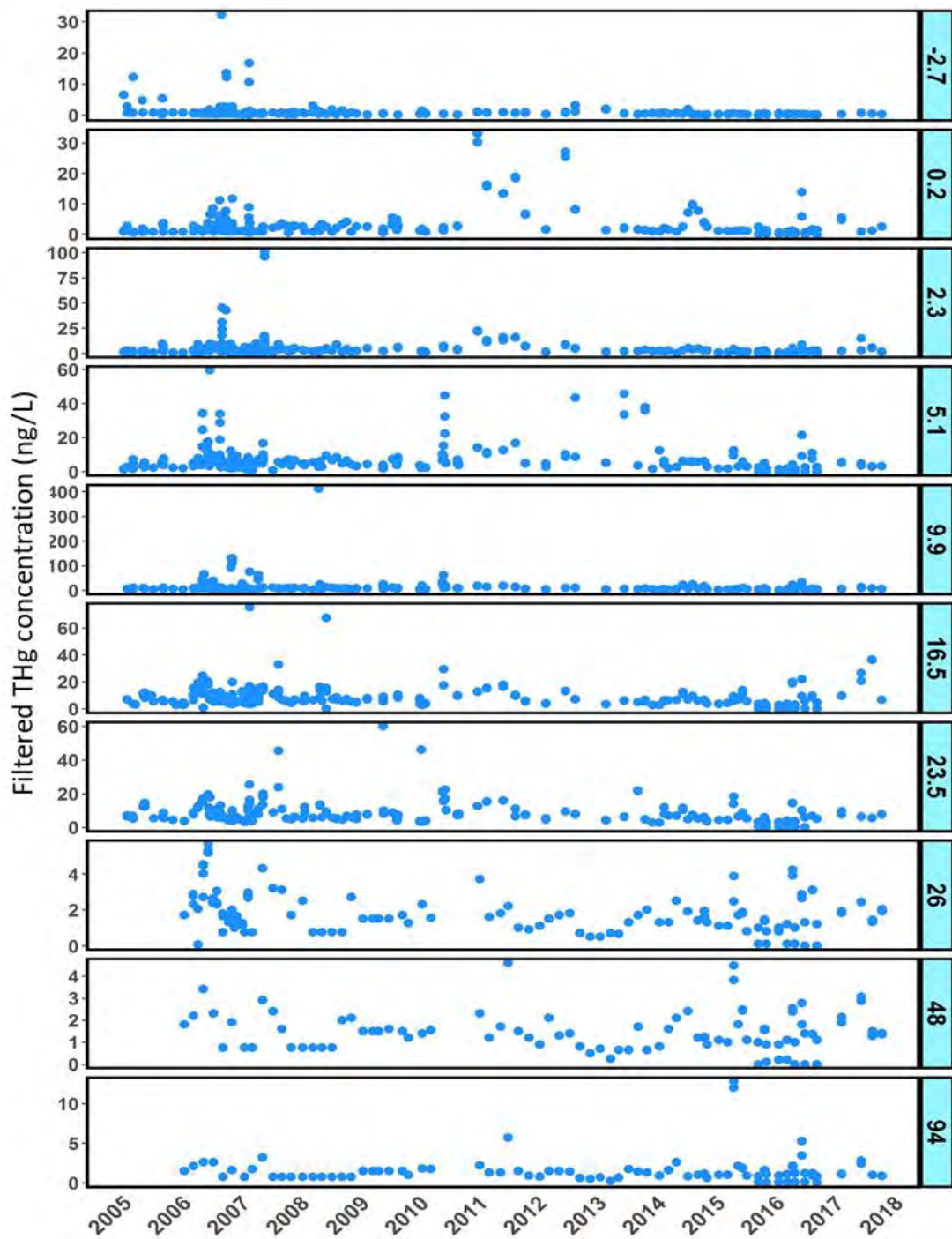


Figure 11. Filtered THg concentrations from 2004-2011 at various locations in the South River. Adapted from Collins (2018b). Numbers in blue shaded areas are distances downstream of the former DuPont facility (Relative River Mile).

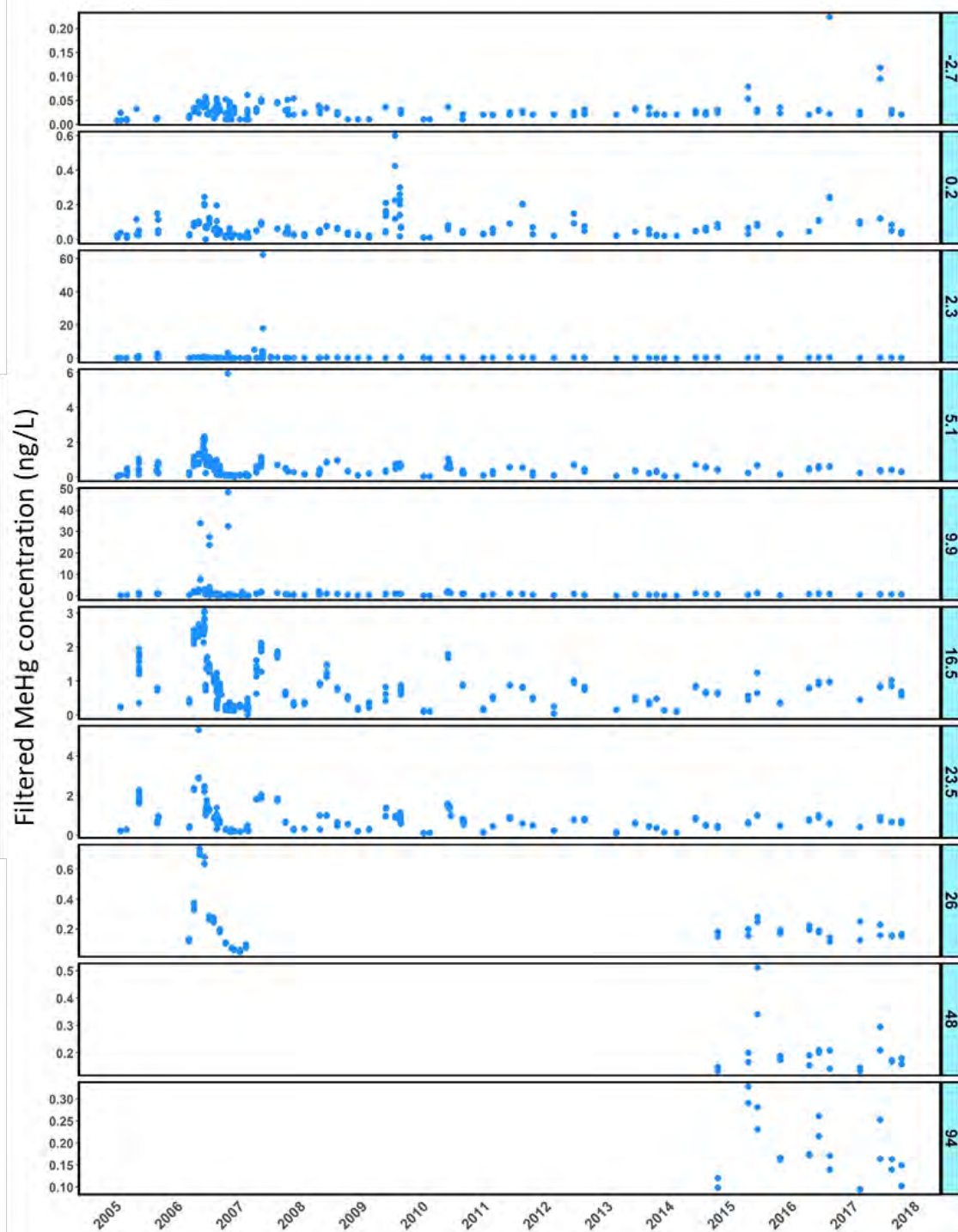


Figure 12. Filtered MeHg concentrations from 2004-2011 at various locations in the South River. Adapted from Collins (2018b). Numbers in shaded areas are distances downstream of the former DuPont facility (Relative River Mile).

Sediments often provide valuable information on the history of Hg loading. To address the confounding effects of mixing, Skalak and Pizzuto (2014) dated sediment deposits at various depths using C, Pb, and Cs isotopes, and developed a reconstruction of the history of Hg contamination in the South River (Figure 13). Their analysis suggested large declines in suspended solids Hg concentrations from the 1950's via natural processes. They also concluded that *".... 100-yr timescales will be needed for the South River to cleanse its channel perimeter of Hg-contaminated sediments through natural processes alone."*

The estimated inventory of 80 kg Hg in fine grain channel margin deposits in 2005 was projected to decline to 20 kg by 2050 if Hg loading rates were instantly reduced to background levels of 0.2 $\mu\text{g/g}$. This rate of recovery, if represented with simple exponential decay, would equate to a half-time of roughly 22 years. For the 9-year period simulated with D-MCM (2006-2014), Hg concentrations in fine-grained channel margin (FGCM) deposits would decline roughly 20%, again assuming an exponential decline and a complete cessation of excess Hg loading. If water Hg concentrations declined in an exponential manner similar to FGCM deposits, a decline of roughly 30% would be expected from 2006-2018. Skalak and Pizzuto (2014) also estimated that the average residence time of solids in FGCM deposits was 1.75 years (1-60 year range). This average rate would enable Hg concentrations in FGCM deposits to recover much more quickly than 100 years if excess Hg loads to these deposits was stopped. As discussed in later sections, a steady rate of response may not be an appropriate assumption in this system over shorter time periods, where particle movement and mixing can occur intermittently based on large flow events. The wide range of residence times reported (1-60 years) also means that some areas have the potential to recover faster than others. In addition, the high uncertainty regarding the load of Hg from eroding banks makes temporal conclusions on the time frame of recovery more challenging to predict.

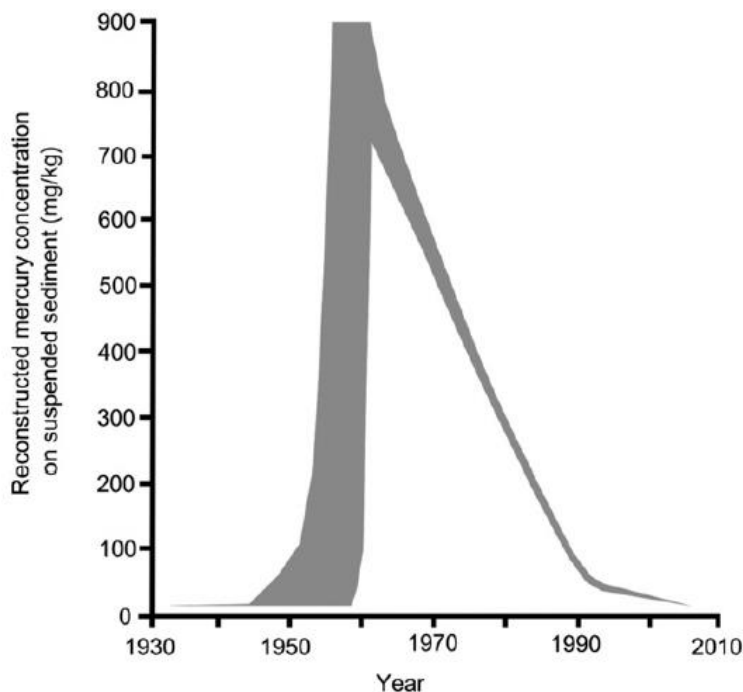


Figure 13. Estimated Hg concentrations in suspended sediments in 20 km segment of South River, reconstructed from fine grain channel margin deposits by Skalak and Pizzuto (2014)

6.3 Relationship Between MeHg and Inorganic Hg

Non-linear relationships between Hg concentrations in fish and THg in water or sediments (most of which is inorganic Hg(II)) have been reported for the South River (Figure 14) (Brent and Kain, 2011; VDEQ, 2008; Dyer, 2009). This is consistent with observations from other ecosystems spanning a wide range of sediment Hg concentrations, suggesting a linear relationship between MeHg and THg in sediments at lower concentrations, *e.g.* less than roughly 1-5 μg THg/g, while MeHg does not increase in proportion to inorganic Hg at some highly contaminated sites.

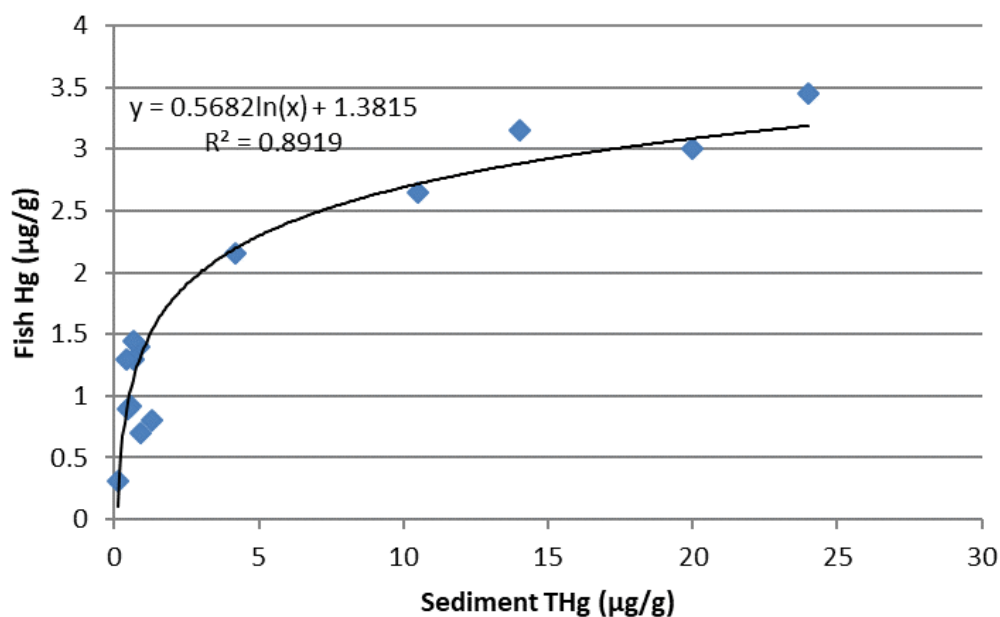


Figure 14. Relationship between mercury in Smallmouth Bass and THg in sediments in the South River.
Derived from Dyer (2009) presentation. Data paired by approximate location.

It was expected that the non-linear relationship reported between Hg in fish and sediments in the South River would be due to MeHg production not increasing in proportion to sediment Hg concentrations. This could occur, for example, if some or all of sediment Hg contamination was not as available for methylation as background Hg. Paired measurements of THg and MeHg concentrations in South River sediment samples, collected in 2006, produced a positive but highly variable relationship (Figure 15). Some of the variability was likely associated with seasonal shifts in the MeHg-THg relationship in sediments but relationships were still weak when examining data from the same months (Figure 16).

When paired sediment MeHg and THg concentrations were averaged for each sampling location along the river, a stronger relationship emerged, even when combining data for all months (Figure 17). Spatial patterns of rising and declining concentrations of MeHg and THg along the river were evident using averaged concentrations at each location (Figure 18).

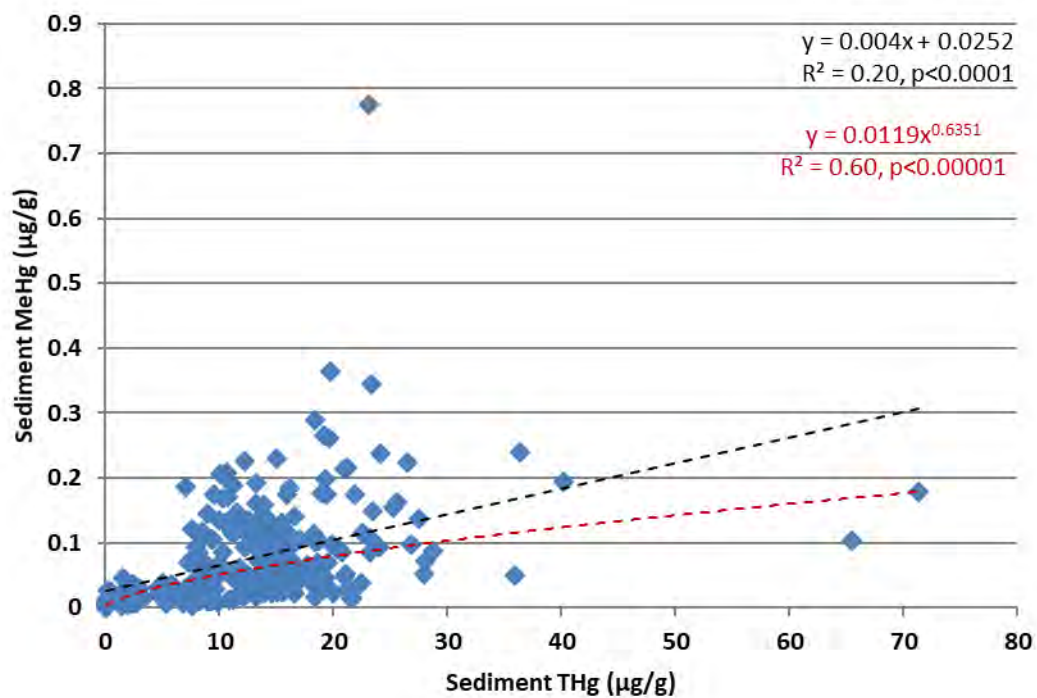


Figure 15. Relationship between MeHg and THg concentrations in South River surface sediments (≤ 5 cm) for RRM 0.6-26. Data are from paired samples collected in 2006 (March-September data combined). Black line and equation represent a linear fit. The red line and equation represent a power function fit. Derived from (Collins, 2018a).

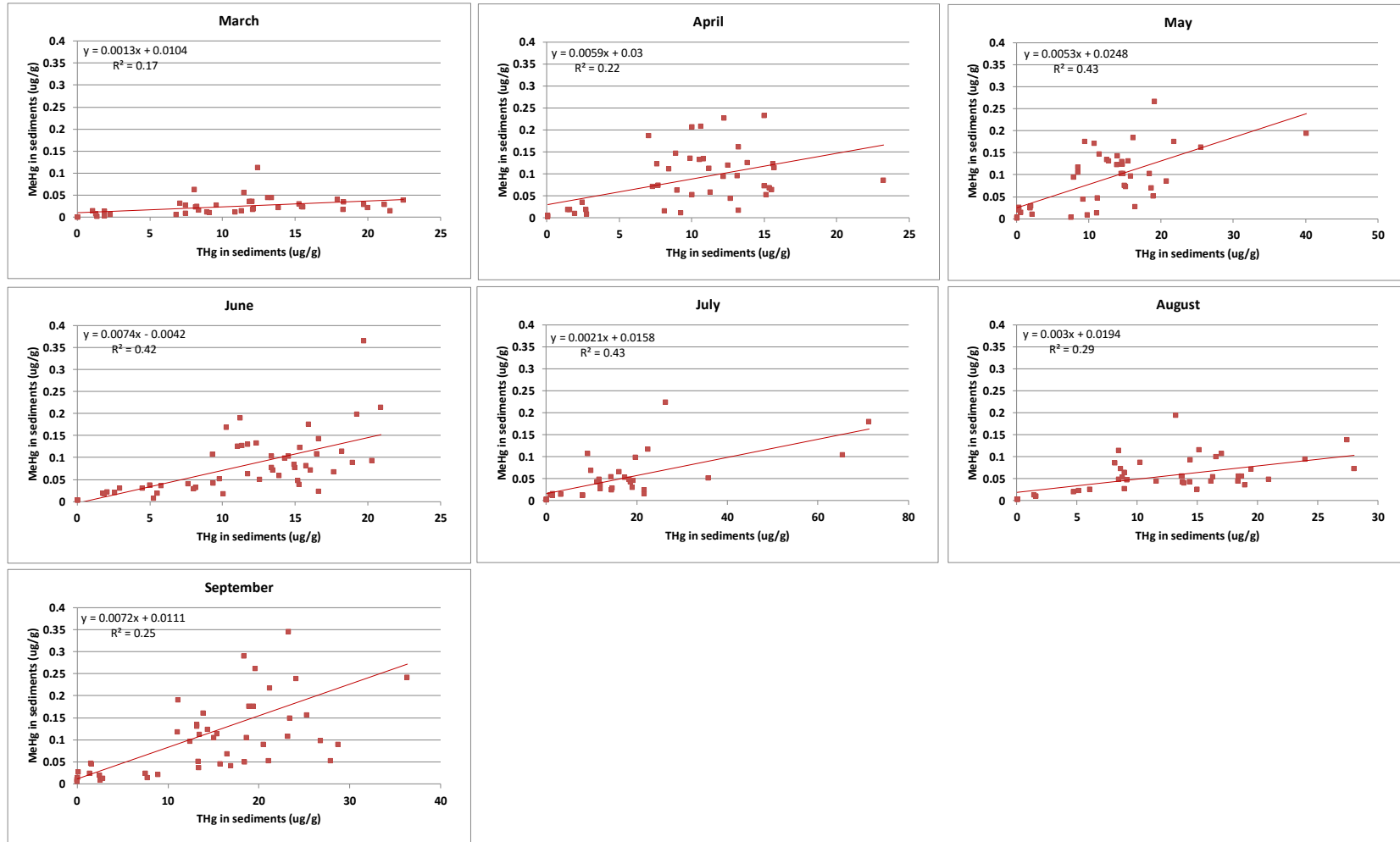


Figure 16. Monthly relationships between MeHg and THg in South River surface sediments (<=5 cm) for RRM 0.6-26 in 2006. Derived from paired data from (Collins, 2018a).

It was expected that the reported non-linear relationship between fish Hg levels (mostly MeHg) and THg in sediments (Figure 14), would also be evident in sediments, where a majority of methylation in this system is assumed to occur. It was not visually obvious in a plot of raw field data for paired MeHg vs THg concentrations in sediments whether a linear relationship existed (Figure 15). This was also the case when concentrations were averaged by sample location along the river (Figure 17). Statistically, R^2 values were higher and “p” values for significance were lower (better) for regressions assuming a non-linear relationship, for the raw and location-averaged data. Power fit regressions had higher R^2 values than other relationships tested including linear, exponential, logarithmic and polynomial. The power fits had declining rates of increase for MeHg concentrations as THg increased. Flanders (pers. comm) also analyzed paired data for total Hg and MeHg concentrations in South River sediments and calculated a slightly lower (better) value for Aikake’s Information Criterion for a non-linear model with less of an increase in MeHg at higher concentrations of total Hg, relative to the linear model. The data can also be examined from the perspective of the fraction of THg that is MeHg. If a linear relationship existed (and the intercept was zero), the percent of THg that is MeHg would be constant, *i.e.* doubling THg concentrations would double MeHg concentrations. A plot of the percent of THg that is MeHg in sediments, again using paired observations from different locations, showed the percent MeHg to be lower near the former DuPont facility site (Figure 19). These properties of the sediment data for MeHg and THg concentrations are consistent with the non-linear relationship reported for fish Hg versus sediment THg. Finally, the regressions in Figure 15 and Figure 17 all exhibited positive relationships between MeHg and THg that were statistically significant at a level of $p < 0.01$. This is consistent with remediation designed to reduce loading of inorganic Hg in order to reduce MeHg concentrations, even if the relative benefits of reducing THg loads and concentrations to reduce MeHg concentrations are not certain.

One hypothesis to explain a non-linear relationship between MeHg and THg in sediments is that a portion of the inorganic Hg contamination is unavailable for methylation. A related hypothesis to explain less available Hg(II) for methylation is that some Hg(II) contamination is more strongly bound to solids and less available to microbes. This can be examined using apparent partition coefficients ($K_d = [Hg]_{\text{solids}}/[Hg]_{\text{filtered}}$), where the solids concentration is dry weight (*e.g.* $\mu\text{g/g}$). Mercury partitioning in surface waters clearly changed as water flowed over contaminated sediments (Figure 20), indicating that contaminated particles from eroding banks or remobilized from the sediment bed were not fully equilibrating with dissolved Hg pools during the time it took water to travel through the contaminated reach to the confluence of the North River. Assuming methylation in the contaminated reach of the South River occurs primarily in sediments, inorganic Hg partitioning in sediments would be of greater relevance to MeHg production than water column partitioning. In sediments, two datasets were examined (Figure 21). The THg K_d was higher for the dataset with measurements specifically from RRM 0-2, compared to values from Flanders et al (2010) for RRM 0-24. It is uncertain if these data describe true spatial differences or differences in methods and approaches used to estimate K_d s for the two datasets.

Overall, available data suggest that MeHg production does not increase in proportion to inorganic Hg at sites with higher levels of contamination, although this is difficult to observe visually in plots of MeHg versus THg in sediments. Another potential source of non-linearity between MeHg concentrations in water or fish and THg concentrations in sediments is that river flows could result in locations of peak water column concentrations of THg or MeHg being downstream of sediment peaks. If fish Hg has an important component of exposure linked to MeHg in water, then pairing fish Hg and sediment Hg

spatially along the river could result in non-linear relationships, even if MeHg production was proportional to Hg(II) concentrations.

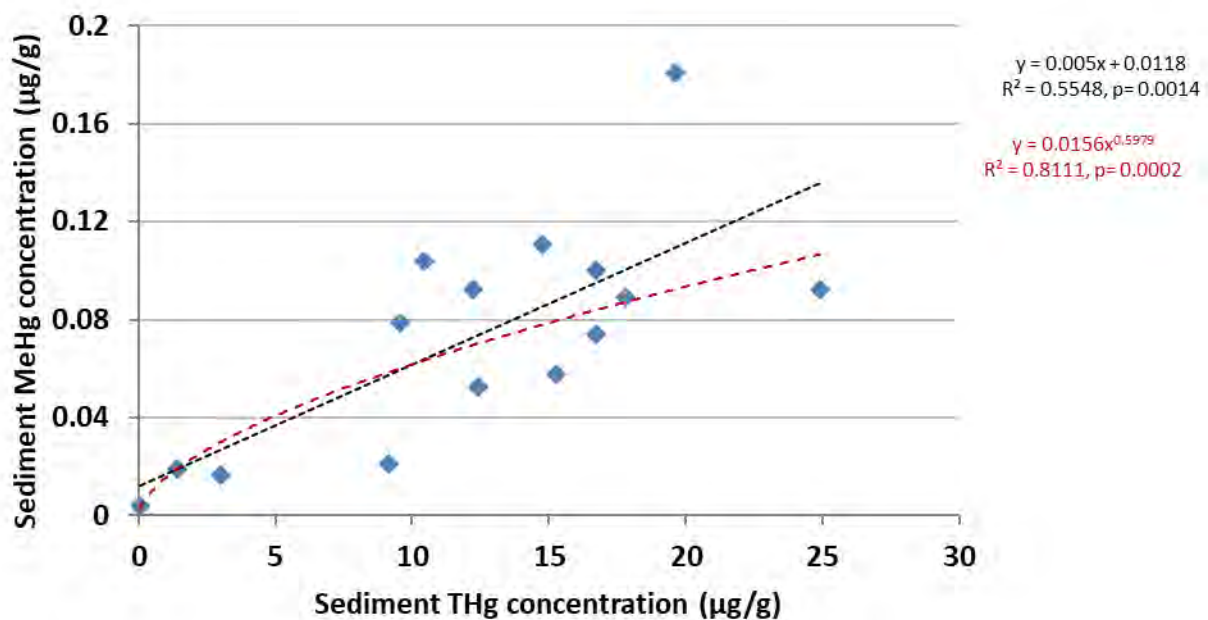


Figure 17. Relationship between MeHg and THg in South River surface sediments (<3 cm) using average concentrations for each sampling location (RRM 0.6 to 26). Each location used paired data from March-September 2006). Derived from (Collins, 2018a).

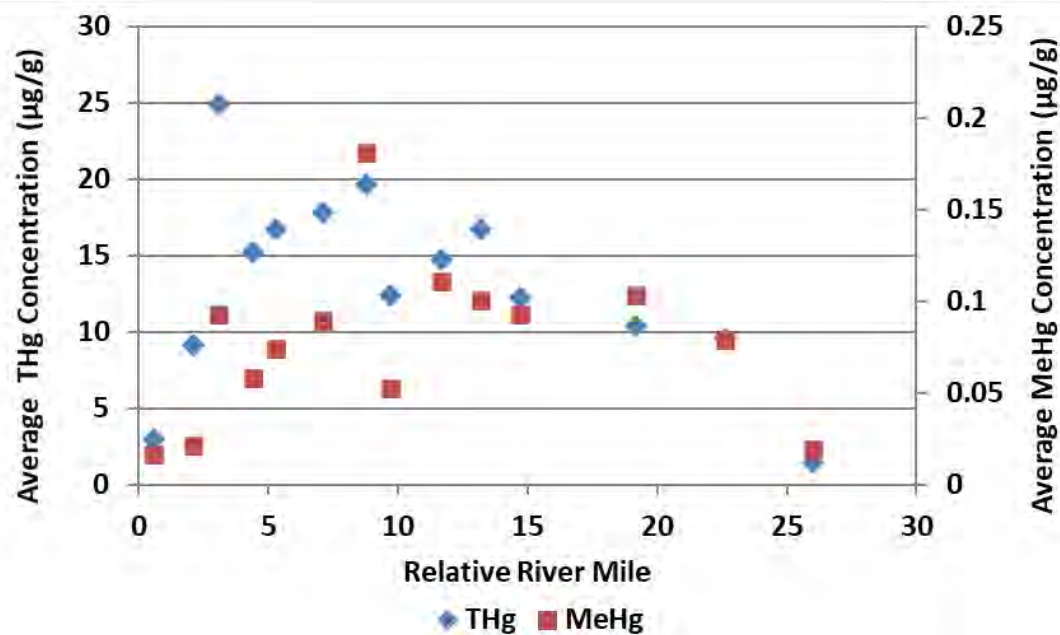


Figure 18. Sediment MeHg and THg concentrations versus relative river mile in South River surface sediments (<3 cm) using average concentrations for each sampling location. Paired samples collected in 2006 (March-September data combined). Derived by D. Hutchinson from Collins (2018a).

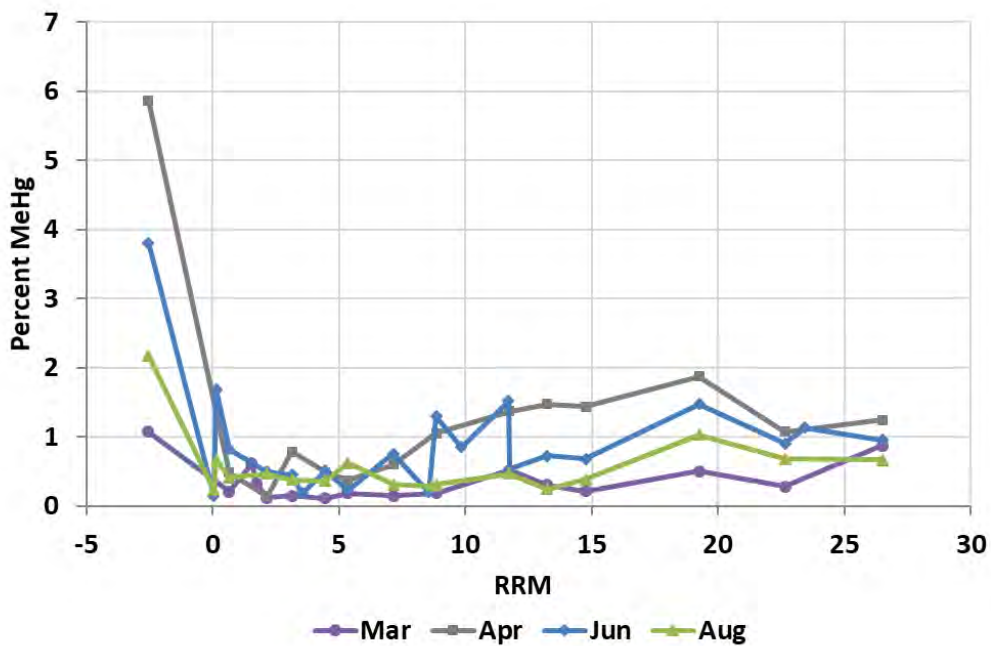


Figure 19. Percent MeHg in South River surface sediments (<3 cm) from RRM -2.5 to 26.4. Paired data from samples collected from 2005-2012. Derived by D. Hutchinson from (Collins, 2018a).

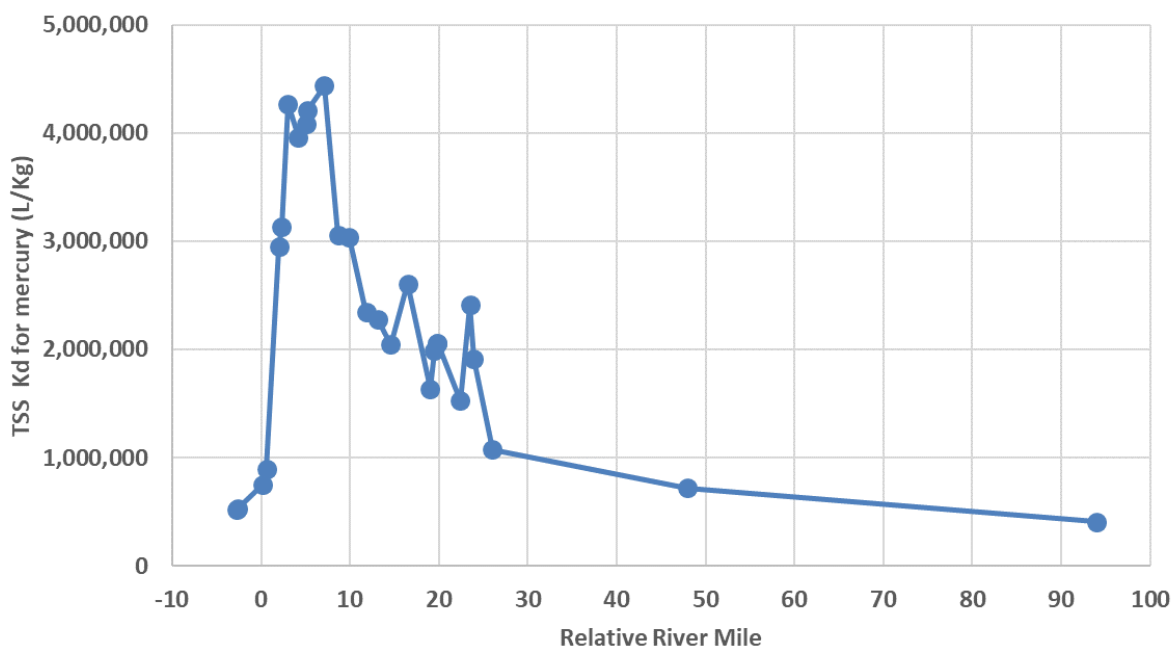


Figure 20. Field-based estimates of mercury partitioning between water column solids and the filtered phase. Data combined from 2006-2016. Derived using data from Collins (2016a).

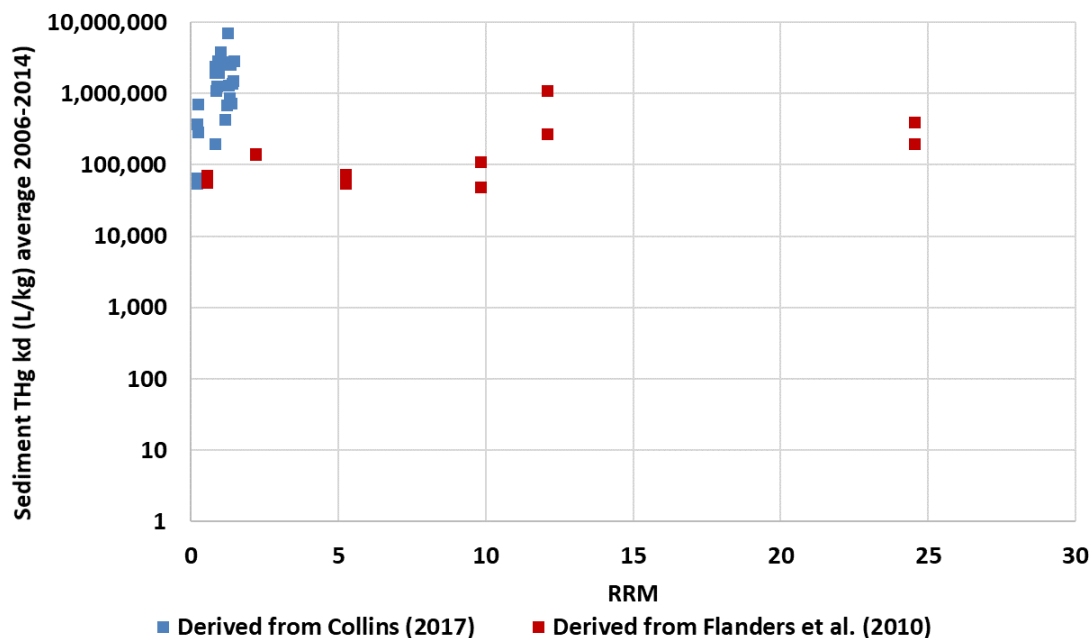


Figure 21. Field-based estimates of mercury partitioning between surface sediment solids and porewater. Both datasets used paired data.

7 MODEL CONFIGURATION AND INPUT VALUES

7.1 Model Grid Configuration

D-MCM was configured to simulate Hg in the South River from the former DuPont facility site to approximately 2 miles downstream of the confluence of the South and North Rivers (RRM 0-26, Figure 22). The modeled river reach was divided into 46 cells, each approximately 0.5 to 1 km in length (Figure 23). The water column within each cell was assumed to be well mixed horizontally and vertically. Water, solids or Hg loads entering a cell were mixed throughout the cell water column, independent of the actual point of loading in the cell. The sediment bed was represented using three layers: a surface layer 2 cm thick, underlain by a 2nd layer 5 cm thick, and a 3rd layer 50 cm thick (Figure 24). The surface layer thickness was chosen assuming that methylation would occur within this zone, and this layer is well mixed vertically. Some sediment bed areas have gravel sizes up to 6 cm diameter and cobbles up to 25 cm in diameter (N. Grosso, pers. comm), and the model results are representative of finer material in interstitial spaces in these areas. Within each cell, the sediment bed is assumed to be uniform horizontally, *e.g.* the mix of particle types is the same at any location within a given cell. Sediment bed conditions vary among model cells. Bathymetry for model cells was derived from thirteen transects taken at irregular distance intervals from RRM 0 through RRM 22.4 (URS, 2006). Each transect provided the river width at a series of elevations. The cross-section of each D-MCM cell was assumed to be constant along its length in the direction of flow (Figure 25) and was assigned the cross-section corresponding to the transect that was closest to its midpoint. Area vs elevation information for cells below the confluence with the North River (cells 44-46) was developed based on channel data from the South Fork Shenandoah USGS gage (USGS 2018g).

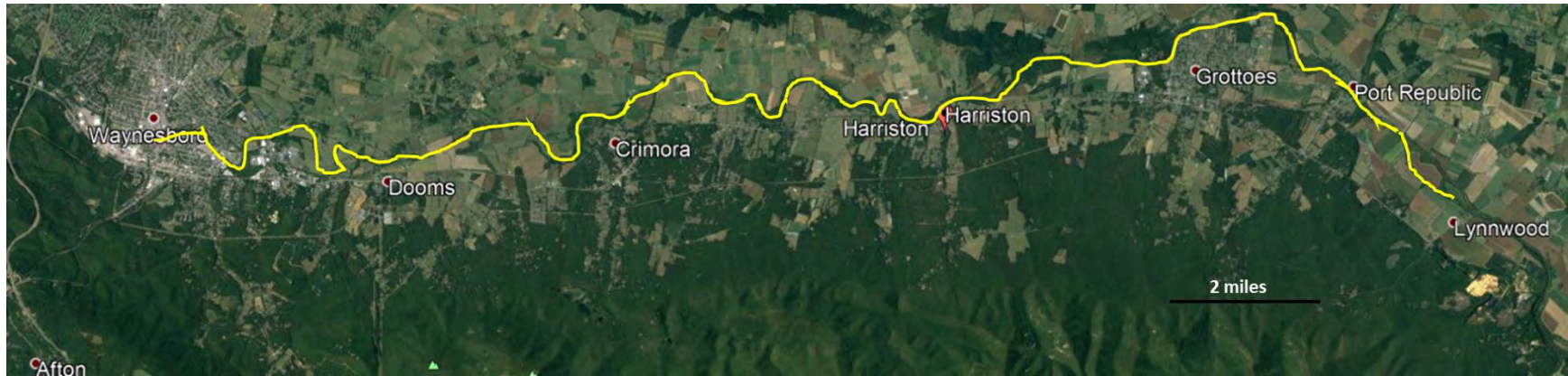


Figure 22. Modeled reach of South River, VA, from Waynesboro to approximately RRM 27 in the South Fork Shenandoah River.

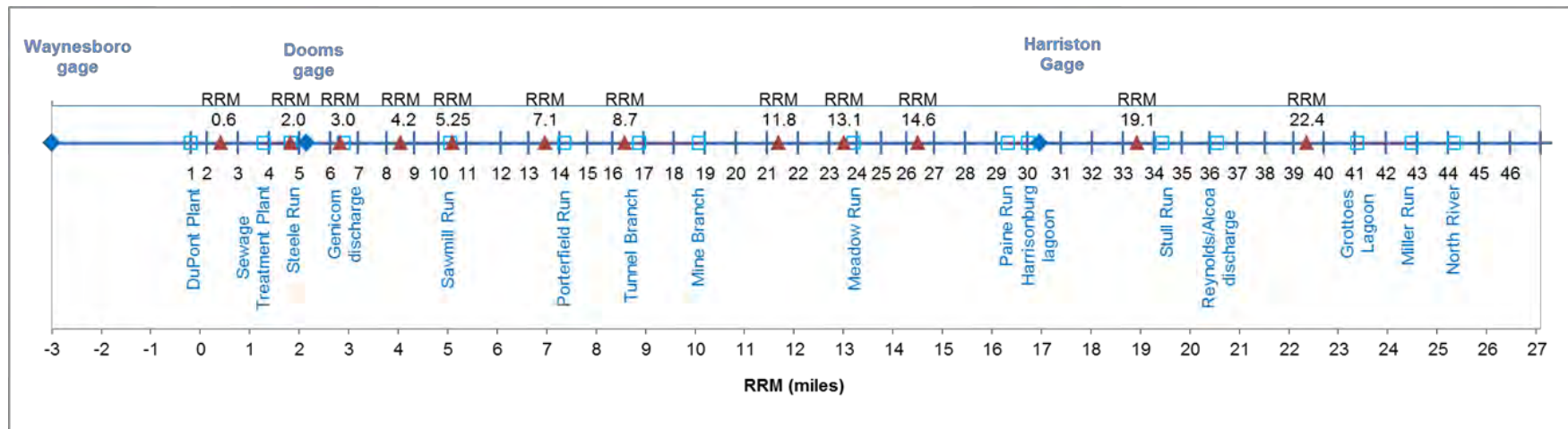


Figure 23. Hydrodynamic gaging stations within model domain. Vertical blue lines define cell boundaries. Red triangles are sampling stations for Ecological Study. Blue diamonds are USGS gaging stations. Open blue squares are locations where tributaries enter the South River.

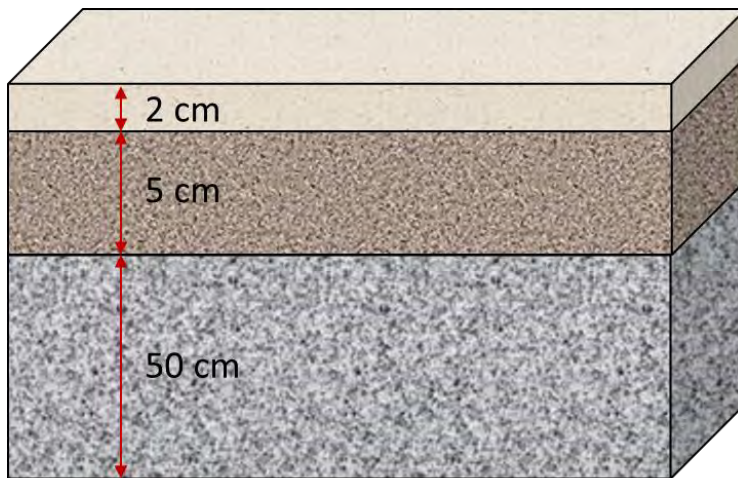


Figure 24. Schematic of sediment bed layers in D-MCM

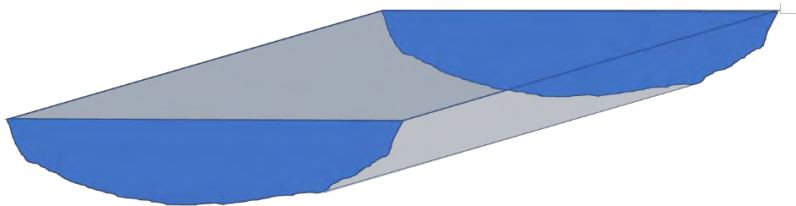


Figure 25. Schematic of approach to estimating cell areas and volumes.

7.2 Hydrology

Three USGS gaging stations exist within or just upstream of modeled reach of the South River, upstream of the confluence with the North River (Figure 23) (USGS 2018a-c).

- Waynesboro (RRM -2.8), USGS station # 01626000
- Doods (RRM 2.0), USGS station # 01626850
- Harriston (RRM 7.1), USGS station # 01627500

Three additional gaging stations were used to estimate flows below the confluence with the North River (USGS 2018d-f):

- South Fork Shenandoah (RRM 28.8, USGS station #01628500)
- North River (USGS station #01622000)
- Middle River (USGS station #01625000)

Flows from the North River and Middle River stations were summed to estimate the flow from the North River at the confluence with the South River. The resulting flow was added to the South River flow to estimate the flow of the South Fork Shenandoah at the confluence. Mean

daily flows were obtained for each of the stations for 2006-2014, *e.g.* flows at Dooms are shown in Figure 26. Median flows for 2006-2014 were 73 cfs at Waynesboro, 107 cfs at Dooms and 133 cfs at Harriston.

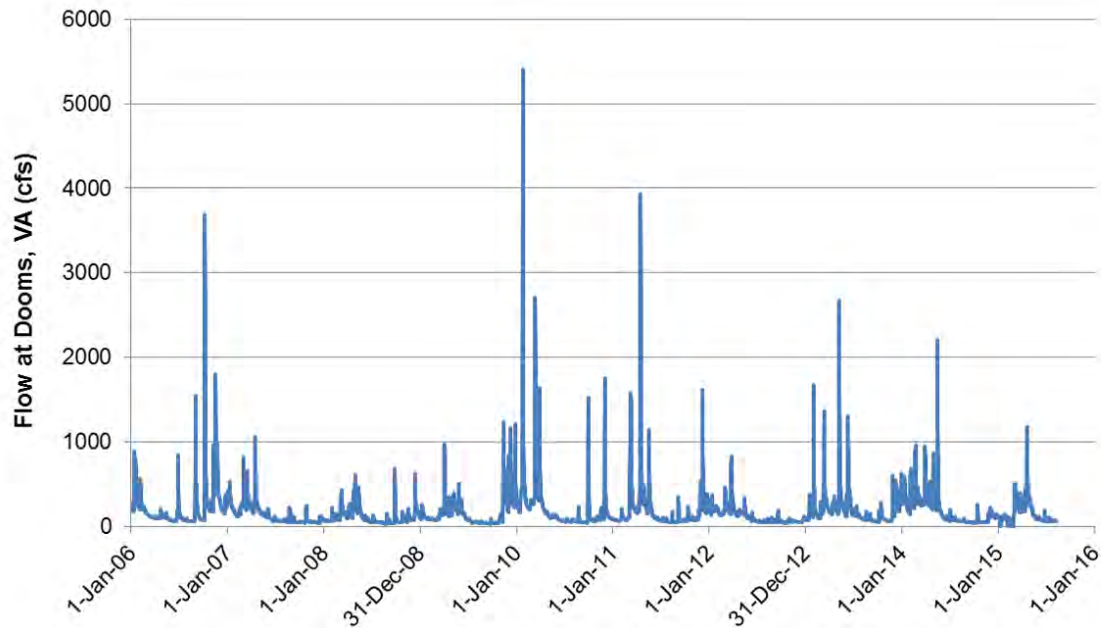


Figure 26. Daily flows at Dooms. Source (USGS 2018b)

Stage-discharge relationships were developed from available rating tables for each of the relevant USGS gage stations (Waynesboro, Dooms, Harriston and South Fork Shenandoah). Three curves were fitted at each station, corresponding to low, medium and high flows/stages. A standard relationship for flow versus stage was used:

$$Q = C (h - h_0)^b$$

Where:

Q = flow rate (cfs)

H = stage (feet)

Rating curves obtained for the Harriston gage are shown in Figure 27.

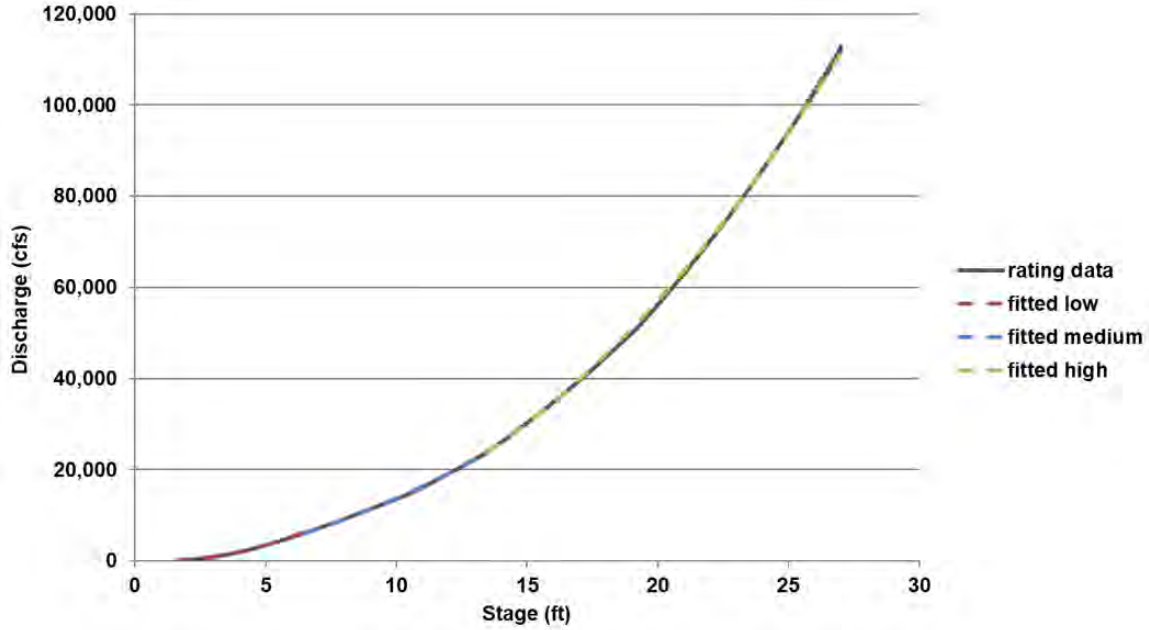


Figure 27 Derived rating curves for low, medium, and high flow conditions at USGS gage at Harrison, VA. Curves based on data from 2006-2014 (USGS 2018c).

A simple dynamic hydrological mass balance was constructed to simulate flows, water levels and average cell velocities for each model cell:

$$\frac{dV_i}{dt} = Q_{i-1} + Q_{gw} + Q_{trib} - Q_i$$

Where:

V = volume
Q = flow
i = cell number (upstream cell = 1)
gw = groundwater
trib = tributary

Differences between flow at the USGS gaging stations were allocated to tributary inflows and groundwater. Tributary inflows (blue text in Figure 23) were allocated based on ratios of tributary flows from Grosso (2006). Groundwater inflows to the river were estimated as follows:

1. Groundwater was assumed to represent 70% of the increase in flow between gaging stations during periods of low flow. This is based on a statement from Grosso (2006): *“Based on hydrograph separation techniques conducted by the USGS (Eggleston, 2005) and numerous groundwater studies conducted by DuPont, the annual contribution of groundwater to flow in the river is between 30% and 70% and may vary over the length of the river.”*

2. Low flow was defined as less than the median value for 2006-2014.
3. For any dates with low flows, the increase in river flow between three gaging stations (Waynesboro to Dooms to Harriston) was calculated on a daily basis. The average increase in flow for the two reaches was then calculated using daily estimates.
4. The resulting groundwater flows were (2006-2014 medians):
 - a. ~9 cfs from Waynesboro to Dooms (~8-12 percent of the median overall flow)
 - b. ~17 cfs from Dooms to Harriston (~13-16% percent of the median overall flow)
5. Groundwater discharges per length of riverbed were assumed to be constant within each reach between gaging stations. Groundwater was assumed to be constant at all times unless the difference between the flow at the downstream gage and the upstream gage was less than the estimated constant groundwater discharge for that reach. This mostly occurred at low flows during a rising hydrograph.

The resulting median flows along the river for 2006-2014 are shown in Table 1 and Figure 28. The largest source of water at RRM 24.6 was the mainstem (54%) followed by tributaries (29%) and groundwater (16%). The modeled flows matched observations from Dooms and Harriston well.

Table 1. Simulated external sources of water from RRM 0-24.6 for 2006-2014.

	Median flow (cfs)	% of total
Upstream River	73	54
Groundwater	22	16
Tributaries	40	29
Total	142	100

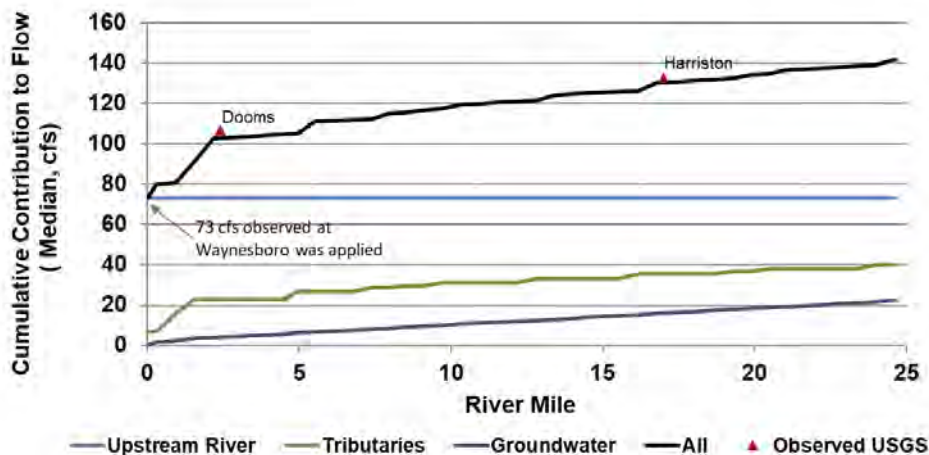


Figure 28 Median estimated flows associated with the main stem at Waynesboro, tributaries and groundwater for 2006-2014.

7.3 Particle Dynamics

D-MCM can calculate mass balances for particles in the water column and sediments. In the water column, solids fluxes include inflows, outflows, settling, and resuspension (Figure 29). No terms are included for internal production or decomposition of solids in surface waters. Within each model cell, the mass balance is used to solve for suspended solids concentrations as a function of time. In the sediment bed, mass balances are used to solve for solids burial or erosion rates as the difference between solids inputs via settling and the sum of resuspension and decomposition losses. Conceptually the 2 cm thick surface layer of constant thickness can be thought of as moving up if burial is occurring or moving down if erosion is occurring. Temperature-dependent decomposition rates were assigned to labile and refractory organic particles in sediments, while inorganic particles were assumed not to decompose.

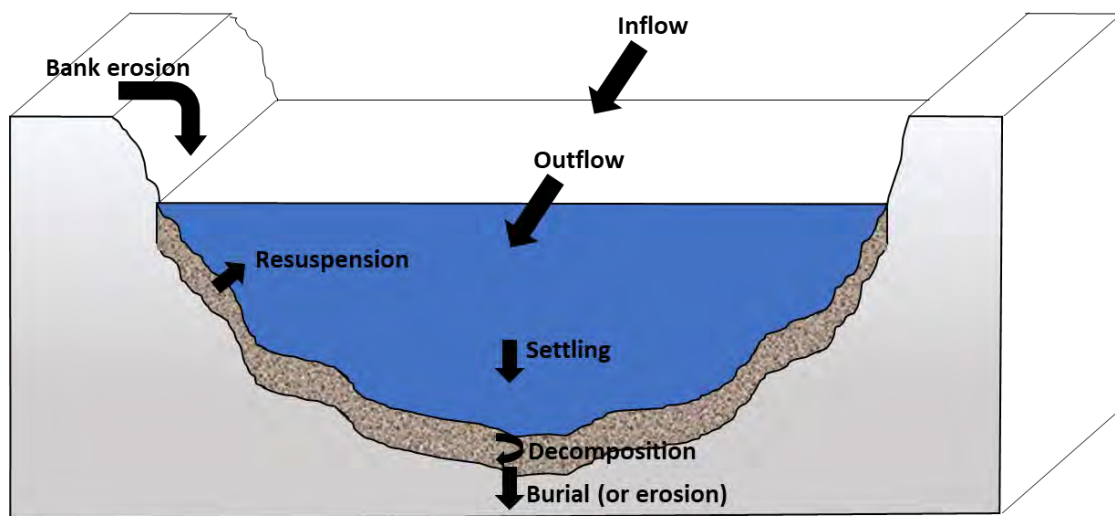


Figure 29. Schematic of internal fluxes for each particle type within a model cell. Inflows and outflow are also shown

Four particle types were included in simulations:

- coarse inorganic solids (*e.g.* sand) that do not decompose,
- fine inorganics (silt and clay) that do not decompose,
- organic particles that decompose slowly, and
- organic particles that decompose readily.

The four particle types were assigned different settling velocities. Due to limited information on mercury partitioning as a function of particle type, all particles were assigned the same partitioning characteristics. Inflowing boundary solids loads, bank erosion, resuspension rates, and settling velocities were assigned as discussed below.

7.3.1 Upstream and Tributary Solids Loads

Solids loads from the main stem of the South River to the upstream end of the modeled river reach were estimated using linear regressions for solids loads versus flow. The regressions were based on pooled data from RRM -2.8 to 0 for 1999-2014 (n=312, Figure 30, derived from Flanders (2016)). Solids loads were converted to suspended solids concentrations by dividing the solids flux by flow (Figure 31). Separate regressions were developed for flows above and below $5 \text{ m}^3 \text{ s}^{-1}$. The “break point” of $5 \text{ m}^3 \text{ s}^{-1}$ was chosen subjectively. There was a high degree of variability in solids loads and concentrations for a given flow, note the log scales on the axes in Figure 30 and Figure 31. This approach captured variation in suspended solids concentrations as a function of flow, but did not capture the variability that can occur at any specific flow value. A more detailed approach was beyond the scope of this analysis.

Suspended solids concentrations data for tributaries were not available and were assumed to have the same concentrations as estimated for the mainstem at Waynesboro.

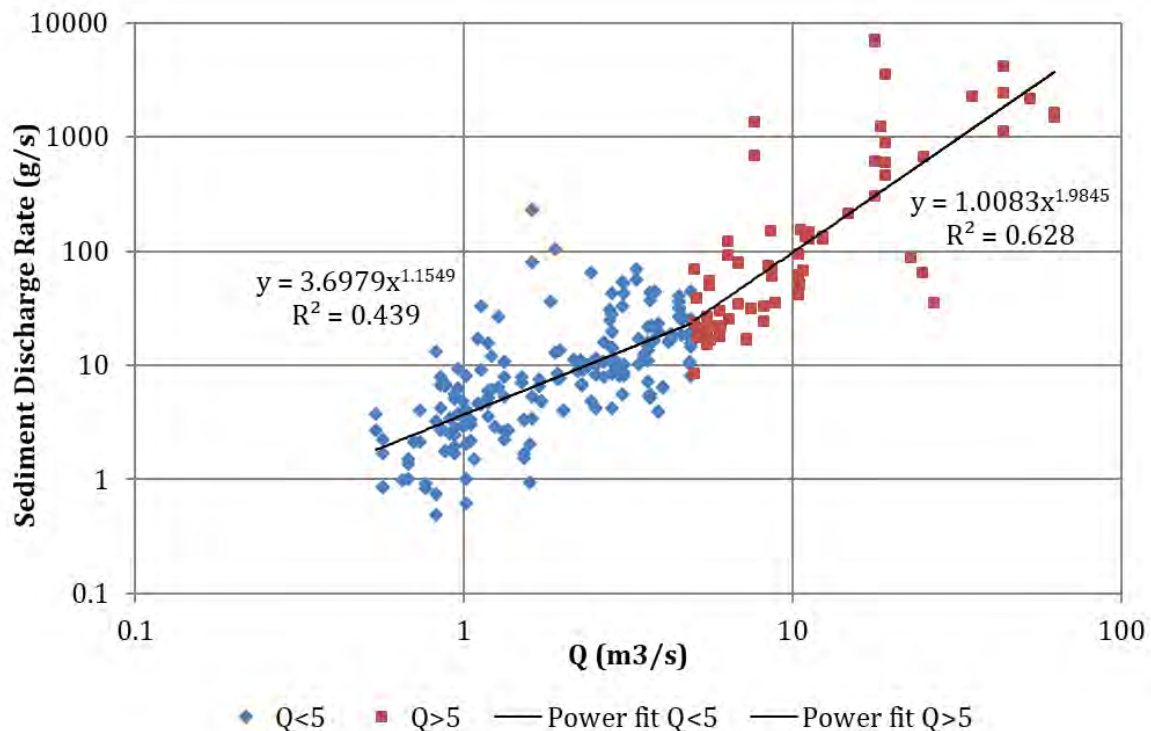


Figure 30. Sediment discharge in the South River as a function of flow for RRM -2.8 to 0. Data from 1999-2014, n=312. Data source: Flanders (2016).

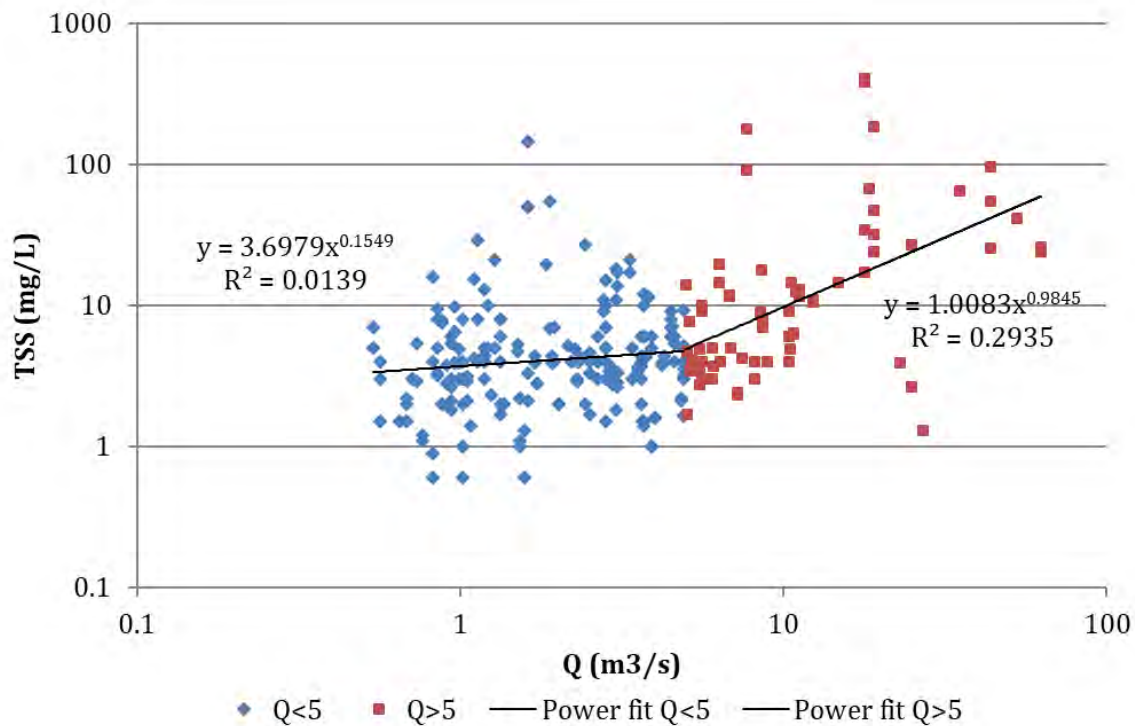


Figure 31. Suspended solids concentrations in the South River as a function of flow for RRM - 2.8 to 0. Data from 1999-2014, n=312. Data source: Flanders (2016).

7.3.2 Bank Erosion

Solids loads from eroding banks were estimated as follows:

- RRM 0-5: Based on DuPont spreadsheet with estimates of pre-remediation solids loads and potential reductions via Phase I and 2 remediation efforts (Grosso, 2018)
- RRM 5-10: Based on Anchor QEA estimates (Flanders, 2016)
- RRM 10-25: Based on Pizzuto *et al.* solids erosion rate estimates within 184 intervals from RRM 0.14 to 23.81, ranging from 0.005 to 0.41 miles in length.
- Cells downstream of confluence with North River: Assumed no bank erosion.

Average annual solids erosion rates (kg yr^{-1}) were estimated for each field segment. Field data from segments within each D-MCM model cell were summed to generate erosion rates for each D-MCM cell. Bank erosion rates were allocated daily over the 2006-2014 period to achieve the overall estimated average rates in Figure 32. Daily “weightings” for erosion rates were developed on the assumption that erosion depends on velocity. Daily velocities were estimated using daily flows divided by the cross-sectional area of the cell. Initially bank erosion was proportional to velocity squared. When this approach was combined with the assumption that there was little net accumulation of solids from 2006-2014, modeled values for the median suspended solids were too high. A relationship with bank erosion related to velocity to the 4th power was ultimately used in simulations, in order to transport solids downstream while

maintaining median concentrations of suspended solids consistent with observations. Additional information is provided later in the report. J. Pizzuto (pers. comm.) noted that bank erosion events do not necessarily happen only during periods of high flow. They can also occur during freeze-thaw cycles, or during periods after large events, when delayed bank slumps may occur. No consideration of these possibilities has been included in the model analysis, but the discharge-solids relationship shown in Figure 31 reflects these processes.

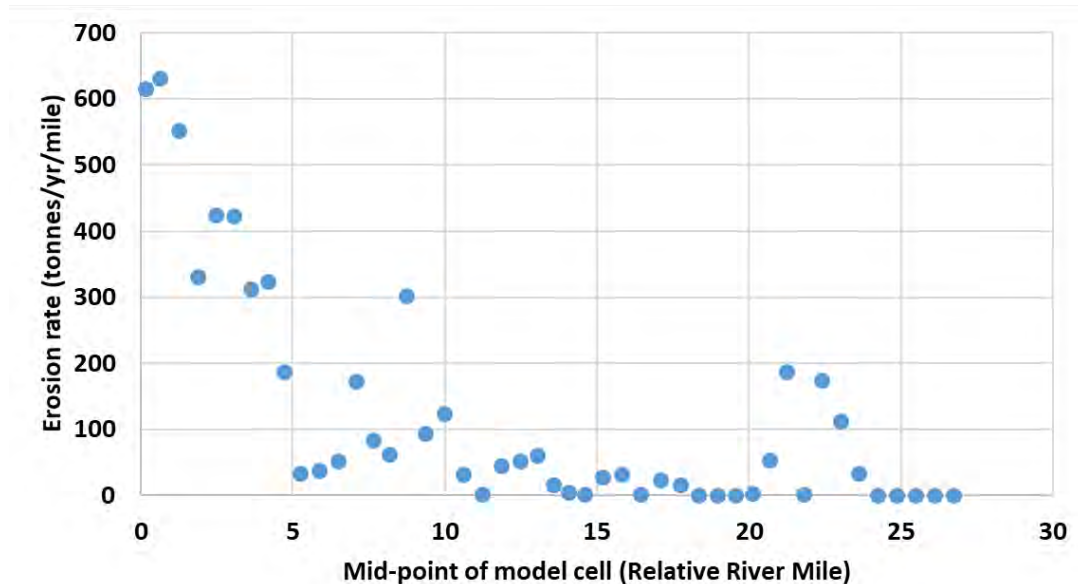


Figure 32. Solids loading estimates to model cells from RRM 0-27. Values are averages for 2006-2014 and vary daily, depending on hydrology. Additional information is provided in Appendix A

7.3.3 Summary of External Solids Loads to Modeled River Reach

A summary of solids loading rates used in D-MCM simulations for the upstream river, bank erosion and tributaries is shown in Figure 33. D-MCM loads from upstream, RRM 0-2, RRM 2-23.8, and tributaries were comparable, roughly 1000 -2000 tonnes per year. Estimates of the same solids sources are also shown in the figure for Pizzuto *et al.* (2006). It is not clear why the Pizzuto estimates for solids inputs from upstream are much larger than estimated for the D-MCM analysis. The time periods are different, which would result in some difference. For example, large storms, and associated elevated particle loads, may have occurred during the period of record used by Pizzuto, but not from 2006-2014 (further discussion below). The relationship between solids loads and flow used in D-MCM was based on South River data between RRM -2.8 and 0, while the Pizzuto *et al.* (2006) regression was based on data from regional waterbodies. The data used in the D-MCM analysis of inflowing suspended solids at Waynesboro were within the overall range used by Pizzuto *et al.* (2006) (Figure 34).

Tributary solids loads from Pizzuto *et al.* (2006) were also larger than currently used in D-MCM simulations and were almost 4-fold greater than the bank erosion loads estimated by Pizzuto *et al.* (2006). In the absence of tributary-specific data, D-MCM simulations assumed that tributaries had the same suspended solids concentrations daily as the main stem of the river near Waynesboro.

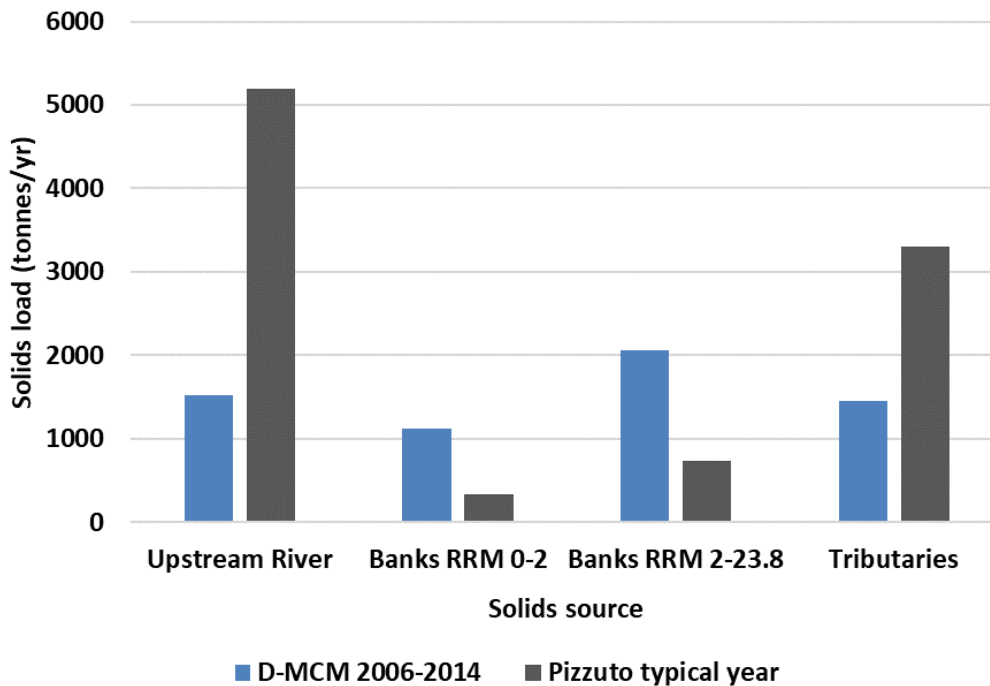


Figure 33. Estimated average annual solids loading rates from the upstream river, banks and tributaries for D-MCM from 2006-2014, and from Pizzuto *et al.* (2006) for a typical year.

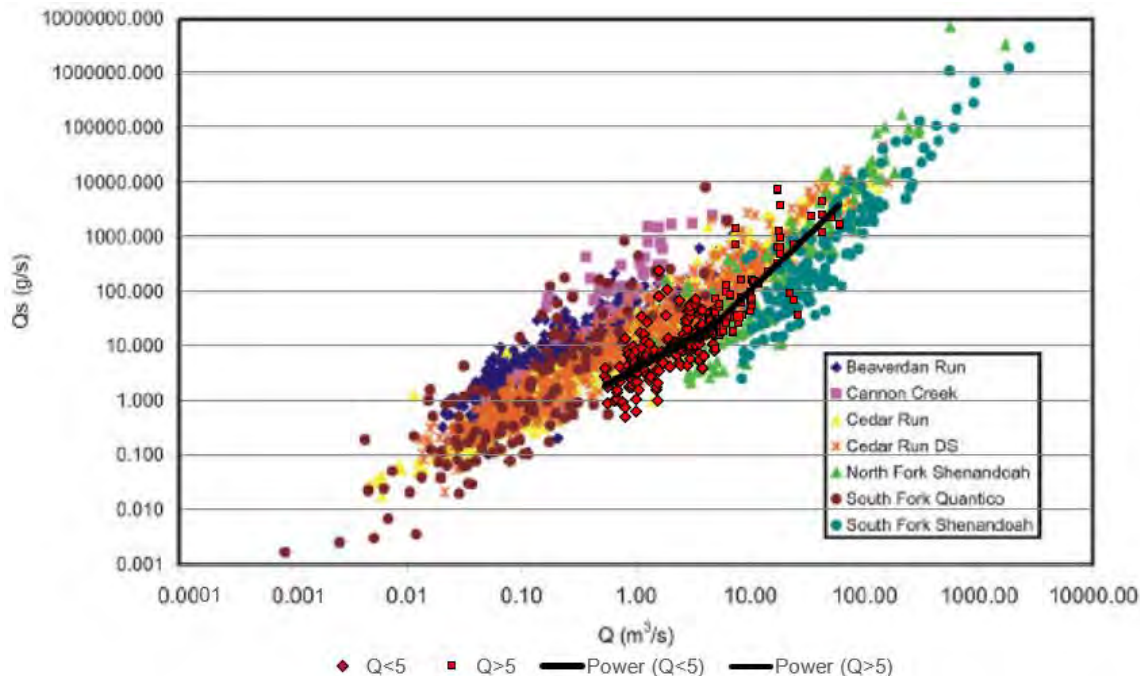


Figure 34. Solids fluxes versus flow for stations used by Pizzuto (2006) and in this study. All points except red diamonds are from Pizzuto *et al.* (2006). Red diamonds are from the South River from RRM -2.8 to 0 from 2006-2014 (Flanders, 2016). Black line is the fit to South River data, used in D-MCM modeling.

7.3.4 Sediment Bed Solids Fluxes

If the ongoing supply of Hg contamination from riverbanks stopped, it would take time for Hg concentrations in the sediment bed to respond and decline. A key factor governing the rate of recovery of total Hg in surface sediments is rate at which new, low-Hg particles replace legacy contaminated particles in surface sediments. New particles are supplied by settling solids, while contaminated particles are removed via burial and resuspension. These Hg losses from surface sediments are not necessarily permanent. Resuspended particles may re-settle locally or downstream, and large storms may erode solids and contamination that had previously been accumulating and buried for years or decades.

Pizzuto *et al.* (2006) described a conceptual model of sediment accumulation in FGCM deposits in the South River, which included three phases (Figure 35). During the formation phase, fine particles accumulate. A second phase is characterized by periods of minor erosion or deposition but no long-term change. The third phase involves events such as large flows or the removal of obstacles providing shelter for FGCM deposits, resulting in erosion of most or all of the fine material in these deposits. It is unclear how frequently FGCM deposits are mobilized and transported. The 2008 analysis by Pizzuto *et al.* suggested a cycle averaging roughly 13 years, although this duration would depend on the occurrence of specific events. More recently Skalak and Pizzuto (2014) estimated that particle residence times in the FGCM deposits were 1.75 years (range 1-60 years). There are also fine grain deposits in interstitial deposits in the coarse

river bed. Pizzuto *et al.* (2006) estimated that this pool is small compared to the FGCM deposits, but these deposits could still be relevant to MeHg production and bioaccumulation.

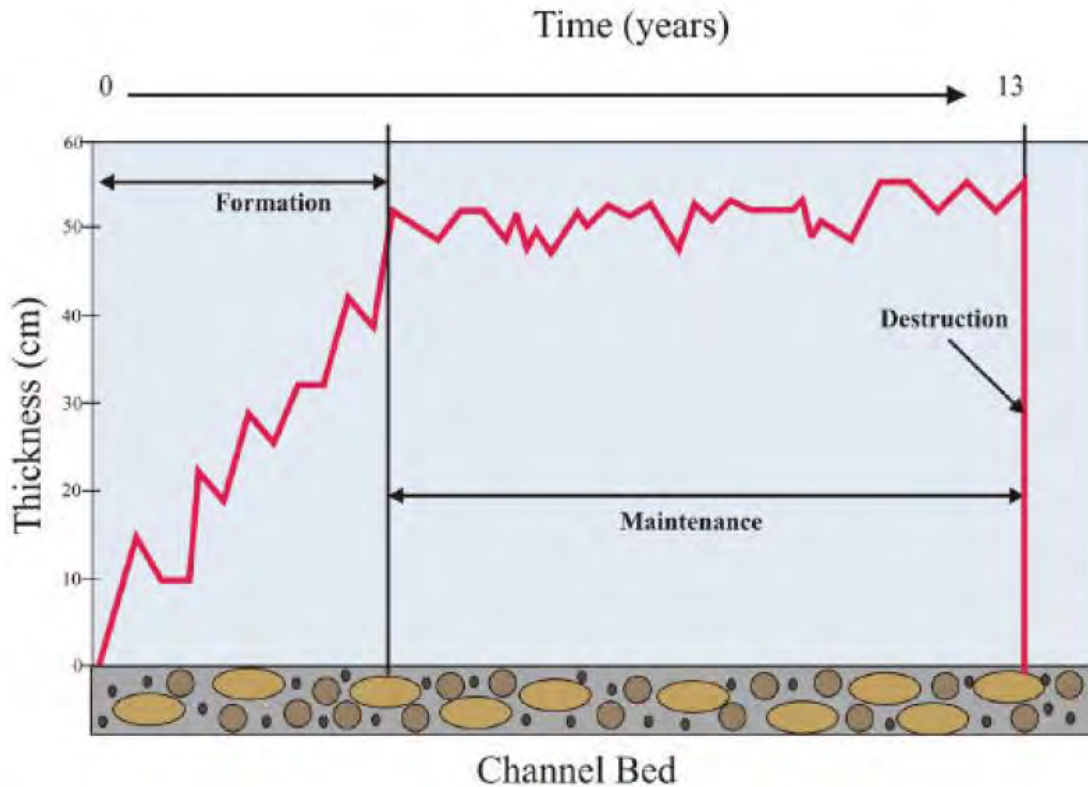


Figure 35 Conceptual model of the temporal evolution of fine-grained channel margin deposits over time. From Pizzuto *et al.* (2006)

An important issue for D-MCM modeling was the stage of the life cycle for fine-grained solids that the system experienced during the model calibration period from 2006-2014. Solids transport rates estimated for 1994-2014 for D-MCM simulations were compared to estimates by Pizzuto *et al.* (2006) at Waynesboro for the period from 1952- 2003 (Figure 36). The comparison suggests the episodes of large transport evident in some years in the Pizzuto record did not occur in the 2006-2014 period. However, D-MCM estimates for 1994-2003 were also systematically lower than Pizzuto *et al.* (2006) by roughly 50%, complicating a comparison of different time periods. The modeled river reach may have been in a period of solids accumulation or neutral accumulation from 2006-2014 (the model calibration period). It was assumed that little or no net accumulation of solids occurred for this study, for the primary calibration of the model. Solids fluxes were adjusted to attempt to achieve this condition. An alternative simulation was also developed where most of the solids from bank erosion accumulated locally during the nine-year simulation.

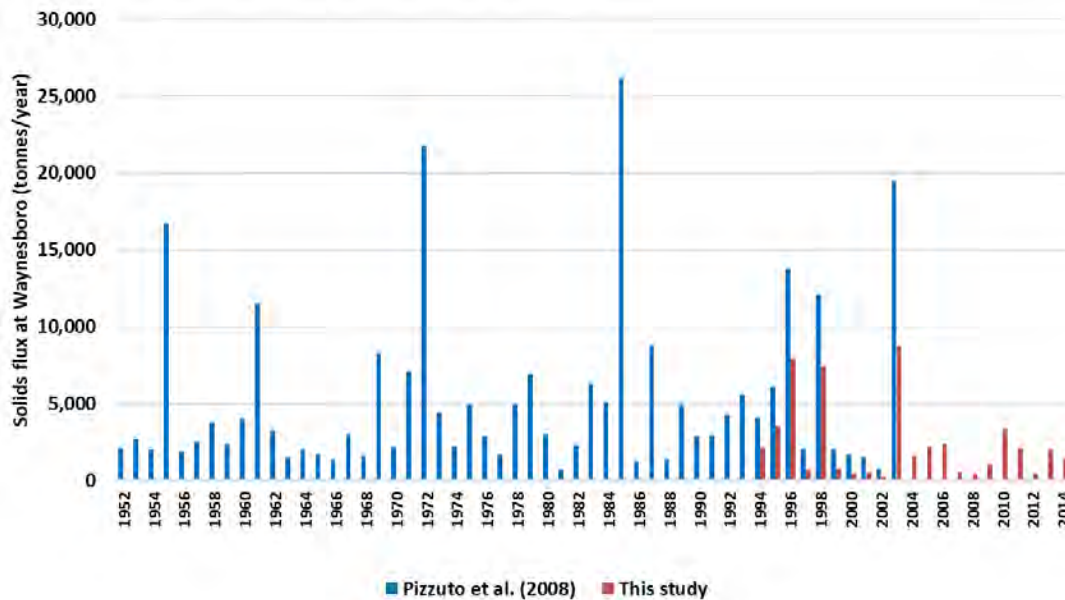


Figure 36. Estimated solids fluxes in the South River at Waynesboro. Estimates for this study were developed using flow data from the gage at Waynesboro and the relationship between TSS and flow shown in Figure 30.

7.3.5 Bank Overtopping

Resuspended particles travel downstream in model simulations until they re-deposit in another model cell or are exported downstream of the modeled river reach. There are no provisions for lateral flow into the floodplain during periods of high flow. Pizzuto *et al.* (2016) indicated that overtopping of riverbanks during large flow events could result in lateral transport of water, solids and Hg, the latter of which could be deposited in the floodplain. Once deposited in the floodplain, further downstream transport would be very slow (J. Pizzuto, pers. comm). D-MCM could be configured with additional cells “on the sides” to allow bank overtopping and deposition of Hg in the floodplain, but this is beyond the current scope of the analysis. Overall, it is possible that the model overestimates the downstream transport of solids and Hg during large events.

7.4 Mercury Loads

7.4.1 Bank Erosion Mercury Loads

Estimated bank erosion rates for Hg are shown in Figure 37 for each model cell, and were calculated by summing field estimates of loads within each model cell. The same sources of information for Hg concentrations on eroding solids were used for RRM 0-5, 5-10 and 10-26 as described previously for solids. D-MCM calculates bank Hg loads as the product of solids erosion rates and Hg concentrations on those solids. Hg concentrations on eroding solids (Figure 38) were calculated by dividing field estimates of Hg loads by field estimates of solids erosion rates (Figure 32). Additional information is provided in Appendix A.

Estimated THg concentrations in banks generally declined with distance downstream. THg loading rates from eroding banks were much greater for the first 5 miles than downstream. No data were identified for MeHg concentrations in bank solids. The percent of THg as MeHg was assumed to be lower than average % MeHg values in river sediments, which were on the order of 0.2% of THg or more (Figure 19). A value of 0.1% THg as MeHg was assumed in riverbanks for all locations (Figure 39).

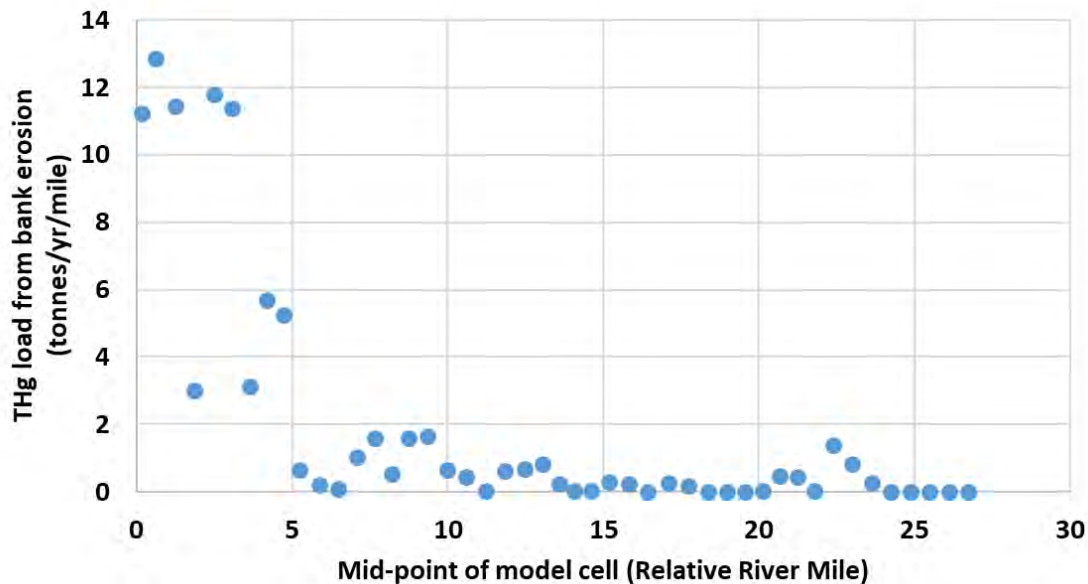


Figure 37. Estimated THg loads from bank erosion in model cells. Values are assumed to be the overall averages for the duration of the simulation from 2006-2014. Each point is the rate for a given model cell whose mid-point is given on the x-axis.

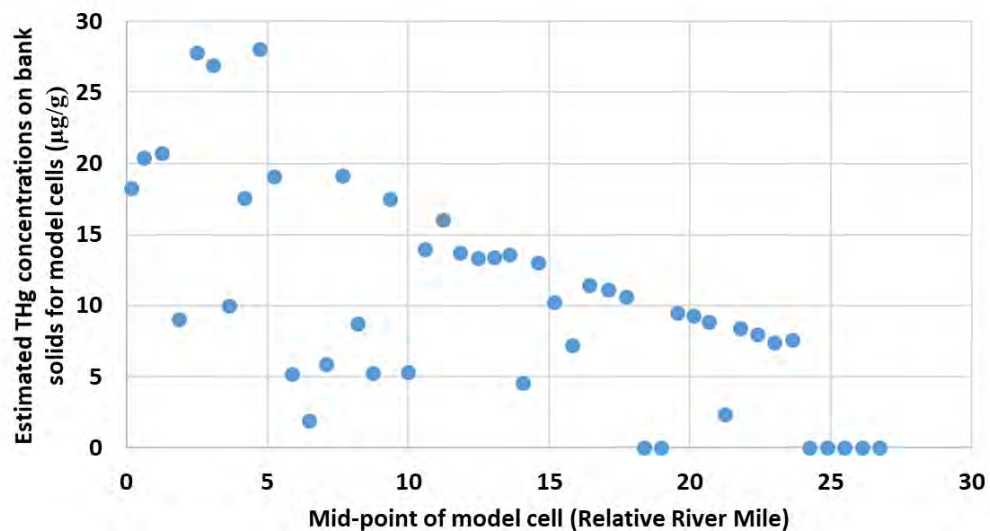


Figure 38. Estimated THg concentrations on bank solid in model cells. Each point is the estimated concentration for a given model cell whose mid-point is given on the x-axis.

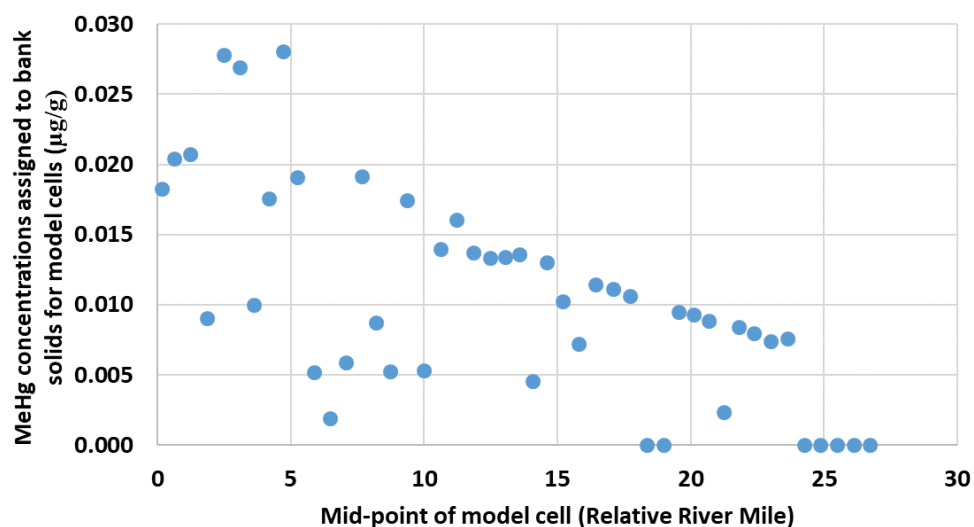


Figure 39. MeHg concentrations assigned to bank solids for each model cell. Each point is the concentration for a given model cell whose mid-point is given on the x-axis. Values were assigned assuming 0.1% of THg as MeHg.

7.4.2 Bank Leaching

The potential exists for dissolved transport of inorganic Hg and MeHg from banks to the river. An analysis by Dyer (2015a, 2014) initially estimated that bank leaching could represent 1-5% of the Hg load to the river system that is relevant to bioaccumulation, later increasing the estimate to 5-15%. Dyer (2015a) estimated a storm flow contribution of 7400 -11090 g THg/yr for RRM 0-10. The volume of water that would flow into bank interstitial spaces and then leach out was estimated and then multiplied by the estimated leachate concentration. It was assumed by Dyer (2015a) that the bank had a porosity of 25% and ratio of 1:2 or 1:3 for the rise in water level relative to the horizontal incursion of water seeping into the bank. The wetted volume was assumed to be a triangular wedge extending 10 miles in the direction of flow. Dissolved THg leachate concentrations for the three storm events were assumed to be 30,000, 56,000 and 68,000 ng/L, respectively, based on DGT probe data. The lower estimate of 7400 g/year from RRM 0-10 was used for this analysis.

Inputs for individual D-MCM cells were estimated by assuming that the annual bank leaching rate declined with distance from RRM 0 with a decay constant of -0.06 per mile. This is the decay rate estimated for THg in bank solids with distance from RRM 0 by J. Pizzuto, and it was assumed leachate concentrations would follow the same spatial pattern as solid phase concentrations. The leaching rate at RRM 0 was calculated to give a total of 7400 g/yr when integrated from RRM 0 to RRM 10 with a decay rate of -0.06 mi^{-1} . The leaching rates for individual cells were then determined by integrating over the length of each cell.

Estimated inorganic Hg(II) leaching rates for individual cells were assumed to be constant for the duration of the simulation. A future improvement would be to scale leaching rates as a function of the hydrograph such that rates are greater during or shortly after periods of greater flow. As discussed later in the report, the current approach may overestimate the importance of bank leaching as a source of Hg during low flow periods. In the absence of data for MeHg concentrations in leachate, it was assumed that MeHg concentrations in were 0.01% of THg in leachate. Estimated bank leaching rates for each model cell are provided in Appendix B.

7.4.3 Lycra Company Site Inputs

The Lycra Company Site was assigned a THg loading rate to the South River of 1 g/day at all times. This was a coarse estimate for base flow conditions from J. Dyer (2015b), who also described the potential for greater releases under stormflow conditions, and during sewer cleanup activities. THg loading from the Lycra Company site has been reduced in recent years (Figure 40). MeHg loads from the Lycra Company site were assumed to be 0.01% of THg loading.

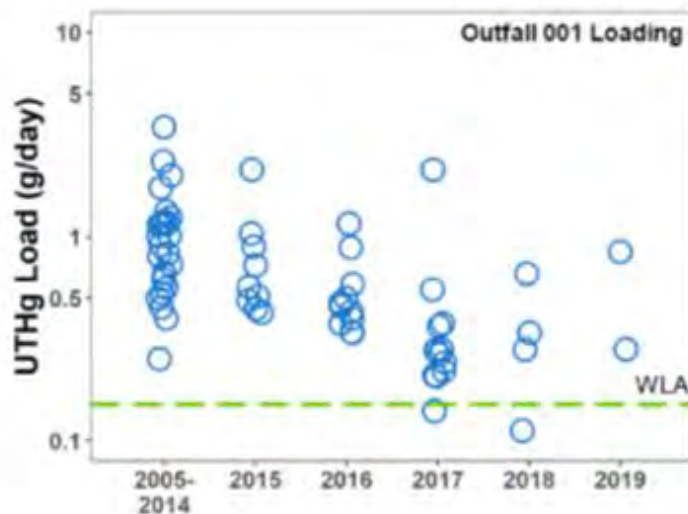


Figure 40. Estimated loads of unfiltered Hg at Outfall 001, Lycra Company site. Figure provided by N. Grosso. WLA = waste load allocation.

7.4.4 Upstream South River and Tributary Loads

Mercury loads from the South River (upstream) and tributaries were estimated by multiplying inflows by estimated Hg concentrations. Water inflow rates to the model domain from the upstream South River and tributaries are described in Section 7.2. Concentrations of THg entering the upstream segment of the model from the South River were estimated using a regression relating THg concentration to flow, and allocating daily concentrations so the average load for the overall simulation matched the average at RRM 0. In the absence of data characterizing tributary Hg concentrations, values estimated for the South River upstream inflows were also assigned to tributaries.

7.4.5 Groundwater Advection

Dissolved inorganic Hg and MeHg were transported in simulations from sediments to overlying water via advection and diffusion. Groundwater advection rates were estimated as described in Section 7.2. The Hg concentrations predicted by the model in sediment porewater were used in combination with groundwater flows to estimate advective transport from sediments to the water column.

7.5 Food Web Structure and Fish Diets

The food web in D-MCM simulations was set up with the compartments shown in Figure 41. This configuration was largely based on a previous application of the US EPA's BASS model to the South River food web by URS (2012). Growth rates, fish condition and fish diets were calibrated for smallmouth bass, redbreast sunfish and common shiner, using information from Reese (2015). Species-specific bioenergetics parameters from the Wisconsin Bioenergetics

Model were used for smallmouth bass (Hanson *et al.*, 1997). In the absence of bioenergetics parameters specifically for redbreast sunfish and common shiner, bioenergetics parameters for bluegill and alewife were used for these species, respectively. Additional information is provided in Appendix C.



Figure 41. Food web compartments in D-MCM simulations in the South River

8 MODEL CALIBRATION RESULTS

This report chapter describes the calibration of the model to conditions from 2006-2014, in terms of solids and inorganic Hg in water and sediments, and MeHg in water, sediments and the food web.

8.1 Model Calibration of Solids Concentrations and Fluxes

Simulated total suspended solids (TSS) concentrations were compared to observations from 2006-2014 from RRM 0.2 to 16.5 in Figure 42 and Figure 43. Features of the model results include:

TSS concentrations:

- The model reasonably represented the magnitude of TSS concentrations under lower flow conditions (Figure 42), and median TSS concentrations on the order of 4 mg/L (Figure 43). Observed and predicted TSS concentrations in the South River did not show clear changes with distance downstream of Waynesboro. Average TSS levels are not represented as well (Figure 43) suggesting the model is reasonably reflecting baseflow conditions but is not matching some high TSS levels that occur during storm events.
- The lack of agreement between the model and TSS observations on some occasions (Figure 42) reflects the fact that the model assigns a single TSS value for a given flow, *i.e.* TSS depends only on the flow at the time TSS is being predicted, while field data clearly show a wide degree of variability in the relationship between TSS and flow (Figure 31). TSS concentrations depend on a range of factors, including hydrologic, bank, and sediment bed conditions prior to the time that TSS is measured. It was beyond the scope of this model exercise to develop a more realistic expression to predict TSS. The goal of the TSS modeling was therefore to reasonably represent the general magnitude of observations under base flow conditions, while reflecting the observed large increases observed on some occasions that were likely associated with high flow events.

Sedimentation rates:

- Model simulations were adjusted to produce an average solids accumulation of 2 mm or less in model cells for the overall simulation period from 2006-2014 (Figure 44). This was the result of accumulation in most years and erosion in a few years (*e.g.* 2006, 2010, 2011). The estimated mass of solids supplied by bank erosion was sufficient to increase average TSS concentrations by roughly 20 mg/L, which is not evident in the field data. This suggests that the rates of bank erosion are over-estimated and/or large quantities of eroded solids are transported during relatively infrequent high flow events.
- True rates for solids settling, resuspension and net accumulation along the river are not known for the calibration period from 2006 -2014. Pizzuto *et al.* (2006) assumed no net sedimentation in the long term in the river, which is reflected in model results presented here. It is possible though that the sedimentation from 2006-2014 could be different than the longer term (decadal) average. An alternative calibration with more settling and less

resuspension deposited the equivalent of roughly 3 cm of solids per year over the entire river bed for 5 miles downstream of the former DuPont facility, which is inconsistent with observations.

- Given the uncertainty regarding particle dynamics, remediation scenarios were simulated for both model calibrations.

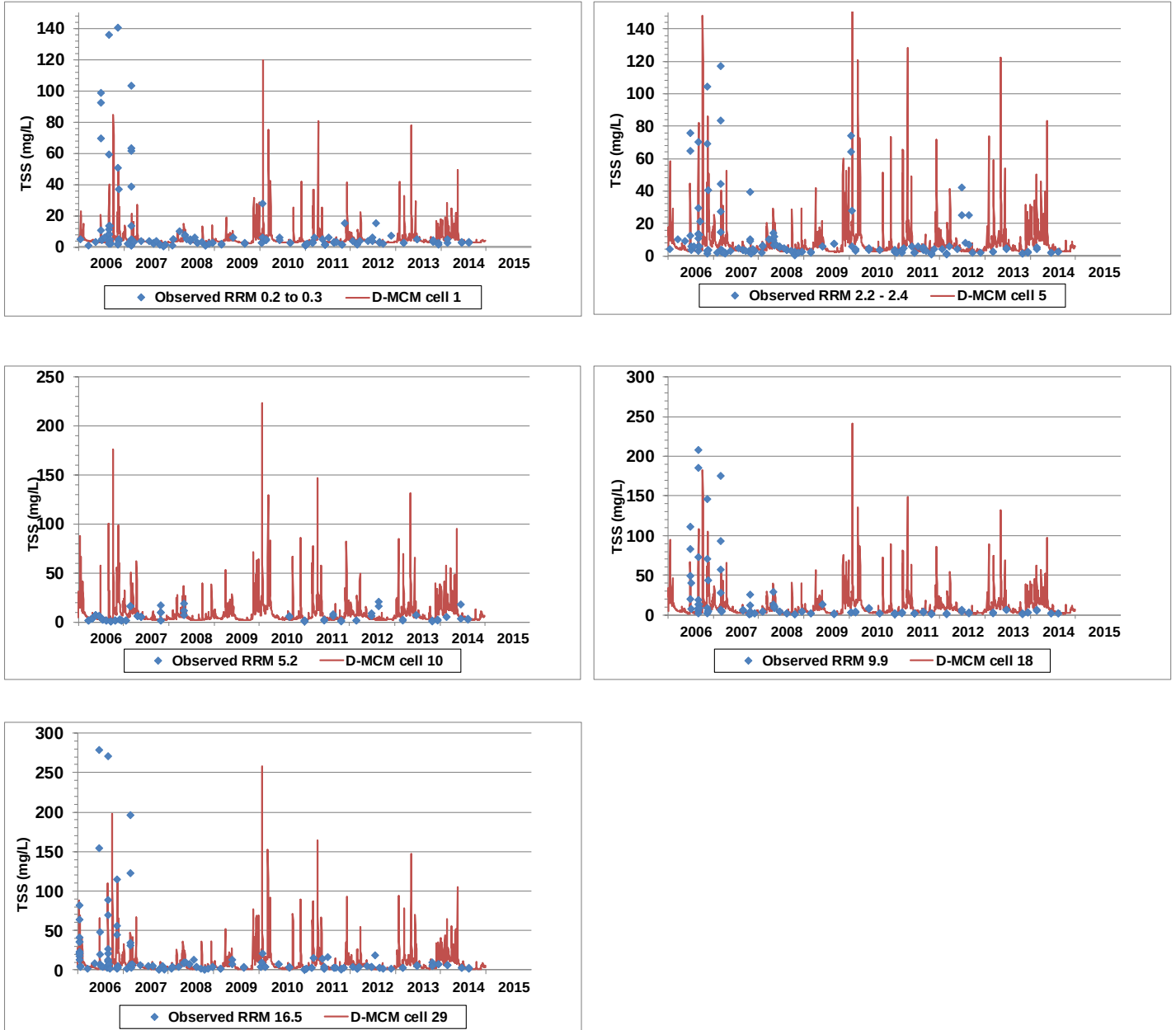


Figure 42. Observed and simulated TSS concentrations from RRM 0.2 to 16.5 from 2006-2014. Observations derived from Flanders (2016).

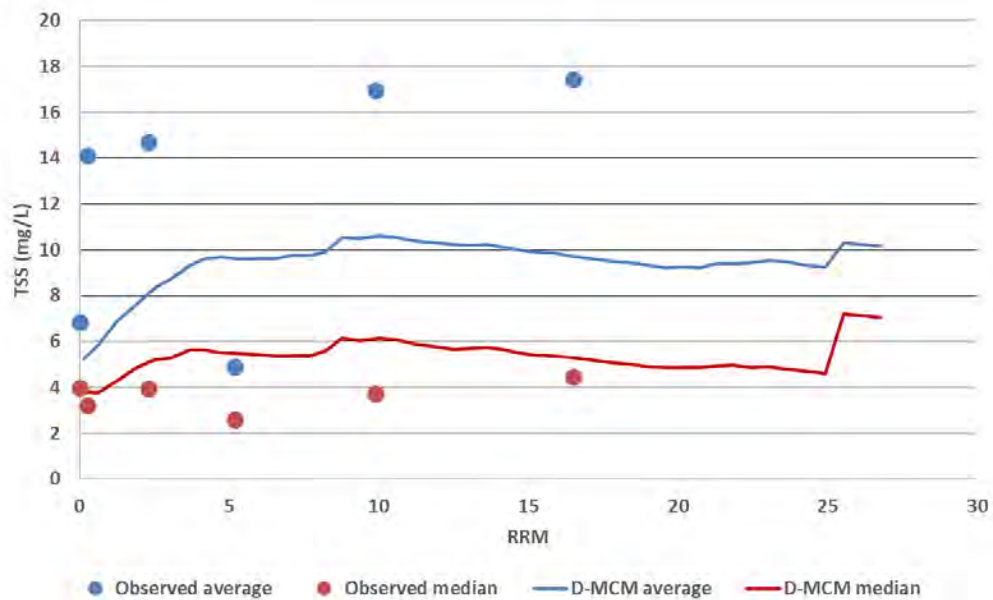


Figure 43. Average and median observed and simulated TSS concentrations in the South River from 2006-2014. Observations derived from 2006-2014 (Flanders, 2016).

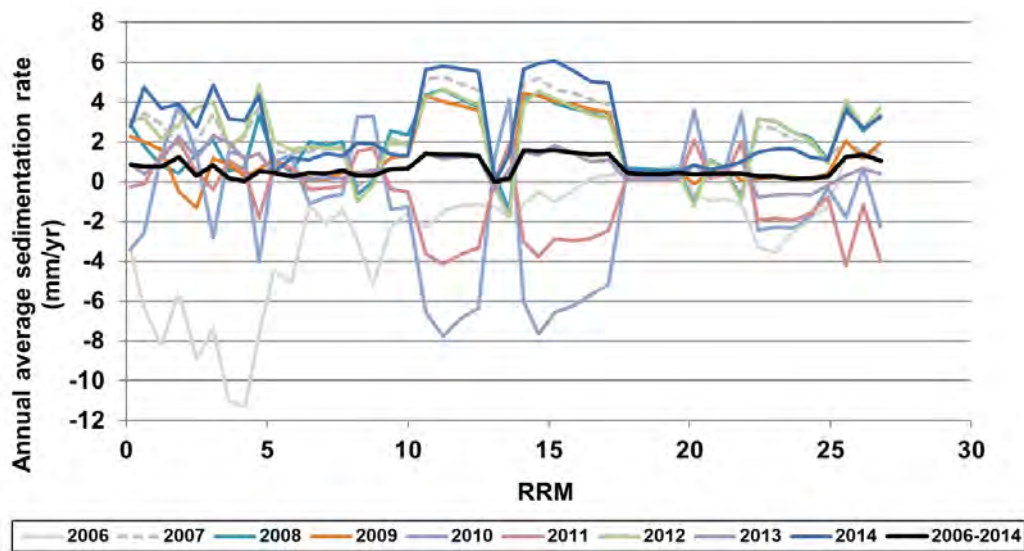


Figure 44. Simulated sediment accumulation rates in the South River from 2006-2014. Each line represents model results for a different year, except the black line which represents the averages overall for 2006-2014.

Particle turnover rates in sediments:

The simulated rapid supply of particles to the sediment bed in the first 5 miles downstream of the former DuPont facility would result in particle residence times in the top 2 cm layer of surface sediments on a scale of months to years (Figure 45). An outcome of the relatively rapid turnover of solids throughout the modeled river reach is that the surface sediment bed has the potential to respond to changes in Hg loading on a scale of years. For example, a well-mixed compartment would purge about 95% of a chemical in ~6 years if the residence time was two years, and 8-17 years if the residence time was 3-6 years (assuming simple first-order responses). Longer residence times would mean that more time would be needed for sediments to recover once excess Hg loading stopped. The South River does not exhibit steady rates of losses that would be associated with a smooth exponential response. Nevertheless, these results imply that while there may be localized areas that are slow to recover from contamination that occurred decades ago, the ongoing supply of Hg contamination is preventing the recovery of the overall system.

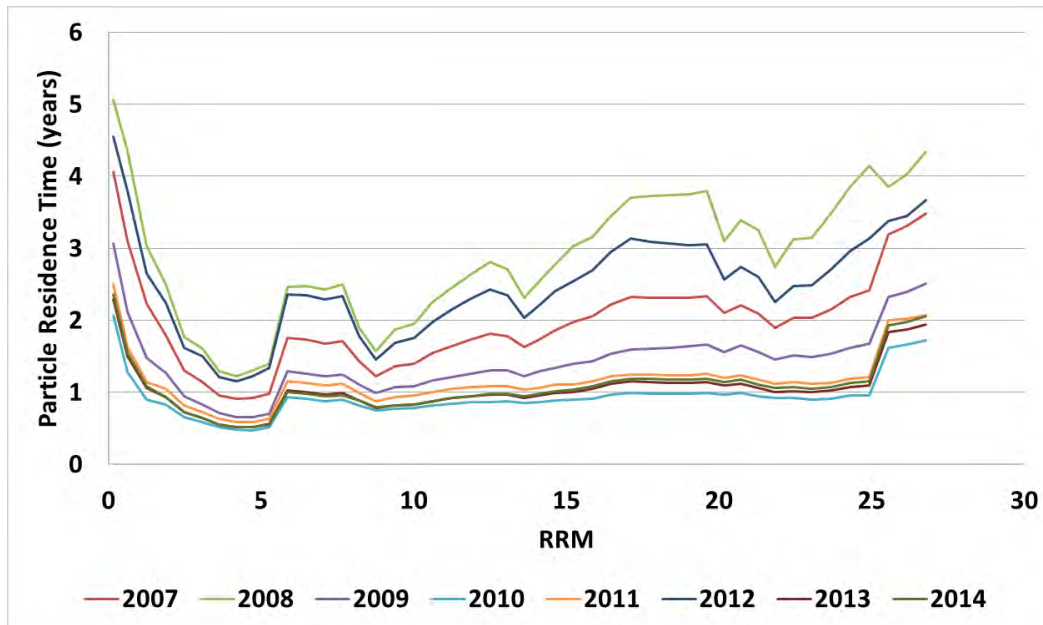


Figure 45. Predicted solids residence times in surface sediments (0-2 cm) from 2006-2014

8.2 Model Calibration of Inorganic Hg Concentrations

Simulated and observed concentrations of unfiltered THg in river waters are shown in Figure 46, by river mile. Each panel shows median values at different locations for a given year. The general magnitude and spatial rise and fall of THg concentrations observed in water is reflected in the simulations. Peak concentrations of unfiltered THg in surface waters tended to occur between RRM 5-10 in the observations and simulations, gradually declining downstream. Model simulations predict a sharp decline in water column THg concentrations after the junction with the North River. No water column observations were identified for the model

calibration period downstream of the junction with the North River, but this decline was evident in earlier studies (Figure 8).

Observed and simulated filtered THg concentrations in surface waters are shown in Figure 47, increasing downstream of the former DuPont facility. Filtered THg concentrations between RRM 0 and the confluence with the North River do not reach a clear peak followed by a downstream decline, in simulations or observations.

Observed and simulated particulate THg concentrations in surface waters are shown in Figure 48. While the model captures observed increases for particulate THg in water, simulated concentrations tend to be underpredicted in the vicinity of RRM 5-10.

Predicted and observed THg concentrations in the unfiltered, filtered and particulate phases are also shown at selected locations as a function of time in Figure 49. These results demonstrate that the model is capturing the magnitude and in some cases seasonality of observations. Observations and simulations both display a high degree of variability in water column THg concentrations, likely related to high flow conditions that mobilize solids and associated mercury.

Predicted and observed THg concentrations in sediments in 2006 are shown in Figure 50. Observed concentrations increase downstream of the Lycra Company site and exceed 10 $\mu\text{g/g}$ within a few miles. Model results reflect this trend. Given that (1) initial sediment concentrations in simulations were assigned values based on field data, and (2) sediment concentrations can take years to respond in the model, it is not surprising that the model results for THg in sediments are close to observations in 2006. Simulated sediment THg concentrations are also shown for 2014 in Figure 50, with concentrations declining in most locations relative to 2006. The exception was the first few miles downstream of the Lycra Company facility, where predicted concentrations increased from 2006 to 2014.

The model also reflected limited observations of porewater Hg concentrations (Figure 51). To achieve these porewater results in simulations, solids/dissolved partitioning of inorganic Hg(II) had to be manually adjusted higher downstream of RRM 8 to produce the observed decline in porewater Hg(II) concentrations downstream of RRM 8 - 10. No data were identified that would explain such a shift in partitioning, if that actually occurs.

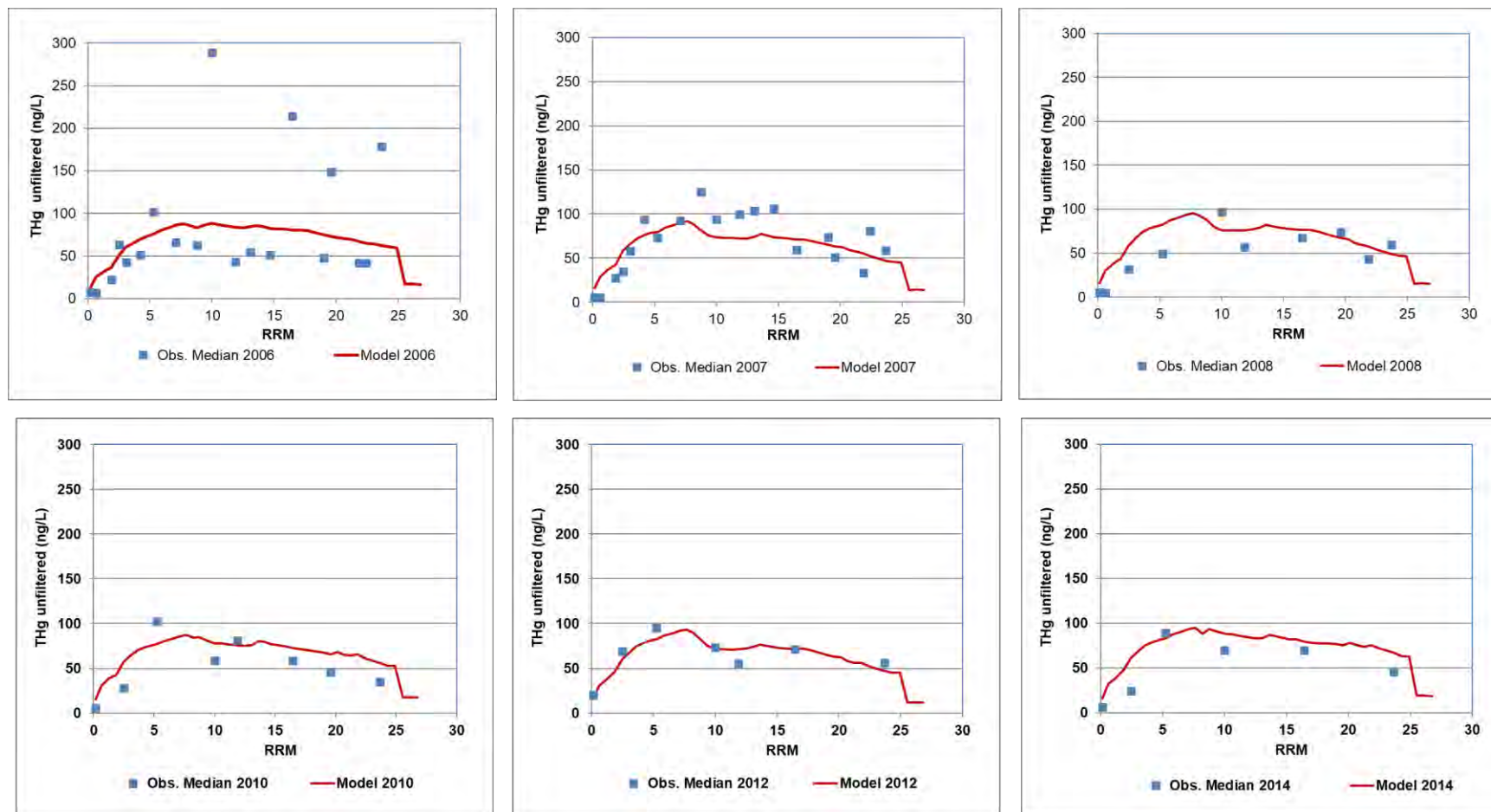


Figure 46. Simulated and observed concentrations unfiltered THg in surface waters. Values are medians for each year at different locations. Observed estimates derived from Flanders (2016).

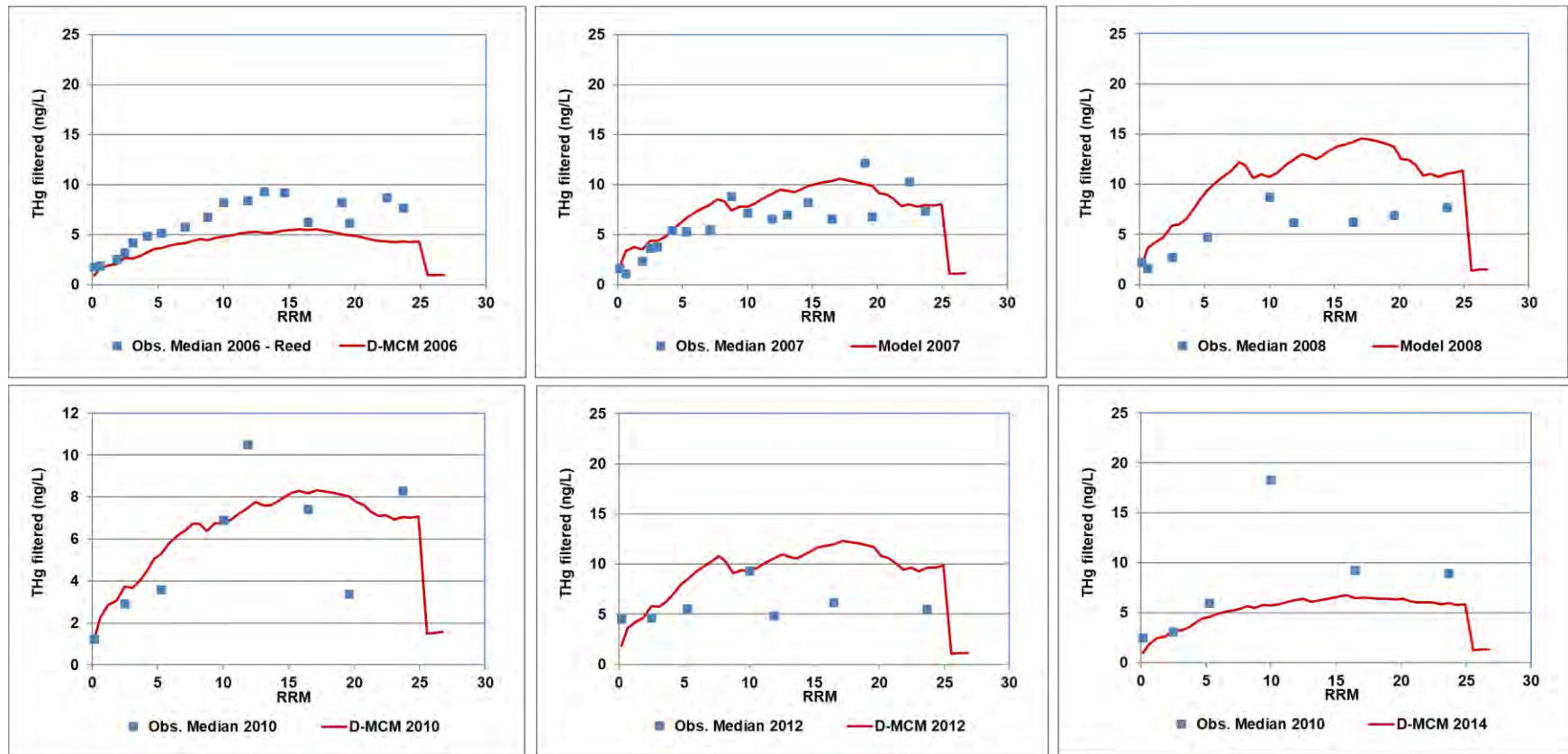


Figure 47. Predicted and observed concentrations of filtered THg in surface waters. Values are medians for each year at different locations. Observed estimates derived from Flanders (2016).

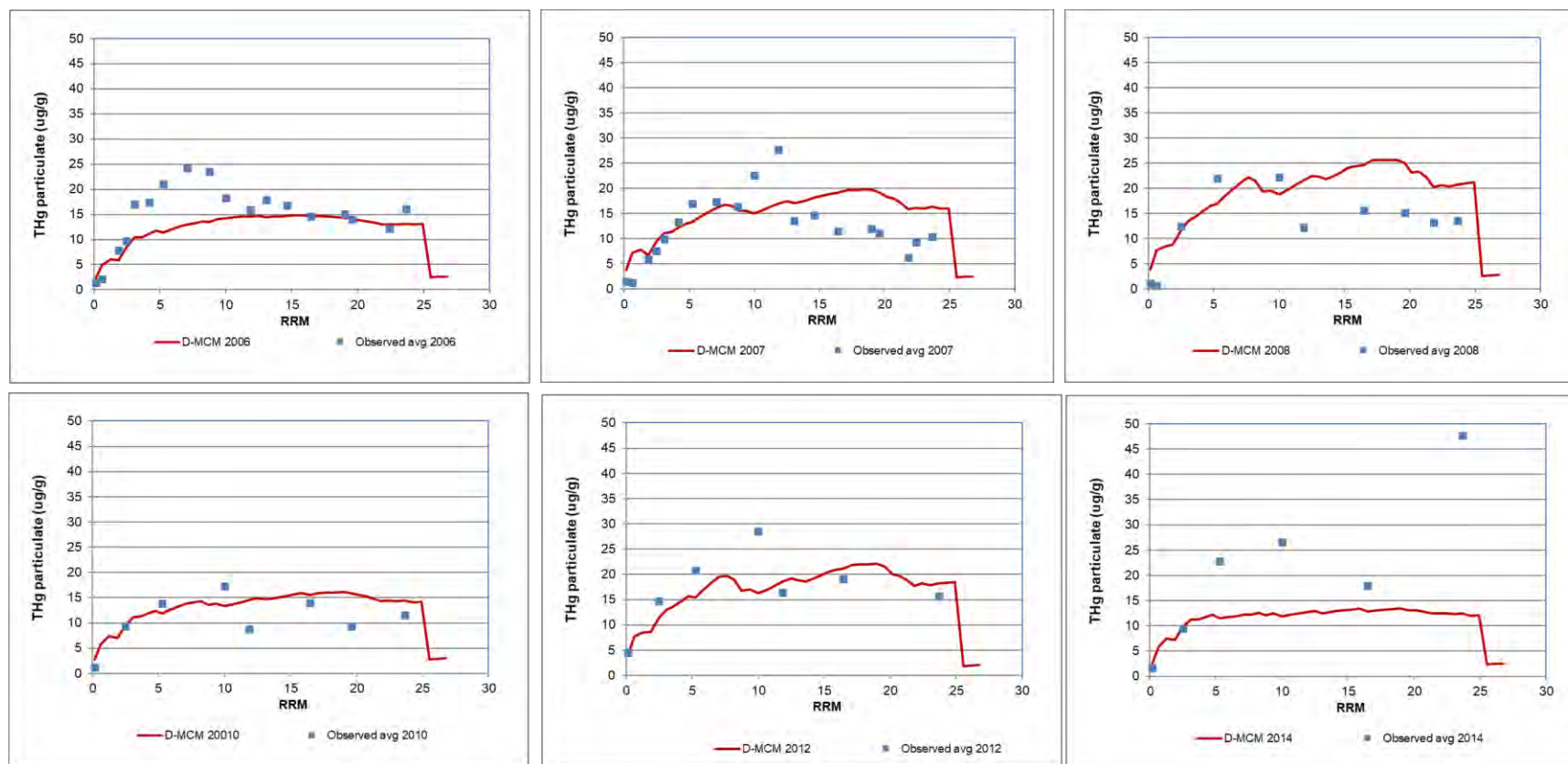


Figure 48. Simulated and observed concentrations of particulate THg in surface waters. Values are medians for each year at different locations. Observed estimates derived from Flanders (2016).

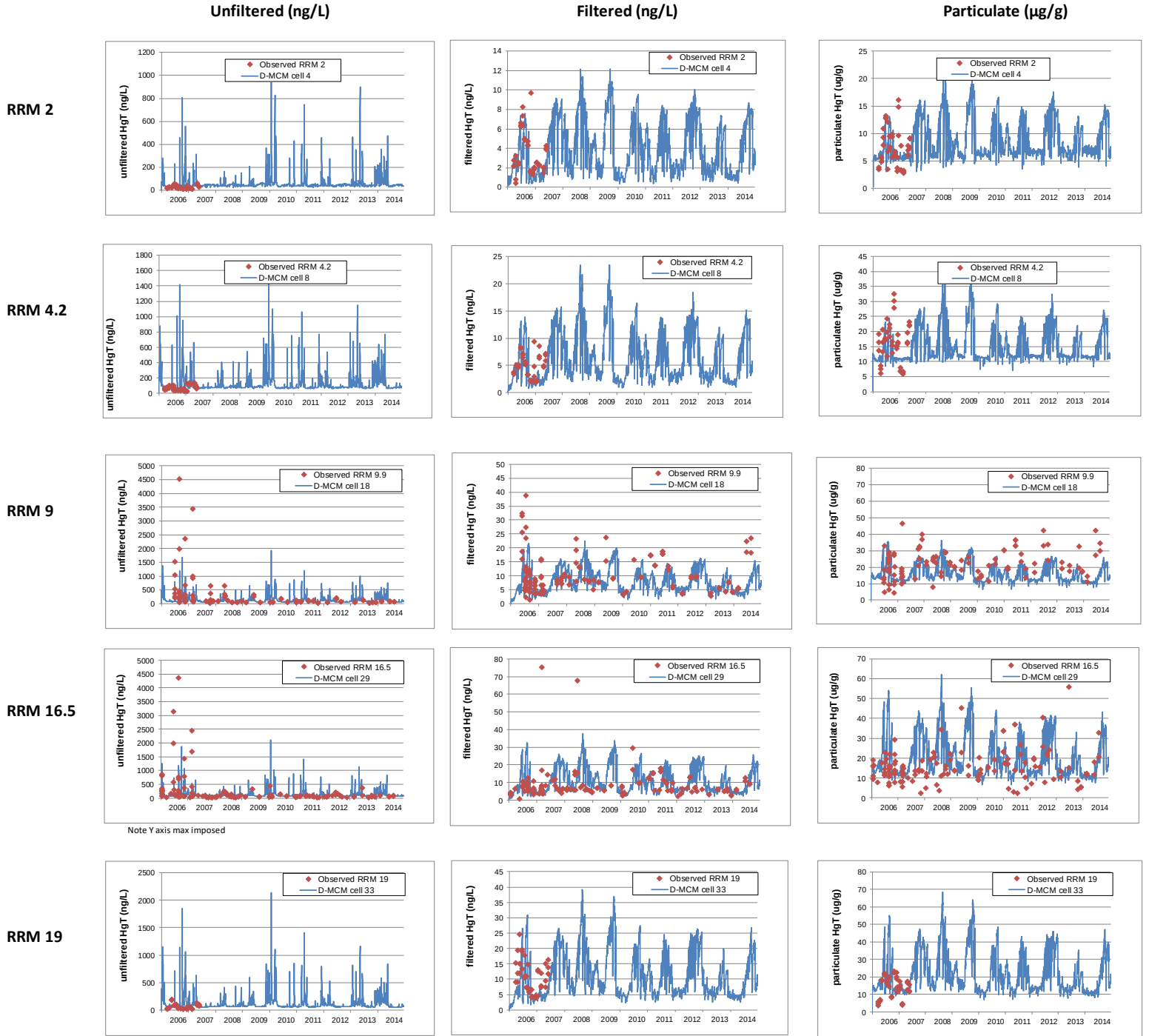


Figure 49. Simulated and observed concentrations of THg in surface waters versus time at selected locations in the South River. Observed estimates derived from Flanders (2016).

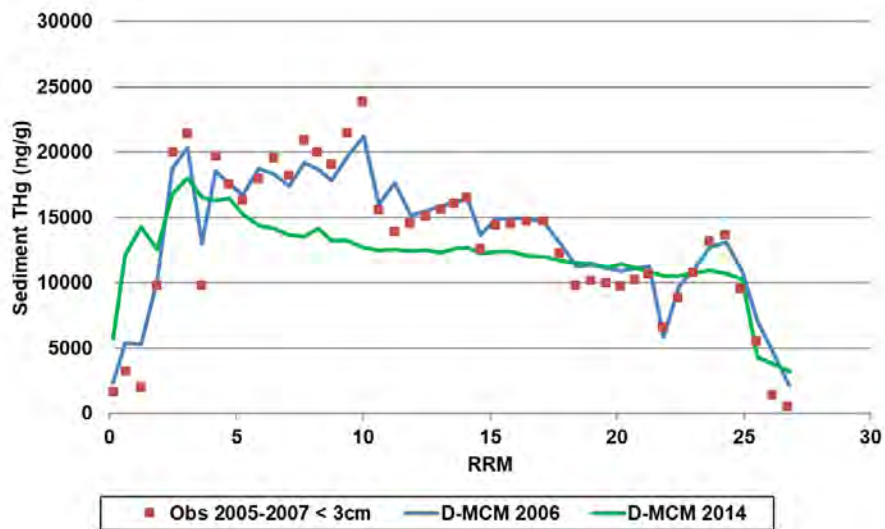


Figure 50. Simulated and observed THg concentrations in surface sediments in the South River. Observations are averages from 2005-2007, derived using data from Collins (2018a)

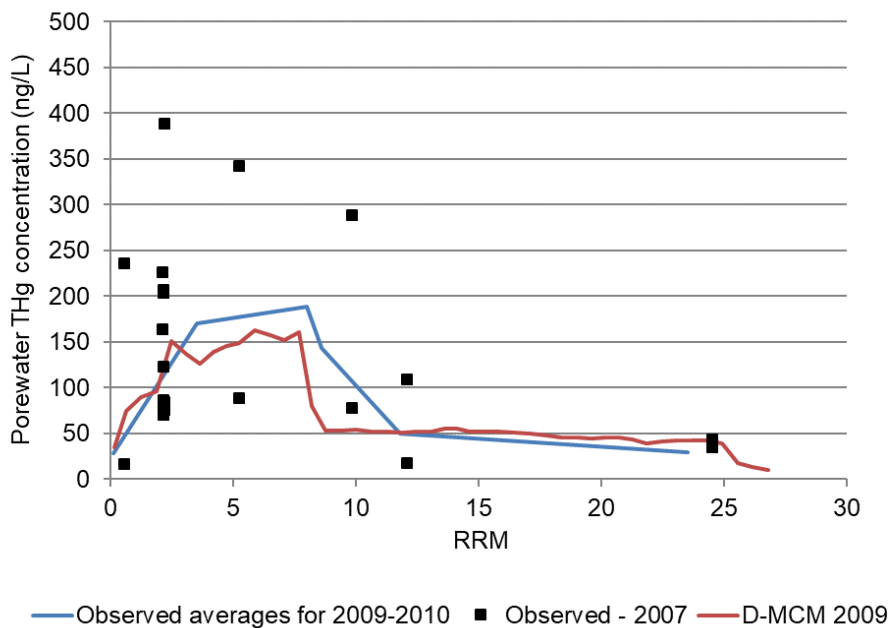


Figure 51. Simulated and observed MeHg concentrations in surface sediment porewater in the South River. 2007 data from Flanders (2017a, 2010). 2009-2010 values derived by D. Hutchinson from Flanders (2017b)

8.3 Model Calibration of MeHg Concentrations

8.3.1 Model Calibration of MeHg Concentrations in Water and Sediments

Simulated and observed median concentrations for unfiltered, filtered and particle phase MeHg for selected years are shown in Figure 52 - Figure 54. The general observed trend of increasing MeHg concentrations in water downstream of the former DuPont facility was captured in the simulations, although the model underpredicted MeHg concentrations in surface waters in 2006 in all phases.

Predicted and observed surface water MeHg concentrations are also shown at selected locations as a function of time in Figure 55. These results also suggest a reasonable model fit to observations, capturing the overall magnitude and variability of MeHg concentrations in surface waters. However, when observations and simulation results are examined on a monthly average basis for MeHg in surface waters, there is clearly more seasonal variation in the field data than in the model results (Figure 56). This is especially evident for April – June when observed MeHg concentrations increase from winter levels while the model does not reach peak concentrations until late summer or early fall. Possible explanations are reviewed in the discussion section of the report.

Average simulated and observed MeHg concentrations in surface sediments (0-2 cm) are shown in Figure 57. Observed concentrations increase downstream of RRM 0 to exceed 50 ng/g by ~ RRM 10 and model results reflect this trend, although simulated sediment MeHg concentrations in 2006 were low (similar to the water column). Reasons have not yet been identified.

Similar to the model results for MeHg in surface waters, averaging on an annual basis masked the tendency of the model to underpredict the seasonal variability of MeHg concentrations in surface sediments (Figure 58, Figure 59). Also similar to the model results for surface waters, simulations underpredicted the pulse in MeHg concentrations in sediments in April-June.

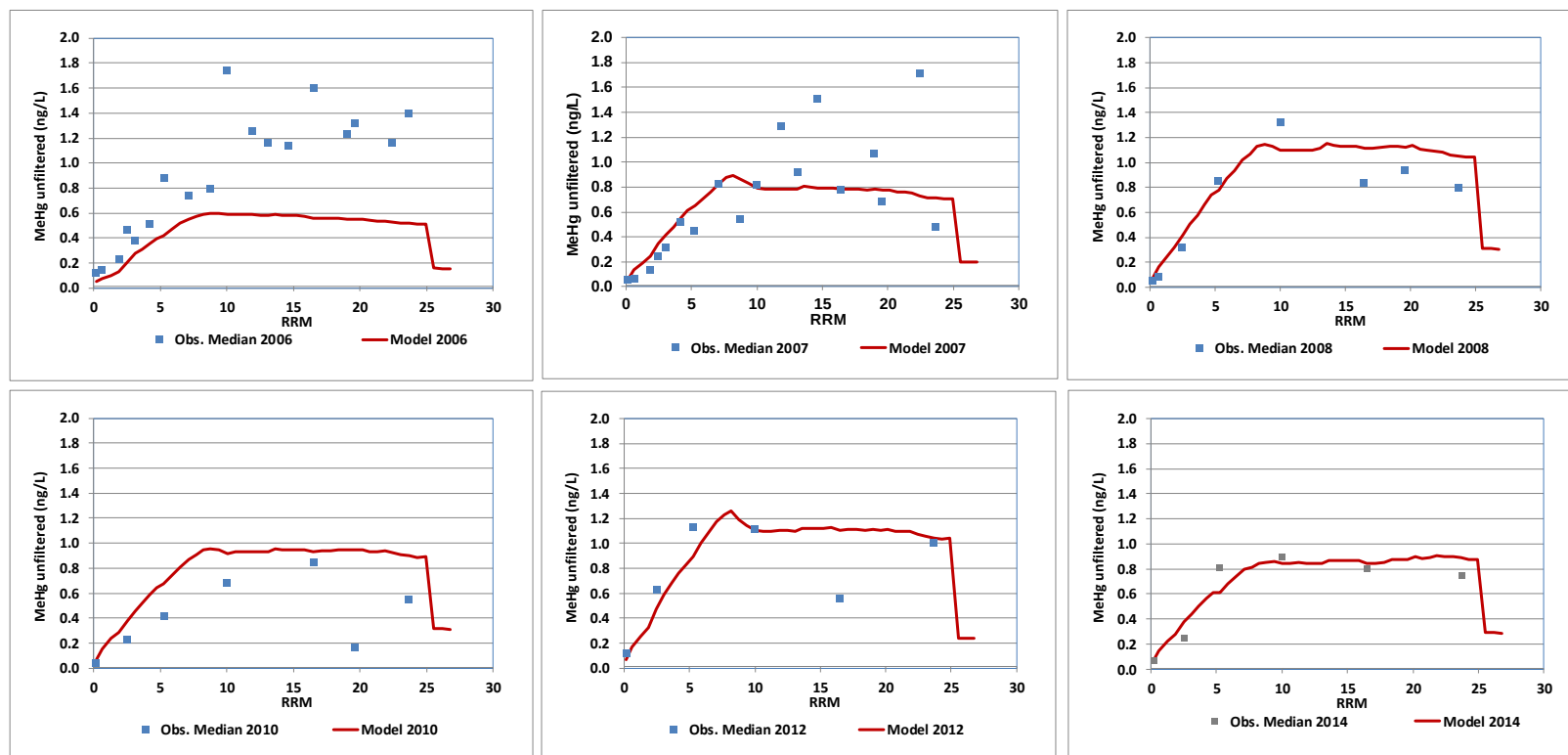


Figure 52. Simulated and observed concentrations of unfiltered MeHg in surface waters. Values are medians for each year at different locations. Observed estimates derived from Flanders (2016).

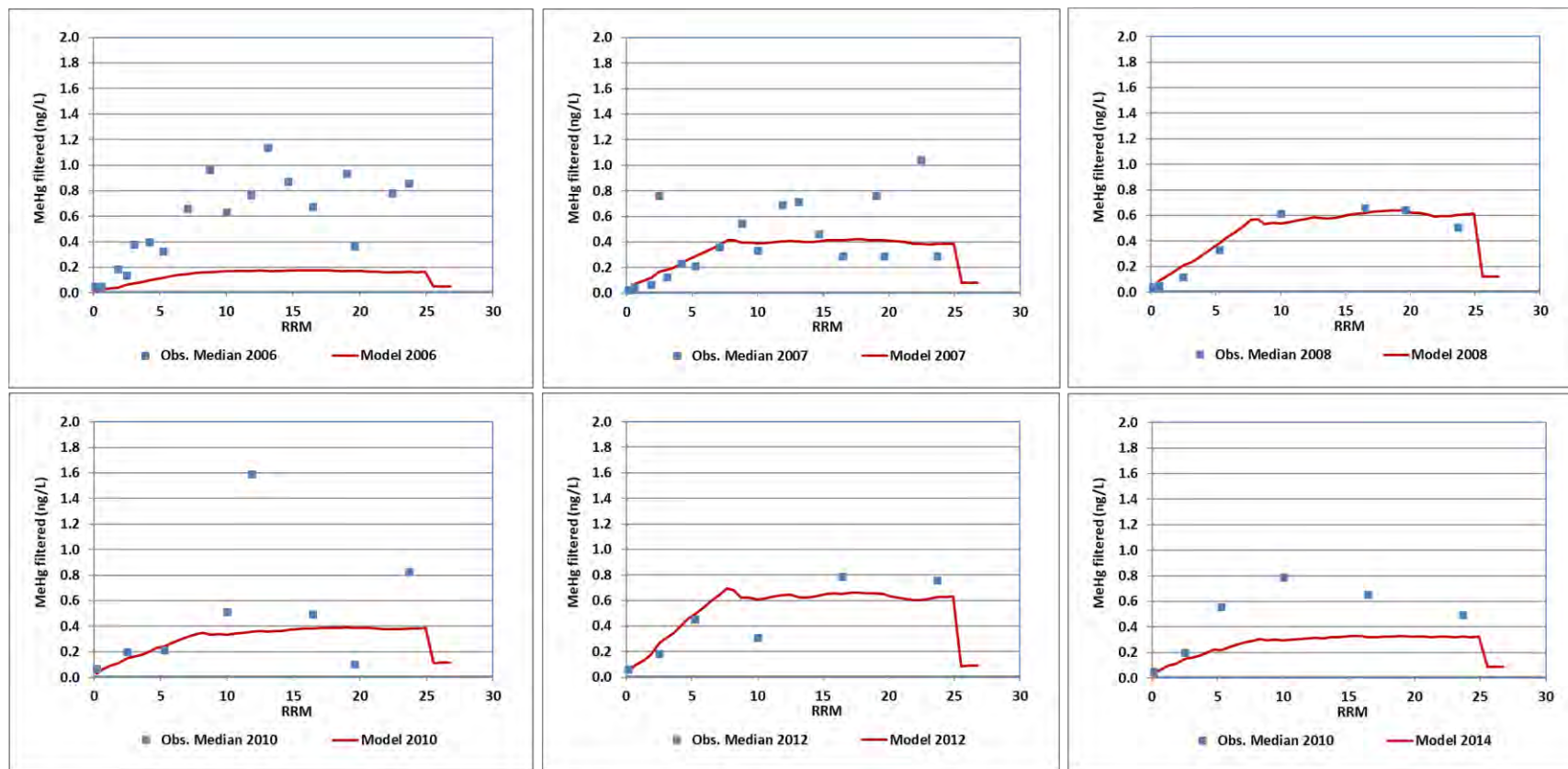


Figure 53. Simulated and observed concentrations of filtered MeHg in surface waters. Values are medians for each year at different locations. Data from Observed estimates derived from Flanders (2016).

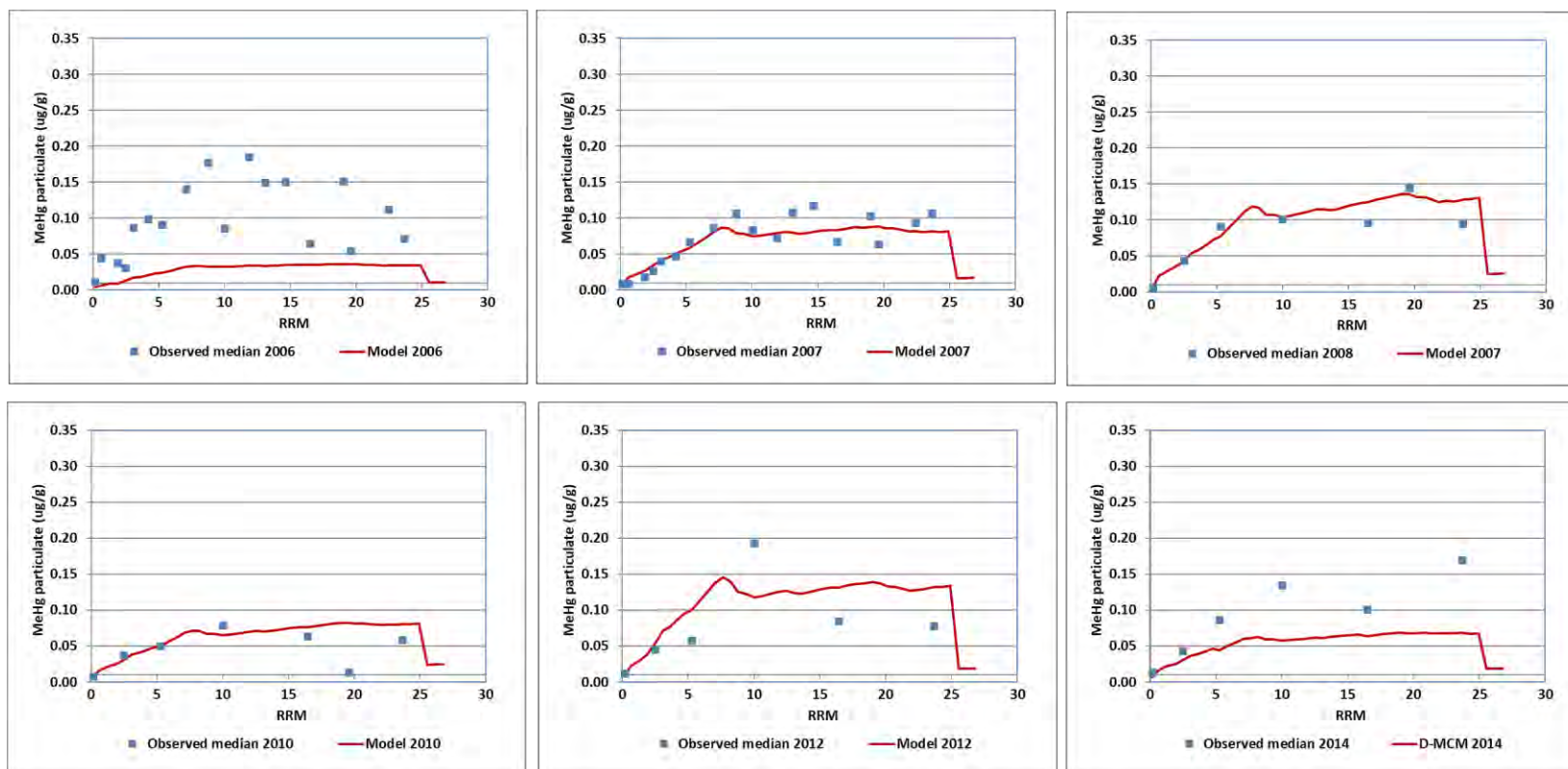


Figure 54. Simulated and observed concentrations of particulate MeHg in surface waters. Values are medians for each year at different locations. Observed estimates derived from Flanders (2016).

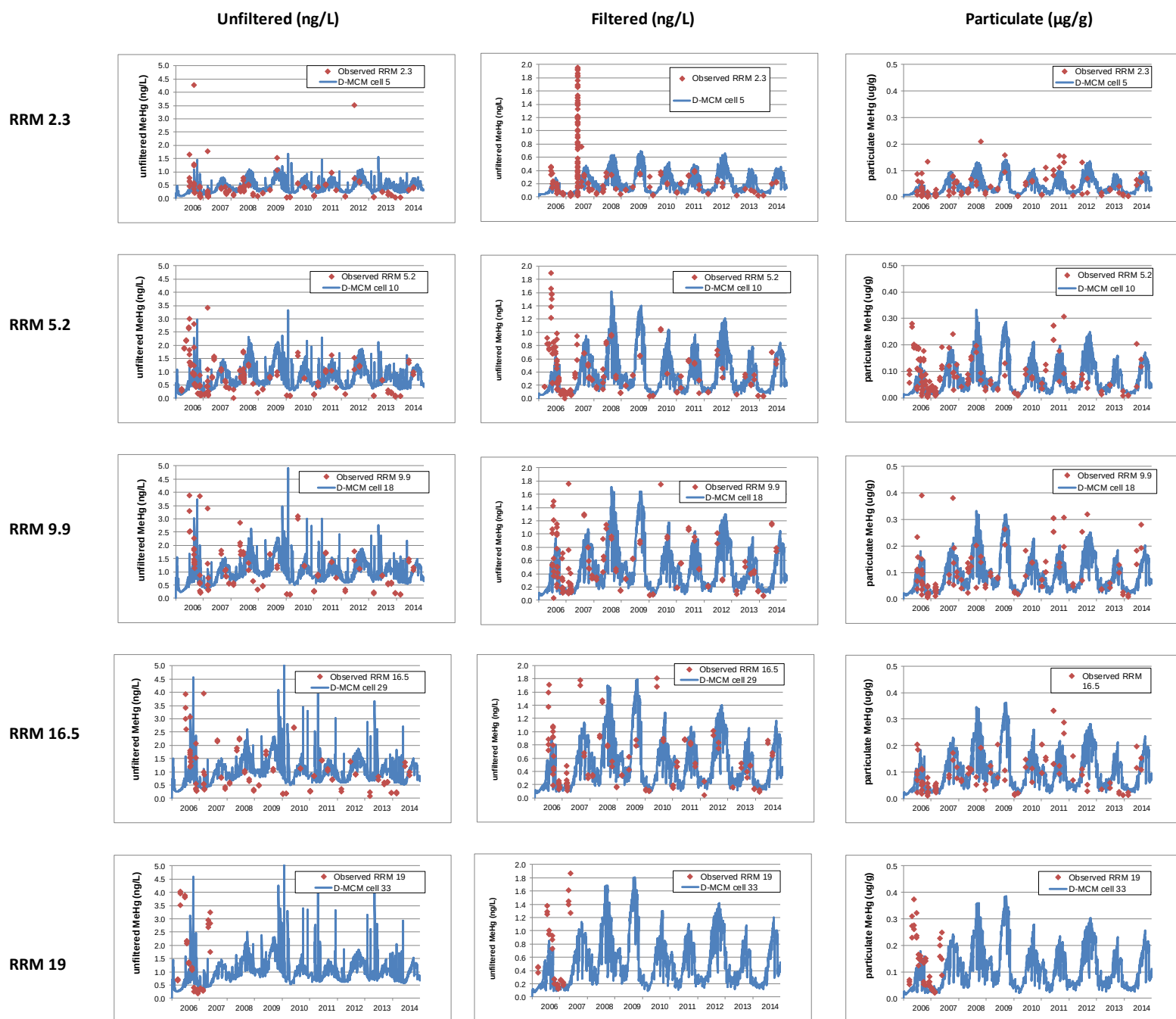


Figure 55. Simulated and observed surface water concentrations of MeHg versus time at selected locations in the South River. Observed estimates derived from Flanders (2016).

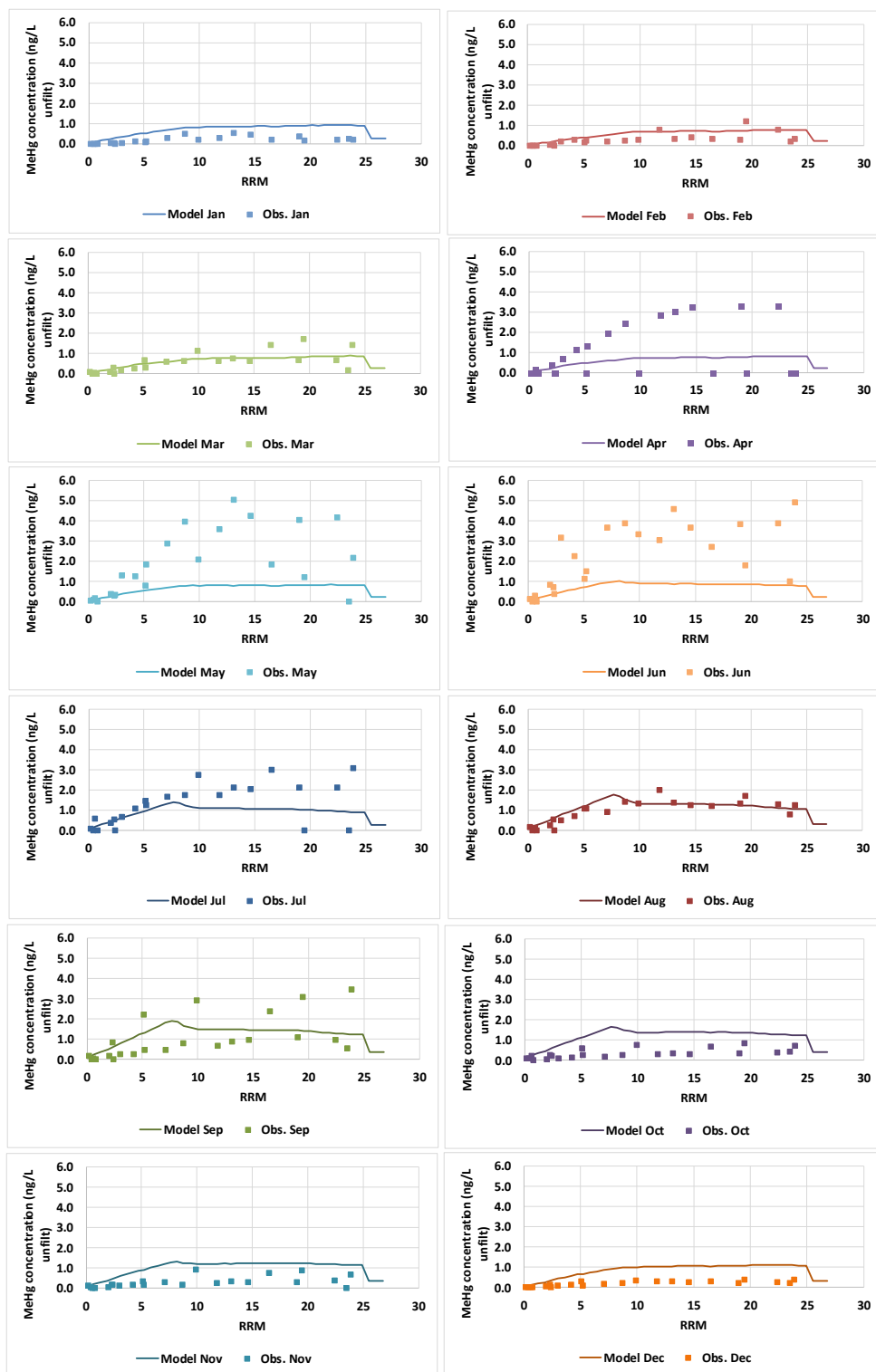


Figure 56. Simulated and observed monthly average concentrations of unfiltered MeHg in surface waters versus river mile in the South River. Simulated values are monthly medians from 2006-2014. Observed estimates derived from Flanders (2016).

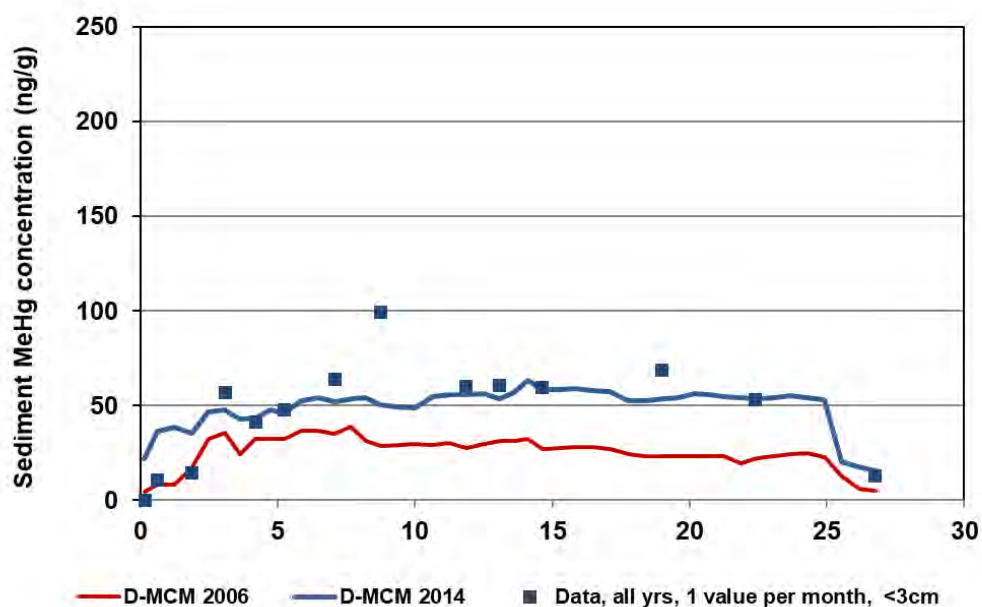


Figure 57. Simulated and observed average MeHg concentrations in surface sediments in the South River. Model averages are based on daily results from 2006-2014. Observations were from 2002-2013, averaged first to obtain an estimate for each month of the year, followed by an averaging of the 12 monthly values to obtain an overall average. Field estimates were derived using data from Collins (2018a).

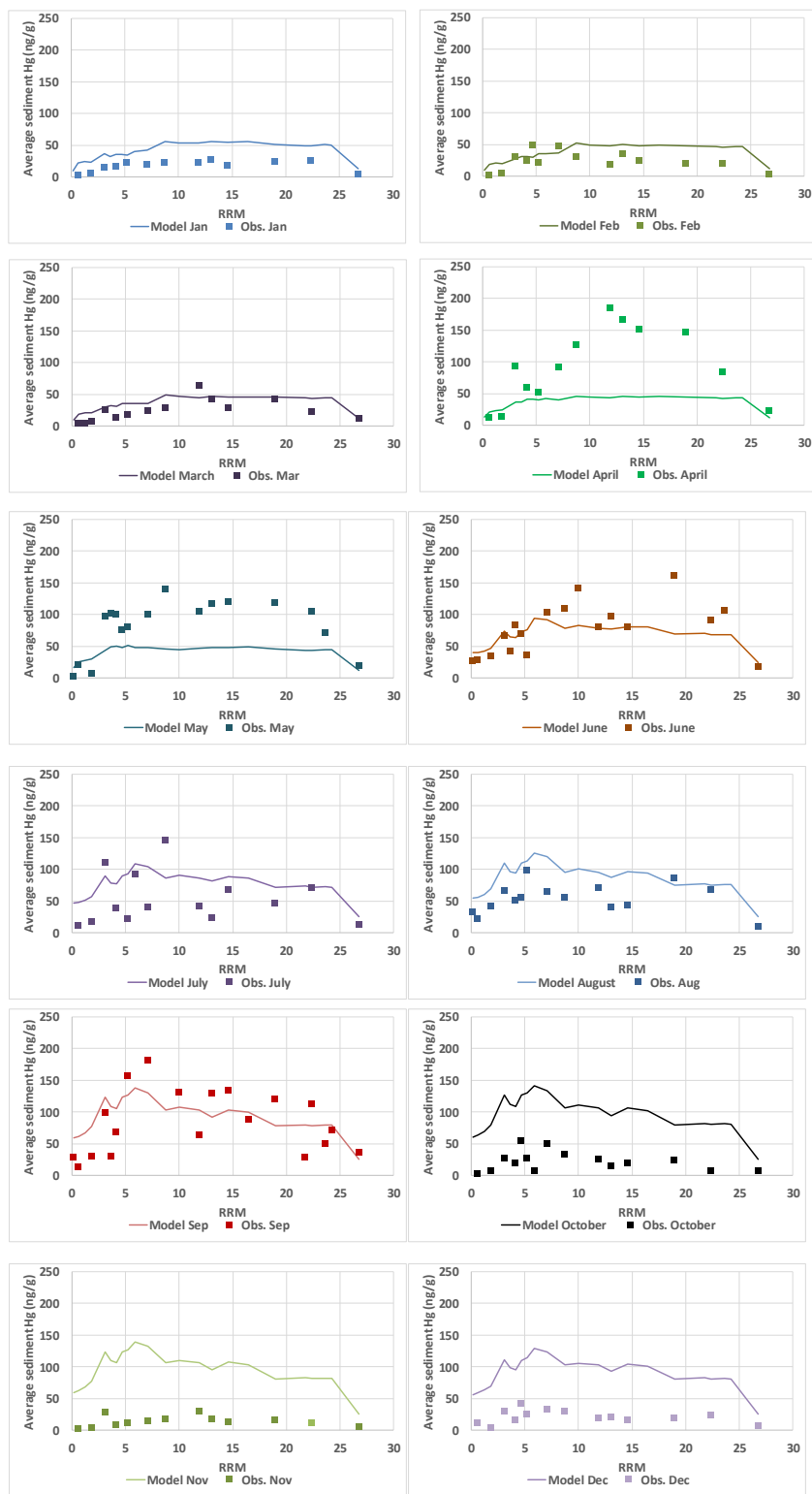


Figure 58. Simulated and observed monthly average MeHg concentrations in surface sediments versus river mile in the South River. Simulated values are monthly averages from 2006-2014. Observations are from 2002-2013, derived using data from Collins (2018a).

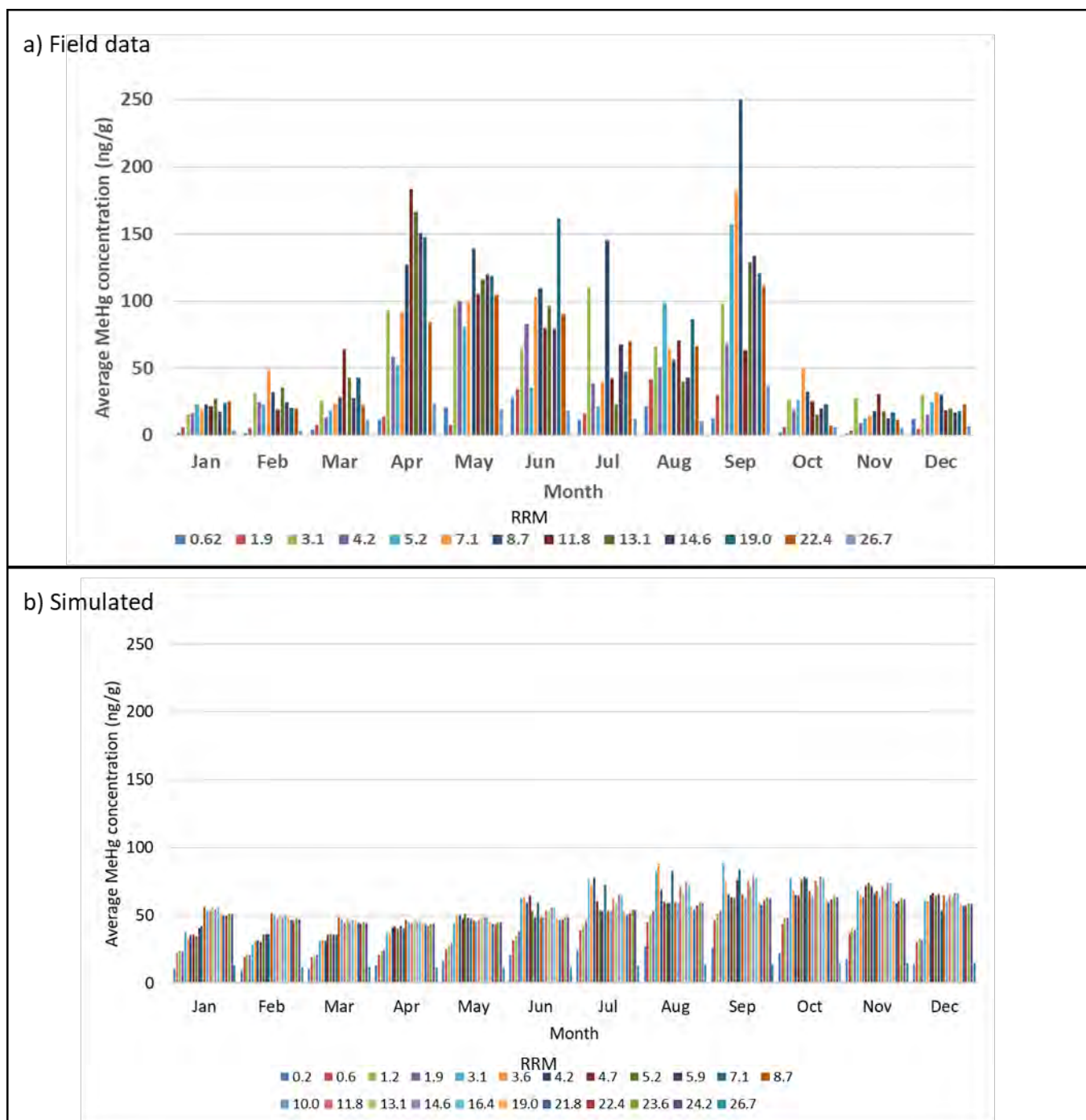


Figure 59. Simulated and observed concentrations of MeHg in surface sediments averaged by month and river mile in the South River. Data derived from Collins (2018a).

8.3.2 Model Calibration of MeHg Concentrations in the Food Web

Simulated and observed MeHg concentrations in the food web are shown as a function of river mile in Figure 60 through Figure 63. The calibrated model reasonably captures the magnitude and spatial patterns of fish concentrations along the river, simulating peak MeHg concentrations in the vicinity of RRM 10-15, consistent with observations for smallmouth bass, red-breasted sunfish, and common shiners (Figure 60 to Figure 62). For fish, all available observations were combined from 2001-2011, assuming MeHg levels in the system were not systematically changing during the simulation period. Model results for the last 5 years of the simulation (2010-2014) were compared to observations to allow conditions to stabilize in the model. MeHg concentration in invertebrates (mayflies, caddisflies, midge and crayfish) were also reasonably simulated (Figure 63). Initial calibrations of the model tended to overpredict MeHg concentrations in common shiners. Clearance rates were increased for MeHg in common shiner to moderate concentration increases simulated by the model.

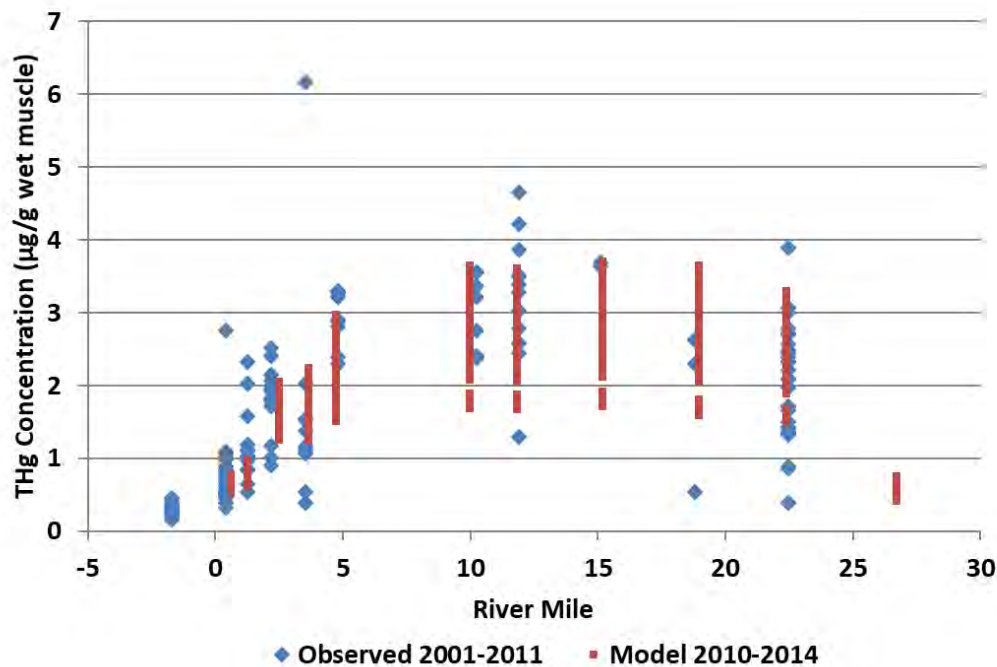


Figure 60. Simulated and observed Hg concentrations in 250-300 mm smallmouth bass. Blue diamonds are individual observations. Red squares are simulated values for any fish in the 250-300 mm length range from 2012-2014. Data from Collins (2016b).

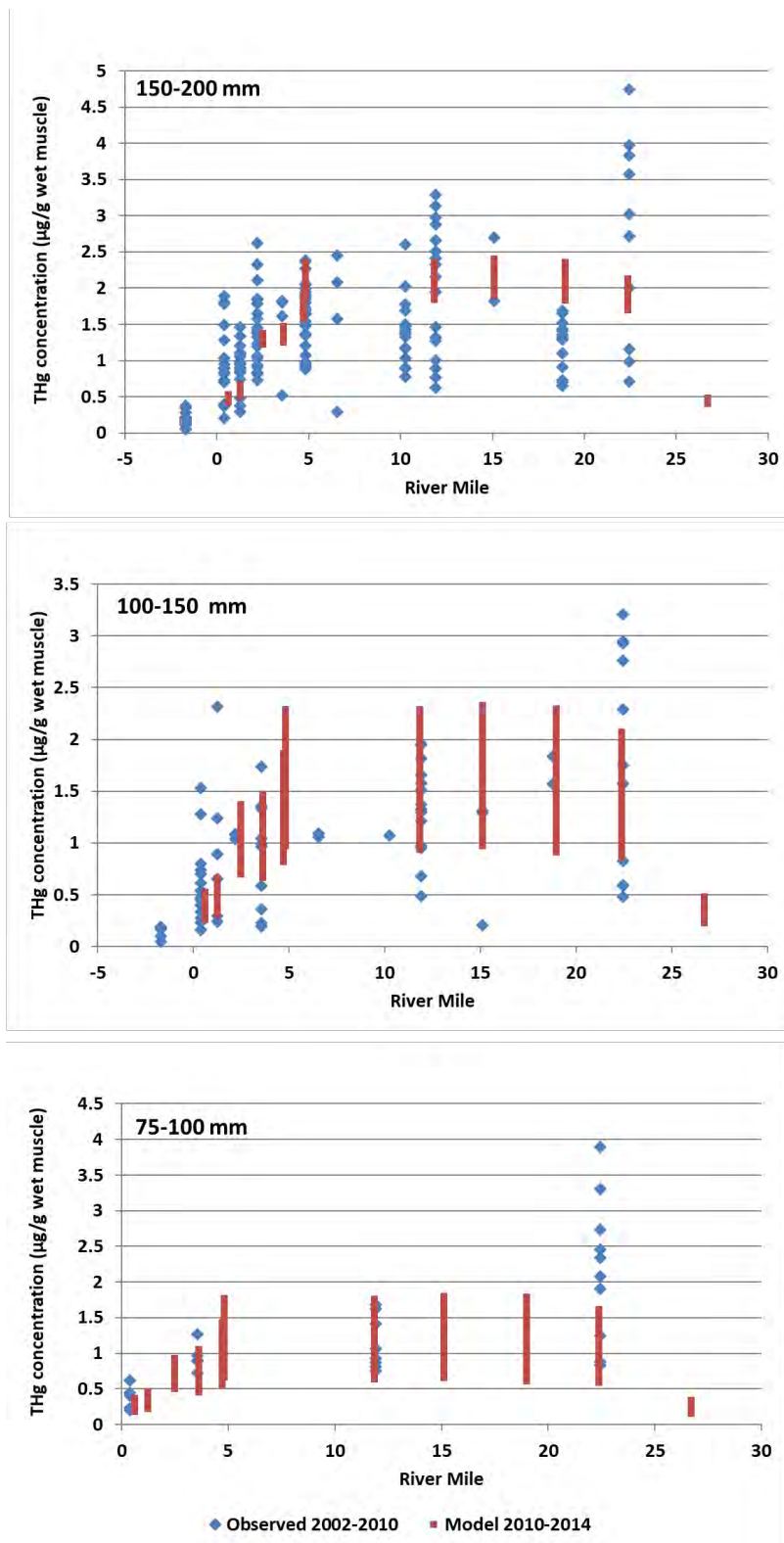


Figure 61. Simulated and observed Hg concentrations in redbreast sunfish for different size categories. Blue dots are individual observations from 2002-2010 (only 2010 for 75-100 mm). Red dots are simulated values for any fish in the identified length ranges from 2010-2014. Data from Collins (2016b).

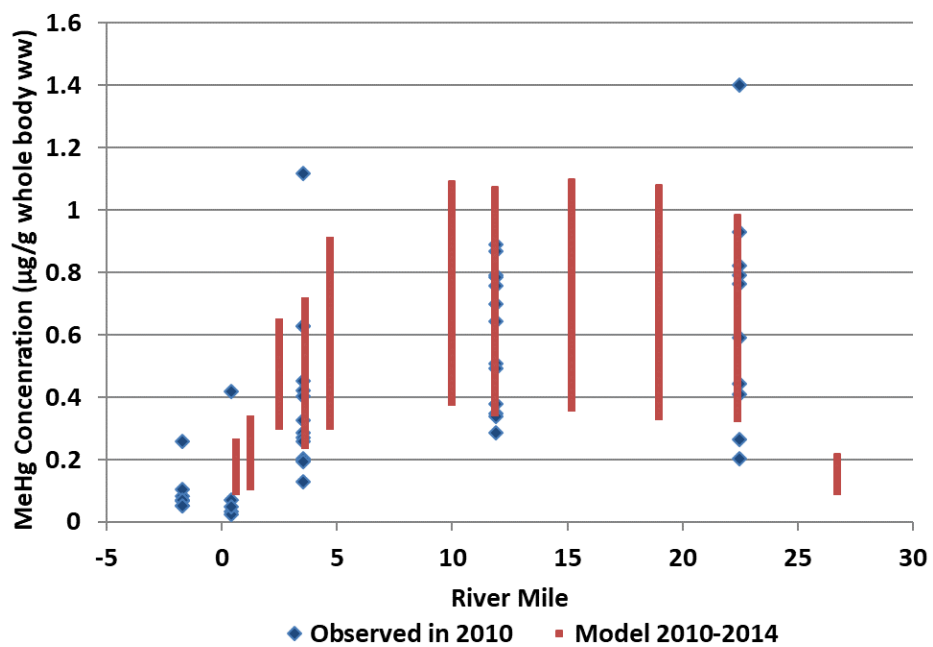


Figure 62. Simulated and observed MeHg concentrations in 100-186 mm common shiner. Blue diamonds are individual fish. Red squares are predictions for any fish in the 100-186 mm length range from 2012-2014. Data from Collins (2016b).

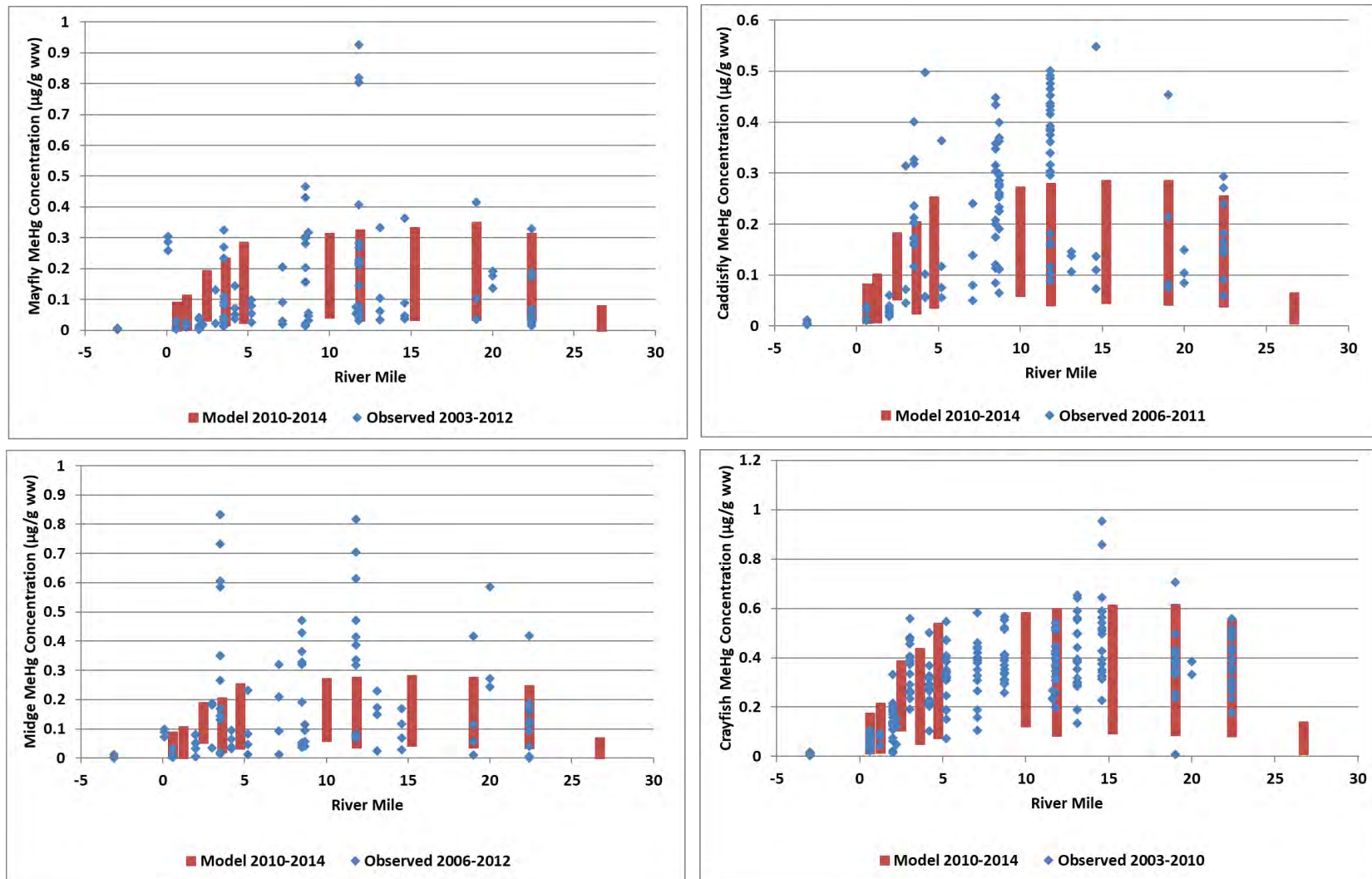


Figure 63. Simulated and observed MeHg concentrations in mayfly, caddisfly, midge and crayfish. Blue diamonds are individual samples. Red squares are simulated values for biota from 2012-2014. Data from Collins (2016b).

8.4 Sources and Sinks of Inorganic Hg and MeHg

Estimated sources and sinks of inorganic Hg and MeHg for RRM 0-24, averaged from 2006-2014 are shown in Table 2 and Table 3, and Figure 64 and Figure 65. The primary estimated external source of inorganic Hg to the modeled river reach was bank erosion, continuing to supply inorganic Hg to sediments. The 2nd largest external Hg input was bank leaching, roughly ¼ of the bank erosion load (although in a potentially more bioavailable form, being dissolved). Together, bank erosion and leaching dominated external inputs to the contaminated river reach in simulations. A large flux of mercury was simulated to be delivered to the sediment bed via settling (Figure 64), but a roughly equal offsetting flux is simulated from sediments back to the water column via resuspension over the 9 year simulation. The Hg load from the Lycra Company site (1 g/day) represented less than 1% of the overall Hg load from RRM 0-24, but would be sufficient to increase concentrations in the median flow of 73 cfs at Waynesboro by ~5 ng/L.

The largest source of MeHg to the river water column was the sediment bed, which supplied roughly 90% of the estimated gross MeHg load to the water column via resuspension, diffusion, and groundwater advection. In the absence of having identified observations, MeHg concentrations in eroding bank solids and leachate were assumed to be low, 0.01 to 0.1% of THg concentrations. This resulted in the banks representing on the order of 10% of the overall MeHg supply to the river water column. The large flux of MeHg from sediments to the water column produced a corresponding large increase in the MeHg outflow at the downstream end of the modeled river reach relative to the external inflows (primarily at Waynesboro) (Figure 65).

Table 2. Model estimates of inorganic Hg sources to the South River from RRM 0-24

	kg/yr	g/day	% of total load to water	% of external load to water/sediment system
Inflow	0.7	1.8	0.4	1
Bank erosion	51	139	8	79
Bank leaching	13	35	7	20
Lycra Co. site	0.4	1.0	0.2	0.6
Wet deposition	0.04	0.1	0.0	0.1
Dry deposition	0.003	0.0	0.0	<0.1
Resuspension	115	315	63	
Diffusion	1.3	3.4	0.7	
Advection up	1	3	0.6	
Total in	182	499	100	100

Table 3. Model estimates of MeHg sources to the South River from RRM 0-24

	g/yr	mg/d	% of total load
Inflow	7	20	1
Bank erosion	51	139	8
Bank leaching	1	3.5	0.2
Lycra Co. site	0.0	0.1	<0.1
Wet deposition	0.1	0.3	<0.1
Dry deposition	0.0	0.1	<0.1
Resuspension	414	1,134	65
Groundwater advection	71	195	11
Diffusion	92	253	15
Total in	637	1,746	100

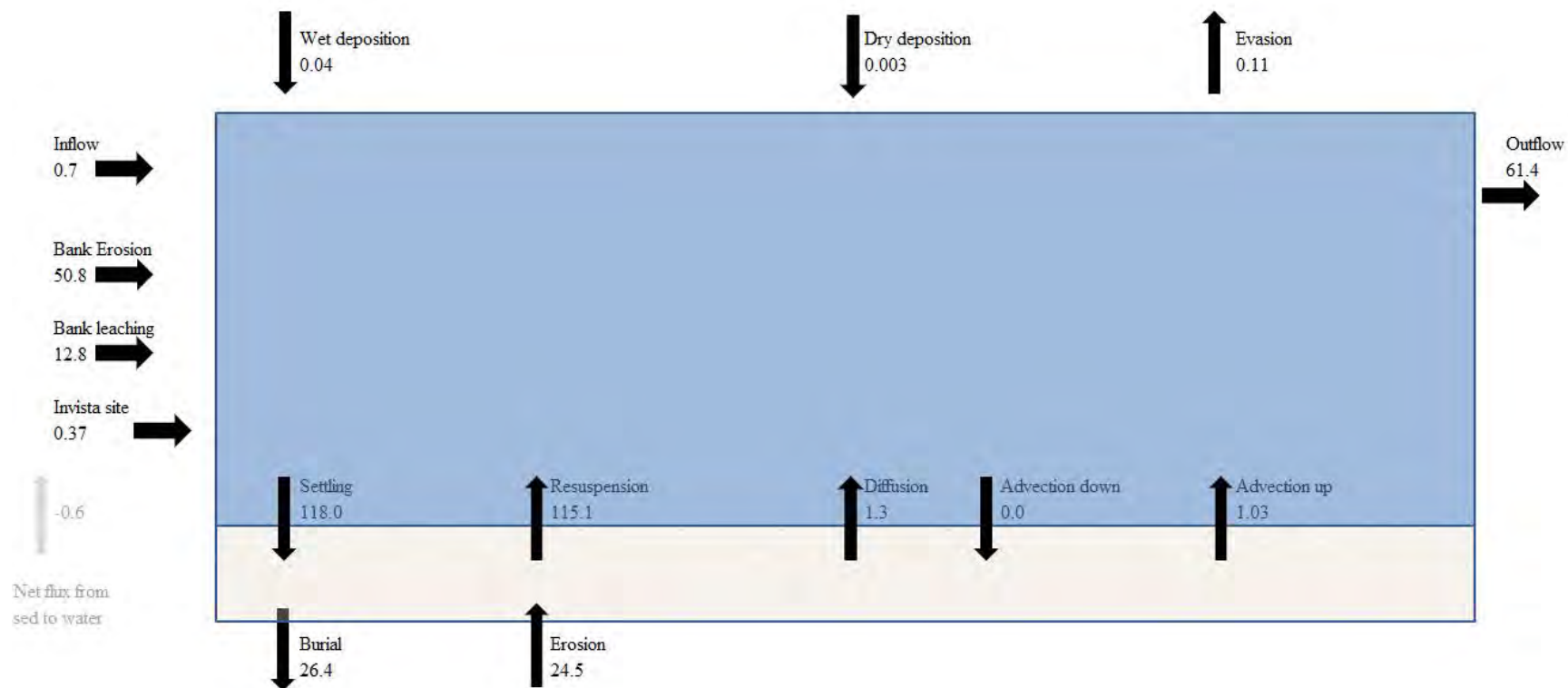


Figure 64. Model mass balance for inorganic Hg in the water column and surface sediments (0-2 cm), averaged from the former DuPont facility site to the confluence with the North River, for 2006-2014 (kg/yr)

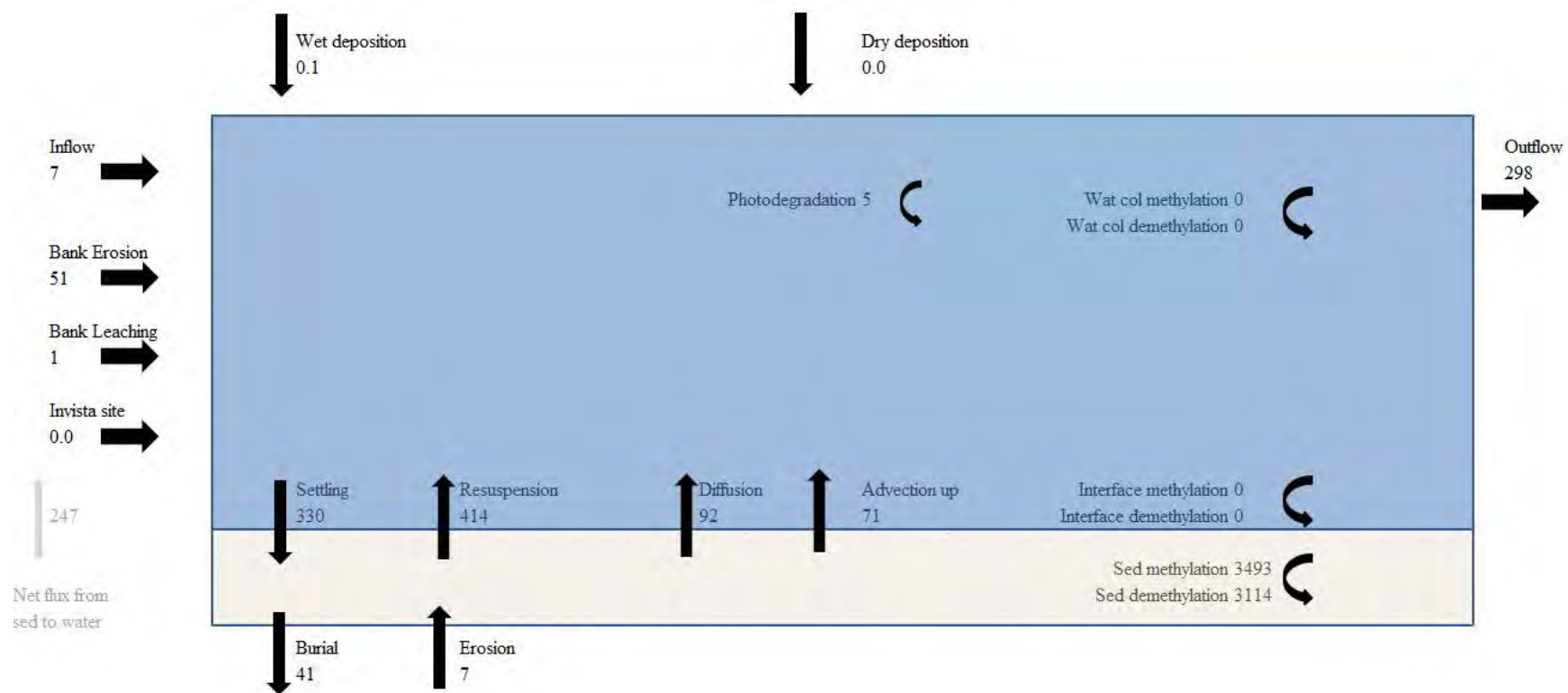


Figure 65. Model mass balance for MeHg in the water column and surface sediments (0-2 cm), averaged from the former DuPont facility site to the confluence with the North River, for 2006-2014 (g/yr).

9 SENSITIVITY ANALYSIS

An analysis was carried out to examine the sensitivity of three model outputs to selected model inputs. The three model outputs were concentrations of THg in water, MeHg in water, and MeHg in age 3-4 smallmouth bass. The model inputs that were adjusted included:

1. Inflow suspended solids at Waynesboro
2. Inflow Hg(II) concentration at Waynesboro
3. Inflow MeHg concentration at Waynesboro
4. Hg(II) load from the former DuPont facility site
5. Hg(II) concentration on eroding bank solids
6. MeHg concentration on eroding bank solids
7. Hg(II) concentration on bank leachate
8. MeHg concentration on bank leachate
9. Water temperature
10. Diffusion constant from sediments to water
11. Settling velocity
12. Resuspension velocity

The base case model calibration was used as the basis for comparison with model sensitivity runs, which were carried out for 2006-2014 (same as base case calibration), varying each input in isolation in separate model runs. Each input was increased 10% except resuspension velocity which was decreased 10% to avoid potential issues related to unrealistically eroding the sediment bed if resuspension was increased. For each sensitivity simulation, the percent change in the predicted concentration of THg in water, MeHg in water, and MeHg in smallmouth bass was calculated as:

$$\% \text{ Change} = 100 * (\text{Sensitivity run result} - \text{Base case result}) / \text{Base case result}$$

The sensitivity of the model to changes in inputs may vary with location and time. Sensitivity calculations were therefore carried out at three locations (RRM 0.4, 10.2 and 22.4) and two times (7 months and 8.5 years after the simulation began) to span a range of locations and times.

Sensitivity analysis results are shown in Figure 66. Simulated THg in water was more responsive to changes to inputs related to bank leaching and erosion (top panels in Figure 66). Surprisingly, THg in water was more sensitive to a 10% change in the Hg(II) concentration in bank leachate than a 10% change in the concentration of Hg(II) on eroding bank solids. This may have been related to the mercury on eroding solids being strongly bound to particles and settling out of the water column quickly. Further

discussion is included later in the report. THg in water was also relatively sensitive to changes in Hg(II) loading from the former DuPont site, but this was only the case at RRM 0.4, *i.e.* close to the facility. The two downstream locations evaluated (RRM 10.2 and 22.4) were not sensitive to changes in inputs from the former DuPont facility.

MeHg concentrations in water were most sensitive to changes in temperature. MeHg in water also showed some sensitivity to Hg(II) concentrations on eroding bank solids, inputs related to fluxes across the sediment water interface (diffusion, settling, resuspension), and inflow MeHg concentrations (only at the upstream end of the modeled reach) (middle two panels in Figure 66). Hg(II) concentrations in bank leachate had less influence on MeHg in surface waters than for THg in surface waters.

Excluding temperature, MeHg concentrations in age 3-4 smallmouth bass showed little sensitivity to any of the changes shown in Figure 66 after 7 months (bottom left panel of Figure). This is not surprising given the fact the fish integrate their exposure over time and a lag between any change in exposure and a change in fish concentration is expected. A 10% increase in temperature resulted in smallmouth bass MeHg concentrations increasing 5-6% after 7.5 months, and 35% after 8.5 years. MeHg in age 3-4 smallmouth bass also showed some sensitivity, although less than for temperature, to changes in Hg(II) concentration on eroding bank solids and inputs related to fluxes between sediments and the water column (diffusion, settling, resuspension).

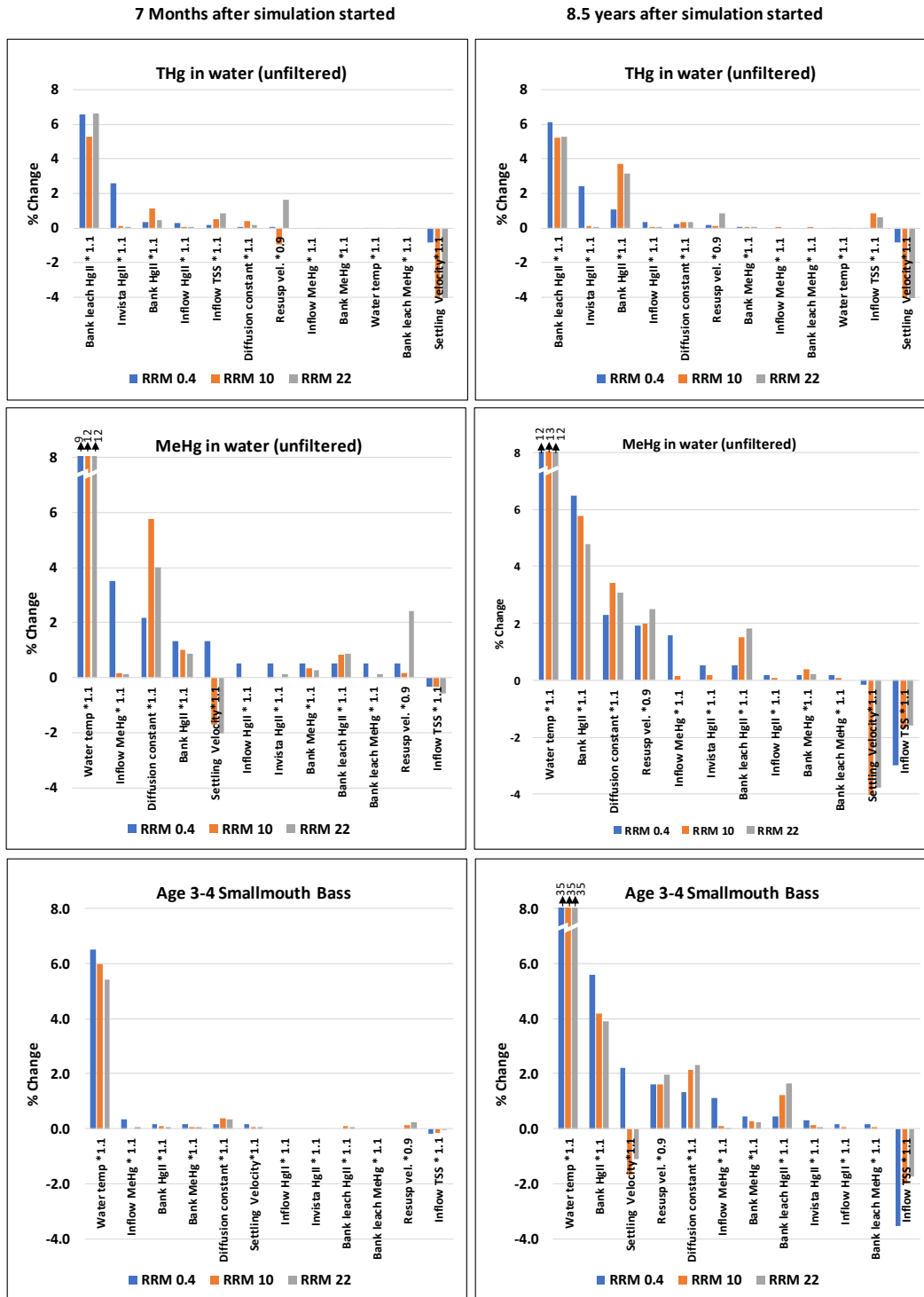


Figure 66. Sensitivity analysis results. Y axis value is the % change in model output, relative to base case simulation, following a 10% increase for the inputs shown on x axis. Model input was changed through the simulation from January 1, 2006 – December 31, 2014. Panels on left represent changes from the base case after 7 months (August 1, 2006). Panels on right represent changes after 8.5 years (August 1, 2014).

10 REMEDIATION SCENARIOS

Two remediation scenarios were simulated, involving bank stabilization for RRM 0-2 (Phase 1) and RRM 2-5 (Phase 2) (Table 4 and Table 5, derived from Grosso (2018)). Phase 1 included a 90% reduction of THg loading via bank erosion, from 20.4 kg yr^{-1} to 2.0 kg yr^{-1} for RRM 0-2. Solids loading from banks was reduced 42 percent. Phase 2 would additionally reduce bank erosion Hg loads from 21.2 kg yr^{-1} to 2.3 kg yr^{-1} for RRM 2-5, also a reduction of approximately 90%. Solids loading for RRM 2-5 would be reduced approximately 60%. Remediation was assumed to be instantly implemented on January 1, 2006 (the first day of the model calibration period). The remediation simulations continued through 2014.

To provide information on the temporal and spatial response to remediation, predicted median THg concentrations in water and sediments for 2006 and 2014 at different locations along the river are shown in Figure 67 for the base case and remediation scenarios. Percent reductions in THg concentrations from the base case to the scenario with Phase 1 and 2 remediation are shown in Figure 68. Spatially, the greatest benefits were closer to areas remediated. The predicted benefits of remediation increased as time progressed. Predicted reductions in THg concentrations in surface sediments are shown as a function of time in Figure 69. Upstream areas responded sooner than downstream. The system had not yet fully responded to remediation when the simulation stopped after 9 years, especially in downstream areas.

Similar trends were predicted for the response of MeHg concentrations in water (Figure 70, Figure 71). The predicted response of MeHg in smallmouth bass (250-300 mm) to Phase 1 and Phase 2 remediation is shown in Figure 72, as a function of river mile and year after remediation. The response again depended on time and location, with the greatest responses occurring near the areas of remediation, up to roughly a 60% reduction by 2014. The same information is presented in Figure 73, with the x axis representing time after remediation was invoked in the simulation. MeHg concentrations in adult smallmouth bass were still declining 9 years after remediation began.

The above results are based on simulations that did not reduce bank leaching of inorganic Hg(II) and MeHg as part of Phase 1 and 2 bank stabilization. A simulation was also carried out where bank leaching of inorganic Hg(II) and MeHg were reduced by the same percentages as bank erosion loads of inorganic Hg(II) during Phase 1 and 2 remediation. The simulated additional benefits of reduced bank Hg leaching are shown for surface sediments and smallmouth bass in Figure 74 and Figure 75 respectively (compare solid and dashed lines of the same color). Simulated reductions in bank leaching had more influence on simulated THg concentrations in surface waters at low flows, up to a decline of 60 ng/L (see green line in Figure 76). This was likely because the annual estimated bank leaching load of inorganic Hg(II) was allocated at constant daily rate throughout each year. This resulted in bank leaching have a greater effect on concentrations at low flow, when flow dilution was less effective. Further discussion of the implications of how bank leaching loads were assigned is provided in the Discussion section.

Table 4. Solids and mercury loads associated with base case and Phase 1 remediation for RRM 0-2 (model cells 1-4).

Derived from Grosso (2018).

Model Cell	Solids load (kg/yr)			THg load (kg/yr)			THg concentration (µg/g)		
	Base Case	Remediation	% Reduction	Base Case	Remediation	% Reduction	Base Case	Remediation	% Reduction
1	190,768	119,915	37	3.48	0.17	95	18.24	1.45	92
2	391,166	216,696	45	7.97	0.67	92	20.39	3.08	85
3	342,694	138,069	60	7.10	0.51	93	20.72	3.71	82
4	205,282	181,897	11	1.86	0.66	64	9.04	3.62	60
Total	1,129,910	656,578	42	20.41	2.01	90			

Table 5. Solids and mercury loads associated with base case and Phase 2 remediation for RRM 2-5 (model cells 5-9).

Derived from Grosso (2018).

Model Cell	Solids load (kg/yr)			THg load (kg/yr)			THg concentration (µg/g)		
	Base Case	Remediation	% Reduction	Base Case	Remediation	% reduction	Base Case	Remediation	% Reduction
5	263,090	103,000	61	7.31	0.58	92	27.79	5.68	80
6	236,166	49,806	79	6.36	0.39	94	26.91	7.83	71
7	173,861	111,256	36	1.74	0.64	63	10.02	5.75	43
8	180,450	79,373	56	3.17	0.42	87	17.56	5.32	70
9	92,777	28,171	70	2.61	0.32	88	28.08	11.51	59
Total	946,344	371,606	61	21.18	2.36	89			

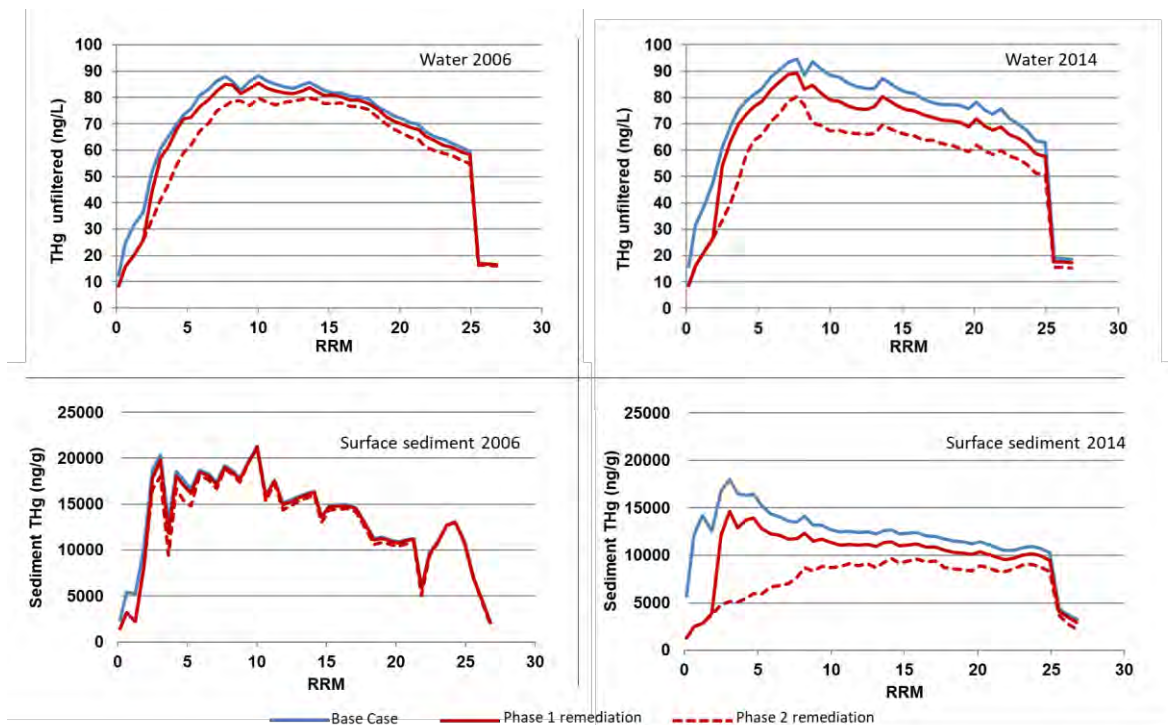


Figure 67. Predicted effect of Phase 1 and Phase 2 remediation (reduced bank erosion from RRM 0-5) on median concentrations of THg in water and sediments. Assumes remediation instantly implemented January 1, 2006. Values are median predicted concentration for a given year.

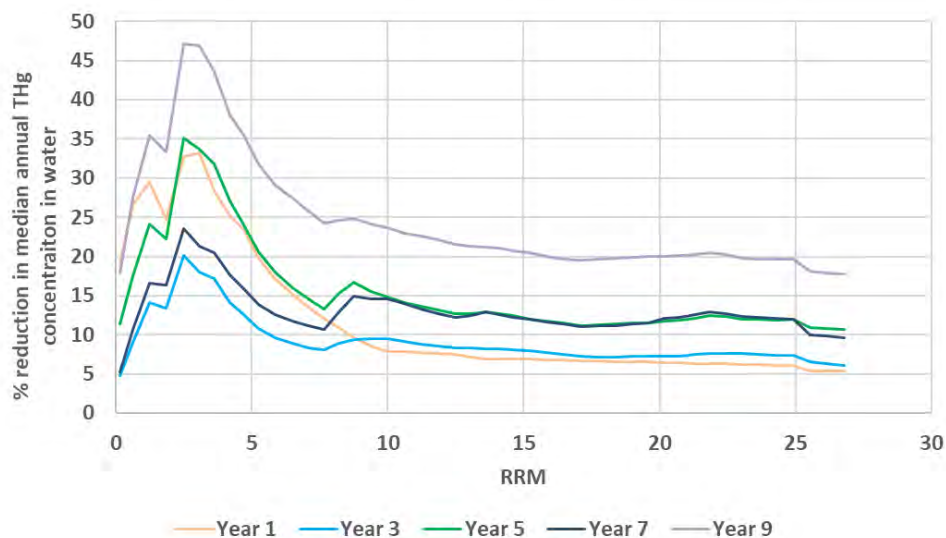


Figure 68. Predicted percent reduction in THg concentrations in surface waters after Phase 1 and Phase 2 remediation. Values are reductions in annual median concentrations from the base case simulation (no remediation). Year = year after remediation initiated. Assumes remediation instantly implemented January 1, 2006.

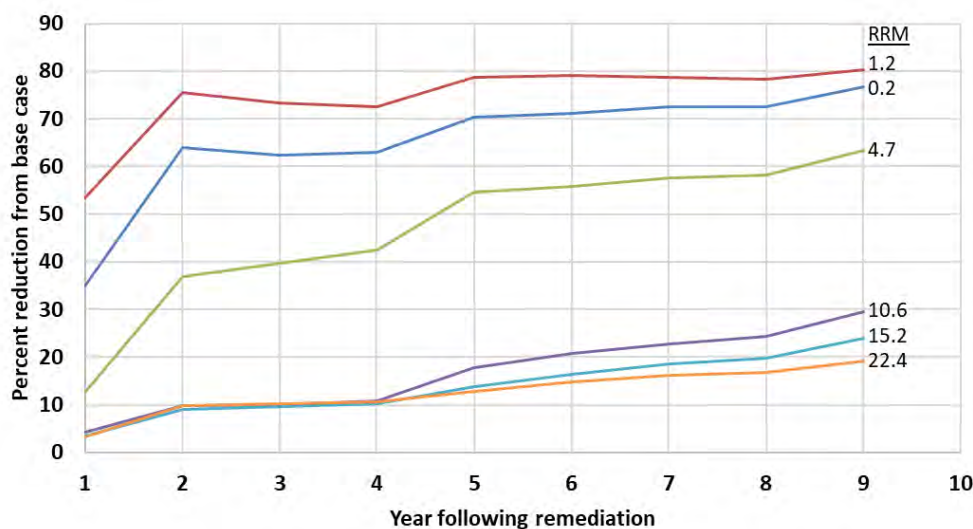


Figure 69. Predicted percent reduction in THg concentrations in surface sediments (0-2 cm) versus time. Values are average declines during year after remediation. Reductions in bank leaching not invoked.

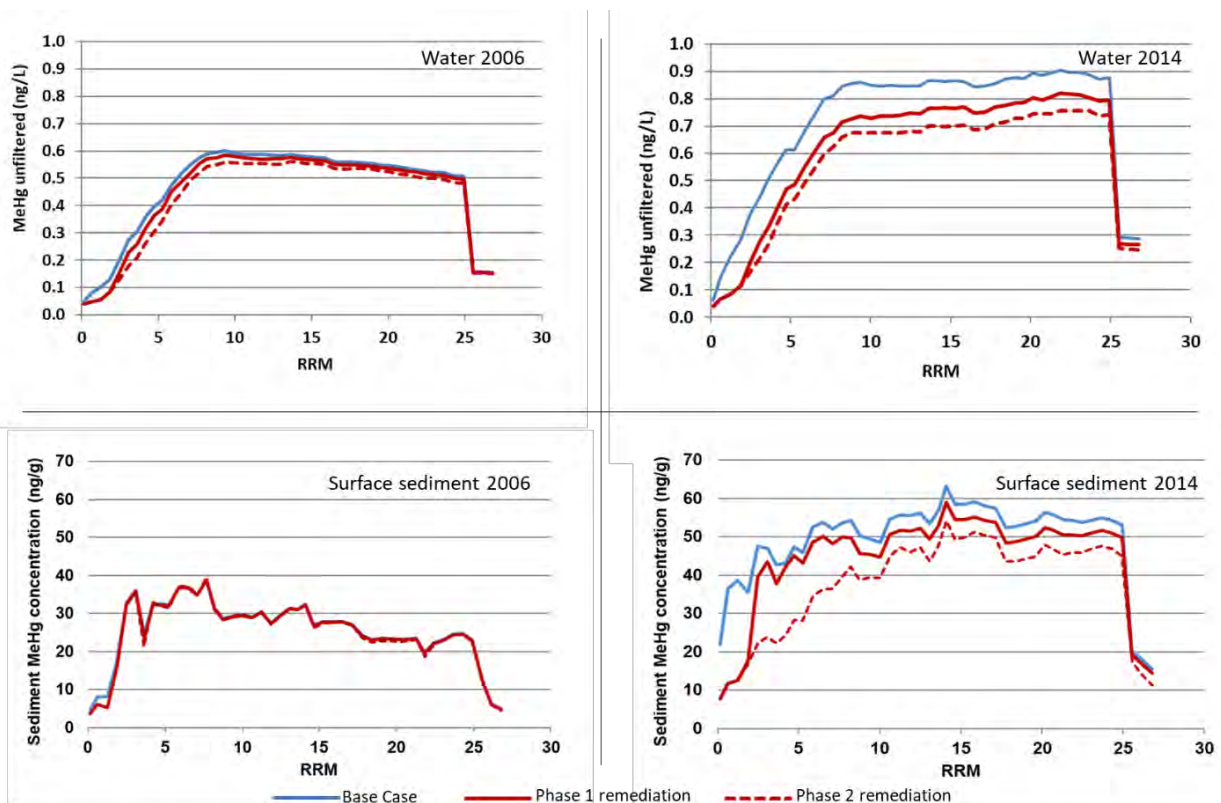


Figure 70. Predicted effect of Phase 1 and Phase 2 remediation (reduced bank erosion from RRM 0-5) on concentrations of MeHg in water and sediments. Assumes remediation instantly implemented January 1, 2006. Reductions in bank leaching not invoked. Values are average concentration for a given year.

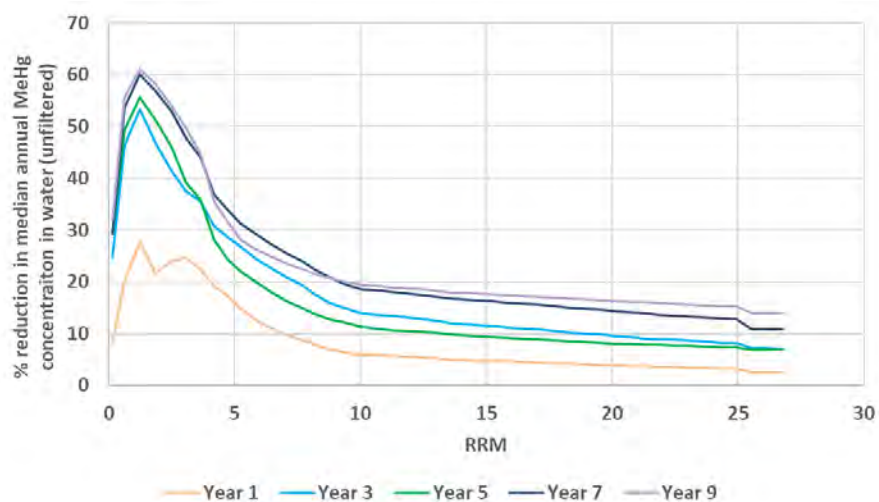


Figure 71. Predicted percent reduction in MeHg concentrations in surface waters after Phase 1 and Phase 2 remediation. Values are reductions in annual median concentrations from the base case simulation (no remediation). Reductions in bank leaching not invoked. Year = year after remediation initiated. Assumes remediation instantly implemented January 1, 2006.

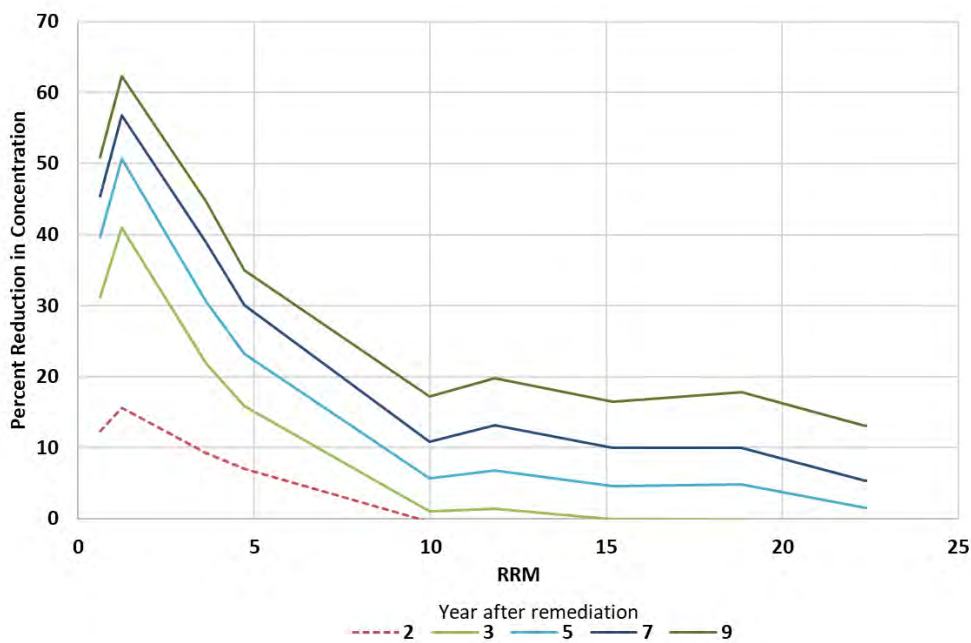


Figure 72. Predicted percent reduction in MeHg concentrations in 250-300 mm smallmouth bass versus river mile. Values are average declines during year after remediation. Reductions in bank leaching not invoked.

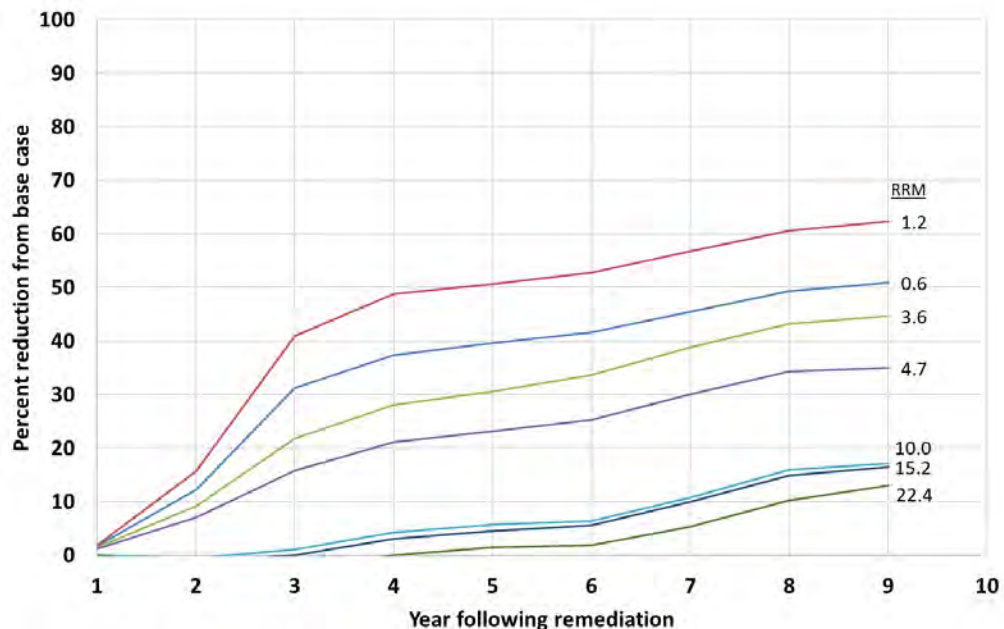


Figure 73. Predicted percent reduction in MeHg concentrations in 250-300 mm smallmouth bass versus time. Values are average declines during year after remediation. Reductions in bank leaching not invoked.

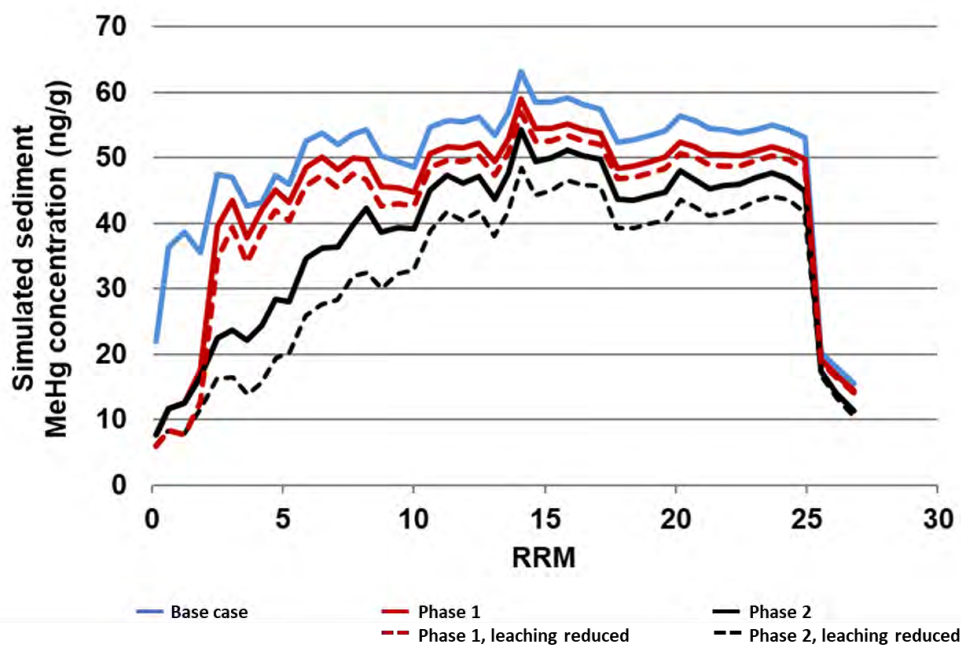


Figure 74. Simulated median MeHg concentrations in surface sediments (0-2 cm) in 2014 for the base case calibration and remediation scenarios. Dashed lines show the predicted incremental effects when bank leaching of inorganic Hg(II) is reduced by the same amounts as inorganic Hg(II) loads for Phase 1 and Phase 2 remediation.

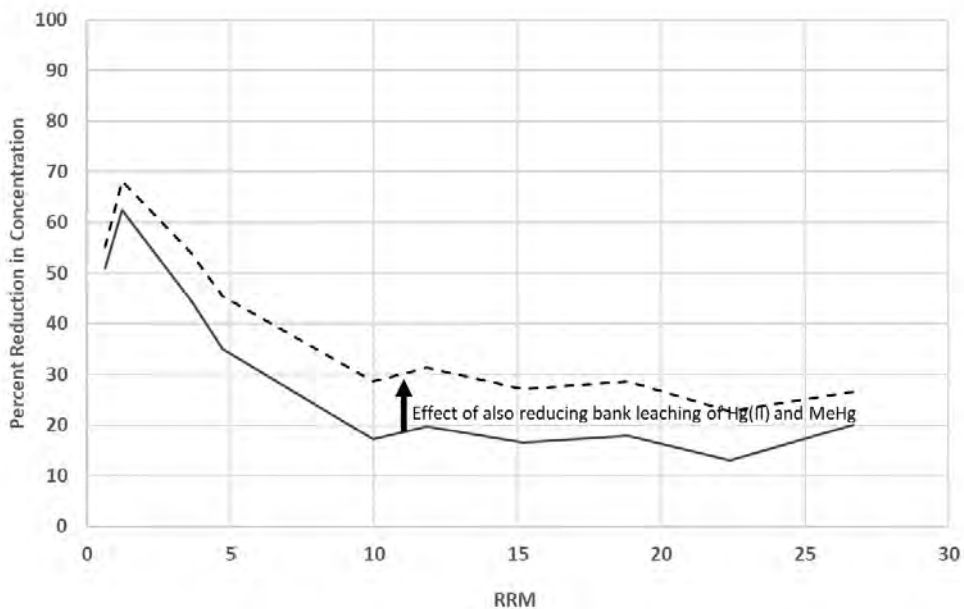


Figure 75. Predicted effect in smallmouth bass (250-300 mm) of reducing bank leaching of inorganic Hg(II) and MeHg by same percentages as inorganic Hg bank erosion loads for Phase 1 and 2 remediation. Results are based on average concentrations for 2014, nine years after remediation initiated.

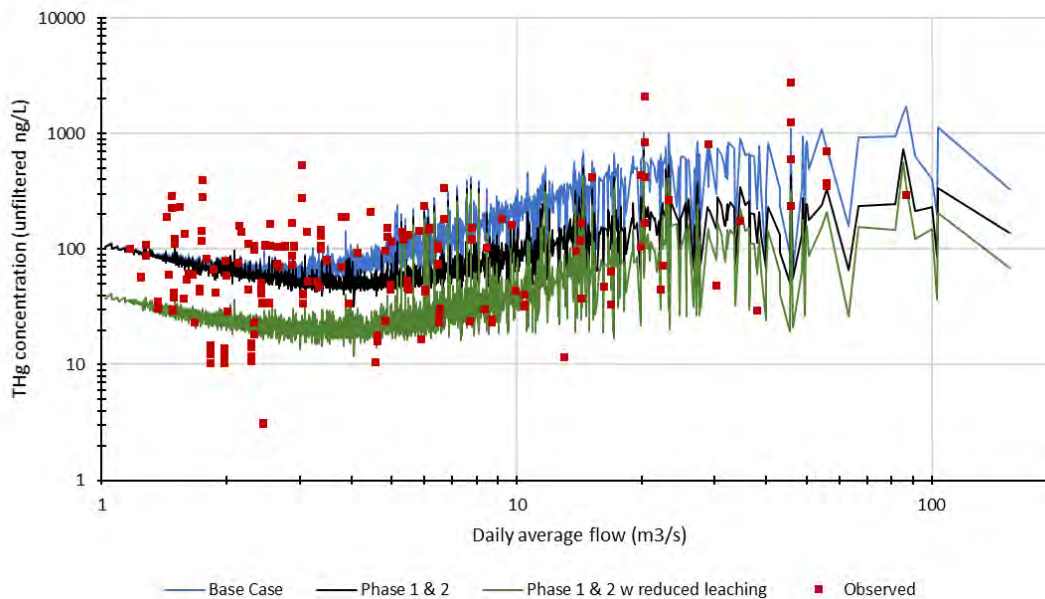


Figure 76. Observed and predicted THg concentrations in water at RRM 5 as a function of daily average flow. Model results are for (a) base case, (b) Phase 1 and 2 remediation without reducing bank leaching loads, and (c) Phase 1 and 2 remediation with bank leaching reduced in same manner as solid-phase mercury loading. Observations and model results are from 2006-2014. Observations are from Flanders (2016) and are from 2006-2014. Model results are daily values from 2006-2014. Flows are model estimates at RRM 5. Log scales are used to better show information at low flows.

11 DISCUSSION

The South River has been studied extensively since 2000 by the South River Science Team to better quantify mercury contamination in the river reach downstream of the former DuPont facility at Waynesboro to the confluence with the North River. Elevated Hg concentrations persist in water, sediments and biota more than six decades after mercury stopped being used as a catalyst for the production of rayon. Mercury cycling in the river is strongly influenced by hydrology and particle transport, which are both highly dynamic, resulting in the ongoing remobilization of historical contamination. A mechanistic model of mercury cycling and bioaccumulation, D-MCM, was used to simulate conditions in the South River from RRM 0-26.7 from 2006-2014, the period with the most complete data available at the time the model analysis began. The model was first calibrated using available data for this period, then used to predict the response to remediation from RRM 0-2 and RRM 0-5, which are areas with significant mercury loading to the river. A sensitivity analysis was carried out to examine which model inputs and processes had greater influence on model predictions. Each of these major components of the model study is discussed below.

Model Calibration

The calibration of D-MCM using data from RRM 0-26.7 from 2006-2014 reflected several key features of the observations, including the general magnitudes and spatial patterns for:

- THg concentrations in water (Figure 46 to Figure 48) and sediments (Figure 50, Figure 51).
- MeHg concentrations in water (Figure 52 to Figure 54), sediments (Figure 57) and food web (Figure 60 to Figure 63).

Field data and model simulations were both characterized by rapidly increasing concentrations of THg in water in all phases (bulk, filtered, particles) in the initial few miles downstream of the former DuPont facility at RRM 0. This occurred in model simulations due to the remobilization of legacy inorganic Hg, originally released years or decades ago, from riverbanks via erosion and leaching, and resuspension from the contaminated sediment bed (Table 2, Figure 64). The river sediment bed is characterized as non-depositional on a time scale of roughly a decade (Pizzuto *et al.*, 2006), although the system may experience periods of sediment accumulation followed by erosion, in a highly dynamic manner. Mercury contamination above background levels in surficial sediments would likely be depleted by now, 6 decades after the use of mercury at the site stopped, unless an ongoing supply is provided to the sediment bed. Potential sources include the former DuPont facility site, riverbanks, and supply from contaminated sediments at depth. Ongoing releases from the site of the former DuPont facility were assigned a rate of 1 g/day in simulations. In the absence of other contamination this would be sufficient to increase THg concentrations in river water by about 5 ng/L (using a median flow of 73 cfs at Waynesboro). It is not sufficient however to explain increases in THg to levels in the range of 100 ng/L (Figure 46). Other ongoing sources to the water column are needed to explain observations.

The conceptual site model for mercury in the South River, and the modeling carried out in this study, estimate that the primary source of ongoing inorganic Hg contamination is from select eroding riverbanks containing elevated mercury. Most of the riverbank supply of inorganic mercury was via bank erosion in model simulations (~50 kg/yr average from 2006 - 2014) (Table 2), with a secondary

component from bank leaching (~13 kg/yr). As discussed later, bank leaching may be over-represented under baseflow conditions.

Simulated and observed THg concentrations in surface waters and sediments reached peak values downstream of the original point of release, roughly from RRM 5-10, and then began to decline farther downstream (Figure 46, Figure 50). This is consistent with historical releases of inorganic Hg from a point source, now ceased or much reduced, and a current situation where legacy contamination released years ago is broadly distributed along a portion of the river. Increasing concentrations occur in the water column traveling downstream as long as Hg supply from contaminated banks and sediments exceeds removal rates. At some point downstream, Hg concentrations in the water column are sufficiently elevated that processes removing mercury from the water column, such as settling, match inputs within a reach. At this point inputs equal losses locally and concentrations reach peak values. Downstream of this location, declining Hg loading to the water column is exceeded by losses in a reach, and water column concentrations begin to decline. This explanation could also apply to MeHg, with loads distributed along the river due to methylation of Hg(II) contamination along the river. It is possible but not necessary that site conditions are also ecologically more conducive to methylation in areas where peak MeHg concentrations occur in water.

Methylmercury concentrations in surface waters also rose quickly downstream of the former DuPont facility, approaching and sometimes exceeding median concentrations of 1 ng/L in field measurements and model simulations (Figure 52). For RRM 0-24, the primary overall predicted source of MeHg to river waters was the sediment bed (~250 g/yr net load on average from 2009-2014 for RRM 0-24, Figure 65), due to the ongoing supply of inorganic mercury for methylation. Much of the supply of MeHg from sediments to overlying water was predicted to occur via resuspension, which would have an important component associated with short term high flow events. Dissolved fluxes of MeHg from the riverbed could play a more important role under lower flow conditions. Riverbanks also contributed methylmercury to the river (~50 g/yr, Figure 65) in simulations. This estimate is directly a result of the fraction of Hg eroding solids and leachate from riverbanks that is MeHg, assumed to be 0.01 to 0.1% in this analysis. This estimate is uncertain due to limited data.

The general seasonal pattern of higher MeHg concentrations in the ice-free season is reflected in the model (Figure 55). When the model is compared to observed monthly median MeHg concentrations in surface waters, it is clear that there is more variability seasonally in the observations than in the model (Figure 56). The same discrepancy between the model and observations is evident for MeHg in sediments (Figure 58, Figure 59), especially from April – June. It is possible that the model does not capture the effects of seasonal changes in the supply of carbon for microbes that methylate mercury. The model was set up with methylation depending on the concentration of available Hg(II) and temperature, but not explicitly depending on the supply of carbon. Perhaps the supply of labile carbon, or other substrates required for methylation, are highest in the spring which is then subsequently depleted. D-MCM has the ability to relate methylation to carbon turnover, but initial efforts to use this feature produced results confounded by simulated differences in the supply of labile carbon along the length of the river, favoring some areas for methylation in a manner that may not be realistic. A more refined consideration of this issue was beyond the scope of the current analysis.

Another feature of the model calibration was the decline of sediment THg concentrations from 2006-2014 in the vicinity of RRM 5-15 (Figure 50). Insufficient recent data were identified to compare with data from 2005-2007, to assess whether this trend is real or an artifact of the model. THg concentrations in sediments predicted by 2014 were similar to concentrations estimated in the riverbanks, which were lower than 2005-2007 estimates of sediment THg concentrations for RRM 5-15 (Figure 9). Given the model residence time of solids in surface sediments on the order of 1-2 years in this river reach (Figure 45), simulated THg concentrations in sediments in 2014 may have adjusted to the concentration of mercury in source material from the banks, rather than indicating ongoing long-term recovery. If that was the case, the question can still be asked why observed sediment Hg concentrations would be higher in 2005-2007, and whether Hg concentrations on solids supplying those sediments were higher in the past.

The model calibration imposed three conditions that resulted in sediment resuspension being a major flux to the water column for both Hg(II) and MeHg:

1. A non-depositional environment over 9 years, requiring that any solids supplied from eroding banks or upstream inputs eventually had to be resuspended and transported downstream
2. A large supply of solids from bank erosion.
3. Median suspended solids concentrations in the water column should be on the order of 3-5 mg/L (the observed median).

Overall, much of the large supply of solids to the water column had to be settled out quickly in order to approximate the median suspended solids concentrations observed. To avoid long term accumulation, solids delivered to the sediment bed had to eventually be remobilized and transported downstream during infrequent high flow events. Other combinations of settling and resuspension could also produce reasonable results. The magnitude of resuspension affects the extent to which mercury in water is connected to mercury in sediments. Faster coupled rates of settling and resuspension mobilize more of the legacy sediment contamination into overlying water, although it can settle back out.

An alternative calibration was developed with large quantities of the solids from bank erosion depositing locally near the point of release (Appendix D). While the alternative calibration is considered less realistic (it would produce sedimentation of several cm per year for RRM 0-5 (Figure D1)), it demonstrated that it is possible to calibrate the model to reasonably represent observed mercury concentrations in water, sediments and biota (*e.g.* Figures D4 and D5) using different assumptions about particle transport, *e.g.* whether most of the eroded bank solids deposited locally and buried or deposited but transported downstream at some future time (Figure 77). Yet particle dynamics are a key influence on the mercury response to bank stabilization, in terms of how quickly mercury concentrations would decline, and how this would vary along the river system.

These model results demonstrate the need to have good information on particle transport and fate identify and reduce uncertainty associated with the response to bank stabilization. Nevertheless, all simulations predict that reducing sources of inorganic Hg concentrations reduce MeHg concentrations in biota.

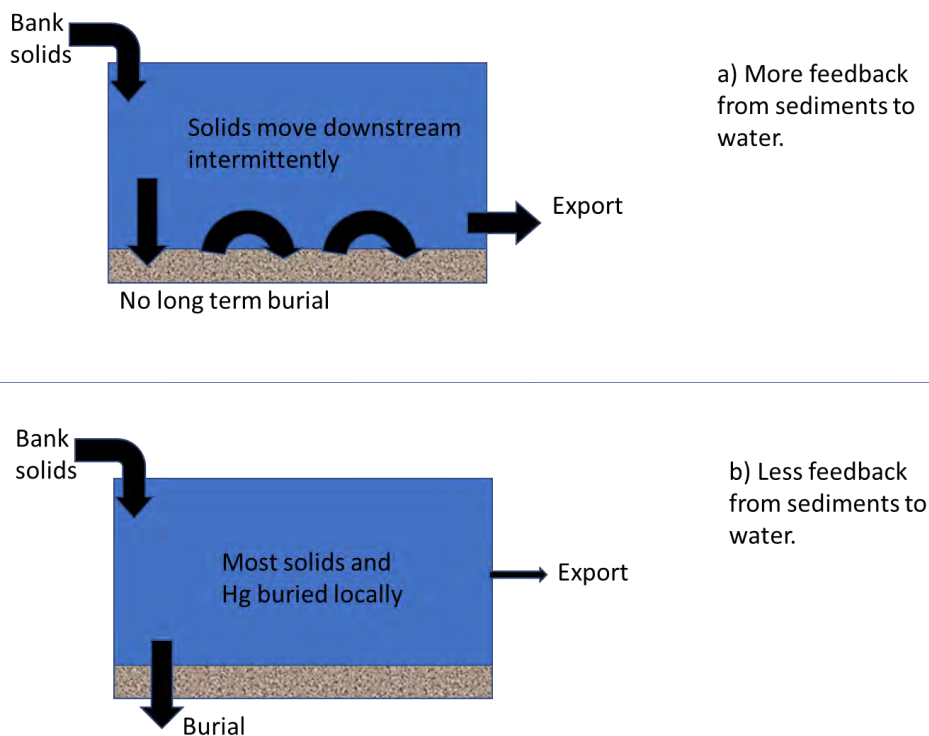


Figure 77. Conceptual sketch showing two alternatives for the transport and fate of solids from bank erosion.

The final aspect of the model calibration discussed here is the relationship between THg and MeHg, which has important implications for the response of MeHg in fish following reductions in inorganic loading from riverbanks. As discussed in Section 6.3, previously reported field data suggested a non-linear relationship between MeHg in fish and THg in sediments, and between MeHg and THg in sediments (this report). A decline in sediment THg concentration may not be followed by a proportional decline in fish MeHg. Model simulations also exhibited a less than linear decline in sediment MeHg production when inorganic Hg concentrations decline, although less pronounced than reported in the relationship between fish Hg and sediment THg (Figure 14). For example, in the final year of the 9-year Phase 1 remediation simulation, the simulated decline in sediment methylation (65%) in cell 1 was not as great as the decline in sediment THg concentrations (80%). This was because simulated porewater concentrations of inorganic Hg(II), assumed to be the pool available for sediment methylation in the model, did not decline as much as solid phase Hg(II), *i.e.* there was a shift in the apparent partitioning of inorganic Hg(II), favoring the dissolved phase. Most of the inorganic Hg(II) on contaminated solids was assumed to be strongly bound, slow to desorb, while mercury on inflowing “background” Hg(II) from upstream was assumed to exchange more readily. These results were likely sensitive to assumptions about the kinetics of Hg partitioning which are not well quantified.

Sensitivity Analysis

The sensitivity analysis supported the conceptual model that fish Hg is responsive to changes in inorganic Hg loading from riverbanks. A 10% increase in Hg(II) loading from bank erosion produced ~4-6% increases in smallmouth bass after 8.5 years, with slightly greater effects at the upstream end of the modeled river reach (Figure 66, bottom right panel). The 10% increase in bank erosion had little effect on simulated MeHg concentrations in adult fish after 7 months, but this is not surprising given that adult fish integrate exposure over time.

Temperature had the greatest effect on fish Hg concentrations in the sensitivity analysis. A 10% increase in temperature produced a 35% increase in MeHg in 3-4 year old smallmouth bass after 8.5 years. There were two components to the increase. First, temperature affected methylation, which is a microbial process and temperature-dependent in the model. Water MeHg concentrations increased 12-13% after 8.5 years. Most of the predicted increase in MeHg concentrations smallmouth bass was however associated with bioenergetics effects. Metabolic rates in fish are predicted to increase with warmer temperature. Fish then need to eat more food to reach a given size, and take in more MeHg as a result. This happens for fish species at each trophic level in the food web, and the bioenergetics effects compounded through the food web to smallmouth bass in simulations. This model result has been predicted previously using D-MCM in a study for the US EPA examining potential effects of climate change on fish mercury concentrations in the Great Lakes Region (Harris *et al.*, 2015). Further model analysis is needed for this issue to test the validity of model predictions regarding temperature effects.

Bank leaching of inorganic Hg(II) had a strong influence on inorganic Hg(II) concentrations in water (Figure 66), greater than the influence of Hg(II) concentrations in eroding bank solids. This seems counterintuitive given that the Hg load from leaching was roughly $\frac{1}{4}$ the load from bank erosion (Figure 64). Two factors may contribute to this result in simulations. First, the model was set up assuming that most of the mercury in eroding bank solids was strongly bound to solids, most of which would not desorb rapidly when mobilized into the water column. This was consistent with the large observed increase in Hg partitioning in suspended solids as water flowed past river sections identified as sources of contaminated bank solids (Figure 20). A large component of eroding bank solids settled out of the water column rapidly in simulations, reducing the time-integrated effect, although it was remobilized later during higher flow conditions. Bank leachate, on the other hand, was loaded to river waters in dissolved form in the model. A second factor affecting the predicted importance of bank leaching was that it was loaded at a constant rate. Leaching rates are probably greater during or shortly after high flow events that generate hydraulic gradients supporting water and Hg transport from banks to the river. A more realistic refinement of the approach used here would be to scale leaching flows with time, based on hydrologic conditions. This could result in lower simulated concentrations of inorganic Hg in surface waters under low flow conditions. Given that the existing calibration reasonably reflects observed elevated concentrations in surface waters, including periods of low flow (Figure 76), less bank leaching during low flow periods would likely need to be compensated with greater loading rates from another source to maintain a fit to observations.

These sensitivity results do not, on a standalone basis, mean that bank leaching is more important than eroding solids as a source of Hg to the water column, as the estimated bank erosion load of Hg was about 4X the load from leaching. They do suggest that model predictions of Hg(II) concentrations in water are sensitive to the magnitude of bank leaching, which are therefore important to quantify reasonably. Bank leaching of Hg(II) had less effect on MeHg concentrations in water or fish than bank

erosion in the sensitivity analysis. This may have been related to better delivery of Hg associated with bank solids to sediments, where methylation occurred in simulations, than inorganic Hg(II) leached from banks. Point source releases of Hg from the former DuPont facility site had a localized effect on THg in water, but little influence at the downstream sites examined at RRM 10.2 and 22.4.

Remediation Scenarios

Phase 1 and 2 remediation simulations imposed reductions in solids and Hg loads on January 1, 2006, and followed the effects through 2014, the same period used for the model calibration. Inorganic Hg and MeHg concentrations were predicted to decline and the response depended on the environmental compartment, location and time after remediation was implemented (Figure 67 - Figure 74). Phase 1 and Phase 2 remediation each produced declines in predicted concentrations of THg and MeHg in water and sediments downstream of RRM 5 (Figure 67 and Figure 70). Benefits of remediation were greatest near the location where remediation was carried out in simulations (RRM 0-5), up to ~60% declines in unfiltered MeHg in water (Figure 71) and age 3-4 smallmouth bass (Figure 72) during the last (9th) year of the simulation. Remediation from RRM 0-5 was also predicted to reduce downstream concentrations of THg and MeHg in water and sediments, but to a lesser degree (*e.g.* ~15% reduction in 250-300 mm smallmouth bass at RRM 23, 9 years after remediation was initiated, Figure 72).

Reductions in predicted Hg concentrations progressed through the 9-year remediation simulations. The timing of the response to remediation for any given mercury form and compartment is directly related to how quickly loading declines, followed by how quickly compartments responds to a change in loading. Because environmental media are linked, one compartment can slow the overall response of a system once external loads are reduced. This is typically sediments when dealing with contaminants in freshwater systems. The water column has the ability to respond to changes in loading very quickly, on a scale of days, because there are processes such as settling and outflow that can remove contamination quickly. Total Hg in sediments is much slower to respond to a change in loading. Sedimentation, for example, often replaces sediment solids with new material on a scale of years or decades in the top few cm. In this model analysis, the average residence time of solids on a cell by cell basis were on the order of 1-4 years in surface sediments (Figure 45). The fact that sediments remain contaminated on a widespread basis more than 60 years after the original contamination points to ongoing sources. Other factors that could prolong the natural rate of recovery beyond the average rates estimated for individual model cells include:

- 1- Intermittent downstream transport (“hopscotch” effect): Contaminated particles are mobilized and transported downstream over time. Contaminated particles in upstream areas can be a source of contamination to downstream areas for a period of time, even if external contamination stops. Downstream areas may take longer to fully recover than upstream contaminated areas.
- 2- Localized hot spots: If there are localized area with slow particle residence times and high mercury concentrations, these areas could contribute to a slower natural rate of recovery.

The primary pathways for sediments to purge contamination are burial, resuspension, and diffusion, although some of the mercury removed by resuspension and upward diffusion may settle back into sediments or be carried downstream to provide mercury to downstream sediments. Thus, the magnitude of resuspension has implications for the rate of recovery locally and downstream. Scenarios with less resuspension may exhibit a greater initial response for Hg(II) in the water column when

mercury loads from bank erosion are reduced. This was the case when Phase 1 and 2 remediation was simulated using the alternative calibration with more solids burial and less resuspension. Concentrations of THg and MeHg in water responded to a greater degree, especially downstream of RRM 5 (Figure D6) than in the simulations where the system was nearly non-depositional (Figure 67).

Reduced bank erosion also reduces the supply of solids to sediments. To the extent that the burial of solids contributes to replacing contaminated surface sediments, this process would slow down due to the lower rate of solids supply. While preventing erosion of contaminated sediments is beneficial, the rate of response would be affected by reduced solids supply. This was reflected in simulations.

Due to uncertainties associated with a range of factors affecting how quickly sediment Hg(II) concentrations available for methylation will change after erosion control measures, the model results to-date are interpreted to suggest that bank stabilization will reduce fish MeHg concentrations, but the timing and magnitude of the response are difficult to quantify. Key uncertainties regarding the timing are related to particle dynamics and the rate at which solids in the surface sediment layer are replaced at different locations following remediation. Also important regarding the ultimate magnitude of the response is the extent to which the bioavailable pool of Hg(II) changes for a given change in overall THg concentration. For example, will a reduction of 50% in sediment Hg result in a reduction of 50% for the available Hg(II) pool.

12 CONCLUSIONS

A mechanistic model of Hg cycling and bioaccumulation was applied to a 26-mile reach of the South River, VA, contaminated with Hg used at a former DuPont facility from 1929-1950 to produce rayon. The model was calibrated to data from 2006-2014, followed by a sensitivity analysis and remediation simulations. Key features of the analysis include:

- The mechanistic model simulated bank erosion to be the largest external source of Hg to the river reach (~80%), consistent with the conceptual model.
- The greatest source of MeHg to the water column in the simulated river reach was from the sediment bed via resuspension, diffusion and groundwater advection (~90% combined) .
- The model calibration to 2006-2014 data reflected observed magnitudes and spatial trends of increases in total Hg and MeHg in water, sediments and biota, and some of the seasonality observed for MeHg in water. Peak concentrations of THg and MeHg in water, sediments and biota remain clearly elevated decades after the original release of Hg.
- Hydrodynamics and particle dynamics exert strong influences on mercury cycling and concentrations in the contaminated river. Short term events are important in terms of the remobilization and downstream transport of solids and Hg from riverbanks and the sediment bed.
- Bank leaching of inorganic Hg(II) was roughly ¼ of the load from bank erosion, but it had a strong influence on simulated THg concentrations in water, especially under low flow conditions. This was partly because bank leaching was assumed to be loaded at constant rate. It is more likely that bank leaching occurs preferentially during periods following larger rain/flood events.
- Remediation scenarios involving bank stabilization were simulated, reducing bank erosion of Hg by roughly 90% for RRM 0-5. The model predicted that inorganic Hg and MeHg concentrations would decline over a period of years, and the benefits were predicted to be greater in areas where remediation was carried out. As a result of Phase 1 and 2 remediation, MeHg concentrations in adult smallmouth bass were predicted to decline up to 60% locally near remediated areas, and to a lesser extent downstream. The response to remediation was not complete after 9 years in the simulations.
- Additional information on particle mobilization and downstream transport, and the role of short-term events, would help reduce uncertainty associated with model predictions regarding remediation. Additional comments are provided in the Recommendations section of the report.

13 RECOMMENDATIONS TO REDUCE UNCERTAINTIES REGARDING REMEDIATION PREDICTIONS

Much effort has been devoted to characterizing mercury contamination in the South River, and better understanding mercury cycling and bioaccumulation in the system. This information was extremely valuable for the mechanistic model analysis. At the same time, there are data and knowledge gaps that constrained the ability to assign high levels of confidence to some model predictions. Factors currently constraining the ability to quantify the benefits of remediation include uncertainty regarding particle loading rates, transport and fate, and uncertainty regarding pools of inorganic Hg(II) available for methylation, and the effects of bank stabilization specifically on those pools.

The following recommendations are provided towards a goal of improving the understanding of mercury behavior in the South River, and improving the ability to anticipate, whether using models or other approaches, the potential benefits of remediation:

1. Consider options to improve estimates of particle budgets (sources, transport, fate) in the system, including an assessment of event-driven particle transport, and the overall long-term rate of downstream particle transport. D-MCM is essentially a mercury model, and is not designed to accurately simulate sediment transport, sedimentation and erosion in highly dynamic river systems. An improved characterization of sediment mobilization and transport in the short and long terms (event to decadal scales) would improve:
 - o the understanding of the transport and fate of mercury in the system,
 - o the rate of natural recovery,
 - o the ability to simulate mercury in the South River and predict the timing and magnitude of the response to remediation.
2. Examine options, if any, to better identify the pools of Hg(II) available for methylation, and the non-linearity of methylation with respect to sediment inorganic Hg concentration. Discuss this with experts on the topic. Recent advances in analytical methods using stable Hg isotopes to identify sources of inorganic Hg contributing to MeHg should continue to be explored.
3. Improve information on the MeHg content of eroding banks and bank leachate. Even a small fraction of THg as MeHg in banks could be meaningful.
4. Revisit estimates of bank leaching of Hg(II). It is not suggested the current estimate is unreasonable, the recommendation is made because this term emerged from the sensitivity analysis as an input for the model as potentially influential, and therefore important to quantify.
5. Consider extending model simulations to be long enough to consider effects of major storms on long term trends and long-term benefits of remediation.
6. Compare field results from Phase 1 remediation with model predictions. This may help refine the site conceptual model and provide insights regarding the potential benefits of additional remediation measures. This could also help inform whether additional model simulations incorporating new data and knowledge would be useful.

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Appendix A
Estimated Bank Erosion Loads of Solids, THg and MeHg

Bank erosion rates were estimated for THg, MeHg and solids in each model cell. Field estimates of sediment solids erosion rates and total mercury loads on both sides of the river were summed for locations within each model cell as described in Report sections 7.3.2 (solids) and 7.4.1 (Hg). The resulting long-term average rates for each cell are given in Table A1. The overall averages were allocated daily using a relationship that assigns erosion as a function of velocity to the 4th power. It is recognized that this is a simplification of processes affecting bank erosion, which also include, for example, previous recent flows and erosion rates, soil moisture and bank stability.

Table A1. Estimated long term average rates of erosion for solids, THg and MeHg, for each model cell.

Model Cell	Start Mile	Finish Mile	Solids load		THg load		THg concentration	MeHg load		MeHg concentration
			tonnes/yr	tonnes/yr/mile	kg/yr	kg/yr/mile	µg/g	g/yr	g/yr/mile	µg/g
1	0.0	0.3	191	615	3.5	11.2	18.24	3.5	11.2	0.018
2	0.3	0.9	391	631	8.0	12.9	20.39	8.0	12.9	0.020
3	0.9	1.6	343	553	7.1	11.5	20.72	7.1	11.5	0.021
4	1.6	2.2	205	331	1.9	3.0	9.04	1.9	3.0	0.009
5	2.2	2.8	263	424	7.3	11.8	27.79	7.3	11.8	0.028
6	2.8	3.3	236	423	6.4	11.4	26.91	6.4	11.4	0.027
7	3.3	3.9	174	312	1.7	3.1	10.02	1.7	3.1	0.010
8	3.9	4.5	180	323	3.2	5.7	17.56	3.2	5.7	0.018
9	4.5	5.0	93	187	2.6	5.3	28.08	2.6	5.3	0.028
10	5.0	5.5	19	34	0.4	0.7	19.07	0.4	0.7	0.019
11	5.5	6.2	26	37	0.1	0.2	5.20	0.1	0.2	0.005
12	6.2	6.8	29	52	0.1	0.1	1.91	0.1	0.1	0.002
13	6.8	7.4	107	172	0.6	1.0	5.91	0.6	1.0	0.006
14	7.4	7.9	47	83	0.9	1.6	19.14	0.9	1.6	0.019
15	7.9	8.4	31	62	0.3	0.5	8.72	0.3	0.5	0.009
16	8.4	9.1	187	302	1.0	1.6	5.26	1.0	1.6	0.005
17	9.1	9.7	58	94	1.0	1.6	17.48	1.0	1.6	0.017
18	9.7	10.3	77	124	0.4	0.7	5.30	0.4	0.7	0.005
19	10.3	10.9	20	32	0.3	0.5	13.98	0.3	0.5	0.014
20	10.9	11.5	2	3	0.0	0.0	16.03	0.0	0.0	0.016
21	11.5	12.2	28	45	0.4	0.6	13.71	0.4	0.6	0.014
22	12.2	12.8	32	52	0.4	0.7	13.34	0.4	0.7	0.013
23	12.8	13.3	34	61	0.5	0.8	13.42	0.5	0.8	0.013
24	13.3	13.8	8	16	0.1	0.2	13.57	0.1	0.2	0.014
25	13.8	14.3	3	5	0.0	0.0	4.54	0.0	0.0	0.005
26	14.3	14.9	1	2	0.0	0.0	13.00	0.0	0.0	0.013
27	14.9	15.5	17	28	0.2	0.3	10.21	0.2	0.3	0.010
28	15.5	16.1	20	32	0.1	0.2	7.22	0.1	0.2	0.007

Model Cell	Start Mile	Finish Mile	Solids load		THg load		THg concentration	MeHg load		MeHg concentration
			tonnes/yr	tonnes/yr/mile	kg/yr	kg/yr/mile	µg/g	g/yr	g/yr/mile	µg/g
29	16.1	16.7	1	1	0.0	0.0	11.43	0.0	0.0	0.011
30	16.7	17.4	16	23	0.2	0.3	11.15	0.2	0.3	0.011
31	17.4	18.0	10	17	0.1	0.2	10.63	0.1	0.2	0.011
32	18.0	18.7	0	0	0.0	0.0	0.00	0.0	0.0	0.000
33	18.7	19.3	0	0	0.0	0.0	0.00	0.0	0.0	0.000
34	19.3	19.8	1	1	0.0	0.0	9.46	0.0	0.0	0.009
35	19.8	20.4	2	3	0.0	0.0	9.28	0.0	0.0	0.009
36	20.4	21.0	30	54	0.3	0.5	8.84	0.3	0.5	0.009
37	21.0	21.5	105	187	0.2	0.4	2.37	0.2	0.4	0.002
38	21.5	22.1	1	2	0.0	0.0	8.40	0.0	0.0	0.008
39	22.1	22.7	108	175	0.9	1.4	7.98	0.9	1.4	0.008
40	22.7	23.3	70	112	0.5	0.8	7.39	0.5	0.8	0.007
41	23.3	23.9	21	34	0.2	0.3	7.56	0.2	0.3	0.008
42	23.9	24.6	0	0	0.0	0.0	0.00	0.0	0.0	0.000
43	24.6	25.2	0	0	0.0	0.0	0.00	0.0	0.0	0.000
44	25.2	25.8	0	0	0.0	0.0	0.00	0.0	0.0	0.000
45	25.8	26.4	0	0	0.0	0.0	0.00	0.0	0.0	0.000
46	26.4	27.0	0	0	0.0	0.0	0.00	0.0	0.0	0.000

Appendix B
Estimated Bank Leaching Rates for Model Cells

Bank leaching rates were estimated for THg, MeHg and solids in each model cell, as described in Section 7.4.2 in the main report. The resulting leaching rates for each cell are given in Table B1. Leaching rates were constant with time. It is recognized that this is a simplification of processes affecting bank leaching, which also include, for example, recent hydrology, bank moisture, and whether the flows on a given day are on the rising or falling limb of a hydrograph.

Table B1. Estimated bank leachate loads of THg and MeHg for model cells.
MeHg concentration in leachate was assumed to be 0.01% of THg.

Cell #	THg load (g/d/cell)	MeHg load (mg/d/cell)
1	0.830	0.083
2	1.614	0.161
3	1.555	0.155
4	1.498	0.150
5	1.443	0.144
6	1.254	0.125
7	1.212	0.121
8	1.172	0.117
9	1.010	0.101
10	1.100	0.110
11	1.296	0.130
12	1.021	0.102
13	1.095	0.110
14	0.951	0.095
15	0.819	0.082
16	0.990	0.099
17	0.954	0.095
18	0.919	0.092
19	0.886	0.089
20	0.853	0.085
21	0.822	0.082
22	0.792	0.079
23	0.688	0.069
24	0.592	0.059
25	0.575	0.057
26	0.627	0.063
27	0.672	0.067

Cell #	THg load (g/d/cell)	MeHg load (mg/d/cell)
28	0.647	0.065
29	0.624	0.062
30	0.660	0.066
31	0.577	0.058
32	0.556	0.056
33	0.535	0.054
34	0.465	0.047
35	0.450	0.045
36	0.435	0.043
37	0.421	0.042
38	0.407	0.041
39	0.436	0.044
40	0.420	0.042
41	0.405	0.040
42	0.390	0.039
43	0.376	0.038
44	0.362	0.036
45	0.349	0.035
46	0.336	0.034
Total	36.1	3.609

Appendix C
South River Fish Growth, Condition, and Food Web Dietary Preferences

Growth rates, fish condition and fish diets were calibrated for smallmouth bass, redbreast sunfish and common shiner (Figures C1-C3, Table C1). Growth rates were calibrated using information from a previously developed bioenergetics model (BASS) for the South River (Reese, 2015). Fish diets were derived using information from Reese (2015). Fish condition (weight vs length) estimates were developed by fitting curves to data from Collins (2016b).

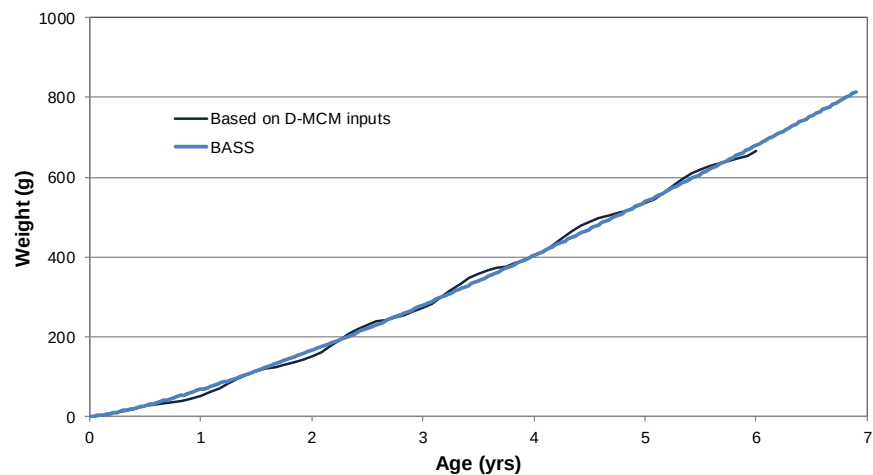
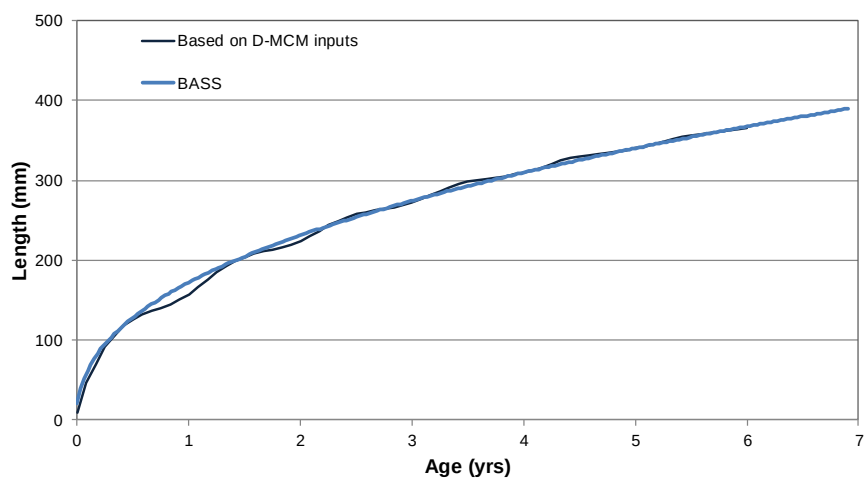
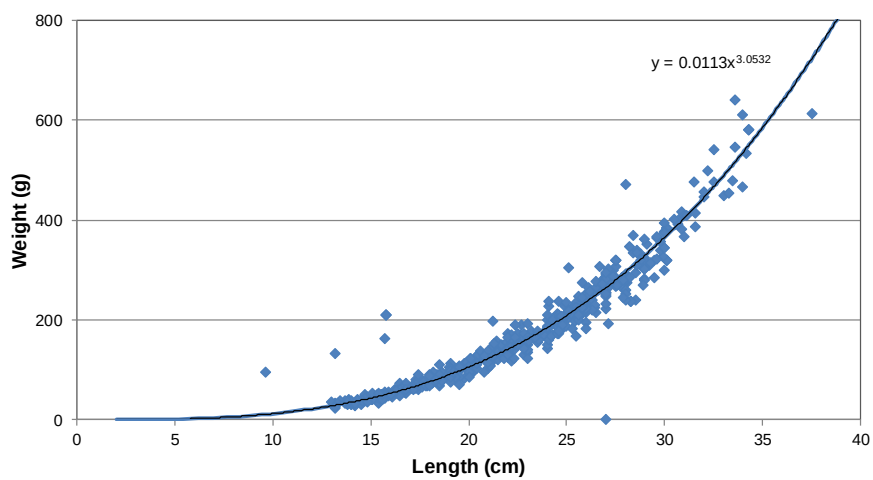


Figure C1. Smallmouth bass relationships for (a) weight vs length, (b) length vs age and (c) weight vs age. D-MCM curves were calibrated to fit BASS model curves. Bass estimates from Reese (2015). Weight vs length data from Collins (2016b)

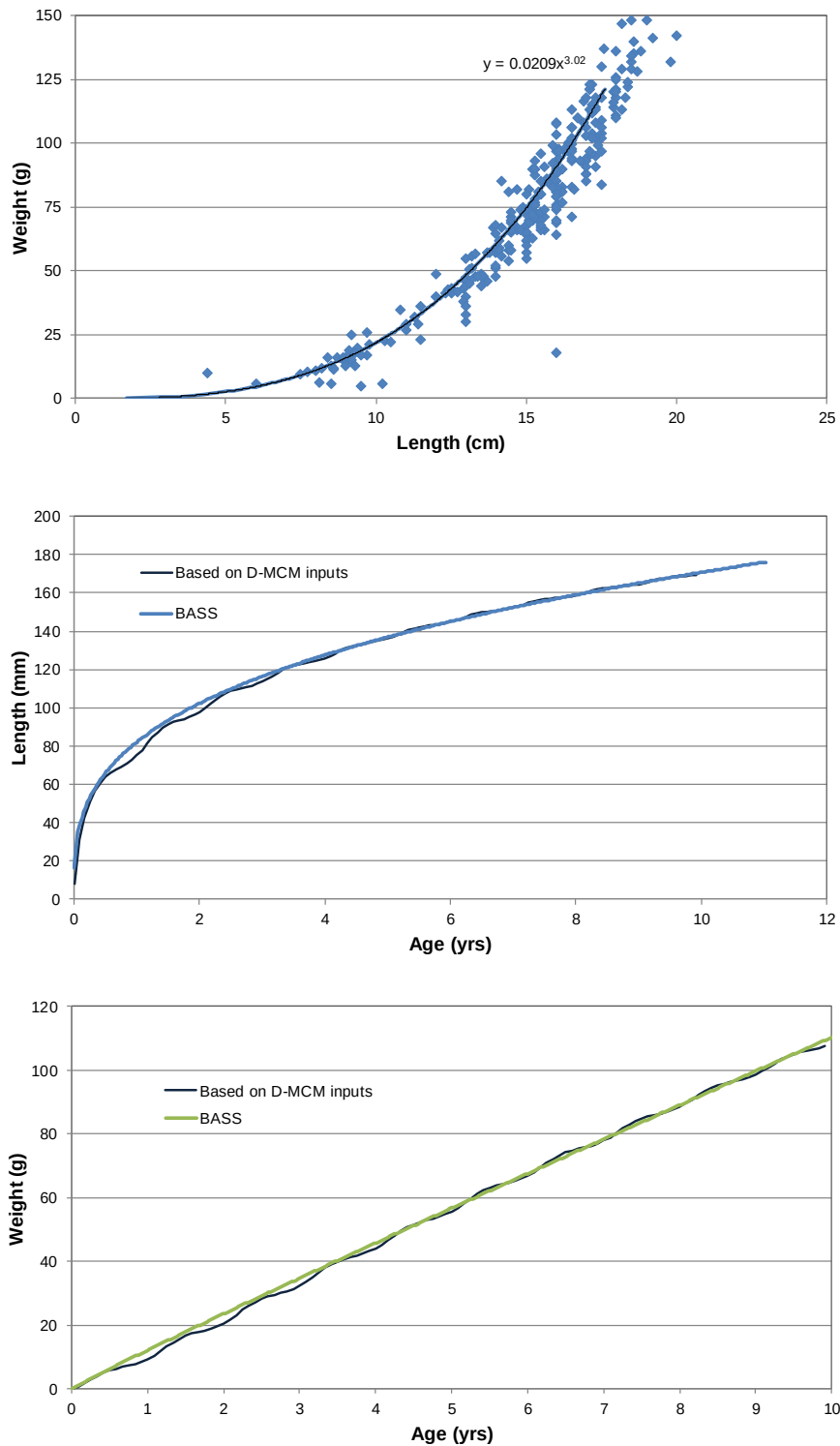


Figure C2. Redbreast sunfish relationships for (a) weight vs length, (b) length vs age and (c) weight vs age. D-MCM curves were calibrated to fit BASS model curves. Bass estimates from Reese (2015). Weight vs length data from Collins (2016b)

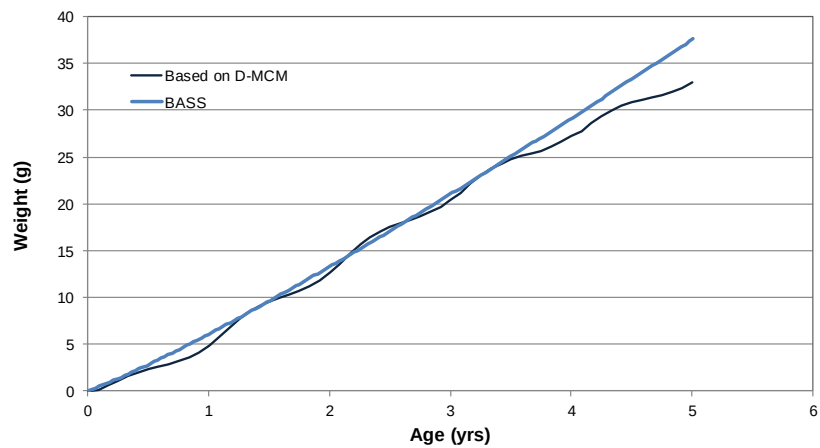
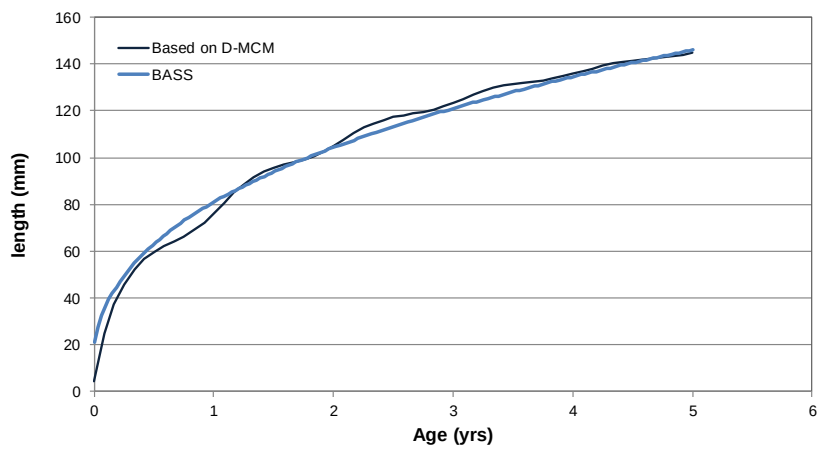
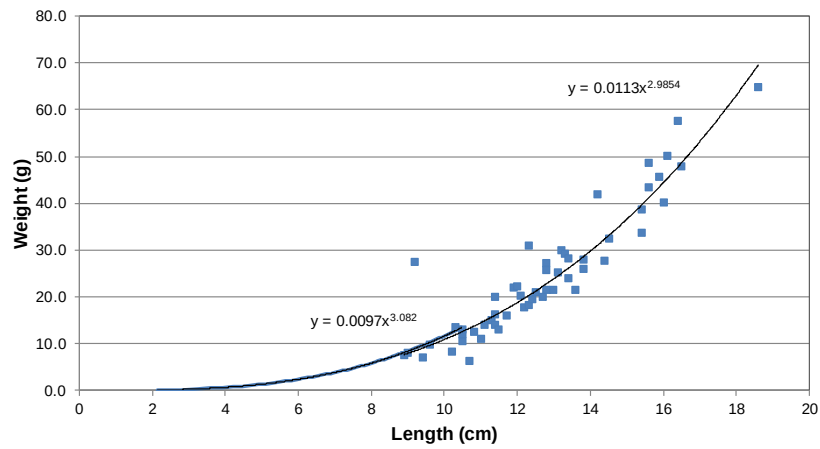


Figure C3. Common shiner relationships for (a) weight vs length, (b) length vs age and (c) weight vs age. D-MCM curves were calibrated to fit BASS model curves. Bass estimates from Reese (2015). Weight vs length data from Collins (2016b)

Table C1. Fish dietary preferences used in D-MCM simulations. Derived from Reese (2015).

Prey	Predator				
	Common shiner	Redbreast sunfish	SMB <116mm	SMB 116 to 185mm	SMB >186mm
Ringed worms	0%	2%	2%	0%	0%
Beetles	1%	2%	0%	1%	0%
Crayfish	0%	4%	1%	10%	34%
Midge	18%	25%	9%	3%	0%
Mayflies	4%	13%	33%	14%	3%
Water boatman, aphids	0%	1%	4%	0%	0%
Moths and butterflies	2%	4%	0%	0%	0%
Dragonfly	1%	4%	1%	2%	2%
Caddisflies	12%	25%	1%	4%	1%
Common shiner	0%	5%	17%	45%	38%
Redbreast sunfish	0%	0%	1%	6%	2%
Insect (Terrestrial)	1%	5%	24%	0%	4%
Macrophyte	16%	3%	0%	1%	0%
Organic Matter / Detritus	27%	7%	7%	14%	16%
Periphyton	18%	0%	0%	0%	0%
Total	100%	100%	100%	100%	100%

Appendix D

Alternative Model Calibration with Increased Local Sedimentation

The primary calibration of D-MCM to the South River for this study was set up to approximate low to non-depositional conditions when averaged from 2006-2014 (Figure D1 – blue line). An alternative calibration was developed such that the river reach from RRM 0-27 was depositional from 2006-2014, especially from RRM 0-5. High supply rate of solids from bank erosion in this area were deposited locally and mostly buried rather than remobilized and transported downstream (Figure D1 – dashed red line). This calibration is unrealistic for RRM 0-5, which would have accumulated roughly 3-3.5 cm/year of solids on average, or 27- 38 cm over the 9-year simulation. Nevertheless the results of this calibration, and remediation scenarios based on this calibration, provide a useful counterpoint to the primary calibration, and help to examine the implications of different assumption regarding particle dynamics, in terms of the response of the system to remediation, as discussed in the main report.

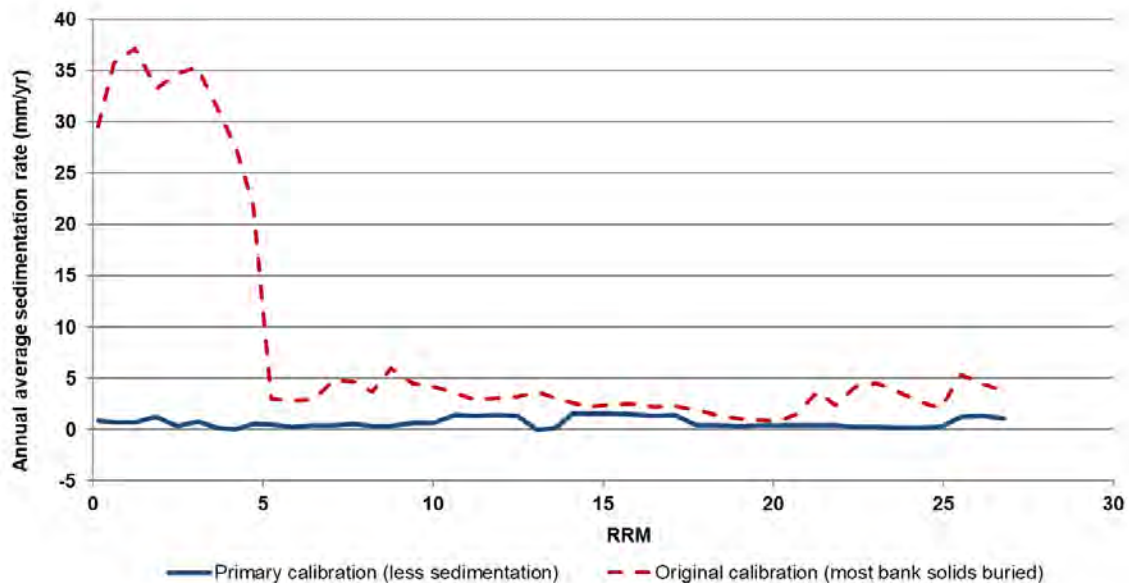


Figure D1. Annual average sedimentation rates from RRM 0-27 for two model calibrations.

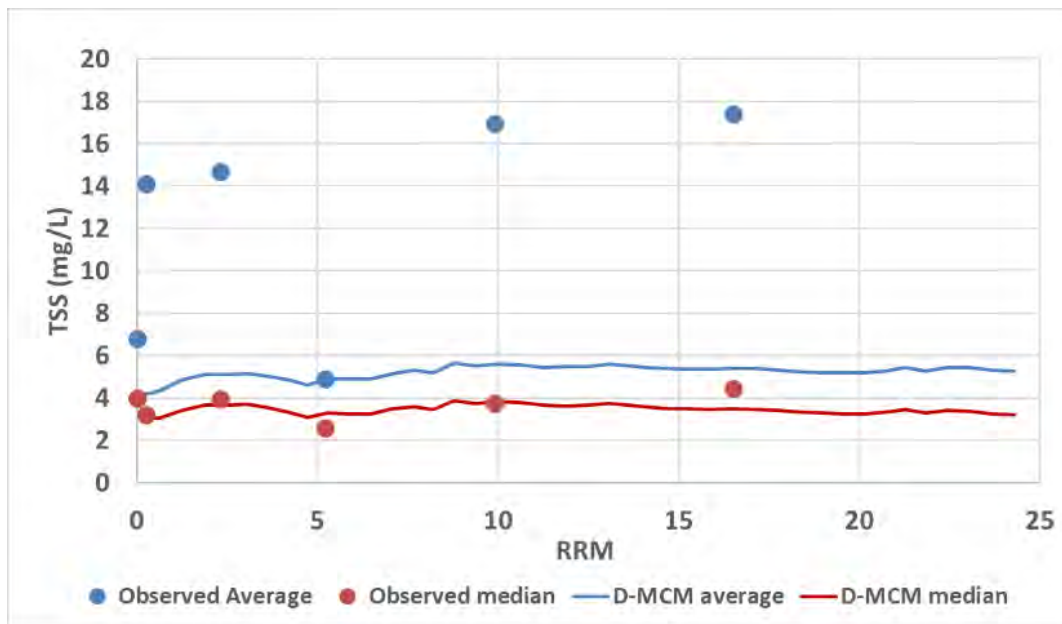


Figure D2. Average and median observed and predicted TSS concentrations in the South River – alternative calibration. Observations derived from 2006-2014 (Flanders, 2016).

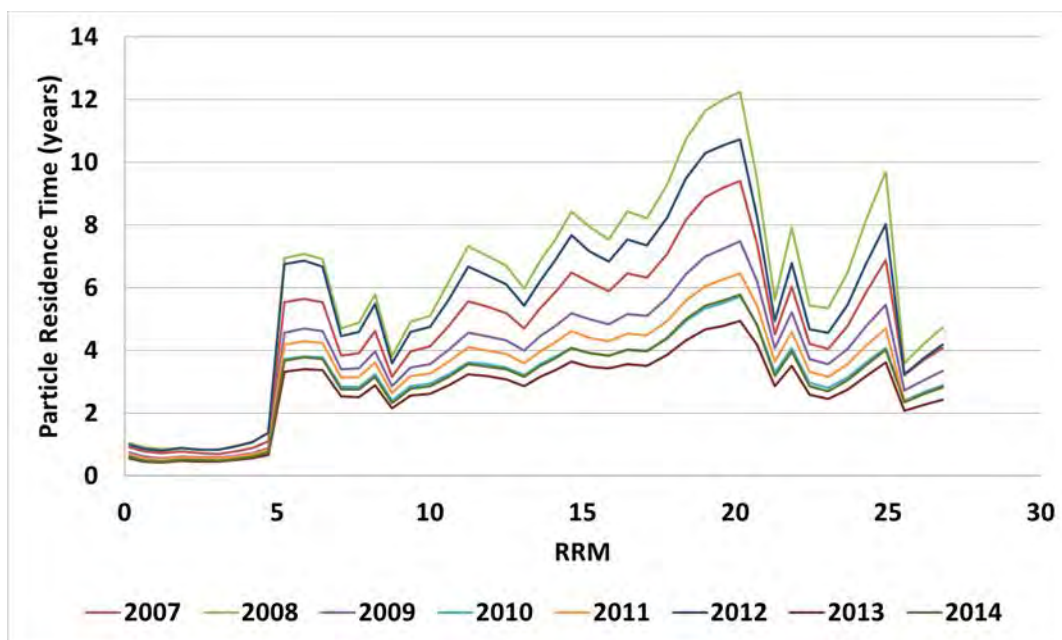


Figure D3. Simulated particle residence times in surface sediments (0-2 cm) from 2006-2014 – alternative calibration

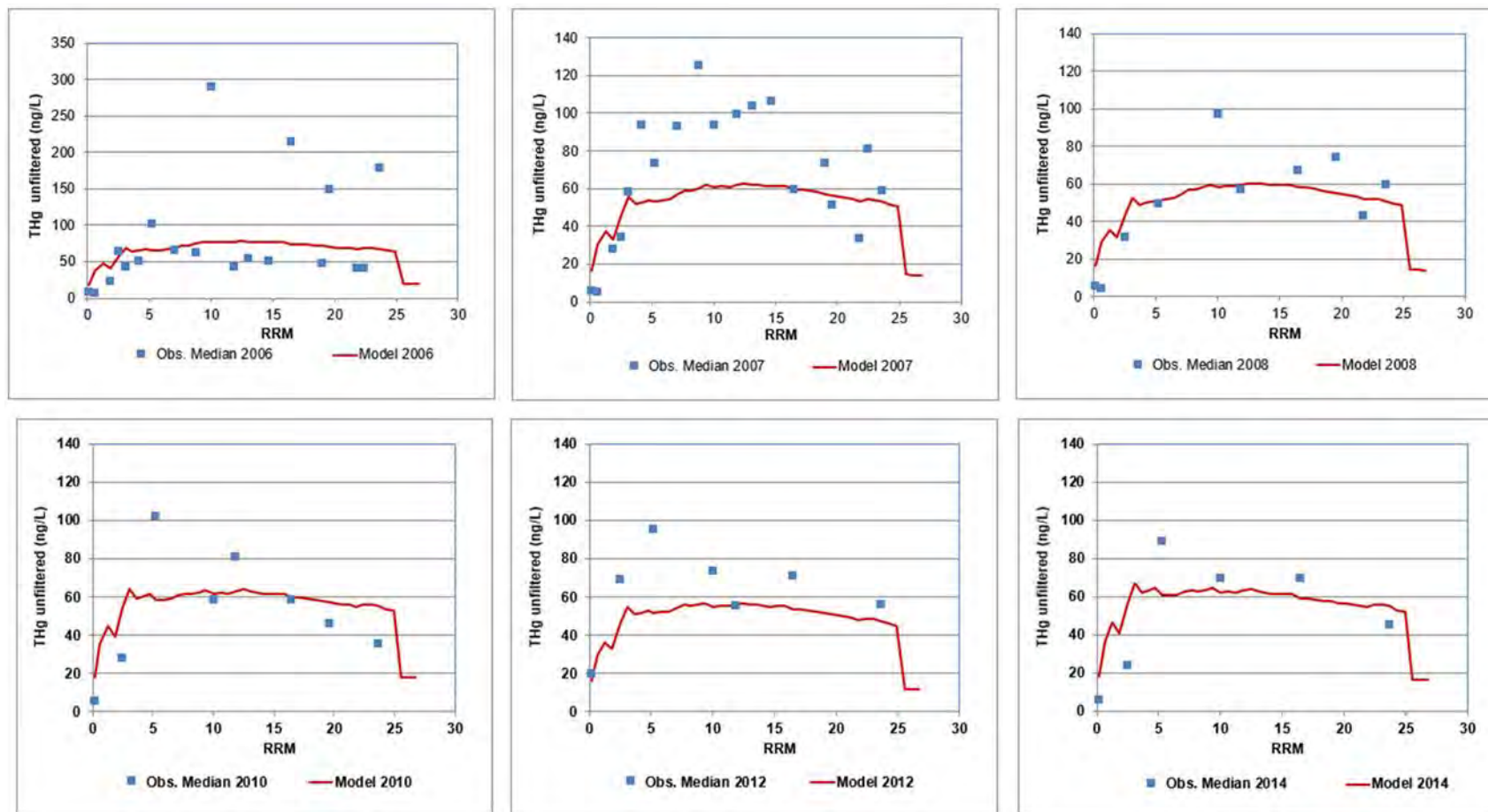


Figure D4. Predicted and observed concentrations of unfiltered total mercury in surface waters – alternative calibration. Values are medians for each year at different locations. Data from Flanders (2016)

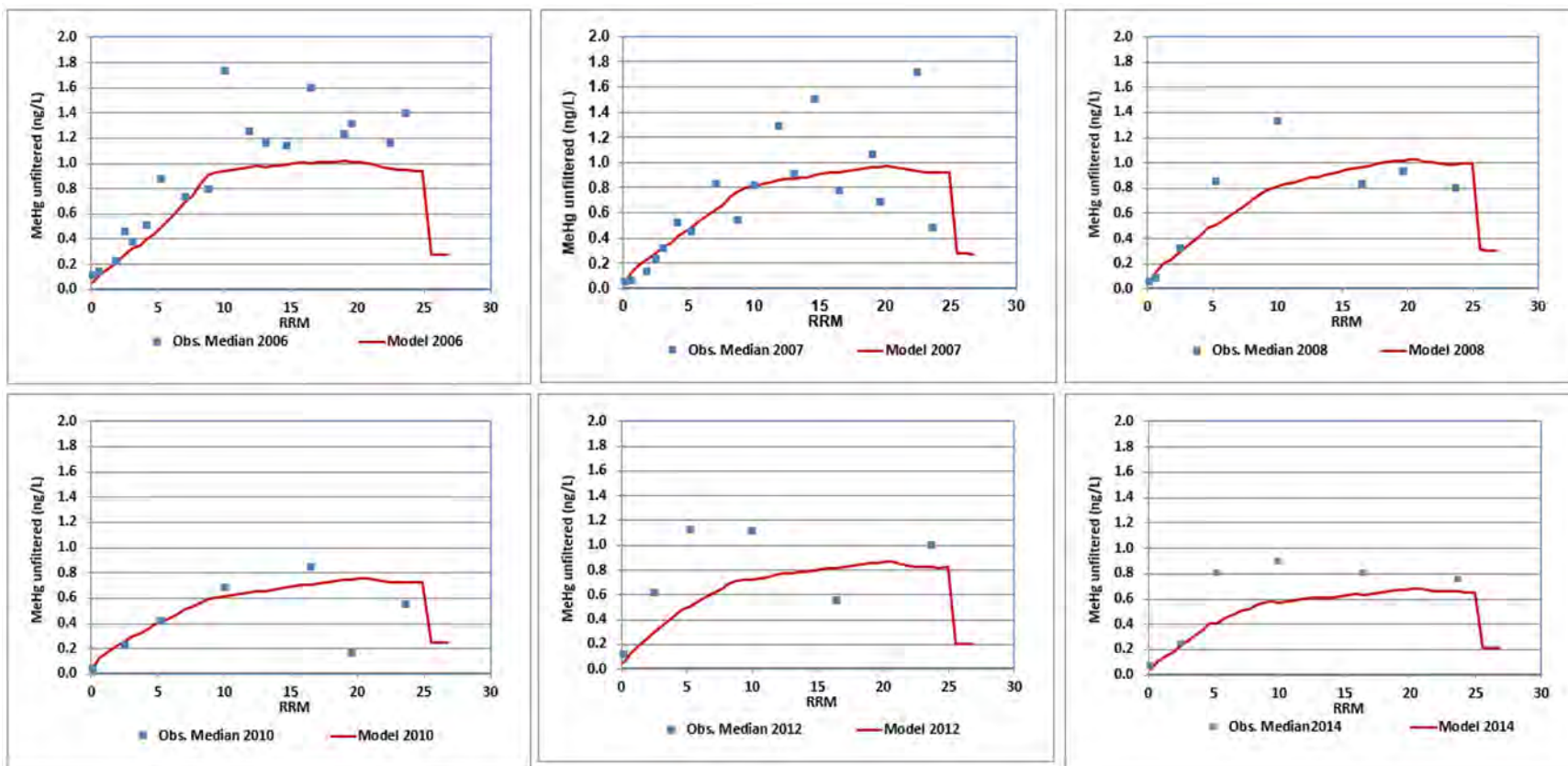


Figure D5. Predicted and observed concentrations of unfiltered MeHg in surface waters – alternative calibration. Values are medians for each year at different locations. Data from Flanders (2016)

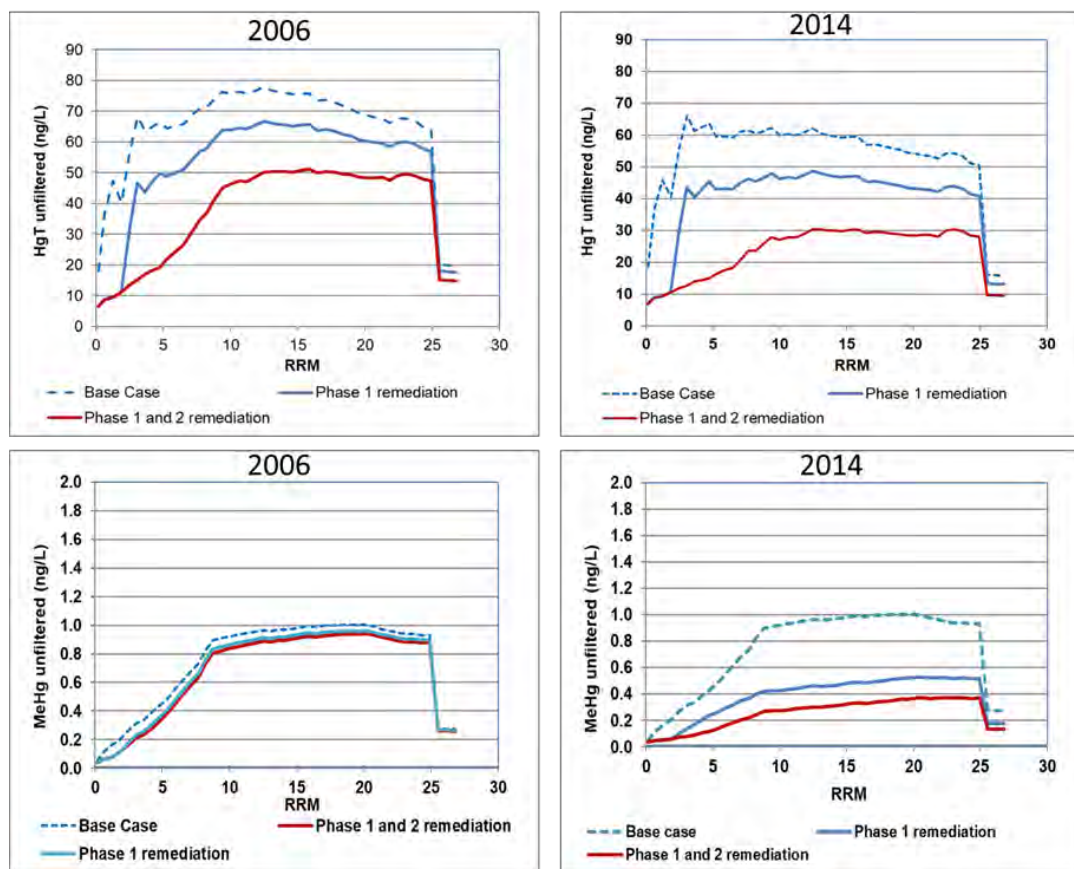


Figure D6. Predicted effect of Phase 1 and Phase 2 remediation (reduced bank erosion from RRM 0-2) on concentrations of THg and MeHg in water. Assumes remediation instantly implemented January 1, 2006. Values are average concentration for a given year.