South River Remedial Options Program (ROPs) – Aquatic Conceptual Site Model

Between 2009 and 2011, a ROPs task team was chartered to develop an evergreen conceptual site model (CSM) for the South River aquatic system to help explain how Hg moves through the ecosystem to biota as well as to assess the potential benefits of remediation options. In particular, the CSM highlights the key processes affecting methylmercury (MeHg) concentrations in the biota of concern in the aquatic system.

Team Members

Jim Dyer (DuPont)
J. R. Flanders (URS)
Nancy Grosso (DuPont)
Reed Harris (Reed Harris Environmental Ltd.)
Rich Landis (DuPont)
Greg Murphy (formerly URS)
Jim Pizzuto (University of Delaware)

Objectives and Approach

Specific objectives for the CSM were to identify

- Hg sources and pathways that are primarily responsible for elevated Hg levels in fish in the contaminated reach of the South River,
- factors controlling the slow rate of natural recovery of the system,
- feasible pathways to intercept in order to reduce fish Hg levels, and
- gaps in the data or state of knowledge of Hg cycling that should be addressed to better assess remedial options.

The CSM was developed using existing information from a wide range of SRST-sponsored studies already conducted along the South River. Multiple lines of evidence were used, where possible, including field studies, laboratory experiments and numerical models. The CSM presented in this briefing paper focuses on base flow conditions for RRM 0 to 10.

Hg fluxes were estimated in terms of the Hg ultimately delivered to smallmouth bass. A key assumption in developing the CSM was that all inorganic Hg sources are equally bioavailable for methylation, although evidence indicates that the leachability of dissolved and colloidal inorganic Hg from freshly eroded bank and floodplain soils is much greater than from water-saturated river sediments that have been exposed to river water for some time. This important assumption regarding the bioavailability of different inorganic mercury sources is subject to ongoing examination.

Sources of Mercury to Fish in the South River

The CSM focuses on Hg sources that are methylated and ultimately bioaccumulate in smallmouth bass. These Hg sources may occur either as direct MeHg loads or as inorganic Hg loads that are subsequently methylated, and include

- residual seepage from the former DuPont plant outfall,
- tributaries,

- groundwater,
- floodplain runoff,
- inflows from upstream,
- bank erosion,
- bank leaching, and
- fluxes from legacy Hg contamination from deeper sediments to surface sediments.

Atmospheric deposition is a negligible contributor (< 0.03%) to Hg loading in the contaminated portion of the South River.

Multiple lines of evidence (mass balance calculations, benthic flux chamber studies, and mass transfer models) suggest that methylation occurs *in situ* in surface sediments located in areas with fine-grained material. In the South River, this includes both the coarse-grained gravel beds, which comprise approximately 85% of the total river bed area, and fine-grained (channel margin) sediment deposits, which account for the remaining 15%. While reported in anoxic freshwaters, water-column production of MeHg is unlikely in this river setting. Zones of methylation within these sediments currently contain legacy inorganic Hg contamination that will take time to dissipate (time scale of decades) even if external sources are completely eliminated. However, there is evidence in the literature and from laboratory studies at the University of Waterloo that "aged" particle-associated (non-colloidal) mercury in the river bed may be less bioavailable than "fresh" inorganic Hg entering the system from eroding banks and the plant outfall. This is a potential contributor to the natural recovery of the system if inputs from eroding banks are reduced.

The area of greatest Hg contamination in the river is from RRM 0 to RRM 10. This reach not only contains the original point source of Hg release, but it also has a shallower river slope and wider floodplain than points farther downstream. A CSM of Hg loading, cycling, and bioaccumulation was first developed for this reach of the river. Independent estimates were made for each potential source of inorganic Hg to zones of methylation in sediments using data from a wide range of existing field and laboratory studies, including the Phase I and II ecological studies, RCRA corrective action studies at the former DuPont plant, Virginia DEQ monitoring studies, the South River Hg TMDL, river morphology studies, laboratory sediment leaching studies, and benthic chamber flux data.

Estimated Hg sources and abiotic fluxes ultimately leading to MeHg accumulation in smallmouth bass from RRM 0 to 10 are presented in Figure 1. The largest source is estimated to be bank erosion of legacy inorganic Hg previously released from the facility and deposited in near-bank areas (40-60%). Statistical models developed independently of the CSM by John Green (DuPont) as well as multiple, independent modeling studies completed by URS, DuPont, HydroQual, University of Delaware (Jim Pizzuto), and USGS (TMDL, Jack Eggleston) strongly suggest that bank erosion is a significant component of the increase in water-column inorganic Hg loading between RRM 0 and 10.

It is important to note that bulk loading of Hg to the water column from bank erosion is not necessarily equivalent to the loading of Hg delivered to sites of methylation. Particles with low sorbed Hg concentrations, for example, might actually adsorb additional dissolved Hg, rather than release it to the dissolved phase. Hg contamination on particles might also be so strongly bound to the surface that little of the Hg loaded to the water column will desorb and become available for methylation. Conversely, sediment and soil leaching experiments at the University of Waterloo have clearly shown that inorganic

Hg is readily desorbed from South River bank and floodplain soils in both dissolved and colloidal forms. While it is difficult to quantify the precise fraction of the Hg on solids that leaches/desorbs and contributes to methylation, the potential for this to occur is high. Filter-passing concentrations of inorganic Hg also increase from RRM 0 to 10.

Attempts to close the mass balance for filtered (dissolved) inorganic Hg in the water column had an insufficient supply of dissolved Hg unless desorption of inorganic Hg from eroding bank soils was included in the mass balance model. Benthic flux chamber data and predictive mass transfer flux models could, at most, account for ~50% (5 g/d) of the filter-passing inorganic Hg load in the water column (9.5 g/d) over the 10-mile reach from RRM 0 to 10. The remaining 4.5 g/d is attributed to desorption from eroding bank soils and/or bank leaching. Independent calculations indicate that less than 0.5% of the total inorganic Hg available in eroding bank soils needs to desorb to close the mass balance for filtered inorganic Hg. This is in contrast to MeHg where both filtered and total loads in the water column can be accounted for by measured and modeled fluxes from the river bed.

The second largest source of inorganic Hg that ultimately bioaccumulates as MeHg in smallmouth bass is advective and diffusive fluxes of inorganic Hg from legacy contamination in deeper sediments (15-35%). Benthic flux chamber studies and mass transfer model calculations indicate that average total Hg flux rates due to advection plus diffusion from the river bed are on the order of 0.5 g d^{-1} per mile from RRM 0 to 10 as compared to Hg loading from banks which ranges from 1 to 4 g Hg d^{-1} per mile from RRM 0 to 10. For MeHg, benthic flux chamber studies and mass transfer model calculations indicate that average total MeHg flux rates due to advection plus diffusion from the river bed are on the order of 0.05 g d^{-1} per mile from RRM 0 to 10.

When averaged over the 10-mile reach from RRM 0 to 10, residual seepage from the former DuPont plant and inflows from upstream are estimated to be less significant sources of inorganic Hg that ultimately bioaccumulate in smallmouth bass as MeHg (Figure 1). Locally, however, the plant outfall will be a more important source of bioavailable inorganic Hg for methylation. Bank leaching is currently estimated to contribute 1-5% of the inorganic Hg that ultimately bioaccumulates in smallmouth bass as MeHg. However, this estimate is currently being revisited as part of the University of Delaware biogeochemical study of HRAD bank soils at RRM 3.5.

Direct external loads of MeHg from bank and the floodplain soils are currently estimated to be of minor importance. Due to the greater presence of coarser-grained embedded gravel beds in the river compared to fine-grained sediment areas (roughly 85% vs. 15% on an area basis), the majority of MeHg supply in the river is expected to be from interstitial areas of the embedded gravel beds. Higher inorganic Hg and MeHg porewater concentrations in fine-grained sediment areas of the river resulted in slightly greater weighting of fine-grained sediment areas compared to using just areal coverage.

Major storms (e.g., flow rate > 1000 $ft^3 s^{-1}$) have the potential to mobilize Hg and induce a newly contaminated system state via mechanisms including:

- Increased erosion rates in river banks and the river bed;
- Higher water levels, resulting in greater areas of inundated banks;
- Increased loading of inorganic Hg to the river via floodplain runoff;

- Increased interflow (soil water drainage);
- Side channels that are not part of the low-flow regime may become inundated and better connected hydrodynamically with the river. These areas may also experience increased erosion compared to low-flow conditions.

The above mechanisms may be at least partly offset by the introduction of low-mercury sediments from upstream and reduced erosion of contaminated soil from stabilized river banks. For example, ecological study data show lower Hg concentrations on particles during periods of high flow in the South River, presumably due to the influx of lower-Hg solids and water from upstream.

Downstream of RRM 10, river conditions change, and it cannot be assumed that the conclusions reached upstream of RRM 10 also apply downstream. The river slope from RRM 10 to 24 is double that for RRM 0 to 10. As a result, fine-grained deposits are less common in the steeper river reach, and the floodplain is narrower. There was therefore less of a tendency for mercury releases from the former DuPont plant to accumulate in this stretch of the river and floodplain. Under base flow conditions, an incremental loading analysis performed by HydroQual in 2009 showed that net loading of total Hg to the water column is often negative downstream of RRM 10. It is expected that the primary source of Hg downstream of RRM 10 under base flow conditions shifts from river banks to inflows from upstream. An implication of this finding is that fish MeHg exposure downstream of RRM 10 might be significantly reduced if Hg contamination upstream is addressed. The HSPF model used by the USGS in the development of the Hg TMDL for the South River suggested that floodplain runoff during storms becomes a more important contributor to annual Hg loading to the water column downstream of RRM 10. During high-flow events ($> 1000\ ft^3\ s^{-1}$), net Hg loading to the water column becomes positive downstream of RRM 10 due to increased contributions from bank erosion and floodplain runoff.

MeHg Bioaccumulation in the South River

MeHg produced in sediments moves into the base of the food web before ultimately being accumulated by smallmouth bass (excluding the minor direct uptake across the gills). Compartments at the base of the food web include periphyton, surface coatings on rocks, seston (TSS), submerged aquatic vegetation, and detritus/fine sediments (Figure 1). Bioenergetics modeling predicted differing degrees of importance for each of these compartments as a source of MeHg that ends up in smallmouth bass (Figure 2). Field studies and modeling were used to identify the trophic structure of the aquatic food web in the South River and associated MeHg fluxes (Figure 2). Field studies included fish capture and stomach content analyses for several fish species, food web C/N isotopic studies, invertebrate dietary studies, and MeHg uptake studies for mayfly nymph and crayfish. MeHg dynamics in smallmouth bass, redbreast sunfish and common shiner were simulated using the BASS bioenergetics model. Consistent with several other studies, 90% or more of the estimated MeHg supply to fish was via the diet, rather than gill uptake. Approximately 90% of the predicted dietary uptake of MeHg by smallmouth bass was via aquatic organisms, while ~10% was via consumption of terrestrial insects. When the origin of MeHg supply to smallmouth bass was traced back to the base of the food web in simulations, an important link to the water column was predicted, with half or more of the MeHg ultimately accumulated by smallmouth bass being derived from seston and filtered water, while roughly one third was taken up by periphyton, surface coatings, and detritus associated with sediments or the sediment-water interface (where a water component to MeHg exposure is also likely involved). It is not clear how quickly MeHg exchange occurs among these various compartments at the base of the food web, but it could be rapid.

Storms have the potential to impact the biological conditions affecting MeHg production and bioaccumulation in aquatic (and terrestrial) biota via:

- Increased MeHg production associated with wet/dry cycling around storms;
- Potential changes in aquatic invertebrate biomasses and community structure, although evidence exists that effects are short-term in duration;
- Shifts in fish food habits, reproduction, bioenergetics, and MeHg uptake.

These hypotheses on the effects of storms require further evaluation, as well as the assumption that all MeHg supplied to different compartments at the base of the aquatic system is quickly exchangeable among compartments.

Implications of the Conceptual Model for Remediation

The current evergreen conceptual model suggests that remedial alternatives which address Hg loading from banks (physical erosion and leaching) may substantially reduce fish Hg levels in the South River, but not necessarily to background levels. In addition to bank inputs, Hg contamination is also supplied to the river to a lesser degree via other pathways, including diffusion from deeper sediments and delivery from the floodplain. Although multiple lines of evidence indicate that the leachability of dissolved and colloidal inorganic Hg from freshly eroded bank and floodplain soils is much greater than from water-saturated river sediments that have been exposed to river water for some time (legacy sediments), this assumption regarding the bioavailability of different inorganic mercury sources requires further examination.

As a result, a suite of actions may be needed to maximize reductions in the supply of legacy Hg contamination and associated fish Hg levels in the river. The solution to elevated fish MeHg concentrations in the South River will require an adaptive management approach that utilizes a number of remedial actions coupled with a well-designed, focused monitoring program for ongoing recovery.

Uncertainty and Future Needs

Conceptual models evolve and are refined as improved information becomes available. In the case of the conceptual model for Hg in the South River, uncertainty currently remains regarding the potential influence of large storms on the benefits of bank stabilization. To what extent will pre-stabilization loadings be renewed or, alternatively, will a large supply of low-Hg content solids from upstream actually accelerate the recovery of the system, as long as stabilized banks remain intact. An assessment of the expected relationships between storm flow, erosion, new deposition of Hg-contaminated and low-Hg particles, and renewal of elevated MeHg production may provide guidance for the necessary extent of bank stabilization (e.g., 90% of stabilized banks must be stable in a 30-year flood event).

As introduced above, one way to manage uncertainty is to use a phased or adaptive implementation approach to remediation. Adaptive implementation permits a plan to be executed in a way that measures results over time and includes a process for adapting the plan (including tactics and timelines) based on feedback received from performance measurement data.

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Figure 1

Hg Sources & Abiotic Pathways Leading to MeHg Accumulation in Smallmouth Bass in the South River Baseflow Conditions, RRM 0 to 10

Values are the percent of MeHg supply to smallmouth bass. The green box represents compartments at the base of the ecosystem that are primary connections to MeHg in the food web.

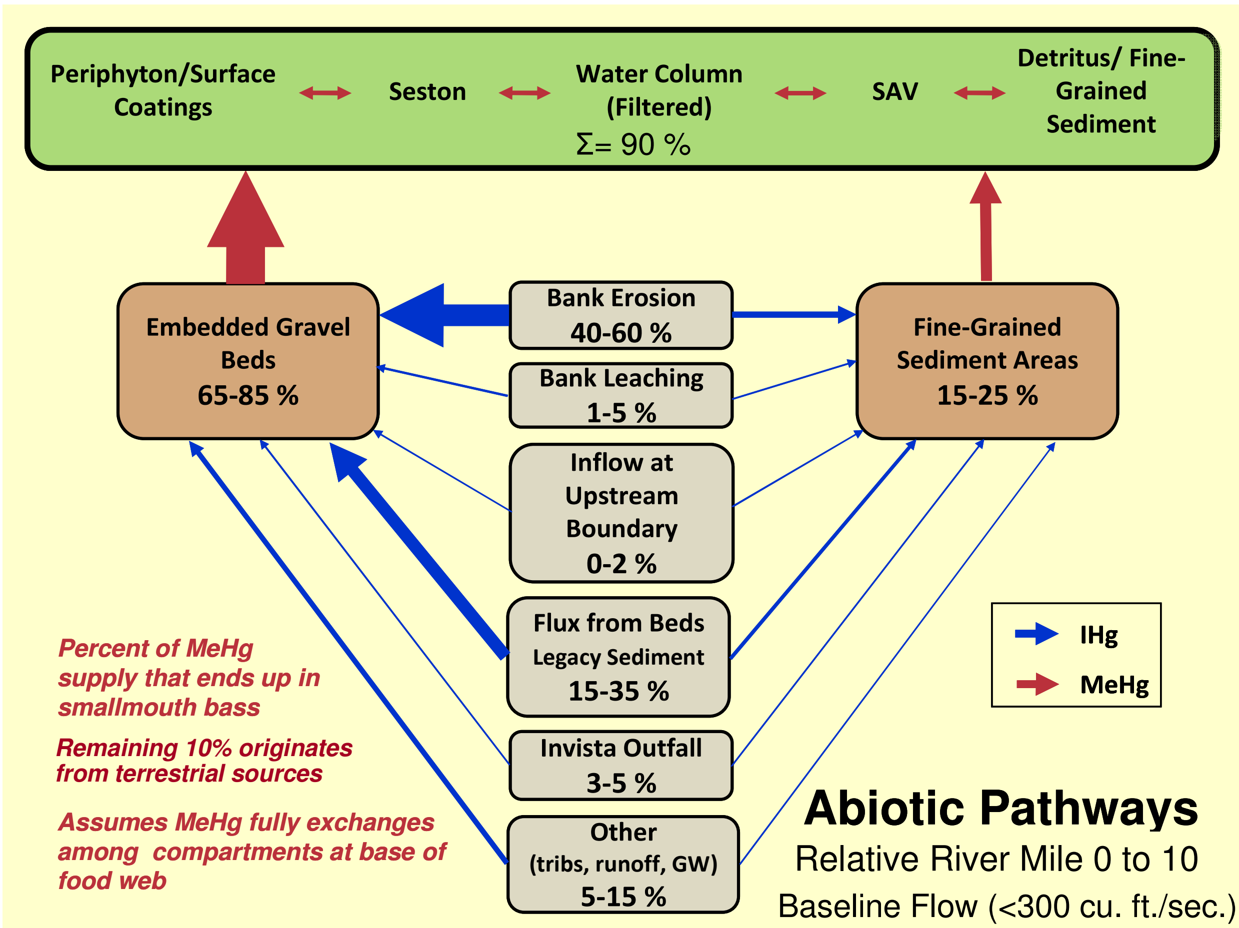

Figure 2

Conceptual Model of the Flow of MeHg Through the Food Web to Smallmouth Bass in the South River