Multiple Working Hypotheses to Explain Total Mercury and Methylmercury in South River Water Sediment and Biota

This monograph outlines the scientific hypotheses that have been, are being, or will be tested to explain the spatial and temporal patterns of mercury in South River water, sediment, and biota. This document also provides documentation for hypothesis testing and details the current status of efforts. Most of the hypotheses are related to mercury and methylmercury in river water and sediment but it is understood that identifying the correct explanations for these media will lead to explanations for mercury in prey species, fish, and aquatic wildlife. The hypotheses are not mutually exclusive, i.e., more than one mechanism or process may explain the distribution and behavior of mercury in the South River. In addition, the list is not intended to be complete or final as new data from the South River or findings elsewhere may suggest additional hypotheses.

General Hypothesis

Ongoing sources of mercury to the South River are present and have prevented the expected decline of mercury in fish tissue. The potential sources for current mercury inputs to the river can be separated into the following:

- Inputs potentially derived from historical releases
- Inputs based on current releases from one or more contemporaneous sources

Potential pathways for historical inputs include the following:

- Bedrock groundwater
- In-channel fine-grained sediments (as discrete deposits, as fine-grained material between cobbles and gravel, or as low density detritus/fine-grained material associated with more quiescent in-channel areas)
- Floodplain soils through bank erosion and floodplain drainage channels
- Landfills
- Dumping
- Dredge spoils
- Storm sewers (residual deposits)
- Quiescent backwaters such as wetlands, oxbows, and abandoned mill races
- Alluvial groundwater from downstream floodplain

Potential pathways for current inputs include the following:

- Atmospheric deposition
- Point source discharges
- Nonpoint source discharges
- Dumping
- Fertilizers
- Other industrial inputs

The sub-elements of this general hypothesis address one of the key questions initially posed by the South River Science Team and subsequently by the ecological study—How is mercury getting into the South River? This monograph details the working hypotheses to explain the following:

- ☐ Total mercury in South River water (see Table 1)
- ☐ Methylmercury in South River water (see Table 2)
- ☐ Total and methylmercury in South River sediments (see Table 3)
- ☐ Changes (or lack thereof) in mercury in South River fish tissue (see Table 4)

References (cited in tables that follow)

Bloom, N. and Preus E. (2003) Anoxic sediment incubations to assess the methylation potential of mercury contaminated solids. *Ecotoxicology, 2nd Intl. Symp. On Contaminated Sediments*, pp. 331-336.

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Table 1. Working Hypothesis to Explain Total Mercury in South River Water

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
1) DuPont plant site is a significant point source. a. Surface water effluents b. Groundwater inputs	1) Sample outfalls over range of flows and calculate loading to river. Compare load to upstream and downstream loads.	Completed and described in a monograph on plant site effluents, stormwater and groundwater as Source(s) of Mercury to the South River.
	2) Measure hydraulic gradients and conductivities. Sample monitoring wells and estimate loading via groundwater pathway.	Completed and described in a monograph on plant site effluents, stormwater, and groundwater as sources of mercury to the South River.
2) Sediments adjacent to plant site are point source(s). Mercury-contaminated sediment, including possibly free elemental mercury, is present in sufficient quantities and/or in "soluble" enough form(s) to account for the observed increase in particulate and dissolved mercury in the South River downstream of the plant.	1) Sample shallow and deep sediments adjacent to plant site. Compare concentrations (e.g., deep vs. shallow) to samples from upstream and further downstream. Is mercury in deeper sediments greater than shallow sediments? Are sediments adjacent to the plant significantly higher in mercury than either upstream or downstream sediments? Are there significant quantities of sediment in the South River adjacent to the plant?	Completed and described in a monograph on the size classified sampling of sediment between and beneath gravel and cobbles in the South River bed.
	2) Sample sediment porewater adjacent to plant site. Compare porewater concentrations to concentrations in overlying surface water. Are porewater mercury values greater than surface water values?	Completed and described in a monograph on the relationship of river fluxes and methylmercury inventories.

Table 1. Working Hypothesis to Explain Total Mercury in South River Water (continued)

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
3) Groundwater and/or tributary inputs *downstream* of the plant are significant source(s) a. Point sources (e.g., springs, tributaries, POTWs, landfill drainage) b. Area sources (seepage through stream bed)	1) Sample all tributaries, springs and POTWs downstream of the plant over range of flows. Measure/estimate flows and calculate loading. Compare load to upstream and downstream loads.	In progress.
	2) Use temperature or other index to detect suspect groundwater inputs.	Limited work in suspect area but no temperature anomalies detected.
	3) Examine water balance for river to detect anomalous changes in flow for each reach.	Preliminary whole river water balances developed and described in monograph on South River geology and hydrogeology.
	4) Use existing monitoring wells (or install new ones) in floodplain or nearby to sample for dissolved mercury and determine hydraulic gradients.	Pending for Genicom wells only. Alluvial groundwater program in planning stage.
	5) Consider using natural (e.g., Ca/Mg) or anthropogenic (contaminants) tracers of groundwater along the river to establish hydraulic connection(s)	Nothing currently planned.
	6) Sample selected reaches of river at close intervals to detect step changes in dissolved mercury. Associate, if possible, such changes to known or suspected inputs.	Partially completed and described in the monographs on the close interval sampling and the clam studies.

Table 1. Working Hypothesis to Explain Total Mercury in South River Water (continued)

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
4) In-stream bed sediments *downstream* of the plant are significant source(s) of dissolved and particulate mercury. a. Historic deposits b. Ephemeral deposits	1) Map bed deposits/substrate, especially fine-grained sediments (silt-clay, organic-rich). Sample for total mercury content and porewater mercury. Compare locations of significant accumulation and/or porewater concentrations to particulate and dissolved mercury concentrations in surface water.	Mapping of deposits in progress as part of geomorphological evaluation and described in the monograph on geomorphology. Porewater work is planned.
	2) Evaluate solubility of mercury in bed sediments with laboratory extractions using river water. Conduct multiple extractions using both “clean” water/contaminated sediments and “contaminated” water/clean sediments. Do bed sediments appear to be sources or sinks for dissolved mercury? Is the relationship between solid and solution concentrations an equilibrium state? Does redox state of sediments affect release?	Preliminary work completed and described in the monographs on ambient mercury incubation experiments and mercury releases from simulated suspended matter.
	3) Sample surface water at mid-depth/mid-stream and compare dissolved mercury values to near-bottom and near-bank. Are mid-stream/mid-depth values less than near-bottom/near-bank? Are near-bank anomalies associated with eroding banks or areas of suspect groundwater inputs?	Preliminary results available; further evaluation needed.

Table 1. Working Hypothesis to Explain Total Mercury in South River Water (continued)

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
5) Floodplain soils are significant source(s) a. In situ leaching (e.g., local groundwater, see 3b) b. Bank erosion (see 4b)	1) Map mercury content and distribution in floodplain soils, especially the contents of eroding/eroded banks. Compare values to those for fine-grained bed sediments and mercury on TSS (particulate Hg $_{ng/L}$/TSS$_{mg/L}$). Compare locations of significant accumulation to particulate and dissolved mercury levels in surface water. Measure/model stability of riparian floodplain soil deposits.	Preliminary work completed and described in the monograph on eroding bank sampling. Additional work is in progress and described in the geomorphology of the South River monograph.
	2) Sample near-bank bed sediments adjacent to eroding/eroded banks. Are values “enriched” compared to bed sediments collected near non-eroding banks and mid-stream?	In progress.
	3) Evaluate solubility of mercury in floodplain soils using laboratory extractions using river water. Conduct multiple extractions using both “clean” water/contaminated soils and “contaminated” water/clean soils. Do soils appear to be sources or sinks for dissolved mercury?	Preliminary work completed and described in the monograph on the ambient mercury incubation experiments and the mercury releases from simulated suspended matter monograph.

Table 1. Working Hypothesis to Explain Total Mercury in South River Water (continued)

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
6) Atmospheric inputs are a significant source a. Historic (watershed soils, see 3b and 5a) b. Current direct deposition	1) Use regional Mercury Deposition Network (MDN) and similar datasets to estimate wet deposition in Shenandoah Valley. Calculate atmospheric loading to river as fraction of loading from known internal loadings.	Assumed to be conducted by the USGS TMDL group.
	2) Measure tributary dissolved mercury concentrations in Rockfish Run, Steele Run, and others that are more distant from Waynesboro but draining otherwise similar watersheds. Compare values to determine if there is a local anomaly near Waynesboro that could be explained by historic or current atmospheric plant emissions.	Pending. Some of this work is described in the monograph on the Steele Run and oxbow sampling.
	3) Measure gaseous and particulate mercury in ambient air over the South River floodplain. Are concentrations higher than expected based on comparisons to regional and global levels?	Air monitoring station (temperature, wind speed/direction, particulate mercury, gaseous mercury) established at Augusta Forestry Station in June 2005.

Table 2. Working Hypothesis to Explain Methylmercury in South River Water

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
1) Ex situ generation and input of dissolved and particulate forms a. Floodplain including riparian wetlands b. Effluents (landfill leachate, STPs, DuPont effluents, groundwater inputs) c. Use of mercury catalyst at plant between 1929-50 unintentionally produced methylmercury (e.g., via side alkylation reaction) that is still being released from contaminated soils/sediments	1) Measure methylmercury concentrations in floodplain/wetland soils and runoff/seepage/shallow groundwater. Compare values to South River bed sediments, $MeHg_{TSS}$, and $MeHg_{diss}$.	In progress.
	2) Measure methylmercury in all significant effluents over range of flows. Compare concentrations and estimated loadings to South River concentrations and loadings.	Partially completed.
	3) Measure methylmercury and possible related organoforms of mercury in soil/sediment layers that have been dated to 1929-1950 period. Are total mercury and methylmercury highly correlated in these layers even though over 60 have elapsed since deposition?	In progress.
2) In situ generation and release to surface water or uptake by biota a. Within bed sediments without periphyton/biofilm b. Within periphyton/biofilm materials c. Within water column	1) Measure methylmercury in biofilms, bed sediments, and sediment porewater. Compare values to surface water. Estimate or measure diffusive/advective fluxes using benthic flux chambers or similar approaches.	In progress and described in monograph on benthic flux chambers. Additional effort is underway by Dr Mike Newman (College of William and Mary)
	2) Conduct time-series surface water and incubations with and without sediment (e.g., ambient mercury incubation experiments).	Initial study completed and described in monograph on ambient mercury incubation experiments.
3) The South River is *not* enriched in mercury-resistant bacteria and thus mer-mediated methylmercury degradation is inhibited, allowing accumulation and uptake of this form of mercury.	3) Assess resistance of the indigenous microbial community to mercury using established methods (see Schaefer et al., 2004)	No activity thus far.

Table 3. Working Hypothesis to Explain Total and Methylmercury in South River Sediments

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
1) Deposits are historic and contemporaneous with 1929-50 releases from former facility and have not been significantly displaced downstream by the normal and extremes of river flow.	1) Collect long sediment cores of deposits for mercury analysis and chronology of deposition. 2) Map locations of current fine-grained deposits and compare to historic aerial photographs.	1) Partially completed and described in the deep core sampling and analysis monograph. Additional work is in progress and planned in association with the geomorphology study (see the geomorphology monograph). 2) In progress and described in the monograph about the geomorphology of the South River.
2) Deposits are recent and originate from floodplain soils that are (a) scoured or undercut by storm flow, (b) displaced by natural freeze/thaw action, or (c) disturbed by agricultural/urban activities (e.g., cultivation, domestic animal grazing/traffic, urbanization)	Prepare sediment budget/model for the South River.	In progress and described in the monograph on the geomorphology of the South River.
3) Sediments are contaminated by current inputs and sorption of soluble total and methylmercury from effluents or groundwater.	Measure concentrations of dissolved total and methylmercury in current inputs and within South River mixing zones. Does dissolved mercury rapidly partition to South River suspended matter?	No activity thus far aside from measurements in selected effluents.
4) Methylmercury in mainstem sediments is produced and exported from episodically flooded soils.	Measure methylmercury in erodible surficial soils of episodically flooded soils seasonally. Compare values to mainstem surficial sediments collected at same time.	Work planned for NRDC ecological study.
5) Methylmercury in mainstem sediments is produced in situ from bioavailable total mercury in sediments.	Measure methylmercury in surficial sediments seasonally. Measure potential methylation in surficial sediments using incubation protocol (e.g., Bloom and Preus, 2003)	Work planned for NRDC ecological study.

Table 4. Working Hypothesis to Explain Changes (Or Lack Thereof) in Mercury in South River Fish Tissue

Working Hypothesis	Sampling/Experimental Approaches To Evaluate	Status
Selenium or other sequestering constituents in South River water and sediment is not present in sufficient quantity to sequester mercury or otherwise prevent/reduce biological uptake.	Measure selenium and mercury/selenium ratios in South River water, suspended matter, sediment, and fish tissue. Compare results to other systems where this hypothesis has been tested or data for both mercury and selenium in environmental media are available (e.g., Southworth et al 2000).	No activity thus far.
The South River is *not* enriched in mercury-resistant bacteria and thus mer-mediated methylmercury degradation is inhibited, allowing accumulation and uptake of this form of mercury.	Assess resistance of the indigenous microbial community to mercury using established methods (see Schaefer et al., 2004)	No activity thus far.
Water quality conditions (e.g., sulfate, chloride, biological oxygen demand, fecal coliform, dissolved oxygen) have changed in the South River over the last 20 years in a manner that favors the formation of methylmercury on a local or more regional scale, and this has resulted in increases in mercury concentrations in fish tissues.	Review information developed by VADEQ and Friends of the Shenandoah to assess trends and correlations. Review experiences at other sites where general water quality changes appear to have affected mercury in fish tissues (e.g., Southworth, 1999).	Preliminary evaluation completed. No trends noted.
Observed changes in fish tissue mercuryconcentrations result from changes in the dietary preferences of important fish species in the South River during the past 20 years.	Conduct fish dietary studies in South River and reference locations.	Completed; see Murphy, 2004.