south river
SCIENCE TEAM

EXPERT PANEL MEETING
OCTOBER 10-11, 2007
BRIEFING PAPERS

FEASIBILITY OF BANK STABILIZATION AS AN EFFECTIVE AND EFFICIENT SR REMEDY

Bank Stabilization Pilot

South River Science Team and Expert Panel Meeting
Nancy Grosso October 2007

Background:

Currently, there are a number of potential sources of total mercury to the SR aquatic system or within the aquatic system, some of which may be dominant in some reaches and not others.

The reintroduction of mercury into the system from eroding banks is currently one of the leading hypotheses for potential on-going sources, at least in certain reaches of the river. This hypothesis is based on mercury profiles of bank soils, the way in which banks are eroding, and sequential extraction tests and "shake and bake" experiments. The Bank Stabilization Pilot will begin to explore what might be done to mitigate bank erosion into the river. A secondary objective of this pilot is to test whether physical stabilization technologies can also cut off interaction between mercury in the bank soils and the aquatic system to reduce the potential for dissolution of mercury through wetting and drying of the banks. Since bank stabilization is a well established technology, the proof of the technology is not an issue. However, we will need to assess whether the physical stabilization also isolates mercury in the banks from the river.

Primary Objective:

Assess the efficacy and feasibility of conventional bank stabilization for isolating mercury-containing bank soils from the South River aquatic system. Other objectives, such as habitat improvement may be identified through dialogue with Core Team members.

Core Team

- DuPont: Nancy Grosso, Rich Landis, Bill Berti, Ed Lutz, Ralph Stahl
- URS: Bruce Bayne, Todd Morrison
- VADEQ: Calvin Jordan
- VADGIF: Larry Mohn
- U of D (Geomorphologist): Jim Pizzuto
- Interfluve (Consultant Contractor): Greg Koonce

The Core Team is currently developing a plan and will work together to explore potential challenges and optimal approaches.

Status of Work

The team is just beginning to solidify some of the needs for the design of a pilot. To date, we have selected a pilot site on the eastern (right) bank of the South River from approximately RRM 0 to RRM 0.16. This site which is 500 to 900 feet long has been selected for a number of reasons: there is evidence of bank erosion, soil Hg concentrations in bank are above background, Dupont owns the land, the layout allows easy access for construction, maintenance and monitoring, the adjacent land use is recreational and is used intermittently, and the site is located in the upper region of the river with respect to sources. The tentative schedule is to have construction plans out for bid 4Q08 and to construct 4Q09. By the end of 2007, our goal is to complete the conceptual design.

Plan

1. Brainstorm with Core Team on Goals and Objectives and Finalize
2. Research and Prepare Permits List
3. Conduct pre-design investigations (groundwater flux, habitat and wetland assessment)
4. Start to develop Public Communications approach
5. Establish measures of success
6. Develop conceptual design with consideration of materials handling
7. Develop 30%, 60% Design
8. Develop 100% Design including baseline and post construction monitoring plans
9. Obtain permits
10. Complete baseline characterization
11. Construct and Monitor

Measures of success for the pilot may involve a hierarchy desired outcomes, and then whether or not these can be measured. Thorough and appropriate characterization of baseline conditions will be necessary to monitor the effects of the pilot. A more extensive monitoring program may help to define just how significant bank erosion is as an ongoing source.
Possible Measures of Success:

- Bank is not eroding or has very low erosion rate as demonstrated by LiDAR and traditional measurements – is a zero erosion goal necessary?
- Bank is not attracting fine particle deposition (?)
- No visual evidence of bank failure (soil clumps at base of bank)
- Measures more difficult to link specifically with pilot –
    - Caged clam tissue concentrations reduced
    - Hg on TSS locally reduced
    - Filtered and total Hg locally reduced,
    - Longer term - reduced flux of Hg out of sediments

A characterization and monitoring program will be developed that will likely include upstream and downstream monitoring as well as a temporal component.

Baseline Characterization Initial Thoughts:

- Current Bank Topology: using LiDAR and conventional methods
- Bank soil profile data
- Point samples of near-bank pore water (and some transects into river)

- Near bank surface samples
- Near bank sediment sweeping
- Caged Clams

South River Remedial Options Program (ROP)
Initial Tasks to Assist in Screening of Remedial Alternatives

Nancy Grosso, DuPont *October 2007*

Background

Over the past several years, a significant data set has been collected to refine our understanding of the physical, chemical and biological elements of the South River system. While many studies are ongoing, it was recognized that a view toward possible remedial actions was needed in order to begin focusing certain study objectives or to optimize current investigation programs. This briefing paper summarizes an initial plan for evaluating remedial technologies.

Overall Remedial Objective for the Aquatic System

Reduce fish tissue Hg levels to concentrations that would allow consumption by humans.

Although the emphasis is currently on fish tissue concentrations, at least some of the learnings from this program are likely to be applicable to floodplain challenges and terrestrial ecology.

Controlling Potential Ongoing Sources

Currently, there are a number of potential sources of total mercury to the SR aquatic system or within the aquatic system, some of which may be dominant in some reaches and not others. These include:

1. Ongoing source of mercury by eroding banks that introduce the floodplain inventory back into the aquatic system.
2. Ongoing source of mercury through wetting and drying cycles of the banks that dissolves / desorbs total mercury
3. Introduction of dissolved mercury into the system by advective flux of groundwater through mercury-bearing sediments or from alluvial groundwater itself
4. Storage of mercury in fine-grained deposits in long pools, bench deposits, deposits associated with point bars, and remnant deposits of historic mill dams that are in contact with the aquatic environment.
5. Partitioning of mercury from fine-grained in channel sediments resident in gravel and cobble bed interstices to pore water and subsequent transport of dissolved mercury through sub-bottom stream lines into the water column (stream pumping).
6. Mercury released from in channel coarse deposits due to physical bed movement and release of formerly trapped pore water (turnover) or fines.
7. Methyl mercury production within the wetted perimeter of the river in low DO environments, in discrete patchy thin zones just below the sediment water interface, in the periphyton biomass, and within biofilm materials.

Using the hypotheses on potential sources of total mercury and methyl mercury, a number of challenges with respect to remediation in the aquatic system were identified. Control of potential sources or bioavailability were rephrased into a series of five questions and a lead for each of these was identified (core team members are shown in parentheses and the lead is underlined).

1. What can be done to reduce or cut off introduction of total mercury from the floodplain sediments through eroding banks? (Grosso, Landis, Lutz, Stahl, Morrison, Bayne, Koonce, Pizzuto, Jordan, Mohn)
2. What can be done to reduce dissolved mercury in water? (Turner, Sherrier, Dyer, Jensen, others TBD)
3. What can be done to inhibit methyl mercury production? (Flanders, Mack, Turner, others TBD)
4. How can we inhibit Hg release from soil and sediment into the biological system? (Dyer, Berti, Others TBD)
5. Is it possible to tweak the food web to reduce Hg concentrations in the food web? How would this be done? (Morrison, Berti, Newman, Murphy)

Approach for the Remedial Options Program (ROP)

1. **Brainstorm** on current Hg treatment technologies that may have application to the South River.
2. **Initial Technology Screening** A draft approach to address each of these questions was prepared, including technology review, laboratory studies, field investigations or monitoring programs to advance the understanding of feasibility for the SR.
3. **Combine / Prioritize Tasks**. The teams met to discuss the approaches and to prioritize or optimize activities/tasks.
4. **Formulate a Draft Approach to Initial Remedy Evaluation**. A draft program was prepared that summarizes our initial approach (see below).
5. **Finalize the core Team Members.** With the help of DEQ, augment the teams to include interested individuals from the SRST to help implement the elements of the plan.
6. **Obtain feedback from Expert Panel on Plan**: Seek input from the expert panel in terms of content, logical sequence of activities, etc.
7. **Formalize the Approach.** After processing expert panel input, construct a framework for conducting "proof of concept feasibility studies." The approach may and probably will continue to evolve, but such a framework may help to keep our program organized and moving forward.

Proposed Short Term Tasks
As a result of the initial prioritization of tasks, a set of tasks to be completed over the next eighteen months is proposed

Papers Studies
- Conduct a review of full-scale or pilot remedies that have been conducted at Hg-contaminated sites and produce case study summaries (Turner)
- Conduct review of current state of technology to physically or chemically remove mercury from water (Dyer)

- Revisit and, if necessary, expand/update Dyer's review of the state of the art in mercury stabilization (Dyer)
- Review literature for information on how nutrients affect the biogeochemistry of a Hg-rich system with applications to the SR such as the STP and agricultural runoff (Flanders)
- Conduct review of literature to identify ligands (e.g., natural DOC, Se) shown to reduce bioavailability (Flanders on Selenium, Dyer on others)
- Review literature for examples of food web management to reduce bioaccumulative contaminants in predatory fish (Newman)

Laboratory Testing or Specialized Characterization/Speciation and Treatment Studies for Aqueous and Solid Phases

- Conduct full characterization of target sediments and soils to understand Hg speciation and physical/chemical properties (University of Waterloo)
- Speciate mercury in 001 discharge
- For water treatment, select one or more ligands for laboratory or mesocosm evaluation based on efficacy, availability/abundance/cost, and toxicity (side effects). Design experiments to verify efficacy and absence of deliterious / unacceptable side effects
- For soils and sediments, screen possible treatment chemistries in lab for viable candidates using SPLP, for example, as a screening tool. Use dissolved mercury as a surrogate for methyl mercury in screening tests (University of Waterloo)
- Adopt LeachXS methodology to fully test the leachability of the preferred option(s). This includes batch pH equilibrium studies, acid neutralizing capacity, and column mass transfer tests (Vanderbilt University).

Laboratory Testing or Specialized Characterization Bioavailability and Methylation Studies

- Evaluate which analytical measure(s) best represents “bioavailability” (e.g., biosensor response, reactivity, molecular weight, uptake by test organism) (Rutgers)
- Measure inherent *potential* rate of methylation through a ^{203}Hg assay which is inexpensive with well established protocols. (Rutgers)

Discussion

1. STABILIZE BANKS

What can be done to reduce or cut off introduction of total mercury from the floodplain sediments through eroding banks?

Currently, the reintroduction of mercury into the system from eroding banks is one of the leading hypotheses for potential on-going sources, at least in certain reaches of the river. This hypothesis is based on mercury profiles of the bank, the way in which banks are eroding, and sequential extraction tests and “shake and bake” experiments. The Bank

Stabilization Project will begin to explore what might be done to mitigate bank erosion into the river. (see 2007 Briefing Paper). A secondary objective of this project is to cut off communication between mercury in the bank and the aquatic system. Since bank stabilization is a well established technology, the proof of the technology is not an issue. However, we will need to assess whether the physical stabilization also isolates mercury in the banks from the river. The reach downstream of the footbridge to Rockfish Run (east bank) has been selected, and data gaps have been identified. The goal is to have a conceptual design by the end of 2007. Anticipated construction completion date is 3Q09.

2. REDUCE DISSOLVED MERCURY IN THE WATER COLUMN

What can be done to reduce the dissolved (bioavailable) mercury in the water column?

This question pertains to technologies or treatments that could reduce dissolved mercury in the water column (including effluents), and not to those that prevent/reduce mercury releases from sediments and soils. It could also include treatments that alter the bioavailability of aqueous Hg without necessarily reducing the "dissolved" concentration (e.g., increasing the concentration of an Hg-binding ligand to complex with the bioavailable species). The latter approach is covered below. The focus currently is on the plant discharges. Current plans are to conduct review of current state of technology to physically or chemically remove mercury from water – is there a technology that can address low levels of Hg? Can we isolate a richer, smaller stream for treatment at the plant? Then, the feasibility, practicality and effectiveness of the technology will be evaluated.

3. INHIBIT METHYLYMERCURY PRODUCTION / REDUCE BIOAVAILABLE MERCURY

What can be done to inhibit methyl mercury production?

Ancillary questions to this are: Given what is known about MeHg production- can we focus efforts on certain reaches of the South River? Where are the Fe and S, etc. reducers present? What experiments or pilots may help answer this question? What is the connection between nutrients in the river and MeHg production? What (if any) are the good and bad effects? What experiments or pilots (e.g. STP upgrades) might help define these areas? Some of these questions will be answered through literature surveys. Laboratory testing of South River sediments with respect to methylation potential will be undertaken by Rutgers University.

4. CONTROL RELEASE OF Hg FROM SOIL AND SEDIMENT TO BIO SYSTEM

What can be done to inhibit mercury release from soil and sediment into the biological system?

Some of the applicable Hypotheses that would justify this remedial approach are:

- There is plenty of leachable mercury available in the floodplain soils and river/bank sediments for desorption and, hence, methylation (i.e., an infinite sink). In other words, we are not mercury limited, now or in the foreseeable future.
- The equilibrium partitioning of Hg in the South River system are in the range of other systems that have been studied. That is, mercury preferentially partitions to the solid phases and the majority of the total mercury in the water column is particulate-bound mercury.
- The desorption mechanisms and kinetics of Hg in the South River are similar to other systems studied. For metals, biphasic desorption kinetics is very common; that is, there is a more labile fraction and a tightly bound fraction.
- The exchangeable or more labile fraction is characterized as Hg sorbed/electrostatically bound to clay minerals or iron oxides. The tightly bound fraction is characterized as Hg precipitated with sulfide or complexed with reduced sulfur groups in the organic matter. It could also be Hg that has diffused deep into the micropores of the soil/sediment particles.
- The floodplain/bank soils are in a more dynamic redox environment because of wetting and drying (oxidizing) cycles and are more susceptible to chemistry changes that increase metal mobility and, hence, bioavailability. It seems to be a common theme in the literature for redox active metals that the cycling action happens at redox interface(s).
- The submerged sediments in low-DO quiescent zones are in a more stable redox environment and are less susceptible to chemistry changes that increase mobility.
- The exchangeable fraction of soils is more susceptible to desorption and, hence, methylation than the tightly bound fraction.
- Any remedial option needs to at least target the exchangeable fraction of the floodplain/bank soils.

There are three general classes of options: Chemical modification to change the speciation to a more stabile, less labile form, Redox modification to minimize conditions that favor methylation, and physical/chemical armoring of the solids to "lock in" mercury. Challenges include the permanence of the solution (for example, HgS is very insoluble under the right conditions, but we know that the river is a dynamic redox environment over the short and long terms). Another challenge is the whether desorption can be slowed down enough to affect bioaccumulation. The initial tasks include a review of state of the art technologies to stabilize mercury in soil and to characterize (speciate) mercury in targeted soils and sediments in the South River.

5. MANIPULATE FOOD WEB TO REDUCE Hg IN FISH TISSUE

Is it possible to tweak the food web to reduce Hg concentrations in the food web? How would this be done?

Conceptually the reduction of aquatic trophic levels or simplification of the food web could result in fewer trophic stages for mercury accumulation between primary producers and top predator fish. The team is currently reviewing the literature for examples of food web management to reduce bioaccumulative contaminants in predatory fish. A life cycle history for targeted prey types and fish species with different feeding behavior in the food web will be developed (components of the prey community which comprise the greatest biomass and/or highest total number of individuals surveyed). Using this and other available data , a SR food web will be constructed and mercury biomagnification rates between trophic levels will be developed. Then, evaluate the feasibility of management of food web to change mercury concentrations in predatory fish.

Hg Treatment Technologies / Strategies identified to Date
Explore Remediation Technologies to Cut off Potential Pathways

- Monitored Natural Recovery (Baseline Conditions)
- Stabilization/isolation of eroding banks
- Flood control measures (e.g. increase storage capacity, levees)
- Chemical manipulation to:
    - Suppress MeHg production
    - Suppress uptake and metabolism of MeHg
    - Increase sorption of Hg (reduce dissolved Hg; e.g. Bauxite, clay, humus)
    - Thermal Desorption
    - Facilitate Ion exchange (thiols – check efficiency)
- Ultrafiltration
- Capping (impermeable and permeable, reactive)
- Hydraulic modification
    - Rerouting river/runs
    - Construct bypasses above a certain river stage

- Administrative Controls/Measures
    - Fish exchange program
    - BMPs for Cattle (alternative water supply)
    - Floodplain Conservation easement
- Soil or Sediment Removal
- Aeration of environment and/or air stripping (and capture)
- Maintenance/ filling of ditches (e.g. cow ponds)
- Management of Large Woody debris
- Phytoremediation
- Sediment Traps to Treat
- Providing clean food supply for fish

Considerations

- Beware of unintended consequences, deleterious effects
- Delivery and permanence of treatment will be a significant challenge
- Employ the adaptive management approach
- Upgrades to STP are planned – how will aquatic chemistry be affected?
- For all options DECIDE ON MEASURES OF SUCCESS – PRE AND POST MONITORING

Waynesboro Plant RFI Background
10/10/07

History

In 1929 DuPont began operations at the Waynesboro site which is situated on 177 acres along the South River. The site was originally chosen because of the abundant water supply, railroad access, and an available workforce. Initial operations included the manufacture of acetate flake and yarn from 1929-1977. This process included the use of mercury from 1929-1950. Other products manufactured at the site include:

- Orlon 1958 – 1990
- Permasep 1960 – 2000
- Lycra 1962 – current
- BCF Nylon 1978 – current

In 2003 the plant assets were sold to Koch Industries (Invista). Upon the completion of the Corrective Action Program, the land will be transferred to Invista.

RFI Investigations

Three phases of the RCRA Facility Investigation (RFI) have been completed to date. The purpose of the RFI is to characterize solid waste management units (SWMUs) where hazardous substances may have impacted the environment. Twenty SWMUs were identified in the corrective action permit. Four of these SWMUs are currently under investigation. Twelve SWMUs were recommended for no further investigation and four were recommended for no further action.

The Phase I investigation conducted in 2000-2001 consisted of soil and groundwater sampling at 10 SWMUs. Eighty six soil samples and forty groundwater samples were collected for VOCs, SVOCs, metals, methyl mercury, HMD, DMF, and DMAC. This included water level measurements and slug testing for hydrogeologic evaluations. The Phase I concluded that SWMU 1 (Mercury Recovery Area) and SWMU 4 (Incineration Area) required further evaluation and that the Northeast Area water level depression should be investigated.

During the Phase II investigation (2004-2005) eight SWMUs and two areas of concern (AOCs) were evaluated. This included the collection of 68 soil samples and 65 groundwater samples for the same constituents as in the Phase I. Also in this investigation were a soil gas sampling program SWMU 1 for the presence of mercury vapor and a geologic investigation at the Northeast Area. The Phase II Investigation concluded that groundwater in the deep clastic zone present in Northeast Area was impacted with mercury. Mercury was further characterized at SWMU 1 and SWMU 4 and benzene and mercury were detected downgradient of SWMU 6/7. No further investigation was recommended for SWMUs 10, 13, 20 and AOCs 1 and 2, however additional investigation was recommended at SWMUs 1, 4, 6/7 and the Northeast Area.

The Phase III Investigation, completed in July 2007, included the collection of 76 soil samples and 5 groundwater samples at three SWMUs for the same constituents as in previous investigations. Soil samples were collected at SWMU 1 to confirm previous soil gas results and the former process ditches at the Chemical Building were sampled for mercury. Geoprobe soil sampling was performed at SWMU 4 for further delineation of mercury and at SWMU 6/7 (former Sludge Pond) for initial characterization of soils. Two new wells were drilled to assess potential migration of constituents from SWMU 6/7. The Northeast Area was investigated by locating and logging plant Well #1 and conducting a long term water level study. The results of the Phase III investigation will be reported in the Phase III Summary Report later this year.

Groundwater

Following the Phase I RFI investigation, a semiannual groundwater monitoring program was initiated. The monitoring plan submitted in 2004 included the monitoring of 38 wells and 55 water level measurements. Findings from three and a half years of sampling (7 events) show that mercury concentrations are localized at SWMU 1, SWMU 4 and SWMU 6/7 and that downgradient perimeter wells are below VGS criteria. However, water level measurements indicate the Deep Water Table Zone water levels (Northeast Area) fluctuate significantly.

Outfall Monitoring

Three phases of outfall monitoring have been performed to assess the loading of mercury under base flow and storm flow conditions. The first phase conducted in 2003 sampled one storm and one base flow event at 8 outfalls and 10 upstream locations. No significant mercury was detected in baseflow or first flush storm samples, however mercury was detected in flow weighted composites (up to 1.7 µg/l) during the storm event. Estimated loading rates were low relative to the mass observed in the South River.

During the Phase II monitoring in 2004-2005, 10 locations were sampled during 3 base flows and one storm flow event. Also sampled were sediments and water in upstream portions of the sewer. This investigation concluded that the amount of mercury that is bioavailable was 20-29% under base flow conditions and 32-33% for storm flow conditions. The highest concentrations of Hg in sewer sediments and water occurred upstream of 001D near the Chemical Building and SWMU-1.

The Phase III program conducted from 2005-2007 included the sampling of 10 locations over an 18 month program to support the TMDL program. Fifteen base flow and 6 storm events were sampled. The data shows that the highest concentrations occur at outfall 011 but it is in diversion to WWTP and does not discharge to the river. The outfall with the highest loading rate to the river is outfall 001.

The Phase IV program was initiated in June 2007 and will continue to monitor 10 outfall locations. The program consists of monthly base flow events and 2 storm events per year.

Sewer Investigation

The first phase of the sewer investigation was completed in January 2007. This program consisted of mapping and verifying sewer locations and structures including the identification of structures and confirmation of flow directions. Conventions for the naming of structures were established and a database was developed for the structures and piping sections, including sizes and materials of construction. Key storm sewer sections were identified and recommendations were made for the Phase II investigation.

Future Activities

- Phase IV Stormwater Sampling (Began in Jun 07)
- Phase II Sewer Investigation (4Q07)
- Groundwater Monitoring (Nov 07)
- Reporting of Phase III RFI (Dec 07)
- Corrective Measures Study (2008/2009)

Phase I System Characterization: Year One Findings and Year Two Direction

J.R. Flanders and Todd Morrison
South River Science Team
Expert Panel Meeting
October 11 – 12, 2007
Harriston, VA

Introduction

The Phase I ecological study is a multidisciplinary project that includes the integration of physical, chemical, and biological data to achieve the study objectives. The overall objective of Phase I system characterization is to more fully characterize the river systems that include the North River, South River, and the South Fork Shenandoah River (SFS), Virginia. Data collection activities are based on the overall project objectives for the ecological study as well as information acquired from ongoing and historic studies, such as those conducted by the South River Science Team. These data collections are not limited to collections of environmental media for chemical analysis because a critical activity of Phase I is to collect and organize geospatial and hydrological information into one database. The Phase I study will continue approximately two years and the baseline river information acquired from these studies will be integrated into a full description of the physical, chemical, and biological characteristics of these areas.

This briefing paper outlines the results of Phase I, Year one loading studies conducted during 2006-2007 and provides a summary of Phase I, Year two activities currently underway in 2007. The results of Phase I will set the stage for Phase II of the ecological study, that is to assess impacts to the environment. At the end of Phase I studies, two years of data will be integrated, resulting in a stratified understanding of the primary study area and its ecological habitats. Points of mercury and methylmercury loading will provide a focus for Phase II activities.

Year One Mercury Loading Studies

The major influences on total mercury (THg) and methylmercury (MeHg) behavior in the South River are discharge and seasonal in nature. Despite significant variation in discharge over the course of year one, the concentrations of filter-passing THg (FTHg) and mercury on particulates (THgP) under baseline conditions change very little, suggesting continuous inputs of THg to the South River. In contrast, the methylmercury concentrations in filtered surface water (FMeHg) and on particulates (MeHgP) were initially low, increased during in spring 2006, and declined thereafter, suggesting that MeHg inputs are seasonally pronounced in the spring and early summer. These temporal patterns for both THg and MeHg were observed in sediment samples.

During storm events, the majority of unfiltered THg is loaded above Harriston and the majority of FTHg is loaded above Crimora. Partitioning coefficients measured during peak flows of storms suggest that the loads measured in lower reaches (study area RRM

16.5 to 23.9) are particle-associated and do not represent additional inputs of THg or MeHg. Peak storm related flows dilute both filter-passing and particulate forms of both THg and MeHg to concentration levels significantly below sediment. The concentrations of FTHg and THgP increase significantly in isolated samples collected on the falling limb of storm events, but only at locations in the upper half of the South River (study area RRM 2.3 to 9.9), suggesting mobilization of potential sources under higher water surface elevations. Sediment THg concentrations confirm this trend and show increasing concentrations up to RRM 3, remaining at similar levels until RRM 8.7.

Tracking the change in THgP and MeHgP under baseline conditions over the course of the South River reveals that low gradient reaches of the South River load mercury species to particles. Loading rates of FTHg under the lowest flow regime (58 - 110 CFS at Harriston) reach a maximum around RRM 12; as discharge increases, the location of the maximum loading rate moves downstream. Maximum loads are observed at Port Republic Road (RRM 23.9) under the highest baseline loads (>270 CFS). Methylmercury loading rates are highest in the spring and summer, and the majority of MeHg loading occurs in the upper half of the South River (study area RRM 3.0 to 11.8). Sediment MeHg concentrations rise until RRM 8.7 and decline thereafter, further supporting that sources appear to be limited to the upper half of the river.

Although MeHg loading at baseline sampling stations are highest in the upper half of the river, MeHg concentrations in biological tissue samples are generally higher in the lower half of the river, where the concentrations in surface water are highest. Results of season tissue collections for algae/vascular plants, invertebrates, and prey fish indicate MeHg concentrations increase with trophic position. Monthly collection of crayfish tissue show little seasonal variation in MeHg at baseline stations. While in contrast, *Corbicula* tissue MeHg concentrations show seasonal trends that are similar to those seen in surface water concentration. These data indicate trophic position and feeding behavior influence MeHg tissue concentrations in the South River aquatic food web.

Year Two Studies

Year two studies focus on refining the study area and providing additional data to characterize the potential sources of mercury and methylmercury in the South River. The emphasis for year two includes geospatial analysis of the geomorphic, hydrologic, and loading data collected in year one. Collectively, these data along with data collected from numerous South River Science Team activities will be used to assist in the development of Phase II studies.

Year two study activities are discussed briefly in the following section, they include:

- Revised baseline monitoring for 2007
- Storm event loading for the upper 10 miles of the South River (RRM 0 to 10)
- Identification and characterization of a reference area(s) on the Middle River
- Baseline characterization of fine-grained sediment deposits

Revised Baseline Monitoring

Programmatic changes to the baseline monitoring study are recommended to focus data collections and integrate surface water and sediment studies going forward in Phase II. The surface water data collected during year one resulted in comprehensive data set regarding the study area. The data characterize water conditions during baseflow along the river but these data are not located coincident with storm event data. By relocating the surface water stations to bridges, the revised sampling design integrates baseflow and stormflow data collections to the same locations. The bridges are spaced at regular intervals along the South River and are conducive to providing a detailed characterization of surface water along the South River (from RRM 0 to 24). These changes will allow for a more systematic review of loading and the relative importance of potential sources to the South River.

The sediment sampling design for year one included the characterization of sediment in one river environment (at the toe of pools). Since the river study area is comprised of riffle pool units, the characterization of mercury in sediment collected from the toe of pools provides data for an important habitat type along the river. The study resulted in comparable data sets at various stations within the study and reference areas. These data have identified the highest methylmercury and total mercury concentrations between RRM 2 to RRM 11.8 of the study area.

In order to understand what role this environment may play in methylmercury production as compared to other environments in the river and along the floodplain, revisions to the year two sampling plan include characterizing methylmercury in sediments in five river environments within the South River including:

- main channel pools with low and high embedded substrates
- depositional areas along the edges of pools
- pools in island side channels and mill races
- open water wetlands within the 0.3-yr floodplain

This revised design will result in sediment data at multiple environments (i.e. habitats), which will be evaluated to characterize methylmercury concentrations and assess potential seasonal changes (or lack thereof). These environments can also be described spatially to integrate areas of potential methylmercury production with other study components such as loading to surface water and food webs directly interacting with these environments.

Targeted Loading Study

A targeted loading study was developed for the upper 10 miles of the South River study area (RRM 0 to 10) based on data collected during various studies including river geomorphology, characterization of sources (historic sediment and floodplain soils sampling), and year one loading studies. Geomorphology data indicate that this reach has a lower river gradient, greater floodplain area, higher percentage of eroding banks, and greater in-channel storage of fine-grained sediment (Pizzuto et al. 2006). In addition, the highest concentrations of total mercury and methylmercury in sediment and soil have been recorded in this reach, which is closest in proximity to the historic release point

(Pizzuto et al. 2006 and Floodplain Soil Sampling South River Technical Monograph). Year one baseline flow and storm flow data confirm that mercury was loaded into the South River along this reach. Collectively these data indicate that this reach (i.e. RRM 0 to 10) has the capacity to store and release mercury into the South River from various major potential sources (e.g. floodplain and/or sediment deposits).

A target loading study is underway in this reach of the South River to evaluate the relative importance of various major potential sources of mercury to the river system during the course of and following two specific storm events. The sampling plan includes data collections for tributaries, direct floodplain runoff points, and bridge crossings on the mainstem river between RRM 0 and 10. It is designed to evaluate total mercury loading during the rising discharge and total and methylmercury loading over seven days during the falling discharges (post-storm runoff) at targeted bridges and various points within the floodplain.

A total of 14 tributaries were identified within the targeted study area with substantial watershed drainages (i.e. total drainage area greater than 0.5-km^2). The total drainage area for each tributary and their drainage areas within the South River floodplain for various storm inundation frequencies were determined using the geospatial database. Eight of these tributaries were selected for the study based on the size of the overall drainage area and/or the size of the floodplain drainage areas. Collectively the eight selected tributaries account for 87% of the total tributary drainage area and 93% of the total drainage area within the 100-yr floodplain of the South River. In addition to the major tributaries, a survey of aerial photos for the floodplain indicates several prominent floodplain drainage features. In most cases these features drain large portions of the floodplain within river meanders. These areas are generally the first features to be inundated when the river overflows its banks and water may remained ponded in some of these features following a storm event, slowly draining back to the river. Several of these features were included in the sampling design to address their overall importance in mercury loading to the South River.

Reference Area Development for the Middle River

The development of a reference location along the Middle River is proposed in order to provide an additional potential reference location for Phase II studies. The results of Phase I loading studies have identified stretches of the South River with higher mercury loading, generally between baseline sampling stations at RRM 3.0 to RRM 11.8. Lower gradient, higher percentages of bank erosion, and greater volumes of fine-grained sediment characterize the habitats along this stretch of the South River, as compared to other reaches within the overall study area (RRM 0 through RRM 24). In addition, two reaches within this stretch of river function essentially as long pools with little to no riffle habitat (RRM 4 to 5 and RRM 8 to 9). As a result of these findings an additional reference area will be developed along the Middle River, since preliminary evaluations indicate stretches of this river have similar habitats and geomorphic features, while current reference areas in along the North River are higher gradient and do not contain long pools. These areas will be evaluated to serve as a suitable reference site(s) for future Phase II studies.

Source Characterization

Year two investigations will focus on characterizing the floodplain and depositional features. An evaluation of floodplain soils with various land uses (including wetlands) and river channel banks will be designed to characterize potentially important sources of external loading of mercury to the river. VADEQ and the greater South River Science Team are undertaking this study.

Sediment depositional features are potentially important internal sources of mercury loading. Previous investigations have characterized fine-grained sediment deposits (FGSD) at several locations along the South River. Year two work will further characterize FGSD to evaluate their role in the storage of mercury in sediment. Previous investigations have identified approximately 56 locations of FGSD along the South River from RRM 0 to the confluence with the North River (Pizzuto et al. 2006). Mapping results suggest that the majority of deposits are between RRM 2 and RRM 14. The previous investigation also determined an approximate volume for each feature and a minimum volume of 30 cubic meters was used as a cut-off point for additional characterization. Year two work will characterize an additional seventeen FGSD for total mercury and methylmercury.

References

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Ralph Turner/Dick Jensen

Mercury Source Tracing and Mechanistic Studies
Status for October 2007 Expert's Meeting

Purposes of Studies: 1) Characterize mechanisms by which non-filterable (<0.45 micron) mercury enters the river and water column and rank according to overall importance. 2) Develop/provide investigative tools and methods for later phases of the ecostudy. These may include field or laboratory protocols to better characterize mechanisms and/or forms of mercury.

Specific locations/objectives of study: 1) Plant reach, from Wayne Avenue to Main Street (RRM -0.5 to RRM 0.3). Under higher flow conditions, this reach consistently shows greater loading than has been accounted for, thus far, from plant outfalls and groundwater. The objective has been to determine the origin of the additional loading. 2) Basic Park (RRM 2.0). This location is within a section of the river consistently showing a high loading of total dissolved mercury to the water column and includes areas for ecostudy baseline monitoring, geomorphology special studies (LIDAR) and benthic flux chamber research. Dissolution of mercury in bioavailable forms from bank soils and/or bed sediments are the chief suspects. 3) In 2007 porewater sampling and special leaching procedures developed at Basic Park were applied at other locations between Constitution Park (RRM 0.5) and Port Republic (RRM 24) to provide comparative longitudinal data. *A common objective at all three study locations is to develop and evaluate tools and procedures for potential adoption by the ecostudy in later phases.*

Status of studies at plant reach:

Stormflow Loading **-** A unique opportunity to evaluate mercury loading within the plant reach during a major storm event (peak instantaneous and mean daily discharges were 3920 and 2700 cfs, respectively on 10/7/06) occurred in October 2006. The two most important mercury loading input reaches above Main Street during this flood were the large upper watershed above Lyndhurst Avenue and the reach between the footbridge and Main Street. A much smaller portion of loading occurred in the operating plant reach between Wayne Avenue and the footbridge. In contrast, at moderate flow, with little re-suspension of riverbed solids in the overall plant reach, the operating reach may supply half or more of the [much smaller] added loading below Wayne Avenue. Based on soil sampling results sufficient mercury concentration exists in the eroding banks below the footbridge to account for the increased mercury on suspended matter during a flood peak. But the amount of erosion to close the mercury balance appears unreasonably high.

Status of studies at Basic Park:

Gravel Bar Hyporheic Water **-** Stainless steel probes have been used to sample hyporheic water within a large gravel bar at Basic Park. Surface water flow over the bar produces zones of upstream entry to, and downstream exit from, the interstitial space (hyporeheic zone) of the bar. Some, but not all, pressure head measurements across the Basic Park bar show negative heads upstream and positive heads downstream and thus generally support the conceptual model of flow through the bar. Hyporheic water extracted from the bar at 6 to 12 inches below the gravel surface are consistently higher in dissolved mercury than surface water flowing over the bar. In contrast, dissolved methylmercury concentrations in hyporheic water is consistently lower than in overlying surface water, suggesting that any methylation that might occur in the bar is occurring at shallower depths than sampled by the probes. On a few occasions surface water collected at the gravel interface at the suspected point of flow exit from the bar has been higher in dissolved mercury than surface water collected mid-depth in the thalweg. Generally dissolved oxygen is somewhat lower in hyporheic water than surface water, but especially where the direction of flow is suspected to be out of the gravel bar. *A reliable means to quantify the contribution of gravel bars to whole river loading of mercury and methylmercury remains elusive, although calculated estimates might be possible based on other known values*

<u>Alluvial Groundwater –</u> Six shallow (water-table) wells have been installed and monitored at Basic Park. All the wells are within 50 feet of the South River, are screened 5 to 8 feet below ground surface and penetrate soils with total mercury concentrations up to 60 ppm near the top (12 to 16 inches) of the profile. Water level elevation data, including continuous monitoring of one well and the adjacent South River, show relatively large hydraulic gradients that vary closely with river stage. At low river stages the adjacent alluvial water table can be up to 2 feet higher than the river surface. Slow recovery of most of the wells and slug testing also suggest low hydraulic conductivites of the aquifer. Dissolved mercury in the Basic Park alluvial groundwater appears to vary seasonally with some wells showing values ranging from < 1 to 60 ng/L over the period of monitoring. *Preliminary estimates of the contribution of alluvial groundwater to "dissolved" mercury loading of the South River, derived from the Basic Park analytical results and the incremental increase in baseflow non-tributary discharge (i.e., groundwater) over the entire river, suggest a wide range of values with a median value of 4%*. Thus far only one well at Basic Park and one well at the Forestry Station have been sampled for methylmercury and thus we cannot estimate the potential groundwater contribution of methylmercury.

<u>Benthic Flux Measurements</u> – Both the Dupont and our custom-designed flux chambers have been used at Basic Park to estimate the flux of total mercury and methylmercury. The chamber designs produced reasonably comparable data, but our group has elected to employ the Dupont chambers for work in 2007 (Thank you Rich Landis for the loan and support!). Our work is focused on using the chambers to conduct "amendments" to stimulate or inhibit generation (or release) of methylmercury. In an initial exploratory study we amended chambers deployed over both rock plates (2) and mud (2) with a floodplain soil extract (10:1 soil:water, 0.45 μm pore filtered) with the intention of elevating dissolved mercury within selected chambers by a factor of 10 while using a paired chamber as a control. All chambers (amended and control) produced "well-behaved" time-series data but amended chambers revealed only a 2X increase in dissolved mercury and showed no significant enhanced flux of methylmercury over the 8-hr duration of the study. Mud chambers produced higher fluxes and a steady rise in methylmercury concentration while rock plate chambers showed a lower flux after 4

hours. *Un-amended fluxes of both dissolved total mercury and methylmercury, measured over near-bank mud deposits have continued to be too low to explain whole river benthic fluxes derived from differences in fluxes between thalweg monitoring stations.* Additional studies using flux chambers to investigate the effects of various amendments are underway.

Porewater from Mud Deposits – Porewater from mud deposits cannot be sampled "in situ" using the stainless steel probes. In 2007 we began recovering porewater from mud deposits using a centrifuge. In April 2007 we collected "muddy" sediments from 9 locations along the right bank of the South River at Basic Park and separated the porewater by centrifugation for analysis of total mercury. Total mercury in the sediments ranged from 7.3 to 102 ppm, dry wt, while porewaters ranged from 84 to 1824 ng/L. Within this limited dataset total mercury in sediment was correlated with total mercury in porewater ($r^2 = 0.96$). Using relatively clean river water from above the plant to extract (10:1, sediment:water) the same sediments produced dissolved mercury values that matched porewater values reasonably well (r2 = .79). *These measurements suggested that either total mercury in sediments or a simple water extract of sediments is a good predictor of porewater total mercury, at least for the Basic Park reach of the South River.* In July 2007 we collected muddy sediments from 6 locations spanning the length of the river from Constitution Park (RRM 0.3) to Port Republic (RRM 24) for separation of porewater and the simple water extraction. Total mercury in these sediments ranged from 0.93 to 54 ppm while total mercury in porewater ranged from 18 to 403 ng/L and total mercury in the water extracts ranged from 28 to 1100 ng/L. The correspondence between total mercury in sediments and either porewater or the water extracts was not quite as good ($r^2 = 0.63$ and 0.84, respectively) as for the Basic Park only dataset. Methylmercury was also analyzed in sediment (13 to 81 ng/g) and porewater (1.5 to 17 ng/L) samples from the whole river group of samples. The correlation between sediment methylmercury and porewater methylmercury values was poor ($r^2 = 0.42$) and non-significant.

Form(s) of Mercury in Aqueous Soil/Sediment Extracts – As reported earlier and above, filtered (0.45 μm pore) aqueous extracts of floodplain soils and river bed sediments can be highly elevated (>1000 ng/L) in total mercury concentrations relative to South River surface water (5 to 20 ng/L). The fraction of this "soluble" mercury that is particulate or colloidal, and possibly unavailable for conversion to methylmercury by microorganisms, remains unknown. To address this issue we performed two assays to begin to describe the nature of these extracts: ultrafiltration with a 5000 molecular weight cutoff (MWCO) and reactivity assay using neutral tin citrate to measure easily reducible mercury. Extracts from one floodplain soil (from Basic Park, 40 ppm) and two sediments (Basic Park and RRM13) were included in this preliminary study. The soil produced a 0.45 μm filter extract of 4200 ng/L of which <1% passed the ultrafilter and 12% was tin-reducible. Both sediments produced much lower 0.45 μm filter extracts (81 and 61ng/L) of which 22% and 25% passed the ultrafilter and 12% and 15% were tin-reducible. *These results suggest that the "bioavailable" fraction of 0.45 μm filter extracts is likely to be far less than indicated by the filter extracts.*

Side Channels as Areas of Methylmercury Accumulation and/or Generation – Previously we have reported on the high concentrations of methylmercury (up to 20 ng/L) observed in surface water in a side channel at Crimora (RRM10). In the past year we investigated three similar side channels elsewhere on the river (two former mill races and a side channel at Basic Park that became progressively less flushed by the main river as discharge declined over the 2007 summer). Volumetric flow from these channels is consistently very small compared with the river at each location and is provided both from the hyporheic zone and upstream direct small overflows from the river. Methylmercury concentrations in all these channels has been significantly higher than in the adjacent river thalweg. For the Basic Park side channel dissolved total mercury increased by a factor of two between the inlet and outlet while dissolved methylmercury increased five-fold. The results are reminiscent of our observations of higher methylmercury concentrations near banks throughout the length of the river, and particularly where eddies have formed. Water caught in such eddies has greater opportunity for interaction with near-bank muddy sediments that we now know may have high porewater concentrations of both total mercury and methylmercury.

Geomorphology Briefing Paper – F07 Expert Panel Meeting

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Bank Erosion

Summary of Historical Bank Erosion Rates, 1937-2005

A statistical analysis of 525 erosion polygons defined using 1973-2005 shorelines indicates that decadally averaged linear bank migration rates are remarkably low along the South River. The median bank erosion rate is 0.02 m/yr, and the modal bank erosion rate is 0.005 m/yr. The 84^{th} percentile erosion rate is 0.07 m/yr, while the 95^{th} percentile erosion rate is only 0.15 m/yr. There are relatively few high erosion rates. The maximum erosion rate is only slightly higher than 0.35 m/yr.

Bank erosion polygons are separated according to different categories of bank erosion. About 1/3 of the total bank erosion occurs in reaches with islands, while 26% of the total erosion occurs at bends. Engineering structures and dams are associated with another 19% of bank erosion, while confluence bar development accounts for about 6% of the total bank erosion. 15% of the total erosion occurs in straight reaches or in other situations that are not otherwise readily classified. Most of the erosion associated with islands occurs between relative river miles 13 and 19.

Erosion rates are controlled by bank material, the density of riparian vegetation, and bend curvature. Erosion rates are highest along banks composed of recent alluvium, while much lower erosion rates are observed along bends where bedrock or terrace deposits are exposed. Trees growing along banks composed of recent alluvium tend to reduce erosion rates. For banks composed of alluvium, bends with low radii of curvature have higher near-bank velocities and erosion rates tend to increase linearly with increasing near-bank velocity. Alluvial banks with relatively low tree densities have bank erosion rates that are about twice as high as alluvial banks with higher tree densities.

The observed linear relationships between near-bank velocity and erosion rates suggest that decadal bank erosion rates might be accurately predicted by existing models of meander migration. To be successful, these models would require considerable calibration, as the regression relationships reported here have low correlation coefficients and limited statistical significance.

Changes in Erosion Rates Through Time

Fourteen eroding bends were selected to study changes in bank erosion rates with time on historical aerial photographs from 1937, 1957, 1974, and 2005. The results indicate that bank erosion rates increased significantly after 1957 compared to the period between 1937 and 1957. The intensity of storm discharges decreased from 1957-1974, and the density of riparian vegetation increased after 1975. Both of these changes should have decreased bank erosion rates, so apparently other factors must be invoked to expain the observed increase in bank erosion rates.

Thirteen dams were in place along the South River in 1937 between Waynesboro and Port Republic. After 1957, 3 dams remained, and all of these had been breached by 1974.

All of the dams immediately downstream of the eroding banks studied in this chapter were breached by 1957. The loss of mill dams could have increased velocities in the river, providing a potential explanation for the observed increased bank erosion rates. However, all of the eroding banks may not have been influenced by downstream dams, and the intensity of increased bank erosion does not appear to be related spatially to the locations of the dams. Further research is needed to better link bank erosion processes to the dams themselves before this working hypothesis can be fully accepted.

Several other factors could also have caused the increase in bank erosion rates. These include changes in climate, such as the frequency or intensity of freeze-thaw, changes in riparian land use unrelated to riparian vegetation (grazing by cattle, for example), and changes in the supply and storage of bed material in the channel. These processes were not investigated as part of this study, and await further research.

Lidar Surveys of Contemporary Bank Erosion

From January, 2006 until July, 2007, we surveyed eroding banks using tripod mounted LIDAR. We surveyed 23 sites located between relative river mile (RRM) 1.5 and RRM 23. 16 of the sites are located upstream of RRM 10. Repeat surveys are available for 6 of the sites (3 sites with 2 surveys, 2 sites with 3 surveys, and 1 site with 5 surveys. Permanent benchmarks have been installed at all these locations to facilitate future repeat surveys to determine contemporary bank erosion rates.

Repeat lidar surveys provide information that is generally consistent with results obtained from studies of historical aerial photographs. Bank erosion rates are generally low, and vary with channel geometry, bank vegetation, and bank sediment type. Other specific conclusions include:

1. Bank erosion processes are spatially variable at all sites, with measured ranges of bank retreat between 0 and more than 1 meter at every site.
2. Where bank materials are composed of noncohesive gravelly sediment, bank erosion rates can exceed 1 m per year.
3. Cohesive silty banks exhibit slow rates of erosion with complex spatial organization. At some sites, erosion is localized in just a few “holes” along the bank.
4. On banks protected by large trees, erosion is “focused” between the trees, and may occur at rates of several decimeters per year. Retreat of the entire bank,

however, will require removal of the trees, a process which can take many years if the trees are “large”.

5. Cohesive, silty banks unprotected by trees can erode at rates approaching a few decimeters per year. Cattle can accelerate these rates to over 1m/year.

Models of Erosion by Individual High Flow Events

A computational model is described for determining the extent of erosion of bank profiles caused by single flow events. The model is entirely empirical, and is based on approximately 240 surveys of eroding bank profiles from a study of the Brandywine Creek near Chadds Ford, Pennsylania from April 1986 through March, 1988. The model is applicable to eroding cutbanks composed of silt and clay on rivers similar in size to the Brandywine Creek, which has a drainage basin area of 287 mi^2. The survey profiles were not vegetated, although the riparian zone of the Brandywine Creek is covered with a forest of boxelder, silver maple, and white ash.

The model is developed by developing empirical equations for erosion 1) directly caused by action of the current (“water erosion”) and 2) related to the failure of overhangs. Empirical relationships governing water erosion include the near-bank velocity, the frequency of freeze-thaw, the water level, and the duration of high flow as important variables. The occurrence of overhang failures is controlled by the geometry of the overhang, such that large overhangs are more likely to fail than small overhangs. All empirical relationships are statistically significant, but all have low correlation coefficients.

The model is used to estimate the relative importance of variables controlling bank erosion and to evaluate potential remediation measures for controlling bank erosion and mercury loading. According to the model, the near-bank velocity is the most important variable influencing the erosion of steep, silty, unvegetated eroding cutbanks. The frequency of freezing and thawing is of nearly equal importance on gently sloping banks. Water levels represent another, though lesser, influence on bank erosion rates. The model also suggests that bank remediation can produce significant reductions in loading of sediment and mercury. In particular, reducing the slope of steep banks and reducing the near-bank velocity to 0 can reduce mercury loading by several orders of magnitude.

Sediment Deposition Related to Shoreline Changes, 1937-2005

We have classified and mapped 6 categories of deposits on the floodplain of the South River in Virginia. All of the deposits are related to shoreline changes mapped on historical aerial photographs from 1937 and 2005. Mapped categories include mill dam deposits, point bar/bench deposits, concave bank bench deposits, islands, cattle deposits, and tributary confluence deposits. A total of 39 deposits have been identified between relative river miles (RRM) 1.5 and 11.6, with particular concentrations of deposits between RRM 3-4 (6 deposits), 5-6 (5 deposits), and 8-9 (10 deposits). Mill dam deposits, point bar/bench deposits, concave bank deposits, and tributary confluence deposits all are likely to preserve silt and clay deposits dating from the period of direct mercury release from the plant at Waynesboro (~1930-1950). Many of these deposits could approach 3 m in thickness, and all are likely to have a significant connection to the stream channel itself though exchanges of alluvial ground water.

2007-2008 Program

1. Bank Lidar Surveys – survey 4 banks 2 times.
2. Monitor Pilot Bank Stabilization Project using lidar and other surveying techniques as appropriate.
3. Assist with floodplain sampling program.
4. Continue to develop and evaluate depositional models for ’37-’05 deposits.
5. “Particle Budgets” and Hg-related particle transport:
    a. Combine existing monitoring data for high and low flows with estimates of bank erosion and exchange with bed.
        i. Use these to refine conceptual models of particle transport during a range of flows.
6. Continue development of bank erosion models so useful approaches are available for analysis of “particle budgets” (#6 above).

Mercury Trophic Transfer: South River Aquatic Food Webs

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The project is part of a three-year study that began in 2005 to define mercury accumulation and trophic transfer in the South River watershed. After the first year, the spatial distribution of mercury and methylmercury in periphyton (natural surface coatings) was defined. Snail and periphyton samples were analyzed for mercury, and N and C isotopes during the first year to facilitate sampling design during the second year. In 2006, available periphyton, invertebrate, and fish samples were used for three sites (Dooms Crossing Rd, Crimora (AFC), and Grottoes Town Park) to successfully quantify mercury biomagnification using N isotopes.

The design was refined and expanded this year by taking triplicate samples of sixteen types of biota at five riffle sites (Constitution Park, North Park, Dooms, Augusta Forestry Center, and Grottoes Town Park). A pool site was added at the request of URS to explore whether mercury biomagnification was distinct in deep areas of the river that might have high methylmercury flux. All samples will be analyzed for total mercury with one replicate also being analyzed for methylmercury so that the change in percentage of total mercury that is methylmercury can be quantified with trophic position changes. Stable isotopes will be measured to determine the trophic positions of each of the sampled organisms. Efficiency of mercury movement through the trophic web will be assessed using these mercury concentration and N isotope data in biomagnification models.

Organisms were collected last May with the help of URS, Calvin Jordan of the Virginia DEQ, and William and Mary colleagues. Periphyton was also grown on substrates and collected in early July. These samples are currently being processed.

Briefing Paper for Bird Study, 2007 (Year 3)
Dan Cristol, College of William & Mary

Objectives for 2007:

1): The first objective was to continue the tree swallow monitoring for a third year to determine whether reproductive effects found in 2006 were evident again, whether they were still limited to inexperienced ("stressed") individuals, and whether they were linked to the higher methylmercury levels detected in 2006. In addition, we proposed to measure more eggs to test the hypothesis that inexperienced breeders on contaminated sites were suffering reproductive deficits because they were producing smaller eggs.

2): The second objective was to explain the differing mercury levels in different terrestrial songbirds by collecting prey items (e.g. spiders) from nestlings at variable distances from the river, and of different sizes and isotope signatures.

Summary of Preliminary Results:

Tree swallows: The tree swallow population once again fully occupied all available nest boxes. The overall mercury level in adult tree swallows dropped back to near 2005 levels, after having doubled unexpectedly in the drought spring of 2006 (2007 contaminated: ~2.42 ± 1.21 ppm, n = 131, reference: ~0.26 ± 0.50 ppm, n = 63). This provided a natural experiment to untangle whether the reproductive effects found in 2006 were due to the higher mercury levels of that year or were the result of accumulation in aging birds. If reproductive effects were found to be less severe in 2007 than 2006, it would have implicated the higher levels in 2006 as the cause of the detected reproductive deficits, and provided a valuable threshold for effects. If reproductive success continued to decline in 2007, despite the drop in blood mercury levels, it suggests that lifetime accumulation produces cumulative impacts on reproduction.

Reproduction – The many reproductive measures we obtain are correlated, so here I report only the one that is perhaps most directly related to fitness. Contaminated swallows produced significantly fewer fledglings (i.e., nestlings that left the nest) than reference swallows (contaminated: 3.49 ± 2.04, n = 98; reference: 4.44 ± 2.07, n = 82). This difference was significant for all ages of birds, as well as for experienced birds. In 2006 the same difference was observed but was driven by the poor performance of inexperienced "first-year" breeders, who appeared to have smaller eggs.

*Surviva*l – Female swallows are site faithful, so that if they breed at a site one year they have a high probability of returning there in the following year if they are still alive. (Nestling swallows are less good about returning to the area of their hatching, although this does occur with some regularity.) Because we capture 100% of the females breeding on our site, and there are very few places for tree swallows to nest near the study area, recapture rate is a good approximation of survival rate. In addition, we have checked the

2005-2006 data to confirm that reference and contaminated swallows that return to the site have the same propensity to move short distances within the study area, so any discrepancy between recapture rate and true survivorship is unlikely to be biased. Birds banded as breeders in 2005 had returned at approximately the same rates in 2006 whether they were on contaminated or reference sites (~56% and 52%, respectively). However, in 2007, only ~15% of the 2005 females returned to the contaminated sites, whereas ~30% returned to the reference sites. These numbers are preliminary because data are still being proofed. Enough data have been obtained from returning males, and the birds banded in 2006, that additional comparisons will be made.

Eggs – Large numbers of eggs were measured (30 contaminated and 63 reference clutches) to test the hypothesis that inexperienced breeders were laying small eggs, thereby explaining the poor performance of this age class on mercury-contaminated sites. However, with a larger sample the eggs, inexperienced breeders did not appear to have smaller eggs in 2007, and poor reproductive performance was evident in experienced birds as well. Additional tree swallow eggs were collected to provide a robust sample for mercury analysis that might explain the poor reproductive success of birds on contaminated sites (66 eggs from 11 contaminated clutches and 68 eggs from 11 reference clutches). These analyses were not part of the original proposal and have not been completed.

***Prey items*:** The ligature technique for sampling invertebrates brought back to nestlings by parents worked well again in 2007, with no mortality from strangulation, and more than 50 samples gathered from each of the four target terrestrial-feeding bird species. Sample sizes of nests were smaller than anticipated. To compensate for this, sweep netting and arrays of pitfall traps were employed to collect additional spiders. Using these additional techniques the targeted sample size of 400 spiders was exceeded, but the most valuable spiders, those collected by the birds themselves, number only 104 (chickadee = 14, Carolina wren = 29, house wren = 26, bluebird = 35). Analysis of these samples is complex and will integrate isotope level, size of prey, distance from river and elevation to determine what places a songbird at risk of collecting contaminated prey.

***Biomarker studies*:** Several collaborative pilot biomarker studies were carried out on tree swallows in 2007. A subsample of birds was “challenged” with an injection of the harmless protein PHA, and resulting swelling was measured as an estimate of immune responsiveness (with former student Dana Hawley, now at Virginia Tech). A subsample of birds was sampled for plasma corticosterone level, which involves holding the bird for an extra 30 minutes after capture to induce a mild “stress” response, and then comparing the baseline and “stressed” corticosterone levels (with Haruka Wada, postdoctoral fellow at Virginia Tech with Bill Hopkins). A drop of blood was taken from the tree swallow samples collected for mercury analysis in order to estimate oxidative damage to DNA using PCR (with Natalie Karouna, Patuxent Wildlife Research Center). When completed, these biomarker studies may provide a mechanistic explanation of differences in survivorship and reproduction in tree swallows.

Conclusion and work products: In the third year of the study tree swallow mercury levels dropped back to 2005 levels, but reproductive output was depressed nonetheless. Because the proportion of the population that has experienced one or more years of exposure to mercury increased from zero in 2005 to ~50% in 2006 and ~75% in 2007, interpretation of the mechanisms underlying reproduction (lifetime accumulation versus delayed impacts of the one-time higher levels in 2006) require careful interpretation and further data. What is clear is that tree swallows on contaminated sites produce fewer fledged offspring and are less likely to return than their counterparts on reference sites. The preliminary biomarker studies that we have initiated can uncover mechanisms behind these effects.

Mercury bioaccumulation in amphibians from the South River: Nondestructive indices of exposure, maternal transfer, and reproductive effects

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Introduction:

Amphibians and reptiles are critical constituents of aquatic and terrestrial communities, playing important roles in the transfer of energy and nutrients through food webs (Beard et al. 2002; Bouchard and Bjorndal 2000; Hopkins 2006; Wyman 1998). Herpetofauna occupy diverse trophic niches (from planktivores to carnivores) and often serve as abundant and important prey items for predatory wildlife, including birds and mammals. In fact, certain species of amphibians represent the single most abundant vertebrate in many aquatic and terrestrial communities, exceeding densities of 40,000 individuals per hectare in portions of Virginia (Jaeger 1980). Regardless of their trophic position, amphibians and reptiles are incredibly efficient at converting ingested energy into biomass (Burton and Likens 1975; Grayson et al. 2005). For example, the conversion efficiency of lizards and snakes is about 10 times higher than in birds and mammals of similar trophic level (Pough 1980). Because of this high conversion efficiency, many herpetofauna can exploit energy poor resources that are suboptimal for other wildlife and thus serve as critical links between the lowest and highest trophic levels within a community. Hopkins (2006) recently suggested that such high conversion efficiency should also be associated with high rates of contaminant bioaccumulation compared to other animals of similar trophic position, and this theoretical framework was recently supported in a food web study using stable isotopes (Unrine et al. 2007). Taken together, available evidence suggests that the high abundance and conversion efficiency of herpetofauna makes them key determinants in the cycling of environmental pollutants in ecological systems. This year, our research focused on several species of amphibians from different habitats and at different life stages to better assess their role in Hg cycling in the South River system.

2007 Primary Objectives:

In 2007 our primary goal was to test the following three hypotheses:
1) Amphibians accumulate high concentrations of mercury (Hg) in their tissues, making them important to the fate and transport of Hg within the South River foodweb.
2) Accumulation of Hg in amphibians follows the same spatial pattern as observed in other biota along the South River.
3) Tail tissue is a useful nondestructive index of Hg exposure for amphibians that exhibit tail autonomy.

We determined that there are at least 3 species of amphibians that occur in sufficient abundance to study Hg accumulation patterns along the South River including two-lined salamanders (*Eurycea bislineata*), red-backed salamanders (*Plethodon cinereus*), and American toads (*Bufo americanus*). To test our hypotheses, we collected adult and larval amphibians from multiple sites upstream and downstream of the Hg contamination source along the South River in all available and accessible habitats for each species. For adult salamanders, the tail was removed using a sterile blade. Bodies and tails were frozen separately until analysis. For toads, approximately 0.6 mL of blood was obtained using a 1-mL heparinized syringe. Bodies, tails, and blood were then analyzed for total Hg (THg), methylmercury (MMHg), and selenium (Se).

Briefly, a large range in THg concentrations (dry mass) was found among species and stages, with concentrations rising for all species and stages within the contaminated portion of the South River after the source of contamination. THg concentrations were low in the reference areas. Within the contaminated portion of the river, *E. bislineata* adults and larvae had the highest THg concentrations (3453 ± 196 ng/g and 2479 ± 171 ng/g, respectively), followed by *B. americanus* tadpoles (2132 ± 602 ng/g), while adults of the more terrestrial *B. americanus* and *P. cinereus* had the lowest concentrations (598 ± 117 ng/g and 583 ± 178 ng/g, respectively). Peak Hg concentrations were among the highest known for amphibians in the literature. Details of spatial patterns and interpretation of findings will be presented at the October SRST meeting.

There was a strong positive relationship between THg concentrations in salamander bodies and tails for both *E. bislineata* ($r^2 = 0.988$, $p < 0.0001$) and *P. cinereus* ($r^2 = 0.946$, $p < 0.0001$). A strong positive relationship was also found between THg concentrations in *B. americanus* adult bodies and blood ($r^2 = 0.839$, $p < 0.0001$). These findings will be extremely important for future work on the South River, as well as at other Hg contaminated sites around the world, because sacrificing amphibians may be avoidable for future risk assessments involving Hg.

2007 Additional Findings:

In addition to meeting our primary goals (above), we conducted an assessment of maternal transfer of Hg in *Bufo americanus.* The transfer of contaminants from a female to her offspring may be an important mechanism of impaired reproductive success in amphibians. While maternal transfer of contaminants has been studied in many fish and wildlife, only two studies have documented maternal transfer of contaminants in amphibians (Hopkins et al. 2006; Kadokami et al. 2004). We found that female toads transferred approximately 5% of their Hg body burden to their eggs in both the reference and contaminated site. THg concentrations in eggs ranged from 11 to 48 ng/g in the reference site and from 9 to 269 ng/g in the contaminated site. There was a significant negative relationship between THg concentrations in eggs and the percentage of eggs that hatched ($r^2 = 0.290$, $p = 0.004$) and between female THg concentration and hatching success ($r^2 = 0.472$, $p < 0.001$). Importantly, there was also a significant negative relationship between THg concentrations in female blood and the hatching success of eggs ($r^2 = 0.178$, $p = 0.029$), suggesting that predictions of egg viability might be possible based on female blood concentrations. This is the most compelling evidence in the amphibian literature (Hopkins et al. 2006) that a contaminant can maternally transfer and influence female reproductive success. However, further research is needed to clarify the ultimate impact of Hg bioaccumulation on embryonic development (e.g., malformation frequencies), larval development, female fitness, and the ecological significance of compromised reproductive success.

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Briefing for the South River Science Team Meeting, October 11-12, Harrisonburg, VA

Mercury in Bats from the South River, Virginia

David Yates and David Evers, BioDiversity Research Institute, 19 Flaggy Meadow Road, Gorham, Maine 04038, (207) 839-7600, dave.yates@briloon.org

Objectives:

PRIMARY EMPHASIS

1. Use Sonobat® technology to determine species type and location on the South River with an emphasis on federally listed species;

2. Emphasize capture and sampling of bats to generate a Hg exposure profile for multiple locations on the SR.

SECONDARY EMPHASIS

3. Physiological Hg effects will be measured with:

   a. Immunosuppression bioassays;
   b. Genetic bioassays for DNA fragmentation;

4. Reproductive Hg effects will be measured with:

   a. Reproductive Condition using lactation frequency;
   b. Stress responsiveness using progesterone;

5. Use stable isotope signatures of foodweb to determine dietary emphasis, trophic level, and percent use of aquatic-based prey items.

From early June to mid August, we captured 5 different bat species from sites along the South River and Middle River to collect blood and fur samples for Hg analysis. We also collected wing punches for isotope (n=127) and genotoxicity (n=40), and plasma for immunosuppression bioassays (n=111), stress hormones (n=50), histology (n=25) and reproductive markers (n=30). We attached radio transmitters to 3 bats and attempted to track them back to their daytime roosts. We captured and collected a blood and fur samples from 166 bats. Sonobat® was used at each site and all the species found on the Sonobat recordings were captured, except for the Hoary bat.
Mercury levels of blood collected from bats on the reference river (middle river) ranged from 0.008 to 0.043 ug/g ww, which has a mean level of 0.028 ± 0.008 ug/g ww for all bat species. Mercury levels in blood from the South River ranged from 0.036 to 3.7 ug/g ww, and had a mean level of 0.949 ± 0.995 ug/g ww. The site with the highest

concentration of blood Hg was the Forestry Center, river mile 13, with mean Hg levels of 1.619± 1.016 ug/g ww, Table 1. The species of bat representing the highest Hg concentration was the Northern Long-eared bat followed the Eastern Pipistrelle, big brown and red bat, Table 2. Fur Hg results are pending from the laboratory. Results for all other biomarkers are still being analyzed.

Table 1. Mean Hg levels in bats, by site, captured during the 2007 field season.

Site	n	Min	Max	Mean	sd +/-
Honeysuckle Hill-MR	16	0.008	0.043	0.028	0.008
Genicom-RM 2	21	0.036	1.050	0.159	0.232
Forestry Center-RM 13	21	0.064	3.700	1.619	1.016
Cosby Mill-RM 16	18	0.068	2.810	1.088	0.903

Table 2. Mean Hg levels by bat species.

Species	n	Min	Max	Mean	sd +/-
Eastern Pipistrelle	9	0.030	2.750	1.578	1.002
Big Brown	29	0.021	0.824	0.142	0.164
Red	5	0.026	0.151	0.067	0.049
Little Brown	1	~	~	~	~
Northern Long-eared	33	0.008	3.700	1.173	1.050

-

Mercury in Mallard Ducks from the South River, Virginia

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Objectives:

1. Determine Hg concentrations in potential breeding Mallards feeding on the South River and reference rivers by sampling blood, feathers, and egg.

2. Compare Mallard Hg levels within the South River and reference rivers with published literature values.

3. Determine the proportion of Mallards from the South River containing Hg levels exceeding available published data on the lowest observed adverse effects levels associated with reproductive impairment.

From late March to mid May, Mallard Ducks (*Anas platyrhynchos*) were live-captured from sites along the South River, Middle River, and North River, to collect blood and feather samples for Hg analysis. We captured and collected a blood and feather sample from 48 Mallards. Six Mallards were passively recaptured and blood was resampled, feather was not. In addition, captured female Mallards were equipped with a radio transmitter in order to track them to their nests and collect eggs for Hg analysis. Five hens were equipped with transmitters. A total of 107 Mallard eggs were collected from the reference and South River.

Mercury levels of eggs collected from Mallards on the reference rivers ranged from 0.01 to 0.03 ug/g ww, and contained a mean level of 0.02 ± 0.004. Mercury levels in eggs from the South River ranged from 0.13 to 1.46 ug/g ww, and had a mean level of 0.61 ug/g ww.

Blood Hg levels in Mallards from the reference rivers ranged from 0.006 to 0.06 ug/g ww and contained a mean Hg level of 0.03 ug/g ww. Blood Hg levels in Mallards from the South River ranged from 0.02 to 2.19 ug/g ww and had a mean Hg level of 0.79 ug/g ww. Feather Hg results are pending from the laboratory.

Preliminary analysis has determined that some eggs collected from Mallards breeding on the South River contained Hg levels exceeding levels associated with adverse effect levels in laboratory based Mallard studies.

Site Conceptual Model: Evaluation of the spatial profiles of mercury and methylmercury loading in the South River

Aaron Redman, Edward, Garland, Robert Santore. HydroQual, Inc

Introduction

Data generated from the Ecostudy on the South River were used to evaluate potential sources of mercury and methylmercury and the potential for mercury and methylmercury to migrated throughout the river system. Pathways of mercury transport to potential methylation sites as well as exposure pathways to fish were also evaluated. Needs for additional data, which will improve the understanding of mercury cycling in the South River were identified. Data collected as part of the storm characterizations and monthly monitoring campaigns were analyzed to identify seasonal patterns and other factors that control mercury input to the South River. Loading calculations were also performed to quantify the input of mercury and methylmerury along the river under different flow conditions.

Results

Total mercury (HgT) in South River surface water samples, measured at lower flows during the monthly monitoring program, did not vary much between months at a given station in contrast to the trend for methylmercury (meHg), which increased by nearly an order of magnitude between cold months and warm months. Total mercury concentrations in water and sediment increase by nearly a factor of 100 from the upstream reference site (RRM –2.8) reaching maximum concentrations near RRM 10, and then decrease gradually (about a factor of 2) out to the confluence with the South Fork of the Shenendoah (RRM 24). Methylmercury and total mercury have similar spatial profiles, except that the peak methylmercury concentrations are found between RRM 10 and 15, slightly downstream of the total mercury peak, which is near RRM 10. Between upstream reference sites and the mid-stream stations. Methylmercury concentrations do not increase as dramatically in relative concentration as total mercury. This results in a spatially variable ratio of methylmercury to total mercury, which is near 1% at the upstream site, and gradually decreases and levels off near 0.1% around RRM 10-15.

The analysis of the storm data shows that TSS and the concentrations of unfiltered mercury and methylmercury increase by nearly a factor of 100 between low and the highest flows. The filtered mercury and methylmercury concentrations do not vary substantially at the same range of flow conditions. Sorbed HgT and meHg concentrations (e.g., ng Hg/g TSS) show a decrease (factor of 2-10) that occurs just following the passage of the peak flows in the river. This effect is more pronounced in upstream sections of the river.

An incremental loading analysis of the monthly monitoring data show that Hg and meHg loading is broadly distributed between RRM 2-15. Unfiltered total mercury loadings reach peak values between RRM 5-10 while meHg loadings reach maximum values between RRM 10-15. The magnitude and location of the peak loading increases and migrates farther downstream as flow conditions increase. This change in the spatial profile of Hg and meHg loading under changing flow conditions coincides with a change in the physical characteristics of the river (e.g, episodic inundation of islands or side-channels).

An integrated loading analysis of the storm surface water data over the entire period of record show large suspended solids loadings, which increases slightly (factor <2) from upstream to downstream. The storm-integrated spatial HgT and meHg loadings increase from upstream to downstream reaching peak loadings around RRM >10. The integrated concentrations: e.g., Hg or meHg loadings (mg) normalized to suspended solids loading (kg), have a spatial profile that is very similar to the soil, sediment and sorbed, particulate HgT and meHg concentrations.

Fish mercury concentrations were analyzed using the database of historic and recent fish mercury concentrations. The fish data were binned according to species, age (e.g., size) class, and collection station to identify trends in fish mercury levels over time. The analysis shows that there are no consistent increases in fish mercury levels over time. Most of the apparent increase in fish mercury is explained by fish size and location at the time of collection. Preliminary bioaccumulation modeling suggests that meHg from dietary sources (e.g., aquatic insects) is the primary route of HgT exposure to fish in the South River.

Discussion

The incremental loading analysis suggests that changes in the physical characteristics of the stream under different flow conditions affect the loading profiles of HgT and meHg. Differences between the HgT and meHg loading profiles under similar flow conditions suggest that mercury methylation is likely a major contributor to meHg present in the South River. It is also likely that soil erosion (including bank erosion) is a major contributor of HgT inputs to the river. It was not possible to quantify separately the contributions of methylation and soil erosion to the meHg inputs to the river system.

Future efforts in this area should focus on identifying areas of mercury methylation such as backwaters or periphyton mats, or other environments. An improved characterization of porewater chemistry (e.g., sulfide, DOC concentrations) as well as a better understanding of general microbial processes that affect mercury methylation (e.g., diagenesis) in the South River will give more confidence to predicted impact of future remedial options for the river. Better characterization of short term erosion rates and processes will generate information necessary to quantify the contribution of soil erosion to HgT and meHg inputs to the river system.

The integrated and storm loading analyses suggest that particle exchange of in-place sediment is a major contributor to the overall suspended solids, HgT, and meHg loadings during high flows. An evaluation of the TSS-flow relationships generally show a clock-wise hysteretic loop which suggest the mobilization of bank or instream solids during initial onset of high flows followed by the introduction of solids from more remote locations some time after the passage of the peak flows. This is consistent with the patterns in the mercury (e.g., HgT, meHg) measurements. Future work on this topic should include an analysis of HgT and meHg distribution on different particle sizes in soils and sediments to improve the understanding of Hg, meHg and solids loading during storm events relative to available sources of TSS, HgT, and meHg as they are currently understood.

The fish data analysis suggests that HgT in fish has not increased significantly over time and that the apparent increase in fish HgT in more recent years can be explained by fish size, species and location of collection. This suggests that mercury bioavailability for uptake has not changed substantially over time within the South River. Future work in this area should include a continuation and refinement of the bioaccumulation modeling to quantify the relationship between water and sediment HgT and meHg, prey HgT and fish HgT.

South River Floodplain Sampling
Calvin Jordan, DEQ

A workgroup was created after the April 2007 South River Science Team meeting to come up with a monitoring plan that would satisfy the requirement of DEQ's 100 year monitoring plan and would also provide data for other projects such as the Ecosystem Study. The proposed plan calls for dividing the river in sections based upon bridge crossings. Those sections will then be divided again by inundation levels and then again by usage (Open space, forest, cropland). About 600 samples are proposed to be collected, analyzed and archived. The archived samples will actually be split based upon depth of sample (0-12 inch, 12-24 inch), so that there will actually be 1200 archived samples.

Use of Benthic Flux Chambers for the Quantification of Filter-passing Mercury and Methylmercury from the streambed of the South River – 2008 Study Proposal

Rich Landis, DuPont

Background:

Benthic flux chambers (BFC) allow the direct measurement of chemical flux from discrete areas of sub-aqueous environments in the South River. The use of a BFC allows for the measurement of the flux of filter-passing total mercury (THg), methylmercury (MeHg), iron (Fe) and manganese (Mn) in the South River, as well as measurements of dissolved oxygen in the chambers. The use of an opaque and a clear BFC allows for the testing of the effects of induced diurnal changes in the redox state within the BFC, such as the dissolution of mineral phases or increase in anaerobic microbial activity.

The overall goal of the study is to:

- Provide direct measurements of flux from dominant substrate types in the South River that are contributing THg and MeHg to the water column.

Substrates that have been hypothesized to be potentially important contributors of filtered MeHg fluxes to surface water are fine-grained channel margin (FGCM) deposits, periphyton attached to main channel cobbles, embedded substrates or gravel bars in the main channel, wetlands or other quiescent areas hydraulically connected to the South River. In 2006 and 2007, the study focused on method development for two dominant substrate types, fine-grained channel margin (FGCM) deposits and periphyton attached to main channel cobbles. The 2008 Benthic Flux Chamber (BFC) study will build on the results of the 2006 and 2007 BFC efforts and the results of the Phase I System Characterization. The preliminary results of the 2006 and 2007 BFC study are:

- BFCs are able to measure fluxes from different substrates in the South River.
- Opaque flux chambers can depress oxygen levels and simulate diurnal redox effects.
- The rocks attached to polycarbonate plates appear to effectively simulate the fine grained sediment trapped between the river cobbles and attached flora of the river bed.
- Dissolution of mineral phases may account for some part of the total fluxes of THg and MeHg caused by diurnal effects.
- THg flux rates varied over two orders of magnitude in South River FGCM deposits and periphyton attached to channel cobble.
- MeHg flux rates varied over one order of magnitude in FGCM deposits, and by a factor of two in periphyton attached to main channel cobble.
- Equipment blanks of the BFCs using the simplified cleaning protocol has been proven not to cause cross-contamination.
- The YSI 550 dissolved oxygen probe has been proven not to adsorb THg or MeHg and therefore can be inserted into the BFCs without biasing the results

The 2006 results of the Phase I System Characterization, Ecological Study (Eco Study) provide a good comparison for the rates detected in the first year of the BFC study, as well as provide a hypothesis to drive the 2007 BFC study. The results of surface water sampling from the Eco Study indicate that MeHg concentrations were highest the spring (April, May and June) and decreased throughout the year. Fluxes predicted from surface water sampling identified two areas as having the highest flux rates: between RRM 3.0 and RRM 4.2, and between RRM 7.0 and RRM 8.7. The fluxes measured during the 2006 BFC study were generally similar to the fluxes predicted from the Eco Study, but the samples were not collected during the Spring, at the time of peak flux. In addition, other results suggested that additional habitats may act as sources of THg or MeHg, such as wetlands or embedded pools and gravel bars. As a result, the 2008 BFC study will attempt to detect seasonal variations in fluxes and quantify fluxes in the different substrate types that may act as internal sources of THg or MeHg.

In the 2008 BFC study, several substrates types will be studied to determine their relative differences in THg or MeHg fluxes, and to determine if fluxes measured from these substrates can account for the fluxes measured over an entire reach from surface water sampling. Four substrates types will be evaluated in the 2008 BFC study; FGCM deposits, embedded gravel substrates, embedded gravel substrates in back waters, and wetland type habitats. Additional methods are needed to measure fluxes in embedded substrates, and the remainder of 2007 will be dedicated to methods development for the embedded gravel substrate that is a dominant South River substrate.

<u>Substrate Comparison Study:</u>

Scope of Work:

Three locations between RRM 3.0 and RRM 4.2 (Figure 1) have been selected based on the results of the 2006 Ecological Study data and proximity to important geo-morphological features. For example, the locations selected are adjacent to floodplain areas that are believed to have accumulated between 1937 and 2005, and may have been accumulating materials during the time that the plant in Waynesboro used mercury. These banks are currently eroding, so it is hypothesized that the FGCM deposits in proximity to these features could be acting as sources of bio-available inorganic mercury and/or as areas of methylation. The locations selected for the 2007 study are downstream of floodplain inputs from the Shifflet farm area, which has been studied by the EPA and has known concentrations of THg in soil. This area also has unique wetland features that are frequently in contact with the water column and drain to the South River after storm events and flooding, and potentially supply inputs of nutrients to the river that could stimulate methylation.

Sampling:

At each of the three study locations, one chamber of each type (clear and opaque) will be deployed on both FGCM deposits and the embedded gravel substrates and sampled simultaneously, providing measures of flux under similar conditions. Each location will be sampled over the course of one day to reduce temporal variability. Samples will be collected at one hour intervals for three hours; a duplicate sample will be collected with the last sample per chamber. Samples will be field filtered using a 0.45 micron filter and analyzed for THg, MeHg, Fe and Mn.

In order to compare the flux chamber results to surface water results, two surface water samples will be collected in duplicate twice each day at RRM 2.3 (Hopeman Parkway) and RRM 5.1 (Holsinger Farms Foot Bridge). Samples will be collected in the morning and evening to better account for potential surface water variations in the river. Samples will be analyzed for THg, MeHg, Fe and Mn.

After the BFC testing has been completed, surficial sediment will be collected from beneath the BFC from a depth of 1 to 2 cm and analyzed THg, MeHg, Fe, and Mn.

Dissolved oxygen (DO) will be monitored within all BFCs, and a 24 hour cycle of DO will be monitored in the immediate vicinity of the chamber installation locations to determine if the oxygen levels observed in the chambers are environmentally relevant. Conductivity will also be monitored over 24 hour cycle to help determine if dissolution of mineral phases is occurring.

Schedule:
The study will be conducted four times in 2008, once early in the year around March, a second time in the May timeframe after surface water temperature reaches roughly 10 degrees Celcius, a third time in the July timeframe during the summer months, and a final time in the fall around September.

Wetland Study:

Scope of Work:
Three wetland locations at RRM 5.3 (Figure 2), RRM 7.4 (Figure 3), and RRM 9.9 (Figure 4) have been selected as preliminary locations. These locations were selected based on previous data showing high MeHg or THg concentrations in surface water or sediment, and proximity to geomorphic features as described above. These habitats are low flow areas such as mill races, island side channels, and remnant channels.

Sampling:

At each of the three study locations, one chamber of each type (clear and opaque) will be deployed in wetland area. Samples will be collected at one hour intervals for three hours; a duplicate sample will be collected with the last sample per chamber. Samples will be field filtered using a 0.45 micron filter and analyzed for THg, MeHg, Fe and Mn.

In order to compare the flux chamber results to surface water results, two surface water samples will be collected in duplicate twice each day at RRM 5.2 and RRM 9.9. Samples will be collected in the morning and evening to account for potential surface water variations in the river. Samples will be analyzed for THg, MeHg, Fe, and Mn.

After the BFC testing has been completed, surficial sediment will be collected from beneath the BFC from a depth of 1 to 2 cm and analyzed THg, MeHg, Fe, and Mn.

Dissolved oxygen (DO) will be monitored within all BFCs, and a 24 hour cycle of DO will be monitored in the immediate vicinity of the chamber installation locations to determine if the oxygen levels observed in the chambers are environmentally relevant. Conductivity will also be monitored over 24 hour cycle to help determine if dissolution of mineral phases is occurring.

Schedule:
The study will be conducted four times in 2008, once early in the year around March, a second time in the May timeframe after surface water temperature reaches roughly 10 degrees Celcius, a third time in the July timeframe during the simmer months, and a final time in the fall around September.

Methods:

The benthic flux chambers that will be used on the South River were developed by DuPont and based upon the BFCs developed at Texas A&M. With input from Dr Gary Gill of Battelle's Marine Sciences Lab, DuPont advanced the BFC design for measuring flux from a broader range of sediment deposits including very soft sediment and advanced much of the BFC's functionality.

All the components of the BFC for the South River that are wetted by the surface water to be sampled are constructed of either Polycarbonate or Teflon. Prior to assembly for field deployment, each component that is wetted by the surface water to be sampled goes extensive cleaning process. This process includes disassembly of the BFCs and a thorough cleaning in a Micron 90 solution. After the cleaning process, the BFCs are thoroughly rinsed with distilled water. The BFC is then air dried within a medical type hood that filters the air preventing dust particles from collecting on the BFC. The focus of this thorough cleaning process is to remove potential trace amounts of mercury that may be present on surfaces of the BFC.

There are two types of BFCs; one is transparent and the other is opaque, but otherwise they are identical and are typically deployed in transparent / opague pairs,. The comparison of the data from the transparent and opaque BFCs aid in the determination of whether or not there is dissolution of mineral phases during a diurnal redox cycle that could influence the flux of MeHg and inorganic Hg.

The sediment area enclosed by the BFC is rough 974 square centimeters (151 square inches) and has an internal wetted volume of roughly 12.5 liters (3.30 gallons). Each BFC has an internal pump that slowing moves the water within the BFC to avoid concentration gradients within the BFC. The impeller of the pump is inductively coupled via magnets to a motor and gearbox that is powered by two 6-volt batteries wired in series contained within a waterproof box. The pump can also pump surface water from the outside of the BFC to the inside of the BFC through a series of valves. This functionality is used primary during the period prior to initiation of sampling events to help maintain the internal water in equilibrium with the external water. The BFC also has 4 two-inch diameter equalization ports that are opened initially to help support the equilibrium processes caused by the natural advective forces of currents and wave motion. Two additional ports have been engineered. The first port is for the collection of seepage via a specialized Tedlar bag and the second port is for the measurement of DO from within the BFC.

The BFC has four gauge plates near the bottom of the BFC, a tapered leading edge around the bottom of the BFC, and four ¾ inch diameter spuds all of which help ensure the BFC is appropriately keyed into the sub-aqueous fine grained channel margin deposit. The gauge plates are transparent polycarbonate and visually “wets” when they are in contact with the sediment. The gauge plates are a visual sign that the BFC’s tapered leading edge is keyed into the sediment. The spuds anchor into the sediments and additional weight is added to the BFC if needed to ensure that BFC does not move after is properly deployed. To study the periphyton attached channel cobble environment, rocks from the South River were attached to a polycarbonate and arranged to fit within the inside perimeter of the BFC. A specialized seal on the outside perimeter of the BFC then seals against the polycarbonate plate and is securely held in place by threaded hooks.

The typical BFC deployment event consists of deploying the BFC through the use of divers if the water is deeper than a few feet, otherwise deployment can be accomplished via leaning over the edge of a boat or by simply wading. If deployment is accomplished by wading, consideration must be made not to disturb the sub-aqueous area of interest and to stand down stream. After deployment of the BFC, no further disturbance of the general surrounding sub-aqueous area is permitted. The BFC is then allowed to equilibrate with the surface water for 30 minutes to and an hour depending upon the nature of the sub-aqueous environment. Upon expiration of the equalization period, the 4 equalization ports are closed, the valves to the internal pump are actuated, and the seepage collection bag is opened.

Once the ports are closed, the valves actuated, and the valve to the seepage collection bag is open, sampling of the BFC begins and continues for 3 to 4 hours. During the sampling period, samples are typically drawn at one-hour intervals and continue until the oxygen content of the sample is 50% of the baseline measurement or time expires. Surface water samples are drawn from with the BFC using eleven 25 milliliter syringes in order to collect sufficient sample to rinse two 250 ml sample bottles,. Dissolved oxygen is measured using a YSI 550 that is inserted into the BFC during emplacement. All sampling is conducted using ultra-clean techniques, the samples are filtered in the field using a 0.45-micron filter, the samples placed on ice immediately, and shipped for analysis using over night methods. Samples are then analyzed using low level detection methods (roughly 0.05 ppt) for filtered total mercury and methylmercury.

Shifflet Farm – Soil and Groundwater Results

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EPA, VADEQ, USGS, and U.S. Army Corps of Engineers conducted studies using soil, surface water, and groundwater sampling on the Shifflet farm on October 16 through 19, 2006. The Shifflet farm includes a flood plain area within a meander bend of the South River, located from river mile 3.1 to 4.3, downstream of Hopeman Parkway and the former Genicom facility. Approximately 58 acres of the farm (the entire area sampled in this study) lie within the 5 year floodplain. The floodplain is characterized by broad flat pastureland and hayfield, incised by erosion channels which trend south to north across the meander bend. These surface channels are flooded periodically (every year) but become dry during extended periods of low river stage. There are several permanent ponds on the property (cow ponds).

Sampling occurred approx. one week after the river peaked on Oct. 7, 2006 following a significant flooding event. Because of the flooding, all surface channels on the property were full of water - with water levels in the ponds at or near ~~the~~ ground level~~surface~~. Surface water runoff flowed to the South River at the northern end of the property which receives drainage from several of the surface channels. We collected surface water samples at this location (the northern end of the property), in addition to water samples from the three cow ponds, is where we collected surface water samples. An ATV-mounted direct-push drill rig was used to collect soil samples and to install two permanent and 16 temporary groundwater monitoring wells, distributed around the floodplain.

Our information demonstrates that surface water runoff passing over formerly dry surface channels contributed dissolved Hg, suspended Hg, and methyl Hg (3.52 ng L^{-1}) to the South River as these areas drained back into the South River after flooding. Hg concentration (filtered methyl Hg, filtered Hg, and unfiltered Hg) in surface water drainage and the permanent cow ponds were similar, while being approx. one to two orders of magnitude greater than Hg concentrations measured in the South River near this location. Groundwater discharge to the South River contributed methyl Hg in localized discharge zones, in association with former channel deposits connected to the cow ponds. Most groundwater in other areas of the flood plain were not impacted by dissolved or methyl Hg. Pressure transducer data collected hourly in 3 permanent shallow monitoring wells show groundwater elevation closely mimicked South River gaging data from the Hopeman Parkway USGS station, indicating that the floodplain aquifer was highly permeable and reacted quickly to river stage.

Soil Hg concentrations occurred in ppm ranges, and were elevated over the entire floodplain. The highest Hg concentrations generally occurred in areas that flood most often (along drainage pathways), and also highest in areas that receive deposited sediments during a major flooding event. In some locations peak Hg concentrations are in the surface (0-6”) interval, while other locations have peak concentrations at greater depth, with elevated concentrations over a greater depth interval. Density separations demonstrated that up to 99 % of the solid phase Hg preferentially partitioned with the organic carbon-rich light density (< 1.5 g cm^{-3}) fraction. X-ray absorption spectroscopy (XAS) showed that soil Hg existed overwhelmingly as the divalent cation. Exchange experiments demonstrated that Hg^{2+} was poorly exchangeable, releasing < 0.8 mg kg^{-1} of solid phase Hg against successively intrusive extractions with 0.5 eq L^{-1} $CaCl_2$ and KCl. Poor exchangeability was linked in part to the preferential Hg bonding to thiol S groups in soils. Fittings of XAS data showed a linear trend between Hg concentration in soil and organic S coordination, implying enhanced bond stability under abiotic weathering conditions.

The results from the solution and solid phase data suggest a relationship between solid phase Hg and flooding on the Shifflet flood plain. Ponded water promotes the dispersion of exposed soil, releasing organic-rich particulates containing elevated levels of Hg (adsorbed) relative to the concentrations dissolved in the South River waters. In this environment, biological activity rapidly accelerates to consume the newly available carbon and adsorbed nutrients, incidentally methylating adsorbed Hg. It is our hypothesis that adsorbed/particulate Hg on sediments in the South River provides a constant source of MeHg throughout the year and that these processes are enhanced by at least one order of magnitude during flooding periods. The vast stores of solid phase Hg, coupled with scant release of Hg by exchange suggests that these processes could be sustained for many years to come and that natural attenuation does not represent a viable option for remediating the South River.

South River Mercury TMDL - Briefing Paper

October, 2007
USGS- Jack Eggleston
VADEQ- Robert Brent

Purpose of Study : The purpose of the TMDL study is to determine fluxes of mercury in the South River basin and to calculate loading reductions needed to lower fish tissue mercury concentrations below the proposed state advisory level of 0.3 ppm.

Study Period : January, 2005 – October, 2008

Recent Results:

- Monitoring Results

  Collection of real-time water-quality data, and periodic water and sediment samples is complete. Data collected for this project, combined with data available from other projects allows the construction of a conceptual mercury transport model for the South River basin.

- Conceptual Model

  A conceptual model has been developed to summarize the most important processes controlling mercury transport and concentrations in the watershed. The conceptual model serves as the basis for the subsequent numerical simulation model. Significant sources of total mercury include atmospheric deposition, groundwater discharge, plant site discharge/runoff, sediment bound mercury dispersal, and desorption of mercury from sediment to river water. Downstream mercury transport occurs primarily (>80%) in the sediment bound phase during high flow events. Mercury moves readily between sorbed and desorbed phases, although in-stream total mercury is primarily sediment bound (92% at Dooms, 83% at Harriston).

- Numerical Simulation Model

  The numerical model represents water, sediment, and mercury transport in the watershed. It is based on the Hydrologic Simulation Program – FORTRAN (HSPF), a watershed simulation software package commonly used in TMDL studies of surface water bodies. The model divides the South River watershed into 5 subbasins, each with its own stream reach. Inputs to the model include spatially distributed properties such as land use, slope, and sediment erodibility as well as time series for such properties as precipitation, wind, and potential evapotranspiration. The primary outputs of the model are hourly time series of streamflow, suspended sediment concentration, and mercury concentration at the end of each stream reach.

  The hydrologic model has been compiled and calibrated. The sediment transport component of the model has been compiled and is currently being calibrated. The mercury transport component of the model is currently being compiled.

- Site-Specific BAF Modeling Approach:

As has been discussed in previous SRST meetings, the TMDL study will represent bioaccumulation of mercury by fish using a site-specific bioaccumulation factor (BAF) approach for total mercury. With this approach, the relationship between measured water column total mercury concentrations and fish tissue mercury is used to set a target water column concentration that will be protective of the 0.3 ppm advisory level for mercury concentration in fish. TMDL modeling will be performed to determine reductions in mercury loading needed to meet the target water column concentration.

The decision to use the BAF approach is based on the very strong relationship between average total mercury concentrations in the water column and fish tissue mercury concentrations. Alternative modeling approaches are available that more explicitly model the transformation of total mercury to methyl-mercury to biotic mercury moving up the food chain. But a review of these modeling approaches indicates that they would have less predictive value due to our lack of understanding about the fundamental processes controlling the detailed mercury pathways and the lack of available data to parameterize these additional processes.

A non-linear technique will be used to establish the target water column concentration that would be protective of fish consumption (Figure 1). While this approach will be refined with additional collected data, it appears that the target water column concentration will be near 2.9 ng/L total mercury.

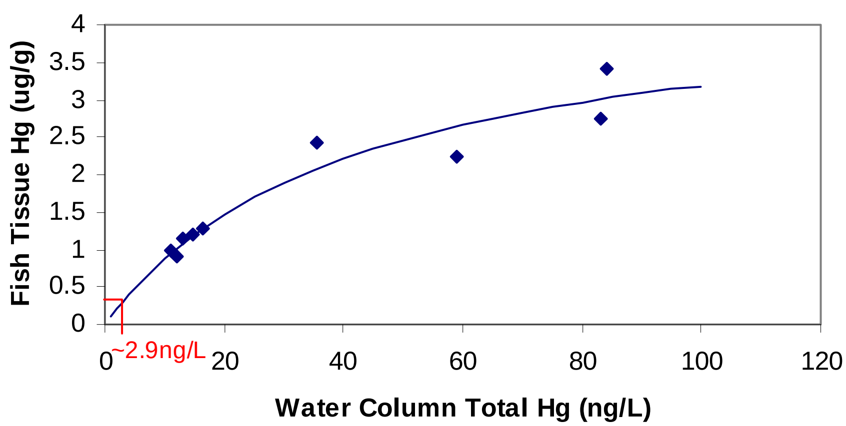

Figure 1. Relationship Between Size-normalized Fish Tissue Mercury Levels and Total Mercury in the Water Column of South River and South Fork Shenandoah River.