

South River Science Team  
Expert Panel Meeting  
October 6-7, 2009

Briefing Papers

## South River Mercury Study

This newsletter issue is devoted to summarizing the status of studies conducted by members of the South River Science Team, as well as describing the initial findings that have resulted from the work conducted over the past several years.

As many of you know, mercury was used at the former DuPont plant in Waynesboro from 1929 to 1950 and was released to the South River as a result of past practices at the plant. A Virginia Department of Health fish consumption advisory has been in place on the South River and South Fork Shenandoah River since the mid-1970s.

The South River Science Team was formed in 2000 as a

nonregulatory, collaborative partnership and has been working since that time to characterize the distribution of mercury in the watershed and identify potential options to decrease mercury availability to aquatic and terrestrial organisms. Science Team studies have included collecting samples from floodplain soil, river sediment and water, birds, bats, crayfish, small mammals, insects, fish, toads, and turtles, among others.



Members of the South River Science Team have been collecting samples from all types of aquatic organisms, including fish.

### About this Newsletter...

**In the Fall 2000, the South River Science Team was formed to serve as a focal point for technical issues concerning mercury in the South River and downstream waterways. The Science Team is a cooperative effort between the Virginia Department of Environmental Quality, Department of Health and the Department of Game and Inland Fisheries and representatives from academia, citizens groups, the Environmental Protection Agency and DuPont. The Science Team provides technical direction for the mercury monitoring program and ensures that there is effective communication provided to the users of the river. The Science Team's goal is to understand why mercury in South River fish has not decreased over time and to identify potential solutions to improve the situation.**

Past issues of this newsletter have summarized the sample collection methods and results of these individual studies. This newsletter issue presents the key findings that the Science Team is using to guide its future work. So much data have been collected that it is difficult to describe the findings in one newsletter without losing some of the more interesting details. Nevertheless, the Science Team hopes that the information contained in this issue is useful to readers.

Questions about any South River Science Team activities can be directed to any of the team members listed on page 4.

## The Big Picture and the Next Steps

The work of the South River Science Team has been extensive. With so many samples being collected, it is important to frame the key findings as part of the bigger picture. The findings are provided in a question and answer format below, along with the team's future plan for the topic.

### How is mercury entering the South River?

Mercury seems to be entering the South River in two primary ways. The main entry appears to be from the erosion of mercury-impacted soil on the floodplain and the river banks. Fine sediments dispersed throughout the river itself also play a role. Other minor sources include residual mercury from the former DuPont plant, atmospheric deposition, and groundwater.

Mercury tends to be tied up or bound when it first comes into contact with soil and sediment particles. When mercury is bound to particles, it typically does not enter the food web (see the Winter 2007-2008 issue of the newsletter for a discussion of food webs). However, under specific and not yet well understood situations in the South River, the mercury on particles transforms and becomes available for uptake by aquatic organisms and enters the food web. Understanding the process of mercury entry into the food web is a major focus of the Science Team.

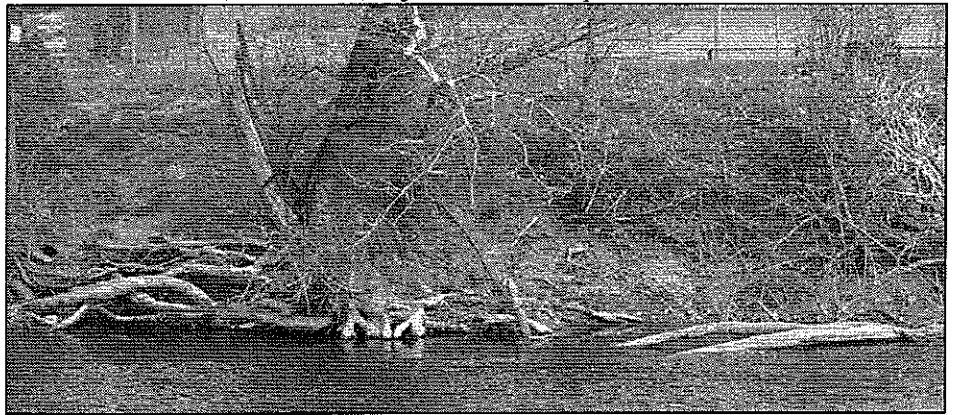
### How does the soil on the floodplain enter the South River and why is this important?

The work of the Science Team has shown that mercury-impacted soil on the floodplain is transported into the river by several different erosion processes. Flowing water during normal and storm conditions erodes river banks and floodplains. Human and animal activities can also cause soil erosion, and river banks can collapse into the river due to the winter freeze and thaw cycle.

The Science Team has measured erosion in many locations on the 25 miles of the South River between

Waynesboro and Port Republic. The findings reveal that more river banks are eroding in the upper stretch of the river between Waynesboro and Crimora compared to the lower stretch between Crimora and Port Republic. When erosion occurs, soil particles containing the mercury enter the river and some fraction of the mercury detaches from the soil particles and enters the food web. This process is one explanation of why mercury is distributed throughout several miles of the South River.

Similar to mercury on soil particles, some fraction of the mercury on sediment particles in the South River



Photograph of a typical eroding bank along the South River.

detaches and enters the river water and the food web. Even though the river bed consists primarily of rocks and gravel, there is sufficient sediment in the South River to provide a small but steady source of mercury to the river and the food web.

The Science Team is unsure exactly how the mercury detaches from soil and sediment particles and how it then enters the food web. The team will try to gain a better understanding of this process in its future work. If the erosion processes that transport mercury-impacted soil to the river can be slowed down or stopped, it is believed that some of the mercury entering the food web could be reduced or eliminated.

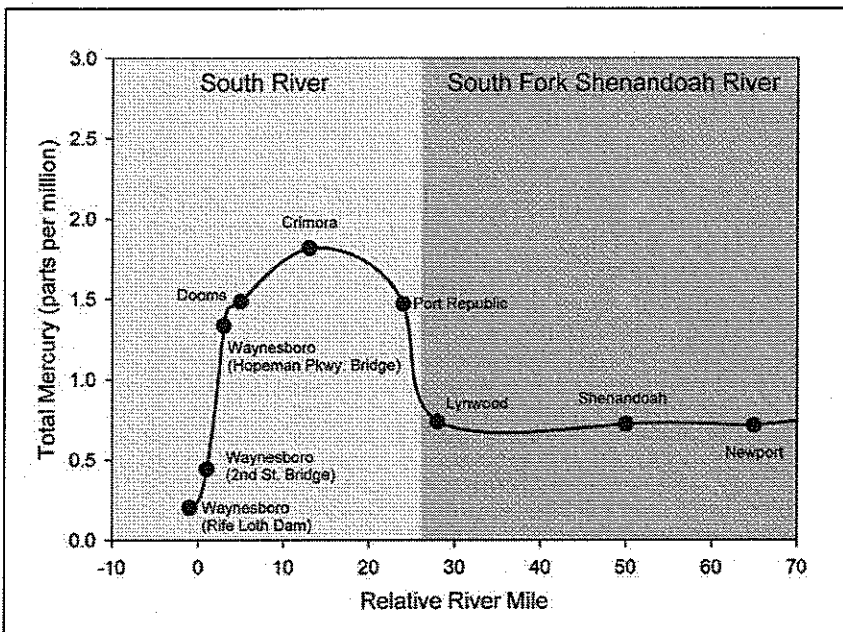
The Science Team will complete a river bank stabilization project in Waynesboro in late summer 2009. Across the river from Constitution Park, approximately 500 linear feet of eroding river bank will be stabilized and vegetation will be planted. This effort is considered a demonstration or pilot project to measure the changes, if any, that might occur when river bank erosion is reduced or stopped. Depending on its success, this approach may be one

option that could be applied to other eroding river banks that contain mercury-impacted soil. Construction activities will be visible from Constitution Park or while driving over the Main Street bridge in Waynesboro.

### What are the key findings of the Science Team’s fish and aquatic organism studies?

Measurements of mercury in fish date back to 1977, and now the Science Team has analyzed many other aquatic organisms in the South River for mercury. The information from these studies has helped improve the understanding of where mercury resides in the South River food web.

The mercury level in aquatic organisms typically increases downstream of Waynesboro, and the mercury level in many organisms is the highest near Crimora. Downstream of Crimora, the mercury level in fish and other organisms begins to decrease and the mercury level declines even more downstream of Port Republic. This rise and fall (i.e., a “hump”) of the mercury level in aquatic organisms can be plotted on a graph, as seen below.



This graph shows the total mercury levels in filets of largemouth bass and smallmouth bass from the South River and South Fork Shenandoah River. Between 1981 and 2007, the Virginia Dept. of Environmental Quality has collected filets from 1,605 fish and analyzed them for mercury.

Why do we see this “hump” in the level of mercury in aquatic organisms? A greater percentage of river banks are eroding in the upper stretch of the South River between Waynesboro and Crimora compared to downstream of Crimora. Mercury levels in river

bank soil tend to be higher in the upper stretch as well. These two conditions seem to support a connection with higher levels of mercury in aquatic organisms in the upper stretch of the South River. In the upper stretch, the South River flows more slowly, the floodplain is wider, and there is more sediment at the base of the river bank compared to the downstream stretch.

Although sufficient measurements of the connection between erosion and the mercury level in aquatic organisms have not yet been made, the connection seems plausible and worthy of further investigation.

### How might humans be exposed to mercury?

The Science Team continues to examine all of the ways in which humans might be exposed to South River and South Fork Shenandoah River mercury, such as eating fish, wildlife, crops, and livestock and through living and recreating on the river.

The fish consumption advisory provides important information about the amount and types of fish that should not be eaten. Less is known about mercury levels in wildlife, and the Science Team has begun sampling waterfowl and game that is typically hunted and consumed.

With the exception of interior locations at the former DuPont plant, mercury levels in the South River and South Fork Shenandoah River, as well as the groundwater in the area are below those identified as safe for drinking. For those people participating in recreational activities, mercury levels are not believed to pose a significant health concern. Science Team activities have focused on potential human exposure to floodplain soil and crops. Results show that the vast majority of floodplain soil samples have low mercury levels. These low levels are below the U.S. Environmental Protection Agency (USEPA) level that is considered safe for people

(including children) who routinely have contact with the soil. Samples with higher mercury levels were collected at a limited number of sample locations (e.g., forested, agricultural, or commercial areas) where direct human contact with soil is expected to


be infrequent and potential risks to humans are expected to be limited to nonexistent. A few samples with higher mercury levels were obtained from areas where more frequent contact might be expected. These areas will be revisited to determine if additional soil samples should be collected. Findings from a floodplain crop study show that mercury in edible crops is not a significant route of exposure to people.

The Science Team also performed an outdoor air study to determine whether mercury levels are higher than normal background levels in the vicinity of the South River and its floodplain. All measured concentrations are comparable to global background concentrations, meaning that the amount of mercury in the air is similar to what is normally found on Earth in places that do not have a local mercury pollution problem.

Shortly after mercury was discovered on the floodplain in the 1970s, samples from edible portions of a limited number of cattle that grazed in the area were analyzed for mercury. No mercury was found at levels that pose a health risk from eating beef from cattle raised on the floodplain. Sampling was limited in the study, so additional investigation may be needed to confirm these findings.

### **What are the next steps?**

There is still much to learn about mercury in the South River and adjacent floodplain environments, so it is important that the Science Team's collaborative efforts continue. Unfortunately, mercury is a difficult material to understand, particularly in a system like the South River that is changing over time through climatic, geologic, and human activities. Mercury can change chemical forms, move about in the environment, and be converted by microorganisms to a more active, toxic form. It is important to understand these dynamic processes in the South River in order to identify potential remediation options that may improve the mercury situation.

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## **SRST Human Exposure Task Team Briefing Paper**

A Human Exposure Task Team of the South River Science Team (SRST) was formed in 2008. The key objectives of the team's efforts are to better identify possible routes of exposure to mercury, define possible risks and uncertainties, and communicate that information to the public.

One activity identified by the team is to produce a fact sheet identifying what is known, what is not known and what the SRST is doing about getting this information related to potential human exposures related to mercury of the South River and its floodplain. The work product "People, Mercury, and The River", which in effect summarized activities of the Exposure Team, is attached. The Team also produced a more general Fact Sheet on the SRST and is working on a third that summarizes floodplain soil sampling efforts. The fact sheets are meant to be made available to the general public.

Ongoing efforts of the Team include evaluating potential dietary exposures via livestock and wildlife consumption; and evaluating the results of a recently completed health-based survey designed to determine how well the fish consumption advisories have reached communities.

# People, Mercury, and the River

Mercury in fish in Virginia's South River and South Fork Shenandoah River has been investigated since its discovery in the 1970s. Mercury is a neurotoxin, meaning it may have harmful effects on the human nervous system and, hence, it may pose a risk to people who are exposed to it in the environment. While the most common potential route of exposure is from eating contaminated fish, other routes of exposure are also possible.

Though human exposure always has been a focus of mercury investigations, the South River Science Team formed a dedicated work group to systematically identify, study, and communicate potential risks and uncertainties associated with human exposure to mercury. This Fact Sheet summarizes what researchers on the Science Team have learned and plans to further understand potential exposure to mercury in these rivers.

## Fish Consumption

The risks associated with eating mercury-contaminated fish have been studied extensively in many locations around the world. As a neurotoxin, mercury is particularly harmful to young children and pregnant women.

Fish consumption advisories have been in place on the South River for more than three decades. The Virginia Department of Health's current advisory on the South River recommends that people eat only trout (no other fish) caught in the South



Fishing is safe as long as you follow the advisory.

River between Waynesboro and Port Republic. Trout are safe to eat because they are stocked as adults and do not live in the river long enough to build up significant amounts of mercury. The fish consumption advisory is listed above.

Signs outlining these consumption advisories are posted in English and Spanish

**South River:** Fish caught in these waters may contain mercury. Mercury may be hazardous to your health. No fish other than trout should be eaten from these waters. Stocked trout have been tested and are safe to eat.

**South Fork River:** Fish caught in these waters may contain mercury, which may be hazardous to your health. No more than two meals (1/2 pound each) of fish per month should be eaten from these waters. Women who are pregnant or may become pregnant, nursing mothers, and young children should not eat fish from these waters.

Users of the river should follow these advisories.

at all public access points along these rivers. Additional information is available at local health clinics and on the Virginia Department of Health's web site at <http://www.vdh.virginia.gov/epidemiology/DEE/PublicHealthToxicology/Advisories/index.htm>.

## River Recreation

Swimming, boating, and wading in any natural water body poses some risk, generally from possible bacterial contamination.

But mercury levels in the South River and South Fork Shenandoah River do not pose a significant health concern to people participating in these recreational activities.



Many people enjoy canoeing down the South River.

## Drinking Water

The U.S. Environmental Protection Agency (USEPA) has established a maximum contaminant level of mercury in water that is considered safe for drinking. With the exception of a few groundwater monitoring wells located on the former DuPont plant site, mercury concentrations in the rivers as well as the groundwater in the area are below this level. In fact, mercury concentrations in these rivers are well below the safe drinking water level, seldom reaching even 1% of the level.

## Floodplain Soil

Periodic flooding has deposited mercury in South River floodplain soil, so the Science Team has been sampling and studying floodplain soil extensively. In general, the Science Team has found that the vast majority of samples have low levels of mercury. These low levels are below the

# People, Mercury, and the River

USEPA level that is considered safe for people (including children) who routinely have contact with the soil. Higher concentrations of mercury were measured at a limited number of sample locations.

The majority of these sample locations were from forested, agricultural, or commercial/industrial areas where direct human

contact is expected to be infrequent, and potential risks to humans are expected to be limited to nonexistent. A few samples with higher concentrations of mercury were obtained from areas where more frequent contact might be expected. These areas will be revisited to determine the current uses of the properties and to determine if additional soil samples should be obtained to further define the extent of elevated mercury concentrations.

## Floodplain Crops

Scientific literature has shown that mercury in soil does not usually find its way into food crops. To validate these findings, the Science Team planted and harvested 17 garden crops over two growing seasons on the South River floodplain in Crimora, Virginia. The results show that mercury in edible crops is not a significant route of exposure to people.

## Mercury in the Air

Mercury can be present in air as it escapes from soil and as emissions from burning fossil fuels. The Science Team performed an outdoor air study in 2005 and 2006 to determine whether mercury concentrations were higher than normal background levels in the vicinity of the South River and its floodplain. All measured concentrations were comparable to global background concentrations, meaning that the amount of



Lettuce, carrots, and sweet corn were some of the crops harvested.

mercury in the air is similar to what is normally found on Earth in places that do not have a local mercury pollution problem.

## Livestock on the Floodplain

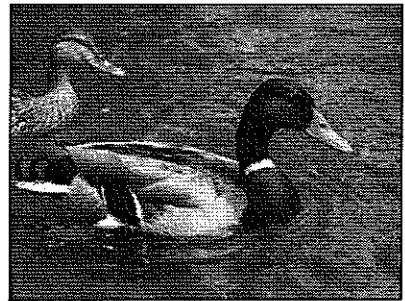
Shortly after mercury was discovered on the floodplain in the 1970s, samples from edible portions of a limited number of cattle that grazed in the area were analyzed for mercury. No mercury was found. Sampling was limited in the study, so additional investigation may be needed to confirm these findings.

## Floodplain Wildlife

Much less is known about mercury concentrations in wildlife than in fish from the South River. Mercury contamination may be a concern for the wildlife itself, as well as for people who eat wild game. The Science Team has begun sampling wildlife and waterfowl.

## Additional Information

Working with the Department of Health, the Science Team will complete a survey in South River health clinics to determine how well the fish



The Science Team is performing studies on waterfowl.

consumption advisories have reached communities. Local health clinics and private physicians along the South River have been informed about mercury contamination in fish and asked to report any signs and symptoms that could be associated with eating fish contaminated with mercury. To date, the Virginia Department of Health has received no such reports.

## Contacts

For more information about the potential for human exposure, contact:

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**South River Science Team  
Remedial Options Program (ROP) Update**

**Co-chairs: Nancy Grosso, DuPont  
Robert Brent, JMU**

**October, 2009**

The Purpose of the SRST ROP Work Group is to review, evaluate and test promising remediation approaches for the South River.

*South River Remedial Action Objectives are to:*

- *Reduce fish tissue Hg levels to concentrations that would allow consumption by humans*
- *Ensure protection of aquatic and terrestrial ecology with respect to Hg exposure*

### **ROP Approach**

The ROP approach involves: refining our understanding of mercury cycling within the South River system, exploring potential remedial options, expanding those options beyond the norm, and testing promising alternatives.

Refining our understanding The team has processed the working hypotheses and conceptual exposure pathway diagrams and posed a number of questions based on our current understanding of exposure/migration pathways to physical and biological compartments.

1. What can be done to reduce introduction of total mercury from eroding banks?
2. How can we reduce bioavailability of mercury in the aquatic and terrestrial systems?
3. Can we shift the system to enhance demethylation potential?
4. Can the food web be manipulated to reduce the mercury levels in the upper trophic levels?

Exploring remedial options The team developed a comprehensive technology matrix to identify a full range of options for the river, floodplain and plant site. These technologies have not been screened but will allow the team to refer to these when evaluating alternatives for different reaches of the river/ floodplain. Promising technologies or approaches may be combined to optimize remedial efforts. Additionally, a review paper of remedial activities planned or implemented at different mercury contaminated fluvial sites was prepared.

Expanding remedial options The team solicited the help of nationally-recognized remediation experts to brainstorm innovative remedial approaches that could provide additional alternatives and expand remedial options beyond traditional approaches.

Testing remedial options The general approach for testing and implementing potential technologies / approaches is to:

1. Characterize the river by reach with respect to sources (internal and external) and identify the processes relevant to transfer of mercury through the food web.
2. For reaches or areas where action may be feasible, conduct an alternatives analysis and identify bench scale studies that may be needed to prove concept or to assess potential unintended consequences.
3. Implement field pilots and monitor for success. Consider adaptive management to optimize activities. Evaluate monitoring results, and if successful, consider larger scale implementation or add to toolbox of potential technologies..

A bank stabilization pilot is currently underway.

## 2009 Activities

A number of activities have occurred or are proposed this year that will aid in exploring and evaluating remedial approaches:

- Developed a Technology Matrix of a broad range of possible remedial technologies and approaches
- Formed Task Team to explore innovative approaches to address the mercury challenge
- Commenced Bank Stabilization Pilot Project, including design refinement, baseline monitoring, and initial construction
- Began lab studies to test amendments that may adsorb mercury and yield it less bioavailable (University of Waterloo) (Exponent, University of Maryland and Smithsonian)
- Initiated geomorphic studies to understand the residence time of Hg-associated fine sediments in the river channel (University of Delaware)
- Proposed geomorphic studies to refine our understanding of the distribution of on-going sources to the river channel (University of Delaware).
- Began river studies to refine understanding of the physical and biological exposure pathways in the system (Phase 2 Ecological Study, URS). Remedies may target cutting off an exposure pathway.
- Initiated Corrective Measures Study for on-site SWMU areas that may be a source of the mercury detected in outfalls
- Drafted Total Maximum Daily Loads (TMDL) for mercury, phosphorus, sediment and bacteria in the South River. The South River is currently listed as impaired, because it does not meet Virginia's bacteria standard, Virginia's general standard for aquatic life, or Virginia's fish consumption use. The draft reports may be found on the DEQ website at: <https://www.deq.virginia.gov/TMDLDataSearch/DraftReports.jspx>.

## Discussion

### **Selected Case Studies of Remediation at Hg-contaminated Fluvial Sites (Ralph Turner, RTGeosciences, Inc.)**

A review paper was prepared describing experiences at sites where remediation of fluvial receiving environments has been carried out or is in final stages of planning. The number of such sites is relatively small and few "large" sites have actually experienced much, if any, remediation. The focus of most remediation at these sites has been on the facilities themselves that originally discharged or lost the mercury. For a few very small sites or small portions of large sites, remediation, typically in the form of complete sediment and soil removal, has been practiced beyond the fence line of the facilities. A more complete review is included in a separate Briefing Paper.

### **Innovative Remedial Approach Task Team (Reed Harris, Mike Newman, Danny Reible, Carol Ptacek)**

The ROP Work Group had assembled a technology matrix of possible remedial approaches that includes physical, chemical, and administrative alternatives. This technology matrix represents a wide range of options that have not yet been screened. In order to explore other innovative options that may be considered, a small Task Team was assembled. Their charge was to identify innovative technologies and approaches for reducing the bioavailability of mercury in the South River aquatic system, without harming the biota. The task team had to consider the feasibility of deploying technology/technologies in a relatively high-energy, sinuous, bedrock, and gravel-bed river. The preliminary results of this Task Team are provided in a separate Briefing Paper.

### **Bank Stabilization Pilot**

Mercury associated with soils that are eroding into the River from banks is believed to be the major source of ongoing inorganic mercury to the river. The Bank Stabilization Pilot was proposed in order to help understand the significance of bank soil loading while also controlling a source to the river of both mercury and sediments. The pilot is located just downstream of the Waynesboro plant site. A separate Briefing Paper is included that further explains objectives and status of the pilot.

### **Testing Amendments to Bind Mercury (Carol Ptacek PI, University of Waterloo)**

The main objectives of this research are to: 1) Characterize the form and geochemical associations of mercury in bank soils and sediment; 2) Characterize the potential geochemical mechanisms leading to release of mercury from soil and sediments and; 3) Identify geochemical approaches which may lead to reductions of mercury release from soil and sediment. This work was initiated in late summer and results are pending.

The characterization of the soil and sediment will include analysis of mercury and other trace metals, sulfur, total carbon, grain size, mineral identification including clays, characterization of elements and other binding mechanisms associated with mercury. The leaching of mercury under aerobic and anaerobic conditions will also be conducted to evaluate the contribution of dissolution processes on mercury release. The leaching experiments are designed to include analysis of short-term release (<15 minutes) of mercury from soils as well as longer term (24 hour) release.

The study of mass transfer mechanisms from soil and sediment (Phase 2) will be conducted using column tests to investigate the roles of advection and diffusion (to simulate transport regimes in the river) and diffusion alone (to simulate storage zones in the river). The focus of the final phase of investigation (Phase3) will be to develop strategies to minimize the release/and or bioavailability of mercury from soil or sediment. Materials for testing have been tentatively identified as: attapulgite clay, organically modified clay, biochar (pyrolyzed biomass), zero valent iron, zero valent copper, and elemental sulfur. Different materials may be co-blended to optimize the effectiveness.

### **"SediMite" Preliminary Bench Tests (Cyndi Gilmour, Smithsonian Institute; Upal Ghosh, University of Maryland; Betsey Henry, Exponent)**

SediMite is a granular material developed to deliver treatment materials such as activated carbon to sediments contaminated by organic chemicals and metals. The material, generally in the form of pellets, can be applied at the water surface and is designed to sink to the bottom. Native benthic organisms perform the mixing into the biologically active zone, thus obviating the need for mechanical mixing. The binding agents then break down, while bioturbation continues, facilitating the sorption of contaminants to the activated carbon.

Amendments of activated carbon, modified organoclay, and a mercury sorbent with incorporated thiol groups have been tested in the lab using sediments from RRM 4.3. Exposures to methyl mercury were reduced by 70% to 90% in the bench-scale demonstrations, as measured by sediment pore water chemistry and bioaccumulation (*Lumbriliculus*). However, concentrations of MeHg in bulk sediments increased in those amended with activated carbon and modified organoclay. Additional investigation of these phenomena is planned.

### **Geomorphic Studies (Jim Pizzuto PI, University of Delaware)**

The focus of a portion of the current and proposed geomorphic study work will support remediation approaches in the river and increase our understanding of natural processes that may aid in the recovery of the river.

Currently, the conceptual understanding of the river is that most of the methyl mercury production is occurring in river bed sediments – both in transport (coarser-grained gravel and cobble/boulder) and storage zones (finer-grained silts, clays and fine sands). Methyl mercury production in the river is facilitated by inorganic mercury on fines that acts as a local source. A question posed by the South River Science Team was, if ongoing sources to the river were halted, how long would it take for the inventory of fine-grained particles (and by association inorganic mercury) now in the river bed to wash out? An objective of the ongoing geomorphic work is to estimate the time required for the river to remove inorganic mercury stored in the river bed through natural bed turnover. More detail is provided in the briefing paper on Geomorphic Studies.

A second study objective is to develop a quantitative method to locate banks with elevated mercury concentrations. The purpose of this study is to refine the current model of river banks responsible for significant inorganic mercury loading to the river. This will allow prioritization of reaches for management options.

**Waynesboro Plant Site Corrective Measures Study for Mercury-impacted soils(URS)**

Three solid waste management units have been identified that may potentially impact environmental media at the plant. A corrective measures study (CMS) is underway. Among the actions considered for source control are removal, treatment, containment and institutional controls. Two treatment technologies have been identified for further testing: physical recovery of mercury and stabilization of mercury impacted soils. CMS work will continue through 2010.

<b>ROP Work Group Members:</b>	
<p><b>VA Department of Environmental Quality</b>          Robert Brent (Robert has joined the faculty of James Madison University as of August, 2009)          Calvin Jordan          Don Kain</p> <p><b>VA Department of Conservation and Recreation</b>          Neshia Mizel</p> <p><b>US Environmental Protection Agency Region 3</b>          Joel Hennessy          Mike Jacobi</p> <p><b>US Army Corps of Engineers – Engineer Research and Development Center</b>          Mark Chappell</p> <p><b>Friends of the Shenandoah</b>          Bob Luce</p> <p><b>University of Delaware</b>          Jim Pizzuto</p>	<p><b>Virginia Institute of Marine Science</b>          Mike Newman</p> <p><b>URS Corporation</b>          Todd Morrison</p> <p><b>Unique Environmental Services</b>          Dick Jensen</p> <p><b>RT Geosciences, Inc.</b>          Ralph Turner</p> <p><b>DuPont Company</b>          Bill Berti          Jim Dyer          Nancy Grosso          Rich Landis          Mike Liberati          Erin Mack          Mike Sherrier</p>

# **Innovative Remedial Options Study**

## **Briefing paper**

Reed Harris<sup>1</sup>, Mike Newman<sup>2</sup>, Carol Ptacek<sup>3</sup> and Danny Reible<sup>4</sup>  
October 2009

*1: Reed Harris Environmental Ltd., 2: Virginia Institute of Marine Science, 3: Waterloo University, 4: University of Texas - Austin*

### **1 Background**

An Innovative Remedial Options workgroup was assembled in March 2009 to identify innovative technologies that could reduce the bioavailability of mercury in the South River aquatic system, without harming the biota. Consideration was given to feasibility and cost-effectiveness in deploying a technology in a relatively high-energy, sinuous, bedrock, and gravel-bed river.

The workgroup included four members external to DuPont (R. Harris, M. Newman, C. Ptacek and D. Reible). Innovative options did not have to be fully developed yet, thus a wide range of ideas was initially considered. The task team met May 7-8, 2009 and June 17, 2009 and continued efforts afterwards to develop remedial options worth considering further. A draft technical memorandum is being prepared that describes the findings of the workgroup. It identifies approaches considered and describes the process of developing a list of options recommended for further consideration. The following information is provided for higher priority options:

- A description of the technology/approach and what it would accomplish,
- Advantages and disadvantages of the technology,
- Uncertainties with respect to "proof of concept" and deployment feasibility,
- Whether the technology is available or needs to be developed, and other previous project applications, if any.
- Next steps to further evaluate or develop highly ranked options.

### **2 Candidate Innovative Remedial Options**

The workgroup recommended a two-track approach: Short term actions related to trophic modifications and habitat restoration that would quickly reduce exposure for sportfish consumers, and a longer term effort related to reducing MeHg supply to biota at the base of the ecosystem. Options identified by the Innovative Remedial Options work group as warranting further attention are shown in (Table 2-1), grouped into four categories:

- Bank stabilization (complementary to a fully engineered approach)

- Sediment capping, including sand/gravel caps and amended caps,
- Reducing the activity of methylating microbes, and
- Food web modifications.

A potential point-source control technology for Hg effluents was also presented briefly, although this was outside the area of focus of the workgroup. Table 2-1 also indicates whether an option would likely contribute to the restoration of trout habitat and/or ultimately help to reduce MeHg levels in the ecosystem.

While no single option was considered likely to entirely remediate concerns regarding mercury contamination in the river, one option was seen as having the potential in the near term to significantly reduce human exposure to mercury via sportfish consumption: favoring the restoration of a trout fishery and replacing bass as the primary sportfish. Restoration of trout would not however reduce MeHg concentrations in lower food web or underlying ecosystem. Additional remedial options should be investigated to complement the armored bank stabilization program being evaluated to reduce mercury loading and methylmercury levels in the overall South River system. It is most likely that a range of options will provide incremental benefits rather than finding a single solution.

A Technical Memo that discusses the findings of the Innovative Remedial Options workgroup is being prepared and will be shared with the ROP Workgroup presently.

Remedial option	Enhances Trout Habitat	Reduces MeHg Levels in Ecosystem
<b>Group 1: Bank Stabilization (complementary to ongoing engineered approach)</b>		
- Vegetative cap	X	X
- Limit livestock access to banks	X	X
<b>Group 2: Caps to inhibit MeHg production and Hg fluxes</b>		
- Sand/gravel cap		X
- Caps amended with sorbent		X
<b>Group 3 : Alter microbial activity to reduce net methylation</b>		
- Reduce load of limiting nutrient	X	X
- Add nitrogen to phosphorus limited systems.		X
- Reduce labile org C (via TP reductions, also including leaves)	X	X
- Modify habitat/flow to prevent plant growth and sedimentation	X	X
- Enhance microbial demethylation		X
<b>Group 4: Food web options</b>		
- Stock trout, remove/reduce bass. Set up fish exchange, reward, or similar mechanism	X	
- Enhance habitat for trout		
- Modify habitat to favor insects	X	
- Reduce forage fish trophic level	X	
- Produce low MeHg habitat for bass or their prey	X	
- Stock sterile fish (triploids)	X	
- Promote faster growth rates (triploids, feed fish, modified habitat, )	X	
- Supply low-MeHg food	X	
- Stock larger fish	X	
<b>Group 5: Point source control of Hg effluent</b>		
- Reduction of Hg(II) by magnetite		X

Table 2-1. Innovative Remedial Options recommended for further consideration

## **BANK STABILIZATION PILOT**

### **Testing the Feasibility of Conventional Bank Stabilization** South River Science Team

Todd Morrison, URS    Nancy Grosso, DuPont

October 2009

#### **Background**

One of the leading hypotheses for potential on-going sources of mercury to the South River system is from eroding banks. In general, introduction of mud from eroding banks hinders the quality of a river system which reduces forage and cover habitat for fish and other beneficial aquatic organisms. In the South River System specifically, the river is impaired for aquatic habitat based on sedimentation and phosphorus loading (TMDL). The bank stabilization pilot will test the efficacy of bank stabilization to reduce erosion of Hg-containing bank soils into the river and to enhance riparian and aquatic habitat.

Conceptually, the bank will be built out into the current channel to construct a more consistent river width (relative to upstream and downstream). Vegetating the bank with native shrubs would further stabilize it and help prevent erosion from re-occurring. In addition, the top of the bank will be planted with shrubs and trees expanding the riparian buffer habitat. Among its benefits, this buffer would restore a resource for wildlife use and provide shade in the summer that cools the water and further improves the aquatic habitat of the river.

#### **Pilot Project Status**

All necessary permits have been obtained. Site preparation and field construction began on September 9, 2009. Construction is anticipated to be complete in November.

#### **Pilot Objectives**

##### **Primary Objectives:**

- Reduce river bank erosion such that there is a reduction in the quantity of mercury-bound soil particles entering the South River
- Enhance existing near-bank aquatic and riparian ecosystems
- Reduce mercury (Hg) loads to physical and biological compartments within the river.

##### **Secondary Objectives:**

- Evaluate changes in groundwater/bank interactions between the river and the floodplain pre and post construction;
- Determine if the mercury methylation environment in adjacent sediment has change appreciably
- Determine if off-site changes in river bank erosion and/or sediment deposition have occurred following bank stabilization.

The stabilization pilot was designed to withstand forces of storm event flows and over bank flows (i.e., the bank withstands storm event stresses based on HEC-RAS modeling). In addition, modifications were made to the design to accommodate potential fish habitat improvements in the stream bed morphology adjacent to the bank.

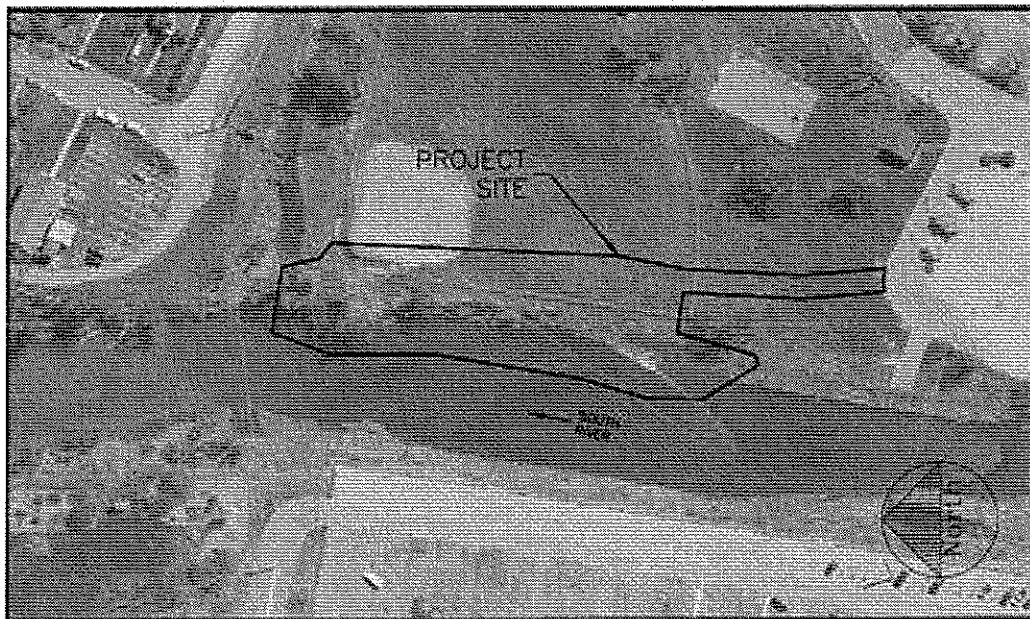
#### **Pilot Location**

The team has selected a pilot site on the eastern (right) bank of the South River from approximately RRM 0.10 to RRM 0.16 (upstream of the confluence with Rockfish Run). This site, which is approximately 500 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 Hg source



#### **Pilot Construction Plan**

The plan is to build the bank out into the river to make the river width more consistent with upstream and downstream of the pilot. The construction plan has three main components: a rock toe at the base of the bank slope for slope protection, soil lifts to engineer a more stable gentler bank slope, and native vegetation on both the slope and top of the bank to provide further stability and habitat. In addition, woody debris will be anchored to the rock toe for fish habitat. Weir rock will be incorporated into the toe design in the center of the pilot to allow for alterations of the stream bed by VA DGIF.

#### **Success Criteria and Monitoring Plan**

The team identified success criteria for the pilot and then defined the monitoring program necessary to establish success.

The success criteria to evaluate primary objectives (primary criteria) are:

- Quantifiable reduction in bank erosion
- Bank treatment undamaged during storm events
- Enhanced habitat diversity and reduced Hg exposure
- Quantifiable reduction in Hg loads.

The success criteria to evaluate secondary objectives (secondary criteria) are:

- Reduction in the potential movement for Hg from bank groundwater to surface water
- Methylmercury (MeHg) concentrations in physical and biological compartments in the near-bank environment decrease
- No substantial change in off-site river bank erosion and/or sediment deposition.

The attached table summarizes the monitoring plan and references the success criteria. The baseline monitoring has been completed. Performance monitoring and post-storm inspections/monitoring are planned through 2010. Periodic inspections and monitoring will be conducted based on the results of the first year of monitoring.

Objective (Primary)	Success Criteria	Metric	Other Supporting Data
Reduce river bank erosion such that there is a reduction in the quantity of mercury-bound soil particles entering the South River	Quantifiable reduction in bank erosion rate	<ul style="list-style-type: none"> <li>Erosion pin exposure (cm/yr)</li> <li>Change in channel geometry (+/-)</li> </ul>	<ul style="list-style-type: none"> <li>Grain size distribution</li> <li>Flow velocity (ft/s)</li> <li>Discharge (cfs)</li> <li>Visual assessment (e.g., slumping, undercutting, rills, gullies, lack of vegetation)</li> </ul>
Maintain a stable bank during storm event flow and over bank flow	Bank remains undamaged at <= design flows and overbank flows	<ul style="list-style-type: none"> <li>Flow velocity (ft/s)</li> <li>Discharge (cfs)</li> </ul>	<ul style="list-style-type: none"> <li>Change in channel geometry (+/-)</li> <li>Grain size distribution</li> <li>Visual assessment (e.g., slumping, undercutting, rills, gullies, lack of vegetation)</li> </ul>
Enhance existing near-bank aquatic and riparian ecosystems	<ul style="list-style-type: none"> <li>Enhanced habitat diversity</li> <li>Reduced exposure to mercury (Hg)</li> </ul>	<ul style="list-style-type: none"> <li>Riparian plant density, survival, % cover, % invasive plants</li> <li>SAV coverage</li> <li>Large woody debris (P/A)</li> <li>Soil/sediment Total Hg concentrations</li> </ul>	<ul style="list-style-type: none"> <li>Channel geometry</li> <li>Grain size distribution</li> <li>Flow velocity (ft/s)</li> <li>Observed wildlife use</li> <li>Plant vigor</li> </ul>
Reduce Hg loads to physical and biological compartments within the river	Quantifiable reduction in Hg loads	<ul style="list-style-type: none"> <li>Loads from soil erosion rate (grams of Hg/kg soil/yr)</li> <li>Near bank sediment Hg concentration</li> <li>Pore water Hg concentration</li> <li><i>Corbicula</i> THg and methylmercury (MeHg) concentrations and loading rates</li> </ul>	<ul style="list-style-type: none"> <li>Grain size distribution</li> <li>Flow velocity (ft/s)</li> <li>Potentially use surface water monitoring data at Main Street bridge and fish tissue data at Constitution Park</li> </ul>

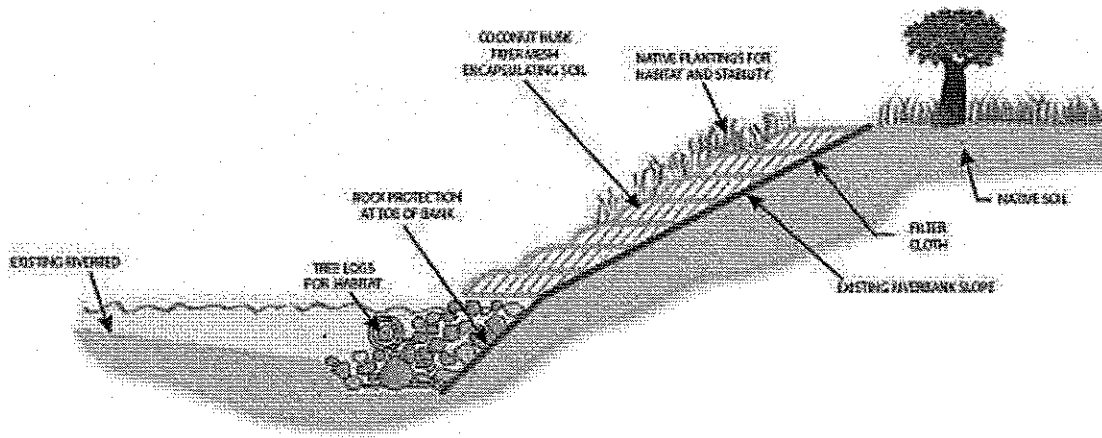
Objective (Secondary)	Success Criteria	Metric	Other Supporting Data
Evaluate changes in groundwater/bank interactions between the river and the floodplain pre and post construction	Reduction in the potential movement for Hg from bank groundwater to surface water	<ul style="list-style-type: none"> <li>Hg and MeHg concentrations in groundwater</li> <li>Well water level elevation data relative to river conditions over various flows</li> </ul>	<ul style="list-style-type: none"> <li>Description of permeability of construction materials</li> <li>Groundwater transmissivity, storativity, and hydraulic conductivity tests</li> </ul>
Determine if the mercury methylation environment in adjacent sediment has change appreciably	MeHg concentrations in physical and biological compartments in the near-bank environment decrease	<p>Qualitative evaluation of various data sets including:</p> <ul style="list-style-type: none"> <li>Changes in sediment deposition and water storage in near-bank environment adjacent to pilot bank</li> <li>Changes in MeHg concentrations and % MeHg in pore water, sediment, and tissue (<i>Corbicula</i>)</li> </ul>	<ul style="list-style-type: none"> <li>Near bank sediment Hg concentration</li> <li>Pore water MeHg concentration</li> <li><i>Corbicula</i> MeHg concentrations and loading rates</li> <li>Grain size distribution</li> <li>Near-bank flow velocity (ft/s)</li> </ul>
Determine if off-site changes in river bank erosion and/or sediment deposition have occurred following bank stabilization	No substantial change in off-site river bank erosion and/or sediment deposition	<ul style="list-style-type: none"> <li>Erosion pin exposure (cm/yr)</li> <li>Change in channel geometry (+/-)</li> </ul>	<ul style="list-style-type: none"> <li>Grain size distribution</li> <li>Flow velocity (ft/s)</li> <li>Discharge (cfs)</li> <li>Visual assessment (e.g., slumping, undercutting, rills, gullies, lack of vegetation)</li> </ul>

#### Bank Stabilization Team

- DuPont: Nancy Grosso, Rich Landis, Bill Berti, Doug Fletcher, Ralph Stahl
- URS: Todd Morrison, Kevin Suter, Marjie Zeff
- VADEQ: Calvin Jordan
- VADGIF: Larry Mohn
- U of D: Jim Pizzuto, Geomorphologist
- Interfluve (Consultant Contractor): Greg Koonce, Bill Norris

Other stakeholders include Invista, City of Waynesboro, Trout Unlimited as well as the SRST.

# Design of Riverbank Stabilization Pilot Project



# Remediation of Hg-contaminated Sites: Selected Case Studies of Sites with Fluvial Receiving Environments - Briefing Paper

Ralph Turner

There are numerous sites in North America and worldwide where mercury has been used historically in industrial/mining processes, often with unfortunate losses to the environment that significantly challenge modern efforts at restoration. Some of the most challenging situations involve contaminated river systems in which historical losses of mercury are incompletely sequestered in floodplain soils and channel sediment deposits and are continuing to enter the water column and biota. Whereas historical mercury losses to lakes and bays can benefit from the natural processes of burial and dilution, and are easier in some cases to recover or confine by conventional engineering methods (dredging, capping), mercury in river channel sediments and floodplain soils are subject to constant resuspension and redistribution and, perhaps most challenging of all, the contamination is distributed over many linear miles.

During 2009 Dupont's ROPS Group requested preparation of a review paper describing experiences at a sites where remediation of fluvial receiving environments has been carried out or is in final stages of planning. The number of such sites is relatively small and few "large" sites have actually experienced much, if any, remediation. The focus of most remediation at these sites has been on the facilities themselves that originally discharged or lost the mercury, and in many cases continue to have mercury losses due a residual soil and groundwater contamination. For a few very small sites or small portions of large sites, remediation, typically in the form of complete sediment and soil removal, has been practiced beyond the fence line of the facilities.

This review was restricted to fluvial sites because of the desire to understand remediation efforts and effectiveness at other sites with at least some similarity to the South River. For the purpose of this review "fluvial" sites includes these four subcategories:

- Free-flowing rivers and creeks
- Rivers and creeks with impoundments
- Rivers and creeks with extensive freshwater wetlands
- Rivers and creeks with estuaries

This subdivision is somewhat important because mercury can behave quite differently in these systems and also because the types of available corrective measures varies among these systems. For example, rivers with impoundments and wetlands, including marine marshes, provide greater opportunity for long-term storage of mercury contaminated sediments. Long-term storage can be beneficial if natural capping with cleaner sediments has occurred but of course poses a future risk if hydrologic conditions evolve to allow disturbance. On the other hand storage of mercury contaminated sediments in wetlands is known to lead to greater conversion of inorganic mercury into methylmercury.

Information for this review was obtained from a variety of sources but mainly from web searches using "(river name)", "mercury" and "remediation" as search terms. Additional sources included USEPA websites that provide relevant documents such as Records of Decision (RODs) and 5-

year Reviews, and direct contact (phone interviews) with site managers or their consultants. Special effort was taken to locate data and reports that documented “remediation effectiveness”. The latter were rarely found because most sites have not always had programs to track effectiveness, especially as reflected in trends in the water, sediment, and tissue concentrations in receiving environments. Cost information was sought but not always obtained.

The sites for which information was accessed and reviewed were:

East Fork Poplar Creek, Oak Ridge, TN  
North Fork Holston River, Saltville, VA  
Abbotts Creek, NC  
St Clair River, Sarnia, ON  
St Lawrence River, Cornwall, ON  
Geddes Brook/Nine Mile Creek, Syracuse, NY  
Idrijca River, Slovenia  
Nura River, Kazakastan  
Acid Brook, Pompton Lakes, NJ  
Sudbury River, MA  
Cache Creek, CA  
Guadalupe River, CA  
Berry Cr, NJ  
Pierson Cr, NJ  
English-Wabigoon River, ON  
Penobscot River, ME  
Walker Creek, CA

### **Summary of Findings**

There are no known examples where complete/comprehensive remediation of a large free-flowing river (comparable to South River) has been undertaken or is in the planning stages (exception might be Nura River in Kazakstan). Many sites, including a few on large rivers, have undertaken limited or selective remediation of sediments and floodplain soils (East Fork Poplar Cr, St Clair R, Abbotts Cr). For a few sites the “formal” remedy selected for offsite creeks and rivers has been “monitored natural recovery” with imposition of administrative controls (e.g., St Lawrence River at Cornwall, English-Wabigoon River). Excavation of soils and/or dredging of sediments, with upland disposal in landfills, are the most common remedies applied. Application of erosion controls and capping of floodplain soils are also implemented at some sites, mainly former mining sites.

Many fluvial sites have long records of biological monitoring (e.g., English-Wabigoon) of tissue concentrations of mercury (fish, clams, crayfish). These records suggest that onsite remediation activities that reduce loading of mercury to the receiving waterbodies have been usually very effective in decreasing tissue concentration but that the decreases are rarely sufficient to allow removal of consumption advisories and never result in full recovery of tissue concentrations to “background” (see Munthe et al 2008). In some cases consumption advisories have been imposed, or re-imposed, because fish guidelines were lowered (e.g., from 1.0 to 0.5 to 0.3 ppm).

The latter is illustrated by Abbotts Creek/High Rock Lake in North Carolina where advisories were lifted in 1992 following decreases in mercury in large mouth bass below 1.0 ppm. Consumption advisories are now often posted when tissue concentrations exceed 0.3 ppm (USEPA ???).

The document search for this review also found one excellent overview paper (Wood. A. 2003. "Remediation Control Strategies and Cost Data for an Economic Analysis of a Mercury TMDL in California". USGS Open File Report 03-284) that, while focused on remediation options and costs for mining sites, provides a good summary of actual remediation experiences and their costs.

South River Geomorphology Studies, 2008-2009

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EXECUTIVE SUMMARY

Two studies were completed during 2008-2009. One involved creating spatially explicit estimates of annual average mercury loading from eroding banks along the South River. The other study used radiometric dating methods to determine the age distribution and residence time of mercury-contaminated fine-grained sediments on the gravel bed of the South River.

Mercury loading from bank erosion gradually decreases in the direction of flow along the South River. Areas of unusually high loading from bank erosion are located between relative river miles 3-5 and 6-10. Mercury loading from bank erosion is much lower in the downstream half of the study area than in the upstream half. Eliminating the loading from 1 mile of those riverbanks with the largest loading would reduce the total mercury loading to the South River by 40%. If 4 miles of river banks were restored, then about 80% of the total mercury loading could be eliminated.

Radiometric dating of fine-grained sediments sampled from a point bar platform at relative river mile 3 indicated that sediments are 80-100 years old at a depth of ~ 25 cm below the sediment-water interface. The data suggest a pattern of long-term deposition at the coring sites of slightly greater than 2 mm/yr. This accumulation could be a result of long-term lateral migration of the channel at this site. If this hypothesis is correct, then these mercury contaminated sediments could ultimately be incorporated into the floodplain, rather than being reworked into the water column.

## UPDATED ESTIMATES OF MERCURY LOADING TO THE SOUTH RIVER FROM ERODING BANKS

This study presents spatially refined estimates of mercury loading from contemporary bank erosion along the South River from Waynesboro to Port Republic, Virginia. The estimates are based on a variety of new and recent data sources documenting rates of bank erosion and mercury concentrations in eroding banks.

The estimates of mercury loading from bank erosion summarized in this report have both greater spatial resolution and greater temporal resolution than previous estimates. Greater spatial resolution is achieved by including visual estimates of the locations of eroding banks, by including bank erosion estimates from tripod mounted LiDAR, by relying on many more analyzes of the mercury content of eroding banks, and by accounting for the geologic and geomorphic setting of banks along the South River. Greater temporal resolution is achieved by including 6 repeat surveys using tripod mounted LiDAR, by analyzing aerial photographs from 1977-2005 (rather than relying on the 1937 aerial photographs to determine past shoreline positions), and by including field observations of the locations of currently eroding banks.

### Methods

We followed the steps outlined in Table 1. The first step involved classifying the banks according to geomorphic setting, an approach that provided insight into the likely extent of bank erosion and the mercury concentration of eroded bank materials supplied to the river. Banks were classified into 6 groups: alluvial banks inundated at least every 2 years ("frequently inundated alluvium"), alluvial banks inundated with a frequency of 2-5 years ("infrequently inundated alluvium"), banks in reaches with islands, banks developed in alluvial fan or terrace deposits, banks with exposed bedrock, and banks created by anthropogenic activity (mostly river engineering projects that involved placement of riprap or fill). Reaches with islands were neglected. Banks composed of terraces, alluvial fans, and "anthropogenic" banks were assumed to provide no mercury through bank erosion.



Table 1. Steps used to determine rates of mercury loading to the South River from contemporary bank erosion.

Step Number	Description
1	Classify riverbanks by geomorphic/geologic setting
2	Estimate Hg concentrations in riverbanks
3	Estimate time-averaged volumetric bank erosion rates
4	Convert volumetric bank erosion rates to sediment mass erosion rates
5	Convert mass erosion to mass of mercury loading
6	Correct long-term average (mostly decadal) loading rates to contemporary annual loading rates

Mercury concentrations in eroding banks were assessed using the available field data (Figure 1). Data fell into 3 groups. The mercury concentrations of samples from “frequently inundated alluvium” decrease systematically with relative river mile, albeit with nearly two orders of magnitude of variation around this trend. Mercury concentrations of samples from “infrequently” inundated alluvium average about 2 ppm; these concentrations did not systematically decrease with distance downstream. In the cutoff area (a meander bend artificially cut off during the mid-1970s to facilitate downstream passage of floodwaters), concentrations are very low, averaging about 2 ppm. These data were used to develop guidelines for estimating mercury concentrations in all the riverbanks of the study area (Table 2).

Bank erosion rates were determined using a variety of modeling and field data. A curvature-based hydrodynamic model was used to quantify the near-bank velocity around bends, and data from aerial photographs was used to correlate forcing of bank erosion due to increased velocity with the observed erosion rate. This model is only appropriate in areas without bedrock, and it failed to predict the locations of some eroding banks. Where the model predictions were lacking, several different types of field data were used to determine bank erosion rates. These included analyses of historical aerial photographs (Rhoades et al., 2009), repeat surveys using tripod-mounted lidar, and field observations

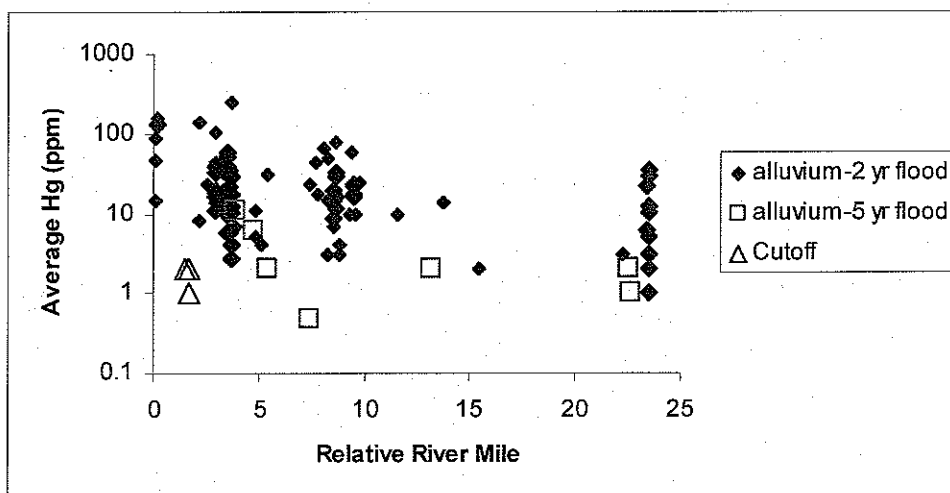


Figure 1. Vertically averaged mercury concentrations in eroding banks of the South River as a function of relative river mile.

Table 2. Mercury concentrations in eroding riverbanks of the South River.

Bank Classification or Location	Mercury Concentration (ppm)
Frequently inundated alluvium	$= 26.3e^{-0.06052RRM}$
Infrequently inundated alluvium	2
Cutoff	2
Islands	0
Alluvial Fan, Bedrock, Terrace	0

of the locations of eroding banks. Field observations of eroding banks do not provide direct observations of the rates of bank retreat, so these banks were assumed to have retreated 1 m from 1937-2005 (this is slightly below the maximum resolution of the aerial photo analysis).

The data described above only provide the areal extent of bank erosion. To obtain bank erosion in units mass per time, the areal rates were multiplied by the height of the banks and also by the bulk density of the soil (represented by a constant value of 1200 kg/m<sup>3</sup>). Bank heights were estimated directly from aerial lidar survey data (Rhoades et al., 2009) and also from the 2 foot contour map of the study area derived from the aerial lidar survey.

Most of the bank erosion data are obtained directly or indirectly from the 1937-2005 aerial photo analysis. Because these time-averaged rates are likely to be lower than current rates, all the long-term bank erosion rates were multiplied by a factor of 1.2 to provide a more accurate estimate of contemporary erosion rates.

## Results

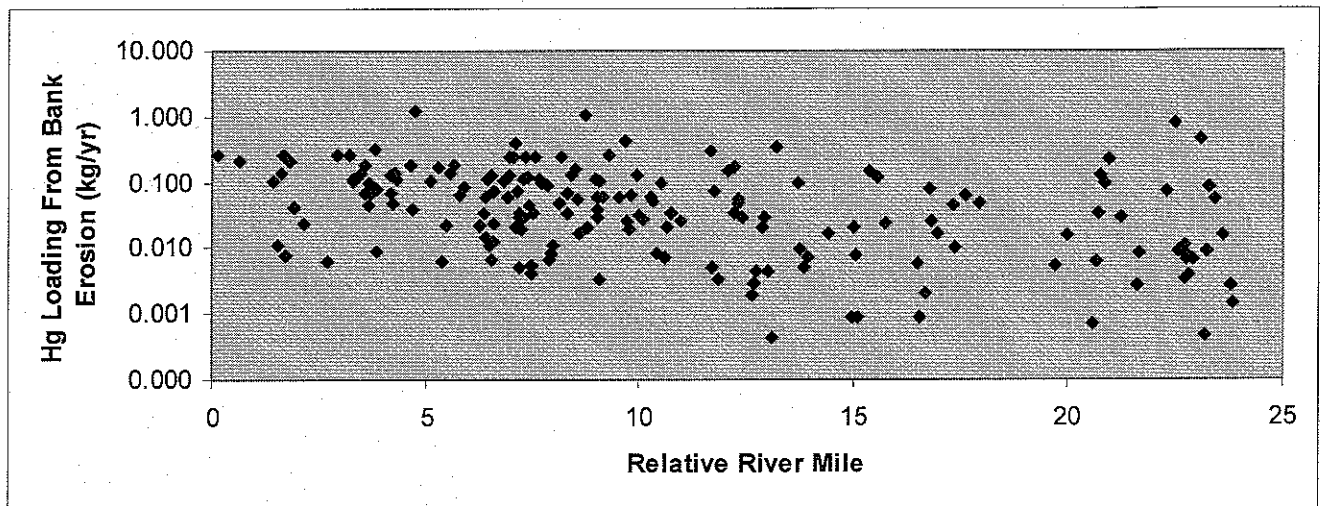


Figure 2. Annual mercury loading from individual eroding river banks as a function of relative river mile.

The annual loading from individual eroding river banks is presented as a function of relative river mile in Figure 2. Rates of loading tend to decrease in the downstream direction, reflecting the trend of decreasing mercury concentration in river banks in the downstream direction. Almost two orders of magnitude of variation is superimposed on the downstream trend, however, that primarily reflects variations local rates of bank erosion and also in the lengths of eroding banks. There are more points plotted upstream of about relative river mile 12 or so compared to the reach between relative river miles 12-24, reflecting the greater number of eroding banks in the upstream half of the study area.

Spatial trends in mercury loading from bank erosion are illustrated in Figure 3, which presents the total loading per river mile throughout the study area. Loading from bank erosion is highest in the uppermost 10 miles of the river, with notable peaks in loading between river miles 3-5 and 6-10.

The fraction of the total mercury loading provided by banks of progressively decreasing mercury loading is presented as a function of cumulative length of bank erosion in Figure 4. Figure 4 allows some "what if" restoration scenarios to be provisionally evaluated. For example, if 1 mile of river banks were restored to reduce erosion to 0, and if sites could be selected so that banks with the largest loading were restored first, then about 40% of the mercury loading to the South River from bank erosion could be eliminated. If 4 miles of river banks were restored, then about 80% of the total mercury loading could be eliminated.

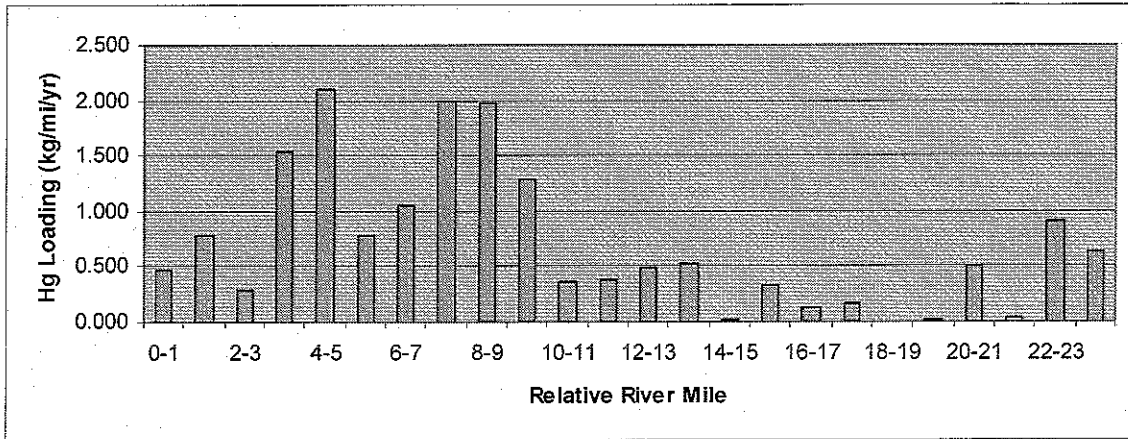


Figure 3. Annual mercury loading per river mile from bank erosion.

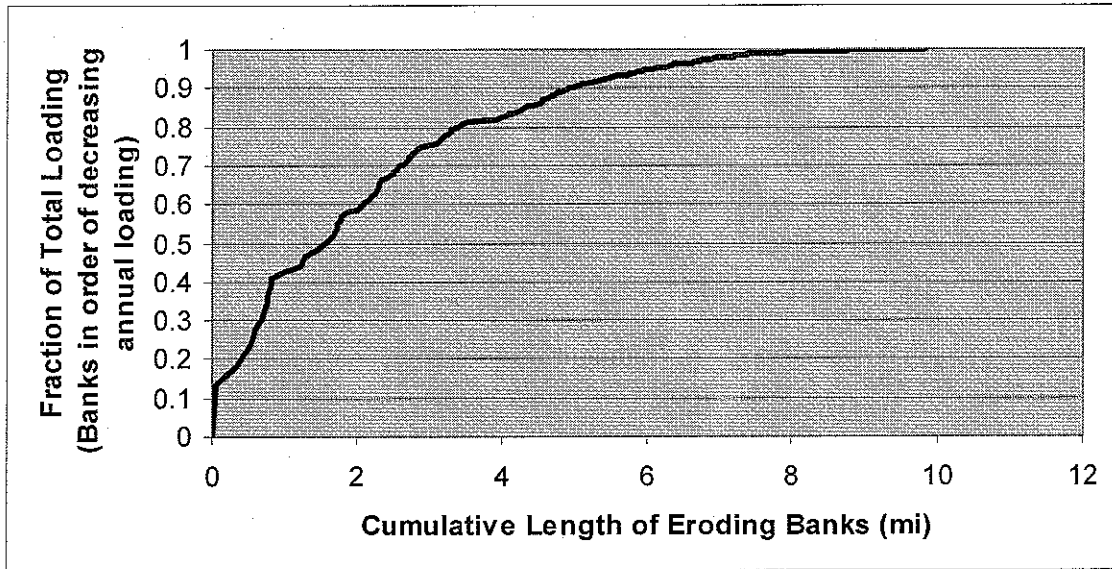


Figure 4. The fraction of total loading from bank erosion as a function of the cumulative length of eroding banks for bank erosion locations ordered by progressively decreasing annual loading.

## RADIOMETRIC DATING OF FINE-GRAINED PARTICLES IN THE BED OF THE SOUTH RIVER

The goal of this study is to determine the age and residence time of mercury-contaminated fine-grained sediment stored within the gravel matrix of the streambed of the South River. This information could, in principle, be used to evaluate how long it would take the South River to cleanse itself of mercury by natural processes if ongoing sources of mercury to the water column could be eliminated by remediation. Because similar studies have not been completed before, this project was conceived as a pilot study to determine 1) if good samples could be obtained from the stream bed, and 2) if traditional radiometric dating techniques could be used to determine the ages of these samples.

### Sampling Location

Samples were obtained from two sites located on a point bar platform of a gentle bend near relative river mile 3 (Figure 5). The upstream and downstream ends of the study reach are bounded by riffle subenvironments (where the bed is predominately composed of cobbles). A pool, locally floored by exposed bedrock, occupies the outside part of the bend, while a sand/pebble point bar platform occupies the inside of the bend. A cross-section of the study site is illustrated in Figure 6, providing greater detail of the morphology of the point bar platform, pool, and adjacent banks. Mercury concentrations from cores taken on the inside and outside banks, and also from a Fine-Grained Channel Margin deposit (Skalak and Pizzuto, in press) along the cross-section, are also illustrated for reference. Reconstructions of the floodplain and locations of the stream banks in 1937 (Figure 7) indicate that the channel at this location has been very slowly migrating towards the northwest, with erosion occurring at the outside of the bend, deposition occurring on steep banks at the inside of the bend, and slow accretion likely occurring over the point bar platform.

### Methods

Two cores were obtained from the streambed at the site (Figure 5). Cores were returned to the laboratory and sectioned into intervals of about 5 cm. Each interval was analyzed for loss-on-ignition, mercury content, and grain size composition. Activities of the radioactive isotopes of Cs-137, Pb-210, and Be-7 were measured using a gamma detector. Pb-210 has a half-life of 22.26 years, while Be-7 has a half-life of 53.3 days. Cs-137 was produced by atmospheric nuclear weapons testing; the peak atmospheric concentration occurred in 1963, providing a useful time marker in sedimentary deposits.

Radioactive decay can only provide age dates if the initial activity of each isotope is known at the time of deposition. To estimate initial activities, we placed 3 plastic bins at the site to collect suspended sediment transported by high flows of the South River. The bins were covered with wire mesh to protect the samples from resuspension. The tops of the bins were placed within a few centimeters of base flow water level, so that even small events could provide useful samples. The samplers are illustrated in Figure 8,

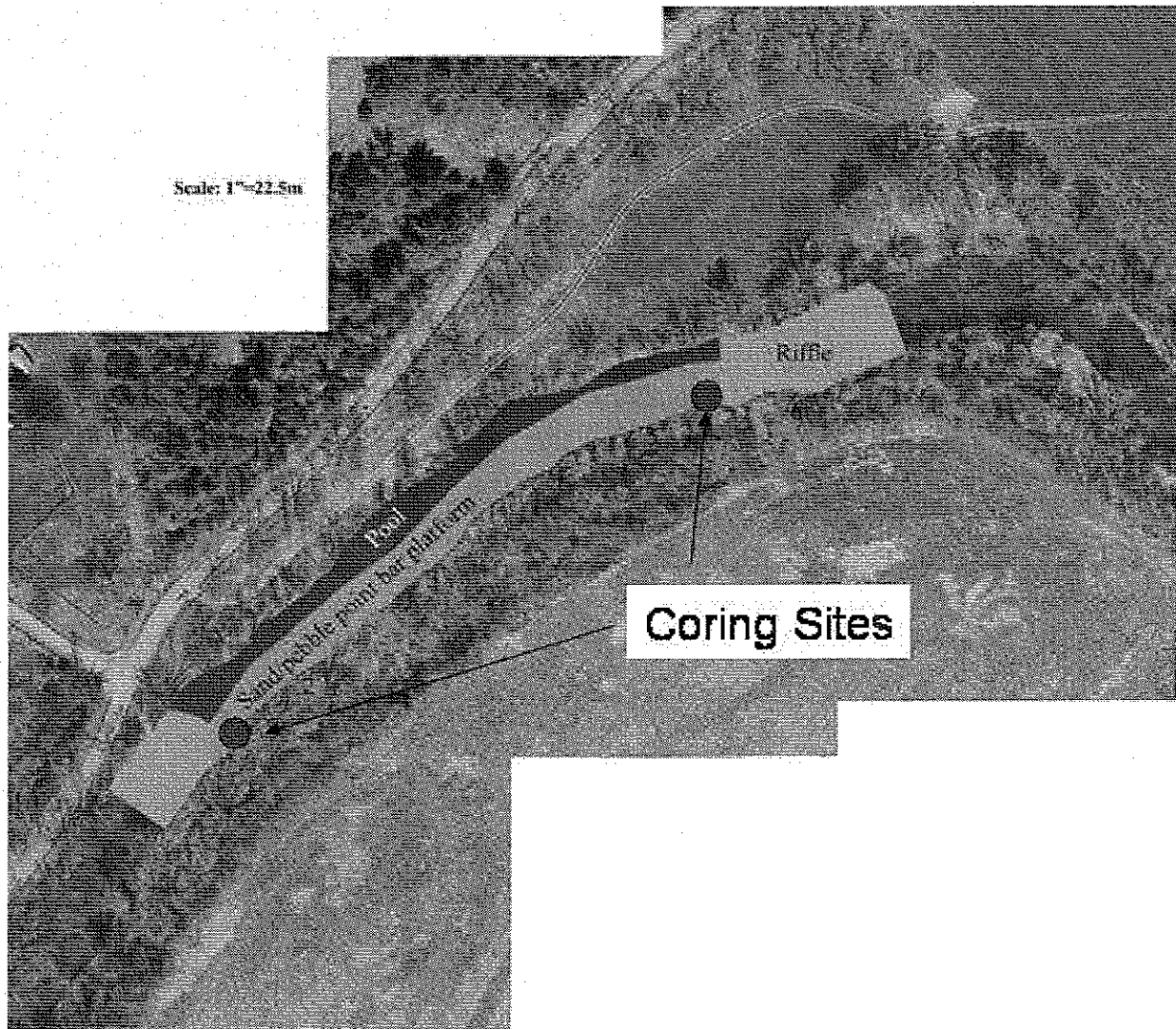


Figure 5. Coring site locations at about relative river mile 3. The river flows from left to right. The locations of selected geomorphic features (pool, riffle, and a sand/pebble point bar platform) are also illustrated.

which also presents a useful illustration of the morphology and setting of the point bar platform surface where cores were obtained.

The suspended sediment samples and samples from the cores varied considerably in grain size composition. A partitioning scheme was developed to account for differences in radionuclide activities that arose as a result of variations in grain size between different samples. This approach will not be described further here.

## Cross-Section RRM 2.98

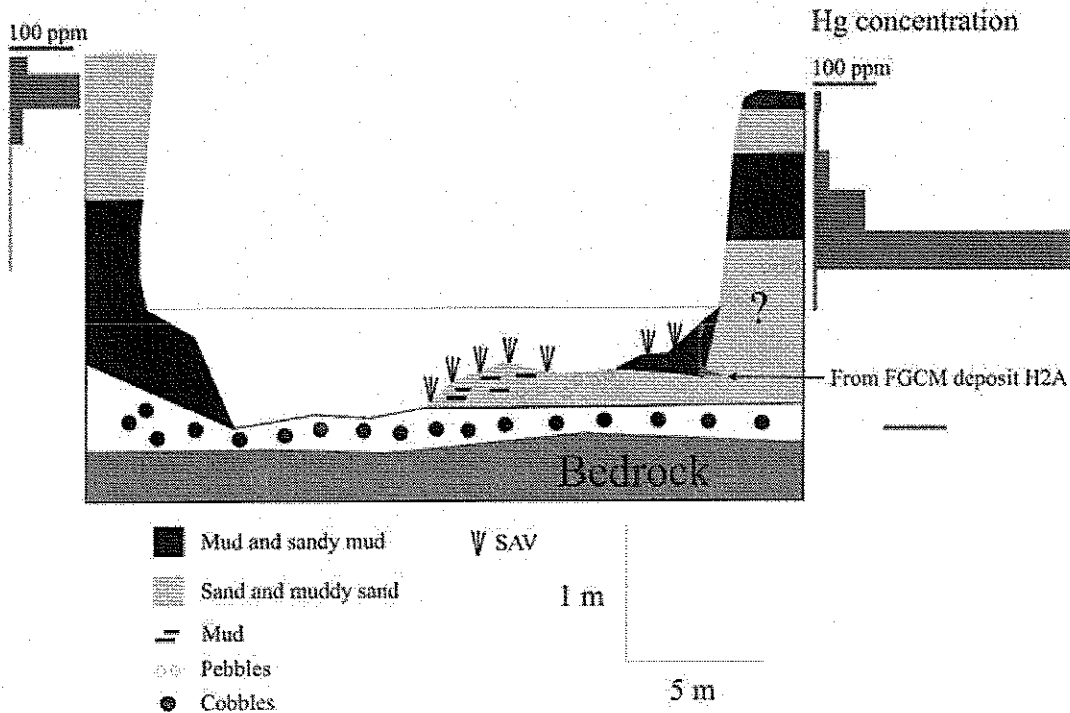


Figure 6. Cross-section at relative river mile 2.98, illustrating the morphology of the channel, underlying deposits, and mercury concentrations from cores obtained on both banks and from a "Fine-Grained Channel Margin Deposit" at the base of one of the banks (Skalak and Pizzuto, in press).

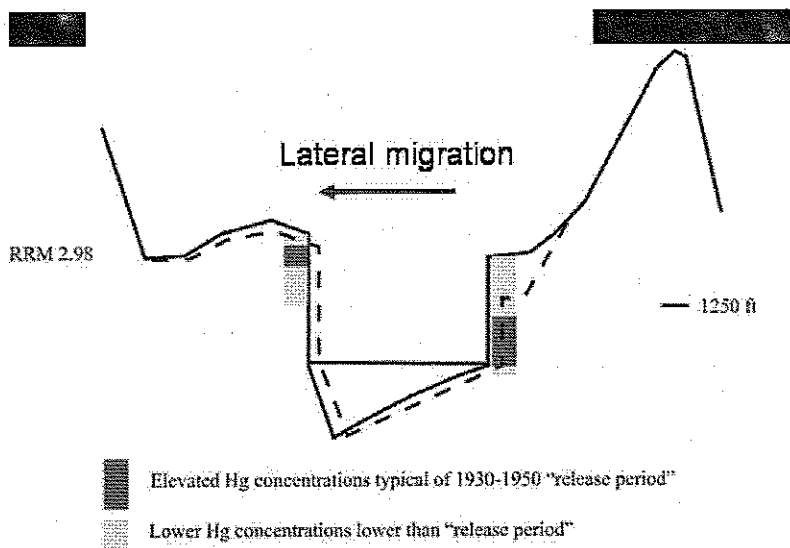


Figure 7. Reconstructed cross-section, 1937 (dashed line) to 2005. High mercury concentrations (illustrated in red) likely were deposited during the period of active mercury release into the river from 1930-1950.



Figure 8. Bins used to sample suspended sediment during high flows. The morphology of the point bar platform is depicted in the foreground – one of the cores was obtained at this location.

### Results

Suspended sediment samples were collected from 3 high flow events (Table 3). Be7 was detected in all of these samples. However, none of the bed samples had any detectable activity from Be7. This could result from differences in texture, but it could also indicate that the bed sediment samples are older than several of the Be7 53.3-day half-lives.

Table 3. Be7 activities of bed samples and suspended sediment samples

Sample	Be7 Activity (Bq/gm)
SR-6-9-09-Qss	0.085
SR-5-7-09-Qss	0.05
SR-4-3-09 Split 1	0.025
SR-4-3-09 Split 2	0.017
SR-4-3-09 Split 3	0.015
All Bed Samples	0



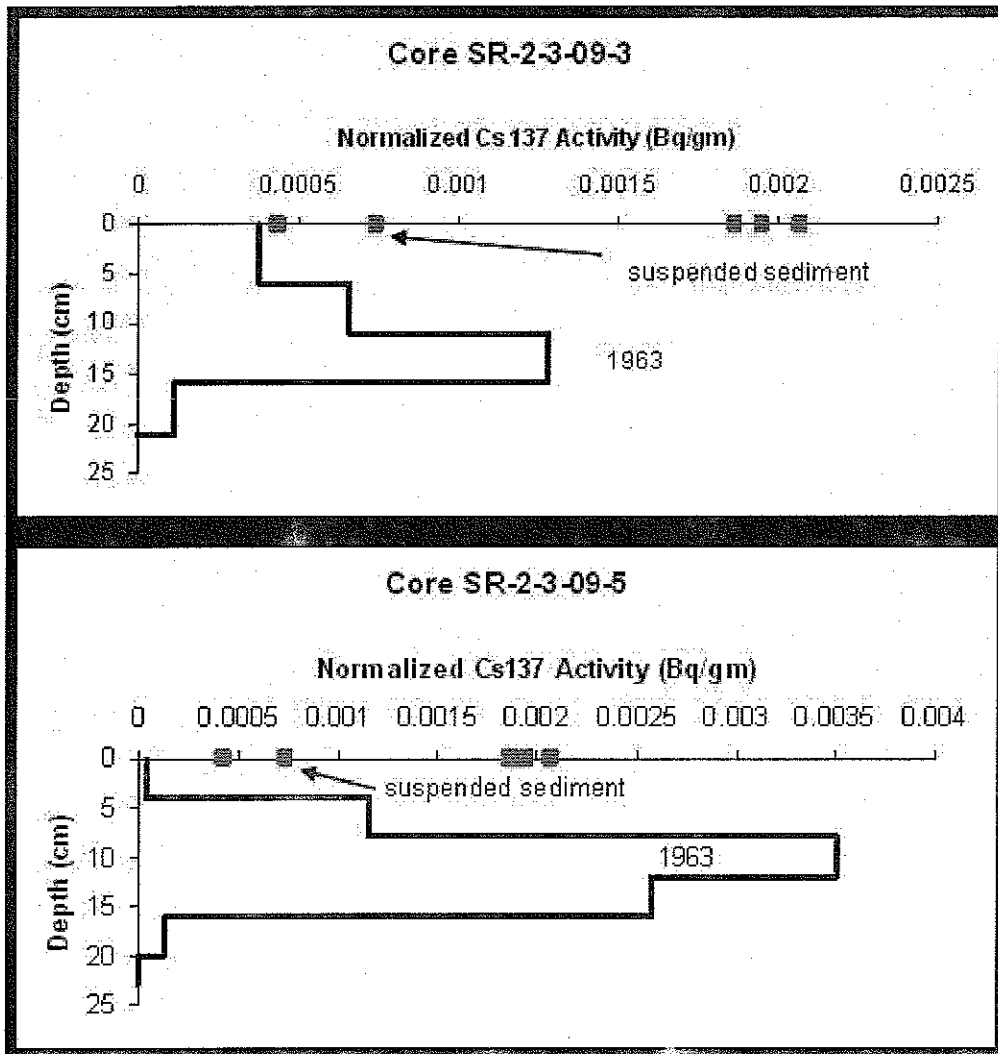


Figure 9. Cs-137 profiles in two cores. All data have been adjusted for differences in texture. The peak Cs-137 concentration is likely associated with a date of 1963. Data from suspended sediment are represented as purple squares plotted at a depth of 0 cm.

Cs-137 activities show distinct peaks at depths of 10-15 cm in each core. The data have been adjusted for differences in concentration, so the peaks are not artifacts of changes in sediment type with depth. These peaks are likely associated with a date of the peak atmospheric Cs-137 concentration: 1963.

Pb-210 chronologies (adjusted for variations in sediment grain size)(Figure 10) show linear increases in age with increasing depth. Analyses from the two cores are in close agreement, and the Cs-137 ages agree well with those obtained from Pb-210. The chronologies suggest that sediments at depths of around 25 cm are 80-100 years old.

The age dating results can be interpreted in at least two ways. If sediments are rarely re-entrained, and if the probability of resuspension decreases linearly with depth, then the age distribution of Figure 10 could be obtained. Alternatively, the age

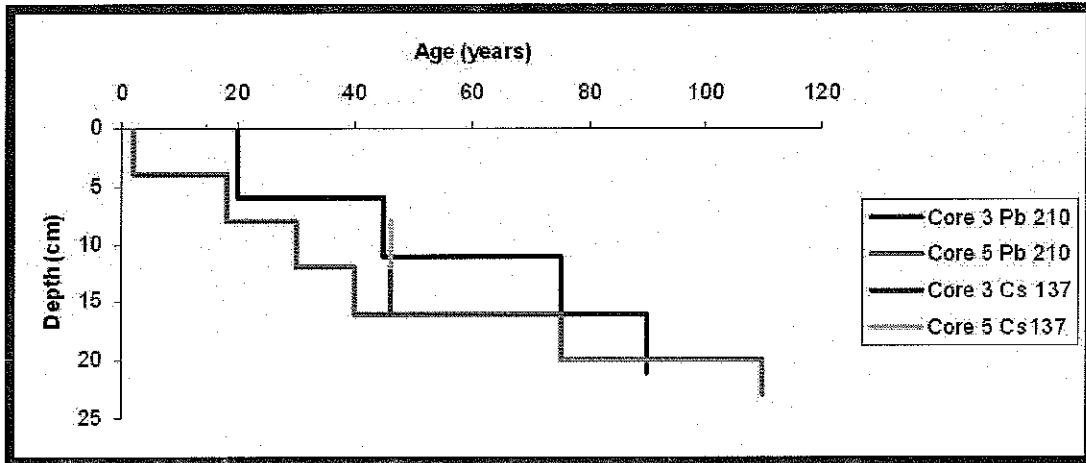


Figure 10. Pb-210 chronologies for two cores. Dates from Cs-137 analyses are also plotted. All data have been adjusted for the effects of changing sediment grain size.

distribution could reflect slow accumulation of sediment at this site, at a more or less constant rate. The required accumulation rate is about 2.2 mm/yr (Figure 11).

One mechanism that could cause sediment to slowly accumulate at the coring site is the slow lateral migration of the channel (as is illustrated in Figure 7). Following this hypothesis, lateral movement of the inclined point bar platform would result in a slow, steady accumulation of sediment. Given the geometry of the cross-section, and the long-term migration rate of about 4 cm/yr, the vertical accumulation rate would be close to that suggested by the radionuclide chronologies (Figure 11). This therefore provides a plausible interpretation for the distribution of sediment ages for these cores.

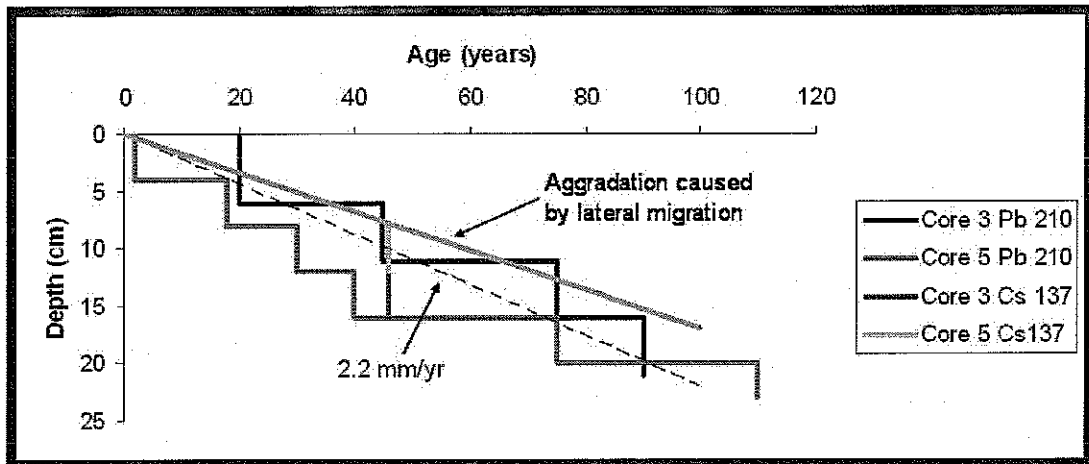


Figure 11. Pb-210 and Cs-137 chronologies interpreted as linear accumulation rates. The accumulation rate associated with lateral migration of the channel and sedimentation on the point bar platform is also indicated.

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## Phase II Ecological Study: Preliminary Findings of the Biological Studies

Todd Morrison, JR Flanders, and Greg Murphy  
South River Science Team  
Expert Panel Meeting  
October 7-8, 2009  
Harrisonburg, VA

### Introduction

This briefing paper summarizes the preliminary findings of the Phase II physical and biological studies conducted in the South River during 2009, including the following:

- Physical loading study to investigate the links between terrestrial inputs and aquatic fate and transport of inorganic mercury (IHg) and methylmercury (MeHg).
- Asian clam (*Corbicula fluminea*) transplant study to evaluate total mercury (THg) and MeHg uptake by caged and seeded clams in zones of hydraulic transport and hydraulic storage of the South River
- Aquatic insect study to evaluate THg, MeHg, and stable isotopes in aquatic insect larvae and adults from select taxa with importance to aquatic and terrestrial food webs of the South River
- Biological monitoring of THg concentrations in the muscle tissue of largemouth bass (*Micropterus salmoides*) and smallmouth bass (*M. dolomieu*) from various size classes using a nonlethal biopsy sampling technique that enables unique individuals to be tracked over time in the South River

### Physical Loading Study

A physical loading study was designed to investigate the links between terrestrial inputs and aquatic fate and transport of IHg and MeHg. Based on previous work conducted by the South River Science Team, the hyporheic zone of the South River is thought to be an important zone of IHg and MeHg exchange between porewater and surface water. For this study, it was hypothesized that IHg and MeHg are loaded to the water column from river substrates, particularly in near-bank areas, through advection and diffusion from the hyporheic zone.

The physical loading study used a small volume porewater sampling method to (1) characterize the distribution of IHg and MeHg in porewater; (2) calculate loads from the hyporheic zone using a numerical framework that combines mass transfer calculations and numerical simulation; and (3) perform a mass balance analysis by comparing hyporheic zone loads to surface water loading rates. Four short (~300 m) study areas were selected along a spatial gradient of mercury in terrestrial floodplain storage areas. Samples were collected during three events starting in June (THg and MeHg), July (THg and MEHg), and August (THg only). At each study area, eight transects were established

perpendicular to flow around important areas of terrestrial THg storage and input<sup>1</sup>, and 3 to 8 samples were collected along each transect and filtered using a 0.45 um filter with a glass pre-filter.

Preliminary findings from June sampling indicate porewater IHg concentrations were more strongly influenced by terrestrial inputs than MeHg. MeHg was higher in areas adjacent to HRADs, but was more strongly influenced by grain size rather than location. MeHg concentrations were significantly higher in fine-grained sediment than in medium or coarse-grained sediment. In near-bank environments, IHg concentrations, but not MeHg concentrations were correlated with THg concentrations in HRAD and eroding bank soils. Mass transfer models indicated that loading of IHg and MeHg from the hyporheic zone accounts for surface water mass loads, and that advection is the dominant mass transfer process for both IHg and MeHg.

### **Asian Clam Transplant Study**

An Asian clam transplant study was developed to evaluate THg and MeHg uptake by caged and seeded clams in zones of hydraulic transport and hydraulic storage in the South River. Asian clams were collected from the North River and transplanted at four study areas in the South River, including RRM 0.1, 3.5, 8.5, and 23.1 in the spring and summer of 2009. Cages were placed in select zones of hydraulic transport and hydraulic storage with tagged clams seeded directly under cages. Transplanted clams were collected at 1, 3, and 5 weeks after deployment, depurated for 48 hours, and analyzed for THg and MeHg. An additional collection of seeded and wild clams was conducted at week 14 to evaluate THg and MeHg concentrations over an extended transplant period.

Preliminary findings from the spring component of the Asian clam transplant study include the following:

- Seeded clams accumulated more THg and MeHg than caged clams, particularly in zones of hydraulic storage (i.e., depositional habitats)
- Caged clams displayed little difference in THg or MeHg concentrations between zones of hydraulic transport and hydraulic storage
- Percent MeHg appears to increase with increasing distance downriver
- Seeded clams displayed better growth (increase in shell width and weight) than caged clams; growth evaluated at RRM 8.5
- No obvious relationship between clam size (shell width or weight) and THg or MeHg concentration; finding consistent with prior SRST studies

### **Aquatic Insect Study**

An aquatic insect study was developed to evaluate THg, MeHg, and stable isotopes in aquatic insect larvae and adults from select taxonomic groups with importance to aquatic and terrestrial food webs of the South River. The sampling plan included the active and passive collection of larvae and adults (Baetidae, Chironomidae, and Hydropsychidae) at

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<sup>1</sup> Terrestrial storage and inputs from the floodplain include Historic Release Age Deposits (HRAD); channel/floodplain accretions formed after 1937, storing THg) and eroding alluvial riverbanks.

RRM 3.5 and 8.5 of the South River in the spring and summer of 2009. Additional aquatic insects were collected at RRM 11.8 and 22.1 in support of the trophic transfer models being developed by researchers from the Virginia Institute of Marine Science (VIMS).

Preliminary findings from the spring component of the aquatic insect study include the following:

- Chironomidae and Baetidae adults displayed higher concentrations of THg and MeHg and a higher percent MeHg than larvae of the same taxa
- Hydropsychidae adults typically had lower THg and MeHg concentrations than larvae which may be influenced partly by the relatively long adult phase
- Adults and larvae were higher in THg and MeHg at RRM 8.5 than RRM 3.5, with the exception of Baetidae larvae

### **Biological Monitoring**

Biological monitoring of fish tissue was conducted in May and September of 2009 to evaluate THg concentrations in the muscle tissue of largemouth and smallmouth bass using a nonlethal biopsy sampling technique. The non-lethal sampling technique was coupled with the use of Passive Integrated Transponder (PIT) tags to allow the unique identification of individuals during future re-sampling events. Sampling was conducted at RRM 0.1, 11.8, and 22.0 on the South River with the help of biologists and equipment from the Virginia Departments of Game and Inland Fisheries and Department of Environmental Quality (VADEQ).

Preliminary findings from the dry run and spring component of the biological monitoring include the following:

- Mean concentrations of THg in muscle tissue biopsies were strongly correlated to THg concentrations in fillets ( $r^2 = 0.96$ )
- THg concentrations increased with the size/age of bass
- Higher THg concentrations were observed at RRM 11.8, which is consistent with patterns observed during prior fish tissue monitoring studies by VADEQ

**Mercury Trophic Transfer Model: South River Floodplain.  
A Cooperative Study Involving VIMS, URS, FWS-Gloucester Point,  
and the BioDiversity Research Institute**

M.C. Newman, Kyle Tom, Xu Xiaoyu  
College of William & Mary's Virginia Institute of Marine Science

**Goals**

**Firstly**, DuPont asked that floodplain trophic modeling begin after modeling for the aquatic food web was done. The South River team agreed that focus should be trophic movement toward the Screech owl. Sampling was done at two sites used in the 2007 aquatic trophic transfer modeling and past avian studies. **Secondly**, exposure models based on the 2008 sediment-to-periphyton study and 2007 trophic modeling were to be explored in order to guide remediation decision making. **Lastly**, VIMS was to help gather initial data for predicting consequences of Phase II manipulations. It was agreed that pre-manipulation data should be gathered and used later to gauge responses of fine sediments, periphyton, and primary consumers.

**Progress**

**Floodplain Modeling** – The VIMS/FWS/BRI team sampled soils, plants, invertebrates (including detritivores and emergent adult insects), rodents, and birds from the two sites. More samples were taken than required by the DuPont contract under the assumption that they might be needed to finish the modeling. However, because many small-mass samples required more expensive microanalytical techniques, it is uncertain if these additional samples can be analyzed for methylmercury with available funding. VIMS can do total mercury analyses in-house at no additional expense.

As anticipated, there was a general increase with trophic position of total mercury, methylmercury, and percent of mercury that is methylmercury. When nitrogen isotope data are sent back from the UC-Davis isotope facility, these trends will be quantified more completely. Also as anticipated, the preliminary exploration of the data indicates more variability in these floodplain data than in the aquatic food web data.

Highest prey concentrations were found in insects emerging from the river, detritivores, and spiders. Other arthropods (tent caterpillar and ladybug) had substantially lower concentrations. Screech owls and Carolina wrens had the highest concentrations of mercury and methylmercury of all sampled biota. Other birds (six species) and rodents (two species) had intermediate concentrations.

**Exposure Models for Aquatic Component** – The VIMS team has generated models for predicting exposure consequences after various remediation-driven reductions of sediment or periphyton mercury/methylmercury concentrations. These models will become useful as various remediation options are explored.

***Initial Information for Phase II Studies*** – The VIMS/URS team gathered sediments, periphyton, and three sets of pre-emergent/emergent insects (mayfly, midge, and caddisfly) with the intent of establishing a baseline prior to any pilot remediation studies. The small mass in samples such as adult midge samples resulted in additional costs.

### **Anticipated Products**

***Floodplain Modeling*** – A semi-quantitative model is anticipated; however, a more accurate model might still be possible if the nitrogen isotope data explain a significant portion of the intraspecies variation in the mercury and methylmercury data. Regardless, a general biomagnification factor will be estimated and used for predicting consequences of and setting goals for any remediation activities.

***Aquatic Exposure Models*** – Available information was incorporated into a straightforward series of parameterized relationships/equations that allow prediction of mercury bioaccumulation in the aquatic food web resulting from changes in fine sediment or procedurally-defined periphyton concentrations. These tools are available now.

***Initial Information for Phase II Studies*** – Samples collected by URS at several sites and VIMS/URS for the Augusta Forestry Center and Grottoes Town Park sites will establish a baseline for the river prior to any remediation activities, and also define more clearly the change in mercury and methylmercury for pre- and post emergence aquatic insects.

### **Pilot Studies in Anticipation of 2010 Activities**

As remediation discussions become more prominent, various physical and chemical techniques will be explored to reduce bioavailable mercury. VIMS anticipates that several issues will require study, and accordingly, began some pilot activities. (1) With three visiting students from the University of Koblenz-Landau (Germany), VIMS is exploring an amphipod-based assay of detrital processing and bioaccumulation. If found to be viable, the assay will be used with others to quantify the reduction in bioavailable mercury in sediments. The students are also planning to deploy leaf packs in the river to quantify *in situ* detrital processing. (2) Two VIMS graduate students are exploring candidate materials including nanomaterials that can be added to sediments in order to reduce bioavailable mercury. In one such study, the focus will be materials that can be added during breeding season to temporary ponds used by amphibians that are putatively impacted by current bioavailable mercury. The second student will explore similar pilot studies focused on invertebrates in the river itself. Response variables being used are bioaccumulation and oxidative stress enzymes that are directly influenced by mercury. These responses will quantify bioavailable mercury in the context of amount available to accumulate and amount available to cause a biochemical response. Finally, M. Newman is working in the innovative remediation committee, exploring remediation options to assess in coming years and defining the information needed to evaluate these options.



## October 2009 Update on Bird Research on the South River, Virginia

Daniel Cristol, College of William & Mary

**Background:** In 2005, nothing was known about mercury levels or effects on birds of the South River. In four field seasons we produced a great deal of knowledge that is of applied/local interest as well as contributing to the body of basic/worldwide knowledge on birds and mercury. Our published findings can be distilled to the following four points:

- South River mercury has accumulated in the avian food chain and most birds living along the river's riparian corridor have mercury levels that are significantly elevated, in both the statistical and biological senses. (Brasso and Cristol. 2008. *Ecotoxicology* 17:133)
- Mercury contamination is not limited to birds with obvious connections to the river, such as ducks and kingfishers. Instead, nearly all species of birds are affected, some terrestrial songbirds even accumulating higher levels than aquatic counterparts. (Cristol et al. 2008. *Science* 320:335)
- The main vector of mercury into songbirds is terrestrial, non-web-weaving spiders (e.g. wolf spiders), which comprise a large portion of the diet (>25%) and deliver a majority of mercury (>75%). (Cristol et al. 2008. *Science* 320:335)
- Detailed study of one species, Tree Swallow, indicates that birds living on contaminated sites differ in a number of ways that could reduce fitness: reduced immune system responsiveness, reduced return rate of adults, reduced number of fledglings, reduced responsiveness of the adrenocortical system in nestlings, reduced ability to recover from experimental stressors such as simulated nest predation or feather plucking. (Hawley et al. 2009. *Ecotoxicology* 18:499; Wada et al. 2009. *Environmental Science and Technology* 43:6031)

**Recent Findings:** 2008 findings have been included in theses but are still undergoing analysis before publication:

- A lower proportion of tree swallows returns to breed again on contaminated sites than reference sites. However, when analyzed using Program MARK, which accounts for return rate and detection rate using mark-recapture statistics, there was no significant effect of an individual's mercury level or whether a bird lived on a contaminated or reference site. This apparent discrepancy can be explained by the fact that the effect of mercury on return rate has a time lag – differences between reference and contaminated birds do not appear until birds are returning for the second or third time (i.e. are 3-4 years old). Thus, the bulk of birds in the study at any time are not experiencing lower return rates because they are 1-2 years old. Inclusion of these birds in the mark-recapture analysis renders the overall effect of mercury non-significant. Despite this, the mark-recapture analysis identified a non-significant but consistent difference in survival rate of 1-

3% between reference and contaminated swallows, and nearly all of the models that best explained the survival of swallows contained one or both mercury terms, suggesting that mercury affects survival in tree swallows, but not as much as other, unmeasured factors (e.g. weather conditions on the wintering range, food availability on the breeding grounds, etc.)

- A second season of collecting floodplain samples of feathers and blood, as well as prey items, from bluebirds, wrens and chickadees, indicated that mercury is elevated in biota for >300 meters into the floodplain. Bird tissues declined, with variation between species, with distance from the river, but spider levels were highly variable and did not decline consistently and are still under analysis. It appears that flood potential (i.e. elevation and probability of flooding as determined by FEMA floodplain designations) is a better predictor of bird mercury than distance alone, suggesting that flooding, rather than annual transfer by emergent insects, may be the driving force behind lateral transfer of mercury into floodplain biota. However, soil mercury level itself, presumably the result of flooding history, did not predict bird mercury level as well as expected.

**Current Activity:** Our next phase of research will center on dosing captive birds of three species (Carolina Wren, European Starling, Zebra Finch) with realistic low doses of mercury (0, 0.1, 0.2, 0.4 ppm wet weight in diet). The objective is to determine the low effects level of dietary methylmercury for songbirds by examining behavioral, reproductive, and physiological endpoints similar to those effects detected from the field studies (e.g. fecundity, longevity, hormone profiles, immune suppression, neurological damage, genotoxicity, learning deficits, etc.).

The project is moving along and has attracted a number of collaborators, but construction delays on the aviary facility have delayed the start of dosing. The essence of the problem is that the existing aviary drainage was to storm sewers. To avoid adding mercury to wetlands the drainage is being rerouted to a sanitary sewer. This necessitated constructing roofs over the entire area to prevent the mixing of clean runoff and aviary outflow. Further delay, and a huge cost increase that was borne by The College of William & Mary, occurred because of fire safety issues due to encroachment on another building. The remainder of the job is now out to bid and construction of the last phase is scheduled for October 1. Barring further delays, the dosing of all three species will begin in November 2009 and Zebra Finch dosing may begin earlier as they are on a separate sewer system.

Carolina Wren Pilot Study  
Anne Condon  
September 2009

A pilot study on Carolina Wren reproductive success was conducted April-August 2009. The intent was to locate territories and suitable sites (especially additional reference sites) and collect preliminary data on nesting success. Approximately 220 nest boxes and nest tubes were set up on reference sites, including: the Waynesboro Nursery and Ridgeview Park upstream of the former Dupont facility on the South River, and at the Whitescarver's property and adjacent properties on the Middle River. Approximately 170 nest boxes and nest tubes were set up on the contaminated South River, focusing on river mile 9-24, including: Bradburn Park, Grottoes City Park, Grand Caverns, the Wolf's (across from the Augusta Forestry Center), and the Wertman's property. Nest boxes were monitored between April 7, 2009 and September 4, 2009 by Anne Condon, Gale Heffinger, and John Schmerfeld, with assistance from Ellie Sheridan (William and Mary), and BRI employees Sarah Folsom, Chris Niven, Lizzie Goodrick, John Diener and Andy McGann. Data collected included: number of eggs laid, nestlings and fledglings, date of initiation and fledging. Adults (mostly females) were caught at the nest box, banded and blood and feather samples were taken. Nestlings were banded only. Mercury analysis of adult blood and feathers is being conducted at William and Mary, and is in progress. Reproductive data are yet to be analyzed and are still being proofed. There were approximately 13 nests on the reference sites (5 successfully fledged young) and 22 on the contaminated sites (7 successfully fledged young). Some nests included in the above count were inactive, possibly dummy nests. Nest failures were seemingly a result of flooding/weather events, box takeovers by other species, predation, or unknown reasons (e.g., some or all nestlings were found dead in the nest, apparently abandoned by the adults). To determine how many nests were lost via predation, we set up 2 motion-sensor cameras on at least four nests, however, none of these nests failed as a result of predation so we just got many pictures of the wrens.

## Avian Summary

BRI

South River Science Team Expert Panel Meeting

October, 2009

Passerines were sampled along the South River (SR) and the South Fork of the Shenandoah River (SFSR) from May 18<sup>th</sup> – August 20<sup>th</sup>, 2009. The purpose of the study was to increase sample sizes of several bird species in order to better characterize injury, and to identify the geographic extent of bird injury along the SFSR. A total of 575 birds were sampled along the two rivers, with 347 individuals sampled on the SFSR and 228 on the SR. Birds were sampled at five locations on the SFSR and three locations on the SR, for a total of eight sampling locations. Mercury results are still pending for all samples collected and are currently being processed at the College of William and Mary under the supervision of Dan Cristol.

## Effects of Maternally- and Trophically-Derived Mercury on Reproduction, Development, and Performance of Amphibians

**Principle Investigator:** Dr. William A. Hopkins, Associate Professor, Dept. of Fisheries and Wildlife Sciences, Virginia Polytechnic Institute and State University

**Students & Postdocs:** Christine Bergeron (Ph.D. candidate), John Burke (senior undergraduate), Dr. Brian Todd (postdoctoral fellow), Dr. Haruka Wada (postdoctoral fellow)

### Conceptual Context

The transfer of contaminants from a female to her offspring has been studied in many fish and wildlife species, but this process is grossly understudied in amphibians which are among the most imperiled vertebrates on earth. Because maternal transfer of pollutants can directly affect reproduction of individuals as well as population-level processes, understanding the effects of maternal transfer should be a top priority for amphibian conservation efforts. Our research on the South River is the first to document amphibian maternal transfer of mercury (Hg), a pollutant of global concern due to its ubiquity, toxicity, and ability to bioaccumulate and biomagnify in food webs. Our overarching research goals are to: 1) Examine the impact of trophically-derived Hg on reproduction in adults, 2) Examine the individual and interactive effects of maternally- and trophically-derived Hg on growth and development in amphibian embryos, larvae, and juveniles, 3) Use the data generated from these studies to project the impact of Hg on amphibian population growth rates using stage-based matrix models (Figure 1), and 4) Use elasticity and sensitivity analyses to provide insight into the contribution of different life stages to population growth rate. This last objective will ultimately be critical towards remediation decisions because the most important lifestages can be identified and become the focal point for restoration efforts. For example, if larvae experience the greatest adverse effects of Hg exposure because of their high trophic exposure and this

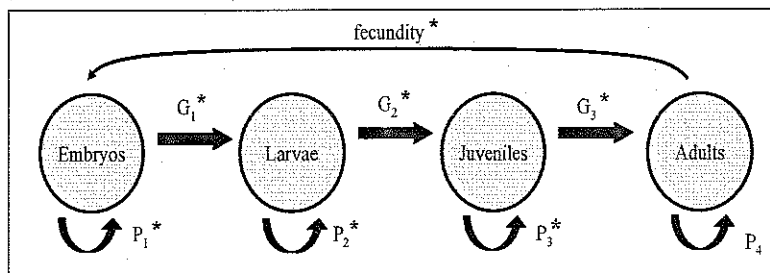


Figure 1: A conceptual diagram illustrating the stage-based population models for an amphibian species with a complex life cycle.  $G$  is the probability of surviving to next stage and  $P$  is the probability of staying in the same stage. The stars (\*) indicate the parameters that will be derived from this study.

subsequently influences local population dynamics, then restoration efforts could be focused on minimizing larval exposure (e.g., by constructing unpolluted vernal pools for their breeding and development) to be

maximally cost effective. Thus, our work not only links dietary and maternal exposure of Hg to effects on reproduction and survival of individuals, but it also explicitly links specific concentrations of Hg to projected changes in population dynamics with the intent of informing practical solutions to this important problem.

## **2009 Research Highlights**

### **Approach**

In all of our studies examining the latent effects of maternally-derived Hg on larval (i.e., tadpole) traits and recruitment (i.e., successful metamorphosis), we monitored larval growth, as well as size, survival, and time at metamorphosis in *Bufo americanus* at two different Hg contamination levels. In 2009, we collected egg masses from 27 breeding pairs from the reference and contaminated portions of the South River and drew blood from females immediately after oviposition in the lab. Because we have shown that Hg concentrations in female blood are closely correlated with THg in female carcass and eggs (Bergeron et al., *In Press*, a), we analyzed female blood samples for Hg within 48 hours of egg collection to confirm correct placement of eggs into our two treatments. Ultimately, we selected 5 females from the reference site (wet wt; reference < 250 ng/g in female blood) and 6 females from the contaminated site (1,000-4000 ng/g) for use in the experiments detailed below. We counted all eggs in clutches and a subset of eggs from each clutch was frozen for Hg analysis. The eggs remained separated by egg mass and were allowed to hatch. Within each treatment, successful hatchlings with "normal" morphology were pooled in order to avoid genetic bias. We transferred subsets of hatchlings into experiments within 4 days of hatching.

### **Project #1: Effects of larval predators and latent mercury exposure on American toad tadpoles**

In 2008, we found a significant difference between the latent and metamorphic responses to maternal Hg exposure between our Hg-exposed and reference treatments. Contrary to our predictions, the overall significance was driven by a 21% decrease in metamorphic success in the reference treatment compared to the Hg-exposed treatment. However, when we took percentage of viable larvae from the laid clutches into account, we found no significant relationship between the percentage of the clutch to metamorphose and the THg in eggs or maternal blood, suggesting that maternal transfer of Hg alone does not affect the number of juveniles recruited into the terrestrial environment in the absence of predators or heterospecific competitors.

Since Hg is a neurotoxicant and has been shown to affect behavior and performance in other organisms, in 2009 we used a 2X2 experimental design to investigate whether the addition of a larval predator (dragonfly larvae) affects recruitment to the terrestrial environment in the Hg-exposed and reference treatments. For this experiment, we transferred hatchlings to 32 outdoor pond mesocosms (2 Hg contamination levels x 2 predator treatments x 8 replicates x 100 hatchlings per replicate = 3,200 hatchlings) constructed out of 1,000 L polyethylene cattle watering tanks containing water, leaf litter, and plankton communities. We monitored mesocosms daily and metamorphosing individuals were moved into the lab at Gosner stage (GS) 42 (front limb emergence) to complete metamorphosis (GS 46). In addition to quantifying the proportion of individuals that successfully completed metamorphosis, we also determined size at metamorphosis and time to complete metamorphosis, as well as other metamorphic traits. This approach allowed determination of latent effects of maternal transfer and/or the presence of predators on larval growth and survival to metamorphosis, which can influence the number and quality of individuals recruited to the adult population (Beebee et al., 1996; Berven, 1990).

The percentage of individuals that successfully metamorphosed was high in all of our treatment groups (treatment means from 57-74%). Overall, we found significant effects of both maternal exposure to Hg and the presence of predators on several tested traits (MANOVA: maternal:  $P=0.008$ ; predator:  $P=0.021$ ) but we found no evidence of an interaction ( $P=0.714$ ). Component ANOVAs revealed a significant effect of maternal Hg exposure on larval growth rates ( $P=0.042$ ) and mass at GS 42 ( $P=0.022$ ); both of which were significantly lower compared to larvae from reference mothers. Similarly, we found a marginally significant effect of maternal Hg on mass at GS 46 ( $P=0.06$ ), but no effects on survival to GS 46, time to GS 42, or days for tail resorption ( $P=0.15$  or greater). Component ANOVAs also demonstrated a significant effect of predator presence on larval growth rates ( $P=0.012$ ), mass at GS 42 ( $P=0.003$ ), and mass at GS 46 ( $P=0.004$ ); all were significantly lower compared to larvae reared in the absence of predators. We also found a marginally significant effect on survival to GS 46 ( $P=0.06$ ) in which larvae reared with predators had lowered survival on average than those without. We found no effects on days to GS 42 or days to tail resorption ( $P \geq 0.373$ ). Overall, our results suggest that both maternal Hg contributions and the presence of predators can influence important larval traits, but the presence of predators did not exacerbate the effects of maternal Hg.

## **Project #2. Individual and interactive effects of dietary and maternal mercury exposure on growth, survival, and performance of American toad tadpoles**

Several studies have shown that tadpoles are efficient accumulators of contaminants because of their benthic omnivorous dietary habits (e.g., Snodgrass et al., 2004; Unrine et al., 2007). Indeed, our work on the South River in 2007 demonstrated that THg concentrations in *B. americanus* tadpoles were 3.6-fold higher than adults collected from the same areas. Such high exposure to Hg during the larval stages could have important implications for amphibian health and the percentage of individuals successfully metamorphosing from contaminated breeding sites (i.e., recruits to the terrestrial population). Because many of these larvae may have been produced by females who maternally transferred Hg to their eggs, it is likely that some of these individuals face the interactive insults of embryonic (maternally-derived) and larval (trophically-derived) exposure to Hg.

We used a 2X3 factorial study to determine if trophic exposure to Hg during the larval period has an interactive effect on development of tadpoles from Hg-exposed females. Because *B. americanus* adults have a large home range and have been known to travel up to 1 km from their breeding pond (Forester et al., 2006), our reciprocal study design addresses the impact of larval development of offspring from "reference" females deposited in Hg contaminated breeding ponds, and the opposite scenario of "contaminated" females laying eggs in reference ponds. We compared the responses of larvae raised under these conditions to the best case scenario (reference females breeding in reference ponds) and what we predicted would be the worst case scenario (contaminated females breeding in contaminated ponds).

Individual tadpoles were randomly selected and allocated among six treatments containing 25 tadpoles per treatment for a total of 150 tadpoles:

- 1) reference tadpoles → control diet,
- 2) reference tadpoles → Low Hg diet,
- 3) reference tadpoles → High Hg diet,
- 4) High Hg tadpoles → control diet,
- 5) High Hg tadpoles → Low Hg diet,
- 6) High Hg tadpoles → High Hg diet.

Husbandry and experimental Hg diet provisioning were similar to methods developed previously (Unrine et al., 2004). We produced diets by combining vitamin-enriched rabbit pellets, trout pellets, TetraMin fish flakes, and SeraMicron algae powder in a matrix of agar and gelatin. Prior to suspension in the agar/gelatin matrix, ground dietary components were mixed with proper quantities of Hg II and MeHg in an ethanol solution to produce desired dietary Hg concentrations. Control diets were prepared using ethanol only. Ethanol was evaporated from the diets under a fume hood. The control diet contained 10.2 ng/g THg dry wt (56.7% MeHg), and the Hg-spiked diets contained 2,503 ng/g THg dry wt (3.2% MeHg) and 10,132 ng/g THg dry wt (1.0% MeHg). Both Hg concentrations are well within the range of concentrations observed in periphyton in the South River (up to 26,000 ng/g, dry wt; Newman, unpublished data). Ratios of MeHg:Hg(II) were calculated using regression equations in Unrine and Jagoe (2004) and the % MeHg in the Hg-spiked diets were consistent with Mike Newman's data for periphyton from the South River.

Tadpoles were fed ~ 6% of their body weight daily and growth rates and survival were monitored closely throughout the study. Tadpoles in all treatment groups exhibited positive growth rates, on average increasing in body size by 20-fold over the first 6 weeks of the study. Survival was high in all treatments to GS 42, ranging from 80 – 96 % among treatments. The first tadpoles began metamorphosing during the 6<sup>th</sup> week of the experiment. We found a significant effect of both dietary and maternal Hg on toad tadpoles at GS 42 but no evidence of an interaction (MANOVA, diet: P=0.03; maternal: P=0.002; interaction: P=0.327). Individual component ANOVAs revealed that mass at GS 42 was significantly affected by diet (P=0.004), with animals fed the high Hg diet being, on average, 16% smaller than those fed the control diet. We also found a significant affect of maternal Hg on mass at GS 42 (P=0.019) with larvae from reference mothers being 10% larger on average than those from contaminated mothers. There were no significant effects on time to GS 42 or larval growth rates. When analyzing toads at GS 46, we found significant overall effects of both dietary and maternal Hg, but no evidence of an interaction (MANOVA, diet: P=0.038; maternal: P=0.001; interaction: P=0.297). Toads fed the high Hg diet were 21% smaller at GS 46 than those fed the control diet (P=0.015). In addition, toads from Hg-exposed mothers took 14% longer to resorb their tails compared to toads from reference mothers (P=0.000). When maternal Hg and high dietary Hg were combined, fewer larvae survived to metamorphosis (24% total) than reference larvae feeding on control diet (56%;  $\chi^2=5.77$ ; P=0.016). We found no evidence of reduced survival in other treatments compared to reference larvae feeding on control diet.

In addition, locomotor performance was evaluated for tadpoles (speed and responsiveness) 1 month after the start of the experiment and toadlets (hopping distance, speed and responsiveness) 24 hours after completing metamorphosis. Videos of performance trials have yet to be analyzed.



### **Projects #3 and #4: Effects of dietary and latent mercury exposure on larval and post-metamorphic American toads in complex environments**

Population dynamics are greatly influenced by post-metamorphic survival (Biek et al. 2002). Because evidence suggests that amphibians retain Hg through metamorphosis (Unrine and Jagoe 2004, Unrine et al. 2007) and first year juvenile survival is important, this experiment specifically tests whether embryonic (maternally derived) and/or larval (trophically derived) Hg exposure has latent effects that manifest as a decrease in size or survival during the first year in the terrestrial environment. The six treatment groups and diet were the same as in Project 2, however, tadpoles were raised communally instead of individually due to the number of postmetamorphic toads needed. Each of the six treatments had six replicates with 50 tadpoles each for a total of 1,800 tadpoles. To minimize competition with cohabitants, tadpoles were fed ~ 9% of their body weight daily and growth rates and survival were monitored closely throughout the study. Tadpoles in all treatment groups exhibited positive growth rates, on average increasing in body size by 25-fold over the first 6 weeks of the study. Survival was high in all treatments to GS 42, ranging from 85 – 95 % among treatments. The first tadpoles began metamorphosing during the 6<sup>th</sup> week of the experiment. We found a significant effect of maternal Hg exposure in our overall MANOVA (maternal:  $P < 0.001$ ) but we found no effect of dietary Hg or its interaction with maternal exposure (diet:  $P = 0.419$ ; interaction:  $P = 0.212$ ). Offspring from Hg-exposed mothers were 14 % smaller than those from reference mothers at both GS 42 and GS 46 ( $P = 0.001$ , for both). In addition, larvae from Hg-exposed mothers took 5% longer to resorb their tails ( $P < 0.001$ ), had 15% slower growth rates ( $P < 0.001$ ), and 155% greater number of gross morphological spinal malformations ( $P < 0.001$ ) than larvae from reference mothers. The effect of maternal Hg exposure on average time to GS 42 was marginally significant ( $P = 0.055$ ) where larvae from Hg-exposed mothers took 2.5% longer than larvae from reference mothers.

In addition, locomotory performance (hopping distance) of recently metamorphosed toads was evaluated 24 h after completing metamorphosis and prey capture efficiency was also evaluated within 72 h of completing metamorphosis. Videos of performance trials are still being analyzed.

After completing metamorphosis, individuals from replicates were either entered into the terrestrial enclosure experiment, used in performance studies (hopping distance and prey capture efficiency), or euthanized to analyze Hg tissue concentrations. We used a 2X2 experimental design for the terrestrial enclosures with 8 replicates each and 9 toads per replicate for a total of 288 juvenile toads:

- 1) reference tadpoles → control diet,
- 2) reference tadpoles → High Hg diet,
- 3) High Hg tadpoles → control diet,
- 4) High Hg tadpoles → High Hg diet.

All toads have been marked and placed in pens. Censuses are conducted at regular intervals and will continue through the first half of 2010 to track growth and survival over the animals' first full year post metamorphosis.

### Additional 2009 Studies

Although our overarching objectives focus on the effects of Hg on American toads, we also completed two studies on other amphibian species that occur along the South River. These studies serve as important complements to our existing work because each species chosen differs drastically in their ecology, life history, and physiology, and thus experiences differing levels of risk along the South River.

#### **Project #5: The effect of excessive dietary mercury on thyroid-mediated processes and fitness-related traits in wood frog tadpoles**

Research on the relationships between Hg and endocrine functions has primarily focused on piscivorous vertebrates in aquatic environments. However, increasing evidence suggests that Hg can disrupt endocrine functions, even in insectivores in terrestrial environments. Such endocrine functions include thyroid and adrenocortical hormonal axes which are important for metabolism, development, and thermoregulation. For example, our work on the South River in 2007 showed that tree swallow nestlings in the Hg contaminated sites had suppressed adrenocortical responses and plasma thyroid hormone concentrations (Wada et al. 2009). In a laboratory study, dietary Hg has been shown to delay tail resorption in southern leopard frogs (*Rana sphenoccephala*) during metamorphic climax, a process mediated by thyroid hormones (TH) (Unrine et al. 2004). To explore the direct link between Hg, hormone disruption, and developmental delays in amphibians, we examined the effects of dietary Hg on TH concentrations and development, growth, performance, and survival of wood frogs (*Rana sylvatica*). Wood frogs were an excellent model for this study because this species are widely distributed in northeastern United States and Canada and are abundant along the South River.

We collected five masses of freshly laid wood frog eggs near Blacksburg, VA and brought them back into the laboratory. After tadpoles reached free swimming stage, two hundred sixteen tadpoles were haphazardly distributed among three diet treatments: control (0.01  $\mu\text{g/g}$  dry wt), low Hg (2.5  $\mu\text{g/g}$  dw), and high Hg (10  $\mu\text{g/g}$  dw) (see above for the composition of the diet). The dose was based on environmental Hg concentrations in periphyton in low and high Hg contaminated areas in the United States. The low dose corresponds to approximately twice the mercury exposure from atmospheric deposition alone (Unrine and Jagoe 2004) and the high dose corresponds to Hg concentrations in periphyton at the Hg-contaminated South River, VA. Tadpoles were fed ~6% of their body weight daily and we monitored their survival and metamorphic progress daily and their growth weekly. Whole-body thyroid hormone concentrations were measured at Gosner stage 37, 42, and 46, and mercury concentrations were measured at Gosner stage 42 and 46. Upon completion of the metamorphosis, we examined their hopping performance.

Tadpoles accumulated Hg in a dose-dependent manner; total Hg concentrations in Gosner stage 42 tadpoles fed the three diets were 0.03, 1.06, 3.54  $\mu\text{g/g}$ , dw, respectively. During metamorphic climax, tadpoles eliminated 35% of the inorganic Hg from their tissues but retained most of the more toxic methylmercury that they had accumulated, resulting in total Hg concentrations of 0.05, 0.85, and 2.57  $\mu\text{g/g}$ , dw, in three treatments, respectively. Because of this differential retention of methylmercury and inorganic Hg,

percent methylmercury rose from 25% to 37% in the low Hg group and 10% to 23% in the high Hg group. Contrary to our predictions, we found no effect of Hg on the duration of larval development, size at metamorphosis, tail resorption time, or hopping performance. Consistent with the lack of effects on development, we also detected no differences in whole-body TH concentrations among our dietary treatments. Our results suggest that wood frogs may have a lower sensitivity to dietary Hg, perhaps due to differences in the length of the larval period or other life history factors.

#### **Project #6: Sublethal Effects of Mercury Contamination on the Northern Two-lined Salamander (*Eurycea bislineata*)**

Little research has examined the effects of Hg bioaccumulation in amphibians. The known effects of Hg on the nervous system suggest that it may also have behavioral and performance costs in fish and wildlife even when present in sublethal tissue concentrations. The goal of this study was to determine the effects of Hg contamination on performance and behavioral endpoints in *Eurycea bislineata* (Northern two-lined salamander). We chose *E. bislineata* for this study because it has the highest Hg concentrations of the three amphibian species studied on the South River and has the highest THg concentrations (up to 5,785 ng/g, dry wt) reported in the literature for amphibians (Bergeron et. al, *In Press*, b). We used two experiments to determine whether *Eurycea bislineata* from the contaminated portion of the South River would exhibit reduced locomotor performance and reduced prey capture ability compared with conspecifics from the reference portion of the river.

We collected adult *E. bislineata* salamanders by hand from under logs or rocks within 1 m of the river from both reference (n = 19) and mercury contaminated (n = 15) portions of the South River, VA. In the first experiment, we conducted locomotion trials to determine speed and responsiveness using a 3 m long racetrack with 1 cm demarcations down its length. Salamanders were encouraged to run by gently prodding them at the base of the tail with a laboratory spatula. Salamanders were raced once a day for two consecutive days and each trial was recorded for subsequent analysis. Responsiveness was calculated as the number of prods necessary for the salamander to travel 1m whereas speed and sprint length were quantified by analyzing videos in slow motion and determining the length of time it took for each animal to traverse 1m. Upon completion of the locomotion test, each salamander was used in a second experiment to test their prey capture and feeding abilities. Salamanders were offered 8 fruit flies (*Drosophila melangastor*) in an enclosed experimental chamber and recorded with a digital video camera for 5 min to assess the number of missed strikes, successful strikes, seconds until first strike, and total number of flies consumed. After the experiments were completed, the salamanders were humanely euthanized and analyzed to determine tissue mercury concentrations.

We found a significant effect of treatment on locomotor performance in Trial 1 in our overall MANOVA (P= 0.03). Treatment had a significant effect on both the number of prods it took for an animal to reach 1m (P= 0.02) and on the total moving time of an animal over that 1m (P=0.01). It took ~5X more prods on average for contaminated salamanders (20.0±6.9 prods) to reach 1m than the reference salamanders (4.2±0.8 prods). The salamanders from contaminated sites also took ~3X longer to reach 1m (17.5±4.2 s) than those from uncontaminated sites (5.8±1.1 s). We did not find a

significant overall effect of treatment on performance in Trial 2 ( $P=0.91$ ). In the prey capture ability experiment, salamanders from reference sites ate on average 2X the number of flies during five minutes than did salamanders from contaminated sites ( $3.7 \pm 0.79$  and  $1.7 \pm 0.69$  respectively), however we did not find a significant effect of treatment ( $P=0.06$ ). These results suggest that Hg may indeed be negatively impacting aspects of salamander performance and behavior, but future research is needed with larger sample sizes for increased statistical power.

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## **Bat Mercury Study Examining Footprint Area with Radio Tracking and Downstream Assessment**

*Authors: David Yates, David Evers, Pedro Ardapple, Casey Huck, Sofia Angelo, and Dominick Fuski*

This year to determine the footprint size we attached 24 bats, two species (little brown, eastern pipistrelle), from RM 10-20 with transmitters. We tracked bats back to their summer roosts and GPS locations. This year we found 14 new roosts and 2 of the bats returned to already known roosts. We tracked 19 bats for two weeks to identify feeding areas and determine core use areas, the other 5 bats transmitters failed, were never located, or fell off the bats. The roosts from previous years demonstrate the bats are traveling at least 1.6 miles each night to reach the river to feed. Two bats caught at AFC traveled at least 5.1 miles from their roost where they were captured and fixed with transmitters. *Myotis sp.* can travel up 10 miles in night to feed (pers. com. Rick Reynolds, VAGF). We will calculate core use areas using the fixed kernel method of estimating home range size. These bats will help us determine the total area used by the bats on the South River.

Our downstream assessment we sampled bats below the confluence of the North River and South River on the South Fork of the Shenandoah River (SFSR). We sampled bats from 5 different sites as far downstream as Bentonville. Sites were at least ten miles apart to not duplicate bats sampled and corresponded with bird sampling. One hundred fifty two fur, isotope, and blood (archieved) samples were taken from 5 different species of bats. The samples are at the UCONN lab and we expect the results late fall.

## **Pilot assessment of methylmercury availability to muskrat and shrews on the South Fork River, Virginia - 2008**

*Authors: David Yates and David Evers*

We examined mercury exposure in one target furbearer and shrews that occupy the SR. Muskrat (*Ondatra zibethicus*) and shrews (*Sorex sp*) are widely distributed throughout the United States. The muskrat commonly forages on shellfish and are less known for their risk to methylmercury availability; however, bi-valve shell middens are relatively common on the SR and are likely the result of foraging muskrats. The short-tailed shrews diet is principally earthworms, snails, and insects but fungus, various invertebrates, and occasionally small vertebrate animals are also eaten.

Furbearer and shrew sampling efforts occurred from 24 November to 7 December 2008. Traps were placed from river mile 9.9 (Chrimora Crossing) to mile 19.6 (Cosby Mills) on the SR where sightings of animals have been recorded, where either anecdotal information suggested their presence, or where suitable trapping locations were identified. Other trapping sites included Augusta Forestry Center (AFC, RM 11.3), Boes (RM 14.2), and Renkin (RM 17.4). A total of 82 tomahawk® boxtraps were deployed over 13 nights, and 90 small mammal snap-traps at 3 sites. The total number of traps available at any one night varied.

We captured 32 muskrats over 13 nights, which yielded a capture efficiency of 0.030 animals/trap/night. We also captured 36 shrews over 13 nights, which yielded a capture efficiency of 0.010 animals/trap/night. We captured 34 short-tail shrews and 2 pygmy shrews. Muskrat mean blood and fur Hg concentrations were 0.011 and 4.13, respectively ( $\mu\text{g/g}$ ). Muskrat blood Hg concentrations ranged from 0.0015 to 0.0413 ( $\mu\text{g/g}$ ). Muskrat fur Hg concentrations ranged from 0.287 to 14.3 ( $\mu\text{g/g}$ ). Shrew mean fur Hg concentrations were 27.38 ( $\mu\text{g/g}$ ) and fur Hg concentrations ranged from 6.08 to 88.4 ( $\mu\text{g/g}$ ). All shrew species were pooled since only two pygmy shrews were captured. The Renkin site had the highest fur Hg concentrations. Mean fur Hg concentrations varied by site as well and the Renkin site were significantly different from Boes and Cosby Mills. Mean mercury concentrations in kidneys were  $38.8 \pm 24.6 \mu\text{g/g}$  for the short-tailed shrew (*Blarina brevicauda*).

An understanding of the species at greatest risk to Hg pollution has improved. Muskrats are likely not at risk for injury from the availability of MeHg on the SR. However, a conclusion about the magnitude of injury toward furbearers, such as the mink and river otter, is less apparent.

## Landscape Patterns of Airborne Hg in Waynesboro, VA

Dean Cocking\*, Zamda Lumbi, Allison Kelley, Amir Allak, and James Wilson  
James Madison University MSC 7801, Harrisonburg VA 22807 (\*corresponding)

A survey of the distribution of airborne Hg concentration at numerous locations within the City of Waynesboro was carried out during three different time periods in 2003, 2004 and 2005.

These data and the analyses were gathered as a group effort over the years by the co-authors and research assistants with Zamda Lumbi subsequently carrying out the synthesis of the three years results in a report that was the primary source for this summary.

Samplers were inverted plastic Petri Plates poured with Tangle Trap® gel which were affixed to random telephone poles located within a mapped grid of the city. (see Addenda) During each study period, the plates were distributed and collected concurrently and then the gel was digested in hot nitric and sulfuric acid. Total Hg in the diluted samples was determined using a Perkin Elmer FIMS dedicated atomic absorption mercury hydride analyzer.

All of the measured values during a sampling period from Waynesboro and two cities remote from the South River, Staunton and Harrisonburg, were dependent on the total amounts deposited during the sample period. These locations, which were presumed to be unaffected by the South River local source, were used as control sites and the third controls were unexposed plates. The Hg concentrations were compared statistically and the summary data for 2005 are presented as an example in Table 1. The demarcation between NE and SW Waynesboro can be seen in Figure 1. This roughly divides the floodplain into downstream and upstream from the point source.

Table 1: T-test Statistical analysis comparing the differences between the means of mercury deposition rates measured from July 2005 to October 2005. The units for means and Standard deviations are  $\mu\text{g Hg/m}^2/\text{mo}$ .

Location	Mean	St Dev	n	
NE Waynesboro	0.695	0.299	60	
SW Waynesboro	0.556	0.306	59	
Harrisonburg	0.312	0.214	18	
Staunton	0.312	0.119	26	
Unexposed	0.082	0.08	19	
Comparison	t statistic	df	Probability	Significant
NE Waynesboro- SW Waynesboro	2.508	117	0.013	Yes
NE Waynesboro- Harrisonburg	6.022	39	4.80E-07	Yes
NE Waynesboro- Staunton	8.486	84	6.39E-13	Yes
Harrisonburg - Staunton	-0.0096	24	0.992	No
NE Waynesboro- Unexposed	14.341	76	2.54E-23	yes
SW Waynesboro- Unexposed	10.818	74	6.73E-17	yes
Harrisonburg- Unexposed	4.272	21	3.30E-04	Yes
Staunton - Unexposed	7.779	43	9.74E-10	Yes

The measured amounts of Hg at the control and Waynesboro field sites were totaled for the time period and a grand mean was determined. The statistical dispersion of the total sample was calculated and each location was characterized by its location in an array of standard deviations from the grand mean. Concentrations below the mean were negative (blue) and those above the mean were positive (red) and were plotted for each year of the study. In Figure 1 they are mapped for the 2005 sample period.

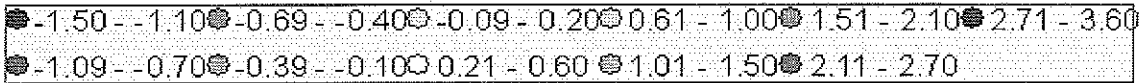
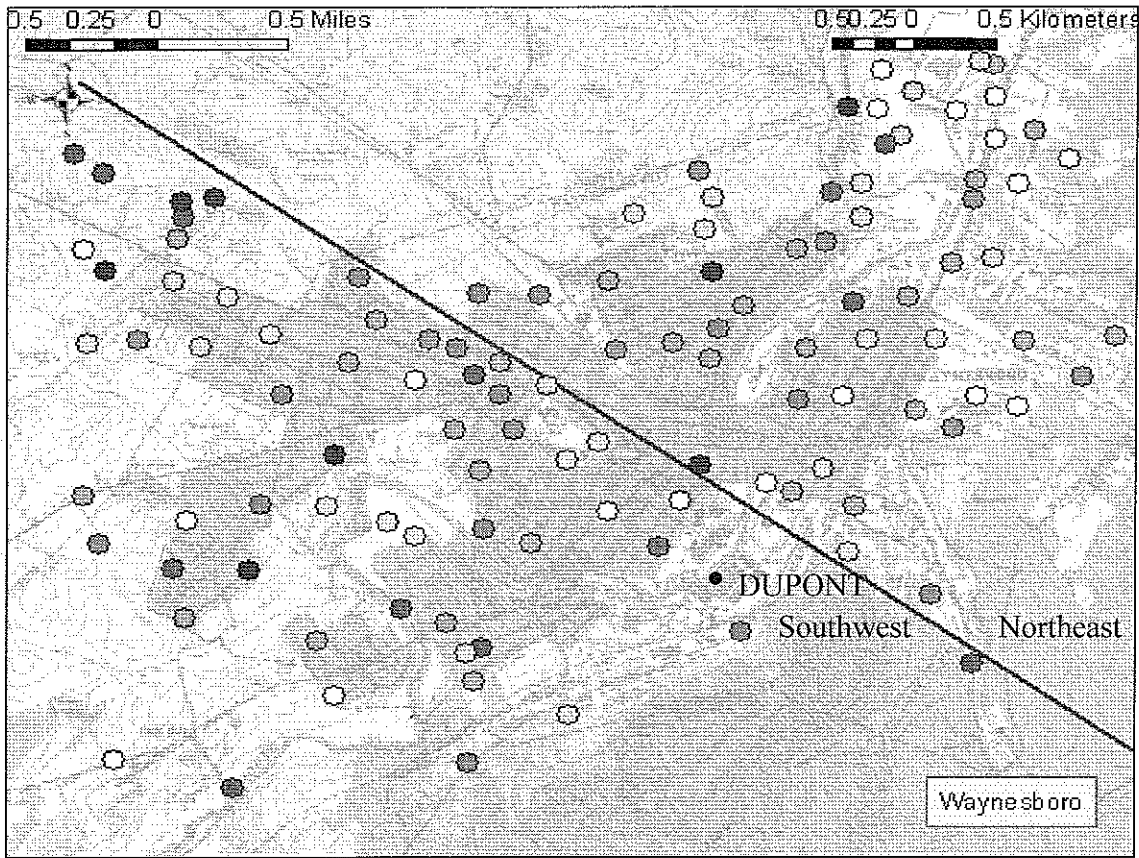
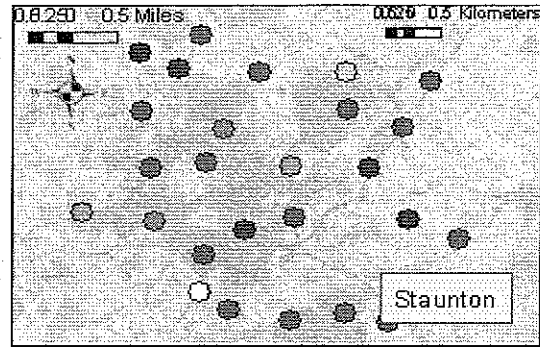
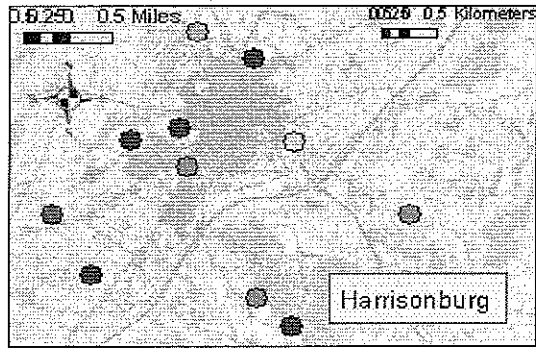


Fig. 1. : Maps of Waynesboro, Harrisonburg and Staunton with standard deviations of each site away from the grand mean of all concentrations for the study conducted between July 2005 and December 2005. The northeast section exhibits more sites with standard deviations above the grand mean than the southwest section. (DUPONT is at river-mile 1 in SRST studies)



Similar analyses were carried out for the other two data sets and the overall picture was consistent but beyond the scope of this three page SRST summary. An exact duplication of the comparative individual sample site variables would not be expected because conditions were different each year. However, the use of a relative ranking with respect to the grand mean of a sample period allows for year to year comparison.

The number of sites on the map is not the same as the "n" in the statistical analysis. That value is the total number of plates harvested. Because some plates were lost or stolen, the number of observations from each telephone pole sample site varied from 1 - 3. If no plates remained at a site it was excluded from the study that year.

It is not possible to convert the THg measurements to specific units of Hg (mass)/unit volume of air/unit time because they are a measure of mixed sources including that attached to particulates, in the vapor phase, dissolved Hg deposited during precipitation and that carried in by small insects. The release of Hg vapor from deposits in the soil adjacent to the sampler is also a possible source. It is not possible to separate inorganic from organic Hg within these data. The purpose of the numbers is different from one of quantitative measurement of Hg contamination levels; they are indices presented to show relative presence in the geo-referenced spatial field. Those locations, which repeatedly demonstrated greater than grand mean Hg concentrations, are ones that may warrant further investigation. The fact that there is a significantly greater frequency of higher concentration sites in the North East section of Waynesboro indicates that there is a correlation between airborne Hg contamination and the relative location with respect to the original point source of Hg input. Even with high sampling site to sampling site variability, there is a greater probability of lower airborne Hg concentrations upstream and higher concentrations downstream.

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Addenda: Photograph of sample plate. The cost of these samplers and subsequent analysis is about 2.5% of commercial passive samplers per unit.

