

**List of Technical Briefing Papers
SRST Expert Panel Meeting
October 8-9, 2014**

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AOC 4 Ecological Risk Assessment: Technical Briefing Paper

This briefing paper summarizes the findings of the Ecological Risk Assessment (ERA) Report for Area of Concern 4 (AOC 4) of the former E.I. du Pont de Nemours and Company (DuPont) Plant (the site), in Waynesboro, Virginia. Mercury was released to the South River system from the site between 1929 and 1950, during the period of mercury use in acetate flake and yarn production. In February 2014, under the authority of the Resource Conservation and Recovery Act (RCRA), Commonwealth of Virginia, Department of Environmental Quality (VDEQ) modified the Hazardous Waste Management Permit for Corrective Action (VAD003114832) for the site to include AOC 4. This ERA Report has been prepared pursuant to the February 2014 permit modification and provides a summary of its key components; additional details are documented in the AOC 4 ERA Report (URS, 2014).

Introduction

The AOC 4 ERA followed EPA guidelines for ecological risk assessment (EPA, 1997 and 1998). The goals of the ERA were (1) to evaluate potential risks to ecological receptors within AOC 4 due to exposure to site-related constituents, including mercury and (2) to support remedial decision-making within AOC 4. AOC 4 includes off-site aquatic and riparian terrestrial

systems (including the floodplain) along approximately 25 miles of the South River downstream of the site, and a segment of the South Fork Shenandoah River (SFSR) in Virginia. AOC 4 was divided into 16 Assessment Reaches for the ERA including:

- ☐ A reference reach upstream of the plant site located between relative river mile (RRM) -2.7 to RRM -0.7;
- ☐ A buffer reach (located between RRM -0.7 and RRM 0);
- ☐ Thirteen reaches between RRM 0 and RRM 24; and
- ☐ A segment of the SFSR downstream of RRM 24.

The ERA uses information from numerous reports and publications regarding conditions in AOC 4. A Retrospective Data Quality Assessment (RDQA) was performed at the request of VDEQ to evaluate existing data sets in terms of their usability for the ERA. Data comparability, sample integrity, accompanying QA/QC elements, and overall representativeness and relevance of the datasets for the ERA were evaluated as part of the RDQA.

Key components of the ecological risk process include problem formulation, ecological effects analysis, exposure analysis, and risk characterization. Summaries of these components are provided in the subsequent sections, along with conclusions of the assessment.

References

- ✓ EPA. 1998. Guidelines for Ecological Risk Assessment. US EPA. Washington, DC 20460, EPA/630/R-95/002F. April, 1998.
 - ✓ EPA. 1997. Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments. US EPA. Washington, DC 20460, EPA/540/R-97/006. June 1997.
 - ✓ URS Corporation. 2014. Ecological Risk Assessment Report for the Former DuPont Waynesboro site, Area of Concern (AOC) 4, South River and a Segment of the South Fork Shenandoah River, Virginia. September 12, 2014. Submitted to VDEQ.
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Problem Formulation

The problem formulation identifies factors to be addressed in the ERA including:

- ❑ Contaminant of potential ecological concern (COPEC);
- ❑ Ecological conceptual site model(s);
- ❑ Fate and transport of COPECs;
- ❑ Potentially complete exposure pathways; and
- ❑ Receptors and assessment and measurement endpoints.

A screening-level ecological risk evaluation was performed to focus the evaluation of ecological risks in AOC 4 and define the boundaries of the baseline ecological risk assessment. The evaluation identified mercury [total mercury (THg) and methylmercury (MeHg)] as COPECs.

An ecological conceptual site model (ECSM, see Figure 1) was developed to represent the current understanding of the mercury source, fate, and transport, and potential exposure of various ecological receptors to mercury within AOC 4. Based on mercury concentrations detected in various media and existing potential ecological habitats within AOC 4, the following exposure routes and exposure pathways were identified:

- ❑ Direct contact with soil, sediment, pore water, and surface water (e.g., aquatic and benthic invertebrates, fish, and soil invertebrates);
- ❑ Incidental ingestion of soil and sediment (e.g., sediment ingestion by mallard ducks and soil ingestion by short-tailed shrew); and
- ❑ Dietary ingestion of mercury containing food items by aquatic organisms, birds, and mammals.

Included in the exposure assessment was the aquatic-to-terrestrial trophic transfer pathway involving terrestrial birds (e.g., Tree swallow) feeding on invertebrates (e.g., emergent insects) and invertebrates that prey on aquatic invertebrates (e.g., wolf spiders).

Based on the potentially complete exposure routes and pathways identified in AOC 4, the following ecological receptor groups and focal receptors were selected for the BERA:

- ❑ **Aquatic Receptors:** Benthic macroinvertebrates and larval and emergent aquatic invertebrates, fish species [largemouth bass (*Micropterus salmoides*) and smallmouth bass (*Micropterus dolomieu*)], and submerged aquatic vegetation;
- ❑ **Semi-Aquatic Receptors:** Amphibians, piscivorous birds [belted kingfisher (*Megaceryle alcyon*)], omnivorous birds [mallard duck (*Anas platyrhynchos*)], piscivorous mammals [river otter (*Lontra canadensis*)]; and
- ❑ **Terrestrial Receptors:** Terrestrial vegetation, soil invertebrates (earthworms), invertivorous birds [Tree swallow (*Tachycineta bicolor*) – an aerial insectivore and American robin (*Turdus migratorius*) – a ground insectivore], carnivorous birds [Eastern screech owl (*Megascops asio*)], invertivorous mammals [Big brown bat (*Eptesicus fuscus*) – an aerial insectivore, short-tailed shrew (*Blarina brevicauda*) – a ground insectivore, and white-tailed deer (*Odocoileus virginianus*) – an herbivore].

Population-level potential risks were evaluated for the above receptor groups and focal species based on measurement endpoints related to population survival, growth, and reproduction. Individual level impacts were considered for the evaluation of potential risks to endangered and/or special status species.

Ecological Effects Analysis

A comprehensive literature review was performed to develop no effects and low effects thresholds or benchmarks to serve as a basis for comparison with estimated exposures as follows:

- ❑ No Observed Effects Concentrations (NOECs) and Lowest Observed Effects Concentrations (LOECs) for THg and MeHg in surface water and pore water, sediment, and soils;
- ❑ No Observed Effects and Low Observed Effects Critical Body Residues (CBR_{NOECs} and CBR_{LOECs} , respectively) for THg or MeHg in tissues of various receptors (whole body, blood, feather, fur, etc.); and
- ❑ Toxicity Reference Values (TRVs) based on No Observed Adverse Effects Level (NOAEL) and Lowest Observed Adverse Effects Level (LOAEL) doses for MeHg and inorganic mercury (IHg) for specific focal species representing the avian and mammalian receptors.

Exposure Analysis

Relationships were established between the chemical stressor (mercury, either as THg, MeHg, or IHg) and the focal receptors through: (1) spatial distribution of mercury concentrations across AOC 4 and reference areas, (2) calculation of exposure point concentrations (EPCs) for exposure medium/focal receptor pairs based on the most likely exposure scenario for each focal receptor, and (3) calculation of reasonable maximum daily mercury intake rates (DMIRs) via the food chain from abiotic and biotic sources by focal avian and mammalian receptors.

Following the standard practice, EPCs for THg, MeHg, and IHg were calculated to be the higher of the maximum detected concentrations or the 95% Upper Confidence Level of the Mean. EPCs were calculated for abiotic media (surface water, pore water, sediment, and soil) and biological tissues (e.g., whole body, blood, fur, etc.).

Reasonable maximum DMIRs were estimated for each Assessment Reach within AOC 4 using food web models (or dose rate models), for each of the following receptors: belted kingfisher, mallard duck, eastern screech owl, tree swallow, American Robin, river otter, short-tailed shrew, big brown bat, and white tailed deer.

Risk Characterization

Deterministic or point estimates of risks were quantified based on the Hazard Quotient (HQ) approach and the evaluation of available site-specific studies provided further information for a weight-of-evidence (WOE) evaluation of the potential risks. A summary of the findings is provided below; measurement endpoints are provided, followed by a risk statement:

- ❑ **Benthic Invertebrates:** abiotic bulk chemistry, sediment toxicity, benthic community analysis, and tissue residue; adverse effects to benthic invertebrates are unlikely.
- ❑ **Fish:** surface water chemistry, age/growth survey, condition survey, community structure survey, and tissue residue; fish population level effects are not likely.
- ❑ **Aquatic Vegetation:** surface water, pore water; adverse effects are not likely.
- ❑ **Amphibians:** surface water, whole body tissues; adverse effects are unlikely.
- ❑ **Terrestrial Plants and Soil Invertebrates:** soils; population-level adverse effects are unlikely.
- ❑ **Avian Receptors:** blood mercury concentrations; potential for adverse effects may exist for several avian receptors, including piscivores (such as belted kingfisher), carnivores (such as Eastern screech owl), and insectivores (such as tree swallow).
- ❑ **Mammalian Receptors:** blood and fur THg EPCs; potential for adverse population level effects to aerial insectivorous mammals (e.g., the big brown bat) exists.

Conclusions

Conclusions for each of the key receptor groups are summarized as follows:

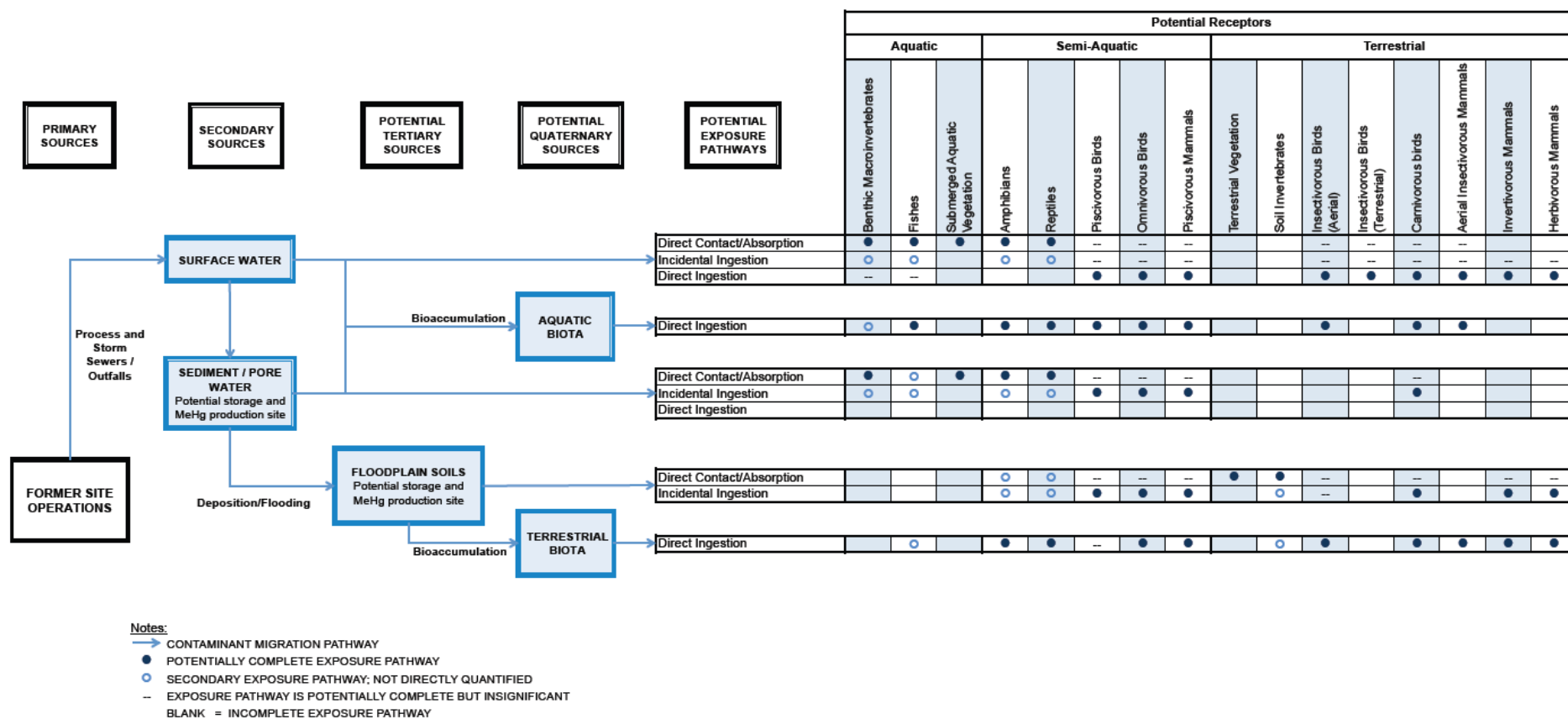
- ❑ **Aquatic Receptors:** Unlike the direct contact pathway which poses no risk, mercury bioaccumulation by the invertebrates and fish species within AOC 4 poses potential risks of adverse effects.
- ❑ **Semi-Aquatic Receptors:** While significant uncertainties bias conclusions toward overestimation of risks, potential risks of adverse effects cannot be ruled out for amphibians and piscivorous birds due to bioaccumulation and/or dietary exposures to mercury within AOC 4 Assessment Reaches beyond RRM 2.7.
- ❑ **Terrestrial Receptors:** Potential risks of adverse effects cannot be ruled out for carnivorous birds, invertivorous songbirds, and bats due to dietary exposures to mercury within AOC 4. However, calculated potential risks for these groups of receptors incorporate significant uncertainties biased toward overestimation of risks.

Recommendations

The results of the ERA indicate that potential adverse effects to the ecological receptors are due to trophic transfer of MeHg originating in the South River system—a finding that is consistent with the current understanding of the system on which the proposed remedial strategy is based. Owing to the size, linear nature, complexity, and spatial variability of the South River system, reduced exposure of ecological receptors (and humans), and subsequent overall risk reduction, will be best achieved in AOC 4 by conducting remedial measures in an adaptive management approach involving integration of various interim measures, monitoring, and community outreach and education. Such an approach is already being planned for the AOC 4 and the results of the ERA provide

further justifications for such an approach in ecological risk management and remedial decision-making.

Figure 1
Ecological Conceptual Site Model (ECSM)
AOC 4 Ecological Risk Assessment Report
Technical Briefing Paper



AOC 4 HHRA Report: Technical Briefing Paper

This briefing paper summarizes the findings of the Human Health Assessment (HHRA) Report for Area of Concern 4 (AOC 4) of the former E.I. du Pont de Nemours and Company (DuPont) Plant (the site), in Waynesboro, Virginia. Mercury was released to the South River system from the site between 1929 and 1950, during the period of mercury use in acetate flake and yarn production. In February 2014, under the authority of the Resource Conservation and Recovery Act (RCRA), Commonwealth of Virginia, Department of Environmental Quality (VADEQ) modified the Hazardous Waste Management Permit for Corrective Action (VAD003114832) for the site to include AOC 4. The HHRA Report was prepared pursuant to the February 2014 permit modification.

This briefing paper provides a

summary of its key

components; additional details are documented in the AOC 4 HHRA Report (URS, 2014).

Introduction

The HHRA was conducted consistent with RCRA requirements to evaluate potential exposure of human receptors to mercury detected in environmental media in the South River watershed. The area of the assessment includes the South River and associated floodplains (designated as AOC 4). AOC 4

includes approximately 25 miles of the South River downstream of the site, the associated floodplain, and a segment of the South Fork Shenandoah River in Virginia. The South River watershed within AOC 4 is composed of agricultural, forested, and developed areas.

The primary goals of the HHRA were (1) to evaluate potential risk for AOC 4 human receptors; and, (2) to provide risk information sufficient for remedial decisions consistent with United States Environmental Protection Agency (EPA) and VADEQ requirements.

To support the risk assessment, conceptual site models (CSMs) were developed in collaboration with VADEQ to summarize potential human exposure pathways for the AOC. The CSMs form the basis of the risk assessment detailed within this briefing paper. The CSMs are provided as part of this briefing paper (see [Figures 1, 2 and 3](#)).

As described below, the technical approach for the HHRA consisted of the following basic steps: data review and identification of constituents of potential concern (COPCs), human exposure assessment, toxicity assessment, risk characterization, and uncertainty analysis.

References

- ✓ URS Corporation. 2014. Human Health Risk Assessment Report for the Former DuPont Waynesboro Plant, Area of Concern (AOC) 4, South River and a Segment of the South Fork Shenandoah River, Virginia.
- ✓ USEPA. 1989. Risk Assessment Guidance for Superfund: Volume I - Human Health Evaluation Manual, Part A. Interim Final. Office of Emergency and Remedial Response, Washington, D.C. December.
- ✓ VADEQ, 2011. Current Risk Based Performance Standard for Hazardous Waste Corrective Action.

Data Review and Identification of Constituents of Potential Concern

The HHRA compiled information from investigations and studies that have been performed as part of on-going investigations of the South River and South Fork of the Shenandoah River over the approximately last 10 years. As part of the data review, DuPont and VADEQ developed an assessment-mechanism [referred to herein as a retrospective data quality assessment (RDQA)] specifically for the data sets to be used in the HHRA. The objective of the RDQA was to document that the analytical data collected during numerous investigations was of sufficient quality for use in risk assessment. The original, historical source of mercury in the South River watershed is the Former DuPont Waynesboro Plant. Potential COPCs for AOC 4 are limited to total mercury (THg) and methyl mercury (MeHg).

Exposure Assessment

Based on an evaluation of the available data compared to screening levels, South River sediment and fish, floodplain area soil and floodplain area pond fish were identified as media of concern. In addition, floodplain area biota (such as wildlife, livestock and garden crops) were evaluated. South river surface water, floodplain area groundwater, floodplain area pond surface water and floodplain area pond sediment were not considered media of concern.

All properties along the approximately 25 miles in the South River watershed were reviewed for land use. Using a landuse-based screening decision logic, potential receptors were identified consistent with land uses in the South River watershed, namely residents, industrial/commercial workers, construction/excavation workers, hunters, farmers, and, recreational users of floodplain area parks and the South River under both current and future conditions.

In addition, a hypothetical future residential scenario and hypothetical future subsistence farmer scenario were evaluated in exposure areas where soil concentrations were above a conservatively adjusted residential screening value of 17 milligrams per kilogram (mg/kg). Potential exposures to all media were combined to provide an upper-bound estimate of potential risk assuming uncontrolled exposures via all possible exposure pathways. The farmer scenario differed from the resident in that potential exposure to livestock was also included.

Exposure via ingestion, inhalation, and dermal contact was evaluated in all exposure scenarios, as applicable. Exposure calculations used reasonable maximum exposure assumptions. Exposure point concentrations were either 95% upper confidence limit (UCL) of the arithmetic mean or the maximum value based on all available data. In some instances for soil data, outliers (THg concentrations greater than 100 mg/kg) were removed and the analysis was repeated.

Toxicity Assessment

Toxicity values for use in the human health risk assessment included reference doses (RfDs) and reference concentrations (RfCs) for THg and MeHg, which are both non-carcinogens. In accordance with EPA guidance, toxicity values for THg specific to the oral and inhalation pathways were obtained from a specific hierarchy of sources

recommended by EPA. Dermal toxicity factors were derived using adjusted oral toxicity values as recommended by EPA.

For the HHRA, the RfD for mercuric chloride was used to assess THg. However, in assessing food sources, it was conservatively assumed that all THg is present as MeHg. Therefore, the MeHg toxicity values were applied to the EPCs calculated for THg.

Risk Characterization

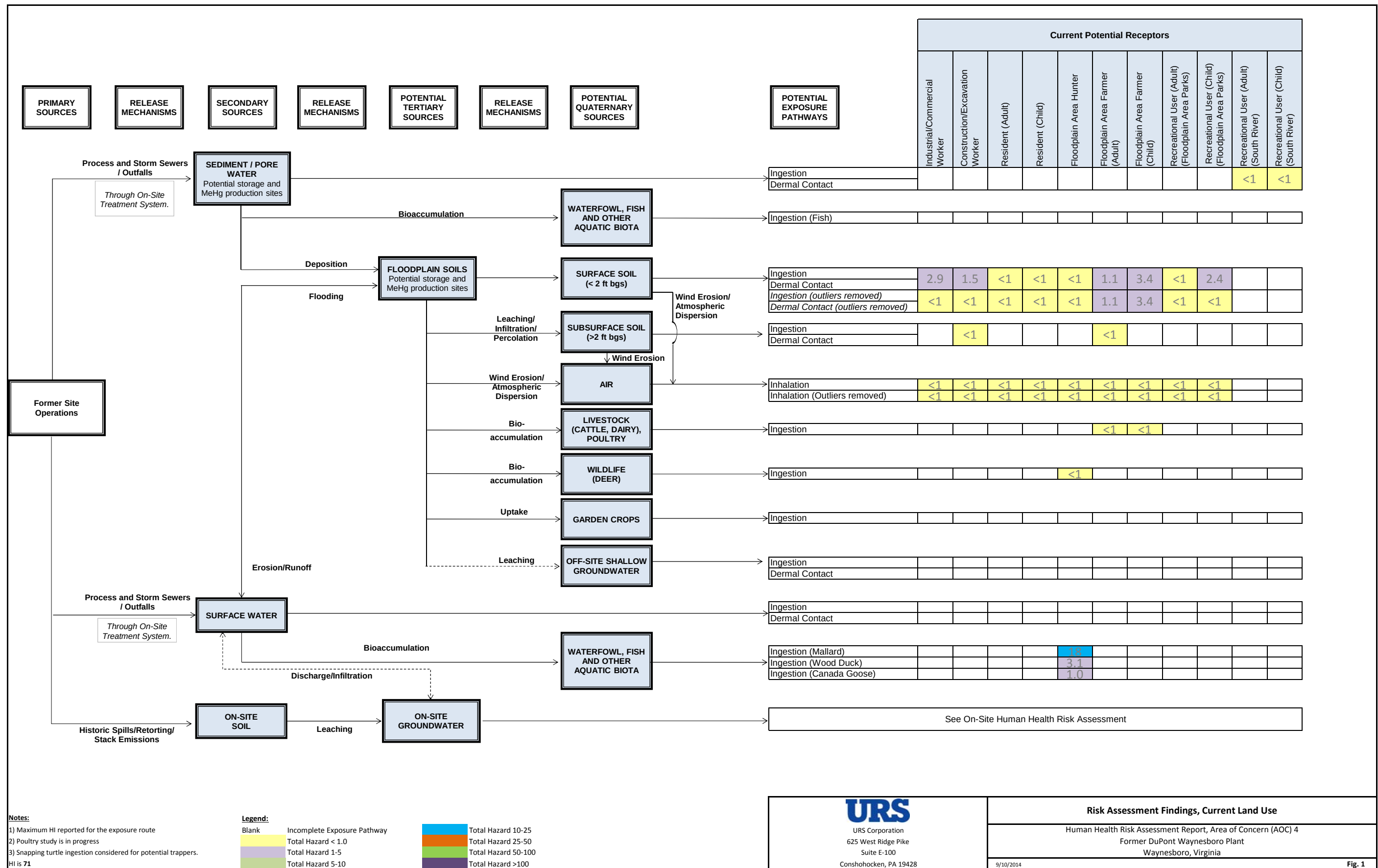
In the risk characterization, the toxicity factors (RfDs and RfCs) were applied in conjunction with COPC concentrations and intake assumptions to estimate noncancer hazards. Potential hazard associated with mercury exposure was evaluated at all properties. Hazard Indices (HI) were compared to EPA's and VADEQ's target hazard quotient (HQ) of 1.0 (EPA, 1989 and VADEQ, 2011).

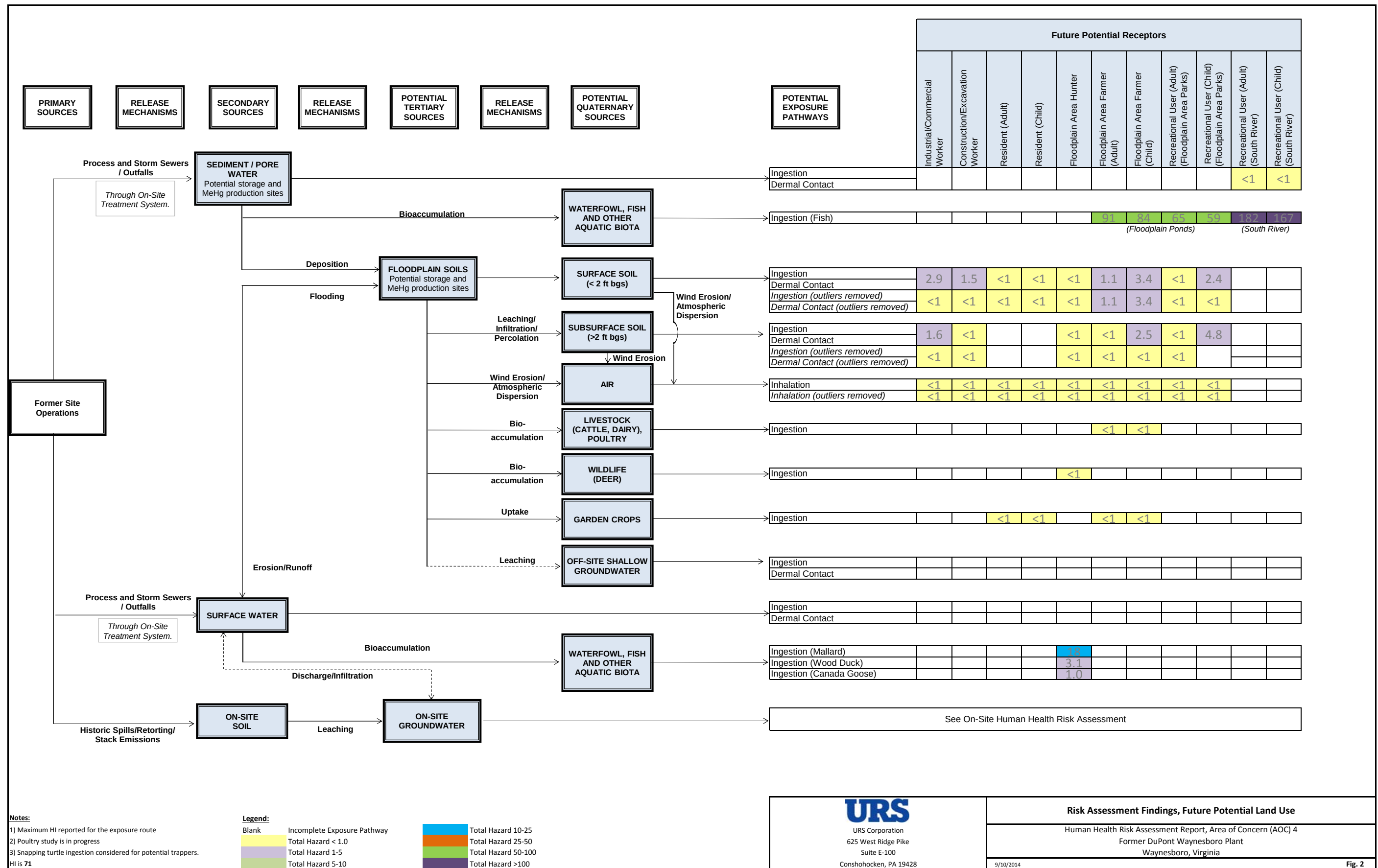
In general the HHRA concluded the following:

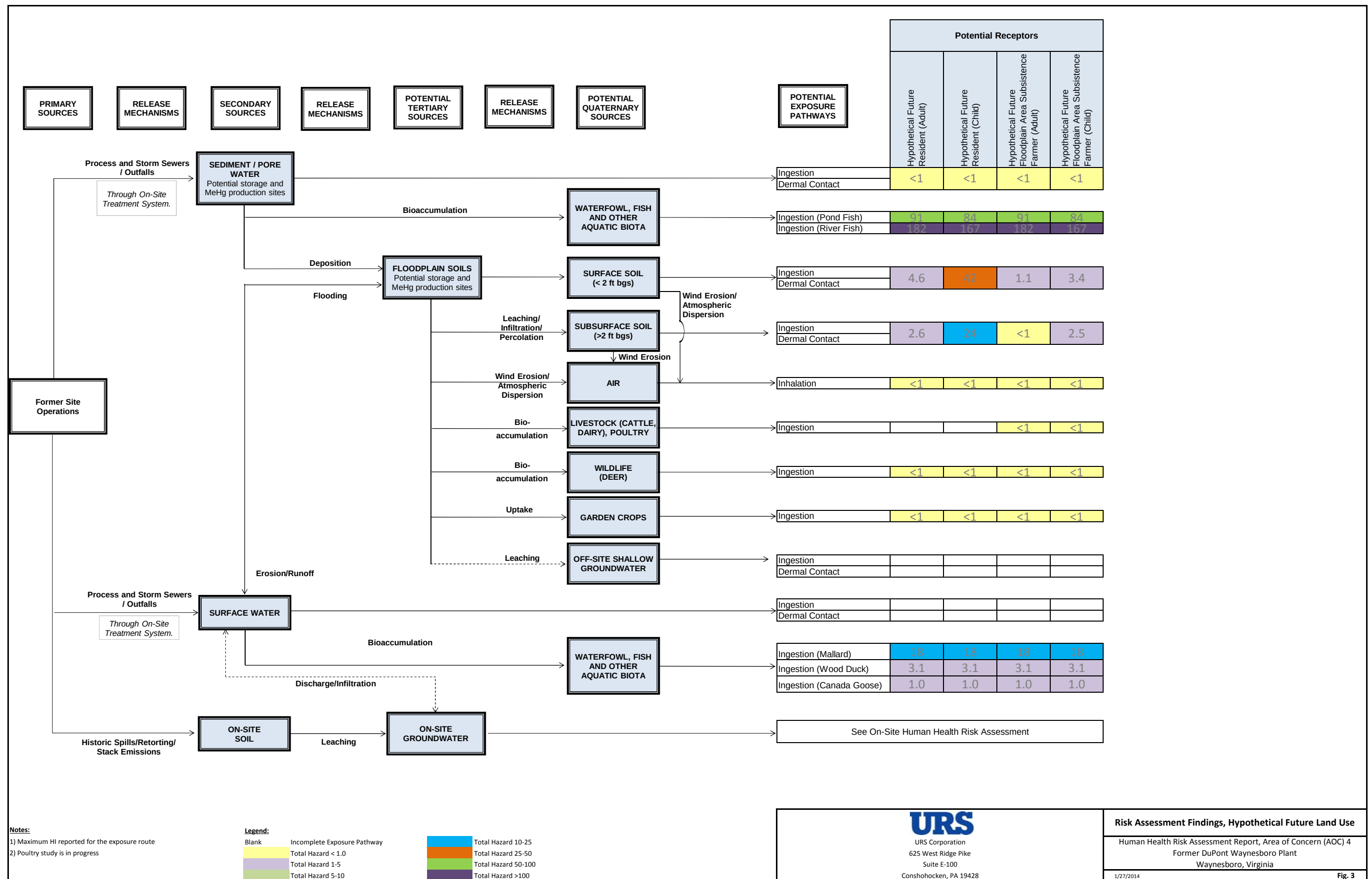
- ❑ For all current potential receptors, HI exceedances were limited to potential exposure to floodplain area surface soil and ingestion of waterfowl (mallards and wood ducks). (The number of soil exceedances is reduced if the outlier analysis is performed.) Maximum exceedances by receptor and pathway are illustrated on [Figure 1](#).
- ❑ For potential future receptors, if floodplain area subsurface soils are assumed to be on the surface and the fish advisory is not in place, these pathways also show HI exceedances. (Similar to above, the number of exceedances is reduced if the outlier analysis is performed). Maximum exceedances under this scenario by receptor and pathway are illustrated on [Figure 2](#).
- ❑ For the both the hypothetical future resident and hypothetical future subsistence farmer, where all pathways are assumed possible on any property where soil concentrations exceed 17 mg/kg, similar pathways exceed the target HQ and maximum HIs are higher. Maximum exceedances under this scenario by receptor and pathway are illustrated on [Figure 3](#).

In all cases, no exceedances are noted for potential exposures directly to sediments and air and indirect pathways associated with consumption of livestock, game (represented by deer) and garden crops.

The report is currently under review by VA DEQ







AOC 4 Monitoring Program: Technical Briefing Paper

This briefing paper summarizes the objectives, approach, and status of the monitoring program for Area of Concern (AOC) 4 of the former DuPont Waynesboro manufacturing facility (site) in Waynesboro, VA. AOC 4 includes the South River downstream of the site and a portion of the South Fork Shenandoah (SFS) River. Interim remedial measures are being designed to control mercury loading from eroding river banks and the site (Anchor QEA et al., 2014). A monitoring program to test the efficacy of remedial measures is appended to the design work plan.

The monitoring program contains both a short-term monitoring plan and a long-term monitoring plan, which differ in terms of relevant spatial and temporal scales, but are both designed to provide information to monitor achievement of remedial action objectives (RAOs) described in the Phase 1 Interim Measures Design, Implementation and Monitoring Work Plan (Anchor QEA et al., 2014). The RAOs are listed in Table 1. Short-term RAOs are expected to be addressed through interim measure construction, while long-term RAOs take into account future corrective actions to be implemented.

References

- ✓ Anchor QEA, LLC, URS Corporation, and E. I. du Pont de Nemours and Company. 2014. Phase 1 Interim Measures Design, Implementation and Monitoring Work Plan. South River, Area of Concern 4. Final Report, August 2014.
 - ✓ URS, 2012. Final Report: Ecological Study of the South River and a Segment of the South Fork Shenandoah River, Virginia. Fort Washington, Pennsylvania. Final report prepared by URS Corporation. September 2012.
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The short- and long-term monitoring plans detail specific monitoring and data interpretation methods to address specific objectives. Both monitoring plans rely on characterization of current baseline conditions in the river system. Existing data sets collected as part of the Ecological Study (URS 2012) and VDEQ 100-Year Monitoring Program for the South River, provide initial background data for establishment of baseline conditions. Additional baseline monitoring will include focused supplemental data collection as necessary, to support ongoing monitoring. The short- and long-term monitoring plans are summarized in the following sections. Additional details are presented in Appendices D and E of the Interim Measures Work Plan (Anchor QEA et al., 2014).

Short-Term Monitoring Plan

The short-term monitoring plan is designed to measure improvements over relatively rapid timeframes (e.g., 2 to 10 years) and small spatial scales, such as adjacent to a particular remedial target (e.g., eroding bank). Short-term monitoring plan elements, including details such as sample frequency and location are included as Table 2.

First and foremost, the short-term monitoring will assess whether the physical specifications of a remedy are being met, and ensure that the physical integrity of the remedy is repaired should it be affected by flooding or other events.

Secondly, the short-term monitoring will provide chemical and biological information that will feed into the relative risk model and the adaptive management approach.

Combined, these data will allow for feedback on the efficacy, integrity, and performance of the remedy, and whether or not the remedial action objectives are being met.

Long-Term Monitoring Plan

The long-term monitoring is designed to measure potential mercury exposures to humans and ecological receptors, as well as monitor habitat improvements and responses to remediation. While the short-term monitoring will be focused primarily in the South River at or near those areas where bank management area remedies are being implemented, the long-term plan is designed to cover a timeframe of many years to decades, and a much larger area, including watersheds of the South River and SFS River. Sample locations and methodologies are based on the extensive data collected by the South River Science Team. The monitoring elements are listed in Table 3 lists along with sampling details, including sample locations, sample frequency and sample sizes.

Similar to the short-term monitoring plan, chemical and biological results from the long-term monitoring will also feed into the relative risk modeling and the adaptive management approach. In this way, both the short- and long-term information will be used as input to management decisions regarding the efficacy of remedial actions, the need to alter approaches or evaluate new or improved technologies, or to maintain and/or repair areas as necessary.

Most importantly, the monitoring information will help in estimating changes in the potential exposures and risks to humans and ecological receptors that result from changes in mercury loading to the South River and SFS River. It is expected that once remedial actions have been implemented in the South River, the mercury loading should decline and be accompanied by a concomitant reduction in potential mercury exposures and potential risks to humans and ecological receptors. There will be open and frequent outreach and communication with local communities, physicians and health clinics, and relevant public-health groups throughout the implementation and monitoring of the remedial strategy.

Table 1
Remedial Action Objectives
AOC 4 Monitoring Program Briefing Paper
South River and a Segment of the South Fork Shenandoah River

Time Frame	General Response Objectives	Performance Objective	Measurable Metric
Short-Term (2-10 years)	Reduce mercury transport and exposure and improve bank habitat functions within the upper two miles of the South River	Conduct and/or maintain bank remediation actions in the upper two miles of the South River to achieve sustainable reductions in mercury concentrations and improve water quality and bank habitat functions within this reach	Bank erosion rates, measured using detailed topographic surveys, and/or root analysis; establishment of bank vegetation; and mercury concentrations in physical media and biological tissues
Long-Term (10+ years)	Reduce MeHg exposure and improve habitat conditions throughout the South River and SFS River	Conduct and/or maintain remediation actions that sustain reductions in tissue MeHg concentrations and improve water quality and habitat functions throughout the South River and SFS River	Mercury concentrations in biological tissues and physical media, and bank and in-channel habitat metrics

Notes:

SFS: South Fork Shenandoah

MeHg: methylmercury

Table 2
Short-Term Monitoring Scope Summary
AOC 4 Monitoring Program Briefing Paper
South River and a Segment of the South Fork Shenandoah River

Short-Term Remedial Action Objectives				Monitoring Plan Designs			Adaptive Management Outcomes	
General Objective	Performance Objective	Measurable Metric	Preliminary Success Criteria	General Station Locations	Monitoring Frequency	Analytical Parameters	Contingency Actions	Decision Analysis
Reduce Mercury Transport and Exposure	Increase in Bank Stability	Topography	Reduced Annual Erosion Rate	Shore Based LiDAR Surveys Conducted at Each BMA	Annually for First 3 Years; Post-storm	Average Annual Erosion Rate	Structural and/or Vegetative Stabilization	Refine Effectiveness Estimates
		Vegetation	>80% Cover; <10% Invasives	Vegetation Plots at Each BMA	Annually for First 3 Years; Post-storm	Cover and Species Composition	Additional Vegetation Enhancement	Refine Effectiveness Estimates
		Design and Implementation	Landowner Approvals and Permits	BMA Properties	NA	NA	NA	Refine Implementation Estimates
	Reduce Mercury Loading from Bank	Surface Sediment	>75% Mercury Concentration Reduction	Downstream of Representative BMAs (Nearshore)	Twice Annually for First 3 Years	IHg and MeHg Concentrations	NA	Refine Effectiveness Estimates
		Periphyton	>75% Mercury Concentration Reduction	Downstream of Representative BMAs (Nearshore)	Twice Annually for First 3 Years	IHg and MeHg Concentrations	NA	Refine Effectiveness Estimates
		Asiatic Clam Sampling	>75% Mercury Concentration Reduction	Downstream of Representative BMAs (Nearshore)	Twice Annually for First 3 Years	IHg and MeHg Concentrations	NA	Refine Effectiveness Estimates
	Reduce In-Channel Mercury Exposure	Periphyton	>50% Mercury Concentration Reduction ^a	Downstream of Representative BMAs (Channel)	Annually for First 10 Years	IHg and MeHg Concentrations	NA	Refine CSM
		Asiatic Clam Sampling	>50% Mercury Concentration Reduction ^a	Downstream of Representative BMAs (Channel)	Annually for First 10 Years	IHg and MeHg Concentrations	NA	Refine CSM
Maintain or Improve Riparian and Aquatic Habitat	Improve Bank Vegetation	Vegetation	>80% Cover; <10% Invasives	Vegetation Plots at Each BMA	Annually for First 3 Years	Cover and Species Composition	Additional Vegetation Enhancement	Refine Effectiveness Estimates
	Improve In-Stream Habitat	Rapid Bioassessment Protocols	Visual Stream Classification	Downstream of Representative BMAs	Quarterly for the First Year and Semi Annually (Q1/Q3) for years 2-10	Rapid Bioassessment Protocol Scores	NA	Refine Effectiveness Estimates

Notes:

NA - Not applicable

IHg - Inorganic Mercury

MeHg - MethylMercury

CSM - Conceptual Site Model

BMA - Bank Management Area

a, May be applicable for long-term evaluations rather than for short-term evaluations.

Table 3
Long-Term Monitoring Scope Summary
AOC 4 Monitoring Program Briefing Paper
South River and a Segment of the South Fork Shenandoah River

Monitoring Element	Objective	Measurements	Proposed Sampling Frequency	Samples per Location	Locations
Monitor Potential Human Exposure					
Largemouth Bass Smallmouth Bass	- Monitor trends in human exposure to MeHg in adult fish - Develop non-lethal mercury monitoring techniques for the South River	- THg and MeHg in filets and biopsy plugs - Total length, weight	Twice annually (May and October)	10 bass (SMB and LMB)	South River: RRM -2.7* RRM 0.1 to 2.3 RRM 5.2 to 11.8 RRM 16 to 23.5
Snapping turtle ¹	Monitor trends in human exposure to MeHg in snapping turtles	- THg and MeHg in turtle blood or nail tissue² - Total length, weight	Once annually (May-July)	3	SFS: Lynwood, VA near Rt. 708 bridge (RRM 26) Shenandoah, VA boat ramp (RRM 48) Newport Landing (RRM 63) Hamburg, VA near Rt. 211 bridge (RRM 72) Fosters Landing near Rt. 684 bridge (RRM 89) Bentonville Landing near Rt. 613 bridge (RRM 106)
Mallard duck ¹	Monitor trends in human exposure to MeHg in mallard ducks	- THg and MeHg in breast muscle tissue - Sex, reproductive status - Length, weight	Once annually [October - January (waterfowl hunting season)]	3	Karo Landing (RRM 115) Shenandoah River: Rt. 17/50 bridge (RRM 143) Berryville, VA near Rt. 7 bridge (RRM 158)
Community outreach	Monitor trends in human exposure to mercury, including adherence to the fish consumption advisory	- Outreach to non-English-speaking communities (e.g., the Promotores de Salud program and outreach to other non-English language groups) - Physician and clinic newsletters - Angler surveys	- Annual outreach to non-English speaking groups, local physicians, and health clinics - Once every 3 years for the angler survey	NA	Focused on Waynesboro, but also including the downstream locales of Dooms, Crimora and Grottoes. Also dependent on locations of local/state health clinics.
Monitor Ecological Exposure					
Aquatic					
YOY fish	- Monitor exposure of YOY fish to MeHg in water and dietary items - Monitor exposure of ecological receptors (e.g., piscivorous birds) to MeHg in YOY fish - Document potential declines in exposure due to remediation	THg and MeHg in whole fish	Once annually (August - October)	10	RRM -2.7* RRM 0.1 to 2.3 RRM 5.2 to 11.8 RRM 16 to 23.5 SFS near Lynwood, VA (RRM 26) SFS near Shenandoah, VA (RRM 48)
Sediment	- Monitor exposure of invertebrates to sediment MeHg - Monitor natural recovery of sediment	THg and MeHg in sediment collected from coarse grained beds	Once annually (May)	3	RRM -2.7* RRM 0.1 RRM 3.5 RRM 11.8 RRM 23.5 SFS near Lynwood, VA (RRM 26) SFS near Shenandoah, VA (RRM 48)
Benthic invertebrates	- Monitor exposure to invertivorous ecological receptors (e.g., YOY fish) - Monitor responses to decreasing mercury loads	Tissue THg, MeHg in Mayfly tissue	Twice annually (May and October)	3	
Periphyton	- Monitor THg and MeHg in periphyton, which is an important exposure medium for benthic invertebrates - Provide a data set for comparison with short-term monitoring elements	THg and MeHg in periphyton	Twice annually (May and October)	3	
Asiatic clam tissue	Provide a data set for comparison with short-term monitoring elements	Tissue THg, MeHg in asiatic clam tissue	Twice annually (May and October)	3	
Terrestrial					
Adult Carolina Wren	Monitor songbird exposure to MeHg	- THg in blood - Weight	Once annually (June - July)	3-8 individuals	South River (Reference): Waynesboro Nursery (RRM -6.2)* Ridgeview Park (RRM -1.2)*
Wolf Spiders (family Lycosidae)	- Monitor exposure of terrestrial ecological receptors to MeHg in spiders - Monitor MeHg transfer between aqueous and terrestrial compartment of the South River	- THg and MeHg in spiders - Size	Once annually (June - July)	5 individuals	South River: RRM 0.1 to 2.3 Wertman Property (RRM 9) Grottoes City Park (RRM 22)
Earthworms	- Monitor exposure of terrestrial ecological receptors to MeHg in earthworms - Monitor potential terrestrial MeHg bioaccumulation	THg and MeHg in earthworm tissue and soil	Once annually (June - July)	3 composite samples	SFS: Power Dam (RRM 31) Shuller's Island (RRM 50) Long Bend Farm (RRM 66) Bealer's Ferry (RRM 85)
Water Quality and Habitat Quality Monitoring					
Water quality**	- Monitor trends in water quality - Provide information on inter-annual - Continue to describe behavior of mercury species in South River	Surface water: THg, MeHg**, TSS, TOC, DOC, water quality parameters (T, pH, DO, conductivity), and nutrients (Phosphorous)*	Monthly**	1 to 2**	South River: RRM -2.7* RRM 0.2 RRM 2.3 RRM 5.2 RRM 9.9 RRM 16.5 RRM 23.5
Benthic invertebrate Community	Monitor improvements to benthic community and benthic habitat	Benthic community (300 count subsampling)	Twice per year	6	RRM -2.7* RRM 0.1 RRM 3.5
		Substrate condition	Once per year	--	RRM 11.8 RRM 23.5 Middle River*

Notes:

DO: dissolved oxygen; DOC: dissolved organic carbon; MeHg: methylmercury; RRM: relative river mile; SFS: South Fork Shenandoah River; T: temperature; THg: total mercury; TOC: total organic carbon; TSS: total suspended solids; YOY: Young-of-Year; LMB: Largemouth bass; SMB: Smallmouth bass

* Reference area

** Sampling conducted in concert with VADEQ routine monitoring; as a result, some parameters are analyzed on a different frequency or for different numbers of replicates

1, Final determination of which additional species, if any, that will be monitored will be made in collaboration with VDH and the regulatory agencies

2, Data have shown good correlation between Hg in muscle and Hg in blood and nails; thus, non-lethal methods will be employed where possible

NA, Not applicable

AOC 4 RFI Report: Technical Briefing Paper

This briefing paper summarizes the findings of the Resource Conservation and Recovery Act (RCRA) Facility Investigation Report (RFI Report) for the Area of Concern (AOC) 4. It provides an introduction, summary of results and investigations, and a description of the anticipated future course of action. The information reviewed and presented herein is not comprehensive; additional details are provided in the AOC 4 RFI Report (URS, 2014).

Introduction

The AOC 4 RFI Report documents the results of a number of investigative activities conducted to characterize the nature and extent of mercury in environmental media in an off-site portion (AOC 4) of the former E.I. du Pont de Nemours and Company (DuPont) Plant (the site), in Waynesboro, Virginia. It was prepared pursuant to a modification to permit VAD003114832, and issued to DuPont by the Commonwealth of Virginia, Department of Environment Quality (VDEQ) in February 2014 under the corrective action provision of RCRA.

References

- ✓ Anchor QEA, LLC and URS Corporation. 2013. Remediation Proposal South River and a Segment of the South Fork Shenandoah River, Virginia. October 2013.
 - ✓ Anchor QEA, LLC and URS Corporation. 2014. Phase 1 Interim Measures Design, Implementation and Monitoring Work Plan. Area of Concern 4. Former DuPont Waynesboro Site.
 - ✓ URS Corporation. 2012. Final Report: Ecological Study of the South River and a Segment of the South Fork Shenandoah River, Virginia. September 2012.
 - ✓ URS Corporation. 2014. RCRA Facility Investigation (RFI) Report Former DuPont Waynesboro site, Area of Concern (AOC) 4, South River and a Segment of the South Fork Shenandoah River, Virginia. August 15, 2014. Submitted to VDEQ.
 - ✓ VDEQ. 2009. Bacteria and Benthic Total Maximum Daily Load Development for South River. Prepared by Engineering Concepts, Inc. July.
-

The AOC 4 RFI Report relies on data provided in the Ecological Study Report (URS, 2012) and the Remediation Proposal (Anchor QEA and URS, 2013) to document the nature, extent, fate, and transport of mercury that has historically migrated from the site into the surface water, sediments, floodplain soils, and biota within AOC 4. Both the Ecological Study Report and the Remediation Proposal were prepared pursuant to the June 2005 Consent Decree (CD) among DuPont, the Natural Resources Defense Council (NRDC), and the Sierra Club (Virginia Chapter).

Summary of Results and Investigations

DuPont and others have extensively investigated the physical, chemical, and biological components of off-site portions of the South River, SFS River, and associated floodplain areas within AOC 4. The Ecological Study Report (URS, 2013) integrated the findings of various studies and concluded that the largest mercury sources are river banks, outfalls from the former Waynesboro facility, and sediment, and they primarily occur in the first 12 river miles. Another important finding was that concentrations of total mercury (THg) in the riverbanks of the South River downstream of relative river mile (RRM) 12 and the upper segment of the SFS River are generally low, but biota inhabiting these areas such as birds and fish, have elevated mercury concentrations. The following paragraphs summarize the chemical/mass balance, physical/geomorphological, and biological characteristics of AOC 4. Also provided is a summary of the Mercury Conceptual

System Model that was developed as a framework to better understand linkages in the aquatic and terrestrial systems. Detailed information can be found in the RFI or source documents cited above.

Chemical/Mass Balance Characteristics

The concentrations of mercury in various media within AOC 4 have been documented through various studies that have occurred over the past two decades. Key findings from the studies are summarized below.

- ❑ ***Floodplain Soils:*** The concentrations of THg in floodplain soils decrease with increasing distance to the floodplain from the river and increasing distance downstream, but were highest in the two- and five-year floodplains and within forested areas. The majority (89%) of soil samples were below the human health screening level of 17 mg/kg.
- ❑ ***Bank Soils:*** A total of 207 river bank transects was sampled from RRM 0.1 to 23.5. The vertically averaged THg concentration in the river bank soils range from 1 to 140 mg/kg, and the maximum concentrations in discrete samples range from 3 to 515 mg/kg. Concentrations of THg vary spatially, but highest concentrations occur between RRM 0 and 11.6.
- ❑ ***Surface Water:*** Under baseline (or non-storm) conditions, the concentration of inorganic mercury (IHg) on particles in surface water generally increases immediately downstream of the outfall (at RRM 0) and reaches a maximum at RRM 5.2. Particulate IHg concentrations remain relatively constant until approximately RRM 12, then decrease.

MeHg concentrations in surface water were generally the highest between RRM 10 and 12, but the areas with the highest surface water MeHg concentrations were more widely dispersed. Surface water MeHg concentrations exhibit strong seasonality, generally increasing when surface water temperatures reach approximately 12 degrees Celsius (°C) and low flow conditions. Surface water MeHg loading is generally higher at temperatures greater than 12 °C compared to temperatures below 12 °C, suggesting a role of methylation at higher temperatures.

- ❑ ***In-Channel Sediment:*** Fine-grained sediment in the South River occurs primarily as channel margin deposits and as interstitial sediment within the coarser substrates of the streambed. THg concentrations were highly variable in the channel margin deposits. Higher concentrations were found at depth, buried below fine sediment with lower concentrations relative to subsurface sediments. THg concentrations in interstitial sediment generally increase between RRM 0 and 8.7 and decline farther downstream.
- ❑ ***Biological Tissues:*** Extensive sampling and analysis of biological tissues across the range of aquatic and terrestrial trophic levels has been performed in AOC 4.

Higher trophic levels tend to have higher concentrations (e.g., smallmouth bass). Areas with relatively high MeHg concentrations in environmental media (e.g., surface water) and biological tissue (e.g., fish) were observed at distances greater than approximately 12 miles from the site.

- ❑ **Mercury Mass Balance:** A present-day mass balance for mercury was developed for the first 10 river miles of the South River. Several different lines of evidence—including incremental loading rates and concentration gradients in surface water, sediment, and pore water—strongly suggest that non-channel (e.g., bank) sources of THg were primarily limited to the first 10 to 12 river miles of the South River. Additionally,
 - Eroding banks were the largest current single source of THg loading to RRM 0 to 10, accounting for 40 to 60% of the THg loading.
 - Site outfalls continue to be a source of mercury to the South River.
 - Although a relatively small source, in-channel sediments in RRM 0 to 12 are both a potential MeHg source to the South River and an exposure medium.

Physical/Geomorphological Characteristics

- ❑ **Sediment and Mercury Transport:** At RRM 0, the South River carries an estimated 54 to 92 metric tons of suspended sediment per year. As suspended sediment is transported downstream, an average of approximately 6% of the annual load is deposited per mile on the floodplain. In addition, approximately 3% of the annual sediment load is deposited as fine-grained sediment deposits in eddies and other low energy areas near the banks, such as behind large woody debris and other obstructions. Newly deposited sediment originates mostly from the eroded banks but also from re-suspended surficial sediments of fine-grained sediment deposits. Bank soil erosion is a relatively small portion of the total sediment budget, but is important for mercury transport.
- ❑ **In-Channel Bed Stability:** The South River bed is stable with no discernible scour. Approximately 80% of the stored sediment in gravel beds and interstices is estimated to be less than 50 years old and the median age of stored sediment is estimated to be about 32 years, indicating that the bed is relatively stable and that sediment residence time in the coarse-grained beds is on the order of a few decades.
- ❑ **Bank Erosion:** Bank erosion rates on the South River average approximately 4 cm/yr throughout the system. Present-day bank erosion rates tend to be higher near islands and at migrating bends.

Biological Conditions

The South River is a generally functional ecological system supporting diverse land types and biological communities. A number of studies on biological conditions are summarized below:

- ❑ **Benthic Community:** Benthic and epibenthic communities were found to be similar in the South River and reference areas based on several widely applied

metrics. These comparisons indicate that that mercury is not adversely affecting benthic community structure in AOC 4 relative to the reference areas.

- ❑ **Bank Habitat:** Riverbanks and the surrounding riparian zones also represent ecologically important habitats of the South River. These areas provide foraging, nesting/burrowing, and refugia opportunities for numerous species of songbirds, piscivorous birds, small mammals, and reptiles/amphibians. The extent and quality of bank and riparian habitats of the South River vary extensively with surrounding land use. For example, the first two miles of the river are mostly surrounded by a mixture of commercial, industrial, and residential land uses with minimal riparian habitats.

Mercury Conceptual System Models

DuPont and others have investigated the physical, chemical and biological components of off-site portions of the South River, SFS River, and associated floodplain areas. The legacy mercury issue at the site was discovered in 1976. A review of VDEQ monitoring data in 2000 showed that mercury remained elevated in the South River fish species, with potential implications for human and ecological exposure. After over three decades of investigation, mercury biomagnification in the aquatic and terrestrial food webs, rather than direct toxicity to existing ecological receptors, has been identified as the primary pathway of exposure within AOC 4. Figures 1 and 2 provide the mercury conceptual system models for AOC 4. These models describe the unique set of conditions within the South River aquatic system and terrestrial systems of AOC 4.

Future Course of Action in AOC 4

The findings summarized in the preceding sections formed the basis for the Remediation Proposal and the Phase 1 Interim Measures Design Implementation and Monitoring Plan (Anchor QEA and URS, 2013 and 2014). The remedy includes site-specific remedial action objectives (RAOs), and evaluates a range of bank remediation alternatives, first to be applied to the upper reach of the South River in a logical upstream-to-downstream implementation sequence. In addition to ongoing efforts to control limited on-site mercury releases, the primary recommended remedy for AOC 4 includes enhanced vegetative and structural stabilization of target banks to substantively reduce mercury loading to the South River and accelerate natural recovery processes within channel areas.

Given the complexity, extent, and the uncertainty of the system(s) involved, an Enhanced Adaptive Management (EAM) approach is proposed to address ongoing mercury exposures in AOC 4. SRST studies will also continue to provide information relevant to the RFI. In addition, the results of the proposed EAM process may warrant investigative work. Resulting additional information will be evaluated as part of the RCRA process. Proposed human and ecological exposure monitoring (short-term and long-term) plans will also generate environmental data used for hypothesis testing within the EAM approach to track potential system responses to remedial actions and effectively integrate lessons learned.

DuPont will also continue to work closely with the various state and federal governmental agencies to conduct education and other outreach efforts for the communities along the South River and SFS River (e.g., via continued collaboration with *Promotores de Salud*, a public health program for the Hispanic community).

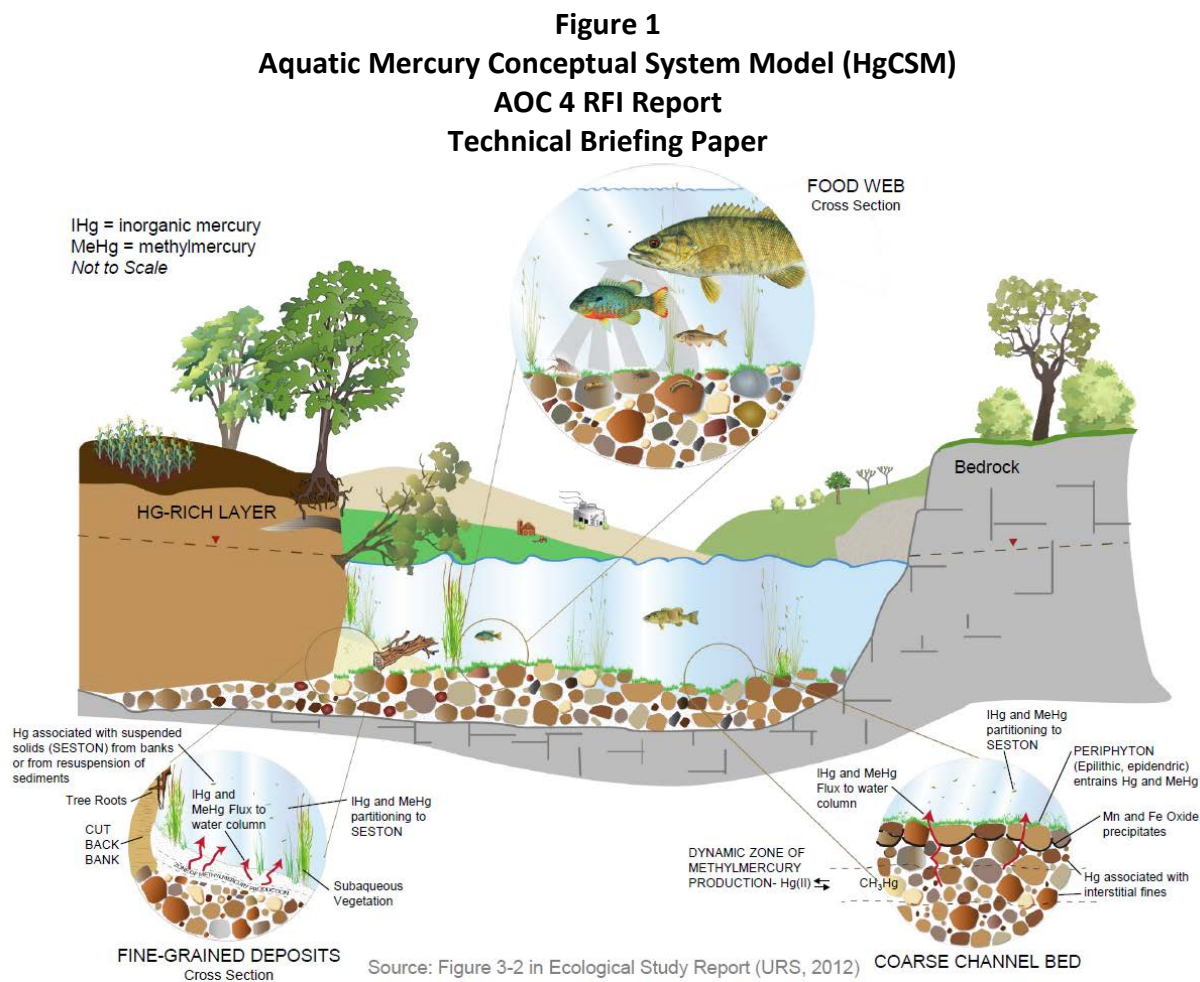
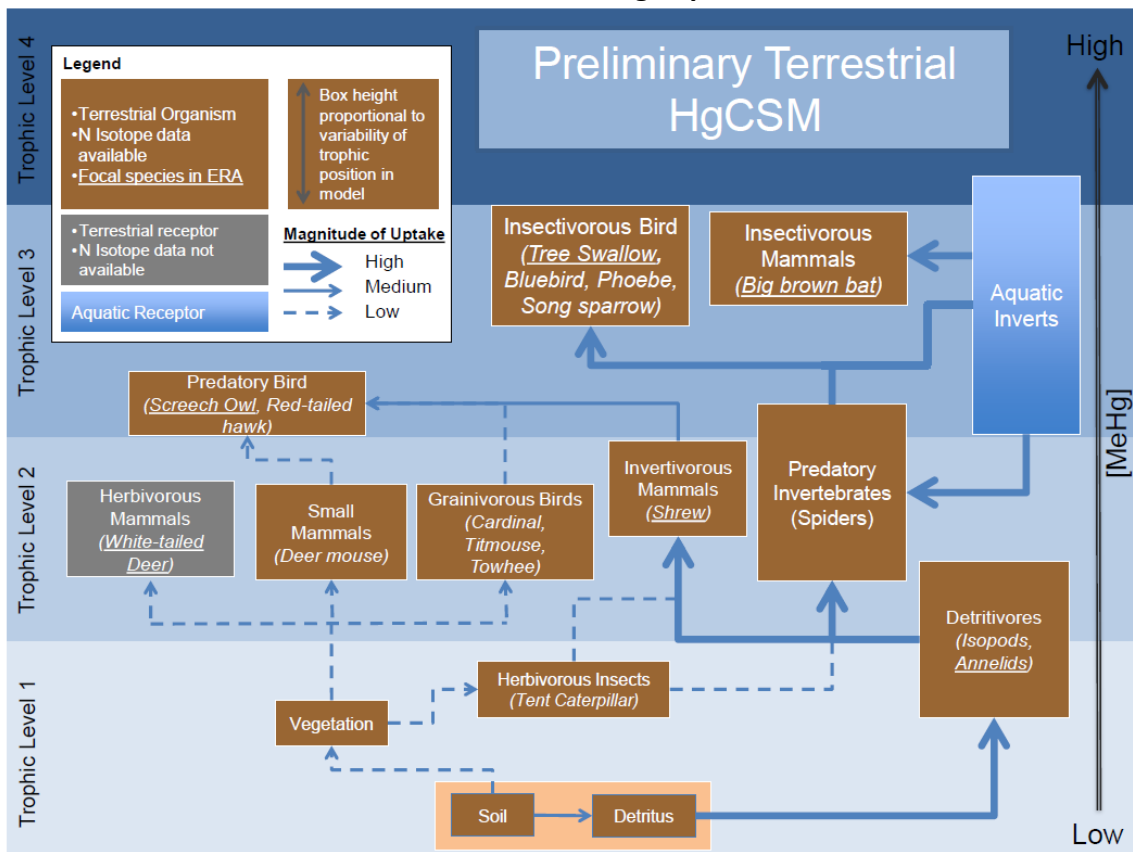


Figure 2
Terrestrial Mercury Conceptual System Model (HgCSM)
AOC 4 RFI Report
Technical Briefing Paper



Bank Stabilization Pilot Study: Technical Briefing Paper

This briefing paper summarizes key findings from performance monitoring studies conducted between 2010 and 2014 as part of the Bank Stabilization Pilot Study. Study findings resulting from the physical, chemical, and biological sampling efforts are summarized below. The information reviewed and presented herein are not comprehensive; additional details regarding the scope of work, methodologies, assessments, and conclusions are documented in URS (2012, 2011a, 2011b, and 2010) and Turner and Jensen (2008).

Introduction

In the fall of 2009, a section of stream bank (Pilot Site) along the South River in Waynesboro, Virginia was physically stabilized and re-planted with a native vegetative community to abate localized bank erosion. The bank stabilization pilot design incorporated three main components: 1. A rock toe at the base of the bank for slope protection; 2. Soil lifts to engineer a more stable and gradually sloping bank; and 3. Native vegetation on both the slope and top of the bank, providing further stability and habitat. The objective of the Bank Stabilization Pilot Study monitoring program is to assess whether control of mercury (Hg) loading to the water column and sediment from eroding bank soil will result in reductions of Hg concentrations in the aquatic environmental media (i.e., pore water, sediment, surface water, and biological tissue). Monitoring also included a geomorphic assessment based on cross sectional information, and plant stock survival, as well as an assessment of the re-established vegetative community. This briefing paper describes key findings of the physical, chemical and biological monitoring thru the 2014 annual monitoring event. Additional monitoring is scheduled for the fall of 2014.

References

- ✓ Bateman, J., 2009. Topographic As Built, South River Bank Stabilization. November 3, 2009
 - ✓ Barbour, M.T., J. Gerritsen, B.D. Snyder, and J.B. Stribling. 1999. Rapid Bioassessment Protocols for Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinvertebrates and Fish, Second Edition. EPA 841-B-99-002. U.S. Environmental Protection Agency; Office of Water, Washington, D.C.
 - ✓ Turner, R. and R. Jensen. 2008. Plant Reach Characterization; Results of 2006-2007 Investigations of Mercury in the South River at Waynesboro, Virginia. February.
 - ✓ URS. 2012. Memorandum: South River Pilot Bank Stabilization-3Q Monitoring Activities. October 5, 2012.
 - ✓ URS. 2011a. Memorandum: South River Pilot Bank Stabilization-Year-Two Update. September 30, 2011.
 - ✓ URS. 2011b. Monitoring Report: Year One South River Bank Stabilization Pilot Study. Waynesboro, Virginia. February 2011.
 - ✓ URS. 2010. Monitoring Work Plan-South River Bank Stabilization Pilot Study-Waynesboro, Virginia. Revised October 29, 2010.
-

Physical

Pre- and post-stabilization channel morphology monitoring was conducted by evaluating eight stream cross sections within the project area: two upstream of the Pilot Site, four within the Pilot Site area, and two downstream of the Pilot Site. Erosion monitoring was also conducted along both the stabilized and opposite banks utilizing erosion pins to determine erosion rates. Monitoring data collected to date demonstrate that the pilot bank has remained stable, withstanding a near 10-year recurrence storm event. However, minor changes to channel morphology within the wetted channel and opposing bank have occurred. These changes included deposition of coarse sand attributed to active bedload transport, and deposition occurring along the left bank upstream of the Pilot Site (Transect Up-3) where a historical side channel/floodplain bench is located. Additionally, mid-channel deposition of boulder material was documented, likely from movement of constructed launchable rock toe material at the Pilot

Site. Small, isolated areas of erosion have been documented along the first fiber encapsulated soil (FES) lift near the confluence of Rockfish Run. These areas are being closely monitored to identify conditions that may require corrective actions such as extensive undercutting and/or erosion.

Chemical

Sediment, pore water, and Asiatic clam (*Corbicula fluminea*) tissue samples were collected and analyzed to detect potential changes in mercury concentrations before and after stabilization.

Sediment

Collection of sediment samples associated with the Bank Stabilization Pilot Study monitoring occurred in 2008 as part of a near-bank characterization event, and in 2009 to provide pre-stabilization data. Post-stabilization monitoring included data collections in November 2009, June 2010, June 2011, March and June 2012, June 2013 and June 2014 (Table 1; Figure 1). Results of the sediment component of the monitoring program indicate the following:

- ❑ Total mercury (THg) concentrations in sediment collected post-stabilization are generally lower than concentrations of THg in pre-stabilization sediment samples (Table 1). THg reduction in nearbank sediment is thought to be a result of decreased erosion due to bank stabilization and partial capping through placement of the rock toe.
- ❑ Variability among post-stabilization near-bank THg concentrations has been reduced compared to pre-stabilization sampling events.
- ❑ Hg concentrations in fine-grained sediments accumulating within the rock toe reflect the concentration of Hg on solids within the water column.

Pore Water

Pore water samples associated with Bank Stabilization Pilot Study monitoring were collected in June, July, and August 2009 to provide pre-stabilization data. Post-stabilization data were collected annually in June from 2010 to 2014 (Table 2; Figure 2). The pore water component of the monitoring program indicates the following:

- ❑ Filtered inorganic mercury (FIHg) concentrations in pore water have generally declined on an average basis; however, these declines are not statistically significant due to the high variability observed in the area adjacent to the rock toe in the pre-stabilization data dataset (Table 2).
- ❑ Filtered methylmercury (FMeHg) concentrations in pore water are variable at the Pilot Site; however, a consistent decline has been documented over time (Table 2).

Asiatic Clam Tissue

Previous studies have demonstrated the utility of using transplanted Asiatic clams to measure mercury uptake; clams were deployed at the Pilot Site as part of the monitoring program using these same methods. To measure Hg uptake rates by Asiatic clams, tissue data were collected from seeded clams in 2009 (pre-stabilization), and 2010 through 2014 (post-stabilization) (Figure 3; Figure 4). The Asiatic clam tissue monitoring program indicates the following:

- ❑ Asiatic clam uptake data indicate significant decreases in IHg uptake in 2010 and increases in IHg uptake observed in 2011 and 2012 (Figure 4). These increases are thought to be related to increased IHg loading from the plant outfall associated with perturbations to the on-site sewer system during remedial activities. Significant decreases

in IHg uptake were observed in 2013; however, an increase in IHg uptake was observed in 2014 (Figure 4).

- ❑ No significant differences in MeHg concentrations over time were observed; however, higher concentrations in the near-bank area compared to mid-channel were identified (Figure 4).

Biological

Biological monitoring included an assessment of the vegetative community and a structural habitat quality assessment following USEPA Rapid Bioassessment Protocols.

Vegetative Community

Prior to construction, opportunistic species, including Grape vine (*Vitis* sp.), Virginia creeper (*Parthenocissus quinquefolia*) and Poison ivy (*Toxicodendron radicans*), dominated the Pilot Site vegetative community. Removal of these species occurred during construction, and they were replaced by a community of native grasses and trees post-stabilization. Results of post-stabilization vegetative community monitoring indicate the following:

- ❑ First year growth upstream and downstream of the Pilot Site reached 100% coverage, while maximum Pilot Site bank cover reached 70%. Additional plant stock that was planted at the Pilot Site in 2011 continues to thrive.
- ❑ Non-native species have become established along the Pilot Site, representing a considerable portion of the vegetative community.
- ❑ Natural recruitment of herbaceous and woody species, such as sycamore (*Platanus occidentalis*) and catalpa (*Catalpa speciosa*) saplings, have colonized the rock toe of the Pilot Site in a similar manner to naturally occurring gravel bar islands.

Habitat Quality

Habitat quality assessments were performed along the Pilot Site following USEPA Rapid Bioassessment Protocols (Barbour et al., 1999) in order to assess bank stability, vegetative protection, epifaunal substrate/available cover, embeddedness, and substrate characterization within the river channel. Results indicate the following:

- ❑ Baseline bank stability and vegetative protection within the Pilot Site were both suboptimal prior to stabilization.
- ❑ Immediately following construction, the Pilot Site bank was categorized as suboptimal or optimal in terms of stability, and poor or suboptimal in terms of vegetative protection. This assessment occurred shortly after construction, during the winter, prior to plant growth.
- ❑ Post-construction surveys in late spring 2010 identified that vegetative protection had returned to pre-construction levels of suboptimal.
- ❑ Surveys conducted through 2012 identified bank stability and vegetative protection as optimal. Epifaunal substrate/available cover and pool substrate characterization were both suboptimal, while embeddedness was optimal.
- ❑ Surveys conducted in 2013 identified an area at the edge of the bank where the geotextile fabric is visible. This area and the area along Rockfish Run is being closely monitored for potential changes that might impact the integrity of the bank stabilization.

- ❑ Surveys conducted in early 2014 documented a slight increase in exposed soils at the base of the first FES lift in isolated areas due to poor herbaceous vegetative cover. In subsequent surveys throughout the growing season, herbaceous vegetation colonized these areas further stabilizing these soils. Aquatic habitat continues to improve, as numerous fish species were documented utilizing the cover provided by the installed large woody debris.

Summary of Findings

A summary of findings from the Bank Stabilization Pilot Study monitoring program through the 2014 annual monitoring event are as follows:

- ❑ The stabilized bank has withstood a 10-year flood event, and exhibits signs of continued stability; however, minor changes in channel morphology are evident. These changes are most notably in the near bank area associated with the launchable toe, as well as in movement of fine sediments below the confluence of Rockfish Run associated with a historical snag being washed away during the 10-year flood event.
- ❑ Chemical monitoring suggests that on average, mercury concentrations in sediment and pore water have declined since stabilization, but that the high variance in the pre-stabilization data set prevents the detection of significant differences. The 2014 chemical monitoring data is relatively consistent; however a slight increase was observed in sediment data. Pore water concentrations continue to show substantial declines compared to data collected in previous years.
- ❑ Biological tissue data support an initial decrease in IHg in transplanted *Corbicula* following stabilization. An increase in IHg concentrations, however, was observed in 2011 and 2012, which is thought to be related to temporal perturbations to the system associated with remedial activities at the former DuPont plant site. A decrease in IHg and MeHg concentrations in transplanted *Corbicula* was observed in 2013; however a slight increase was documented in 2014. Concentrations of MeHg in near-bank *Corbicula* continue to be higher than those deployed in mid-channel environments.
- ❑ The vegetative community is well established and aids in stabilization of the Pilot Site.

Future events are likely to be integrated into the monitoring effort for the AOC 4 interim remedial measure.

Table 1
Mercury Concentrations in Sediment
Bank Stabilization Pilot Study
Technical Briefing Paper

Sample ID	Sediment Type	Sample Date	THg (mg/g)	Average THg (mg/kg)	Standard Deviation	Relative Standard Deviation
<i>Pre-Stabilization</i>						
T1	Interstitial	August 2008	54	19	24	128%
T3 T5			19			
T6			1.2			
C	Bulk	March 2009	2.4			
<i>Post-Stabilization</i>						
A	Interstitial	November 2009	0.4	0.43	0.15	34%
B			0.3			
C			0.6			
UP		June 2010	1.9	1.1	0.8	78%
A			1.6			
B			0.3			
C			0.4			
UP		June 2011	3.9	3.8	1.1	28%
A			2.6			
B			3.6			
C			5.2			
UP		March 2012	1.7	3.1	1.9	62%
A			2.2			
B			2.6			
C			6.0			
UP		June 2012	4.1	3.1	0.8	27%
A			2.1			
B			3.2			
C			3.1			
UP		June 2013	1.3	1.3	0.40	30%
A			1.1			
B			1.9			
C			1.0			
UP		June 2014	3.5	2.2	0.96	44%
A			1.6			
B			2.1			
C			1.5			

Notes:

Bank Stabilization occurred in Fall 2009

10-Yr Storm event occurred April 2010

Table 2
Pore Water FIHg and FMeHg Monitoring Summary
Bank Stabilization Pilot Study
Technical Briefing Paper

Sampling Date	Mean FIHg (ng/L)	FIHG Range (ng/L)	SD	Mean FMeHg (ng/L)	FMeHG Range (ng/L)	SD
June 2009	53	2.26 - 131	42	10	1.04 - 40.5	11
July 2009	51	5.23 - 292	83	3.9	0.36 - 14.4	4.0
August 2009	82	2.73 - 510	153	2.3	0.04 - 6.83	2.0
June 2010	27	2.94 - 176	48	4.4	0.14 - 20.9	6.6
June 2011	27	14.1 - 47.8	13	3.3	0.13 - 13.7	4.5
June 2012	25	5.37 - 32.7	9	3.4	1.1 - 7.18	2.0
June 2013	8.7	4.48 - 21.1	4	2.1	0.26 - 4.49	1.4
June 2014	8.5	5.43 - 13.5	2	2.0	0.35 - 3.69	0.97

Notes:

Bank stabilization activities occurred after the August 2009 sampling event

Samples were collected at transects A-C"

FIHg: Filtered inorganic mercury

FMeHg: Filtered methylmercury

SD: Standard deviation

10-Yr. Storm event occurred April 2010

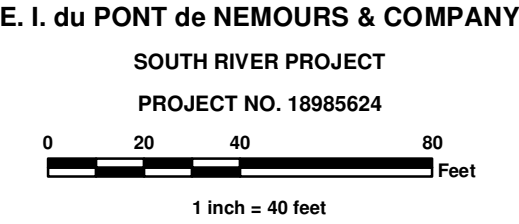
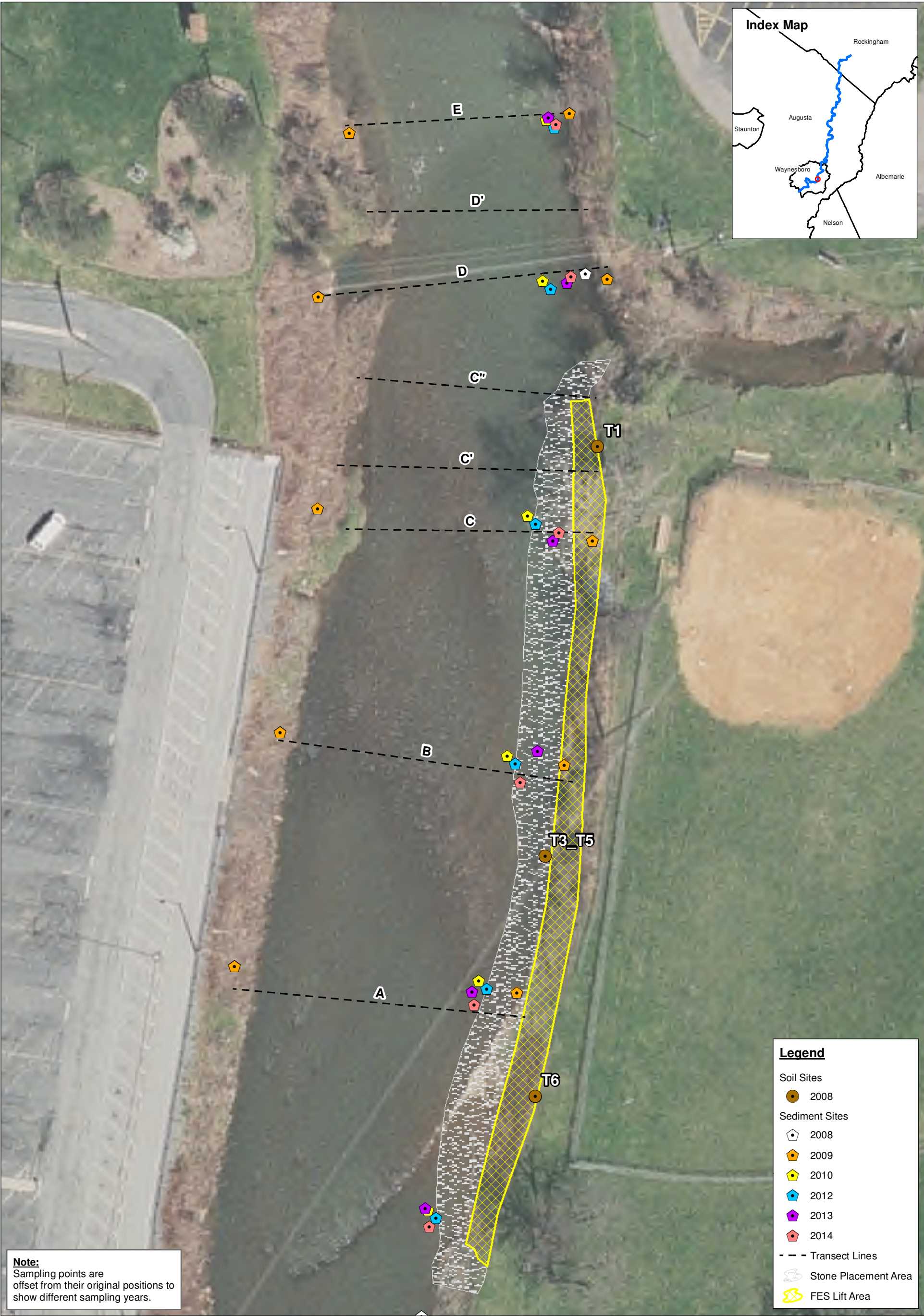
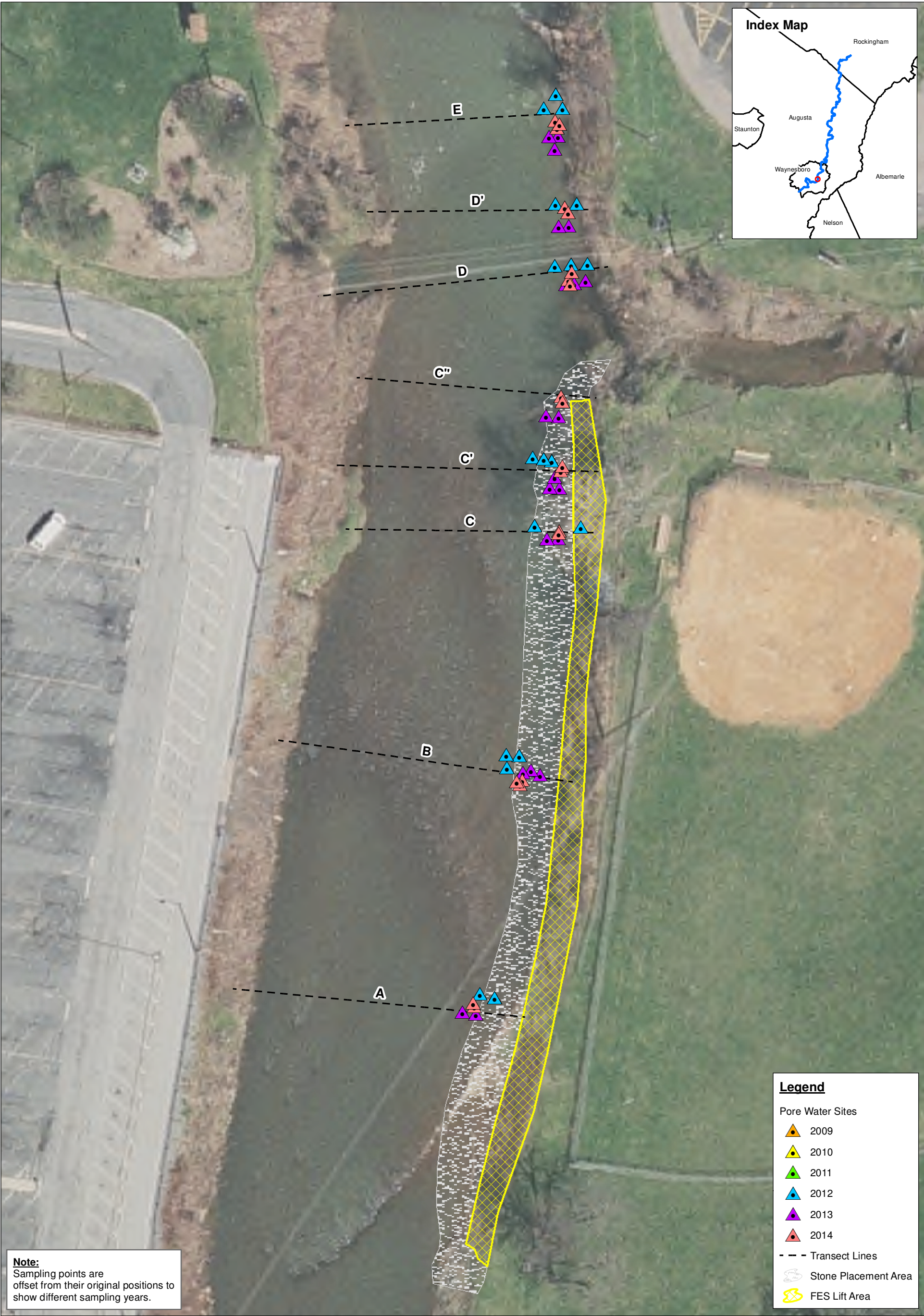


Figure 1
Sediment Sampling Locations
Bank Stabilization Pilot Study
Technical Briefing Paper

Source: Aerial Photography - SURDEX 2005



Note:
Sampling points are offset from their original positions to show different sampling years.

Legend

Pore Water Sites

- 2009
- 2010
- 2011
- 2012
- 2013
- 2014

- - - Transect Lines

Stone Placement Area

FES Lift Area



E. I. du PONT de NEMOURS & COMPANY

SOUTH RIVER PROJECT

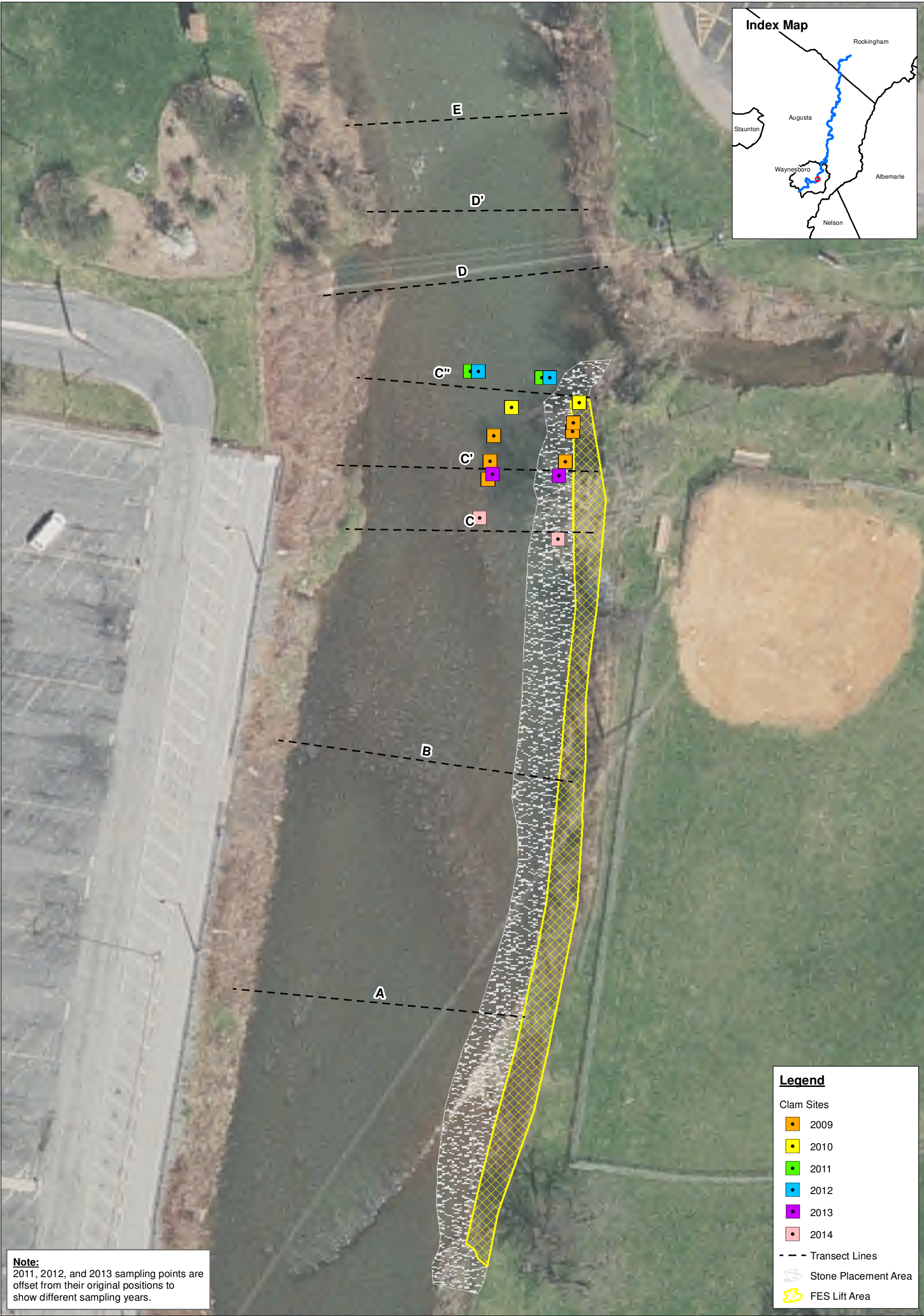
PROJECT NO. 18985624

0 20 40 80 Feet

1 inch = 40 feet

Figure 2
Pore Water Sampling Locations
Bank Stabilization Pilot Study
Technical Briefing Paper

Source: Aerial Photography - SURDEX 2005



E. I. du PONT de NEMOURS & COMPANY
SOUTH RIVER PROJECT
PROJECT NO. 18985624

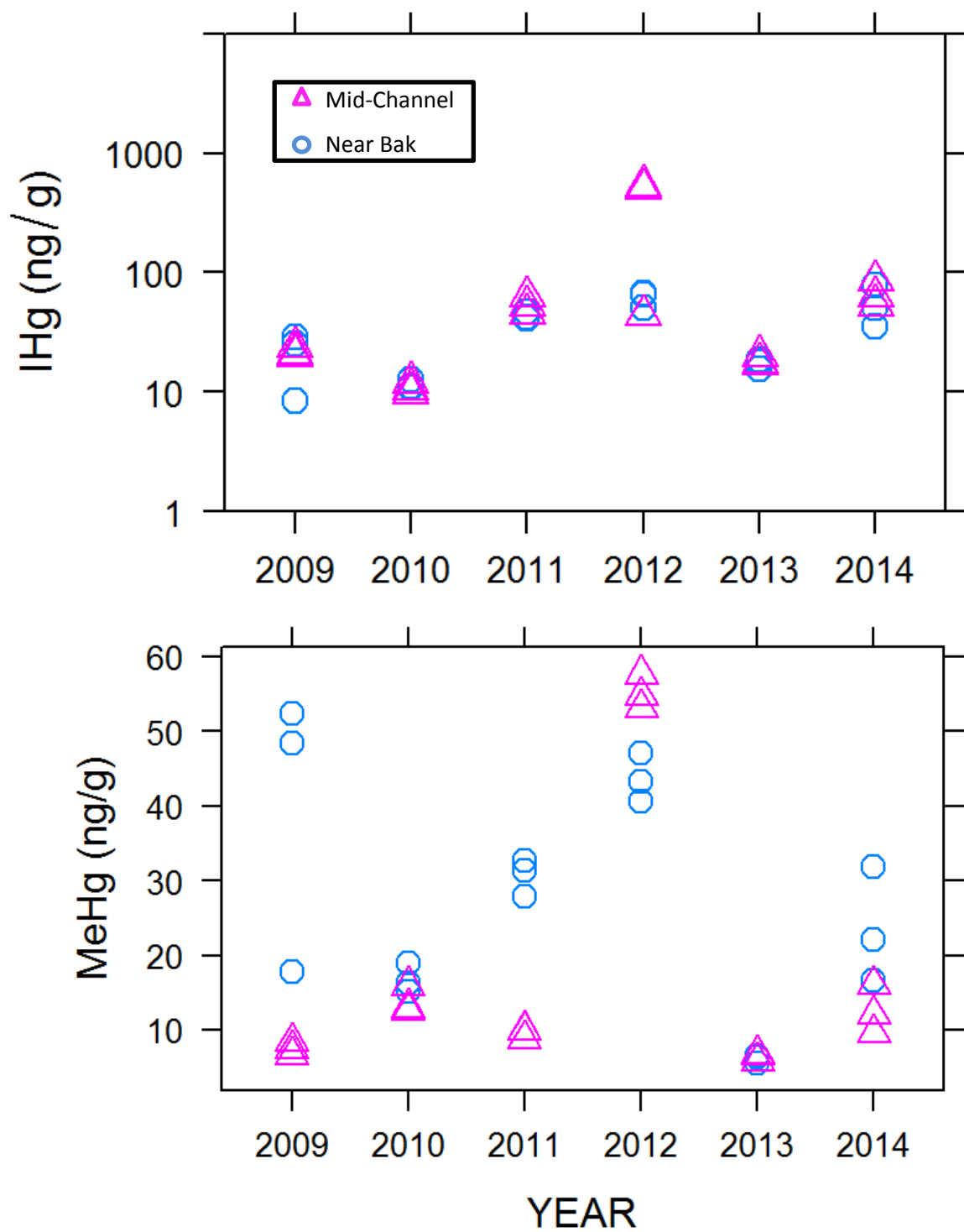
0 20 40 80 Feet

1 inch = 40 feet

Figure 3
Asiatic Clam Sampling Locations
Bank Stabilization Pilot Study
Technical Briefing Paper

Source: Aerial Photography - SURDEX 2005

Figure 4
 Asiatic Clam IHg and MeHg Uptake
 Bank Stabilization Pilot Study
 Technical Briefing Paper



Community Involvement Plan for AOC 4

This briefing paper summarizes the Community Involvement Plan for Area of Concern (AOC) 4, which includes the aquatic and riparian terrestrial systems of part of the South River downstream of the former DuPont Waynesboro facility and parts of the South Fork Shenandoah River. The Community Involvement Plan presents several traditional and innovative methods that will be used to inform and seek feedback from community stakeholders prior to and during remedial activities. Equally important, DuPont will continue its existing community involvement and outreach efforts to enhance the understanding and compliance with the fish consumption advisories. The plan will be revised as the project progresses and project needs change.

DuPont is committed to implementing remedial actions on the South River and South Fork Shenandoah River in a manner that protects human health and the environment. DuPont is equally committed to involving the public during the project. To achieve this goal, DuPont will provide (1) access to accurate, timely, and understandable information about the project as it progresses, (2) the opportunity for informed and meaningful participation, and (3) adequate time and opportunity for participation using the tools and activities listed below.

Tools	Activities
SRST Office	Remediation Advisory Panel (RAP)
UPDATE	Meetings with Landowners
Information Bulletin Boards at Fishing Access Areas	City of Waynesboro Meetings
SRST Website	Public Information Sessions
SRST Fact Sheets	SRST Meetings
Frequently Asked Questions Flyer	Promotores Program
Mailing Lists	Community Events
Telephone and Electronic Mail	School Outreach
	Media Briefings

Highlights of some of the new activities are as follows:

- ❑ **RAP**
The mission of the RAP is to facilitate communication and understanding between DuPont and community stakeholders about remedial efforts associated with mercury in the South River watershed so that DuPont gains input and insight from a diverse community audience and information about the project's progress and plans are disseminated broadly.
- ❑ **Meetings with Landowners**
For properties that will be impacted by remedial activities, DuPont will meet individually with each landowner prior to initiating pre-design efforts and twice more to provide the landowners with the final design package for approval prior to construction.
- ❑ **Public Information Sessions**
DuPont will hold an annual public meeting prior to the construction season each year to provide information about planned work along the river and other RCRA activities. These sessions will be designed to enable community stakeholders to ask questions in a comfortable and informal setting. The first public information session will be held in late 2015 or the spring of 2016 prior to the start of the first phase of bank stabilization construction. Per the RCRA permit, DuPont will hold a public information session in late October 2014.

Briefing Paper – DGT Monitoring of THg and MeHg in Porewater, South River VA

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Texas Tech University

Assessing Hg speciation taken up by DGT

The monitoring undertaken by the Reible group has focused on using diffusion gradient in thin film (DGT) devices to measure total mercury (THg) and methyl mercury (MeHg). These devices accumulate THg and MeHg onto a sorbing thiol-resin separated from the surrounding medium by a thin diffusion layer. The rate of uptake is dependent upon the rate of diffusion through this layer and the concentration of the species in the porespace of the surrounding medium. THg is generally associated with porewater ions including chloride and sulfides, dissolved organic matter or suspended particulate matter rather than freely dissolved. Work has been undertaken during 2014 to better understand which of these species pass the diffusion layer and are therefore measured by the DGT. It is believed that the biologically relevant mercury species are those that readily pass a cell wall and therefore potentially limited to molecular and nanometer sized complexes. The purpose of the DGT is to measure THg in these species rather than 100-450 nm colloidal and particulate associated Hg which would still be expected to pass a 0.45 μm filter that operational defines “dissolved Hg” by conventional water and porewater sampling. We undertook various experiments to demonstrate the ability of the DGT device to reject Hg associated with larger particles and to evaluate the uptake of Hg associated with dissolved organic matter.

The results of the studies are summarized in the two figures below. In the first, thiol resins of two particle sizes, 60 μm and 0.2 μm (200 nm), were used to evaluate particle rejection by the DGT gel. The Hg was expected to be strongly associated with these resins and if these particles are rejected by the diffusion gel, little or no Hg should be taken up by the DGT when exposed to aqueous solutions of these resins. This was observed with significant uptake from Hg in the absence of particles and essentially no detectable uptake (background uptake) in the presence of Hg associated with the 60 and 0.2 μm particles. Aggregation was noted with the 0.2 μm particles which may limit the ability to categorically state that a 0.2 μm does not pass the diffusion layer, but no evidence of uptake of particulate bound Hg was noted.

In the second of the two figures, Hg was exposed to different size fractions of natural organic matter (NOM) in aqueous solutions. The NOM solutions were prepared by wetting Suwanee River NOM and different size fractions were produced by sequential ultrafiltration. The largest size fraction would be expected to be of the order of 10 nm in size. Very little difference between uptake from solutions with no NOM and uptake with different NOM sizes was noted. This may also reflect the difficulties of separating the NOM due to NOM aggregation during ultrafiltration (i.e. small molecular weight NOM may have been retained on high molecular weight filters) or weak binding between Hg and the NOM. If NOM was not migrating through the DGT, however, a more significant reduction in Hg uptake would have been expected.

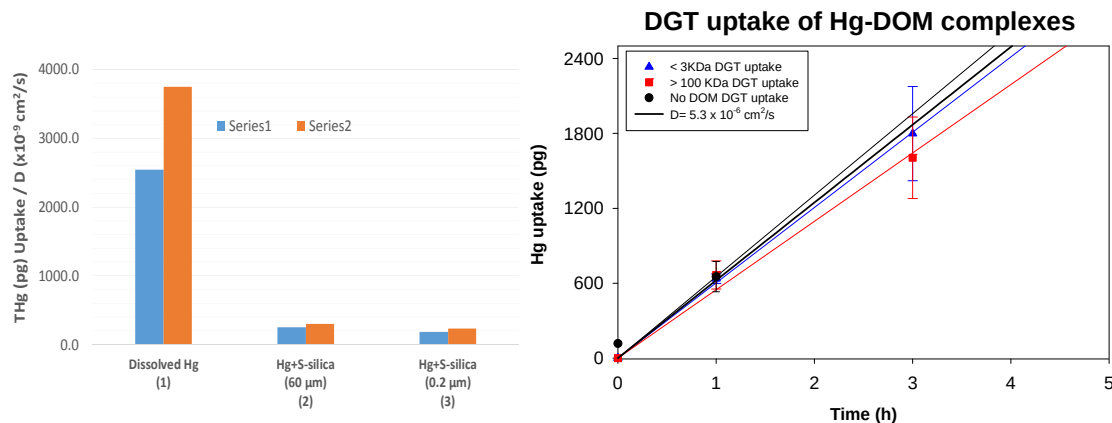


Figure 1 (a) Uptake from dissolved and particulate bound Hg and (b) uptake over time of dissolved and DOM associated Hg

As a result of the two experiments and other supporting information, it is believed that only freely associated Hg and Hg associated with molecular sized complexes (<10 nm) are believed to be taken up by the DGT. The DGT appears to successfully reject particulate bound Hg associated with colloidal particles that might pass a conventional filtration with 0.45 μm filters. This is consistent with the work of Fatin-Rouge et al. (2004) who demonstrated that aqueous agarose gels similar to that used for the diffusion layer do not allow appreciable diffusion of particles larger than around 50 nm.¹

As a result of the apparent rejection of particulate bound Hg, it is believed that the DGT provides a better indication of bioavailable Hg than filtered porewater samples. Hg associated with particles larger than 100 nm are unlikely to be biological relevant, at least by passive cell uptake processes. Preliminary experiments have in fact shown that the DGTs provide a better correlation with bioaccumulation in deposit feeding organisms than organic carbon normalized solid Hg concentration (see separate briefing paper Reactive Cap Assessment, South River, VA, Reible et al., 2014)

Summary of DGT monitoring in South River

DGT porewater measurements of THg and MeHg have been conducted since 2010. Monitoring has focused in surficial sediments at RRM 0.1, RRM 3.5 and RRM 11.8. Typically monitoring with both piston (approximately 0-2 cm) and depth profiling (0-10 cm) DGTs was conducted at locations near the bank (2-5 ft from the bank), in transitional sediments (5-15 ft from shore) and channel sediments (>15 ft from shore). At RRM 11.8, the near shore sediments were fine grained channel margin deposits while increasing coarse sand and gravel deposits were noted as you moved offshore. A similar trend was noted at RRM 3.5 although substantial amounts of sand and gravel was found at all sampling locations at that station. Fine sands were noted at RRM 0.1 at all sampling locations, likely the result of deposition from the adjacent runoff channel. Additional sampling was conducted at the bank-water interface at RRM 3.5 and 11.8 in 2013 and 2014 and at RRM 0.1 at the bank stabilization pilot in 2014.

Typical concentrations of THg as a function of depth at RRM 3.5 (left) and 11.8 (right) are shown in Figure 2. At RRM 11.8 peak concentrations were generally of the order of 1000 ng/L (ppt) or 1 μg/L of THg. At RRM 3.5 similar concentrations of THg were noted offshore in sand and gravel deposits but near the bank in this HRAD area, elevated THg concentrations were noted in the range of 1000-10,000 ng/L

¹ Fatin-Rouge et al., Biophysical Journal, 2004

or 1-10 $\mu\text{g/L}$. Sampling until 2010 was entirely during low river stage and flows (100-300 ft^3/sec) and the concentrations in Figure 2 are associated with these baseline flow conditions. In 2014, peepers were used as an independent measure of THg in porewater and also showed 1000-10,000 ng/L at the base of RRM 3.5 bank during these baseline flow conditions and serve as a confirmation of the DGT measurements.

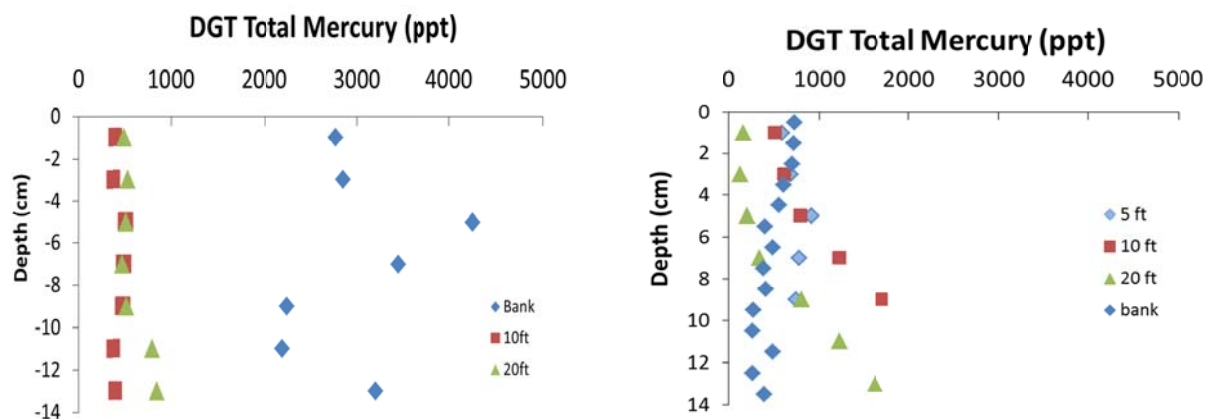


Figure 2 (a) THg in porewater under baseline flow conditions at RRM 43.5 and (b) THg in porewater under baseline flow conditions at RRM 11.8

MeHg concentrations in the near surface sediments under baseline conditions were typically 1-10 ng/L although 10-100 ng/L MeHg was noted in the fine grained channel margin deposits at RRM 11.8 and 50-300 ng/L was noted in the bank and near shore areas of RRM 3.5. The MeHg levels were typically less than 1% of the THg measured in the porewater at the same location which suggests that the system is not very productive relative to methylation. Typically, highly methylating sediments (e.g. organic rich salt marshes) exhibit porewater MeHg to THg levels of >10% (1-10% bulk solid basis).

In May 2013, sampling coincided with a declining stage after a storm related high flow event in the river. Peak river flows immediately before the beginning of sampling were in excess of 3000 ft^3/sec and declined during the 2 day sampling period to about 1000 ft^3/sec . THg concentrations in the riverbed and at the bank at RRM 11.9 were similar to that under baseline flow conditions. THg concentrations at the base of the bank at RRM 3.5, however, were significantly increased with peak concentrations of nearly 200,000 ng/L or 200 $\mu\text{g/L}$. During May of 2014, sampling was conducted both immediately before a storm event and during the declining stage after a storm event as shown in Figure 3.

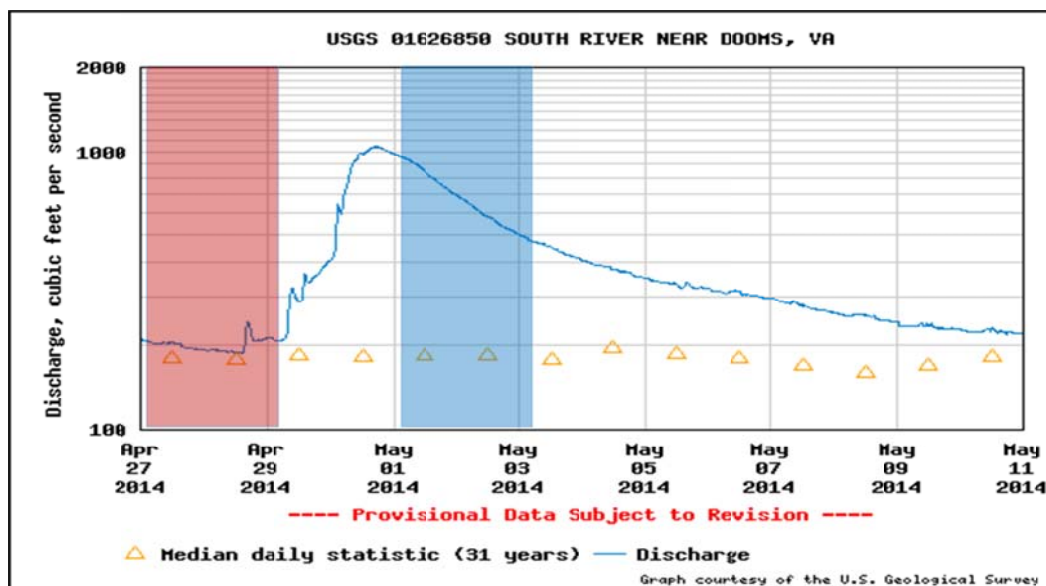


Figure 3 Sampling periods (shaded) and river hydrograph at Dooms, VA

The THg porewater concentration at the base of the bank during these two periods is shown in Figure 4 with the left hand figure showing typical baseline flow concentrations of <10,000 ng/L (<10 µg/L) THg and an order of magnitude higher concentrations at the same locations a few days later during the declining stage conditions.

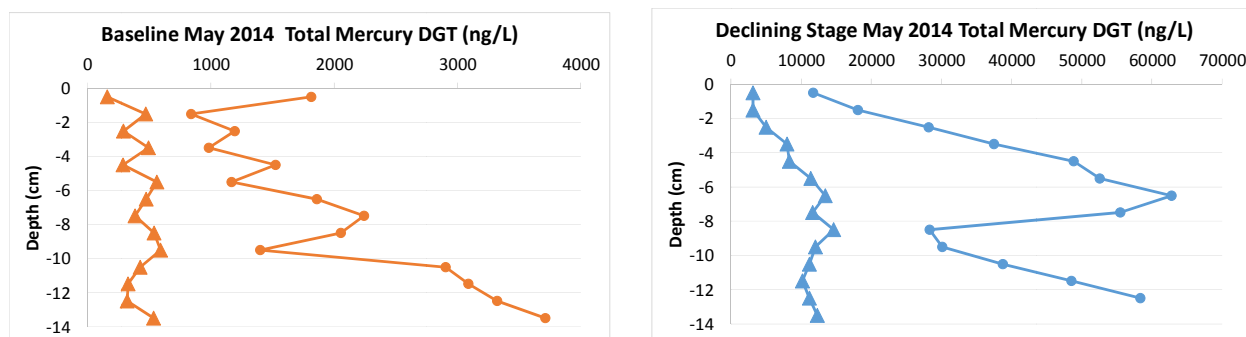


Figure 4 THg porewater concentration during the baseline (left) and declining stage (right) conditions of May 2014

The likely mechanism for this phenomena is the rapid rise of water into the RRM 3.5 bank sediments during periods of high water, wetting zones that had previously been unsaturated and oxic. Oxidic conditions lead to reduced amounts of THg in low solubility reduced phases and also typically leads to higher amounts of DOM due to great degradation of organic carbon. Both of these lead to the observation of greater amounts of THg in porewater per unit concentration in the bulk solids in oxic environments (i.e. a lower effective Hg partition coefficient). Once this area is inundated and begins to drain, the water returning to the river contains these elevated levels of THg. This is depicted in Figure 5. THg is released into the draining water and that water either returns to the river at the base of the bank or moves vertically down where it is diluted by the relatively rapid flushing of water in the sand-gravel zone at the base of the bank. Regardless of the flow movement, however, the THg released into the inundation water is carried into the river as the bank drains. The sampling wells in the bank soils at RRM 3.5 are believed to be largely connected to the relatively well flushed zone at the base of the bank

and this was borne out by simultaneous measurements of THg in the wells and in DGTs placed in the wells. These measurements were similar to each other but showed <100 ng/L THg compared to the >10,000 ng/L at the undiluted face of the bank. Well concentrations may also be lower than the seepage face as a result of lower soil Hg concentrations at those locations in the bank and thus lower concentrations in the draining water.

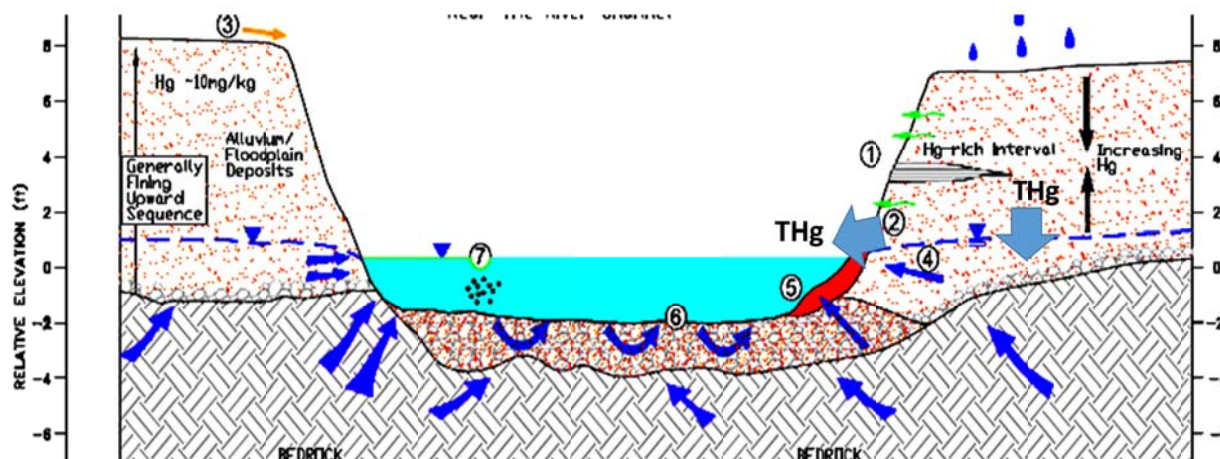


Figure 5 Conceptual model of THg release during bank drainage

During May 2014, the river stage during the storm event and presumably the resulting inundation of the bank, was approximately half as much as during the May 2013 monitoring event. As a result, the concentrations of THg in the bank seepage face peaked at approximately 60,000 ng/L (60 µg/L) during May 2014 compared to almost 200,000 ng/L (200 µg/L) during May 2013. This remains an order of magnitude higher than the typical 1-10 µg/L during baseline flow conditions.

Methyl mercury concentrations were also monitored at the base of the bank and are typically an order of magnitude *lower* during the bank drainage period. This is consistent with the conceptual model that the elevated THg is associated with drainage of oxic water from the bank and also consistent with voltammetry measurements at the bank-water interface that shows that oxygen is near saturation at all depths during the drainage cycle. These conditions would limit any methylation. During the baseline flows oxygen is observed in only the upper 1-2 cm at the bank-water interface and there is evidence of reduction deeper in the profile, leading to greater amounts of methylation.

Significant storm events followed by inundation and then drainage of the banks occur of the order of once per month in the South River and more often during certain times of the year. It is not known if there are other areas of the river giving rise to elevated THg releases during drainage cycles. During July 2014, additional DGT sampling was conducted at the bank stabilization pilot at RRM 0.1 and showed that at least during baseline flow conditions the concentrations of THg at the base of the bank are substantially lower (168 ng/L) than at RRM 3.5. Additional sampling should be conducted at the base of the stabilization pilot and at other potential HRAD locations during drainage cycles to assess the significance of this mechanism on mercury loading in the river. If this mechanism leads to substantial mercury loading elsewhere in the river, it may be appropriate to consider leachate control as part of the bank stabilization efforts. Potential approaches to manage leachate are under investigation in the reactive capping assessment (see separate briefing paper, Reactive Cap Assessment, South River, VA, Reible et al., 2014).

Ecological effects of biochar on stream benthic communities

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Background

Results of field experiments (e.g., Wertman Pond), streamside mesocosm studies and laboratory experiments conducted by DuPont, private subcontractors and University researchers have suggested that biochar is a cost-effective approach for reducing Hg bioavailability. Although numerous studies have been conducted to assess effects of biochar in soil ecosystems, our understanding of potential effects on aquatic ecosystems is greatly limited. Recent experiments conducted by Newman and colleagues (SRST Meeting, October 2013) compared effects of biochar and sedimite on detritus processing by freshwater amphipods. Results showed relatively little effects of biochar, but demonstrated significant reduction of detritus processing in containers containing sedimite. Oleszczuk et al. (2013) observed significant toxicity of several different types of biochar to aquatic organisms (*Daphnia magna*). Toxicity was closely associated with the levels of polycyclic aromatic hydrocarbons (PAHs), natural byproducts of the process used to produce biochar, which varied significantly among biochar types.

In addition to potential toxicological effects of biochar on aquatic organisms, physical effects associated with transport and deposition of these materials are also possible. Loss of interstitial habitat as a result of biochar deposition in stream substrate may influence several different macroinvertebrate groups. Because of variation in particle size of biochar, there is the potential that this material may affect several different groups of benthic macroinvertebrates. For example, filter-feeding organisms such as caddisflies, mayflies and some dipterans will likely be exposed to small biochar particles suspended in the water column. Deposition of small biochar particles to the streambed may affect food resources for grazing insects and collector-gatherers. Before sediment amendments such as biochar can be applied on a larger scale to a natural system such as the South River, it is critical that we understand the potential effects of these materials on stream communities. The community-level mesocosm experiments proposed here will assess potential effects of biochar on each of the major macroinvertebrate functional groups (filter-feeders, collector-gatherers, grazers, predators) present in stream ecosystems.

Objectives and hypotheses

The goal of this proposed research is to examine the potential effects of biochar on the structure and function of aquatic ecosystems. Experiments will be conducted with natural communities of macroinvertebrates exposed to biochar under controlled conditions in stream mesocosms and in the field. Specifically, we will test the hypothesis that exposure to biochar has effects on: survival and community composition of benthic macroinvertebrates, macroinvertebrate drift, immigration rate and community metabolism. Because potential effects are likely to vary with particle size, experiments will also investigate responses of aquatic communities to different size fractions of biochar.

Experimental Approach

The Stream Research Laboratory

Mesocosm experiments will be conducted at the Colorado State University Stream Research Laboratory (SRL), Fort Collins, CO. The SRL consists of 18 stream mesocosms (**Fig. 1**) housed in a greenhouse that receives natural water directly from a deep, mesotrophic reservoir. Water quality in the mesocosms is typical of mountain streams and was characterized by low water hardness (30-38 mg/L CaCO₃), alkalinity (25-29 mg/L CaCO₃) and dissolved organic carbon (2.5- 3.0 mg/L), cool temperature (12-16.6 °C), circumneutral pH (6.7-7.8) and low conductivity (57-89 µmhos). Current in the 20 L microcosms is provided by paddlewheels that maintain a constant current velocity of 0.45 m/s. Each flow-through stream receives water from a headbox at 1.0 L/min, resulting in a turnover time of approximately 20 min. Benthic communities will be collected using a technique that was developed in our laboratory and has been employed for over the past 25 years to assess ecological responses to a variety of anthropogenic stressors (Clements et al. 1988; Kashian et al. 2007; Clements et al. 2013). Briefly, benthic communities will be established on 10 x 10 x 6 cm trays filled with pebble and small cobble substrate placed in the field (**Fig. 1**). Our previous experiments have shown that benthic communities colonizing these trays are very similar to those collected from the natural substrate (Courtney and Clements 2000). After 30 d of colonization, the trays with their associated communities will be removed from the stream, transferred to the SRL and randomly assigned to biochar treatments.

Experimental Design

Mesocosm and field experiments will be conducted to assess the direct and indirect effects of biochar on macroinvertebrate communities. In the field experiment, we quantified macroinvertebrate colonization rates of substrate-filled trays containing biochar placed in small mesh bags. Mesh bags in control trays contained a similar size fraction of gravel. Replicate trays (n = 4) were sampled after 7, 17 and 30 days to test the hypothesis that the presence of biochar would reduce macroinvertebrate colonization.

Different size fractions of biochar may pose different risks to filter feeders, collectors, and grazers, the dominant macroinvertebrates in the South River. In the first mesocosm experiment, benthic communities were exposed to 2 size fractions of biochar during a 10 day period. The experiment consisted of 4 treatments (n = 4): control, large biochar (>1.0 mm), small biochar (<1.0 mm) and large + small biochar. Endpoints (see details below) included macroinvertebrate drift, community metabolism, immigration rate, survival and community composition. Routine physicochemical analyses were conducted throughout the experiment. This experiment is completed and samples are currently being processed. Preliminary analyses of these data indicate a potential effect of the small biochar treatment on community metabolism.

The second microcosm experiment was designed to compare the effects and effectiveness of biochar in the presence of a standard reference toxicant. We choose copper (Cu) for this experiment because it readily binds to biochar and because our previous mesocosm studies allow us to predict direct toxicological effects on benthic communities. This experiment consisted of 4 treatments (n = 4): control, Cu only (50 µg/L), biochar only and Cu + biochar. We predict that the Cu only treatments will reduce abundance of certain metal-sensitive groups (e.g., mayflies), whereas the toxic effects of Cu will be reduced in the Cu + biochar treatments. These experiments are currently underway.

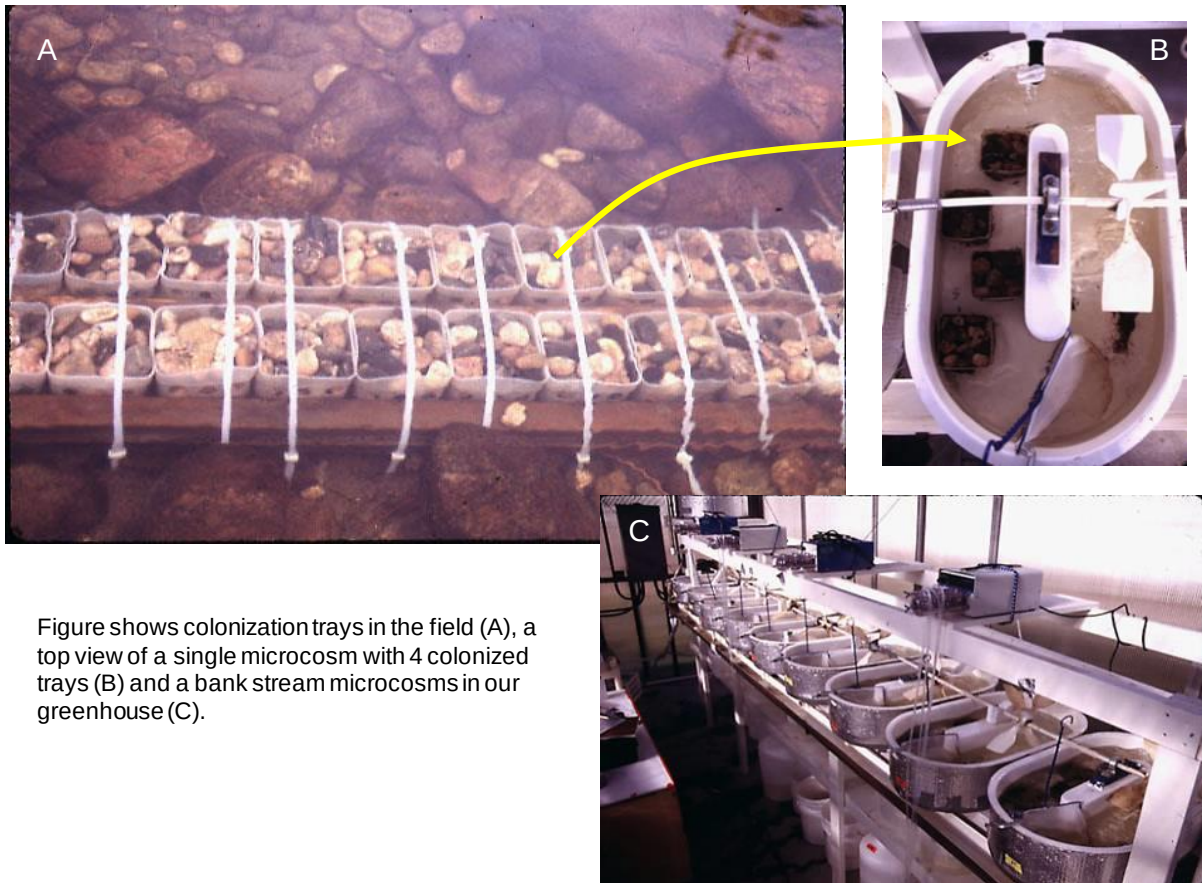


Figure shows colonization trays in the field (A), a top view of a single microcosm with 4 colonized trays (B) and a bank stream microcosms in our greenhouse (C).

Macroinvertebrate drift

We have previously shown that macroinvertebrate drift is highly sensitive to anthropogenic stressors in stream mesocosms (Kiffney et al. 1997; Clements 1999). Macroinvertebrate drift will be measured by placing a small net immediately downstream from the trays in each experimental stream. Organisms caught in the drift net will be removed from the stream and preserved in 80% ethanol.

Community metabolism

At the end of each mesocosm experiment net community metabolism (gross productivity – total respiration) will be determined using light and dark chambers. Two trays from each mesocosm will be removed and placed individually in either a transparent or an opaque 3.0-L airtight incubation chamber. Each chamber will be filled with mesocosm water and incubated in a water bath to maintain temperature. Community metabolism will be measured as a change in dissolved oxygen concentration in the overlying water in chambers after one-hour incubation.

Immigration rate

It is possible that the presence of biochar in natural substrate will reduce immigration and colonization rates of macroinvertebrates. We will assess the potential avoidance of biochar by measuring macroinvertebrate colonization of natural and biochar substrate in each mesocosm.

Trays (6 cm x 10 cm x 6cm) filled with either natural cobble substrate or substrate mixed with biochar will be placed downstream from the macroinvertebrate communities. At the end of the experiment trays will be removed and organisms will be preserved in 80% ethanol.

Survival and community composition

At the end of the experiment, the 4 trays from each stream mesocosm will be removed and organisms will be preserved in 80% ethanol for determination of effects on survival and community composition. In the laboratory organisms will be counted and identified to the lowest practical level of taxonomic resolution (genus and species for mayflies, stoneflies and caddisflies; tribe for chironomids). We will develop concentration-response relationships between levels of biochar and measures of macroinvertebrate abundance, richness and community composition.

Statistical analyses

All statistical analyses will be conducted using SAS (SAS Institute Inc., Cary, NC, USA). We will use general linear models (PROC GLM) to estimate effects of different size classes of biochar and to establish concentration-response relationships between biochar and benthic community responses (macroinvertebrate drift, community metabolism, immigration, survival). Multivariate analyses (PROC CANDISC) will be used to examine separation and overlap of benthic communities among treatments and to identify sensitive taxa.

Literature Cited

- Clements, W.H. 1999. Metal tolerance and predator-prey interactions in benthic macroinvertebrate stream communities. *Ecol. Appl.* 9:1073-1084.
- Clements, W.H., D.S. Cherry, and J. Cairns, Jr. 1988. The impact of heavy metals on macroinvertebrate communities: a comparison of observational and experimental results. *Can. J. Fish. Aquat. Sci.* 45:2017-2025.
- Clements, W.H., P. Cadmus, and S.F. Brinkman. 2013. Responses of aquatic insects to Cu and Zn in stream microcosms: understanding differences between single species tests and field responses. *Environ. Sci. Technol.* 47: 7506–7513
- Courtney, L.A. and W.H. Clements. 2000 Sensitivity to acidic pH in benthic invertebrate assemblages with different histories of metal exposure. *J. North Amer. Benthol. Soc.* 19:112-127.
- Kashian, D.R., R.E. Zuellig, K.A. Mitchell and W.H. Clements. 2007. The cost of tolerance: sensitivity of stream benthic communities to UV-B and metals. *Ecol. Appl.* 17: 365-375.
- Kiffney, P.M., E.E. Little, and W.H. Clements. 1997. Influence of ultraviolet-B radiation on the drift response of stream invertebrates. *Freshw. Biol.* 37: 485-492.
- Lehmann J., M. C. Rillig, J. Thies, C. A. Masiello, W.C. Hockaday, D.Crowley. 2011. Biochar effects on soil biota - A review. *Soil Biology & Biochem* 43: 1812-1836.
- Oleszczuk P., I. Joško, M. Kuśmierz. 2013. Biochar properties regarding to contaminants content and ecotoxicological assessment. *J. Hazard Mat* 260: 375-382.

Evaluating Mercury in Poultry from the South River Floodplain

Background and Objectives

In February 2001, DuPont, VADEQ, and US Environmental Protection Agency (EPA) agreed to voluntarily establish an interdisciplinary team of individuals from industry, government, citizens' groups, academic institutions, and private research to revisit the issue of mercury contamination and its consequences on the South River. This group is called the South River Science Team (SRST). An Exposure Task Team (ETT) of the South River Science Team (SRST) was formed in 2008. The key objectives of the team's efforts are to identify possible routes of human exposure to mercury in the South River watershed, define possible risks and uncertainties, and communicate that information to the public.

Specific Objective: To sample eggs, selected organs and muscle to determine the potential for chickens reared on the South River floodplain to accumulate mercury. The information will be used to inform decisions about exposure through potential food consumption of eggs and chickens reared on the floodplain.

As a first step, ETT first commissioned a literature review of studies that have evaluated mercury uptake in animal species (including both game and livestock). The results are reported in *Literature Review of Mercury Exposure in Animals* (URS, 2012). Several studies were reviewed regarding THg and MeHg concentrations in chicken meat and eggs exposed to mercury. Total mercury concentrations in chicken muscle were less than 4 ng THg/g in Poland (Falandysz (1991) and from poultry farms in Pakistan (Shah et al. 2010). Liver tissue tends to have higher mercury concentrations than muscle tissue or other organs (Shah et al. 2010). A study from Brazil reported higher levels (0.5-30 ng THg/g) in chicken meat (Batista et al. 2012); it is not known what accounts for regional differences in mercury levels in chicken meat. Kamamanoli-Dimou et al. (1989) reported that MeHg concentrations were <56 ng MeHg/g in chicken meat and eggs in Greece. Higher MeHg concentrations are detected in eggs due to their high lipid content, as was the case in two studies, which found that egg MeHg concentration ranged between 10 and 40 ng MeHg/g (Sell et al., 1975; Shafer et al., 1976).

A potential environmental factor affecting concentrations of mercury in eggs is free-range foraging due to the increased likelihood of soil ingestion. Numerous factors influence the amount soil ingestion in free range chickens including vegetative cover of the soil, number of chickens per unit area, time spent outside of the coop, and specific feeding practices (Waegeneers et al., 2009a). Van Overmeire et al., (2006) reported THg concentrations up to 4 times higher in free-range eggs (2 µg THg/kg) than commercial eggs (0.5 µg THg/kg). In a follow-up study, Waegeneers et al., (2009b) documented mean THg concentrations in eggs ranging 3.15 to 4.44 µg/kg in eggs from private free-range farms in Belgium. These concentrations are within the range of THg concentrations (1.3 – 4 µg THg/kg) reported in chicken eggs from three other European Union states; however, these studies do not differentiate between battery farm and free range eggs (Waegeneers, 2009a). There was no difference in mercury concentration in chicken meat between free-range and confined chickens (Batista et al. 2012).

For the South River, a survey of how poultry are raised and used on the floodplain was performed. While no commercial farming operations were observed, five (5) locations were

noted where chickens were raised on the floodplain to varying degrees. Based on this survey, it appears that current practice does not suggest a consumption concern since rearing of these animals are limited (between 6 and possibly 24 chickens) and the locations are in areas that have limited to no contamination.

However, since it is possible that chickens may be reared in a free range manner in the future, this study was designed to represent reasonable worst-case exposure of poultry raised on the floodplain (as described below).

General Approach

In evaluating potential exposure via consumption of poultry reared on the floodplain, a two-step approach will be used. First, samples will be collected from edible parts (including eggs) of chickens reared under reasonable worst case conditions on the South River Floodplain. Second, the results of the sampling along with conservative consumption assumptions will be used to determine potential human exposure to mercury from consumption of chicken that are reared in a free-ranged manner on the floodplain.

As a general approach, mature (i.e., of egg-laying age) birds of a common backyard breed are being reared in coops at the Augusta Forestry Center for a period of approximately 6 months. Eggs and muscle from birds are being sampled initially and at four other times over the six (6) months. Soils have been extensively sampled at the AFC and chickens have been placed in coops that allow them to forage in areas of contaminated soils in the 2-5 year floodplain (5-year floodplain) and in control areas (62 year floodplain) over the duration of the study. In addition, background samples of chicken muscle and eggs have been obtained from a local area farm (out of the contaminated area) and local area markets to provide context. Supplemental feed also was sampled to check that feed would not be a significant contributing source of mercury.

Samples are being analyzed for THg and MeHg by Brooks Rand, LLC, a NELAP-certified laboratory specializing in trace metal analysis of environmental samples, including animal tissue. Total mercury will be analyzed following the appendix to USEPA Method 1631 (USEPA 2001a), with a method detection limit of 0.04 ng/g in tissue samples. Methylmercury is analyzed following USEPA Method 1630 (USEPA 2001b), with detection limits of 0.07 ng/g in tissue samples. These limits fall below the ranges reported for tissue from poultry in the literature (URS, 2012).

The study is slated to conclude in late 2014 or early 2015. Limited data have been received from the analytical laboratory at this point in time. Modifications to the original study plan have also been made to account for predation of some chickens by a variety of predators.

References

Batista, B. L., Grotto, D., Carneiro, M. F. H., & Barbosa, F. (2012). Evaluation of the Concentration of Nonessential and Essential Elements in Chicken, Pork, and Beef Samples Produced in Brazil. *Journal of Toxicology and Environmental Health, Part A*, 75(21), 1269–1279.

Falandysz J. 1991. Manganese, copper, zinc, iron, cadmium, mercury and lead in muscle meat, liver and kidneys of poultry, rabbit and sheep slaughtered in the northern part of Poland. *Food Additives and Contaminants* 8(1):71-83.

Kambamanoli-Dimou A, Kilikidis S, Kamarianos A. 1989. Methylmercury concentrations in Broiler's meat and hen's meat and eggs. *Bulletin of Environmental Contamination and Toxicology*. 42(5):728-734.

Schafer ML, Rhea U, Campbell JE. 1976. Mercury in chicken eggs. *J Agric Food Chem* 24(5): 1078-81.

Sell JL, Deitz FD, Buchanan ML. 1975. Concentration of mercury in animal products and soils of North Dakota. *Arch Environ Contam Toxicol*. 3(3): 278-88.

Shah, A. Q., Kazi, T. G., Baig, J. A., Afridi, H. I., Kandhro, G. A., Khan, S., ... Wadhwa, S. K. (2010). Determination of total mercury in chicken feed, its translocation to different tissues of chicken and their manure using cold vapour atomic absorption spectrometer. *Food and Chemical Toxicology* 48(6), 1550–1554.

URS (in progress): Off-Site Human Health Risk Assessment Report for the South River Former DuPont Waynesboro Plant Waynesboro, Virginia

URS. 2012. Preliminary Draft - Literature Review of Mercury Exposure in Animals. South River Science Team Exposure Group.

USEPA. 2001a. Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation. Office of Water. EPA 821-R-01-013.

USEPA. 2001b. Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS, EPA 821-R-01-020.

Waegeneers, N., De Steur, H., De Temmerman, L., Van Steenwinkel, S., Gellynck, X., & Viaene, J. (2009a). Transfer of soil contaminants to home-produced eggs and preventive measures to reduce contamination. *Science of the Total Environment*, 407(15), 4438-4446.

Waegeneers, N., Hoenig, M., Goeyens, L., & De Temmerman, L. (2009b). Trace elements in home-produced eggs in Belgium: levels and spatiotemporal distribution. *Science of the Total Environment*, 407(15), 4397-4402.

Van Overmeire I, Pussemier L, Hanot V, De Temmerman L, Hoenig M, Goeyens L. 2006. Chemical contamination of free-range eggs from Belgium. *Food Addit Contam.* (11): 1109-22.

Evaluation of Potential Treatment Methods for Mercury-Bearing Riverbank Sediments and Soils from the South River, Virginia (USA)

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Waterloo, Ontario, Canada**

Introduction

The sediments and soils in the South River watershed contain elevated concentrations of mercury (Hg) which can be released to the local ecosystem. Studies were conducted at the University of Waterloo to evaluate the effectiveness of passive treatment methods for controlling the release and biological uptake of Hg. The goal of the studies was to evaluate the effectiveness of reactive media to remove or stabilize both dissolved and particulate Hg. The reactive media included in the studies are biochar-based materials, common adsorbents, and other reagents. After initially screening materials for control of inorganic Hg, more detailed studies were conducted to evaluate Hg removal under dynamic flow conditions, potential formation of methyl Hg (MeHg) during treatment, and removal of Hg over longer time frames.

Sample Locations

Sediment and soil samples selected for evaluation were collected from the riverbank along the South River and within the floodplain (Figure 1). The treatment experiments focused on sediments and soils with elevated concentrations of Hg from locations RRM 0.1, RRM 1.6, RRM 1.65, RRM 3.5, and RRM 22.1.

Overview of Studies

Analyses were conducted to determine the concentrations and speciation of Hg, bulk chemistry and mineralogy and other chemical parameters for each sediment sample collected. Initial screening studies evaluated the potential for stabilizing Hg using a range of solid-phase reactive media. These studies involved combining reactive media with sediment or soils using batch style experiments, and monitoring the concentration of Hg after a limited mixing time. After the initial screening, more detailed studies were conducted to further evaluate the potential for sustained control of Hg. The studies were designed to answer a series of questions, including:

- a) Do concentrations of Hg decrease in aqueous solutions in contact with sediments that are amended with solid-phase reactive media relative to concentrations in unamended sediments?
- b) Does the addition of reactive media control both dissolved and colloidal forms of Hg?
- c) Does the addition of reactive media control Hg under dynamic flow conditions?
- d) Are the reactions promoted by amendments easily reversed if geochemical conditions change?
- e) Do the concentrations of MeHg decrease in systems containing reactive media?

f) As the reactive media age, are the reactions reversed, or methylation reactions promoted?

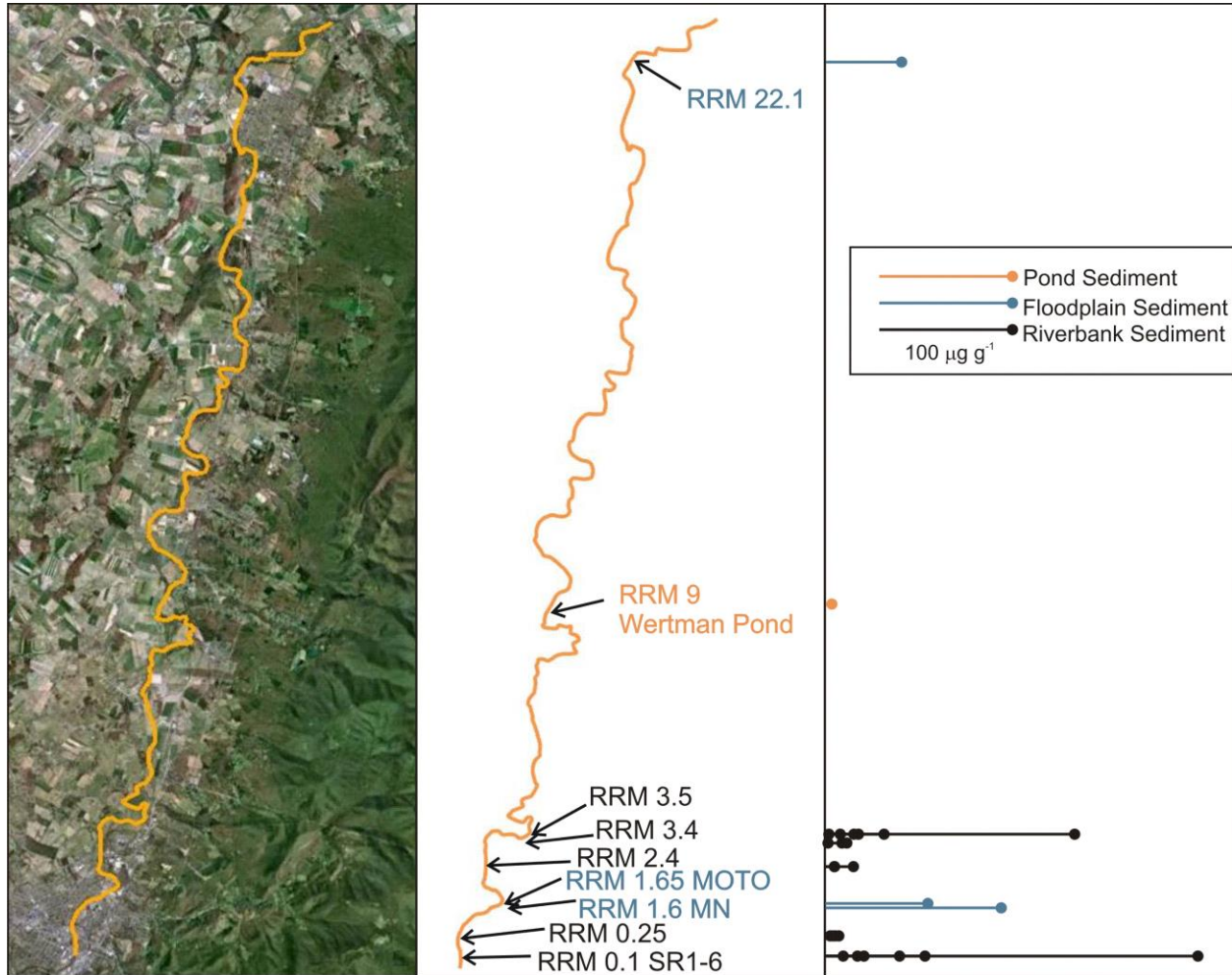


Figure 1. Map showing sampling locations, expressed as relative river mile (RRM) downstream from Hg source area, type of sample, and concentrations of total Hg expressed on a dry weight (d.w.) basis.

Experiments to Evaluate Hg Control through Addition of Reactive Media Amendments

Batch experiments were conducted to evaluate the change in Hg release from sediments in response to amendments with solid-phase reactive media. These experiments involved initially mixing South River water and sediment at a 4:1 ratio, followed by the addition of reactive amendments, either as single solids or as combinations of solids. The mixtures were allowed to equilibrate under stagnant conditions for 14 days. After equilibration, the mixtures were gently mixed, and the water sampled for filtered Hg and other geochemical parameters.

For the majority of the mixtures evaluated, the aqueous concentrations of Hg after the addition of reactive media were lower than those observed for the unamended sediment (data not shown). For the amendments which resulted in the greatest reductions in Hg, further testing was completed to evaluate the influence of adding different masses of reactive media to the sediment (Figure 2). For these tests, aqueous concentrations of Hg in contact with the sediments decreased

to values that were < 3% to up to 80% of concentrations observed for the unamended sediments (Figure 2). The greatest reductions in Hg concentrations were observed for attapulgite clay, organically modified clay, and most of the mixtures of zero-valent iron and elemental S. The reductions in Hg concentrations were slightly less for hardwood-based biochar (CL2- Cowboy Charcoal Biochar). The results suggest that, under stagnant conditions, reductions in aqueous Hg concentrations were observed for a range of amendments.

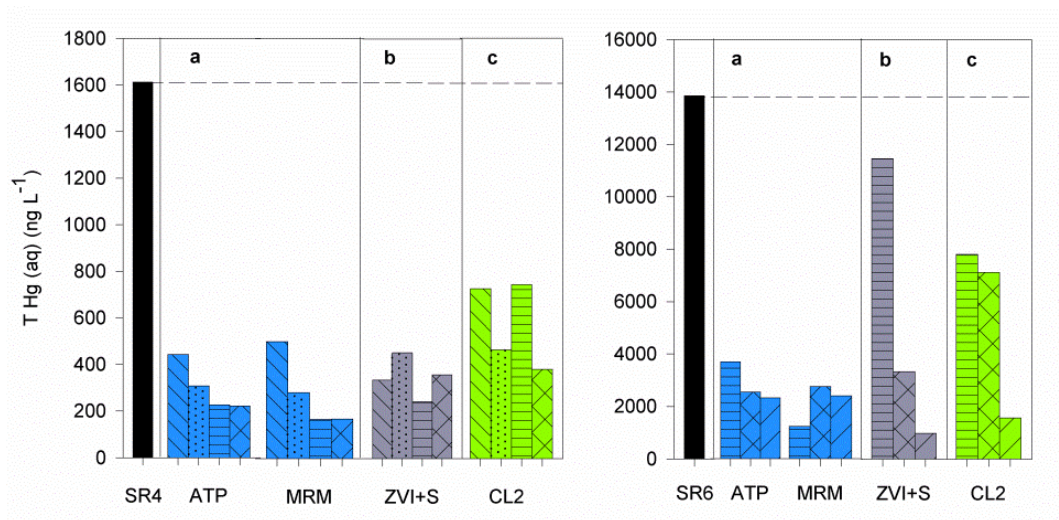


Figure 2. Concentrations of Hg after variable masses of reactive material were added to RRM 0.1 samples SR4 (a) and SR6 (b). Black bars indicate the initial Hg concentration without the addition of a reactive-amendment. Diagonal stripes from left-top to right-bottom represent 0.5%, dry weight (d.w.), dots represent 1% d.w., horizontal lines represent 2% d.w., criss-cross represents 5% d.w., and diagonal stripes from right-top to left-bottom represent 8% d.w. ATP=attapulgite clay; MRM = organically modified clay; ZVI = zero-valent iron; S=elemental sulfur; CL2= hard-wood based biochar.

Experiments to Evaluate Removal of Hg from Flowing Water

Experiments were conducted to evaluate the potential effectiveness of reactive media at removing discharged Hg under dynamic flow conditions. The experimental apparatus consisted of two columns connected in series; the purpose of column 1 was to simulate Hg leaching from Hg-bearing bank sediment using South River as an input solution and the second column was to remove Hg contained in the effluent of column 1 (Figure 3). Two sets of these combined experiments were conducted. The first columns in these sets contained sediment from RRM 0.1 (SR3 and SR6) and the second columns both contained a mixture of 50% hard-wood based biochar (CL2) and 50% Ottawa sand. This experimental design was selected to provide an indication of treatment effectiveness under continuous Hg loading under flow rates and solid-water ratios typical of field conditions.

The results of the experiments indicate that the total Hg concentrations released from both the SR3 and SR6 leaching columns gradually declined over time. The 0.45 μm filtered Hg declined from 1.8 to 0.3 $\mu\text{g L}^{-1}$ in the SR3 column effluent over 14 months and from 13 to 2.5 $\mu\text{g L}^{-1}$ in the SR6 column effluent over 7 months (Figure 4).

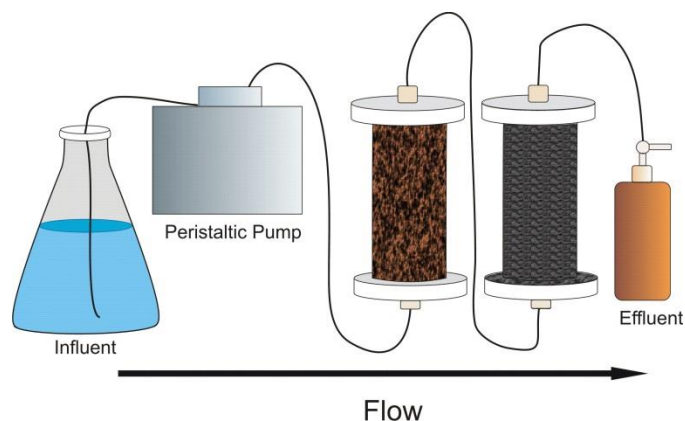


Figure 3. Schematic diagram showing experimental design: Effluent from the first column containing sediment is treated using reactive media in a second column connected in series to the first column. The influent was South River water.

The concentrations of Hg in effluent collected from the treatment column attached to the SR3 column were approximately 20 ng L^{-1} , representing $>98\%$ removal of Hg. The concentrations of Hg in effluent collected from the SR6 treatment column reached a maximum of 146 ng L^{-1} ; this reduction also represented $>98\%$ removal of Hg. The treatment effectiveness for these columns was sustained over many months of treatment.

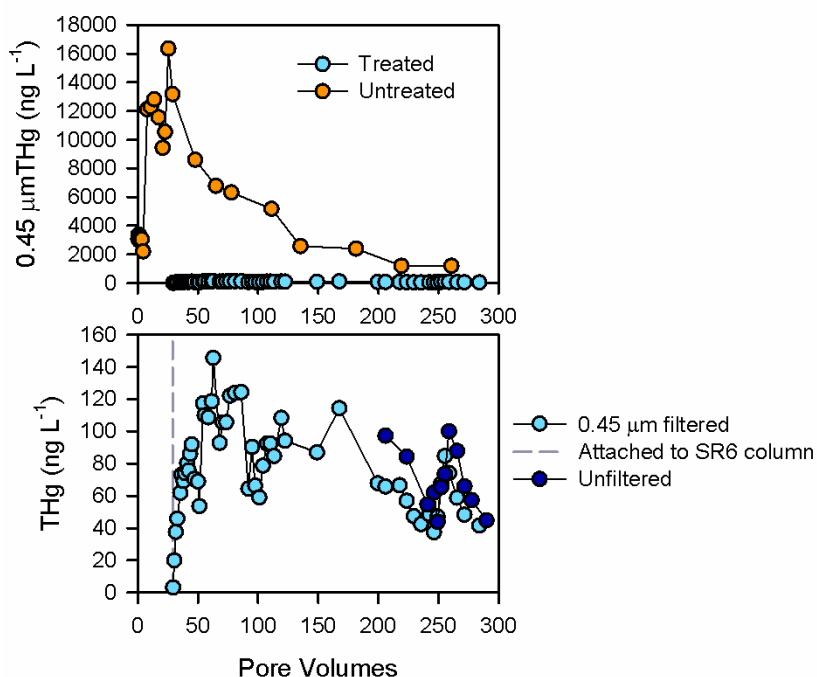


Figure 4. Comparison of Hg concentrations in the treated and untreated column effluent for SR6 sediment for $0.45 \mu\text{m}$ filtered and unfiltered samples over time. Top) Orange symbols show effluent Hg concentrations from the column containing sediment; blue symbols represent effluent from the treatment column. Bottom) Light blue symbols show Hg concentrations for filtered samples and dark blue symbols show the results for unfiltered samples. Note the expanded scale in the bottom diagram.

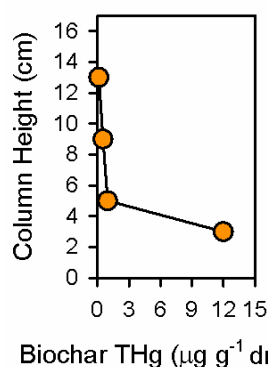


Figure 5. Concentrations of THg observed on the biochar solids after sectioning of the SR6 biochar treatment column.

After 314 pore volumes of flow (687 days), the biochar treatment column from the SR6 column was sectioned at 2 cm intervals and the solid biochar analysed for THg and MeHg. The greatest concentration of Hg on the biochar solids was observed on the first 2 cm of material, with a concentration of $12.0 \mu\text{g g}^{-1}$ (Figure 5). There was a rapid decline in THg concentrations from $12 \mu\text{g g}^{-1}$ to $0.97 \mu\text{g g}^{-1}$ by the next 2 cm interval, suggesting the majority of the aqueous Hg was effectively removed within the first 2 cm of biochar material. The first 2 cm of biochar material also was analysed to determine concentrations of MeHg accumulated on the biochar. A solid phase MeHg concentration of 0.16 ng g^{-1} was observed on the first 2 cm of material, representing 0.0013% of the THg and not a significant accumulation of MeHg. Additional analyses using synchrotron based techniques currently are underway to identify mechanisms of Hg binding with the biochar material.

After 182 pore volumes of flow, the influent solution from the SR3 sediment was switched to South River water to evaluate the potential for desorption of Hg from the biochar. Very low concentrations of Hg ($4\text{--}6 \text{ ng L}^{-1}$) were observed in the effluent from the treatment column over 16 pore volumes of flow. The input then was switched to simulated acid rain water (denoted by the red vertical line in Figure 6). With the exception of one sample when concentrations of THg approached 80 ng L^{-1} , the concentrations remained $< 10 \text{ ng L}^{-1}$ for an additional 70 pore volumes of flow. These results suggest that the Hg accumulated in the treatment column was strongly bound to the biochar.

The biochar material from the SR3 treatment column was analysed using synchrotron radiation-based XAS techniques at the Argonne National Laboratory, IL, USA. Micro-XRF maps were created from thin sections made from the first 2 cm of biochar material (Figure 7).

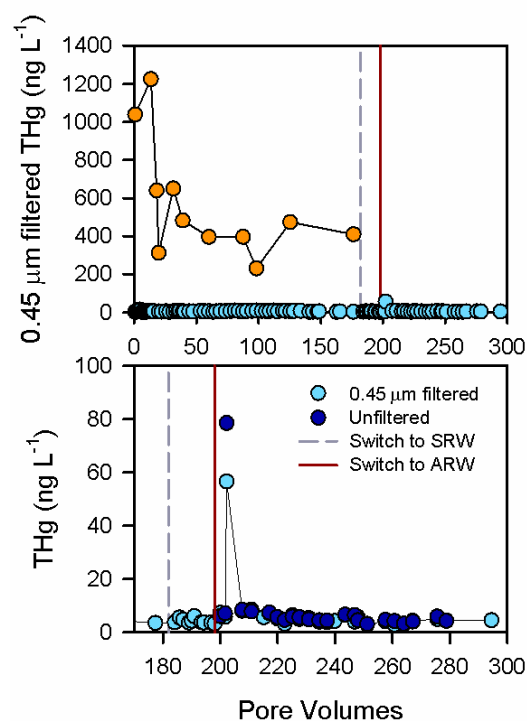


Figure 6. Concentrations of Hg in the effluent of treatment column showing nearly complete removal. At ~ 182 pore volumes, the input was switched to South River water (SRW), and then acid rain water (ARW) at 198 pore volumes to evaluate the potential for Hg leaching from the treatment material.

The higher counts of Hg observed in the elemental map appear to correspond to the presence of pore-like areas of the biochar particle. This association suggests these zones in the biochar are more accessible to water containing dissolved Hg, and potentially represent the physical accumulation of Hg-bearing particles. The absence of release of dissolved and particulate Hg from the biochar column observed in the effluent after long-term subjection to ARW suggests that the Hg is strongly bound likely due to a combination of physical and chemical processes.

Experiments are currently in progress to evaluate the effectiveness of co-blending reactive media with sediment from the low-Hg containing riverbank transects under saturated flow conditions.

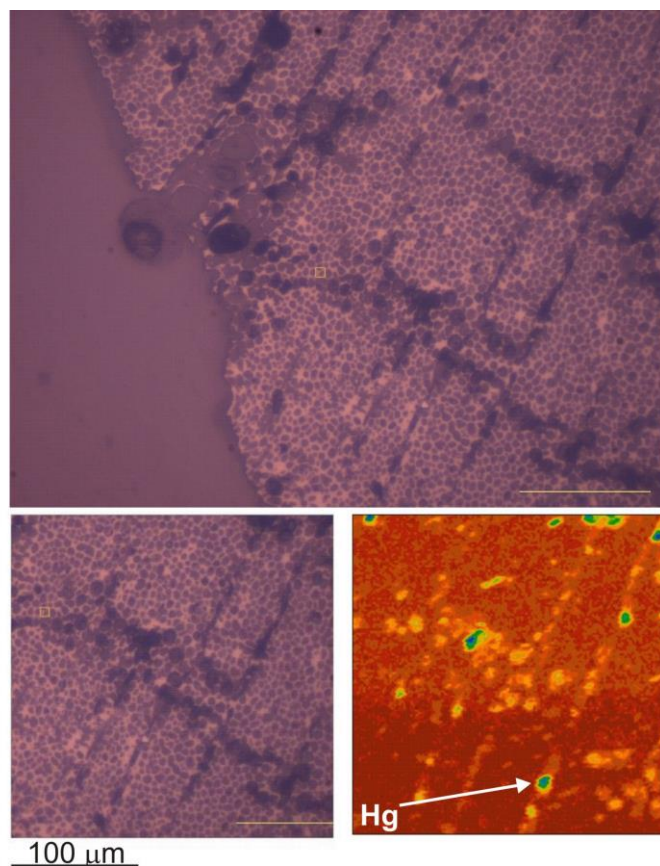


Figure 7. Optical image of biochar particle on thin section (top) and zoomed-in (bottom left) with the corresponding μ -XRF map of Hg (bottom right) showing hot spots of Hg in green.

Experiments to Evaluate Treatment Effectiveness under Variably Saturated Conditions

Two types of experiments were conducted to evaluate the effectiveness of amending floodplain soil with biochar to limit the release of Hg. These involved experiments in which columns were packed with co-blended mixtures of soil and reactive media, and experiments where effluent from unamended soil was directed through a second column containing reactive media. Each of the cells was subjected to alternating flooding and drying periods following the standard humidity test cell protocol for accelerated weathering (ASTM, 2012).

For the co-blending experiments, humidity cells were packed with a) floodplain soil (RRM 1.65; MOTO) as a control, b) floodplain soil with 16 % dry weight (d.w.) biochar, and c) floodplain soil with 8% d.w. biochar (Figure 8). Either simulated acid rain water or South River water were used to flood the soil mixtures. The results of the experiments indicate that the effluent from the column amended with 8 % biochar had Hg concentrations that were similar to those observed for the unamended soil, suggesting little improvement in Hg control. For the 16 % amendment, the concentrations of Hg were slightly lower than the control, however a direct comparison between the 16% column and the unamended soil was not possible due to differences in flooding

conditions for the two columns. The overall influence of co-blending the soils with biochar appears negligible.

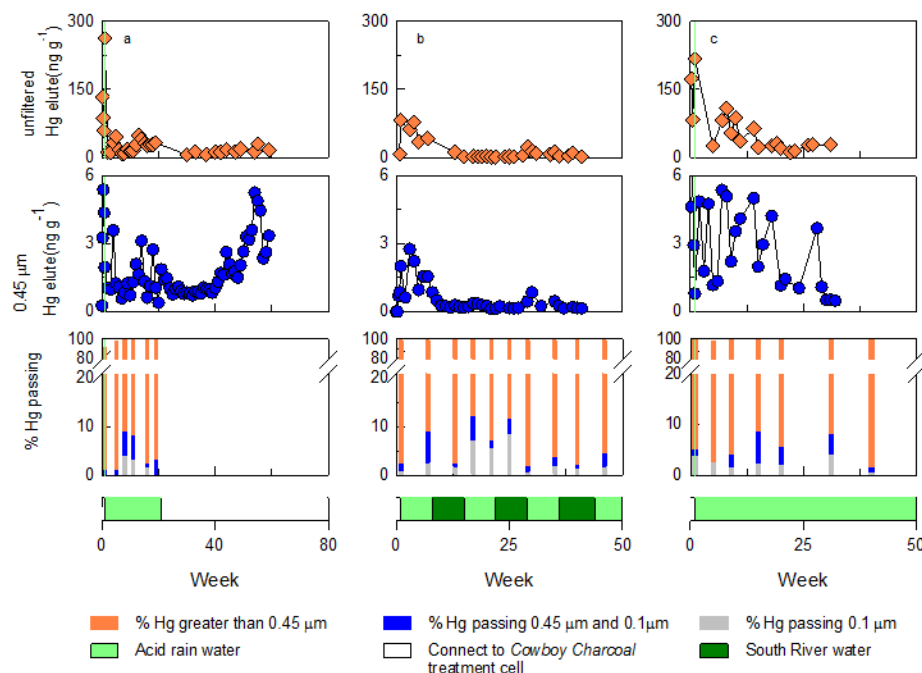


Figure 8. Concentrations of Hg, including different filter fractions, in column effluent collected from humidity test cells. a. Floodplain soil, b. Floodplain soil amended with 16 % biochar, and c. Floodplain soil amended with 8% biochar. Note alternating composition of influent solution between simulated acid rain water and South River water.

For the second type of experiments, effluent from cells containing sediment or soil was directed through treatment columns containing a 1:1 mixture of biochar (C12) and Ottawa sand. These columns also were subjected to alternating flooding and drying conditions on a weekly basis. The effluent collected from a cell packed with soil (MOTO) and flooded with simulated acid rain water released elevated concentrations of Hg, up to $60 \mu\text{g L}^{-1}$ unfiltered Hg, and up to $10 \mu\text{g L}^{-1}$ filtered Hg (Figure 10a). After directing this effluent through a treatment column, 70% of the particulate Hg and 68% of $0.45 \mu\text{m}$ filtered Hg was removed by the biochar treatment column. For riverbank sediment (SR6) flooded with South River water, concentrations of Hg also were highly variable with effluent concentrations reaching maximum values of $15 \mu\text{g L}^{-1}$ unfiltered Hg and 750 ng L^{-1} filtered Hg. After directing this effluent through the treatment column, approximately 90% of the particulate Hg and 80% of the $0.45 \mu\text{m}$ filtered Hg was removed (Figure 9b). These results suggest that biochar may be an effective material for removing Hg under rapid flow conditions.

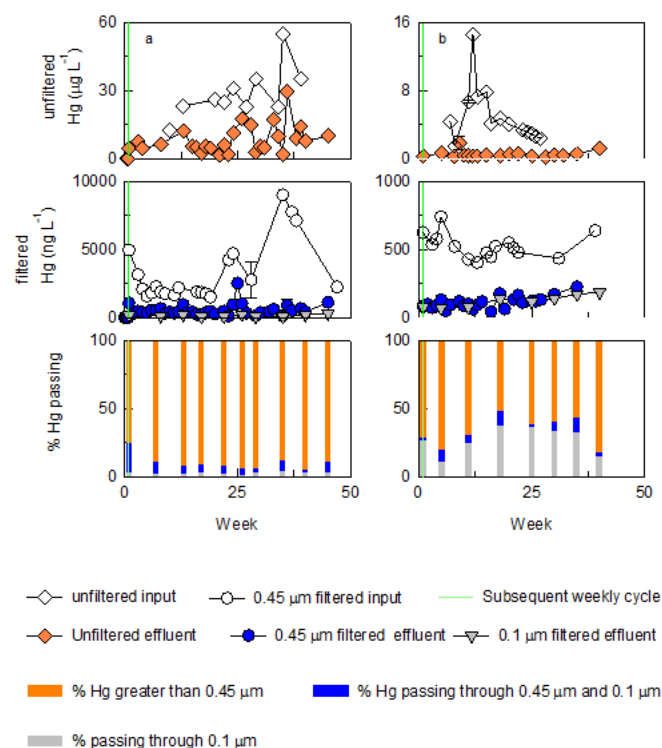


Figure 9. Concentrations of Hg in the effluent from a) floodplain soil (MOTO) flushed with acid rain water and b) riverbank sediment (RRM 0.1 SR6) flushed with South River water (open symbols), and concentrations of Hg in the effluent from the treatment cells for a) effluent from MOTO cell and b) effluent from SR6 cell (coloured symbols).

Experiments to Evaluate a Broad Range of Biochar Materials for Hg Control

Laboratory experiments were conducted to evaluate the effectiveness of a broader range of biochar materials for removing Hg from water. Thirty-nine biochar materials were prepared from different source materials and pyrolyzed at two temperatures. The biochars were characterized for properties which might influence the extent of Hg uptake and potential use in field settings. These properties include bulk density, particle-size distribution, specific surface area, carbon and sulfur content, surface functional groups, surface morphology and chemical composition. Measurements of Hg uptake were made using batch-style equilibration experiments. The biochar samples were added at a 1:75 mass ratio to South River water spiked with $10 \mu\text{g L}^{-1}$ Hg added as a HgCl_2 salt. The spiked river water and biochar were mixed thoroughly, and then allowed to settle and equilibrate. After equilibration, water samples were passed through $0.45 \mu\text{m}$ filters and analysed for pH, alkalinity and aqueous concentrations of Hg, dissolved metals, anions, nutrients, short-chain organic acids and dissolved organic matter.

The specific surface area (SSA) varied substantially for the different biochars. The SSAs for biochars prepared at 300°C varied from 1.06 to $11.3 \text{ m}^2 \text{ g}^{-1}$, much lower than those for charcoal and granular activated carbon, which had SSAs ranging from 1.93 to $597 \text{ m}^2 \text{ g}^{-1}$ (Figure 10). The SSAs of biochars pyrolyzed at 600°C also varied substantially from 1.93 to $229 \text{ m}^2 \text{ g}^{-1}$. The

feedstocks did not appear to play a key role in the SSA values, but the preparation temperatures did. The ratio of SSA of biochars prepared at 600 °C over that of biochars prepared at 300 °C ranged between 0.67 and 131.

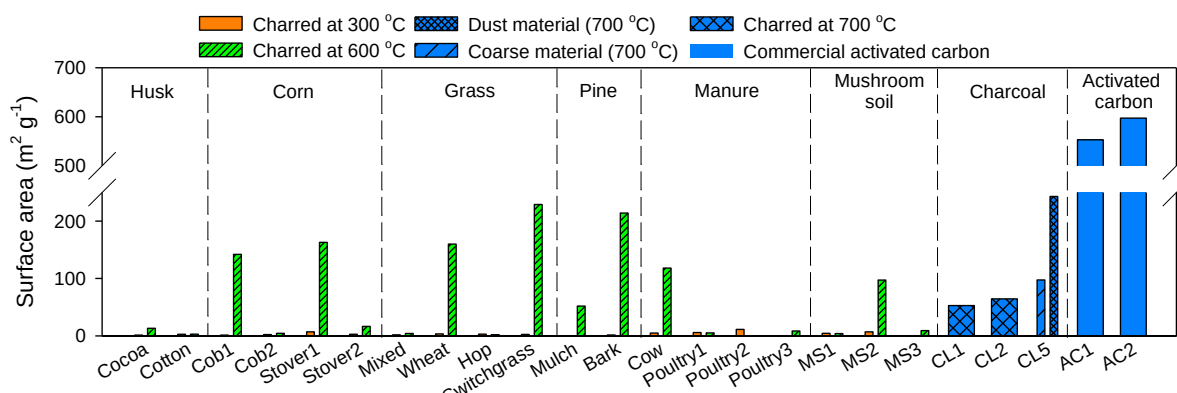


Figure 10. Specific surface areas (SSA) of biochar samples.

In the aqueous treatment systems, concentrations of Hg decreased by > 90% in the mixtures containing activated carbon, charcoal and biochars pyrolyzed at 600 °C (Figure 11). In the systems containing other biochars, concentrations of Hg decreased by 40-90%, with the lowest removals observed for biochars made from husk, corn and pine bark prepared at low temperature. In this study, the higher removal rates corresponded to higher surface area material, which is consistent with literature studies which often show a positive correlation between surface area and treatment efficiency.

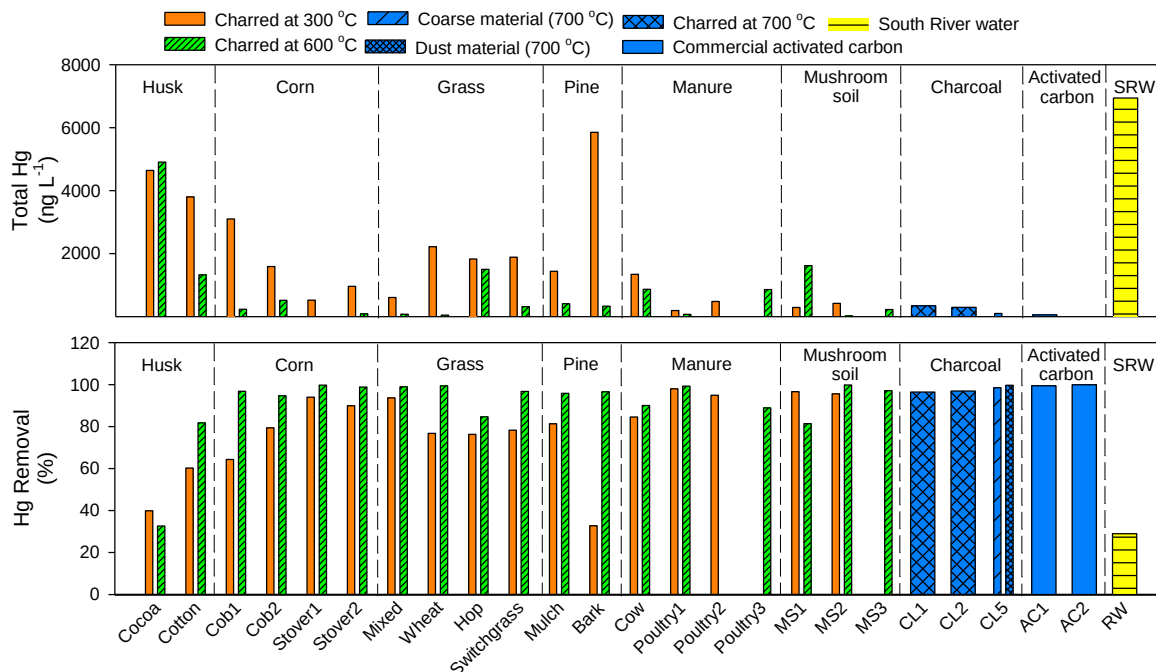


Figure 11. Concentrations of total Hg and % removal for mixtures containing biochar and Hg spiked South River water.

A number of substances can be released from biochars which can contribute to soil fertility (e.g. nutrients) (Lehman and Joseph, 2009), but also can stimulate microorganisms which methylate

Hg (e.g. Gilmour et al., 1992). The activities of Hg methylators are greatest in reducing systems which contain elevated concentrations of labile electron donors (e.g. short chain organic acids) and SO_4^{2-} as an electron acceptor. In this study, the release of short-chain organic acids, nutrients and sulfate was monitored for the different biochar samples. The release of short-chained organic acids was observed to vary with feedstock and pyrolysis temperature (Figure 12), with the greatest concentrations observed for the biochars prepared at 300 °C and for husk, corn, grass, and mushroom soil.

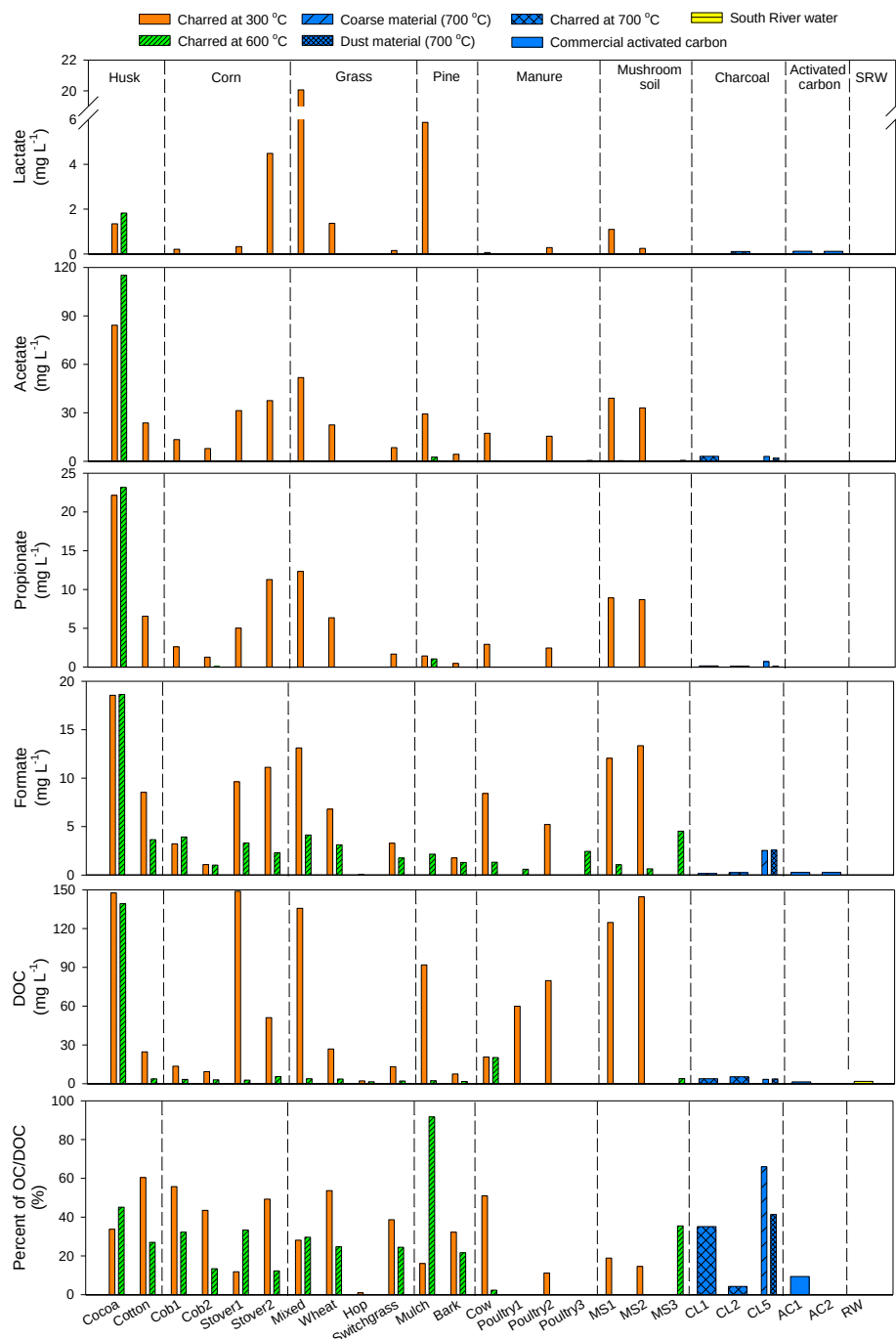


Figure 12. Concentrations of organic acids and total dissolved organic carbon for aqueous solutions mixed with biochars.

Concentrations of Cl^- were variable for the different groups of biochars, with slightly higher concentrations observed for the higher temperature biochars. In contrast, the concentrations of NO_3^- and SO_4^{2-} were higher for the lower temperature biochars (Figure 13). The release of Cl^- was greatest for corn, grass, manure and mushroom-soil biochars. The release of NO_3^- was more consistent across the groups. Concentrations of SO_4^{2-} were highly variable, with elevated concentrations observed for grass, manure and especially mushroom-soil based biochars.

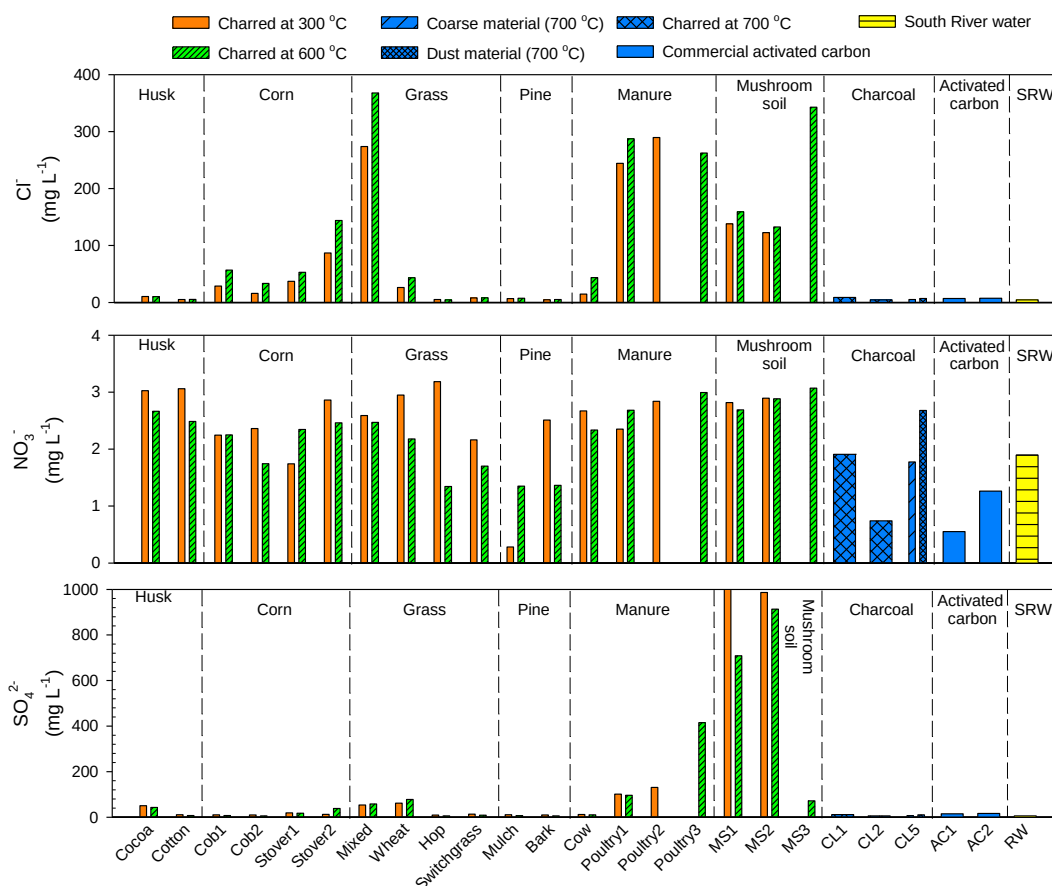


Figure 13. Aqueous concentrations of Cl^- , NO_3^- , SO_4^{2-} for river water mixed with biochars.

The results of these studies on different types of biochars indicate variable Hg uptake, and highly variable release of short-chained organic acids and sulfate. Some biochars evaluated in this study, such as biochar produced from hardwood, showed high Hg uptake with limited release of substances which can stimulate methylation reactions. In contrast, some biochars, such as biochar produced from mushroom soil, released elevated concentrations of SO_4^{2-} , which could promote methylation reactions in the presence of labile organic carbon sources. Others promoted the release of nutrients which could be used to enhance growth of plants in agricultural settings.

Summary

Studies were conducted to evaluate the potential removal of Hg from water and stabilization of Hg in sediment and soils under static and dynamic flow conditions. More detailed studies were focused on solid-phase reactive media which are readily available and provide sustained removal

or stabilization of Hg. The studies also included assessment of Hg methylation potential through the direct measurement of MeHg or through analysis of substances which can stimulate methylation reactions. Some of the main findings of the studies suggest that a number of solid-phase reactive media can remove aqueous phase Hg. However, although some reactive media have the potential to remove Hg, they also appear to have the potential to stimulate methylation reactions. Further studies are focused on evaluating the long-term effectiveness of reactive media at limiting Hg concentrations and at suppressing the generation of MeHg. Alternative treatment approaches also are being evaluated.

References

ASTM, 2012. International Standard Test Method for Laboratory Weathering of Soil Material using a Humidity Cell. D5744-12, 1-19.

Gilmour, C.C., Henry, E.A., Mitchell, R., 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* 26, 2281-2287.

Lehmann, J., Joseph, S., 2009. *Biochar for Environmental Management: Science and Technology*. Earthscan Publishers, London, UK

Floodplain Pilot Study: Technical Briefing Paper

This briefing paper summarizes the objectives, study approach, and findings of the South River Floodplain Pilot Laboratory Study (Laboratory Pilot Study), and the plans for the South River Floodplain Field Pilot Study (Field Pilot Study). Laboratory Pilot Study findings are summarized below and plans for future Field Pilot Study are briefly discussed. The information reviewed and presented herein are not comprehensive; additional details regarding the scope of work, methods and results are documented in the Floodplain Laboratory Pilot Final Report (URS, 2014).

Introduction

Remedial options are currently being evaluated for their ability to reduce mercury uptake by South River floodplain soil biota. One option involves amending the floodplain soils with physical and chemical controls to decrease mercury bioavailability in soils. The Laboratory Pilot Study was designed to assess the viability and efficacy of a soil amendment (biochar) as a potential remedial option via its effect on soil mercury toxicity and uptake by earthworms and plants. Based on the results of the Laboratory Pilot Study, a Field Pilot Study is being planned for a field evaluation of the potential remedial option.

Objectives

The purpose of the Laboratory Pilot Study was to test the efficacy of a soil biochar amendment in limiting the mercury bioavailability (and hence toxicity) toward biological receptors. Specific objectives were to evaluate biochar's:

- ☐ Potential to reduce mercury uptake by earthworms and plants from floodplain soil;
- ☐ Effects on mortality, weight change, and reproduction of earthworms;
- ☐ Effects on seed germination and shoot production in plants;
- ☐ Effects on potential bioavailability of mercury in soil to other ecological receptor; and
- ☐ Effects on mercury methylation in soil.

References

- ✓ Office of Economic Cooperation and Development (OECD). 2004. Test 222: OECD Guideline for the Testing of Chemicals. Earthworm Reproduction Test (*Eisenia fetida*/*Eisenia andrei*). Adopted 23-November-2004.
 - ✓ Office of Economic Cooperation and Development (OECD). 2006. Test 208: OECD Guideline for the Testing of Chemicals. Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test. Adopted 19-July-2004.
 - ✓ EPA. 2013. Ecological Soil Screening Levels (Eco-SSLs). Accessed at: <http://www.epa.gov/ecotox/ecossl/index.html>
 - ✓ URS Corporation. 2014. Floodplain Laboratory Pilot, Final Report for AOC 4, Former DuPont Waynesboro Plant, Waynesboro, Virginia. May 6, 2014.
 - ✓ Berti, W.R., Guiseppe-Elie, A., Quinn, E., Jensen, R.H., Cocking, D. 2013. Evaluation of Garden Crop Mercury Uptake and Potential Exposure from Consumption of Garden Crops grown on Floodplain Soils. Human and Ecological Risk Assessment. 13(1): 215-231.
 - ✓ Fagervold, S.K., Chai, Y., Davis, J.W., Wilken, M., and Ghosh, U. 2010. Bioaccumulation of Polychlorinated Dibenzo-p-Dioxins/Dibenzofurans in *E. fetida* from Floodplain Soils and the Effect of Activated Carbon Amendment. Environ. Sci. Technol. 44, 5546-5552.
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Soil Sample Collection and Characterization

Soil samples were collected on August 20, 2013 from two locations at the Augusta Forestry Center, approximately at relative river mile (RRM 11.8): one location to serve as the low total mercury (THg) “background soil” (outside of the 100-year floodplain), and the other with higher THg as the high THg test soil (within the 2-year floodplain). One composite soil sample was analyzed for a suite of chemical and physical characteristics, including metals, pesticides, herbicides soil properties [grain size; pH, total organic carbon (TOC), and cation exchange capacity (CEC) and % solids]. Three replicate samples were collected from homogenized soil and analyzed for THg to ensure that laboratory replicates had similar THg concentrations.

Laboratory Toxicity Testing

Wildlife International (Easton, MD) conducted the toxicity tests for the earthworm (*Eisenia fetida*) and three plant species, wheat (*Triticum* spp.), soybeans (*Glycine max*) and radish (*Raphanus sativus*). Procedures for both the earthworm and plant toxicity tests followed the standard protocols developed by the Office of Economic Cooperation and Development (OECD): OECD Test No. 222, Earthworm Reproduction Test (*Eisenia fetida*/*Eisenia andrei*) (OECD, 2004) and OECD Test No. 208, Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test (OECD, 2006).

Toxicities were tested on the two soils with three biochar amendments: 0% (control), 5% and 10% biochar in soils (on dry weight basis). Cowboy charcoal, a biochar derived from hardwood, was used to amend the soils. Tests were conducted in soils sieved to < 2 mm and amended with biochar sieved to < 1.25 cm.

Earthworm Test

Adult earthworms were exposed to six groups of soils (two soils each at 0, 5, and 10% biochar). Four replicates for each group were tested. Test duration was eight (8) weeks. Adult mortality and growth (weight change) were measured after 4 weeks. The adults were then removed from the soils and reproductive effects (number of offspring) were evaluated following another 4 weeks. Earthworm tissue and soil samples were collected and analyzed for THg and MeHg.

Terrestrial Plant Test

Seeds for each plant species (wheat, soybeans, and radish) were planted in the six soil groups and grown for 14 to 21 days, after which seedling emergence and plant growth endpoints (shoot weight and height) were measured. Following endpoint determination, two composite samples from each species were prepared from the six replicate samples and analyzed for THg and MeHg.

Soil Characterization Results

The mean THg concentration ($\pm$ standard deviation) was 57.4 ± 0.3 mg/kg in the high THg soil and 0.05 ± 0.01 mg/kg in the background soils. The low standard deviations indicate that the soils were thoroughly homogenized and that exposure conditions in the toxicity test cells would be similar among replicates. Other conclusions include:

- ❑ Soil properties (pH, TOC, % solids, and CEC) were generally similar between the two soils.

- ❑ Concentrations of several metals (cobalt, copper, manganese, selenium, and zinc) in the high THg soil exceeded EPA's Ecological Soil Screening Levels (Eco-SSLs) for plants and/or invertebrates (EPA, 2013), suggesting that these metals in the high THg soil may contribute to potential toxicity in the soil samples.
- ❑ The two soils had similar characteristics in other respects and they are not impacted by herbicides, pesticides, or polychlorinated biphenyls.

Earthworm Test Results

Overall results indicate that biochar amendment is not expected to cause any adverse effects on invertebrates. The 4-week earthworm adult exposure was repeated (Experiment I and Experiment II) to collect sufficient adult tissues for mercury analysis because several adult worms from Experiment I escaped during depuration. The results of both Experiments I and II are discussed below.

- ❑ **Mean Mortality:** Results indicate that biochar amendment reduced the mortality in the high THg soil to levels observed in the background soil. Mean adult mortalities in Experiment I and II were greater than 30% in the untreated high THg soil, 5% in untreated background soil, and less than or equal to 5% in both soils (background and high THg soils) treated with biochar at 5% and 10% (Figure 1).
- ❑ **Growth and Deformities:** All surviving worms were normal in appearance (no deformities) in the background soil (all treatments) and the high THg soil at 10% biochar. In the high THg soil, deformities in survivors were generally reduced at 5% biochar compared with the control and deformities were altogether absent from the surviving worms in the 10% biochar treatment. Mean body weights (initial and final) and mean changes in the body weights in each treatment were not statistically different from the respective controls or between high THg or background soil.
- ❑ **Reproduction:** No statistical differences were observed between treatments and respective controls and between the high THg soil (all treatments including control) and control background soil.
- ❑ **Mercury Uptake:** Uptake of MeHg by the adult and juvenile worms is generally greater in the high THg soils than in the background soil. Uptake of MeHg by juveniles, but not adults, is statistically lower ($p < 0.001$) in the soils treated with biochar (for both soils) (Figure 2).

Plant Test Results

Overall results indicate the biochar amendment (at 5% and 10% levels) do not cause any appreciable adverse effects on plants grown in the high THg soil. Beneficial effects were apparent (compared to the corresponding controls) as demonstrated by the growth of wheat and radish seedlings grown in biochar-treated high THg soils.

- ❑ **Seedling Emergence and Survival:** No adverse effects of biochar amendments (compared to corresponding controls) were apparent on seedling emergence or

survival, except for soybean seedlings grown in background soil at 5% amendment. Soybean seedling emergence was statistically different at all three measurement times in the 5% amendment level compared to the control.

- ❑ **Seedling Growth:** Adverse effects of biochar treatments on mean seedling heights were not apparent, except for soybean grown in biochar-treated background soil, which were statistically shorter compared to the corresponding control. Apparent beneficial effects demonstrated dose-dependence in wheat seedlings in both the background and the high THg soils and radish seedling in only background soil. Mean seedling biomass results were similar to the mean seedling height results.
- ❑ **Mercury Uptake:** Consistent with other findings of plant uptake of mercury in the South River (Berti et al., 2013), seedlings of all three species had low THg concentrations. THg concentrations in seedlings among all treatments were low with only two exceptions, but unrelated to the concentration of biochar. In general, THg and MeHg concentrations were higher in seedling grown in the high THg soils. Addition of 5% or 10% biochar did not have any effect on MeHg concentrations (Figure 3).

Test Soils

In high THg soils, MeHg concentrations were reduced over the course of the *E. fetida* experiments (i.e., 28 days and 56 days) by 50% in the 10% biochar treatment in Experiment II. In contrast, MeHg concentrations increased by 2 to 18-fold in background soils. The higher increases in the background soil were mostly due to the low starting MeHg concentrations. However, these changes were observed in a single replicate, indicating a relatively high degree of uncertainty (Figure 4).

Overall Findings of the Pilot Study

The Pilot Study found that biochar amendment of soils produced no apparent negative effects on earthworms or plants, and may have reduced mercury or metal-related toxicity on earthworms. In addition, MeHg uptake may be reduced by biochar in juvenile earthworms. Specific findings include the following:

- ❑ Based on mortality, growth, or reproduction in earthworms, biochar-related adverse effects are not apparent in soils amended with biochar. Biochar appeared to reduce mortality of adult earthworms in the high-THg soils from RRM 11.8, which was >30% in 0% biochar controls, but absent in 5% or 10% biochar treatments.
- ❑ In addition, there were apparent biochar-related increases in growth of worms in RRM 11.8 soils. There were no effects of biochar on plant emergence, growth, or biomass.
- ❑ Methylmercury concentrations in juvenile *E. fetida* were lower in biochar treatments in both high-THg and background soils. MeHg concentrations in adult *E. fetida* were reduced in biochar amended background soil, but not in biochar-amended high THg soil.
- ❑ It is unclear whether the elevated adult mortality and apparent sub-lethal effects (e.g., deformities) observed in the control high THg soil is due to mercury (at 57.4

mg/kg dw) or due to one or more metals exceeding the corresponding Eco-SSLs for soil invertebrates.

- Biochar amendment did not affect mercury concentrations in plants. In test soils, MeHg concentrations decreased by 5% to 50% over the course of the experiments, suggesting that biochar decreased mercury methylation in soil. The opposite pattern was observed in background soils, with increases of 50% to 95%.

Planning for the Field Pilot Study

Based on the results of the Laboratory Pilot Study, a Field Pilot Study is being planned to provide further information on the efficacy of carbon amendments to reduce mercury bioavailability in the floodplain soils. The objectives are similar to those of the Laboratory Pilot, but the overall objective is to demonstrate effectiveness and safety of using carbon amendments on a field scale. Many aspects of the Field Pilot are in development, but the following provides a general description of the study design.

The Field Pilot Study will be performed in the 0.3 to 2-year floodplain of the South River. The Field Pilot will likely be conducted at the August Forestry Center. Two different types of carbon amendments will be tested: cowboy charcoal and activated carbon. The amendments will be sieved to less than 0.25 mm and added to final concentrations of 5% dry weight in soil. The amendments will be tilled into test plots in the fall of 2014 and allowed to age.

Sampling will be conducted the following spring, and will involve two types of sampling: caged earthworms and native invertebrates (e.g., earthworm, predatory mite, collembolans, enchytraeid worms, spiders). Caged earthworms will be employed to reduce the ability for earthworms to travel below the zone where biochar is applied. Earthworms will be collected from an area outside the 100-year floodplain, measured and weighed and then added to earthworm cages made from PVC pipe with screened openings. Soil from the 0.3 to 2-year floodplain will be mixed with a carbon amendment and added to the cages which will be driven into the soil for a 28-day exposure. In addition, native invertebrates will be collected from the test plots; for soil-dwelling invertebrates (e.g., earthworms) a co-located soil sample will be collected. Invertebrates and soil will be sampled for the following analytes:

- THg and MeHg (Tissue, soil)
- % lipids (invertebrate tissue; f_{lipid})
- TOC (soil; f_{oc})

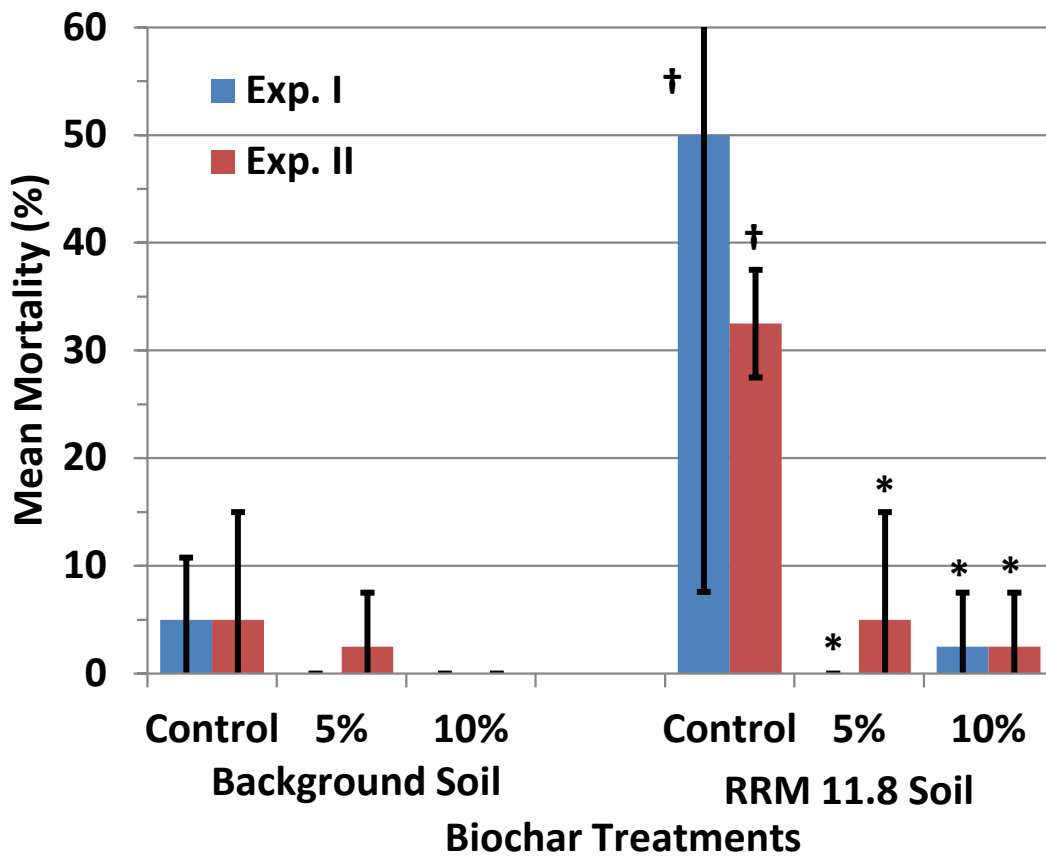
This analyte list will allow calculation of biota-soil accumulation factors (BSAF), which will control for the variability in the soil concentrations between controls and amended plots:

$$\frac{C_{worm}/f_{lipid}}{C_{soil}/f_{oc}}$$

Where C_{worm} is the concentration of mercury in invertebrates and C_{soil} is the concentration of mercury in soil (Fagervold et al., 2010). Invertebrates will be measured and weighed following collection. In addition, test soils will be collected for analysis of ancillary parameters (black carbon and nutrients).

Sampling will be conducted for two successive years to test the efficacy period in soil. Because the life span of earthworms is typically one or two years, and the Laboratory Pilot Study only observed effects on uptake in juvenile earthworms, it will be important to sample earthworms that have been exposed to carbon amendment throughout their life.

Figure 1
Mortality in Adult Earthworms
Floodplain Laboratory Pilot for AOC 4
Former DuPont Waynesboro Plant, Waynesboro, Virginia



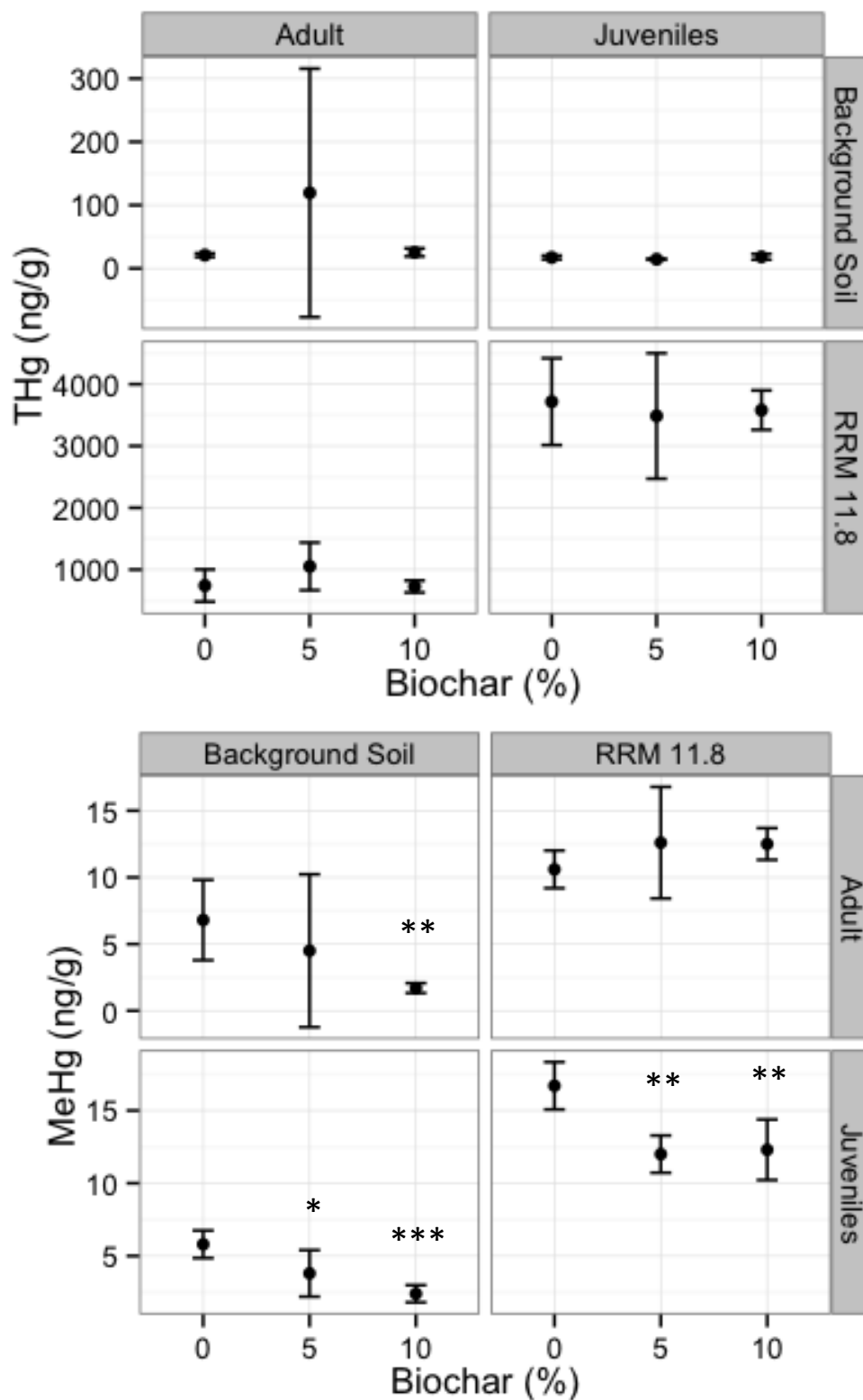
Notes:

Mean Standard Deviation shown; Exp. I - Experiment I; Exp. II - Experiment II;

*Statistically different (at $p < 0.05$) from corresponding control;

† Statistically different (at $p < 0.05$) from background control.

Figure 2
Mercury Concentrations in Earthworms
Floodplain Laboratory Pilot for AOC 4
Former DuPont Waynesboro Plant, Waynesboro, Virginia



Notes:

Mean Standard Deviation shown.

*p<0.05; ** = p<0.01; ***p<0.001

Figure 3
Mercury Concentrations in Seedlings
Floodplain Laboratory Pilot for AOC 4
Former DuPont Waynesboro Plant, Waynesboro, Virginia

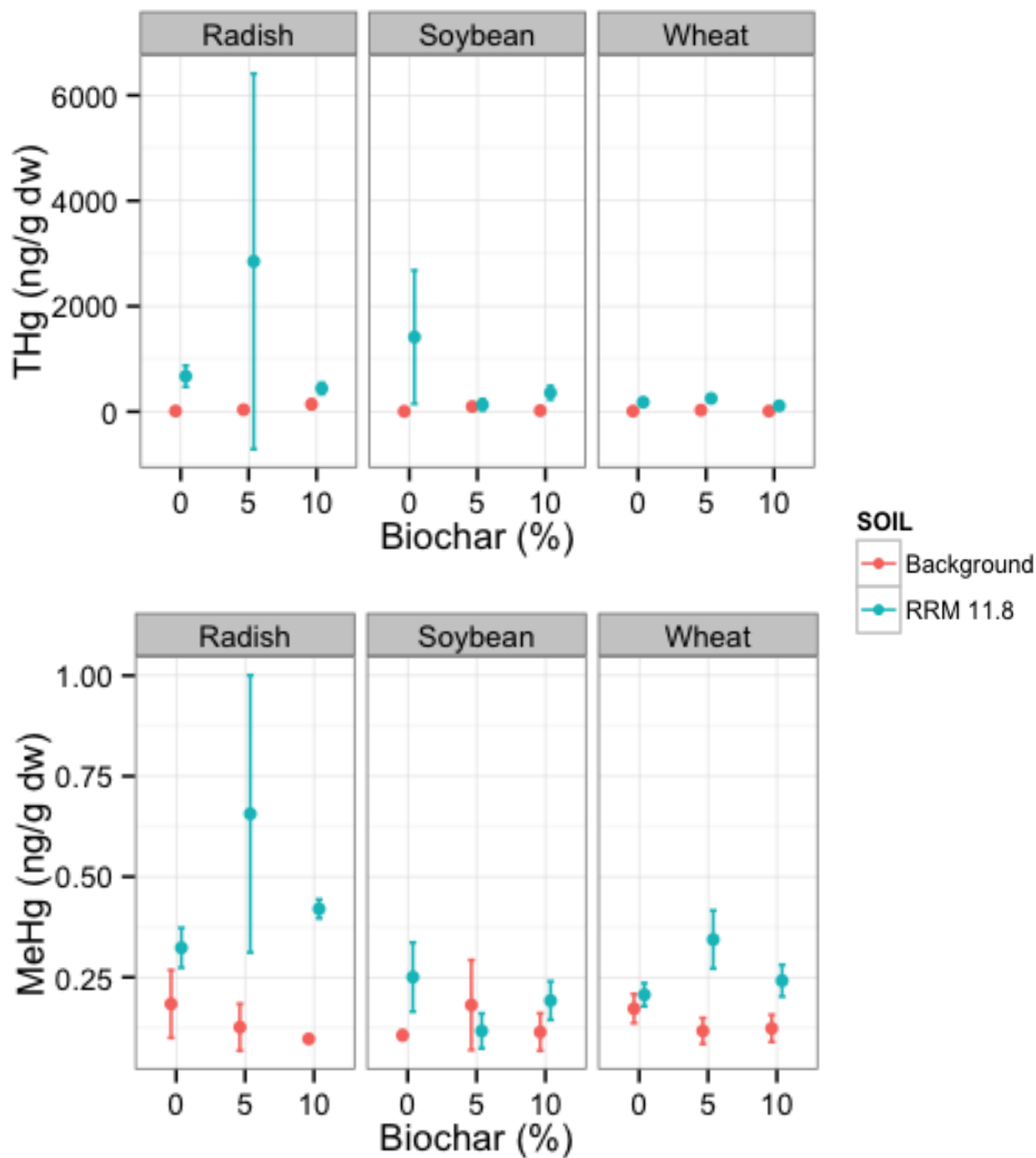
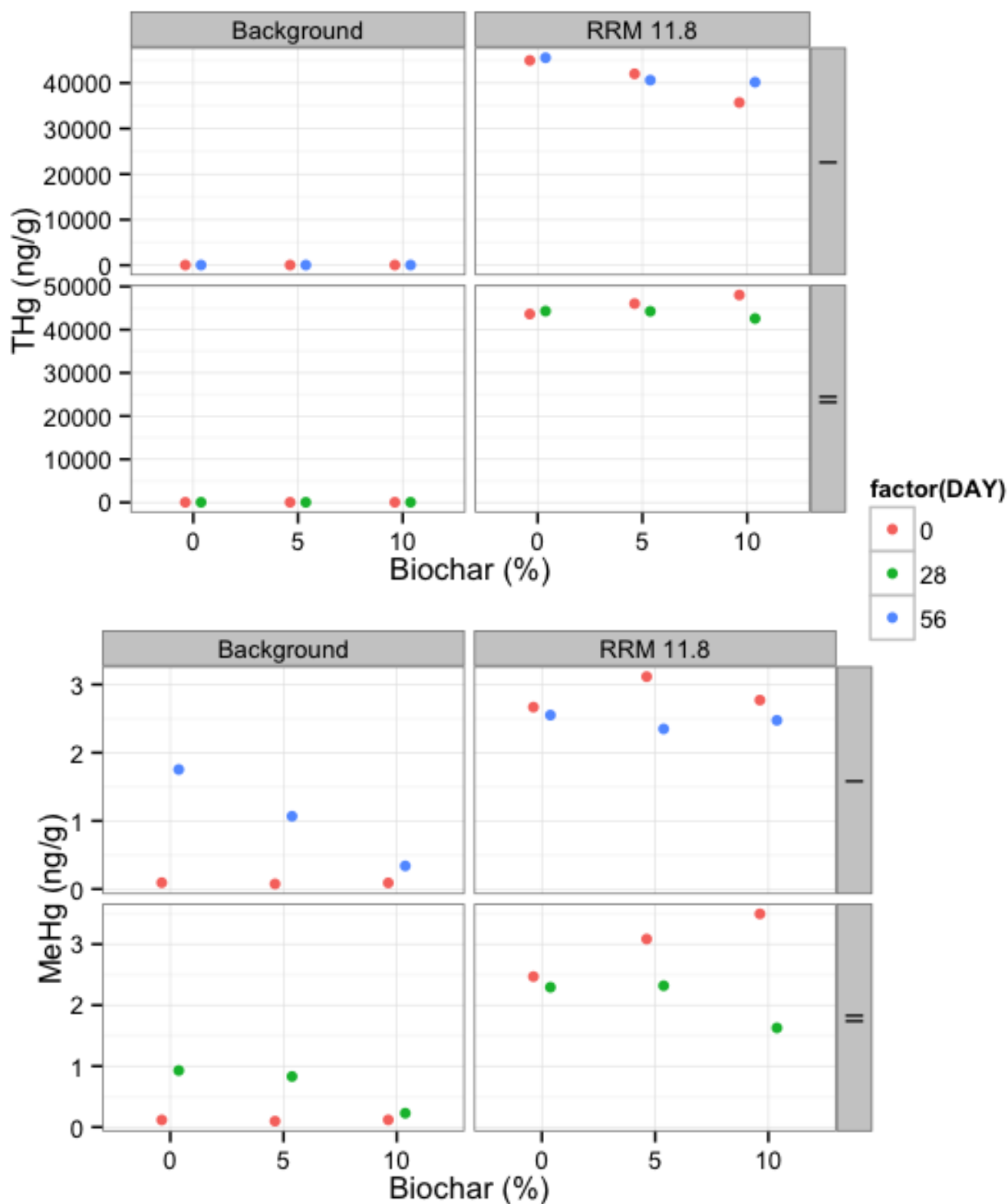


Figure 4
Mercury Concentrations in Test Soils
Floodplain Laboratory Pilot for AOC 4
Former DuPont Waynesboro Plant, Waynesboro, Virginia



Geochemical Characterization of Mercury-Bearing Riverbank Sediments and Soils from the South River, Virginia (USA)

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Introduction

The sediments beneath and adjacent to the South River, near Waynesboro, VA, contain elevated concentrations of mercury (Hg). As these sediments erode, Hg-bearing particles enter the river and can release Hg to the water in dissolved or particulate forms. Flooding and precipitation events can induce infiltration of water through soils and sediments and potentially lead to additional input of Hg to the river. This infiltration can lead to changes in soil moisture content which can subsequently promote a series of reactions in the aqueous and solid-phase chemistry and changes in Hg speciation and transport. Studies are being conducted at the University of Waterloo to evaluate the extent of Hg release through sediment resuspension events and through enhanced groundwater transport associated with precipitation and flood events. An overview of the experiments that have been completed or are underway is provided. The results of the studies will aid in the prediction of Hg release to the river and design of remedial systems.

The studies include 1) measurements to characterize the bulk sediment to determine the composition of sediment particles and potential for Hg binding, 2) experiments to provide an indication of Hg release as sediments are eroded and enter the river, and 3) leaching experiments to evaluate Hg release under fully saturated and variably saturated conditions with input solutions of different compositions including river or acid rain water. Sediment and soil samples were collected from locations with elevated concentrations of Hg, and from sites with low concentrations of Hg (RRM 0.25, 2.4 and 3.4). The low-Hg samples were selected to quantify the potential for Hg release from sections of the river which represent a large portion of the river channel. Additional samples were collected from the river floodplain at locations with known elevated concentrations of Hg.

Specific tools that are being applied in the studies include:

chemical analyses to determine masses of Hg, other elements and nutrients;

mineralogical analyses, including optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersion x-ray analyses (EDXA), to determine particle morphology, bulk mineralogy, and chemical composition of particles;

synchrotron radiation-based X-ray absorption spectroscopy (XAS) to determine oxidation states and nature of binding of Hg to other elements;

sequential extraction assays to determine the stability of Hg when sediments are exposed to different reagents;

batch resuspension tests to evaluate the mass of Hg released when sediments are mixed with South River water;
long-term saturated column tests to evaluate Hg leaching under saturated flow conditions;
humidity test cells to simulate wet / dry cycling when sediments are exposed to South River water and simulated acid rain; and
geochemical modeling

The results obtained from these and other tools will be integrated to develop an improved understanding of Hg behavior at the South River site and processes leading to its release, transport and attenuation, and potential availability for methylation.

Sample Collection Locations

Sediment and soil samples were collected from the riverbank along the South River and within the floodplain (Figure 1). These samples cover a range in concentration of total solid-phase Hg, from near background values to concentrations representative of the highest concentrations observed in the study area.

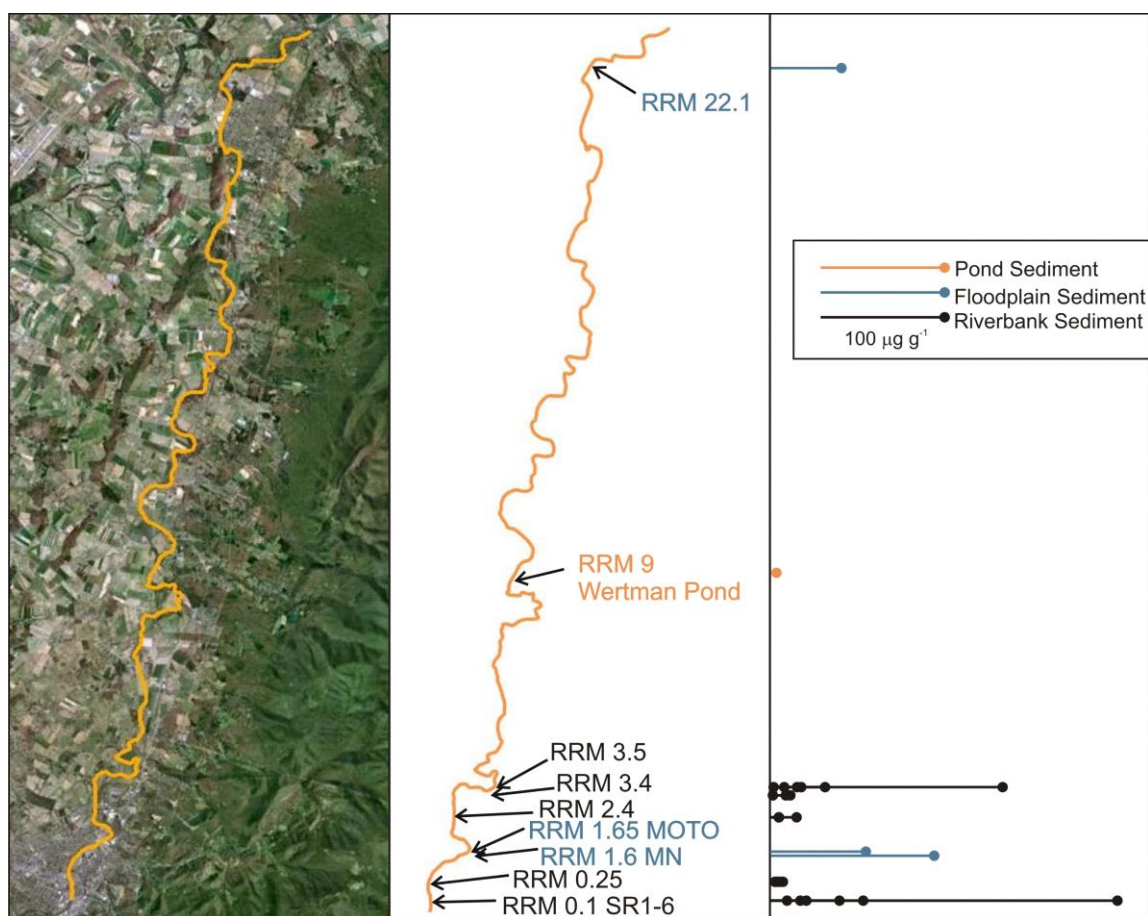


Figure 1. Map showing sampling locations, expressed as relative river mile (RRM) downstream from Hg source area, type of sample, and concentrations of total Hg expressed on a dry weight basis.

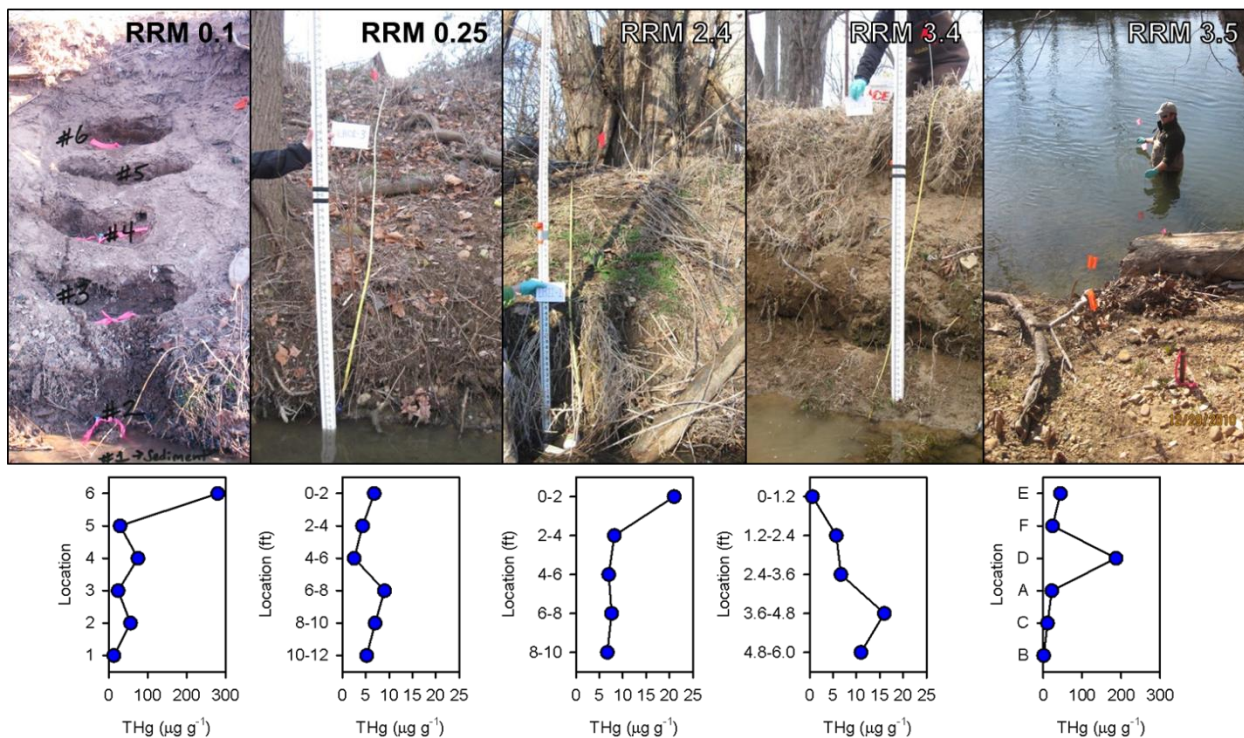


Figure 2. Photographs showing sample collection locations (top) and corresponding THg concentrations (bottom) at transects at RRM 0.1, 0.25, 2.4, 3.4, and 3.5. These locations were selected for more detailed study due to the presence of both low and elevated concentrations of Hg.

Overview of Results and Status of Studies

Solid-phase Chemical Analyses: Chemical analyses of solid-phase samples indicate highly variable concentrations of Hg at the site and generally elevated concentrations of Fe (Table 1).

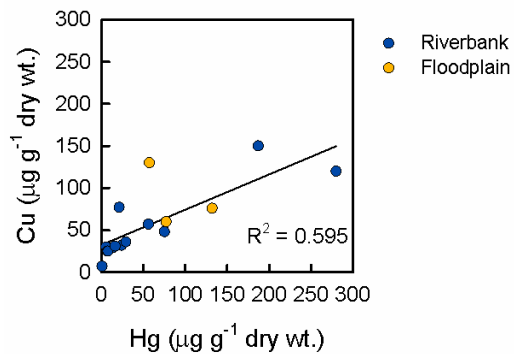


Figure 3. Correlation between total Hg and total Cu present in the riverbank and floodplain sediments.

Concentrations of Hg in the riverbank sediments ranged from $0.6 \mu\text{g g}^{-1}$ to $280 \mu\text{g g}^{-1}$, and in the floodplain sediments from $57 \mu\text{g g}^{-1}$ to $132 \mu\text{g g}^{-1}$. The concentrations of Hg are correlated strongly with solid-phase Cu concentrations, consistent with the chalcophile nature of these two elements (Figure 3).

Table 1. Concentrations of Hg and other elements in selected samples collected from the study area, including sample ID and location reported as relative river mile. For transects 0.25, 2.4 and 3.4 only those sediments which were chosen for column experiments are shown.

Sample ID	Location (miles)	Hg	Cu	Fe	K	Mg	Mn	Ni	Pb
		$\mu\text{g g}^{-1}$, dry weight							
SR1	0.1	13	29	12000	1500	710	140	8.8	14
SR2		56	57	20000	1000	870	320	14	23
SR3		24	32	29000	2000	1200	340	10	13
SR4		75	48	17000	1000	910	310	9	23
SR5		29	36	20000	1300	1100	420	13	26
SR6		280	120	16000	820	930	300	8.5	23
10-12'	0.25	5.2	30	14000	1000	13000	240	9.3	82
0-2'		6.8	25	16000	990	2300	320	9.4	32
MN-38	1.6	132	76	27000	1800	1300	460	10	30
MOTO	1.65	77	60	14000	1600	760	290	6.3	18
6-8'	2.4	7.6	25	25000	1900	2100	560	13	20
0-2'		21	77	22000	1200	1900	380	13	54
3.6-4.8'	3.4	16	31	15000	1100	1100	240	8.0	29
0-1.2'		0.6	7.1	17000	910	1200	390	7.2	6.0
SRD	3.5	187	150	16000	760	1200	230	8.2	21
RRM 22.1	22.1	57	130	24000	780	1100	1500	22	27

Mineralogical Analyses: Mineralogical studies are currently underway and include a variety of techniques to identify the morphology and composition of particles in the sediments and soils in samples collected along the South River and within the floodplain. A number of samples collected from RRM 0.1 and RRM 3.5 were prepared for analysis using SEM, TEM and other methods. Preliminary results of analyses of river bank sediments indicate that the dominant phase observed in polished thin sections was quartz. The next most common phases consisted of agglomerates of Al-rich silicates (most likely clays) and fragments of quartz, feldspar, and Fe-silicate (much less common). Lesser quantities of mid-to-highly weathered feldspars (orthoclase/microcline and albite) were observed in agglomerates, but also as separate grains. Other particles were composed of Fe and Ti (hydr)oxides. Elevated concentrations of Hg were observed in fine-grained particles enriched in C, S, and often Al and alkali elements such as Na, K, and Ca which were attached to agglomerates. These studies will be continued to further quantify the nature of the Hg associations.

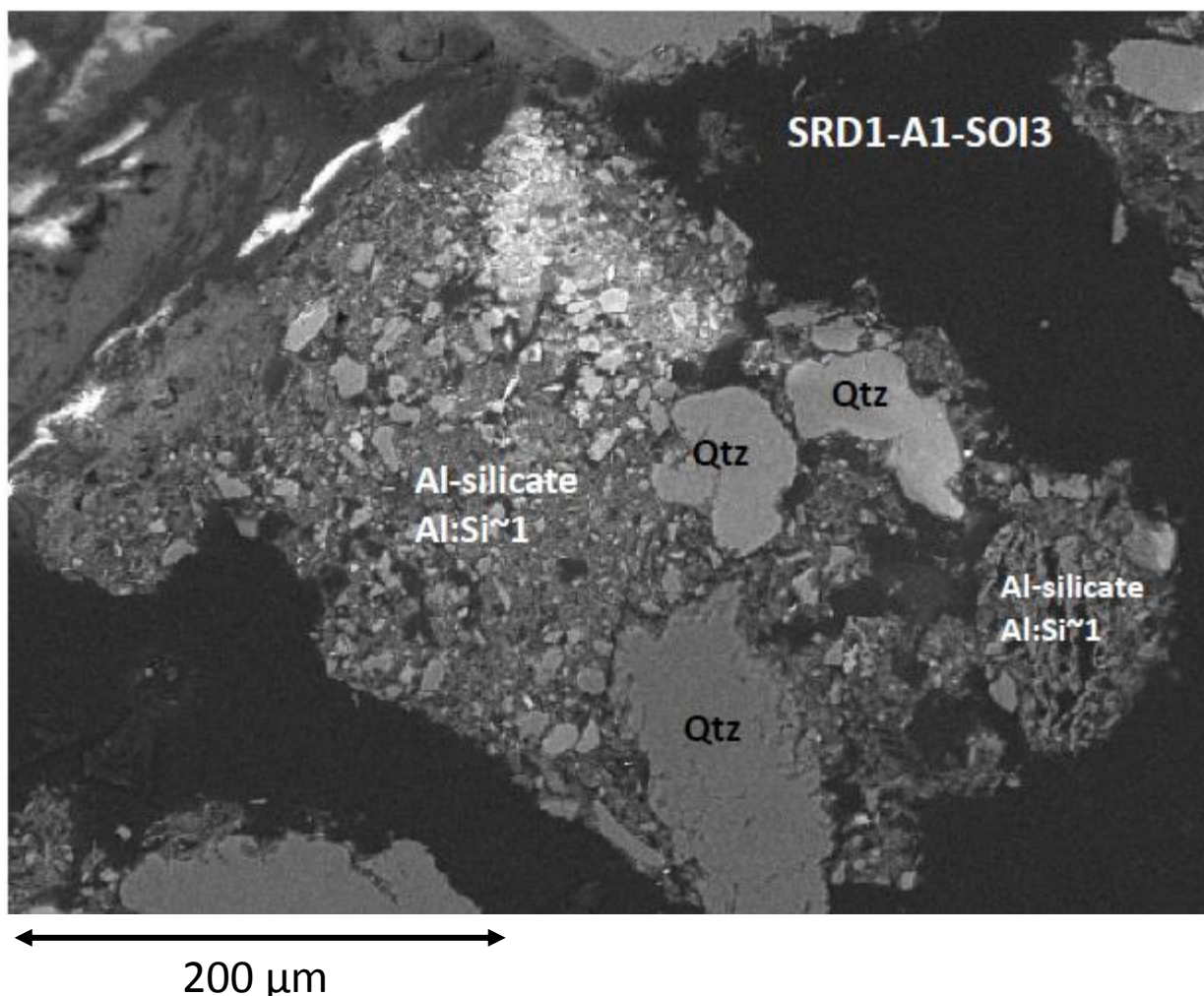


Figure 4. Example SEM image of bank sediment collected from location RRM 3.5 – SRD showing typical grain morphology observed in thin section samples.

Synchrotron Radiation Analyses: Synchrotron radiation-based XAS techniques were employed to characterize the form of Hg in the bank sediments and floodplains soils. Six samples from RRM 0.1 (SR1 to SR6), five samples from RRM 3.5 (SRA, SRB, SRC, SRE, and SRF), and floodplain samples from the motocross area at RRM 2.4 (labelled MOTO) and RRM 22.1 were analyzed on Beamline 13-BM-D-GSECARS at the Advanced Photon Source (Argonne National Laboratory, Lemont, IL, USA). A 13-element Ge detector (Canberra Industries Inc., Meriden, CT, USA) and a defocused beam measuring approximately 1000 x 300 μm was used for collection of XANES spectra for Hg. Data processing was performed with the program ATHENA (Ravel and Newville, 2005). XANES spectra were collected on the same beamline for Hg bearing standards (Figure 5).

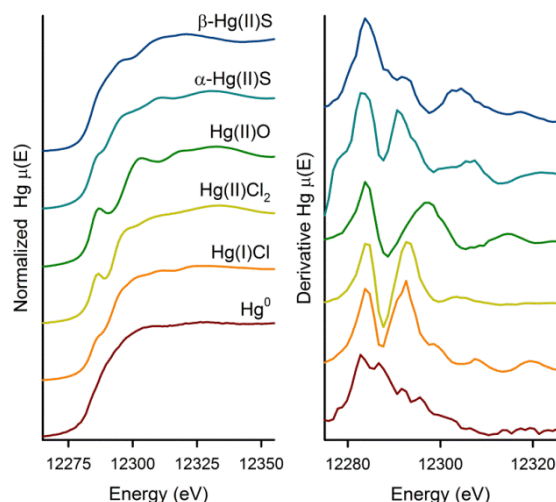


Figure 5. Hg XANES reference spectra for selected standards.

The minimum concentration for analysis of Hg by XANES was approximately $100 \mu\text{g g}^{-1}$. As such, Hg was difficult to detect in many of the samples. Mercury XANES spectra were obtained for the lowest and highest elevation samples at RRM 0.1 (SR1 and SR6), the floodplain sample at RRM 2.4 (MOTO), a high-Hg sample at RRM 3.5 (SRD), and the floodplain sample at RRM 22.1 (Figure 6).

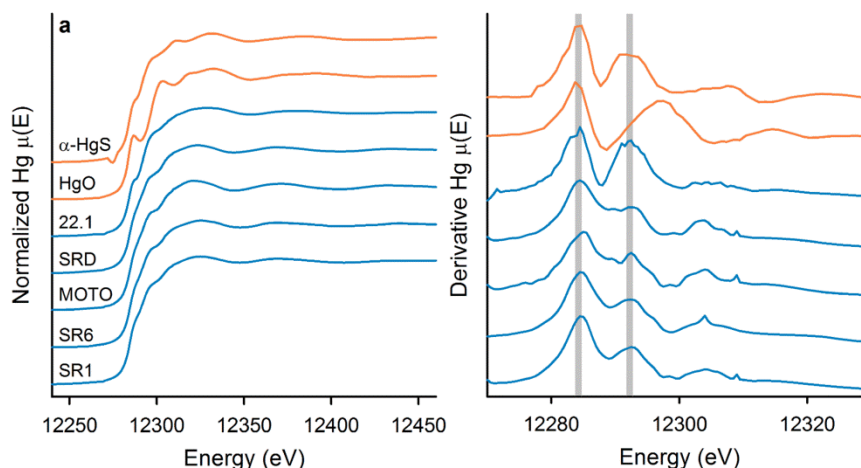


Figure 6. Hg L-edge XANES spectra for selected standards and sediment samples collected from the riverbank and floodplain. The grey lines on the Hg XANES derivative plot show first and second peak locations typical of cinnabar [α -HgS]

At each location, Hg appeared to be bound to sulfur with spectra resembling either cinnabar or metacinnabar and possibly as Hg bound to thiol groups in organic matter. A detailed analysis of the extended fine structure region would be required to differentiate between inorganic and organic Hg-S bonding, however the spectra collected in this study were too weak to perform this analysis.

Sequential Extraction Assays: Sequential extraction analyses were conducted on river bank and floodplain samples to assess the potential bioavailability of Hg through a five-step extraction

process: deionized water (targets HgCl_2 , HgSO_4), 0.1 M CH_3COOH + 0.01M HCl at pH 2 (targets HgSO_4 , HgO , adsorbed Hg), 1M KOH (targets organo-chelated Hg , Hg_2Cl_2), 12M HNO_3 (targets Hg^0 , thiol-bound Hg), and aqua regia (targets HgS , HgSe , HgAu) (Bloom et al., 2003). These extractions can be used to infer the presence of target phases, but do not provide definitive identification of these phases. The results of the extractions indicate release of Hg under all five extraction steps for all samples (Figure 7), suggesting a range in potential availability of Hg for biological uptake and other reactions. The F4 and F5 fractions dominate the Hg forms for the majority of the sediments, though for the low- Hg samples collected from RRM 0.25 and RRM 2.4 there is a greater proportion of the F3 fraction, especially in the sediments from locations further away from the base flow of the river. The analyses, however, are static tests and only represent release of Hg for sediment:extract ratios used in the assays.

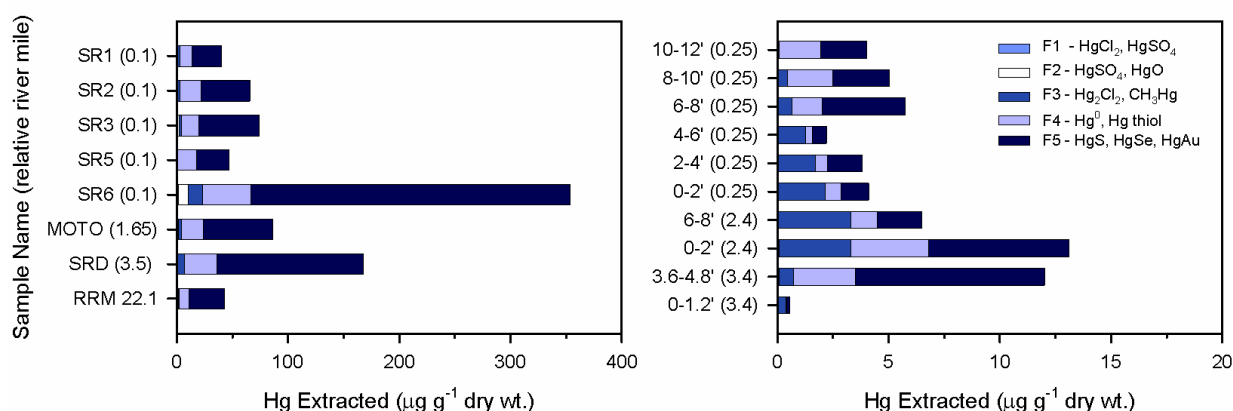


Figure 7. In-house Hg sequential chemical extraction data for soil and sediment samples. Left: High- Hg samples, and Right: Low- Hg samples. Note: The presence of all five fractions for all samples, but the predominance of the F4 (targeted phases are Hg^0 and thiol-bound Hg) and F5 (targeted phases are HgS , HgSe and HgAu) fractions.

Resuspension Tests: A modified elutriate test protocol described in the EPA Inland Testing Manual (US EPA, 1996) was employed to determine the potential for Hg leaching as sediment erodes from the riverbanks into the river from the low- Hg sediments and compared to the higher Hg sediments results determined previously. Sediment and South River water were combined at 40:1, 20:1, 10:1 and 4:1 ratios and gently agitated for 30 minutes. The aqueous supernatant was filtered (0.45 μm) and the samples analysed for Hg and other chemical parameters.

Concentrations of Hg were observed to generally increase with a decrease in liquid-solid ratios (Figure 8). Concentrations of Hg ranged from 0.2 to 80.2 $\mu\text{g L}^{-1}$ for water in contact with sediment collected along the riverbank, and ranged from 6 to 30 ng L^{-1} for cobblestone samples collected within the riverbed (SRB and SRD). The highest concentrations of Hg were observed for the SR6 sediment. The greatest aqueous THg released from the low- Hg sediments of 1020 ng L^{-1} was observed with the sediment from RRM 2.4 (0-2') with a 1:4 sediment to SRW ratio. The resuspension tests show that of the low- Hg sediments, the sediments that could potentially leach large amounts of Hg were: RRM 0.25 (10-12'), RRM 2.4 (0-2'), RRM 3.4 (3.6-4.8'). Based on the resuspension test results, two sediment samples each from the 0.25, 2.4, and 3.4 transects were selected for saturated flow-through column experiments.

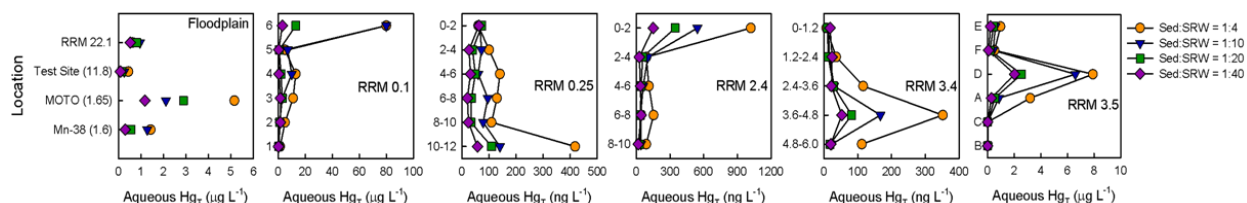


Figure 8. Concentrations of Hg in 0.45 µm filtered water samples released during sediment resuspension experiments reported as a function of the mass ratio of water and sediment.

Leaching of Hg under Saturated Flow Conditions: Saturated flow column experiments provide a direct measurement of the release of Hg as water flows through sediment at solid:water ratios representative of field conditions. Sediments from transects 0.25, 2.4 and 3.4 were packed into columns and the water was pumped at a flow rate of 100 mL week⁻¹ yielding calculated average linear velocities ranging from 16 to 40 cm d⁻¹.

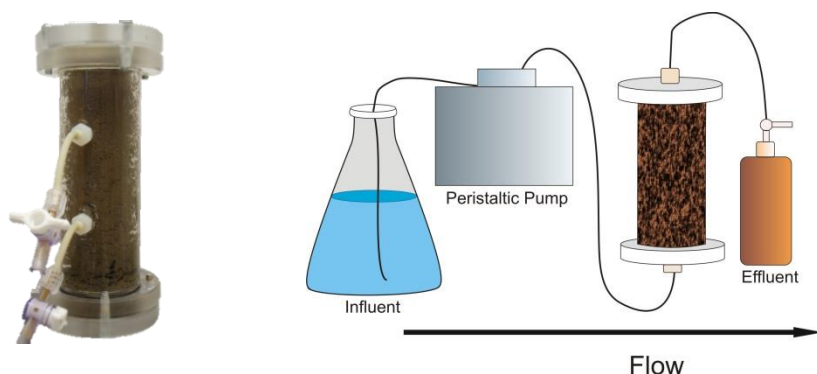


Figure 9: Photograph of column packed with sediment collected from RRM 2.4 (6-8') (left) and schematic diagram of experimental set-up (right).

Analyses of water samples collected over the first 50 pore volumes of flow from the low-Hg columns (Figure 10) indicate that the effluent from RRM 0.25 (10-12') had the highest concentrations of THg. Relatively low concentrations of solid-phase Hg were observed at this site, and low concentrations of Hg were leached in the resuspension tests, suggesting that there is a poor correlation between leaching under dynamic flow conditions and the total Hg concentrations and leaching during resuspension tests. In all three low-Hg transects the highest concentrations of Hg were observed in the effluent from the columns containing sediment obtained closest to the base flow of the river rather than the sediment collected from higher up the bank. The maximum concentrations of MeHg of 25 ng L⁻¹ were observed in the effluent of the column containing sediment from RRM 2.4 (6-8') followed by 0.25 (0-2') where a maximum of 8.8 ng L⁻¹ of MeHg was observed.

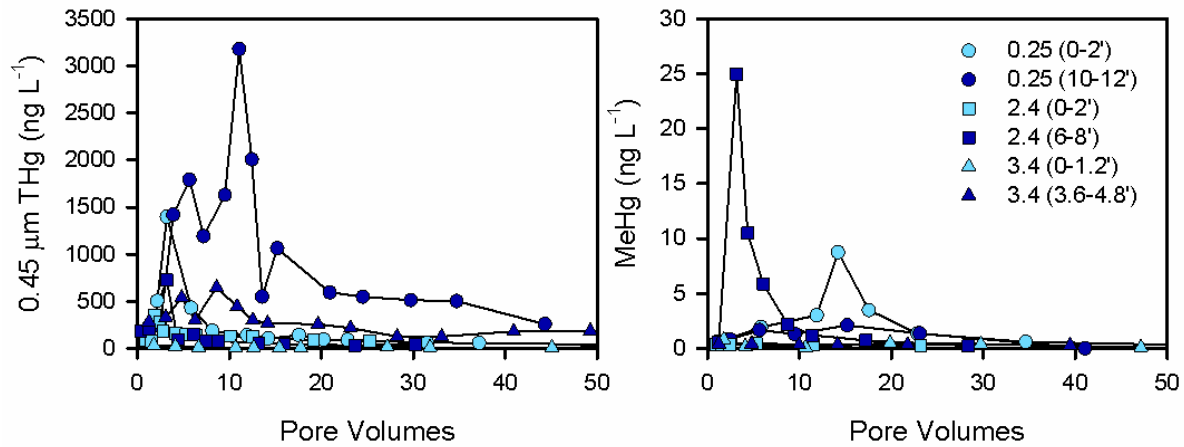


Figure 10: Concentrations of 0.45 µm filtered Hg in the effluent from the columns containing low-Hg sediments (left) and the corresponding effluent MeHg concentrations (right).

Comparison of Hg Release from a Range of Sediment Samples: The concentrations of Hg in the effluent collected from the low-Hg saturated column experiments were compared to the concentrations observed in column experiments conducted with sediment containing elevated concentrations of Hg. The greatest cumulative release of Hg was observed for columns containing sediments collected from locations closest to the base flow of the river (*e.g.*, RRM 0.25 10-12' and RRM 0.1 -3) (Figure 11). The release of Hg under saturated flow conditions appears to be directly correlated to the degree of saturation at the time of sample collection.

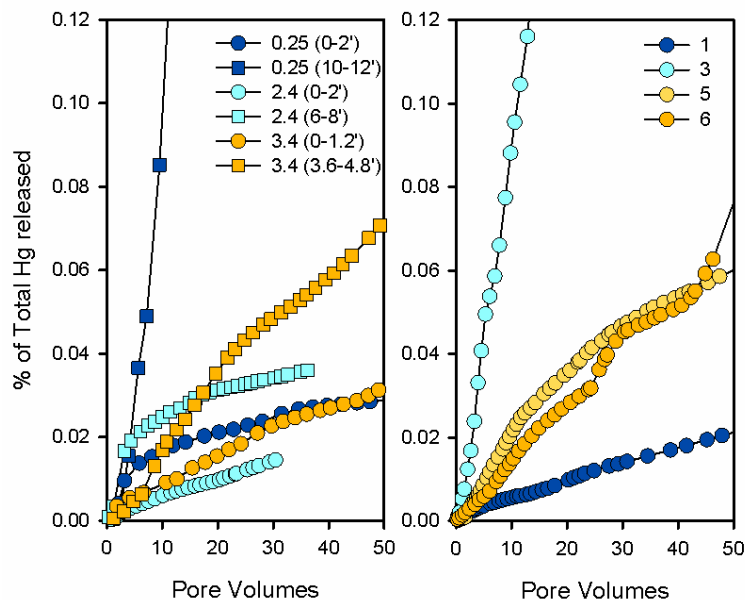


Figure 11. Comparison of cumulative Hg observed in the effluent of the low-Hg columns from low-Hg locations (left) and high-Hg locations (RRM 0.1; right).

Release of Hg under Variable Moisture Contents: Changes in moisture contents can lead to the generation of alternating oxidizing and reducing conditions, which can promote weathering reactions and, in turn, induce changes which may influence Hg release. Humidity test cell experiments were conducted following a standardized protocol (ASTM, 2012) to promote cyclic changes in moisture contents. Slight modifications to the procedure were made to evaluate the influence of input solution composition and holding times on Hg release. Simulated acid rain water (pH 4.6) was used for the input solution for the floodplain soils (MOTO and RRM 22.1) and South River water was used as input solution for the river bank sediments (RRM 0.1 SR6 and RRM 3.5 SRD). In addition, simulated acid rain water was used for the input solution for a second column containing SR6. After addition of the input solutions, the cells were exposed to dry air and then wet air and then rewet on a weekly basis. The cells with river sediments were allowed to stagnate for 4 days prior to exposing to dry air and wet air, whereas the cells with floodplain soils were not allowed to stagnate between flushing events.

The concentrations of unfiltered Hg in the humidity test cell effluent initially exceeded $150 \mu\text{g L}^{-1}$ for all three columns with simulated acid rain water as the input solution (Figure 12). The concentrations then declined steadily for the two soil samples (MOTO and RRM 22.1), approaching a few $\mu\text{g L}^{-1}$ by the end of week 60 (Figure 11, subplots a and b). For the SR6 sediment, the concentrations in the effluent were more sporadic exceeding $100 \mu\text{g L}^{-1}$ in several samples during the experiment (Figure 11, subplot c). For all three sediments, the concentrations of filtered Hg ($0.45 \mu\text{m}$ filter passing fraction) released from the floodplain soils were less than $10 \mu\text{g L}^{-1}$ and generally averaged around $3 \mu\text{g L}^{-1}$. The majority of the Hg ($> 80\%$) was released in the colloidal form ($>0.45 \mu\text{m}$ fraction).

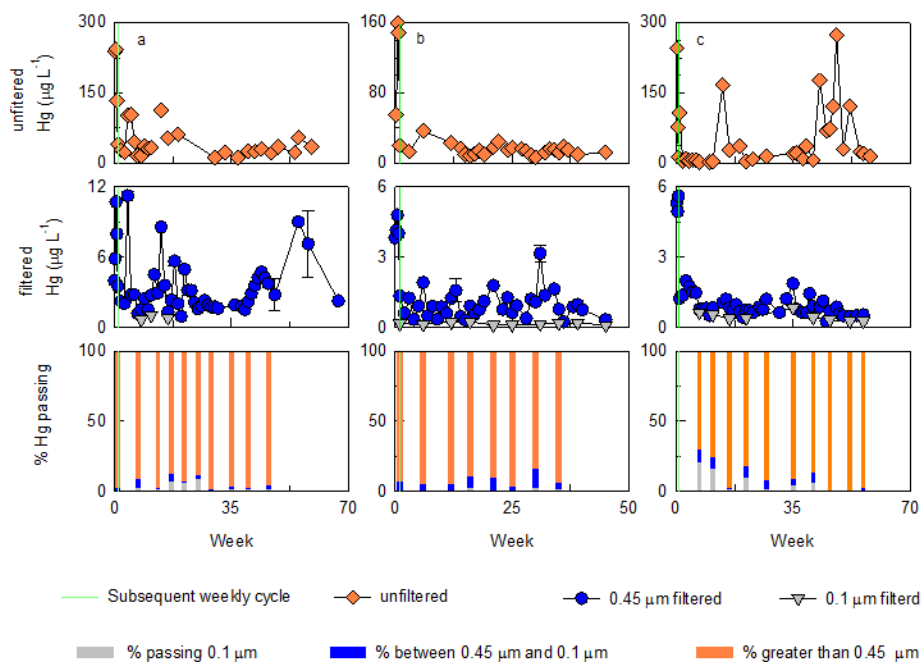


Figure 12. Release of Hg from humidity test cells packed with floodplain soils and riverbank sediment and flushed with simulated acid rain water, including unfiltered Hg, filtered Hg, and Hg filter fractions. a) MOTO soil, b) RRM 22.1 soil, and c) RRM 0.1 SR6 riverbank sediment.

For the cells flushed with South River water (Figure 13), the concentrations of unfiltered Hg and filtered Hg were substantially less than observed for cells with acid rain input (Figure 12). The concentrations of unfiltered Hg approached $50 \mu\text{g L}^{-1}$ from SR6 flushed with the South River water. The concentrations of dissolved Hg (0.45 μm filter passing fraction) from SR6 and SRD were approximately 500 ng L^{-1} as the experiments progressed. The majority of the Hg was present in colloidal forms for both columns during the subsequent weekly cycles.

These results suggest that the transport of Hg in the form of fine-grained particles was likely enhanced due to the combination of both rapid flow rates and alternating wet/dry conditions in the cells. The transport of Hg was greater for the columns with the acid rain water as the input solution. A comparison of the results suggest that the acidic conditions generated in the column with simulated acid rain water as input solution may have promoted the disaggregation of particles allowing greater transport through the sediments.

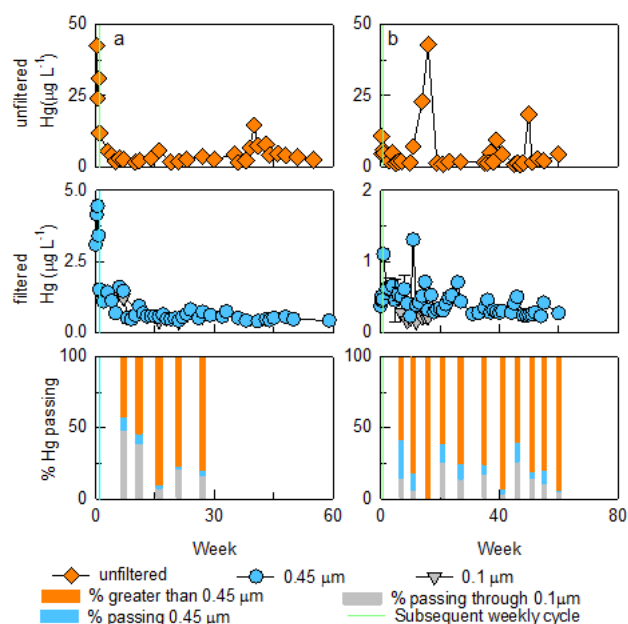


Figure 13. Release of Hg from humidity test cells packed with river bank sediment and flushed with South River water, including unfiltered Hg, filtered Hg, and Hg filter fractions. A) RRM 0.1 SR6, and B) RRM 3.5 SRD

Summary

The studies to date indicate that the distribution and speciation of Hg in the South River sediment and soils are highly variable. The Hg appears to be bound within aggregates of fine sediment particles, some of which is associated with reduced S, likely as metacinnabar. In addition to bound Hg, a portion is readily available for leaching, as indicated by the elevated concentrations of Hg observed in filtered water samples in contact with the sediment, including water collected in resuspension tests, saturated column experiments and humidity test cell experiments. In the low-Hg saturated column experiments with South River water as input solution, the release of Hg was relatively high in comparison to the concentration of Hg in the sediment (*e.g.*, RRM 0.25 (10-12') sediment). These results suggest that the potential for sediments to release Hg cannot be predicted from Hg concentrations in the sediment alone. The low-Hg sediments that were

derived from locations closest to the base flow of the South River appear to leach a greater % of the total Hg in the sediment than those derived from locations further from the water. The application of simulated acid rain water in the humidity test cell experiments also led to greater release of Hg than for South River water as an input solution. Current efforts are directed at completing the mineralogical analyses for the low-Hg and floodplain samples, completing solid-phase characterization and experiments for the new RRM 11.8 test site Hg samples, and integrating the data collected to date.

Acknowledgements

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References

Bloom, N.S., Preus, E., Katon, J., and Hiltner, M. (2003). Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Analytica Chimica Acta*, **479**, 233-248.

Ravel B. and Newville M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* **12**, 537–541.

U.S. EPA (1996). Evaluation of dredged material proposed for discharge in waters of the U.S. – Testing Manual. EPA 823-B-98-004.

Results Summary Update for the Integrated Regional Risk Assessment for the South River and Upper Shenandoah, Virginia

September 2014

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(Photo courtesy of W.G. Landis, 2013)

Project Summary

The briefing paper summarizes objectives, status, major outcomes / conclusions, and any recommendations going forward.

Objective 1: Updated ecological risk assessment for South River Study Area

1. Implement Phase IV of the South River regional scale ecological risk assessment to integrate the ecological with the human health risk assessment.

Status: We have conducted a regional scale risk assessment using Bayesian networks (Ayre and Landis 2012) structured on the relative risk model (RRM) as described by Landis and Weigers (2005). The Bayesian networks relative risk model (BN-RRM) calculations were performed in three parts (**Figure 1**):

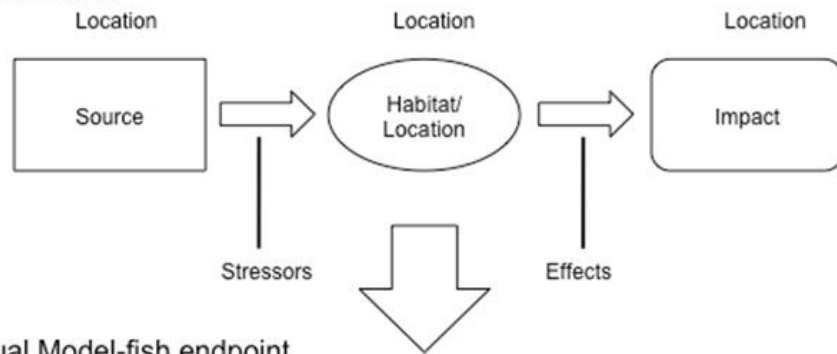
1. We conducted the risk assessment using two fish species and two bird species as biotic endpoints (Summers 2012).
2. Concurrently, a BN-RRM was constructed and applied to four water quality parameters that are specifically tied to ecosystem services delivered by the South River.
3. The outputs of the two BN-RRM models were then combined using Monte Carlo analysis to provide an overall characterization of relative risk within the South River watershed.

Outcome: An increasing gradient of risk was identified that extends from Region 1 north until the merger of the South River with the South Fork of the Shenandoah River (**Table 1**). The smallmouth bass had the highest risk scores, with regions 4 and 5 being the areas of highest risk to them. Carolina Wren were also at high risk in these regions, but had lower risk scores than the smallmouth bass. White sucker and Belted Kingfisher had the highest risk scores in region 2. All biotic endpoints except white sucker had lower risk in region 6 (the South Fork of the Shenandoah) compared to region 5.

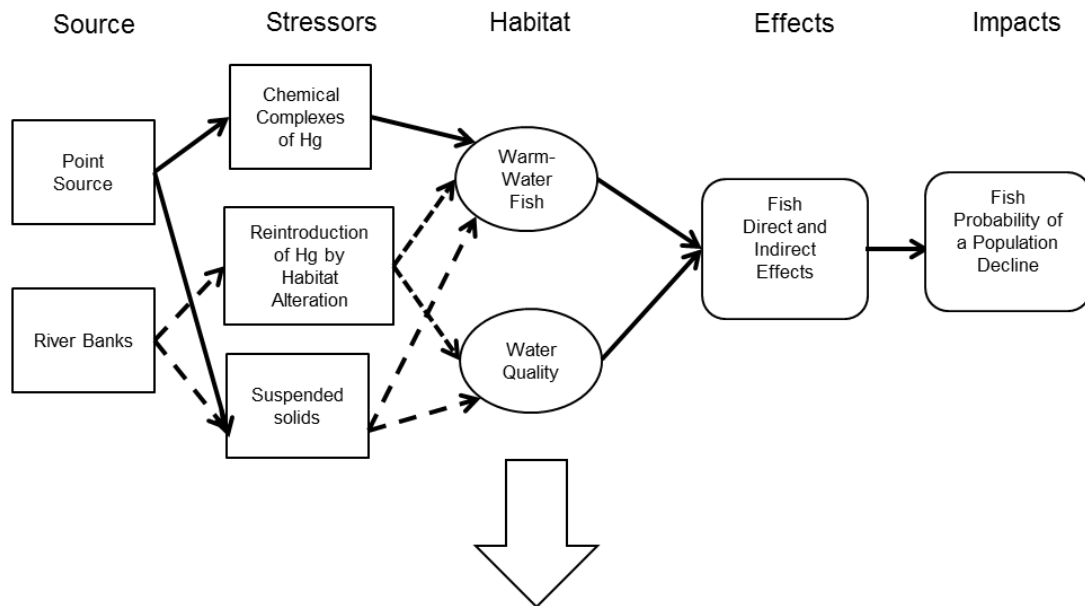
Table 1. Risk Scores for the different endpoints by risk region. SMB-smallmouth bass, WS-white sucker, BK-Belted Kingfisher, CW-Carolina Wren, WQ-water quality standards, WF-fishing standards, WS2-swimming standards, WB-Boating standards. To provide perspective for the total risk scores a maximum risk score would be 48 (24 from each the biotic and WQ).

Biotic Endpoints					Water Quality				Totals		
Region	SMB	WS	BK	CW	WQ	WF	WS2	WB	Biotic	Water	Overall
2	2.4	3.6	2.5	1.1	4.9	1.6	4.5	4.4	9.6	15.4	25
3	2.7	3.1	1.5	1.9	4.5	1.5	4.6	4.6	9.2	15.2	24.4
4	4.3	2.4	2.1	3	4.5	2.1	4.3	4.2	11.8	15.1	26.9
5	4.5	1.3	2.2	2.9	4.8	1.9	4.8	4.7	10.9	16.2	27.1
6	3.3	1.7	1.5	2.5	4.3	1.2	4.6	4.5	9	14.6	23.6

Relative Risk Model



Conceptual Model-fish endpoint



BM-RRM Smallmouth Bass endpoint

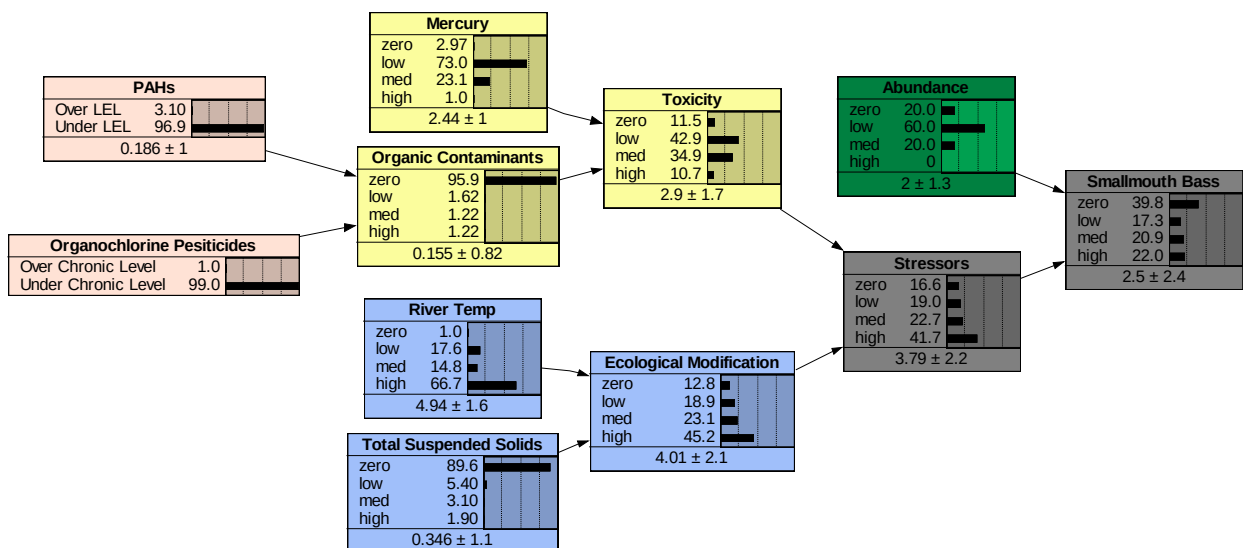


Figure 1. Derivation of a Bayesian Networks RRM. The basic form of the RRM (top) is converted into a conceptual model that describes the cause-effect linkages that will be used to estimate risk (middle). Finally a Bayesian Network is built that describes these pathways and incorporates the likelihood distributions for each variable (bottom).

2. **Uncertainty Reduction:** To reduce uncertainty, additional analyses were conducted to better describe the toxicity of Hg to fish and temperature tolerances of smallmouth bass.

- A. Hg Toxicity to Fish: An analysis of the exposure-response data, summarized in Dillon et al. (2010), by curve fitting allowed a better description of the toxicity at lower levels of Hg exposure. Raw Hg concentration data and model predicted mercury fillet concentration values for the smallmouth bass, white sucker and fishing river use endpoints were used (**Figure 2**).

Outcome: The BN-RRM output showed only a slight change in the probability of risk to smallmouth bass. Overall, this output resulted in an increase in the total risk score for all risk regions.

- B. Temperature Tolerances of Smallmouth Bass: A detailed analysis of the temperature tolerances of smallmouth was constructed by referring to data from the scientific literature. The analysis of these data for both high and low temperature ranges allowed the construction of an exposure-response curve that included both extremes (**Figure 3**).

Outcome: After applying the alternative temperature ranking schemes to the BNs, very little change was observed to the smallmouth bass risk scores in any risk region, however, overall there was a slight decrease in risk.

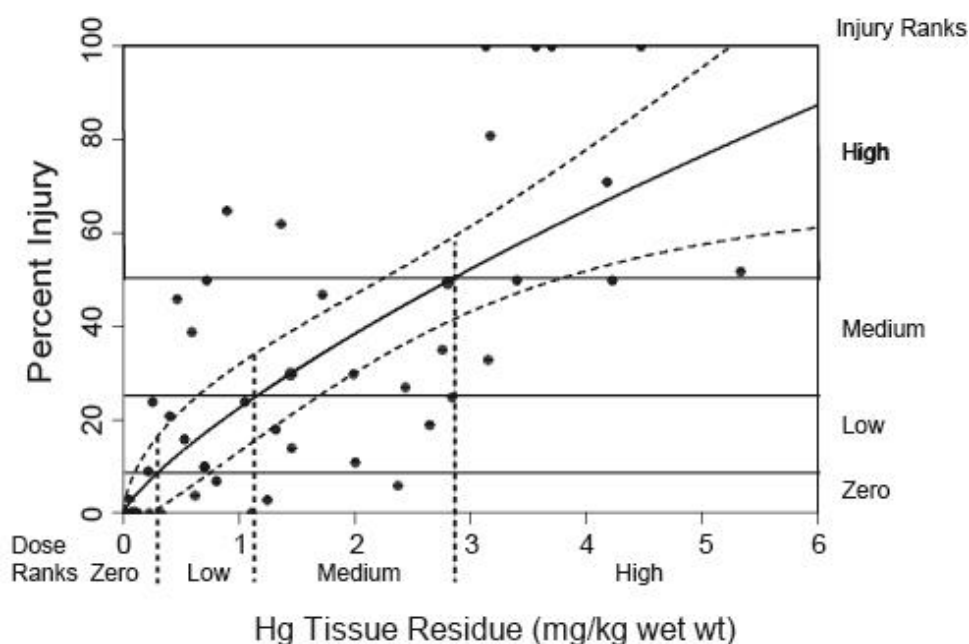


Figure 2. Exposure-response curve for determining exposure ranks based on tissue residue in fish to Hg.

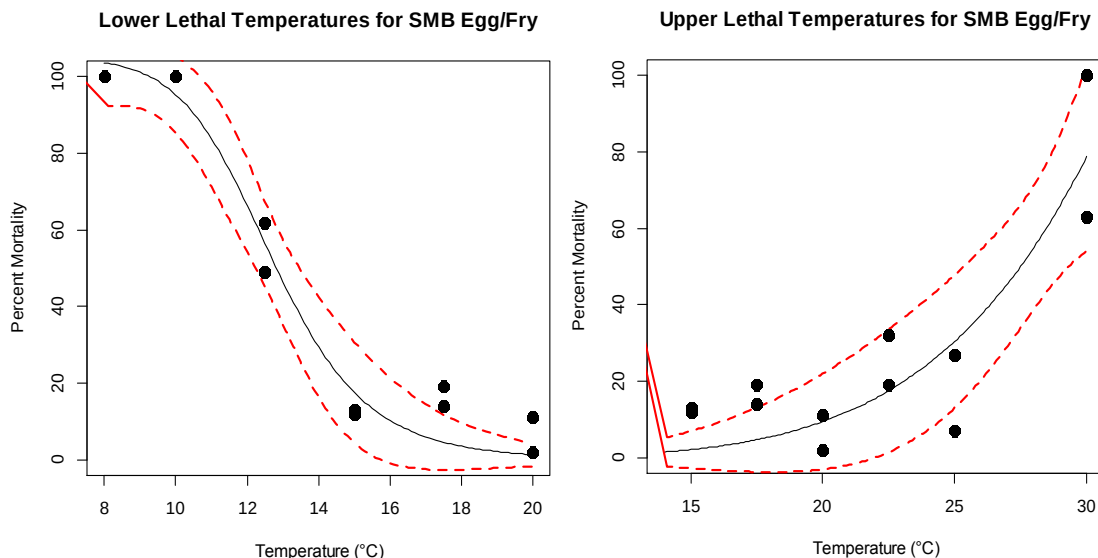


Figure 3. Temperature and percent mortality data for smallmouth bass egg and larval stages. This is a log-logistic model; dashed lines indicate 95% confidence intervals (CI). The 63% mortality point at 30°C represents eggs that hatched, but larvae died soon after hatching. Data source: Kerr 1966, also see Shuter et al. 1980.

We also incorporated the latest data obtained earlier in the year from the South River Science Team as compiled by URS into our analysis. The data included the more current monitoring information for a number of variables included in the risk assessment.

3. Risk from Combining Alternative Mercury Concentration and Temperature Scenarios

Status: We explored combinations of the alternative temperature and methylmercury concentration scenarios to identify the highest and lowest probabilities of risk associated with each region.

Outcomes: Cold temperatures in combination with lower Hg concentrations (lower confidence intervals in Figure 2) resulted in a shift from high to lower risk, especially in the northernmost risk region, Region 6 where risk declined from 38% to 25.5%.

Objective 2: Integration to Adaptive Management and Monitoring

Status: The two current management alternatives for the South River have been evaluated. The management options included agricultural best management practices (BMPs) and bank stabilization. We adapted our initial BNs to include nodes specific to the effects that each will have within the watershed.

Outcomes: Agricultural BMPs did not increase risk to any assessment endpoint. The bank stabilization management option resulted in a shift to lower risk for some biotic endpoints (e.g. smallmouth bass), but at the potential cost of increasing risk to Belted Kingfisher by removing nesting habitat (**Figure 4**).

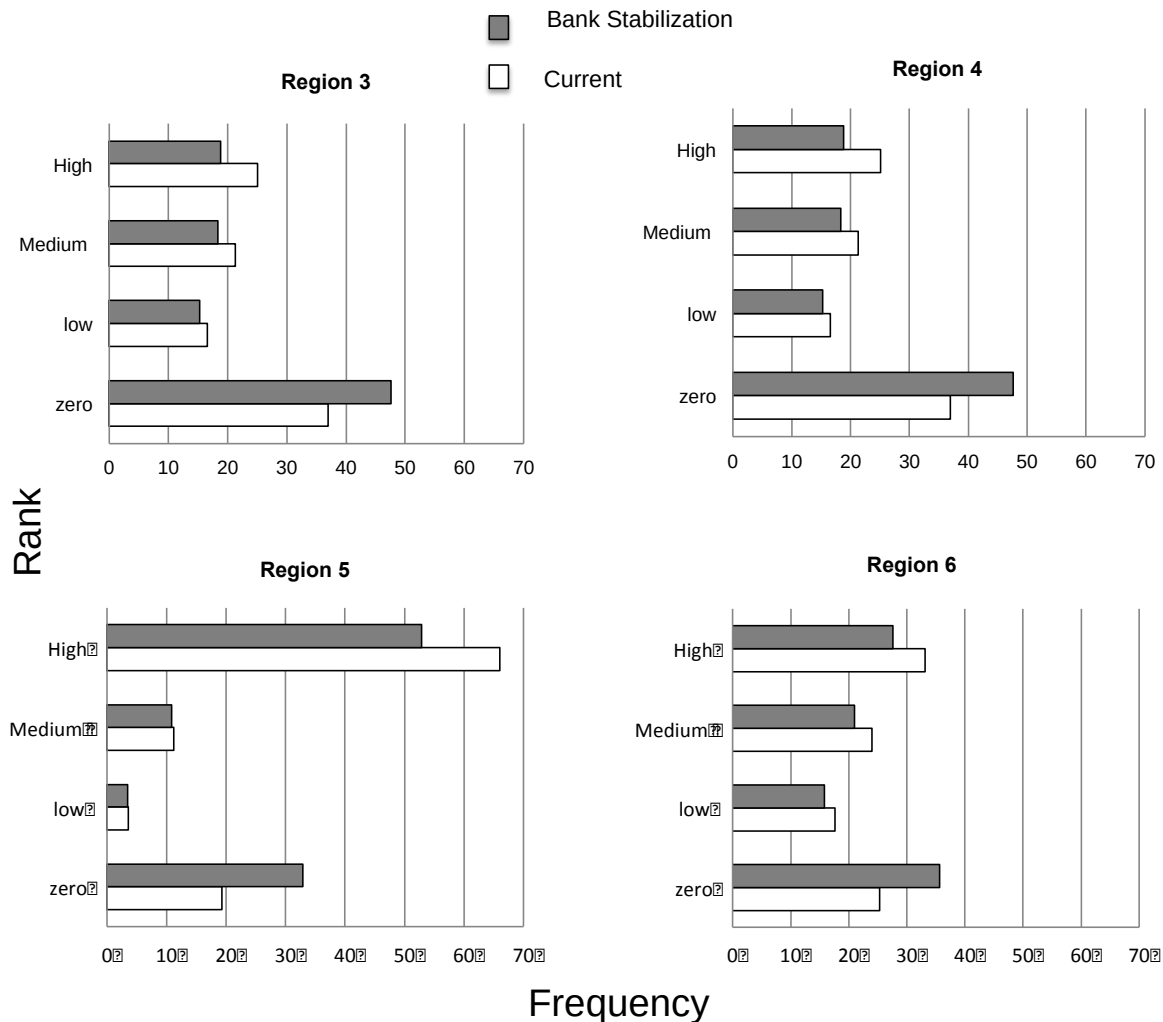


Figure 4. Effects of bank stabilization on risk to smallmouth bass. Graphical representations from Netica™ show the current risk distributions for smallmouth bass, and predicted risk distributions after bank stabilization management is employed in the South River. The frequency of the high and medium ranks decreased and the low and zero risk ranks increased compared to current risk.

The risk assessment process has also provided a list of variables associated with each assessment endpoint that should be measured as part of the long-term monitoring program of the South River Science Team (**Table 2**). The variables are listed for each endpoint and by the importance of each variable to be sampled. From the management alternatives assessment, a list of measurements was developed for both the BMP and the bank stabilization activities (**Table 3**).

Table 2. Monitoring to support the risk analysis. The monitoring parameters for each of the endpoints are based on the parameters that have the greatest influence on the risk to the fish, birds, and water quality endpoints. The parameters are listed from top priority down, and the numbers in parentheses indicate in how many regions the parameter was important. The parameters in **BOLD** font are the parameters that we would like SRST to monitor, the other data we obtained from outside sources.

Belted Kingfisher**Mercury (5)** – Blood samples**Fish Length (5)****Potential Habitat (2)** – Land use type (%)**Territory (3)** – Nests per length of river section (m)**Carolina Wren****Mercury (4)** – Blood samples

Nest Predation (5)

Potential Habitat (2) – Land use type (%)

Winter Air Temperature (4)

Smallmouth Bass**River Temperature (5)****Mercury (5)** – fish fillet mercury conc.**White Sucker****River Temperature (5)****Stream Cover (5)** – Submerged aquatic vegetation cover (%)**Mercury (4)** – Fish fillet mercury Conc.**Organic Contaminants (1)****Water Quality Standards****Dissolved Oxygen (5)** - Summer DO**Bacteria (4)** – Bacteria indicators (E. coli)**River Temperature (3)** – Winter temp.**River Discharge (3)** – Summer & winter discharge**Fishing River Use****Dissolved Oxygen (5)** – Summer DO**Methyl Mercury (4)** – Fish fillet MeHg conc.**River Temperature (5)** – Summer & winter temp.**Swimming River Use****Bacteria (4)** – Bacteria indicators (E. coli)**River Temperature (5)** – Summer & winter temp.**River Discharge (1)** – Summer Discharge**Boating River Use****River Temperature (5)** – Summer & winter temp.**Bacteria (4)** – Bacteria indicators (E. coli)**River Discharge (1)** – Winter Discharge

Table 3. Adaptive Management Parameters: The lack of site-specific data added to the difficulty of parameterizing the management models. As adaptive management alternatives are implemented, monitoring the following parameters would decrease the uncertainty of our subsequent management assessments.

Agricultural best management practices

Total suspended solids

Total phosphorus

E. coli levels**Bank stabilization**

Total suspended solids

Fish fillet mercury concentrations

Bird blood mercury concentrations

Stream cover

Habitat alteration (habitat loss for the Belted Kingfisher)

Dissolved oxygen

Discharge

Objective 3: Human Health and Integrated Risk Assessment

Status: The integration of human health risk assessment with the ecological risk assessment (HHRA-ERA) is underway and a conceptual model and preliminary Bayesian network are complete (**Figure 5**). This assessment will have two focuses: risk to human health from mercury exposure via dietary sources and risk to recreational activities in the South River watershed. The integration process began with endpoint selection and construction of the conceptual model, and will continue through risk analysis and risk communication.

South River RRM Human Health Conceptual Model

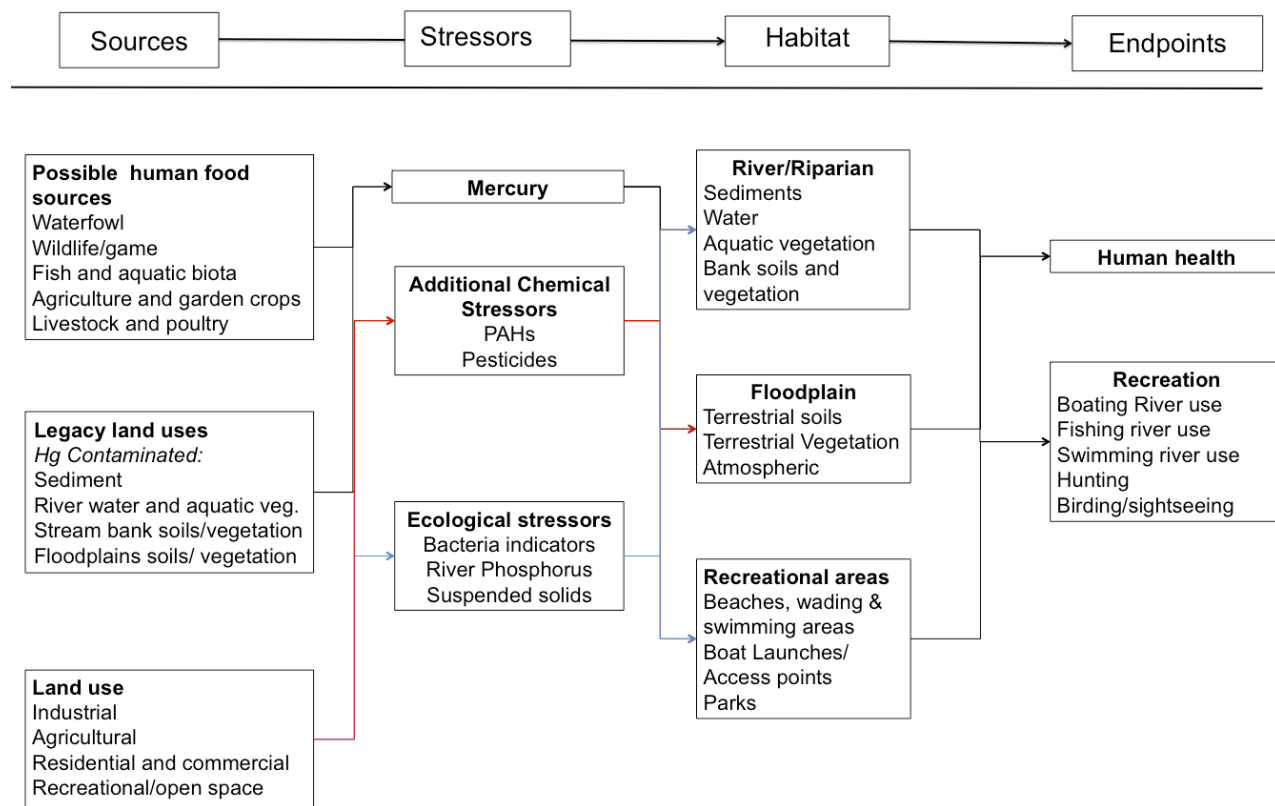


Figure 5. Conceptual model for the human health risk assessment. The model fits the overall structure of the relative risk model.

Isotopic Characterization of Mercury in the South River, Virginia
Briefing Paper
September 30, 2014

Prepared for the South River Science Team Remediation Options Program October Meeting by
Spencer Washburn and Joel Blum, Dept. of Earth and Environmental Sciences, University of
Michigan

1. Introduction

The measurement of mercury (Hg) isotope ratios in environmental reservoirs has been used in recent studies to identify sources of anthropogenic Hg and trace the movement of Hg between and within reservoirs. High precision measurements of Hg isotopic composition are made possible by separation and concentration of Hg from samples followed by introduction of a cold Hg vapor into the plasma source of a multi-collector inductively coupled mass spectrometer (MC-ICP-MS). Hg has seven stable isotopes (with masses 196, 198, 199, 200, 201, 202, and 204) and participates in a variety of redox reactions, which can cause isotope fractionation. Hg can undergo two general types of isotope fractionation: mass-dependent fractionation (MDF) and mass-independent fractionation (MIF). MDF occurs in reactions with nuclear mass selectivity, and is generally reported as the $\delta^{202}\text{Hg}$ value¹, where:

$$\delta^{202}\text{Hg} (\text{‰}) = \left(\left[\frac{(^{202}\text{Hg}/^{198}\text{Hg})_{\text{Sample}}}{(^{202}\text{Hg}/^{198}\text{Hg})_{\text{NIST3133}}} \right] - 1 \right) \times 1000$$

MDF has been observed in a number of biological reactions, including microbial methylation and reduction. MIF occurs in reactions with nuclear spin selectivity, and is reported as $\Delta^{199}\text{Hg}$ or $\Delta^{201}\text{Hg}$, calculated as the deviation of the odd-mass isotopes from the predicted kinetic isotope fractionation law in units of ‰. For Hg, MIF has mostly been observed as the result of photochemical reactions^{2,3}.

2. Proposed Work

The objective of this project is to utilize variations in natural Hg stable isotope composition to enhance understanding of Hg sources, mobility, speciation and bioavailability in the South River. An emphasis will be placed on providing new constraints on the chemical and biological processes that lead to methylmercury (MeHg) production, degradation, transport and uptake by aquatic organisms. The Hg stable isotope method has proven useful at other similar sites such the area near Oak Ridge Tennessee⁴, and there is great potential for adding new insight to the factors and mechanisms leading to methylation, transport and biological uptake of Hg in the contaminated South River ecosystem and other nearby stream ecosystems. Specific objectives of the proposed work include:

1. Characterize the spatial variability of the Hg isotopic composition in channel, bank and overbank sediments in a longitudinal transect of the South River from 1 mile upstream of the DuPont facility to 20 miles downstream and in several reference sites.
2. Characterize the Hg isotopic composition of the plant outfall and potential point sources of mercury downstream of the DuPont site to the South Fork of the Shenandoah River.

3. Characterize the Hg isotopic composition of creek bottom periphyton, select benthic organisms, and several fish species such as stoneroller minnows (*Camptostoma anomalum*), redbreast sunfish (*Lepomis auritus*) and smallmouth bass (*Micropterus dolomieu*) from sites in South River within the first ten miles after the outfall to obtain the isotopic signature of IHg and MeHg in the creek at various sites.
4. Evaluate the concentration of chemically labile Hg in sediment using dilute acid extraction and measure the Hg isotopic composition of this more biologically available pool to determine whether it is the same or different from Hg in bulk sediment.
5. Characterize the Hg isotopic composition of filtered stream water, suspended sediment and stream bank piezometer water to explore interconnections of flood plain pore groundwater with streamwater.

3. Field Sampling

An initial field sampling campaign to acquire samples for isotope analysis was conducted by Rich Landis and Scott Gregory on April 9th and 10th, 2014. During this initial sampling, sediment and bank soil samples were collected from the following locations within the South River: SR-01 reference site, Outfall-011, Relative River Mile (RRM) 0.25 (Constitution Park), RRM 1.7, RRM 3.5, RRM 8.5, RRM 11.8, RRM 22.1, and floodplain site Wertman Pond. Sediment and bank soil samples were shipped frozen to the BEIGL lab at The University of Michigan.

A second field sampling campaign to collect filtered stream water, suspended sediment and stream bank piezometer samples was conducted between June 24th and 26th, 2014 and involved three members of the Blum lab group and Rich Landis. Filtered water and suspended sediment samples were collected at each of the locations where sediment and bank soil had been collected during the initial field sampling effort, as well as at reference sites on the Middle River (MR-01) and the South Fork Shenandoah (SFR-01). The stream bank piezometers at the RRM 3.5 site were sampled for filtered water and suspended sediment using a portable peristaltic pump. Water samples were collected, filtered, and preserved in the field, using trace-metal clean sampling methods involving a hand operated vacuum-pump and disposable, pre-cleaned 45µm filter housings. Filters and water samples were placed in refrigerated storage at the end of each sampling day, and transported in coolers back to the University of Michigan.

4. Laboratory Status

As of the time of writing, all of the sediment and bank soil samples collected during the April field sampling effort have been analyzed. The filters collected during the June sampling trip, representing the suspended mercury load, have been processed for analysis and combusted. Surface water samples collected in June have not yet been processed, but we plan to begin the processing this fall.

5. Results

The THg concentrations of the sediment and bank soils collected along the longitudinal transect of the South River are presented in Figure 1 (see Appendix 1). The concentration

profiles are in general agreement with previous studies. The bank soil THg concentrations peak at 65ppm directly downstream of Outfall 011, while the sediment concentrations peak at 45ppm around RRM 3.5, with concentrations decreasing dramatically farther downstream.

The longitudinal variation in $\delta^{202}\text{Hg}$ values in the South River is shown in Figure 2. The $\delta^{202}\text{Hg}$ values for the upstream reference site SR-01, presumed to be representative of the regional background $\delta^{202}\text{Hg}$ values, are -1.01‰ for the bank soil and -1.27‰ for the sediment. This is isotopically distinct from the first contamination impacted site, Outfall 011, where the bank soil and sediment $\delta^{202}\text{Hg}$ values are -0.65‰ and -0.60‰ respectively. Within the initial reach below Outfall 011, sediment and bank soil samples have very similar $\delta^{202}\text{Hg}$ values, indicating that the mercury came from the same source and has not been modified by fractionation. Wertman Pond samples (floodplain pond) appear to be isotopically similar to mercury in sediment directly upstream, in line with the hypothesis that movement of sediment loads during flood events is a source of mercury to floodplains. At site RRM 22.1, $\delta^{202}\text{Hg}$ values trend toward a mixture between regional background and contaminated source signals.

The longitudinal change in the $\Delta^{199}\text{Hg}$ values of the bank soils and sediments along the longitudinal transect is depicted in Figure 3. As with the $\delta^{202}\text{Hg}$ data, we observe a significant difference between the regional background values at SR-01 (-0.21‰ for sediment and -0.18‰ for bank soil) and the contamination impacted sites (0.04‰ for sediment and 0.03‰ for bank soil). At sites farther downstream, the increased $\Delta^{199}\text{Hg}$ values may be evidence of photochemical reduction and subsequent loss of $\text{Hg}(0)$ from bank soils.

Through a comparison of MDF and MIF, represented by $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$, we can explore interactions between various Hg reservoirs. The sediment and bank soil data are plotted as $\delta^{202}\text{Hg}$ vs. $\Delta^{199}\text{Hg}$ in Figure 4. The sediment data falls into two groupings, representing the influence of the regional background Hg isotopic value and the contaminated source value. The two distinct groupings suggest that the Hg in the sediments in the South River follows a simple two end-member mixing model. The sediment samples do not appear to be influenced by a third isotopic end-member, such as the atmospheric end-member that was observed to influence the sediments in the contaminated East Fork Poplar Creek near Oak Ridge, TN⁴. Several of the bank soil samples do not appear to fit a simple two end-member mixing model. This suggests either an additional Hg source or isotopic fractionation due to changes in Hg speciation, but more research is necessary to determine what processes may be influencing the bank soils.

6. Preliminary Conclusions

Some of the preliminary conclusions we can draw from the sediment and bank soil data are presented below. We expect to fill in many of the gaps in our understanding of the system with mercury isotope analyses of the suspended and dissolved Hg loads of the South River system. An important conclusion we can draw from the initial sediment and bank soil samples is that the regional background mercury source is isotopically distinct in both $\Delta^{199}\text{Hg}$ and $\delta^{202}\text{Hg}$ from the mercury derived from the source of contaminated media. The difference between source and regional background isotopic signatures is significantly large to allow for determination of the source for various pools of mercury within the South River fluvial system. The mercury load in the streambed sediments of the South River follow a two end-member mixing model, unlike a previously studied contaminated fluvial system at Oak Ridge, TN⁴. We also observed that within the initial reach below Outfall 011, sediment and bank soil samples have very similar $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values, suggesting the mercury came from the same source and has not been modified by

fractionation. Further downstream sediment and bank soil samples deviate in $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ values suggesting different sources or fractionation processes. Finally, there is preliminary evidence from the $\Delta^{199}\text{Hg}$ data that photochemical reduction and loss of $\text{Hg}(0)$ is occurring within the South River at downstream locations, although further work needs to be done to better understand the role of photochemical reactions within the system.

References

1. Blum, Joel D, and Bridget a Bergquist. 2007. "Reporting of Variations in the Natural Isotopic Composition of Mercury." *Analytical and Bioanalytical Chemistry* 388 (2) (May): 353–9.
2. Blum, Joel D., Laura S. Sherman, and Marcus W. Johnson. 2012. "Mercury Isotopes in Earth and Environmental Sciences." *Annual Review of Earth and Planetary Sciences* 42 (1)
3. Bergquist, Bridget A, and Joel D Blum. 2007. "Mass-Dependent and -Independent Fractionation of Hg Isotopes by Photoreduction in Aquatic Systems." *Science*. 318 (5849) (Oct): 417-420
4. Donovan, Patrick M, Joel D Blum, Jason D Demers, Baohua Gu, Scott C Brooks, and John Peryam. 2014. "Identification of Multiple Mercury Sources to Stream Sediments Near Oak Ridge, TN, USA." *Environ. Sci. Technol.*, 48 (7), pp 3666–3674

Appendix 1: Figures

Figure 1- THg Concentration Along Longitudinal Transect of South River

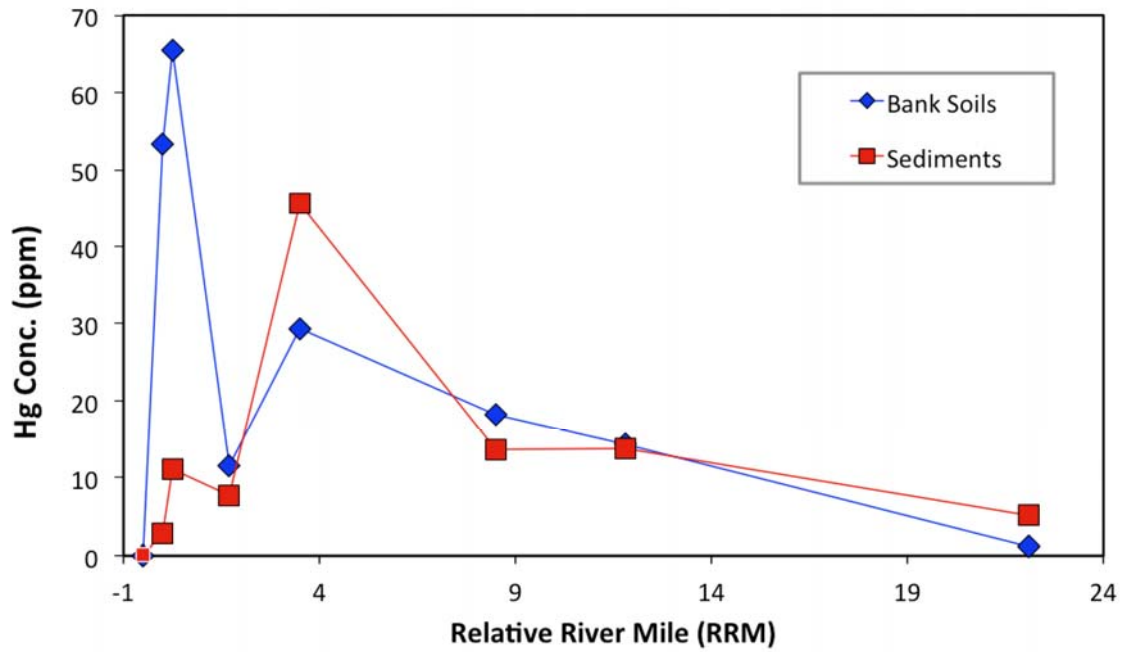


Figure 2 - $\delta^{202}\text{Hg}$ Values Along a Longitudinal Transect of the South River

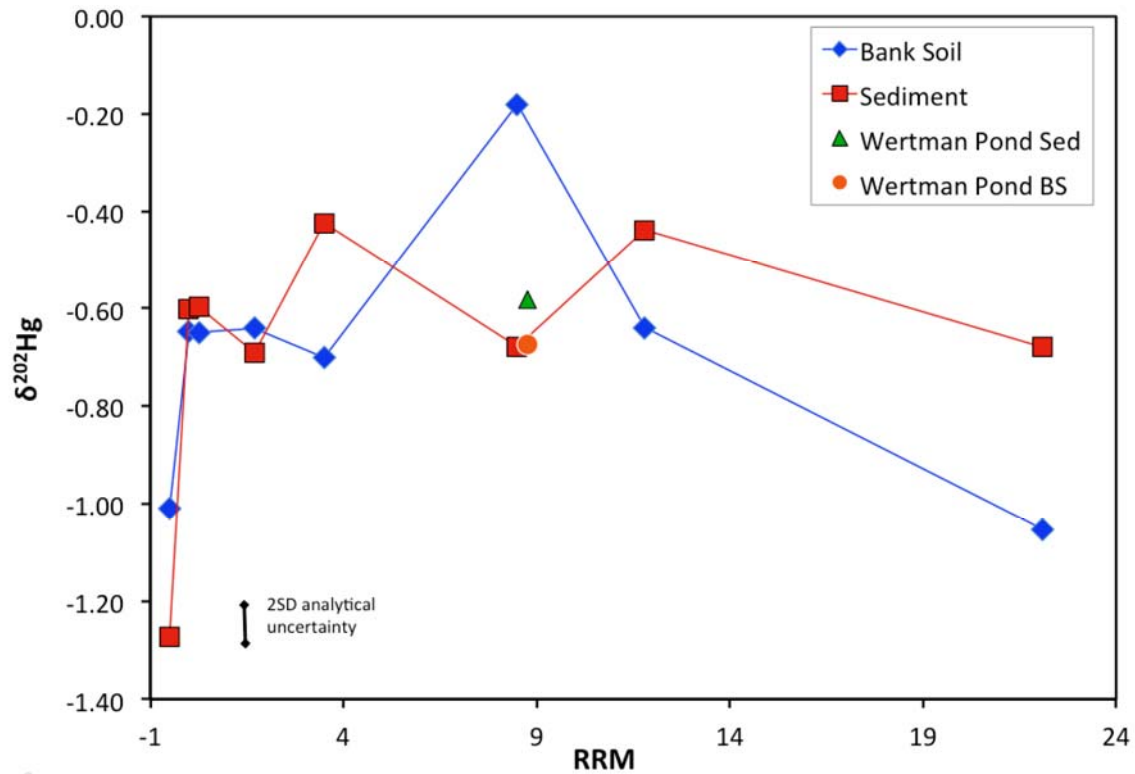


Figure 3 - $\Delta^{199}\text{Hg}$ Values Along a Longitudinal Transect of the South River

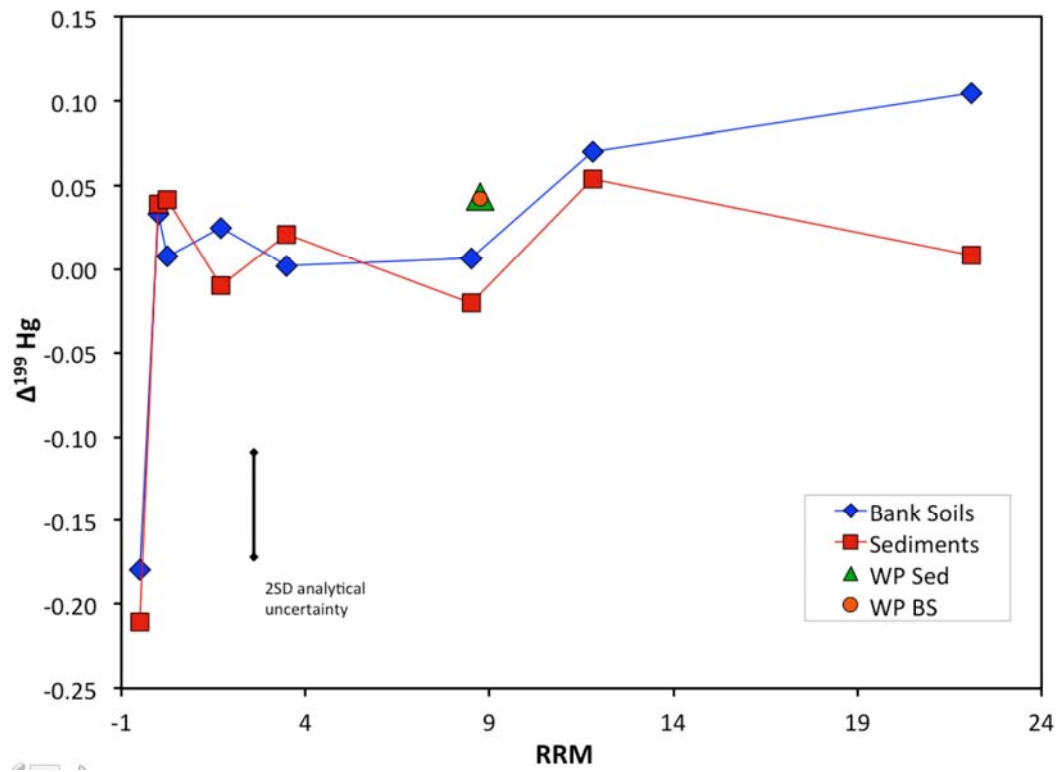
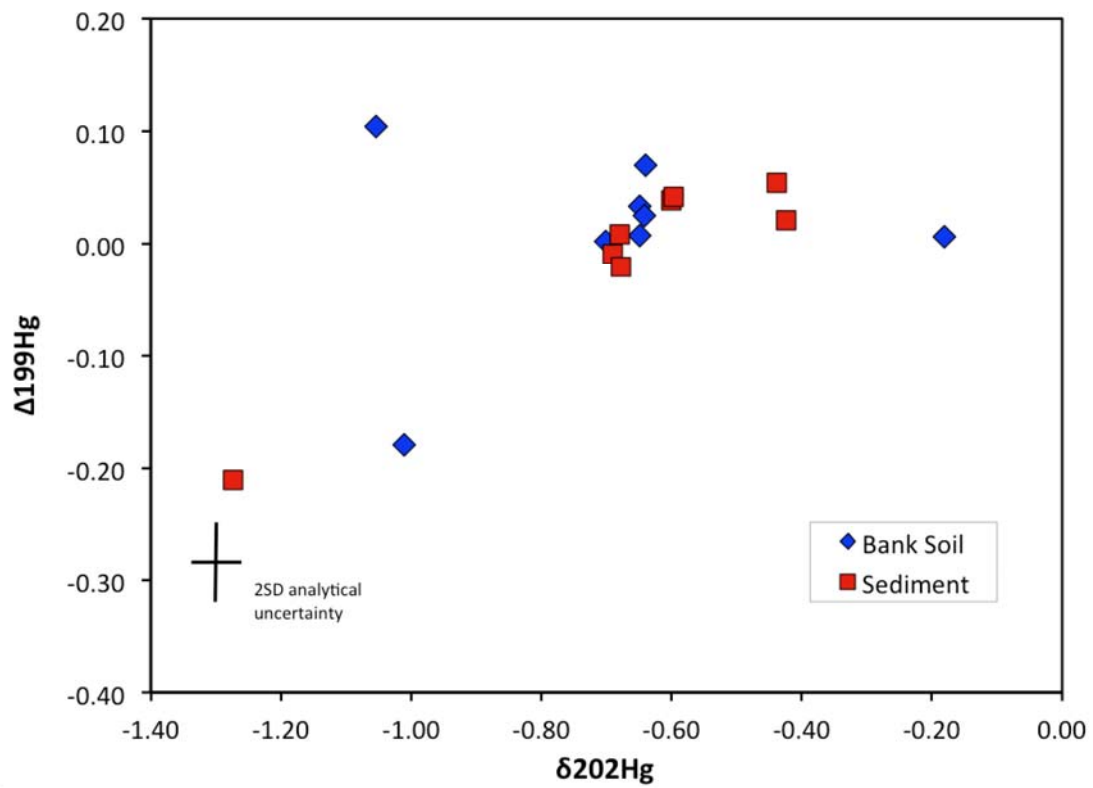


Figure 4 - Plot of $\Delta^{199}\text{Hg}$ (MIF) vs. $\delta^{202}\text{Hg}$ (MDF)



Mercury Bioaccumulation from Unamended and Amended South River Sediments – September 2014 Update

M.C. Newman - VIMS

Background

As the DuPont team moves into the remediation stage for the South River, sediment amendment with sorbents has emerged as one promising tool. Candidate materials range from expensive thiol SAMM[®] nanoparticles, to fabricated iron sulfide nanoparticles, to Exponent's moderately priced Sedimite[®], to low-cost biochars. The ongoing Wertman pond amendment trial and results from the VIMS 2013 study indicate that Cowboy[®] biochar is a viable candidate for final remediation activities. A previous South River study (Bundschuh et al. 2011)¹ and the assays from the VIMS 2013 study suggested that Sedimite[®] might have the drawback of reducing detrital processing in the detritivory-dominated South River.

The VIMS 2013 study documented general shifts in both bioaccumulation and detrital processing at 0, 1.5, 3, and 6 months after sorbent mixing with Dooms Crossing sediment. Bioaccumulation was significant after 10 days of exposure to sediments but sediment amending did reduce the degree of bioaccumulation. The influence of sediment-amendment mixture ageing on efficacy was not definitive at the end of 2013 study although there did seem to be a decrease in efficacy with time. Explicit bioaccumulation modeling and relative bioavailability estimation were needed to clearly define any remediation-associated bioaccumulation reduction.

The freshwater amphipod, *Hyalella azteca*, was selected as the model collector/shredder for the VIMS studies because it is a common North American collector/shredder, is used widely for ecotoxicological studies, and was used successfully by the VIMS team for an initial study of South River remediation with Sedimite[®] (Bundschuh et al. 2011). It represents the epibenthic invertebrate guild that dominates the base of the South River food web. It is amenable to field exposures in small screened enclosures so that it can potentially be used for future *in situ* post-remediation studies.

Specific 2014 Objectives

1. To model mercury bioaccumulation from contaminated sediments², determining the decrease in bioavailability of mercury in sediments amended with Sedimite[®], or one of three size-grades of Cowboy[®] biochar (<0.25mm, 0.25-1mm, and 1-2mm sieved). Bioavailability is estimated relative to that of unamended sediment.
2. To model mercury bioaccumulation and estimate relative bioavailability from sediments 0, 2 and 4 months after amendment of the sediment. The intent is to document any decrease in efficacy with time.

¹ Arch. Environ. Contam. Toxicol. 60: 437.

² Sediments used in these 2014 assays were collected by Scott Gregory and Richard Landis at the Augusta Forestry Center during the spring of 2014. The mean total mercury in this sediment was 13.7 ug/g DW (SD = 4.7, n = 20). Organic matter, measured as percentage weight loss on ignition, averaged 8.3% (SD = 1.6%, n = 5).

Preliminary 2014 Results

This study estimates mercury bioaccumulation from amended sediments from South River and compares that bioaccumulation to that of unamended sediment. Sediment amended with Sedimite[®] or one of several size classes of Cowboy[®] biochar were studied. Cowboy[®] biochar treatments involved biochar sieved into three size classes: <0.25, 0.25-1, and 1-2 mm. Amending was done at 0.1 gm of material per gm of dried sediment. Treatments were established and the bioaccumulation quantified over 20 day periods immediately, 2, and 4 months after blending. Each treatment was done in duplicate during each period with 100 amphipods per replicate. Two assays are complete at this time and a final one (4 months) is underway. The bioaccumulation of total mercury in amphipods was measured during each time course (0, 1, 2, 3, 4, 5, 7, 9, 12, 15, 20 days) and fit to the following model by nonlinear regression (SAS program),

where $[Hg]_t$ = concentration in amphipods at time, t , $[Hg]_{source}$ = mercury concentration in source sediment, $[Hg]_0$ = mercury in amphipods at time 0, k_e = elimination rate constant, and k_u = uptake clearance rate. The results are presented below as the predicted whole body concentration after 20 days exposure. The concentration at 20 days reflects the concentration at practical equilibrium, i.e., the predicted 95% equilibrium concentration.

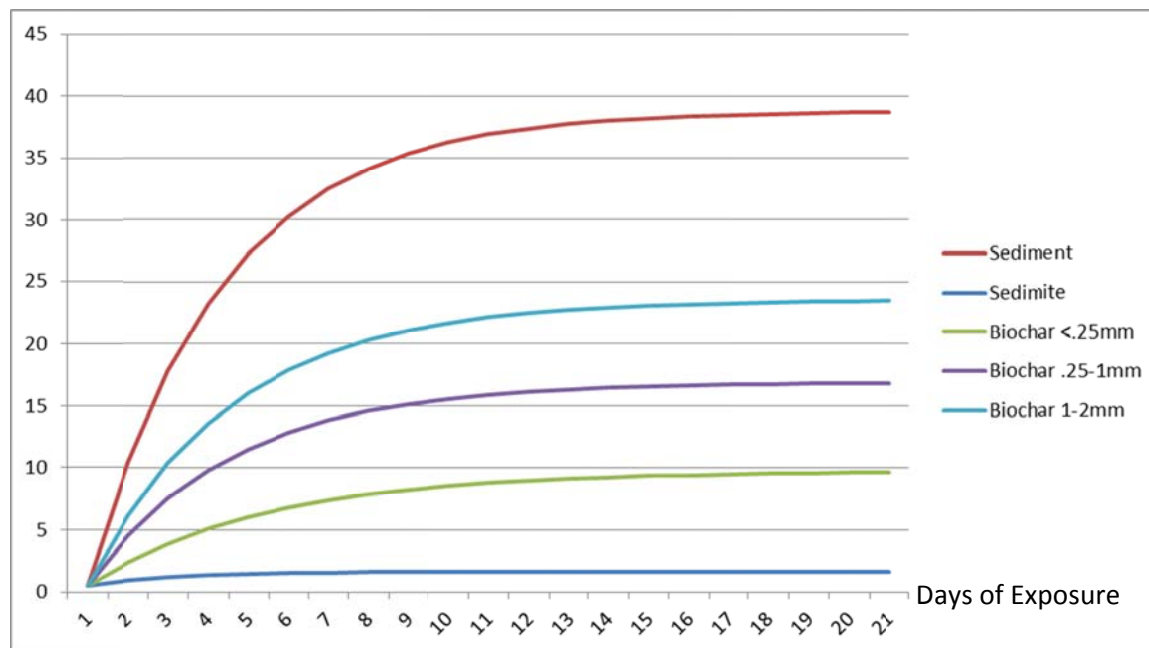


Figure 1. Assay 1 started immediately after blending the sediment and amendments. Relative bioavailability (%) is estimated as 100 times the predicted concentration at 20 days divided by the same for the sediment-only treatment. 38.8 mg/kg is the predicted Hg concentration of amphipods after 20 days exposure to untreated sediment (13.7 mg Hg/kg DW, red line). This assay was conducted in a dark, constant temperature incubator (Mean Temperature = 23.3 C, SD = 0.1 C, n = 41). An initial sample of amphipods used in the assay produced a mean amphipod dry weight of 0.35 mg (SD = 0.11 mg, n = 31). Replicate (n = 45) analyses of the DORM 3 standard material were used to estimate mercury analysis accuracy (percent recovery = 99.7%) and precision (RSD = 3.0%).

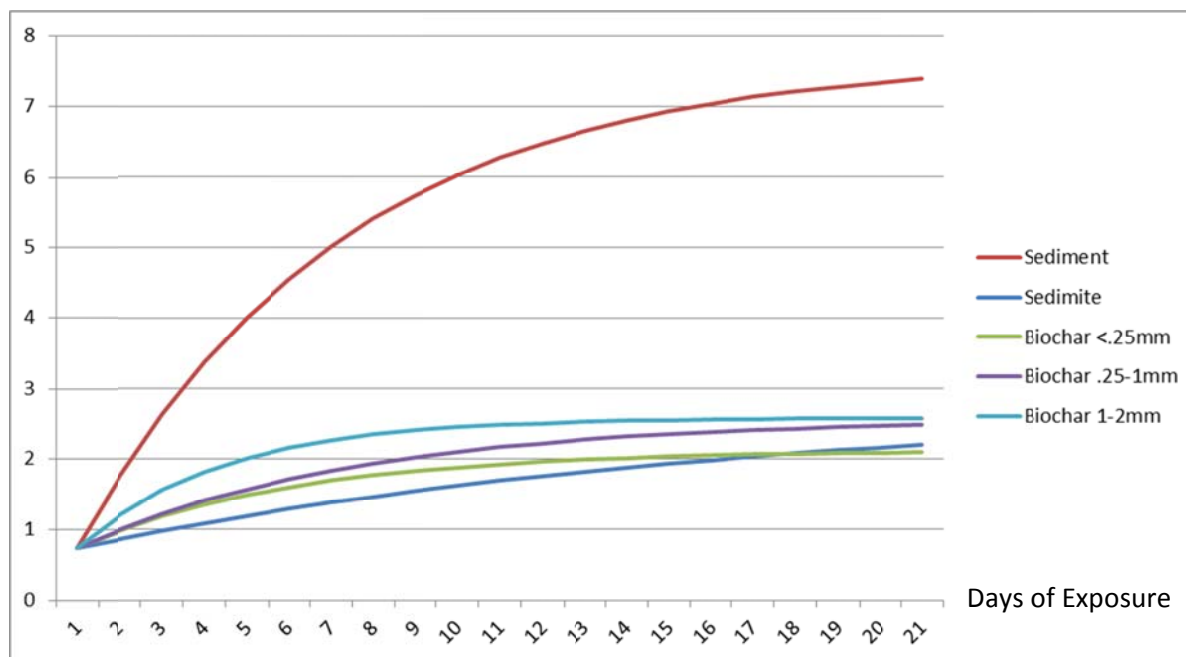


Figure 2. Assay 2 conducted two months after blending the sediment and amendments. Relative bioavailability is expressed as a percentage of the availability from the untreated sediment (red line). This assay was conducted in a dark, constant temperature incubator (Mean Temperature = 23.3 C, SD = 0.1 C, n = 40). An initial sample of amphipods used in the assay produced a mean amphipod dry weight of 0.33 mg (SD = 0.13 mg, n = 40). Replicate (n = 42) analyses of the DORM 3 standard material were used to estimate mercury analysis accuracy (percent recovery = 99.0%) and precision (RSD = 2.4%).

Summary of Results To-date

The mercury from the DooMS sediments was more readily available to amphipods initially than 2 months post-blending. Initially the Sedimite[®] was the most effective sorbent and smaller diameter Cowboy[®] biochar granules were more effective than larger diameter biochar granules. After 2 months, the mercury in the sediments was less bioavailable and all sorbent materials substantially reduced its bioavailability during the assay, i.e., 23 to 35% as bioavailable as that in unamended sediment.

Next Steps

The third (4 months) assay will be completed in November, achieving the two 2014 objectives. To find a possible explanation for the substantial changes in bioavailability in the unamended sediments through time, samples of sediments from the three assays will be sent to CEBAM for methylmercury analysis. Also, samples of the sorbent materials are being analyzed for available surface area so that differences among materials can be explored relative to differences in surface areas of the four materials.

The promise of successful remediation by biochar amendment is apparent from these results. What remains to be done is to move the investigations into the field. Leaf pack deployment to measure detrital processing (to establish a baseline prior to any amendment activities) and also mesocosms to quantify bioaccumulation and detrital processing differences upon field treatment seem very appropriate at this time.

SOUTH RIVER PHASE 1 INTERIM MEASURES DESIGN, IMPLEMENTATION, AND MONITORING WORK PLAN

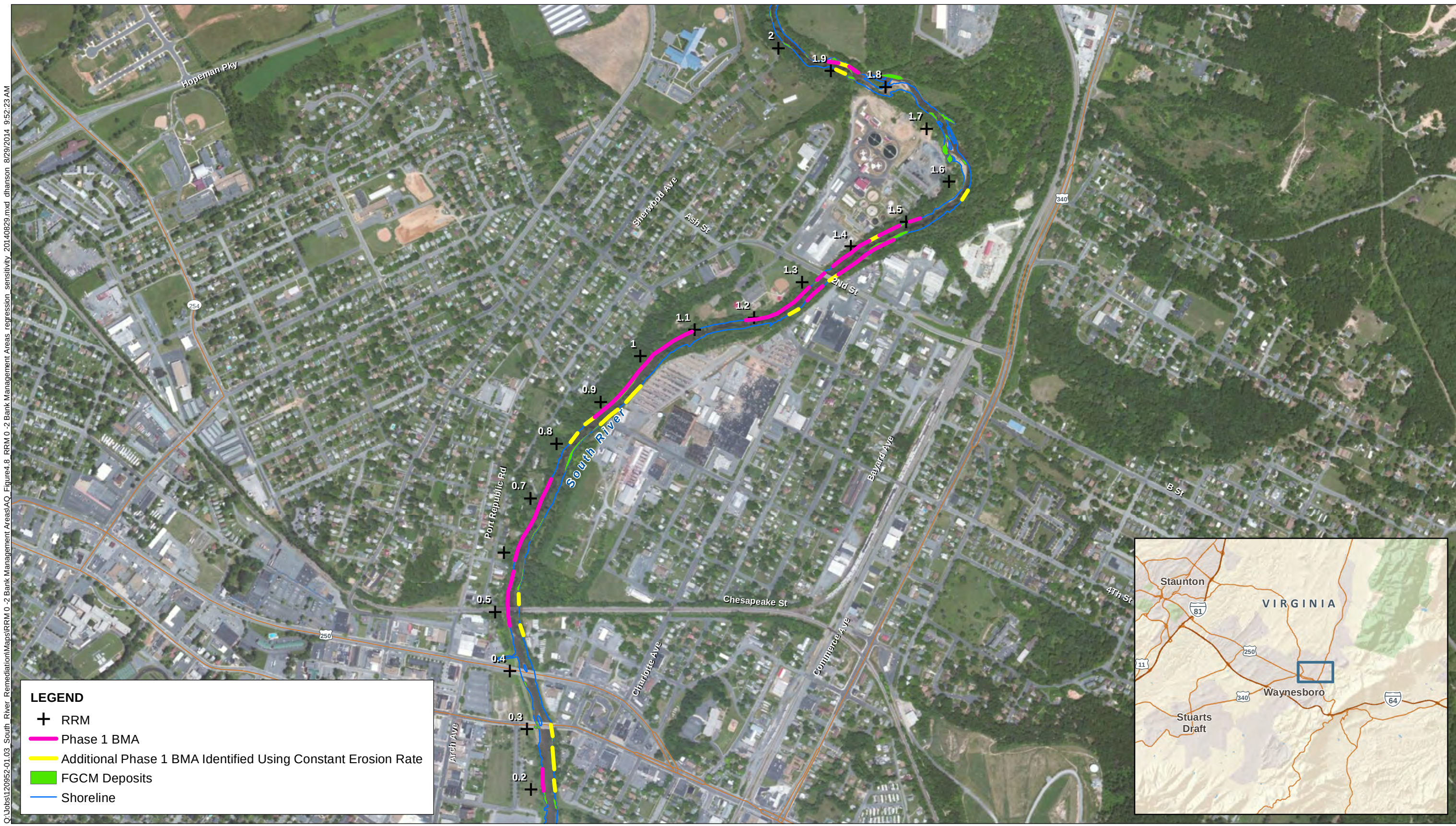
The August 2014 *Interim Measures Design, Implementation, and Monitoring Work Plan* (IM Work Plan) prepared by Anchor QEA, URS Corporation, and E. I. du Pont de Nemours and Company (DuPont) under oversight by the Virginia Department of Environmental Quality outlines the rationale for remediating riverbanks in the South River, Virginia, within an adaptive management framework, and describes the process to design and permit actions in the first 2 relative river miles (RRM) below Waynesboro. The IM Work Plan is part of a larger remedial strategy designed to address mercury historically released from the former DuPont Waynesboro facility to the South River and a portion of the South Fork Shenandoah River. It also reflects the technical and legal frameworks for addressing legacy mercury, agreed to by DuPont with the various governmental and non-governmental parties involved with the South River. The main working hypothesis is that reducing the loading of mercury to the South River in a stepwise, upstream-to-downstream manner will result in progressive improvements within the river and the adjacent riparian zone and floodplain terrestrial environment. Careful monitoring of the outcome of the first set of interim measures (Phase 1) will help adjust the scope of subsequent phases as part of an iterative learning process. As has been the case for collaborative work done since 2001, stakeholder engagement on Phase 1 and subsequent work will take place primarily through the South River Science Team. However, additional outreach to local communities along the South River will be conducted as required under the Resource Conservation and Recovery Act.

Detailed evaluations of shear stresses in the river, bank erosion rates, bank heights, and bank face mercury concentrations were performed to identify those banks that contribute disproportionately to bank erosion loading of total mercury to the South River. Using hydrodynamic and regression models relating peak river shear stress to measured bank erosion rates, approximately 90% of the estimated bank mercury loading to RRM 0 to 2 is likely attributable to roughly 23% (0.9 miles) of the banks. However, because of uncertainties in calculated loadings using the regression model, additional bank segments with relatively higher bank height and bank face total mercury concentrations (with total mercury loadings calculated assuming a constant bank erosion rate) were also included,

providing a more conservative approach to Phase I implementation. Thus, a total of approximately 1.3 miles of banks have been identified as Phase 1 bank management areas (BMAs), and are depicted in the attached figure. Many of these BMAs are also adjacent to existing fine-grained channel margin (FGCM) deposits that can serve as areas of mercury storage and release to the South River, and likely reflect recent erosion from the BMAs. These FGCM deposits will be incorporated into the final design of the BMA interim measures as practicable, resulting in an efficient remediation approach.

The IM Work Plan outlines pre-design sampling and analysis efforts to complete the interim measures design, including additional bathymetric surveys, geotechnical data collection, hydrodynamic modeling, and other activities. Site access/landowner agreements, permit applications, treatability studies, and baseline monitoring will occur concurrent with pre-design efforts. The interim measures design will include Preliminary Design and then Final Design documents. Depending on landowner, permitting, and other requirements, interim measures at the Phase 1 BMAs may include a combination of institutional controls, enhanced vegetative stabilization, structural stabilization, capping, and/or removal options. Construction of the Phase 1 interim measures is currently targeted to begin in early 2016, shortly after completion of source controls at the former Waynesboro facility. Phase 1 construction will likely continue through 2017.

Q:\Jobs\120952-01.03 South River Remediation\Map\RRM 0 - 2 Bank Management Areas\AQ_Figure4.8_RPM 0 - 2 Bank Management Areas regression sensitivity_20140829.mxd dhanson 8/29/2014 9:52:23 AM



Use of a Carbon Amendment to Reduce Bio-uptake of Mercury in a South River Floodplain Pond: Technical Briefing Paper

This briefing paper summarizes the objectives, study approach, and findings of the South River Pond Pilot Study. Ongoing annual monitoring has been conducted since the study pond was amended in the spring of 2011. The data reviewed and presented herein includes results and findings from monitoring conducted in 2011, 2012, 2013, and 2014.

Introduction

Mercury was used between 1929 and 1950 at DuPont's Waynesboro, Virginia site, and was released and transported into surface water, sediments, soils, and biota of the South River. Remedial options are currently being evaluated for their ability to reduce the bioavailability of mercury to South River biota; one involves the use of carbon based sediment amendments. To assess the viability and efficiency of a sediment amendment remedial option, the Pond Pilot Study was implemented in 2011 in a South River floodplain pond using a two-phased approach (URS, 2011). Phase I included pond site selection, characterization of the pond, permitting, strategy development, and delineation of water/wetlands surrounding the pond. Phase II included amendment selection and deployment, engineering activities, and post-amendment annual monitoring (on-going).

References

- ✓ Hopkins, W. A. 2009. Reproduction and Development in *Bufo Americanus* from the South River, VA. 2008-2009 Annual Report. Prepared for E.I. DuPont de Nemours Company.
 - ✓ Ptacek C. and D. Blowes. 2010. *Riverbank Sediment Characterization and Preliminary Treatment Results*. University of Waterloo Powerpoint Presentation. South River Science Team Expert Panel Meeting, October 2010, Virginia.
 - ✓ Reible, D., P. Bireta, and R. Landis. 2012. Field measurement of porewater Hg using DGT. South River Science Team Expert Panel Meeting, October 2012, Virginia.
 - ✓ URS Corporation, 2011. Amendment Pilot Work Plan, South River Amendment Pilot Study, Waynesboro, Virginia. Wilmington, Delaware.
 - ✓ URS. 2012. Final Report: Ecological Study of the South River and a Segment of the South Fork Shenandoah River, Virginia. September 2012.
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Objectives

The purpose of the study is to test the efficacy of a sediment carbon amendment in limiting the bioavailability of mercury to biological receptors. Specific objectives are listed below:

- ❑ Assess the efficacy of the carbon amendment in reducing mercury concentrations in environmental media and bioavailability to biological receptors.
- ❑ Assess potential unintended consequences of the carbon amendment on water quality, sediment characteristics, and the benthic community.

Study Area Selection Process

A review of aerial imagery was performed to identify ponds within the South River floodplain for potential carbon amendment. The following descriptive information was gathered for each pond: accessibility, pre-existing data, presence of suitable monitoring organisms, and location on the floodplain. Based on review of this information, a candidate pond near relative river mile (RRM) 8.7 was chosen for the Pond Pilot Study (Figure 1).

The Pond Pilot Study site (pond) is adjacent to a smaller pond which was included in a previous study concerning mercury concentrations in the tissue of American toads (*Anaxyrus americanus*) (Hopkins, 2009). The property is not easily accessible by the public and is not located near public roads. The property is part of the Conservation Reserve Enhancement Program (CREP), and has broad areas that are planted with a variety of hardwood saplings. The property will be restored to pre-disturbance conditions at the conclusion of the pilot study, including vegetative cover.

The pond is approximately 42 feet by 103 feet, but physical features vary with groundwater elevation, river stage, and flood inundation. During the initial study period in 2011, the pond had a surface area of 3,365 ft² and volume of 2,580 ft³. The surface water level in the pond varies seasonally from approximately 2.5 to 6.0 feet in depth. The pond is an isolated, groundwater-fed floodplain feature, which also receives input from the river during flooding conditions. The direction of groundwater flow in the vicinity of the pond is toward the southeast based on groundwater elevation data. The substrate of the pond is not uniform—the margins are primarily silt, which increases in depth on the northwestern edge; the central area of the pond is primarily cobble.

Investigation Approach

In June 2011, a ‘semi-impermeable’ barrier was installed in the pond to create two discrete study areas or cells. The southern cell received the carbon amendment and is referred to as the amended cell. The northern cell remained untreated, serving as a control. The primary materials used to construct the barrier consisted of galvanized pipe, high-density polyethylene (HDPE) membrane (20-30 mm thickness), and sandbags.

In July 2011, approximately 2,000 pounds of commercially available biochar (i.e., Cowboy Charcoal®) were saturated with water and applied to the amended cell of the pond by way of a pneumatic biochar applicator. Biochar is a carbon-rich product created from biomass (e.g., hardwood) that is heated to elevated temperatures under oxygen deficient conditions. Biochar has proven effective in reducing biological uptake in metal-contaminated sediments (Ptacek, 2010).

Physical media (i.e., surface water, sediment, and pore water) and biological tissues [*Caenis* sp. (Mayfly nymph), Chironomidae (midge larvae), Planorbidae (aquatic snail), young-of-year bluegill (*Lepomis macrochirus*), green sunfish (*Lepomis cyanellus*) and wood frog tadpoles (*Rana sylvatica*)] have been monitored for inorganic mercury (IHg) and methylmercury (MeHg) as part of the Pond Pilot Study. Pore water IHg has also been monitored using diffusion gel thin film (DGT) devices (Reible et al., 2012). Additionally, the benthic macroinvertebrate community, *in situ* water quality, and sediment characteristics have been monitored to assess potential unintended

consequences of the carbon amendment. Monitoring took place prior to barrier installation (“pre-barrier”), prior to adding the carbon amendment (“baseline”), and at the monitoring frequency shown in Table 1.

Table 1
Monitoring Frequency
South River Pond Pilot Study:
Technical Briefing Paper

Monitoring Frequency (Weeks Post-Amendment)	Sampling Event (Month, Year)
1	July, 2011
2	July, 2011
4	August, 2011
8	September, 2011
12	October, 2011
16	October, 2011
20	November, 2011
43	May, 2012*
50	June, 2012
61	September, 2012
97	May, 2013**
104	July, 2013
117	October, 2013
150	May, 2014
157	July, 2014

Notes:

*Prior to this sampling event, barrier breach occurred between December, 2011 and January, 2012, likely following a significant storm even on December 8, 2011.

**Flooding occurred prior to this sampling event on May 8, 2013.

Study Results

A summary of results thru the 2014 annual monitoring from the South River Pond Pilot Study is provided below. While the setup of the pilot study occurred in such a way to eliminate differences between the amended and control cells, not all conditions can be controlled for in a field pilot. For example, a barrier breach and a flooding event (see Table 1) occurred that may have compromised the intended segregation of the control and the test areas. Hence, these results should be reviewed in the context of uncertainties associated with any dynamic natural system such as the effects of surface water mixing from overtopping barrier during natural flooding events, redistribution of biochar over

time, water depth, fresh particulate mercury deposition due to periodic runoff or flooding, baseline sediment physical and chemical differences between the amended and control side, biological and chemical factors.

Study results from the South River Pond Pilot Study thru the 2014 annual monitoring are as follows:

- ❑ Surface Water: Filtered inorganic mercury (FIHg) and filtered methylmercury (FMeHg) concentrations in surface water were generally significantly lower in the amended cell than the control cell (Figure 2).
- ❑ Aquatic Macroinvertebrates:
 - IHg concentrations in *Caenis sp.*, Chironomidae, and Planorbidae tissue were generally lower in the amended cell (Figure 3).
 - MeHg concentrations in *Caenis sp.* and Planorbidae tissue were generally significantly lower in the amended cell (Figure 4). Chironomidae tissue MeHg results were less consistent.
- ❑ Wood Frog Tadpoles: MeHg concentrations in wood frog tadpole tissue were significantly lower in the amended cell at post-amendment weeks 43 and 97 (Figure 5). There was no difference in IHg tissue concentrations at week 43. However, concentrations of IHg in tadpole tissue were significantly lower in the amended cell at post-amendment weeks 97 and 150.
- ❑ Sunfish: MeHg concentrations in young-of-year sunfish tissue were significantly lower in the amended cell at post-amendment weeks 50 and 157 (bluegill only). However, concentrations of MeHg in fish tissue were significantly lower in the control cell at week 104. (Figure 5). There was no difference in IHg tissue concentrations.
- ❑ Pore Water: IHg and MeHg concentrations in pore water were generally lower in the amended cell (Figure 6).
- ❑ Sediment: Consistent overall trends in grain-size-normalized sediment IHg and MeHg concentrations between cells were not evident (Figure 7).
- ❑ Benthic Community: Unintentional consequences of the carbon amendment on the native benthic community composition in the Pilot Study pond were not evident.

Summary of Findings

The application of biochar appeared to remove mercury from the water column, as evidenced by the significant decline in water mercury concentrations (prior to and following the barrier breach and the flooding event). The amendment appeared to reduce MeHg uptake by ecological receptors that are more closely associated with surface water exposures, including snails, wood frog tadpoles, and young of the year bluegill. This is consistent with the current conceptual model for mercury exposure in low trophic level and young organisms, which may receive 50% of their mercury load via aqueous exposures (URS, 2012).

The results of the DGT sampling, which showed a 50% decrease in pore water MeHg concentrations, strongly suggest that either methylation is suppressed in sediment or that partitioning is affected, reducing the labile MeHg (Reible et al., 2012). MeHg concentrations were lower in sediment following amendment consistent with the hypothesis that methylation was suppressed.

Findings from the South River Pond Pilot Study thru the 2014 annual monitoring are as follows:

- ❑ The carbon amendment may have had a positive effect, reducing MeHg concentrations in surface water and biological receptors monitored during the high methylation periods in Spring 2012 and 2013.
- ❑ The carbon amendment may be causing a reduction in the concentrations of IHg and MeHg in environmental media, and the bioavailability of MeHg to biological receptors.
- ❑ To date, no adverse effects of the sediment carbon amendment on water quality, sediment characteristics, or the benthic community have been observed.
- ❑ Increases in mercury concentrations in the water column were evident following the barrier breach and the flooding event; although the impacts of these events on the pilot study are unclear, these events likely interfered with the overall study goals (including the evaluations of biochar's efficacy in reducing mercury bioaccumulation).
- ❑ Results and findings of the South River Pond Pilot Study provide input to the potential use of amendments in remedial option strategies for reducing the bioavailability of mercury to South River biota.

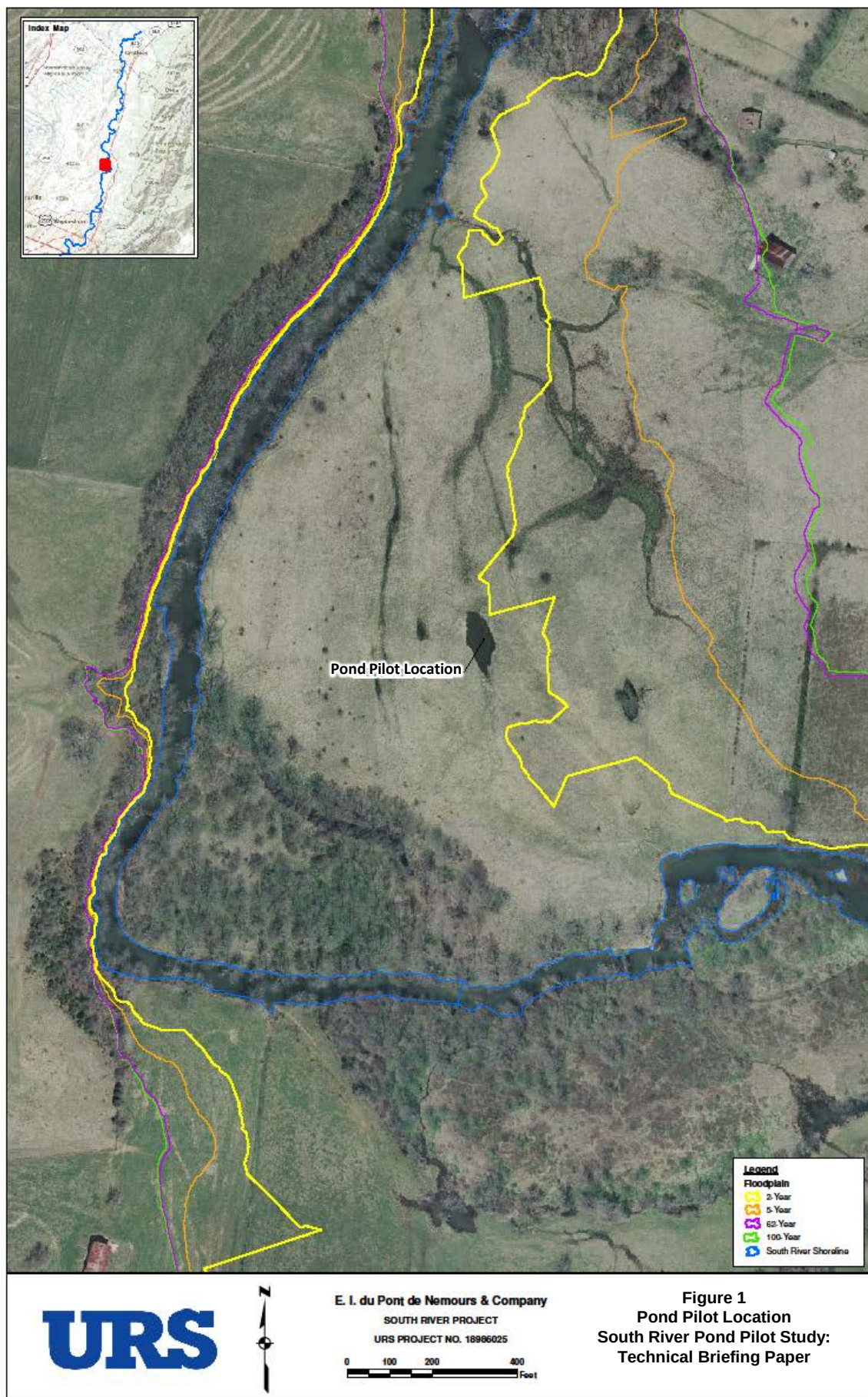
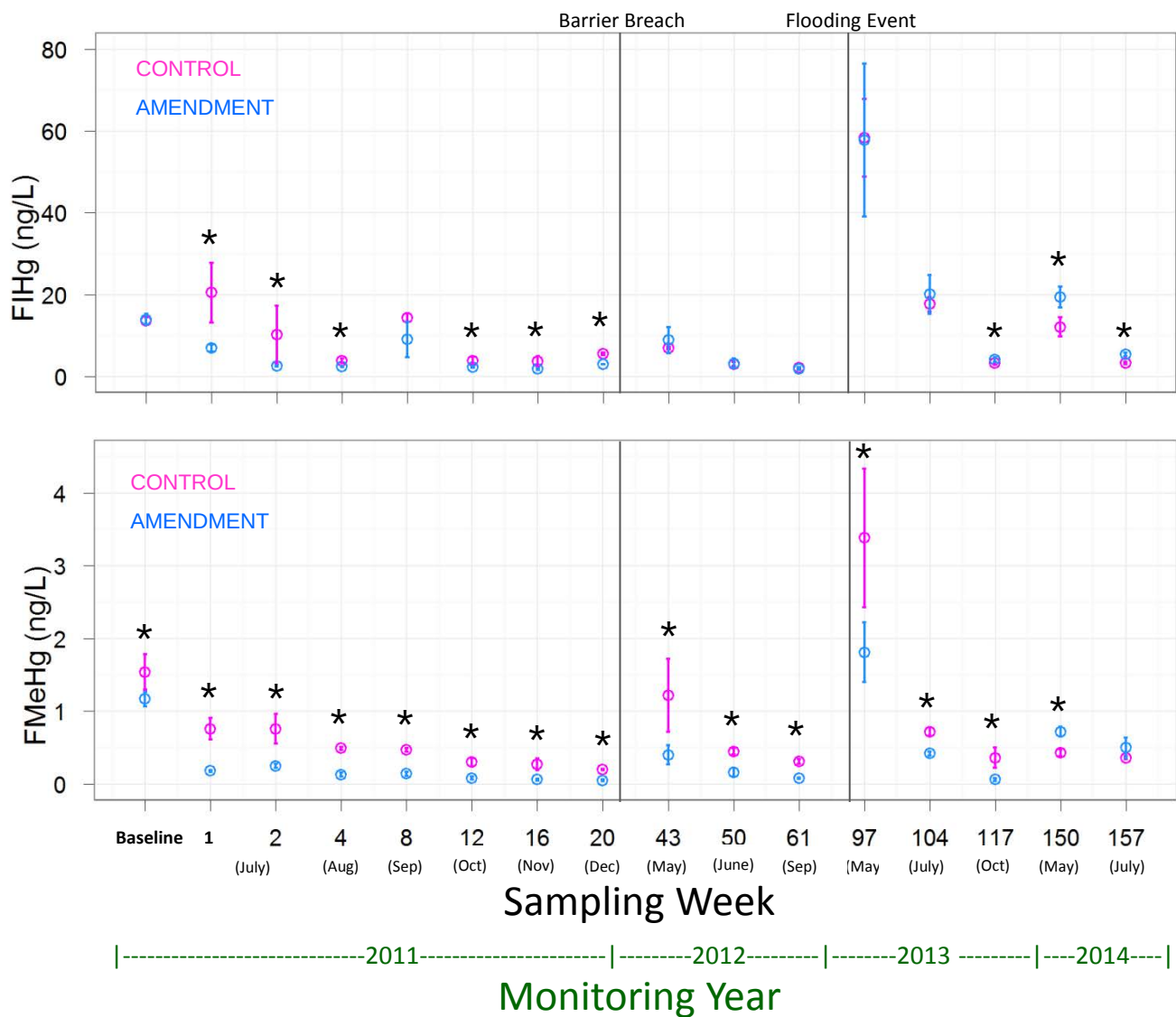
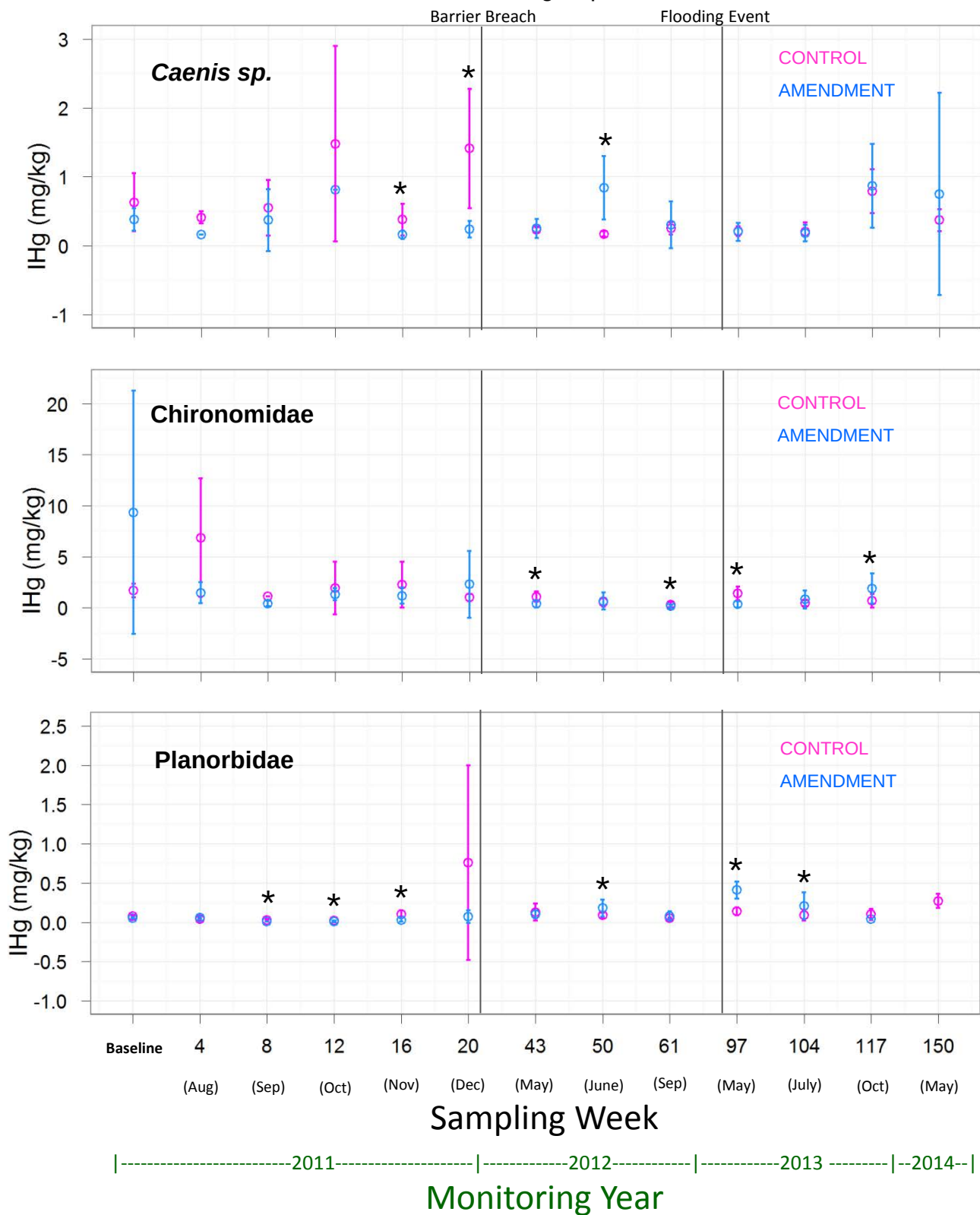


Figure 2
 Filtered Surface Water Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
 South River Pond Pilot Study:
 Technical Briefing Paper



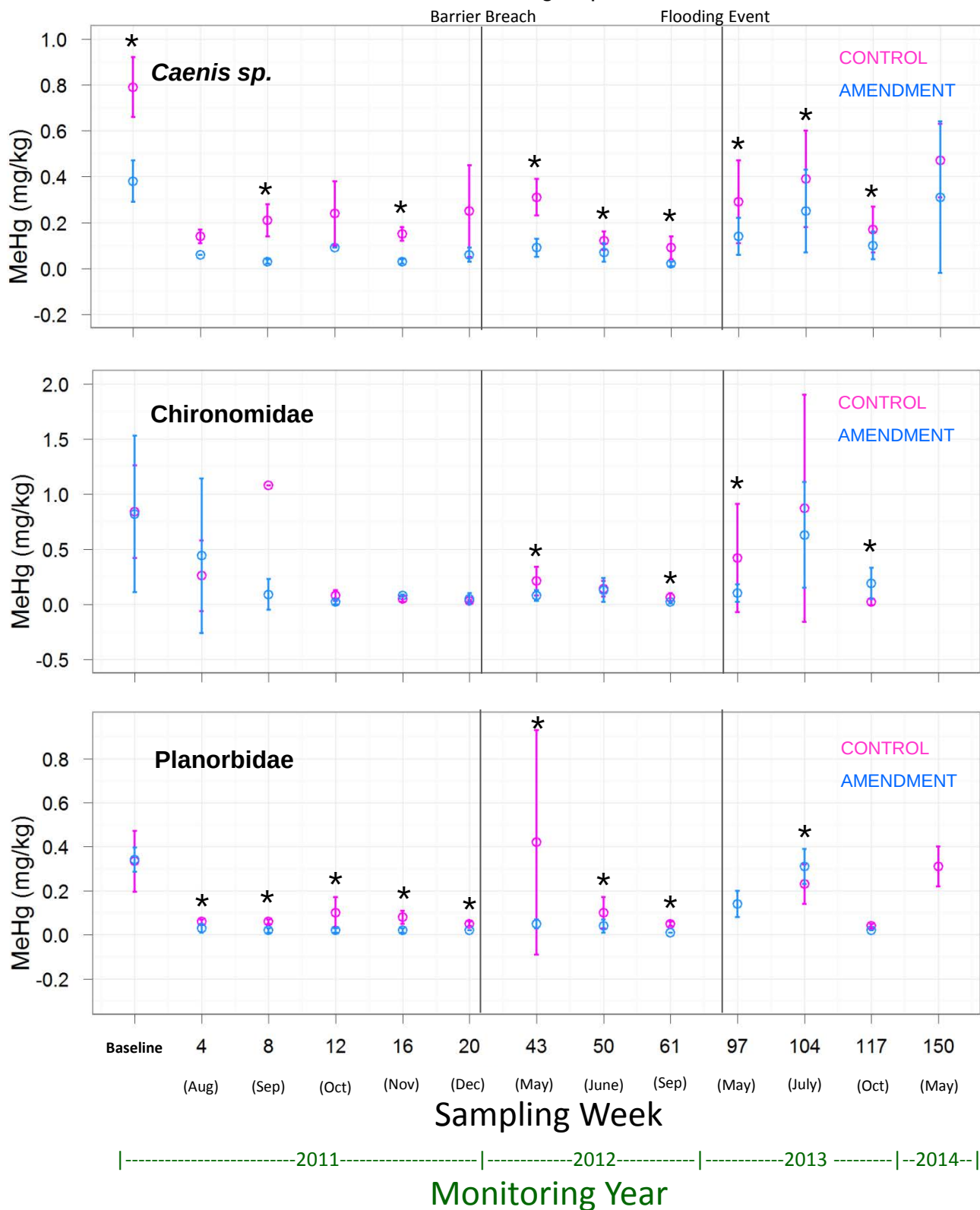
Note:
 Surface water mixing occurred between cells on several occasions after slight failure of barrier beginning January, 2012.
 Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference ($\alpha=0.05$) indicated by an asterisk (*).

Figure 3
Benthic Invertebrate Tissue Inorganic Mercury (IHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper



Note:
Due to lack of data for weeks 117 and 150. Chironomidae was not monitored in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference ($\alpha=0.05$) indicated by an asterisk (*).

Figure 4
Benthic Invertebrate Tissue Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper

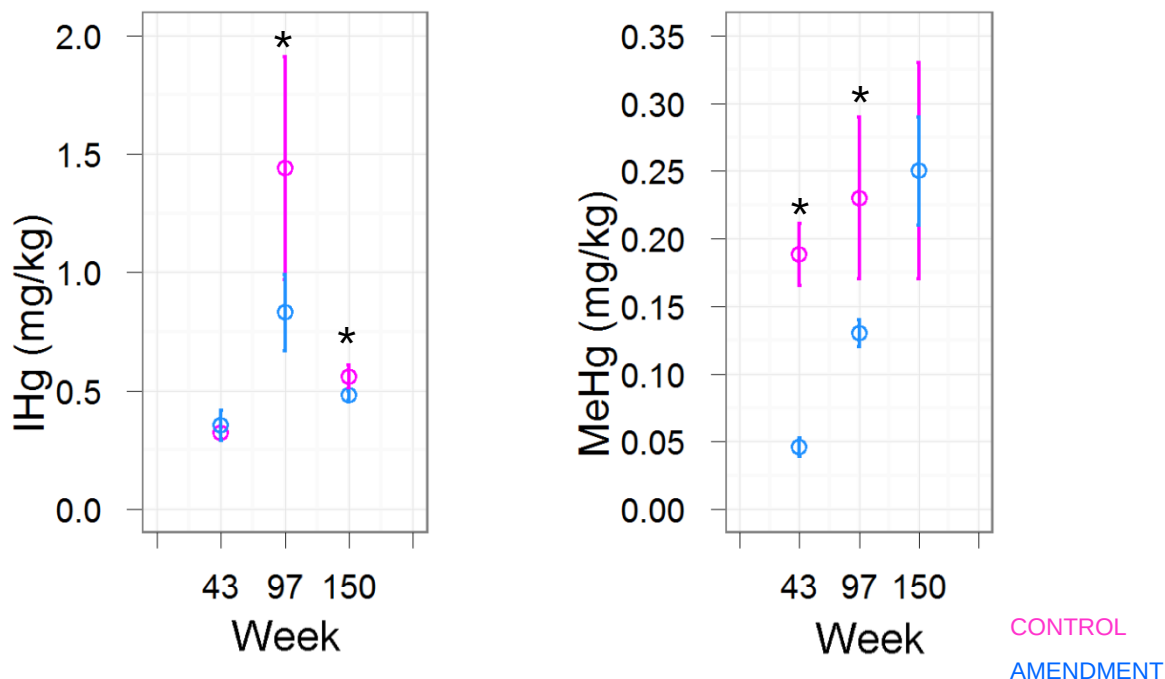


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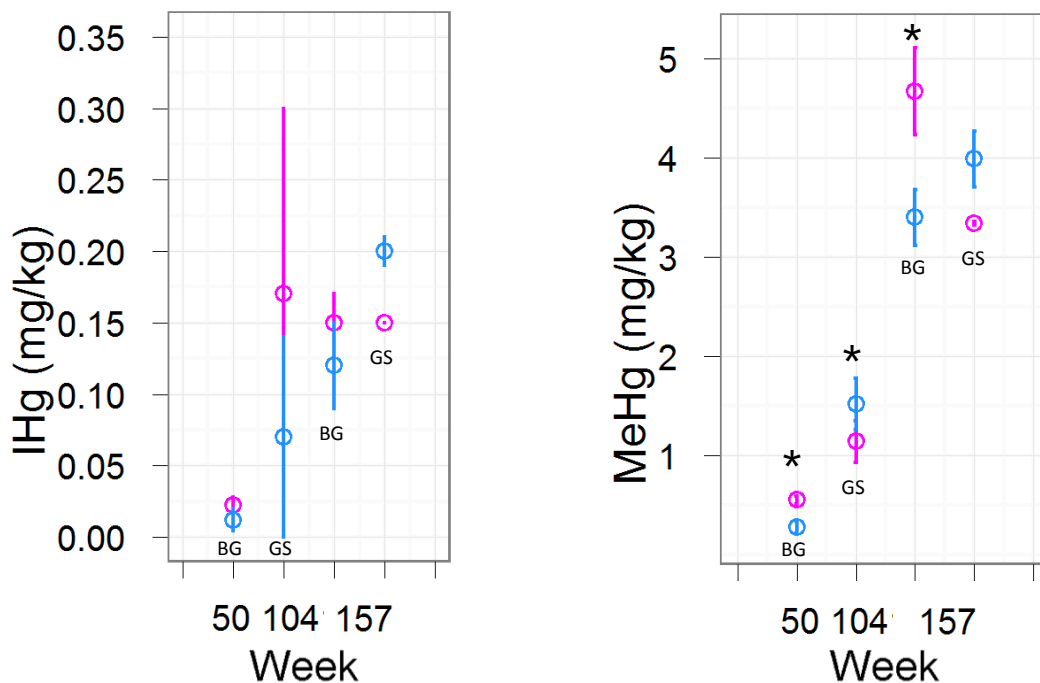
Due to lack of sample replicates, statistical tests were not conducted for *Caenis* at weeks 4 and 12, Chironomidae at week 8, and Planorbidae at weeks 117 and 150. Chironomidae was not monitored in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference ($\alpha=0.05$) indicated by an asterisk (*).

Figure 5
Wood Frog Tadpole and Young-of-Year Sunfish
Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper

Wood Frog Tadpole

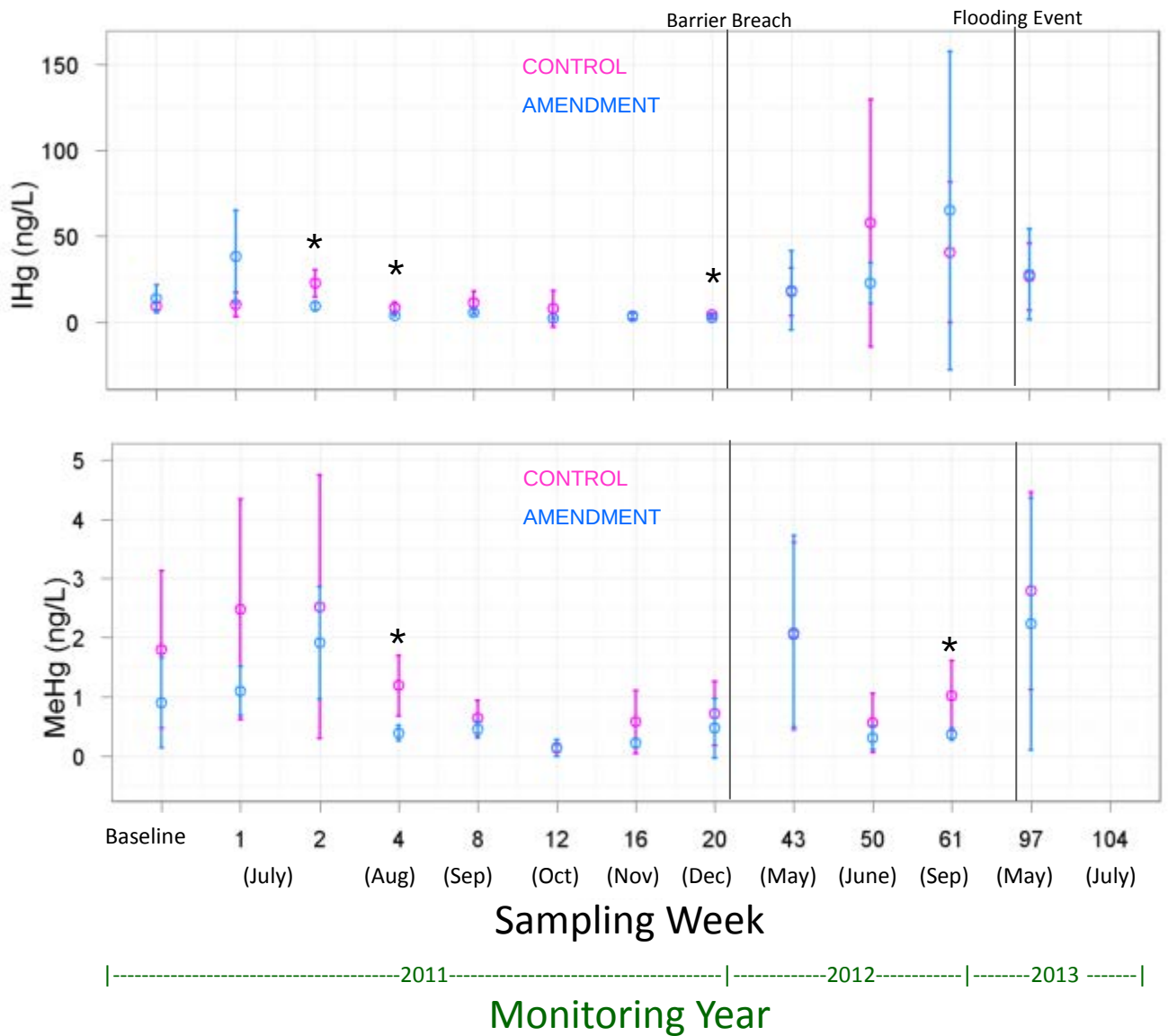


Young-of-Year Sunfish



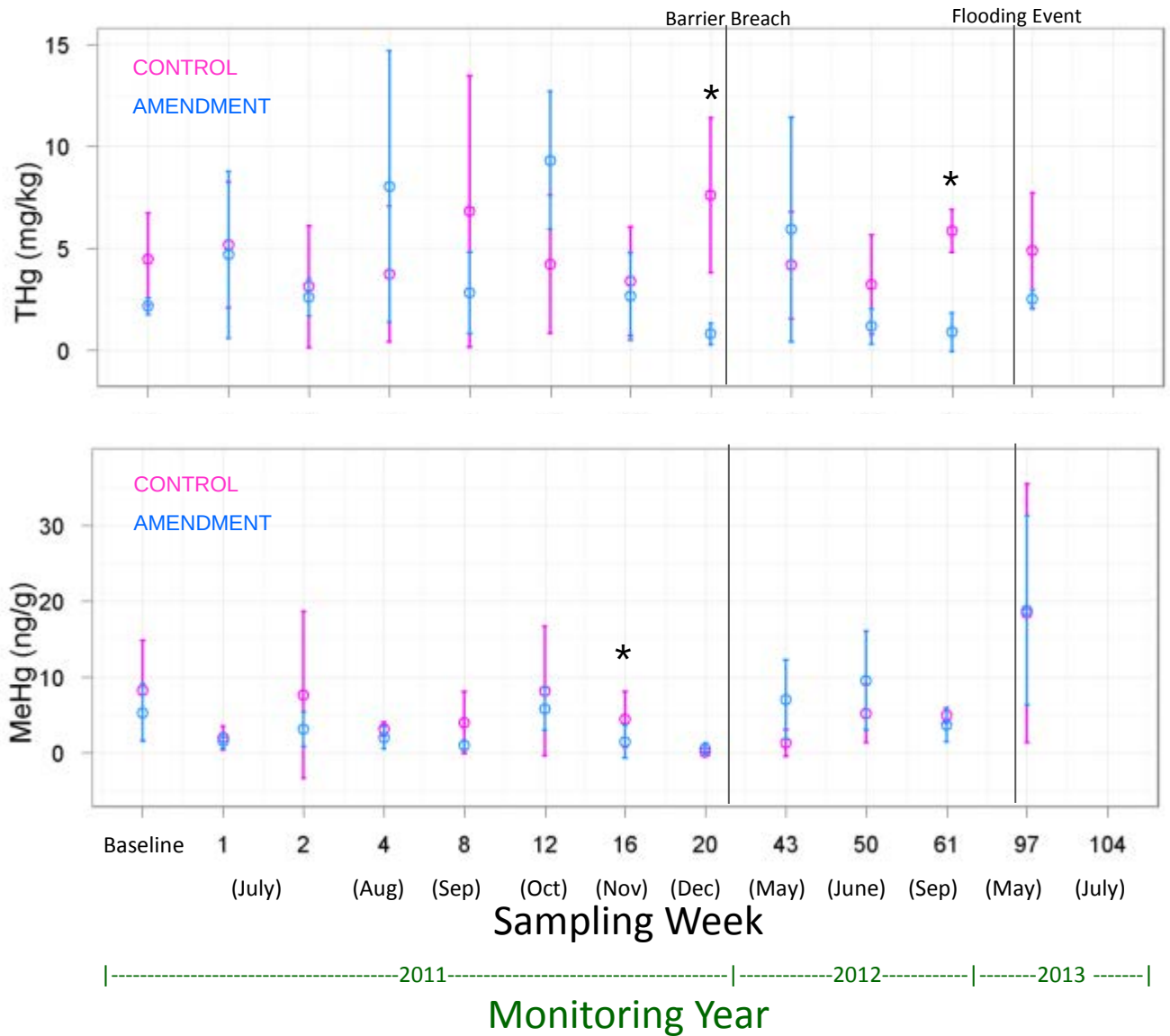
Note:
BG= Bluegill; GS= Green sunfish. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test).
Significant difference ($\alpha=0.05$) indicated by an asterisk (*).

Figure 6
Pore Water Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper



Note:
Pore water was not sampled in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference ($\alpha=0.05$) indicated by an asterisk (*).

Figure 7
Sediment Inorganic Mercury (IHg) and Methylmercury (MeHg) Monitoring Results
South River Pond Pilot Study:
Technical Briefing Paper



Note:
Sediment was not sampled in 2014. Compared log-transformed concentrations between amended and control cells (one-tailed, two-sample t-test). Significant difference ($\alpha=0.05$) indicated by an asterisk (*).

Proposed Mechanistic Modeling of Mercury in the South River, VA

Reed Harris

Reed Harris Environmental Ltd.

1 Introduction

An Enhanced Adaptive Management (EAM) framework is being developed to help design and assess the benefits of remedial actions. This framework requires estimates of the effects of remedial actions on fish mercury concentrations. A conceptual model has been developed to help understand how Hg moves through the ecosystem to biota, and to help assess the potential benefits of remediation options. This semi-quantitative model includes estimates of mercury sources to the river, but does not impose a mass balance for Hg in the system. Here we propose to apply a quantitative mass balance simulation model to help synthesize existing data, better understand mercury cycling and remedial options, and interpret results of monitoring programs as a component of the EAM framework for the South River.

2 Objectives

The primary objectives of the proposed modeling are to:

- 1- Help predict the benefits of remedial actions such (e.g. bank stabilization).
- 2- Help interpret monitoring carried out to assess the benefits of remedial actions.
- 3- Help test the conceptual model for Hg in the South River
- 4- Help understand Hg cycling in the South river and processes controlling the natural rate of recovery.
- 5- Provide information to the EAM framework.

3 Proposed Approach

Mechanistic modeling will be used to inform the Enhanced Adaptive Management framework established for mercury in the South River. In particular, modeling proposed here is meant to help estimate the relationship between mercury loading/remediation scenarios and the response of mercury concentrations water, sediments and biota.

Mercury cycling in water and sediments will be simulated using D-MCM Version 4. D-MCM is a mechanistic, time-dependent model that simulates three forms of mercury in aquatic systems: Methylmercury, inorganic Hg(II) and elemental Hg. Compartments include the water column sediments and optionally a food web (Figure 1). External Hg loads (e.g. atmospheric inputs, terrestrial inputs, bank erosion, point sources) are provided as inputs to simulations. The model can represent rivers as a series of connected segments (e.g. Figure 2). The bioavailability of mercury for reactions such as methylation

or photoreduction can be adjusted by selecting specific dissolved complexes as substrates. Mercury partitioning between solids and the dissolved phase can also have fast and slow components (e.g. mercury could adsorb quickly but desorb slowly if desired). This may also affect the bioavailability of mercury for reactions.

Methylmercury bioaccumulation will be simulated using either the food web model within D-MCM or by passing D-MCM outputs to the BASS model already set up for the South River. Further discussions are needed to assess which option is preferred.

Processes in the numerical model will be compared to the conceptual model for mercury in the South River, to ensure that key processes in the conceptual model are represented in the numerical model.

Simulations will first be carried out to calibrate the model to existing conditions in the contaminated portion of the South River, and the slow ongoing rate of natural recovery. The river will be divided into a series of connected segments. The calibrated model will then be used to test future scenarios involving additional bank stabilization or other remedial actions (e.g. Figure 3).

Hydrology and particle transport play important roles in the mobilization and fate of mercury in the South River. D-MCM includes hydrology and particle-related inputs in simulations, but does not predict these inputs directly. This information will need to be estimated external to the modeling, at a coarse scale suited to the model grid.

4 Next Steps

Discussions will be carried out to determine the optimal approach to represent MeHg dynamics in the South River food web (BASS or D-MCM). Discussions are also needed regarding estimates of particle concentrations and fluxes (e.g. TSS, sedimentation rates) to use in simulations. A full proposal will be developed by mid-October.

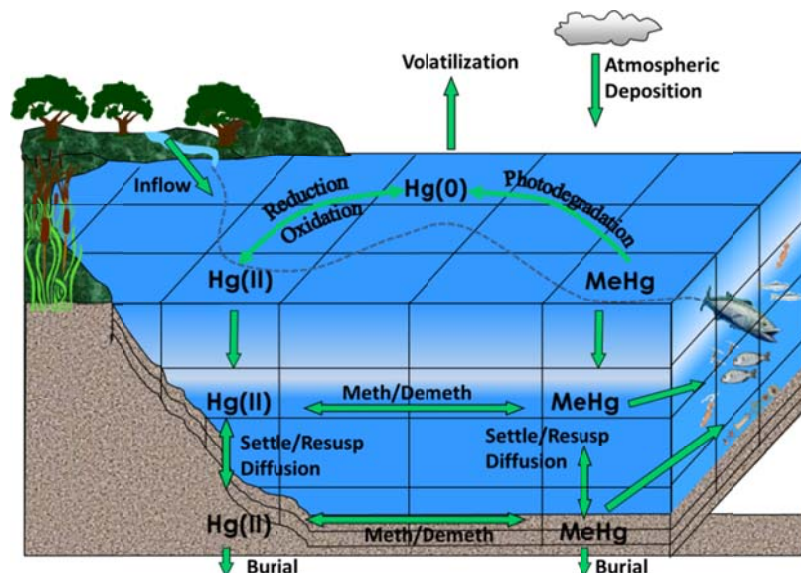


Figure 1. Conceptual diagram of mercury cycling in D-MCM.

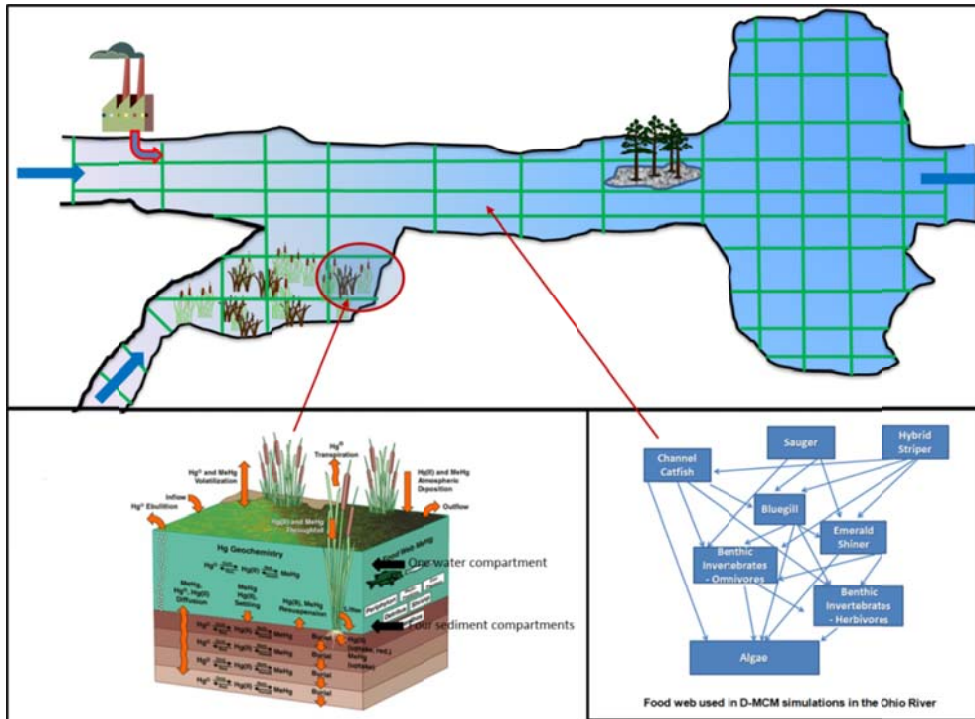


Figure 2. Multi-cell approach in D-MCM version 4.

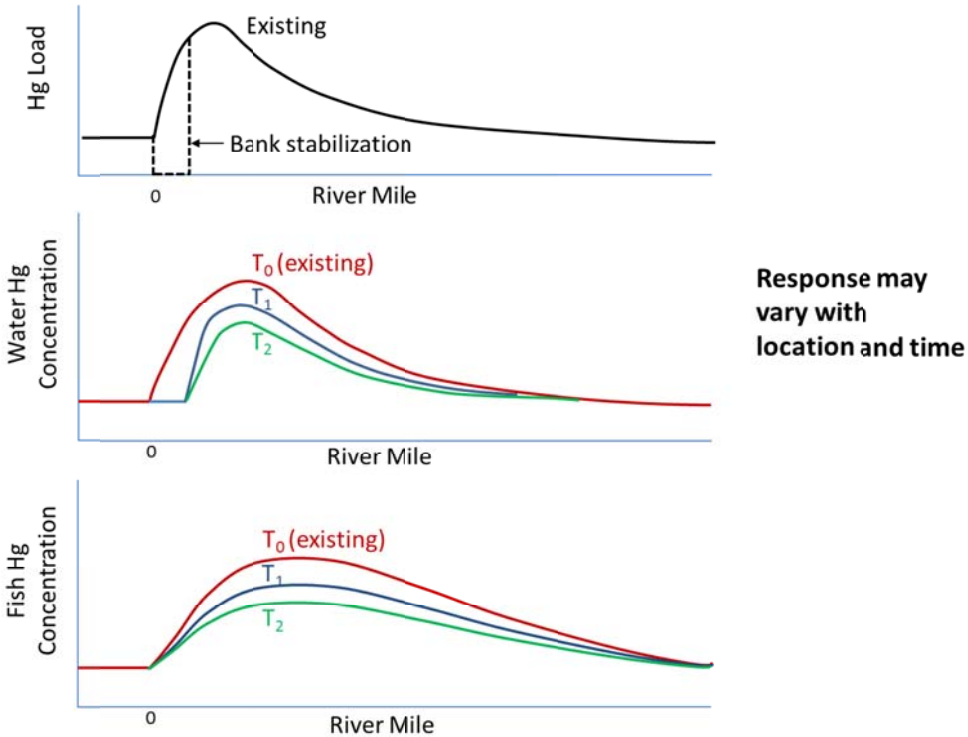


Figure 3. Conceptual illustration of model outputs for Hg concentrations in water and fish at different locations and times following bank stabilization in a section of the South River..

Briefing Paper – Reactive Capping Assessment, South River VA

Danny Reible, Alyssa Offut, Paul Bireta, Ariette Schierz, Balaji Rao

Texas Tech University

Introduction

Monitoring of the South River by both DGTs and conventional approaches have shown that there is mobile and potentially bioavailable mercury (Hg) leaching from the sediment bed and from bank deposits. The results of DGT monitoring are detailed in a separate briefing paper (DGT Monitoring of THg and MeHg in Porewater, South River VA, Reible et al. 2014). In brief, the results suggest that porewater containing the order of 1 $\mu\text{g/L}$ total mercury (THg) is commonly observed in surficial bed sediments with higher levels, 1-10 $\mu\text{g/L}$, in particular environments including the near shore of more highly impacted banks such as the HRAD at RRM 3.5. In addition, the DGT measurements suggested that an order of magnitude higher concentration of THg is observed seeping from the base of some banks (specifically the HRAD at RRM 3.5) during transient bank drainage. Methyl mercury (MeHg) in near surface porewaters is typically 0.1-1% of THg, suggestive of marginally productive sediment environment with respect to methylation. During bank drainage, MeHg is typically an order of magnitude lower due to oxic conditions in the drainage. The THg and MeHg release vectors are shown in Figure 1.

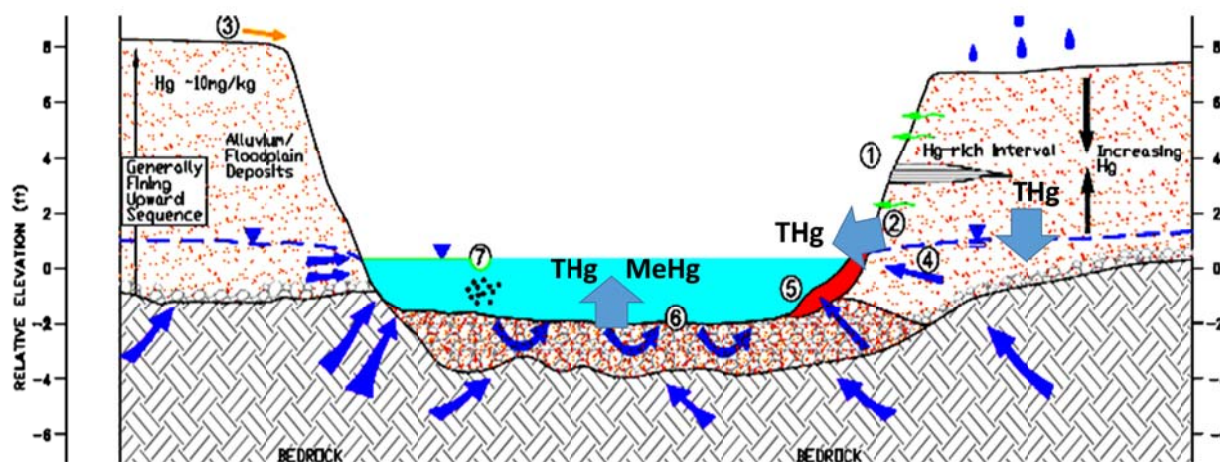


Figure 1 THg and MeHg release vectors in the river

Management of these releases may be possible with sorbing amendments introduced on or in the surface sediments of the river and at the bank. The goal of the project summarized herein is to evaluate potential in-situ capping or treatment options for the South River. The preliminary efforts in this assessment have been directed toward three efforts

1. Baseline studies with benthic organism populated mesocosms with sediment from RRM 11.8.
2. Screening studies of potential sorbing amendments to identify the best choices of amendments for the mesocosm studies.

3. Capping and treatment mesocosm studies with sorbing amendments and conventional caps with sediment from RRM 3.5 to evaluate the performance of potential amendments

Baseline Studies – RRM 11.8

These studies were designed to explore Hg availability and mobility under baseline or unremediated conditions and to evaluate DGTs as a physico-chemical measure of availability by comparing to bioaccumulation in benthic organisms. Mesocosms as depicted in Figure 2 were employed with measurements including profiling voltammetry to assess redox conditions and dynamics and profiling DGTs to measure porewater profiles of THg and MeHg.

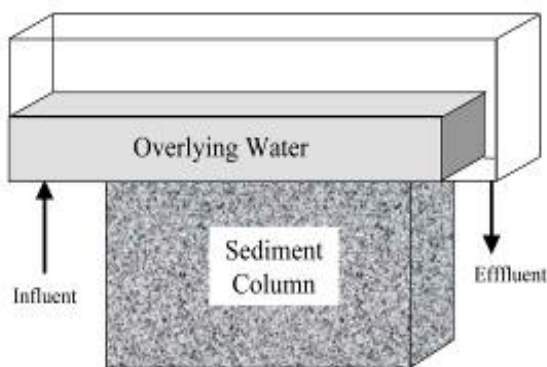


Figure 2 T-cell mesocosms used to evaluate redox dynamics and Hg availability and mobility

A deposit feeding tubificid organism, *Tubifex tubifex*, were introduced to these mesocosms in order to evaluate bioaccumulation and compare to DGT measurements of porewater THg and MeHg. These organisms are not dominant species in the South River ecosystem but are intense sediment mixers through burrowing and conveyor belt feeding and rapidly achieve equilibrium with respect to bioaccumulation. They process 10-20 times their weight in sediment every day by ingesting sediment particles in the organic rich 0.5-10 μm size range. They thus may represent an upper bound to bioaccumulation whereas uptake in other organisms is often less due to slow uptake, insufficient exposure duration, or lack of significant contact with the source substrate (e.g. surface foraging organisms for sediment based contaminants).

Each mesocosm is approximately 120 cm^2 in area and contains sediment about 8 cm deep. The mesocosms were allowed to develop natural redox gradients with a slow overlying water flow over 6-8 weeks before organism introduction. *T. tubifex* was introduced at a density of approximately 25,000/ m^2 , a typical density of deposit feeding worms in the environment although higher than would be expected in the South River. Voltammetry was used to monitor redox changes in the sediments and DGTs were employed at the end of the experiment to determine porewater concentrations of THg and MeHg. Sediment cores were collected to measure sediment concentration and the entire mesocosm was sacrificed to collect organisms for measurement of bioaccumulation at the end of the 28 day period of exposure.

The bioaccumulation results are shown in Figure 3. The figure shows the bioaccumulation of THg and MeHg in the organism. The organism achieved concentrations approximately 100 times greater than the sediment concentration during the 28 day exposure (after depuration for 24 hours). The bulk of the

mass of Hg in the organism was associated with THg which is typical of benthic organisms whereas MeHg is the dominant Hg species in higher order organisms, e.g. fish.

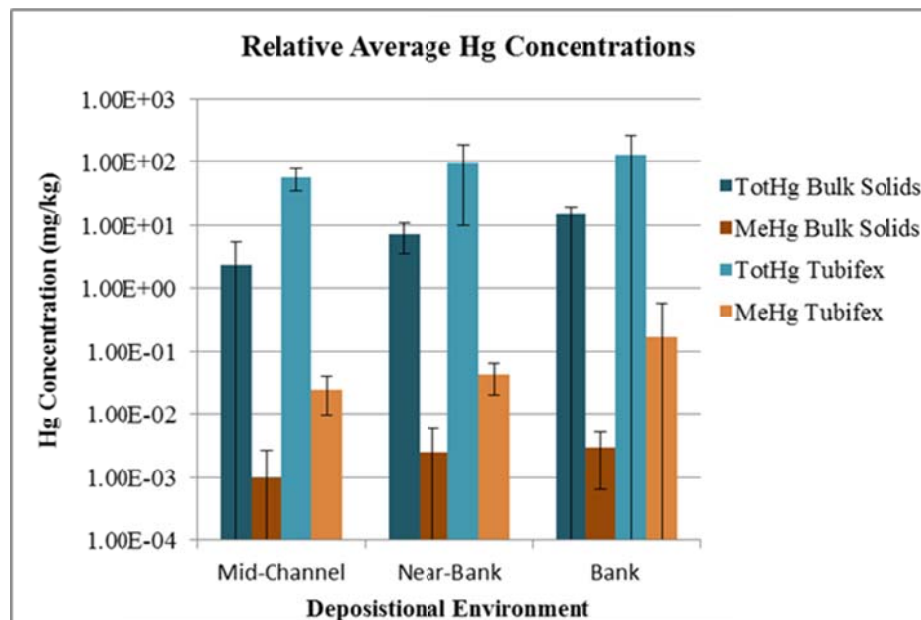


Figure 3 Bioaccumulation of THg and MeHg in *T. tubifex* after 28 day exposure to the sediments

This bioaccumulation was then correlated with organic carbon normalized bulk solid concentration (as an indicator of the feed to the organisms) and DGT measured THg porewater concentration. The results are shown in Figure 4. The left figure shows a very poor correlation with organic carbon normalized sediment concentration while the right figure shows a weak but better correlation with DGT porewater concentration. This is despite the fact that the fine organic carbon rich sediment is the primary source of food to the organism. A constant biota sediment accumulation factor model of bioaccumulation would presume that there should be a constant slope positive correlation between organic carbon normalized bulk solid Hg concentration and bioaccumulation, which was clearly not observed. Instead, the DGT measured porewater concentration appears to be a better indicator of availability of THg to the organism, despite the fact that the uptake is likely the result of sediment ingestion.

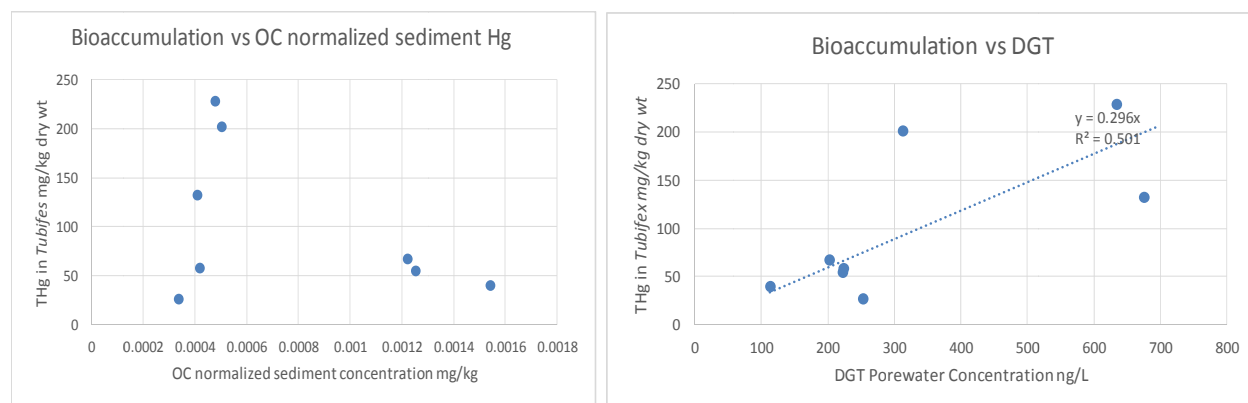


Figure 4 Bioaccumulation vs organic carbon normalized sediment concentration (left) and DGT measured porewater concentration (right). Both measures represent the 0-4 cm average, the approximate depth of organism interactions with the sediment

The DGT-measured porewater concentration profile with depth was also compared to the voltammetry measured redox profile. The results (Figure 5) showed that the porewater concentrations of THg were approximately an order of magnitude higher in the zone where oxygen was detected (shaded area). This is a common observation and is presumably associated with the greater organic carbon oxidation in this layer (increasing natural organic matter, NOM) and the oxidation of low solubility reduced Hg species (e.g. HgS). It is this phenomena that likely leads to the elevated concentrations during drainage from the RRM 3.5 bank (separate briefing paper on DGT monitoring in the river (Reible et al., 2014)).

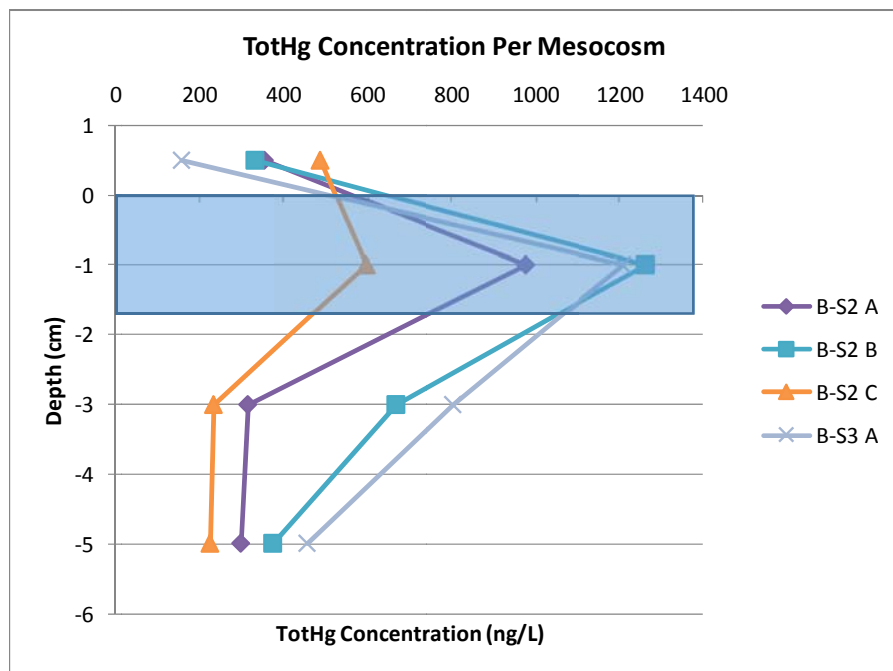


Figure 5 Hg depth profiles showing elevated porewater THg in oxic layer (shaded region)

Sorbing Amendment Studies

Conceptually, we view methylation as the product of desorbed Hg in the porewater, speciation of this Hg into a bioavailable form and finally microbial processes under reducing conditions to give rise to methylation. Amendments can interfere with any of these three steps to reduce methylation. Initial efforts have been focused on reducing the amount of porewater Hg, the first step in this process, by adding a strong sorbent to the sediment or in a cap layer. By attacking Hg availability and mobility, the amount of Hg available for methylation at that location and the amount of Hg that can migrate elsewhere and methylate.

A variety of sorbents were evaluated by conducting sorption studies in freshwater systems. Artificial porewater similar to the river waters was used for these studies due to the lack of large volumes of porewater that could be generated for these studies. The effective partition coefficient of mercury was estimated by measuring the reduction in solution concentration due to the addition of sorbent. The estimated partition coefficients for a variety of sorbents are shown in Table 1.

Table 1 Effective partition coefficients for selected Hg sorbents in freshwater

		Matrix
Material Type	Sorbent	Freshwater
		K_d [L/kg]
Carbon based material	GAC	14300
	Biochar-wood	1310
	Biochar-Rice Husk	190
organophilic clay based materials		
	PM199 granular	460
Natural materials	Kaolinite	1490
	Sand	6

On the basis of these results, activated carbon and wood-based biochar have been selected for cap amendments in the capping mesocosm studies. Kaolinite has a performance similar to that of biochar but is even more difficult to place than biochar. Organophilic clays were not as effective in this application although this media has proved very effective at other sites, particularly when Hg is primarily associated with NOM. In general, activated carbon has proved the most effective in all conditions and there has been no measurable advantage noted of using sulfur based activated carbons that were primarily developed to treat sulfur containing gas streams.

Capping Mesocosm Studies

The capping mesocosm studies will explore amended caps and in-situ treatments for the South River sediments. The initial studies will focus on near shore and bank sediments from RRM 3.5. Mesocosms like those described above for RRM 11.8 have been set up and redox conditions have been equilibrating. Screening sorption tests (described above) have been conducted to identify appropriate caps for the mesocosm testing. These caps have been tentatively identified as a granular activated carbon cap, a wood-based biochar cap and a conventional sand cap for comparison. A low permeability cap (bentonite in a reactive core mat) will also be evaluated as a tool to control inundation for possible application in leaching bank environments.

The activated carbon and biochar amended caps will be mixed in an approximate loading of 1 lb/ft² and mixed throughout a thin (3 cm) sand cap. The mesocosm tests with these and the sand cap will be monitored in the following ways

- Voltammetry to monitor changes in redox conditions after cap placement
- Overlying water measurements before and after cap placement to demonstrate flux reduction
- DGT profiling of porewater THg and MeHg concentration to evaluate response of these parameters in the underlying sediment as well as any migration over time into the overlying cap

Initial efforts (to be completed by Jan 2015) will be focused on static cap conditions similar to those observed on the river bottom. Subsequent experiments in 2015 will be focused on the dynamic environment typical of the banks wetting, drying cycles and the performance of the low permeability cap layer as well as the amended caps to manage the resulting bank leaching.

Stabilization of Mercury and Methyl Mercury by Biochars in Water/Sediment Microcosms

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Introduction

Previous studies have focused on the addition of biochar to South River sediments as an amendment to control dissolved Hg concentrations and to limit the production of methyl mercury (MeHg). These studies were either conducted as short-term laboratory experiments in a controlled environment, or as longer-term field experiments in a less controlled setting. The studies described here focus on evaluating the effectiveness of biochar amendments for controlling Hg and MeHg in saturated, anaerobic microcosm experiments in a laboratory setting over longer time-frames than has previously been investigated. The effectiveness of amending South River sediment with multiple sources of biochars also was evaluated over these longer time frames to provide a direct comparison of treatment effectiveness for different biochar materials.

Specific Questions Addressed

- 1) Will the amendment of sediments with biochar promote Hg binding over an extended time period?
- 2) What is the nature of the binding mechanism between Hg and biochar?
- 3) Will net MeHg production increase due to the release of elevated sulfate, dissolved organic carbon (DOC), and organic acids (OA) associated with the addition of biochar?
- 4) Are there differences in Hg stabilization and MeHg production for the difference biochar sources?

Experiments

Cowboy charcoal (CL2), low- and high-T switchgrass biochar (GR4L and GR4H), high-T poultry manure (MP1H), and activated carbon (AC) were selected as amendments to South River sediment collected from RRM 3.5 (labelled SRD). The biochar, sediment, and South River water (SRW) were mixed at a ratio of 1:20:80 by mass (5 g, 100 g, and 800 mL) (Figure 1). Mixtures containing SRW and biochar only, and SRW and sediment only, were used as controls. The microcosm experiments were conducted in an anaerobic glovebox.

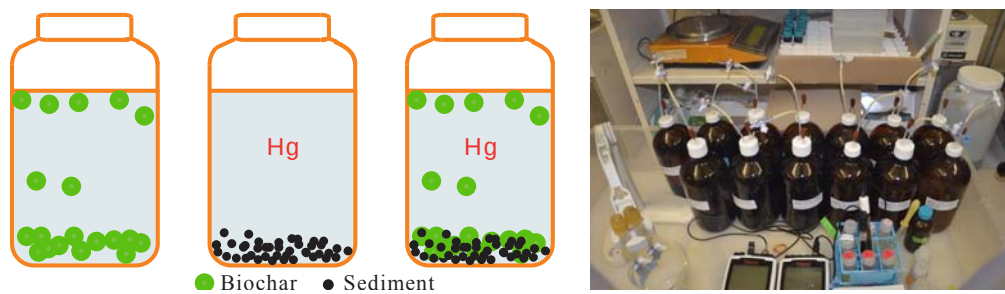


Figure 1. Microcosm experimental setup.

The aqueous phase was sampled as a function of time for analyses of pH, Eh, alkalinity, total Hg (tHg), MeHg, anions, cations, $\text{NH}_3\text{-N}$, $\text{PO}_4\text{-P}$, organic acids (OAs), and DOC. The solid phase was sampled as a function of time for analyses of tHg, MeHg, Hg sequential extraction, and pyrosequencing analyses. The biochar particles were separated and prepared for thin-sections. The thin-sections were analyzed for X-ray fluorescence (XRF) mapping of S, Hg, Cu, Fe, and Mn and X-ray spectroscopy (XAS) of S, Hg, Cu, and Fe.

Results

Chemical composition of aqueous solutions:

Determinations of aqueous concentrations of tHg as a function of time showed elevated concentrations of tHg in the sediment control, reaching values of approximately $40 \mu\text{g L}^{-1}$ (Figure 2). During the first few weeks of the experiment, there was little difference in tHg between the control and the mixtures containing biochar. Reductions in tHg concentrations of 50% relative to the control were observed after 30 days for the activated carbon (AC), after 90 days for the high-T poultry manure biochar (MP1H), and 120 days for the low-T switchgrass biochar (GR4L) and the high-T switchgrass biochar (GR4H) amendments. Similar decreases in aqueous concentrations of tHg were not observed in the duplicate amendment systems containing Cowboy Charcoal (CL2) over the duration of the experiment. The concentrations of tHg in the control and amendment systems were highly variable over the duration of the experiments, especially in the mixtures containing low-T switchgrass biochar (GR4L) and high-T switchgrass biochar (GR4H). The tHg concentrations in the duplicate amendment systems containing Cowboy Charcoal (CL2) were more variable than those observed in the high-T poultry manure biochar (MP1H) amendment. The tHg concentrations in the high-T switchgrass biochar (GR4H) amendment were lower than the low-T switchgrass biochar (GR4L) amendment during the first 120 days, and then increased at later times. The observed reductions in tHg in the aqueous phases were: activated carbon (AC) > high-T poultry manure biochar (MP1H) > low-T switchgrass biochar (GR4L) > high-T switchgrass biochar (GR4H) > Cowboy Charcoal (CL2).

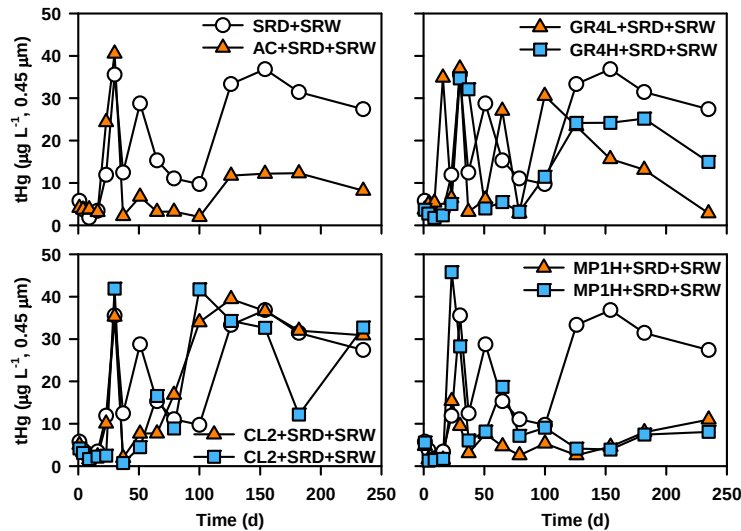


Figure 2. Aqueous concentrations of tHg (0.45 µm filtered) in SRD control (open circles) and amendment systems (triangles and squares) versus time.

Concentrations of MeHg as a function of time reached maximum values of close to 40 ng L⁻¹ in the sediment control (Figure 3). Similar or lower concentrations of MeHg were observed in the mixtures containing biochar. The peak concentration in activated carbon (AC) amendment system was higher than the control. The MeHg concentrations in the duplicate Cowboy Charcoal (CL2) amendment systems were the lowest compared to the control and the other amendment systems. The MeHg concentrations in the low-T switchgrass biochar (GR4L) and high-T switchgrass biochar (GR4H) were lower than those in the control during the first 100 days, but higher after 180 days. The peak concentrations in the high-T poultry manure biochar (MP1H) amendments were lower than that in the control, but persisted at elevated concentrations for longer. The MeHg concentrations in the mixtures containing activated carbon (AC) and high-T poultry manure biochar (MP1H) were lower than the control after 90 and 150 days, respectively. The rank in order of removal efficiency of MeHg was: Cowboy Charcoal (CL2) > high-T switchgrass biochar (GR4H) > low-T switchgrass biochar (GR4L) > activated carbon (AC) > high-T poultry manure biochar (MP1H).

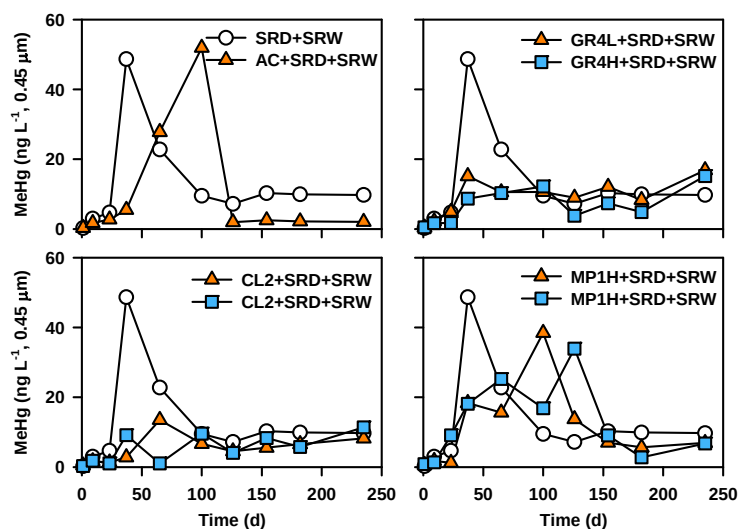


Figure 3. Aqueous concentrations of MeHg (0.45 µm filtered) in SRD control (open circles) and amendment systems (triangles and squares) versus time.

The highest sulfate concentrations were observed in the duplicate batch with high-T poultry manure biochar (MP1H) as an amendment (Figure 4), which is consistent with previously reported results showing elevated aqueous sulfate concentrations in short-duration batch systems containing high-T poultry manure biochar (Ptacek et al., 2013). The concentrations of sulfate in the amendment containing Cowboy Charcoal (CL2) decreased at a rate similar to the control. The concentrations of sulfate in the activated carbon (AC) and high-T switchgrass biochar (GR4H) mixtures were higher than in the control. The higher sulfate concentrations in the activated carbon (AC) amendment system are attributed to the leaching of sulfate from activated carbon (AC) (Ptacek et al., 2013). The relatively rapid decrease in sulfate concentrations in the low-T switchgrass biochar (GR4L) may be due to the activity of SRB coupled to the presence of elevated acetate in the low-T switchgrass biochar (GR4L) amendments.

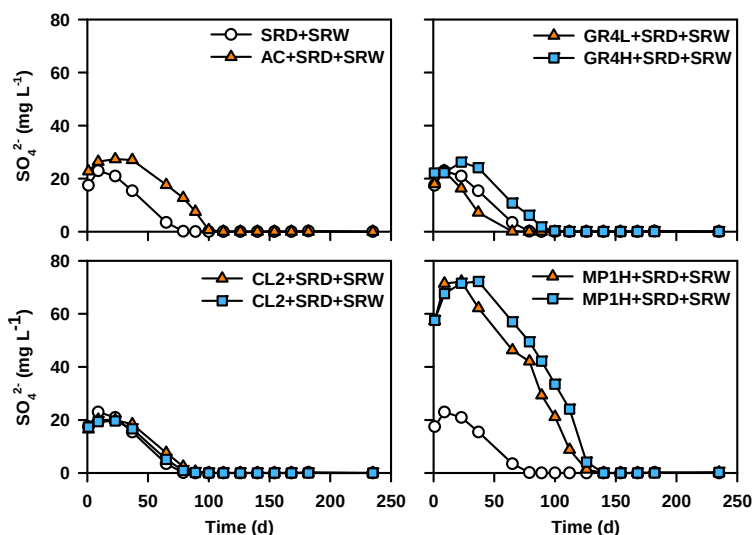


Figure 4. Aqueous sulfate concentrations in the SRD control (open circles) and amendment systems (triangles and squares) versus time.

Sulfate-reducing bacteria are the major contributors to Hg methylation (Benoit et al., 2001; Gilmour et al., 1992). The low MeHg concentrations in Cowboy Charcoal (CL2), high-T switchgrass biochar (GR4H), and low-T switchgrass biochar (GR4L) are consistent with the low sulfate concentrations in these amendments (Figure 3). The elevated sulfate concentrations observed in activated carbon (AC) and high T poultry manure biochar (MP1H) amendment systems correlate to elevated MeHg concentrations. The low tHg concentrations in these amendments also may partly be due to the elevated concentrations of sulfate which can be converted to sulfide. Sulfide can scavenge Hg by forming mercury sulfide precipitates.

Solid-phase characterization:

The X-ray fluorescence (XRF) mapping is an elemental analysis technique which allows the examination of the distribution of an element of interest in a particle or a small area of a particle. The XRF mapping can simultaneously illustrate the spatial distribution of several elements at one time, which can help to define the binding environment and hot spots of an element of interest. The XRF maps are presented for Hg and Fe in a fresh SRD particle (Figure 5, top) and for Hg, S, Fe, Cu, and Mn in a reacted particle of Cowboy Charcoal (Figure 5, bottom) at day 235 of the experiment. Maps for S, Cu, and Mn in the fresh SRD particle were also collected, however the signals were poor, which indicates that the concentrations of these elements also were low in this particle. The results indicate that the particle of fresh SRD had an elevated Fe content and the Hg hot spot was near the surface of this particle. This particle was likely iron oxide. The Hg on the surface was not associated with S, given that a low S content was observed.

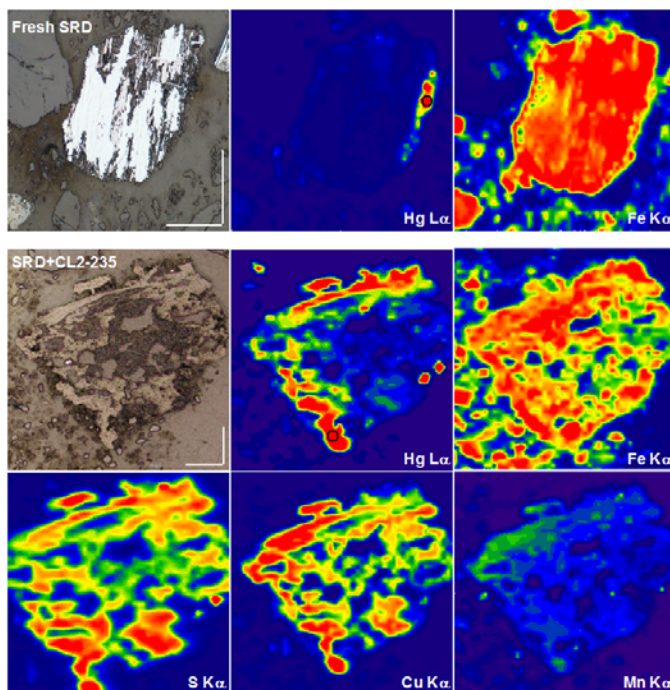


Figure 5: Top: Microscope photo of fresh SRD sediment and X-ray fluorescence maps for Hg L α and Fe K α X-ray fluorescence (XRF), and Bottom: Microscope photo and XRF maps for Hg L α , Fe K α , S K α , Cu K α , and Mn K α for a grain of Cowboy Charcoal (CL2) after 235 days in thin-sections. The white bars in the microscope photo represent 0.1 mm. The EXAFS spectra for modeling were collected inside the black circles.

The Hg in the particle of Cowboy Charcoal in the CL2 amendment were observed to co-exist with S, Fe, Cu, and Mn. The Hg, Cu, and Fe were likely in sulfide forms as high S contents were observed. The Cu and Fe were also likely in reduced forms. The thin-section samples of activated carbon (AC), low-T switchgrass biochar (GR4L), high-T switchgrass biochar (GR4H), and high-T poultry manure biochar (MP1H) amendments and the control at day 235 were also mapped with XRF, however similar particles were not observed.

X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) are regions of the spectra acquired from X-ray absorption spectroscopy (XAS). XANES spectra can help to define the oxidation state of an element and its primary binding environment. EXAFS spectra can help to define the local structural information (binding elements, coordination number, bond length, etc.) of the atom of interest. The EXAFS spectra were modeled for Hg in the hot spot observed in the fresh SRD sediment and for Hg and Cu in the Cowboy Charcoal (CL2) particle (Figure 6). The best fit of the Hg spectra collected for fresh SRD was obtained using Hg_2Cl_2 as the model compound, whereas the best fit of the Hg spectra collected for the Cowboy Charcoal (CL2) particle was obtained using cinnabar as a model compound. The best fit for the Cu spectra was obtained using Cu_2S as a model compound. The Hg spectra for the particle in the Cowboy Charcoal (CL2) amendment is consistent with cinnabar, which is relatively stable in the environment. These observations suggest the potential transformation of Hg as Hg_2Cl_2 to Hg in cinnabar. This transformation to a more stable form of Hg within the biochar grain may be associated with a decrease in bioavailability of Hg in Cowboy Charcoal (CL2) amendment.

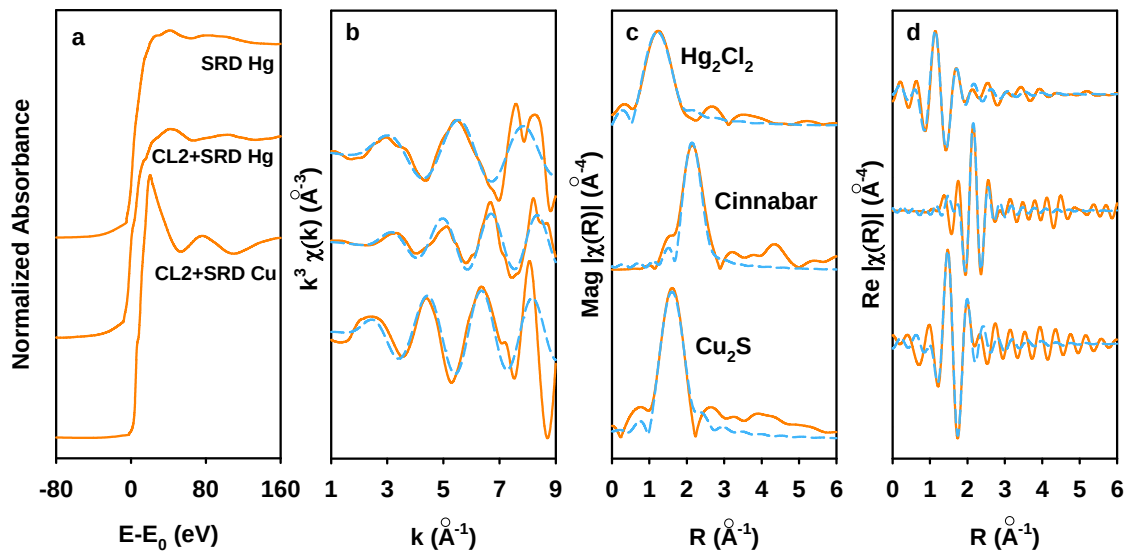


Figure 6. ^a Edge-step normalized Cu K-edge and Hg LIII-edge XANES spectra of fresh SRD and Cowboy Charcoal (CL2) in an amendment after 235 days. ^b k^3 -weighted chi spectra (orange solid line) and the best fit data (light blue dash line). ^c Fourier-transform magnitude spectra and the best fit data. The spectra were best fitted by these reference materials. Fourier transform data were not corrected for a phase shift. ^d Fourier-transform real part and the best fit data. The Hg and Cu XANES spectra are plotted relative to E_0 of 12 284 and 8 979 eV, respectively.

Summary and Implications

Long-term batch experiments were conducted to evaluate the effectiveness of biochar as an amendment for controlling Hg in South River sediments. Different biochar materials were co-blended with the sediments and maintained under saturated conditions in an anoxic environment. These mixtures were periodically sampled to determine the aqueous concentrations of Hg, MeHg and other geochemical parameters. Solid-phase samples were periodically collected and analysed for mineralogical and geochemical parameters. Large reductions in aqueous Hg concentrations were not observed at early times, but were followed by larger reductions in total Hg as the experiments progressed. Concentrations of MeHg in Cowboy Charcoal (CL2) and low- and high-T switchgrass (GR4L and GR4H) were lower than the sediment control. The sulfate concentration decreased in the sediment control and amendments as the experiments progressed. The XAS studies indicated Hg in Hg_2Cl_2 form was near the surface of a Fe-bearing particle in fresh SRD sediment. Hg in cinnabar form was observed to be co-precipitated with S, Fe, Cu, and Mn in a particle from Cowboy Charcoal (CL2) amendment. Similar particles were not isolated from other biochar mixtures.

The decrease in Hg and sulfate concentrations from aqueous solution and the characterization of Hg in the XAS studies suggest a potential transformation pathway for Hg from a soluble form to the insoluble cinnabar during long-term contact with Cowboy Charcoal biochar. A possible pathway leading to this transformation was: 1) After Hg_2Cl_2 -bearing sediment, Fe(III) oxide particles and Cowboy Charcoal (CL2) particles were blended, the system became progressively reduced causing dissolution of the Fe(III) oxide phases, possibly releasing Cu and Hg into solution, 2) Meanwhile sulfate from the sediment was reduced to form sulfide. 3) A suitable environment was provided within the Cowboy Charcoal (CL2) particle for the co-precipitation of Hg, S, Fe, Cu, and Mn.

The occurrence of cinnabar within the biochar particle indicates that the accumulation of Hg is within the biochar structure. This result suggests that in addition to Hg being present as an insoluble phase, it is present within the biochar structure. Biochar contains reduced C which may provide a geochemical environment where cinnabar may be more resistant to reoxidation.

This document describes the major findings of this study to date. Additional analyses are currently being conducted using XAS and other techniques to evaluate whether the phases identified occur elsewhere in the biochar or are relatively sparse.

References

Benoit, J.M., Gilmour, C.C., Mason, R.P., 2001. Aspects of bioavailability of mercury for methylation in pure cultures of *Desulfobulbus propionicus* (1pr3). *Appl. Environ. Microbiol.* 67, 51-58.

Gilmour, C.C., Henry, E.A., Mitchell, R., 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* 26, 2281-2287.

Ptacek, C., Blowes, D., Desrochers, K., Liu, P., Paulson, K., 2013. Evaluation of potential treatment methods for mercury-bearing riverbank sediments and soils from the South River, Virginia (USA). SRST Briefing Report.

Use of an Enhanced Adaptive Management Approach for Integration of Mercury Cycling Modeling, Relative Risk Modeling and Monitoring Data

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Background

Uncertainties about future conditions and the effects of remedial actions, as well as increasing resource scarcity, have been driving forces in the utilization of adaptive management strategies. However, many applications of adaptive management have been criticized for shortcomings including lack of direct links between anticipated outcomes and management alternatives and the complexity of coordination of the series of decisions with stakeholder input or values. We supplement existing adaptive management approaches with a decision-analytical approach that guides initial selection of management alternatives and also allows for incorporation of stakeholder values and learning based on monitoring information. The model provides the remedial implementation team with a transparent set of recommendations for further consideration. We illustrate the use of this enhanced adaptive management (EAM) framework to analyze remedial alternatives at the South River near Waynesboro, VA based on an understanding of mercury loading and behavior in the river. The results show that the performance of alternatives is highly influenced by the importance placed on different evaluation criteria, by uncertainty in the contaminant loading model and by cost estimates. The process demonstrates that a decision model can link environmental models and short- and long-term monitoring information with management choices to help inform a remediation approach and provides information useful for adaptive incremental implementation.

Introduction

A conceptual EAM framework has been developed that integrates decision analysis with monitoring information to provide managers and decision-makers with a tool for visualizing how remedial approaches may be modified or changed based on additional information. The EAM approach requires integration of several research projects, modeling efforts and observations: (1) A decision framework specifying the criteria to be used in evaluating the remedial alternatives (evaluation criteria); (2) Enumeration of the relative importance or trade-offs among these criteria (relative weights); (3) Empirical results and physical models relating the hypothesized effects and the stated aims; (4) Linkages, assumptions, or models providing a basis to hypothesize the effects of management actions or remedial alternatives on the stated aims.

EAM requires specification of the remedial action objectives, clear hypotheses about the potential impacts of remedial actions, and suggests a monitoring plan that increases the certainty and accuracy of the remedial outcomes. The short term remedial action objectives for the South River are to reduce exposure and transport of mercury and to enhance ecological habitat. The evaluation criteria for the decision model include effectiveness of the action in achieving the

remedial action objectives, implementability including stakeholder acceptance, and cost including construction and long term maintenance and monitoring costs (see Remediation Proposal, 2013). The Phase 1 remedial action is proposed to begin in the first two-mile stretch of the river adjacent to the former plant's outfall. The EAM approach was designed to be utilized to support decisions in the context of planning and implementation of South River remediation. The initial EAM framework application was designed to demonstrate the utility of this approach.

The objective for the current effort is to refine, apply and transfer the EAM approach to the SRST ROP Work Group. The approach needs to be refined to encompass output from the Relative Risk Model (RRM) under development by Wayne Landis (Western Washington University) and the Mercury Cycling Model (MCM) under development by Reed Harris. In order to do this, the evaluation criteria may need to be modified and aligned across the projects. The EAM approach will be aligned with the remedial objectives including development of specific performance metrics that inform those objectives. Following these modifications, the model and supporting user documents will be delivered.

Materials and Methods

Adaptive management requires that decision makers hypothesize the potential outcomes and mechanisms behind the effectiveness of remedial actions, so that they may test those elements after remedial actions are performed. The relationships between the effects and the outcomes should be based on modeling, empirical relationships, previous research, or expert hypotheses that can be measured and updated. One evaluation criterion, the effectiveness in the reducing smallmouth bass tissue MeHg, may be predicted by the MCM which utilizes the specifics of a remedial action to determine potential changes in Hg concentration at the downstream end of the remediation reach. Another evaluation criterion, reducing the risk to ecological receptors, can be modeled using the Landis RRM. The decision model allows quantitative effects analysis, and provides an archive of the most up-to-date understanding of the system and the relative priorities of stakeholders. The predictions and relationships in the model are updated with monitoring results.

Decision Model. The decision model needs to reflect the decision process for selecting the best remedial alternative and the expected effects of that alternative. The initial set of evaluation criteria in undertaking remedial action were considered to be (1) effectiveness in achieving the remedial action objectives (2) implementability and (3) cost. The long term remedial objectives include reduction in MeHg in smallmouth bass tissue and the preservation or enhancement of ecological resources, as reflected in the potential of an alternative to create habitat and avoid risks to the ecological community. To this we add a criterion to consider the change in habitat conditions associated with any remedial actions.

An initial set of remedial alternatives have been developed to use for the integration effort. The alternatives are different combinations of technologies including vegetative bank stabilization, MNR, and outflow source control in the reaches closest to the outfall. Each alternative can then be evaluated based on its collective performance on all the objectives. The model uses the performance of the alternatives on each evaluation criterion (?) to calculate the relative value of each alternative. Multi-attribute value theory is used to compare the alternative using a local

scale for each criteria and objective (Linkov and Moberg, 2012). The “value” of each alternative is a normalized score for each objective with the highest performing alternative(s) given a value score of 1, and the lowest performing alternative given a 0. The total utility, $U(\mathbf{a})$, for that alternative, $\mathbf{a}$, is then calculated as a weighted sum across the four objectives,

$$U(\mathbf{a}) = w_1 \cdot V_1(a_1) + \dots + w_n \cdot V_n(a_n) , \text{ (Keeney and Raiffa, 1976)}$$

where a_i is the performance score of alternative $\mathbf{a}$ on objective O_i for $i = 1$ to n , $V_i(a_i)$ is the value of alternative $\mathbf{a}$ reflecting its performance on criterion O_i and w_i is the weight of criterion O_i where $\sum w_i = 1$.

Incorporating the Remediation Proposal and the Interim Measures Work Plan. The Remediation Proposal (2013) and the Interim Measures Work Plan (2014) specify a set of remedial action objectives that need to be met in order for a remedial action to be considered effective. From those documents, a comprehensive set of ultimate objectives and metrics for assessing success will be developed. These will be refined with input from stakeholders, the SRST and other decision makers.

Mercury Cycling Model. The MCM will be developed that will provide a prediction of the concentrations of Hg in specific environmental compartments in the river, based on the anticipated efficacy of remedial alternatives. The MCM output includes predictions of resulting concentrations in surface water and sediment and can include resulting concentrations in biota, or the sediment and surface water concentration output can be used in the BASS model to anticipate changes in key food web biota. Additionally, Hg concentrations can be represented as a distribution range of predicted outcomes in different environmental compartments that can be input into the EAM Model.

Relative Risk Model. The RRM predicts the risk of population continuity for four endpoint species: belted kingfisher, Carolina wren, smallmouth bass, and white sucker and for four water quality parameters tied to ecosystem services. Each remedial alternative under consideration is predicted to alter the environmental conditions that are inputs to the RRM, such as bank stabilization, sediment loading, etc. Therefore, the impact of each remedial alternative can be associated with a change in the relative risk of population continuity for the four ecological receptors of interest. The change in risk predicted under each remedial alternative (the output of the RRM) provides metrics to assess the potential ecological disruption associated with each remedial plan. A soft linkage for the models is anticipated; a series of RRM runs will provide a set of values and probabilities that will be entered as inputs to the EAM model.

Monitoring Plan. The EAM model is designed to reflect an understanding of the current conditions within the river. An important aspect of the application of the model, therefore, is specification of a series of measurements that should be taken in order to update the model, reduce uncertainty and increase understanding of the relationship between parameters that influence the predicted outcomes. The parameters form the basis of a short- and long-term monitoring plan which is necessary to inform the ranking of alternatives in subsequent phases of implementation. Initial discussions with the team suggest that certain monitoring parameters

will be useful in assessing success such as Hg and MeHg in surface water, sediment, mayflies, clams, and young of year fish.

Progress

Each of the 5 components of the integration effort is in a different stage of development. Initial EAM model structure and function has been presented to the group, allowing the first iteration of what an EAM approach integrating all the components would look like. The first steps will be to make a comprehensive list of objectives, and metrics by which to measure a successful remedial action. The next steps will be to collect the input parameters for the RRM and MCM that may be influenced by any remedial action plan. A hypothetical monitoring data set will be developed based on anticipated parameter changes that result from the current proposed action. This hypothetical data set will be used to test the evaluation process and the overall adaptive management approach.

Implications

The EAM approach is designed to assist and focus decision-making under adaptive management. EAM includes a decision model which is used to predict the expected outcomes in response to implementation of different remedial alternatives. The decision model serves as both an archive of the understanding of the system as it relates to the decision objectives, and a way to compare different courses of action. It is not an ecological or conceptual site model. It provides a simple description of the relationship between actions (remedial alternatives) and their impacts on the evaluation criteria (reduction in MeHg in smallmouth bass, cost, etc.). The decision model forces a quantitative evaluation of alternatives and a relative value score is calculated for each one. This score is based on a combined evaluation of how well the alternative meets the objectives and other evaluation criteria. As subsequent phases of remediation are implemented, the EAM may be updated improving the accuracy of the evaluation for each remedial alternative.

References

- Foran, C. M., K. M. Baker, N. R. Grosso and I. Linkov. 2015. An Enhanced Adaptive Management Approach for Remediation of Legacy Mercury in the South River. Submitted.
- Keeney L, Raiffa H (1976) Decisions with Multiple Objectives: Preferences and Value Trade-Offs. Wiley, New York.