Quantitative Basis for Design of Monitoring of Remedial Effectiveness in a River System

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ABSTRACT

The South River is a high-gradient stream in central, VA with elevated mercury (Hg) concentrations in soil, sediment, surface water and biological tissue as the result of historic industrial Hg use. In addition, benthic invertebrate communities have been degraded in certain locations due to increased phosphorous (P) loading and suspended sediment deposition from degraded riparian zones. Remedial actions to address elevated Hg concentrations in environmental media (e.g., bank soils and sediment) and the impaired benthic invertebrate communities are being considered for implementation. A monitoring regime for the South River has been designed to measure potential post-remedy short-term and long-term improvements.

The short-term remedial action objectives (RAOs) are to reduce mercury transport and improve river bank habitat from a focused area of the South River. Short-term RAOs will be linked with specific projects (e.g., bank stabilization projects) and will be designed with a before-after type of monitoring design. Short-term monitoring will focus on river bank habitat and concentrations of Hg in near-bank media; results will be evaluated within an adaptive management framework.

Long-term monitoring RAOs are to reduce methylmercury (MeHg) exposure and to improve habitat conditions throughout the South River. Reductions in MeHg concentration in fish tissue may take several years following Hg loading reductions. As a result, the long-term monitoring needs to quantify interannual variability and build on the substantial existing baseline data set.

The long term monitoring regime has three components: annual young of the year (YOY) smallmouth bass tissue mercury concentrations, monthly surface water monitoring for mercury and water quality parameters, and biannual habitat quality and benthic invertebrate community monitoring. YOY smallmouth bass sample sizes were determined through a power analysis based on BASS model predictions of range of MeHg in YOY fish (~75mm total length). Collection of approximately 10 YOY smallmouth bass should detect a 30% decline in MeHg concentration at 70% power. Monthly baseline water quality monitoring has observed significant variation in MeHg resulting from changes in water temperature. Biannual monitoring of the benthic invertebrate community will be compared to baseline data and incorporated into a multivariate statistical framework to identify stressors and long-term changes.

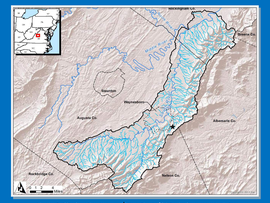


Figure 1: Site location map. ● Location of historical mercury point source. Distances from this location are listed in relative river miles (RRM).

SHORT-TERM MONITORING

The short-term RAOs are to reduce mercury transport and improve river bank habitat from a focused area of the South River. Short-term monitoring elements are listed in Exhibit 1.

- Short-term RAOs will be linked with specific remediation projects (e.g., bank stabilization projects) and will be designed with a before-after type of monitoring design (Table 1)
- Focus on river bank habitat and concentrations of Hg in near-bank media.
- Short-term monitoring results will be evaluated within an adaptive management framework.

- **Reduce Mercury Transport and Exposure**
  - **Reduce Bank Erosion**
    - Topography
    - Bank Pins
    - Vegetation
    - Bank Characteristics
    - Design and Implementation
  - Reduce Mercury Loading from Bank
    - Surface Sediment
    - Periphyton
    - Asiatic Clam
  - Reduce In-Channel Mercury Exposure
    - Periphyton
    - Asiatic Clam
- **Maintain or Improve Riparian and Aquatic Habitat**
  - Improve Bank Vegetation
  - Vegetation
  - Improve In-Stream Habitat

Exhibit 1: Short-term monitoring elements.

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	Reduce Bank Erosion	Topography	Low-Range Bank Erosion Rate	Transects Across Each BMA	Annually for First 3 Years; Post-storm	Bank Angles and Average Annual Erosion Rate		Structural and/or Vegetative Stabilization	Refine Effectiveness Estimates
		Bank Pins	Low-Range Bank Erosion Rate	Transects Across Each BMA	Twice Annually for First 3 Years; Post-storm	Average Annual Erosion Rate		Structural and/or Vegetative Stabilization	Refine Effectiveness Estimates
		Vegetation	≥70% Root Density; ≤ 0 Root Depth/Bank Height	Transects Across Each BMA	Annually for First 3 Years; Post-storm	Root Density and Depth; Bank Height		Additional Vegetation Enhancement	Refine Effectiveness Estimates
		Bank Characteristics	Minimal Undercutting or Slumping	Transects Across Each BMA	Annually for First 3 Years; Post-storm	Extent of Undercutting and Slumping		Structural and/or Vegetative Stabilization	Refine Effectiveness Estimates
		Design and Implementation	Landowner Approvals and Permits	BMA Properties	N/A	N/A		N/A	Refine Implementation Estimates
	Reduce Mercury Loading from Bank	Surface Sediment	>75% Mercury Concentration Reduction	Downstream of BMAs (Nearshore)	Twice Annually for First 3 Years	Irhg and MeHg Concentrations		N/A	Refine Effectiveness Estimates
		Periphyton	>75% Mercury Loading Reduction	Downstream of BMAs (Nearshore)	Twice Annually for First 3 Years	Irhg and MeHg Accumulation Rate		N/A	Refine Effectiveness Estimates
		Asiatic Clam Cage Sampling	>75% Mercury Loading Reduction	Downstream of BMAs (Nearshore)	Twice Annually for First 3 Years	Irhg and MeHg Accumulation Rate		N/A	Refine Effectiveness Estimates
	Reduce In-Channel Mercury Exposure	Periphyton	>50% Mercury Concentration Reduction	Downstream of BMAs (Channel)	Annually for First 10 Years	Irhg and MeHg Accumulation Rate		N/A	Refine CSM
		Asiatic Clam Cage Sampling	>50% Mercury Concentration Reduction	Downstream of BMAs (Channel)	Annually for First 10 Years	Irhg and MeHg Accumulation Rate		N/A	Refine CSM
Maintain or Improve Riparian and Aquatic Habitat	Improve Bank Vegetation	Vegetation	>80% Cover; <10% Invasives	Transects Across 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 Characterization	Downstream of BMAs	Annually for First 10 Years	Rapid Bioassessment Protocol Scores		N/A	Refine Effectiveness Estimates

Table 1: Short-term monitoring plan RAOs, designs and potential adaptive management outcomes. Remedial action objectives have pre-defined metrics and success criteria that will be evaluated through an adaptive management framework.

LONG-TERM MONITORING

Long-term monitoring RAOs are to reduce methylmercury (MeHg) exposure and to improve habitat conditions throughout the South River. Subsequent to the publishing of this abstract; other elements were added to the long-term monitoring plan to track human and ecological exposure over time; these items are listed in Exhibit 2. Numerical approaches for two of the elements of the long-term monitoring are discussed in detail here:

- Young of the year (YOY) smallmouth bass tissue mercury concentrations
- Surface water monitoring for mercury and water quality parameters

Reductions in MeHg concentration in fish tissue may take several years following Hg loading reductions. As a result, the long-term monitoring needs to quantify interannual variability and build on the substantial existing baseline data set. An analysis of surface water data illustrates the approach that the monitoring plan will take to address this.

- **Potential Human Exposure**
  - Largemouth Bass
  - Smallmouth Bass
  - Snapping turtle
  - Mallard duck
  - Community outreach
- **Ecological Exposure**
  - Aquatic
    - YOY fish
    - Sediment
    - Benthic invertebrates
    - Periphyton
    - Asiatic clam tissue
  - Terrestrial
    - Adult Carolina Wren
    - Wolf Spiders (family Lycosidae)
    - Earthworms
- **Water quality**
- **Benthic invertebrate Community**

Exhibit 2: Long-term monitoring elements.

YOUNG-OF-YEAR FISH

YOY fish are an ideal monitoring element to track long-term changes in mercury exposure due to the relatively short exposures they experience and their site fidelity or small home range. YOY fish have been successfully used to track short-term (i.e., annual) changes in mercury exposure in several studies. For example, mercury loaded to an experimental lake via atmospheric deposition was detectable in YOY fish within 2 months (Harris et al. 2007); YOY fish are an important component of many regional mercury-monitoring plans (e.g., Slotton 2008). In addition to the rapid responses to mercury loading, YOY fish are more spatially restricted (Minns 1995) because they are subject to more intense predation and associate with protective cover (e.g., large woody debris).

YOY fish have not been collected in the South River, so the Bioaccumulation and Aquatic System Simulator (BASS) model was used to predict the concentration range for a YOY smallmouth bass between relative river mile (RRM) 2.4 – 5. The BASS model predictions of THg in fish is in good agreement with the empirical data over the range of total fish lengths for specimens collected in the South River (Figure 2). In addition, the model predicts a relatively narrow range of concentrations for fish up to 125 mm in total length.

The minimum, maximum, and average THg concentrations predicted were used to simulate a THg concentrations in a YOY smallmouth bass population (n=1000) (Figure 3). The average THg of this population was 0.23 ± 0.09 mg/kg.

These data were used in a power analysis to determine number of samples necessary to detect small declines in YOY THg concentration. Cohen's d (Cohen, 1969) was calculated for two cases: a 30% decline or 5% decline (Table 2 and Table 3). It was found that approximately 10 samples would be adequate to measure a 30% decline in THg concentration in YOY tissue at a 70% power; it would not be feasible to measure a 5% decline at any power.

YOY smallmouth bass will be collected from six sample locations including one reference area at RRM ~2.7, three areas from the South River, and two areas in the SFS River. The rationale for collecting fish from larger areas is to avoid oversampling the smallmouth bass or non-target species population. Smallmouth bass ranging from 60 to 110 millimeters (mm) total length will be collected in the fall of each year, following four or five months of exposure, beginning in 2013.

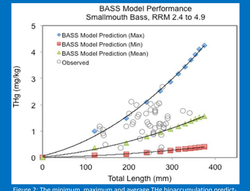


Figure 2: The minimum, maximum and average THg bioaccumulation predicted by the BASS model, compared with observed THg concentrations in smallmouth bass.

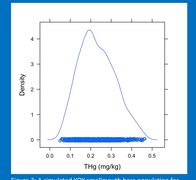


Figure 3: A simulated YOY smallmouth bass population for the South River.

Class	THg (mg/kg)	SD
Smallmouth Bass at RRM 3.5	0.226	0.088
30% decline	0.158	0.062
5 % decine	0.215	0.084

Table 2. The mean and standard deviation (SD) of individual replicates from river bank samples. SD was used to compute the combined σ' (Table 3).

Alternative Hypothesis	σ'	d
30% decline	0.08	0.89
5 % decine	0.09	0.13

Table 3. The combined σ', used to calculate the effect size (d) for each of the comparisons. Note that the σ' and d were calculated on log-transformed values.

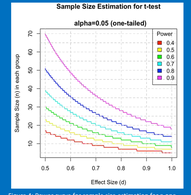
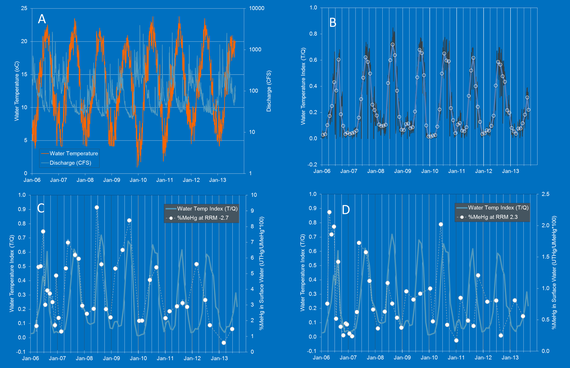


Figure 4: Power curve for sample size estimation for a one-tailed t-test. Curve created in R (R Development Core Team 2013) using the *pwr* package (Champely 2009).

SURFACE WATER MONITORING REVEALS PATTERNS IN INTERANNUAL VAIRIABILITY



A challenging aspect of long-term mercury monitoring in aquatic systems or watersheds is understanding how changes in climate and river hydrology affect the concentrations of mercury in environmental media. This is due to the role that bacteria play in mercury cycling (i.e., methylation) and the role of the biological food web in controlling ecological exposure. In addition, physical processes like dilution can reduce exposure over biologically relevant timeframes.

The relationship between MeHg and climate can be used to understand the status of MeHg production in the South River. For example, daily South River discharge and surface water temperature as measured at Waynesboro (RRM 2.7) show highly variable but repeatable seasonal patterns of high discharge and low temperatures in the first and third quarters of each year (Panel A). This pattern is more evident in the water temperature quotient, which is calculated by dividing the surface water temperature by the discharge (Panel B). Higher values of this quotient indicate periods of time where surface water temperatures are high and discharges are low. This value tracks closely with the percentage of MeHg in unfiltered surface water in a South River reference area (Panel C), and an area with high inorganic mercury in the water column (Panel D). A clear interannual pattern is observed where certain years appear to have warmer and drier conditions than other years. For example, 2008 data show relatively high water temperature quotient values and correspondingly high percent MeHg values. In contrast, 2013 has had the lowest quotient values and the lowest percent MeHg observed in the second or third quarter of the year.

Analysis of surface water samples for THg and MeHg in the water column of the South River and SFS River builds on the extensive baseline data set, provides a measurement of mercury exposure for the base of the food web, and provides important information on interannual variation in MeHg production. The South River surface water mercury database has low-level mercury data beginning in 1999, providing extensive characterization of pre-remediation conditions. Samples are collected on an approximately monthly basis, providing high frequency data on mercury loading rates and mercury behavior. Interannual variability can be evaluated by comparison of MeHg concentrations in various phases of surface water (i.e., filter-passing vs. particulate) on a monthly or annual basis and combined with an evaluation of climatological data and water quality (e.g., temperature data).

References:

- Champely, S. 2009. pwr: Basic functions for power analysis. R package version 1.1.1. http://CRAN.R-project.org/package=pwr.
- Cohen, J. 1969. Statistical power analysis for the behavioral sciences. New York, NY: Academic Press.
- Flanders, J.R., R.R. Turner, T. Morrison, R. Jensen, J. Pizzuto, K. Skalak, and R. Stahl, 2010. Distribution, behavior, and transport of inorganic and methylmercury in a high gradient stream. Applied Geochemistry 25: 1756-1769.
- Harris, R.C., J.W.M. Rudd, M. Amyot, C.L. Babiarz, K.G. Beaty, P.J. Blanchfield, R.A. Bodaly, B.A. Branfireun, C.C. Gilmour, J.A. Graydon, A. Heyes, H. Hintelmann, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S.E. Lindberg, R.P. Mason, M.J. Paterson, C.L. Podemski, A. Robinson, K.A. Sandilands, G.R. Southworth, V.L. St. Louis, and M.T. Tate, 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. PNAS 104(42): 16586-16591.
- Minns, C.K., 1995. Allometry of home range size in lake and river fishes. Canadian Journal of Fisheries and Aquatic Sciences 52(7): 1499–1508.
- R Development Core Team. 2011. R: A language and environment for statistical
- computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL http://www.R-project.org/.
- Slotton, D., 2008. The UC Davis Biosentinel Mercury Program: Using Small Fish to Monitor Fine-scale Patterns of Methylmercury Contamination in the Watershed Fact Sheet. The Fish Mercury Project. San Francisco Estuary Institute Contribution No. 552.
- VADEQ (Virginia Department of Environmental Quality), 2009. Bacteria and Benthic Total Maximum Daily Load Development for South River. Prepared by Engineering Concepts, Inc. July 2009.