

Remedial Options (ROPs) Program Update

October 26, 2016

Robert N. Brent

*James Madison
University*

SRST ROPs Activities 2016

1. Characterization and Use of Biochars for Treatment of SR Soil and Sediment (Carol Ptacek, Waterloo)

Objective: Characterize various biochar sources and evaluate biochar for use in limiting Hg leaching from SR soils.

2. Floodplain Soil Amendment Pilot (Josh Collins, AECOM)

Objective: Test the efficacy of biochar application in floodplain soils to reduce uptake of Hg or MeHg by biota.

3. Biochar Effects on Macroinvertebrate Community (Will Clements, Colorado State University)

Objective: Estimate community-level effects of biochar on macroinvertebrates in field and mesocosm settings.

4. Reactive Capping Simulations (Danny Reible, Texas Tech University)

Objective: Identify capping design element parameters through laboratory mesocosms and modeling.

SRST ROPs Activities 2016

1. Characterization and Use of Biochars for Treatment of SR Soil and Sediment (Carol Ptacek, Waterloo)

Objective: Characterize various biochar sources and evaluate biochar for use in limiting Hg leaching from SR soils.

2. Floodplain Soil Amendment Pilot (Josh Collins, AECOM)

Objective: Test the efficacy of biochar application in floodplain soils to reduce uptake of Hg or MeHg by biota.

3. Biochar Effects on Macroinvertebrate Community (Will Clements, Colorado State University)

Objective: Estimate community-level effects of biochar on macroinvertebrates in field and mesocosm settings.

4. Reactive Capping Simulations (Danny Reible, Texas Tech University)

Objective: Identify capping design element parameters through laboratory mesocosms and modeling.

University of Waterloo Biochar Studies

1. Initial batch tests of various biochars
 - Hg removal
 - Leaching of unwanted constituents
2. Evaluation of Cowboy Charcoal for Hg removal under various conditions
 - Sequential columns
 - Layered columns
 - Co-blended columns
 - Variably saturated
3. Comparison of new large batch Cowboy Charcoal with previous batch
4. Characterization of new biochars

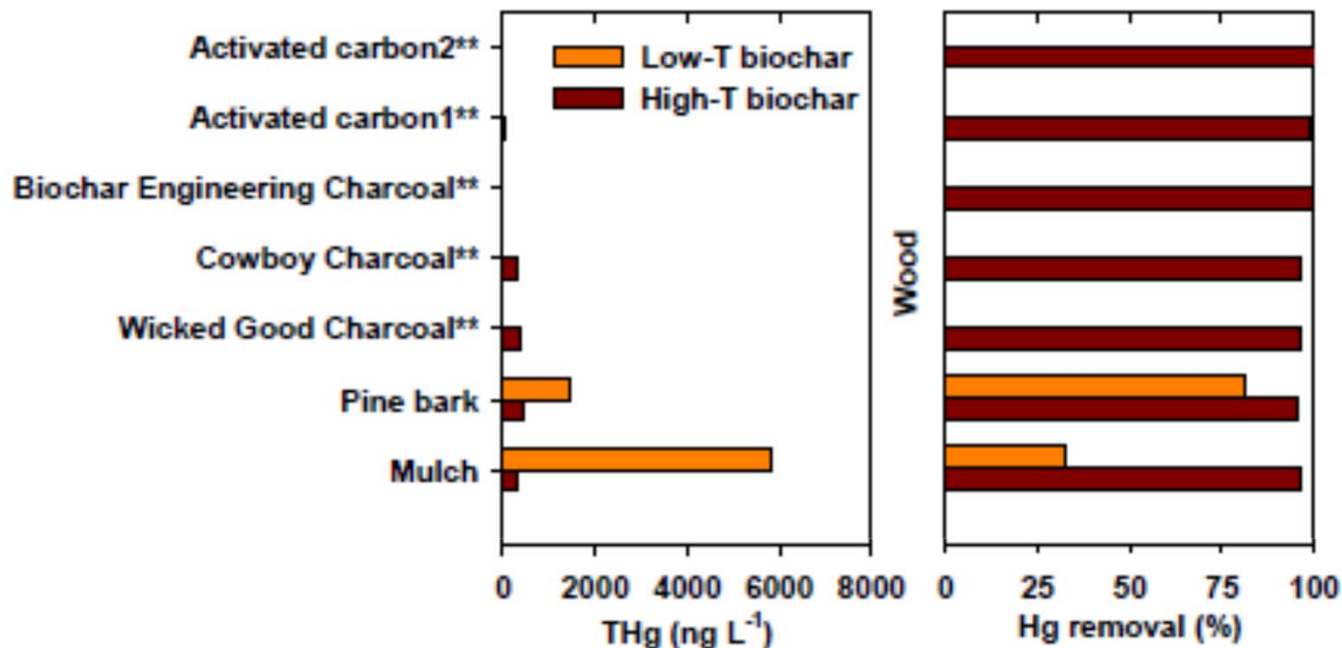
My Take-Home Message



FOR
DUMMIES

1. Initial batch tests of various biochars

- Many different biochar sources tested
- Cowboy Charcoal was about the best for Hg removal and didn't leach much else (nutrients, DOC, sulfate)
- Cowboy Charcoal is a good choice for biochar



My Take-Home Message



FOR
DUMMIES

2. Evaluation of Cowboy Charcoal for Hg removal under various conditions

- As a reactive layer, biochar is effective at removing Hg under both saturated and variably saturated conditions
- A relatively thin layer can be effective for a relatively long time
- Hg seems to be held rather tightly on the biochar
- Co-blending is not very effective



My Take-Home Message



FOR
DUMMIES

3. Comparison of new large batch Cowboy Charcoal with previous batch

- Different batches fairly consistent
- Hg removal best when biochar is crushed

4. Characterization of new biochars

- Some other biochars are promising (digestate biochar)



SRST ROPs Activities 2016

1. Characterization and Use of Biochars for Treatment of SR Soil and Sediment (Carol Ptacek, Waterloo)

Objective: Characterize various biochar sources and evaluate biochar for use in limiting Hg leaching from SR soils.

2. Floodplain Soil Amendment Pilot (Josh Collins, AECOM)

Objective: Test the efficacy of biochar application in floodplain soils to reduce uptake of Hg or MeHg by biota.

3. Biochar Effects on Macroinvertebrate Community (Will Clements, Colorado State University)

Objective: Estimate community-level effects of biochar on macroinvertebrates in field and mesocosm settings.

4. Reactive Capping Simulations (Danny Reible, Texas Tech University)

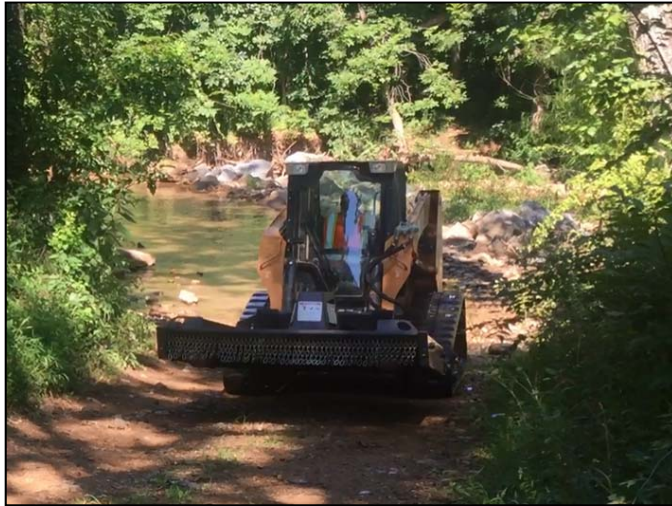
Objective: Identify capping design element parameters through laboratory mesocosms and modeling.

Floodplain Field Pilot



- Phase I – Laboratory Study
 - Biochar seemed promising for reducing Hg uptake in floodplain biota
- Phase II – Field Study
 - Worms don't like to be caged in
 - Unclear results
- Phase III – Field Pilot
 - Test methods for field applying biochar
 - Evaluate effects on uptake by biota

Floodplain Pilot Study- Phase III Feasibility Test



Floodplain Pilot Study- Phase III Feasibility Test



Floodplain Pilot Study- Phase III Schedule

Task	Date
Application Technique Feasibility Test	Complete
Work Plan Development	Fall 2016
Amendment Application	Late Winter 2017
Post-Amendment Monitoring	2017/2018
Data Evaluation and Reporting	2018

SRST ROPs Activities 2016

1. Characterization and Use of Biochars for Treatment of SR Soil and Sediment (Carol Ptacek, Waterloo)

Objective: Characterize various biochar sources and evaluate biochar for use in limiting Hg leaching from SR soils.

2. Floodplain Soil Amendment Pilot (Josh Collins, AECOM)

Objective: Test the efficacy of biochar application in floodplain soils to reduce uptake of Hg or MeHg by biota.

3. Biochar Effects on Macroinvertebrate Community (Will Clements, Colorado State University)

Objective: Estimate community-level effects of biochar on macroinvertebrates in field and mesocosm settings.

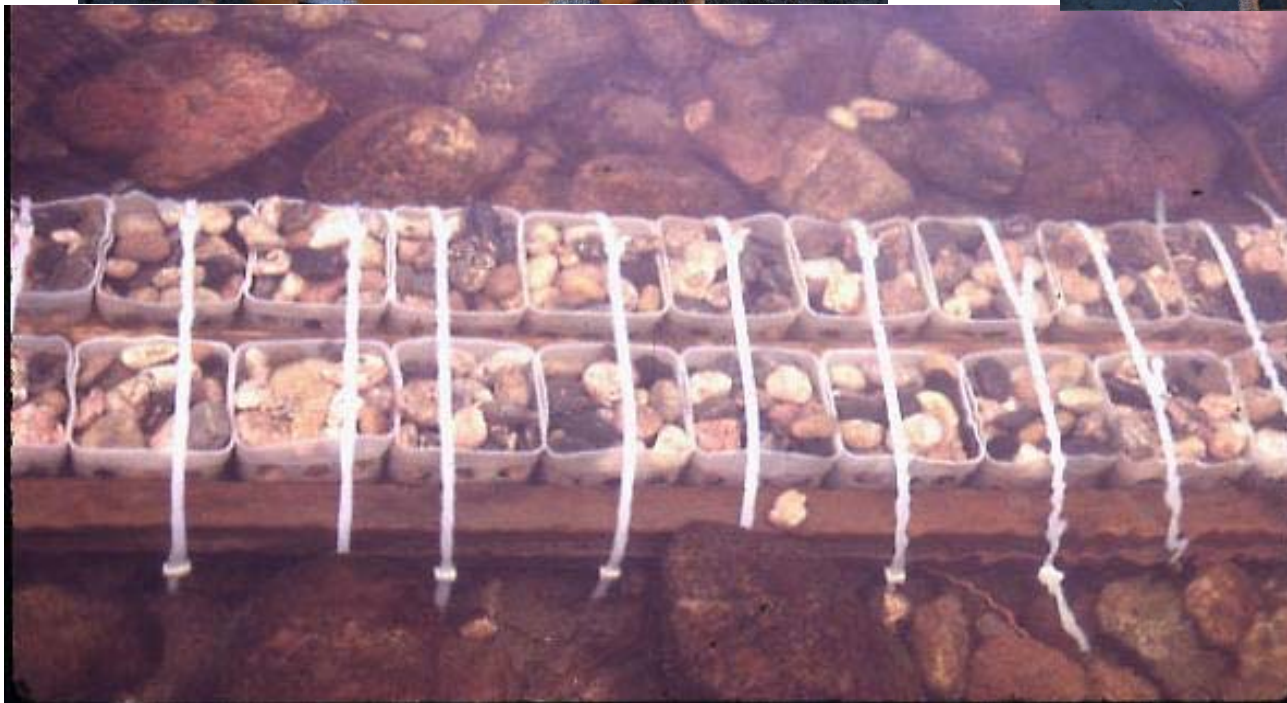
4. Reactive Capping Simulations (Danny Reible, Texas Tech University)

Objective: Identify capping design element parameters through laboratory mesocosms and modeling.

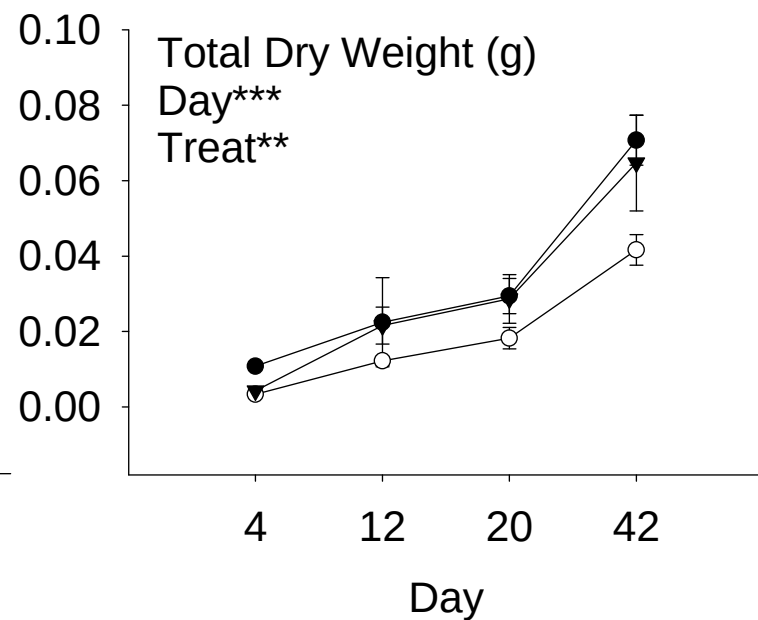
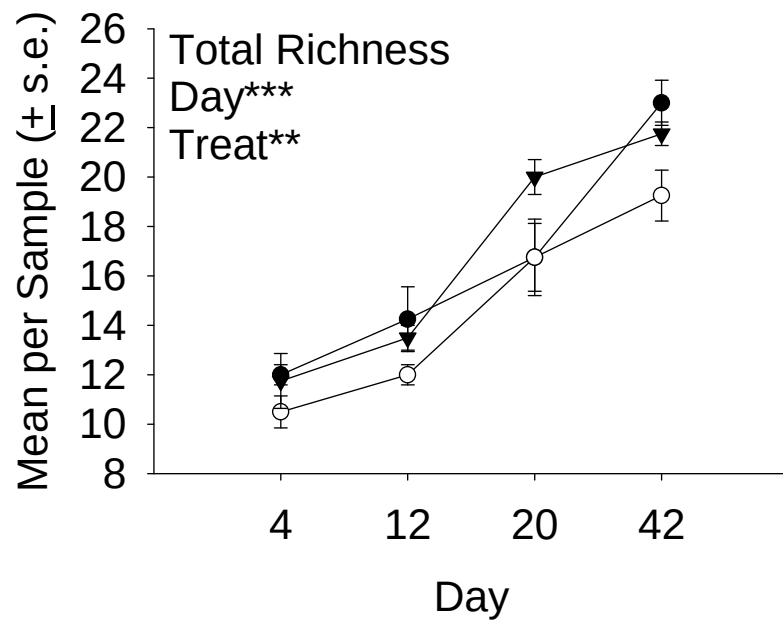
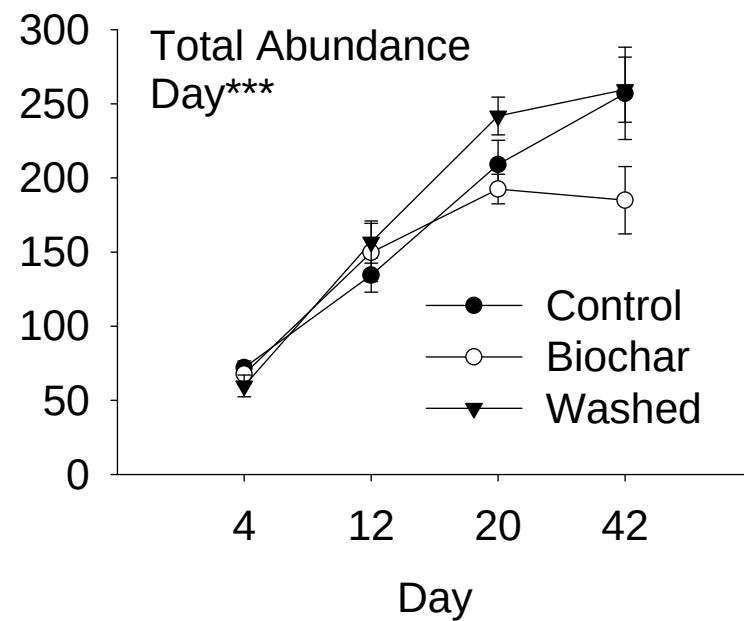
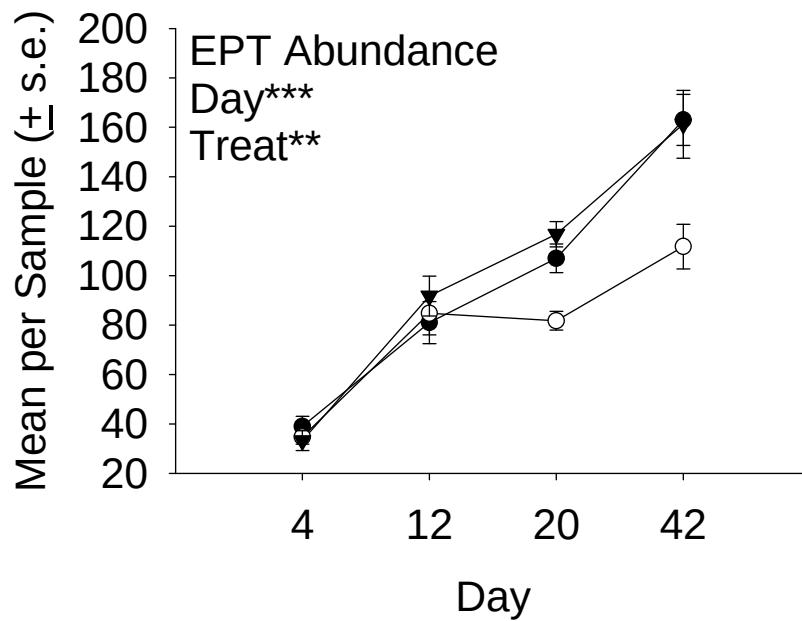
Mesh bags filled with either gravel
(Control), Biochar, or Washed Biochar



Covered with pebble & small
cobble substrate



Deployed in the
field & collected
after 4, 12, 20 &
42 d



My Take Home Message



- Biochar does seem to have a modest but statistically significant effect on benthic macroinvertebrate community measures
 - EPT abundance, total dry weight, richness
 - Perhaps an avoidance response
- Washing biochar seems to remove this effect

SRST ROPs Activities 2016

1. Characterization and Use of Biochars for Treatment of SR Soil and Sediment (Carol Ptacek, Waterloo)

Objective: Characterize various biochar sources and evaluate biochar for use in limiting Hg leaching from SR soils.

2. Floodplain Soil Amendment Pilot (Josh Collins, AECOM)

Objective: Test the efficacy of biochar application in floodplain soils to reduce uptake of Hg or MeHg by biota.

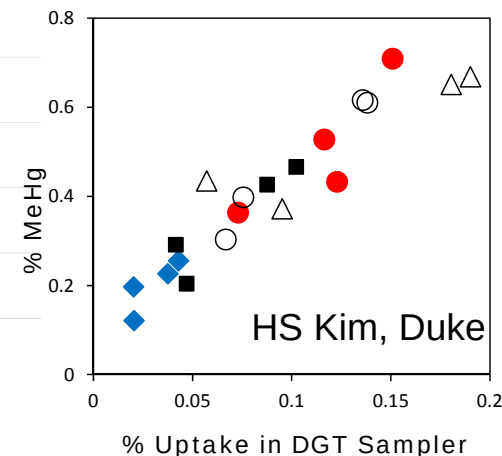
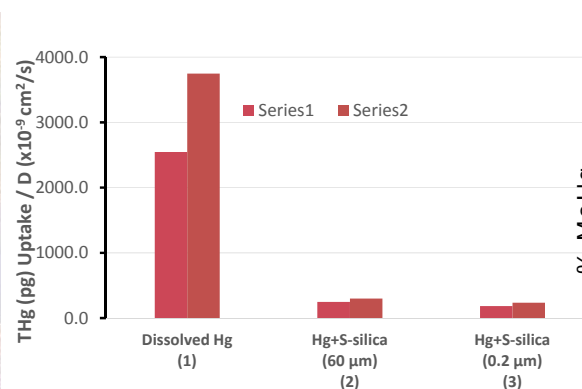
3. Biochar Effects on Macroinvertebrate Community (Will Clements, Colorado State University)

Objective: Estimate community-level effects of biochar on macroinvertebrates in field and mesocosm settings.

4. Reactive Capping Simulations (Danny Reible, Texas Tech University)

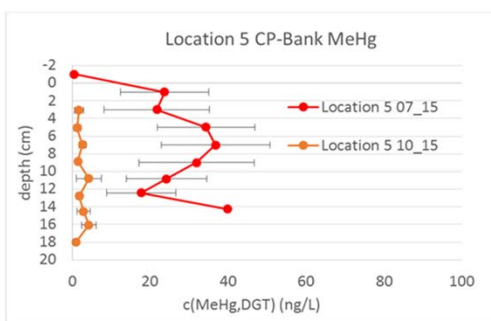
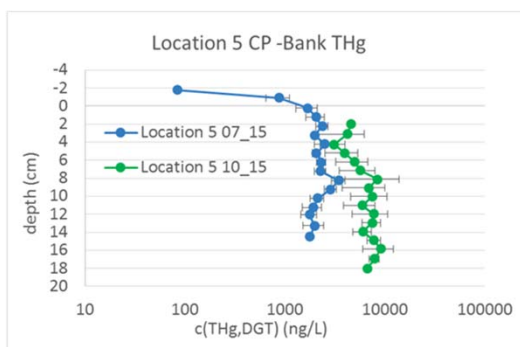
Objective: Identify capping design element parameters through laboratory mesocosms and modeling.

Passive Sampling of Bank Drainage via DGTs



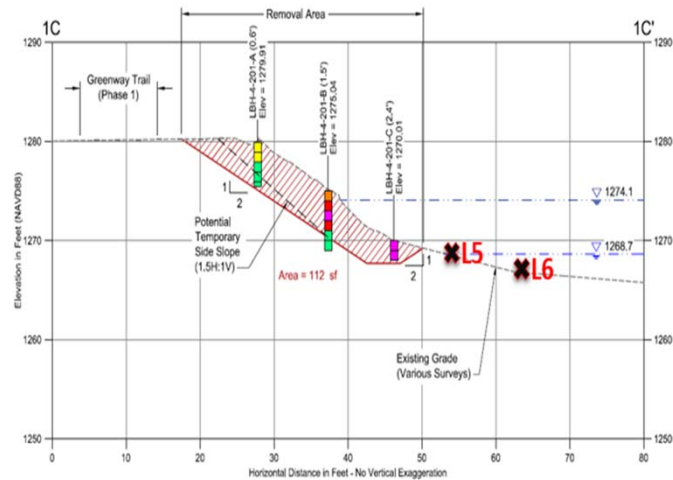
DGT uptake largely limited to freely available Hg and correlates well with bioavailability as measured by methylation

Constitution Park
Sampling base of bank and in channel



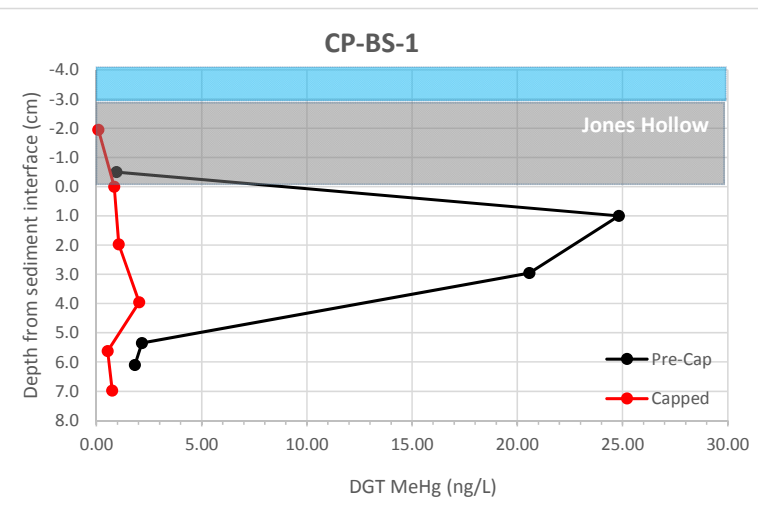
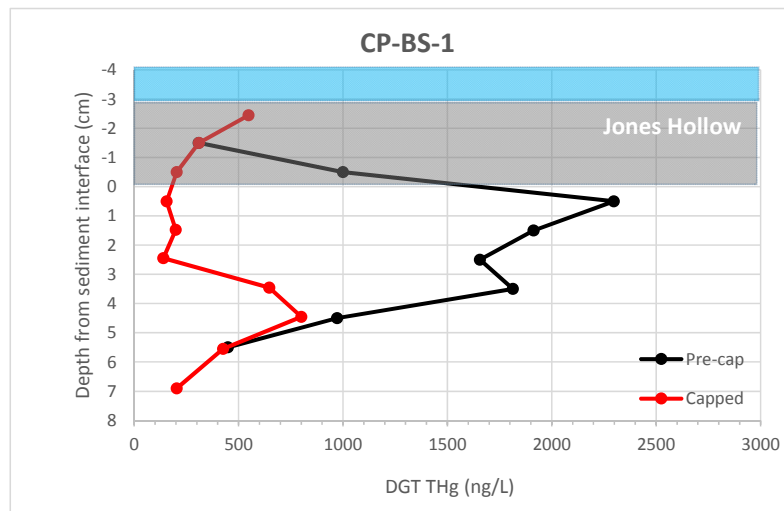
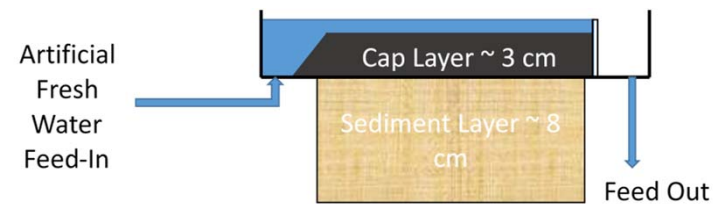
Sampling during low flow
Loc 5 - elevated
THg similar in July and October
MeHg much lower in October
(less reduction and microbial activity)

Lab Evaluation of Amended Capping



Evaluation of potential amended cap as part of stabilization design to control non-particle related leaching

Long term modeling also being pursued



Typical- sequestration of THg and reductions in MeHg in underlying sediment after capping

My Take Home Message



- DGT probes indicate that leaching from contaminated banks can be significant
- Capping can be effective at reducing that leaching
- MeHg in pore water much higher in July than October

SRST ROPs Activities 2015

5. Use of XRF for Field Measurement of Hg (Robert Brent, JMU)

Objective: Evaluate the method accuracy, precision, and sensitivity of handheld XRF for measuring Hg in SR bank and floodplain soils.

6. Stable Isotope Analysis (Joel Blum, U Michigan)

Objective: Explore stable Hg isotopes as a forensic tool for understanding Hg fate and transport.

7. Real-time Hg Monitoring (Todd Martin, Integral)

Objective: Develop and test a multi-parameter monitoring system that can estimate real-time Hg concentrations in the SR.

8. Dynamic Mercury Cycling Model (Reed Harris)

Objective: Develop a mechanistic mercury cycling model for the SR.

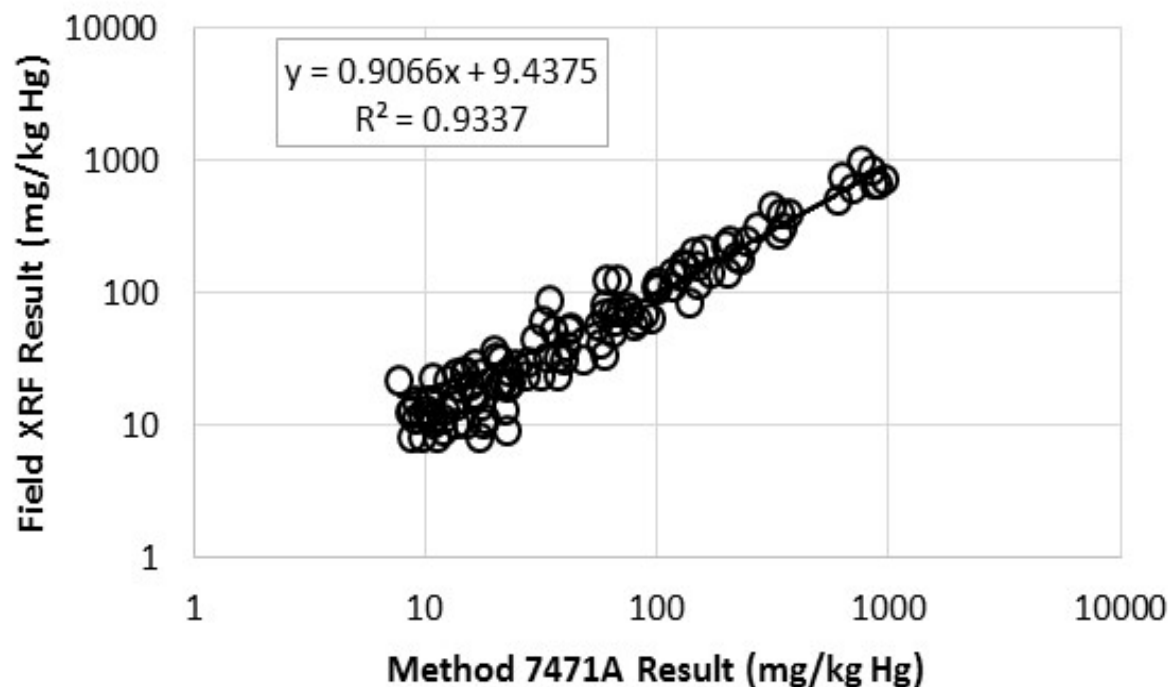
9. Enhanced Adaptive Management Model (Christy Foran, USACE)

Objective: Develop a decision tool that can assist in the SR adaptive management process.

XRF Study Findings



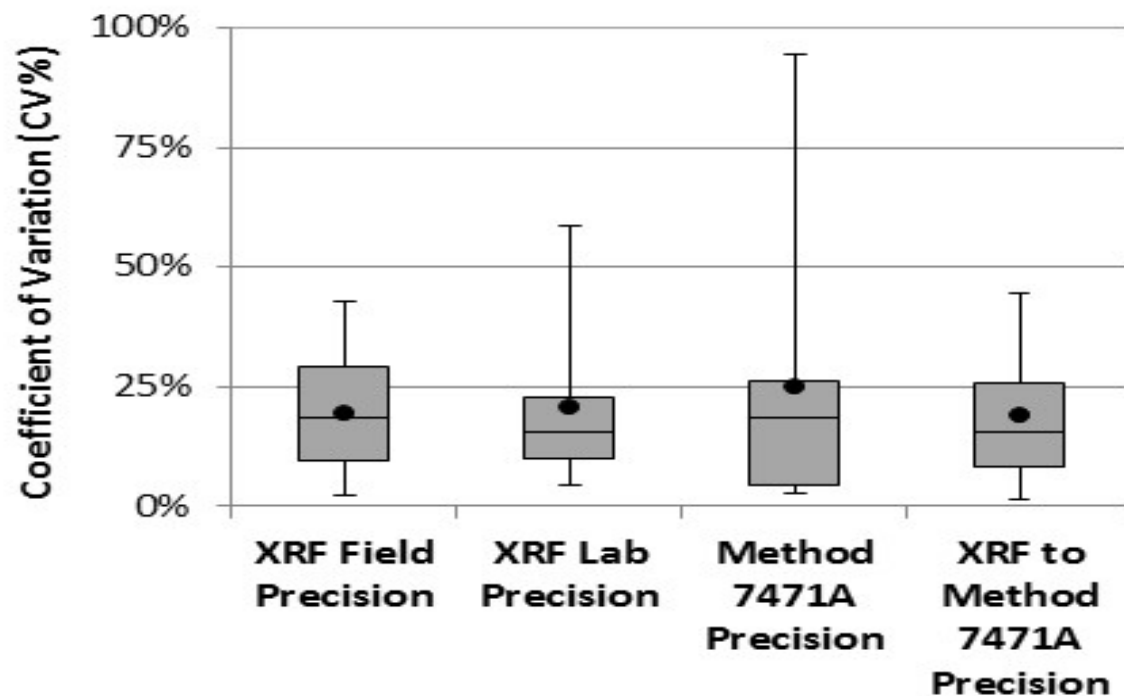
- Accuracy at the detection levels was very good – XRF results agreed with 93% of samples that were <7.4 ppm according to Method 7471A
- Accuracy throughout the range of 7.4 to 1000 ppm was very good



XRF Study Findings



- Precision was comparable to Method 7471A and constrained by sample heterogeneity
 - Median XRF precision = 18% CV
 - Median Method 7471A precision = 19% CV



SRST ROPs Activities 2015

5. Use of XRF for Field Measurement of Hg (Robert Brent, JMU)

Objective: Evaluate the method accuracy, precision, and sensitivity of handheld XRF for measuring Hg in SR bank and floodplain soils.

6. Stable Isotope Analysis (Joel Blum, U Michigan)

Objective: Explore stable Hg isotopes as a forensic tool for understanding Hg fate and transport.

7. Real-time Hg Monitoring (Todd Martin, Integral)

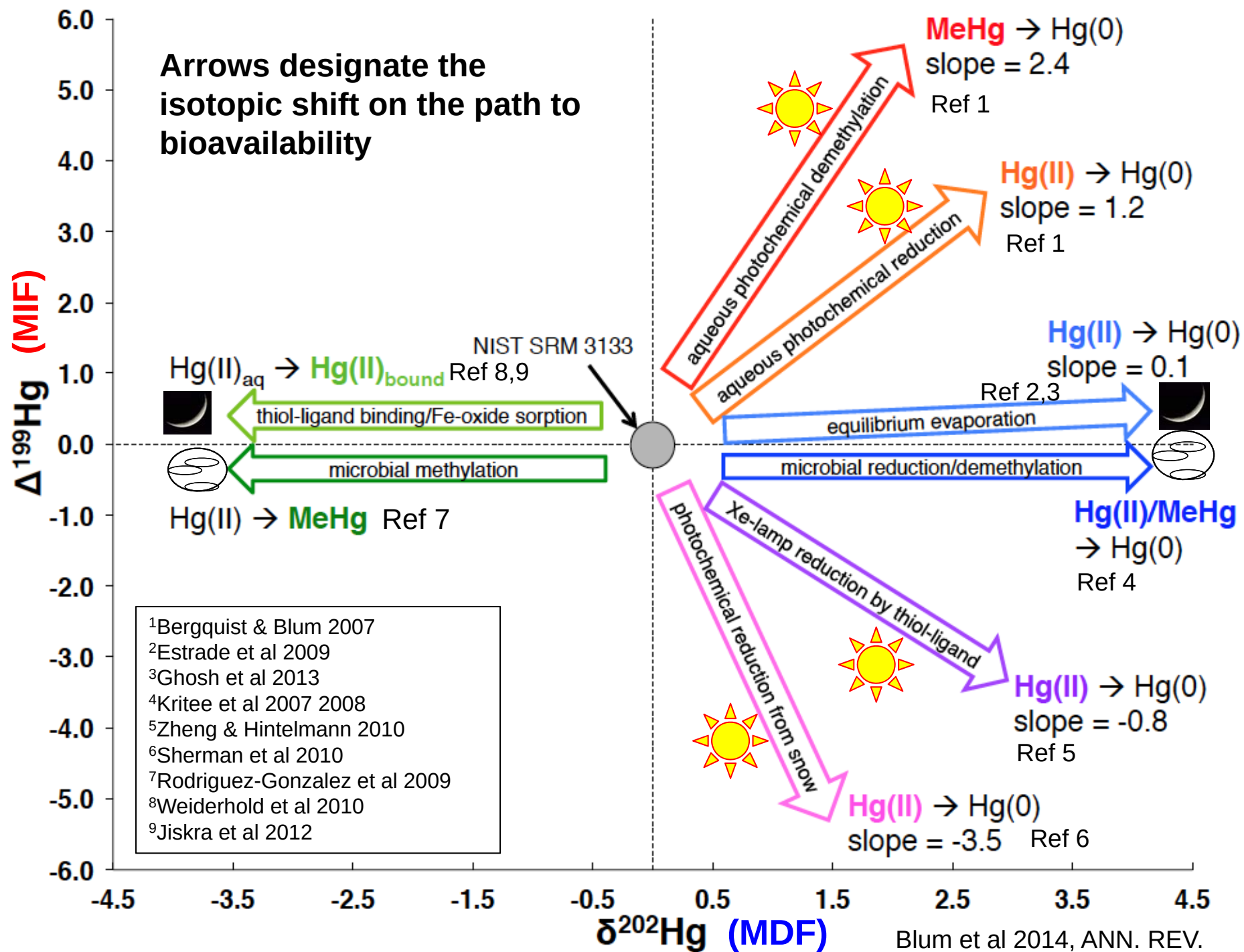
Objective: Develop and test a multi-parameter monitoring system that can estimate real-time Hg concentrations in the SR.

8. Dynamic Mercury Cycling Model (Reed Harris)

Objective: Develop a mechanistic mercury cycling model for the SR.

9. Enhanced Adaptive Management Model (Christy Foran, USACE)

Objective: Develop a decision tool that can assist in the SR adaptive management process.





Isotopic Characterization of Hg in the South River

Spencer Washburn and Joel Blum, University of Michigan

Major Findings from Phase I Work (June '14 – Dec '15)

- Established that the isotopic composition of Hg entering the river channel in the river reach adjacent to the industrial facility is distinct from Hg entering downstream of the facility, as well as Hg sourced from upstream of the facility
 - The observed isotopic composition in the river channel is a mixture of these three isotopic endmembers
- Observed a consistent offset in the Hg isotopic composition of suspended particulate versus dissolved Hg ($<0.45 \mu\text{m}$ size fraction) in the South River
 - We believe this is due to fractionation caused by a kinetic process related to preferential binding of Hg to thiol-containing binding sites on colloidal size particles
- Observed reaches of the South River with significant mass-independent fractionation of Hg, indicating photochemical reduction is occurring within these reaches to a significant extent



Phase II

Objectives:

- Explore the temporal variability of the Hg isotopic composition of legacy Hg released from the former industrial facility
- Characterize the end member isotope compositions influencing Hg in the South River channel in a variety of sample types with greater spatial coverage
- Investigate whether observed variability in Hg isotope compositions downstream of the former industrial facility are related to in-situ, site specific processes
- More accurately determine the Hg isotopic composition of portions of the South River unaffected by industrial inputs

Progress:

- Field Sampling campaign conducted in May-June '16
- Collected samples currently being processed and analyzed for Hg isotopes

My Take-Home Message



- It looks like isotopic analysis can be used in the South River to investigate Hg sources, movement, and transformations
- Different isotopic signatures are observed for
 - Natural background (upstream inputs)
 - Plant site inputs
 - Legacy Hg (downstream inputs)
- Different isotopic signatures are observed for
 - Dissolved Hg
 - Particulate Hg

SRST ROPs Activities 2015

5. Use of XRF for Field Measurement of Hg (Robert Brent, JMU)

Objective: Evaluate the method accuracy, precision, and sensitivity of handheld XRF for measuring Hg in SR bank and floodplain soils.

6. Stable Isotope Analysis (Joel Blum, U Michigan)

Objective: Explore stable Hg isotopes as a forensic tool for understanding Hg fate and transport.

7. Real-time Hg Monitoring (Todd Martin, Integral)

Objective: Develop and test a multi-parameter monitoring system that can estimate real-time Hg concentrations in the SR.

8. Dynamic Mercury Cycling Model (Reed Harris)

Objective: Develop a mechanistic mercury cycling model for the SR.

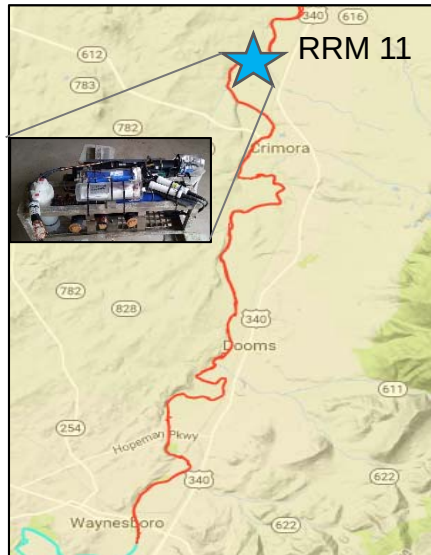
9. Enhanced Adaptive Management Model (Christy Foran, USACE)

Objective: Develop a decision tool that can assist in the SR adaptive management process.

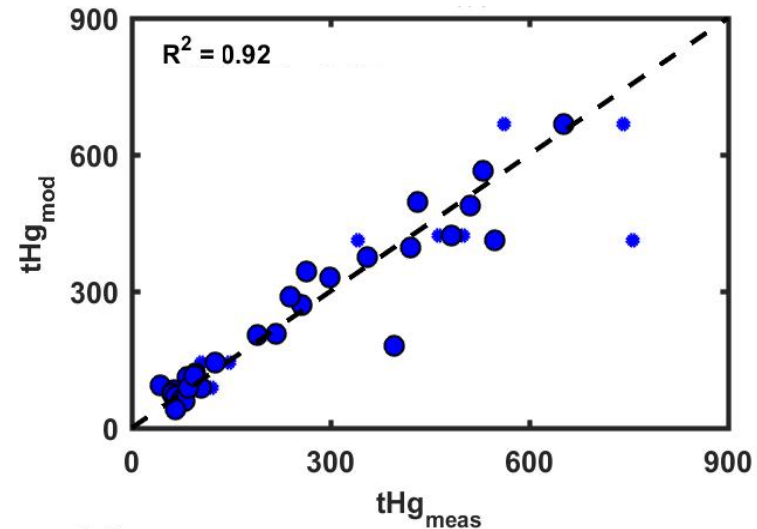
South River OPTICS Field Studies



6 week pilot study to evaluate particulate and dissolved Hg and MeHg

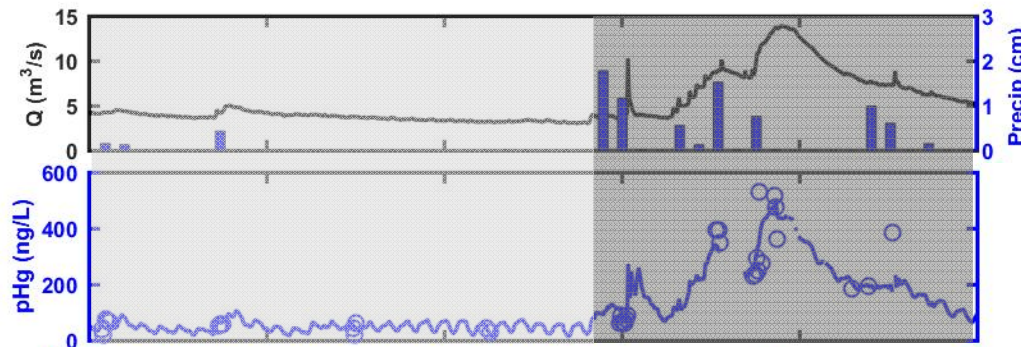


Excellent agreement between statistical models and laboratory analytical data



Diurnal Variability Under Baseflow Conditions

Storm-induced particulate resuspension



Baseflow

- Patterns in TSS, PIC, POM and particulate Hg/MeHg indicative of nocturnal bioturbation seen at other sites

Storm Flow

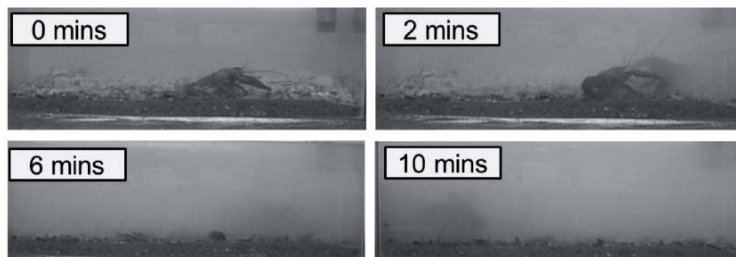
- Patterns indicative of particulate mobilization due to stream bed resuspension and bank engagement during storm flows

South River Mass Flux

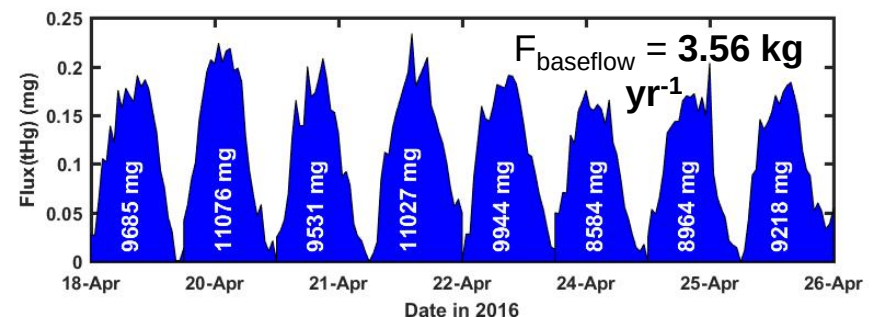
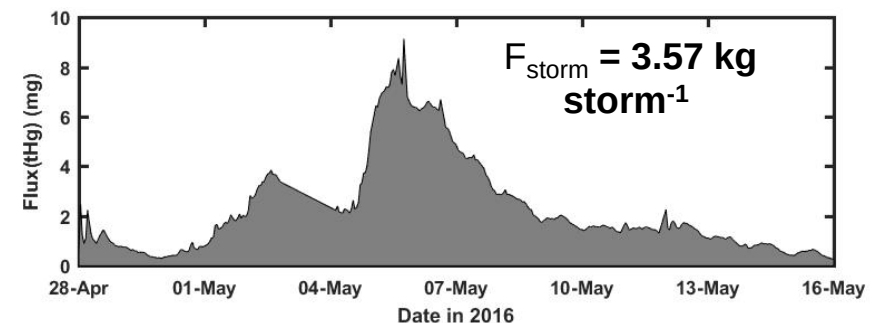
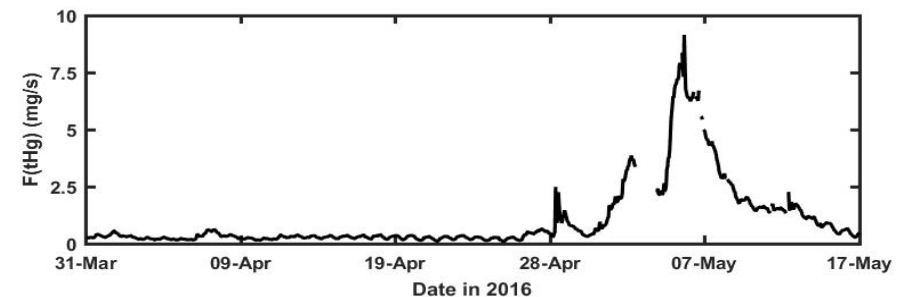


High frequency OPTICS data support estimation of mass flux over monitoring period

- Hg mass flux during the monitoring period is dominated by the 3-4x per year storm flow event
- However, integration of baseflow mass flux across the year suggests that bioturbation is also important



Rice et al. (2014) Diel patterns of suspended sediment flux and the zoogeomorphic agency of invasive crayfish, Cuadernos de Investigación Geográfica, 40 (1), 7-27.



My Take-Home Message



- Good agreement between modeled and measured results
- Diurnal fluctuations observed under baseflow due to bioturbation
- Annual Hg flux dominated by large storm events
 - But, baseflow load can also be important (equivalent to a large storm)

SRST ROPs Activities 2015

5. Use of XRF for Field Measurement of Hg (Robert Brent, JMU)

Objective: Evaluate the method accuracy, precision, and sensitivity of handheld XRF for measuring Hg in SR bank and floodplain soils.

6. Stable Isotope Analysis (Joel Blum, U Michigan)

Objective: Explore stable Hg isotopes as a forensic tool for understanding Hg fate and transport.

7. Real-time Hg Monitoring (Todd Martin, Integral)

Objective: Develop and test a multi-parameter monitoring system that can estimate real-time Hg concentrations in the SR.

8. Dynamic Mercury Cycling Model (Reed Harris)

Objective: Develop a mechanistic mercury cycling model for the SR.

9. Enhanced Adaptive Management Model (Christy Foran, USACE)

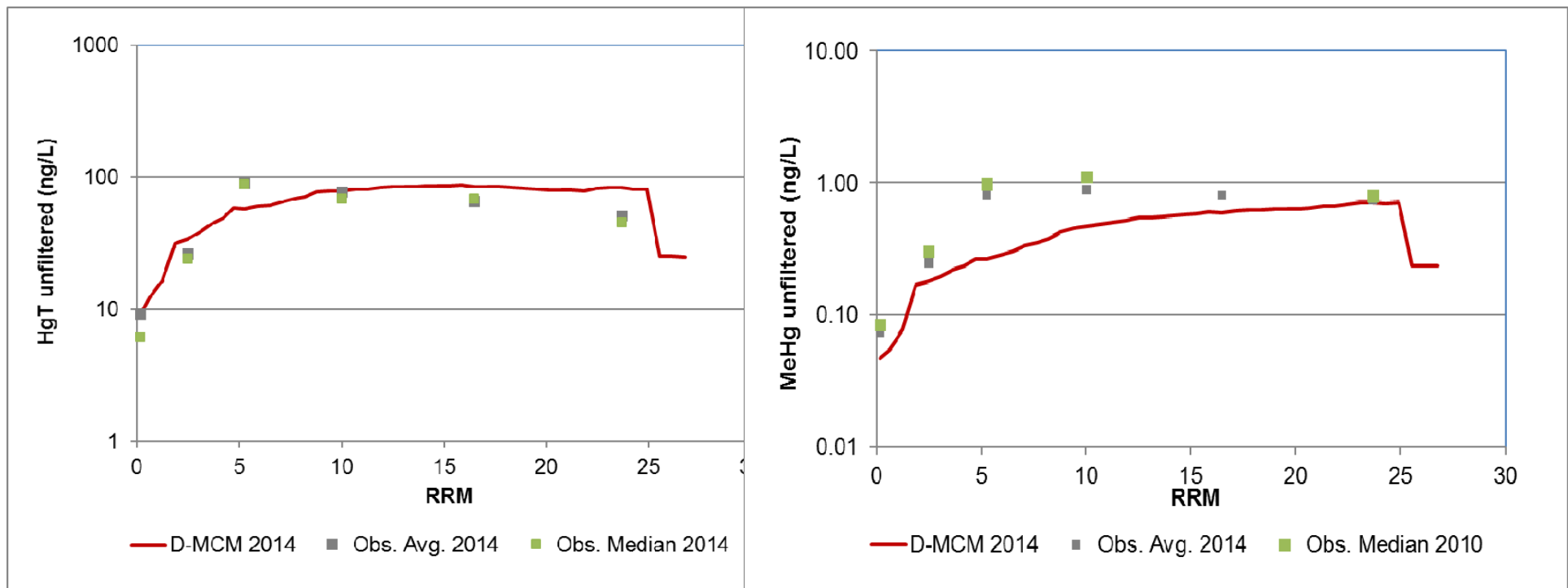
Objective: Develop a decision tool that can assist in the SR adaptive management process.

My Take-Home Message



FOR
DUMMIES

- Mechanistic Hg Dynamics Model is a work in progress, but calibration is nearly complete
 - Total Hg simulations approximate actual conditions
 - MeHg simulations are a little low

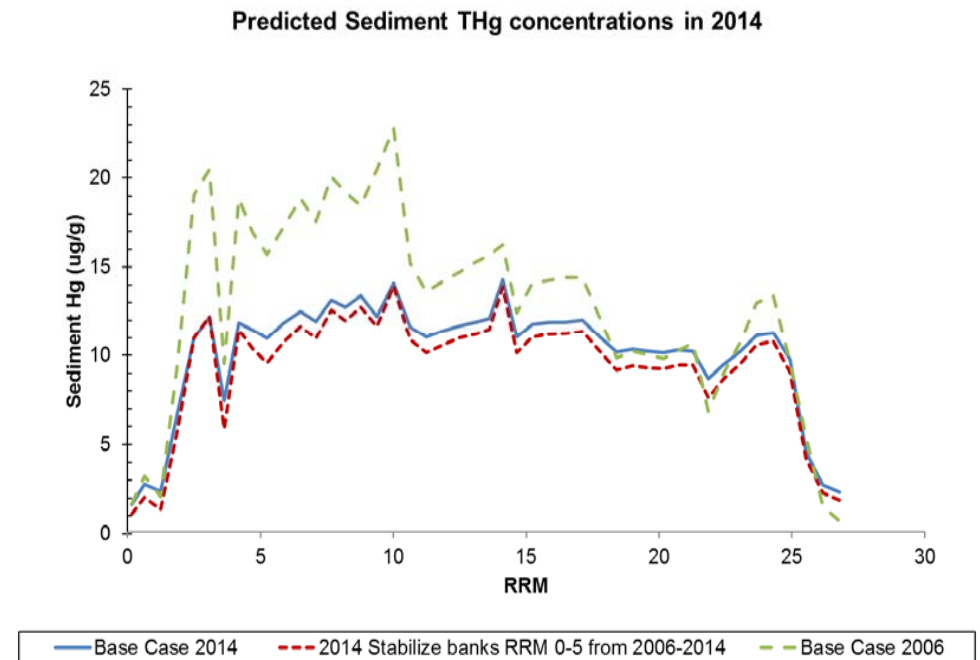
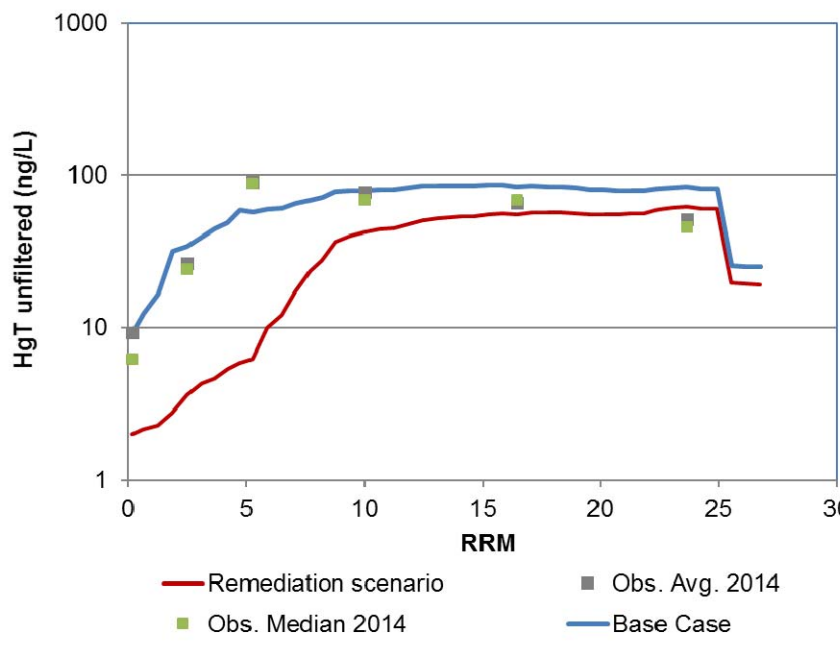


My Take-Home Message



FOR
DUMMIES

- Results are generally consistent with conceptual model
 - Bank erosion is the greatest source of Hg to the river
- Simulated results with plant and (0-5mi) bank inputs shut off
 - Show significant improvements in water, not as much in sediment
 - Show measurable natural recovery?



SRST ROPs Activities 2015

5. Use of XRF for Field Measurement of Hg (Robert Brent, JMU)

Objective: Evaluate the method accuracy, precision, and sensitivity of handheld XRF for measuring Hg in SR bank and floodplain soils.

6. Stable Isotope Analysis (Joel Blum, U Michigan)

Objective: Explore stable Hg isotopes as a forensic tool for understanding Hg fate and transport.

7. Real-time Hg Monitoring (Todd Martin, Integral)

Objective: Develop and test a multi-parameter monitoring system that can estimate real-time Hg concentrations in the SR.

8. Dynamic Mercury Cycling Model (Reed Harris)

Objective: Develop a mechanistic mercury cycling model for the SR.

9. Enhanced Adaptive Management Model (Christy Foran, USACE)

Objective: Develop a decision tool that can assist in the SR adaptive management process.

EAM Update...



- **Survey developed and implemented to collect different perspectives**
 - 34 responses
 - overview of the responses presented

- **Training to demonstrate the use of the tool**
 - 3 scenarios:
 - anticipated course of action
 - natural attenuation
 - aggressive removal

- **Use and methods behind the tool**
 - learning from implementation
 - archiving current best understanding
 - supporting communication