Characterizing Hg Cycling in the Aquatic System
Expert Panel Question

1. Has the SRST sufficiently characterized the South River aquatic environment, so that we can reach consensus on the predominant pathways by which inorganic mercury and other constituents/conditions necessary for methylation enter and move through the aquatic system to sites of methylation, and how the mercury subsequently bioaccumulates within the food web to fish?
We Have Analytical Data for Characterization

• Water
  – Approximately 42,336 measurements on 5,581 samples
• Sediment
  – Approximately 10,800 measurements on 1,788 samples
• Soil
  – Approximately 13,325 measurements on 2,585 samples
• Biota
  – Approximately 14,715 measurements on 9,797 samples
• Fish Tissue
  – Approximately 16,109 measurements on 8,918 samples
Talks

• Updated Conceptual Pathway and Exposure Diagrams for IHg & MeHg

• South River Geomorphology and Hg Cycling

• Summary of Findings for Physical Studies and Aquatic Food Web Interactions
South River Aquatic System
Key Questions

• What are the primary sources of inorganic Hg being methylated & transferred to the food web?

• How is inorganic mercury being transported to sites of methylation?

• Where, when, and how is the transfer of MeHg to the food web taking place?

• What are the rate-limiting mechanisms controlling methylation in the river ecosystem?
  - bioavailable Hg(II), organic carbon, nutrients, bacteria, temperature, etc.
Task Team Objectives

• Define physical & chemical processes/mechanisms for Hg transport, transfer, & transformation

• Define & rank sources of IHg that “feed” methylation production compartments
  - primary (1o) or secondary (2o) source?
  - rank H, M, or L based on magnitude of contribution to methylation (i.e., mass load x bioavailability)

• Define & rank MeHg production compartments that “supply” the food web
  - rank H, M, or L based on magnitude of MeHg production
  - rank H, M, or L based on biological ranking as food source

• Develop conceptual pathway diagrams for IHg & MeHg, focusing on dominant sources over first 5-10 miles of river

• 80/20 rule in effect
## Sources of FIHg and HgR Feeding Methylation in the South River

<table>
<thead>
<tr>
<th>Source</th>
<th>Primary Processes</th>
<th>Source Type</th>
<th>Importance to Methylation (initial assessment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bank erosion/collapse (includes exposed HRADs)</td>
<td>resuspension/deposition, adsorption/desorption, oxidation/reduction</td>
<td>1&lt;sup&gt;o&lt;/sup&gt;</td>
<td>H</td>
</tr>
<tr>
<td>Shallow, near-bank, fine-grained sediment</td>
<td>adsorption/desorption, methylation, diffusion, advection, resuspension/deposition</td>
<td>2&lt;sup&gt;o&lt;/sup&gt;</td>
<td>H</td>
</tr>
<tr>
<td>Coarse- &amp; medium-grained gravel beds</td>
<td>adsorption/desorption, methylation, diffusion, advection, hyporheic flow</td>
<td>2&lt;sup&gt;o&lt;/sup&gt;</td>
<td>H</td>
</tr>
<tr>
<td>Invista outfalls</td>
<td>deposition, adsorption/desorption, volatilization, oxidation/reduction</td>
<td>1&lt;sup&gt;o&lt;/sup&gt;</td>
<td>M</td>
</tr>
<tr>
<td>River input (upstream of Invista plant)</td>
<td>resuspension/deposition, adsorption/desorption, demethylation</td>
<td>1&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>Floodplain soil (ex. banks)</td>
<td>surface runoff, methylation/demethylation, oxidation/reduction</td>
<td>1&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>Direct precipitation</td>
<td>infiltration + interflow</td>
<td>1&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>Deeper, buried sediment</td>
<td>resuspension</td>
<td>2&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>Interflow/GW advection through river banks</td>
<td>diffusion, advection</td>
<td>2&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>TSS</td>
<td>adsorption/desorption, resuspension/deposition, oxidation/reduction</td>
<td>2&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>Tributaries and millraces</td>
<td>resuspension/deposition, adsorption/desorption, methylation/demethylation</td>
<td>2&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L</td>
</tr>
<tr>
<td>Contaminated GW at source</td>
<td>diffusion, advection</td>
<td>2&lt;sup&gt;o&lt;/sup&gt;</td>
<td>L?</td>
</tr>
</tbody>
</table>
IHg Sources Feeding MeHg Production in South River

To Food Web

- Low
- High

MeHg on TSS

IHg on TSS

Surface Coatings on Coarse- & Medium-Grained Gravel Beds (Transport Zones)

Medium

IHg on TSS

Invista Outfalls

Bank Erosion/Collapse

Shallow, Near-Bank, Fine-Grained Sediment (Storage Zones)

High MeHg Production Ranking

High

High
Production Compartments for TMeHg and FMeHg in South River

<table>
<thead>
<tr>
<th>Production Compartment</th>
<th>Biological Ranking as Food Source *</th>
<th>MeHg Production Ranking *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface coatings on coarse- &amp; medium-grained gravel beds</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Shallow, near-bank, fine-grained sediment</td>
<td>M</td>
<td>H</td>
</tr>
<tr>
<td>TSS</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Water column colloids</td>
<td>L</td>
<td>N/A</td>
</tr>
<tr>
<td>Upstream river input</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Gravel/cobble areas</td>
<td>L</td>
<td>M</td>
</tr>
<tr>
<td>Banks</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Floodplain</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Invista outfalls</td>
<td>N/A</td>
<td>L</td>
</tr>
<tr>
<td>Tributaries and millraces</td>
<td>L</td>
<td>L</td>
</tr>
</tbody>
</table>

* Note: H, M, L rankings are based on collective experience of task team
South River Geomorphology and Hg Cycling

October 6, 2009
Jim Pizzuto
Summary of Findings for Physical Studies and Aquatic Food Web Interactions

October 6, 2009
Todd Morrison, JR Flanders
Big Picture Topics

- Can we identify and rank potential sources of THg and MeHg for the South River?
- What are the most important factors providing IHg to the river?
- What factors influence MeHg concentrations in physical media and ultimately MeHg production?
- Where are the likely sites of methylation?
- What are the key linkages between MeHg sources and the aquatic food web?
Can we identify and rank potential sources of THg for the South River?

THg Sources by Relative Importance:
1) Floodplain soils
2) Fine-grained sediment deposits
3) Groundwater

THg Loading Mechanisms to River by Relative Importance:
1) Floodplain soils via river bank erosion
2) Runoff from tributaries and floodplain drainages and groundwater discharge (<10%)
2008 Mass Balance Studies Indicate Importance of “Bank-to-bank” Sources

- Tributaries, outfalls, and groundwater contributed relatively small amount of mass
- Diffusive flux alone does not account for mass

Percent of Total Load for FIHg
RRM -2.7 to 9.9

- Unclassified 91%
- Gravel 2%
- Groundwater 1%
- Tributaries 1%
- Wetlands/Mill Races 0%
- FGCM Deposits 0%
- Point Sources 5%
Pore water IHg concentrations at 5-cm within the South River bed more than account for the “unclassified” source in mass balance.
Can we identify and rank potential sources of MeHg for the South River?

MeHg Sources by Relative Importance:
1) In river near-bank habitats more important river sources than floodplain wetland contributions

MeHg Loading to River by Relative Importance:
1) Flux from in-river habitats
2) Tributaries, floodplain wetlands, and groundwater (<10%)
2008 Mass Balance Studies Indicate Importance of “Bank-to-bank” Sources

- Wetlands / mill race areas, tributaries, and groundwater contributed relatively small amount of mass
- Diffusive flux important but does not account for mass

Percent of Total Load for FMeHg
RRM -2.7 to 9.9

- Gravel 20%
- Unclassified 73%
- Wetlands/Mill Races 0%
- Tributaries 3%
- Point Sources 2%
- FGCM Deposits 0%
- Groundwater 1%
Pore water MeHg concentrations at 5-cm within the South River bed more than account for the “unclassified” source in mass balance.
What are the most important factors providing IHg to the river?

- Location
- Erosion
- Dispersion (Entrainment / Transport / Deposition)
- Dissolution
Soils Have High Capacity to Release Hg to Surface Water

Notes: Figure taken from multiple extraction experiments performed by Ralph Turner
FIHg in Pore Water is Related to Distance from Bank

Log(FIHg)~DR
$R^2 = 0.23$
$P = 0.003$

Log(FIHg)~DL
$R^2 = 0.25$
$P = 0$

Log(FIHg)~D2B
$R^2 = 0.002$
$P = 0.3$

Log(FIHg)~D2B
$R^2 = 0.03$
$P = 0$
What factors influence MeHg concentrations in physical media and ultimately MeHg production?

- IHg
- Temperature
- Substrate
- Electron Acceptors
- Others (e.g. DOC)
IHg Concentrations in Sediment and FIHg Concentrations in Pore Water are Significantly Related to MeHg, but not Strongly Predictive

Note:
Sediment results are fine-grained sediments collected by suction from within river pool coarse grained substrates (i.e. cobble / boulder, and sand / gravel areas).

*Sediment samples collected in January and February 2007 and March 2006
Temperature as a Control for MeHg

**Surface Water**

FMeHg and MeHgP concentrations are significantly ($p=0$) and positively correlated with water temperature (ANCOVA).

**Sediment**

MeHg in sediment is highest when temperatures are between 15 and 20°C, and declines at temperatures $>20$°C.
FMeHg Pore Water Concentrations are Significantly Higher in Fine-Grained Sediment

- Coarse- and medium-grained substrates can support high FMeHg concentrations in pore water
- Coarser substrates likely have higher advection rates/connectivity with the hyporheic zone
## Physical Conditions in River Sediments are Similar During Spring

### Sediment Data: May 2008

<table>
<thead>
<tr>
<th>Habitat Type</th>
<th>RRM</th>
<th>MeHg (ng/g)</th>
<th>AVS (μmol/g)</th>
<th>Fe(II):Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floodplain wetland</td>
<td>1.6</td>
<td>5.3 (0.4)</td>
<td>&lt;1.75</td>
<td>1.3 (0.01)</td>
</tr>
<tr>
<td>Toe of pool</td>
<td>3</td>
<td>55.5 (2.8)</td>
<td>&lt;1.9</td>
<td>1 (0.02)</td>
</tr>
<tr>
<td>Embedded pool</td>
<td>4.6</td>
<td>76.7 (11)</td>
<td>&lt;2</td>
<td>2.4 (0.08)</td>
</tr>
<tr>
<td>Mill race</td>
<td>5.2</td>
<td>57.6 (5)</td>
<td>&lt;1.2</td>
<td>2 (0.03)</td>
</tr>
<tr>
<td>FGCM deposit</td>
<td>6.2</td>
<td>114 (9)</td>
<td>&lt;2.6</td>
<td>3 (0.36)</td>
</tr>
<tr>
<td>Embedded pool</td>
<td>7.4</td>
<td>97 (0.9)</td>
<td>&lt;2.3</td>
<td>1.3 (0.04)</td>
</tr>
<tr>
<td>Floodplain wetland</td>
<td>8.6</td>
<td>99.9 (3.2)</td>
<td>&lt;2.5</td>
<td>1.7 (0.1)</td>
</tr>
<tr>
<td>Toe of pool</td>
<td>8.7</td>
<td>47.4 (0)</td>
<td>&lt;2.5</td>
<td>0.4 (0)</td>
</tr>
<tr>
<td>Mill race</td>
<td>9.9</td>
<td>39.2 (9.9)</td>
<td>6.1 (1.5)</td>
<td>7.7 (0.07)</td>
</tr>
<tr>
<td>FGCM deposit</td>
<td>12.8</td>
<td>102.4 (21.7)</td>
<td>3.7</td>
<td>4.3 (0.26)</td>
</tr>
</tbody>
</table>

- Low AVS suggests that sulfate reducing bacteria are present
- Higher Fe(II) concentrations suggest iron reducing bacteria may also be important methylating bacteria
Where are the likely sites of methylation?

- Soils
- Bedrock
- Sand
- FGCM deposits and HRADs
- Gravel
- Cobble Boulder
- Redox Zone

**Working Hypothesis:** A preferential redox zone exists for MeHg production within the hyporheic zone throughout the bed of the river and likely within dense periphyton mats.
Near-Bank Environments and Fine-Grained Areas Have the Highest MeHg Pore Water Concentrations
Surface Water and Sediment Habitats Can Change From Spring to Summer

South River RRM 8.7

Spring 2006          Summer 2006
Macroinvertebrates are the Key Linkage Between MeHg Sources and the Aquatic Food Web

Aquatic Insects:
- Grazers/Scrapers
- Deposit Feeders
- Suspension Feeders

Potential Methylmercury Sources

- Shallow, Near-Bank, Fine-Grained Sediment
- Suspended Solids (TSS)
- Surface Coatings on Cobble/Gravel Beds

Algae
Biological Exposure is Widespread Within Habitats Along the South River

Surface Water

- Surface water MeHgₚ concentrations are highest during base flow conditions

Sediment

- Sediment MeHg concentrations are generally similar across habitat type

- Toe of Pool (2006 - 2007)
- Toe of Pool (2007-2008)
- Embedded Gravel (2007-2008)
- FGCM Deposit (2007-2008)
- Wetland (2007-2008)
Linkages Between Sediment and Periphyton

Algae + Sediment and Bacterial Surface Coatings on Cobble/Gravel = Functionally Defined Periphyton

Significant and predictive correlation between MeHg concentrations in interstitial sediment and functionally defined periphyton on rocks in pool habitats during Spring and Summer

Notes: Linkages between sediment and periphyton developed by Mike Newman
Linkages Between Sources and Aquatic Invertebrates

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Deposit Feeders</th>
<th>Detritus from dead algae deposited as sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>Suspension Feeders</td>
<td>Algae or detritus particles suspended in the water</td>
</tr>
<tr>
<td>Surface Coatings</td>
<td>Grazers/Scrapers</td>
<td>Periphyton on rocks</td>
</tr>
</tbody>
</table>

Chironomidae

Hydropsychidae

Baetidae

www.smcvt.edu
www.bugguide.net
www.cityofaustin.org
www.bugguide.net
www.discoverlife.org
www.discoverlife.org
South River Fish Community Assemblages Center Around Macroinvertebrates

Aquatic Invertebrate Community Composition by Functional Feeding Designation

- 11.6% Suspension Feeders
- 17.0% Deposit Feeders
- 60.2% Grazers/Scrapers
- 0.2% Predators
- 1% Shredders
- 1.0% Omnivore, Parasite, or Unclassified

Fish Community Composition by Trophic Designation

- 18% Piscivore
- 68% Invertivore
- 3% Omnivore
- 11% Herbivore

Notes: Percent community composition for aquatic invertebrates is based on total numbers of organisms collected during four sampling events in 2006/2007 (seasonal collections). Data from 6 stations within the study area along the South River (RRM 0.6, 5.2, 11.8, 14.6, 19.0, 22.4) were combined. Station collections included three composited surber samples along the right, left, and center of a riffle and one composited pool sample comprised of ten D-net sweeps throughout the pool.

Percent community composition for fish is based on total numbers of organisms collected during May 2006. Data from 6 stations within the study area along the South River (RRM 0.6, 5.2, 11.8, 14.6, 19.0, 22.4) were combined.
These Findings Were Used to Develop a MeHg-based Predictive Aquatic Trophic Transfer Model

Periphyton THg of 0.6 ug/g DW would result in bass whole body concentrations of 0.5 ug/g ww

Notes: MeHg-based trophic transfer model developed by Mike Newman
What’s Next?

• Continued data evaluations for 2009 physical loading studies
• Statistical evaluations for data sets
• Findings to feed into Remedial Options Planning group
Questions to Facilitate Discussion

• What information was unclear & needs further clarification?
• What do you lack that will limit your ability to respond to the feedback questions?
• What strengths & weaknesses can you identify in our program?
• Can you identify any significant holes in our data collection programs, hypotheses, laboratory & field studies, etc. that will limit our decision making ability?
• What areas can be marked as "Complete?"
• What conflicts with "accepted mercury wisdom" can you identify in our results to date?
• Please comment as you are able (non-CBI) on efforts by others to address the issues we confront in the South River, including similarities & differences between approaches & programs.
Additional Information
Glossary of Terms Commonly Used in Presentations

- **Hg**: Mercury, no form specified
- **THg**: Total mercury
- **MeHg**: Methylmercury
- **IHg**: Inorganic mercury (THg - MeHg)
- **MeHgp**: Methylmercury on particles
- **IHgp**: Inorganic mercury on particles
- **FIHg**: Filtered IHg
- **FTHg**: Filtered total mercury
- **FMeHg**: Filtered MeHg
- **AVS**: Acid volatile sulfide
- **Fe(II)**: Reduced iron
- **Fe(III)**: Oxidized iron
- **LOI**: Loss on ignition

- **HRAD**: Hg-Release Age Deposits
- **LiDAR**: Light detection and ranging (remote sensing used to measure erosion rates)
- **BFC**: Benthic flux chamber
- **RRM**: Relative river mile
- **FGS**: Fine grained sediment
- **FGCM**: Fine grained channel margin deposit
- **DGT**: Diffusive gradients in thin-films
- **PIT**: Passive integrated transponder tags

Characterizing Hg Cycling in the Aquatic System
2009 Expert Panel Meeting
Can we identify and rank potential sources of THg and MeHg for the South River?

The first 12-miles of the South River study area contain the highest source concentrations, greatest increases in surface water loading, highest concentrations in fish tissue.

Notes:
Figure adapted from presentation reported to the South River Science Team on 10-21-2008 by C. Jordan of Virginia Department of Environmental Quality on 2007 fish tissue monitoring results. THg = total mercury, RRM = relative river mile
Significant Potential Sources of THg in the Upper 10 Miles of the South River

- SRST studies regarding HRADs, eroding banks, and FGCM deposits
IHg Concentrations in Interstitial Sediment Increase Rapidly Over Upper 10 Miles

- Highest concentrations at RRM 3.0
- Relatively little change in THg concentration except at locations RRM 3.0 and RRM 4.2 (after storm events)
Baseline Filtered MeHg Loading, 2006 - 2007

(A) April 2006 – September 2006; April, May 2007

(B) March 2006; October 2006 – February 2007

Positive Load
Negative Load
Average THg on Particles in Surface Water, River-bank and HRAD Soils, and FGCM Deposit Sediment, 2006 – 2008

Notes:
Particles in surface water; data shown are averages (n = 16 to 42 per location) and one standard deviation collected between 2006 and 2008 HRADs, eroding banks, and FGCM deposits: data shown are vertically averaged total mercury concentrations collected between 2005 and 2008
Pore Water Collections at RRM 0.1 During June 2009

FIHg (ng/L)  FMeHg (ng/L)

LEGEND

Sediment - Total Mercury
Surface Total Mercury - (ng/g)
- 0.01 - 5.00
- 5.01 - 10.00
- 10.01 - 15.00
- 15.01 - 20.00
- 20.01 - 25.00
- 25.01 - 30.00
- 30.01 - 35.00
- 35.01 - 40.00
- 40.01 - 44.00
- > 44.00

Sediment - Average Total Mercury
Average Total Mercury - (ng/g)
- 0.01 - 5.00
- 5.01 - 10.00
- 10.01 - 15.00
- 15.01 - 20.00
- 20.01 - 25.00
- 25.01 - 30.00
- 30.01 - 35.00
- 35.01 - 40.00
- 40.01 - 44.00
- > 44.00

Soils - Total Mercury
Total Mercury - (ng/g)
- 0.01 - 5.00
- 5.01 - 10.00
- 10.01 - 15.00
- 15.01 - 20.00
- 20.01 - 25.00
- 25.01 - 30.00
- 30.01 - 35.00
- 35.01 - 40.00
- 40.01 - 44.00
- > 44.00

Soils - Average Total Mercury
Average Total Mercury - (ng/g)
- 0.01 - 5.00
- 5.01 - 10.00
- 10.01 - 15.00
- 15.01 - 20.00
- 20.01 - 25.00
- 25.01 - 30.00
- 30.01 - 35.00
- 35.01 - 40.00
- 40.01 - 44.00
- > 44.00

Bank Soils - Average Total Mercury
Average Total Mercury - (ng/g)
- 0.01 - 5.00
- 5.01 - 10.00
- 10.01 - 15.00
- 15.01 - 20.00
- 20.01 - 25.00
- 25.01 - 30.00
- 30.01 - 35.00
- 35.01 - 40.00
- 40.01 - 44.00
- > 44.00

Sediment - Total Mercury
Sediment - Average Total Mercury
Soil - Total Mercury
Soil - Average Total Mercury
Bank Soil - Total Mercury
Bank Soil - Average Total Mercury

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Pore Water Collections at RRM 3.5 During June 2009
Pore Water Collections at RRM 8.5 During June 2009

Characterizing Hg Cycling in the Aquatic System
2009 Expert Panel Meeting
Pore Water Collections at RRM 23.1 During June 2009
IHg and MeHg in Porewater at Two Depths

Methylmercury in Porewater

Total Inorganic Mercury in Porewater
FIHg in Pore Water by Substrate

- No statistical difference in pore water FIHg between grain sizes in June 2009 data
FIHg Pore Water Summary

- Higher than observed in surface water
  - SW: 0.85 to 8.90 ng/L
  - PW: 0 to 3217 ng/L
- Pairwise comparisons show that FIHg concentrations in pore water are:
  - Lower at Study Area (SA) SA 1 than at the other areas
  - Similar at SA 3 and SA6
  - Lower at SA 8 than SA3 and SA6
- No difference between grain sizes
- Higher in zones of hydraulic storage
- FIHg in the near-bank environment is correlated with sediment THg concentrations, but not soil
- Inversely correlated with pore water conductivity
- Higher than concentrations predicted by Dyer (2008) to complete mass balances
FMeHg Pore Water Summary

• Concentrations detected in pore water are higher than in surface water
  – SW: 0.13 to 1.42 ng/L
  – PW: <0.07 ng/L to 78.5 ng/L

• In contrast to FIHg, FMeHg is more similar between SAs
  – Difference between SA1 and SA3 likely driven by grain-size rather than concentration

• Fine-grained areas, regardless of distance to bank have higher FMeHg concentrations

• Not correlated with conductivity or soil and sediment THg concentrations

• Highly correlated with FIHg concentration
Sediment/Periphyton Relationship Spring and Summer 2008

\[ y = 1.144x + 2.1188 \]
\[ R^2 = 0.8502 \]

Notes: Data from study conducted by VIMS in spring and summer 2008. Linkages between sediment and periphyton developed by Mike Newman.
Average Methylmercury (MeHg) Uptake in Transplanted Asian Clams - Weeks 1, 3, and 5

Notes:
Preliminary Data from May-June 2009
MeHg Concentrations in Aquatic Biota

Notes:
Mean concentrations of methylmercury in aquatic biota collected in the South River, VA. Data were categorized according to major taxonomic group and plotted as box plots to represent the central tendency and spread of methylmercury concentrations at each station (SYSTAT 11, SYSTAT Software, San Jose, CA). RRM = relative river mile, MeHg = methylmercury. Adapted from URS (2007).
Notes:
Adapted from Murphy et al. (2005).
Data represents the diet composition by weight across all size classes of fish and stations evaluated in the South River.
The diet items listed as other insects and other invertebrates were comprised of taxonomic groups that generally accounted for less than 1% of the diet by weight.
Unidentified insects were insects not identifiable due to partial digestion.