South River Science Team Agenda
October 21-23, 2003

Tuesday, Oct 21

1:00	Welcome, Introductions, etc.	Don Kain
1:15	Background / Working Hypotheses	Ralph Stahl
Biological Issues		
1:30	Fish tissue statistics	John Green
2:15	Clam study proposals	Tom Benzing Doug Graber-Neufeld
3:00	Fish diet studies	Greg Murphy
3:45	Crop study	Bill Berti Dean Cocking
4:30	Birds (if time allows)	Ralph Stahl Paul Bugas

Wednesday, Oct 22

Water Issues		
9:00	Intensive water sampling	Ted Turner
9:30	Stormwater, trib study	Mike Sherrier
10:15	Flow balances	Annette Guiseppi-Elie
11:00	TMDL development	Robert Brent
Soils and Sediments		
11:30	Floodplain sampling	Annette Guiseppi-Elie
Lunch		
1:00	Coring results, next steps	Erin Mack
1:45	Sediment sampling	Ted Turner
Special Reports		
2:15	Report on bioavailability of Hg	John Rudd
3:00	Report on SETAC Hg meeting	Mike Newman
3:45	Proposal for "technical workshop"	Ralph Stahl

Thursday, Oct 23

Group Discussions - Where do we go from here?		
9:00	Revisit Working Hypotheses	Ralph / Don
9:45	If-then analysis	Ralph
10:30	Putting the puzzle together	Ralph / Don
11:15	Wrap-up, Action Items, Next Meeting	

Meeting Summary:
Expert Panel Meeting
Day 1: 21 October 2003

Welcome and Introductions. Self-introductions were made and an outline of the meeting agenda and schedule was discussed.

Background / Working Hypotheses. Ralph Stahl

- From DEQ dataset, no observed trends in phosphate, TSS that might explain lack of observable decrease in fish tissue
- Nancy Grosso wondered if wet/dry cycling (w/in and between years) might enhance methylation
- Fish tissue [Hg] appears positively correlated with high flow years; total Hg also pos. correlated to flow (and TSS)
- For floodplain contributions probably should make observations during periods of max. effect (during spring tilling, spring flooding/high water, cover die-off, etc. From field observations, even dead cover is very effective at reducing erosion)
- See Presentations folder for full details.

Fish tissue statistics. John Green

- With only 1 statistically insignificant exception, tissue [Hg] at all stations have decreased from 1996 values
- Trends for most stations for both bass (large and smallmouth) and sunfish (redbreast, bluegill, etc) since 1996 are decreasing. However, tissue concentrations still elevated over "baseline" average of data from '77-'83.
- Note that 2002 tissue levels are lower than in recent past. 2002 was worst drought year in valley since early '30s.
- Not much difference between response of all bass (large and smallmouth) compared to just smallmouth.
- In general, tissue [Hg] starts to rise at 2nd St./ Hopeman Pkyway, peaks from Dooms to Grottoes, then drops at Lynnwood, and is pretty much "flat" after that (but still above advisory levels)
- Maybe plot tissue [Hg] vs spring flows (averaged over Jan. through April?)
- See Presentations folder for John's powerpoint slides.

Clam study proposals. Tom Benzing and Doug Graber-Neufeld

- Didn't detect any correlation between shell size and [Hg]
- No apparent differences Doug's (2001) and Tom's (2002) data
- Doug wants to put clean clams in contaminated water to determine uptake rate
- Rob Mason suggested putting contaminated clams in clean water to determine depuration rate
- Previous studies showed decrease from Sept. to Oct. from 250 ppb to ~125 ppb in contaminated clams moved to clean sites
- Mike Neuman observed that clams move around (not completely sessile) can move downstream relatively easily (by floods etc.)
- Rob Mason suggested that in follow up studies, that MeHg be measured also.
- Determining ratios of MeHg vs. inorg. Hg might yield info regarding sources
- Someone (Dick Jensen?) mentioned using clean clams and placing them at the "hot spot" we found doing the Phase II sweep adjacent to the DuPont Plant in Waynesboro (1BSTH025.50)
- Refer to Presentations folder for Tom's presentation slides.

Fish Diet Studies. Greg Murphy

- Results of study show interesting result in adult June beetles collected in Basic Park ; total Hg was 12 ppm, but MeHg was only 3%; maybe due to contaminated soil on exoskel.
- 60% MeHg in snails, 80% in crayfish
- See Presentations folder.

Crop Studies. Bill Berti and Dean Cocking

- Flooding from Hurricane Isabel covered garden, but two remaining plants for harvest (carrots and onions) were protected below ground
- Carrots only plant with Hg greater than Limit of Quantitation (LOQ)
- most plants below detection limits**;** all others below LOQ
- Fall crop planted 30 Sept. 2003, will try to harvest in Nov.
- Will check for soil in carrot samples to see if this caused detectable [Hg].
- See Presentations folder.

Expert Panel Meeting
Day 2: 22 October 2003

Avian Studies. Ralph Stahl, Paul Bugas

- Literature search provides info., mostly based on mallard ducks
- Mallards more sensitive than piscivores; eagles, ospreys, kingfishers probably tolerate higher [Hg] adaptively
- May want to look at cliff swallows, bats (big insectivores; Basic Park June beetles had high [Hg]; mayfly swarms might be big Hg contributors to insectivorous birds
- Some picivorous birds may feed in both contaminated and clean streams; may complicate attempted analyses
- Bottom line is that probably is some risk to birds, but fixing fish contamination will probably fix any potential bird ecological effects.
- See Presentations folder for complete Powerpoint presentation.

Intensive Survey Follow-up. Ted Turner

- Downstream segment near Hopeman parkway sampled to verify previous high Hg sample of 449 ppt; didn't see nearly as high, but did see almost 2x increase over the average for the reach, just downstream of original spike site
- Sampled new reach adj. DuPont; only sampled right bank (DuPont side).
- Ran ions at all sites; didn't see any significant blips except for sodium. Biggest sodium change just upstream of Jones Hollow/Rockfish Run and downstream of outfall 011
- Obs. 2 spikes in total Hg; one just above Jones Hollow and one just below outfall 001 (from background of 5 ppt total Hg to ~11 ppt, and from a background of 3 ppt to ~26 ppt total Hg respectively)
- Will plan to bracket large spike more closely soon; may revisit smaller one also
- See Presentation folder.

DuPont Stormwater/Tributary Investigation. Mike Sherrier

- All baseflow samples are below detection limits of 0.15 ppb (150 pptrillion)**;** this includes contribution from Baker Spring
- Will look more at ratios of flow contributions within outfalls
- Need to sample Baker Spring and main outfall at lower detection limits
- No data yet from storm event sampling
- See Presentation folder.

South River Water Budget. Nancy Grosso (presented by Mike Sherrier)

- Nancy Grosso's info. suggests that about 30% of the flow in the South River adjacent to the plant is subsurface groundwater contribution (doesn't include surface springs)
- John Rudd - may be inputs or methyl hotspots between Dooms and Crimora; should look at MeHg in top 3 cm of sed.
- Bill Van Wart noted that problem isn't too spotty; relatively smooth curve from DuPont to junction with North River
- Bigham – if there's an active source, it would be more likely to influence fish tissue Hg levels than sediment born Hg.
- Metallic Hg in deep sediments could be methylated, if ground water is welling up through it
- Rudd suggests looking at % MeHg in sed.
- If suspect upwelling through metallic Hg, could use conventional grab water samples to home in on suspect sites, then use pipe to pump water from near bottom to get water closest to sed./water interface (similar to Ralph Turners pump apparatus)
- See Presentation folder.

Sediment Deposited by Isabel.

- Sediment is being tested for total Hg, TOC, and particle size analysis
- One sample split, then fines sieved, settled, and submitted for analysis
- Photos attached in Presentations folder.

South and South Fork Shenandoah TMDL. Robert Brent

- Difficult to define, allocate, and reduce loading
- Will need to address sediment dynamics; bioavailability of Hg in water and sed., floodplain, banks
- Need to determine extent of atmospheric contributions (but controls to date in North River, and upstream in South River suggest no significant impact from atmospheric input)
- Refer to Presentations folder.

Floodplain Sampling. Annette Guiseppi-Elie

- Recommend sampling within 35 mi. downstream of plant for soil Hg
- Ralph Turner recommends sampling just the top ½ cm for soils (if it's not there, it probably isn't mobile in the system)
- Ralph Turner also suggests looking at scour routes, and along natural levees,etc., since they can be important influences
- See Presentations folder.

Coring results, next steps. Erin Mack

- Looks like Hg peak in core at Dooms occurs ~1942 (from Cesium dating) and that Hg begins to increase around 1929 (all consistent with knowledge of operations and timeframe at DuPont)
- Estimates of time deposits occur assumes constant deposition rate (may not be accurate though)
- Sedimentation rates difficult to tease out, since deposition rates may have changed over life of millpond
- Some peaks in Hg look like results of discrete releases, rather than chronic dribbles
- Erin Mack observed that since soils appear to be continuing to be deposited at about 10 ppm, there may be an ongoing source
- 10 ppm Hg is about the concentration on TSS in water samples taken for bimonthly clean metals in South River
- More information can be gained from upcoming stormwater data in river and tribs (and DuPont Plant)
- See Presentations folder.

DEQ 10 year sediment sampling. Ted Turner

- Want to develop method that yields most useful measure of sediment Hg
- Pumping may yield higher percentage of fines occurring in natural sediment, but will increase equipment load, sample time, decrease mobility
- Ralph Turner suggests pumping, then decanting to reduce sample volume
- Definitely want to represent fines in sample
- Will plan on experimenting with various methods prior to 2007 (next sched. sed. sampling event on 100 yr timeline)
- See Presentations folder.

Report on bioavailability of Hg. John Rudd

- New bioassay uses mer-lux bacteria; bioluminesce when they transport Hg into cytoplasm
- Light production increases with increased bioavailable Hg
- Light production increased with time at all concentrations
- Mechanism of transport into cells appears to be facilitated transport
- Bacteria method not refined enough to use as routine assay
- Increase Hg bioavailability in sed. and water under lower pH conditions
- High DOC tends to reduce bioavailability
- See Presentations folder.

Report on SETAC Hg meeting. Mike Neuman

- main topic of meeting was to determine the best way to document changes to environment resulting from changes in Hg resulting from regulatory actions (to determine effectiveness of actions)
- See Presentations folder.

Technical Workshop. Ralph Stahl

- Primary function to educate local community fate and effects of Hg

Expert Panel Meeting
Day 3: 23 October 2003

- Suggest we look more at MeHg in food chain, rather than total
- Rob Mason – said that predatory insect Hg was ~100% methylated
- General consensus (Rudd, Mason, Bigham, Neuman, Turner) that we need MeHg in water and sediment
- Suggestion to have John Green do an analysis to find out what %Δ in Se would result in significant changes to Hg in fish tissue (R.Turner thinks this would have to be about 2-3x change)
- Gary Bigham suggests having Greg Murphy provide food web diagram
- Mike Neuman thinks it'd be useful to have trophic status for each animal in Greg's study; based on analysis of Nitrogen isotopes (N^{14}, N^{15})

Birds:

- Swallows (and Bats) might still be useful to examine, as insectivores
- Any data in birds wouldn't lead to different strategies in remediation; whatever will fix the fish will probably address the birds (/bats)
- Might be appropriate to gather some data on ducks and geese
- Expending a lot of resources on birds limits resources for more pressing issues

Water Quality:

- Rudd- suggests looking more into potential methylation sites (scale may be important; do we look at macro-zones like Dooms/Crimora, or might myriad micro-zones occurring along entire length be just as significant?)
- Mason –look at Se in sediment, since it may have potential for mitigating Hg
- No long term data on water Hg; 'till ~'96, all water data were non-detect
- No apparent trends in water quality parameters (Nutrients, Se, TSS, etc.) that might exacerbate Hg accumulation in fish

- If water running off Blue Ridge is acidic, could this result in increased methylation rates (Sawmill Run near Dooms; Mine Branch and Tunnel Run near Crimora? Might result in “hot-spots”?)
- Suggested that we collect clean water samples at high/cold flows, then again at low/warm flows, send to Rob Mason for MeHg analysis.

Sediments:

- Is methylation occurring in algal mats and within sediments?
- Rudd – notes there’s lots of sediment among cobbles, might be impt. methylation sites; represents a large percentage of the river bed in South River
- Wetting and drying cycles with changing flows might enhance methylation (moves the RPD through “fresh” layers of Hg in sediment)
- Rudd thinks if there’s a discrete Hg input, that once it’s stopped, river should begin to show measurable improvement
- #1 priority: Look for a source
- #2 priority: determine methylation process in an area of high Hg in water and sediment.

Hypotheses. Ralph Stahl, Panel

- See Presentation folder for Ralph’s working hypothesis attachment.
- If we have a new source slowly “dripping” into the system, we would need to do more, closely spaced sampling, filtering as we go (Ralph Turner’s high flow system)
- focus on total and dissolved Hg in water, tightly bracket any [Hg] peaks, sample at multiple occasions and replicate
- Check for [MeHg] downstream, since there’s likely to be lag in MeHg production
- Could have multiple scenarios involving either new sources or old sources; steady methylation along river length or hot spots, any and all possible combinations could be occurring (see “Knowledge Status” presentation above)
- If problem is primarily groundwater upwelling through contaminated bed sediments and trapped Hg globules, then low flow years (when groundwater input is greater fraction of system flow) should have higher avail. Hg; but fish tissue doesn’t seem to reflect that pattern
- Ralph Turner has Lumex (hg “Sniffer” measures volatilized elemental Hg sparged out of water sample) that could be used for continuous measurement with real-time results; would be very useful in helping determine whether Hg is spotty or continuously distributed (but only detects elemental Hg; possible that might not get species that are also bioavailable?)
- R. Turner thinks Hg° will only be in river bed gravel

Upcoming Tasks/Priorities:

1) Perform follow-up Intensive study to verify/ resolve location of peak near DuPont
2) Proceed with clam studies

3) Shake and Bake sediment experiment
4) Head space analysis for Hg° w/ Lumex

- **Ask DGIF if they can harvest a few water fowl from the river for Hg analysis**
- **Arrange to have tot. and diss. clean Hg water samples sent to Rob Mason for MeHg analysis; one set from high flow/cold, one from low flow/warm**

Next Meeting: February 10, 2004

Attachment 1.

Filling Data Gaps

Ongoing or Completed

- **Sediment Sampling and Coring**
- **Corbicula Studies, Phase 1 (& intensive around plant site)**
- **Fish Diet Studies**
- **DuPont Site Stormwater Investigation**
- **Intensive Water Followup**
- **Tributary & Bridge Sampling**
- Investigate Floodplain (& for purposes of CSM) / Vegetation / Biota
- River / land use survey
- Food Crop Study, Phase 1
- **Publications (need some common definitions)**
- Water Column Sampling (ions, etc.)
- Atmospheric Deposition Studies (summer 04 results)
- Initial Estimate of Bird Exposure and Risk
- Water and Flow Balance

Planned or Proposed

- **Investigate 2nd St. Landfill**
- Sampling Periphyton / Aquatic Vegetation (Bill made presentation)
- Sediment Sampling & Analysis
- Re-emergent Hg (globules under sediment surface in river bed)
- Outreach (website, workshop)
- Sediment Traps – sedimentation rate
- Corbicula, Phase 2
- Stormwater repeat for plant site
- Food crops, Phase 2
- Water column Hg at DuPont site and downstream
- Shake and bake of soils, sediments (maybe clams added)
- Non Trust-fund Fish Sampling (forage fish for TL3 estimates)
- Bird exposure (feather or tissue analysis – geese, ducks)
- Develop set of bioindicators (including fish)
- Modeling Help
- Hg Speciation

Suggestions from 2003 Expert Panel meeting – testing hypotheses

1. Are floodplain soils a source of bioavailable mercury
   Shake and bake study using soils, river water and measuring MeHg production over time

2. Are river bed sediments a source of bioavailable mercury
   Shake and bake study using sediments, river water and measuring MeHg production over time (could combine with clam uptake studies)

3. In 1 and 2, add organic matter to provide food source for bacteria (to stimulate microbial activity) – stack the deck. Maybe have a streamside flow through system – soils / sediments, river water, and clams (and enhancements to microbes) to see if bioavailable mercury is released.

4. For slow drip hypothesis, or new source hypothesis: need intensive water column study with total and dissolved Hg along with low detection limit. Sample at low flow period if possible. Include tributaries and other potential inputs other than the point at which the transect is specified. Need to check the ratio of total to methyl along with the change in this ratio downstream. Separate inorganic data from methyl data. The change in these will be reflective of new inputs to system – may need a statistical power test to help identify how many samples are needed to determine whether we'll be able to detect a difference.

5. For slow drip, hot spots of methylation: need intensive water column study and target areas in river conducive to methylation for MeHg analysis. Need to include flow measurements with this effort, particularly when going to areas where methylation might occurs. Have to combine upstream, in the zone, and downstream of these areas.

6. For hypothesis # 3, for this to work, there would have to be an erosional process in the sediments and soils that would provide the continued input of inorganic Hg to the system. In the absence of the erosional process, it is likely that the levels in fish would have gone down.

7. For the globules hypothesis – difficult to distinguish from other hypothesis. Headspace analysis in water, sediment or soil samples (using inert gas like Argon) and measure elemental mercury content. Might be able to use PIMS or similar type of sampler. Difficult to distinguish among various forms particularly when adding air or other medium drives changes in speciation. Soil / vapor analysis might be useful for soils but it is unlikely that elemental mercury will be present. Might be helpful for studies on the plant site, particularly along river bank that are wetted during rain

events (but need 10-20 ppm in soils to be able to measure any elemental mercury; need to have about 100 ppm before able to measure anything in vapor).

8. Mass balance estimate: how much biomass is produced each year and knowing the MeHg, how much mercury would be required to maintain this level.

Briefing Papers

- **Clam Study Proposals – Tom Benzing, James Madison Univ.
Doug Graber-Neufeld, Eastern Mennonite Univ.**
- **Fish Diet Study – Greg Murphy, Virginia Tech**
- **Vegetable Crop Mercury Study – Bill Berti, DuPont
Dean Cocking, James Madison Univ.**
- **Bird Surveys – Ralph Stahl, DuPont**
- **DEQ Water Sampling – Ted Turner, Virginia DEQ**
- **Water Flow / Budget Evaluation – Nancy Grosso, DuPont**
- **TMDL for South River – Robert Brent, Virginia DEQ**
- **Floodplain Soil Assessment – Annette Guiseppi-Elie, DuPont**
- **Coring Study – Erin Mack, DuPont**
- **DEQ South River Sediment Assessment – Ted Turner, Virginia DEQ**
- **If – Then Analysis – Ralph Stahl, DuPont**

Clam Studies

Background: Two recent studies of Corbicula, a non-native freshwater clam, have shown that this organism acts as a reliable biomonitor for mercury concentrations in the South River. In November 2001, Dr. Doug Graber-Neufeld at Eastern Mennonite University (EMU) collected clams from 5 locations and found tissue concentrations ranging from 0.80 ppm to levels that were below detection. In this study, mercury concentrations increased significantly between Constitution Park in Waynesboro and Dooms and again between Crimora and Grottoes.

A subsequent study in November 2002 focused on the reach from Constitution Park to Dooms. Dr. Thomas Benzing at James Madison University (JMU) collected clams from 16 locations in this 5-mile stretch of South River and found tissue concentrations ranging from 0.84 ppm to levels that were below the limit of practical quantitation. The study concluded that no significant differences existed in samples collected from right bank, middle, and left bank locations across the stream channel. Also, tissue concentrations did not depend on clam size within the 15 – 30 mm size range. However, significant differences were shown to distinguish several subpopulations. In this study, the mercury concentrations increased at Constitution Park, at a point just upstream from Bridge Street, and at a point just upstream from the Dooms mill pond.

The Issue: The South River Science Team is faced with two questions:

1. What is happening to mercury concentrations further downstream in the reach between Dooms and Port Republic?
2. What are the uptake rates for Corbicula? Is it possible to transplant clean clams to identify source areas in the channel?

Proposed Path Forward:

In November 2003, clams will be sampled from 10 locations along the South River from Waynesboro to Port Republic. This sampling event will replicate many of the locations from the earlier studies and include new stations at Harriston and Port Republic. From each location, three 10-clam composite samples will be collected. The clams will be processed at a JMU laboratory with the help of JMU, VADEQ, and VDGIF staff and shipped to a contract laboratory for analysis of total mercury and methyl mercury. Control samples will be collected at Ridgeview Park in Waynesboro and from North River. This part of the study is intended to identify reaches along the river below Dooms that may be acting as source areas. In addition, these samples will provide the team with information about methyl mercury levels in clams.

The second part of this study will establish a protocol for using caged, transplanted Corbicula as a biomonitoring tool that would aid in localizing source areas in the river. This preliminary study will establish 1) the methodology for transplanting clams in the river, and 2) the minimum time needed for clams to accumulate levels of tissue mercury that reflect the environment. Corbicula taken from a clean area will be moved into mesh cages on the river bottom at a contaminated site (near Crimora). Starting in November, three groups of 10 clams each will be removed at monthly intervals for the analysis of total mercury. Simultaneously sampling of a control group—clams taken from the contaminated site and moved into cages—will allow us establish the time period required for transplanted clams to reach a mercury content that is not significantly different from the control group.

The Uptake of Mercury and Relationship to Food Habits of Selected Fish Species in the South River and South Fork Shenandoah River, Virginia

Update: October 2003

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Background: The purpose of the current study is to elucidate the pathways of mercury (Hg) bioaccumulation by channel catfish, redbreast sunfish, smallmouth bass, and white sucker in the South River and South Fork Shenandoah River. The study is divided into 3 main objectives which include: (1) determining food habits of selected fish species; (2) determining Hg concentrations of food items consumed by selected fish species; and (3) predicting Hg concentrations in selected fish species based upon alternative management scenarios aimed at remediation of the South River and South Fork Shenandoah River.

During 2002, research activities focused on determining food habits of selected fish species. Fish ranging from juveniles to adults were sampled in spring, summer, fall, and winter by electrofishing at 18 sites in the South River, South Fork Shenandoah River, and North River (reference reach). A total of 1,276 fish were collected and analyzed for food habits. Overall, food habits of selected fish species observed in this study followed similar patterns to those observed in other studies conducted in North America and in the southeastern United States. Fish fed upon a variety of items such as aquatic earthworms, aquatic and terrestrial insects, clams, crayfish, detritus, algae, fish, and snails. Important differences in food habits were observed between fish species, river reaches, seasons, and sizes of fish.

Current Activities: Once food habits were known, the next research focus was to collect food items consumed by selected fish species for Hg analyses. Target food items were selected from study reaches based upon importance in the diet among all selected fish species. The final list of target food items consisted of a diverse group of organisms such as ephemeropterans, trichopterans, crayfish, fantail darters, and margined madtoms. Target food items were sampled in spring, summer, and fall at 5 sites in the South River, South Fork Shenandoah River, and North River. Final analytical results should be received by December 2003. Preliminary results from spring and summer indicate that Hg concentrations in food items show similar patterns to those observed in selected fish species such as differences between sites and trophic levels.

Future Work: Results from food habit analyses and Hg analyses of food items along with existing data will be used to predict Hg concentrations in selected fish species based upon alternative management scenarios aimed at remediation of the South River and South Fork Shenandoah River. Management scenarios will be evaluated using the Bioaccumulation and Aquatic System Simulator, a contaminant bioaccumulation model developed by the U.S. Environmental Protection Agency. Final results of this study will provide resource managers with an enhanced understanding of the Hg bioaccumulation processes occurring in fish in the South River and South Fork Shenandoah River, so that assessment and measurement endpoints can be determined which are essential for establishing remedial and restoration goals.

Mercury Uptake from Soil into Vegetable Garden Plants

William Berti, DuPont Central Research & Development and
Dean Cocking, James Madison University

A field study has been established to determine the extent, if any, to which Hg may be taken-up by vegetables from soil and if this may be a significant route of human exposure. The objective is to examine edible plant organs that have been prepared in a manner suitable for domestic consumption to test the Null hypothesis that there is no difference between the Hg content of food grown on floodplain and non-floodplain soils. . The field study is located at the Augusta Forestry Center, Virginia Department of Forestry, on the South River about 10 river-miles downstream of Waynesboro. Two gardens have been established at the Center. The floodplain garden is located within 50 m of the South River riverbank. Total Hg concentrations in the floodplain garden soil are estimated to range from greater than 12.5 to 53.5 µg Hg g^{-1} soil (dry wt.) in the surface 15 cm of soil. The control garden is in an upland area about one km from the floodplain garden. The total soil Hg concentration in this location is estimated to average about 0.03 µg Hg g^{-1} soil (dry wt.), which is below the Limit of Quantification (LOQ) of the analytical method.

The gardens were established the week of June 23, 2003, when the first planting of vegetables occurred. Several tomato, onion, cabbage, green pepper, and squash plants were transplanted into their respective 1.5 m x 3.0 m plot. Carrots, spinach, and sweet corn were planted from seed. A fall planting was performed on September 30, 2003, when lettuce, radish, and spinach were seeded into their respective plots in both the floodplain and control gardens. Each vegetable in the floodplain garden was replicated four times in a completely randomized design. Vegetables were planted into one of ten randomly selected plots within the control garden. The control garden plots were not replicated.

Fully-grown, edible portions of squash, cabbage, green pepper, spinach, tomato, sweet corn, onion, spinach, and carrot were harvested. With the exception of the sweet corn, all of the vegetables were washed with tap water after harvest. The sweet corn was husked and the seed cut from the cob. A soft vegetable brush was used to remove any soil particles from the other non-leafy vegetables. The top layers of the onions were removed after washing. The carrots were washed but not pealed. After blot drying using a paper towel, an amount of each replicate vegetable sufficient for analysis and subsequent storage was cut into small pieces. From each harvest date, at least one vegetable from the floodplain garden was submitted to the laboratory in duplicate for Hg analysis. In addition, one vegetable sample from the control garden was spiked with Hg to check for matrix effects from each harvest date.

The results thus far have been below the LOQ for Hg measured on fresh vegetables samples. Generally, Hg was not detected in the samples; however six of the 34 samples showed traces of Hg between the MDL (Method Detection limit of 0.0028-µg Hg kg^{-1} vegetable [wet weight basis]) and the LOQ, including one vegetable sample from the control garden. Mercury analysis of oven-dried or freeze-dried samples is being considered as a reasonable alternative to Hg analysis on fresh vegetable samples. Drying at 60 ºC or freeze-drying should decrease the LOQ and MDL of the vegetables on a dry-weight basis, since the vegetables are at least 90% moisture. Replicate wet and dried sub-samples were reserved and stored when adequate material was available.

Later this fall, composite soil samples will be collected from individual plots for total Hg analysis. In each case, soil will be sampled to 15 cm deep from at least eight points within each plot, a composite of which will be analyzed for total Hg. Aliquots of soil from each floodplain plot sampled for total Hg will be mixed and submitted for an agronomic soil test. An agronomic soil test will also be performed on a composite soil sample collected from the control plots that are sampled for total Hg. Soil test results will be used to determine the need to apply limestone fertilizer for the 2004 growing season.

Questions

- Does the sample preparation as outlined seem sufficient to meet the primary objective?
- Should soil samples be collected in a different way than that outlined in the summary?
- Do you have comments on our plot design (i.e., completely randomized designed)? Should additional locations in the floodplain with lower and higher soil-Hg concentrations be considered?
- Should the same vegetable be planted in the same plots in 2004 as in 2003 or should plots be re-randomized?
- How many years/growing seasons should a garden be continued at a single location?
- Is it important to differentiate between Hg that is taken-up and translocated or is soil contamination?
- If the Hg is mostly not detected in the wet vegetables, is it necessary to analyze samples that have had water removed (freeze-drying or oven-drying)?
- The gardens were planted too late this year to include potato. For 2004, however, we plan to include potato in addition to the vegetables that were planted in 2003. Should additional vegetables be considered? If so, what? There is no room to include additional vegetables without expanding the floodplain garden, reducing the plot size, reducing the number of replications from four, or substituting one of the vegetables that we are currently growing with another, no other vegetables can be included.1

Bird Surveys and Preliminary Exposure Evaluation

A review of web-based information on the diversity of bird species in the South River watershed was conducted and presented to the South River Science Team (SRST) in September 2003. The results of this review suggested that the diversity of bird species was high in the watershed, and relatively consistent through to the upper part of the South Fork Shenandoah River. Based on these observations, there does not appear to be a reduced number of bird species in the South River watershed.

Despite the above information, the team has decided to undertake a screening level exposure analysis for piscivorous bird species known to inhabit the watershed. Estimates will be made using literature-based food consumption rates of the two or three main piscivorous species as well as the potential levels of mercury in the prey. These results will be presented at the SRST meeting in October 2003.

Water Column Hg Assessment

Background: As part of the ongoing monitoring program established in the late '70s, ambient water has been sampled in the South and South Fork Shenandoah Rivers at approximately 5 year intervals. Almost all samples collected through the 90's were at concentrations below the Hg detection limit for CVAA (Cold Vapor Atomic Absorption) which was used through that time. Starting late in the 90's, the use of CVAF (Cold Vapor Atomic Fluorescence) analysis and Clean Metals sampling methods yielded detection limits of 1.5 parts per trillion, which were sufficiently low to observe ambient concentrations of total and dissolved Hg in the rivers.

Since 2000, the South and South Fork Shenandoah Rivers waters have been sampled for Hg bimonthly. Additionally, a more focused effort to precisely locate any sites with elevated Hg concentrations was conducted in July 2002. Samples were collected along a 1.5 mile reach in Waynesboro at 0.1 mile intervals, starting approximately 0.4 miles upstream of the 2nd St. bridge and ending just downstream of Hopeman Parkway. This section of river begins approximately 1.5 miles downstream of the DuPont, Waynesboro plant, believed to be the point where the majority of mercury historically entered the river. A spike in total Hg concentrations was observed near the Hopeman Parkway bridge, which initiated a follow-up survey in August 2003 to verify the original spike. In addition to resampling the site of the observed spike, the 1-mile stretch of the South River along the DuPont, Waynesboro plant was also sampled to determine if high Hg concentrations existed in this area.

The Issue: By examining $TSS_{45\mu m}$ and total and dissolved clean metal Hg data, it is hoped that Hg transport models can be refined to better predict clearance of mercury from the system. The information might also be useful in identifying [Hg] trends that could be used to recalculate estimates of time required for fish tissue levels to recover below consumption advisory levels. Also, the data may provide for estimates of population and community-level impacts on non-fish species affected by mercury, including piscivorous birds, mammals and reptiles. Finally, the identification of high [Hg] areas may facilitate future remediation efforts.

Proposed Path Forward: The DEQ will continue the bimonthly program to evaluate Hg loading under varying flows and seasons, and will survey additional reaches suspected to include high concentration sites. Should remediation efforts commence at some future time, measurements of water column Hg will be used to assess the effectiveness of whatever actions are taken.

South River Water Budget Evaluation – Watershed Balance

Background**: The purpose of the water budget evaluation was to: Characterize general hydrology in the basin; determine a range for groundwater contribution to South River flow; evaluate potential for sub-aqueous springs; and eventually expand the evaluation to include a solids balance in the basin. The data sources for this evaluation included: USGS Gauging Stations (continuous 1970s to 2002, sporadic from 1927 to 1970s); State Climatologic Data; VADEQ Discharge/Withdrawal Permits; Engineering Feasibility Study for DuPont (LMS, 1981); Hydrogeologic Study of the Waynesboro Nurseries Inc. (Tethys, 1988); Geology of Waynesboro Quadrangles (Gaithright et. al., 1977); and personal communication with Maptech, Inc. who is preparing the bacteria TMDL for the upper part of the South River.**

Approach and Observations**: The approach was to use mean annual statistics to evaluate the hydrologic data and the climatologic data, and to resolve any discrepancies between the two data sets. Significant anomalies in river flow from one station to the next, if present could indicate increased groundwater influence (three gauging stations on the river are monitored by the USGS). The stretch in the river that has substantially increased flow is in the City of Waynesboro but this can be attributed to a number of point discharges and outfalls along this stretch of the river.**
The general evaluation presented here is considered a first step. Average daily flow in the river is greater than the annual mean approximately 30% of the time. Because the river is so flashy, evaluating the response of the system on an event related scale should be considered.

Results**: The drainage area from the South River from its source to the confluence with North River is 234.4 mi^2. The ratios of river flow to drainage area are relatively consistent at approximately 1.2 cfs/ mi^2 based on 3 gauging stations (upstream of Waynesboro, at Hopeman Parkway and in Harriston). This ratio was used to interpolate and extrapolate river flows when only drainage basin areas were available. Therefore, the mean annual flow of the South River at Port Republic is estimated to be 282 cfs (16.3"/yr).**

Hydrographs suggest that the groundwater contribution to river flow is approximately 30% of total river flow. For MapTech's *Basins Modeling* upstream of the Waynesboro site, a groundwater contribution of about 50% is estimated; Tethys (1998) estimated the groundwater contribution in the alluvial plain to the river to be approximately 70% of total river flow.

Mean annual water balance in the South River Watershed:
Precipitation: 35.54"/yr (614 cfs) to 36.18"/yr
Evapotranspiration: 19.34"/yr (332 cfs)
River flow: 16.31"/yr (282 cfs)
Contributions to South River Flow of 282 cfs at Port Republic (annualized):
GW + Overland Runoff and tributaries – net consumption
Groundwater: 30% of flow or 64.6 cfs (4.89")
Runoff and tributaries: 212.4 cfs (11.42")
Consumption: 5 cfs

Discrete Contributions to flow (tributaries estimated) in South River (Note that withdrawals are mainly through GW)

River Mile	Name	Mean Flow in cfs
-0.30	Baker Springs overflow	4.46
0.00	DuPont Discharge	5.42

1.46	Waynesboro STP	4.18
2.00	Steele Run	(6.12)
3.06	Genicom Discharge	0.17
5.20	Sawmill Run	(12.36)
7.50	Porterfield Run	(6.96)
9.00	Tunnel Branch	(2.04)
10.20	Mine Branch	(4.8)
13.30	Meadow Run	(6.84)
16.40	Paine Run	(8.16)
16.80	Augusta Co. - Harris. Lagoon	0.05
19.50	Stull Run	(3.0)
20.60	Reynolds/Alcoa Discharge	3.63
23.41	Grottoes Lagoon	0.23
24.50	Miller Run	(5.88)
	Total	**74.31**

Mean Annual Flow for the three gauging stations are:

Upstream Waynesboro: 149 cfs (mile -2.9)
Hopeman Parkway: 214 cfs (mile 2.6)
Harriston: 262 cfs (mile 17)

Estimated Flow of North River just before confluence with South River: 700 cfs
Measured Flow South Fork Shenandoah at Lynwood: 1,033 cfs

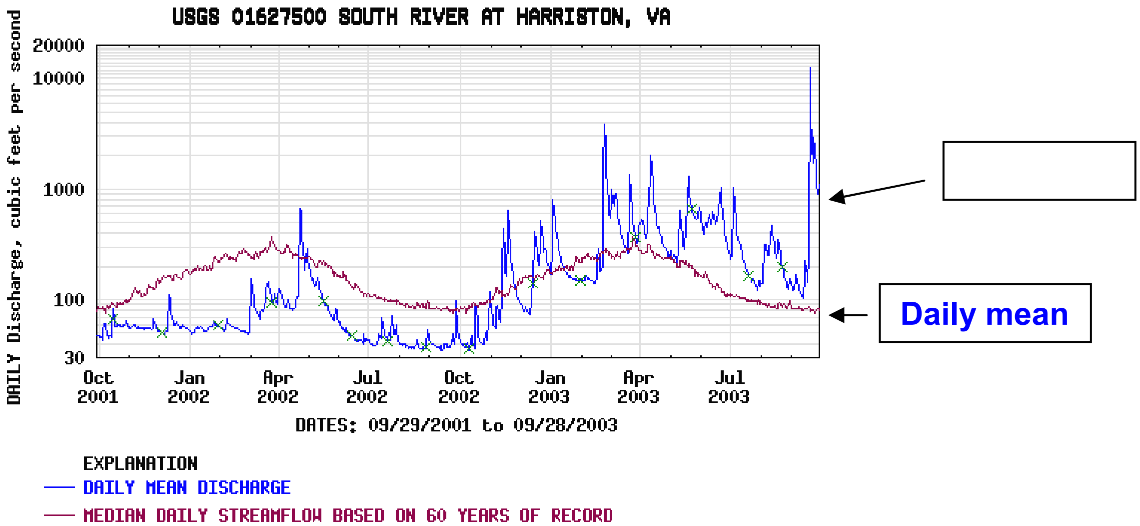
Spatial and Temporal Considerations

Inputs to and withdrawals from the river system are not equally spaced up and down the river and small-scale changes in water quality data or local scouring may result from local inputs. Alternating dry/wet years could influence trends seen in monitoring data.

Hydrographs suggest that the last thirty years are wetter than the previous thirty. More controls on TSS in discharges and erosion control (BMP) suggest less sediment loading. Wetter conditions and less sediment load could result in net erosion.

Water Budget - Conclusions

- **Hydrologic data and climatologic data agree in the 234 mi^2 watershed**
- **Total budget available to river (overland and groundwater seepage) is 16 to 16.31"/yr but the proportion of groundwater contribution is still uncertain.**
- **GW discharge could make up 30% to 50% of total river flow**
- **Data does not have the spatial resolution to identify specific areas of higher GW discharge (i.e., springs)**
- **Groundwater flow under river is possible (Genicom site) but groundwater flow probably shortly returns to river at some point downstream (flow in alluvial deposits or limestone bedrock).**
- **Temporal (monthly, annual and seasonal) variations in rainfall may be a factor influencing trends in fish data.**
- Longterm trends could be changing and result in changing depositional/erosional regimes



Possible Next Steps:

- Conduct a solids balance for the watershed as a whole and then specifically for solids in the floodplain
- Collect solids data under varying flow conditions at an appropriate scale to understand solids movement
- Evaluate the river floodplain and watershed from a geomorphologic perspective – For example:
- Determine if the river is in an erosional phase
- Determine erosion, deposition, accretion on a local scale and attempt to track solids particle movement in the floodplain

South River Mercury TMDL

The South River is under a TMDL for mercury in fish tissue. The stream was listed in 1998 and is scheduled for TMDL development in 2008. Details to be developed.

2002 303(D) Impaired Waters Fact Sheet

CLEAN WATER ACT GOAL AND USE SUPPORT: Fish Consumption Use - Partially Supporting

Part: 1A

RIVER BASIN: POTOMAC AND SHENANDOAH RIVER BASIN
CITY/COUNTY: Augusta, Rockingham, Page, Warren, Waynesboro, City of
STREAM NAME: South River/S.F. Shen R./N.F. Shen R./Shenandoah R.
HYDROLOGIC UNIT: 02070005
SEGMENT SIZE: 128.82 - Miles
INITIAL LISTING: 1998
TMDL SCHEDULE: - 2010
SEGMENT ID(s): VAV-B32R VAV-B33R VAV-B35R VAV-B37R
UPSTREAM LIMIT:
DESCRIPTION: Begins at DuPont foot bridge
RIVER MILE: 128.82
LATITUDE: 380340.0
LONGITUDE: 785312.0
DOWNSTREAM LIMIT:
DESCRIPTION: Warrenton Power Dam
RIVER MILE: 0.00
LATITUDE: 385715.0
LONGITUDE: 780854.0

LOCATION INFORMATION:
Segment begins at the DuPont foot bridge over the South River in Waynesboro, continues downstream to the headwaters of the S.F. Shenandoah River (23.89 0.00) . The entire S.F. Shenandoah River is included (100.97 - 0.00). The segment ends on the main stem of the Shenandoah River at the Warrenton Power Dam (41.62 - 38.09). This segment also includes a small section of the lower N.F. Shenandoah River from its mouth upstream to the Riverton Dam (0.43 - 0.00).

IMPAIRMENT CAUSE: VDH Health Advisory (Mercury) Mercury has been found in fish tissue and sediments at values high enough for the VDH to issue a fish consumption advisory.

1BSTH000.19 - 5 PAH result exceeded the screening value in 1996 in 1 fish species resulting in a
Partially Supporting assessment assessment for 3.64 miles beginning at Rt 677 (Luray Ave) and
continuing downstream to the confluence with the North Fork Shen River.
1BSSF000.19 - 6 total phosphorus values exceeded the screening value out of 58 samples and USGS
01631000 - 20 total phosphorus values exceeded the screening value out of 76 samples during the

2002 assessment period resulting in a threatened assessment for 9.53 miles. Rt 677 (Luray Ave)
downstream to the confluence with the N.F Shen River (3.64 miles) and from Gooney Run
downstream to the 619 bridge (5.89 miles).
The source of the Mercury is from a process that was abandoned by DuPont in the early 1950s.
The source of the benzo(k)flouranthene in fish tissue is unknown.
The source of the total phosphorus is unknown.
IMPAIRMENT SOURCE: VDH Health Advisory (Mercury), Unknown - Threatened, Unknown

Floodplain Soil Assessment

Background: The floodplain has been identified as a potentially significant residual source of mercury (Lawler, Matusky and Skelly, 1981). Elevated mercury concentrations have been measured in both surface and subsurface soils in the 100-year flood area with surface soils (3-19 miles downgradient) having the highest concentrations (Hendricks, 1981). A study of the flood plain ecosystem ((Cocking *et al.* 1991) hypothesized that there is widespread distribution of Hg throughout the floodplain ecosystem, including vegetation, invertebrates and small vertebrates. A critical issue is that the dataset is 10 – 20 years old. In addition, although average concentrations are below health-based criteria, earlier datasets used a composite strategy that may not be adequate for current evaluations.

Issue: The Team is considering sampling floodplain soils. The objectives of the sampling will be (1) to determine general "representative" levels of mercury in floodplain soils relative to data currently available and (2) to leverage this activity with data gathering for helping to refine the conceptual site model including potentially defining continuing sources. A statistical review of the available data was used to develop a preliminary scope that defined the number of sample locations and replicates. A river reconnaissance was performed to help defined potential sample locations. Actual locations will have to take into account access issues.

The preliminary scope identifies 15 locations along the South River from Waynesboro to the confluence in Port Republic with a maximum of six sites per location (three on either bank, as appropriate). Typically, at each site a series of replicates will be composited to a single sample. Hand auger equipment will be used. The majority of the samples will be taken as surface samples (0-24"). In one or 2 locations, a more comprehensive sample design will be employed. Individual rather than composite samples will be taken. Samples will also be taken at depth to evaluate potential concentration changes with depth.

Path Forward: Obtain feedback from the Science Team and finalize the Scope. At the same time, the team expects to begin getting access permission from property owners.

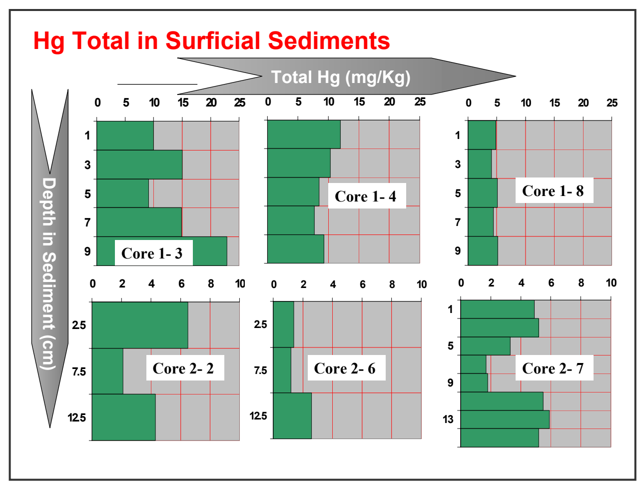
South River Sediment Coring Project

E. E. Mack, DuPont Corporate Remediation Group

Hypothesis: Areas where sediment has accumulated without disruption will contain a history of mercury inputs into the South River.

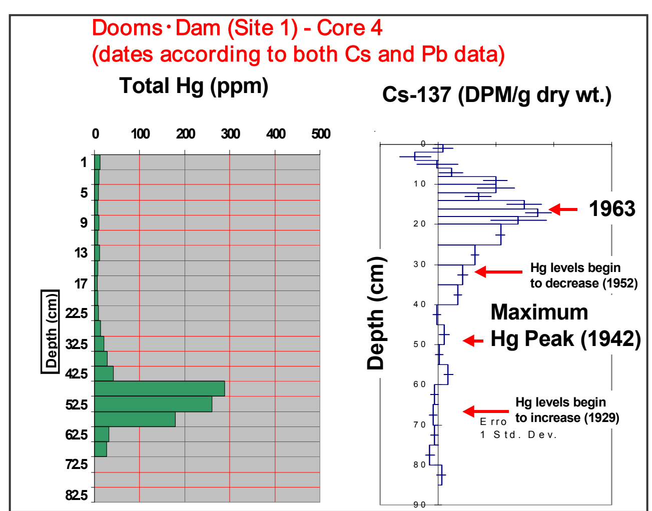
Goals: Develop understanding of historic and current inputs of mercury into the South River system using mercury concentrations in vertically stratified sediment cores. Data on depth profiles of total mercury, Cs-137 and Pb-210 will be used to assign dates to specific periods of mercury input to South River sediments.

Methods: Two depositional sites downstream from the DuPont plan were chosen. Site 1 is a pocket of sediment located upstream of Doom's Dam in the main channel of the river. Site 2 is located downstream of site 1 within the channel of a small tributary that crosses the floodplain of the South River. Cores were collected either by driving the corer in with a mallet or by vibra-corer until refusal. Nine cores were collected from each site and logged and photographed for geological characteristics. Three of the nine cores from each site were selected for further analysis for total and methylmercury (Lancaster Labs and Frontier Geosciences respectively). Based on the total mercury data, one core from each site was further analyzed for Cs-137 (Flett Laboratory). After review of the Cs-137 data, a single core from site 1 was analyzed for Pb-210 (Flett Laboratory).



Results / Discussion: Core lengths ranged from 70 to 100 cm long (most cores were at least 80 cm). In most cases, mercury concentrations increased with depth. In several cases (at both sites) there were distinct depths at which mercury concentrations were elevated. In all cases, mercury concentrations in the surficial sediments (top 15-cm) ranged from 1.5 to about 15 ppm, well above background for the area. Methylmercury values followed expected trends in that ratios of methylmercury to total mercury were highest in the surficial sediments and much lower in the deeper sediments where total mercury levels were highest.

Of the two cores that were analyzed for Cs-137, only one core (site 1, core 4) showed a distinct maximum for Cs-137. Based on the depth of the Cs-137 maximum a sedimentation rate of 0.4 cm/yr is predicted.



However, this produced a history of mercury inputs inconsistent with the known history of mercury use in the area (e.g. using this sedimentation rate, mercury inputs began in the early 1800's and ended in the early 1900's). This core was further analyzed for Pb-210 using the regression slope model (because the core was not long enough to include background Pb-210 activity). The results, as reported by Dr. Flett, indicate that there is some mixing of the surficial (top 10-cm) sediments and that there is an "approximately exponential drop in Pb-210 activity as a function of depth". Based on the Pb-210 data, the regression slope model predicts a sediment deposition rate of 1.0 - 2.3 cm/yr, much higher than predicted by the Cs-137 data. The discrepancy can be resolved if it is assumed that some of the surficial sediments are not represented in this core. Dr. Flett estimates that the core is missing the top 43-cm of sediment. If this is assumed to be true, a sedimentation rate of ~1.5 cm/yr is derived from the placement of the Cs-137 peak and Pb-210 data. Using this sedimentation rate, mercury inputs occur at times consistent with the known history of the site (e.g. Hg inputs began in 1929).

Given that it appears that mercury inputs have decreased over the last 40 years, the source of the elevated levels of mercury in the surficial sediments indicate the possibility of an ongoing source of mercury to the river. Data from the recent intensive water column sampling suggests that particle associated mercury during normal flows is about 10 ppm, enough to account for the elevated levels observed in the surficial sediments. Possible sources for this mercury include contaminated floodplain and river banks or movement of internal sediments. A plan is in place to sample the river water column during a storm even to examine the possibility that mercury rich particles are moving from the floodplain or plant site under high flow conditions.

South River Sediment Assessment

Background: As part of the ongoing monitoring established in the late '70s, sediment has been sampled in the South and South Fork Shenandoah Rivers at approximately 10 year intervals. Studies conducted in the 80's by the engineering firm Lawler, Matusky and Skeller (LMS) concluded that the fate of mercury in the river system is primarily a function of sediment trasnsport in the form of scour and deposition. Models developed by LMS to predict recovery rates of the rivers were largely based upon sediment Hg concentration changes over time. Each time interval of observations of mercury concentrations in sediment are used to validate and refine the model. Since the discovery of Hg in the South River, sediment has been collected and analyzed for total Hg three times; once each in 1978, 1986, and 1997. Results of these sample events have not revealed any trends of reduced Hg concentration in sediment.

The DEQ is scheduled to perform another round of sediment sampling in 2007, and is currently investigating whether past sampling methods and strategies were adequate to observe spatial and temporal trends. Collection of sediment in the past was largely limited to bank sampling, since bed sediments were impractical to sample. These samples were collected systematically at regular river mile intervals. There is now some concern that bank sampling might not be representative of overall Hg concentrations in the rivers. Additionally, past efforts have not provided information about the concentration of Hg in physically distinct river features such as pools, riffles, and glides. If large amounts of Hg exist in these zones within the stream channel then model predictions based on these results would be inaccurate.

The Issue: The DEQ is now investigating whether new sampling methods might provide data to more accurately model the system and predict river recovery rates. It is anticipated that these approaches would also provide information useful in developing remediation strategies. The goals of a new sediment monitoring plan would be 1) to quantify relative partitioning of Hg into varying stream bed features; 2) to provide representative data to be used to assess sediment [Hg] trends and transport; and 3) to provide data to determine if remediation would be effective and practical.

Surveys of the South River downstream of the initial contamination site have revealed a great deal of variation in the river bed structure, and in the type and distribution of sediment within the bed. Any new method of sediment collection would need to be able to measure Hg concentrations in the spectrum of sediment/bed conditions spanning the length of the system. Methods considered to date have included McNeil samplers, suction/dredge samplers, and sediment traps. Limitations of each method must be considered to establish which is most appropriate. Once a method of sediment sampling is selected, then characterization of the river would be necessary to estimate the distribution of Hg throughout the entire contaminated length of the river.

Proposed Path Forward: DEQ would like to develop a sediment sampling plan and have it in place well in advance of the next scheduled sediment sampling event (2007). The primary objective of the plan would be to determine spatial and temporal trends of mercury levels in sediments. Secondary objectives would be to address modeling, fate, and potential remediation issues by determining relative mercury levels in different types (grain size or material) of sediments; quantifying sediment types (and, therefore, mercury) in portions of the river, and evaluating input from “new” sediments via sediment traps. Finally, efforts to locate “hot pockets” of mercury in sediments will be pursued in the Waynesboro area.

If – Then Analysis

Over the past 2 ½ years, the South River Science Team (SRST) has devoted considerable time and effort to understanding more fully the dynamics of remnant mercury in the water, sediment, floodplain and biota of the South River. A more complete conceptual model has resulted, which will continue to be refined as new and important information are obtained.

To help refine the types of studies and information that might be needed to augment what currently exists, the SRST would like to undertake an analysis of the working hypothesis. In this situation the team would engage in an interactive session where the existing data (the if) are contrasted with the working hypothesis (the then). This will help eliminate or modify working hypothesis are not congruent with existing knowledge, or will stimulate suggestions for how additional data might be needed to resolve the issue.