Briefing Papers
South River Science Team
November 9-10, 2004

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Phase II Storm Water Sampling at the Invista Waynesboro Plant

Mike Sherrier, URS Corporation

The Phase I Storm Water Monitoring Program at the Invista Waynesboro Plant was completed in 2003. Mercury was not detected in any of the base flow or first-flush storm flow samples collected from the outfalls discharging to the South River (MDL = 0.16 µg/l) during the Phase I sampling. Mercury was detected at low concentrations (up to 1.7 µg/l) in the flow-weighted composite samples collected from 4 of the plant outfalls that discharge to the South River.

The Phase II Storm Water Monitoring Program was initiated in early 2004. The primary objective of this program is to estimate the bioavailable percentage of the mass of mercury discharging to the South River. This objective will be met through additional base flow and storm flow sampling at the main plant outfalls. A secondary objective is to further characterize the up-stream portions of the storm water system where mercury was previously detected. This objective will be achieved through characterizing the sediment and water quality within the affected portions of the storm water system.

The Phase II program will include multiple base flow and storm flow sampling events with the aim of characterizing the concentration of mercury in the plant discharges under varying flow conditions. Three base flow sampling events will be completed. Samples will be collected at 8 outfalls and 2 up stream location (within the storm-water sewer system) during each base flow sampling event. At least 2 storm flow sampling events will be completed. During each storm sampling event, first-flush and flow-weighted (or time-weighted) composite samples will be collected from the 7 outfalls that receive storm flow.

Portable, automated samplers (ISCO 6712) will be used to collect samples at the 7 locations where storm-flow samples (first-flush and flow-weighted composites) will be collected. All Phase II storm monitoring samples will be analyzed for total and dissolved total mercury as well as TSS. Mercury analyses will be performed using the low detection limit 1631 methodology in order to quantify the mercury concentration in the plant discharges where previous results were below the method detection limit.

Base flow samples for dissolved total mercury will be filtered in the field. First flush and flow-weighted composite samples for dissolved total mercury will be filtered in the lab. At least two storm-flow split samples (either first flush or flow-weighted composite) will be filtered at the time of collection to allow direct comparison of field-filtered and lab-filtered dissolved total mercury results.

To identify potential sources of mercury to the storm water sewer system at the site, a limited sediment and water quality survey will be conducted under base flow conditions as part of the Phase II program. The survey will include collection of water and sediment samples from accessible junction boxes along the portions of the storm-water system that are up-stream of locations where mercury was detected during previous storm water sampling. Water samples will be analyzed for total and dissolved total mercury (using EPA method 1631). All sediment samples will be analyzed for total mercury.

The Isco samplers were installed at the site in August and September 2004. The three base flow sampling events will be completed in November and December, 2004. If weather conditions allow, one or both of the storm sampling events will be completed during the same time period. The sediment and water quality survey will also be completed in November 2004.

Surveying Air-borne Mercury at the Landscape Level

Cocking, Dean, Amir Allak and Allison Kelley
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Atmospheric deposition of mercury on water and land surfaces is now recognized as a significant component of its overall geochemical cycling. Routine network sampling of regional background concentrations within the US is ongoing and is revealing information about temporal variability and the relative contributions of Hg vapor, wet and particulate deposition. These studies are complimented by extensive local sampling at sites known to contain sources of Hg.

The purpose of this study is to develop an inexpensive method of surveying terrestrial habitats at the landscape scale to identify locations which repeatedly have higher than average air-borne deposition of Hg. For the purpose of this study, the definition of air-borne Hg is that which adheres to a thin layer of sticky material poured into plastic Petri dishes which are exposed to air while attached to telephone poles. These locations were dispersed within the city limits of Waynesboro, Harrisonburg and Staunton VA.

From the outset it is realized that each sample which is collected is not complete and subject to various sampling errors such as variability in the impaction of insects and dust due to air movement, and the inability of the samplers to hold the entire sample during more intense precipitation events such as thunderstorms and hurricanes. Therefore, the technique is likely to underestimate Hg presence and does not provide an absolute measure of atmospheric Hg. However, all of the plates are exposed to similar sources of error which for the moment are considered to be random.

The samplers are simple in design with “tangle trap” (a commercial insect trap coating) being used to create a sticky surface which remains after repeated exposure to precipitation. The materials cost approximately one dollar per sampler and replicate samplers were stapled adjacent to each other on each telephone pole. These samplers cost only a fraction of the amount that must be invested in any of the various other passive units on the market, and are even more economical in comparison with automated fixed position deposition and pump dependent atmospheric gas sampling units. Furthermore the costs are kept down by doing the Hg analysis locally on the James Madison University campus with a Perkin Elmer FIMS continuous flow cold vapor atomic absorption spectrophotometer. We can sample 100 locations, with 200 samplers total for example, at a cost less than $500. Whereas, 200 passive samplers at $250 each would cost $50,000 initially and 200 total Hg analyses from a contract laboratory would conservatively be $10,000; about 120X the cost. Our contention is that if locations of interest within the landscape can be identified with this relatively inexpensive screening process, then more detailed and precise studies can follow where appropriate.

The present status of this screening process is that we have established networks of plates within the city limits of Waynesboro during three different years. Duplicate samplers were set out at 135 locations in the most recent and extensive study. Because of damage and vandalism, only about two thirds of the initial number of samplers were collected each time. Because the duration of each study was different, the Hg deposition was calculated as μg Hg/m^2/day for comparison. Similarly, in the most recent studies smaller samplings of 25 locations each were distributed within the city limits of both Harrisonburg and Staunton, VA. It was anticipated that these locations would represent random ‘background’ levels of Hg deposition in comparison with Waynesboro, VA, which has documented floodplain soil Hg contamination associated with the South River situation. For each of the study periods, the grand mean Hg concentration of all plates that were recovered in that group was calculated. Each sample location was scored with respect to the standard deviation from this grand mean and the high and low locations determined for each study. The landscape distribution patterns were compared and those which repeatedly had higher (or lower) air-borne Hg concentrations were identified. The locations have been mapped and a fourth year study is under way. Several interesting observations have already emerged from the data including the presence of some consistently high Hg locations near the South River downstream from the center of Waynesboro and several locations within the Harrisonburg, VA ‘control location’ which appear to have Hg concentrations as great as those found in Waynesboro. This unanticipated result is also presently under study. We do not think that the traces of air-borne Hg which are being detected are sufficient to cause environmental alarm in themselves; however, this particular study was not designed to make that determination. This could be evaluated by the establishment of a permanent atmospheric deposition (and Hg vapor) monitoring station at one or more of the locations identified as having consistently high survey concentrations.

South River Surface Water

Ralph Turner, Ted Turner, and Dick Jensen

Summary

In August 2004, Ralph Turner and Dick Jensen conducted a South River surface water survey, from the USGS station above the plant to the McGaheysville Dam below Port Republic. At each of 16 stations, filtered and unfiltered samples were taken for total and methyl mercury. At each station a liter of water was submitted for high resolution TSS. From these analyses, the TSS-bound values of total and methyl mercury can be accurately calculated. Additional control samples were included from the North River in Port Republic. These results are in hand and will be reported at the November meeting.

In September 2004, Ted Turner of DEQ and Dick Jensen repeated many of the August sampling stations during an unusually high water event: Hurricane Jeanne. The water was very muddy. In addition, Ted was able to obtain samples at Harriston as the water was rising the day prior to this river sampling event. Filtered Hg and TSS samples were obtained. These data have not been received as of this writing, but results should be in hand by the November meeting.

Results from August

Data are still being reviewed, and Science team and Expert Panel analysis will be invited. Initial review of the August results suggests that this data set is very well-behaved. Both dissolved total and dissolved methyl mercury appear to rise steadily from the plant to near Crimora, where they both then assume an approximately steady value (~10 ppt for total and ~0.6 ppt for methyl) to Port Republic. At Port Republic, the levels of both dissolved total and dissolved methyl are diluted to a lower value by the North River. Outside the main stream, a sample from the Ox Bow near Basic Park was unusually high in methyl mercury, relative to total mercury, and the samples from the North River were at background levels, as expected.

Mercury levels on TSS in August had risen to above 10 ppm (dry) by Dooms and remained high until Port Republic, where they dropped to below 5 ppm with the North River dilution. The level exceeded 30 ppm at Harriston but dropped to slightly greater than 10 ppm by Grand Caverns and Port Republic.

The August data were consistent with earlier samplings, such as the high intensity samplings in 2002 and 2004, but they greatly expanded the overall range of river miles.

Floodplain Soil Assessment

Annette Guiseppe Elie, DuPont

The floodplain has been identified as a potentially significant residual source of mercury (Lawler, Matusky and Skelly, 1981). A critical issue was that this original dataset is now very 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.

Recent sampling activities have taken a phased approach. In the spring of 2003, samples were collected at the Forestry station,primarily to support an understanding of whether mercury in the floodplain soils is available at levels that could present a health risk from vegetable ingestion. However, all data collected has been used to help understand the role of floodplain soils as a potential “source”.

A second phase of sampling was performed in the summer/fall of 2004. The objectives of the current sampling were (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.

In this most recent round of sampling, a statistical review of the available data was used to develop a scope that defined the number of sample sites and replicates. Fifteen sites along the South River from Waynesboro to the confluence in Port Republic were identified for sampling. At each site, specific locations were sampled. Typically, at each sample location a series of replicates were composited to a single sample using hand auger equipment.
The majority of the samples were taken as surface samples (0-24"). A total of 12 separate sites were sampled 2004, with a total of 55 sample locations divided between the locations. Of these 55 locations, 23 were composited at two depths for representative concentrations. An additional 29 locations were sampled at 3 depths to further improve the conceptual model. Two 3 ft deep cores were obtained at one location and divided into 11 individual slices for analysis. And one eroded bank sample was obtained with 10 individual increments from water to top of bank. The core and bank samples were obtained to improve the conceptual model. Most recently, in October 2004, two additional eroded bank samples were obtained, with results pending.

Results of other sampling events (Deep Cores taken in the Wetlands in 2002 and Greenway Sampling in 2003) will be included in the evaluation.

Not all results are available but the initial results are consistent with 1980 findings. Surface soils above Port Republic are order-of-magnitude 10 ppm dry wt but variable. Deeper soils are sometimes higher but not always. No high concentration bands have been found in eroded bank locations but such samples have been few. The most recent eroded bank samples will add to these datasets.

Path Forward:

- Get results for outstanding samples
- Review data for Conceptual Site Model refinement
- Statistical analysis by John Green
- Determine need for additional samples

- Prepare report

An Examination of the Release of Mercury and Methylmercury from River Sediment and Bank Soils, and the Potential for Mercury Net Methylation During Sediment Resuspension Typical of High River Flow Conditions.

Robert Mason, University of Maryland-Center for Environmental Science
Chesapeake Biological Laboratory

It has been hypothesized that the source of methylmercury (MeHg) to fish in the river could be either due to methylation of mercury (Hg) input from external sources or due to physical processes that disturb the Hg and MeHg that is contained in sediment and floodplain soils and result in its release and/or methylation. Elevated Hg concentrations have been measured downstream of the plant and a variety of samples were collected to study, in the laboratory, the impact of physical disturbance on the release of Hg and MeHg from these sediments, and the potential for Hg methylation. The specific objectives of the study were to: 1) examine the mobility and bioavailability of Hg found in various surficial sediments and soils, of varying Hg content; and 2) investigate the potential for Hg methylation within these sediments/soils after resuspension/disturbance and the role of the disturbance period and/or the availability of organic carbon in influencing the rate of methylation and of MeHg release into the water column.

Sediment samples were analyzed for Hg and MeHg prior to the study and showed varying total Hg concentration but generally relatively low %MeHg compared to other ecosystems. Upon resuspension, samples were collected over 96 hours from twelve treatments of four sediment site locations, with varying resuspension time and analyzed for total and dissolved Hg and MeHg. In addition, the sediment was also analyzed at the end of the experiment, and ancillary parameters were also measured. Total Hg concentrations increased dramatically with increasing suspended sediment load (TSS) but rapidly decreased in concentration after the cessation of resuspension. Dissolved Hg increased accordingly with disturbance but also decreased in concentration rapidly after the stirring stopped, and by the end of the experiments dissolved concentrations were generally <5 ng/L for the Dooms and GS site samples, but were higher for the soil samples (10-30 ng/L). Such high concentrations may reflect the presence of "colloidal" material in the water column at the end of the experiment. For these sediments, Hg on TSS in the water column at the end of the experiment, on a mass basis, appeared to be higher than that of the bulk sediment suggesting that the fines remaining suspended at the end of the experiment had higher Hg concentrations. In contrast, for the Dooms site, the TSS Hg concentration per gram was lower at the end of the experiment than that of the bulk sediment.

For MeHg, water column concentrations also increased with resuspension. At the end of the 96 hours, dissolved MeHg concentrations were <0.5 ng/L for essentially all the treatments, and concentrations appeared to be little related to treatment conditions, resuspension time or sediment MeHg concentration. DOC was added to some treatments in an effort to stimulate methylation. The results in terms of MeHg in the water column and MeHg in the sediment at the end of the experiment were inconclusive as the variability between treatments was relatively high and the DOC-treated samples were not substantially different from the other treatments. The %MeHg in the final sediments was similar to that of the initial sediments, giving further proof that little net methylation occurred during the experiments. In addition, for MeHg, the TSS MeHg concentration (mass basis) at the end of the experiment was comparable to that of the bulk sediment.

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

Gregory W. Murphy

ABSTRACT

Mercury poses significant challenges to human health and fisheries management. Historical industrial practices in Waynesboro, Virginia left portions of the Shenandoah River basin contaminated with mercury and stringent health advisories for fish consumption. I investigated processes affecting the bioaccumulation of mercury in *Catostomus commersoni*, *Ictalurus punctatus*, *Lepomis auritus*, and *Micropterus dolomieu* by studying food habits, total mercury and methylmercury in common prey items, and bioaccumulation dynamics of methylmercury in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River. Additionally, I evaluated sexual and seasonal variations of total mercury in *M. dolomieu* in the South Fork of the Shenandoah River.

Algae, aquatic insects, crayfish, detritus, and fish accounted for 75-97% of the diet. Total mercury in aquatic invertebrates and forage fish in contaminated rivers ranged from 66.7-398.3 and 198.0-594.9 ng/g wet weight, while total mercury in aquatic invertebrates and forage fish in the reference river were 4.4 and 29.3 ng/g. Model simulations indicated that dietary pathways accounted for 87% of methylmercury uptake by fish in contaminated rivers, but only 57% in the reference river. Total mercury in *M. dolomieu* was 19-20% higher in females than males and 14-21% higher during spring than summer and fall. Results of this study indicate that bioenergetics-based bioaccumulation models are valuable tools for evaluating field data, identifying processes critical to contaminant accumulation, and comparing outcomes of alternative management options associated with pollution control, ecosystem management, and/or restoration activities for management guidance prior to costly expenditures.

Transplanted Clam Studies

Thomas R. Benzing and Doug Graber-Neufeld

Background: 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 (Graber-Neufeld, 2001; Bowles and Benzing, 2003; Benzing and Graber-Neufeld, 2004.) Taken together, these studies indicate that source areas continue to exist in a 5-mile reach of the river beginning at the plant site in Waynesboro. In particular, clam tissue concentrations increased at Constitution Park, at a point just upstream from Bridge Street, and at a point just upstream from the Dooms mill pond. So far, all studies have relied on wild (i.e. stream-bred) clams that were sampled directly from the river channel.

Summary of Results: Pilot Study & Monthly Sampling

A preliminary study was initiated in November 2003 to establish both the methodology for transplanting clams in the river, and the minimum time needed for clams to accumulate tissue mercury. Two groups of *Corbicula* were moved into mesh cages: 1) "Transplant" clams were taken from a clean (North River) site and moved to the South River at the Augusta Forestry Center (AFC), and 2) "Control" clams from AFC were caged and placed adjacent to the cages containing transplanted clams. Monthly sampling from cages continued through August 2004. Major conclusions from this section of the study include:

- Clams appeared to be unaffected by caging. Survival of clams was excellent until mid-summer (June-July), when both caged and uncaged clams showed increased mortality. There was no difference in mercury levels of control clams that were caged vs uncaged.
- Mercury turnover in clams is relatively rapid. "Clean" clams moved to a contaminated site accumulated the majority of their mercury within one month, and major seasonal changes in clam mercury levels occurred within a matter of several weeks.
- Despite nine months exposure to contaminated conditions, clams from the "clean" site never reached levels of mercury as high as those of clams taken from the contaminated site.
- Clams from the August collection had a higher percentage of methylmercury (50-60%) than those from the March collection (25-30%).

Summary of Results: Transplant Study on Plant Reaches

During Summer 2004, 20 groups of *Corbicula* were transplanted from North River to cages along the Dupont plant boundary in both South River and Jones Hollow. These cages were placed at 100-meter intervals in the river channel, collected after 3 months of exposure, and analyzed for total mercury and methylmercury in tissue. The caged clams showed good survival and growth during the exposure period, and the cages themselves had not moved significantly from the locations in which they were placed.

In South River, tissue concentrations increased significantly within a reach located 400-600 meters below the Wayne Avenue bridge. These increases occurred primarily in the non-methyl fraction and suggest the presence of a mercury source in the river channel at this point.

In Jones Hollow, tissue concentrations were higher than background levels and increased near the confluence with South River. The Jones Hollow clams also showed higher methylmercury concentrations that suggest a difference in methylation rates in the two river systems.

Assessing Garden Crops as an Exposure Route for Soil Mercury

William Berti, DuPont Central Research & Development
Dean Cocking, James Madison University Department of Biology

We are investigating mercury uptake from soil into garden crops and the significance of this potential route of human exposure to mercury. Our objective is to determine if soil-mercury is taken-up by vegetables at concentrations sufficient to be a health risk. Locations for two experimental vegetable gardens were identified at the Augusta Forestry Center, which is about 16 river-km downstream from Waynesboro, VA, along the South River. The 15 x 15 m floodplain garden had soil mercury concentrations ranging from 4.2 to 78 mg $Hg \cdot kg^{-1}$ dry weight in the surface 15 cm. A control garden located outside of the 100-year floodplain of the South River but relatively close to the floodplain garden had total soil mercury concentrations that ranged from 0.16 mg $Hg \cdot kg^{-1}$ to less than the Limit of Quantitation (LOQ was no greater than 0.12 mg $Hg \cdot kg^{-1}$ dry wt.). The soil mercury concentrations were determined in soil samples collected in November 2003 after the first growing season.

Each crop in the floodplain garden was planted in four replicate plots using a completely randomized design in 2003 and a randomized complete block design in 2004. The plots in the control garden were not replicated during the 2003 growing season; however, duplicate plots have been planted for 2004. Fully-grown, edible portions of lettuce, squash, cabbage, green pepper, spinach, tomato, sweet corn, onion, radish, and carrot were harvested in 2003. In 2004, beets, turnips, potatoes, scallions, cauliflower, bush peas, and bush beans were added to list of crops planted. Sweet corn was not planted in 2004 to make room for the additional crops.

In 2003, mercury concentrations in fresh tissue samples were generally less than the MDL (Method Detection Limit of 0.003-mg $Hg \cdot kg^{-1}$ plant tissue [wet weight basis]). Twenty-five of 53 samples from the floodplain garden and 9 of 12 samples from the control garden had non-detectable concentrations of mercury. Of the 31 samples with mercury concentrations greater than the MDL, all but three were less than the LOQ, which was about 0.1-mg $Hg \cdot kg^{-1}$ (wet weight basis). Three of five carrot samples from the floodplain garden had mercury concentrations that ranged from 0.188 to 0.103-mg $Hg \cdot kg^{-1}$. The carrots in 2003 were harvested after a flooding event that appears to have affected mercury concentration, based on 2004 results.

In 2004, mercury concentrations of bean, beet, pea, pepper, radish, red onion, and potato fresh tissue samples from both gardens were below the MDL. Mercury concentrations in samples of carrots, lettuce, scallions, spinach, and tomatoes from the control garden and unpeeled carrots from the floodplain garden were generally less than the MDL. Trace levels of mercury that were below the method LOQ in these crops harvested from the floodplain samples could not be quantified by the method used to measure mercury.

Using information from the US EPA Exposure Factors Handbook (1996), mercury screening level values of 0.3 and 0.8 $mg \cdot kg^{-1}$ were calculated for methyl mercury and inorganic mercury, respectively, for homegrown vegetables. These screening level values for mercury in vegetables were calculated using several conservative assumptions, such as a reference dose (R_fD) for methyl and inorganic mercury of 0.0001 and 0.0003 mg $Hg \cdot (kg\ Body\ Wt.\text{-}day)^{-1}$, respectively, a 30-year exposure duration, an exposure frequency of 350 $days \cdot y^{-1}$, a lifetime of 70 years, a body weight of 70 kg, and 100% mercury bioavailability. The LOQ of 0.1-mg $Hg \cdot kg^{-1}$ (wet weight basis) for the method used to measure mercury in the plants was about one-third of the methyl mercury screening concentration calculated from the information in the exposure handbook.

This demonstrates that for the two years of the study, trace estimated levels of mercury in the vegetables are not at concentrations sufficient to be a health risk.

Our plans for the garden include:

- Harvest and analyze fall crops planted 28-Aug-04 (radish, carrots, lettuce, spinach, turnips and beets)
- Evaluate the Limit of Quantitation (LOQ) for mercury in plants to insure that it is adequate to meet the study objective
- Collect floodplain and control garden soils in fall 2004 for mercury analysis
- Evaluate 2004 results and plan for 2005

Use of Flux Chambers for the Quantification of Dissolved Mercury and Methylmercury Flux from South River Sediments

Richard Landis, DuPont

Introduction:

Flux chambers allow direct measurement of chemical flux from discrete areas of sediment. Flux chamber measurements in the South River System can facilitate determination of which sediments are the most important contributors to methylmercury (meHg) in the South River system. The resulting data can be used to help our understanding of mercury cycling in the South River System.

There are two main objectives for the flux chamber work:

1) Direct measurement of the flux of dissolved Hg and meHg from several locations representing the range of total sediment Hg concentrations and environments in the South River System and reference sites.

2) Simultaneous comparisons of dissolved Hg and meHg measurements of flux from the sediment with surface water and pore water.

Accurate measurements of the flux of mercury species from the sediments will allow conclusions to be drawn regarding the relative contribution of sediments to the overall mercury budget of South River System.

Materials and Methods:

The flux chambers are designed as dual systems allowing for either replicate measurements or testing the effect of variable conditions. The chambers are constructed of Polycarbonate and Teflon, and go through an extensive cleaning process to remove any potential trace amounts of mercury that may be present in the chamber construction materials.

The collaboration between Dr. Gill with TAMU and DuPont has produced several improvements to Dr. Gill's original flux chamber design. The improved chambers have additional support plates and adjustable stilts to assist their deployment in soft sediments. Based upon some recent efforts by the USGS (Groundwater: January – February 2004: "Use of Electromagnetic Seepage Meter to Investigate Temporal Variability in Lake Seepage"; D.O. Rosenberry, R.H. Morin), the capability to measure very low water flow from the sediments has been added.

The deployment of the flux chambers consists of a one-hour equalization period followed by a five-hour sampling period. During the sampling period, samples are drawn at regular intervals until the oxygen content of the sample is 50% of the baseline measurement. The samples are analyzed for mercury species and possibly additional ancillary parameters relevant to mercury cycling.

South River Mercury TMDL

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The South River has been listed as an impaired water on Virginia's 303(d) list since 1998. The listing was based on a fish consumption advisory for mercury issued by the Virginia Department of Health. The 2004 impaired segment extends from the DuPont foot bridge to the Warrenton Power Dam (~129 miles) and includes the South River, the South Fork Shenandoah River, and small sections of both the mainstem Shenandoah River and the North Fork Shenandoah River. A Total Maximum Daily Load (TMDL) for this segment is due no later than May 1, 2010 as specified in 1999 Federal Court Consent Decree.

A TMDL describes the amount of a pollutant that a stream can assimilate and still meet water quality standards. TMDLs identify all sources of the pollutant, set pollutant allocations for both point sources (permitted discharges) and nonpoint sources (non-permitted discharges), and quantify the reductions needed for each source to meet these allocations.

The Virginia branch of the US Geological Survey recently prepared a proposal to develop a mercury TMDL for the South River. The proposal was shared with the South River Science Team and subsequently discussed in separate conversations with DuPont and EPA staff. DEQ also received a comment letter from DuPont suggesting alternatives to TMDL development as well as pointing out the need for close cooperation between the Science Team and the TMDL team.

DEQ discussed the proposed TMDL alternatives both internally and with EPA Region III staff. Based on existing EPA guidance, both agencies believe that there are no programs currently in place that are expected to result in attainment of the water quality standard and would thus justify a "TMDL not needed" classification. Also, DEQ does not anticipate pursuing any change in a designated use such as fish consumption unless it can be demonstrated that effluent limits and cost-effective and reasonable best management practices have been implemented to control the impairment. The best way to document such a situation is through the TMDL and TMDL implementation process.

DEQ believes it is prudent to start the TMDL development process now and with a three-year timeline will allow us time prior to submitting the TMDL to EPA to make any changes to the proposed approach if warranted. Also, once a TMDL is approved by EPA, adaptive implementation is an integral part of Virginia's TMDL program. This staged implementation approach allows for iterative implementation of corrective actions during the TMDL implementation phase.

With respect to cooperation between the TMDL team and the South River Science Team in sharing existing data, in identifying and filling data gaps and in locating mercury sources, DEQ has always envisioned the South River Science Team as a major partner and contributor in the TMDL development effort. DEQ expects to avoid duplication of effort in the USGS work and to target additional data collection where it is most needed based on the data already collected and analyzed by the Science Team. Thus DEQ anticipates a focussed effort to quantify the known loadings and processes causing elevated mercury in fish tissue. DEQ would like to explore DuPont staff's suggestion of having members of the Science Team act as the technical advisory committee during the TMDL development effort. DEQ agrees, and USGS has revised their proposal to more clearly state, that working together on this project will result in a more credible and effective effort.

Based on these comments and discussions, USGS revised their proposal to reflect the following TMDL approach:

- The TMDL will focus on the South River as the area of greatest concern and highest mercury levels.
  - Downstream data will be assessed to determine if significant additional loads are entering the system.
  - Air deposition rates will be assessed to determine if this load is significant.
- The TMDL will focus on methylmercury as the pollutant of concern.
  - Data collected to characterize methylmercury cycling/flux/production will guide the development of the ultimate TMDL endpoint (e.g. MeHg, total Hg or a surrogate)
  - Fish tissue criteria are expected to drive the allowable in-stream loads, i.e. the water column criteria are most likely not stringent enough.
- The TMDL process will include review of existing data, establishment of additional monitoring stations for MeHg characterization, data collection, creation of a conceptual model and finally creation of a numerical model to derive the allocations.

Public participation during the TMDL process will include technical advisory committee meetings as well as public meetings. There will be at least two public meetings, one at the beginning of the process and one to present the draft TMDL. Since the project is longer-term than typical TMDL projects, one or two interim public meetings may be necessary. The technical advisory committee will meet periodically on an as needed basis.

Questions

- What is the best way to formalize the link between the TMDL team and the Science Team? Propose members of the Science Team serve as Technical Advisory Committee for the duration of TMDL development. How to proceed (member selection, meeting dates, data exchange)?
- Feedback on proposed technical approach? Project elements? Public participation process?

SEDIMENTATION AND GEOMORPHOLOGY – PLAN FOR 2005

Jim Pizzuto and Kathrine Skalak, Dept.of Geology, U. of Delaware

Study Area

South River and its floodplain from Waynesboro to Port Republic, VA.

The Preliminary Sediment Budget – The Hypothesis to be Tested

Reconnaissance of the study area defined the following areas of sediment storage: “mature” floodplain, “immature” floodplain, channel bed, “near bank” and bank areas, and backwater areas. Estimates of the extent of fine-grained sediment storage in these areas, and estimates of fluxes between the storage areas based on literature values and preliminary field study, provided the basis for a preliminary budget of fine-grained sediment. During the next year, these estimates will be refined with actual data.

Some hypotheses to be are:

1. Bank erosion is a significant source of suspended sediment in the study area, though it is likely smaller than input from the total watershed area upstream of the study reach;
2. Suspended silt and clay entering the study area is stored for significant periods of time in the bed and “near-bank” regions before leaving the study area. It is expected that length of storage will be variable, but a mean value of this distribution should be on the order of 0.5 – 2 years.
3. Annual rates of sediment storage on “mature” and “immature” floodplains are low enough that they may be neglected in an annual budget.

Tasks to be Completed

These hypotheses will be addressed by completing the following tasks:

1. Map the distribution of sediment storage areas at present and in the past;
2. Monitor current rates of bank erosion;
3. Measure floodplain accumulation rates;
4. Estimate suspended sediment supply from upstream reaches;
5. Measure the volume of silt and clay in storage on the streambed;
6. Obtain basic geomorphic data for the study reach;
7. Develop and test methods to assess rates of exchange of fine-grained sediment between the channel perimeter and the water column;
8. Begin development of a 1+ dimensional numerical model to predict the movement of fine-grained sediment through the study area on decadal timescales.

South River Conceptual System Model Refinement 2Q 2005

Nancy Grosso, DuPont

A conceptual system model (CSM) is a representation of known or suspected contaminant sources, contaminant migration pathways, exposure mechanisms, and potential human health and ecological receptors. The reason for constructing a CSM is to determine complete pathways to receptors, and assess whether the complete pathways pose a risk. The existing risk or potential future risk may then be addressed. In a general sense, CSMs help us achieve a shared understanding by:

- Defining management objectives
- Guiding problem formulation
- Identifying potential sources and extent
- Analyzing exposure and effects
- Identifying sources of uncertainty in our analysis
- Guiding remedial planning and alternatives analyses

A preliminary CSM has been developed for the South River, which includes potential sources and Hg migration pathways as well as potential exposure pathways. More specific conceptual models, for example food web models or geomorphological models contribute to the overall understanding of the system represented by the Conceptual System Model. Another model - a very general watershed-scale annualized water balance has been prepared. A number of studies designed to evaluate potential sources and pathways are on-going and all feed into the Conceptual System Model.

DuPont has requested and received a proposal from Hydroqual, Inc. to further refine the CSM by incorporating mass balance calculations based on existing data. Hydroqual will evaluate the water budget, the hydrodynamics, the solids balance, and to the degree possible, the mercury mass balance, and compare to observed/existing data. The quality and quantity of existing data may limit the accuracy of the mass calculations, but at the very least, range-finding estimates will be conducted to give approximate qualitative patterns. The early modeling conducted in the 1980s that indicated a natural recovery mechanism is feasible will also be reviewed. The revised CSM will be supported with more detailed conceptual representations and a compilation of existing data such as temporal plots at individual stations or zones and spatial plots at specific times.

In order to conduct this study efficiently, Hydroqual will use the GIS-based relational database that is currently being constructed, and which is scheduled to be completed in early January 2005. The goal of the South River CSM refinement is to eliminate, if possible, some of the working hypotheses regarding Hg sources and migration pathways, and to define critical data gaps that need to be filled to better understand mercury in the river system. The refined CSM and the data gaps defined can also form a good basis for the numerical model development that is planned for South River /South Fork Shenandoah TMDL development.

Hydroqual will work closely with the Science Team and Expert Panel in order to maximize the quality of the refined CSM and to help define critical data gaps.

South River and South Fork of the Shenandoah River Hg

Sediment Assessment Methods

Ted Turner, VA DEQ

Background: As part of the ongoing monitoring program established in the late '70s, stream bed sediment has been sampled in the South and South Fork Shenandoah Rivers at approximately 10 year intervals, with 3 sampling events conducted to date. Sediment has been collected near the water line along the banks, at stations systematically located at 1 mile intervals along the South River downstream from DuPont, and then at 5 mile intervals on the South Fork of the Shenandoah River from Port Republic to the West Virginia state line. Sediment data were intended to indicate the rate of Hg transport through and out of the river system.

The Issue: Recently, concerns regarding the heterogeneity of the sediment collected in the past have prompted a reassessment of the collection methods previously employed. Primary among these concerns is that sediments collected in the past were comprised of differing ratios of fine particles and TOC content. Additionally, there was also concern that bank samples may not be representative of actively transported sediments that would tend to reside in the stream bed proper, and would therefore not yield the most useful comparisons of spatial and temporal trends along the river. Several previous attempts to collect bed sediments had failed using traditional techniques such as ponar grabs, since these devices do not work well in high gradient, rocky streams. The DEQ, in anticipation of the upcoming 10 yr. sediment collection event scheduled for 2007, sought to develop an alternative collection method that would yield more homogeneous samples to facilitate inter-station comparisons.

With input from the South River Science Team, a method has been developed and tested. During collection, a hand powered bilge pump that is used to collect the thin layer of sediment that covers the streambed, along with a copious amount of water. Approximately 4 gallons of a water/sediment mixture is collected into a 5 gallon bucket. This mixture contains sand which is excluded by stirring the water rapidly, then allowing it to settle for about 20 seconds. The supernatant is then decanted into a second bucket and allowed to settle for approximately 20 minutes (conveniently, about the time it takes to move from one station to another via canoe). At this time, the overlying water is discarded, and the sediment remaining is poured into a 250 ml plastic bottle.

Projected Path Forward: Preliminary sampling demonstrates that this method yields approximately 50 grams dry weight of sediment. It is anticipated that this will provide enough material to perform Hg, TOC and particle size analyses. There will be at least one trial run before the 10 yr. sampling, to provide for testing and method adjustment. If this approach proves effective and representative, it will also likely be used to sample deep pools and other features of the stream that have until now remained inaccessible.

Potential Future Studies of Mercury Accumulation in the South River

Marcella Kelly, William Hopkins, Don Orth
Virginia Tech, Department of Fisheries and Wildlife Sciences

Bioaccumulation of mercury in terrestrial amphibian components of the riparian ecosystem

Hg is a contaminant that readily accumulates in female tissues, and can then be maternally transferred to young. Once in the egg, it is highly teratogenic and can result in reduced reproductive success due to embryo-larval mortality and developmental malformations. Few studies have examined maternal transfer of any contaminant in amphibians. We are very interested in examining maternal transfer of mercury at the South River site and quantifying its effects on development and reproductive success of native amphibian species. We would examine multiple species representing different trophic positions, associated with the aquatic environment. For example, wood frog (*Rana sylvatica*) larvae are omnivorous grazers whereas most salamander larvae are carnivorous. We would compare a streamside salamander species with the wood frog to examine exposure scenarios based on different ecology of the species. This study would collect individuals from the contaminated site and a reference site and breed them under controlled conditions to assess maternal transfer of mercury, clutch size, hatching success, embryo survival, etc.

One of the other factors that is missing in amphibian ecotoxicology is the link between contaminants and population-level change. We can quantify female reproductive success by measuring maternal transfer, clutch size, embryo survival, larval survival, and metamorphic recruitment. We can then make higher level predictions about how these effects translate into population level changes. This could even be further enhanced if we can focus on a species that has been well studied (e.g., wood frog) where other data exists on their vital rates.

Additionally, because fish are highly mobile, a study of less mobile species, such as terrestrial amphibians, may provide more insight as to where the contamination is occurring.

Bioaccumulation of mercury in mammalian components of the riparian ecosystem

Methylmercury (MeHg) biomagnifies through the food chain as predators eat other organisms and absorb the contaminants that their food sources contained. Over time, an individual who consumes plants or prey contaminated with methylmercury will acquire levels greater than in either its habitat or its food. As a result, top predators will acquire greater body burdens of mercury than the fish they consume. Elevated mercury levels in predatory species may cause behavioral changes, neurological defects, reproductive failures, and/or mortality depending on degree of exposure. Detrimental effects will depend on the level of exposure, the species diet, and the susceptibility of the species (among other things). To interpret how environmental exposure in a river will accumulate up a food chain, wildlife benchmarks need to be established. These species could be used as "biosentinels" helping assess the risks to wildlife and allow landscape-level extrapolations of the hazards. Studying bioaccumulation in mammals is also relevant as a model for studying bioaccumulation in humans.

The terrestrial species most likely to be affected by mercury levels in rivers are those closely associated with the riparian environment. These include: the river otter (*Lontra canadensis*), the mink (*Mustela vison*), the beaver (*Castor canadensis*), the muskrat (*Ondatra zibethicus*), and the raccoon (*Procyon lotor*). Of these species, it is likely that the river otter, the muskrat, and the raccoon, occur in the South River. These three species would be interesting to study and compare as their diets go from mostly herbivorous (muskrat) to almost entirely piscivorous (otter). This study proposes examining mercury levels in these 3 species in the South river and in a reference population for comparison. In addition, population level affects can be examined through live capture and radio collaring of individuals. This would allow examination of general health, behavior, and reproductive success of exposed and unexposed individuals and allow population level predictions.

Continuation of the accumulation and mercury dynamics model development and analysis

We propose exploratory analysis of the BASS model and potential expansion to the Olin-Mills (Hg) site on the North Fork of the Holston River. James Vance can conduct this exploratory analysis next semester and this may lead us to attract other research co-sponsors in Fall 2005.

2005 Fish Tissue Monitoring – South River Mercury

Bill Van Wart, VA DEQ

Since mercury contamination was discovered in the South River system in the mid 1970s, fish have been collected regularly to determine the risk of human consumption. Samples were collected by DEQ in the initial characterization of the problem every year from 1977 to 1981. After the 100-year monitoring program was developed, AMRL collected fish in 1992, 1994, and 1996. DEQ and DGIF continued collecting fish in 1999 and 2002.

Until 1999, collections were targeted to trophic levels rather than individual species. One collection event could include ten fish of any species within a trophic group. Because of this, earlier data are inconsistent in sample size for each species. In 1999, we switched to a design targeting individual species.

We are proposing to sample the same sites sampled in 2002. The sampling will include the collection of samples from 17 sites on the South River, North River, South Fork Shenandoah River and main-stem Shenandoah River. Sampling will take place during spring 2005. At each location 10 fish from each of 3 trophic groups will be collected, as follows:

- Predators – smallmouth bass will be the target species, with largemouth bass as the alternate.
- Foragers – redbreast sunfish will be the target species, with rock bass as the alternate.
- Bottom Feeders – white suckers will be the target species, with carp as the alternate.

Target and alternate species will not be mixed for samples of a trophic group at each site.

Additional smallmouth bass (10 individuals each season) will be collected from Grottoes (STH004.21) in the summer and the fall to determine seasonal variation in mercury.

Channel catfish (10 individuals per site) will be collected from the following locations:

- SSF078.24 (Shenandoah, VA)
- SSF054.20 (White House Landing)
- SSF010.18 (Karo Landing)
- SHN038.48 (Rt. 17/50 Landing)

Trout (10 individuals per site) will be collected from the South River at designated stocking locations in Waynesboro and Grottoes. In addition, ten individuals will be collected from the fish hatchery prior to stocking and ten individuals that are marked holdovers from the previous year's stocking will be collected from Waynesboro.

Table B1.1 – Sampling sites and collection goals.

Station	Trophic Groups	Seasonal Smallmouth	Channel Catfish	Trout
STH026.12	30			
STH025.10	30			20
STH023.73	30			
STH022.75	30			
STH020.44	30			
STH014.49	30			
STH004.21	30	20		10
NTH004.10	30			
SSF100.10	30			
SSF078.24	30		10	
SSF063.17	30			
SSF054.20	30		10	
SSF037.60	30			
SSF020.70	30			
SSF010.18	30		10	
SHN038.48	30		10	
SHN022.63	30			
Hatchery				10
Total	**510**	**20**	**40**	**40**

Total sample numbers to be analyzed are <u>610 samples for total mercury, and 61 samples (one for each species at each site) for methyl mercury</u>.

Examining impacts of mercury contamination on birds in the Shenandoah River watershed.

Daniel Cristol, Biology Department, College of William & Mary

1. Overview: A 3-year study designed to detect and quantify effects of mercury contamination on the avifauna of the Shenandoah River. Belted Kingfisher and Tree Swallow have high potential for mercury (Hg) impact, so Year 1 focuses on reproductive success and Hg availability in these species. Bird diversity surveys will also be carried out, and Hg availability will be examined in 3 additional species. In Years 2-3, sample size increases for target species, and more species and their prey will be examined as necessary.

2. Objective: To compare the reproductive success and physiological condition of individual birds between mercury contaminated sites and uncontaminated sites in the same watershed. In addition we will compare the species richness of the avian communities to identify severely impacted populations. We will also provide a robust quantification of the current levels of mercury availability in the watershed's avifauna.

3. Plan of work: We will erect 200 swallow nesting boxes along the water's edge, evenly distributed across the contaminated and uncontaminated sites. Nests (n = 20 each from contaminated and uncontaminated sites) will be monitored to compare basic reproductive health parameters. Hg accumulation in adults and young will be measured in blood and feathers, as well as one egg per clutch. We will employ the ligature method, in which prey are harmlessly collected from the throats of nestlings, to determine the species and biomass of invertebrate prey. In Years 2-3, after the swallows have recruited to the boxes in large numbers, we may destructively sample 15 adults and 15 young to determine how egg, feather and blood Hg correlate with levels in kidney, brain, liver and breast muscle. We may also sample the prey base directly to assess mercury availability if these data are not available.

We will locate Belted Kingfisher nests at the contaminated and uncontaminated sites from a boat. The nesting cycle will be monitored using a burrow probe to examine nest contents by video. Nests will be entered from above by digging to allow direct sampling of blood from young and attending adults. Kingfisher hunting success and prey will be identified through a spotting scope, allowing us to pinpoint the size and numbers of fish fed to the young. Expected annual sample size of 5-10 nests per site will necessitate 2 years of study on kingfishers for a final sample size of 10-20 nests from each of contaminated and uncontaminated sites.

We will do preliminary screening of the entire avian community to identify major effects such as extirpation of entire populations from the contaminated study sites, or extreme reduction in density. This will be done with 30 point count surveys of breeding birds in Year 1.

Using mist nets we will sample blood and feathers from 10 each of 3 breeding migratory species that forage on insects near the water. We will also sample an egg from 5 nests of each of these species. This sampling will be repeated on uncontaminated sites for a total of 20 adult and 10 eggs of each species.