### <u>Agenda</u> South River Science Team December 11, 2002. Harrisonburg, Va. 9:00 a.m. – 3:00 p.m.

Time	lssue	Responsible
9:00	Welcome	Don Kain
9:15	Soils / floodplain investigation proposal	Bill Berti
10:15	Update on 2002 fish tissue / water column results	Billy Van Wart Ted Turner
10:30	Break	
10:45	Basic hydrodynamic model	Nancy Grosso Mike Sherrier
11:15	Sediment Sampling & Coring Results	Erin Mack Dick Jensen
12:00	Lunch	
12:30	Floodplain CD	Dick Jensen
1:00	Corbicula Update	Tom Benzing
1:30	Newsletter / Communications	Mike Liberati
1:45	Publications – scope / outline	Ralph Stahl
2:15	Working Hypotheses	Ralph Stahl
2:45	Wrap-up, next meeting	Ralph / Don
3:00	Adjourn	

### Meeting Summary

**Welcome, Introductions.** Attendance was reduced, due to an overnight ice storm. The meeting started at 10:00 a.m and ended shortly after 2:00 p.m. Don Kain welcomed the attendees and outlined housekeeping and the agenda for the meeting. Self-introductions were made. Attendees are listed on Attachment 1. Don also informed all that the summary of the October 8-9 meeting was available and had been sent to all attendees electronically. If you wish to have a CD with summaries of all Science Team meetings to date, please contact Don.

**Soils / floodplain investigation proposal.** Bill Berti, DuPont gave back-to-back presentations on floodplain soils and potential for crop uptake and transmission of mercury to those who eat the crops (refer to Presentations folder). The first presentation outlined aspects, such as literature review and the conceptual approach for conducting a floodlpain crop study. The second presentation included a more specific "scope of work"-type outline for a crop study in the South River floodplain and included the following:

- Study objectives
- Recommendations for greenhouse and garden approaches
- Site selection criteria
- Target vegetables
- Processing and analytical protocols
- Sources of guidance
- Projected timeline

Dean Cocking of James Madison University (JMU) has conducted considerable work on soils, plants and animal mercury levels in the South River floodplain during the past 15 years and has provided the Science Team with a proposal for a study with many similarities to the DuPont proposal. One consideration would be to proceed with a joint study, incorporating concepts from DuPont's and JMU's proposals. Proposals from DuPont and JMU are included as Attachments 2 and 3, respectively.

Attendees were in favor of a study, but agreed to wait until the proposal was discussed with Virginia Department of Health (VDH) (whose staff were unable to attend the meeting) before proceeding. Don Kain will set up a conference call between DuPont, DEQ, JMU and VDH shortly after the first of the year.

**Update on 2002 fish tissue / water column results.** DEQ's fish tissue results from 2002 are not yet available from the lab. They are expected in February 2003.

DEQ requests input for follow up work to address issues and questions from the summer 2002 intensive water column sampling and bimonthly clean metals runs. If there is sufficient need to conduct follow-up sampling, DEQ will develop a sampling plan to present to the science Team.

**Basic hydrodynamic model.** Nancy Grosso presented an update to the South River conceptual model and hydrology (see Presentations folder). Considerable effort is underway to assemble a complete hydrologic picture of the river. Based on known inputs

and drainage areas, the base flow of the South River at Hopeman Parkway (at 52 cfs) is 16 cfs higher than expected. Likely contributors to this base flow include dischargers and ground water input. Nancy is in the process of gathering discharger data, but asked for input on methods to obtain flows from ground water, springs, and tributaries. Dean Cocking mentioned a software package (STELLA?) that may be of use in this application. Nancy will look into this and will continue to update and refine the model.

**Sediment Sampling & Coring Results.** Erin Mack presented preliminary results for the fall 2002 sediment core sampling in the Dooms area (Presentations folder). Data suggested relatively low levels exist in a fairly uniform pattern in shallow sediments, but there appear to be 1-2 bands of higher concentrations (up to 500 ppm) at greater depths. Dating (cesium and lead-210) results are due in February. Dating results and follow-up sampling proposals will be presented at the February Science Team meeting.

Dick Jensen suggested that the deposition of high concentrations at certain depths may be variable and related to different erosional and sediment patterns. He will pursue the possibility of follow-up work to address this issue.

**Floodplain CD.** Dick Jensen shared the updated floodplain CD and gave a brief demo of the information included in this interactive report. In addition to the original mud mapping information, similar overlays, with maps, photos, and comments, now exist for floodplain features, including dwellings, crops, livestock holding, etc. These features are easily identified within flood boundaries along the river. Dick shared paper and CD copies of this report.

**Corbicula Update.** Tom Benzing provided a recap of work completed to date on the <u>Corbicula</u> project, including a photo history of field and laboratory activities (Presentations folder). Samples have been collected, clams shucked, and tissue sent to the lab. Preliminary data will be available shortly after the first of the year, followed by a presentation at the Spring 2003 meeting.

**Newsletter / Communications.** Mike Liberati shared circulation information regarding the newsletter. The fall 2002 issue was mailed to about 400 addressees, and another dozen or so individuals or groups have requested to be added to our distribution. The next issue will be in the May/June timeframe. Suggestions for articles are solicited. Ralph Stahl suggested that articles on the sediment coring and the JMU *Corbicula* work be considered. Tom Benzing suggested that the newsletters be available on the web. Don Kain agreed to see if he could get a link added to the DEQ web site. Mike will provide .pdf files of the newsletters to Don for this purpose.

**Publications – scope / outline.** Ralph Stahl has assembled an outline for a manuscript describing the multi-faceted work of the Science Team to date (Attachment 4). This paper would "tell the story" of the South River mercury studies and the collaborative approach of the many stakeholders. The "publication team" will review the outline and work together after the first of the year to identify focus areas which need to be developed to support the overall manuscript. Ralph will begin looking into possible journals or other publications that may have an interest in this type of manuscript. We will soon need to decide whether to pursue "hard-core" scientific/technical journal or technical "magazine"-type publications.

**Working Hypotheses.** Ralph Stahl presented an updated "working hypotheses" outline (Attachment 5) to the group. A number of new concepts/actions have come out of discussions at recent science team meetings and are highlighted on the attachment. Ralph asked that participants review the outline and provide comments.

**Next Meeting.** Don suggested the winter or spring meeting be held at the DuPont facility in Waynesboro and that a tour of the site be included on the agenda. Most members of the science team have not been on the DuPont property. The tour will acquaint participants with the areas described in the RFI presentations at earlier meetings. Brenda Kennell suggested the meeting at DuPont be held in April, during warmer weather.

# The next meeting was set for February 11 at DEQ in Harrisonburg (later moved to February 25). Meeting will begin at 9:00 a.m. and end at 3:00 p.m.

### Meeting "Action Items."

- Don Kain will see if we can assemble DEQ WQ data on South River and DuPont sulfate values from the DuPont discharge and provide to Ralph.
- Brenda Kennell will make arrangements for meeting and tour at DuPont in April
- Don will check with NRCS in Verona for high quality aerial photos of the South River and floodplain.
- Ted Turner will see if he can find any selenium data on South River.

### Attachment 1. South River Science Meeting Attendees December 11, 2002

Name	Organization	Phone	E-mail Address
Don Kain	DEQ	540-574-7815	dgkain@deq.state.va.us
Bill Berti	DuPont	302-366-6762	William.r.berti@usa.dupont.com
Mike Liberati	DuPont	302-892-7421	Michael.r.liberati@usa.dupont.com
Stephen Reeser	VDGIF	540-248-9360	sreeser@dgif.state.va.us
Bill VanWart	DEQ	540-574-7861	wjvanwart@deq.state.va.us
Ralph Stahl	DuPont	302-892-1369	ralph.g.stahl-jr@usa.dupont.com
Dick Jensen	DuPont	302-547-6286	richard.h.jensen@usa.dupont.com
Ted Turner	DEQ	540-574-7858	rtturner@deq.state.va.us
Tom Benzing	JMU	540-568-2794	benzintr@jmu.edu
Erin Mack	DuPont	302-366-6703	elizabeth-
Paul Bugas	VDGIF	540-248-9360	pbugas@dgif.state.va.us
Brenda Kennell	DuPont	540-946-1320	Brenda.I.kennell@usa.dupont.com
Dean Cocking	JMU	540-568-6566	cockinwd@jmu.edu
Nancy Grosso	DuPont	302-992-6783	Nancy.r.grosso@usa.dupont.com

### Attachment 2. DuPont Proposal

### Request for Input

Exploratory Effort to Evaluate Plant Uptake of Mercury from Floodplain Soils

### Hypothesis:

Mercury in floodplain soils is not available for uptake by crops in sufficient levels to be a health risk.

### Background:

Much of the mercury in the South River system is assumed to be bound up in the floodplain soils and is unavailable for plant uptake (LMS, 1981, 1982). Background information from additional sources (e.g., EPA Biosolids Rule, 1995, NAS, 1997, Mercury Report to Congress, 1997) support this assumption. However, the public may be skeptical without empirical data. The current landuse survey suggests some backyard gardening and farming does occur in the floodplain. Various tasks to obtain empirical data to address concerns that may be raised by the public are proposed below to start this discussion.

### Goal:

To collect sufficient empirical data to support hypothesis that mercury in floodplain soils are not available.

### Proposed Tasks:

- Develop and execute a sampling plan to tests soils for Hg and MeHg at the forestry station. Sampling should be sufficient to quantify a statistical difference. Samples should be taken on the surface and at depth to characterize vertical profile/differences.
- If there is sufficient difference between the floodplain and upland area, plant relevant crops in the floodplain area (single or multiple growing seasons). Crops should include ones that allow for distinction between windblown dust and actual uptake from the soils.
- Harvest these crops and determine, mercury content in various components, e.g., surface, roots, leaves.
- Collect samples from wayside stands and local "factory" and perform similar analyses.

### Timing:

Summer of 2003

### **Resources:**

DuPont

### **Request for Input:**

Is it reasonable to try to test this hypothesis? Are the proposed tasks appropriate? What other tasks should be considered?

### **References:**

Mercury contamination of the South, South Fork Shenandoah and Shenandoah Rivers. State Water Control Board, Basic Data Bulletin 47, March 1980.

- Mercury contamination of the flood plains of the South and South Fork Shenandoah Rivers. Virginia State Water Control Board, Basic Data Bulletin 48, May 1981.
- Engineering feasibility study of rehabilitating the South River and South Fork Shenandoah River. Vol I., Lawler, Matusky & Skelly, 1981.
- Engineering feasibility study of rehabilitating the South River and South Fork Shenandoah River. Vol II., Lawler, Matusky & Skelly, 1982.
- Cooking, et al, 1991. Water, Air, and Soil Pollution 57-58: 159-170
- USEPA (1995) Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule, EPA/832-B-93-005
- NAS (1996) Use of Reclaimed Water and Sludge in Food Production
- Hg Study Report to Congress, Volume III:Fate and Transport of Mercury in the Environment EPA-452/R-97-005 (12/97)
- U.S. Department of Energy (1998) Empirical Models for the Uptake of Inorganic Chemicals from Soil by Plants

Attachment 3.

## Survey of Mercury Uptake by Domestic Garden Plants in Mercury Contaminated South River Floodplain Soils

Exploratory Preliminary Proposal - November 22, 2002

Dean Cocking, Department of Biology, James Madison University

# This is not a contract proposal or formal agreement and does not constitute a legal commitment by James Madison University or the primary investigator.

Objective: Determine whether washed and unwashed common garden plant species are susceptible to mercury accumulation when growing in South River floodplain soils.

Site: The study will be carried out at the Augusta Forestry Center in Crimaora, VA. Mr Larry Estes, Forestry Assistant Senior, was contacted and two test garden locations were examined. One is on the lowland flood plain, which has been submerged numerous times in recent history and is suspected to contain Hg contaminated soils. The other is up-slope closer to Route 340 and according to Mr. Estes, it has not been flooded for a long time. Superficially the soils appear similar and therefore it probably has received some river sediments in the past. Soil samples were collected on November 20, 2002, and will be tested in our lab for Hg to determine the suitability of the sites. Both garden sites have water available for irrigation and/or application by sprinkler systems.

Experimental Design: Five different species will be planted in a randomized design with two blocks of each species seeded in each garden.

Species: This will be determined at a later time, but the following are possibilities:

- 1) Spinach This leafy species has been used in our growth chamber experiments and the leaf tissues are consumed by humans.
- 2) Carrots This tap root species has been used in our growth chamber experiments and the roots are consumed by humans.
- 3) Tomato This is a commonly planted garden species. While it is highly unlikely that Hg will be found in the fruits, it is a plant that would be of interest to the public. (A variety with small fruits would be chosen to facilitate air drying the samples.)
- 4) Red Skin Potato This is a small tuber producing garden species which might accumulate Hg. The effect of washing the tissue prior to consumption would be particularly important.
- 5) Onion This would be the only monocot species in the study. The edible portion, the bulb formed from leaf and stem tissue, is under the soil and potentially exposed to Hg uptake. Our previous studies have shown that fibrous onion roots have associated Hg which is probably both adsorbed to surfaces and internal.

Planting: This would occur in the Spring, 2003. The crops will be grown to normal agricultural harvest.

Sampling: Leaf, root, and edible portion (fruit, tuber, bulb) tissues will be collected at optimal harvest time for each species.

Sample processing: Split samples with washed and unwashed tissues will be obtained. The "unwashed samples" will be rinsed to remover obvious superficial soil, but not "kitchen" cleaned. The "washed" samples will be cleaned with criteria to be developed. The goal, however, would be to simulate what a reasonable consumer would consider to be adequate washing for food preparation. Because the focus of the experiment is on potential inclusion in dietary materials, the samples will not be acid washed prior to analysis (If resources allow, some acid washed samples will be prepared, but this would be a 50% increase in tissues for analysis if done for all sample combinations.)

Analysis sample preparation: Washed tissues from each of the blocks will be air-dried, fragmented and manually mixed. The mixed samples will then be sub-sampled and three aliquots ground in a Wiley Mill to produce a powdered sample suitable for analysis. (50 g supply of each would be desirable;  $\sim 1$  g / digestion has worked in the past) These air-dried samples will be stored in plastic vials. The plastic vials will be placed in a container with silicon gel (not heated) for 24 hr prior to capping. Vials opened during subsequent analyses would have this process repeated before continuation of storage.

This would result in:

2 plots (Hg contaminated vs uncontaminated control)

- X 2 blocks per plot
- X 5 species
- X 3 tissue types
- X 2 washing conditions
- X 3 aliquots

or a total of 360 samples for analysis

Sending them to the DEQ laboratory at \$125 per number = \$45,000 Our lab is not EPA certified and therefore gives "screening level" results.

My suggestion would be for us to analyze the samples as a student project and reserve the prepared dried samples. Depending on the capabilities of DEQ, some selected samples (preferably at least a few dozen) would be sent for comparison of techniques. If "samples of interest" are found in the survey, then they could be sent for certified analysis. (DEQ analysis costs are not included in the budget.)

Analysis: Our laboratory has a Perkin Elmer FIMS cold vapor atomic absorption spectrophotometer. Our digestion procedure has been a concentrated sulfuric/concentrated nitric acid "leaching" process. It has not resulted in the complete digestion of all cell wall tissues in plant materials, but has obtained reasonable relative numbers in the past. Some additional calibration and comparison with standards is needed because physically the lab was moved to a different location from where previous work was done.

#### Budget:

I do not presently have a student lined up for this project. Therefore, everything that we discuss is contingent on the availability of personnel. Because of increased of grant supported research within the department and other external summer research opportunities, it is virtually impossible to find technician help for free. The combination of a stipend and academic credit has been attractive in the past year. Because the plants will require the summer growing season to mature, this project by its nature will include both Summer and Fall 2003 work. Preparation for the project in the Spring means that I would have to commit as the Primary Investigator to the calendar year, 2003 with the final objective being a report that would be completed by May, 2004, the end of the Spring academic semester. In order to increase the chances of recruiting a suitable student, an early decision is necessary if the project is to be carried out this year.

#### Personnel:

Undergraduate Research Student technician \* Summer Stipend # \$3,500 for 10 weeks Travel allowance and lodging\$1,000 (approximately) # \* Fall stipend \$2,000 # based on JMU NSF Research Experience for Undergraduate support, 2002 Primary Investigator – serve as student mentor and hands on work with project Project stipend paid in summer  $3,789 \quad 1/2 \text{ month salary } (75,779 / 10 \text{ mo})$ \$ 697 **FICA** University overhead on salaries (\*) \$4,087 (\$9,289 x 44%) TOTAL PERSONNEL \$15.073 Supplies for sampling and analysis \$1,550 Travel \$1,500 58 mile round trip to Crimora, VA x 20 = 1160 miles and professional meeting report Equipment maintenance \$1,000 TOTAL NON-PERSONNEL \$4,050 **GRAND TOTAL** \$19,123

This assumes that the VA Department of Environmental Quality will cover costs of Hg analysis in Richmond laboratory and that there would be no charges for the space, water, and garden maintenance at Crimora. We would plant and harvest crops.

NOTE: This project would be carried out as basic scientific research and there would be no restrictions on the public presentation of the results at scientific meetings and through publication

### Attachment 4 (Ralph Stahl).

# Assessing Long-Term Mercury Dynamics in the South River, Virginia: Results of a multiple stakeholder approach.

### I. Introduction / Background

Site history Genesis of the mercury problem Initial decisions on remedy Establishing a multiple stakeholder working group Use of outside experts

### II. Methods

Data Collection and Evaluation General hydrogeology Sampling and locations Chemical analyses Surface water Groundwater Sediments (includes mud mapping) Floodplain Biota Conceptual Model Development Sources Pathways Receptors Exposure Assessment Statistical analyses

### III. Results

### Surface waters

Groundwater Sediments Floodplain Biota Exposure Assessment

### IV. Identifying Data Gaps

Developing working hypotheses Refining the conceptual model Pathways of continued Hg input into the river system Surface water Hg concentrations Groundwater Hg in sediments at depth Floodplain Point sources (e.g. landfill) Hydrodynamics of South River Additional biological sentinels

## V. Conclusions and Next Steps

- VI. Acknowledgements
- VII. References

## Attachment 5 (Ralph Stahl)

Working Hypothesis	Experimental Concepts / Actions			
<ol> <li>Ongoing sources of Hg to the South River are present and have prevented the expected decline of Hg in fish tissue. The potential sources for existing Hg inputs to the river can be separated into: (a.) existing inputs potentially derived from historical releases; and (b.)</li> </ol>	<ul> <li>a. Utilize information on Hg in water column collected during bi-monthly sampling of South River for TMDL.</li> <li>b. Examine potential for old landfill near 2<sup>nd</sup> st. bridge area to have received Hg contamination and now act as a source to the South River.</li> </ul>			
existing inputs based on current releases.	<ul> <li>c. Determine significance of floodplain soils as source of Hg to South River.</li> </ul>			
Potential pathways for historical inputs include: Groundwater     Sediments	d. Develop approach to conduct intensive sampling of water column downstream of DuPont footbridge to verify and expand on results obtained by Ralph Turner.			
<ul> <li>Floodplain soils</li> <li>Landfills</li> </ul>	e. Review historical records and / or obtain anecdotal results of dredging activities in South River after flooding events.			
<ul><li>Dumping</li><li>Dredge spoils</li></ul>	f. Consider additional sampling of plant environs to determine if Hg inputs are occurring; stormwater ?			
<ul> <li>Potential pathways for current inputs include:</li> <li>Groundwater</li> <li>Atmospheric deposition</li> <li>Point source discharges</li> <li>Non-point source discharges</li> </ul>	<ul> <li>g. Conduct sediment studies / coring at selected locations on the South River.</li> <li>h. Determine whether pockets of metallic Hg are present in the main channel close to the DuPont plant. Pan for Hg in sediments.</li> </ul>			
<ul> <li>Dumping</li> <li>Fertilizers</li> </ul>	<ul> <li>i. Ion profiles and / or temperature profiles in the South River to investigate potential locations for GW input.</li> <li>j. Conduct RFI on plant site and review results with team (groundwater pathway).</li> </ul>			
2. Water quality conditions (e.g. sulfate, chloride additions) have changed in the South River over the last 20 years in a manner that favors the formation of MeHg and this has resulted in continued elevated Hg concentrations in fish tissues.	a. Review information developed by Friends of the Shenandoah and DEQ – look for trends and correlations.			
3. Observed changes in fish tissue Hg concentrations result from changes in the dietary preferences of important fish species in the South River during the last	a. Conduct fish dietary studies in South River and other locations (as reference).			

20 years (locational differences).		
4. Wetland areas in the South River	a. Map locations and test against locations where fish tissue levels	
watershed have increased during the last	have remained high. Review historical maps and photos.	
20 years and are contributing larger		
amounts of MeHg to the surface water.	b. Consider in-situ studies of MeHg production in selected wetland	
-	iocations, develop nux estimates.	
	c Wetland sediment coring analysis and dating	
	ongoing	
	ongoing.	
5. Changes in water levels, providing a	a. Map flow / flood conditions over the past 20	
regular wetting and drving cycle leads to	vears against fish tissue data results for the same	
periodic increased production of MeHg in	period.	
the South River (similar to filling and		
draining of lakes and reservoirs) which	b. Consider in-situ studies in floodplain.	
in turn keeps levels in fish tissue from		
declining.	c. Conduct plant uptake (total and MeHg) and soil	
	characterization studies in the floodplain.	
6. Clearing of forested areas (or other	a. Review historical aerial maps to look for trends.	
land use activities that may expose		
deeper soils) along the South River	b. Consider in-situ studies in floodplain.	
watershed over the last 20 years has		
altered the availability of Hg from soils in	c. Conduct plant uptake (total and MeHg) and soil	
these areas and resulted in increased	characterization studies in the floodplain.	
inputs of total Hg to the surface water.		
7. The observed changes in fish tissue	a. Adjust statistical methods to account	
Hg levels over the last 20 years result	for size, weight of fish and analyze	
from sampling artifacts and variability,	data accordingly.	
e.g. changes in tissues sampled and	b. Determine whether season and gender	
method of collecting tissues, changes in	have an influence on the level of MeHg	
analytical methods and laboratories, or	in fish tissue.	
changes in data inputs – non detects vs		
zero, etc.		
8. Changes in agricultural practices in	a. Consider analyzing for Se in floodplain soils,	
the floodplain and watershed have	sediments and the water column.	
changed minimal Se levels in the South	b. Review clean metals data and see if Se has	
River and thereby increased the	been analyzed (and / or detected).	
availability of Hg in the system.		
9. The South River has an unusually low	a. Review clean metals data and see if Se has	
level of Se organics or other constituents	been analyzed (and / or detected).	
which provide a mechanism for Hg to be	b. Review non-Hg water quality data.	
more bioavailable.		
10. Mercury levels in South River biota	a. Consider additional biological indicators –	
have actually decreased over the past 20	Corbicula or other.	
years but are not reflected in the fish.	b. Review Hendrick's insect data from past	
	study.	