South River Remedial Options Program (ROP) and Bank Stabilization / Restoration Pilot

Initial Tasks to Assist in Screening of Remedial Alternatives

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Background

Over the past several years, a significant data set has been collected to refine our understanding of the physical, chemical and biological elements of the South River system. While many studies are ongoing, it was recognized that a view toward possible remedial actions was needed in order to begin focusing certain study objectives or to optimize current investigation programs. This briefing paper summarizes a plan for evaluating remedial technologies and their potential application to specific areas of the river.

Overall Remedial Objectives for the South River

- Reduce fish tissue Hg levels to concentrations that would allow consumption by humans
- Ensure protection of aquatic and terrestrial ecology with respect to Hg exposure

Controlling Potential Ongoing Sources

Currently, there are a number of potential sources of total mercury to the SR aquatic system or within the aquatic system, some of which may be dominant in some reaches and not others. These include:

1. Ongoing source of mercury by eroding banks that reintroduce the floodplain inventory to the aquatic system.
2. Dissolved Hg detected in plant site outfalls
3. Ongoing source of mercury through wetting and drying cycles of the banks that dissolves / desorbs total mercury
4. Introduction of dissolved mercury into the system by advective flux of groundwater through mercury-bearing sediments or from alluvial groundwater itself
5. Storage of mercury in fine-grained deposits in long pools, bench deposits, deposits associated with point bars, and remnant deposits of historic mill dams that are in contact with the aquatic environment.
6. Partitioning of mercury from fine-grained in channel sediments resident in gravel and cobble bed interstices to pore water and subsequent transport of dissolved mercury through sub-bottom stream lines into the water column (stream pumping / Hyporheic flow).
7. Mercury released from in channel coarse deposits due to physical bed movement and release of formerly trapped pore water (turnover) or fines.
8. Methyl mercury production within the wetted perimeter of the river in low DO environments, in discrete patchy thin zones just below the sediment water interface, in the periphyton biomass, and within biofilm materials.

Using the hypotheses on potential sources of total mercury and methyl mercury, and the manner in which Hg may cycle through the system a number of challenges with respect to remediation in the aquatic system were identified. Control of potential sources or bioavailability were rephrased into a series of five questions and a lead for each of these was identified.

1. What can be done to reduce or cut off introduction of total mercury from the floodplain sediments through eroding banks?
2. How can we inhibit Hg release from soil and sediment into the biological system in general?
3. What can be done to reduce dissolved mercury in water?
4. What can be done to inhibit methyl mercury production?
5. Is it possible to tweak the food web to reduce Hg concentrations in the food web? How would this be done?

Criteria for Evaluation of Actions based on the USEPA NCP Criteria

The remedial action:

- Achieves the remediation objectives
- Complies with laws and regulation
- Is effective in the long-term in protecting human health and the environment
- Reduces toxicity (bioavailability), mobility or volume
- Is technically feasible and can be implemented
- Protects workers, the community and environment during implementation
- Has costs that are commensurate with benefits of the action
- Is accepted by the Public and by Regulators

Approach for the Remedial Options Program (ROP)

The steps below were initially identified for formation of a ROP. As our understanding of the river system as well as the technology limitations/capabilities evolve, this approach will also evolve.

1. **Brainstorm** on current Hg treatment technologies that may have application to the South River (completed).
2. **Initial Technology Screening** A draft approach to address each of these questions was prepared, including technology review, laboratory studies, field investigations or monitoring programs to advance the understanding of feasibility for the SR (completed).
3. **Combine / Prioritize Tasks**. The teams met to discuss the approaches and to prioritize or optimize activities/tasks (completed).
4. **Formulate an Approach to Technology Evaluation**. A draft program was prepared that summarizes our initial approach (see below).
5. **Finalize the Team Members.** Augment the team to include interested individuals from the SRST to provide input and comment to the plan.
6. **Obtain regular feedback from Expert Panel on Plan**: Seek input from the expert panel in terms of content, logical sequence of activities, etc.
7. **Identify Specific Locations or targeted Hg sources in the River System that may be amenable to remediation and test appropriate technology (ies).** The conceptual system model is updated as new information becomes available. As sources of mercury (including bioavailable mercury, methyl mercury) are identified, the feasibility of applying some remedial technology will be assessed. This will be accomplished through a remedial alternatives analysis drawing from the larger set of technologies identified through the ROP process.

Proposed Short Term Tasks

As a result of the initial prioritization of tasks, a set of tasks is proposed

Papers Studies (completion of this set by June 2009)

- Conduct a review of full-scale or pilot remedies that have been conducted at Hg-contaminated sites and produce case study summaries (Turner, *in progress*)
- Conduct review of current state of technology to physically or chemically remove mercury from water (Dyer)
- Revisit and update review of the state of the art in mercury stabilization (Dyer)
- Review literature for information on how nutrients affect the biogeochemistry of a Hg-rich system with applications to the SR such as the STP and agricultural runoff (Flanders, *in progress*)
- Conduct review of literature to identify ligands (e.g., natural DOC, Se) shown to reduce bioavailability (Flanders on Selenium *completed*, Dyer on others)

- Review the literature of river restoration projects to assess whether stated objectives have been met (Flanders, *in progress*)
- Review literature for examples of food web management to reduce bioaccumulative contaminants in predatory fish (Newman)

Laboratory Testing or Specialized Characterization/Speciation and Treatment Studies for Aqueous and Solid Phases

- Conduct full characterization of target sediments and soils to understand Hg speciation and physical/chemical properties. Conduct studies to assess the effects of wetting and drying on the solubility of soil associated mercury (University of Waterloo, 2008-2009)
- Speciate mercury in 001 discharge (DuPont – 4Q08)
- For water treatment, select one or more ligands/sorbents for laboratory or mesocosm evaluation based on efficacy, availability/abundance/cost, and toxicity (side effects). Design experiments to verify efficacy and absence of deleterious / unacceptable side effects
- For soils and sediments, screen possible treatment chemistries in lab for viable candidates. Use extractable dissolved mercury as a surrogate for methyl mercury in screening tests (University of Waterloo)
- Test the effectiveness of powdered activated carbon and organoclays in reducing the bioavailability of Hg in soil and sediment (Exponent / University of Maryland, 2008)

Laboratory Testing or Specialized Characterization Bioavailability and Methylation Studies

- Evaluate which analytical measure(s) best represents "bioavailability" (e.g. merlux bioreporter response, reactivity, molecular weight, uptake by test organism) (Rutgers)
- Measure inherent *potential* rate of methylation through a ^{203}Hg assay and demethylation through a ^{14}C assay, which are inexpensive with well established protocols. (Rutgers)
- Explore the feasibility of developing / develop a probe to measure in-situ pore water concentrations of different mercury species (University of Texas at Austin, 2009)

Pilots

- Bank Restoration-Stabilization Pilot to assess efficacy and feasibility of restoration techniques to isolate mercury in bank soils from eroding into the river

Discussion

1. ISOLATE Hg-CONTAINING SOILS IN IDENTIFIED BANKS

What can be done to reduce or cut off introduction of total mercury from the floodplain sediments through eroding banks?

Currently, the reintroduction of mercury into the system from eroding banks is one of the leading hypotheses for potential on-going sources, at least in certain reaches of the river. This hypothesis is based on mercury profiles of the bank, the way in which banks are eroding, and sequential extraction tests and "shake and bake" experiments. The Bank Restoration - Stabilization Project will begin to explore what might be done to manage bank soil erosion to the river. A secondary objective of this project is to cut off communication between mercury in the bank and the aquatic system. We will attempt to assess whether the physical stabilization also isolates dissolved phase mercury in the banks from the river. The reach downstream of the footbridge to Rockfish Run (east bank) has been selected, and data gaps have been identified. The goal is to have a 90% design by the end of 2008. Anticipated construction completion date is 3Q09.

2. CONTROL RELEASE OF Hg FROM SOIL AND SEDIMENT TO BIO SYSTEM

What can be done to inhibit mercury release from soil and sediment into the biological system?

There are three general classes of options: Chemical modification to change the speciation to a more stabile, less labile form, Redox modification to minimize conditions that favor methylation, and physical/chemical armoring of the solids to "lock in" mercury. Challenges include the permanence of the solution (for example, HgS is very insoluble under the right conditions, but we know that the river is a dynamic redox environment over the short and long terms). Another challenge is the whether desorption can be slowed down enough to affect bioaccumulation. The initial tasks include a review of state of the art technologies to stabilize mercury in soil and to characterize (speciate) mercury in targeted soils and sediments in the South River.

3. REDUCE DISSOLVED MERCURY IN THE WATER COLUMN

What can be done to reduce the dissolved (bioavailable) mercury in the water column?

This question pertains to technologies or treatments that could reduce dissolved mercury in the water column (including effluents), and not to those that prevent/reduce mercury releases from sediments and soils. It could also include treatments that alter the bioavailability of aqueous Hg without necessarily reducing the "dissolved" concentration (e.g., increasing the concentration of an Hg-binding ligand to complex with the bioavailable species). The focus currently is on the plant discharges. Current plans are to conduct review of current state of technology to physically or chemically remove mercury from water – is there a technology that can address low levels of Hg? Can we isolate a richer, smaller stream for treatment at the plant? Then, the feasibility, practicality and effectiveness of the technology will be evaluated

4. INHIBIT METHYLYMERCURY PRODUCTION / REDUCE BIOAVAILABLE MERCURY

What can be done to inhibit methyl mercury production?

Ancillary questions to this are: Given what is known about MeHg production- can we focus efforts on certain reaches of the South River? Where are the Fe and S, etc. reducers present? What experiments or pilots may help answer this question? What is the connection between nutrients in the river and MeHg production? Upgrades to STP are planned – how will aquatic chemistry be affected? What (if any) are the good and bad effects? What experiments or pilots might help define these areas? Some of these questions will be answered through literature surveys. Laboratory testing of South River sediments with respect to methylation/demethylation potential will be undertaken by Rutgers University.

5. MANIPULATE FOOD WEB TO REDUCE Hg IN FISH TISSUE

Is it possible to tweak the food web to reduce Hg concentrations in the food web? How would this be done?

Conceptually the reduction of aquatic trophic levels or simplification of the food web could result in fewer trophic stages for mercury accumulation between primary producers and top predator fish. The team is currently reviewing the literature for examples of food web management to reduce bioaccumulative contaminants in predatory fish. A life cycle history for targeted prey types and fish species with different feeding behavior in the food web will be developed (components of the prey community which comprise the greatest biomass and/or highest total number of individuals surveyed). Using this and other available data, a SR food web will be constructed and mercury biomagnification rates between trophic levels will be developed. Then, evaluate the feasibility of management of food web to change mercury concentrations in predatory fish.

Hg Treatment Technologies / Strategies identified to Date without Screening

Explore Remediation Technologies to Cut off Potential Pathways

- Monitored Natural Recovery (Baseline Conditions)
- Physical Actions
    - Stabilization/isolation of eroding banks
    - Flood control measures (e.g. increase storage capacity, levees)
    - Capping or covering (impermeable and permeable, reactive)
    - Hydraulic modification
        - Rerouting river/runs
        - Construct bypasses above a certain river stage
    - Soil or Sediment Removal
    - Management of Large Woody debris
    - Sediment Traps to capture or isolate contaminated sediment.
- Treatment
    - Aeration of environment and/or air stripping (and capture)
    - Maintenance/ filling of ditches where methylation may occur
    - Phytoremediation
    - Chemical manipulation to:
        - Suppress MeHg production
        - Suppress uptake and metabolism of MeHg
        - Increase sorption of Hg to soil/sediment in order to reduce dissolved Hg (e.g. Bauxite, clay, humus, "Sedimite", new organoclay types)
        - Facilitate Ion exchange (thiols – check efficiency)
    - Ultrafiltration of water
- Administrative Controls/Measures
    - Fish exchange program
    - BMPs for Cattle to prevent erosion (alternative to river for water supply)
    - Floodplain Conservation easement
    - Providing clean food supply for fish

Considerations

- Beware of unintended consequences, deleterious effects
- Delivery and permanence of treatment will be a significant challenge
- Employ the adaptive management approach
- For all options DECIDE ON MEASURES OF SUCCESS – PRE AND POST MONITORING