Investigation of Increased Mercury Levels in the Fisheries of Lower East Fork Poplar Creek (Lefpc), Oak Ridge Reservation, Tennessee

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ABSTRACT

The DOE Western Environmental Technology Office (WETO) is supporting remediation efforts on the U.S. Department of Energy Oak Ridge Reservation in Oak Ridge, Tennessee by performing this study. MSE Technology Applications, Inc. (MSE) has performed a series of literature reviews and bench-scale testing to further evaluate the mercury problem in the Lower East Fork Poplar Creek (LEFPC) at Oak Ridge. The primary problem is that total mercury (HgT) levels in LEFPC water decrease, while HgT levels in sunfish muscle tissue increase, with distance away from the National Security Complex (NSC), despite extensive source control efforts at the facility and within downstream reparian zones. Furthermore, dissolved methylmercury (d-MeHg) levels increase downstream from the NSC, especially during warm weather and/or high flow events.

MSE performed four test series that focused on conversion of aqueous phase elemental mercury (Hg°A) to methyl mercury (MeHg) by algal-bacterial biofilms (periphyton) present in the streambed of LEFPC. Small (mg/L) quantities of unsulphured molasses and peptone were added to some of the Hinds Creek samples to stimulate initial bacterial growth. Other Hinds Creek samples either were dosed with glutaraldehyde to preclude microbial growth, or were wrapped in aluminum foil to preclude Hg photochemical redox effects. The bench-scale testing for Phase II was completed August 2006. The final reporting and the planning for Phase III testing are in progress.

INTRODUCTION

MSE completed three literature reviews regarding various aspects of biogeochemical controls on Hg methylation, and potential means of lowering MeHg uptake into the fisheries of LEFPC. MSE also performed two phases of bench-scale testing to evaluate and provide a "first approximation" of Hg°A's contribution to d-MeHg levels in surrogate (Hinds Creek) waters. The first phase (FY05) was conducted under both oxic and sub-oxic conditions. The second phase (FY06) was conducted under oxic conditions with variations in nutrients, light, and microbial activity.

PROJECT BACKGROUND

Large amounts of inorganic mercury (Hg) were used in the 1950s and 60s at the Y-12/National Security Complex (NSC) to separate stable isotopes of lithium. The total inventory of elemental mercury was in the millions of pounds, while many tons of mercury was discharged to the creek over this time period. Over the past ten years, Hg source control actions within the East Fork Poplar Creek (EFPC) watershed have resulted in decreased concentrations of inorganic Hg in the headwaters of the stream. During this time, Hg levels in muscle tissue of adult redbreast sunfish (Lepomis auritus) sampled from within the NSC have declined and then stabilized at concentrations ≥ 0.5 micrograms per gram (μg/g) wet weight. Concurrently, levels in sunfish residing in the Lower East Fork Poplar Creek (LEFPC) have increased. Limeted long-term data on waterborne MeHg concentrations suggest that it has paralleled fish concentrations, or at least not changed inversely. Presently, mercury concentrations in LEFPC fish exceed the U.S. Environmental Protection Agency's ambient water quality criterion for protection of human health from (methyl) mercury exposure (i.e., ≤ 0.3 μg/g tissue wet weight).

Project Goals

The series of literature reviews and evaluations culminated with suggestions for follow-on research regarding biogeochemical controls on Hg methylation, and subsequently lowering MeHg uptake into the fisheries of LEFPC was presented to Oak Ridge. These reports were used, in part, to prepare the following hypotheses [1] for mercury behavior in this watershed:

- ***Hypothesis 1 –*** Waterborne methylmercury has increased in LEFPC because microbial demethylation (destruction of methylmercury) rates have decreased in response to lower inorganic mercury concentration, or reduction in some other agent that stimulated the growth and activity of demethylating microorganisms.
- ***Hypothesis 2 –*** The nature of inorganic mercury exported from Upper East Fork Poplar Creek (UEFPC) has changed to a form that is initially less available for conversion to methylmercury but gradually reverts to more bioavailable forms. Accumulation of this precursor material in LEFPC, where sediment transport rates are slower, allows time for readily methylated precursor mercury to be formed.

Dissolved (<0.2 μm-filtered) inorganic mercury (HgA) and d-MeHg levels in LEFPC for December 2002 – June 2004 [1,3] indicate that:

- The nonlinear decline in HgA concentrations, away from the putative Hg source at NSC, is similar for both December and June sampling events; while
- d-MeHg levels tend to increase nonlinearly away from the NSC, especially during the June sampling events.

In general, net MeHg production appears to increase as dissolved mercury (HgA) levels decrease. Such a result could be due to either proportionate decreases in MeHg demethylation rates or proportionate increases in HgA biomethylation rates, with increasing distance away from the NSC. The demethylation concept is reflected in the literature review reports [2]. Hypothesis No. 2 recognizes the likelihood of continuous release of dissolved and colloidal (<1 μm) forms of aqueous elemental mercury (Hg^oA) from both NSC and LEFPC (e.g., sediment) sources. Given the presence of 1-3 ng/L of Hg^oA in LEFPC waters, this species may be an environmentally significant factor in MeHg production throughout the watershed.

Furthermore, very little research has been done regarding the nearly direct methylation of Hg^oA, as opposed to MeHg production from Hg (II) species. Therefore, the goal of this investigation (bench-scale

testing) was to provide a "first approximation" of Hg^oA's contribution to d-MeHg levels in surrogate (Hinds Creek) waters, under oxic conditions with variations in nutrients, light, and microbial activity.

Summary of FY05 Test Results

The testing included four series:

- Aerobic Test No. 1 (AE1) – Nutrients added ("Eutrophic")
- Anaerobic Test No. 2 (AN1) – "Eutrophic"
- Aerobic Test No. 2 (AE2) – Replication of AE1
- Aerobic Test No. 3 (AE3) – No nutrients ("Oligotrophic")

Table I shows the summary of the Phase I (FY05) testing results.

Table I. Summary of Phase I (FY05) Testing Results.

Test No.	HgV Dosing[a] (ng/flask)	Monitoring Flask No. 4[b]					Mercury (ng/L)[d]			
					Aerobes (CFU/mL)[c]		HgD		d-MeHg	
		Water (C)	ORP (mV)	pH(s.u.)	Min.	Max.	Undosed	Dosed	Undosed	Dosed
AE1	9.1	22.6 ± 1.2	230.3 ± 34.3	8.85 ± 0.47	1.6 x 10^6	6.6 x 10^7	2.94 ± .08	2.75 ± 0.71	0.57 ± 0.31	0.80 ± 0.03
AN1	10.4	22.0 ± 1.6	109.9 ± 58.3	8.53 ± 0.25	4.2 x 10^5	1.1 x 10^7	6.18 ± .53	7.50 ± 0.80	0.62 ± 0.30	0.32 ± 0.08
AE2	10.8	21.6 ± 1.5	208.4 ± 52.8	8.34 ± 0.22	2.3x 10^5	7.3 x 10^7	5.02 ± 0.82	5.27 ± 1.24	0.70 ± 0.05	0.68 ± 0.14
AE3	10.5	20.8 ± 1.4	253.0 ± 48.0	8.27 ± 0.17	2.3x 10^5	5.3 x 10^6	2.53 ± 0.58	3.95 ± 0.16	0.20 ± 0.02	0.13 ± 0.05

Notes:
[a] Daily dosing, based on vaporizer calibration with the Mercury Tracker 3000; 0.45 ng/d theoretically simulates EFK6.3.
[b] Mean ±one standard deviation for 10 (daily) readings.
[c] For entire test period, with 5 samples taken per test (including background).
[d] Represent mean ±one standard deviation for triplicate measurements.

The summary results of the FY05 (Phase I) bench-scale testing are as follows:

- pH-E_H conditions in AE1/AE2 sediments were sufficient to stimulate MeHg production by facultative anaerobic sulfate reducing bacteria (SRBs)—yet not to the degree of stimulating MeHg degradation by iron reducing bacteria (IRBs)
- pH-E_H conditions in AN1 sediments were sufficient to stimulate both MeHg production and degradation – resulting in net d-MeHg levels were less than those associated with the "aerobic-eutrophic" tests (AE1/AE2)
- pH-E_H conditions in the AE3 sediments were sufficiently aerobic (and bacterial numbers sufficiently low) that either MeHg production was minimal or MeHg degradation exceeded MeHg production
- Changes in physicochemical conditions in the solid (sediment) phase produced changes in microbial community size and composition – which resulted in different levels of net d-MeHg production between the four tests

Phase II Test Objectives (FY06)

It is hypothesized that enrichment of Hinds Creek water and sediment with elemental mercury vapor (HgV) will result in elevated production of d-MeHg. Background levels of HgA and d-MeHg for Hinds Creek in June 2005 were reported to be 14 ng/L and 1.1 ng/L, respectively. These concentrations are considerably higher than the 2.5 ng/L HgA and 0.2 ng/L d-MeHg results observed for the undosed, low-nutrient AE3 test performed in FY05. However, the MSE data is more in-line with the 1.8 ng/L HgA and 0.2mg/L d-MeHg levels reported for Hinds Creek in June 2004.

Acid–extractable ("total") Hg levels in periphyton and sediment used in the FY05 investigations were typically <0.05 mg/kg dry weight. Given the apparent variability in Hg levels in the environmental materials, MSE determined HgA and d-MeHg levels in Hinds Creek water plus total Hg in solids, prior to their use in the FY06 study:

Therefore, the principal objectives of the bench-scale study are as follows:

- Characterize the environmental materials from Hinds Creek, plus determine Hg levels in the nutrients and glutaraldehyde, before their use in the experiments
- Determine HgA and d-MeHg levels in the various test solutions following dosing with elemental mercury vapor
- Assess predominant terminal electron acceptor (bacterial) processes involved with biomethylation of HgA or dissolved gaseous mercury.

MATERIAL DESCRIPTIONS

Bench-scale testing of these hypotheses utilized 0.5L microcosms containing "clean" water and biomass/sediment from Hinds Creek. Dissolved HgA and d-MeHg levels in Hinds Creek are typically 2 and 0.02 ng/L, respectively [1]; total Hg in biomass/sediment is typically ≤0.05 mg/kg dry weight. Small (mg/L) quantities of unsulphured molasses and peptone were added during one of the tests to Hinds Creek samples to stimulate initial bacterial growth. Light was excluded from one of the tests to address photochemical affects on aqueous mercury speciation.

Purified air was used to flow through the flasks aqueous phase to create aerobic conditions. MSE attempted dosing of the tests flasks with sufficient elemental mercury vapor calculated to achieve target levels of ≤0.5 ng/L $Hg^{o}A$ and ≤20 ng/L HgA, as is often observed in waters from LEFPC [1]. The control flasks received carrier gas (air), only. Physicochemical and microbiological parameters were measured throughout the 10-day incubation period. Aqueous phase samples were collected at the end of each experiment for d-MeHg and HgA analyses. The Phase II (FY06) testing used a smaller permeation tube for better control of the mercury vapor dosing.

Test Materials

The test materials used for the bench-scale testing were:

- Hinds Creek water, sediment, and periphyton
- Molasses and peptone amendments
- Elemental mercury (from permeation tube/vaporizer)
- Purified air.

Oak Ridge collected side-by-side samples of stream water, stream sediment, and organic matter from Hinds Creek; these materials were used as the surrogates for the bench-scale test. Given that

Chickamauga limestone is the predominant geologic parent material beneath the LEFPC channel, and LEFPC waters being of calcium-magnesium-bicarbonate type, MSE requested calcareous sediment and Ca-Mg-HCO_3 type water for this investigation. The organic matter is comprised of periphyton scraped from the surfaces of submerged stones from the creek bottom; given a recent storm event, the periphyton sample was unavoidably coated (mixed) with silty stream sediment.

Upon receipt of the cubitainers, each was gently shaken to resuspend any solid material; a 1:1:1 volumetric composite water sample (1000 mL total volume) was prepared for laboratory characterization. The results of the water chemistry for the FY05 study was essential the same as that shown in Table II (FY06 study).

Table II. Summary of Laboratory Results for the Hinds Creek Samples[a,b]

Part A. Creek Water	
Parameter	**Concentration (mg/L)**
Total Metals	
Al	0.275
Ca	47.340
Fe	0.436
Mg	15.460
Mn	0.082
Hg	<0.0002
K	2.432
Si	4.332
Na	3.590
Dissolved Metals	
Al	<0.045
Ca	47.560
Fe	<0.015
Mg	15.580
Mn	<0.003
Hg	<0.0002
K	2.381
Si	4.010
Na	4.061
Major Anions	
Alkalinity (as $CaCO_3$)	160
Chloride	5.1
Sulfate	12.1
Nitrogen Species	
Ammonia	0.050
Nitrate/Nitrite-N	0.63
PH	8.0
Phosphorous, total dissolved	0.060
Total Organic Carbon	1.6
Total Dissolved Solids	202
Total Suspended Solids	2
Part B. Solids	
Parameter	**Concentration (mg/kg, dry weight)**
Total Hg in Organic Matter ("Periphyton")	<0.0548
Total Hg in Stream Sediment	0.01643

Note: [a] Data package (with QC) received from MSE Laboratory on July 7, 2006.
[b] Reagent grade (Type 1) water had <0.0002 total Hg level.

Other Materials and Reagents

During the FY05 study, the periphyton/sediment material was maintained in a 1L beaker at (varying) room temperature and lighting duration since receipt. The beaker had been cleaned with warm, soapy water, rinsed with tap water, then Type 1 water (total Hg < 100 ng/L) and finally with Hinds Creek water before adding the environmental material. The slurry had been stirred lightly to maintain aeration, and creek water added occasionally to maintain sufficient liquid volume. In the FY06 work, all materials were kept refrigerated (in the dark) until ready for use in preparing the test flasks.

Aliquots of slurry were removed and centrifuged (at 2000rpm for 20 minutes, T = 25 ºC) prior to use in the microcosms. The liquid layer was returned to the "stock" beaker, while 1g aliquots of the solid were weighed (to nearest mg) onto previously cleaned (as above), tarred glass slides. This process was repeated for all test and control flasks, and any residual solid then returned to the "stock" beaker. All equipment used (e.g., centrifuge tubes, spatulas, slides) was cleaned as discussed above. The lab area was clean, the HgV levels were less than 100 ng/m^3 inside and outside of the laboratory hood. HgV levels are typically 200-400 ng/m^3 ; therefore the lab area was "clean".

Test Apparatus

The three main pieces of equipment used for this testing were:

- Vaporizing system (Elemental mercury permeation tube/vaporizer)
- Test flasks with gas delivery (±HgV) manifolds
- Excess HgV physicochemical traps.

The overall test apparatus used in FY06 is shown in Fig. 1 and the setup for both FY05 and FY06 is shown in Figure 2. No electronic data acquisition occurred in the FY05 study; while the less sensitive Mercury Tracker 3000 was used to monitor HgV levels emanating from the vaporizer box.

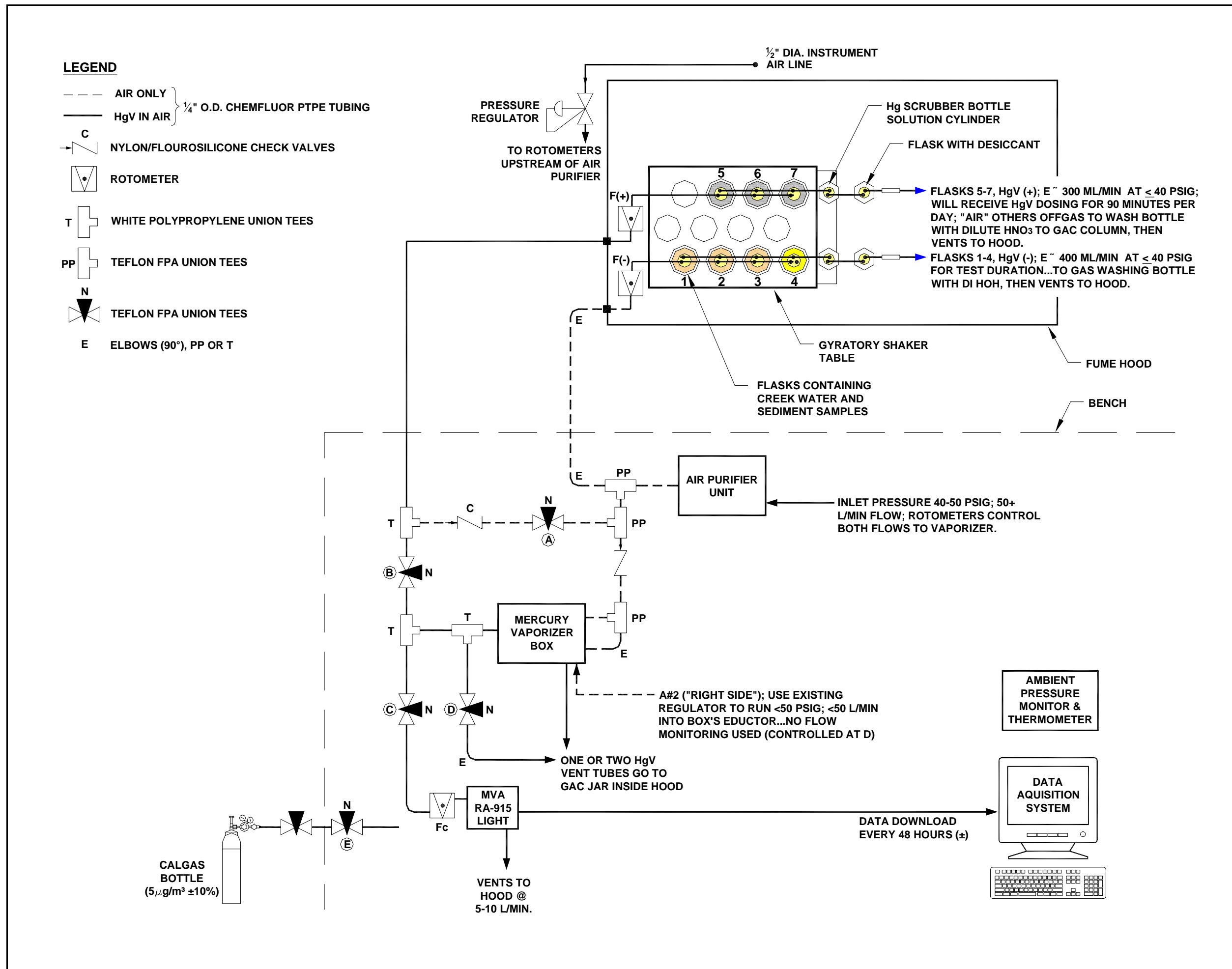

Fig. 1. Test apparatus diagram (FY06).

Fig. 2. Test setup (FY05 and FY06)

The test design was set up with seven flasks mounted on a shaker table. The seven flasks were arranged in two rows, the first row of flasks 1 through 4 did not receive gaseous elemental mercury (HgV) and served as the control flasks for three of the four tests. Flask 4 was the monitoring flask; while flasks, 5 through 7 received the HgV addition. All flasks did have creek water, sediments and periphyton.

The experimental liquids were contained in 500 mL widemouth Erlenmeyer flasks. The two-holed stoppers allowed introduction of HgV and venting of excess HgV plus carrier/fermentation gases from the flasks. The flasks were mounted on a New Brunswick Scientific Co. (Edison, NJ) GIO Gyratory Shaker having adjustable rpm settings. Treatment occurred under environmental conditions existing within MSE's test facility during the duration of this study (i.e., 15-30 °C, 40-60% relative humidity). Standard volumetric and nonvolumetric glassware, analytical balances (0.1mg accuracy), test meters, and general expendables were used as needed during this study.

Elemental mercury vapor (HgV) was delivered to the test flasks using a vaporizing system fabricated by MSE in 2003 (see Fig. 3). The vaporizer utilizes a sonic orifice and dilution eductor to provide a reliable and consistent inlet $Hg^{o}V$ concentration to the test flasks. A hot-cell, situated within the mercury vaporizer, contains a commercially available mercury permeation tube. By accurately controlling the temperature of the hot cell and permeation tube, a known and repeatable concentration of mercury vapor is eluted from the permeation tube. The mercury vapor is removed from the hot-cell using a 20 mL/min. gas purge, controlled by a sonic orifice connected to the suction side of a dilution eductor. The "motive-fluid", used in the dilution eductor, was air. By adjusting the eductor inlet pressure to maintain a "motive-fluid" flow rate of 4.5–5.0 L/min., the vacuum produced on the suction side of the eductor is approximately -7 in. Hg, which draws the mercury vapor and purge gas into the eductor. The "motive-fluid" and mercury vapor mixture exiting the dilution eductor is then plumbed directly to the flasks. To minimize the potential of amalgamating or condensing mercury vapor within the dilution eductor, the "motive-fluid" is preheated to 120 ºC; and the dilution eductor is maintained at the system operating temperature. By varying the operating temperature of the hot-cell and the flow rate of "motive-fluid", the mercury concentration in the vaporizer effluent gas can be varied from 15 µg/dscm to 475 µg/dscm. As a safety feature, the components comprising the mercury vaporizer are contained in a sealed enclosure. Any mercury fumes, resulting from a leak were vented from the enclosure and into the fume hood. The laboratory hood is

chemical proof, with a fiberglas interior and an epoxy-coated steel exterior. The air flow is approximately 125 fmp.

Fig. 3. Vaporizing system.

Calculations based on the solubility and fugacity of HgV (i.e., gaseous elemental mercury) indicated that a 90-minute per day dosing of 3.0 ± 0.1 μg/m^3 HgV would result in HgA and Hg°A concentrations of ≤ 20 ng/L and ≤ 0.5 ng/L respectively in the FY06 test solutions (microcosms).

A diversion system was plumbed into the vaporizer to allow either air or N_2 carrier gas delivery to the test flasks during the non-HgV dosing intervals. Excess HgV from the 4.5 SLPM "motive-fluid" flow was purged from the vaporizer through a vent line and then into a granulated activated carbon trap. Mercury concentrations in the various gas streams plus ambient HgV level in the hood was quantified using a Mercury Tracker 3000 gas analyzer (in FY05) or Ohio Lumex RA-915L (in FY06).

EXPERIMENTAL ACTIVITIES (TEST DESIGN)

The testing included four test series:

- Aerobic Test No. 1 (AEL1) – No nutrients ("Oligotrophic"), light
- Aerobic Test No. 2 (AEL2) – Nutrients ("Eutrophic"), light
- Aerobic Test No. 2 (AEL3) – No nutrients, dark (Al-foil covered)
- Aerobic Test No. 3 (AEL4) – No nutrients, light, glutaraldehyde in controls.

The test matrix for AEL1, AEL2, and AEL3 is presented in Table III, IV, and V. Flasks 1 through 3 represented the control flasks; they did not receive gaseous elemental mercury (HgV). Flask 4 was the

monitoring flask where pH, ORP, and microbial activity were measured. Flasks 5 through 7 were the actual testing flasks that received HgV.

Table III. Test Matrix

Flask No.[a]	Test Duration (hrs)	Parameters Measured
1 (-)	8	d-MeHg and HgA on Day-10 Sample[b]
2 (-)	8	d-MeHg and HgA on Day-10 Sample
3 (-)	8	d-MeHg and HgA on Day-10 Sample
4 (-, m)	8	pH/orp plus hetertrophs, days 2, 4, 6, 8, 10[c]
5 (+)	8	d-MeHg and HgA on Day-10 Sample
6 (+)	8	d-MeHg and HgA on Day-10 Sample
7 (+)	8	d-MeHg and HgA on Day-10 Sample

Notes:
[a] Flasks without gaseous elemental mercury (HgV) are designated "-"; while those with HgV addition are designated "+"; "m" = pH/ORP plus microbial activity monitoring flask.
[b] Ca. 200 mL unfiltered samples were sent to CEBAM Analytical, Inc. for "clean" 0.45 µm-filtering and d-MeHg and dissolved mercury (HgA) analyses by c and 1631E, respectively. Sampling followed EPA Method 1669 to the extent practicable.
[c] At least pH and oxidation-reduction potential measurements were taken by MSE prior to collection of the microbiological samples; ca. 42 mL aliquot per sampling event was sent to CFI (Bozeman, MT) for the aerobic and anaerobic heterotroph plate counts.

Table IV. Test Matrix

Flask No.[a]	Test Duration (Days)	Parameters Measured
1 (c)	10	d-MeHg and HgA on Day-10 Sample
2 (c)	10	d-MeHg and HgA on Day-10 Sample
3 (c)	10	d-MeHg and HgA on Day-10 Sample
4 (m)	10	pH/orp plus hetertrophs, days 2, 4, 6, 8, 10[c]
5 (n)	10	d-MeHg and HgA on Day-10 Sample
6 (n)	10	d-MeHg and HgA on Day-10 Sample
7 (n)	10	d-MeHg and HgA on Day-10 Sample

Notes:
[a] c = addition of chemical sterilant (glutaraldehyde); m = monitoring of at least pH/orp plus aerobic and anaerobic microbial activities; n = "new" test conditions.

Table V. Test Series Specifics

Start	Code	Test Condition Flasks 1-4	Test Condition Flasks 5-7
6/19/06	AEL1	Air only, no nutrients, no chemical sterilant, no light exclusion	3±1 µg HgV/m^3 air for 1 ½ hours per day, no nutrients, no chemical sterilant, no light exclusion
7/10/06	AEL2	Air only, nutrients added, no chemical sterilant, no light exclusion	3±1 µg HgV/m^3 air for 1 ½ hours per day, nutrients added, no chemical sterilant, no light exclusion
7/24/06	AEL3	Air only, no nutrients, no chemical sterilant, flasks covered with aluminum foil to exclude light	3±1 µg HgV/m^3 air for 1 ½ hours per day, no chemical sterilant, flasks covered with aluminum foil to exclude light
8/7/06	AEL4	Air only, no nutrients, chemical sterilant added, no light exclusion	30±1 µg HgV/m^3 air for 1 ½ hours per day, nutrients, no chemical sterilant, no light exclusion

Aerobic Test No. AEL1

The purpose of this test was the determination of d-MeHg) levels in surrogate LEFPC water, as produced by biomethylation of dissolved elemental mercury Hg°A under oxygenated, low nutrient conditions. Except for the monitoring flask, each test volume included 250 mL surrogate LEFPC water (e.g., from Hinds Creek), 2.0 g sediment, and 1.0 g periphyton/sediment. The aerated flask contents were stirred using a gyratory shaker operating at about 80 rpm.

Aerobic Test No. AEL2

The purpose of this test was the determination of d-MeHg levels in surrogate LEFPC water, as produced by biomethylation of DGM under nutrient rich conditions. The experimental design was essentially the

same as for the AEL1 test, except that 0.050 g each of peptone and molasses were weighed in, or added gravimetrically, to each flask.

Aerobic Test No. AEL3

The purpose of this test was the determination of d-MeHg levels in surrogate LEFPC water, as produced by biomethylation of Hg°A under low nutrient (oligotrophic) conditions in the absence of light. This test essentially replicated the AEL1 test, except that all flasks were covered with aluminum foil to exclude laboratory lighting.

Aerobic Test No. AEL4

This test assessed biotic vs. abiotic contributions to d-MeHg production (in flasks 1-4), and elevated HgV dosing in flasks 5-7. The prepared contents of flasks 1-3 were chemically sterilized via addition of 13.2 (±) mL of 50 volume-percent glutaraldehyde solutions and 15.8 (±) mL into flask number 4. The resulting concentration of glutaraldehyde was 2.5 percent and should have been sufficient to maintain "abiotic" conditions for about 15 days total.

DATA REDUCTION AND EVALUATION

Sampling and Environmental Methods

Determination of HgA in test waters utilized EPA Method 1631E. MeHg levels in these matrices were determined using EPA Method 1630. Essentially, the cool (4 °C), unpreserved sample received from MSE was filtered (0.45 µm), then split into two 100 mL-aliquots. The first aliquot was used for dissolved mercury (HgA) analysis, while the second was used for d-MeHg analysis at CEBAM Analytical, Inc.

The data received from the various contract laboratories has been reviewed. Parameter-specific arithmetic means and standard errors were calculated from those data of acceptable quality and will be evaluated in the final report.

Synopsis of the Data

Table VI and VII show the summary of the Phase II (FY06) testing results.

Table VI. Summary of Phase II (FY06) Testing Results.

			Monitoring Flask No. 4[b]					Mercury (ng/L)[d]			
						Aerobes (CFU/mL)[c]		HgD		d-MeHg	
Test No.	HH (ppbv)	HgV Dosing[a] (ng/flask)	Water (C)	ORP (mV)	pH(s.u.)	Min.	Max.	Undosed	Dosed	Undosed	Dosed
AE1	300/ 352	24.2	21.4 ± 2.3	76.4 ± 47.4	8.83 ± 0.15	1.3 x 10^5	2.3 x 10^6	4.18 ± 0.56	3.98 ± 0.53	0.17 ± 0.02	0.06 ± 0.03
AN1	995/ 972	23.9	26.0 ± 1.1	86.5 ± 26.8	8.81 ± 0.26	3.7 x 10^4	4.9 x 10^6	3.67 ± 0.71	7.47 ± 1.92	0.32 ± 0.06	0.37 ± 0.01
AE2	826/ 581	24.6	23.7 ± 2.9	100.1 ± 30.9	8.98 ± 0.25	1.6 x 10^4	8.4 x 10^5	3.02± 0.40	6.18 ± 1.64	0.20 ± 0.05	0.19 ± 0.01
AE3	3,728/ 501	113.5	22.7 ± 1.3	121.8 ± 27.9	6.95 ± 0.46	4.4 x 10^4	<5.5 x 10^2	2.41 ± 0.49	3.55 ± 0.65	0.40 ± 0.04	0.20 ± 0.09

Notes:
[a] Daily dosing, based on vaporizer calibration with the Ohio Lumex RA 915-L; 0.45 ng/d theoretically simulates EFK6.3.
[b] Mean ±one standard deviation for 10 (daily) readings.
[c] For entire test period, with 5 samples taken per test (including background).
[d] Represent mean ±one standard deviation for triplicate measurements.
[e] HH = headspace hydrogen levels in control/treated samples; IRB range is typically 260-770 ppbv, for ORP in 50-600 mV range; while SRB range is 1,000-5,000 ppbv and ORP< 0mV.

Table VII. Summary of Methylation Reference Data used to Interpret the Phase II (FY06) Testing Results.

	Water Column (d^{-1})		
Nutrient Status	MeHg Production	MeHg Destruction	P/D
Oligotrophic	0.0001-0.0005	0.001-0.002	0.05-0.50
Eutrophic	.0014-0.003	0.0025-0.005	0.28-1.20
Source: USEPA 600-R-06-073 (2006)			

The preliminary summary of the FY06 data is as follows;

- Predominant Hg source was in the nutrients, not the HgV that was added during the test
- The net MeHg production appears to increase with nutrient addition
- Based on headspace H_2 levels, the IRBs are "doing the work"
- The testing indicated that lower net MeHg production might be achieved via complexing mercuric ion(s) with a suitable anion.

Figure 4 shows a graphical summary of the FY05 and FY06 summary results.

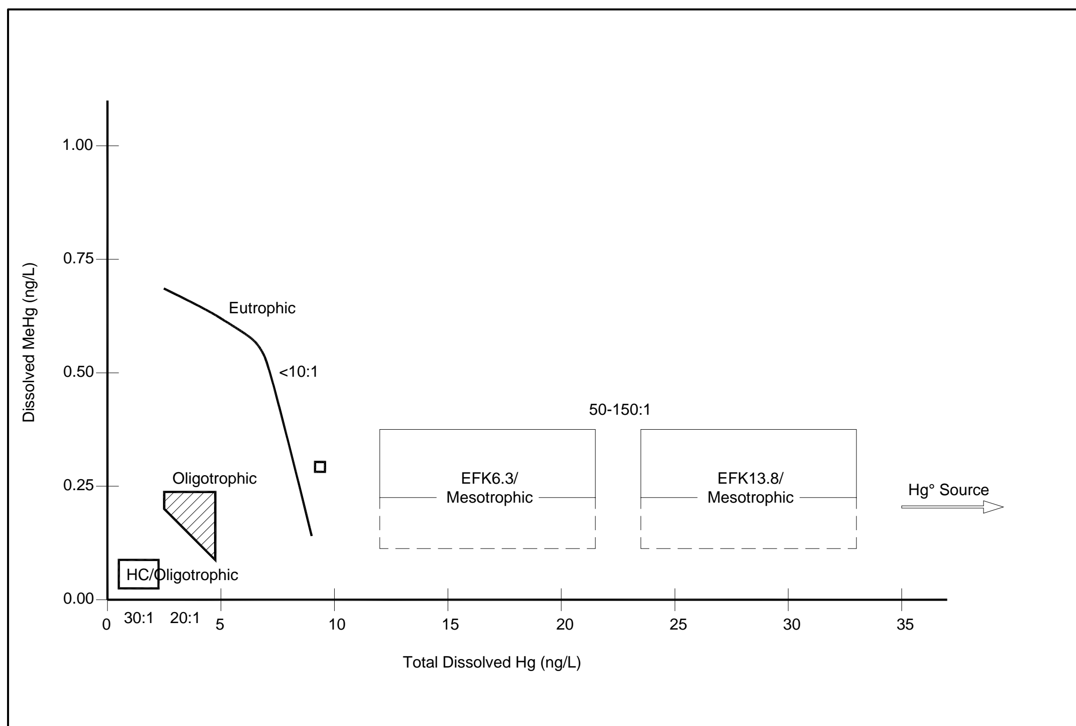

Fig. 4. Graphical summary of FY05 and FY06 results.

CONCLUSION

Reporting

The final report for FY06 (Phase II) testing and the additional testing that is in the planning phase, will be completed by August 2007. The report will include the following:

- Qualitative acceptance or rejection of the hypothesis that the increased HgV dosing regimen will increase both HgA and d-MeHg levels relative to those seen in phase I
- Qualitative acceptance or rejection of the hypothesis that d-MeHg production from Hg°A is greater under eutrophic/elevated heterotroph conditions than oligotrophic/low hetertroph conditions
- Qualitative acceptance or rejection of the hypothesis that d-MeHg production will be very low in the absence of microbial activity
- Evaluation of general HgA chemistry in the defined test environments.

MSE is planning additional testing using East Fork Poplar Creek (EFPC) water (vs. Hinds Creek water, as used in previous testing). The purpose of the four additional tests is to better approximate "baseline" biomethlylation of mercury, and to investigate potential measures for lowering net mercury methylation in the creek. The four test series will include:

- Evaluation of particulate-illumination interactions in "untreated" EFPC water
- Evaluation of thiosulfate-mercuric ion complexation effects on Hg methylation
- Evaluation of selenite-mercuric ion complexation effects on Hg methylation
- Replication of one of the three tests or a "to-be-determined" test.

REFERENCES

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