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 Oak Ridge's remediation efforts 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. 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 dissolved and colloidal forms of elemental mercury (Hg°A) to methyl mercury (MeHg) by algal-bacterial biofilms (periphyton) present in the streambed of LEFPC; MeHg production by these biofilms under anoxic versus oxic conditions was the critical measurement taken. The bench-scale testing for Phase I was completed November 2005. The final reporting and the planning for Phase II 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 bench-scale testing to evaluate and provide a "first approximation" of Hg°A's contribution to d-MeHg levels in surrogate (Hinds Creek) waters—under both oxic and anoxic conditions.

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. 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 with increasing distance downstream from the NSC. 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. Concurrent levels in sunfish residing in the Lower East Fork Poplar Creek (LEFPC) appear to be increasing inversely with warm weather concentrations of both total and dissolved monomethyl mercury (MeHg; $H_3C\text{-}Hg\text{-}OH_2^+$) species [1].

However, in LEFPC the little data available for looking at long-term trends suggests that MeHg and possibly HgT have paralleled fish concentrations, or at least not changed inversely. Presently, this condition exceeds 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 weight).

During fiscal year 2005, MSE finalized a series of literature reviews and evaluations of site-specific information regarding the above issues [2]. Given the present uncertainties regarding the above relationship of Hg in water versus fish tissue, it is imperative to better understand the Hg contamination source term (i.e., gHg/day to LEFPC) as well as the biogeochemical controls on Hg methylation in LEFPC. Such knowledge will be crucial to refining Hg remedial design/action within the LEFPC watershed.

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. The draft (2004) versions of 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 (<0.2μm-filtered) inorganic mercury (HgA) and methylmercury (d-MeHg) levels in LEFPC for December 2002 – June 2004 [3][1] 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 (<1μm) 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 is to provide a "first approximation" of Hg^oA's contribution to d-MeHg levels in surrogate (Hinds Creek) waters, under both oxic and anoxic conditions.

Test Objectives

It is hypothesized that algal-bacterial "bioreactors" occur throughout LEFPC, and convert dissolved and colloidal phase Hg^o (Hg^oA) from upstream sources to MeHg. It may be that MeHg production per g dry biomass day $^{-1}$ is much greater than MeHg production per g dry stream sediment day^{-1}. Furthermore, the MeHg flux would increase in the downstream direction if there were a general increase in algal-bacterial biomass, especially below the outfall from the municipal wastewater treatment plant. The proposed mechanism involves ad(b)sorption of Hg^oA on or into the biofilm, with methylation then occurring in hypoxic zones at the film-substrate (e.g., rock) surface. The MeHg produced then diffuses back through the biofilm and into the water column, or is released as particulate MeHg in biomass sloughed from the biofilm.

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

- Determination of dissolved MeHg levels in surrogate LEFPC water containing different dosing levels of aqueous elemental mercury under aerobic and anaerobic conditions;
- Evaluation of the relative contributions of inorganic (sediment) and organic (plant) particulate matter on methylation of dissolved mercury species present in surrogate LEFPC water.

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 0.02ng/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 several of the tests to Hinds Creek samples to stimulate initial bacterial growth.

Purified air and nitrogen (N_2) were used to flow through the flasks aqueous phase to create aerobic (oxic) and anaerobic (anoxic) conditions, respectively. The test flasks were dosed with sufficient elemental mercury vapor calculated to achieve target levels of ≤3ng/L Hg^oA and ≤80ng/L HgA, as is often observed in waters from LEFPC [1]. The control flasks received carrier gas (air or N_2), 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.

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); and
- Purified air or nitrogen

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 (1000ml total volume) was prepared for laboratory characterization. The results are shown in Table I.

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

Part A. Creek Water

Parameter	***Concentration (mg/L)***
Total Metals	
Al	0.177B
Ca	37.800
Fe	0.290
Mg	12.100
Mn	0.044
Hg	0.0001U
K	2.070B
Si	4.080
Na	2.930B
Dissolved Metals	
Al	0.041U
Ca	38.900
Fe	0.018B
Mg	12.400
Mn	0.007B
Hg	0.0001U
K	2.140B
Si	3.940
Na	3.550B
Major Anions	
Alkalinity (as $CaCO_3$)	140
Chloride	3.9
Sulfate	16.0
Nitrogen Species	
Ammonia	<0.05
Nitrate/Nitrite-N	0.43
pH	7.8 S.U.
Phosphorous, total dissolved	0.070
Total Organic Carbon	1.7
Total Dissolved Solids	132
Total Suspended Solids	4.0

Part B. Solids

Parameter	***Concentration (mg/kg, dry weight)***
Total Hg in Organic Matter	0.057
Stream Sediment	
Total Hg	0.046B
Leachable Hg	0.051

Note: [a] Data package (with QC) received from HKM Laboratory on July 7, 2005.
[b] Reagent grade (Type 1) water had 0.0001U total Hg level.

Other Materials and Reagents

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 < 100ng/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.

Aliquots of slurry were removed and centrifuged (at 2000rpm for 20 minutes, T = 25ºC) 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.

Test Apparatus

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

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

The overall test apparatus is shown in Fig. 1 and Fig. 2.

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. 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 500ml 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) plus 24-hours/day lighting within the hood. 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 designed and fabricated by MSE; the system was initially applied during successful demonstration of the Plasma Enhanced Electrostatic Precipitation System (an EPRI-funded project) in 2003 (see Fig. 3). The vaporizer utilizes a sonic orifice and dilution eductor to provide a reliable and consistent inlet HgºV 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 20mL/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,

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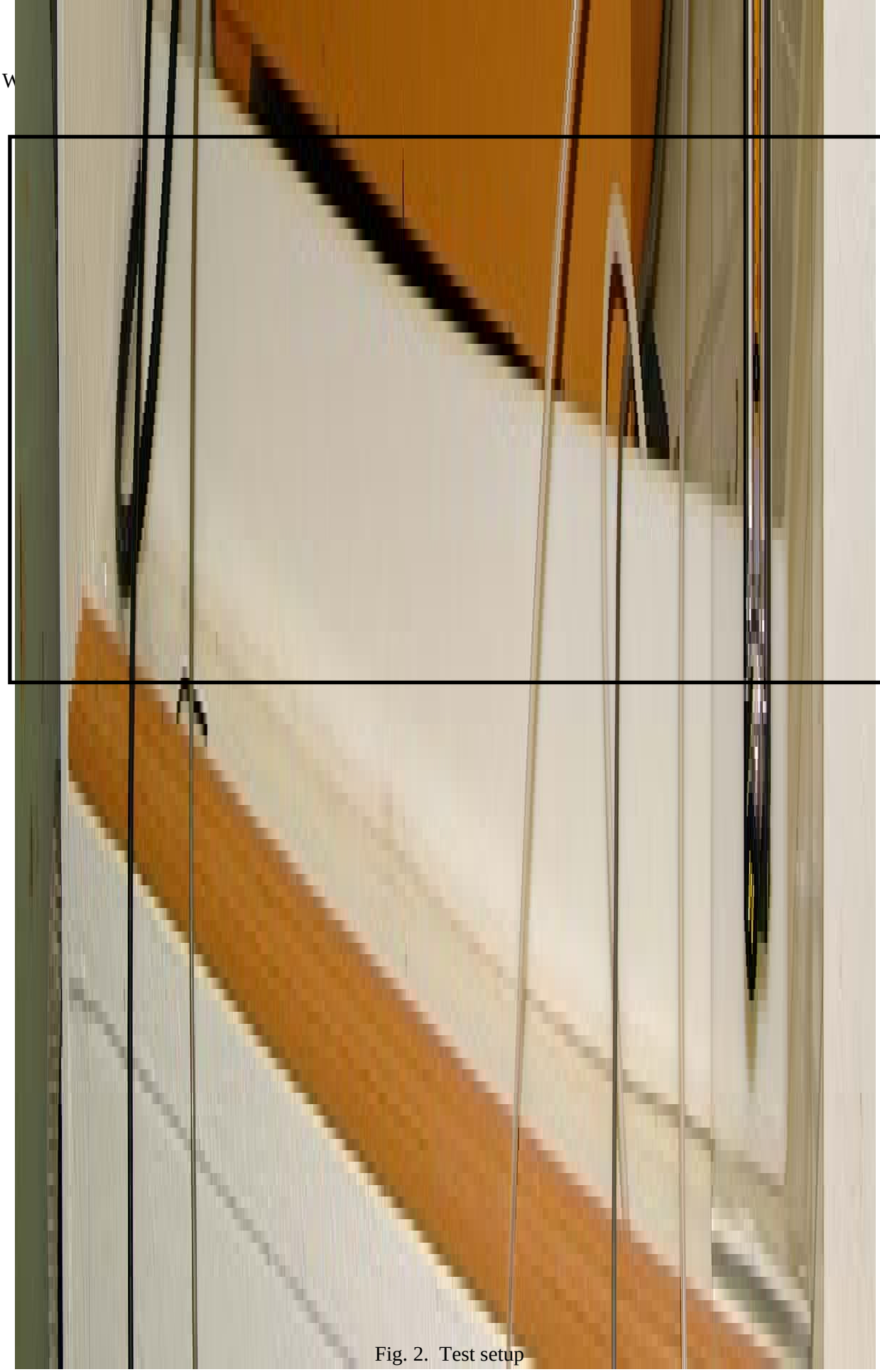

Fig. 2. Test setup

was either nitrogen or 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 120ºC; 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 15µg/dscm to 475µg/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.

Fig. 3. Vaporizing system

Calculations based on the solubility and fugacity of HgV (i.e., gaseous elemental mercury) indicated that a two-minute per day dosing of 30 ± 2 µg/m^3 HgV would result in HgA and Hg°A concentrations of ≤ 80 ng/L and ≤ 3 ng/L respectively in the 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.

EXPERIMENTAL ACTIVITIES (TEST DESIGN)

The test matrix is presented in Table II. Flasks 1 through 3 represented the control flasks; they did not receive gaseous elemental mercury (HgV). Flask 4 is the monitoring flask where pH, ORP, and microbial activity were measured. Flasks 5 through 7 were the actual testing flasks that received HgV.

Table II. Test Matrix

Flask No.[a]	*Test Duration (hrs)*	*Parameters Measured*
1 (-)	10	d-MeHg and HgA on Day-10 Sample[b]
2 (-)	10	d-MeHg and HgA on Day-10 Sample
3 (-)	10	d-MeHg and HgA on Day-10 Sample
4 (-, m)	10	pH/orp plus hetertrophs, days 2, 4, 6, 8, 10[c]
5 (+)	10	d-MeHg and HgA on Day-10 Sample
6 (+)	10	d-MeHg and HgA on Day-10 Sample
7 (+)	10	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" 0.45µm-filtering and D-MeHg and dissolved mercury (HgA) analyses by EPA Methods 1630 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. 42ml aliquot per sampling event was sent to CFI (Bozeman, MT) for the aerobic and anaerobic heterotroph plate counts.

The testing included four test series:

- Aerobic Test No. 1 (AE1)
- Anaerobic Test No. 2 (AN1)
- Aerobic Test No. 2 (AE2)
- Aerobic Test No. 3 (AE3)

Table III. Test Series Specifics

Start	*Code*	*Test Condition*	*HgV Dosing*
7/25/05	AE1	Aerobic (air)	30±1 µg/m^3
8/08/05	AN1	Anaerobic (nitrogen)	32±1 µg/m^3
9/12/05	AE2	Aerobic (air)	33±3 µg/m^3
9/26/05	AE3	Aerobic (air, no nutrients)	32±2 µg/m^3

Aerobic Testing Phase

The purpose of this phase was to determine dissolved methylmercury (d-MeHg) levels in surrogate LEFPC water, as produced by biomethylation of dissolved elemental mercury (Hg^{o}A) under oxygenated conditions. Each test volume included 250ml surrogate LEFPC water (e.g., from Hinds Creek), 2.0g sediment, and 1.0g periphyton/sediment, plus 0.050g each of peptone and molasses; the molasses was added gravimetrically. The aerated flask contents were stirred using a gyratory shaker operating at about 80 rpm.

Anaerobic Testing Phase

The purpose of this phase was to determine d-MeHg levels in surrogate LEFPC water, as produced by biomethylation of Hg^{o}A under hypoxic conditions. The experimental design was essentially the same as for the aerobic test series, with the following exceptions:

- Purified N_2 was used to "carry" the Hg^{o}V, as well as to create/maintain anaerobic conditions, in the liquid phase; and

- Ca. 42ml (bubble-free) samples were sent to CFI for completion of the aerobic and anaerobic heterotroph plate counts.

Additional Test Phase

This additional test (AE3) did not include the nutrients (peptone or molasses). The purpose of the test was to determine "background" methylmercury production under low-nutrient conditions.

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 (0.45μm) , then split into two 100ml-aliquots; the first aliquot was used for dissolved mercury (HgA) analysis, while the second was used for dissolved 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 IV. provides the arithmetic means for the respective measurements.

Table IV. Synopsis of the Data

Start Date	***Test***	***THg, (ng/L)***	***MeHg (ng/L)***	***CFU/mL on Brewer's***	***CFU/mL on R2A Media***	***Water Temp (℃)***	***PH (S.U.)***	***ORP (mv)***
7/25/05	AE1	2.84	0.674	1.0×10^2	1.7×10^7	22.6	8.85	230.3
8/08/05	AN1	6.84	0.471	2.6×10^6	3.6×10^6	22.0	8.53	109.9
9/12/05	AE2	5.22	0.689	2.4×10^5	1.9×10^7	21.6	8.34	208.4
9/26/05	AE3	3.24	0.164	4.5×10^3	1.6×10^6	20.8	8.27	253.0

The data in Table IV. indicates that:

- Aerobic activity has generally declined (AE1>AE3), but anaerobic activity has increased (AE3>AE1) due to declining aeration in the original sample bottles; while
- Anaerobic heterotroph activity is highest in AN1, although still less than the aerobic activity over test duration.
- The pH for all four test runs averaged 8.5.
- The ORP was lowest in AN1 and highest in AE3.

CONCLUSION

The results indicate that parts per trillion (ppt) levels of elemental mercury can be converted to environmentally significant MeHg levels under both aerobic and anaerobic conditions. Furthermore, the

results indicate that a 10-fold increase in aerobic microbiological activity (over background levels) is sufficient to achieve this conversion.

Reporting

The final report will be completed by March 2006. The report will include the following:

- Qualitative acceptance or rejection of the hypothesis that ppt levels of dissolved elemental mercury (Hg°A) can be biomethylated to d-MeHg;
- Qualitative acceptance or rejection of the hypothesis that d-MeHg production from Hg°A is greater under anaerobic than aerobic conditions; and
- Evaluation of general dissolved elemental mercury's environmental behavior under the given test conditions.

Furthermore, the final report will recommend the path forward for follow-on testing. Presently, such recommendations will include:

- Use of a smaller permeation tube to deliver continuous, low-level, dosing of HgV to the flasks (while keeping HgA levels similar to those used to date); and

- Evaluating the potential for lowering biomethylation rates via complexing aqueous Hg species with various levels (e.g., 5, 10 and 15 mg/L) of thiosulfate ion.

ACKNOWLEDGEMENTS

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