

Y-12

**OAK RIDGE
Y-12
PLANT**

LOCKHEED MARTIN

PROPOSED EXPERIMENT FOR
SnCl₂ TREATMENT OF OUTFALL 200
FOR THE PURPOSE OF MERCURY REMOVAL
FROM EAST FORK POPLAR CREEK
Y-12 PLANT
OAK RIDGE, TENNESSEE

MARCH 1997

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for the Y-12 PLANT
managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract DE-AC05-84OR21400

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Unclassified
Derivative _____
Classifier L. Wayne McMan
Name _____
Date 3/12/97 Title ADC

Experimental Removal of Mercury From East Fork Poplar Creek by Natural Volatilization and Air Stripping Following Stannous Chloride Reduction

Identification and treatment/elimination of point sources of mercury (Hg) to East Fork Poplar Creek (EFPC) within the Y-12 Plant have reduced base flow mercury concentrations considerably; but, after all such actions are completed, nonpoint sources will continue to add mercury to the creek. Studies conducted in 1996 on the use of air stripping to remove elemental mercury from Outfall 51, a mercury-contaminated natural spring, demonstrated that the addition of trace concentrations of stannous chloride (SnCl_2) converted a large fraction of the dissolved mercury in the outfall to elemental mercury, which could subsequently be removed by air stripping.

Dissolved mercury is the dominant form in EFPC at the north/south (N/S) pipes, where it emerges from the underground storm drain network. More than 50 percent of that mercury is capable of being rapidly reduced by the addition of a 3-5 fold molar excess of stannous chloride. Upon conversion to the volatile gaseous (elemental) form, mercury would be lost across the air-water interface through natural volatilization. EFPC within the Y-12 Plant is shallow, turbulent, and open to sunlight and wind, providing conditions that facilitate natural evasion of volatile chemicals from the water. Preliminary calculations estimate that 75 percent or more of the elemental mercury could be removed via evasion between the N/S pipes and the Y-12 Plant boundary (Station 17). Alternatively, elemental mercury might be removed from EFPC in a short reach of stream below the N/S pipes by an in-situ air stripping system which bubbles air through the water column. The purpose of these proposed experiments is to test whether natural volatilization or in-situ air stripping may be used to further reduce baseflow concentrations of mercury in EFPC. If either test appears to offer promise for achieving long-term reduction in mercury exposure to aquatic life, a proposal for longer-term (several months) testing will be prepared.

Results of this experiment will be useful for understanding the transport and fate of other volatile chemicals in the upper reaches of EFPC. Chlorinated solvents such as perchloroethylene, carbon tetrachloride, and trichloroethylene should volatilize from EFPC at rates similar to that of mercury. Polychlorinated biphenyls, because of their high Henry's Law constants, would also be expected to escape to the atmosphere if present in dissolved form.

Experiment 1 Natural Volatilization of Elemental Mercury Across the Air/Water Interface in EFPC

Initial experiments will consist of short-term (less than eight hours) addition of stannous chloride to EFPC at the N/S pipes in conjunction with downstream sampling for total and elemental mercury in EFPC water. Mercury in air above the creek will also be monitored during the experiment, which will be run on two separate dates. Depending upon results of initial experiments, follow-up studies will be undertaken to investigate the role of variables such as wind, temperature, and sunlight. Results of studies associated with natural evasion of elemental mercury (such as the persistence of elemental mercury in oxygenated stream water, reaction of SnCl_2 with Hg in creek water) will also be used to assess the viability of in-situ air stripping and design a test system, if the concept appears to have potential.

Trace concentrations (0.002-0.005 mg/L) of stannous chloride will be added to EFPC at the N/S pipes. Concentrations of total mercury and dissolved gaseous mercury will be measured in grab samples of creek water at sites downstream at times roughly corresponding to travel time for a water mass moving downstream and then compared to similar measurements made before the stannous chloride addition started. Samples will be collected for mercury analysis at 500-m intervals downstream from the N/S pipes. Gaseous (elemental) mercury in air and water will be measured on site using a Jerome portable mercury analyzer. Total mercury will be measured using the same technique following overnight oxidation with bromine chloride (BrCl). The amounts of SnCl_2 and hydrochloric acid (HCl) added to EFPC in these experiments will not be detectable by routine chemical analysis (detection limit for Sn is 0.05 mg/L); therefore, no measurements of aqueous tin concentrations in EFPC will be made.

Assumptions

- 1) Volatilization of mercury is described by a two film-model:

where $k = (Hk_g k_l / Hk_g + k_l) / \text{day}$

k = first order rate constant describing loss of mercury from water as a function of time

H = Henry's Law constant, 0.4

k_l = gas phase mass transfer coefficient, assumed to be 1000 cm/h

k_g = liquid phase mass transfer coefficient, assumed to be 16 cm/h

(In-stream measurements of mercury evasion by S. I. Lindberg, ORNL/ESD in Jan. 1997 indicate that k_g is in the range of 15-25 cm/h)

d = stream depth, assumed to be 15 cm

thus, $k = 1.0 \text{ h}^{-1}$

The concentration of mercury in water at any time (t) following start of volatilization is:

$$[\text{Hg}]_t = [\text{Hg}]_0 (e^{-kt}) \quad (1)$$

- 2) Stream dimensions are assumed to be 3.4 m wide and 15 cm deep, giving a cross section of 0.53 m². Flow is 0.26 m³/s ($22.8 \times 10^6 \text{ L/day}$, 6 mgd), yielding a current velocity of 0.5 m/s.

If the rate constant for evasion is converted to units of distance along the stream, the result is 0.00056 m^{-1} . The predictive equation then becomes:

$$[\text{Hg}]_d = [\text{Hg}]_0 (e^{-0.00056d}) \quad (2)$$

where d is distance (m) from point of SnCl_2 addition.

The predicted distance required to remove 50 percent of the elemental mercury is 1240 m. Thus, it appears theoretically possible to remove 75 percent of the reducible mercury entering EFPC at the N/S pipes in 2.5 km, roughly the entire reach from Station 17 upstream.

The stannous chloride concentration needed to reduce 0.7 $\mu\text{g}/\text{L}$ mercury would be approximately 0.002-0.005 mg/L, corresponding to an input rate of 15-38 g SnCl₂ per day. A metering pump would be used to feed approximately 10 ml/minute of stannous chloride stock solution into creek water pumped through a mixing/distribution manifold placed in the stream. The stock solution (1 g/L stannous chloride in 0.01 Normal [N] HCl) would be held in a double-contained 8 L carboy on the stream bank. The lower input rate roughly corresponds to that approved by Tennessee Department of Environment and Conservation personnel for stannous chloride inputs to EFPC associated with the Outfall 51 air stripper (< 22 g/day) before the Flow Management Project (which adds raw water to EFPC at the N/S pipes to achieve 7.0 mgd minimum flow at Station 17) went into effect. The latter input rate roughly represents the same in-stream stannous chloride concentrations approved for testing the Outfall 51 air stripper, but reflects the additional dilution associated with flow management.

Concerns

Short-Term

Ecological - Ecological concerns associated with the short-term addition of stannous chloride to EFPC are the same as those addressed in the request for permission to add stannous chloride to the creek in conjunction with operation of the Outfall 51 pilot air stripper unit. Concentrations of SnCl₂ in the creek will be far below levels associated with acute toxicity; duration of each experiment will be eight hours or less.

Atmospheric Mercury - If EFPC at the N/S pipes (before addition of water from flow management) is assumed to contain 1 $\mu\text{g}/\text{L}$ total mercury, of which 0.7 $\mu\text{g}/\text{L}$ is reducible, and a flow of 2.0 mgd ($10 \times 10^6 \text{ L/day}$), the hypothetical rate of transfer of mercury to the atmosphere is 5.3 g/day, or 4.2 lb/year. This is far below the continuous discharge rate requiring a permit (200 lb/year for prevention of significant deterioration).

If natural in-situ volatilization is effective at removing mercury from EFPC, increased concentrations of mercury in the air in the vicinity of the creek are to be expected. If all mercury lost from the creek in one hour is retained in a volume of air 20-m wide, 10-m high, and 2000-m in length, the atmospheric concentration would be 3 $\mu\text{g}/\text{m}^3$. This concentration is well below levels requiring respiratory protection in the workplace. Retention of mercury in such a small volume of air is very unlikely; this rough calculation probably vastly overestimates possible atmospheric concentrations. Y-12 Plant Industrial Hygiene staff will be requested to monitor concentrations of mercury in the air over the creek during the experiments, and Y-12 Plant and Environmental Sciences Division (ESD) staff conducting the experiments will also monitor mercury in air over the course of the experiment. If atmospheric concentrations reach 25 $\mu\text{g}/\text{m}^3$ at any point in the creek bed, the stannous chloride addition will be halted.

Long-Term (concerns associated with permanent operation)

Effects on Hg Bioavailability - Dissolved elemental mercury is at least as bioavailable as other dissolved inorganic species and should have a lower tendency to become particle associated. Increased concentrations of this species in water could result in significant changes in mercury transport and transformations in the aquatic system, but we cannot predict whether such changes would be adverse or beneficial. The present Y-12 Plant Biological Monitoring and Abatement Program (BMAP) would detect any substantial changes in bioaccumulation or ecological effects associated with increasing the concentration of elemental mercury in creek water.

Chronic Toxicity - The low toxicity of tin, coupled with the very low concentrations being added, indicate little concern for chronic toxicity in EFPC. The BMAP in place on upper EFPC would detect any changes associated with chronic toxicity, if they occurred.

Formation of Organotin Compounds - There is evidence in the literature of inorganic tin being converted in the environment to organotin compounds by microbial action. However, the compounds formed are generally short chain aliphatic compounds such as monomethyltin, and the rates and extent of conversion are low. These substances are not extremely toxic like tributyltin and, if formed, would be present at extremely low concentrations.

Atmospheric Mercury - Although atmospheric release of 5-10 g/day of elemental mercury should be acceptable from a regulatory perspective, this action will be subject to criticism for dispersing a contaminant suspected of being a global pollution concern. Before such a procedure is implemented on a long-term basis, careful evaluation of the consequences of transferring mercury from the aquatic environment to the atmosphere will need to be undertaken in order to demonstrate that the environmental benefits outweigh the drawbacks.

Experiment 2 In-Situ Air Stripping at the N/S Pipes Site

Mercury in water exiting the N/S pipes is in a predominantly dissolved reactive form that can be reduced by the addition of trace concentrations of stannous chloride. The pool in the stream where it exits the pipe has sufficient volume and depth that streamflow is retained for several minutes, allowing the possibility of removing reduced mercury by passing a stream of air through the water in the pool. This test envisions placing an array of diffusers on the streambed at this site, and blowing air through the water column at a rate several times the volumetric flow of the creek. Stannous chloride will be added at the head of the pool, using the system described for Experiment 1. If successful, the procedure has the potential for reducing mercury loading to upper EFPC by 3-4 g/day.

Assumptions

- 1) Creek section (pool) is 3-m wide x 6-m long x 0.5-m deep = 18 m³ = 18000 L
- 2) Flow = 2 mgd = 7.6×10^6 L/day = 5280 L/m (upstream from flow management)

Therefore, **Retention time = 3.4 minutes**

- 3) Air needed is assumed to be 10 x stream flow = 53,000 L/min (1873 cfm)
- 4) Hg in water is 1.0 $\mu\text{g}/\text{L}$, 0.7 $\mu\text{g}/\text{L}$ tin reducible
- 5) In-situ stripping assumed to remove 60-80 percent of the reduced Hg
(Amounts to 3.2-4.3 g/day Hg)
- 6) Amount of SnCl₂ needed = 2-5 $\mu\text{g}/\text{L}$, 15-38 g/day

If all mercury was removed by 53,000 L/min air, concentration in the air exiting the creek (assuming 70 percent efficiency) would be 0.05 $\mu\text{g}/\text{L}$ (50 $\mu\text{g}/\text{m}^3$). This concentration could be an industrial hygiene concern if not rapidly mixed with ambient air.

Concerns

Short-Term

Ecological - Ecological concerns associated with the short-term addition of stannous chloride to EFPC are the same as those addressed in the request for permission to add stannous chloride to the creek in conjunction with operation of the Outfall 51 pilot air stripper unit. Concentrations of SnCl₂ in the creek will be far below levels associated with acute toxicity (Enclosure 2), and the duration of each experiment will be less than eight hours.

Atmospheric Mercury - If EFPC at the N/S pipes (before addition of water from Flow Management) is assumed to contain 1 $\mu\text{g}/\text{L}$ total mercury, of which 0.7 $\mu\text{g}/\text{L}$ is reducible, and a flow of 2.0 mgd (7.6×10^6 L/day), the hypothetical rate of transfer of mercury to the atmosphere is 5.3 g/day, or 4.2 lb/year. This is far below the continuous discharge rate requiring a permit (200 lb/year for prevention of significant deterioration).

Industrial Hygiene - This procedure will vent gaseous mercury into a much smaller air volume than natural volatilization. If a volumetric air/water ratio of 10 is used, 88 L/s of air containing 50 $\mu\text{g}/\text{m}^3$ would enter the atmosphere at the site. Rapid dilution of this stream with ambient air would be required to prevent localized mercury concentrations at the site from exceeding levels requiring respiratory protection (25 $\mu\text{g}/\text{m}^3$). Y-12 Plant Industrial Hygiene staff will be requested to monitor concentrations of mercury in the air over the creek during the experiments, and Y-12 and ESD staff conducting the experiments will also monitor mercury in the air over the course of the experiment. If atmospheric concentrations reach 25 $\mu\text{g}/\text{L}$ in the air at a height of 6 ft over the

stream bank, stannous chloride addition will be halted. Operational or National Pollutant Discharge Elimination System sampling would not be conducted in this area during the test.

Resuspension of Sediment-Associated Mercury - Preparation of the site may require removal or relocation of some gravel and associated fine deposits that have accumulated on top of the concrete bottom at the N/S pipes, and some increased loading of fine particles in the creek will occur at that time. Mixing and turbulence associated with air injection at the site would also tend to resuspend fine particles. It may be necessary to cover the streambed under the diffuser array with heavy plastic or a metal plate to reduce resuspension. In both cases, the amount of total suspended solids generated would be far less than typical response to stormflow; and the duration would be short. It may be necessary to operate the air injection system several days prior to stannous chloride injection to reduce the mercury contributed by resuspension to levels that do not interfere with the experiment.

Long-Term (concerns associated with permanent operation)

Effects on Water Chemistry - Effective air stripping would be expected to remove carbon dioxide from stream water, raising the pH. Atmospheric CO₂ would reenter the stream 1-2 km downstream from the N/S pipes, returning the pH to normal conditions. Mercury has been shown to be less bioavailable at higher pH; hence, this might have a beneficial effect on mercury bioaccumulation.

Effects on Hg Bioavailability - This is less of a concern for in-situ air stripping than for enhanced natural volatilization because the elemental mercury generated would be removed in a localized site. The concerns associated with altered bioavailability described in Experiment 1 would also pertain to any residual elemental mercury not removed by the in-situ air stripping.

Chronic Toxicity - Same as Experiment 1. The low toxicity of tin, coupled with the very low concentrations being added, indicate little concern for chronic toxicity in EFPC. The BMAP in place on upper EFPC would detect any changes associated with chronic toxicity, if they occurred.

Formation of Organotin Compounds - Same as Experiment 1. There is evidence in the literature of inorganic tin being converted in the environment to organotin compounds by microbial action. However, the compounds formed are generally low degree of alkylation, short chain aliphatic compounds such as monomethyltin; and the rates and extent of conversion are low. These substances are not extremely toxic like tributyltin and, if formed, would be present at extremely low concentrations.

Atmospheric Mercury - Same concerns as in Experiment 1. Although atmospheric release of 5-10 g/day of elemental mercury should be acceptable from a regulatory perspective, this action will be subject to criticism for dispersing a contaminant suspected of being a global pollution concern. Before such a procedure is implemented on a long-term basis, careful evaluation of the consequences of transferring mercury from the aquatic environment to the atmosphere will need to be undertaken in order to demonstrate that the environmental benefits outweigh the drawbacks.

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M98004781



Report Number (14) Y/TS--1663

Publ. Date (11) 199703

Sponsor Code (18) DOE/DP, XF

UC Category (19) UC-702, DOE/ER

DOE