Mercury removal from East Fork Poplar Creek using chemical reduction and volatilization

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INTRODUCTION

East Fork Poplar Creek (EFPC) in Oak Ridge, TN receives inputs of mercury caused by legacy of contamination at the Department of Energy Y-12 plant. Most of that mercury leaves the storm drain network at a single discharge point. This mercury is highly reactive because of the presence of residual chlorine in the water. This project investigated removing the residual chlorine in the water and chemically converting the dissolved mercury (Hg (II)) to gaseous Hg (0). Natural volatilization across the air-water interface and/or air stripping within the storm drain itself could then be used to remove the Hg(0). This work studied the reactivity of dissolved Hg in creek water with the reductant stannous chloride ($SnCl_2$), photochemical re-oxidation of Hg (0) in daylight and the possible interferences from the de-chlorinating agents. A model was developed to describe the rate of volatilization of gaseous mercury from water flowing through a pipe as a function of flow, depth, velocity, and pipe dimensions. Preliminary design of a system for *in situ* air stripping was initiated.

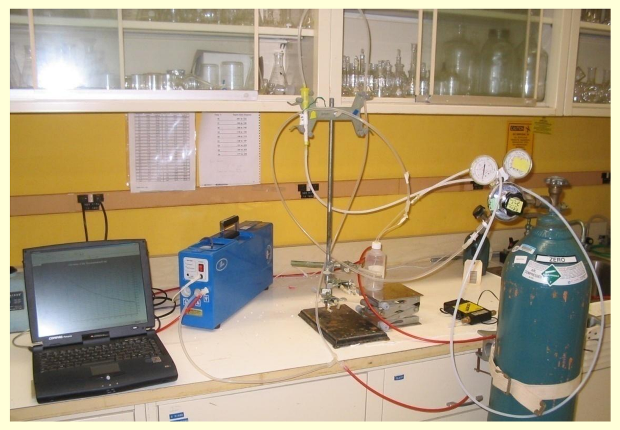
HISTORY

In the 1950's around 11,400 metric tons of Hg were processed in the plant Y-12 (Oak Ridge) which led to mercury contamination of ground and surface waters. East Fork Poplar Creek (EFPC) continues to receive dissolved inorganic mercury from groundwater. Remedial efforts started in the 1980's included cleaning/relining pipes, rerouting flows, and treatment of sump discharges and contaminated spring water in the Y-12 plant. These actions reduced Hg concentrations in upper East Fork Poplar Creek (UEFPC) by ~ 90%. However, Hg in fish remains elevated above regulatory standards, and further reductions in waterborne Hg concentrations (from present 200 - 300 ng/L) will be needed.

Location of the source of Upper East Fork Poplar Creek surface flow within the Y-12 plant in Oak Ridge

HYPOTHESIS

- Trace concentrations of $SnCl_2$ would transform of Hg(II) to volatile Hg(0) in EFPC water
- The rate of photo-oxidation of Hg(0) by direct sunlight in the creek would require that Hg(0) removal occur in the dark
- Natural evasion of Hg(0) from water in the storm drain network would be rapid enough to substantially reduce total Hg concentration in the stream at the point where flow exits the system
- In situ air stripping could be a low cost alternative to increase the rate of removal of Hg(0).



Measurements of Hg(0) concentrations using the Lumex Mercury analyzer and the Mercury Guru software

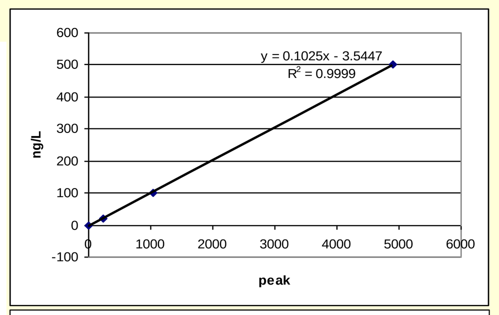
METHODS

- **Simulation in the lab**

  Tap water with Hg standard was mixed, added sodium thiosulfate as a de-chlorinator and $SnCl_2$ in different concentrations to determine the production of Hg(0) versus $SnCl_2$ (Fig.1 and 2) using the spectrometer Lumex RA-915 mercury analyzer. Alternatives de-chlorinators, like sodium sulfite and hydroxylamine were investigated.

Graphs of Hg(0) versus concentration of $SnCl_2$

1: Make up 0.5ug/L Hg in tap water (pH 7.48)							
2: Added 60uL Na-thiosulfate to 100ml of this Hg solution to dechlornate							
3: Put 10ml of 0.5ug/L Hg solution in a clean vial and purge, then add different con. of $SnCl_2$							
using fresh Hg solution for each running							
100ug/L $SnCl_2$ was made freshly from 10mg/L $SnCl_2$							
$SnCl_2$.2H2O	$SnCl_2$.2H2O	Hg(0)	Sn	Hg	Hg		
uLof 100ug/L	ug/L in 10ml	peak	µM/L	µg/L	µM/L		
or 10mg/L			0		0		
10	0.1	811	0.000443	0.079583	0.000398		
20	0.2	1685	0.000886	0.169168	0.000846		
40	0.4	3009	0.001773	0.304878	0.001524		
10	10	4270	0.04432	0.43413	0.002171		
100	100	4406	0.443203	0.44807	0.00224		
peak	std(ng/L)						
0	0						
242	20						
1039	100						
4905	500						



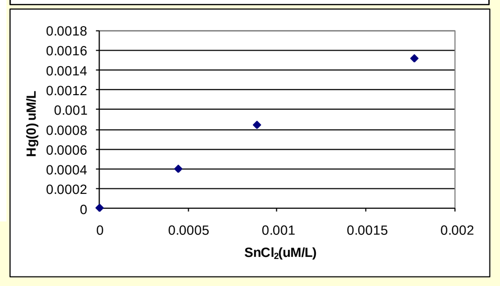


Fig 1

Different concentrations of SnCl2 dissolved with Standard Hg in dechlorinated tap water (2 tests)

- 0.5 ug/L of Hg in tap water
- Na thiosulfate as a de-chlorinator

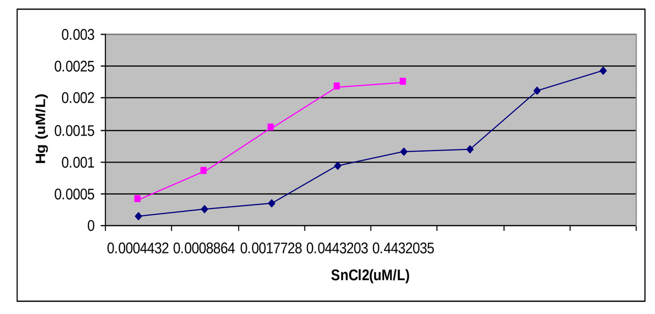


Fig 2

- **Experimental data**

  Samples of water were collected from upper East Fork Poplar Creek (UEFPC) at the point where it emerges from the storm drain system at Y-12. These samples were mixed with different concentrations of stannous chloride ($SnCl_2$) to evaluate the efficacy of the reduction reaction and the possible interference from excess de-chlorinating agent (ammonium bisulfite). Some samples received direct sunlight to evaluate the photo-oxidation of the Hg(0) (Fig. 3 & 4).

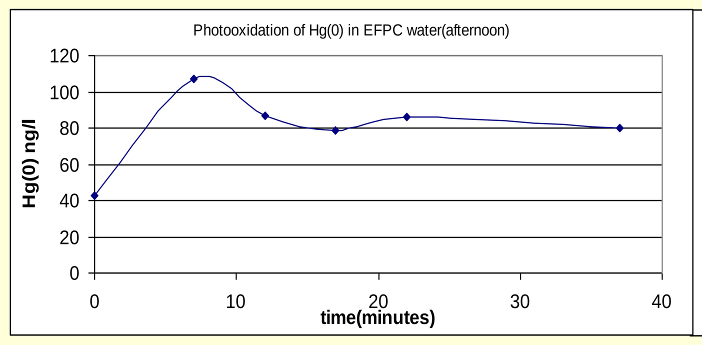


Fig 3 shows a balance between photo-oxidation and photo-reduction.

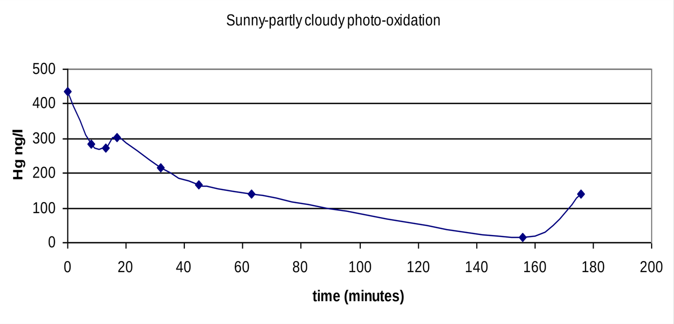


Fig 4 shows that Hg(0) in EFPC is rapidly oxidized to Hg (II) by sunlight (half life=28 minutes).

Sign showing Hg contamination in the EFPC

METHODS CONT'D

- **Modeling data**

  A simple mass transfer model was used to describe the rate of volatilization of Hg(0) as a function of depth, temperature and velocity of water. The model successfully predicted the downstream decrease in Hg(0) observed under low light conditions in a December 2007 study (Fig. 5), and was then applied to predict Hg(0) volatilization within pipes of various lengths, diameters, and flows. (Fig 6).

Modeled and observed concentrations of Hg(0) in EFPC versus distance from storm drain exit point

- Modeled using mass transfer coefficient (K), which varies as function of velocity and depth
- Hg(0) for any t is $Hg(o)(t)= 3*e^{-kt}$
- $K=23.51(v^{0.969}/R^{0.673})(32/Mol.wt\ Hg)^{2/3}$

  Where v= velocity of current at determined point, R is the depth of the creek (variable) and Mol wt Hg is 200
- Hg Flux = K * concentration of Hg(0)

  $(ng/cm^2/h)= (cm/h)(ng/cm^3)$

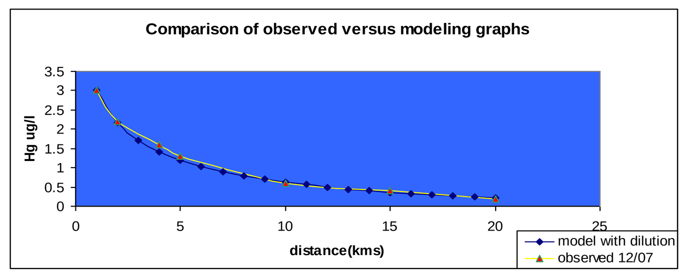
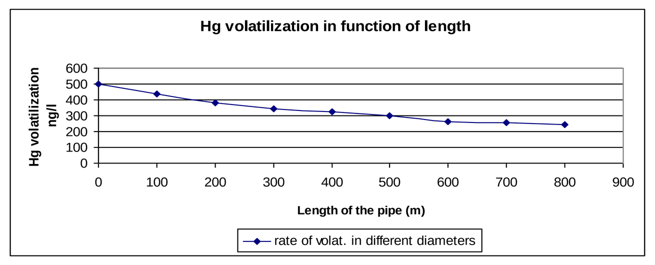


Fig 5

Mass transfer coefficient from creek applied to storm drain



- Predict 40% removal of Hg(0) in 500 m of storm drain
- Calculating wetted area of each pipe: $A=1/2r^2*(\Phi-\sin\Phi)$, $\Phi=2\cos^{-1}((r-depth)/r)$, Average depth=A/ Φ*r=R
- Velocity=Flow/area where flow=0.0694m3/sec
- Using $Hg(0)t=Hg(0)o*e^{-kt}$ where $k=(23.51*v^{0.969}/R^{0.673})*(32/200)^{2/3}$

Fig 6

Predicted of Hg Flux at storm drain exit, $SnCl_2$ added to each outfall

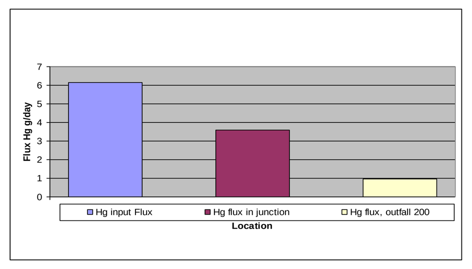


Fig 7

Comparison what happens if stannous chloride is added to each pipe in the drain network (Fig 7) or only to the main trunk line (Fig 8).

Predicted Hg flux at storm drain exit, $SnCl_2$ added 500 m upstream

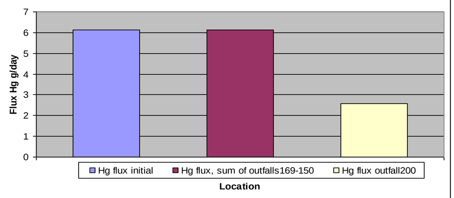


Fig 8

- **Design of air sparging system**

  Some calculations were made to design an efficient air sparging system in the storm drain. The ideal pressure and the power of the compressor were determined (5Hp). This system together with the application of the $SnCl_2$ in the storm drain will reduce mercury concentration in the creek more than 50%.

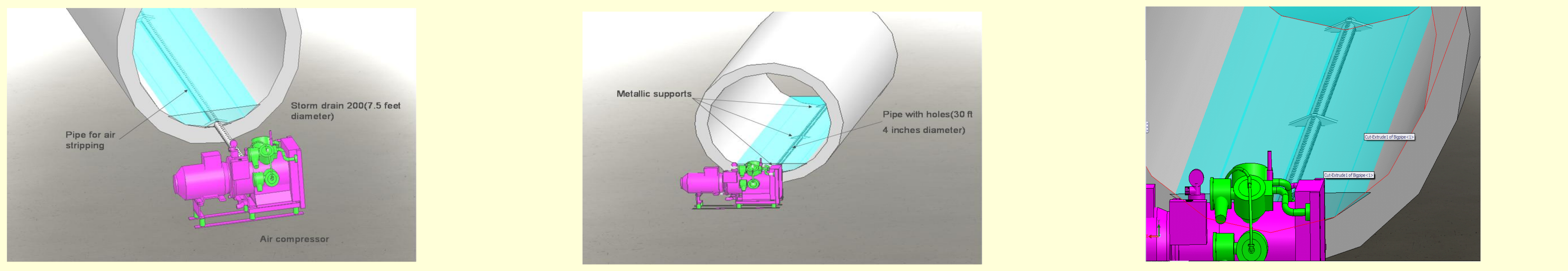


Fig 9 Design of air sparging system

CONCLUSIONS AND FUTURE RESEARCH

The results of the experiments showed that very low concentration of reductant (~5ug/L Sn(II) were able of convert 75% of mercury in the outfall to volatile Hg(0), but that excess de-chlorinating agent (HCl) interfered with the reaction. Using sodium thiosulfate as a alternative de-chlorinator did not interfere with the reaction. Sunlight rapidly oxidized Hg(0) to Hg(II), for that reason all removal of Hg(0) from water had to occur in the absence of sunlight. The model predicted that 35% of the Hg in the outfall could be removed by natural volatilization in a well ventilated pipe. To achieve more effective removal of Hg, volatilization would have to be enhanced by in situ air stripping. The combination of techniques analyzed in this study could be economically feasible and practical to reduce mercury in EFPC but more calculations and research are necessary to implement this system in larger scale.

ACKNOWLEDGEMENTS

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