**REACHING PARTS PER TRILLION CLEAN-UP CRITERION FOR MERCURY IN WATER**

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## ABSTRACT

In the last couple of years, emphasis on environmental mercury contamination and elimination of mercury use has increased. The U.S. Department of Energy has for many decades maintained a stockpile of elemental mercury for operations and, as a consequence of its routine use, spills have occurred. These historical spills have resulted in some contamination of water streams and soils. In this work we examine a newly developed technique for removal of mercury from contaminated groundwater. In this application the mercury concentration was approximately 2.3 parts per billion and the treatment criterion was 200 parts per trillion. Several forms of mercury species contributed to the contamination. The treatment technique developed for this water was to convert all forms of mercury, through a series of fast chemical reactions, to elemental mercury, which was air-stripped from the water. This paper presents preliminary laboratory work on the method.

## INTRODUCTION

Mercury poses unusual environmental hazards because minute concentrations [less than 10 ng/L (=10 ppt)] of mercury in water can result in the accumulation of mercury in fish to levels that are unsafe for human consumption. Mercury contaminated groundwater at the U.S. Department of Energy Y-12 Plant in Oak Ridge, TN is the major source of mercury in the surface flow of Upper East Fork Poplar Creek, where total mercury concentrations exceed the state water quality standard by several fold. Mercury contaminated groundwater at this site does not comprise of a diffuse groundwater plume, but rather occurs where elemental mercury comes in contact with water flowing through subsurface conduits. Mercury contamination of surface waters at this site arises as a consequence of shallow groundwater flow through preferential flow paths in a limestone karst system containing metallic mercury and mercury vapor in the headspace.

Over the past ten years, Oak Ridge Y-12 Plant's Reduction of Mercury in Plant Effluents (RMPE) program has carried out an aggressive investigative program in identifying sources of mercury that have influenced the levels of mercury in Upper East Fork Poplar Creek and exiting the site at the plant boundary. The RMPE program has also implemented several point-source treatment technologies in order to reduce the mercury levels in the creek. The current focus is on an underground spring, fed with water from the karst system, that surfaces and empties into the creek at a location known as Outfall 51. The average concentration of elemental mercury [Hg(0)] in the spring water is high, typically 900 ppt, and the soluble Hg(II) concentration is 1,500 ppt (1, 2). There is also a fraction of mercury with unknown speciation that amounts to 600 ppt. Relative proportions and concentrations of mercury species vary over time, as does flow of the spring. Any full-scale treatment system must handle 330 gallons per minute. The goal for any treatment system is 200 ppt total mercury.

Two characteristics of these mercury-conduit systems act to make it likely that mercury chemistry is atypical of natural waters. The first is the presence of elemental mercury [Hg(0)], which has substantial solubility in water and also appreciable volatility. The presence of elevated concentrations of Hg(0) in water is atypical of surface waters, even in contaminated systems such as East Fork Poplar Creek, where Hg(0) occurs at sub-ppt concentrations (3). It is likely that the near steady-state aqueous Hg(0) concentration maintained in conduits provides a source of precursor mercury for oxidation to Hg(I) and Hg(II) species (4). The second characteristic of concern is the potential for unusual chemical composition

of groundwater at industrial sites. Much of the flow in the storm drain network is process water discharged from the Oak Ridge Y-12 Plant. This water contains residual chlorine, chloride, and additives (such as zinc polyphosphate) to minimize deposit formation and pipe corrosion. Metal complexing agents, such as organophosphates, that were previously used within the facility may also be present in the groundwater. Oxidized mercury species [Hg(I) and Hg(II)], present in the ground water, may be complexed by some of these atypical groundwater constituents. These unknown complexes may alter the environmental transport characteristics and treatability potential. Mercurous mercury [(Hg(I)] complexes are unstable under the chemistry typical of most natural waters, breaking down into Hg(II) and Hg(0) (5), and hence little is known about the environmental behavior of Hg(I) complexes. It is possible that some of the unknown mercury species (which we will refer to as refractory from now on) are present as these Hg(I) complexes.

Treatment technologies applicable to the treatment of the spring water include precipitation/filtration, sorption, and air stripping. However, the success of these technologies requires mercury to be in a form suitable for treatment. Of these treatment technologies, air stripping has been tested at the underground spring in 1996–97 (3). In the air stripping technology, soluble Hg(II) is converted into dissolved gaseous mercury, Hg(0), with a reducing agent (stannous chloride, $SnCl_2$) and the mercury is stripped from the water with air and captured on activated carbon. This methodology is also the basis for laboratory mercury analysis (6). In the large-scale pilot testing at the site, air stripping was effective in removing the elemental and soluble mercury but was unable to remove the refractory mercury (3). Bench-scale studies conducted at the DOE Savannah River Site concluded that air stripping was effective in the treatment of a specific water stream containing approximately 150 ppt Hg(II) (7). They were able to reduce this to less than 10 ppt using chemical reduction with $SnCl_2$ combined with air stripping.

**MATERIALS AND METHODS**

Unfiltered water was collected from the contaminated spring in Teflon bottles on the same day that experiments were conducted. In conjunction with each experiment, three samples were prepared from the untreated water in the following fashion:
1. 40 mL was poured into a 40-mL glass vial and 200 μL of BrCl preservative (10.8 g KBr and 15.2 g $KBrO_3$ per L HCl) was added. The result of mercury analysis of this sample yielded the total mercury concentration.
2. 40 mL was poured into a 40-mL glass vial and air was bubbled through the water for 10 min a rate of approximately 1 L/min after which time the air flow was stopped and 200 μL of BrCl was added. The result of mercury analysis of this sample yielded the total combined Hg(II) and Hg(refractory) concentration.
3. 40 mL was poured into a 40-mL glass vial and 25 μL of $SnCl_2$ solution (1.8 mM $SnCl_2 \cdot 2H_2O$ in 20 mM HCl) was added and air was bubbled through the water for 10 min a rate of approximately 1 L/min after which time the air flow was stopped and 200 μL of BrCl was added. The result of mercury analysis of this sample yielded the Hg(refractory) concentration.

The above procedure allowed calculations of the individual Hg(0), Hg(II), and Hg(refractory) concentrations.

To treat the water, the volume of a vertically-mounted ultraviolet water sterilizer unit (Model SP-1, Aquafine, Valencia, CA), mounted, was filled with water and ozone/oxygen was sparged through the water at a rate of 53–105 mL/min for a predetermined time. Sometimes the UV light was turned on, sometimes not. Two ozone generators were used during the experiments: one was a small Aqua-Flo, Inc. (Baltimore, MD) Model CD06, the other an Ozonology (Northbrook, IL) Model Labozone L-100. Both of these systems were supplied dry oxygen from a compressed gas cylinder. After the water was treated in the ozone/UV reactor it was handled in the following manner:
1. 40 mL was poured into a 40-mL glass vial,

2. 8 µL of 0.86 M $NH_2OH$-HCl was sometimes added,
3. 25–30 µL of $SnCl_2$ solution (1.8 mM $SnCl_2·2H_2O$ in 20 mM HCl) was added,
4. air was sparged into the vial at a rate of approximately 1 L/min, and
5. 200 µL of BrCl preservative was added.

Other details are given in the figure captions. The unit was rinsed with distilled water between each use and analysis of the rinse water showed no significant carry-over from experiment to experiment.

Mercury analysis was performed using the Cold Vapor Atomic Absorption technique with a Leeman Lab, Inc. (Hudson, NH) PS200 mercury analyzer. Briefly, 8 mL of BrCl-oxidized sample (or standard) was reduced with 20 µL of a hydroxylamine solution (4.3 M $NH_2OH$-HCl). This solution was fed into the analyzer at a rate of approx. 5 mL/min and combined with approx. 1 mL/min of 4.4 mM $SnCl_2·2H_2O$ in 0.1 M HCl and continuously purged with nitrogen gas, which after evaporating the reduced mercury passed through a drying bed of packed magnesium perchlorate and into the light absorption cell. Six standards (0, 0.25, 0.5, 1, 1.5, and 2 ppb) of mercury were used to calibrate the instrument.

Measurement of gas-phase ozone was performed by injecting a known volume of gas into a sealed test tube with indigo blue solution and measuring the disappearance of the blue color at 600 nm (8). The detection of ozone in the liquid phase was determined in a similar fashion by adding a known volume of water to a test tube containing the indigo blue reagent (9).

## RESULTS AND DISCUSSION

The treatment method investigated the potential of ozone/UV systems to convert mercury in water samples to soluble Hg(II), which could be reduced with $SnCl_2$ and air-stripped out of solution. Experiments conducted in the ozone/UV reactor with continuous ozone/oxygen with, or without, UV irradiation showed the benefit of UV light. In Fig. 1, it is noted that prolonged exposure of the water to ozone/oxygen was beneficial in converting the mercury species to Hg(II), but that shorter exposure times were needed if UV irradiation was used in conjunction with ozonation.
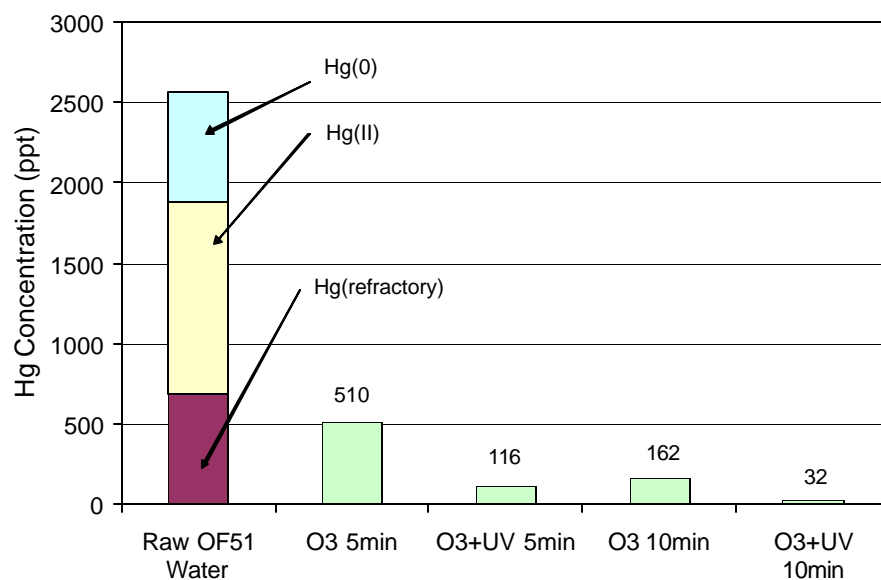


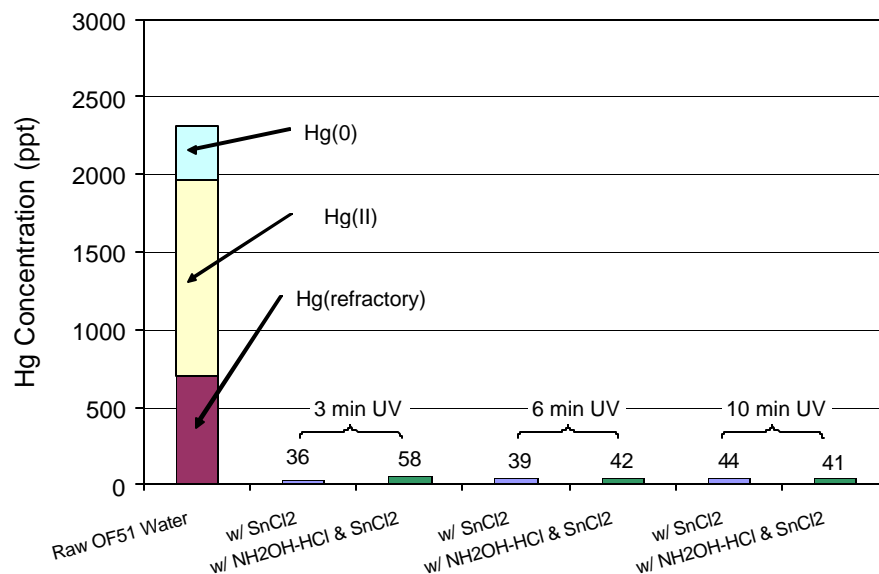**Fig. 1. Effect of ozonation and UV radiation.** Ozone concentration in the sparge gas was 25 mg $O_3$/L and the flow rate was 105 mL/min.

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To study the effect of combined ozonation/UV irradiation time, a set of experiments was conducted where the time for treatment was monitored more closely.  Based on this study, we concluded that treatment times over 5 minutes did not improve the conversion efficiency.  Concentrations of less than 100 ppt were obtained for most of the conditions even though the ozonation sparge rate was half of the one used in previous experiments.
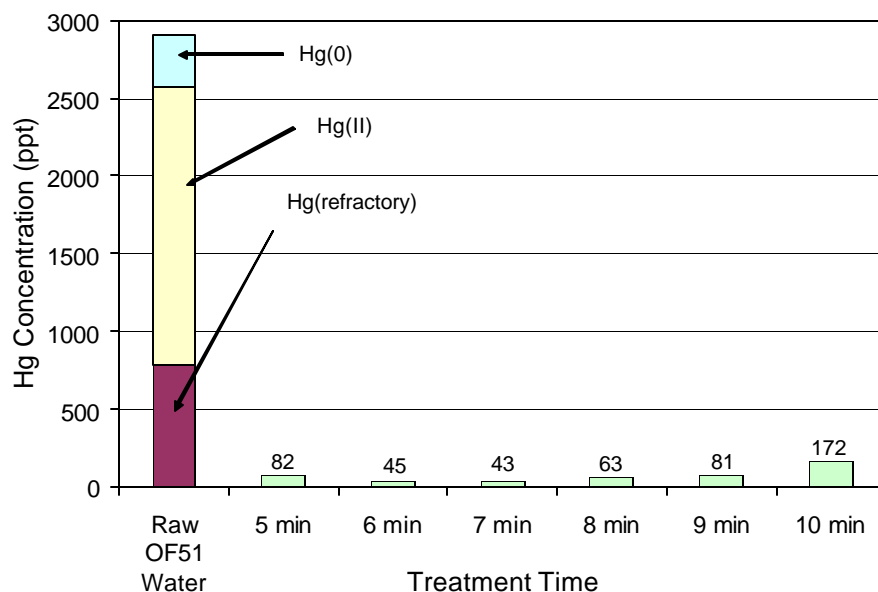


**Fig. 2.  Effect of treatment time on the conversion of mercury to Hg(II).**  Ozone concentration in the sparge gas was 28 mg $O_3$/L and the flow rate was 53 mL/min.

In the experiments corresponding to the results presented in Figs. 1 and 2, a small amount of hydroxylamine was added to the treated samples to remove any remaining ozone in the liquid, which would interfere with the Hg(II) reduction by $SnCl_2$.  To investigate if UV irradiation would serve the same purpose, several experiments were conducted in which the ozone/UV treated samples were exposed to additional UV radiation without ozone/oxygen sparging.  Samples from this approach were treated with or without hydroxylamine prior to the $SnCl_2$ addition.  The results showed that UV irradiation of ozonated samples destroyed the ozone to the point that it did not interfere with the next step of treatment (Fig. 3).  In other experiments, we have shown that the time needed for ozone destruction in our system is less than a minute.

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**Fig. 3.  The effect of UV irradiation as a method for reducing excess liquid ozone.**  The ozone concentration in the sparge gas was 25 mg $O_3$/L and the flow rate was 105 mL/min for 10 min. Then, the sparging was turned off and the water was exposed to additional UV radiation for the specified times.  The  water  was  then  treated  either  with  $SnCl_2$+air sparging+BrCl or with $NH_2OH$-HCl+$SnCl_2$+air sparging+BrCl.

In a practical application of the proposed treatment method, it is desirable to use standard equipment. Ozone generator/contactors are standard equipment in many water systems; so are UV irradiation units. However, systems that expose the water to ozone and UV light at the same time are scarce.  Thus, a set of experiments was conducted where the water was exposed (by sparging) to different concentrations of ozone/oxygen gas.  Then, this exposure was halted and the water was exposed to UV radiation for a short time to generate radicals to convert mercury, not already converted, to Hg(II) as well as remove the ozone before the $SnCl_2$ addition and air-stripping.  The results show that higher concentration of ozone in the water (following the ozonation) resulted in better overall conversion to Hg(II), once exposed to  UV radiation (Fig. 4).
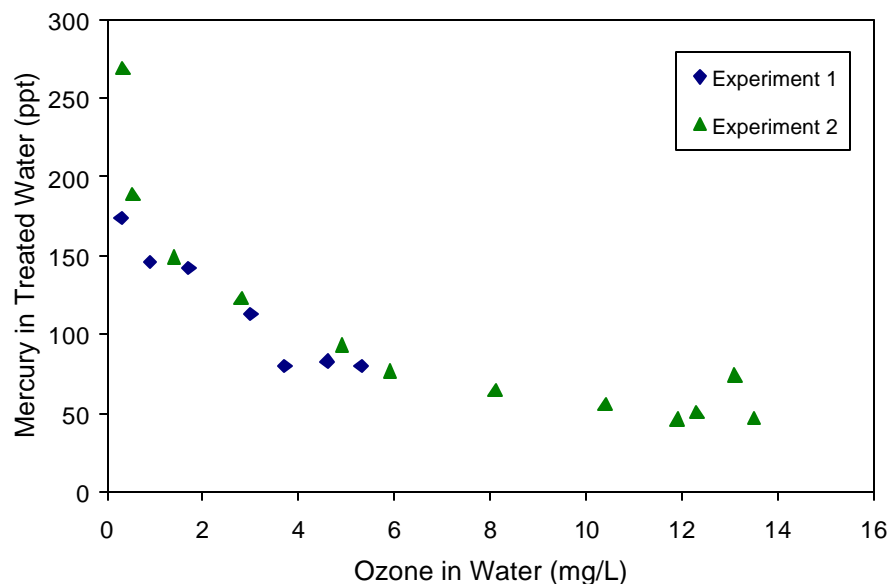
**Fig. 4. Effect of liquid phase ozone concentration (prior to UV irradiation) on the mercury conversion.** The ozone concentration in the gas was variable but the flow rate, 105 mL/min, and the sparging time (4 min.) were held constant. The UV-irradiation duration after ozonation was 30 sec. and $SnCl_2$ was added immediately after this, without any prior $NH_2OH$-HCl addition.

Based on these results, it was concluded that ozonation of water to a level corresponding to 5 mg/L $O_3$ in the liquid, followed by a short burst (30 sec.) of UV light was sufficient enough to reduce the mercury to 100 ppt, or half the targeted level.

**CONCLUSIONS**

It has been demonstrated in laboratory experiments that waters containing different mercury species can be almost entirely converted to a form [presumably, Hg(II)] that can easily be reduced by $SnCl_2$ and air-stripped out of the water. Dependent on the degree of ozonation/UV treatment, different conversion efficiencies can be obtained. For the purpose of treating the natural spring water, which was the objective of our study, ozonation achieving 5 mg $O_3$/L in the water, followed by 30 sec. UV light exposure was sufficient to reach the imposed treatment goal (200 ppt). Future work will concentrate on continuous flow systems and optimization of the reaction conditions.

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