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The effects of a stannous chloride-based water treatment system in a mercury contaminated stream

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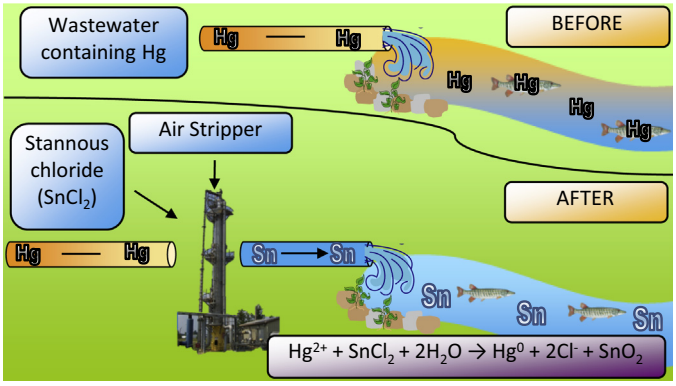
HIGHLIGHTS

- Stannous chloride and air stripping reduced Hg concentrations in stream water > 90%.
- The decrease in aqueous Hg concentrations led to 75% reduction in Hg in fish.
- The treatment resulted in a measurable increase in aqueous tin concentrations.
- Tin bioaccumulation was measurable but not at levels of concern.
- Tin did not affect mercury methylation.

GRAPHICAL ABSTRACT



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ABSTRACT

We assessed the impacts of an innovative Hg water treatment system on a small, industrially-contaminated stream in the southeastern United States. The treatment system, installed in 2007, removes Hg from wastewater using tin (Sn) (II) chloride followed by air stripping. Mercury concentrations in the receiving stream, Tims Branch, decreased from >100 to ~10 ng/L in the four years following treatment, and Hg body burdens in redfin pickerel (*Esox americanus*) decreased by 70% at the most contaminated site. Tin concentrations in water and fish increased significantly in the tributary leading to Tims Branch, but concentrations remain below levels of concern for human health or ecological risks. While other studies have shown that Sn may be environmentally methylated and methyltin can transfer its methyl group to Hg, results from our field studies and sediment incubation experiments suggest that the added Sn to the Tims Branch watershed is not contributing to methylmercury (MeHg) production or bioaccumulation in this system. The stannous chloride treatment system installed at Tims Branch was effective at removing Hg inputs and reducing Hg bioaccumulation in the stream, but future studies are needed to assess longer term impacts of Sn on the environment.

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1. Introduction

Mercury has historically been used for hundreds of applications worldwide because of its unique properties (e.g. density, liquid at room temp, volatility, redox chemistry). In many cases, industrial uses have led to environmental releases of Hg – in the United States alone, there are currently >500 Hg-contaminated sites on the National Priorities List for remediation (U.S. Environmental Protection Agency (EPA), 2010). Some of the same properties which make Hg so useful to industrial applications also make Hg difficult to contain and recover from the environment (Turner and Southworth, 1999). Aquatic systems are particularly susceptible to Hg contamination because Hg is subject to complex biogeochemical interactions and transformations in the aquatic environment.

While the sources of Hg to contaminated systems are most often inorganic Hg (Hg^{2+}, Hg^0), a small proportion of this inorganic Hg is transformed by aquatic microbes into MeHg, which is both more toxic and more bioaccumulative than inorganic Hg. In contrast to most other metals, Hg (especially in its organic form, MeHg) biomagnifies or becomes increasingly concentrated as it is transferred through aquatic food chains so that the consumption of Hg-contaminated fish is the primary route of this toxin to humans. This is why guidelines and remediation targets for Hg often include fish tissue concentrations which are considered to be more consistent indicator of exposure and risk.

Effective Hg remediation at point-source contaminated sites requires an understanding of the nature and magnitude of Hg inputs, and also knowledge of the extent to which these inputs must be controlled in order to achieve the desired reduction of Hg contamination in biota. One of the challenges to remediation is that Hg body burdens in fish are more closely linked to aqueous MeHg than to inorganic Hg concentrations, but MeHg production is not easily controlled. Regulations and "achievable" remediation goals are thus typically developed based on total Hg (Hg_T) concentrations that are dominated by inorganic Hg in many settings.

In the present study, we examine the net impacts of an innovative Hg treatment system which uses Sn(II) chloride (stannous chloride; $SnCl_2$) and air stripping (Looney et al., 2003) to remove aqueous inorganic Hg from wastewater entering Tims Branch, a stream on the Department of Energy's (DOE) Savannah River Site (SRS) in Aiken, South Carolina. This treatment system is an extension of the basic principles used in many analytical methods for Hg (Southworth, 1996), where $SnCl_2$ is used to reduce Hg^{2+} to Hg^0 (Eq. (1)) which is sparged into the gaseous phase by bubbling with air (Jackson et al., 2013).

$$HgCl_2^0 + Sn^{2+} + 2H_2O \rightarrow Hg(0) + 2Cl^- + SnO_2(s) + 4H^+ \quad (1)$$

While the goal of this treatment system is to remove Hg inputs to the watershed, its operation introduces inorganic Sn to the ecosystem. In the present study, we evaluated the effectiveness of the Sn-based remediation system in (1) removing Hg inputs to water in Tims Branch, (2) the effect of removing aqueous Hg inputs on reducing fish tissue Hg concentrations, (3) potential exposure to Sn as a result of treatment, and (4) the potential for Hg methylation in sediments with elevated Sn concentrations.

2. Methods

2.1. Study site

Tims Branch is a second-order tributary stream to Upper Three Runs, a tributary of the Savannah River (Fig. 1). Tims Branch has been the subject of numerous ecological and geochemical research studies (Edwards, 2012) and the Hg contamination (including detailed assessments of water, biota, and atmospheric deposition) has been characterized in the vicinity of the Savannah River Site (Halverson et al., 2008). The headwaters of Tims Branch originate from facility outfalls in two areas-the Savannah River National Laboratory to the north (sometimes referred to as "A area") and the fuel and target manufacturing facility to the west ("M area"). Several beaver dams and pools ("Beaver Ponds") are associated with this stream. From the 1950s until 1982, industrial process wastes were discharged from the M area directly into the headwaters of an unnamed tributary (hereafter referred to as "Outfall Tributary") leading to Tims Branch (Fig. 1). A stannous chloride-based Hg treatment system was installed in 2007 at an air stripper tower (which was originally designed to treat groundwater for organic contaminants) located at the Outfall Tributary (Fig. 1) (Jackson et al., 2013).

2.2. Mercury and tin monitoring in water and sediment

Monthly (unfiltered) water samples were collected for Hg_T analysis from the outfall leading to Tims Branch as part of National Pollutant Discharge Elimination System monitoring. Sediment samples were collected from three locations: (1) the outfall tributary, (2) Tims Branch just upstream of Steed's Pond (approximately 3 km downstream of outfall), and (3) Tims Branch at confluence with Upper Three Runs (approximately 7.8 km downstream of outfall) (Fig. 1) in summer 2011. Sediment was collected with plastic sediment core liners to an average depth of 11.5 cm below the surface. Cores were partitioned into ~0.5 in. segments, air dried at 65 °C and then homogenized with mortar and pestle. The sediment samples were analyzed by X-ray fluorescence (Niton XL3t-GOLDD+ analyzer).

2.3. Biological samples

The target species for monitoring temporal changes in Hg and Sn bioaccumulation pre- and post-$SnCl_2$ treatment is the redfin pickerel (*Esox americanus*). This species is widespread throughout coastal drainages of the southeastern United States and represents the upper trophic level in the Tims Branch watershed. Pickerel were collected by electrofishing and with minnow traps in (September–December) 2006 (pre-treatment) and in (April–July) 2010 (4 years after the start of $SnCl_2$ treatment) from Tims Branch beaver ponds both upstream (Beaver Pond 1) and downstream (Beaver Ponds 2, 3, and 4) of the mouth of the Outfall Tributary (Fig. 1). Because the size of fish varied greatly across sites, and Hg concentrations in fish are correlated with fish size, we used regression analysis to calculate the Hg concentrations in a nominal fish of 150 mm length in order to be able to compare Hg concentrations between sites for similarly sized fish. This method of extrapolation has been shown to be robust when the average size for each dataset is relatively close to the selected nominal length (Fig. A1) (Sonesten, 2003).

To evaluate the potential impacts of adding Sn to the system, fish and invertebrates were collected in November 2011 from various sites within the stream closest to the Sn inputs, including Beaver Pond 2. Target organisms for Hg and Sn monitoring in Tims Branch included the redfin pickerel and some of their potential prey items: dusky shiners (*Notropis cummingsae*), golden shiners (*Notemigonus crysoleucas*), crayfish (*Cambarus* spp.), and immature aquatic insects (various species of Odonata; *Nigronia*, *Corydalus cornutus*, and *Tipula*). Forage fish and insects were analyzed as whole body composites, while pickerel and crayfish were dissected to assess Sn and Hg accumulation in gills, gut, muscle, and remaining carcass. Fish were collected by electrofishing and with minnow traps. Crayfish were collected with minnow traps, and other macroinvertebrates were collected with a D-frame aquatic kick net. Collected specimens were brought back to the laboratory on ice, where they were weighed, measured, and dissected. All