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

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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 redbfin 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.

1. INTRODUCTION

Mercury has historically been used for hundreds of industrial 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 consider 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).

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 1950’s 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 inch 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-SnCl₂ treatment is the redbfin 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 SnCl₂ 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 redbfin 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 fish and invertebrate samples (composites, individual fish tissue samples) were freeze dried, homogenized, and kept frozen until analysis. For each tissue type, the sample was weighed, freeze dried, and percent moisture was determined. Mercury and Sn concentrations for each tissue were analyzed and reported on a dry weight (d.w.) basis.

Biofilm samples were collected by removing a substrate (rock or mass of root fibers) by hand. Samples collected in this manner contained significant quantities of detritus and particulate matter (relative to traditional biofilm samples collected from flat plates after a period of colonization. Samples were dried at 60°C for 12 hours and were separated from substrate by agitation before homogenization with mortar and pestle.

2.4 Mercury and tin analysis of biota samples

Whole body pickerel samples were analyzed for Hg using thermal decomposition, amalgamation, and atomic absorption spectrophotometry (Milestone, DMA-80). All other biota Hg samples were digested in acid ($\text{HNO}_3/\text{H}_2\text{SO}_4$) and analyzed by cold vapor atomic absorption spectrometry (Ohio Lumex, RA-915+) following SnCl_2 reduction. One duplicate fillet sample was digested and analyzed for every six fish, and procedural blanks and standard reference materials (NIST Lake Michigan Fish Tissue or DORM-2) were analyzed for quality control and

demonstrated Hg recovery from standards >90%. Blanks are typically below detection limits, and duplicates are on average < 5% different from their parent sample.

The Sn analysis of tissue samples was performed by ICP-MS following microwave digestion with 9 mL of HNO₃ and 3 mL of HCl. All samples were run in duplicate, and procedural blanks and standard reference material (NRC PACS-2) were analyzed for quality control and demonstrated Sn recovery from standards >90%. Blanks were below detection limits. Biofilm samples were analyzed in the same way as sediment samples, X-ray fluorescence (Niton XL3t-GOLDD+ analyzer).

2.5 Sediment incubations

To evaluate the effect of Sn on Hg methylation potential in sediments, short term sediment incubation experiments were conducted in sediments with high and low Hg and Sn concentrations using ²⁰¹Hg spikes to quantify methylation potential as the concentration of Me²⁰¹Hg produced (Table A1). Sediments were collected from the Tims Branch watershed and East Fork Poplar Creek (EFPC), a Hg contaminated site in East Tennessee with no Sn inputs (Mathews et al. 2013) . The concentration of the ambient and enriched isotope of Hg_T and MeHg were determined using a Hg purge and trap system (Brooks Rand MERX) followed by detection on an inductively coupled plasma-mass spectrometer (ICP-MS; Perkin Elmer Elan DRC)(Moberly et al. 2012). Sediments were incubated in a glove bag for 3 days under anoxic conditions. Detailed methods are presented in Appendix A.

3. RESULTS AND DISCUSSION

3.1 Effects of treatment technology on aqueous mercury concentrations in Tims Branch

The SnCl₂-based treatment system installed in 2007 effectively reduced mean aqueous Hg_T concentrations in the Outfall Tributary from > 100 ng/L to <10 ng/L in the first few weeks after implementation, and concentrations have remained low since treatment began (Fig. 2). The mean aqueous Hg concentrations currently observed in this tributary are below the National Pollution Discharge Elimination System (NPDES) permit limit of 51 ng/L and are comparable to those found in rainwater collected at the SRS (Halverson et al. 2008), suggesting that the treatment system was effective in removing direct anthropogenic sources of Hg to the Tims Branch watershed.

Our results are consistent with smaller scale studies that used SnCl₂ and air stripping to remove aqueous Hg from surface water (Southworth et al. 2009) or Sn filters to remove Hg from groundwater (Biester et al. 2000), but our study has demonstrated a positive effect at a much larger scale. The efficacy of the treatment system at Tims Branch is related to the nature and extent of the Hg inputs to this stream. Over 95% of the Hg entering the air stripper is Hg(II)(Looney et al. 2003) which is amenable to the SnCl₂ treatment – the Sn-based reduction and stripping process does not effectively remove most organic forms of Hg (e.g. MeHg) and is not efficient at removing strongly bound Hg complexes or particulate Hg (Southworth et al. 2010). The treatment system therefore has relevance to many point-source, industrially contaminated sites (e.g. mining sites, chloralkali and other chemical plants, pulp mills, etc.), but would be less suitable for sites with a diffuse source of Hg (e.g. atmospheric deposition).

3.2 Effects of treatment technology on mercury concentrations in fish in Tims Branch

The change in fish tissue Hg concentrations in the Tims Branch system following SnCl₂ treatment is shown in Fig. 3. Mercury concentrations in fish collected from all three pond

sampling locations downstream of the treatment system decreased significantly between 2006 and 2010 (ANOVA, $p < 0.05$), while no significant change was observed in Hg in fish collected from Beaver Pond 1, the upstream reference site. The observed differences in Hg concentrations in fish between pre- and post-treatment were greatest in the pond closest to the treatment system, and decreased with increasing distance from the treatment system. For example, in Beaver Pond 2 (the pond closest to the treatment system), the mean whole body Hg concentration in pickerel of 150 mm length decreased approximately 72%, from 3.4 $\mu\text{g/g}$ in 2006 before treatment to 0.96 $\mu\text{g/g}$ (d.w.) in 2010 after treatment, whereas in Beaver Pond 4 (the pond furthest away from treatment system) the mean whole body Hg concentration only decreased by approximately 5%.

The 2006 Hg concentrations in pickerel collected throughout the Tims Branch watershed decreased with increasing distance from the Hg inputs prior to SnCl_2 treatment. No such spatial gradient was apparent in 2010 after treatment, as mean Hg concentrations in whole body pickerel were not statistically different from each other across sampling sites within the stream in 2010 ($p < 0.05$; ANOVA; Fig. 3). In the Outfall Tributary that receives the treated water, 2010 Hg concentrations in pickerel were lower than those in Tims Branch and the downstream Beaver ponds (Fig. A2). The beaver ponds contain higher aqueous organic carbon and retain sediments (including legacy Hg-contaminated sediment), creating environments that are more favorable to Hg methylation and bioaccumulation in fish than in the Outfall Tributary.

Previous work in contaminated streams has often shown a weak relationship between aqueous and fish tissue Hg_T concentrations, particularly when aqueous Hg_T concentrations are high (Mathews et al. 2013). This is likely because fish tissue concentrations are more closely related to MeHg, rather than Hg_T concentrations. Methylmercury, however, is often not routinely measured because of cost; therefore many monitoring data sets consist solely of Hg_T

concentrations. Mathews et al. (2013) suggested that at contaminated sites, there may be a threshold aqueous Hg_T concentration at which fish tissue concentrations decline in response to decreases in aqueous Hg_T concentrations. The aqueous Hg_T concentrations measured in Tims Branch since the installation of the $SnCl_2$ treatment system are comparable to (or less than) the threshold concentrations at other Hg-contaminated sites (<100 ng/L) (Fig. 2).

3.3 Effects of treatment system on aqueous and sediment tin concentrations in Tims Branch

While aqueous Hg concentrations have decreased since implementation of the treatment system, aqueous Sn concentrations in the treatment system effluent have increased significantly, from below detection limits (< 5 $\mu\text{g/L}$) prior to $SnCl_2$ additions to ~ 12 $\mu\text{g/L}$ (Fig A3) post-treatment. These concentrations are elevated with respect to reported stream and river water concentrations, which are generally between 0.1- 1 $\mu\text{g/L}$ (Narasaki and Ikeda 1990), but inorganic Sn is seldom measured in surface waters and there is great variation among reported aqueous concentrations. Concentrations in drinking water supplies in the United Kingdom are generally < 10 $\mu\text{g/L}$ and the maximum permissible limit for Sn in water in Germany is 20 $\mu\text{g/L}$. Aqueous Sn concentrations in the U.S. average 6 $\mu\text{g/L}$ but can be as high as 30 $\mu\text{g/L}$ (Howe and Watts 2005). The aqueous Sn concentrations in the Tims Branch watershed are thus within the range of concentrations seen in uncontaminated freshwater systems (Weber 1985).

Tin concentrations in sediments collected throughout the Tims Branch watershed show spatial patterns typical of point source inputs, with the highest mean concentrations (~ 60 $\mu\text{g/g}$) closest to the $SnCl_2$ source in the Outfall Tributary, and decreasing concentrations to below detection limits (< 12 $\mu\text{g/g}$) in Beaver Pond 2 (approximately 1 km downstream) (Fig. A4). Typical background Sn concentrations in soils range from 2-15 $\mu\text{g/g}$ (Howe and Watts 2005), though

concentrations of 50-300 $\mu\text{g/g}$ have been reported in soils with high peat content which are not obviously ‘contaminated’ but have accumulated Sn from atmospheric deposition (Chillrud et al. 1999, Griffiths and Milne 1977). Sites affected by mining can have concentrations as high as 800-1000 $\mu\text{g/g}$ (Park and Presley 1997, Bryan and Langston 1992). While the Sn sediment concentrations in the Outfall Tributary are within the range of concentrations seen in uncontaminated sites, the constant input of Sn to the system may lead to Sn accumulation in sediments over longer time periods; longer term studies to characterize Sn dynamics in the Tims Branch watershed are warranted.

The thermodynamically favored species of Sn in stream systems are inorganic Sn oxides which have low solubility and precipitate out of solution (U.S. Department of Health and Human Services 2005) (Fig. A5). As a precipitate, inorganic Sn is relatively inert, immobile, not bioavailable, and non-toxic, so is not often measured in soils because it is considered to have “limited environmental significance” (Hooda 2010). In fact, metal oxides are commonly used in the remediation of contaminated soils and sediments because they are able to adsorb, complex or co-precipitate other contaminant metals in soil. The most commonly used metals for soil remediation are iron (Fe) and aluminum (Al) oxides, which behave similarly to Sn oxides (Hooda 2010).

3.4 Effects of treatment system on tin concentrations in biota in Tims Branch

While Sn concentrations in water and sediments in Tims Branch were moderately elevated, Sn concentrations in biofilm samples showed significantly elevated concentrations in the Outfall Tributary (up to $\sim 10,000 \mu\text{g/g}$, d.w.), with concentrations dropping orders of magnitude with increasing distance downstream to Beaver Pond 2 ($< 100 \mu\text{g/g}$) (Fig. A6). Aquatic plants have

been shown to be efficient accumulators of Sn, but there is no evidence in the literature of inorganic Sn toxicity in plants, even at elevated concentrations (Hooda 2010). For this reason, using plants to remove excess Sn from the environment (i.e. phytoremediation) has been suggested in Sn mining areas (Ashraf et al. 2011).

Despite the elevated Sn concentrations in biofilm in the Outfall Tributary, Sn does not appear to be efficiently transferred through the food chain. Measured Sn concentrations in grazers (crayfish, aquatic insects, and forage fish) in the Outfall Tributary are orders of magnitude lower than in biofilm, with concentrations in grazers ranging from 1-8 $\mu\text{g/g}$ (Fig. A7). In general, concentrations in grazers were higher in the Outfall Tributary closest to the SnCl_2 inputs than in Tims Branch (further downstream of Sn inputs), but concentrations in pickerel were not significantly different between the two sites ($p > 0.05$; Fig. A7). Tin concentrations were fairly comparable between consumers at different trophic levels, suggesting that while Sn may be accumulated by aquatic plants, it is not bioavailable and is not assimilated by animals. These patterns of bioconcentration are typical of Class A (or “hard acid”) metals such as Sn, which can accumulate on the external membranes of primary producers, but are not absorbed but rather egested from consumers (Reinfelder and Fisher 1991).

Tissue distribution of Sn in pickerel showed very low concentrations in the gills and viscera, suggesting that absorption through the gills is not likely important (Fig. A8). Tin concentrations in whole body pickerel collected from Beaver Pond 2 were significantly higher post- SnCl_2 treatment (mean concentration of 0.57 $\mu\text{g/g}$ in 2010 and 2.48 $\mu\text{g/g}$ in 2011) than in 2006 pre-treatment (mean concentration 0.06 $\mu\text{g/g}$; ANOVA, $p < 0.05$, Fig. 4). However, when comparing Sn concentrations between the D1 pond reference site and Beaver Pond 2 within a given year

(2011), mean concentrations were actually higher at the reference site (4.49 µg/g), which was never impacted by anthropogenic activities or wastes. Thus, while the data suggest a statistically significant increase in Sn concentrations in Tims Branch fish since implementation of the SnCl₂ treatment system, these differences may not be biologically significant. Indeed, Sn concentrations in fish collected from the wild generally range from 0.1-8 µg/g, with most concentrations falling between 4-8 µg/g (d.w.), comparable to concentrations seen in Tims Branch (Ikem and Egiebor 2005, Ikemoto et al. 2008, Mansour and Sidky 2002, Maguire et al. 1986).

As with aqueous Sn concentrations, inorganic Sn data for fish collected in the wild are limited. However, because fish are commonly packaged for human consumption in tin cans, there is a fairly extensive literature on Sn concentrations in canned fish (Biego et al. 1999, Millour et al. 2012, Blunden and Wallace 2003), where reported concentrations range between 4-8 µg/g (d.w.). These concentrations are similar to those seen in the limited studies of fish caught in the wild (Weber 1985). Though there are no guidelines for Sn in food in the U.S., the recommended maximum permissible concentration for Sn in food ranges between 200-250 µg/g in Europe (Blunden and Wallace 2003), orders of magnitude higher than the Sn concentrations seen in whole body pickerel collected from the Tims Branch watershed post-SnCl₂ treatment. While there was considerable variability in fish Sn concentrations in Tims Branch, which ranged between 0.1-8.6 µg/g (d.w.), the concentrations seen in Tims Branch post-SnCl₂ treatment system are within the normal range of concentrations seen in fish from uncontaminated sites, and are orders of magnitude lower than concentrations considered to be safe for human consumption.

3.5 Effects of Sn on Hg methylation

In short term anaerobic sediment incubations, we found that the methylation potential of sediment was not related to the initial Hg or MeHg concentrations in the sediment (Fig. 5; Table A1). Of the unamended sediments, those from Beaver Pond 1 (BP1) had a higher potential for Hg methylation than either the Outfall Tributary or EFPC despite the higher ambient Hg concentrations in the latter two sediments. The methylation potential in sediment from EFPC amended with a solid phase Sn spike (EFPC + Sn) was not different from unamended EFPC, suggesting that inorganic Sn added to sediments with high ambient Hg concentrations did not have an effect on Hg methylation. In the two sediment mixture treatments (Outfall Tributary + EFPC and BP1 + EFPC), the methylation potential of the mixture was not different than the sum of the methylation potentials based on the mass fraction of each sediment type in the mixture ($p > 0.05$).

Our results suggest that, while we did not directly measure methyltin production in the present study, other environmental factors such as sediment organic content (Table A1) or microbial activity had a larger impact on Hg methylation than Sn. The ambient MeHg concentration in the sediments from the two sites in the Tims Branch system (Table A1) and the methylation potential incubations both indicate that Sn is not a major driver in the production of MeHg in stream sediments. This is corroborated by the decrease in Hg concentrations in fish observed in Tims Branch since the implantation of the SnCl_2 treatment (Fig 3), which would not be expected if MeHg concentrations were increasing at sites with Sn inputs.

4. CONCLUSIONS

As with any remediation decision, the benefits and disadvantages of using the SnCl_2 treatment system described in this study will depend on many factors including: cost, potential

effectiveness (e.g. this treatment will not be effective at removing certain forms of Hg, including methylmercury), and potential harmful effects (e.g. Sn methylation is thought to be more favorable in brackish conditions (Gilmour et al. 1987)) . Because inorganic Sn is considered non-toxic while mercury is known for its widespread toxicity and can have both regulatory and financial implications at contaminated sites, this treatment system may offer more benefits than drawbacks in many cases. There are many examples where amendments that could be harmful in some systems (coal ash, humic material, etc.) are used to immobilize a contaminant that is considered to be a greater risk.

In Tims Branch, the SnCl_2 treatment system was successful in cost effectively removing Hg from the water column and reducing Hg bioaccumulation in fish. Because the air stripper was originally installed to treat groundwater for organic contaminants, the costs to implement and operate the SnCl_2 -based Hg treatment at this site were negligible (a storage tank and chemical metering pump and small quantities of SnCl_2 reagent). Based on standard cost estimation guidance (Federal Remediation Technology Roundtable 2014), the full costs for implementation and operation of this technology, including the air stripper, would range from \$0.10 to \$0.20 per m^3 . These costs are substantially less than the costs for alternative Hg treatment technologies such as liquid phase carbon (\$0.32 to \$1.65 per m^3).

While more studies are needed to assess the potential longer term impacts of the treatment system, this initial study did not find Sn bioaccumulation to be at levels of concern for human or ecological risk 5 years after treatment began. While this time period may not be sufficient to assess sublethal multi-generational effects which could have impacts at the population and/or ecosystem level, there was no evidence either from the literature, or from the present 5-year study, that the Sn additions resulted in concentrations or species of Sn that would have an

immediate or acute effect on the organisms living in the Tims Branch watershed. Further, evidence from both the field sampling and the incubation study suggests that the added Sn in the Tims Branch system is not exacerbating Hg methylation in the environment.. Additional studies to address longer term effects are either planned or are currently underway e.g., (Edwards 2012).

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Figure 1. Map of sampling sites along the Tims Branch watershed on the Savannah River Site (SRS).

Figure. 2 Aqueous total mercury concentrations (ng/L) in outfall leading to the unnamed tributary to Tims Branch, 2004-2014.

Figure 3. Estimated mercury concentration for nominal 150 mm length redfin pickerel collected from Tims Branch ponds in 2006 (pre-treatment) and 2010 (post-treatment). Data points represent means and error bars show the 95% confidence interval. Italicized numbers represent sample size. BP = Beaver Pond (sites shown in Fig. 1).

Figure 4. Tin concentrations in whole body pickerel from Beaver Pond 2 (grey boxes; 2006 (n=10), 2010 (n=8), 2011(n=4)) and from D1 reference pond (white box; 2011 only; n=8). Asterisks denote whole body concentrations that were calculated as the sum of the Sn content in dissected tissues (gills, fillet, viscera, and carcass). See Fig. A8 for dissection data.

Figure 5. Mercury methylation potentials determined in sediment incubation experiments. Each bar represents the mean of triplicate samples, and error bars represent 1 standard deviation.

FIGURE LEGENDS

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ASSOCIATED CONTENT

Appendix Available

- Fig. A1. Relationship between Hg concentrations and size of redbfin pickerel pre- and post- SnCl_2 treatment

- Fig. A2. Spatial trends in Hg concentrations in whole body fish post-SnCl₂ treatment (2011)
- Fig. A3. Aqueous Sn concentrations in water entering Tims Branch post-SnCl₂ treatment
- Fig. A4. Geochemical speciation of tin in water in outfall
- Fig. A5. Spatial trends in Sn concentrations in sediments collected from the Tims Branch watershed post-SnCl₂ treatment (2011)
- Fig A6. Spatial trends in Sn concentrations in biofilm samples collected from the Tims Branch watershed post-SnCl₂ treatment (2011)
- Fig A7. Whole body Sn concentrations in pickerel and prey collected from Outfall Tributary and Tims Branch post-SnCl₂ treatment (2011)
- Fig A8. Tin concentrations in tissues of pickerel collected from Outfall Tributary and Tims Branch post-SnCl₂ treatment (2011)
- Table A1. Concentrations of total Hg (Hg_T) and methylmercury (MeHg), tin (Sn), and organic carbon (OC) and methylation potential for sediments used in the incubation experiment.