CHLOR-ALKALI PLANT CONTRIBUTES TO MERCURY CONTAMINATION IN THE SAVANNAH RIVER

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Abstract. For many years the Savannah River has suffered fish consumption warnings. While several potential sources of mercury may contribute to this contamination, the chlor-alkali facility in Augusta, which produces chlorine by electrolysis using mercury-cell technology, is a major potential contributor. To examine this possibility samples of sediment were collected from the river above and below the facility and from the channel leading to the river from the facility. Sediment mercury concentrations and sediment toxicities to amphipods were measured.

Mean sediment mercury concentrations in the chlor-alkali discharge channel 62,708 +/- 62,216 ppb dry weight. Upstream and downstream of the chlor-alkali facility channel mean mercury concentrations of dried sediments were 24.4 +/- 14.7 and 46.6 +/- 51.2 ppb, respectively. Channel sediments and downstream river sediments were significantly toxic to amphipods as compared with river sediment samples upstream. Tissue levels of mercury in half of 34 catfish caught within 20 miles downstream of the chlor-alkali facility and 60% of the 32 bass caught in the same region of the river exceeded the 0.3 ppm that trigger a fish consumption warning.

It is apparent that the extremely high mercury levels in the sediment of the outfall channel of the chlor-alkali plant contribute to the mercury problems in the river. Amphipod toxicity and mercury triggered fish consumption warnings are indicators that mercury is a significant problem in the Savannah River.

INTRODUCTION

There are fish consumption warnings for mercury on the Savannah River from Augusta to the ocean. For several months in 2001 there was a TMDL for mercury on the river. A previous study comparing the presence of heavy metals in fish and wildlife at the Department of Energy's Savannah River Site to control sites upriver discovered that bass and raccoons harvested upriver had higher mercury levels.[1] The chlor-alkali facility near Augusta uses an antiquated mercury–cell method to manufacture chlorine.[2] These investigations examined the possibility that the use of mercury by the chlor-alkali facility might have contributed to the contamination in the fish and wildlife.

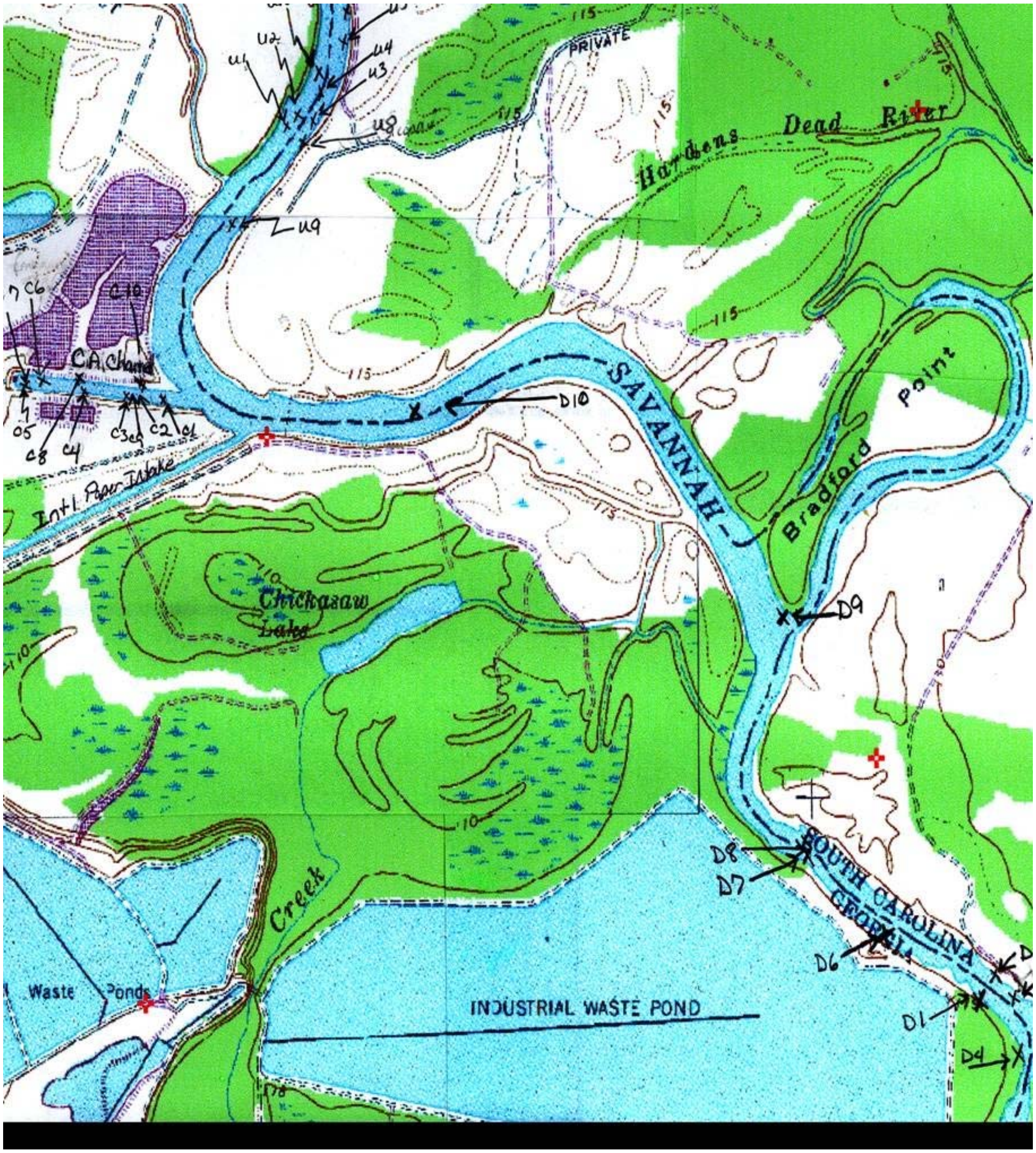
MATERIALS AND METHODS

Ten sediment samples were collected from each of three regions in the river above Olin, in the Olin channel, and in the river down-stream from Olin (See Map). Within each region 5 samples were taken on the left side of the flow and 5 from the right. The locations were recorded by a GPS. Sediments were collected using an Eckman dredge, transferred to plastic bags and labeled. The sediments were returned to the laboratory in field-moist condition and maintained refrigerated until analysis. After wet samples had been air dried and another set had been freeze-dried all samples (field-moist, air-dried, and freeze-dried) were labeled and placed in trays and the weight was measured and recorded. Each sample was analyzed for mercury using a Milestone DMA-80 analyzer, which isolates mercury by thermal decomposition, concentrates mercury with a gold amalgamation, and quantifies mercury by atomic absorption spectroscopy (EPA method 7473). A student's t-test was used to determine significance of differences.

Amphipods (*Gammarus kischineffensis*) were obtained from Carolina Biological Supply Company and maintained in aerated spring water with plant matter (Carolina Biological) for food. Breeding containers were pre-equilibrated by setting them to room temperature prior to arrival. Ten amphipods were exposed to each of five random sediment samples from each of the three river regions using a 1:4 sediment to incubation water ratio. Survival rates were recorded at 24, 48 and 72 hours. The results were analyzed by ANOVA.

RESULTS

Mercury concentrations in the sediment samples from the channel were three orders of magnitude greater than the concentrations in the upstream sediment (Table 1). Sediments were analyzed as "field moist" (concentrated only by settling and decantation), as air dried, and as freeze dried. As expected mercury concentrations increased as drying efficiency increased (Table 1).



Map. Map of the Savannah River immediately below the New Savannah Bluffs Lock and Dam showing where the sediment samples were taken.

Table 1. Statistical parameters of drying techniques.

	Mean	SD	p
Upstream			
field moist	16.3	7.0	*
air dried	26.6	18.6	*
freeze dried	24.4	14.7	*
Channel			
field moist	11961	10016	0.004
air dried	36316	32362	0.006
freeze dried	62709	62216	0.011
Downstream			
field moist	21.2	19.8	0.541
air dried	29.0	26.0	0.826
freeze dried	46.6	50.1	0.238

* Upstream averages were used as the control.

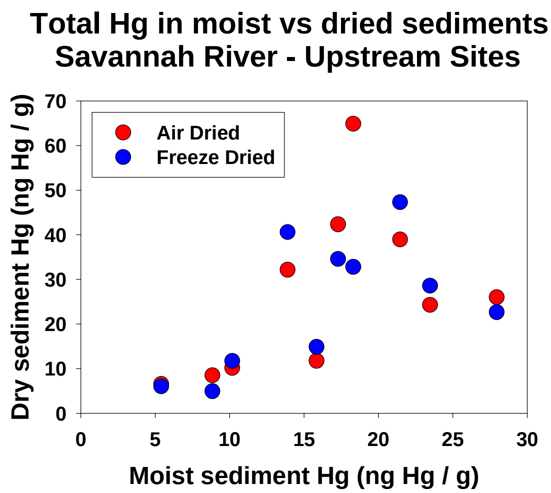


Figure 1. Comparison of drying methods for upstream samples. Samples were dried by one of three methods, settling and decantation (field moist), air drying (exposure to desiccated air for three days) and lyophilization (freeze dried). "Dry weight" values were plotted (ordinate) for the latter two methods against the field moist value (abscissa).

While the average sediment concentrations from the samples collected from downstream all had higher mercury concentrations (independent of water content) than the sediments collected from upstream, none of these differences was statistically significant. The sediments collected in the chlor-alkali facility channel had higher water content than those from upstream or downstream in the Savannah River as indicated by the increased concentrations as the samples were more thoroughly dried (Table 1). Figure 1 shows that air drying and freeze drying yielded relatively consistent results for the upstream samples, while Figures 2 and 3 indicate that dry weight mercury concentrations are higher in the freeze dried samples. This may indicate differences in the mercury speciation between these sites.

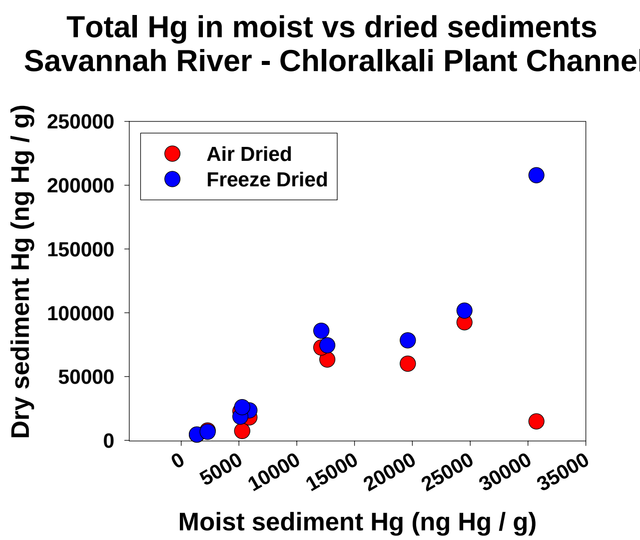


Figure 2. Comparison of drying methods for channel samples. Samples were dried by one of three methods, settling and decantation (field moist), air drying (exposure to desiccated air for three days) and lyophilization (freeze dried). "Dry weight" values were plotted (ordinate) for the latter two methods against the field moist value (abscissa).

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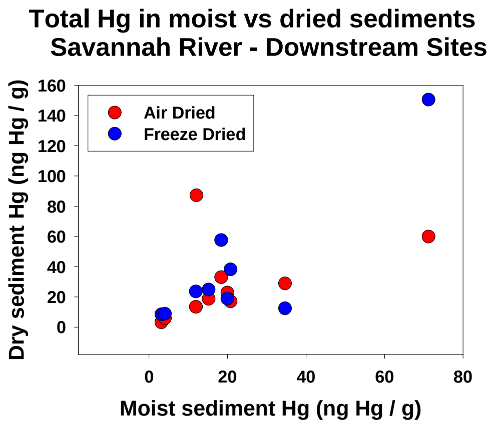

Figure 3. Comparison of drying methods for downstream samples. Samples were dried by one of three methods, settling and decantation (field moist), air drying (exposure to desiccated air for three days) and lyophilization (freeze dried). "Dry weight" values were plotted (ordinate) for the latter two methods against the field moist value (abscissa).

Mercury levels were measured using total mercury methods, which do not reveal whether the mercury detected was metallic, ionic, or organic. All forms of the mercury present are included in the results.

In correlating the GPS coordinates of each of the channel samples with proximity to the chlor-alkali facility, it was found that the five freeze dried sediment mercury levels closer to the facility averaged 97,637 ppb and the five freeze dried levels further from the facility averaged 27,798 ppb, indicating that the mercury is originating from the facility.

Figure 4 shows the survival rates of amphipods at 24, 48, and 72 hours of incubation with sediment samples from each site. Survival rates were significantly decreased in the channel sediment after 24 hours and in the downstream sediment after 48 hours. Although increased incubation times appeared to reduce survival rates the additional exposure time did not produce significant effects within the limited exposure time of this study. However, at 72 hours of incubation survival in the downstream sediment was 72%, significantly less than survival in the upstream sediment, and 32% in the channel sediment, very significantly lower than survival in the upstream sediment.

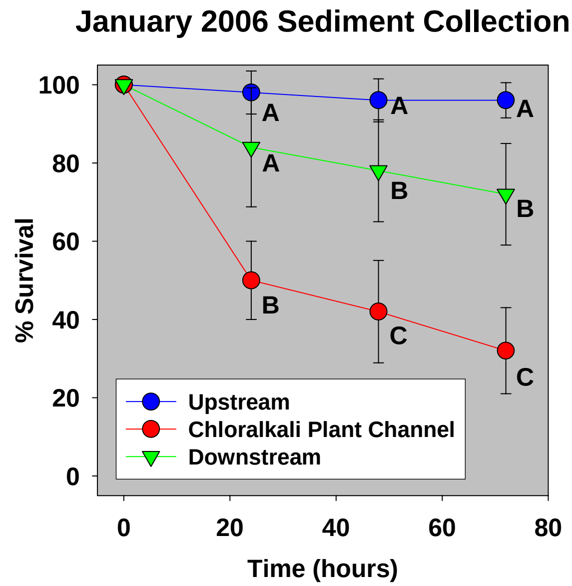

Figure 4. Survival percentages for amphipods exposed to the sediments from upstream, the channel, and downstream. Ten amphipods were placed in each of 15 incubations, five using upstream sediment, five using channel sediment, and five using downstream sediment. Survival was determined at 24, 48 and 72 hours. ANOVA indicated that different sediment exposures affected the survivals differently. Different letters labeling the points indicate that survival is significantly different between locations. Even though the survival appeared to decrease with time of exposure this effect was not significant for the limited time period used.

DISCUSSION

Average channel sediment mercury concentrations over 60,000 ppb (freeze dried) or over 30,000 ppb (air dried) represent a serious contamination problem. Both are three orders of magnitude higher than background (upstream) sediment concentrations. The National Oceanic Atmospheric Administration (NOAA) has published Screening Quick Reference Tables (SQRT) for inorganics in freshwater sediment.[3] Freshwater sediment background is 4-51 ppb, the threshold effect level (TEL) begins at 174 ppb and the upper effect thresholds (UET) for mercury in freshwater sediment is 560 ppb. The mercury levels found in the channel are at least 60 times the UET. Indeed, the levels of mercury found in the channel violate the standards of the Resource Conservation and Recovery Act which dictates that the site be mitigated.

Considering the concentration of mercury in the channel sediment it is not surprising that it is toxic to amphipods.

However, downstream sediment is also toxic to amphipods, but the mercury concentration in downstream sediments is much smaller than the channel mercury concentration. It is possible that there are other unmeasured toxins in the channel that might account at least partially for both the channel and downstream toxicities to amphipods.

The drying data are interesting (Figs 1-3). Metallic mercury has a significant vapor pressure. If the mercury in the sediment were in the metal form, it would be expected that some might be lost during the freeze drying process that exposes it to a relatively strong vacuum. On the other hand, freeze drying should remove more water from the sample than air drying and result in higher dry weight concentrations. Since the upstream samples are evenly split, for half of the paired samples the air dried concentrations are higher and for the other half the freeze dried concentrations are higher, both of these processes might be at work.

For the channel and downstream samples the freeze dried mercury concentrations are higher in 17 of 20 pairs indicating that the efficiency of the freeze drying technique at removing water is the prevailing factor in these samples. This observation suggests that the mercury in these samples is present in a non-volatile form, i.e. non-metallic. This observation may be significant in that the non-metallic forms are more bioavailable. This observation indicates that the mercury concentration from this channel might be contributing to the elevated concentrations found in the bass and raccoons upstream from the Savannah River Site.[1]

LITERATURE CITED

Chlor-alkali Mercury-Free Campaign – http://www.savannahriverkeeper.org/projects.shmtl#mercury

Heavy metal migration from the Savannah River Site – http://www.savannahriverkeeper.org/projects.shmtl#legacy

NOAAs Screening Quick Reference Tables – http://response.restoration.noaa.gov/book_shelf/122_aquirt_cards.pdf