

Draft Memorandum

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Subject: Mercury Fate in the LCP Marsh

This memorandum presents the results of our preliminary evaluation of the potential fate and attenuation rate of mercury in the Purvis Creek marsh, adjacent to the Linden Chemicals and Plastics (LCP) site in Brunswick, Georgia. This memorandum is a deliverable under NOAA contract number 56-DSNC-90031, Task Order 56-DSNC-10006 (as amended) to provide technical NRDA support for the LCP site.

The objective of this memorandum is to provide a brief, qualitative evaluation of the potential fate and attenuation of mercury that has been released from the LCP site to the neighboring environment. The results presented here are based in part on a preliminary fate, transport, and bioaccumulation model for Aroclor 1268 and PAHs that contaminate the marsh system (Hickie, 2001). As part of the technical work conducted for that preliminary model, Hickie in consultation with Stratus Consulting concluded that site-specific information was not sufficient to construct a model with the same level of detail for mercury. This memorandum was prepared to provide the site Trustees with information that may also be useful in estimating the length of time into the future for which mercury-related injuries may continue. This memorandum is not intended to be precise or quantitative, but rather is intended to provide information to Trustees to guide their preliminary assessment of the potential for mercury to persist in the LCP marsh system. Further, it serves to highlight what types of additional information would need to be collected if Trustees determine that a more precise model is warranted.

1. Environmental Fate of Mercury

Once released into natural aquatic environments, mercury can exist in several forms, including ionic, elemental, and methyl. Ionic mercury (Hg^{2+}) is typically the predominant form of mercury in water, soil, and sediment, but because elemental mercury was used in the chlor-alkali process and released from the LCP site, it is likely that a significant portion of the mercury in the marsh is elemental. Methylmercury is formed primarily as a metabolism byproduct of sulfate-reducing bacteria, and hence its concentration is more directly correlated to the presence of reducing conditions and the activity of sulfate-reducing bacteria than the concentration of total mercury.

Mercury speciation in the environment is complex. Speciation is determined by the interaction of various geochemical conditions such as temperature, dissolved oxygen, pH, oxidation-reduction conditions, and the concentration of other species that may form complexes with mercury, and

biological factors such as microbial populations. As a result, predicting the speciation of mercury under specific environmental conditions (such as in the Purvis Creek marsh) can be difficult.

The fate of mercury in the environment is, in turn, dependent on mercury speciation. Mercury does not degrade in the environment. Once released into an environment such as the Purvis Creek marsh, it can be buried in deep sediment, volatilized and lost to the atmosphere, or transported out of the marsh via surface water (advection or dispersion), groundwater, or migrating biota. Ionic mercury interacts strongly with sediment and organic matter; thus its fate is closely linked to sediment fate and transport processes. Elemental mercury has a high vapor pressure relative to other mercury species, and volatilization to the atmosphere can be an important loss process for this form in some systems. Methyl mercury is the most water soluble of these three forms, and thus solubilization is relatively more important in determining its environmental fate than for other forms of mercury. Finally, mercury speciation in abiotic media also determines, in large part, the uptake and accumulation of mercury into food webs (Windom et al., 1976). Thus, the speciation of mercury in an environmental system such as the Purvis Creek marsh affects both the long-term fate of the mercury, and the distribution of the mercury into the different abiotic and biotic compartments.

2. Mercury in the Purvis Creek Marsh System

As in most mercury contaminated natural systems, sediment is the primary storage compartment for mercury in the Purvis Creek marsh (Windom, 1976). For example, sediment total mercury concentrations in the contaminated portion of the marsh are in the parts per million range, whereas water total mercury concentrations in this area are in the parts per billion range, with the majority of the water mercury mass associated with suspended solids (PTI and CDR, 1998; Matta et al., 1998). In addition, total water column mercury concentrations exceeded the Georgia State water quality standards for ecology and human health (25 ng/L).

In aquatic systems contaminated with mercury, uptake from sediment is typically the primary route by which mercury enters the food chain. For example, studies in the salt marsh near the LCP site indicate that inorganic mercury introduced into the marsh has accumulated in the sediment and can be remobilized by methylation in the sediment column (Windom, 1976). Methyl mercury is then accumulated by lower trophic level, sediment-dwelling organisms, which can in turn be ingested by higher trophic level organisms (Windom et al., 1976). In addition, studies at Lavaca Bay, Texas, have shown that sediment is the main source of mercury in the bay, and that the main uptake route for biota is through ingestion of sediment-dwelling organisms (Texas General Land Office et al., 2000).

Most of the mercury present in the sediments of the Purvis Creek marsh is ionic or elemental. For example, the maximum concentration of methylmercury as a percentage of total mercury in

surface sediment samples collected from contaminated portions of the marsh was 0.6% (PTI and CDR, 1998). Two factors could contribute to the low percentage of mercury in the methylmercury form: the relatively high water solubility of methylmercury once it is formed in sediment, and the low rate of mercury methylation in Purvis Creek sediment relative to the mass of mercury present in the sediment. The fact that methyl mercury was detected and that the total mercury mass in the marsh is large does indicate that mercury methylation and subsequent bioaccumulation is an issue of concern in the marsh.

3. Using the Results of the Preliminary Aroclor 1268 Model to Estimate Mercury Persistence

The persistence of mercury in the active sediment layer of the Purvis Creek marsh is expected to be similar to the fate of Aroclor 1268, at least to a first approximation. This is because the persistence of Aroclor 1268, like that of mercury, is expected to be determined in large part by sediment burial processes (Hickie, 2001). In contrast, much of the PAH in the Purvis Creek marsh sediments may be lost because of degradation, a process that does not act on mercury (Hickie, 2001).

The results of the preliminary model by Hickie (2001) indicate that burial is an important factor in the decrease of mass of Aroclor 1268 in the active surface sediment layer. Biological and chemical transformation, surface particle resuspension, and transport of dissolved and sorbed Aroclor 1268 to the Turtle River accounted for the remaining mass lost from surface sediment. For modeling purposes, burial is defined as the entrainment of particles and associated contaminants below the active sediment layer.

For purposes of this qualitative preliminary evaluation, a comparison of relevant fate and transport parameters used in the preliminary Aroclor 1268 model to parameters estimated for mercury indicates the potential applicability of the Aroclor 1268 results to mercury. Octanol-water partition coefficients (K_{ow}) are presented in the model documentation for Aroclor 1268. These values can be used to estimate the particle/water partition coefficient (K_d) using the following equation (Thomann and Mueller, 1987):

$$K_d = 0.617 * f_{oc} * K_{ow} ,$$

where f_{oc} is the fraction organic content (estimated to be between 0.02 and 0.2 in the modeling report). Using this equation and the estimated $\log K_{ow}$ for Aroclor 1268 of 7.7 (Hickie, 2001), $\log K_d$ for Aroclor 1268 is estimated to be between 5.8 and 6.8. This value is similar to the results of studies of partitioning of total mercury between particles and water which indicate a $\log K_d$ range of 4 to 6 (Looney et al., 1987; Hurley et al., 1994), although the lower K_d of

mercury indicates that dissolved concentrations would be somewhat higher for mercury than for Aroclor 1268. The relatively high K_d values for Aroclor 1268 and mercury indicate that mercury has a similar propensity to sorb to sediment as Aroclor 1268, at least as modeled in the preliminary fate and transport model. Consequently, the fate and attenuation rate of mercury in the Purvis Creek marsh is expected to be dominated by processes associated with sediment transport and burial, as is the case for Aroclor 1268 (Hickey, 2001).

In contrast, the preliminary model indicates that the fate of PAH in the Purvis Creek sediment may be dominated by degradation processes rather than sediment processes (Hickie, 2001). The model estimates that the half-life for PAH is 3 to 5 years, much shorter than the estimated half-life of Aroclor 1268 which is dominated by the burial of contaminated sediment with clean sediment thereby reducing the concentration of Aroclor 1268 in the active surface layer.

One environmental process that can act on sediment mercury but not on Aroclor 1268 is methylation. Methylation of inorganic mercury in anoxic sediment, which is mediated by bacteria, can increase the mobility of the mercury. This increase in mobility can, in turn, increase the removal of mercury from the sediments, through either surface water or groundwater transport. Although not much work has been done estimating methylation rates, one study (Windom et al. 1976) concludes that the rate of mercury methylation in Purvis Creek marsh sediment is very low relative to the overall mass of mercury. Using data collected from sediment and primary consumers in the Purvis Creek marsh (marsh vegetation, snails and fiddler crabs), Windom et al. (1976) estimated that only 0.005% annually of the total mass of mercury in the sediment is methylated. Thus, methylation and subsequent mobilization is not expected to be a significant loss mechanism for mercury in the Purvis Creek sediments.

Based on the first-order similarity between the physical-chemical properties of Aroclor 1268 and mercury in the Purvis Creek marsh, the half-life for mercury in sediment should be similar to Aroclor 1268. The results of the preliminary model indicate that the half-life of Aroclor 1268 in the Purvis Creek marsh may be approximately 10 to 20 years. The half life is the time it takes for the concentration in the active surface layer (5 cm for this case) to become one-half its initial concentration, and for Aroclor 1268 in the Purvis Creek Marsh, the magnitude of the half life is dominated by burial by uncontaminated sediment. Using a larger active surface layer, which may be appropriate for this site given the abundance of deeper burrowing animals, would result in a longer half life.

Unfortunately, there are insufficient mercury data for the Purvis Creek marsh to be able to evaluate whether an estimated half-life of approximately 10 to 20 years can be supported by actual observations. Although there are data available for some biota from both the early 1970s (Odom, 1975; Gardner et al., 1978) and the early to mid-1990s (primarily Georgia DNR data), differences in taxa, sampling locations, and analytical methods make direct comparisons difficult. There are comparable data available for 1992 to 1997 (just before the EPA removal

action), but the sample sizes and time span are not sufficient for a definitive evaluation (see preliminary injury evaluation report, Stratus Consulting, 2001). However, the continued presence of mercury in water, sediment and biota indicates that mercury is persistent in the marsh.

In addition, data from the Lavaca Bay, Texas, site can be used to evaluate mercury half-life in an estuarine system with mercury-contaminated sediment. Total mercury concentrations in two types of fish (black and red drum) decreased by a factor of two between the cessation of mercury waste discharge in 1981 and 2000 (Texas General Land Office et al., 2000). Consequently, the half-life for mercury in Lavaca Bay drum is approximately 20 years. Because sediment is the primary source of mercury in Lavaca Bay, it is likely that the active sediment concentration has a similar half-life to that for drum. Therefore, an estimated half-life of approximately 10 to 20 years for mercury in the sediments of the Purvis Creek marsh is consistent with that observed at Lavaca Bay.

4. Potential Modifying Factors

As described in the introductory section of this memorandum, the environmental fate of mercury is controlled in part by its speciation, which in turn is complex. However, given that both mercury and Aroclor 1268 adsorb strongly to sediment (thereby limiting mobility) and that sediment burial is the primary mechanism for reducing mercury concentrations in the surface layer, as a first-order approximation, it is reasonable to assume that the fate of mercury in the Purvis Creek marsh is similar to that of Aroclor 1268. However, several factors beyond sediment transport and burial could result in the half-life of mercury being either less than or greater than that of Aroclor 1268 in the Purvis Creek Marsh, including:

- ▶ Differences in water solubility and/or sediment sorption characteristics. Although generally similar in their sediment/water partition coefficients and hence the propensity to bind to sediment, the fact that mercury is metal and Aroclor 1268 is an organic compound together with the lower K_d of mercury compared to Aroclor 1268 may result in differences in the exact solubility and sediment binding characteristics (e.g., propensity and capacity for binding to different kinds of particulate matter). These differences may result in different sediment attenuation rates over the long term.
- ▶ Other physical-chemical differences that could result in differences between mercury and Aroclor 1268 in their diffusion rate from deeper, more contaminated sediment to surface sediment. Buried contaminants can diffuse upward via sediment porewater to contaminate cleaner, surface sediment. The complex speciation characteristics of mercury may make the mobility of mercury in the geochemically complex sediment environment different from that of Aroclor 1268. For example, under the anoxic conditions that occur in deeper sediment, mercury may become methylated, thus increasing its relative water

solubility and its potential for upward migration. In contrast, because Aroclor 1268 is an organic compound that may bind more readily to the particular forms of dissolved organic carbon that are present in the deeper portions of the marsh sediment, it may be transported more readily to surface sediment. Although these mechanisms are different, they both serve to increase the mobility of the compounds in sediment.

- ▶ Differences in localized sources or sinks between mercury and Aroclor 1268 that result from differences in the timing and/or location of historical releases into the marsh. Such differences could result in either an increase or decrease in the half-life of mercury relative to Aroclor 1268.
- ▶ The relative rates of volatilization from marsh sediment or surface water. For example, the Henry's Law constant for a compound is the ratio of the aqueous concentration to the partial pressure of the compound in the gas phase, so compounds with a higher Henry's Law constant would tend to have a lower gas phase partial pressure and hence not volatilize as readily. The Henry's Law constant for Aroclor 1268 is 2.5 M/atm, whereas the Henry's Law constant for mercury is 0.1 M/atm (Sander, 1999), indicating that mercury is more likely to volatilize.

The potential modifying factors point out uncertainties in assuming that the half-life of mercury in the Purvis Creek marsh will be the same as that of Aroclor 1268. Nevertheless, deep sediment burial is expected to be the dominant loss process for both contaminants, and the factors that control deep sediment burial (rates of sediment deposition and resuspension) will be similar for both contaminants. Therefore, to a first approximation, it is reasonable to assume that the sediment half-life will be similar for both contaminants.

The link between sediment mercury, mercury speciation, and bioaccumulation is also important. The accumulation of mercury from sediment into biota is a function of both the total sediment mercury concentration and the rate of mercury methylation. If the environmental conditions that affect mercury speciation remain relatively constant over the next several decades, then the half-life estimated for mercury in sediment can be reasonably applied to biota as well. However, if changes occur either in abiotic or biotic factors that affect speciation and bioaccumulation, an increase or a decrease in bioaccumulation from sediment and persistence in the biota could result. As described previously, the sediment-water-biota relationship for mercury is quite complex and difficult to model. Nevertheless, for purposes of this preliminary qualitative estimation, we will assume, as a first approximation, that conditions will remain fairly constant over the next few decades, and that the estimated half-life for mercury in sediment is also applicable to mercury in biota at the site. We recognize that if other conditions arise that would alter the current state of the system significantly (like the Brunswick Harbor deepening project), the estimates will also be expected to change.

5. Refinement of the Estimate of Mercury Persistence

A refined estimate of the environmental persistence of mercury in the Purvis Creek marsh could be achieved through obtaining several types of site-specific information:

- ▶ Factors that influence sediment-water transport processes that were estimated for the preliminary fate and transport model (Hickie, 2001), including the water concentration of suspended solids, the fraction organic matter in sediment, the “active” sediment depth, and the sedimentation, resuspension, and burial rates for sediment.
- ▶ The total mercury/sediment partition coefficient to refine the estimate of the sorption characteristics of mercury as compared to Aroclor 1268.
- ▶ Mercury speciation studies. Previous studies (e.g., PTI and CDR, 1998) have evaluated total and methylmercury concentrations in both the dissolved and suspended sediment phases, but no recent studies have evaluated mercury speciation in marsh sediment.

Refining factors used in the preliminary fate and transport model would likely lead to a substantial increase in the confidence in the mercury persistence estimate, while mercury partitioning and speciation studies would serve to further refine this estimate.

6. Summary and Conclusions

The fate and bioaccumulation characteristics of mercury in the environment are complex, and highly dependent on speciation (e.g., whether mercury exists in ionic, elemental or methyl form), which is in turn determined by environmental variables such as temperature, dissolved oxygen, pH, oxidation-reduction conditions, and the concentration of other species that may form complexes with mercury, and biological factors such as microbial populations. Nevertheless, because the majority of the mass of mercury in the Purvis creek marsh resides in the sediment and total mercury sorbs strongly to sediment, burial is most likely the dominant long-term process that determines the fate of mercury in the marsh. Because both total mercury and the PCB compound Aroclor 1268 sorb strongly to sediment and do not readily degrade in aquatic environments, their fate and transport characteristics should be similar. Model results for Aroclor 1268 indicate that burial is the dominant factor in reducing sediment near-surface concentrations, and these results indicate that the half-life for Aroclor 1268 in sediment can be estimated as approximately 10 and 20 years. Consequently, a first approximation of the total mercury half-life in the marsh would also be between 10 and 20 years.

Because the sediment-water-biota relationship is complex, it is more difficult to estimate the half-life of mercury in organisms. However, if the future geochemical and corresponding speciation characteristics of mercury remain similar to current conditions, it is reasonable to assume that the half-life in organisms in the marsh will be similar to that for sediment (i.e., 10 to 20 years). This estimated half-life for biota in the Purvis Creek marsh is consistent with the measured half life for drum in Lavaca Bay (20 years).

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