

# **Evaluating the Consequences of Mercury Emissions from a Point Source**

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## **ABSTRACT**

U.S. EPA fate-and-transport algorithms were applied to estimate the local effect of mercury emissions from a large cement kiln. Applied with default parameters and facility-specific measurements of mercury emissions, the algorithms predicted that the facility could be responsible for a substantial share of the mercury found in fish in a local lake. While plausible, the similarity of the concentrations of mercury in fish from the local lake with those found in more distant lakes cast doubt on the realism of the model predictions. A more careful examination of the underlying fate-and-transport modeling suggested that the default assumptions lead to overestimates of the facility's contributions to mercury in local fish. The most critical factor involved the assumed mercury speciation in stack emissions, for which default parameters predicted a significant fraction of the mercury emissions to deposit in the proximity of the facility. Other model parameters, however, were found to be inconsistent with empirical data and in some cases in violation of physical constraints. The uncertainties associated with multi-step fate-and-transport modeling demand considerable refinement and verification of algorithms if the model predictions are to be considered reliable enough to form the basis of sound regulatory decisions.

## **INTRODUCTION**

As mercury cycles through the environment, introduced to the air by both natural and anthropogenic sources, its various forms and species have a direct bearing on its behavior. The bulk of airborne mercury is vapor-phase elemental mercury, but the species that dominate deposition to soil and surface water are believed to be oxidized forms associated with particulate matter.<sup>1</sup> As a consequence, the forms associated with emissions from an individual source (such as cement kiln or a coal-fired power plant) can profoundly affect the near-field behavior of emissions compared with that of the background distribution. For example, if a facility's emissions are dominated by particle-bound forms of mercury, deposition rates of facility-related mercury could be elevated near the source, resulting in significant gradients, as compared with the

expectation of more or less uniform deposition of background-related mercury. In this case, it is plausible that an individual source could perceptibly influence the amount of mercury that enters soils, vegetation, and surface waters, and ultimately bioaccumulates in local fish populations.

The U.S. EPA's Mercury Report to Congress<sup>2</sup> contains fate-and-transport algorithms for predicting the disposition of mercury released from combustion sources. The Human Health Risk Assessment Protocol (HHRAP)<sup>3</sup> extends these algorithms to provide case-specific guidance directed explicitly toward modeling stack emissions from hazardous waste combustors. This latter guidance was applied to a large cement kiln located in southwest Indiana as part of U.S. EPA permitting requirements. The kiln, located in Greencastle, Indiana and operated by Lone Star Industries (LSI), utilizes both coal and high-BTU hazardous wastes as fuels. Stack-gas from the kiln is cleaned with an electrostatic precipitator, a baghouse, and scrubbers..

Detailed stack testing of the LSI/Greencastle facility was performed to characterize kiln emissions under worst-case operating conditions.<sup>4</sup> Measured emission rates were in general many times lower than the applicable MACT emission limits established by the U.S. EPA. In the case of mercury, the measured emission rate was twenty-four times smaller than the permissible emission rate corresponding to the MACT emission limit of 120 : g/dscm for hazardous waste combustion.<sup>5</sup>

Initial application of the HHRAP algorithms to the LSI/Greencastle facility yielded perplexing results. Adopting mostly default values, the predictions of the fate-and-transport models produced risk estimates in excess of regulatory guidelines, *i.e.*, the modeled exposure to mercury by a hypothetical subsistence fisher was greater than the U.S. EPA's reference dose. Interpretation of the initial results was not straightforward. The U.S. EPA reference dose for mercury is set at a protective level, and it is exceeded by a mercury concentration in fish of about 0.1 ppm (mg/kg) when combined with high-end exposure assumptions within the HHRAP. As a point of comparison, many states issue fish consumption warnings at 0.5–1 ppm levels of mercury in fish, and fish at many locations are found to contain mercury concentrations at or near this range.

Thus, it is not surprising that the HHRAP algorithms yield risk estimates for mercury that exceed the U.S. EPA's reference dose, and that background levels of mercury in fish also produce similarly high risk estimates. The difficult aspect of evaluating the HHRAP's predictions for the LSI/Greencastle facility, however, lays in the assessment of the plausibility of the model predictions. The HHRAP algorithms predicted that the LSI/Greencastle facility was contributing a substantial portion of the mercury found in the fish of a local lake (located about 10 miles south of the facility). Mercury levels in fish sampled from this lake, however, contained levels of mercury indistinguishable from the concentrations found in fish from other Indiana lakes. Moreover, the implications of emissions at the MACT limit were sobering: if the LSI/Greencastle were to emit mercury at this legally permissible level, the HHRAP algorithms (barring changes discussed further on) would predict mercury to accumulate to a level of 25 ppm in fish! Thus, although the HHRAP predictions at the measured mercury emission rate were of a plausible

magnitude, they were questionable, especially in consideration of the implications for other cement kilns operating at or above the MACT emission limit.

The HHRAP, like other U.S. EPA guidance, is constructed in a conservative manner, meaning that uncertainties are generally resolved in a way that likely leads to higher-than-actual levels of exposure. Given the many steps involved in predicting the path whereby airborne mercury deposits and makes its way through the environment and ultimately into fish, there are many opportunities to introduce bias into the overall fate-and-transport modeling. Working from this premise, an attempt was made to refine the HHRAP algorithms and assumptions to produce more realistic estimates of the likely fate of mercury emissions from the LSI/Greencastle facility. The remainder of the paper describes a number of the measures adopted to make more realistic estimates of the local impact of mercury stack emissions from the LSI/Greencastle facility.

## MERCURY SPECIATION

The distribution of mercury within stack emissions is perhaps the most important factor in influencing model predictions. The HHRAP recommends that 20% of mercury in cement kiln stack emissions be treated as particle-bound  $\text{HgCl}_2$ , 60% be treated as vapor-phase  $\text{HgCl}_2$ , and 20% be treated as vapor-phase elemental Hg. These values are taken from the U.S. EPA's Mercury Report to Congress,<sup>2</sup> a category that represents uncontrolled municipal waste combustors. However, markedly different distributions are provided for sources closer in character to a cement kiln utilizing waste-derived fuels. For hazardous waste incinerators, listed values are 58% elemental Hg vapor, 20% divalent Hg, and 22% particulate Hg.<sup>2</sup> For Portland cement manufacturing facilities, listed values are 80% elemental Hg vapor, 10% divalent Hg, and 10% particulate Hg.<sup>2</sup>

The HHRAP algorithms are most sensitive to the portion of mercury assumed to be present in oxidized forms. In contrast, the portion treated as elemental Hg has little influence on local modeling, since almost all of it is assumed to enter the global mercury pool that remains in the atmosphere for extended periods. Hence, by assigning only a small fraction to elemental mercury in its default mode, the HHRAP guidance makes 3–4 times as much mercury available to deposit in local watersheds than would be suggested by potentially appropriate source categories. These differences could also reflect the substantial variation of mercury speciation measurements found among sources, including those in common industrial categories.

Due to the sensitivity of fate-and-transport algorithms to mercury speciation, an in-depth examination of stack testing results was used to derive facility-specific estimates. U.S. EPA Method 0060 Multi-Metals Sampling Train<sup>6</sup> does not directly distinguish among mercury species, but speciation can be inferred from the combination of cement kiln chemistry, chemical properties and behavior, and measurements taken in individual sections of the sampling train. The sampling train includes a glass fiber filter to collect particulate forms,  $\text{HNO}_3$  /  $\text{H}_2\text{O}_2$  impingers to collect soluble forms, and  $\text{KMnO}_4$  /  $\text{H}_2\text{SO}_4$  impingers to collect vapor-phase elemental Hg. Laboratory analyses separately examined Hg in:

1. the rinse and digestion solutions from the probe and filter,
2. the contents and rinse solutions from the HNO<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> impingers,
3. a rinse of the empty, middle impinger,
4. the contents and rinse solutions from the KMnO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> impingers, and
5. a final HCl rinse of the KMnO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> impingers.

Table 1 gives the analytical results for these five Hg analyses from the three runs of the LSI/Greencastle facility stack test, which was conducted under stressed operating conditions designed to produce worst-case emission levels. The only portion of the sampling train in which Hg was measured above the detection limit was in the KMnO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> impingers, indicating that only elemental, vapor-phase Hg was positively identified in the emissions.

**Table 1.** Results from mercury stack testing of a cement kiln

Solution analyzed	Likely Hg species captured	Amount of Hg detected (: g)		
		Run 1	Run 2	Run 3
Probe and filter rinse	Hg <sup>2+</sup> Particulate	<0.2	<0.2	<0.2
Contents and rinse from the HNO <sub>3</sub> / H <sub>2</sub> O <sub>2</sub> impingers	Hg <sup>2+</sup> Vapor	<6.34	<6.03	<5.98
Empty impinger rinse	Hg <sup>2+</sup> Vapor	<0.36	<0.41	<0.43
Contents and rinse from the KMnO <sub>4</sub> / H <sub>2</sub> SO <sub>4</sub> impingers	Hg <sup>0</sup> Vapor	18.3	15.8	8.02
Final HCl rinse	Hg <sup>0</sup> Vapor	<0.46	<0.46	<0.46

Because the detection limits for Hg<sup>2+</sup> in the HNO<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> impinger solutions and rinse are significantly higher than the limits for any of the other stages, the potential for a significant presence of Hg<sup>2+</sup> vapor cannot be ruled out, as this species could be present at any level below analytical detection limits. Based on averages of the three runs in Table 1, Hg<sup>2+</sup> vapor in the HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> impingers could be present anywhere from 0–44% of the detected level of Hg<sup>0</sup> in the KMnO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> impingers.

Consequently, equilibrium partitioning calculations were developed to refine estimates of the Hg<sup>2+</sup> vapor-phase fractions. Appendix A provides details of the equilibrium partitioning modeling for the sampling train. In summary, the modeling suggests that most of the mercury is expected to be present as Hg<sup>0</sup> vapor. The three-run average predictions assign 97.5% of the mercury as Hg<sup>0</sup> vapor, and only 2.5% as oxidized Hg<sup>2+</sup> (combined vapor and particulate).

The large fraction of mercury estimated to be present as  $\text{Hg}^0$  vapor has a substantial impact on bottom-line risk estimates since the HHRAP algorithm assumes that the majority (99%) enters the global mercury pool, and hence does not deposit in the vicinity of its source. Reducing the portion of assumed  $\text{Hg}^{2+}$  from 80% (the HHRAP default) to 2.5% translates into large decrease in estimated exposure levels to facility-related mercury emissions.

## MERCURY DEPOSITION

The fish ingestion route, which serves as the critical exposure pathway for mercury, is one of many potential routes of indirect exposure to stack emissions from a combustion source. Whereas inhalation is the obvious source of exposure to chemicals in air, indirect exposure pathways result from the transfer of airborne chemicals to land, water, and vegetation, with subsequent exposure through the ingestion of media (water, food and soils) that have incorporated the chemicals.

The removal processes that drive indirect exposure pathway analysis are categorized as either dry or wet (the latter mediated by precipitation) and differ in relative significance among chemicals present in air as gases or bound to particles. Models and empirical data are available to predict dry deposition velocities and wet scavenging ratios for particle-bound chemicals. For gases, however, empirical data are available for only a limited number of chemicals. Importantly, few data exist to model coefficients for removal rates of gaseous mercury species, especially divalent (oxidized) species such as mercuric chloride. Consequently, the U.S. EPA<sup>2</sup> has treated these species as being similar to nitric acid, a compound readily deposited by both dry and wet processes. This use of a surrogate deposition velocity is based on a similarity in solubility between the chemicals. Unfortunately, there are no data available to test the validity of the nitric acid analogy, despite the critical importance of deposition and scavenging models in fate-and-transport modeling.

For dry deposition, the HHRAP recommends a deposition velocity of 3 cm/s. This value is at the higher end of limited empirical measurements of nitric acid deposition to vegetative surfaces, which range from 1–4 cm/s and are higher than values measured for chemicals such as ozone and sulfur dioxide. Based on these measurements, researchers have concluded that the leaf cuticle seems to provide little or no resistance to nitric acid deposition, whereas the cuticle does inhibit the deposition of gases such as sulfur dioxide and ozone, which must enter plants through stomata.

The reason, however, that nitric acid deposition to leaves is unimpeded by the cuticle does not seem to be known. In reviewing the literature, no studies were found that described the mechanism whereby nitric acid passes through the cuticle. It is not obvious that high solubility in water should be related to a chemical's ability to penetrate the waxy, largely lipid tissue that composes the leaf cuticle. Sulfur dioxide, which has a relatively high solubility in water, is known to be resisted by the leaf cuticle. Since mercuric chloride's solubility in cold water (6.9 g/100 cc)<sup>10</sup> is lower than sulfur dioxide's (22.8 g/100 cc);<sup>10</sup> the suggestion that mercuric chloride should

deposit to leaves in a manner analogous to nitric acid on the basis of commonly high solubilities is not supported by the contradictory tendency of sulfur dioxide.

Thus, some factor other than solubility is likely responsible for nitric acid's high deposition rate into leaves, and solubility is perhaps not a reliable indicator of mercuric chloride's ability to bypass the cuticular resistance and readily deposit to leaves (as does nitric acid). One arguably similar property shared by nitric acid and mercuric chloride is reactivity — both chemicals burn human skin when contacted at concentrated levels (*i.e.*, levels much higher than those present in the atmosphere). Since human skin serves some of the same functions as a leaf's cuticle, it is plausible that both would react with lipids present in the skin/cuticle. Reactivity may in fact be the reason that nitric acid deposition is not resisted by the cuticle. Since mercuric chloride is highly corrosive, it might plausibly behave in a similar manner.

Consequently, the HHRAP's recommended default value of 3 cm/s was maintained for the default deposition velocity of mercuric chloride vapor. The value is selected from the high end of the range of measured values for nitric acid, and thus likely serves to overestimate dry deposition on average. Moreover, since studies of nitric acid deposition have mostly focused on vegetation, the appropriateness of the value in predicting dry deposition to surfaces such as soil and water is not known. The overall dearth of knowledge concerning dry deposition of mercury vapors suggests the need for basic research studies.

The wet scavenging of vapors is also modeled in a potentially inappropriate manner in the HHRAP, which treats all vapors as small particles, thereby removing any dependence on chemical-specific properties such as solubility and vapor pressure. Elemental mercury, which is known to have a long atmospheric lifetime, would be inappropriately modeled if treated as a small particle, as its low solubility greatly limits the amount that can be scavenged by precipitation. The HHRAP compensates for this factor by assigning the bulk of elemental mercury to a global pool that is assumed not to deposit in the local area. Mercuric chloride, on the other hand, may be scavenged more readily based on its higher solubility. For this chemical, the appropriateness of the HHRAP default method cannot be evaluated, but any agreement with reality would be fortuitous coincidence given the fact that the physicochemical mechanisms of removal differ. Like dry deposition velocities, wet scavenging coefficients for mercuric chloride and other mercury species should be the topic of further research.

## **WATERSHED MODELING PARAMETERS**

Watershed modeling involves prediction of the various ways mercury makes its way into a surface water body, and once there, the manner in which it speciates and distributes within the sediment and water column. Multiple steps and many assumptions are involved in the modeling, beginning with mercury scavenging and deposition (as described above) directly to the surface water and indirectly by its deposition to soil, followed by erosion and transport. Cagles Mill Lake, located about 10 miles to the south of the LSI/Greencastle facility, was evaluated within the risk assessment as the most proximate and plausible source of fish for a person practicing sustenance

fishing (the worst-case risk assessment scenario). Due in part to its large size and use for recreational fishing, a variety of environmental sampling data were available for Cagles Mill Lake. These data served in some cases as sources of site-specific input parameters, and more importantly as useful checks and bounds on modeling estimates. Such efforts do not necessarily validate model predictions, however. For example, the modeled value for total suspended solids was found to be about the same as values measured within the lake, but one cannot conclude that the modeling is accurate as the measured values may reflect resuspended sediment, or streambed scouring, all of which would serve as additional sources of suspended solids that are not reflective of the soil erosion estimates that serve as the source considered in the watershed modeling.

In addition to its role in reality checking, the detailed consideration of watershed modeling can identify inappropriate assumptions and sources of uncertainty. One aspect of relevance to the watershed modeling involved the modification of the HHRAP guidance to account for the explicit inclusion of a soil erosion loss term. The HHRAP recommends that the relevant loss parameter *kse* should be set equal to zero based on the assumption that the amount of soil eroding off of a parcel of land is countered by a roughly equal amount of soil eroding onto the parcel from adjacent lands. While this is perhaps a valid assumption for parcels the size of a residential property or farm, it is not a valid assumption for the evaluation of a watershed as a whole because, by definition, there is no countering source of erosion into a watershed from areas outside its boundary. The consequence of including the *kse* term resulted in the modeling of a roughly 45% reduction in the rates of mercury loading into the lake (as compared with the case with the *kse* term omitted).

## **MERCURY BIOACCUMULATION IN FISH**

The concentration of mercury in fish is estimated from the modeled concentration of methyl mercury in surface water by scaling the latter value by a water-to-fish bioaccumulation factor (BAF). The HHRAP recommends a value of  $6.8 \times 10^6$  L/kg for this purpose, to be applied to the total of the dissolved-phase concentrations of  $\text{Hg}^{2+}$  and methyl mercury (MHg). This BAF value is for trophic level 4 (piscivorous) fish and is referenced to the U.S. EPA Mercury Study Report to Congress.<sup>2</sup> The recommended BAF value is derived from empirical data, but is not appropriate for the mercury species of interest to the HHRAP. Rather, the BAF value of  $6.8 \times 10^6$  L/kg is intended to be applied only to the dissolved methyl mercury concentration, and not the total dissolved concentration.<sup>2</sup>

Three options were explored for estimating mercury concentrations in fish based on application of data for consistent mercury species. First, the HHRAP default BAF was applied to the dissolved MHg concentration in the water, as described in the BAF definition.<sup>2</sup> The second approach was to apply a BAF based on the total dissolved mercury concentration in the water, taken from the Mercury Report to Congress as  $5.0 \times 10^5$  L/kg (a value more than ten-fold lower than the value based on methyl mercury alone).<sup>2</sup> The third method (and that ultimately selected) was to derive an empirical value based on lake-specific measurements of mercury. Based upon available data, a

BAF value of  $4.8 \times 10^5$  L/kg was derived as the ratio of total Hg in fish divided by the total Hg in surface water.

Choosing the best option among the three approaches is not straightforward. Given that empirical observations have shown the most reliable relationship to be based on methyl mercury concentrations, the first option might be endorsed. However, the modeling of methyl mercury in surface water depends on the fraction of dissolved mercury that is present in methylated form (an assumed quantity). This fraction varies among lakes, and hence the use of a non-specific default value is quite uncertain. Additionally, because U.S. EPA guidance emphasizes the substantial degree of uncertainty associated with the use of generic BAF values,<sup>2,3</sup> the use of the lake-specific bioaccumulation factor was selected.

The implications of the three options with respect to the default HHRAP recommendation are demonstrated in Table 2. These values are based upon the detailed fate-and-transport modeling developed for Cagles Mill Lake<sup>7</sup> assuming that the LSI/Greencastle facility releases mercury at the MACT emission limit. As can be seen, all three options yield lower values than would result from rote application of the HHRAP's default BAF value, with the lake-specific BAF producing the mid-level estimate of the three options. Note that the default HHRAP estimate of 0.25 ppm in Table 2 contains adjustments for factors discussed previously (*e.g.*, mercury speciation assumptions), and hence is about a factor of 100 lower than that previously stated in the text. Also, the predicted levels of mercury in fish at the measured rate of mercury emissions from the LSI/Greencastle are about a factor of twenty smaller than those listed in Table 2. These modeled values are much smaller than the measured mean levels of mercury in fish in Cagles Mill Lake, as collected among several species and sampling rounds, have ranged from 0.12 to 0.25 ppm in recent years.<sup>8</sup>

**Table 2.** Predictions of Mercury Concentrations in Fish (Based on MACT-Level Emissions)

Scenario	Predicted concentration of mercury in fish tissue (ppm, or mg/kg)
Default HHRAP guidance <sup>3</sup>	0.25
Option 1: HHRAP corrected for total mercury species	0.019
Option 2: HHRAP made consistent for methyl mercury	0.14
Option 3: Empirical lake-specific data	0.058

## CONCLUSIONS AND RECOMMENDATIONS

Predictions of the fate-and-transport of mercury by the U.S. EPA's HHRAP algorithms were found to yield results that seemed likely to overestimate the degree to which mercury in stack emissions from the LSI/Greencastle cement kiln would find its way into the fish in local lakes. The algorithms predicted levels of mercury in media such as soil and fish that were within background levels, but constituted significant fractions of observed levels in the environment. While these model predictions cannot be validated or verified, the implications for higher levels of emission (such as the regulatory MACT limit) suggested that the algorithms likely overpredict the rate at which airborne mercury deposits and bioaccumulates.

A detailed examination of the HHRAP algorithms identified several sources of bias, all of which tended to overestimate the amount of mercury that might end up in fish living in a lake near the LSI/Greencastle facility. By refining the HHRAP algorithms and assumptions, and including facility- and site-specific data, the estimated levels of mercury in fish seem more consistent with measured levels, and it is likely that the uncertainty of the modeling was substantially reduced.

The assumed mercury speciation was found to be the most critical factor in developing fate-and-transport estimates for mercury emissions. Facility-specific stack testing, combined with appropriate knowledge of the species of mercury likely to be present, can be used to estimate the various species and forms of mercury if analyses of the individual sampling train components are developed. Care should be taken, however, to achieve sufficiently low limits of detection in the stages in which one expects to find oxidized forms of mercury, given that these species principally influence the predictions of the fate-and-transport algorithms embedded within the U.S. EPA's risk assessment guidance documents.

Additional factors found to be important were mercury deposition parameters, the soil erosion loss term within watershed modeling, and the fish-to-water bioaccumulation factor. Watershed modeling was found to benefit from the consideration of area-specific parameters, and empirical data such as lake-specific sedimentation rates, suspended particle measurements, and measurements of mercury in fish and surface water provided useful bounds and checks on model predictions. Despite the use of site-specific data, model comparisons with empirical data should not be interpreted as model validation. Since the model predictions suggest that the LSI/Greencastle facility may directly account for only a small portion of observed mercury levels, there is no way to measure or segregate that portion with respect to empirical data (*e.g.*, mercury levels measured in fish). However, the empirical data were useful in evaluating model results. Based on the notion that local mercury levels in fish are not significantly higher than values from other (more distant) Indiana lakes<sup>8</sup> is consistent with the finding that the fate-and-transport model predictions do not imply a significant contribution from the LSI/Greencastle facility at its measured rate of emissions. In contrast, estimates made with the default (unrefined) HHRAP default assumptions resulted in predictions of significant local impacts that would have led one to anticipate notably higher levels of mercury in fish (with respect to other Indiana lakes).<sup>8</sup> The fate-and-transport algorithms comprise many steps and assumptions, and are based on many theoretical constructs, limited empirical data, and extrapolations from data from other chemicals. However, few (if any) components of the algorithms have received detailed study and evaluation. Placing confidence in the model predictions is difficult to justify, and their inherent uncertainties

— if they could be quantified — likely would be far greater than the estimated effects. It is therefore recommended that significant research efforts be devoted to the study of specific areas of mercury fate-and-transport, as the current algorithms predict levels of concern to human health but cannot be judged to be reliable.

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## APPENDIX A

### PARTITIONING OF MERCURY IN THE SAMPLING TRAIN

Estimates of the vapor/particle partitioning of mercuric chloride within the sampling train were performed through consideration of the sampling probe characteristics and the specific measurements obtained in stack testing. Equilibrium conditions were assumed to hold within the sampling train and glass filter, which was maintained at a temperature of 248°F = 120°C. Other necessary parameters included the measured particle concentration  $C_{part}$  (reported on a dry basis at standard temperature) and the moisture content  $f_w$ . The actual concentration of particles in the probe at the filter was calculated as:

$$C_{actual} = 0.6975 \cdot C_{part} \frac{T_{std}}{T_{probe}} (1 - f_w)$$

where the terms are:

$C_{actual}$	concentration of particles in the probe at actual probe conditions (g/m <sup>3</sup> )
$C_{part}$	particle concentration, as reported at standard temperature on a dry basis (gr/dscf, grains per dry standard cubic foot)
$T_{std}$	standard temperature (20°C = 293.15°K)
$T_{probe}$	temperature of the sampling probe (120°C = 393.15°K)
$f_w$	fractional water content
0.6975	dimensional factor to convert units of grains/ft <sup>3</sup> (gr/ft <sup>3</sup> ) to grams/m <sup>3</sup> (g/m <sup>3</sup> ).

The concentration of particles in the probe was used in conjunction with the surface area per unit mass of the particles ( $A_{TSP}$ ) to calculate the surface area of the particles per unit volume (2):

$$\theta = 0.01 \cdot A_{TSP} \cdot C_{actual}$$

where the additional variables and their respective units are:

2	particle surface area to volume ratio (cm <sup>2</sup> /cm <sup>3</sup> )
$A_{TSP}$	surface area of particles per unit mass (m <sup>2</sup> /g)
0.01	dimensional factor to convert units of m <sup>2</sup> /m <sup>3</sup> to cm <sup>2</sup> /cm <sup>3</sup>

Following U.S. EPA guidance,<sup>9</sup> the fraction of the compound that can be expected to partition to particles is given as:

$$\Phi = \frac{c \cdot \theta}{p_L^o + c \cdot \theta}$$

where the additional terms and units are:

$M$	fraction of the compound absorbed to particles (unitless)
$c$	constant related to the heat of desorption of the particle surface and the heat of vaporization of the compound (Pa-cm)
$p_L^o$	saturation liquid-phase vapor pressure of the pure compound at ambient temperature (Pa).

For a compound that is a solid at standard conditions,  $p_L^o$  is estimated as the sub-cooled liquid vapor pressure from the solid-phase vapor pressure  $p_S^o$ :

$$p_L^o = p_S^o \cdot \exp\left(\frac{\Delta S_f (T_m - T_{probe})}{R \cdot T_{probe}}\right)$$

where the additional terms and units are:

$\Delta S_f$	entropy of fusion (J/mol-°K)
$T_m$	melting point of the compound (°K)
$R$	Universal Gas Constant, equal to 8.314 J/mol-°K

$\Delta S_f$  is calculated from the thermodynamic relationship:

$$\Delta S_f = \frac{\Delta H_f - \Delta G_f}{T}$$

At a temperature of  $T=298.15^\circ\text{K}$ ,  $\Delta H_f = -53.6$  kcal/mol and  $\Delta G_f = -42.7$  kcal/mol for mercuric chloride.<sup>10</sup> These values yield an entropy of fusion value of:

$$\Delta S_f = \frac{(-53.6 - (-42.7)) \text{ kcal / mol}}{298.15^\circ \text{ K}} \times \frac{4186.8 \text{ J}}{1 \text{ kcal}} = -153.06 \text{ J / mol-}^\circ \text{ K}$$

Also, the solid-phase vapor pressure of mercuric chloride at the probe temperature can be estimated from the correlation

$$p_S^o = 10^{\left(\frac{-0.05223a}{T_{probe}+b}\right)} \times \frac{101,325 \text{ Pa}}{760 \text{ mm Hg}}$$

where  $a$  and  $b$  are empirical constants of 85,030 and 10.888, respectively.<sup>10</sup> With these values, a solid-phase vapor pressure

$$p_S^o = 52.08 \text{ Pa}$$

is calculated at the probe temperature  $T_{probe} = 393.15^\circ\text{K}$ . Given a melting temperature of  $276^\circ\text{C} = 549.15^\circ\text{K}$ , the sub-cooled liquid-phase vapor pressure is estimated as:

$$p_L^o = 0.0358 \text{ Pa}$$

To estimate  $M$ , a value of 17.2 Pa-cm is used for the parameter  $c$ , and a representative (mid-range) value for the surface area-to-mass ratio  $A_{TSP}$  is  $5.5 \text{ m}^2/\text{g}$ .<sup>9</sup> With these values, the above equations were used to estimate run-specific values of  $M$  as listed in Table A.1. The average value of  $M$  is 0.271, or 27.1%, over the three stack test runs.

**Table A.1.** Estimation of  $M$  (fraction of mercuric chloride sorbed to particles)

Parameter	Run 1	Run 2	Run 3
$C_{part}$ (gr/dscf) (as reported in particulate stack test)	0.0119	0.0118	0.0127
$f_w$ (as reported in particulate stack test)	0.338	0.347	0.325
$C_{actual}$ (g/m <sup>3</sup> ) (calculated)	0.0134	0.0131	0.0146
$Z$ (cm <sup>2</sup> /cm <sup>3</sup> ) (calculated)	0.000739	0.000723	0.000804
$M$ (calculated)	0.266	0.262	0.283

Based on the vapor to particle fractionation ratios calculated above, it is possible to estimate the distribution of Hg forms within the sampling probe. Table A.2 shows these values for the sampling train data given in Table 1 (in the body of the paper). The calculations use half the detection limits for the non-detected Hg particulate measurements and the Hg analysis of the final HCl impinger rinse, and a calculated value for vapor-phase Hg<sup>2+</sup> based on the particulate measurements and the ratios  $M$  from Table A.1.

Table A.2 Calculated Hg Emission Partitioning

<b>Hg species</b>	<b>Measured Amount of Hg (: g)</b>		
	<b>Run 1</b>	<b>Run 2</b>	<b>Run 3</b>
Hg <sup>2+</sup> Particulate	0.10	0.10	0.10
Hg <sup>2+</sup> Vapor	0.28	0.28	0.25
Hg <sup>0</sup> Vapor	18.5	16.0	8.25