ABSTRACT
On May 18, 1993, the United States Environmental Protection Agency (EPA) announced a series of steps that the Agency would undertake, first, to achieve reductions in the amount of hazardous waste generated in this country and, second, to ensure the safety and reliability of hazardous waste combustion in incinerators, boilers, and industrial furnaces. With this announcement, EPA released its Draft Hazardous Waste Minimization and Combustion Strategy. Eighteen months later, EPA’s released its Final Strategy, which solidified the Agency’s policy on “how best to assure the public of safe operation of hazardous waste combustion facilities.” In short, EPA’s Final Strategy specifically recognized the multi-pathway risk assessment as a valuable tool for evaluating and ensuring protection of human health and the environment in the permitting of hazardous waste combustion facilities.

In keeping with EPA’s Final Strategy, Region 6 believes that combustion facilities in close proximity to population centers and ecologically important areas can be evaluated by a multi-pathway risk assessment to ensure that permit limits are protective of human health and the environment. Furthermore, EPA Region 6 believes that the multi-pathway risk assessment should consider the specific nature of process operations and the type of combustion units and air pollution control equipment utilized at each facility in order to be representative of actual facility operations. Therefore, although certain provisions of the Resource Conservation and Recovery Act (RCRA) program have since been delegated to the States, EPA Region 6 is committed to reviewing facilities on a site specific basis to evaluate the protectiveness of permits for combustion operations.

In July 1998, EPA published its Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, Peer Review Draft (1), commonly referred to as the HHRAP. In the following year, EPA staff worked through several implementation issues in applying this guidance document and in July 1999, EPA issued an Errata to the HHRAP (2) that addressed issues specific to conducting human health risk assessments. This paper will focus on one of the specific issues addressed in the Errata to the HHRAP: the handling of mercury in combustion risk assessments. The HHRAP and Errata are consistent with recommendations and assumptions used in EPA’s 1997 Mercury Study Report to Congress (3), referred to as EPA’s MSRC in this paper. However, evaluation of mercury in combustion risk assessments was and is still an evolving process.

INTRODUCTION

As a naturally occurring, chemically active element, mercury is pervasive in both environmental media and biota. As it cycles between the atmosphere, land, and water, mercury undergoes a series of complex chemical and physical transformations, many of which are not completely understood. However, scientists do agree that mercury’s cycle in the environment is a result of
both natural and human (anthropogenic) activities. Additionally, mercury is known to accumulate most efficiently in the aquatic food web. In 1997, EPA’s MSRC reported that thirty-five states had at least one water body under mercury health advisory, with six states having statewide advisories.

The growing number of health advisories specific to mercury contaminated water bodies issued throughout the United States has led to concern about the source of mercury contamination as well as interest in technologies to minimize such contamination from known sources as much as is technically feasible. In general, current scientific understanding of the relative contribution of mercury from anthropogenic sources is limited due to uncertainties regarding the level of natural emissions as well as the amount and original source of mercury that is re-emitted to the atmosphere from soils, watersheds, and ocean waters (3,4). For these reasons, various federal and state agencies, as well as private entities, have recognized that mercury contamination is a valid concern requiring closer evaluation in order to protect human health and the environment. Even prior to completing human health risk assessments for combustion facilities, EPA Region 6 was aware of intense interest by different stakeholders in the specific evaluation of mercury in the combustion risk assessment process.

This paper will present EPA’s current perspective on how mercury can be modeled and evaluated in human health risk assessments for combustion facilities. In addition, the last section of this paper will present possible risks attributable to mercury for two example facilities which meet the recently released Maximum Achievable Control Technology (MACT) standards for mercury at incinerator facilities (5) and briefly discuss why the MACT standards may not be protective for site-specific facilities. From a risk-based evaluation of current regulatory standards for mercury emissions, speciated emission rate calculations, air dispersion modeling, transport and fate considerations after deposition, and potential exposure profiles, EPA has attempted to utilize the best science available in assessing potential health effects attributable to mercury in stack emissions on a site-specific basis. However, as new information and data become available for understanding mercury’s fate and transport in the environment, EPA’s perspective remains open and the current way of handling mercury emissions from hazardous waste combustion units will evolve.

MERCURY BASICS

Mercury can exist in three oxidation states: metallic or elemental (Hg⁰); mercurous (Hg₂²⁺); and mercuric (Hg³⁺). Mercury’s properties and chemical behavior strongly depend on its oxidation state. Mercury can form ionic bonds with inorganic compounds as well as many stable complexes with carbon-containing, or organic, compounds. Depending on the chemical form and the dose received, mercury can be toxic to both humans and wildlife. In people, toxic doses of mercury can cause developmental effects in the fetus, as well as effects on the kidney and the nervous system in children and adults (3,5).

Elemental mercury is a silver-white, heavy, mobile, liquid metal at ambient temperatures. Virtually insoluble in water, elemental mercury is a volatile metal with fairly low viscosity and high surface tension. The vaporization rate of elemental mercury approximately doubles for every 10 degrees Centigrade increase in temperature and its saturation level in air increases
logarithmically with increasing temperature (4). Other forms of mercury such as mercuric acetate and mercuric chloride are white, heavy powders or crystal solids, which are more soluble in water and have higher vapor pressures depending on the compound (4,6).

Methyl mercury is an organic mercury compound that is somewhat soluble in water. Dimethyl mercury, another organic mercury compound, is much less soluble (4,6). Inorganic mercury can be methylated by microorganisms indigenous to soils, sediments, fresh water, and salt water, to form organic mercury. Invariably, microbial processes can also lead to demethylation, where methyl mercury is reduced back to elemental mercury. However, elemental mercury that has been reduced back from methyl mercury is believed to volatilize into the atmosphere (3,4).

Elemental mercury is the most common form of mercury found in the atmosphere whereas in all other environmental media, mercury is found in the form of inorganic mercuric salts and organo-mercury compounds (3,4). In soils and surface waters, predominately the mercuric and mercurous states of mercury exist as ions with varying solubility. Since mercurous mercury is rarely stable under ordinary environmental conditions, mercuric chloride, a simple salt, is the predominant form in many surface water bodies (3,4). This is due to the differences in physical and chemical properties between the various forms of mercury.

Methyl mercury and mercuric chloride have much lower Henry’s Law Constants than elemental mercury (3,4,6). Henry’s Law Constants are a measure of the extent of chemical partitioning between air and water at equilibrium. Similarly, the soil water partition coefficients for these compounds (1,3,6) show that mercuric chloride may adhere to soil particulates much more than methyl mercury or elemental mercury. Therefore, relative to the other forms of mercury, elemental mercury partitions much more strongly to the atmosphere than either methyl mercury or mercuric chloride due to its low water solubility, high Henry’s Law Constant, and low soil water partition coefficient. Methyl mercury and mercuric chloride partition much more strongly to water and sediments, respectively.

Although most of the mercury in aquatic systems is in the inorganic form, greater than 95% of the mercury accumulated by fish is in the form of methyl mercury (3). The high affinity of methyl mercury for sulfhydryl groups of proteins causes rapid absorption in living organisms. The elimination of methyl mercury by fish is very slow relative to the rate of uptake, allowing it to accumulate (7,8). Biological retention of methyl mercury in pike has been shown to be in the order of several years (9). Inorganic mercury, while absorbed almost as readily as methyl mercury, is depurated at a much faster rate (10,11). Therefore, almost all of the mercury found in animal tissues is in the form of methyl mercury (3,4).

Bioavailability of methyl mercury is determined by a combination of physicochemical characteristics of the aquatic system, the amount and rate of contamination, and the biological structure and function within the system (12). However, methyl mercury is one of the most highly toxic forms of mercury and is also the one most easily accumulated in the aquatic food chain. Therefore, humans and wildlife—such as bald eagles, kingfishers, otter and mink—that feed on fish are particularly at risk because of the potential for methyl mercury to bioaccumulate in freshwater fish (3,4).
Due to the nature of possible human health and environmental impacts associated with mercury, EPA’s goal is to minimize mercury emissions from combustion sources regardless of existing mercury concentrations in environmental media surrounding the stack. Therefore, hazardous waste combustion risk assessments are aimed at predicting the risks associated with a particular facility’s specific mercury contribution to the local environment. The mercury loss to the global cycle is accounted for in EPA risk assessments for hazardous waste combustion units only in terms of subtracting out the amount lost outside of the study area. However, risk management decisions may involve evaluating existing mercury contamination in surrounding media.

PARTITIONING OF EMISSIONS

For hazardous waste combustion facilities, EPA first assumes that stack emissions containing mercury include both vapor and particle-bound phases. Additionally, EPA assumes that mercury exits the stack in only the elemental and divalent species. Methyl mercury formation is addressed only after deposition has occurred. In other words, environmental fate and transport calculations account for methylation of mercury after deposition onto soils or water bodies within the study area. The phase allocation and speciation for mercury recommended in the HHRAP, and applied as a default by EPA Region 6, are based upon emissions data for combustion sources found in published literature and presented in the MSRC (a).

Of the total mercury measured in the stack of a combustion source, EPA assumes 80% is in the vapor phase and 20% is particle-bound. In addition, EPA assumes that speciation of the total mercury is actually 80% divalent (20% in the particle-bound and 60% in the vapor phase) and 20% elemental (all 20% in the vapor phase). Both the vapor and particle-bound phases of the divalent mercury emitted are thought to be subject to much faster atmospheric removal than the elemental form emitted. Furthermore, the reactivity and solubility of divalent mercury vapor are much greater than the divalent mercury particle-bound phase. Therefore, the divalent vapor mercury is thought to be more rapidly and effectively removed by deposition (both dry and wet) than the divalent particle-bound mercury (3,4). EPA also allows a loss to the global cycle for each form of mercury: EPA assumes that 99% of the elemental vapor form, 32% of the divalent vapor form, and 64% of the particle-bound divalent form of mercury are lost to the global cycle and does not deposit within the localized study area.

Figure 1 depicts the mercury cycle within the air media for an example combustion source that measures 100 grams of total mercury exiting the stack. In this example, EPA’s default assumptions are shown as percentage splits which result in reduced mass for each form of mercury that deposits to the surface. Given the example of 100 grams of total mercury exiting the stack, the speciated forms of mercury that are modeled to deposit within the study area are as follows: 48 grams of divalent mercury (7.2 grams particle-bound plus 40.8 grams vapor) and 0.2 grams of elemental mercury (all vapor). Since the air model uses an emission rate of 1 gram per second, emission rate calculations for elemental and mercuric chloride can then be based upon the speciated splits shown in this example so that the loss to the global cycle corresponds to 51.8% and deposition corresponds to 48.2% of the total mercury emitted from the stack (1,3).
Assume 100 g Total Hg

Global Cycle
64% Loss

20 g Elemental Hg (v)
60 g HgCl$_2$ (v)

Global Cycle
99% Loss

40.8 g HgCl$_2$ (v)

Deposited

48.2 g Total Hg Deposited

HWC Facility

Emission Rates
Hg$^0$ = 0.2% of Total Hg
HgCl$_2$ = 48% of Total Hg

Vapor Phase Fractions, Fv
Fv for Hg$^0$ (0.2/0.2) = 1.0
Fv for HgCl$_2$ (40.8/48.0) = 0.85

Only 48.2 g Total Hg Deposited
TRANSPORT AND FATE AFTER DEPOSITION

Once mercury deposits upon either soils or surface water bodies, transformation of specific forms of mercury may occur in each media in addition to fate and transport processes specific to each media. Transformation reactions may include the following: oxidation of total elemental mercury; reduction and methylation of total divalent mercury; and demethylation of total methyl mercury. In soil, each mercury component is subject to leaching and runoff of the dissolved phase, erosion of the particulate phase, and volatilization of the gas phase. In water, each mercury component is subject to advective export of all phases in the water column, volatilization and pore water exchange of the dissolved phase, settling, resuspension and/or burial of the particulate phase (3). Methylation and transport and fate parameters used in EPA combustion risk assessments are consistent with those values used in the MSRC, with the exception of available site-specific factors such as the Universal Soil Loss Equation parameters.

In soils, EPA assumes that 2% of the mercury from deposition will become methylated, while the remainder (98%) essentially stays in the form of mercuric chloride. Since elemental mercury which may deposit is assumed to be all in the vapor form (Fv =1.0), EPA further assumes that elemental mercury deposition onto soils is negligible or zero (this same assumption is also applied for the air to plant transfer for above ground produce). From this point, the transport and fate of each mercury component can be evaluated separately (i.e., divalent mercury versus methyl mercury). For example, soil loss constants are then calculated for both divalent mercury and methyl mercury.

Given that some of the mercury losses from watershed soils may impact the corresponding water body, mercuric and methyl mercury “loads” from watershed soils are added to the deposition loads from the air prior to assessing methylation in the water body. In other words, EPA first calculates the total load to the water body from: 1) both wet and dry particle-bound phase deposition; 2) vapor phase deposition; 3) runoff from impervious watershed surfaces; 4) runoff from pervious watershed surfaces; and 5) contribution from the erosion of watershed soils. Once the total load to the water body is determined for each form of mercury, EPA assumes that 15% of the total mercury concentration in the water column is methyl mercury while the remainder (85%) is in the form of mercuric chloride. From this point, EPA then uses separate transport and fate properties for each form of mercury to calculate the partitioning between water and sediments and water and air to determine the concentration of dissolved phase mercury in the water column.

EPA currently assumes equilibrium partitioning between water and sediments. Methylation in water bodies can range from below 1% to almost 100%. EPA’s assumed split of mercuric and methyl mercury in the water column is based upon the higher end of the beta distribution reported for “the fraction of total dissolved mercury in the water column existing as the methylated species” reported in EPA’s MSRC (b).

Figure 2 picks up from the example started in Figure 1 and continues the mass balance, in simplistic terms, for the mercury cycle within both the soils and water media. For the 48 grams of mercuric chloride deposited onto soils, only 0.96 gram will be converted to methyl mercury (47.04 grams will remain mercuric chloride) prior to losses associated with volatilization,
Figure 2: Mercury Transport & Fate After Deposition

Deposition to Soils & Water Body
\[ = (7.2 \text{g HgCl}_2)_{pb} + (40.8 \text{g HgCl}_2 + 0.2 \text{ g Hg}^0)_{v} \]

Soil Losses
\[ K_s = K_{sg} + K_{se} + K_{sr} + K_{sl} + K_{sv} \]

Prior to Soil Losses
47g HgCl\(_2\); 0.96g MeHg

Prior to Loads from Soils
40.8g HgCl\(_2\); 7.2g MeHg

Total Load to Water Body
\[ L_{total} = L_{dep} + L_{diff} + L_{ri} + L_{r} + L_{e} \]

Volatilization
\[ K_{sv} \]

Runoff
\[ K_{sr} \]

Erosion
\[ K_{se} \]

Leaching
\[ K_{sl} \]
leaching, runoff, and erosion. Conversely, 48 grams of mercuric chloride deposited onto a surface water body, with no contribution from watershed soils, would result in 7.2 grams methyl mercury and 40.8 grams mercuric chloride.

However, contribution from watershed soils is taken into account by partition coefficients respective to each form of mercury. Therefore, once watershed soil runoff and erosion loads are determined for mercuric and methyl forms of mercury, the mercuric loads would undergo additional methylation in the water body. This is taken into account and clarified by the revised load equations presented in the Errata to the HHRAP (2). Specifically, the amount of mercuric chloride loads entering the water body would be multiplied by 15% and then added to the methyl mercury loads entering the water body. At this point, water column concentrations of methyl mercury and mercuric chloride are calculated independently.

**FOOD CHAIN BIOTRANSFER AND BIOACCUMULATION**

EPA also accounts for transport and possible methylation of mercury compounds in plants and animals. These pathways are mainly addressed by following through each mercury compound separately from soils and water to calculate media and exposure point concentrations.

For example, in vegetables and fruits, uptake of both forms of mercury present in the soils can be directly calculated based upon each compound’s bioconcentration factor specific to the type of vegetable or fruit evaluated. For below ground produce, EPA uses bioconcentration factors for root vegetables (Br,rootveg) that are available for both mercuric and methyl mercury. Aboveground produce (fruit and vegetables) and forage bioconcentration factors (Br,ag and Br,forage) are also available for both mercuric and methyl mercury. In the case of above ground produce, EPA also accounts for mercury contribution from the atmosphere by using the air-to-plant biotransfer factor for mercuric chloride. Consistent with the assumption that elemental mercury reaching the surfaces of above ground fruits and vegetables is negligible and methyl mercury is not emitted from the stack, only mercuric chloride is assumed to initially enter above ground produce from the air.

EPA accounts for methylation in above ground produce since information was available from the MSRC to address this pathway: EPA assumes a 22% methyl mercury to 78% mercuric chloride split in above ground produce. However, methylation is not assumed within below ground produce since the MSRC assumed that all methyl mercury via root uptake originated from the soil (c). Therefore, all mercury in below ground produce is assumed to come from soil to plant transfer while mercury in above ground produce is attributable to soil-to-plant transfer, air-to-plant transfer, and also methylation of mercuric chloride within the plant.

In animals, the biotransfer factor (Ba) is the ratio of a compound concentration in a specific type of fresh weight animal tissue (e.g., beef, pork, chicken) to the daily intake of the compound by the animal. Subsequent biotransfer to cow’s milk and poultry eggs (Ba,egg and Ba,milk) also occurs. EPA assumes a split of 13% methyl mercury to 87% mercuric chloride for total mercury in herbivore animal tissues, other than fish. Assuming equilibrium with the body, this same split is used for cow’s milk and chicken’s eggs.
As already discussed, bioaccumulation of methyl mercury in fish tissues is a significant concern for potential exposure in the human health risk assessment. EPA’s MSRC analyzed three different methodologies for determining bioaccumulation in fish, for both trophic levels 3 and 4, and compared the results statistically (d). The recommended values in the MSRC for both trophic levels are the geometric mean values (50th percentile) for statistical analysis of BAFs directly estimated from field data. The recommended BAF is defined in the MSRC as “the average methyl mercury concentrations in piscivorous fish (trophic level 4) divided by average dissolved methyl mercury concentrations in water, accumulated by all possible routes of exposure” (3). Therefore, consistent with the MSRC, EPA assumes that 100% of the mercury in fish tissues exists or is converted into methyl mercury and uses the Bioaccumulation Factor (BAF) for a trophic level 4 fish which is recommended in the MSRC (e).

**RISK ESTIMATE RESULTS**

The aquatic pathway is the predominant pathway of concern for potential mercury exposure and resulting human health hazard estimates in all risk assessment efforts completed to date by EPA Region 6. Based upon the observed health effects of mercury on developing neurological systems, the three subpopulations of greatest concern are pregnant women, women of child-bearing age (i.e., between the ages of 15 and 44), and children ages 14 years and younger (3). An example calculation for the complete adult fisher exposure scenario is available on EPA’s Region 6 web page (http://www.epa.gov/earth1r6/6pd/rcra_c/pd-o/mercury.pdf) updated per the Errata to the HHRAP (2).

Although EPA’s HHRAP evaluates a fisher scenario, the consumption rate used (82 g/day for an adult and 11 g/day for a child) is more in line with a “high-end” consumer than a true “subsistence” fisher. A total of 100 g/day of fish or shellfish is roughly only 3.5 ounces, only ½ serving of fish according to the Food and Drug Administration (3). Results of a cross-sectional survey show that approximately 5% of women within the overall population of the United States consume fish and shellfish in the amount of 100 grams per day or more, on any single day, and approximately 3% of women consistently consume 100 grams of fish/shellfish per day or more. In a 1973 longitudinal (long term) survey conducted by the National Purchase Diary, Inc., the 99th percentile of fish and shellfish consumption among adults was 112 grams per day (3).

*Regulatory Maximum Allowables* - “Tier” limits (either waste feed rates or emission rates) which are applicable to hazardous waste Boiler and Industrial Furnace (BIF) facilities are maximum allowable limits based upon possible inhalation health impacts only (13). Therefore, these levels typically do not demonstrate protective permit limits when used in site-specific risk assessments that evaluate indirect risks over the long term. This is especially true for facilities that are located near small recreational water bodies (small lakes or ponds used for recreational fishing). For larger rivers that have high flow rates, the impacts may be less significant, but risk estimates may still fall above human health levels of concern based upon other site-specific factors and consideration of special subpopulations.

The newly released MACT standards for mercury, applicable to either new or existing incinerators (MACT standards are not yet available for BIF facilities), are more protective than the Tier levels since they are numerically lower. This is not surprising since risk estimates for mercury are directly proportional to the emission rate (mass of mercury) used in the risk model.
However, MACT standards are *technology-based standards* not *health-based standards*. EPA did evaluate the protectiveness of the MACT Standards on a national level by conducting a multi-pathway risk assessment, however, the assessment utilized only generalized assumptions for a hypothetical set of circumstances. Actual site-specific considerations may differ from the generalized assumptions used as part of the MACT evaluation and resulting risk estimates, based upon site-specific information, may exceed EPA levels of concern for certain hazardous waste combustion units.

For example, Table I shows risk estimates for two hazardous waste combustion facilities located in Region 6. Both of these facilities have nearby water bodies used for recreational fishing. The results demonstrate that the MACT standards clearly result in excessive potential health hazards for mercury in both cases.

**Table I: Site-Specific Risk Estimates for Mercury MACT Standards Application**

<table>
<thead>
<tr>
<th>MACT Standards Application</th>
<th>Example 1</th>
<th></th>
<th>Example 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Existing Incinerator</td>
<td>New Incinerator</td>
<td>Existing Incinerator</td>
<td>New Incinerator</td>
</tr>
<tr>
<td>Particulate Matter @ 0.015 gr/dscf</td>
<td>Met @ 0.004 gr/dscf</td>
<td>Met @ 0.004 gr/dscf</td>
<td>Met @ 0.00087 gr/dscf</td>
<td>Met @ 0.00087 gr/dscf</td>
</tr>
<tr>
<td>Total Hg (ug/dscm) =&gt; 130 ug/dscm</td>
<td>45 ug/dscm</td>
<td>130 ug/dscm</td>
<td>45 ug/dscm</td>
<td></td>
</tr>
<tr>
<td>Total Hg Emission Rate based upon MACT Standard &amp; facility-specific Stack Gas Flow</td>
<td>5.048E-4 g/s</td>
<td>1.748E-4 g/s</td>
<td>8.332E-4 g/s</td>
<td>2.884E-4 g/s</td>
</tr>
<tr>
<td>HQ, Methyl Mercury</td>
<td>341</td>
<td>118</td>
<td>1591</td>
<td>551</td>
</tr>
</tbody>
</table>

**Notes:** Stack gas flow rates and particulate matter emissions were measured during risk burn testing and corrected to 7% O$_2$ per MACT Standard specifications. Site-specific Universal Soil Loss Equation parameters were used. The air modeling was conducted based upon site-specific conditions (e.g., flat terrain) and facility-specific conditions (e.g., risk burn data). The HQ (Hazard Quotient) for methyl mercury corresponds to the Total Hg Emission Rate based upon the MACT Standards shown.

**CONCLUSIONS**

*Due to the nature of possible human health and environmental impacts associated with mercury, EPA’s goal is to minimize mercury emissions from combustion sources regardless of existing mercury concentrations in environmental media surrounding the stack.* Therefore, hazardous waste combustion risk assessments are aimed at predicting the risks associated with a particular facility’s specific mercury contribution to the local environment. The loss to the global cycle is accounted for in EPA risk assessments for hazardous waste combustion units only in terms of *subtracting out* the amount lost outside of the study area.
This paper has presented a brief overview of EPA’s current perspective on how mercury can be modeled and evaluated in human health risk assessments for combustion facilities. The complex nature of mercury’s cycle in the environment makes any attempt to model possible human health hazards a challenging endeavor. However, given the few cases already evaluated for the recently released MACT standards for mercury, EPA Region 6 believes that site-specific information can be used to conduct multi-pathway risk assessments. Information from these assessments can then be used to supplement the regulatory maximum allowable standards in order to provide more protective permit limits for mercury emissions.

From a risk-based evaluation of current regulatory standards for mercury emissions, speciated emission rate calculations, air dispersion modeling, transport and fate considerations after deposition, and potential exposure profiles, EPA has attempted to utilize the best science available in assessing potential health effects attributable to mercury in stack emissions on a site-specific basis. However, as new information and data become available for understanding mercury’s fate and transport in the environment, EPA’s perspective remains open and the current way of handling mercury emissions from hazardous waste combustion units will evolve.

ENDNOTES

a. Vol III, Page ES-5 and Table 4-2.
e. Vol III, Page D-18 (Table D-10).

REFERENCES

2. US EPA Errata to the HHRAP. EPA Memo and Attachment (July 1999).


