

Atmospheric Mercury Research Update

Technical Report

Atmospheric Mercury Research Update

Final Report, March 2004

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PRODUCT DESCRIPTION

Atmospheric Mercury Research Update is a summary and analysis of research findings on utility and environmental mercury from 1997-2003. The update categorizes and describes recent work on mercury in utility-burned coal and its route through power plants, the measures for its control, and its fate in the environment following emissions from utility stacks. This fate includes atmospheric chemistry and transport, deposition to land and water surfaces, aquatic cycling, the dynamics of mercury in freshwater fish food webs, and the exposure of and health effects on humans consuming fish tainted with excess levels of mercury. Several aspects of mercury cycling are not addressed: marine cycling, fate in solid material streams, ecosystem risk, and exposure and health effects via non-fish consumption or non-consumption routes of exposure.

Results & Findings

The key findings of the *Atmospheric Mercury Research Update* were that major uncertainties remain in the understanding of mercury dynamics in the environment for clarifying quantitative relationships between nearby and distant mercury sources and community exposure to mercury via fish consumption. Among the primary uncertainties are contributions of background and natural emissions to downwind concentrations and deposition; long-term effectiveness and ancillary costs of mercury controls for high-efficiency mercury removal in power plants; the chemistry of mercury redox reactions in power plant plumes; the rate of mercury movement through watersheds in varying environments to lake and river receiving waters; the range of uptake of mercury among fish communities in widely scattered watersheds; whether high-end fish consumers are subject to local fish concentrations of mercury to a greater degree than to commercial and marine fish levels; and whether tests used to gauge sensitivity of human children to mercury intake are being biased by co-exposures to other neurotoxins.

A key aspect of the research update is a description of recent integrative analysis of the potential for mercury management schemes to reduce human exposure to the substance by lowering the concentrations in fish consumed by members of the community (vs. accidental or workplace exposures, usually through exposure to vapors of elemental mercury through spillage of liquid mercury). Work published in May 2003, and continuing, modeled changes in mercury emissions that might ensue following then-proposed mercury control schemes publicly considered by the U.S. EPA. These schemes included one that entailed each coal-burning electric generating unit in the United States being limited to mercury emissions of 2.2 lbs/10¹² Btu heat capacity. When this scenario constraint was applied to every U.S. power plant, some units already met that limit while others were required to attain it (but with no assumed change in the proportion of emitted mercury that is elemental Hg(0) vs. divalent Hg(II)).

Challenges & Objective(s)

Mercury source-receptor relationships are increasingly subject to quantification and separation of source contributors as detection and analysis methods improve. Yet, key components of mercury cycling are still poorly understood, and “cause and effect” determinations as mercury emissions change are still unable to be well-supported. The emerging research priorities for mercury should be focused on those areas where substantial progress in quantifying changes in receptor concentrations following source changes can be accomplished most readily. One such approach, the natural enrichment of stable mercury isotopes through atomic mass discrimination, has the potential to allow identification of mercury by source pool, if not source category, in the near future.

Applications, Values & Use

This report presents a framework for understanding where substantial progress is possible in the short term. Periodic re-examination of the state of mercury research can enrich the planning process for work on the separate specialties that have mercury as a common issue of concern: neurotoxicology, trace substance sources and transport, multimedia transfer, human exposure, and human health risk.

EPRI Perspective

Substantive support for regulatory decision-making requires a robust understanding of the key contributors to public health risk and the manner in which those contributors can be controlled, either by source regulation or by exposure management. The goal of the EPRI mercury research program is to provide full and balanced evaluation of the remaining uncertainties in these source-receptor relationships to allow a balanced judgment about where resources and effort should be focused to manage issues of public concern. One approach is to provide a synoptic view of our understanding of the issue of concern.

Approach

Key reporting on mercury research, both in the peer-reviewed literature and in proceedings and other technical reports, was surveyed for findings of significance in the understanding of mercury dynamics. Primary contributors to this research were queried for more detailed discussion of key findings and their importance to an overall understanding of mercury cycling and effects. Where conflicting conclusions were drawn in the primary literature, interpretive evaluations of alternative findings were prepared by primary researchers or project contributors. Several peer-review cycles raised additional questions about the currency, relevance, or significance of the various research contributions and additional sources were sought out for supplemental material.

Keywords

Mercury Methylmercury Cost-effectiveness Control policy Deposition
Emissions Health effects Health risk

ABSTRACT

“Atmospheric Mercury Research Update” is a summary and analysis of research findings on utility and environmental mercury provided in the period 1999-2003. The update seeks to categorize and describe the recent work on mercury in utility-burned coal and its route through power plants, measures for its control, and its fate in the environment following emissions from utility stacks. This fate includes atmospheric chemistry and transport, deposition to land and water surfaces, aquatic cycling, the dynamics of mercury in freshwater fish food webs, and the exposure of and health effects on humans consuming fish tainted with excess levels of mercury. Several aspects of mercury cycling are not addressed: marine cycling; fate in solid material streams; ecosystem risk; and exposure and health effects via non-fish consumption or non-consumption routes of exposure.

A key aspect of the research update is a description of recent integrative analysis of the potential for mercury management schemes to reduce human exposure to the substance by lowering the concentrations in fish consumed by members of the community (vs. accidental or workplace exposures, usually through exposure to vapors of elemental mercury through spillage of liquid mercury). Work published in May 2003, and continuing, modeled changes in mercury emissions that might ensue following then-proposed mercury control schemes publicly considered by the U.S. EPA. These schemes included one that entailed each coal-burning electric generating unit in the United States being limited to mercury emissions of 2.2 lbs/10¹² Btu heat capacity. When this scenario constraint was applied to every U.S. power plant, some units already met that limit, while others were required to attain it (but with no assumed change in the proportion of emitted mercury that is elemental Hg(0) vs. divalent Hg(II)).

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1

MERCURY SOURCES AND EMISSIONS

1.1 Introduction

Mercury, the chemical element with atomic number of 80, is classified as a heavy metal. Several forms of mercury occur naturally in the earth's crust, and are associated in trace amounts with coal and other minerals. Mercury's unique physical and chemical properties lead to its ubiquitous presence in the natural and human environment. Releases of mercury to the human environment predominantly occur by discharge to water bodies, or emissions to the atmosphere. Some biogeochemical processes can change the mercury in the environment from one chemical or physical form to another, including transforming inorganic mercury into one or more organic forms. The most common organic mercury compound that microorganisms (such as bacteria and fungi) and natural processes generate from other forms is monomethylmercury, commonly occurring as monomethylmercuric chloride. As a result of natural and human activities, mercury cycles through the environment in both organic and inorganic forms.

Elemental mercury, Hg(0), is considered to be essentially inert chemically because of its relatively slow reactivity with common atmospheric oxidants (e.g. ozone). Mercury is present in the atmosphere as gaseous elemental mercury, gaseous divalent mercury [Hg(II)], and particulate-phase divalent mercury [Hg_p]. The predominant form of mercury occurring in the human environment is gaseous elemental mercury. At most locations, the remainder of mercury species are composed largely of particulate-phase divalent mercury, gaseous divalent mercury (commonly termed "reactive gaseous mercury", RGM), and trace amounts of monomethylmercury, CH₃HgR, where R is typically a halide, commonly chlorine, Cl. Generally monomethylmercury is abbreviated as "MeHg".

Releases of mercury to the atmosphere as well as to aquatic and terrestrial environments typically result in mass fluxes of mercury among these environmental compartments. As a chemical element, mercury is persistent and cannot be chemically transformed to other substances. The speciation or chemical form of the released mercury varies depending on the source types and other factors. The specie of mercury influences the potential effects on human health and the environment since toxicity varies among mercury species.

1.2 Overview

At the time of EPRI's prior research update on mercury (EPRI 1996), there was general scientific agreement that atmospheric mercury has many natural and anthropogenic sources, although there was no consensus on the relative contribution by each category. In the intervening years, no scientific consensus has developed on the relative amount each category of emission source contributes to mercury deposition at each of local, regional, and global scales.

Anthropogenic emissions are releases of mercury due to current, ongoing human actions. Background emissions include both natural emissions (such as volcanoes and geothermal sites) and continuing emissions from former human activity sites (also known as legacy sources), such as mine tailing sites that are currently inactive, as well as re-emission of anthropogenic releases of mercury from natural settings.

Prior studies have shown that atmospheric transport is the primary pathway by which mercury is deposited in the environment on regional and global scales. In previous work, scientific investigators reached consensus that mercury atmospheric cycling has a global dimension as well as local and regional dimensions (EPRI 1996). This chapter provides a discussion of recent studies regarding the global balance and cycling of mercury as well as our current understanding of mercury sources and emissions.

1.3 Global balance

The calculated atmospheric lifetime of elemental mercury is computed as the inverse of the net removal rate of mercury based on global measurements of deposition, balanced against the sum of sources (anthropogenic, background terrestrial, and oceanic). The assumption in these calculations is that atmospheric mercury is well-mixed vertically (although there is a latitudinal gradient due to the predominance of sources and land area in the Northern Hemisphere). Recent measurements of background emissions, of atmospheric mercury vertical profiles, and of deposition are casting doubt on a number of these assumptions, and the reservoir and flux rates that flow from them. There is a wide range of estimates of the amount of mercury present in the global atmosphere. Based upon recent findings, several researchers report that the amount of mercury in the atmosphere at any time may range as high as 6,000 to over 7,000 metric tons¹ (tons) (Nriagu and Pacyna 1988; Nriagu 1989; Fitzgerald 1986; Lindquist et al. 1991; Mason et al. 1994, Pirrone et al., 1996; Lamborg et al. 2002). Table 1-1 provides global totals as estimated by several authors. As can be seen, these estimates of the overall global burden of mercury vary widely.

For example, recent measurements in terrestrial environments in the eastern and western U.S. indicate that the mercury emitted to the atmosphere from natural areas and disturbed natural sites (mining sites and sites of former anthropogenic activity) may cumulatively equal the amount of all current U.S. industrial emissions combined (Radke et al. 2002, Gustin 2003). The most recent work on background sources indicates that mercury emissions from diffuse anthropogenic “legacy” and natural sources are greater than currently estimated in global models. Revising the estimate of background emissions could raise the significance that these sources have within the global mercury biogeochemical cycle. If the background sources of atmospheric mercury are greater than predicted, this implies there must be either unrecognized mercury sinks, or the atmospheric residence time for gaseous elemental mercury must be shorter than previously estimated. These research findings for background source contributions are discussed in more detail in a later section.

¹ 1 metric ton = 10³ kg = 10⁶ grams

Table 1-1
Estimates of Total Releases of Mercury to the Global Environment (UNEP 2002)

Process	Lindquist <i>et al.</i> 1984	Nriagu & Pacyna 1988,Nriagu 1989	Fitzgerald 1986	Lindquist <i>et al.</i> 1991	Mason <i>et al.</i> , 1994	Pirrone <i>et al.</i> , 1996	Lamborg <i>et al.</i> , 2002
Anthropogenic releases	2000-10,000	3560 (910-6200)	2000	4500 (3000-6000)	5550 *1	2200	3000 *2
Natural releases	<15,000	2500 (100-4900)	3000-4000	3000 (2000-9000)	1650	2700	1400
Total present releases	2000- <25,000	6060 (1010-11,100)	5000-6000	7500 (5000-15,000)	7200	4900	4400

- 1 Anthropogenic releases and totals: Numbers include an estimated re-emission (net increase of evasion from oceans) of 1400 metric tons/year originating from previous anthropogenic releases (new anthropogenic releases are thus estimated at 4150 metric tons/year in this study).
- 2 Anthropogenic releases and totals: Numbers include an estimated re-emission (net increase of evasion from oceans) of 400 metric tons/year originating from previous anthropogenic releases (new anthropogenic releases are thus estimated at 2600 metric tons/year in this study).

This atmospheric burden, or resident mass, of mercury is primarily in the form of gaseous elemental mercury, which has been assumed to be well-mixed with height in the global troposphere. However, there is recent evidence to the contrary from measurements of mercury over various terrestrial and ocean environments. Current studies indicate that tropospheric mercury may not be as well-mixed as thought earlier, with evidence of vertical gradients in mercury concentrations found locally over the ocean and near mercuriferous geological areas (Radke et al. 2002, Gustin 2003). Measurements made over the open ocean indicate longitudinal gradients in total gaseous mercury (TGM) concentrations in the boundary layer, and also vertical gradients of divalent mercury concentrations (or RGM) (Radke et al. 2002). Sampling by aircraft of ambient atmospheric mercury concentrations at various altitudes in the troposphere demonstrate that TGM is poorly mixed vertically, evidenced by observed spatial and temporal variations in concentrations. All the factors that cause this lack of mixing are not known. These findings, from observations over both terrestrial and ocean environments, counter previous assumptions that mercury in the atmosphere is well-mixed and at relatively uniform concentrations vertically, i.e., with height above a given location. For mercury to be well-mixed vertically implies that atmospheric mercury is relatively chemically inert with small sources and sinks at the top and bottom of the atmosphere (versus the assumption that mercury is well-mixed in all three dimensions).

Estimates developed in the 1990s indicate that gaseous elemental mercury has a global atmospheric lifetime of about one year, with estimates ranging between 6 months and 1.5 years (Hall 1995, Schroeder and Munthe 1998, Bergan et al. 1999, Shia et al. 1999). Recent work by Sommar et al. (2001) and Radke et al. (2002) has suggested that the atmospheric lifetime for gaseous elemental mercury may be considerably shorter, about 4 to 7 months or 100 days,

respectively. In a scenario with a shorter atmospheric lifetime for gaseous elemental mercury, gaseous divalent mercury and particulate mercury tend to be removed more rapidly, with their lifetimes estimated at one day and one week, respectively. A shorter atmospheric lifetime for elemental gaseous mercury of approximately 100 days at remote locations would imply a sum of combined natural and anthropogenic sources of mercury equal to about 15,000 tons per year (Radke et al. 2002), and would result in a doubling of the highest current estimates of the atmospheric burden.

If both the remote TGM vertical gradient and revised residence times are confirmed by additional research for remote locations on a global scale, these two findings would force major revisions in atmospheric reservoir, source emission, and sink estimates. Assuming current estimates for man-made emissions are more certain than estimates of background emissions, the term for background sources of mercury would require a threefold increase for the global reservoir to be in balance. Further studies needed include measurements to confirm observations of the TGM tropospheric gradient, investigate Hg(0) depletion in the stratosphere, and determine whether the salt oceans are net source or sink for Hg(0).

1.4 Anthropogenic emissions

Using 1999 U.S. data on mercury in utility coals and utility mercury emissions to air, as well as other sources of information, EPRI developed a global inventory of anthropogenic mercury releases to the atmosphere (EPRI 2000). This inventory has been recently updated (Seigneur 2003); those emissions estimates are provided here. Current global emissions of mercury amount to 6386 metric tons (T/y). These numbers take into account recent mercury control requirements for municipal incinerators in the U.S.. Natural emissions were estimated to be 1064 T/y. Since natural emissions from land include 500 T/y from land ore deposits and 90 T/y from volcanoes, natural emissions from oceans amount to 474 T/y. Re-emissions constitute the remainder of the background emissions, comprised of 1525 T/y from the oceans and 1670 T/y from land. Figure 1-1 presents a schematic summary of this global mercury budget. The amount of mercury re-emitted corresponds, therefore, to about 50% of the amount of mercury deposited on average. These re-emissions are allocated to both natural and anthropogenic emissions, proportionately to those emissions. Note that this is roughly consistent with the latest results from the international METAALICUS experiment in western Ontario, which preliminarily indicated about 20% re-emissions from terrestrially deposited mercury, and 80% from direct aquatic surface deposition. This U.S. anthropogenic mercury emission inventory is summarized by source category in Table 1-2, while Table 1-3 summarizes this global emission inventory.

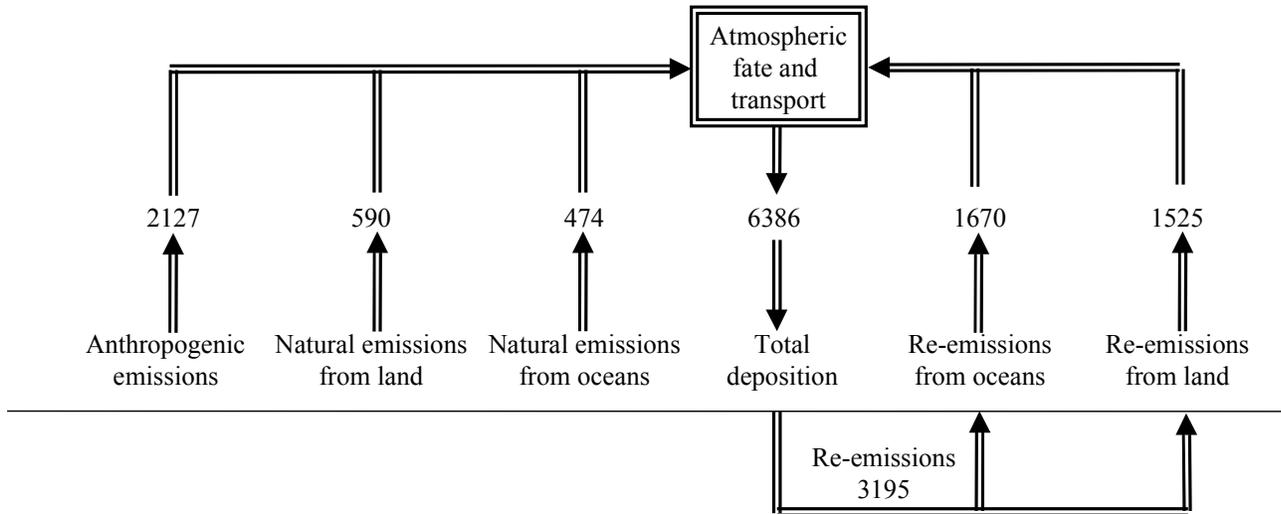


Figure 1-1
Schematic Summary of the Global Atmospheric Mercury Cycle (Annual Emission and Deposition Rates are in Metric Tons/y) (Seigneur et al. 2003)

Table 1-2
Global Emissions Inventory (Seigneur et al. 2003)

Anthropogenic sources	Emissions (metric tons/y)
Africa	246
Asia	1138
Europe	326
North America	193
South America	176
Oceania	48
Total	2127
Natural sources	
Land ore deposits	500
Oceans	474
Volcanoes	90
Total	1064

Table 1-2 (continued)
Global Emissions Inventory (Seigneur et al. 2003)

Re-emissions of anthropogenic mercury	
Land	1113
Oceans	1017
Total	2130
Re-emissions of natural mercury	
Land	557
Oceans	508
Total	1065
Total global emissions	6386

Table 1-3
Anthropogenic Hg Emissions in the North American Domain (metric tons/y)
(Seigneur et al. 2003)

Source Category	United States	Southern Canada	Northern Mexico	Total
Electric utilities	41.5	1.3	9.9	52.7
Waste incineration	28.8	3.4	(a)	32.2
Residential, commercial, and industrial coal burning	12.8	(a)	(a)	12.8
Mining	6.4	0.3	(a)	6.7
Chlor-alkali facilities	6.7	.05	(a)	6.8
Mobile sources	6.2	(a)	(a)	6.2
Other sources	30.6	9.6	23.6	63.8
Total	133.0	14.7	33.5	181.2

(a) included under "other sources"

For North America, it is estimated that the United States emits 133 T/y of the 193 T/y total mercury (divalent plus gaseous elemental) emitted. The industrialized areas of southern Canada and northern Mexico contribute about 15 T/y and 34 T/y, respectively. Of the U.S. portion, electric utilities contribute about 42 T/y, or about 32% of the U.S. total. The global total of anthropogenic emissions is estimated at 2127 T/y.

These U.S. emissions make up about 6% of the mercury due to total global anthropogenic emissions, while U.S. coal utilities make up 2% of these world anthropogenic emissions (other utility emissions, from oil- and gas-fired plants, make up less than 1/50th of the utility total, so are a small component of the global total) (EPRI 2000, Seigneur 2003). In the last decade, anthropogenic emissions of mercury have decreased in North America (Seigneur et al., 2001) and Europe (Pacyna et al., 2001). For emissions over the past ten years, trends analysis indicates that estimates of mercury emissions show increased emissions for India (UNESCAP, 2000) and China (Weidou and Sze, 1998; Ho et al., 1998) of about 27% and 55%, respectively. In China, this is due to substantial increases in coal-fired electricity generation.

Elemental and inorganic mercury enter the atmosphere from mining deposits of mercuriferous ores, from the emissions of coal-fired power plants, from the burning of municipal and medical waste, from the production of cement, and from uncontrolled releases from industrial facilities that utilize mercury in processes and products.

Mercury emissions from coal-fired power plants in the United States are better understood than those of many other source categories because the U.S. Environmental Protection Agency (EPA) conducted a mercury Information Collection Request (ICR) in 1999-2000. This activity analyzed the mercury content of the different types of coal burned at every U.S. coal-fired power plant, and conducted stack sampling at over 80 coal-fired power plants. The results indicated that the actual amount of mercury emitted from the stacks is dependent on the coal type and the sulfur and particulate control system installed.

Mercury emissions of other source categories (particularly those with diffuse emissions, such as landfills) have typically not been as well-characterized. Some key uncertainties are mercury releases from chloralkali plants, several of which use mercury as electrode material (in the production of industrial chlorine gas and caustics). Also, emission inventories for North America and Europe are likely to be more accurate than those for other continents due to variations in data collection by government and private agencies. Therefore, significant uncertainties currently exist for global anthropogenic mercury emissions in selected regions and for several industrial source categories. Nevertheless, they are more certain than natural and legacy estimates.

Mercury releases from products via normal use, spills, breakage, and scrap metal processing and disposal are significant sources that may be under-estimated in some release inventories. For example, metallic mercury has been found at 714 hazardous waste sites nationwide (US ATSDR 1999). As noted by United Nations Environment Programme researchers in the recent Global Mercury Assessment (UNEP 2002), much of the mercury used in products and for consumer purposes is incinerated or disposed of in landfills with collected waste. In many parts of the world mercury in products may be lost, dumped or incinerated directly into the environment from a variety of widely scattered sources. Therefore, a significant part of the total mercury in consumer products could be expected to end up in the environment, directly and quickly.

The release of mercury from waste treatment and storage is more difficult to assess. Regional and national balances (“substance flow assessments”) can cast light on some of the aspects of this uncertainty. Such substance flow assessments have been performed in varying detail in Europe and the U.S. and provide insights regarding source category contributions that may influence local and regional levels of mercury concentrations (UNEP 2002, Husar and Husar 2001). Additional assessments of this source category may help to further explain the effect of local and regional sources on local mercury concentrations, particularly in urban settings.

Anthropogenic emissions consist of several mercury species, $\text{Hg}(0)$, $\text{Hg}(\text{II})$, and Hg_p with the composition of the emissions varying widely among sources. The chemical speciation of mercury emissions is not well known by source category. Emission speciation is an important source of uncertainty when assessing the atmospheric fate of mercury because $\text{Hg}(0)$, $\text{Hg}(\text{II})$, and Hg_p have very different physical and chemical characteristics and, consequently, have very different atmospheric lifetimes. Until now, speciated mercury sampling has been conducted only for a few source categories (such as coal-fired power plants). Even for power plants studied in the ICR, a comparatively well-studied category, there are wide variations in mercury species emitted. These uncertainties are likely to affect the plant-specific estimates but will have less of an effect on national inventories. Fossil-fueled power plants as a source of mercury emissions will be specifically addressed in detail in the next chapter.

1.5 Background Emissions

Background sources of mercury emissions include natural sources (such as geologic formations, forest fires, and volcanic emissions) and legacy sources (historic human activity sites still emitting mercury, such as former smelting sites). Geologic sources of atmospheric mercury include areas of fossil and current geothermal activity, recent volcanic activity, precious and base metal deposits, and organic rich sedimentary rocks. Geologic source areas can also provide legacy emissions. Most natural sources are diffuse and difficult to characterize. Early estimates of global mercury emissions from natural sources were not based upon actual measurements of mercury fluxes, but instead were computed, based on the global mass balance difference between emissions from anthropogenic point sources and wet/dry deposition estimates. Mercury releases from mid-ocean tectonic ridges (e.g., hydrothermal vents) can be significant, and Garrett (2000) estimated annual fluxes of Hg from these sources at 1,860 to 14,680 T/yr

The most recent work on background sources indicates that mercury emissions from diffuse anthropogenic and natural sources are greater than currently estimated in global models. Revising the estimate of natural emissions raises the significance of natural sources in the global mercury biogeochemical cycle. Estimates of annual global emissions from natural sources vary considerably. Early estimates assumed that globally 1,000 metric tons per year originate from non-anthropogenic (natural) sources (Mason et al. 1994). Field measurements by Schroeder and Munthe (1998), however, suggested 1,400 to 3,000 tons are released annually from natural sources. According to Rasmussen et al. (1998), estimates of the total emission of elemental mercury vapor to the atmosphere from natural sources have varied by orders of magnitude among researchers, with the uncertainty due to the scarcity of temporally and spatially representative measurements from direct observations of mercury flux originating from natural surfaces. While significant advances have been made in quantifying mercury emissions from background terrestrial sources, scientists are finding that the global mercury cycle is more

complex than previously thought (Engle and Gustin 2002). For example, studies have shown that mercury emissions from naturally mercury-enriched areas are greater than earlier thought (Rasmussen et al. 1998; Engle et al. 2001; Gustin et al. 1999, 2000, 2001; Engle and Gustin 2002). Recent field investigations indicate that contributions from these natural sources may be comparable to anthropogenic sources in impact upon regional and global atmospheric mercury pools (Gustin et al. 1999, Zehner and Gustin 2002).

An underlying area of uncertainty in global mercury budgets is whether background emissions have remained constant over time, which has yet to be demonstrated (Gustin et al. 2001). Disturbance of naturally enriched areas, through processes such as mining and land development, has resulted in an increase of the exposed surface area and likely atmospheric mercury emissions from naturally enriched substrate over time. Thus, it is unlikely that emissions have remained constant; rather, background emissions have probably increased due to anthropogenic activity.

1.5.1 Mercury-enriched terrestrial sources

Recent estimates of mercury emissions from natural sources have been made at regional and local scales based on substrate mercury concentration, and have been shown to exhibit a strong positive correlation with soil mercury fluxes measured in the field (Zehner and Gustin 2002). These estimates are the result of significant developments over the last decade in several areas. These include: automated analysis of field data; design and operation of flux chamber enclosures; and improvements in tower-based micrometeorological gradient methods that measure gas-phase mercury fluxes directly over waters, soils, and vegetation (e.g. Meyers et al. 1996, Lindberg et al. 1995, Poissant and Casimir 1998, Rasmussen et al. 1998; Gustin et al. 1999, 2000, 2001; Wallschlager et al. 1999; Coolbaugh et al. 2002; Engle and Gustin 2002; Zehner and Gustin 2002; Environment Canada 2002). Numerous groups have now applied these methods around the world, and the database on mercury fluxes has expanded significantly (Lindberg et al. 2000).

An important milestone was reached in 1997 when scientists from several countries collaborated in an EPRI-sponsored field study that compared mercury flux measurements using seven field flux chamber designs and four micrometeorological approaches at the Steamboat Springs Geothermal Area near Reno, Nevada (Gustin et al. 1999). This study assessed and quantified for the first time important factors governing hourly and daily mercury fluxes from a diffuse mercury-enriched, desert landscape (Lindberg et al. 1999; Poissant et al. 1999; Wallschlager et al. 1999), developed new theories of mercury vapor emission from soils (Zhang and Lindberg 1999), and led to important improvements in flux measurement methods (Zhang et al. 2002) (Lindberg et al. 2000).

Recent studies have demonstrated a positive relationship between mercury flux from soil surfaces and substrate mercury concentration, particularly in mercury-enriched areas, as shown in Figure 1-2. (Gustin 2003, Rasmussen et al. 1998; Gustin et al. 1999; Zehner and Gustin 2000, 2002; Engle et al. 2001; Coolbaugh et al. 2002; Environment Canada 2002). Tables 1-1 and 1-4 summarize these data; Table 1-4 provides a ranked summary of data for mercury-enriched sites in Nevada and California, and Table 1-5 provides the ranking for similar sites in Canada, Alaska, Spain, and Michigan.

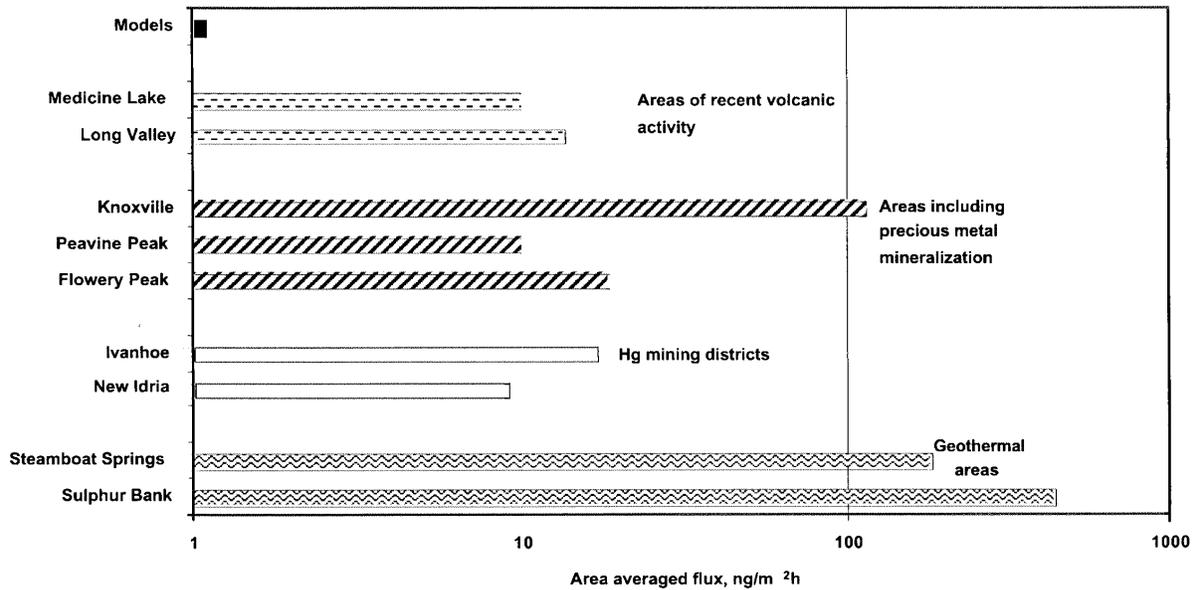


Figure 1-2
Area Average Mercury Emissions (ng/m²-h) Estimated for Each Study Area (Gustin 2003)

Mercury concentration in soil substrate is a dominant factor governing emissions and may be used to predict emissions from regions of mercury enrichment (Gustin et al. 2000). Naturally mercury-enriched soils (greater than 0.1 ppm) are typically contained in major mercuriferous belts located around the earth and are associated with plate tectonic boundaries, recent volcanism, precious and base metal mineralization, high crustal heat flow, and organics-rich sedimentary rocks. These natural sources of mercury are long lived (>10⁴ years) and primarily emit gaseous elemental mercury (Gustin et al. 2001).

Mercury emissions from enriched soils using field-based analytical methods have been measured and result in emission factors significantly higher than those previously used to represent emissions from mercury-rich mineral belts. In order to represent large-scale average emissions from these mercuriferous zones, a flux of 1.5 ng/m²-h had been widely used (e.g. Lindqvist et al. 1991; Mason et al. 1994).

Before the use of field-based analytical methods, there were no published studies that quantified mercury emission from naturally enriched areas (Engle et al. 2001). Emission factors had been derived from the difference between global anthropogenic emissions and deposition (Nriagu and Pacyna, 1988; Nriagu, 1989, Lindqvist et al. 1991; Mason et al. 1994), neither of which were well-constrained (Porcella et al. 1995; Pai et al. 1998, Gustin et al. 2001).

Table 1-4
Ranked Summary of Scaled Mercury Emissions from Natural Source Areas (mercury-enriched geology) (after Gustin 2003)

Areas	Area Average Flux (ng/m²-h)	Annual Flux (kg/yr)	Total Area (km²)	Reference
Sulphur Bank, CA (surficial geothermal activity; prior mercury mining site)	436.0	5.5	1.4	Gustin et al. (2002a)
Steamboat Springs, NV (surficial geothermal activity)	181.0	12.5	8.0	Coolbaugh et al. (2002)
Knoxville, CA (precious and base metal mineralization)	114.0	37.6	37.6	Gustin et al. (2002b)
Flowery Peak, NV (precious and base metal mineralization)	18.5	41.0	251.0	Engle and Gustin (2002)
Ivanhoe, NV (inactive mercury mining district)	17.1	87.0	586.0	Engle et al. (2001)
Long Valley, CA (calderas with recent volcanic activity)	13.6	110.0	945.0	Engle and Gustin (2002)
Peavine Peak, NV (precious and base metal mineralization)	10.0	10.0	108.0	Engle and Gustin (2002)
New Idria, CA (inactive mercury mining district)	9.2	18.0	229.0	Coolbaugh et al. (2002)
Medicine Lake, CA (calderas with recent volcanic activity)	1.2	2.4	242.0	Coolbaugh et al. (2002)
Models	1.1			Lindqvist et al. (1991)

Table 1-5
Mercury Concentrations Observed in Substrate and Estimated Flux in Recent Literature

Literature	Area	Hg Concentrations (ng/g) (average or range)	Total Area (km ²)	Observed Flux (ng/m ² -h) (average or range)	Annual Flux (kg/yr)
Rasmussen et al. 1998	Clyde Forks sulphide anomaly, Ontario, Canada	125,000 ^c	NA	1,928	NA
	Clyde Forks background site, Ontario, Canada	167 ^c	NA	23	NA
	Thunder Bay black shale, Ontario, Canada	845 ^d	>= 295	35	NA
Ferrara et al. 1998	Almaden Hg Mining District, Spain ^e	0.6 – 840 µg m ⁻² d w ⁻¹	4	100 – 400,000	5,256 – 10,512
Environment Canada 2002 (Canadian sites)	Earn and Road River black shale sequences, Yukon Territory	18 -340 ^f	1,479	7.4 –9.2 ^g	70-84 ^h
	Natural soils Kejimikujik National Park, Atlantic region	100 - 330	NA	-0.4 – 2.2 ^j	NA
	Impacted soils ^k , Kejimikujik National Park, Atlantic region	700 - 5400	NA	0 – 237 ^j	NA
Zhang et al. 2001	Tahquamenon River watershed, Upper Peninsula, Michigan ^l	4 - <100	2,124	1.4 +/- 0.3 to 7.6 +/- 1.7	NA

Table 1-5 (Continued)
Mercury Concentrations Observed in Substrate and Estimated Flux in Recent Literature

Notes:

NA Not available

- ^a ~89% of Hg released from district is from naturally enriched non-point sources and ~11% is emitted from areas of anthropogenic disturbance where mercury was mined
- ^b Fluxes during 6 months of the year of snow cover are assumed to be zero
- ^c Average total Hg concentration in B soil horizon.
- ^d Average total Hg concentration
- ^e Includes mining and refining complex plus village
- ^f Includes measurements of Hg concentration in rock and fine substrate materials
- ^g Average emission rates measured using micrometeorological and flux chamber methods, respectively
- ^h Summertime flux estimates for regional extrapolation based on in situ measurements in combination with detailed spatial analysis
- ⁱ Includes forest, glacial till, and granite/till soils
- ^j 24-hour mean Hg flux
- ^k Includes disturbed soil and mine tailings
- ^l Includes shaded forest and open field sites

Tables 1-4 and 1-5 present results of several studies performed in the U.S., Canada, and Spain. For each study area, the substrate mercury concentration, study area size, mercury flux, and mercury loading rate are shown. Remarkably, the mercury fluxes presented in these two tables are 1 to 5 orders of magnitude greater than the value (1.5 ng/m²-h) historically applied to mercuriferous zone fluxes (Gustin et al. 2002a; Gustin et al. 2002b; Engle et al. 2001; Engle and Gustin 2002, Coolbaugh et al. 2002; Ferrara et al. 1998; Rasmussen et al. 1998; Zhang et al. 2001). Several of the studies presented in Tables 1-4 and 1-5 used methods to “scale up” individual mercury flux rates to regional-based flux and loading rates. A direct comparison of emissions from point and non-point sources is difficult unless individual flux measurements from non-point sources are scaled up to provide emissions for areas. This is done by multiplying fluxes by the appropriate surface area for the time period chosen.

When scaling over surface area, heterogeneities in flux caused by geology, vegetative cover, and anthropogenic disturbances must be considered. When scaling over time, adjustments must be made for 24-hour cyclic variations in flux caused by environmental factors as sunlight intensity and temperature. Seasonal weather changes must be accounted for as well (Coolbaugh et al. 2002).

Only a few scaled estimates of diffuse or non-point source mercury emissions have been reported in the literature (Ferrara et al. 1998; Gustin et al. 2000; Engle et al. 2001; Engle and Gustin 2002, Coolbaugh et al. 2002; Zehner and Gustin 2002). With the exception of Ferrara et al. (1998) who investigated mercury emissions from the Almaden Mercury Mining District in Spain, these studies investigated mercury emissions from mercury-enriched soils in Nevada and California associated with the global mercury belt that runs along the western continental U.S.

Pertinent results of several recent scaling studies are presented here. These results suggest that non-point background sources may be significant contributors to atmospheric mercury since more than 2,000 well-defined areas of natural occurrences of mercury enriched geology are reported in the western U.S. alone (Gustin et al. 2000). Zehner and Gustin (2002) scaled up emissions from measurements within Nevada to the entire state and estimated that 10.4 Mg/yr of mercury emissions are released from natural substrate in Nevada alone. A recent report reviewed past measurements from nine study areas located in both Nevada and California and that lie within a belt of geologic mercury enrichment (Gustin 2003). *In situ* measurements of elemental mercury emissions were derived using field flux chambers and micrometeorological methods. Data for reactive gaseous mercury (RGM) concentrations in air were available for two sites.

Table 1-4 provides a ranked summary of these scaled emissions from natural source areas. Coolbaugh et al. (2000) calculated area-averaged bare soil mercury emissions for three naturally enriched areas: Steamboat Springs geothermal area, New Idria mercury mining district, and the Medicine Lake volcano. Annual emissions from bare ground at these three sites totaled ~34 kg. In general, the calculated average fluxes for the two geothermal areas were greater than for the other study areas (Figure 1-2) largely due to the high heat flux of the area (to geothermal activity), and to high substrate mercury concentrations, respectively. Similar to the geothermal areas, areas of mining disturbance with relatively high concentrations of mercury have significantly greater fluxes than surrounding areas with low mercury enrichment.

However, the small areas of mining disturbance contribute significantly less mercury annually to the atmosphere than the large undisturbed areas with low to background concentrations of mercury surrounding them. Thus, in scaling emissions from geologic sources it is important to factor in the low level emissions from large areas of weak hydrothermal alteration and substrate with background mercury concentration surrounding the area of high natural enrichment.

If too small an area is applied to the averaging, the value obtained may be too high or too low to be representative of the area. As the scale gets larger, a value representative of a regional average flux will eventually be obtained. Studies of large areas need to address the smaller anomalies of mercuriferous geology (e.g., mining districts) within. Thus, in scaling mercury emissions, the size of the study area should be carefully chosen to produce an estimate that is representative.

Area emissions based on these sites of mercuriferous geology were estimated to be about 3 times as high as the value for such areas currently used in global models. Natural-source emissions from the State of Nevada are approximately equal to the current anthropogenic emission estimate for the state, which is primarily due to gold ore processing and coal combustion.

Since natural source emissions of mercury appear to be greater than previously realized, discrepancies in the global cycling of mercury need to be resolved. Potential issues with the cycle may be manifested in several ways: some significant sinks may be overlooked in global mercury models; the atmospheric residence time of Hg(0) may be shorter than previously realized; or the total atmospheric burden of mercury may be mischaracterized due to a vertical structure that is not well-mixed vertically. Since these values are intended to represent emissions from substrate with background mercury concentrations and they exceed the value used for mercuriferous belts in global models, researchers may need to reassess the role of soils as sinks and sources for atmospheric mercury. The studies presented here are specific to the global mercury belt situated along the western continental U.S. Regions of mercury-enriched soil

substrate are spread across the globe. Scaling studies similar to those presented are needed from other mercury-enriched regions in the world. Results of such studies will aid in understanding the magnitude of emissions from non-point sources relative to anthropogenic sources.

Volcanoes, fumaroles, and related sources have long been recognized as a source of atmospheric mercury. Estimates of worldwide volcanic mercury fluxes, however, have differed significantly. Recent estimates have ranged from 0.6-1.3 T/yr (Ferrara et al. 2000) to 20-90 T/yr (Fitzgerald 1996). Global mercury emission estimates from volcanoes have historically been calculated by computing a ratio of Hg/SO₂ emissions from the few eruptions where both are measured and applying it to SO₂ volcanic emissions, which are better constrained. Assuming these calculation methods are valid, global mercury emissions from volcanoes may represent only a small fraction of the annual natural mercury emission to the atmosphere (Ferrara et al. 2000). However, taking into account a large variability of data available in literature on mercury fluxes from volcanoes, further measurements are necessary in order to better characterize the global mercury output from volcanogenic origin (Ferrara et al. 2000). A recent estimate by Pyle and Mather (2003) re-evaluated the volcanic input to atmospheric mercury, and arrived at a long-term average input by volcanism of about 700 Mg/y.

1.5.2 Non-enriched background soils and substrate

While mercury-enriched soils appear to be a significant source of mercury to the atmosphere, mercury emissions from non-enriched background soils must not be overlooked. Our knowledge of mercury air/surface exchange at background soils still remains insufficient. Zhang et al. (2000) measured mercury air/surface exchanges over background soils of the Tahquamenon River watershed in the Michigan Upper Peninsula (see Table 1-5). Environmental factors affecting the exchange such as soil temperature, solar radiation, and precipitation were also investigated. Mercury fluxes observed were similar to those found at other similar background source sites (Poissant and Casimir 1998; Capri and Lindberg 1998; Lindberg et al. 1998). These results from non-enriched soils are very important in that they, too, dispute emission factors previously used (Lindqvist et al. 1991; Mason et al. 1994) to model global belts of mercury-enrichment and average continental sources as well as provide evidence that regional and global atmospheric budgets need to be reassessed.

1.5.3 Biomass Fires

To understand the release of mercury in the environment through vegetation and subsequent biomass fires, an understanding of the mechanism involved in the uptake of mercury is needed.

The interactions between mercury in soil, vegetation, and the atmosphere consist of a complicated set of fluxes, which are not yet well-defined quantitatively. Forests are sinks for mercury already present in the atmosphere, thus the wildfire “source” is part of the overall recycling of mercury originating from other sources. Gaseous elemental and divalent mercury as well as particulate mercury are deposited onto plant surfaces and can be assimilated into plant tissue, predominantly leaves, needles, and bark. Gaseous elemental mercury can move in and out of plants through stomata. Some of the mercury compounds accumulated on foliage are washed off when precipitation falls on foliage (throughfall), resulting in higher concentrations in

throughfall than in precipitation. In addition, mercury is accumulated in vegetation through upward transport of ionic mercury in xylem-sap from soil to foliage. However, under normal conditions the xylem contribution to mercury content in the green part of plants is minor relative to mercury from dry or wet deposition. The accumulation of mercury in plants is proportional to foliage during the growing season; after the growing season, mercury contained in foliage is deposited as litterfall to surface soil (St. Louis et al. 2001). Relatively few measurements have been made of mercury release in biomass burning, making it difficult to constrain estimates of the global contribution of biomass burning to the atmospheric mercury budget (Radke et al. 2002).

Recent research suggests that forest fires are a major source of mercury to the atmosphere. Yet to be determined, however, is whether such fires are a source of additional mercury that would otherwise not enter the atmosphere or simply an enhanced transfer mechanism for mercury to the atmosphere that would occur otherwise, but over a longer time period. In vegetation, mercury is predominantly contained in leaves and needles and its concentration increases with plant mass during the growing season (Salt et al. 1998) and is species-specific (Rea et al. 2000). Upon senescence, the leaves and needles falling to the ground generally appear to contain the highest mercury concentration found in plant material (Friedli et al. 2001). Measurements of the combustion of litter and green vegetation under controlled burn conditions found essentially complete release of mercury contained in fuel (Friedli et al. 2001, 2003). Mercury in these cases was emitted almost exclusively as elemental mercury (>95%) (see Table 1-6) Based on those results, it was suggested that fire-emitted mercury is an important and (to date) unrecognized source of atmospheric mercury (Friedli et al. 2001, 2003). Based on estimates of global mercury emissions from natural and all sources, estimates for mercury release from biomass fires bracketed the range of 3.5 to 17.5% of the natural emissions and 1.6 to 8.0% of all emissions globally (Friedli et al. 2001, 2003).

Table 1-6
Mercury Release Budgets from Laboratory and Airborne Experiments (Friedli et al. 2003)

Experiment	Emission Factor (g Hg/kg fuel)	Extrapolated Release of Mercury			
		From Temperature/ Boreal (t/yr ^b)	From All Biomass		
			(t/yr ^b)	% of Natural Releases ^a	% of Total Releases ^a
Lab (Fuel-Ash)					
Low: green conifers	14 x 10 ⁻⁶	7.4	104	3.5	1.6
High: deciduous litter	71 x 10 ⁻⁶	37.7	526	16.5	8.0
Lab (Plume)					
Montana Ponderosa Pine litter	18.2 x 10 ⁻⁶	9.6	133	4.4	2.03
Wildfire (Plume)					
Black spruce	112 x 10 ⁻⁶	59.5	853	28.5	13.0

An investigation of the burn behavior and mercury emission characteristics of various biomass fuels collected from different geographic regions of the U.S. was also undertaken (Radke et al. 2002). The biomass fuels from coniferous and deciduous forests (leaves, needles, branches) were combusted in the laboratory, and the resulting data compared with measurements made on a wildfire in a temperate forest in July 2000 (near Hearst, Ontario). The combined data were then used to estimate the contribution of wildfires and other biomass fires to the atmospheric burden of mercury.

Mercury contained in vegetation (live, dead, coniferous, and deciduous) was essentially completely released in laboratory burns in the form of gaseous elemental mercury and mercury bound to particulate matter. Replicate burns of dry Ponderosa needles indicated a linear relationship between emitted mercury and fuel mass loss. Regionally collected fuels showed the same behavior as the replicate burns, i.e., essentially total removal of mercury. Mercury released from the fuel could be accounted for as gaseous and particulate mercury in the smoke. The mercury content of regionally collected fuels varied between 14 and 70 ng/g on a dry mass (dm) basis (Radke et al. 2002). Measurements of both gaseous and particulate mercury in the wildfire smoke plume supported the conclusion that most of the mercury was emitted in the gaseous elemental form.

During trial burns in the laboratory, the difference between emission factors for the high and low mercury content in fuel samples is believed to be the contribution of mercury released from fire-heated soil during wildfires. Estimates for mercury emissions from temperate/boreal and from all biomass burning as well as their relationship to levels of published natural and total mercury releases are shown in Table 1-6. Estimates of mercury releases from wildfires must be refined and included in future regional and global models.

The mercury emissions from biomass burned in laboratory experiments and in a wildfire were found to be in qualitative agreement. Results suggest that the higher emission factor observed for the wildfire is the result of additional mercury release from compacted organic matter and soil caused by heating from the fire. The results of this study support the conclusion that essentially all mercury in plant material is released in biomass fires in the form of gaseous elemental mercury and mercury contained in particles; gaseous reactive mercury was not detected above background values. The fraction of total mercury that is particulate-bound is fuel-dependent, with higher results for mostly green vegetation at about 13 percent and about 1 percent for dry fuel. The primary uncertainty remains in the emission of mercury from soil during wildfires.

The mercury content of vegetation was found to be highly variable. Variables include the local dry/wet deposition rate of mercury compounds, species-specific absorption of mercury compounds on plant surfaces, and the age of the plants. These first biomass budget estimates of mercury were unexpectedly high. Biomass fires as a mercury source may be large enough to require recalculation of the average mercury atmospheric lifetime. The incorporation of terms for biomass sources of mercury will require collection of additional data, particularly from large wildfires on a continental and global scale, and additional study to provide an understanding of the contribution from fire-heated soils.

Forests are sinks for atmospheric mercury originating from anthropogenic and natural sources and wildfires provide a mechanism for redistribution of mercury back into the atmosphere. Some wildfires appear to be large enough to alter atmospheric levels of mercury extending to the upper

troposphere. Further measurements from wildfires are needed to verify and quantify balances as inputs to regional and global models.

1.5.4 Re-emissions

Mercury that has been deposited can be re-emitted to the atmosphere only in its elemental form, since other forms have to low a vapor pressure to transfer from the surface. The term re-emission is sometimes applied to anthropogenic mercury only; however, since the origin of deposited mercury is unknown, we apply the term re-emission to both natural and anthropogenic mercury. There is considerable evidence that Hg, once deposited, has the capability to be re-emitted from environmental surfaces (e.g. Mason et al. 1994; Kim et al. 1995), and that transpiration-like processes of green plants significantly enhance re-emission (Lindberg et al. 1998). Re-emission of mercury from soils is believed to occur primarily from the uppermost few centimeters (Carpi and Lindberg 1997).

The magnitude of the natural emissions and re-emissions is poorly documented (Fitzgerald, 1986; Pacyna, 1986; Nriagu, 1989; Lindberg et al., 1998; Ebinghaus et al., 1999; Nriagu, 1999). First, it is infeasible to distinguish between natural emissions and re-emissions, except in cases where there is a strong natural source signal (e.g., areas geologically enriched in mercury). Second, there are few measurements available to date, and current estimates are to a large extent extrapolated from a few data points and constrained by global mass balance estimates.

Only a small percentage of deposited mercury need be re-emitted to make a significant contribution to the atmospheric budget on regional and even global scales. Such flux estimates can vary widely and carry a large uncertainty because they represent large areas. The remaining question of mercury re-emissions relative to natural emissions is to what extent “natural” emissions include re-emitted mercury (Lindberg et al. 2000). Results reported by Hintelmann et al. (2002) suggest that newly deposited mercury is generally more available for re-emission than is the “old” native mercury stored on vegetation or the upper soil pool. Reactivity rapidly decreases as deposited mercury becomes bound to soil and plant organic matter over the course of time.

1.5.5 Environmental factors

Recent studies aimed at quantifying mercury emissions from mercury-enriched and non-enriched soils have also investigated the effect of environmental factors upon mercury emission rates. Factors that are known or appear to influence mercury emissions through vegetation include shading and foliar exchange (Zhang et al. 2001; Benesch et al. 2001; Environment Canada 2002); episodic events such as rainfall (Lindberg et al. 1999; Gustin et al. 1999; Engle et al. 2001) and forest fire (Friedli et al. 2001); solar radiation (Carpi and Lindberg 1997; Gustin et al. 1998a; Rasmussen et al. 1998; Engle and Gustin, 2002; Zehner and Gustin 2002; Environment Canada 2002); temperature (Lindberg et al. 1995; Gustin et al. 1997; 1998a,b; Zhang et al. 2000; Environment Canada 2002); soil gas concentrations (Ebinghaus et al. 2000); and humidity (Poissant et al., 1999). Experimental data have shown that emission of mercury from soil increases after precipitation has occurred (Gustin and Lindberg, 2000).

Mercury flux has been found to follow a diel pattern, (it is driven by light and temperature), that peaks midday, when sun intensity is greatest, Figure 1-4 (Engle et al. 2001; Environment Canada 2002). This diel pattern varies generally as the sine of the solar zenith angle (Zehner and Gustin 2002; Engle et al. 2001). When scaling over time, adjustments must be made for 24 hour cyclic variations in flux caused by environmental factors such as sunlight intensity and temperature. Incident solar radiation enhances mercury emissions from soils (Gustin et al., 2002). Seasonal weather changes must also be accounted for (Coolbaugh et al. 2002; Environment Canada 2002); however, no comprehensive information is currently available on the seasonality of mercury emissions. The relative importance of these various factors is not clearly understood. For naturally enriched areas, at least, substrate mercury concentration is a dominant parameter controlling flux (Rasmussen et al. 1998; Gustin et al. 2000; Engle and Gustin 2002).

1.6 Global cycling and sinks

Hg(II) has a much lower residence time in the atmosphere than Hg(0) because Hg(II) compounds are more reactive and more highly soluble in water (by roughly 6 orders of magnitude, for Hg(II) as HgCl₂), enhancing removal via precipitation. Over the open oceans, concentrations of Hg(0) increase from the southern hemisphere (about 1 ng/m³ at 60 degrees south) to the northern hemisphere (about 3 ng/m³ at 60 degrees north), reflecting larger sources of mercury in the northern hemisphere (Fitzgerald 1995, Lamborg et al. 1999). It should be noted that there are different underlying approaches to these estimates of atmospheric mercury and there can be differences in their context as well.

A major advance in the study of mercury cycling was the development of methodologies for determining the speciation of atmospheric mercury. The discovery of measurable levels of water-soluble mercury compounds (as reactive gaseous mercury, RGM) in both flue gas, and, more recently, ambient air has significant implications for modeling the fate of airborne mercury. Methods have been published and now are in routine use for measuring concentrations of divalent mercury at low concentrations in ambient air (Stratton and Lindberg 1995, Landis and Stevens 2000, Feng et al. 2000, Landis et al. 2002). Recent studies have demonstrated that RGM can represent a few percent of total airborne mercury in ambient air that is distant from local sources (concentrations 20-50 pg/m³), but can reach concentrations several hundred times as high (and up to about 10% of total mercury) near anthropogenic point sources that emit RGM as a primary form of mercury (Lindberg et al. 2000).

Recent studies support the conclusion that there has been a general increase in atmospheric mercury background levels due to anthropogenic emissions. Based upon data from the Greenland ice cap, Fitzgerald et al. (1998) conclude that despite uncertainties in current understanding, there is a broad and geologically consistent data base indicating that, over large regions of the globe, anthropogenic mercury emissions have increased relative to natural sources since the onset of the industrial period (taken as the early 19th century onward). Mercury levels in ice cores collected from the Upper Fremont Glacier in Wyoming, and analyzed for the deposition record of the past 270 years, suggested a ratio of about 20 between pre-industrial (pre-1840) deposition rates and a peak deposition (circa 1984) noted in the recent record. A decline in deposition was observed over the final 10 years of the ice record (Schuster et al. 2002, Krabbenhoft and Schuster 2002). This estimate for deposition rate ratios since pre-industrial times based on ice cores is up to 10 times as high as increases determined from sediment cores and precipitation. Historical

mercury emission events such as major volcanic eruptions, the California Gold Rush, and industrialization associated with the past century are demonstrated in the historical pattern of mercury deposition found in these glacial ice cores. This study by the U.S. Geological Survey found that during the past 270 years, volcanic events contributed 6 percent of total atmospheric mercury input with other natural background sources contributing 42 percent (Krabbenhoft and Schuster 2002). The percent of total mercury attributed to anthropogenic sources has increased from about 41 percent in the first 170 years (predominantly from the 19th century gold rush) to 70 percent during the last 100 years. Significant decreases in total mercury observed in the last 15-20 years of the ice-core record indicate reductions in deposition corresponding to the period since the mid-1950s when other cores (from bogs, lake sediments, etc.) also indicate drops in emissions. This recent period matches use records for mercury in industrial products and processes, indicating an 80% or more drop in such direct uses and their waste streams, partially atmospheric. Figure 1-3 provides an overview of the historic atmospheric mercury deposition pattern that the authors have indicated correspond to documented volcanic and anthropogenic events over the past 270 years (Krabbenhoft and Schuster 2002). The recent paper by Slemr et al. further documents an evident decline in global concentrations at mid-ocean locations. Lacerda (1997) estimated that unregulated gold mining in Brazil releases about 137 t/yr of Hg to the atmosphere. Ongoing studies are evaluating the occurrence, as well as the fate, and transport characteristics of mercury in the environment. Included in these studies is a look at differences in contributions of "old" mercury resulting from emissions over the past 100 years, as well as "new" mercury from current emissions. One of these projects is discussed later in Chapter 4 of this report, an internationally conducted effort known as METAALICUS (Mercury Experiment To Assess Atmospheric Loading In Canada and the United States), which is assessing the effects of intentional applications of experimental doses of mercury to a watershed in western Ontario, Canada.

The tropospheric chemistry of mercury has been much discussed in the last four or five years since the publication of the results of long-term measurements from the Arctic (Schroeder et al., 1998). Contemporaneously with tropospheric ozone depletion events, periodically after polar dawn, the concentration of Hg(0) diminished to as low as 10-20 percent of its typical value over a period of three or four days. Since then, this phenomenon has been confirmed by further measurements of the concentration of Hg(0) and also of gas phase oxidized mercury compounds (Lindberg *et al.*, 2002a) and mercury associated with particulate matter (Lu *et al.*, 2001), and mercury depletion has also been seen in Antarctica (Ebinghaus *et al.*, 2002). The results are consistent with gas phase oxidation of Hg(0), probably by halogen atoms or halogen-containing radicals (Boudries and Bottenheim, 2000), and subsequent condensation on to particulates or deposition to the snow pack.

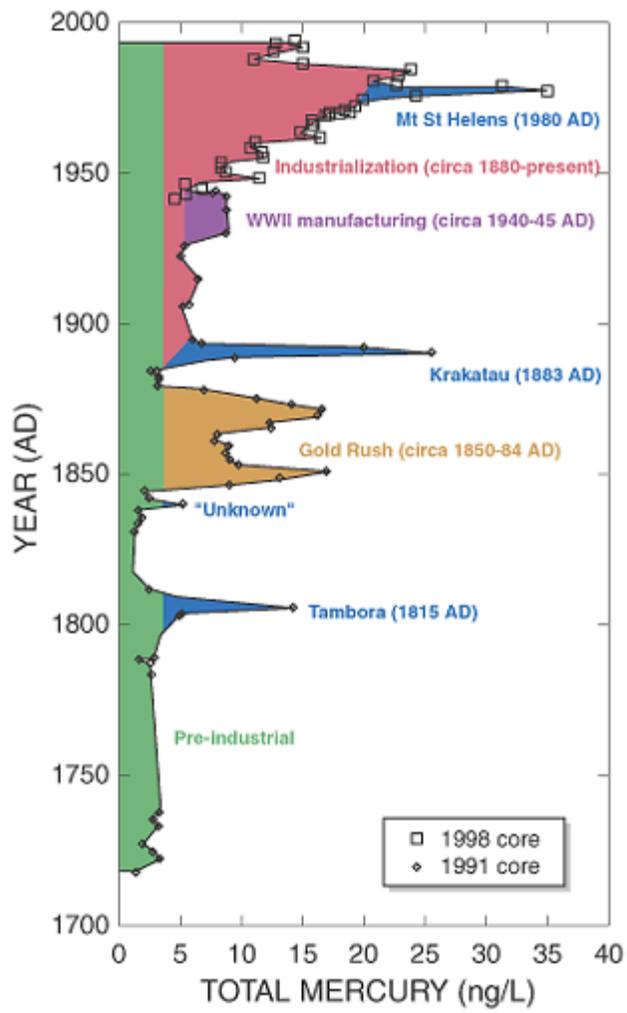


Figure 1-3
Historical Atmospheric Mercury Deposition Patterns from Glacial Ice Cores (from
Krabbenhoft and Schuster, 2002; Schuster, et al, 2002)

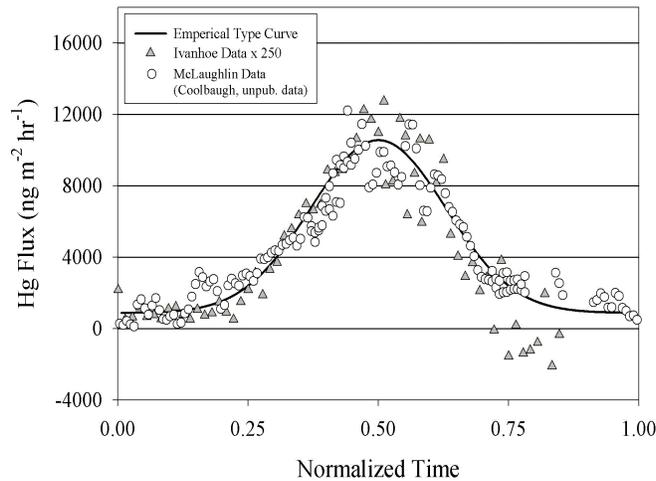


Figure 1-4
Diel mercury flux measurements from Ivanhoe, NV and McLaughlin, CA. Gaussian curve best fit is shown for all data. Despite more than two orders of magnitude difference between the data sets, these data fit the curve. (Engle et al. 2001)

1.7 Summary

- Although there is general scientific agreement that atmospheric mercury has many natural and anthropogenic sources, to date there has been no scientific consensus on the relative amount each category of emission source contributes to mercury deposition at each of local, regional, and global scales.
- For the overall global mercury balance to be credible, accurate measurement and speciation estimates of the evasion or flux from a number of surfaces (the marine boundary layer, soils, geological substrates, and forest fires) will continue to be needed to confirm recent findings.
- The understanding of the relative significance of local versus regional and global sources of mercury has allowed a more complete understanding of the global life cycle of mercury. There is currently a tentative consensus that the lifetime of atmospheric mercury is about one year, but recent findings on source strengths and possible removal mechanisms continue to support major uncertainties in that calculation.

- To account for the levels of natural source emissions being measured, reassessment should be made of the atmospheric residence time of mercury and the biogeochemical cycling of mercury. In order to balance the mercury biogeochemical cycle and determine impacts of atmospheric mercury on local, regional and global ecosystems, the emissions from background sources should be more completely quantitatively characterized on regional and global scales.
- In EPRI's most recent emissions inventory update, current global emissions of mercury amount to 6386 metric tons (T/y), accounting for recent mercury emissions reductions due to control requirements for municipal incinerators. Natural emissions were estimated to be 1064 T/y. Estimates were revised based on recent work that identified natural and other background sources as a larger contributor of mercury emissions than previously thought.
- Within North America, it is estimated that the United States emits 133 T/y of the 193 T/y total mercury (divalent plus gaseous elemental) mercury. The industrialized areas of southern Canada and northern Mexico contribute about 15 T/y and 34 T/y, respectively. Of the U.S. portion, electric utilities contribute about 42 T/y, or about 32% of the U.S. total.
- The global total of anthropogenic emissions is estimated currently at 2127 T/y. The U.S. contributes 6% of the mercury to the total global anthropogenic emissions, while U.S. coal utilities make up 2% of world anthropogenic emissions.
- In the last decade, anthropogenic emissions of mercury have decreased in North America and Europe. For emissions over the past ten years, trends analysis indicates that estimates of mercury emissions show increased emissions for India and China of about 27% and 55%, respectively.
- Mercury emissions from coal-fired power plants in the United States are better known than those of many other source categories because the EPA conducted a mercury Information Collection Request (ICR) in 1999-2000. This study analyzed the mercury content of the different types of coal burned at every U.S. coal-fired power plant, and conducted stack sampling at over 80 coal-fired power plants. The results indicated that the actual amount of mercury emitted from the stacks is dependent on the coal type and the SO₂ and particulate control system installed.
- Mercury emissions of other source categories (particularly those with diffuse emissions, e.g., chloralkali plants, landfills) have typically not been as well characterized. Some key uncertainties are mercury releases from chloralkali plants, several of which use mercury as electrode material (in the production of industrial chlorine gas and caustics). Clarification of the remaining uncertainties would occur with additional efforts to characterize global anthropogenic mercury emissions in selected regions and for several industrial source categories.
- Mercury releases from products via normal use, spills, breakage, and scrap metal processing and disposal are significant sources that may be under-estimated in some release inventories. A more complete assessment and characterization of these source category contributions would better explain local and regional sources on local levels of mercury concentrations, particularly in urban settings.
- In the past five years significant progress has been made in three important areas of research: methods development for the measurement of mercury emissions, definition of the factors

most important in governing mercury emissions, and scaling up emissions from natural source areas. Advances from all three of these areas of research facilitated important advances to refine the understanding of the contribution of sources of mercury to the global budget.

- Field measurements of mercury fluxes from naturally mercury-enriched areas suggest that regional scale emissions are orders of magnitude higher than previously thought. To fully assess the contribution of mercury to the atmosphere from natural sources, emissions from a variety of geologic terrain should be measured to verify recent measurements.
- Emissions data need to be developed for source categories of mercury enriched areas which are not well characterized including black shales and metalliferous belts not within the “defined” global mercury belts.
- Regional natural emissions need to be scaled to larger areas for use in regional and global emission models. With a shift of scaling activities into different climatic regimes, model parameters will need to be developed for soil moisture, vegetation cover, relative humidity, and soil types not typical of arid environments. In addition, the seasonality of natural and background mercury emissions in different climatic regimes needs to be established.
- To enhance our current understanding of mercury emissions from volcanoes and forest fires, a wider representation of mercury emissions from these sources will require additional field studies aimed at quantifying emissions from vegetation as well as from fire-heated soils and identifying important governing factors.
- Re-emissions are still poorly understood and techniques need to be developed for distinguishing between primary emissions and re-emissions of earlier deposited mercury from natural surfaces.
- Research studies accomplished in the last seven years provided the basis for a developing consensus that the level of significance of natural sources to global cycling of mercury in the environment has increased due to sources disturbed by human activity. This research has contributed to a better understanding of the relative contribution of natural mercury sources including mercuriferous geology, forest fires, and volcanic eruptions, as well as legacy sources.
- Current results suggest that newly deposited mercury is generally more available for re-emission than is the old native mercury stored on vegetation or the upper soil pool. Reactivity rapidly decreases as deposited mercury become bound to soil and plant organic matter over the course of time. Additional study is needed to confirm this finding and to further characterize the proportion of newly deposited mercury versus old native mercury in re-emissions.
- Gas phase oxidation and subsequent condensation may play an important role in mercury deposition in Arctic ecosystems. Additional field measurements and analyses could further characterize the kinetics and dynamics of this process.

References

- Benesch, J.A., M.S. Gustin, D.E. Schorran, J. Coleman, D.A. Johnson, and S.E. Lindberg, 2001. Determining the role of plants in the biogeochemical cycling of mercury on an ecosystem level. Presented at the 6th International Conference on Mercury as a Global Pollutant, Minamata, Japan; AT-39.
- Carpi, A. and S.E. Lindberg, 1998. Application of a TeflonTM dynamic flux chamber for quantifying soil mercury flux: tests and results over background soil. *Atmos. Environ.* 32: 873-882.
- Chu, P. and D.B. Porcella, 1995. Mercury stack emissions from U.S. utility power plants. *Water, Air, and Soil Pollut.* 80: 135-144.
- Coolbaugh, M.F., M.S. Gustin, and J.J. Rytuba, 2002. Annual emissions of mercury to the atmosphere from natural sources in Nevada and California. *Environ. Geol.* 42: 338-349.
- Ebinghaus, R., H. Kock, and M. Hempel, 2000. Determination of mercury in ambient air using highly time resolved online methods. *Gefahrstoffe-Reinhaltung der Luft.* 60, 5, 205-211.
- Engle, M.A., M.S. Gustin, and H. Zhang, 2001. Quantifying natural source mercury emissions from the Ivanhoe Mining District, north central Nevada, USA. *Atmos. Environ.* 35: 3987-3997.
- Engle, M.A. and M.S. Gustin, 2002. Scaling of atmospheric mercury emissions from three naturally enriched areas: Flowery Peak, Nevada; Peavine Peak, Nevada; and Long Valley Caldera, California. *Sci. Tot. Environ.* 290: 91-104.
- Environment Canada, 2002. Estimation of Mercury Emissions from Natural Sources/Processes in Canada. *Toxic Substances Research Initiative Project #105*. Environment Canada, Toronto, Ontario. Final Report. December.
- EPRI, 2000. Assessment of Mercury Emissions, Transport, Fate and Cycling. TR-1000522.
- EPRI 1996. Mercury in the Environment, A Research Update. Palo Alto, CA. TR-107695.
- Ferrara, R. B.E. Maserti, M. Andersson, H. Edner, P. Ragnarson, P. Svanberg, and A. Hernandez, 1998. Atmospheric mercury concentrations and fluxes in the Almaden district (Spain). *Atmos. Environ.* 32: 3897-3904.
- Ferrara, R. B. Mazzolai, E. Lanzillotta, E. Nucaro, and N. Pirrone, 2000. Volcanoes as emission sources of atmospheric mercury in the Mediterranean basin. *Sci. Tot. Environ.* 259: 115-121.
- Fitzgerald, W.F., 1986. Cycling of mercury between the atmosphere and oceans. In: P. Buat-Ménard (ed), *The Role of Air-Sea Exchange in Geochemical Cycling*, D. Reidel Publishing Co., pp. 363-408.

- Fitzgerald, W.F., 1996. Mercury emission from volcanoes. *4th International Conference on Mercury as a Global Pollutant*, August 4-8, 1996, Hamburg, Germany.
- Friedli, H.R., L.F. Radke, and J.Y. Lu, 2001. Mercury in Smoke from Biomass Fires. *Geophys. Res. Lett.* 28: 3223-3226.
- Gustin, M.S., G. Taylor, and R. Maxey, 1997. Effect of temperature and air movement on the flux of elemental mercury from substrate to the atmosphere. *J. Geophys. Res.* 102: 3891-3898.
- Gustin, M.S., R.A. Maxey, P. Rasmussen, and H. Beister, 1998a. Mechanisms influencing the volatile loss of mercury from soil. *Symposium Volume Air and Waste Management Association on the Measurement of Air Toxics and Related Air Pollutants*. September 1998, Cary, N.C, USA: 224-235.
- Gustin, M.S., S. Lindberg, F. Marsik, A. Casimir, R. Ebinghaus, G. Edwards, C. Hubble-Fitzgerald, R. Kemp, H. Kock, T. Leonard, J. London, M. Majewski, C. Montecinos, J. Owens, M. Pilote, L. Poissant, P. Rasmussen, F. Schaedlich, D. Schneeberger, W. Schroeder, J. Sommar, R. Turner, A. Vette, D. Wallschlaeger, Z. Xiao, and H. Zhang, 1999. Nevada STORMS project: measurement of mercury emissions from naturally enriched sources. *J. Geophys. Res.* 104: 21831-21844.
- Gustin, M.S., M Coolbaugh, and M. Engle, 2000. Annual emissions of mercury to the atmosphere from natural sources in Nevada and California. *25th International Conference on Heavy Metals in the Environment*, Ann Arbor, MI.
- Gustin, M.S., S.E. Lindberg, K. Austin, M. Coolbaugh, A. Vette, and H. Zhang, 2001. Assessing the contribution of natural sources to regional atmospheric mercury budgets. *Sci. Tot. Environ.* 259: 61-71.
- Gustin, M.S. and S.E. Lindberg, 2000. Assessing the contribution of natural sources to the global mercury cycle: The importance of intercomparing dynamic flux measurements, *Fresenius J. Anal. Chem.*, **366**, 417-422.
- Gustin, M.S., H. Biester and C.S. Kim, 2002. Investigation of the light-enhanced emission of mercury from naturally enriched substrates, *Atmos. Environ.*, **36**, 3241-3254.
- Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott, and V.L. St. Louis, 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. *Environ. Sci. Technol.* 36: 5034-5040.
- Krabbenhoft, D.P. and Schuster, P.F., 2002 , Glacial Ice Cores Reveal A Record of Natural and Anthropogenic Atmospheric Mercury Deposition for the Last 270 Years: 2002 U.S. Geological Survey Fact Sheet FS-051-02.

Kim, K-H., S.E. Lindberg, and T.P. Meyers, 1995. Micrometeorological measurements of mercury vapor fluxes over background forest soils in Eastern Tennessee. *Atmos. Environ.* 29: 267-282.

Lindberg, S.E., K-H. Kim, T.P. Meyers, and J.G. Owens, 1995. Micrometeorological Gradient Approach for Quantifying Air/Surface Exchange of Mercury Vapor: Tests Over Contaminated Soils. *Environ. Sci. Technol.* 29: 126-135.

Lindberg, S.E., 1996. in Baeyens, W., R. Ebinghaus, and O. Vasiliev, (eds), *Global and Regional Mercury Cycles: Sources, Fluxes, and Mass Balances*, Elsevier Amsterdam, The Netherlands, pp. 359-380.

Lindberg, S.E., P.J. Hanson, T.P. Meyers, and K-Y Kim, 1998. Air/surface exchange of mercury vapor over forests--the need for a reassessment of continental biogenic emissions *Atmos. Environ.* 32: 895-908.

Lindberg, S.E., H. Zhang, M. Gustin, A. Vette, J. Owens, F. Marsik, A. Casimir, R. Ebinghaus, G. Edwards, C. Fitzgerald, J. Kemp, H.H. Kock, J. London, M. Majewski, L. Poissant, M. Pilote, P. Rasmussen, F. Schaedlich, D. Schneeberger, J. Sommar, R. Turner, D. Wallschlager, and Z. Xiao, 1999. Increases in mercury emissions from desert soils in response to rainfall and irrigation. *J. Geophys. Res.* 104: 21879-21888.

Lindberg, S.E., M. Gustin, H. Zhang, and S. Brooks, 2000. Mercury Emission and Re-emission from Diffuse Area Sources: The Dilemma of Small Emissions from Large Surfaces, The "Inert" Nature of Elemental Mercury Vapor, and Missing Sinks in the Global Mercury Cycle. 2000 EPA Conference on Hg, San Francisco, November 28-30.

Lindqvist, O., K. Johansson, A. Astrup, A. Anderson, L. Bringmark, G. Hovsenius, A. Iverfeldt, M. Meili, and B. Timm, 1991. Mercury in the Swedish environment. *Water Air Soil Pollut.* 55: 1-261.

Mason, R.P., W.F. Fitzgerald, and F.M. Morel, 1994. The biogeochemical cycling of elemental mercury: anthropogenic influences. *Geochimica et Cosmochimica Acta* 58: 3191-3198.

Meyers, T.P., M.E. Hall, and S.E. Lindberg, 1996. Use of the modified Bowen-ratio technique to measure fluxes of trace gases. *Atmos. Environ.* 30: 3321-3329.

Nriagu, J., 1989. A global assessment of natural sources of atmospheric trace metals. *Nature* 338: 4749.

Nriagu, J. and J. Pacyna, 1988. Quantitative assessment of worldwide contamination of air water and soil by trace metals. *Nature* 333: 134-139.

Nriagu, J.O., 1999. Global Climate Change and Cycling of Mercury in North America: a Background Report to the Commission for Environmental Cooperation. University of Michigan, Ann Arbor, MI, USA.

- Pacyna, J.M., 1986. Atmospheric trace elements from natural and anthropogenic sources, *Advances in Environmental Science and Technology*, **17**, 33-52.
- Pacyna, E.G., J.M. Pacyna and N. Pirrone, 2001. European emissions of atmospheric mercury from anthropogenic sources in 1995, *Atmos. Environ.*, **35**, 2987-2996
- Pai, P., S. Heisler, and A. Joshi, 1998. An emissions inventory for regional atmospheric modeling of mercury. *Water Air Soil Pollut.* 101: 298-308.
- Poissant, L. and A. Casimir, 1998. Water-air and soil-air exchange rate of total gaseous mercury measured at background sites. *Atmos. Environ.* 32: 883-893.
- Poissant, L, M. Pilote, and A. Casimir, 1999. Mercury flux measurements in a naturally enriched area: Correlation with environmental conditions during the Nevada Study and Tests of the Release of Mercury from Soils (STORMS). *J. Geophys. Res.* 104: 21845-21857.
- Porcella, D. M. Chu, and M.A. Allan, 1995. Inventory of North American mercury emissions to the atmosphere. In: Baeyens, W., R. Ebinghaus, and O. Vasiliev, editors. *Global and regional mercury cycles: sources fluxes and mass balances*. NATO ASI-Series, 21. Dordrecht, Netherlands. Kluwer Academic Publishers: 359-380.
- Pyle, D.M., and T.A. Mather, 2003. The importance of volcanic emissions for the global atmospheric mercury cycle. *Atmos. Environ.* 37(2003) 5115–5124
- Rasmussen, P.E., G.C. Edwards, J.R. Kemp, C.R. Fitzgerald-Hubble, and W.H. Schroeder, 1998. Towards an improved natural sources inventory for mercury. In *Proceedings on the Metals in the Environment: An International Symposium*: Skeaff, J. Ed. Pp. 74-82.
- Rea, A.W., S.E. Lindberg, and G.J. Keeler, 2000. Assessment of dry deposition and foliar leaching of mercury and selected trace elements based on washed foliar and surrogate surfaces. *Environ. Sci. Technol.* 34: 2418-2425.
- Salt, D.E., R.D. Smith, and I. Raskin, 1998. Phytoremediation, *Ann. Rev. Plant Physiol. Plant Mol. Biol.* 49: 643-668.
- Schroeder, W.H. and J. Munthe, 1998. Atmospheric mercury—an overview. *Atmos. Environ.* 32(5): 809-822.
- Schuster, P.F., Krabbenhoft, D.P., Naftz, D.L., Cecil, L.D., Olson, M.L., Dewild, J.F., Susong, D.D., and Green, J.R., 2002, Atmospheric mercury deposition during the last 270 years—A glacial ice core of natural and anthropogenic sources. *Environ. Sci. Technol.* 36: 2303-2310.
- Seigneur, C., P. Karamchandani, K. Lohman, K. Vijayaraghavan and R.-L. Shia, 2001. Multiscale modeling of the atmospheric fate and transport of mercury, *J. Geophys. Res.*, **106**, 27795-27809.

St. Louis V. L., J. W. M. Rudd, C. A. Kelly, B. D. Hall, K. R. Rolffhus, K. J. Scott, S. E. Lindberg, and W. Dong. 2001. Importance of the Forest Canopy to Fluxes of Methyl Mercury and Total Mercury to Boreal Ecosystems. *Environ. Sci. Technol.* **35**, 3089-3098.

UNEP Chemicals (United Nations Environment Programme) 2002. Global Mercury Assessment. Geneva, Switzerland.

U.S. Agency for Toxic Substances Disease Registry (ATSDR) 1999. Public Health Statement for Mercury. CAS# 7439-97-6. March 1999

U.S. EPA 1998. White Paper on Mercury.

Wallschlager, D. R. Turner, J. London, R. Ebinghaus, H. Kock, J. Sommar, and Z. Xiao, 1999. Factors affecting the measurement of mercury emissions from soils with flux chambers. *J. Geophys. Res.* 104: 21859-21871.

Weidou, N. and N.D. Sze, 1998. Energy supply and development in China, Chapter 2, 67-117, in *Energizing China*, M.P. McElroy, C.P. Nieslen and P. Lydon, eds. Harvard University Press, Cambridge, USA.

Zehner, R.E. and M.S. Gustin, 2000. Estimation of Mercury Vapor Flux from Natural Geologic Sources in Nevada. *Assessing and Managing Mercury from Historic and Current Mining Activities*; Symposium Volume, San Francisco. Pp 135-140

Zehner, R.E. and M.S. Gustin, 2002. Estimation of Mercury Vapor Flux from Natural Substrate in Nevada. *Environ. Sci. Technol.* 36: 4,039-4,045.

Zhang, H. S.E. Lindberg, M.O. Barnette, A.F. Vette, and M.S. Gustin, 2001a. Simulation of gaseous mercury emissions from soils measured with dynamic flux chambers using a two-resistance exchange interface model. *Atmos. Environ.* 36: 835-846.

Zhang, H. S.E. Lindberg, F.J. Marsik, and G.J. Keeler, 2001b. Mercury air/surface exchange kinetics of background soils of the Tahquamenon River watershed in the Michigan Upper Peninsula. *Water, Air, and Soil Pollut.* 126: 151-169.

2

MERCURY EMISSIONS FROM COAL-FIRED POWER PLANTS

2.1 Introduction

In the previous chapter, an overview of anthropogenic and natural sources of mercury to the atmosphere at the global, regional and local scales was provided. This chapter focuses upon mercury from one source category – fossil-fuel fired electric generation by utilities. Power plant emissions account for about one-third of the mercury emitted to the air from all industrial sources in the U.S. There is increasing evidence that a significant portion of the oxidized mercury in power plant emissions may be rapidly converted to the more insoluble elemental form by other emission constituents, potentially sulfur. The circumstances of this chemical reduction are as yet poorly understood, and its general applicability to coal-fired power plants unknown. The relative amounts in utility boiler emissions of the two mercury forms, oxidized and elemental, at the stack exit and at locations downwind is important to understanding the contribution of power plant mercury emissions to the mercury found in waterways. Reactive gaseous mercury is roughly 10^6 times as soluble in water as the elemental form.

Even though the concentrations of mercury species in these emissions are quite low, the technology is developing to make it possible to measure any such chemical changes both directly and indirectly. Significant advances have been made in the development of reliable methods for measurement and speciation of mercury in power plant emissions since EPRI's earlier comprehensive review of mercury science in 1996 (EPRI 1996). In addition, a substantial number of field measurements of flue gas and stack emissions have been accomplished, with some including longer emissions testing periods.

This chapter reviews recent research work to quantify and characterize mercury in fossil fuels, develop mercury emission factors for fossil fueled power plants, refine measurement methods for mercury in flue gas, mercury speciation measurements and methods, and finally, to fully characterize the combustion emissions from electricity generation by coal fueled power plants in the U.S.

2.2 Mercury Content of Fossil Fuels

Mercury is found in trace amounts in the three major fossil fuels used in utility boilers: gas, oil, and coal. Concentrations of mercury vary widely within a single fuel classification. Mercury may exist in the combustion fuel as elemental mercury (Hg(0)), or ionic mercury (Hg(I) or Hg(II)). In the flue gas, particulate-bound mercury, primarily Hg(II), may occur in very small ratios.

Mercury extracted from the earth in oil and gas, including that in waste streams associated with extraction and production, contributes to the global mercury cycle. While the amount of mercury from burning coal is known with reasonable confidence, the amount from fuel oil cannot be stated with equal confidence at present (USEPA 2001). With additional data collection and analysis, it may be possible to estimate the total amounts of mercury emissions from oil and gas combustion with better accuracy. The mercury content levels of coal tend to be 1 to 4 orders of magnitude greater than in fuel oil, while levels in natural gas are generally at near-detection limits. Table 2-1 shows the typical average concentration of mercury by fuel types (USEPA 2002).

**Table 2-1
Typical Average Concentration of Mercury by Fuel Types (USEPA 2002).**

Fuel	Mercury Concentrations
Coal	4.8-36.4 lb/10 ¹² Btu
Residual fuel oil	0.48 lb/10 ¹² Btu
Natural gas	0.00014 lb/10 ¹² Btu

2.2.1 Mercury in Coal

A greater number of trace element analyses have been conducted for coal than for oil or gas, in part because of the predominance of domestic sources of the fuel, allowing production stream monitoring to proceed. Prior measurements of 154 coal samples on as-fired or as-received coals sponsored by EPRI and reported in 1994 and 1995 indicated a range of 0.02-0.25 ppm, translating to emission factors of 1.15 to 23 lb/10¹² Btu (EPRI 1996). Measurement data based on the 1999-2000 mercury Information Collection Request database indicated mercury levels were generally lower than in earlier analyses. However, in some coal types found among a few states, levels ranged up to 36% higher than in the prior measurements, corresponding to an emission factor of 4.8 to 36.4 lb/10¹² Btu (EPRI 2000a,c). In general, the data for ICR coals were significantly lower in mercury than estimates used for as-received coals used by EPA in their *Mercury Study Report to Congress* (Figure 2-1). As Figure 2-1 indicates, twelve of 16 state coal categories were lower in coal mercury content than levels that were reported in the EPA *Mercury Study Report to Congress*.

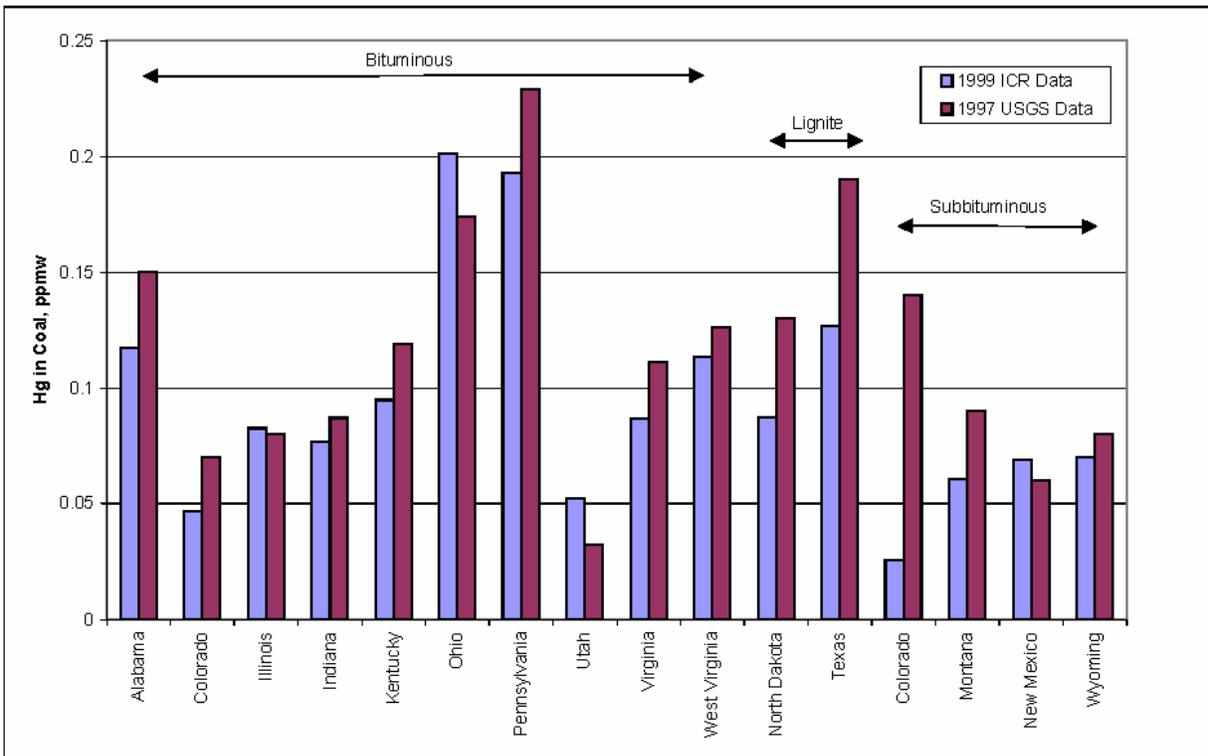


Figure 2-1
1997 EPA Coal Hg Levels Versus 1999 ICR Data
(EPRI 2000a)

Our understanding of coal mercury content was extensively updated by two recent analyses of significant datasets. First, an analysis of the mercury coal concentrations in the U.S. Geological Survey's (USGS) COALQUAL database is discussed in this section, followed by a discussion of analyses of data collected during EPA's Information Collection Request (ICR).

Mercury coal content data for U.S. coal deposits was covered by the U.S. Geological Survey's (USGS) COALQUAL database. COALQUAL contains analyses of approximately 7500 full-bed core and channel samples each representing the entire thickness of a coal bed. Total mercury concentrations in coal, based on data collected since 1993, are relatively constant across the U.S. (20 to 120 parts per billion on a weight basis, or ppbw) with more than 75% of the coals having concentrations below 100 ppbw (Brown et al. 1999). There are a few exceptions with some coal mercury concentrations ranging between 200 and 300 ppbw. Based upon the COALQUAL database analysis by Toole-ONEil et al. (1999), Table 2-2 provides a ranked summary of mercury by coal types in the U.S.

Table 2-2
Statistics for mercury values for selected coal areas from COALQUAL database (mercury content levels ranked by heat rate)

(Toole-O'Neil et al. 1999)

Coal Area	Mean mercury content ($\mu\text{g g}^{-1}$)	Maximum ($\mu\text{g g}^{-1}$)	Mean mercury content (lb/10¹² Btu)
Hams Fork	0.09	0.60	36.4
Fort Union	0.13	1.20	21.8
Wind River	0.18	0.80	18.7
W Interior	0.18	1.60	16.1
Appalachian	0.20	2.90	15.4
Penn. Anthracite	0.18	1.30	15.4
Powder River	0.10	1.40	12.6
So West Utah	0.10	0.50	11.0
Eastern Interior	0.10	0.40	8.2
San Juan River	0.08	0.90	7.7
Uinta	0.08	0.60	7.3
Green River	0.09	1.00	6.6
Raton Mesa	0.09	0.50	6.6
Gulf Coast	0.22	1.00	4.8

The impact of coal cleaning upon mercury coal concentrations is significant and was reviewed in EPA's Report to Congress (USEPA 1997a) as well as in a later journal article (Toole-O'Neil et al., 1999). In their report, EPA applied a coal cleaning factor of 0.79 to the USGS COALQUAL mercury concentrations for bituminous coals from primarily eastern states. This cleaning factor, 0.79, suggested a 21% removal of mercury prior to coal combustion. Toole-O'Neil et al. (1999) evaluated the tendency of coal cleaning to preferentially remove mercury. Of the 24 cases of coal cleaning cited, the average decrease in mercury concentration was 37% on an energy basis, ranging from 12% to 78% overall. On a mass basis, the average mercury reduction from coal cleaning was 30%, which indicates a coal cleaning factor of 0.70, a lower cleaning factor value and higher rate of mercury removal than that applied by EPA in 1997 (Brown et al. 1999).

The U.S. EPA's Mercury Information Collection Request (ICR) required all coal-fired plants with greater than 25 MW capacity to analyze their feed coal, more than 40,000 coal samples, for mercury and chlorine content over a one-year period, beginning in January 1999. In addition, EPA selected about 80 power plants to conduct flue gas mercury speciation measurements. Along with results of stack sampling analyses, the EPA used the coal data to estimate nationwide mercury emissions from coal-fired plants for making a regulatory determination regarding mercury controls.

EPRI also conducted an analysis of EPA's ICR data by coal category and determined that the average mercury coal content ranged from 3.32 lb/10¹² Btu in petroleum coke to 20.7 lb/10¹² Btu in anthracite (EPRI 2000a). Table 2-3 provides the average and 95th percentile confidence interval coal mercury content on an energy basis for tested coals (EPRI 2000a).

During the ICR, coal mercury content analyses were performed by numerous laboratories using a wide range of test methods. EPRI identified laboratory test method adequacy as a potential source of uncertainty in the resulting emissions estimates and sponsored two studies to evaluate analytical methods for measuring mercury and chlorine in coal (EPRI 2000c, 2000d). Results of the EPRI study indicated that laboratory variability did not significantly impact the ability of most electricity generators to meet the ICR quality control limits for mercury.

Some limitations were identified in the analysis methods used, however. The EPRI study concluded that Direct Combustion Cold Vapor Atomic Absorption and Acid Extraction Cold Vapor Atomic Absorption methods give superior analytical performance for measuring mercury in coal and ash, compared to the commonly used ASTM D 3684 Bomb Combustion Cold Vapor Atomic Absorption method (EPRI 2000c). EPRI also evaluated the impact of the analytical method used on the quality of the resulting ICR data for coal mercury content. About 20 percent of the ICR coal samples were measured by ASTM D 3684 and had a mercury concentration below the method's lower quantitative limit. However, because low-mercury coals make a relatively small contribution to nationwide mercury emissions, the measurement uncertainty was not found to impact the use of the ICR coal data to estimate mercury emissions.

About one-third of ICR coal samples had chlorine levels below the lower quantitative limits identified, however, the methods used for each of the ICR samples were not known. In further testing, none of the routinely used laboratory methods could consistently reproduce quantitative results below 200 ppm chlorine in coal (EPRI 2000c). Since more than a third of U.S. coals have less than 200 ppm chlorine, improved chlorine analysis methods were evaluated. Those that were evaluated included ASTM D 4208 Bomb Combustion Ion Selective Electrode, Bomb Combustion Ion Chromatography, and Eschka Ignition Ion Chromatography. None of these methods met all performance criteria for coal analysis, with repeatable detection at lower quantitative limits for chlorine. Furthermore, the methods were not suitable for coal ash analysis. Overall results indicate the need for improved chlorine measurement methods. In a follow-on EPRI study, a new analytical method for chlorine in coal, based on oxidative hydrolysis microcoulometry, was identified, evaluated and produced rapid and reliable results for measurements down to 10 ppm chlorine. (EPRI 2000d).

Table 2-3
Comparison of Correlation and Average Value Characters

Control Class	MWe	Number of Units	10 ¹² Btu	10 ¹⁵ J	Fuel Hg (lb/yr kg/yr)		Gas Hg (lb/yr kg/yr)		% Removal
<i>Results using Correlations</i>									
ESP cold	185,036	674	10,260	10,825	78,746	35,719	53,586	24,306	32%
ESPc FGDw	55,940	117	3,579	3,776	33,670	15,272	15,703	7,123	53%
ESP hot	31,816	120	1,769	1,866	11,067	5,020	9,674	4,388	13%
ESPh FGDw	8,478	20	565	596	3,289	1,492	2,579	1,170	22%
FBC FF	4,134	39	304	321	6,813	3,090	773	351	89%
Fabric Filter	12,478	58	782	825	5,777	2,620	1,943	881	66%
FF FGDw	6,988	14	486	513	2,948	1,337	582	264	80%
IGCC	557	2	22	23	142	64	137	62	4%
SD/ESP	1,623	5	117	123	601	273	482	219	20%
SD/FF	8,820	47	511	539	3,117	1,414	1,689	766	46%
Venturi Scrubber	11,865	32	652	688	4,400	1,996	3,903	1,770	11%
Total		1,128	19,047	20,096	150,570	68,297	91,050	41,300	40%
<i>Results Using Class Averages</i>									
ESP cold	184,322	674	10,260	10,825	78,746	35,719	57,485	26,075	27%
Bit (60%)			6,156	6,495	52,943	24,015	34,413	15,609	35%
Lig (5%)			513	541	4,976	2,257	4,876	2,212	2%
Sub (35%)			3,591	3,789	20,828	9,447	16,871	7,653	19%
ESPc FGDw	55,940	117	3,579	3,776	33,670	15,272	17,172	7,789	49%
ESP hot	31,816	120	1,769	1,866	11,067	5,020	10,624	4,819	4%
ESPh FGDw	8,478	20	565	596	3,289	1,492	2,434	1,104	26%
FBC FF	4,134	39	304	321	6,813	3,090	954	433	86%
Fabric Filter	12,478	58	782	825	5,777	2,620	2,427	1,101	58%
FF FGDw	6,988	14	486	513	2,948	1,337	354	161	88%
IGCC	557	2	22	23	142	64	137	62	4%
SD/ESP	1,623	5	117	123	601	273	492	223	18%
SD/FF	8,820	47	511	539	3,117	1,414	1,933	877	38%
Venturi Scrubber	11,865	32	652	688	4,400	1,996	4,224	1,916	4%
Total		1,128	19,047	20,096	150,570	68,297	98,234	44,558	35%

2.2.2. Mercury in Fuel Oil

Since EPA's 1997 *Mercury Study Report to Congress*, EPA has estimated concentrations of mercury in residual fuel oil (based upon data cited in the literature) ranging from 7 to 17 ppbw (parts per billion by weight = $\mu\text{g/L}$) (USEPA 1997b). For purposes of evaluating control technologies for oil plants, EPA used an average of approximately 10 ppbw of Hg in residual fuel oil (USEPA 1998).

Additional evidence concerning mercury in fuel oils is available from cooperative studies (EPA, EPRI, DOE and utilities) of hazardous air pollutants from electric utility boilers (USEPA 1998). EPA determined mercury emission factors for several furnace types used by utilities. In this study, the EPA cited mercury in residual fuel oil as $0.6 \text{ lbs}/10^{12} \text{ Btu}$ (pounds per trillion Btu) based on the analysis of 4 samples of fuel oil (average standard deviation = 0.3). The conversion factor applied was 150,000 Btu/gallon of oil, at a density of 8.2 lb/gallon, thus yielding a mean mercury concentration of approximately 10 ppb. Recent EPA-reported estimates cite a concentration for mercury in residual fuel oil utilized in national modeling calculations as $0.48 \text{ lbs}/10^{12} \text{ Btu}$ (USEPA 2002).

2.2.3. Mercury in Natural gas

The total mercury in natural gas concentration utilized in calculations of emissions factors in the 1998 study by EPA, EPRI and DOE cited above was $0.5 \mu\text{g}/\text{m}^3$. Thus, current data in the literature and EPA estimates (USEPA 1998) imply that the amounts of mercury in natural gas are insignificant, both *in toto* and as compared to residual oil or coals. In 2002 EPA cited a concentration of mercury in natural gas utilized in modeling calculations as $0.00014 \text{ lbs}/10^{12} \text{ Btu}$ (USEPA 2002).

Two interesting points are further noted. First, mercury removal systems are commercially available and widely applied to gas having sufficient mercury concentration to affect petrochemical processing (USEPA 2001). However, the percentage of total gas processed that is treated for mercury removal is currently unknown. Secondly, pipeline walls are reported to be quite efficient scavengers of mercury in gas, and it may be that major portions of mercury that enter a pipeline never exit but are retained on pipe interior surfaces indefinitely. Thus, the concentration of mercury at the point of consumption is expected to always be less than the concentration upstream of potential mercury sources such as compressors at gas processing facilities (USEPA 2001). With the increasing importance of natural gas consumption for electricity generation, this issue of pipeline scavenging of mercury deserves further examination.

2.3 Mercury Emission Factors for Fossil Fuel Fired Power Plants

There are a number of factors that influence the mercury levels in coal-fired boiler stack emissions. The primary factors include the existing SO_2 and particulate pollution control technology as well as the coal type or coal mix burned (specifically the chlorine and sulfur content). There are many additional factors such as unburned carbon, flue gas temperature, and fly ash constituents which also affect mercury removal and speciation. In this section, current

emission factors used for estimating mercury in stack emissions from fossil-fuel fired power plants are discussed.

2.3.1 Coal-fired Power Plants

Power plant emissions of mercury from fossil fueled power plants vary due to flue gas cleanup systems and other operational procedures at the power plant with a variable impact on combustion conditions and trace element removal. This section provides a discussion of the emission factors that have been developed based upon two parameters: coal type and control technology type. Using the data collected as part of EPA's 1999-2000 ICR, both EPA and EPRI used essentially the same data, employed different approaches to estimating mercury emissions, but developed mercury emission inventory estimates that are generally consistent with one another.

2.3.1.1 EPA ICR

The EPA issued an Information Collection Request (ICR) in 1998 that required owner/operators of coal-fired electric utility steam generating units to report for calendar year 1999 the quantity of fuel consumed and the mercury content of that fuel (Part I). In addition, 84 power plants were randomly selected (based on 36 categories of fuel type and SO₂ and particulate controls) to conduct flue gas measurements of mercury emissions and its chemical form (Part II).

EPA developed the ICR under authority of Section 114 of the Clean Air Act. Part I of the ICR requested information on fossil fuel fired boilers in the U.S. and was used to select Part II and Part III participants. Part II of the ICR required all owner/operators of coal-fired electric utility steam generating units with a capacity greater than 25 megawatts electric [MWe] to report to EPA on a quarterly basis during 1999 the quantity of fuel shipped and the mercury content of that fuel. Each facility also reported the type (coal rank) of each fuel shipment received, and the source of each coal (by state, county, and, optionally, the coal seam). Use of alternate fuels (such as petroleum coke or waste tires) was also reported. Initially, for every sixth shipment, the facility was to test each coal type for percent ash, sulfur, heating value, mercury and chlorine content. Depending on statistical performance, the sampling frequency was either increased or decreased. The definition of a shipment was complex and differed depending on whether the coal was shipped by rail car, barge or ship; by truck; or by conveyor belt from a mine or coal pile.

Part III required the owners/operators of coal-fired electric utility steam generating units selected at random from a total of 36 categories to conduct, at some time during a 1-year period, in accordance with an EPA-approved protocol, simultaneous measurement of mercury speciation in the flue gas before and after the final air pollution control device located upstream of the stack. The testing consisted of three runs at each sampling location. The owner/operator of each selected electric utility steam generating unit was also required to collect and analyze, in accordance with an acceptable procedure, a statistically appropriate number of coal samples from the coal fed to the pulverizer during each stack test. The results of the flue gas tests and the coal analyses were submitted to the EPA.

To supplement the ICR, the EPA requested that coal-fired power plants also report the coal type and quantity burned each month in each boiler. Unlike the ICR Phase II reporting, the coal was not identified by source; this information provides a direct indication of quantities consumed in each unit.

EPA required less than 10% of the power plant population, 84 plants (out of 1086 power plants), to sample their flue gas for mercury emissions. Therefore, in order to estimate mercury emissions from all coal-fired power plants in the U.S., a procedure was needed to estimate emissions from the units that were not tested, as well as to compute annual emission estimates for those that were tested. EPA and EPRI each developed such a method; these are described in the sections below.

2.3.1.2 EPA Emission Estimates

Based upon ICR data, EPA developed a data summary for mercury emissions reductions after installation of a control system or process that would be realized if 100% of the mercury entering the subsystem or unit process remain behind in the flue gas. EPA's initial analysis of the ICR data was later revised to correct data processing and other errors (USEPA 2000b, 2001b, 2002b). Table 2-4 provides a summary of these ICR data by boiler type and SO₂/particulate control equipment (USEPA 2002b). A power plant is typically equipped with an ESP or fabric filter (FF) for particulate removal, low-NO_x burners, and post-combustion flue gas treatment devices for NO_x and SO₂ control. Examples of the latter devices are selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) technologies for NO_x control and high efficiency FGD scrubbers for SO₂ control. EPA did not include consideration of facilities with SCR and SNCR.

Table 2-4
Summary of ICR data by boiler type and SO₂/particulate control equipment. Mean Mercury Emission Reductions for pulverized coal-fired Boilers. (USEPA 2000b).

Add-on Controls	Type of Coal		
	Bitum.	Subbitum.	Lignite
PM Only			
CS-ESP	46	16	0
HS-ESP	12	13	NT
CS-FF	83	72	NT
PM Scrubber	14	0	33
Dry FGD Scrubbers			
SDA + ESP	NT	38	NT
SDA + FF	98	25	17
SCR + SDA + FF	98	NT	NT
Wet FGD Scrubbers			
CS-ESP + Wet FGD	81	35	44
HS-ESP + Wet FGD	55	33	NT
CS-FF + Wet FGD	96	NT	NT

^a Based on OH train data. NT= not tested. Mean reduction from 3-test averages for each unit.

EPA found that the best levels of control of mercury are generally obtained by emission control systems that use FFs. The amount of mercury captured by a given control technology is better for bituminous coal than for either subbituminous coal or lignite. The lower levels of mercury capture in plants firing sub-bituminous coal and lignite is attributed to low fly ash carbon content and the higher relative amounts of elemental mercury in the flue gas from combustion of these fuels (EPA 2000b).

The estimated national total of mercury emitted from all coal-fired electric utility steam-generating units for 1999 is approximately 48 tons. This amount of mercury was emitted from 1,143 units at 461 facilities. This total is composed of 1.48 tons/yr of particle-bound mercury, 20.41 tons/yr of oxidized mercury, and 26.10 tons/yr of elemental mercury (USEPA 2001b).

2.3.2 EPRI Emission Estimates

In separate, parallel analyses employing the ICR coal and stack data, EPRI developed estimates for total and speciated mercury emissions from coal-fired power plants. Using the available mercury ICR stack data, EPRI developed predictive relationships for mercury removal and speciation for the purposes of developing a national emission inventory of mercury emissions from every U.S. coal-fired power plant for the year 1999 (EPRI 2000e). [EPRI's analyses of ICR data are summarized in EPRI 2000a.] EPRI focused on using publicly available information for all the US coal power plants and the available data from the ICR. The ICR data from the stack tests were grouped by control device and fuel properties to develop correlations for both mercury removal and speciation (percentage of elemental mercury).

EPRI study results determined that both mercury speciation and removal are functions of the chlorine content in coal (EPRI 2000e). An example of this is provided for the cold-side ESP category in Figure 2-2. Further, to provide a perspective first, on the population of power plants versus those in the ICR dataset, and second, on the relative number of sites by control technology type and coal mercury consumption, EPRI evaluated these data presented in Table 2-5. Table 2-6 summarizes the EPRI results for estimated emissions of total mercury for each control technology category using the correlation approach, with the results (in the bottom half of the table) obtained by using the average removal for various control classes (EPRI 2000e). Correlations by control equipment type were made between the mercury in fuel and in gas streams after particulate removal. For the calculation of an average removal rate, the averages of control technology class were used. As can be seen the least efficient existing control devices for mercury are venturi scrubbers and hot-side ESPs. The average percentage removal of mercury by existing pollutant control systems was determined to be 40%. The mercury removal by existing control systems derived using correlations generally provide the same overall industry emission inventory as an average emission factor, e.g., EPA's emissions factors. However, there are likely differences in plant-specific estimates.

In summary, there is general agreement between the approaches used by EPA and by EPRI to calculate mercury emissions from coal fired power plants.

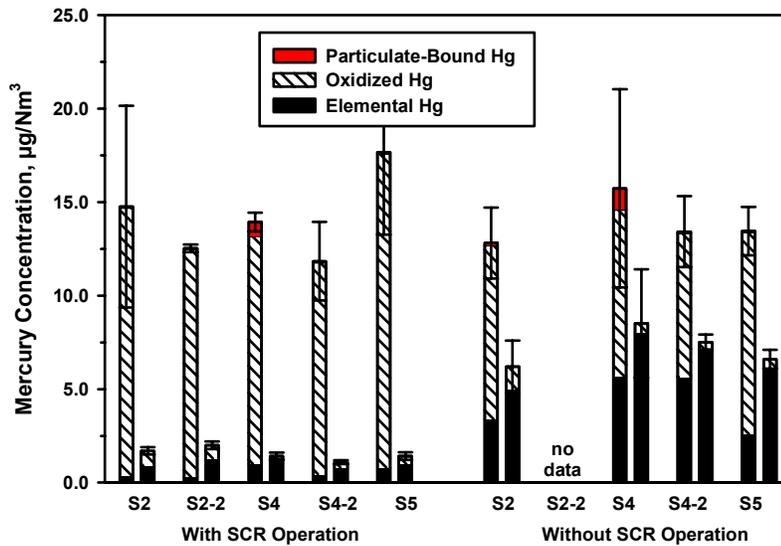


Figure 2-2
Mercury Speciation of SCRs and FGDs in Coal Power Plant Emissions (Chu et al., 2003; EPRI, 2003). Comparison of Mercury Concentrations at PCD Inlet and FGD Outlet, With SCR (left bar) and Without SCR (right bar)

Table 2-5
Control Technology Categories for Developing Correlations

Control Device	Number of Sites tested in ICR Part III	Number of US Power Plants
Primary Particulate Removal Devices		
Cold side ESP ^a	18	674
Hot side ESP	9	120
Fabric filter	9	58
FBC ^b -fabric filter	5	39
Venturi scrubber	9	32
Spray dryer / fabric filter	10	47
Spray dryer / cold side ESP	3	5
IGCC ^c (Note 1)	2	2
FBC – cold side ESP (Note 1)	1	1
Wet FGD Systems After Primary Particulate Control Devices (Note 2)		
After cold side ESP	11	117
After hot side ESP	6	20
After fabric filter	2	14

a ESP – Electrostatic precipitator

b FBC – Fluidized bed combustor

c IGCC – Integrated gasification/combined cycle

Note 1. Averages were developed for these categories because of the limited available data and the small population of power plants in these categories.

Note 2. Incremental Hg removal across wet FGD

**Table 2-6
Correlation Coefficients**

Control Class	% Mercury Removal				% Elemental Mercury			
	Multiplier	Constant	Minimum	Maximum	Multiplier	Constant	Minimum	Maximum
ESPc	0.1233	-0.3885	0%	55%	-0.1283	1.2251	12%	85%
ESPc FGDw	0.1157	-0.1438	24%	70%	-0.039	1.107	81%	98%
ESPh	0.0927	-0.4024	0%	27%	-0.1639	1.5495	34%	91%
ESPh FGDw	0.2845	-1.3236	4%	65%	-0.0945	1.4545	80%	99%
FBC FF	0.1394	0.1127	66%	99%	-0.1198	1.2038	44%	68%
FF	0.1816	-0.4287	40%	85%	-0.1182	0.8803	3%	33%
FF FGDw	0.1943	-0.2385	79%	96%	-0.426	3.0957	45%	84%
SD/ESP	-0.1087	0.6932	5%	25%	-0.0355	1.126	91%	98%
SD/FF	0.2854	-1.1302	0%	99%	-0.1125	1.478	64%	99%
VS	0.0582	-0.1932	3%	24%	-0.021	1.0514	86%	96%
FBC ESPc								
IGCC								

Legend:

ESPc – Electrostatic precipitator (cold)

ESPh - Electrostatic precipitator (hot)

FGDw – Flue gas desulfurization (wet)

FGDd - Flue gas desulfurization (dry)

FBC – Fluidized bed combustion

FF – Fabric filter

SD – Spray dryer

VS – Venturi scrubber

IGCC – Integrated gasification/combined cycle

Note – EPRI chose to not extrapolate the correlations beyond the available data, and thus minimum and maximum removals were established. The User should carefully consider whether to extrapolate the correlations or choose to accept the constraints of the available data.

2.3.3 Control Technology Considerations

It should be noted that generating units with SCRs or SNCRs were not incorporated into either the EPA or EPRI emission inventories of mercury from coal-fired power plants described above. The effect of SCRs and SNCRs on power plant emissions of mercury is an important issue since these control devices are expected to be installed on a significant fraction of electricity generating boilers (from ~55 to 60%) by 2010.

A major program on the effects of post-combustion NO_x controls on mercury was co-sponsored by EPRI, the U.S. Department of Energy, and the U.S. Environmental Protection Agency (EPRI, DOE and EPA 2002). Several regulatory activities such as newly proposed fine particulate (PM_{2.5}) ambient air quality standards, more stringent ambient ozone standards, and restrictions on nitrogen oxides (NO_x) may result in more stringent NO_x emission limits. As a result, a number of generators are either installing or considering installing SCR or SNCR systems to reduce NO_x emissions.

In general, ammonia or urea is used to reduce NO_x in the presence of a catalyst in SCR systems. Catalyst designs are available using layers of ceramic or metal substrates in a honeycomb formation.

To evaluate the potential effects of the SCR catalyst and ammonia injection on mercury speciation and removal, EPRI initiated a pilot-scale screening evaluation jointly with U.S. and Canadian utilities and agencies at a test facility (EPRI, DOE, EPA 2000). The facility consisted of a pilot combustor, a pilot SCR, and a pilot ESP. Four different coals were tested, including three eastern bituminous coals of varying sulfur and chlorine content, and a Powder River Basin (PRB) coal. For some coals, ammonia and/or the SCR catalyst appeared to increase the amount of particulate-bound mercury, which led to increased mercury capture in the ESP. For both the ammonia injection (without SCR) test and the SCR/ammonia test, the amount of particulate-bound mercury appeared to increase compared to tests on units without either SCR or ammonia injection. Thus, the potential effect of SCR and/or ammonia on mercury appears to be highly coal-specific.

Because of the issues of representativeness of pilot results, EPRI, EPA, and DOE conducted full-scale measurements in 2001, 2002, as well as on-going studies in 2003 to confirm these results. Full-scale sampling at six coal-fired power plants investigated the role that SCR, SNCR, and flue gas conditioning have on mercury speciation (EPRI, DOE and EPA 2002; EPRI 2003c). Six plants with SCR systems were tested (with retests at two of these sites). The samples were evaluated using two approaches: the wet-chemistry Ontario Hydro method and near real-time continuous mercury monitors (CMMs).

Four different types of CMMs were used, each employing atomic fluorescence-based analysis: the Semtech Hg 2010, a PS Analytical Sir Galahad, a Tekran, and an Ohio Lumex detector; each used a conversion system to enable measurement of speciated mercury. Measurements were conducted at the inlet and outlet of the SCR, as well as in the inlet and outlet of the particulate and SO₂ controls both with and without SCR operation. Additional sampling involved EPA Method 26A to test for chlorides, a selective condensation method to measure SO₃, and EPA

Method 27 for NH₃ slip. Fly ash and coal samples also were collected to estimate mercury mass balance across control devices. A range of different coals was evaluated, including eastern bituminous and PRB coals. The effects of catalyst space velocity (residence time) and catalyst age were evaluated to better understand the potential for their influence upon mercury conversion and removal.

Oxidation of mercury was found to occur across the SCR reactor for the eastern bituminous coal power plants. Figure 2-2 provides a comparison of the speciation of mercury emissions of the flue gas entering and leaving the SCR. The extent of oxidation was variable and seemed to be affected by the coal type (chlorine and sulfur content) and catalyst design (EPRI, DOE, and EPRI 2002).

Two sites were retested in 2002 to evaluate the effect of an additional ozone season on catalyst mercury oxidation. Both sites burned a high-sulfur eastern bituminous coal and employed an FGD. The results suggest a small, possible drop-off in mercury oxidation across the SCR, however, the extent of mercury oxidation entering the FGD system was not affected, nor was the overall mercury removal. In addition, both power plants may have been operating under slightly different operating conditions, including different coals, which further complicated the analyses.

For one of the six power plants tested which burned a PRB coal, this site did not exhibit significant mercury oxidation across the SCR catalyst. It has been hypothesized that catalyst aging may be important. Additional measurements are planned in late-summer 2003 at a pulverized-coal-fired power plant burning a PRB coal and employing an SCR. A pilot SCR study operating on a PRB flue gas is on-going to evaluate catalyst aging effects. Results after ~3200 hours indicate little drop-off in mercury oxidation.

Of the five bituminous coal plants tested, two employed SCR catalysts with “low” space velocity [~2000 hr⁻¹] (larger catalyst and longer residence times) and three operated with higher space velocities [~3700 hr⁻¹]. The limited results to date would suggest that “significant” oxidation could be possible for the “high” space velocity SCR designs for bituminous coal-fired plants (EPRI 2003c).

2.3.4 Oil and natural gas fired plants

Trace amounts of mercury are present both in coal and oil. Consequently, whenever these fuels are used, such as in the generation of electricity, some of this mercury is emitted into the air along with exhaust gases.

Since emissions estimates were made for oil and natural gas fired utility plants in EPA’s 1997 *Mercury Study Report to Congress*, additional information has become available. In 1998, EPA estimated the mercury emissions from all U.S. utility boilers that burn fuel oil as approximately 200 kg per year (or 441 lbs) (USEPA 1998), based upon an assumption of 10 ppb Hg in fuel oil. Emissions data used were obtained from 12 emission tests conducted by EPRI and individual utilities. Wilhelm (2001) predicted, based on re-analysis of petroleum and petroleum fractions, that total emissions of mercury due to all recovery, processing, and combustion of petroleum products in the U.S. totals no more than 19 Mg/y, or about 40% of U.S. coal utility emissions.

It appears, based on currently available data, that about half of the entire amount of mercury associated with oil and gas (exploration, production, transportation, processing, fuel combustion) enters the atmosphere in fuel combustion (USEPA 2001). Some unknown portion of this amount is captured by pollution control equipment. However, the total overall emissions from oil and gas are less than 6 Mg/y (1 Mg/y = 10⁶ grams or 1 metric ton per year) (if the mean amount of mercury in crude oil is less than 10 ppb) (USEPA 2001). This suggests that, while oil and gas account for about the same mass of fossil fuel combusted annually in the U.S., the amount of mercury in combusted petroleum and gas is one-tenth or less that which derives from coal (based on EPA estimates of 66 Mg/y, U.S. EPA 1997).

Since analytical uncertainties exist with currently published data, especially in regard to the percentage and species identities of suspended forms of mercury in fuel oil, additional data would have to be collected to develop more refined emissions estimates.

2.4 Flue Gas Mercury Measurement Methods

2.4.1 Overview

The chemical species, or valence state and combined form, of mercury in flue gas determines its behavior in the ambient environment. First, the chemical species of mercury in flue gas governs the effectiveness of flue gas control technologies in removing mercury. Second, the chemical species in emissions governs the mercury's atmospheric fate and transport. The percentage of each chemical species of mercury formed during the coal combustion process and post-combustion conditions varies significantly from one plant to another. When different ranks of coal are fired in utility boilers, there is a substantial variation in the concentrations of elemental mercury (Hg(0)) versus oxidized mercury (Hg(II)(II)) as measured at the inlet to the particulate control device. The percentage of Hg(0) varies from 10% to greater than 90% indicating that speciation is very dependent on coal type and coal chlorine content. As mentioned earlier, results from an EPRI study of ICR stack test and coal analysis data determined that mercury speciation and removal are functions of the chlorine content in coal (EPRI 2000e). Understanding the speciation of vapor phase mercury (elemental versus oxidized mercury), and particulate-bound mercury is critical to predicting the mercury contributed to atmospheric transport by power plants and evaluating effective mercury control technologies for coal-fired utility boilers.

Both EPRI and DOE have sponsored extensive research on alternative flue gas measurement methods for total and speciated mercury from electric utility boilers. Research characterized mercury emissions from coal-fired utility boilers using a number of speciation and measurement methods. Results to date indicate that the mercury measurement technology is advancing with current developments that appear promising. Recently, the Ontario Hydro Method was validated as a method for flue gas mercury speciation. The current generation of Continuous Mercury Monitoring (CMM) instruments provide near real-time results, but the current technologies are labor-intensive, and still unproven. Neither the absolute accuracy nor the operational performance of continuous emission monitoring has been validated for compliance purposes. EPA has an on-going program to evaluate CMMs at several coal-fired power plants. However, CMMs may be useful for R&D purposes.

2.4.2 Ontario Hydro Measurement Method

Recent tests of several methods demonstrate that the technology has advanced to enable a greater demonstration of promise in reliable flue gas mercury measurement methods.

The Ontario Hydro Method, an ASTM-approved method, was developed by EPRI (1999). It is the method of choice for mercury speciation measurements, and was required by EPA in the ICR. This method was extensively tested at the Energy & Environmental Research Center (EERC) in a program funded by EPRI and DOE. These tests showed the method accurately measured speciated mercury in coal-fired flue gases. However, testing took place primarily at the pilot-scale level. Thereafter, EPRI and DOE funded a project to further evaluate the Ontario Hydro method at a Midwestern power plant using a modification of the EPA Method 301 validation procedures. Although there was some data variability, EPRI study results show that the Ontario Hydro mercury speciation method is valid according to the criteria established in EPA Method 301 (EPRI, 1999).

2.4.3 Continuous Mercury Emissions Monitoring Methods

A mercury monitor measures speciated or total mercury concentrations in a gas stream over short time spans, to allow for collection of a large enough sample of the substance to avoid detection limit issues. The gas stream must first be conditioned by removing moisture and acid gases to avoid instrumental interference or clogging of sampling lines. A typical sampling set up consists of a sampling probe, particulate filtration, heated transfer line (from the probe to the conditioning system), a conditioning system, and a continuous mercury monitor (CMM). The Tekran CMM instruments employ atomic fluorescence technology.

Over the last several years, despite attempts to demonstrate the application of continuous mercury analyzers on flue gas from various combustion sources, there is no clear consensus on a proven technology. Generally, commercial instrumentation has not performed well in continuous, unattended applications. This has usually been due to a lack of understanding of the sampling environment, the mercury species present, and the low levels of mercury in the flue gas.

EPRI has conducted projects to describe commercially available mercury analyzers, address ongoing verification programs for evaluating CMM systems and summarize information on field evaluations of mercury analyzers (EPRI 2000f, 2002a). Semi-continuous analyzers have been used extensively to monitor mercury emissions during short-term tests for characterizing emissions or evaluating control technology options. These applications have provided valuable field experience. The EPRI study found that the monitors commercially available today are based on sound, well-developed analytical techniques (EPRI 2002a). The instrumentation hardware is comparable to the hardware installed in compliance monitoring systems. However, the complexity of the mercury speciation in flue gas and the potential interference of particulate and sulfur compounds have made the sampling and sample conditioning more challenging when applying existing analytical methods to flue gas at electric generating plants.

A concern remains that the accuracy of mercury monitors for total mercury measurement in utility flue gas has not yet been validated. And two key issues remain: i) how to ensure that the

speciation and concentration of the sample delivered to the analyzer are the same as in the flue gas, and ii) how to verify non-elemental mercury conversion efficiencies. As a result, EPRI believes that mercury monitors should be included in ongoing mercury measurement research. Mercury monitors continue to provide near real-time indication of elemental mercury concentrations in gaseous streams, and remain useful to evaluate the efficiency of controls to reduce certain species of mercury.

EPRI conducted mercury field method testing programs for coal-fired flue gas starting in the summer of 2002. In this study, field tests were conducted of two additional techniques, both the “Quick Silver Emission Monitor” (Quick-SEM™) and the Mercury Sampling Conditioning System (Hg SCS) to determine their reliability and applicability. The Quick-SEM™ could provide a low-cost solution for measuring the time average total mercury emissions at a plant. The Hg SCS would enable real-time monitoring of total vapor-phase mercury, elemental mercury, and total mercury (particulate and vapor), using commercially available mercury analyzers. (EPRI, 2002b)

Field evaluations of the Quick-SEM were conducted in conjunction with semi-continuous mercury analyzers and/or manual mercury measurements using the Draft Ontario Hydro Method. The Hg SCS was evaluated at two field sites in 2002. Testing included an assessment of the performance of the SCS and analyzer assembly following the EPA’s draft Performance Specification 12 for continuous mercury analyzers. Testing at both sites used a cold vapor atomic absorption spectrometry (CVAAS) mercury analyzer from Apogee, Inc., which is not available commercially. Testing at the second field site used a commercially available analyzer from PS Analytical with plans for use of another analyzer, the Ohio Lumex instrument, at a later date. (EPRI, 2002b).

Results from field evaluations of both systems showed promise. Additional extended field testing of both techniques at more sites is still needed. The present challenge is to translate the experience obtained using these analyzers into systems that can be operated in an unattended mode for extended periods. There are extensive efforts underway by EPRI, the EPA, and others to develop improved sampling and sample conditioning for mercury monitors. Potential solutions for testing gas-phase elemental mercury and mercuric chloride are close. Potential solutions for sampling particle-bound mercury require further study (EPRI, 2002b).

2.4.4 Mercury Emissions Variability

An additional significant area of recent EPRI research involved an evaluation of the variability over time of mercury stack emissions. Understanding the variability over time of mercury in stack emissions will aid in considerations of a mercury emissions rate that is both realistic and achievable. The stringency of an emission limit is determined not just by the numerical value of the standard, but also by the averaging time and the measurement method.

To clarify how the concentration of mercury in emissions from coal-fired power plants varies with time, over longer periods of time, EPRI conducted a study of the variability in mercury emissions (EPRI 2003d). Prior tests of mercury emissions from coal-fired boilers have primarily been confined to short-term, manual stack test results using the Ontario Hydro method, providing a “snapshot” of emissions for about 2 hours. Mercury was measured using the CMM for mercury

installed at the particulate control outlet (i.e. stack, if no FGD was present). The Ontario Hydro (OH) mercury speciation method was used to confirm the CMM results.

Twelve coal-fired generating units in the U.S., ranging from 215 to 1025 MW in unit size, were tested. The coal types used in these boilers included two lignite coals, eleven eastern bituminous coals, and one subbituminous PRB coal. The plant configurations for air pollution control devices (APCDs) included SCR reactors, ESPs, low NO_x burners (LNB), wet scrubbers (although measurements were not conducted at the outlet due to the complexities of a wet stack), combination SO₂/PM scrubber, fabric filters and spray dryer fabric filters.

The results of the first test recorded approximately 400 individual measurement values from each of the two CMM systems, with a subsequent test collecting over 100 individual measurement values. Until this work was initiated, the largest mercury emission dataset was the results from EPA's ICR. The ICR dataset consists of a total of about 480 unit operating hours ($80\text{units} \times 3\text{test runs} \times 2\text{hours/run}$). In contrast, the EPRI CMM dataset contains over 4000 hours for the twelve units tested, rendering this body of work a significant mercury emissions dataset for coal fueled utility boilers in the U.S. (EPRI 2003d).

Analysis of the CMM dataset demonstrates that there is considerable temporal variability in mercury emissions from coal-fired utility boilers, persisting across all coal ranks and unit configurations tested. The cumulative frequency distribution plots of the hourly average concentrations of mercury in stack emissions appear consistent across the test locations. Hourly mercury emissions are variable; hourly relative standard deviations (RSDs) range from near 8 percent to more than 60 percent. These plots indicate that while most units operate with periods with low concentrations of mercury in emissions, there is a percentage of time when mercury emissions concentrations are higher than the mean. These study results support a conclusion that mercury emission concentrations from coal fired utility boilers vary with time. Figure 2-3 provides an example of the variability of mercury emissions with plots of the hourly and daily averages for one site over about a 1 month period. Note that hourly averages vary almost ten-fold and that daily averages vary about three-fold over about a one month period (EPRI 2003d).

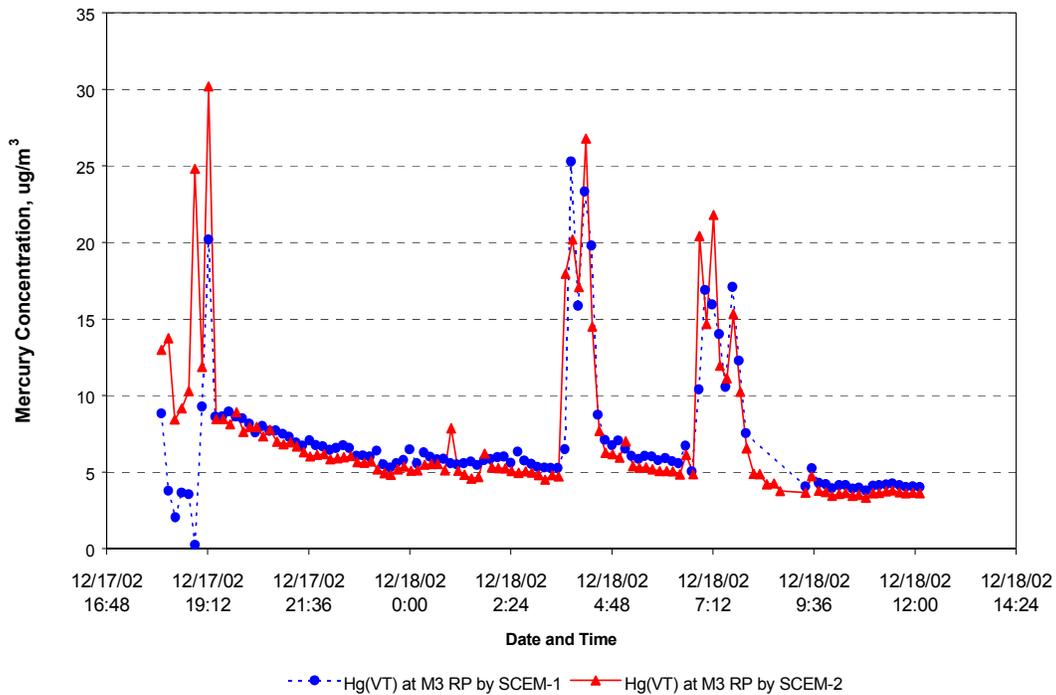


Figure 2-3
Simultaneous Mercury Measurements with Two CMM Analyzers (EPRI 2002b)

2.4.5 Speciation Field Measurements

Recent field measurements of mercury in power plant emissions plumes showed rapid conversion of divalent to elemental mercury in the plume prior to full dispersion. In order to test whether chemistry in power plant emissions might cause conversions from elemental to oxidized or oxidized to elemental mercury, EPRI helped develop a test chamber to simulate the natural behavior of these emissions in a laboratory. That chamber came in two capacities, with experimental voids of either 0.5 Or 1m^3 , and was equipped with pumps, internal lights to simulate solar irradiation, and water sprays. The chambers were operated by being evacuated to a slightly negative pressure with regard to ambient, then drawing in flue gas streams via conduit from stack ports, and then reaching ambient pressure by bleeding in ambient atmospheric gases. The test conditions were varied by using lights, water sprays, or combinations of the two in the test voids. Studies using these test chambers have been carried out at power plants in Maryland, Michigan, Georgia, and Wisconsin. In a pilot-scale test on gases generated by coal combustion in a North Dakota laboratory facility, there was rapid conversion of the more reactive oxidized mercury to the more stable element form. These experiments indicated that, in emissions from coal-fired power plants, mercury measured at the stack exit might not remain in the forms measured, but might be rapidly and preferentially converted to the elemental form, which is some six orders of magnitude less soluble in water than the divalent form.

Measurements at a field site near a power plant confirm the rapid conversion of oxidized to elemental mercury. Using mercury deposition data from a site in rural Georgia about 35 miles outside of Atlanta, measurements of mercury concentrations in the atmosphere were compared to

source estimates of mercury from a large coal fired power plant about 15 miles away. Mercury concentrations in the coal being burned were measured, then used in a mercury chemistry model to predict the mixture of mercury species expected to be emitted from the plant stack. This mixture of forms should be identical to the one found in the air sampled at the measurement site 15 miles away from the power plant source. The expected mix in the air at the measurement site, based on what was emitted at the source, should have been 40% elemental, 60% oxidized. In fact, the mix observed at the downwind deposition measurement site was 91% elemental and 9% oxidized. There are several possible explanations for this difference. The emissions model used might be incorrect, or the oxidized mercury may have deposited before reaching the measurement site ; or chemical reactions converted mercury from one form to another. Later measurements at the plant stacks consistently demonstrated that the emissions model tends to underestimate the fraction of emitted mercury that is divalent, so that the estimate used for comparison to ground data should be viewed as conservative. The short travel time from stack to sampling station, roughly three hours, implies either poor source characterization or chemical conversion. If the latter, approximately 2/3 of the oxidized reactive mercury was apparently converted to elemental mercury, the form that is much less likely to deposit in waterways and surfaces.

2.5 Total Mercury Emissions from U.S. Fossil-Fueled Power Plants move in front of 2.3.4

Based upon EPA's data on coal mercury content and flue gas measurements from the ICR in 1998, EPRI developed correlations by control device and fuel properties for both mercury removal and speciation (percentage of elemental mercury) for 12 categories of particulate and SO₂ control technologies, shown above in Tables 2-5 and 2-6 (EPRI 2000b). The results indicated that the fraction of incoming mercury emitted from the stacks is chiefly dependent on the coal type and the SO₂ and particulate control system installed. Correlations were applied along with the coal analyses data to calculate removals and subsequent mercury emissions.

The total amount of mercury emissions from coal-fired power plants was estimated to be 41 metric tons per year (T/y) for 1999. These 41 tons of mercury emissions consists of 16 T/y of oxidized mercury, 24 T/y of elemental mercury, and about one ton of particulate mercury. The total mercury levels entering power plants in the fuel are estimated at 68 T/y. Therefore, the national average mercury removal is 40 percent across the existing particulate and SO₂ control technologies. Measured removals are highly variable among the various control technology categories, as well as within-category for some of the control technology categories. An alternative estimation technique using average removal efficiencies for categories of control technologies yields a total for mercury emissions of about 44 T/y, compared with 41 T/y using the correlation approach (EPRI 2000b).

The reason for this discrepancy is that the ICR test data set does not contain a representative percentage of sites with high chlorine coal. Higher chlorine coals tend to yield higher mercury removals and lower the average emission. Uncertainty analyses show that EPRI's national inventory estimate of 41 T/y is likely to be accurate to within plus or minus 10 percent. Plant-specific estimates tend to be more uncertain. The sources for this plant-specific uncertainty include: (1) sampling and analytical issues, (2) process changes such as use of different coals,

and (3) the effect of additional independent variables not incorporated into the correlations (EPRI 2000b)

This inventory was more recently updated by EPRI based upon consideration of recent findings from field and laboratory studies (Seigneur et al. 2003). Of the U.S. portion of global anthropogenic mercury emissions, electric utilities contribute about 42 T/y, or about 32% of the U.S. total. The global total of anthropogenic emissions is estimated at 2127 T/y.

Recent information on the chemistry of mercury in power plant emissions plumes implies a potentially lower proportion of utility mercury emissions depositing to waterways or other receptors close to the exit stack. Measurements of mercury emissions within power plant stacks show that, on average, 40% of utility emissions (and up to 95% at some facilities) are in the reactive oxidized form. This is the form likely to deposit more closely to power plant sources, since the solubility of Hg(II) as HgCl_2 is about 6 orders of magnitude greater than that of Hg(0). Yet measurements of ambient mercury in the surrounding atmosphere have consistently found that only about 1 to 3% of the mercury is oxidized, with virtually of the remainder occurring as the elemental form. The recent results on mercury chemistry in power plant emissions appear to indicate that there is a rapid conversion of a portion of the emitted oxidized mercury to the elemental form, thus accounting for this measured discrepancy.

2.6 Summary and Conclusions

- Based on data collected during the 1999-2000 utility Information Collection Request, both EPRI and EPA estimated coal-fired emissions to be ~45 metric tons (1 metric tons = 106 grams) in 1999.
- New ICR data indicate that Hg means in coal are at least 4 orders of magnitude greater than in oil or gas.
- The valence state of mercury as well as its removal rates are a function of chlorine in coal. Speciation is critical for controls as well as fate and transport.
- The Ontario Hydro “wet chemistry” method was used for stack measurements under the ICR, while CMMs are now being used for research, including characterizing the variability of Hg emissions. Hg CEMs are still developmental and are currently being evaluated by EPA.
- Emission inventories by EPA and EPRI do not account for new NO_x controls – SCR and SNCR. Based on recent and on-going studies by EPRI, DOE, and EPA, the results indicate that for bituminous coals, SCRs may catalytically convert elemental Hg to oxidized Hg, which may be removed in the downstream wet FGD, if one is available.
- EPRI’s analysis of EPA’s ICR data by coal category determined that the average mercury coal content ranged from 5.77 lb/10⁶ Btu for subbituminous and 8.65 lb/10⁶ Btu for bituminous to 20.7 lb/10⁶ Btu for anthracite.
- Analyses of the total mercury concentrations indicate that more than 75% of U.S. coals have concentrations below 100 ppbw, with coal cleaning now shown to reduce mercury by 30%.
- There is a substantial variation among coal ranks burned in the resulting concentrations of elemental mercury (Hg(0)) versus oxidized mercury (Hg(II)) as measured at the inlet to the

particulate control device. The percentage of Hg(0) varies from 10% to greater than 90%, indicating that speciation is very dependent on coal type and chlorine content.

- The mercury capture effectiveness of existing controls varies significantly, and depends on the proportions of Hg(0), Hg(II), or particulate-bound mercury in the flue gas. Oxidized mercury is captured effectively by wet and dry SO₂ scrubbers and also appears to be captured more readily by ESPs. Particulate-bound mercury may be associated with unburned carbon in the fly ash, and is generally captured by the particulate control device.

References

Brown T.D., et al, R.A., . 1999. Mercury Measurement and its Control : What we Know, Have Learned, and Need to Further Investigate, J. Air & Waste Manage. Assoc., pp. 1-9. June.

Chu, P., D. Laudal, L. Brickett, C. Lee, 2003. *Power Plant Evaluation of the Effect of SCR Technology on Mercury*. Paper presented at the Combined Power Plant Air Pollutant Control Mega Symposium (MEGA Symposium), May 19-22, 2003. Washington, D.C.

EPRI, DOE, and EPA 2002. Power Plant Evaluation of the Effect of Selective Catalytic Reduction on Mercury. Final Report. Palo Alto, CA. TR-1005400.

EPRI, 2003a. Development and Demonstration of Mercury Control by Dry Technologies. Palo Alto, CA. TR 1004261.

EPRI, 2003b. Effects of Mercury Controls on Removal and Emissions of Trace Elements and Acid Gas Species. Palo Alto, CA. TR-1004264. Technical Update.

EPRI, 2003c. Impact of NO_x Controls on Mercury Controllability: Update 2002. Palo Alto, CA. TR-1004268. Technical Update.

EPRI, 2003d. Characterizing Variation in Mercury Emissions from Coal-fired Power Plants, Palo Alto, CA. TR -1005041.

EPRI, 2002a. Measuring Mercury in Coal-Fired Power Plant Flue Gas. TR 1004176. November. Interim Report.

EPRI 2002b. Status of Continuous Emission Monitors for Mercury: 2002 Update. Palo Alto, CA. TR 1004076. March.

EPRI, 2002c. Mercury Releases from Coal Fly Ash. Palo Alto, CA. TR-1005259.

EPRI, 2001a. Mercury Removal Options for Power Plants. Palo Alto, CA. TR-1004072.

EPRI 2001b. Fate of Mercury in Combined Particulate and SO₂ Scrubbers. Palo Alto, CA. TR-1004073.

EPRI 2000a. An Assessment of Mercury Emissions from U.S. Coal-Fired Power Plants. Palo Alto, CA. TR-1000608.

EPRI 2000b. An Assessment of Hg Emissions, Transport, Fate and cycling. Palo Alto, CA. TR-1000522.

EPRI 2000c. Evaluation of Methods for Analysis of Mercury and Chlorine in Coal. Palo Alto, CA. TR-1000287.

EPRI 2000d. Technical Evaluation: Analysis of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry. Palo Alto, CA. TR-1000846.

EPRI. 2000e. Estimation Methodology for Total and Elemental Mercury Emissions from Coal-Fired Power Plants. Palo Alto, CA. TR-1001327

EPRI 2000f. Status of Continuous Emission Mercury Monitoring Systems. Palo Alto, CA. TR-1000930.

EPRI, 1999. Power Plant Validation of the Mercury Speciation Sampling Method. Palo Alto, CA. TR-112588.

EPRI 1996. Mercury in the Environment, A Research Update. Palo Alto, CA. TR-107695.

Redinger, K.E. et al, *Wet FGD Mercury Control for Coal-Fired Utility Boilers*, Mercury Emissions Workshop, Scientech, Clearwater Beach, Florida, Jan 21-22, 2002 .

Seigneur, C., K. Vijayaraghavan, K. Lohman, P. Karamchandani and C. Scott, 2003. Modeling Mercury Atmospheric Deposition in the United States. CP142-03-01. Prepared for EPRI.

Tewalt, S. J., Finkelman, R. B., Toole-O'Neil, B., and Akers, D. J., 1998, Mercury Concentration in U.S. Coal (abs.) in Proceedings of the 1st Air Quality - Mercury, Trace Elements, and Particulate Matter Conference: Energy and Environmental Research Center, Dec. 1-4, 1998, Mclean, Virginia, unpaginated.

Toole-O'Neil, B. et al, Mercury Concentrations in Coal—Unraveling the Puzzle, *Fuel* 78, p. 47-54, 1999.

U.S. EPA, 1997a, *Mercury Study Report to Congress*, EPA/452/R-97/003 (NTIS PB98-124738), Office of Air Quality Planning and Standards, Research Triangle Park, NC and Office of Research and Development, Washington, DC.

U.S. EPA, 1997b, Locating And Estimating Air Emissions From Sources Of Mercury And Mercury Compounds, EPA-454/R/97-012 (NTIS PB98-117054), Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA, 1997c, Procedures For Preparing Emission Factor Documents, EPA/454/R-95-015, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

US EPA 1998. Pollutant Emissions from Generating Units - Final Report to Congress, EPA/453/R-98/004a (NTIS PB98-131774), Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. EPA, 1999, Method 1631: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry, EPA/821/R-95/027 (NTIS PB95-252433), Office of Water, Washington, DC.

U.S. EPA, 2000a, Unified Air Toxics Website: Electric Utility Steam Generating Units, Section 112 Rule Making, Office of Air Quality Planning and Standards, Research Triangle Park, NC. www.epa.gov/ttn/uatw/combust/utiltox/utoxpg.html

USEPA 2000b. Technical Memorandum, Control of Mercury Emissions from Coal-fired Electric Utility Boilers. By National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC 27711. October 25, 2000.

US EPA, 2001a. Mercury in Petroleum and Natural Gas: Estimation of Emissions from Production, Processing, and Combustion. EPA-600/R-01-066.

US EPA 2001b. MEMORANDUM, To: William Maxwell, EPA/OAQPS/ESD/CG, From: Jeffrey Cole, RTI. Subject: Updated Draft Interim Report on Data Analyses, June 19, 2001.

US EPA, 2002a. Documentation of EPA Modeling Applications (V.2.1) Using the Integrated Planning Model: 8: Fuel Assumptions. Chapter 8. EPA 430/R-02-004. March. <http://www.epa.gov/airmarkets/epa-ipm/chapter8.pdf>

USEPA 2002b. Control of Mercury Emissions from Coal-Fired Electric Utility Boilers: Interim Report Including Errata dated 3-21-02. National Risk Management Research Laboratory, Research Triangle Park, NC 27711. EPA-600/R-01-109. April 2002.

Wilhelm, S. M., 2001, Estimate of Mercury Emissions to the Atmosphere from Petroleum. *Environ, Sci. Tech.* 35, 24:4704.

3

ATMOSPHERIC MERCURY: TRANSPORT AND FATE

3.1 Introduction

Since 1996, significant advances in research on mercury atmospheric chemistry in both homogeneous and heterogeneous atmospheric environments have been made. Field measurement and laboratory analytical methods have been further developed and improved, generating a better understanding of atmospheric mercury reaction kinetics. Improved characterization of emission sources has been achieved, both in an understanding of processes, and in inventories of source strengths and locations. All of the research in these three categories contributed considerably to reducing the uncertainty in understanding mercury atmospheric fate and transport processes. This chapter summarizes the current state of understanding with regard to the atmospheric cycling of mercury, particularly transport, transformation, and deposition. The chapter is organized into four sections representing fate and transport aspects of atmospheric mercury research: 1) atmospheric transport, 2) chemical and physical transformation, 3) deposition, and 4) source-receptor modeling. The areas of scientific uncertainty and data gaps identified by recent literature are highlighted and discussed.

3.2 Atmospheric Transport

Mercury is found in the atmosphere predominantly in its elemental form, Hg(0), because of that species' lower reactivity with common atmospheric oxidants (e.g. ozone). Hg(II) has a much shorter residence time than Hg(0) because Hg(II) compounds are mostly less volatile and more water-soluble (by five to six orders of magnitude, as mercuric chloride). This results in higher wet and dry deposition rates for Hg(II). The oxidation of elemental mercury is faster in water than in air but its very low solubility limits its oxidation rate on a per-volume basis in air. Aqueous phase chemistry models of mercury show that, in the presence of clouds or fog, the most important route from Hg(0) to Hg(II) can be aqueous phase oxidation (Pleijel and Munthe 1995). Figure 3-1 indicates the atmospheric chemistry of mercury, as it is currently understood (EPRI 2000).

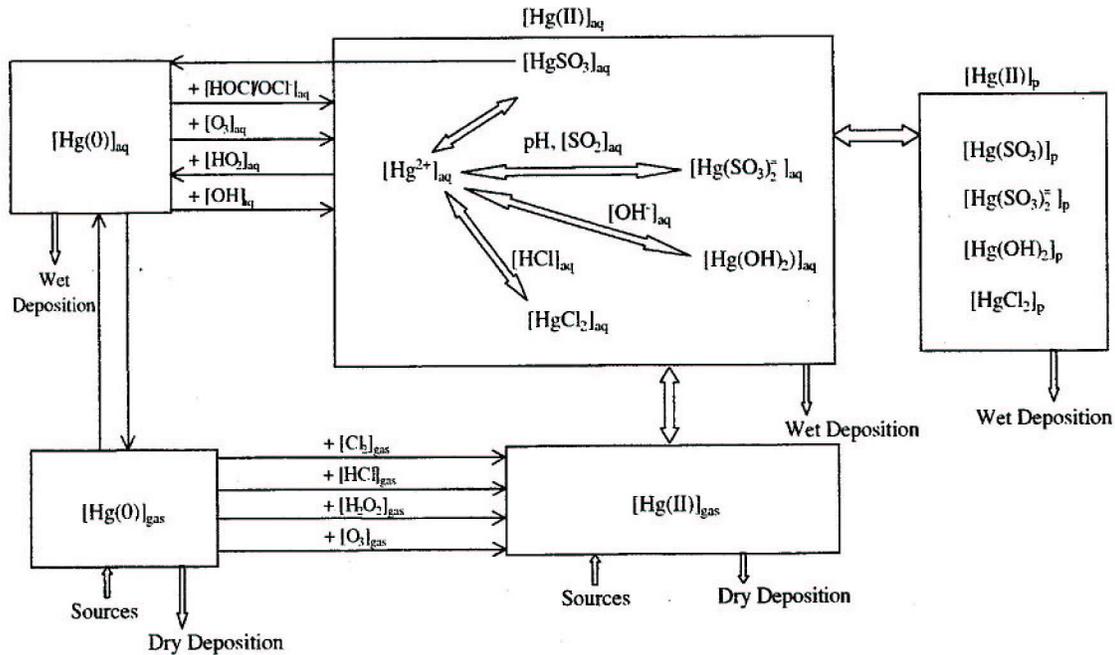


Figure 3-1
Atmospheric Chemistry of Mercury (EPRI 2000)

3.2.1 Mercury Speciation

A major advance in the study of atmospheric transport and mercury cycling was the development of methodologies for determining the speciation of atmospheric mercury. The speciation or chemical form of the released mercury varies depending on the source types and other factors. Speciation influences the atmospheric residence time of the emitted mercury. Once mercury has been liberated from either ores or fossil fuel and mineral deposits in the Earth's crust and released into the biosphere in its elemental form or as salts, it can be highly mobile, cycling between the earth's surface and the atmosphere. The chemical form of mercury strongly determines the mode and speed of transport through the various segments of the mercury cycle. Atmospheric conditions and meteorological variables are also key determinants in transformation from one mercury species to another. Soils, water bodies, and bottom sediments are thought to be the primary biosphere sinks for mercury. Under natural conditions mercury exists in six primary states:

- 1) As elemental vapor or liquid metallic mercury;
- 2) Bound in mercury-containing minerals (as salts, primarily the divalent form);
- 3) As ions in solution or bound in ionic compounds (inorganic and organic salts);

- 4) As soluble ion complexes;
- 5) As gaseous or dissolved non-ionic organic compounds; or
- 6) Bound to inorganic or organic matter (often as particles or aerosols in aqueous or gaseous media) by ionic, electrophilic, or lipophilic adsorption.

Methods have been published and now are in routine use for measuring concentrations of divalent mercury at low concentrations in ambient air (Stratton and Lindberg 1995, Feng et al. 2000, Landis et al. 2002). The detection of measurable levels of water-soluble mercury compounds (reactive gaseous mercury, RGM) in both ambient air and flue gas has significant implications for modeling the fate of airborne mercury, which was previously mischaracterized (Lindberg et al. 2000; Feng et al. 2000, Landis et al. 2002; EPRI 2002).

3.2.2 Atmospheric Transport Studies

An important question regarding atmospheric mercury on the global scale is whether concentrations and fluxes are at steady state. Based upon new methods for speciation of mercury, recent field measurements have pointed out the significance of the role of transport in the variability of atmospheric mercury levels. Over the open oceans, concentrations of Hg(0) increase from the southern hemisphere (about 1 ng/m³ at 60 degrees south) to the northern hemisphere (about 3 ng/m³ at 60 degrees north) reflecting stronger sources of mercury in the northern hemisphere, which is more industrialized and heavily populated than the southern hemisphere (Fitzgerald 1995, Lamborg et al. 1999, Temme et al., 2003). Fitzgerald (1995) estimated a range of 770-2300 Mg/y [1 Mg = 10⁶ grams = 1 metric ton] for ocean emissions. Mason and Sheu (2002) recently estimated ocean emissions at 2600 Mg/y with a significant fraction being oxidized within the marine boundary layer and rapidly deposited as Hg(II), thereby leading to a net emission flux out of the marine boundary layer of about 1500 Mg/y as Hg(0). Recent studies have demonstrated that RGM can represent a few percent of total airborne mercury in ambient air sampled far from atmospheric sources (concentrations 20-50 pg/m³), but can reach concentrations several hundred times as high and concentration ratios 4 times as high near anthropogenic point sources that can emit RGM as a primary source (Lindberg et al. 2000).

Recent modeling results using the Acid Deposition and Oxidant Model (ADOM) examined the regional transport and deposition fluxes of atmospheric mercury species in Europe (Petersen et al. 2001). The ADOM model-predicted concentration and deposition pattern of mercury species over Europe agreed with concentrations of total gaseous mercury in ambient air and total mercury in precipitation observed in data from the monitoring network on the Baltic coast. The modeled mercury concentrations in air agreed within a factor of about two with observations. Observed monthly average concentrations of mercury in precipitation from the Baltic Sea coast were reproduced by the ADOM model within a factor of 1.3. Based upon these results, it appears that the atmospheric transport and chemical scheme for mercury in the ADOM model is based on an adequate understanding of aqueous phase chemical processes that are significant on a regional scale (Petersen et al. 2001).

3.3 Chemical and Physical Transformation

Chemical and physical transformations govern the complex behavior of mercury in the atmosphere as well as mercury's phase state in the environment. Chemical form governs the phase state (whether mercury exists in the gas, liquid, or solid state), the valence state (for example, divalent Hg(II) or elemental Hg(0)), and the chemical form (inorganic versus organic compounds). Since 1996, important advances in atmospheric mercury chemistry have led to a better understanding of mercury transformation, and, therefore, of atmospheric mercury fate and transport. Table 3-1 supplies a summary of the equilibrium process or chemical reactions of atmospheric mercury along with the literature reference.

Due to the disparate atmospheric residence times of Hg(0) and Hg(II), chemical reactions enhancing oxidation of mercury in the atmosphere play a significant role in mercury atmospheric cycling. Once formed, Hg(II) compounds, which have much lower vapor pressure than does Hg(0), can deposit to terrestrial and aquatic ecosystems within a matter of days. Deposition and scavenging are the main loss mechanisms at play for Hg(II). Gas-phase reduction of Hg(II) to Hg(0) seems unlikely under typical atmospheric conditions where reductant concentrations are minimal. However, recent modeling found the aqueous-phase reduction of Hg(II) to Hg(0) to be significant (Ryaboshapko et al., 2002; Seigneur et al. 2001, 2003a,b). Additionally, EPRI (EPRI 2002) and Vijayaraghavan et al. (2002) have demonstrated and discussed, respectively, evidence for Hg(II) reduction in plumes from coal-fired power plants. And recent independent re-evaluations of the kinetics of those reactions suggest that there are still considerable uncertainties in our understanding of mercury chemistry (Seigneur et al. 2003a, 2003b).

The major oxidation pathways of atmospheric Hg(0) have been assumed to be the homogeneous gas phase reaction with ozone and hydroxyl radicals (OH) and the heterogeneous aqueous phase oxidation by ozone in fog and cloud droplets (Pleijel and Munthe 1995; Tokos et al. 1998; Lin and Pehkonen 1998a, 1999; Sommar et al. 2001). To an extent, aqueous phase oxidation by ozone in deliquesced aerosol particles is another pathway for mercury (Pirrone et al. 2000). The oxidation of Hg(0) is faster in water than in air but the very low solubility of Hg(0) limits the total oxidation rate on a per volume of air basis. Some aqueous-phase models of mercury chemistry show that the presence of clouds or fog can be the most important route to formation of Hg(II) (Pleijel and Munthe 1995). The concentration of steady-state Hg(II) in the aqueous phase may double with the inclusion of gas phase Hg(0)-ozone reactions, using the lowest conversion rate in the literature (Lin and Pehkonen 1998a). Interactions between direct scavenging of Hg(II) and oxidation of Hg(0) in the aqueous phase were shown to limit the total concentration of Hg(II) in cloud water (Xu et al. 2000). While ozone is well-recognized as a critical factor in Hg(0) oxidation, it should be noted that (1) ozone kinetics with mercury are slow relative to other potential oxidants, and (2) the ozone cycle produces ozone and other precursors to additional oxidants, and therefore, there may be other important oxidation routes. In remote locations where ozone concentrations are low, it was suggested that the OH radical can play a role of almost equal importance (Lin and Pehkonen 1997). Sommar et al. (2001) showed that the hydroxyl radical can oxidize elemental mercury much faster than ozone, which led to recalculated atmospheric chemical lifetime for elemental mercury of 4 to 7 months.

Table 3-1
Equilibria and reactions of atmospheric Hg (Seigneur et al. 2003b)

Equilibrium Process or Chemical Reaction	Equilibrium or Rate Parameter ^a	Reference
$\text{Hg}(0) (\text{g}) \rightleftharpoons \text{Hg}(0) (\text{aq})$	0.11 M atm^{-1}	Sanemasa, 1975; Clever et al., 1985
$\text{HgCl}_2 (\text{g}) \rightleftharpoons \text{HgCl}_2 (\text{aq})$	$1.4 \times 10^6 \text{ M atm}^{-1}$	Lindqvist and Rohde, 1985
$\text{Hg}(\text{OH})_2 (\text{g}) \rightleftharpoons \text{Hg}(\text{OH})_2 (\text{aq})$	$1.2 \times 10^4 \text{ M atm}^{-1}$	Lindqvist and Rohde, 1985
$\text{HgCl}_2 (\text{aq}) \rightleftharpoons \text{Hg}(\text{II}) + 2 \text{Cl}^-$	10^{-14} M^2	Sillen and Martell, 1964
$\text{Hg}(\text{OH})_2 (\text{aq}) \rightleftharpoons \text{Hg}(\text{II}) + 2 \text{OH}^-$	10^{-22} M^2	Sillen and Martell, 1964
$\text{Hg}(\text{II}) + \text{SO}_3^{2-} \rightleftharpoons \text{HgSO}_3$	$2.1 \times 10^{13} \text{ M}^{-1}$	van Loon et al., 2001
$\text{HgSO}_3 + \text{SO}_3^{2-} \rightleftharpoons \text{Hg}(\text{SO}_3)_2^{2-}$	$1.0 \times 10^{10} \text{ M}^{-1}$	van Loon et al., 2001
$\text{Hg}(\text{II}) (\text{aq}) \rightleftharpoons \text{Hg}(\text{II}) (\text{p})$	34 l/g	Seigneur et al., 1998
$\text{Hg}(0) (\text{g}) + \text{O}_3 (\text{g}) \longrightarrow \text{Hg}(\text{II}) (\text{g})$	$3 \times 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Hall, 1995
$\text{Hg}(0) (\text{g}) + \text{HCl} (\text{g}) \longrightarrow \text{HgCl}_2 (\text{g})$	$10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Hall and Bloom, 1993
$\text{Hg}(0) (\text{g}) + \text{H}_2\text{O}_2 (\text{g}) \longrightarrow \text{Hg}(\text{OH})_2 (\text{g})$	$8.5 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Tokos et al., 1998
$\text{Hg}(0) (\text{g}) + \text{Cl}_2 (\text{g}) \longrightarrow \text{HgCl}_2 (\text{g})$	$2.6 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ariya et al., 2002
$\text{Hg}(0) (\text{aq}) + \text{O}_3 (\text{aq}) \longrightarrow \text{Hg}(\text{II})$	$4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Munthe, 1992
$\text{Hg}(0) (\text{aq}) + \text{OH} (\text{aq}) \longrightarrow \text{Hg}(\text{II})$	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1997
$\text{HgSO}_3 (\text{aq}) \longrightarrow \text{Hg}(0) (\text{aq})$	0.0106 s^{-1}	van Loon et al., 2000
$\text{Hg}(\text{II}) (\text{aq}) + \text{HO}_2 (\text{aq}) \longrightarrow \text{Hg}(0) (\text{aq})$	$1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Pehkonen and Lin, 1998 ^b
$\text{Hg}(0) (\text{aq}) + \text{HOCl} (\text{aq}) \longrightarrow \text{Hg}(\text{II})$	$2.09 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1998
$\text{Hg}(0) (\text{aq}) + \text{OCl}^- \longrightarrow \text{Hg}(\text{II})$	$1.99 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Lin and Pehkonen, 1998

Hg(II) refers to divalent Hg species

^a The parameters are for temperatures in the range of 20 to 25°C, see references for exact temperature; temperature dependence is included in the model for the Henry's law parameter of Hg(0) and for the kinetic rate parameter of the HgSO₃ reaction.

^b This reaction is currently being re-investigated by the authors following the challenge made by Gardfeldt and Jonsson, 2003.

The capacity or potential of an atmospheric aqueous phase reaction to produce oxidized mercury species depends both on the availability of oxidants and the complexing ligands in the aqueous phase (Hedgecock and Pirrone 2001). It has been shown that reactive halogen chemistry involving chlorine (Cl_2) and bromine (Br_2) is very important in this respect (Pirrone et al. 2000, Hedgecock and Pirrone 2001, and Lindberg et al. 2002). RGM is generally assumed to be HgCl_2 , although recent research has shown the existence of gaseous $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Stratton et al. 2001), HgI_2 , and monomethylmercuric chloride (CH_3HgCl) (Schaedlich, 2002). A modeling study (Lin and Pehkonen 1998b) indicates that oxidation of $\text{Hg}(0)$ may be an important pathway contributing $\text{Hg}(\text{II})$ concentration in cloud water, especially in the nighttime marine troposphere where chlorine concentrations are high. Modeling results reported by Xu et al. (2000) demonstrated that the chlorine- $\text{Hg}(0)$ reaction was a contributor to aqueous $\text{Hg}(\text{II})$ concentrations in the night time marine troposphere. In that study, concentrations of aqueous $\text{Hg}(\text{II})$ (by reaction with ozone and chlorine) were very sensitive to chlorine concentration and pH in cloud water. Thus, recent studies indicate that the aqueous phase of mercury chemistry produces oxidized mercury dependent upon the availability of oxidants and reactive halogens including chlorine and bromine; this phenomena has been observed and modeled in a multitude of settings and is discussed further below.

3.3.1 Sea-Salt Aerosols and the Marine Boundary Layer

The role of sea-salt aerosol in the oxidation of $\text{Hg}(0)$ in the marine boundary layer (MBL) has been a recent focus of atmospheric mercury research. The formation of reactive halogen species in sea-salt particles has significant effects upon the chemistry of ozone, sulfur dioxide, and mercury in the MBL (Anastasio et al. 2002). In sea-salt aerosols, there is an order of magnitude difference between the chloride ion concentration range usually found in cloud and fog droplets (0.013-2.7 mM) and that in sea-salt aerosol (5.4 M) (Lin and Pehkonen 1998b and references therein as cited by Hedgecock and Pirrone, 2001). Sea-salt aerosol, unlike fog, is continuously present in the MBL, as a result of continuous production and deposition. The humidity of the MBL and the hygroscopicity of salt are such that these particles are solution droplets and consequently provide a small but constantly available atmospheric aqueous phase for the oxidation of $\text{Hg}(0)$. Sea-salt aerosol scavenges $\text{Hg}(0)$ from the gas phase and cycles it via re-release of HgCl_2 . In coastal areas where measurements of RGM are available, the cycling of $\text{Hg}(\text{II})$ by the sea-salt aerosol may account for up to 20 percent of the total (Hedgecock and Pirrone 2001).

Anastasio et al. (2002) provided experimental evidence that the hydroxyl radical-induced oxidation of bromide involving oxidized chloride leads to a pH-dependent release of Br_2 from sea-salt particles. Their model of sea-salt aerosol indicates the hydroxyl radical could be a significant source of Br_2 in the marine boundary layer. This is important because Br and other halides, when reacting with ozone, contribute to the formation of RGM in the Arctic. Recently discovered mercury depletion phenomena in the Arctic are discussed later in this section. Lastly, it is important to note that these studies show the importance of halogens in mercury oxidation near oceans. However, over the continents, halogen concentrations in the lower troposphere are much lower and the likelihood of halogens acting as a major oxidizer for mercury is unlikely.

3.3.2 Mercury Depletion Events

Schroeder et al. (1998) provided the first evidence that conditions may exist in the upper Arctic following polar sunrise that promote mercury depletion events (MDEs), that is, depletion of airborne Hg(0) via oxidation to Hg(II) and subsequent deposition. Prior to polar sunrise, TGM concentrations and ozone levels showed normal variation and ranged between 1 and 2 ng/m³ and 30-50 parts per billion (ppb), respectively. During the three-month period after polar sunrise, TGM levels frequently dropped well below 1 ng/m³, and those of ozone were often less than 10 ppb and sometimes below the detection level of the ozone analyzer. Springtime conversion of mercury vapor was found to produce one or more mercury species with much shorter atmospheric times than Hg(0).

Between 1998 and 2001, as part of the Barrow Arctic Mercury Study, Lindberg et al. (2002) completed several sampling campaigns to characterize mercury species and their ultimate fate to better understand MDEs. Their data were the first evidence that MDEs could be a widespread phenomenon of Arctic dawn and that RGM only appears at significant levels when Hg(0) is depleted. These data show that rapid, photochemically driven oxidation of boundary layer Hg(0) after polar sunrise, probably by reactive halogens, creates RGM in the remote Arctic troposphere. Production of RGM may be attributed to the same photochemically active halogen species, particularly bromine (Br), involved in ozone destruction, suggesting that the overall process is heterogeneous. Gaseous and aerosol Br exhibited strong seasonal cycles at Barrow. Peak RGM production and Hg(0) depletion generally occurred at midday under maximum UV. Meteorological factors strongly influenced extreme levels of RGM.

A simple predictive model demonstrated that boundary layer entrainment rates and deposition velocities explained about 70% and 80% of the measured variance in airborne Hg(0) and RGM, respectively (Lindberg et al. 2002). The highest RGM concentrations consistently occurred during periods of reduced wind and maximum UV-B. Elevated RGM also coincided with periods characterized by increased levels of BrO. During one elevated BrO event, RGM reached 900-950 pg/m³ (relative to less than 100 pg/m³ in background areas). RGM was formed continuously as long as ozone and reactive bromine are present during polar spring. These data suggest that approximately 30-40% of depleted Hg(0) appears as airborne RGM and the remainder is deposited to the snow surface directly as RGM and/or is scavenged by fine aerosols. Arctic MDEs appear to be recent phenomena, resulting from changes in Arctic climate that have increased atmospheric transport of photo-oxidants and production of reactive halogens (Br/Cl) in the Arctic. If this phenomenon results in higher yearly mercury deposition rates in the Polar Regions than in other regions of the world, this could mean that the Polar Regions serve as “mercury cold traps” collecting a disproportionately high part of the global mercury emissions (UNEP 2002).

These studies taken together suggest a potential relationship between mercury, ozone depletion chemistry and increased UV/ambient temperatures in the polar regions. An important future area of research is to explore whether there is a consistent chemical process that can explain increases in RGM to trends in increased ambient temperatures/UV levels and also to trends in ozone depletion chemistry. Research is needed to examine the relationship between ozone depleting species and increasing RGM production in the arctic and Antarctic regions, perhaps with a look at RGM fluxes in mid-latitude regions where, for example, BrO and levels of atomic bromine are significant.

3.3.3 Meteorological Variables

In addition to tropospheric oxidants, other meteorological and air quality variables have been linked to atmospheric mercury chemistry in analyses of measurement data from Canada, Japan, and Baltic Sea coastal sites. Poissant (2000) reported TGM and ozone concentrations measured at four stations along the St. Lawrence River in Quebec, Canada in 1998. At all four Canadian sites, TGM concentrations were maximum in winter and minimum in summer. Diurnal variations were site-specific. TGM concentration and air temperature were not correlated at these four Canadian sites.

Tomiyasu et al. (2000) measured atmospheric vapor phase mercury daily for one year in Kagoshima City, Japan, to estimate the influence of mercury emissions from Sakurajima volcano. Mercury concentrations varied by season with high concentrations in summer and autumn, and lower concentrations found in winter. When winds were not blowing from the direction of the volcano, background TGM levels were temperature-dependent, and showed a positive correlation. The impact of fumarolic activity of the volcano on mercury concentrations in ambient air in the city was evident in the disappearance of temperature dependency when winds were from the direction of the volcano.

TGM was significantly correlated with local meteorological parameters at two Baltic Sea coastal stations (Urba et al., 2000). TGM was positively correlated with temperature, solar radiation, and wind speed. On a longer time scale, TGM correlated better with temperature than with solar radiation, whereas on a shorter scale, the correlation was better with global radiation, and even better with UV radiation than with the temperature. Very slight but clearly resolved diurnal variability was detected for both stations. The correlation with meteorological data and diurnal variability led to the conclusion that the sea surface acted as a local mercury source controlled by temperature, solar radiation, and (in all likelihood) wind.

3.4 Deposition

Since 1996, there have been significant advances in the understanding of the deposition of different mercury species, historical trends of atmospheric mercury deposition, factors and processes contributing to dry and wet mercury deposition, and the fate of mercury as it deposits to ecosystems. In addition, progress has been made in allocating mercury depositional fluxes to sources at different spatial scales (i.e. local vs. global). This section summarizes recent findings pertaining to atmospheric mercury deposition.

Wet deposition is understood to be the primary mechanism for delivering mercury from the atmosphere to aquatic and terrestrial receptors; however, in regions of lower precipitation, gaseous and particle mercury dry deposition fluxes may be relatively more significant. As discussed in Pirrone et al. (2000) and cited by Forlano et al. (2000), according to aqueous chemistry modeling results, the amount of Hg(II) deposited with particles depends on the nature of the particles and the relative humidity. In areas subject to prolonged dry periods and especially in such regions with large bodies of water, dry deposition via the atmospheric aerosol can be important (Forlano et al. 2000).

Because of its higher water solubility and reactivity, Hg(II) exhibits a far higher dry deposition rate and wet deposition washout coefficient than does Hg(0) and may contribute to local ecosystem loading far in excess of its contribution to the atmospheric burden (Lindberg et al. 2000). Lacking direct measurements of dry deposition, researchers have primarily relied on the assumption that the dry deposition rate of Hg(II) is comparable to that of nitric acid (0.06-5 cm/sec; Seinfeld 1986.). Hg(II) is estimated to dry deposit 100 times as fast as and is 10^5 times as water soluble as Hg(0) (Prestbo et al. 1999 as cited by Poissant 2000).

A sensitivity analysis (Xu et al. 2000) indicated that mercury deposition was sensitive to ambient concentrations of ozone and soot particles due to their direct impact on the aqueous chemical reactions. Tan et al. (2000) measured concentrations of mercury species in air samples from industrial areas of China, subject to emissions from uncontrolled coal combustion sources. Tan et al. attributed relatively high proportions of monomethylmercury in TGM measurements to high SO₂ concentrations in air from coal combustion enhancing the methylation reaction rate of mercury in the atmosphere.

3.4.1 Temporal and Spatial Aspects

Studies involving direct measurement of atmospheric mercury deposition and use of models in data interpretation have led to better understanding of spatial and temporal trends of modern deposition. According to Pirrone et al. (2001) as cited in UNEP (2002), since long-range transport of mercury was observed in the late seventies in Sweden (Brosset 1982), long-term monitoring activities in Scandinavia have shown a clear gradient in wet deposition of mercury with elevated mercury fluxes in the southwestern part of the region; i.e. closer to the main emission sources in Central Europe (Iverfeldt 1991; Munthe et al. 2001a).

Similar patterns have been shown in North America. According to model results, in and around most industrial regions (Europe, North America, southeastern China) the net deposition rate of mercury is likely to have increased by a factor of 2-10 during the past 200 years (Bergan et al. 1999). The magnitude of the direct man-made mercury emissions into the atmosphere are likely to be at least 30% of the magnitude of the natural emissions, implying that the global-average deposition rate has increased by at least 50% since pre-industrial times. Assuming furthermore that there is a re-emission of previously deposited mercury of man-made origin, this increase may be as large as a factor of three (Bergan et al. 1999).

Coring studies of ice and sediments have enabled scientists to evaluate spatial and temporal trends of historic atmospheric mercury deposition. Schuster et al. (2002) measured mercury in ice core samples collected from the Upper Fremont Glacier (UFG), Wyoming. Although the resolution of the UFG ice cores is considered low by polar ice-core research standards, it provides a chronology of sufficient resolution over its 270-year record to support conclusions made about historical changes in mercury deposition. The increase in mercury deposition rates from pre-industrial times to the mid-1980s, as indicated by the ice cores, is up to 10 times as high as increases determined from sediment cores and precipitation. Since the industrial maximum, mercury concentrations in the UFG ice core have declined from the 20-fold increase since pre-industrial times to an 11-fold increase during the 1990s. The declining trends during the last 10 years are consistent with the last 7 years of precipitation data (USEPA 1997 as cited by Schuster et al. 2002).

Lamborg et al. (2002) used peat bog and lake sediments core to estimate the historical fluxes of mercury deposition in the northern and southern hemispheres. They estimated that current global emissions were about four times pre-industrial emissions.

A nearly 50 percent decline in mercury accumulation in the top of the ice core compares very favorably in magnitude with independent estimates of recent global declines of industrial mercury production and use (Engstrom and Swain 1997 and Pacyna and Pacyna 2002). More research is needed to address how ice-core response to changes global atmospheric cycling and deposition may be amplified for snow. In addition, more research is needed to address effects of altitude on deposition and reemission of mercury in snowpacks due to photochemical redox reactions.

3.4.2 Tracking Deposition to Ecosystems

Researchers have tracked atmospheric deposition of mercury as it reaches ground level and enters ecosystems. In forested ecosystems, vegetation appears to be influential in delivering and storing mercury deposited from the atmosphere. As part of the Mercury Experiment to Assess Atmospheric Loadings in Canada and the United States (METAALICUS) program, deposition of atmospheric mercury to boreal ecosystems within the Experimental Lakes Area of northwestern Ontario, Canada is under investigation. St. Louis et al. (2001) measured flux of methylmercury and TGM in direct wet deposition and in throughfall and litterfall of forested areas. The estimated fluxes of methylmercury and TGM in throughfall plus litterfall below the forest canopy were two and three times as great as annual fluxes by direct wet deposition of methylmercury and TGM. Almost all of the increased flux of methylmercury and TGM under the forest canopy occurred as litterfall. In another METAALICUS study, Hintelmann et al. (2002) investigated the dynamics of mercury newly deposited onto a terrestrial ecosystem by spraying an enriched stable isotope of mercury (^{202}Hg) onto a boreal forest catchment. Results suggest that upland runoff may respond very slowly to changes in deposition. In fact, mercury bound to vegetation may only become incorporated into the larger soil pool of mercury when the vegetation dies and decomposes (Lindberg 1996 and St. Louis et al. 2001 as cited by Hintelmann et al. 2002). In an Alaskan polar ecosystem, Lindberg et al. (2002) investigated the fate of RGM and dynamics of mercury in snow following polar sunrise. Their data suggest that approximately 30-40% of depleted $\text{Hg}(0)$ appears as airborne RGM and the remainder is deposited to the snow surface directly as RGM and/or is scavenged by fine aerosols.

These studies indicate that a portion of mercury in snow evaded back to the atmosphere and was influenced by melting processes. Total mercury concentrations in runoff from snowmelt indicated that a portion of the snowpack mercury enters the local ecosystem during snowmelt.

3.4.3 Emission Reductions and Deposition

A prevailing question regarding atmospheric deposition is whether significant reductions in anthropogenic point source emissions will result in notable decreases in mercury deposition and subsequent decreases in bioaccumulation of mercury in fish and other biota, and within what time period. Changes in deposition are expected to be most responsive to source changes, with ensuing changes in receiving waters and in fish less well understood. According to model results

presented by Xu et al. (2000), deposition rates were largely influenced by surface re-emission and regional or global scale transport, and consequently rates were less sensitive to emissions from point sources. Thus, moderate reduction in point source emission may lead to little change in the total wet deposition (Xu et al. 2000). The Scandinavian studies revealed a significant decrease in wet deposition, approximately 50%, after a reduction in mercury emissions around 1990 (Iverfeldt et al. 1995; Munthe et al. 2001). Complicating the linkage between source changes, deposition changes, and biota reductions is the concomitant change in sulfate deposition, which may impact the methylation rate in sulfur-limited waterways.

Recent research suggests that, despite the significant decreases in mercury emissions since 1991, the anthropogenic influence on atmospheric mercury levels is still significant in Europe compared to pre-industrial times (Pirrone et al. 2000 and Munthe et al. 2001b as cited by UNEP 2002). The use of atmospheric mercury models is integral to evaluating how deposition will change as a function of mercury emission reduction scenarios, and in tracing both current concentrations and potential changes in the future to sources and alterations to those sources. Since no benign tracer substance has been found which can mimic the complex biogeochemical cycling of mercury between source and ultimate receptor, these models are essential to a full understanding of the substance and its fate. The status of atmospheric mercury modeling is discussed next.

3.5 Source-Receptor Modeling

Atmospheric mercury fate and transport models are critical to assess source-receptor relationships between mercury emission sources and impacts of deposition to aquatic and terrestrial receptors. Computer models are typically used for assessing source-receptor relationships such as the impacts of power plant emissions on human health and ecosystem viability, evaluating mercury cycling on local to global scales, investigating contributions from different sources, and predicting effects of mercury control strategies on receptors. Since EPRI's earlier report on mercury in the environment (EPRI 1996), atmospheric mercury modeling has become more sophisticated due to advances in data collection techniques, better resolution of mercury emission and deposition data, refinement of kinetic reactions and corresponding rates, and a more precise understanding of the factors affecting mercury fate and transport. Researchers have continued to develop and apply models for investigating mercury at local, regional, and global scales.

Modeling studies have combined atmospheric and watershed models to evaluate atmospheric mercury deposition into lakes (Lohman et al., 2000a, 2000b). UNEP (2002) prepared a brief review and chronology of atmospheric mercury fate and transport modeling studies, evaluations, and workshops between 1996 and 2001. EPRI (2002) identified databases as well as data gaps and areas of uncertainty that are critical to modeling. In this section, applications of atmospheric models of different scales and levels of complexity since 1996 are presented. The development of one particular modeling system, in which a global chemical transport model (CTM) and a continental model are used in sequence, is discussed.

Lastly, recommendations for future work are provided aimed at filling data gaps and resolving areas of uncertainty for atmospheric mercury models.

Studies suggest that the chemical behavior of mercury in the atmosphere, specifically in cloud and fog water, is rather involved (Pleijel and Munthe 1995; Lin and Pehkonen 1999 as cited by Bullock 2000) and may be too complex for Lagrangian parcel modeling to provide scientifically defensible assessment of the sources or source types responsible for observed mercury deposition in precipitation (Bullock 2000). Atmospheric modeling systems employing more complex Eulerian computational frameworks are being developed (Pai et al. 1997, Petersen et al. 1998 as cited by Bullock 2000). These models were initially used to identify atmospheric processes most critical to site-specific wet and dry deposition.

3.5.1 Global models

A climatological transport model, MOGUNTIA, was used to simulate the global distribution of Hg(0) and Hg(II) compounds (Bergan et al. 1999). MOGUNTIA is a 3-D global tracer Eulerian transport model. The main purpose for using the model was to see whether present estimates of sources, sinks, and atmospheric transformation processes are consistent with observed concentrations of mercury in air, in precipitation, and in sediment records. Particularly, the authors wanted to estimate the man-made impact on mercury levels in different parts of the world. Recent observations of a large decrease of TGM over the Atlantic during the 1990s were hard to explain with the model using current estimates of sources, transformation, and sinks. These data seem to indicate that the relative magnitude of man-made emissions has been underestimated or that large variations occur in the natural part of the mercury cycle (Bergan et al. 1999). Another global model, the CTM described in detail by Shia et al. (1999) and Seigneur et al. (2001), was used in conjunction with the EPRI Trace Elements Analysis Model (TEAM) to evaluate the relative contributions of local, regional, and global sources of mercury to deposition across the U.S. and individual regions and states. Results suggest that reducing mercury deposition will require global strategies, particularly in areas where deposition is predominantly influenced by global background sources (AER 2003a; Seigneur et al., 2003c). Further discussion of the combined CTM/TEAM application is provided below.

3.5.1.1 Case Study: TEAM and the Global Chemical Transport Model

The potential effects of atmospheric mercury emissions may range from local impacts such as wet deposition of Hg(II) and Hg_p and dry deposition of Hg(II) to global impacts such as long-range transport of Hg(0) and, under dry conditions, transport of Hg_p. Because of the long-range transport potential of mercury species, it is essential to assess the relative importance of local, regional, continental, and global sources of Hg that may produce deposition in sensitive watersheds. This information is necessary to develop effective emission control strategies (Seigneur et al. 2003b). Accomplishing this requires both global and regional scale processes to be simulated together, which is difficult due to the need to integrate regional and global scale spatial resolutions.

The use of a multiscale modeling system has been applied to investigate the contributions of such sources to deposition in the U.S. and smaller geographic regions within the U.S. The modeling system includes a global CTM and a nested continental Eulerian model (TEAM) to simulate transport, transformations, and deposition of mercury (Seigneur et al. 2001, 2003c). The global CTM provides the boundary conditions (i.e. upwind mercury concentrations) for TEAM. The global CTM is run until steady state is achieved between emissions of mercury into the

atmosphere and deposition to the earth. Emissions and atmospheric mercury chemistry are the same in both models. The modeling system was applied to estimate the relative contributions of regional and global sources to mercury deposition across the continental U.S. (EPRI, 2000; Seigneur et al. 2003a), in New York State (Seigneur et al. 2003b), and in Wisconsin (Vijayaraghavan et al., 2002). The remainder of this section provides an overview of the global CTM and TEAM model formulations and presents the approach and major findings of a recent application of the modeling system (Seigneur et al. 2003a).

The formulation of the global mercury model is described in detail by Shia et al. (1999) and Seigneur et al. (2001). The model is based on the three-dimensional CTM developed at the Goddard Institute for Space Studies (GISS), Harvard University, and the University of California at Irvine. The 3-D model provides a horizontal resolution of 8° latitude and 10° longitude and a vertical resolution of nine layers ranging from the Earth's surface to the lower stratosphere. Seven layers are in the troposphere (between the surface and about 12 km altitude), and two layers are in the stratosphere (between 12 km and 30 km altitude). Transport processes are driven by the wind fields and convection statistics calculated every 4 hours (for 1 year) by the GISS general circulation model (Hansen et al., 1983). This 1-year data set is used repeatedly for multiyear simulations until steady state is achieved.

The mercury transformation processes include gas-phase transformations, gas/droplet equilibria, ionic equilibria, solution/particle adsorption equilibrium, and aqueous-phase transformations as described above. Since its initial application, atmospheric mercury chemistry and depositional processes simulated by the model have undergone a series of modifications (EPRI 2000, Seigneur et al. 2003a, 2003b, 2003c). A summary of the current understanding of mercury chemical processes is shown in Table 3-1. The gas-phase transformations include the oxidation of Hg(0) to Hg(II) by ozone, hydrogen chloride, hydrogen peroxide, and molecular chlorine. Aqueous oxidation of Hg(0) is dominated by the chlorine nighttime reaction over the oceans but by the ozone reaction over land. The aqueous-phase chemistry includes the reduction of Hg(II) to Hg(0) and is primarily governed by its reaction with hydroperoxy radicals. Adsorption of Hg(II) species on atmospheric particulate matter (PM) is simulated using an adsorption coefficient ($K = 34 \text{ l/g}$) (Seigneur et al. 1998). Chemical species reacting with mercury that are spatially and temporally varying include ozone, SO_2 , OH, HO_2 , and H_2O_2 . Concentrations of HCl and with PM are spatially and temporally constant.

Dry deposition rates were varied by species (Seigneur et al. 2003a). Wet deposition is simulated only for Hg(II) and Hg_p since Hg(0) is relatively insoluble. The wet deposition flux is calculated as the product of the cloud droplet concentration of the mercury species and the precipitation amount. Scavenging of these mercury species by rain below the cloud (washout) is treated as a transient process using scavenging coefficients that depend on precipitation intensity as described by Seigneur et al. (2001).

The formulation of the continental CTM, TEAM, was described in detail by EPRI (1996), Pai et al. (1997) and Seigneur et al. (2001). In its application to mercury fate and transport over North America, the horizontal grid resolution is 100 km, and the vertical resolution consists of six layers from the surface to 6 km altitude with finer resolution near the surface. Transport processes include three dimensional mean wind flow and dispersion by atmospheric turbulence. The module that simulates the chemical and physical transformations of mercury is the same

module as that used in the global model. Three mercury species, Hg(0), Hg(II), and Hg_p are simulated.

Dry deposition is simulated using the resistance transfer approach. Since there are no direct measurement of the dry deposition rates for Hg(0), Hg(II), and Hg_p and rates simulated in models are based on best professional judgment (EPRI 2000). The deposition process is simulated as a series of three mass transfer steps: (1) turbulent transport from the bulk atmosphere to near the surface, (2) diffusion through a laminar layer near the surface, and (3) uptake of the gas or particle by the surface. For Hg(0), background emissions and dry deposition are assumed to balance each other over North America. Treatment of Hg(II) dry deposition rate in TEAM is consistent with the global CTM. Dry deposition velocities calculated by TEAM for Hg(II) and Hg_p over various surface types (forest, agricultural land, and water) are those used by Pai et al. (1997) with the updates described by Seigneur et al. (2001).

The multiscale modeling system consisting of the global CTM and TEAM was used to analyze regional and global source contributions to mercury deposition in the contiguous U.S. (Seigneur et al. 2003a). The analysis consisted of a base case scenario in which simulated deposition results based on a 1998 mercury emissions inventory were evaluated and compared with observed data. In addition, sensitivity simulations were run corresponding to mercury emission reduction scenarios. Global simulations were run to estimate relative impacts of global anthropogenic and natural sources on mercury deposition in the U.S. Source-receptor relationships between U.S. power plant emission and mercury deposition at selected locations within the contiguous U.S. were also developed.

The emission inventory used in this study was based on that of Seigneur et al. (2001) and consists of anthropogenic and background mercury emissions into the atmosphere. The inventory of anthropogenic emissions was changed to reflect updates to U.S. anthropogenic emission data (Seigneur et al. 2003a). Important changes were the use of an emission inventory for U.S. coal-fired power plants (EPRI 2002), the addition of a Wisconsin chloralkali plant, and the inclusion of mobile sources (i.e. passenger vehicles). Total U.S. anthropogenic emissions were calculated to be 133 Mg/yr —approximately six percent of the total global anthropogenic emissions (2127 Mg/yr) simulated in the model. Background emissions consist of natural emissions and re-emissions of previously deposited mercury. Since it is not possible to differentiate between natural and anthropogenic mercury after it has been emitted, re-emissions must necessarily reflect both classes of re-emitted mercury (Seigneur et al. 2003a). Background emissions are assumed to amount to 2000 Mg/y from the oceans and 2260 Mg/y from land. These emission rates are commensurate with those used in previous modeling studies (Bergan et al., 1999; Seigneur et al., 2001).

Natural emissions consist of three source categories: oceans, mercury ore deposits on land, and volcanoes. Emissions from land deposits were estimated at 500 Mg/y. Annual volcano emissions were estimated to be 90-112 Mg/y on average (Ebinghaus et al., 1999; Nriagu and Becker, 2003). Natural emissions were estimated at 1064 Mg/y. Natural emissions from oceans amount to 474 Mg/y. Re-emissions constitute the remainder of the background emissions, comprised of 1525 Mg/y from the oceans and 1670 Mg/y from land. The amount of mercury re-emitted corresponds to about 50% of the amount of mercury deposited on average. (A comparison of mercury re-emissions estimates will be possible once analysis of the data from the METAALICUS study is completed.) These re-emissions are allocated to both natural and

anthropogenic emissions, proportionately to those emissions. Table 3-2 presents the inventory of global anthropogenic and background emissions used in the model for North America. As shown, total global emissions are assumed to be 6386 Mg/yr. Figure 3-2 presents a schematic summary of the global mercury budget used in the modeling system.

Table 3-2
Anthropogenic Hg emissions in the North American domain for modeling. (Mg/y)
 (Seigneur et al 2003b).

Source Category	United States	Southern Canada	Northern Mexico	Total
Electric utilities	41.5	1.3	9.9	52.7
Waste incineration	28.8	3.4	(a)	32.2
Residential, commercial, and industrial coal burning	12.8	(a)	(a)	12.8
Mining	6.4	0.3	(a)	6.7
Chlor-alkali facilities	6.7	.05	(a)	6.8
Mobile sources	6.2	(a)	(a)	6.2
Other sources	30.6	9.6	23.6	63.8
Total	133.0	14.7	33.5	181.2

(a) included under "other sources"

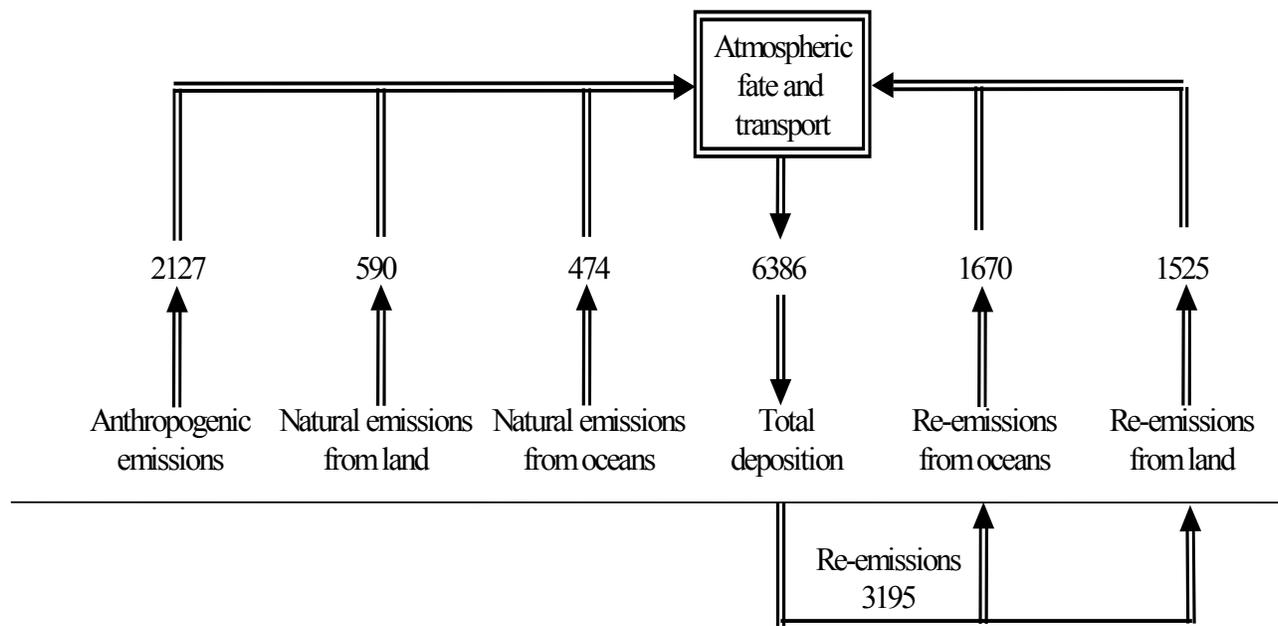


Figure 3-2
Schematic summary of the global atmospheric mercury cycle (annual emission and deposition rates are in Mg/y). (Seigneur et al. 2003a)

Using the emissions inventory described previously, the modeling system was devised so that output from the global CTM was used as boundary conditions for the west coast of the U.S. and at the borders with Mexico and Canada. Model performance was judged to be satisfactory at global and continental scales (Seigneur et al. 2003a). In the global CTM, an average atmospheric lifetime of mercury was calculated to be 1.2 years. The model was shown to reproduce well the north-south latitudinal concentration gradients and vertical gradients, as well as background speciated mercury concentrations (Seigneur et al. 2003a). The surface Hg(0) concentrations display a strong latitudinal gradient with background concentrations mostly in the range of 1.2 to 1.6 ng/m³ in the southern hemisphere and mostly in the range of 1.6 to 1.9 ng/m³ in the northern hemisphere. This latitudinal gradient is consistent with data from Slemr et al. (1992). Concentrations above 1.9 ng/m³ are simulated over the large source areas of eastern Europe and eastern Asia. In the southern hemisphere, South Africa shows as a large source area with Hg(0) concentrations ranging up to 1.7 ng/m³. The Hg(II) concentrations show stronger spatial variations than the Hg(0) concentrations due to their stronger correlations with source areas, such as South Africa, North America, Europe and Asia (Seigneur et al. 2003a). The large contribution from South Africa is not surprising given the local volume of coal combustion for power generation and the frequency of grassland fires.

The highest Hg(II) concentrations (in the range of 200 to 300 pg/m³) are simulated over eastern China, due to the fact that Asia accounts for half of the global anthropogenic emissions. The Hg_p concentrations are solely of anthropogenic origin and, therefore, they provide footprints of the major source areas. Concentrations of Hg_p in eastern Asia are in the range of 100 to 200 pg/m³. Table 3-3 presents a comparison of simulated mercury concentrations derived from the model with background concentrations measured on the west coast of Ireland. Model-simulated concentrations of Hg(0) and Hg(II) are within the range of the measurements. The concentrations of Hg_p are lower than the measured range, possibly because the model does not simulate the adsorption of Hg(II) on atmospheric particulate matter in the absence of clouds (Seigneur et al. 2003a).

Table 3-3
Comparison of simulated mercury concentrations with ambient background data,
Mace Ireland, September 1995. (Seigneur et al. 2003b)

	Simulated	Measured ^(a)
Hg(0) (ng/m ³)	1.6	1.44 to 3.0
Hg(II) (pg/m ³)	27	14 to 94
Hg _p (pg/m ³)	3	5 to 115

(a) Ebinghaus et al., 1999a

TEAM was then run using the U.S. emissions inventory and output from the global CTM. According to model results, Hg(0) concentrations are higher in the eastern United States than in the western United States except for a few isolated grid cells in the West showing concentrations above 1.7 ng/m³. Maximum Hg(0) concentrations reach 2.9 ng/m³. Hg(II) concentrations are mostly below 100 pg/m³, except for a few grid cells that show concentrations in the range of 100 to 191 pg/m³. In northern California, a single high Hg(II) concentration occurrence corresponds to the Geysers geothermal area. High Hg(II) concentrations have been measured in that area.

However, Hg(II) may not actually be directly emitted as Hg(II) but may result from rapid conversion of emitted Hg(0) to Hg(II) in the geothermal flue gases (Gustin 2002). Hg_p concentrations reach 120 pg/m³ in some grid cells but are primarily below 50 pg/m³.

The modeled wet deposition fluxes are highest on the west coast and in the eastern U.S. The high wet deposition fluxes on the west coast are due to the high Hg(II) concentrations at the upwind boundary as well as high precipitation along the mountain ranges of the Cascades and Sierra Nevada. The high wet deposition fluxes in the eastern U.S. result from the influence of local/regional sources (e.g., in the Northeast) or high precipitation (e.g., Florida). Dry deposition fluxes are highest in the northeastern United States. High dry deposition fluxes in the Northeast result from the impacts of local/regional emission sources. The total deposition fluxes reflect the characteristics mentioned above for the wet and dry deposition fluxes. The highest total deposition flux (100 µg/m²-y) occurs near Baltimore and is likely a result of deposition of mercury emitted from local waste incineration prior to imposition of MACT controls for mercury from that source category. For North America, modeled wet deposition fluxes of mercury were compared to observations available from the Mercury Deposition Network (MDN). These results show slightly improved model performance compared to previous modeling efforts (Seigneur et al., 2001, 2003b).

The continental model was applied to simulate how various power plant mercury emission reduction scenarios recently proposed publicly might affect mercury deposition within the contiguous United States. The overall reductions in coal-fired power plant mercury emissions from the base case range from 16% to 83% for five scenarios. These values correspond to reductions in mercury emissions based on the coal content of mercury of 49% to 90% for the same five scenarios. The emissions of the continental North American domain were modified accordingly and a TEAM simulation was conducted for each scenario. Reductions in mercury deposition from the base case were found to be less than 10% over most of the U.S, averaging . 1.2% to 6.2% for the five scenarios (Seigneur et al. 2003d). Table 3-4 indicates changes in wet, dry and total mercury deposition fluxes over the contiguous United States for the five power plant emission scenarios (in percent difference in mercury deposition from the base case).

Table 3-4
Changes in wet, dry and total mercury deposition fluxes over the contiguous United States for five power plant emission scenarios in Seigneur 2003c. (% difference from the base case).

Scenario	% Mercury Emissions Reductions	Percentage Change in Mercury Deposition from Base Case		
		Wet Deposition	Dry Deposition	Total Deposition
1	47%	-2.6%	-5.4%	-3.4%
2	30%	-2.0%	-4.4%	-2.7%
3	16%	-0.9%	-2.1%	-1.2%
4	75%	-4.5%	-9.1%	-5.9%
5	83%	-4.7%	-9.8%	-6.2%

The poor correlation obtained in the regional simulation results to a large extent from the fact that the model predicts an increasing gradient in Hg wet deposition from Minnesota to Pennsylvania, which is not observed in the monitoring network as shown in Figure 3-3. The use of a finer spatial resolution (20 km) improves model performance in Minnesota and Wisconsin (upwind of major Hg emission sources) but degrades model performance in Pennsylvania (downwind of major Hg emission sources). These results suggest the hypothesis that some key chemical transformations for local mercury emissions are likely missing in current regional models (Seigneur et al. 2003c).

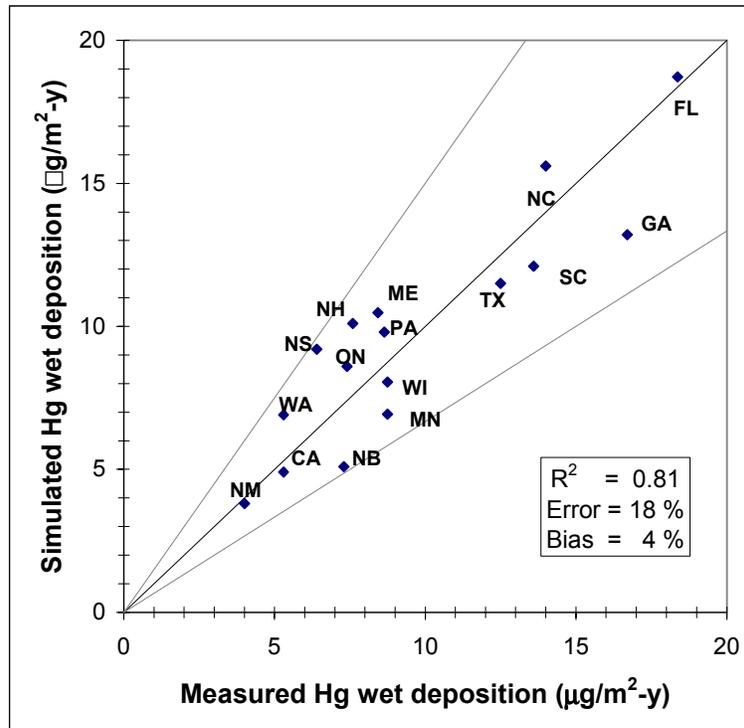


Figure 3-3
Comparison of simulated and observed mercury wet deposition fluxes for 1998 by state/province. (Seigneur et al. 2003a)

Seigneur et al. (2003c) have shown that TEAM overestimates mercury wet deposition in this area, in a geographical swath east and northeast of the Ohio River valley. As discussed by Vijayaraghavan et al. (2002), there is some evidence that reduction of Hg(II) to Hg(0) may occur in power plant plumes, which is not currently accounted for by models such as TEAM. This could explain, at least partially, the reason for higher modeled results for Pennsylvania since the Hg(0) is less likely to be deposited than the Hg(II). If this is the case, a larger fraction of power plant emissions would enter the global background rather than depositing closer to the sources involved, and the decreases in mercury deposition simulated in the five scenarios would represent upper bounds (Seigneur et al. 2003a).

The global and continental models were used in combination to investigate the relative contributions of major source categories (anthropogenic emissions from individual continents and natural emissions from land and the oceans) to deposition in the U.S. Twenty receptor areas

were selected including nineteen individual grid cells and the entire contiguous United States. The contribution of North American sources to deposition ranged from 9 to 86%. Asia showed the largest contribution among other continents with values ranging from 5 to 32%. Natural emissions contributed from 3 to 38%. With the understanding that the model overpredicts mercury wet deposition in the northeastern U.S., North American contribution estimates should be seen as upper bounds. The estimated contribution of North American emissions to mercury deposition in the Everglades National Park, Florida is 17%; this value is significantly different from previous estimates that ranged from 30 to 70% (Dvonch et al., 1999; Guentzel et al., 2001), thereby emphasizing that significant uncertainties remain in understanding of mercury atmospheric fate and transport. These results also suggest that reducing mercury deposition will require a global strategy, particularly for areas such as the Everglades where atmospheric deposition of mercury is dominated by the global background (Seigneur et al. 2003a).

The contribution of mercury emissions from various source areas to mercury deposition at a given receptor depends on a myriad of factors including the speciation of these emissions, the location of the source area with respect to the receptor area, and the atmospheric conditions (i.e., meteorology, chemistry, and deposition processes) that affect air parcels transported from the source area to the receptor area. Therefore, a reduction of mercury emissions will have different effects on a given receptor area depending on which source areas are affected. Trading of mercury emissions among source areas may take such considerations into account. Thus, it is of interest to develop quantitative source-receptor relationships among major source areas and receptor areas.

A simplified version of the continental model (response-surface model) was developed to represent the impacts of fifteen power plant source areas on twenty receptor areas. Because the atmospheric mercury model is a linear system, the response-surface model provides an accurate representation of the original model. The response surface model can be applied to investigate the potential effects of various emissions trading scenarios and to conduct cost-benefit analyses (Seigneur et al. 2003a). The results of cost-benefit analyses conducted with this model are discussed in a later chapter.

3.5.2 Regional and continental models

Atmospheric mercury models designed for simulating atmospheric mercury cycling on regional to continental scales were used to evaluate fate and transport of mercury emissions deposition across the contiguous U.S. and sensitive regions of the country. As part of USEPA mercury study reported to Congress in 1997, the Regional Lagrangian Model of Air Pollution (RELMAP) was modified, beginning in 1995, and used to assess long-range transport and deposition of industrial and residential sources of mercury within the U.S. (Bullock et al. 1997, Bullock 2000; USEPA 1997). Originally developed by USEPA in 1985 to investigate acid rain and particulate deposition, the modified RELMAP was used to simulate three forms of atmospheric mercury: Hg(0), Hg(II), and Hg_p. Anthropogenic sources of atmospheric mercury not represented by emission inventories; recycled anthropogenic mercury, natural sources and wet deposition of Hg(0) were based on methods of Petersen et al. (1995). Seasonal dry deposition rate tables developed by Walcek et al. (1986) and Wesely (1986) were used to estimate Hg(II) dry deposition rates over various surface types, rather than a single value for all surfaces and seasons as in Petersen et al. (1995). Scientific value of comparisons (Bullock et al. 1997) of simulated

and observed mercury wet deposition rates for sites around the U.S., especially near the Canadian border, was limited due to a lack of Canadian mercury emissions data (Bullock 2000). A Canadian mercury emissions inventory that became available from Environment Canada after 1997 was then incorporated into RELMAP as input. The addition of Canadian mercury emissions did not have a significant effect on simulated wet deposition of total mercury over the U.S. Contributions from Canadian sources constituted less than 4 percent additional wet deposition. Researchers have used the RELMAP data to estimate that approximately 98% of the elemental mercury emitted from combustion sources is transported outside the U.S. (EPA 2002).

Xu et al. (2000) performed a sensitivity analysis to examine the ambient concentrations and depositions in response to changes in anthropogenic emissions, environmental conditions, and inclusion of some additional chemical reactions, using a model based on the SARMAP Air Quality Model (SAQM). The newly developed model is described by Xu (1998) and Xu et al. (1999). The model is a three-dimensional Eulerian air quality model that considers Hg(0), Hg(II), and Hg_p. Air-surface exchange of Hg(0) was treated by explicitly applying both dry deposition to, and emission from, bare soil, vegetation, and water surfaces. Aqueous phase chemical reactions of mercury largely followed Petersen et al (1995), but included three types of clouds—precipitating, co-existing non-precipitating, and fair weather clouds—and the interaction between the in-cloud transformation of Hg(0) and direct scavenging of ambient Hg(II) was considered.

Results of the sensitivity analysis indicated that mercury deposition was sensitive to ambient concentrations of ozone and soot particles due to their direct impact on the aqueous chemical reactions (Xu et al. 2000). General ambient concentrations and wet deposition were heavily influenced by re-emission from natural surfaces and regional/global scale transport. Total deposition was dependent upon the fraction of gaseous mercury bound to particles. Both regional and global scale transport were less sensitive to point source emissions.

TEAM, a three-dimensional Eulerian model originally developed under EPRI sponsorship for simulation of long-range acid rain processes, has been used in a series of applications investigating atmospheric concentrations and deposition fluxes of mercury in the U.S. Initial use of the TEAM modeling system for simulating regional mercury fate and transport is described by EPRI (1996). TEAM was used for simulation of fate and transport of mercury emissions from the contiguous U.S. and portions of Mexico and Canada (Pai 1997). In areas near point sources, artificial spreading of source emissions due to 100-km horizontal grid resolution resulted in dilution of simulated mercury concentrations and depositional fluxes. A finer 20-km horizontal grid resolution was then embedded (Pai et al 2000) into the previous model domain representing a portion of the northeastern U.S encompassing 50 percent of the largest mercury point sources in the regional inventory. Ranges in simulated daily average concentration and dry deposition were larger near point sources than at more remote locations.

3.5.3 Local Models

At the local scale, atmospheric mercury models have been used to evaluate small-scale mercury fate and transport on the order of one diurnal cycle. Hedgecock and Pirrone (2001) modeled the MBL using gas and aqueous phase mechanisms based for the most part on the database of reactions in the model of chemistry considering aerosols (MOCCA), first developed by Sander

and Crutzen (1996). The study evaluated the precise part played by the sea salt component of the marine aerosol in the remote MBL using a combination of models to describe photolytic, gas phase, and aqueous phase and heterogeneous chemistry of the MBL, in conjunction with inter phase mass transport and mercury chemistry. Particular attention was paid to halogen chemistry. They concluded that, first, the outgassing of sea-salt aerosol is a source of RGM and, second, the major contribution of the sea-salt aerosol to mercury cycling in the MBL is that of a continuous source of oxidized mercury.

Based on data collected by Lindberg et al. (2002), Brooks and Lindberg (2002) developed a simple predictive model for airborne mercury depletion and dry deposition using local meteorological data and an inverse boundary-layer approach. Taken together, boundary layer entrainment rates and deposition rates explained about 70 to 80 percent of the measured variance in airborne Hg(0) and RGM, respectively. Forlano et al. (2000) linked a hybrid single-particle Lagrangian integrated trajectory model (HYSPLIT_4) (Draxler and Hess 1997, 1998) to the gas-particle partitioning meteorological model GASP (Pirrone et al. 2000) to investigate the fate and transport of emissions from a single Hg(0) source near La Spezia, Italy. Fluxes and speciation of mercury compounds were calculated. Modeling results demonstrated the importance of relative humidity to Hg(II) deposition. The quantity of Hg(II) deposition was dependent upon the nature of aerosol particles and relative humidity. Increases in relative humidity were accompanied by increases in deposition. Earlier experience with models developed by EPRI and others, ROME and TRUE, was discussed in detail in the EPRI Mercury Report published in 1996 (EPRI 1996).

3.6 Summary

- Since 1996, significant advances have been made to improve field measurement and laboratory analytical methods, to increase the understanding of atmospheric mercury reaction kinetics, and to better characterize emission sources. All of these advances have contributed considerably to reducing the uncertainty in understanding atmospheric mercury fate and transport processes.
- A major advance in the study of mercury cycling was the development of methodologies for determining the speciation of atmospheric mercury. Methods have been published and now are in routine use for measuring concentrations of divalent mercury at low concentrations in ambient air and flue gas.
- Results from recent studies have demonstrated that reactive gaseous mercury (RGM) represents a few percent of total airborne mercury in ambient air distant from local sources, however, concentrations can be several hundred times higher near anthropogenic point sources directly emitting RGM.
- The aqueous phase of mercury chemistry has been found to produce oxidized mercury, dependent upon the availability of oxidants and reactive halogens including chlorine and bromine. This phenomenon has also been observed and modeled in a multitude of settings including in the nighttime marine troposphere, the marine boundary layer, and the Arctic troposphere.
- Several study results taken together document a relationship between the rate of oxidation of elemental mercury and the presence of reactive halogens (in various forms) and increased

UV/ambient temperatures. For example, the reactive halogen, chlorine, in various forms including sea-salt aerosols, has been associated with increased oxidation of mercury in various ocean and near ocean settings (MBL, marine troposphere, and Arctic troposphere). And, the UV factor is demonstrated in the Arctic sunrise phenomenon accounts for huge local conversions of elemental mercury to RGM.

- Modeling at the local scale has shown that the quantity of Hg(II) deposition is dependent upon the nature of aerosol particles and relative humidity, with increases in relative humidity accompanied by increases in deposition.
- There are several sources of uncertainties associated with long-range simulation of atmospheric fate and transport of atmospheric mercury. One of the most significant model input data gaps would be improved by collection of field data for Hg(II) dry deposition fluxes over a variety of Earth surfaces under varying meteorological conditions.
- Data gaps for model formulation would benefit from further field and laboratory experimentation to enhance our understanding of complex chemical and physical mercury transformations. Specifically, our understanding would be improved with further research on the: completeness of the redox chemical mechanism of aqueous mercury, the kinetics of the reactions that have been identified, the fraction of mercury that can adsorb on particulate matter [and whether or not the adsorption is reversible], and the values of reactant concentrations. Additional investigative work is needed regarding wet removal of mercury species and specifically, the completeness of Hg(II) and Hg_p scavenging below clouds. Model evaluation would be improved by both speciated ambient measurements of Hg and of fluxes of wet and dry deposition.

References

Anastasio, C., B. Matthew, and I. George, 2002. OH-Initiated Release of Br₂ from Sea-Salt Particles. *Eos Trans. American Geophysical Union (AGU)* 83(47), Fall Meet. Suppl. Abstract A12F-04.

Atmospheric and Environmental Research, Inc., (2002). Contributions of Global and Regional Sources to Mercury Deposition in New York State. Prepared for the New York State Energy Research and Development Authority and Electric Power Research Institute. July. 114 pp.

Baeyens, W. R. Ebinghaus, and O. Valiliev, eds., 1996. Global and regional mercury cycles: sources, fluxes, and mass balances. NATO ASI Series, 2. Environment – Vol. 21. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Bergan, T., L. Gallardo, and H. Rodhe, 1999. Mercury in the Global Troposphere: A Three-dimensional Model Study. *Atmos. Environ.* 33: 1575-1585. *Sci. Tot. Environ.* 259: 145-157.

Brosset, C., 1982. Total airborne mercury and its origin. *Water, Air, Soil, Pollut.* 17:37-50.

Bullock, O.R., W.G. Benjey, and M.H. Keating. The modeling of regional-scale atmospheric mercury transport and deposition using RELMAP. In: Baker, J.E., editor. Atmospheric

deposition of contaminants to the Great Lakes and Coastal Waters. Pensacola: SETAC Press, 1997: 323-347.

Bullock, O.R., 2000. Modeling assessment of transport and deposition patterns of anthropogenic mercury air emissions in the United States and Canada. *Sci Tot Environ* 259: 145-157.

Draxler, R.R. and G.D. Hess, 1997. Description of the HYSPLIT_4 modeling system, NOAA Technical Memorandum ERL ARL224.

Draxler, R.R. and G.D. Hess, 1998. An overview of the HYSPLIT_4 modeling system for trajectories, dispersion, and deposition. *Austr Meteorol Mag* 47: 295-308.

Ebinghaus, R., et al., 1999a. International field intercomparison measurements of atmospheric mercury species at Mace head, Ireland, *Atmos. Environ.*, **33**, 3063-3073.

EPRI 1996. Mercury in the Environment, A Research Update. Palo Alto, CA.

EPRI, 2000. Assessment of Mercury Emissions, Transport, Fate, and Cycling for the Continental United States: Model Structure and Evaluation. Palo Alto, CA. TR-1000522.

EPRI, 2002. Measuring Mercury in Coal-Fired Flue Gas. TR- 1004176. November.

Engstrom, D.R. and E.B. Swain, 1997. Recent declines in atmospheric mercury deposition in the upper Midwest. *Environ. Sci. Technol.* 31: 960-967.

Ferrara, R. B. Mazzolai, E. Lanzillotta, E. Nucaro, and N. Pirrone, 2000. Temporal trends in gaseous mercury evasion from the Mediterranean seawaters. *Sci. Tot. Environ.* 259: 183-190.

Fitzgerald, W.F., 1989. Atmospheric and oceanic cycling of mercury, in chemical oceanography, 10. San Diego: Academic Press: 151-186.

Fitzgerald, W.F., 1995. Is mercury increasing in the atmosphere? The need for an atmospheric mercury network (AMNET). *Water Air Soil Pollut.* 80: 245-254.

Forlano, L., I.M. Hedgecock, and N. Pirrone, 2000. Elemental gas phase atmospheric as it interacts with the ambient aerosol and its subsequent speciation and deposition. *Sci. Tot. Environ.* 259: 211-222.

Gardfeldt, K. and M. Jonsson, 2003. Is bimolecular reduction of Hg(II)-complexes possible in aqueous systems of environmental importance? *J. Phys. Chem.*, in press.

Gustin, M. 2002. Personal communication.

Hall, B., 1995. The phase oxidation of elemental mercury by ozone. *Water Air Soil Pollut.* 80: 301-315.

Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott, and V.L. St. Louis, 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. *Environ. Sci. Technol.* 36: 5034-5040.

Iverfeldt, A., 1991. Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water, Air, Soil Pollut.* 56: 251-265.

Iverfeldt, A., J. Munthe, C. Brosset, and J. Pacyna, 1995. Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia. *Water, Air, Soil Pollut.* 80: 227-233. As cited by von Rein and Hylander (2000).

Lamborg, C.H, and W.F. Fitzgerald, 1996. Modeling the Atmospheric Chemistry of Mercury Using Naturally Occurring, Particle-Reactive Radionuclides. In R. Ebinghaus et al. (eds.), *Book of Abstracts. Fourth International Conferences on Mercury as a Global Pollutant. Germany.*

Lamborg, C.H., K.R. Rolfhus, W.F. Fitzgerald, and G. Kim, 1999. The atmospheric cycling and air-sea exchange of mercury species in the South and equatorial Atlantic Ocean. *Deep-Sea Res II* 46: 957-977.

Lamborg, C.H., Fitzgerald, W.F., Damman, A.W.H., Benoit, J.M., Balcom, P.H. and D.R. Engstrom, 2002. Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications, *Global Biogeochem. Cycles*, 16:doi:10.1029/2001GB001847.

Landis, M.S., Stevens, R.K. Schaedlich, F., and Prestbo, E.M. 2002. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environ. Sci. Tech.* 36:3000-3009.

Lin, C-J, and S.O. Pehkonen, 1997. Aqueous free radical chemistry of mercury in the presence of iron oxides and ambient aerosol. *Atmos. Environ.* 31: 4125-4137.

Lin, C-J, and S.O. Pehkonen, 1998a. Two-phase Model of Mercury Chemistry in the Atmosphere. *Atmos. Environ.* 32(14/15): 2543-2558.

Lin, C-J, and S.O. Pehkonen, 1998b. Oxidation of Elemental Mercury by Aqueous Chlorine (HOCl/OCl⁻): Implications for Troposphere Mercury Chemistry. *J Geophys Res* 103(D21): 28093-28102.

Lin, C-J, and S.O. Pehkonen, 1999. Chemistry of Atmospheric Mercury: A Review. *Atmos. Environ.* 33:2067-2079.

Lindberg, S.E., 1996. In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*; Baeyens, W. , R. Ebinghaus, and O. Vasiliev, eds. NATO ASI Series 21. Kluwer Academic Publishers, Dordrecht, The Netherlands. Pp. 359-380.

- Lindberg, S.E. and W.J. Stratton, 1998. Atmospheric Mercury Speciation: Concentrations and Behavior of Reactive Gaseous Mercury in Ambient Air. *Environ. Sci. Technol.* 32:49-57.
- Lindberg, S.E., M. Gustin, H. Zhang, and S. Brooks, 2000. Mercury Emission and Re-emission from Diffuse Area Sources: The Dilemma of Small Emissions from Large Surfaces, The “Inert” Nature of Elemental Mercury Vapor, and Missing Sinks in the Global Mercury Cycle. 2000 EPA Conference on mercury, San Francisco.
- Lindberg, S. and H. Zhang, 2000. Air/water exchange of mercury in the Everglades II: measuring and modeling evasion of mercury from surface waters in the Everglades Nutrient Removal Project. *Sci Tot Environ* 259: 135-143.
- Lindqvist, O. and H. Rodhe, 1985. Atmospheric mercury – A review. *Tellus*, 37B, 136-159.
- Lu, J.Y., W.H. Schroeder, L. Barrie, A. Steffan, H. Welch, K. Martin, L. Lockhart, R. Hunt, G. Bolia, and A. Richter, 2001. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophysical Research Letters* 28: 3219-3222.
- van Loon, L.E., E. Mader, and S.L. Scott, 2000. Reduction of the aqueous mercuric ion by sulfite: UV spectrum of HgSO₃ and its intramolecular redox reactions. *J. Phys. Chem.* 104: 1621-1626.
- Mason, R.P., W.F. Fitzgerald, and M.M. Morel, 1994. The biogeochemical cycling of elemental mercury: anthropogenic influences. *Geochim Cosmochim Acta* 58: 3191-3198.
- Mason, R.P. and G.R. Sheu, 2002. Role of the ocean in the global mercury cycle, *Global Biogeochem. Cycles*, 16, doi:10.1029/2001GB001440.
- Munthe, J. I. Wangberg, A. Iverfeldt, G. Petersen, R. Ebinghaus, S. Schmolke, E. Bahlmann, O. Lindqvist, D. Stromberg, J. Sommar, G. Gardfeldt, X. Feng, K. Larjava, and V. Siemens, 2001. Mercury species over Europe (MOE). Relative importance of depositional methylmercury fluxes to various ecosystems. Final report for the European Commission, Directorate General XII, September 2001.
- NESCAUM, 1998. NESCAUM and Eastern Canadian Provinces Mercury Study: A Framework for Action, NESCAUM, Boston, MA.
- Nriagu, J. and C. Becker, 2003. Volcanic emissions of mercury to the atmosphere: global and regional inventories. *Sci. Tot. Environ.* 304: 3-12.
- Pacyna, J.M. and Pacyna, P.E. 1996. Global emissions of mercury to the atmosphere. Emissions from anthropogenic sources: A report for the arctic monitoring and assessment programme (AMAP), Oslo, June 1996. As quoted in UNEP 2002.
- Pacyna, J.M, and E.G. Pacyna, 2001. An Assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* 9: 269-298.

- Pai, P., Karamchandani, P., and C. Seigneur, 1997. Simulation of the regional atmospheric transport and fate of mercury using a comprehensive Eulerian model. *Atmos Environ* 31: 2717-2732.
- Pai, P., Karamchandani, P., and C. Seigneur, 2000. On artificial dilution of point source mercury emissions in a regional atmospheric model. *Sci Tot Environ* 259: 159-168.
- Petersen, G., J. Munthe, K. Pleijel, R. Bloxam, and A. Kumar, 1998. Atmospheric mercury species over central and northern Europe. Model calculations and comparison with observations from the Nordic Air and Precipitation Network for 1987 and 1988. *Atmos Environ* 29: 47-68.
- Petersen, G., Bloxam, R., Wong, S., Munthe, J., Krüger, O., Schmolke, S. and Kumar, A. V. (2001): A comprehensive Eulerian modeling framework for airborne mercury species: model development and applications in Europe. *Atmospheric Environment* 35, 3063-3074.
- Pirrone, N., Keeler, G.J., and Nriagu, J.O., 1996. Regional differences in worldwide emissions of mercury to the atmosphere. *Atmos Environ* 30: 2981-2987.
- Pirrone, N., Hedgcock I.M, and L. Forlano, 2000. The role of the ambient aerosol in the atmospheric processing of semi-volatile contaminants—a parameterised numerical model (GASPAR). *J Geophys Res D* 105(8): 9773-9790.
- Pirrone, N., J. Munthe, L. Barregard, H.C. Ehrlich, G. Petersen, R. Fernandez, J.C. Hansen, P. Grandjean, M. Horvat, E. Steinnes, R. Ahrens, J.M Pacyna, A. Borowiak, P. Boffetta, and M. Wichmann-Fiebig, 2001. EU Ambient Air Pollution by Mercury (Hg) – Position Paper. Office for Official Publications of the European Communities.
- Pleijel, K. and J. Munthe, 1995. Modeling the atmospheric mercury cycle-chemistry in fog droplets. *Atmos Environ* 29:1441-1457.
- Poissant, L., 2000. Total gaseous mercury in Quebec (Canada) in 1998. *Sci Tot Environ* 259: 191-201.
- Radke, L.F. , H.R. Friedli, and B. Heikes, 2002. Observations of Gaseous Mercury Over Eastern North America: Gradients, Transports, Variability, and Lifetime Calculations. *Eos Trans. AGU* 83(47), Fall Meet. Suppl., Abstract A62B-0163.
- St. Louis, V.L, J.W.M. Rudd, C.A. Kelly, B.D. Hall, K.R. Rolfhus, K.J. Scott, S.E. Lindberg, and W. Dong, 2001. Importance of the Forest Canopy to Fluxes of Methyl Mercury and Total Mercury to Boreal Ecosystems. *Environ Sci Technol* 35: 3089-3098.
- Sander, R. and P.J. Crutzen, 1996. Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *J Geophys Res D*: 101:9121-9138.
- Schroeder, W.H. and J. Munthe, 1998. Atmospheric mercury—an overview. *Atmos Environ* 32: 809-822.

- Schroeder, W.H., K.G. Anlauf, L.A. Barrie, L.Y. Lu, A. Steffen, D.R. Schneeberger, and T. Berg, 1998. Arctic Springtime Depletion of Mercury. *Nature* 384:331-332.
- Schuster, P.F., D.P. Krabbenhoft, D.L. Naftz, L.D. Cecil, M.L. Olson, J.F. Dewild, D.D. Suson, J.R Green and M.L. Abbott, 2002. Atmospheric mercury deposition during the last 270 years: a glacial ice core record of natural and anthropogenic sources.
- Seigneur, C., H. Abeck, G. Chia, M. Reinhard, N. Bloom, E. Prestbo, and P. Saxena, 1998. Mercury adsorption to elemental carbon (soot) particles and atmospheric particulate matter. *Atmos. Environ.* 32: 2649-2657.
- Seigneur, C, P. Karamchandani, K. Lohman, K. Vijayaraghavan, and R. Shia, 2001. Multiscale modeling of the atmospheric fate and transport of mercury. *J. Geophys. Res.* 106: 27795-27809.
- Seigneur, C., K. Vijayaraghavan, K. Lohman, P. Karamchandani, and C. Scott, 2003a. Modeling mercury atmospheric deposition in the United States. Prepared for EPRI. Document Number CP142-03-01, January.
- Seigneur, C. K. Lohman, K. Vijayaraghavan, and R. Shia, 2003b. Contributions of global and regional sources to mercury deposition in New York State. *Environ. Poll.* 123(3): 365-373.
- Seigneur, C., P. Karamchandani, K. Vijayaraghavan, R. Shia, and L. Levin, 2003c. On the effect of spatial resolution on atmospheric mercury modeling. *Sci. Tot. Environ.* 304: 73-81.
- Seigneur, C., K. Vijayaraghavan, K. Lohman and P. Karamchandani, 2003d. Modeling the atmospheric fate and transport of mercury over North America: Power plant emission scenarios, *Fuel Processing Technol.*, in press.
- Schaedlich, F. 2002. Personal communication.
- Shia, R.L, C. Seigneur, P. Pai, M. Ko, and N.D. Sze, 1999. Global simulation of atmospheric mercury concentrations and deposition fluxes. *J Geophys Res D*: 104: 23747-23760.
- Sommar, J., K. Gardfeldt, D. Stromberg, and X. Feng. 2001. A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury. *Atmos. Env.* 35.:3,049-3,054.
- Stratton, W.J. and S.E. Lindberg. 1995. Use of a refluxing mist chamber for measurement of gas-phase mercury (II) species in the atmosphere. *Water, Air & Soil Poll.* 80:1269-1278.
- Stratton, W.J., S. Lindberg, and C.J. Perry, 2001. Atmospheric mercury speciation: Laboratory and field evaluation of a mist chamber method for measuring reactive gaseous mercury. *Environ. Toxicol. Chem.* 35: 170-177.
- Tan, H., J.L. He, L. Liang, S. Lazoff, J. Sommer, Z.F. Xiao, and O. Lindqvist, 2000. Atmospheric mercury depositions in Guizhou, China. *Sci Tot Environ* 259: 223-230.

- Temme, C., F. Slemr, R. Ebinghaus and J.W. Einax, 2003. Distribution of mercury over the Atlantic Ocean in 1996 and 1999-2001, *Atmos. Environ.*, 37, 1889-1897.
- Tokos, J.J.S., B. Hall, J.A. Calhoun, and E.M. Prestbo, 1998. Homogeneous Gas-phase Reaction of Hg(0) with H₂O₂, O₃, CH₃I and (CH₃)₂S: Implications for Atmospheric Hg Cycling. *Atmos. Environ.* 32(5): 823-827.
- Tomisyasu, T., A. Nagano, H. Sakamoto, and N. Yonehara, 2000. Background levels of atmospheric mercury in Kagoshima City, and influence of mercury emission from Sakurajima Volcano, Southern Kyushu, Japan. *Sci Tot Environ* 259: 231-237.
- United Nations Environment Programme, 2002. Global Mercury Assessment DRAFT. April 25, 2002.
- U.S. EPA, 1997. *Mercury Study Report to Congress*. Volume III: Fate and Transport of Mercury in the Environment. EPA-452/R-97-005.
- U.S. EPA, 2002. *Proceedings and Summary Report. Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments*. EPA/625/ R-02/005. June.
- Urba, A., K. Kvietkus, and R. Marks, 2000. Gas-phase mercury in the atmosphere over the southern Baltic Sea coast. *Sci Tot Environ* 259: 203-210.
- von Rein, K. and L.D. Hylander, 2000. Experiences from phasing out the use of mercury in Sweden. *Reg Environ Change* 1: 126-134.
- Vijayaraghavan, K., K. Lohman, P. Karamchandani, and C. Seigneur, 2002. *Modeling Deposition of Atmospheric Mercury in Wisconsin*. Report to EPRI, EPRI, Palo Alto, CA.
- Walcek, C.J, R.A. Brost, J.S. Chang, and M.L. Wesely, 1986. SO₂, sulfate, and HNO₃ deposition velocities computed using regional land use and meteorological data. *Atmos Environ* 20: 949-964.
- Wangberg, I., J. Munthe, N. Pirrone, A. Iverfeldt, E. Bahlman, R. Ebinghaus, X. Feng, R. Ferrara, K. Gardfeldt, H. Kock, E. Lanzilotta, Y. Mamane, F. Mas, E. Melamed, E. Nucaro, E. Prestbo, J. Sommar, G. Spain, F. Sprovieri, and G. Tuncel, 2001. Atmospheric mercury distribution in northern Europe and in the Mediterranean region. *Atmos Environ* 35: 3019-3025.
- Wesely, M.L. On the parameterization of dry deposition of acidifying substances for regional models. Interagency Agreement DW89930060-01 to the US Department of Energy. Internal Report Nov. 1986. USEPA. Research Triangle Park, NC.
- Wiener, J.G., Krabbenhoft, D.P., Heinz, G.H., and Scheuhammer, A.M., 2002, Ecotoxicology of mercury, in Hoffman, D.J., Rattner, B.A., Burton Jr., G.A., and Cairns Jr., J., eds., *Handbook of Ecotoxicology* (2nd ed.): Boca Raton, Florida, CRC Press, p. 407-461.

- Xu, X. A Regional Scale Modeling Study of Atmospheric Transport and Transformation of Mercury. Ph.D. Dissertation. The University of Connecticut. Storrs, CT.
- Xu, X. X. Yang, D.R. Miller, J.J. Helble, and R.J. Carley. Formulation of Bi-directional Air-surface Exchange of Elemental Mercury. *Atmos. Environ.* 33(27): 4345-4355.
- Xu, X. X. Yang, D.R. Miller, J.J. Helble, H. Thomas, and R.J. Carley. A Sensitivity Analysis on the Atmospheric Transformation and Deposition of Mercury in North-eastern USA. *Sci. Tot. Environ.* 259: 169-181.
- Zannetti, P., 1990. Air Pollution Modeling - Theories, Computational Methods and Available Software, 444 pp. Van Nostrand Reinhold, New York, NY.
- Zehner, R. and M. Gustin, 2002. Estimation of mercury vapor flux from natural substrate in Nevada. *Environ. Sci. Technol* 36: 4039-4045.
- Zhang, H. and S. Lindberg, 2000. Air/water exchange of mercury in the Everglades I: the behavior of dissolved gaseous mercury in the Everglades Nutrient Removal Project. *Sci Tot Environ* 259: 123-133.

4

MERCURY IN AQUATIC ECOSYSTEMS

Mercury in aquatic ecosystems is a continuing environmental and public health concern. Fish advisories for mercury have been issued in more than 40 U.S. states, informing the public that mercury concentrations in local fish occur at levels of concern for human health effects, sometimes at levels of concern for adults. Mercury levels in fish now account for over 80% of fish advisories for all pollutants in the United States. Elevated mercury concentrations in natural populations of fish are also of concern because of toxic effects on birds and other wildlife that feed on fish. Recent studies have discovered the potential for mercury effects within fish populations (e.g., Hammerschmidt et al., 2002; Latif et al., 2001; Wiener et al., citations are inconsistent Hammerschmidt et al., 2002; Latif et al., 2001; Wiener et al. (yes or no see e.g. on pg 3 1st paragraph)2002), contrary to the common perception that mercury is typically an issue for fish consumers, but not the fish themselves. Most of above-mentioned studies involved exposing laboratory fish to mercury-spiked water and/or food items. Actual in-situ population effects are inherently more difficult to elucidate, thus the frequency and magnitude of such effects are relatively unknown at present.

The unique nature of the mercury in aquatic ecosystems is indicated by the U.S. EPA's first-ever issuance in 2001 of an ambient water quality criterion (for methylmercury) to be expressed as a fish and shellfish tissue residue concentration (0.3 µg/g wet weight), rather than as a concentration in the ambient water (USEPA 2001a). Clearly, the shift from water column criteria to fish tissue-based criteria has scientific merit for pollutants that are known to exhibit high bioaccumulation potential.

Research in several national and international programs, including ACME (Aquatic Cycling of Mercury in the Everglades), STAR (Science to Achieve Results) Mercury Research Program, METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the United States), and the CALFED Ecosystem Restoration Program, have contributed significantly to our understanding of mercury cycling in aquatic environments (USEPA 2002). These programs have involved the U.S. EPA, the U.S. DOE, USGS, EPRI, a number of states (including Florida, California, and Wisconsin), and several international bodies. Of government agencies directly involved in mercury research, the USGS has a particularly robust program investigating mercury cycling in the hydrosphere and cryosphere.

This chapter provides an overview of the generally understood concepts pertaining to mercury transformations in aquatic systems and uptake by biota that have been developed through research in the past two decades, with a focus upon the last seven years. Finally, this chapter presents a summary of ongoing and recently completed EPRI research on mercury fate and transport in aquatic systems.

4.1 Biogeochemistry of Mercury in the Aquatic Environment

In 1997, U.S. EPA issued an eight-volume mercury report to Congress (USEPA 1997) that served as a primary source of information for the development of the agency's methylmercury water quality criterion. Since 1997, however, the state-of-the-science has expanded rapidly. This section summarizes our understanding of the biogeochemistry of mercury in the aquatic environment.

The key steps in the cycling and bioaccumulation of mercury by fish in the aquatic environment, as they are understood currently, are summarized in Figure 4-1, discussed further below. This section is based upon a more detailed summary of these biogeochemical processes contained in a 2003 report issued by EPRI (Tetra Tech, 2003).

- Mercury enters natural waters from a number of sources including atmospheric deposition, municipal and industrial discharges, and terrestrial runoff. Currently, for most U.S. waterways, one of these source categories generally dominates, with the others usually minor contributors.
- Mercury entering aquatic ecosystems undergoes a variety of transformations that affect its ultimate concentration in biota. Site conditions can significantly affect the efficiency of converting and delivering methylmercury to fish.
- Sulfate-reducing bacteria (SRB) are important methylators, but iron reducing bacteria can also mediate methylation. Abiotic methylation by natural organic matter has also been demonstrated.
- In-situ methylation within lake sediments or waters is an important source of methylmercury, but watershed inputs may also be significant, particularly in hydrologic basins with wetlands.
- Methylmercury typically constitutes a minuscule fraction of the total mercury in aquatic ecosystems, but it is the critical form that is incorporated into and magnified by organisms in the food web.

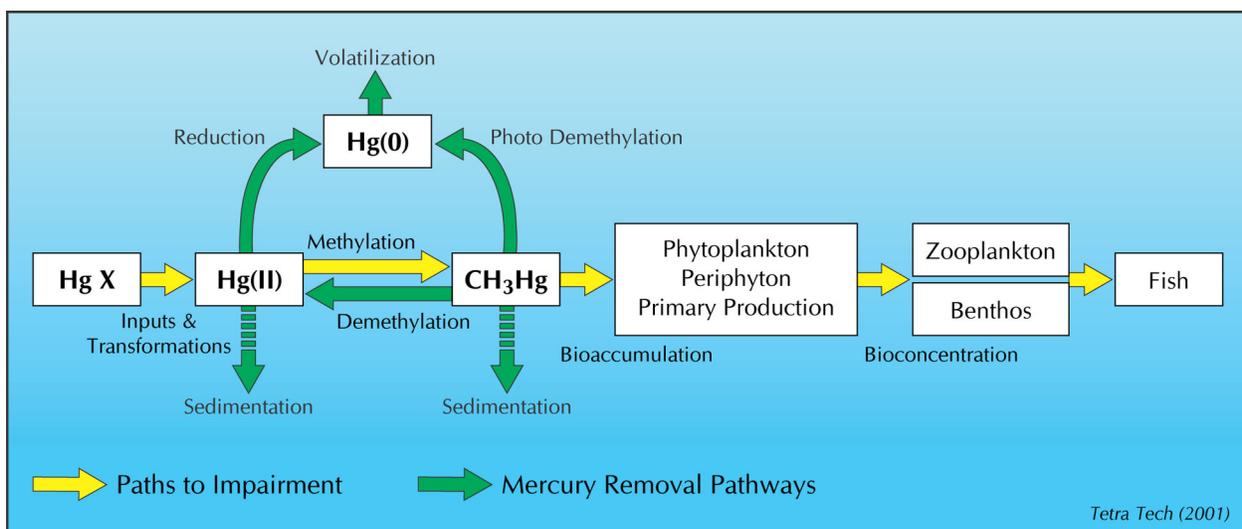


Figure 4-1
Mercury Uptake Pathways

The same physicochemical processes that affect the fate and transport of other metals entering the aqueous environment also affect mercury: adsorption/desorption onto particles, diffusion into and out of sediments, re-suspension of those sediments, and sediment burial. The biogeochemical processes (Figure 4-1) that lead to multiple forms of mercury in the aquatic environment include: reduction of inorganic (divalent) mercury [Hg(II)] to elemental mercury [Hg(0)] and the reverse reaction, photo-oxidation of elemental mercury to inorganic Hg(II), volatilization of elemental mercury, mercury methylation and demethylation, and photodegradation of methylmercury to Hg(0). Note that there are other biogeochemical processes, not shown in Figure 4-1, that also affect the chemical form of mercury in the aquatic environment.

The rates and relative importance of the processes shown in Figure 4-1 are influenced by: 1) abiotic conditions including water temperature, suspended solids, extent of light penetration; pH, alkalinity, dissolved organic carbon (DOC), ions such as chloride, sulfate, and sulfide, and the presence of anoxic conditions in the water column or sediments, and by 2) biological conditions including the composition of the resident microbial community and the productivity of the waterbody. The cycling and conversion processes may vary considerably in both space and time within a single water body.

Hg(II) binds strongly to inorganic and organic particulate matter in freshwater bodies and forms chemical complexes with dissolved organic matter and anions such as chloride and sulfide. DOC can complex with mercury, limiting the adsorption of mercury to settling particles and decreasing the formation of mercury sulfide precipitates such as metacinnabar and cinnabar (e.g., Hudson et al., 1994; Ravichandran et al. 1999). DOC can also affect mercury photochemical reactions depending on its concentration (Driscoll et al. 1995) and the chemical nature of the DOC (Aiken, personal communication)

Not all the dissolved Hg(II) is available for methylation. Processes that reduce availability of Hg(II) for methylation, and/or increase the rate of demethylation, influence the level of methylmercury in the environment. The reduction of Hg(II) to elemental mercury is light-driven and thus is influenced by suspended solids and DOC concentrations. The loss of Hg(II) via reduction to Hg(0) and subsequent volatilization is thought to be greater in alkaline waterbodies (Hudson et al. 1994)

Besides internal production, methylmercury is also supplied to aquatic systems by direct atmospheric deposition (due to its very small unexplained presence in some atmospheric samples) and via export from terrestrial uplands and wetlands. Since actual, *in situ* net methylation rates have not yet been quantified, it has not been possible to directly compare the relative importance of *in situ* methylation, runoff, and atmospheric deposition, although the first two are likely to be dominant. However mass balance budgets and modeling suggest that *in situ* methylation is important while atmospheric deposition of methylmercury is less significant (Harris 2003). Atmospheric deposition may be more important in situations where in-situ methylation and terrestrial methylmercury loading are low. The potential also exists for gas-phase exchange of methylmercury between surface waters and the atmosphere (Hudson et al., 1994). This process has received inadequate attention.

Methylmercury can follow a number of pathways. Of major concern is movement through the food web and bioaccumulation in fish. Trophic factors such as fish growth rates and diets affect

methylmercury concentrations in fish. Food web dynamics are especially important, explaining (at least in part) why, in some cases, adjacent lakes may have similar fish species, but the mercury content in a given species is markedly different between the lakes (e.g., Scheuhammer and Graham, 1999). Methylmercury uptake by fish is typically from food rather than directly from the water (Hall et al. 1998; Rodgers 1994, Harris and Snodgrass 1993). Thus differences in diet and food web structure can directly impact fish mercury concentrations. Slower growth rates can lead to higher fish mercury concentrations (Harris and Bodaly 1998) for the same size fish. A slower growing fish takes longer to reach a standard size, and consumes more food overall due to maintenance metabolic demands.

4.1.1 Methylation

In-situ methylation is bacterially mediated at oxic-anoxic interfaces where sulfate-reducing bacteria (SRB) are most active. Oxic-anoxic interfaces occur in biomass clumps, surface sediments, and in the lower portions of stratified water bodies. The active zone of methylation varies. Methylation in lakes occurs in the upper 5 to 10 cm of sediments and in the water column, as anoxia develops there (Gilmour and Riedel 1995). Recent results from experiments in Canada and Florida indicate that the active layer may be less than 1 cm., because of relatively rapid partial response of fish to reduced or enhanced mercury deposition to waterways. Dissolved rather than adsorbed or solid phase Hg(II) is much more readily methylated. Once methylmercury has been produced, it is readily bioconcentrated into organisms at the lowest trophic levels (level 1 or 2) (e.g., algae) from which it bioaccumulates as it moves to the higher trophic levels. Methylmercury is biomagnified to a much greater extent than inorganic mercury. Methylmercury's strong affinity for sulfhydryl groups, and sulfide and disulfide linkages, results in it being strongly concentrated in the muscle tissue and organs of fish. In addition, methylmercury has a very low octanol-water partition coefficient (approximately 2.0), explaining relatively low levels in lipid tissue (Rand, 1995).

Methylation rate can be influenced by multiple factors that can be grouped into those affecting the activity of the methylating microbes and those affecting the bioavailability of Hg(II) to methylate. DP: Low pH appears to associate with higher net methylation because less substrate is available at high pH due to reduction and volatilization. The availability of labile organic carbon appears to accelerate methylation. Elevated temperature increases the rate of methylation to a much greater extent than the rate of demethylation. The bioavailability of Hg(II) appears to be highest for newly input Hg(II). Within days to weeks, this mercury becomes relatively unavailable due to complexation with very strong ligands.

Photodegradation is thought to be the main demethylation pathway in oxic waters with low mercury concentrations (Morel et al., 1998). Methylmercury can also diffuse from the sediment-water interface into the overlying water or be buried in deeper sediment layers. In addition to photodegradation, methylmercury can be decomposed to Hg(0) by several different mechanisms. An oxidative pathway involves the co-metabolism of monomethylmercury (MeHg) by sulfate-reducing or methanogenic bacteria under anaerobic conditions resulting primarily in the formation of carbon dioxide and Hg(II) with some methane produced (Oremland et al 1991). In systems that are highly contaminated with mercury, a reductive pathway (*mer*-detoxification) occurs under anaerobic conditions where microbes demethylate mercury in a two-step process (Marvin-DiPasquale et al. 2000). Another reductive pathway, which does not involve the *mer*-

operon genes, forms an unstable dimethylmercury sulfide compound that quickly decomposes to dimethylmercury, methane, and metacinnabar (Baldi 1993).

Wetlands are known to remove most dissolved and suspended water pollutants. A few substances, however, such as boron, appear to pass through wetlands unchanged. Although total mercury concentration is typically reduced by wetlands, wetlands have been shown to be significant sources of methylmercury (Kelly et al. 1987; St. Louis et al. 1996; Branfireun et al. 1996; Krabbenhoft et al. 1995). A ten square mile wetland constructed for the Florida Everglades has been producing very high concentrations of methylmercury (SFWMD, 2003). Wetlands are sources of labile organic material that serves as substrate for sulfate-reducing bacteria. Wetlands also typically have shallow warmer waters. Because of abundant natural organic acids, wetlands often have lower pH. These factors all favor methylation. Unlike upland catchments, wetlands have little, if any, vertical hydraulic gradient. This minimizes Hg(II) and MeHg contact with strongly adsorbing soils. Methylation has also been shown to occur in riparian wetlands along streams (Bishop et al 1994; Wiener and Shields, 2000) and in estuarine marshes (Marvin DiPasquale, 2003).

4.1.2 Effect of Sulfur on Mercury Cycling

Since mercury methylation was found to be carried out principally by sulfate-reducing bacteria, a great deal of research has been directed at the effect of sulfur chemistry on methylation. Sulfur species influence the fate of mercury in several ways. The solubility of Hg(II) is increased in the presence of high concentrations of sulfide (Benoit et al. 1999a). When higher concentrations of sulfide are present (e.g., 0.01 to 1 mM), charged polysulfide species may form to allow the dissolved mercury concentrations to increase (Benoit et al. 1999a).

Geochemical modeling over a range of pH and sulfide conditions predicts that polysulfide species are important at pH values above 7 at sulfide concentrations of 1 mM and at pH 8 for sulfide from 0.03 to 10 mM (Jay et al., 2000). While the total dissolved mercury increases when higher sulfide is present, the proportion of neutral $\text{HgS}^0(\text{aq})$ decreases, as confirmed in laboratory experiments (Benoit 1999b). Dissolved, neutral mercury species such as $\text{HgS}^0(\text{aq})$ or $\text{HgCl}_2(\text{aq})$ may be more easily methylated than charged complexes, since they can readily move through cell membranes by passive diffusion (Hudson et al. 1994; Benoit et al. 1998 and 1999a). However, this passive diffusion mechanism has recently been questioned based on new experiments that suggest that facilitated or active uptake of some mercury species may occur across cell membranes, meaning that charged species could potentially be methylated (Golding et al, 2002). In the latter process, the cell takes up mercury instead of the desired nutrient, e.g., zinc.

Further laboratory experiments (Benoit et al., 2001a) have confirmed that as sulfide concentrations increased, less methylmercury was produced, although the mechanism could be different from that hypothesized by Benoit et al., i.e., a reduction in the fraction of the neutral complex, $\text{HgS}^0(\text{aq})$. Experiments with sediments from the Patuxent River estuary and the Everglades showed lower methylation concentrations at increasing sulfide concentrations (Benoit et al. 1999a). The reason for the decrease was thought to be that the charged Hg-bisulfide complexes are less bioavailable to sulfate-reducing bacteria (SRB) (Benoit 1999a and 2001a).

The above experiments suggest that methylation would decrease in higher sulfide environments due to the decreased availability of neutral mercury species to the SRB. However, methylation has been shown in other experiments to occur when only neutral HgCl_2 species were present and by one SRB species without sulfate via a fermentation pathway (described in Benoit, et al., 2001b). There are multiple species of sulfate-reducing bacteria that can methylate mercury. Yet not all SRB carry out Hg-methylation, as shown in recent experiments by King et al. (2000). The rates of methylation differed among the species by a factor of five. Two of these species did not produce methylmercury in the absence of sulfate. Other species exhibited increased methylation rates in acetate and lactate-amended sediments, indicating the importance of carbon sources. One of the early experiments on methylation showed that addition of a known inhibitor of methanogenic bacteria resulted in increased methylation, while addition of 20 mM of Na_2MoO_4 , a known inhibitor of sulfate-reducing bacteria, suppressed all mercury methylation (Compeau and Bartha 1985).

The role of sulfur is not completely understood, and differs from one set of conditions to another. For example, in freshwater sediments with low sulfate concentrations, addition of sulfate stimulated sulfate reduction, and hence methylation (Gilmour et al. 1992 and Gilmour, 2003). When sulfate concentrations were 500 to 1000 mg/L (5.2-10.4 mM), which is considerably above the concentration thought to be limiting for the sulfate-reducing bacteria (10 mg/L or 0.1 mM), additions of sulfate did not stimulate methylation (Choi and Bartha 1994). Addition of sulfate in experiments with peat soils showed an increase in the production of MeHg using up to 40 mg/L (0.42 mM) sulfate (Braunfireum et al. 1999). However, other experiments using Everglades sediments showed decreased methylation in response to added sulfate due to the build-up of porewater sulfide concentrations (Marvin-DiPasquale et al., 2001). The bioavailability of the sulfide and sulfate is an important factor, affected by speciation changes and precipitation of mercury sulfide minerals (Gagnon et al. 1997). Methylation has also been observed when high sulfate and sulfide concentrations are present such as in estuarine systems (e.g., Compeau and Bartha 1987 and Langer et al., 2001).

4.1.3 Bioconcentration and Bioaccumulation

Methylmercury typically constitutes a minuscule fraction of the total mercury in aquatic ecosystems (< 1% in sediments and the water column), but it is the chemical form of mercury that is incorporated into and magnified in the food web. The greatest bioconcentration occurs between the water column and phytoplankton (Lindqvist et al 1991; Watras and Bloom 1992; Mason et al 1996). The bioconcentration factor for phytoplankton uptake can be as high as 300,000.

The corresponding bioaccumulation factors (BAFs) for zooplankton or benthos and lowest trophic-level fish, based on methylmercury levels in the water column, could be on the order of 1,000,000 and 3,000,000. As a rule of thumb, the log of BAF values for MeHg increase by a factor of 3 per trophic level after the initial uptake by phytoplankton. Thus, the concentration of MeHg in predatory fish tissue can be more than 3 million times the water concentration.

Dietary uptake is the dominant pathway for MeHg accumulation in fish (Wiener et al. 2002). The bioavailability of MeHg to fish is controlled by digestive processes rather than by constrained transfer across the gills, skin or intestinal epithelium (Leaner and Mason, 2002). Fish have been

estimated to assimilate from 65 to 80% of the MeHg present in the food they eat (Wiener et al, 2002). Not only is methylmercury readily assimilated, but it is slowly eliminated, resulting in increasing MeHg in fish as a function of age, size and trophic level (Gray, 2002). The assimilated mercury is distributed throughout the tissues and organs of the fish, but a large portion of the MeHg eventually relocates to skeletal muscle where it becomes bound to the muscle protein.

The results of a nation-wide survey of mercury contamination in aquatic ecosystems (Krabbenhoft et al. 1999; Brumbaugh et al. 2001), sponsored by the U.S. Geological Survey (USGS), explored the associations between water quality and sediment variables, and mercury bioaccumulation in fish. The study results also provide information on whether fish in waterbodies nationally were likely to fall above or below the fish tissue residue criterion for methylmercury (0.3 µg/g wet weight). This nationwide, systematic survey of mercury contamination of aquatic ecosystems identified the primary ecosystem characteristics that favor the production and bioaccumulation of methylmercury (MeHg) and compared bioaccumulation rates on a national basis.

Water samples to be analyzed for both total mercury and methylmercury were collected from 106 sites for 20 U. S. hydrologic basins. The selected basins span a west-to-east mercury atmospheric wet deposition gradient and represent a wide range of environmental settings (wetland density, surface water pH, sulfate, TOC) and suspected or known mercury loadings. Numerous fish species were collected, but the focus of the sampling program was on the collection of 3-year old largemouth bass (*Micropterus salmoides*) and other black bass (*Micropterus* sp.). Composite samples of the axial muscle from 5 fish per site were collected for mercury analysis. The results for the analysis of all 159 fish samples are summarized in Table 4-1.

The average mercury concentration for all fish species collected (0.48 µg/g) exceeded the EPA mercury fish-tissue criterion (0.3 µg/g wet weight). Fifteen of the 20 watershed basins sampled had at least one sample above the 0.3 µg/g criterion value. The average concentration of mercury in largemouth bass (0.51 µg/g) also exceeded the EPA criterion. However, the median value of 0.29 µg/g for largemouth bass samples at all locations indicates that half of the sample locations were below the criterion value.

Table 4-1
Summary of Statistics for Mercury Concentrations (µg/g wet wt.) in Fish Fillet Samples
(USGS National Pilot Study of Mercury in Fish, Brumbaugh et. al., 2001)

Statistic	All Samples (n = 159)	Largemouth Bass (n = 50)	Smallmouth Bass (n = 37)
Mean	0.48	0.51	0.24
Median	0.21	0.29	0.21
Geometric Mean	0.22	0.33	0.19
Minimum	0.02	0.05	0.04
Maximum	5.8	4.2	1.1

The results of the USGS studies show that mercury levels exceeding the Fish Tissue Criterion in the aquatic environment are widespread, and also indicates the site-specific nature of the exceedances. Differences were observed among the occurrences of elevated mercury levels by water basin. All of the highest-ranking sites for MeHg water-column concentrations also ranked highest for fish mercury concentrations. Statistical analyses showed a high correlation between mercury concentrations in fish of all fish species and those for largemouth bass as a function of MeHg concentration in water. Based upon average conditions in the waterbodies and fish species investigated, the following associations were identified:

- Water-MeHg concentrations of 0.12 ng/L correspond to a fish mercury concentration of 0.30 µg/g for an age-3 fish (3 year old fish) when all species were considered; the corresponding bioaccumulation factor (BAF) for MeHg in water to mercury in all fish is 2,500,000.
- Methylmercury concentrations in water of 0.058 ng/L correspond to a largemouth bass mercury concentration of 0.30 µg/g, giving a BAF of 5,200,000.

The concentrations of mercury in fish were only moderately correlated with MeHg in sediment or total mercury in water. There was little correlation between mercury in fish and total mercury in sediment.

The authors concluded that their results suggest that, on a national basis, MeHg in water is a much better predictor of concentrations in fish than is MeHg in the sediment. They also identified the need for additional studies to define the limitations in estimating fish concentrations from MeHg concentrations in water and to determine the sampling conditions that maximize the predictive power of water analyses.

This last finding is especially important, since individual states are delegated the responsibility by EPA to develop their own water quality standards for MeHg using the new fish tissue-based mercury criterion. Differences in MeHg concentrations in different ages and species of fish, as well as site-specific water quality conditions that affect mercury bioaccumulation, impact the resulting fish tissue levels. These site-specific factors must be taken into account in any attempt to translate the tissue residue criterion to a water column concentration through the use of bioaccumulation models. There is a need to improve our understanding of these factors to improve the predictive ability of bioaccumulation models.

The bioaccumulation of MeHg in aquatic organisms, in particular fish, is primarily a function of interacting factors, including the rate of introduction of new inorganic mercury into the system (mercury loading), the net mercury methylation rates (methylation efficiency), food web length, and total mass. Maximum MeHg concentrations will be observed in fish when there is an ample inventory of bioavailable mercury [i.e., Hg(II)], sediment and/or water-column conditions promote methylation (e.g., in wetlands), and a multi-step food-web structure exists. Complete information on any single factor is not yet sufficient to predict MeHg concentrations in fish with certainty.

4.1.4 Atmospheric Mercury Levels and Bioaccumulation

For many aquatic ecosystems, atmospheric deposition is thought to constitute the primary source of mercury. The observed elevated concentrations of mercury in fish in North American lakes,

for example, have been attributed to increased industrial activity and global mercury emissions worldwide. However, there is recent evidence of decreases in both mercury emissions to and deposition rates from the atmosphere (Engstrom and Swain 1997; Munthe et al, 2001), and it is anticipated that changes in atmospheric loadings of mercury will result in changes to aquatic systems, specifically reductions in mercury concentrations in lake waters and fish tissue.

Direct measurements made over the period 1994-2000 have demonstrated concomitant reductions of mercury concentrations in precipitation, lake water, and fish tissue in an intensively monitored seepage lake in northern Wisconsin (Watras et al 2000; Hrabik and Watras 2002). Atmospheric mercury deposition decreased by approximately 50% between 1994 and 1999, and mercury concentrations in lake waters decreased an average of 40% between 1988 and 2000 (Watras et al 2000). Fish tissue measurements and statistical modeling indicate that fish mercury concentrations decreased between 35 and 65% between 1994 and 2000 (Hrabik and Watras 2002). The range in the decrease of mercury concentrations in yellow perch was attributed to differences in the existing conditions in two separate basins of the lake, one of which was artificially acidified over a 6-year period and then de-acidified. Overall, the mercury in yellow perch was estimated to decrease at a rate of 5% per year due to decreased atmospheric mercury loading and an additional 0.8% per year due to decreased sulfate loading from the atmosphere. The drop in fish mercury concentrations due to the reduction in atmospheric loading in the treatment basin was believed to be increased by an additional 5%/y due to the effects of accelerated de-acidification.

These investigations at Little Rock Lake provide one of the first demonstrations that atmospheric deposition can propagate rapidly through a precipitation-dominated aquatic ecosystem. These results are consistent with the concept, also implied by initial METAALICUS experimental results described below, that inputs of “new” mercury to the aquatic system is more important than the cycling of “old” mercury already in the system.

Atkeson and Pollman (2002) examined the relationships between estimated reductions in local mercury emissions and recent trends in mercury concentrations in south Florida biota. Consistent reductions in largemouth bass mercury concentrations throughout Florida were observed in the mid-1990's. Frederick (2001) also reported comparable declines in mercury in wading birds in the Everglades. Using historical emissions inventory compiled for the period 1980-2000 (RMB Consulting & Research, 2002) and estimated mercury emissions based on mercury use ascribed to various use categories (Husar and Husar 2002), Atkeson and Pollman (2002) show that estimated changes in atmospheric emissions of mercury in south Florida (approximately 93% between 1991 and 2000) are in agreement with the overall magnitude of decreases in mercury concentrations measured in fish and wading birds (both 80%). While these data are not as compelling as the direct measurements made at Little Rock Lake (Watras et al 2000; Hrabik and Watras 2002), they provide additional evidence for a link between changes in atmospheric loading of mercury and observed responses within the aquatic ecosystem..

4.2 Current Ongoing Research on Aquatic Mercury Cycling

Past assessments of mercury in the aquatic environment confirm the need for an expanded mechanistic understanding of mercury behavior in the aquatic environment. Research by EPRI on mercury in aquatic systems has supported field and laboratory experiments to examine the

processes controlling the behavior of mercury and the development of simulation models and predictive methodologies to calculate mercury accumulation by fish in relation to mercury inputs and to all the site-specific factors that control the rate of accumulation. A comprehensive field study is the focus of current research at EPRI on mercury in the aquatic environment.

4.2.1 METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the United States)

During the period since the last EPRI mercury research update (EPRI 1996), an extensive field and modeling research program, METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the United States), has been initiated in collaboration with an international team of mercury experts to develop a better understanding of the transport, behavior and fate of mercury in lake ecosystems with a special emphasis on the response of mercury cycling to changes to atmospheric mercury deposition. METAALICUS is a whole-ecosystem experiment in which mercury loading to a headwater lake and its watershed is being altered experimentally. These events represent the first whole-ecosystem additions of stable mercury isotopes anywhere. The transport, behavior and fate of the newly added and ambient mercury are both being followed using newly available techniques to directly investigate the question: What happens to fish mercury concentrations when there is a change in atmospheric mercury deposition? This is a critical issue since there are human and environmental health risks to humans associated with mercury exposure via fish consumption.

Inorganic mercury is being added in the form of stable, non-radioactive isotopes of mercury. Furthermore, different mercury stable isotopes are being added to the upland, wetland and lake surface (^{200}Hg , ^{198}Hg and ^{202}Hg respectively) to determine the relative contributions of these sources to fish mercury levels. The power of using isotopes lies in the ability to follow the newly deposited mercury separately from background mercury, and to discriminate the source locations of the mercury mixture in the top trophic level biological compartments.

The METAALICUS program consists of six primary study elements (Figure 4-2). A combination of field, laboratory and modeling studies is being used during METAALICUS. Field programs include pilot studies and baseline work that began in 1999, and the full scale experiment from 2001 through 2003. Long-term follow-up studies are expected in 2004 and beyond.

Mercury concentrations are being tracked in all major compartments in the lake, watershed, and atmosphere. Detailed process studies are also being carried out to follow the movement and transformations of mercury through the watershed and lake, as well as air/surface exchange of mercury. Production of MeHg is being studied in the lake sediments, upland and wetland, as is the bioaccumulation of MeHg into benthic organisms, plankton and fish.

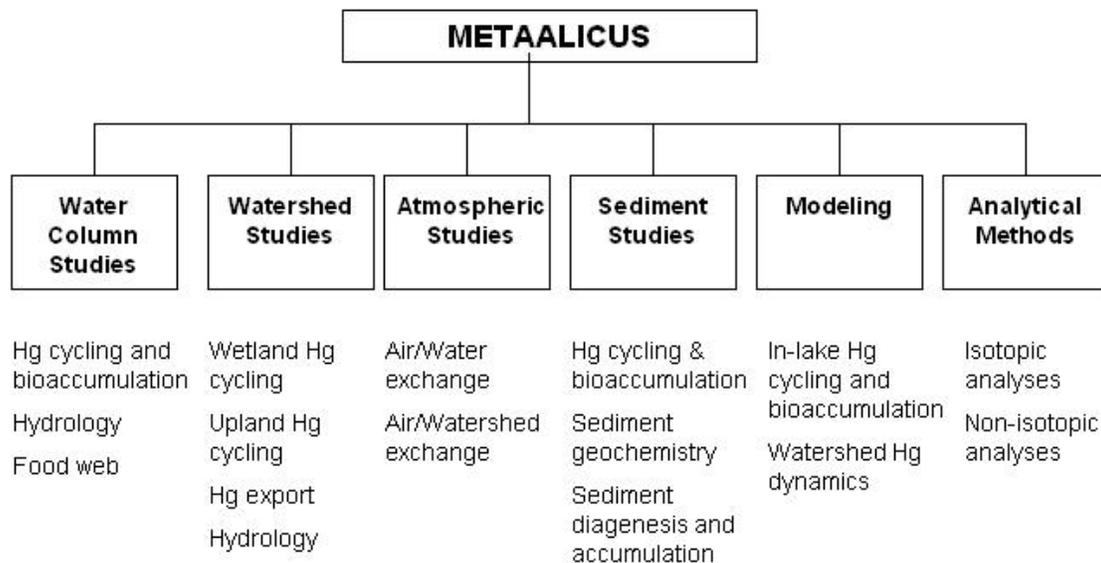


Figure 4-2
METAALICUS Study Elements

The whole-ecosystem approach is based upon studies associated with the first four elements in Figure 4-2: water column, watershed, atmospheric and sediment studies. One of the goals of METAALICUS is to determine the relative contribution of mercury deposited to uplands, wetlands, and the lake surface to fish mercury levels. Wetlands have been identified as net producers of methylmercury in several situations, but the reasons for this observation have not yet been clearly demonstrated. METAALICUS is examining this issue. The export of isotopes (as Hg(II) or methylmercury) to the lake is also critical to follow as terrestrial isotopes move on a pathway than could lead to fish. Hydrologic behavior plays a key role in mercury cycling and export, and is thus being quantified. In forested areas, literature suggests that the mercury deposition is greater than direct deposition in the absence of a foliar canopy. An important question is whether this increase in loading as mercury passes through the canopy is due to additional supply from the atmosphere, or instead represents mercury recycled from soils back through the canopy.

The watershed element of METAALICUS is also critical because the timing of the response of the watershed to changes in atmospheric mercury deposition can potentially affect the overall timing of the fish mercury response. Hintelmann et al. (2002) found that when mercury isotopes were applied to a small upland sub-catchment in METAALICUS, very little was exported in

runoff in the short term (e.g. within a year). The initial results suggest a lag between changes in atmospheric mercury deposition and mercury export in runoff, although the duration of this lag remains to be clarified. Since many lakes receive substantial portions of their inorganic mercury supply from runoff, these results are of central interest to parties wanting to know how long it will take for fish mercury concentrations to respond to changes in atmospheric mercury deposition.

As previously noted, once mercury enters the lake, a complex set of reactions and pathways exists for Hg(II) and MeHg. There remain several important scientific gaps regarding the rates and governing factors for mercury cycling and bioaccumulation in lake water columns and sediments. Following each of these steps is critical if one wants not just to document what happens to fish mercury concentrations, but also to understand why it happens. This is essential if the results of the study will be used to make predictions for other locations. The approach will also provide critical information for EPRI's Dynamic Mercury Cycling Model (D-MCM) (Tetra Tech 2002) that predicts fish mercury concentrations in lakes and the effects of remedial actions such as reductions in mercury loading. Finally, the sixth element of the study is associated with new analytical methods that are a pre-requisite to carrying out the experiment.

Lake 658 at the Experimental Lakes Area, Ontario, was selected as the field site for the METAALICUS investigation. It is a small, oligotrophic, headwater lake on the Canadian Shield and is one of the lakes reserved for research at ELA. Characteristics for Lake 658 are shown in Table 4-2.

Table 4-2
Characteristics of Lake 658

Parameter	Value
Lake area	8.3 ha
Wetland area	1.9 ha
Upland area	42 ha
Drainage pattern	Surface flow headwater lake
Maximum depth	~14 m
Hydraulic retention time	~ 4 years
PH	~ 6.5
Dissolved organic carbon	~ 9 mg L ⁻¹
Predatory fish	Northern pike

ELA is in an area of low atmospheric deposition of mercury, with approximately 7 µg m⁻² yr⁻¹ of wet mercury deposition. The low mercury deposition rate at ELA means that adding the equivalent of about half a teaspoon (2.42 ml) of mercury over a 3-year period is enough to increase wet mercury deposition to the lake and watershed by a factor of three to four. This will

result in a mercury wet deposition rate comparable to rates currently observed in Florida ($>20 \mu\text{g m}^{-2} \text{yr}^{-1}$).

Initial results from METAALICUS also show that when mercury is added directly to the lake surface, transformation to methylmercury and bioaccumulation in the food web occurs quickly, e.g. within weeks in the lower food web (EPRI 2001a; Hintelmann, et al. 2002)). Isotopic methylmercury was observed in fish within 2-3 months of the mercury additions but the isotopic mercury signal in fish was low during this initial period. The newly added mercury is more bioavailable for methylation in sediments than the background mercury at the study site. Methylmercury production rates also depend on the sizes of the new and older mercury pools that are being methylated, and the overall impact of new versus older mercury remains to be quantified in the experiment.

4.3 Mercury Cycling Model Development and Application

For the past ten years EPRI has supported the development of simulation models and empirical approaches to predict the response of aquatic systems to changes in mercury loading. This work includes the development and enhancement of EPRI's Dynamic Mercury Cycling Model (D-MCM) (Hudson, Gherini et al. 1994; EPRI 1996b, 2000, 2001; Tetra Tech 2002), the development of the Watershed Mercury Loading Framework (EPRI 2003), and the Watershed Analysis Risk Management Framework (WARMF) (EPRI 2001).

4.3.1 Dynamic Mercury Cycling Model (D-MCM)

EPRI's Dynamic Mercury Cycling Model (D-MCM) is a Windows-based simulation model (Tetra Tech 2002). It predicts the cycling and fate of the major forms of mercury in lakes, including methylmercury, Hg(II), and elemental mercury. D-MCM is a time-dependent mechanistic model, designed to consider the most important physical, chemical and biological factors affecting fish mercury concentrations in lakes. The D-MCM model can be used in scientific studies to develop and test hypotheses, scope field studies, and improve understanding of cause/effect relationships. In application for regulatory studies, the D-MCM can predict responses to changes in loading, and to evaluate alternative mitigation options facilitating the design of mercury management strategies.

An overview of the major processes in D-MCM is shown in Figure 4-3. These processes include inflows and outflows (surface and groundwater), adsorption/desorption, particulate settling, re-suspension and burial, atmospheric deposition, air/water gaseous exchange, industrial mercury sources, *in-situ* transformations (e.g. methylation, demethylation, MeHg photodegradation, Hg(II) reduction), mercury kinetics in plankton, and bioenergetics related to methylmercury fluxes in fish.

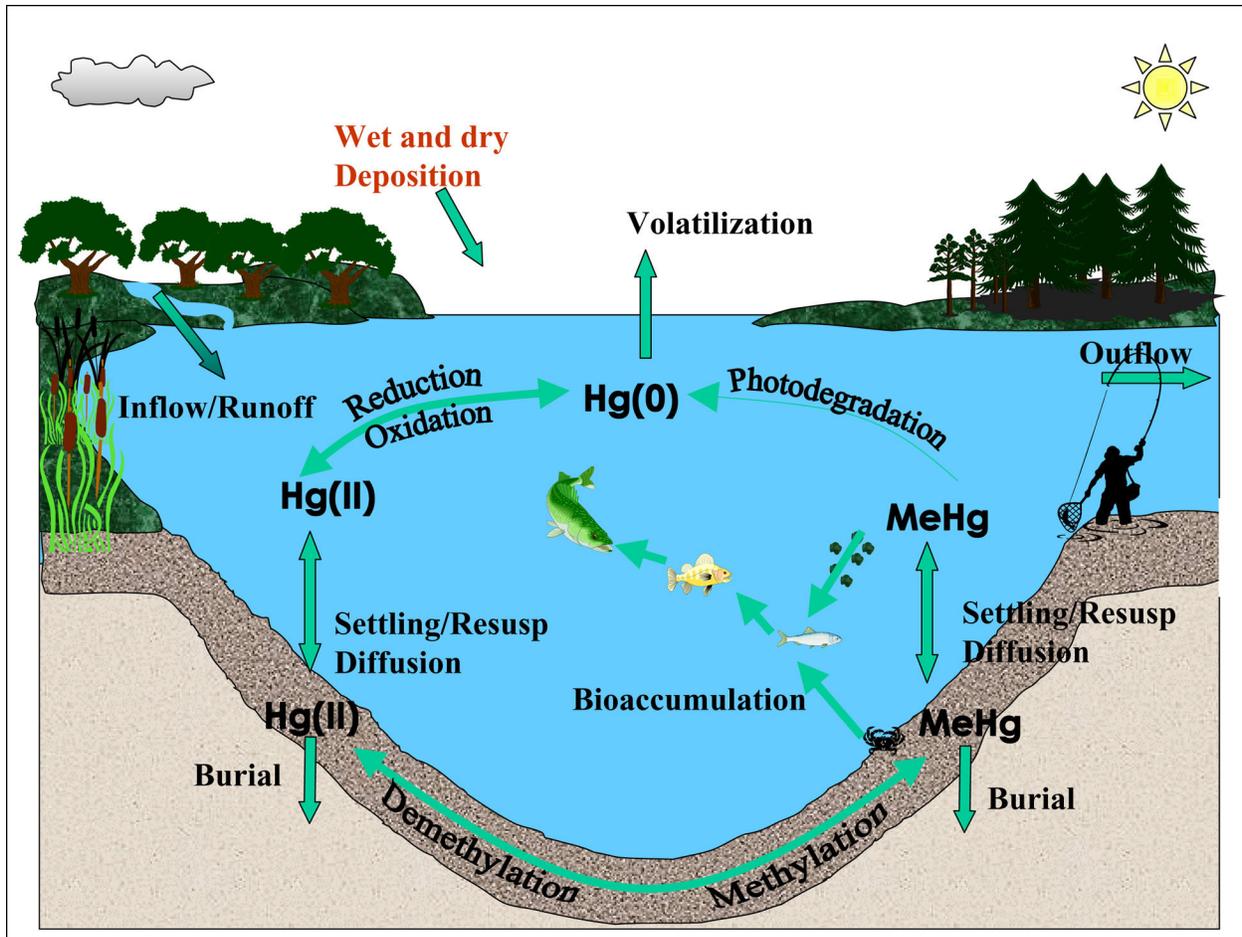


Figure 4-3
Schematic of Hg cycling in D-MCM (Tetra Tech 2002)

Model compartments include the water column, sediments and a food web that includes three fish populations. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry deposition). Similarly, watershed loadings of Hg(II) and methylmercury are input directly as time-series data, not modeled. For lake simulations the user provides inputs for flow rates (surface and groundwater) and associated mercury concentrations, which are combined to determine the watershed mercury loads.

The model food web consists of up to six trophic levels (phytoplankton, zooplankton, benthos, non-piscivore fish, omnivore fish, and piscivore fish). Specific fish species can be selected. Fish mercury concentrations tend to increase with age, and are therefore followed in each year class. Bioenergetics equations for individual fish have been adapted to simulate year classes and entire populations.

The development of D-MCM has been funded by EPRI and the Wisconsin Department of Natural Resources. D-MCM is an extension of previous mercury cycling models, including the original Macintosh-based MCM model developed during the EPRI-sponsored Mercury in Temperate Lakes Project in Wisconsin, and the subsequent steady-state Regional Mercury

Cycling Model (R-MCM). The MCM models have been applied to a wide range of lake conditions in North America. Research and development applications of the MCM models have been carried out in seepage lakes in Wisconsin and Florida, drainage lakes in Ontario and Nova Scotia, and Lake Superior. D-MCM has also been used in US EPA TMDL studies for Devil's Lake, Wisconsin, McPhee Reservoir, Colorado, and Arivaca Lake and Pena Blanca Lake in Arizona.

The predictive capability of D-MCM is currently constrained by gaps in the scientific knowledge. These gaps include the true rates and governing factors for methylation and Hg(II) reduction, factors governing methylmercury uptake at the base of the food web, and the effects of anoxia and sulfur cycling on the behavior of mercury. The role of inorganic mercury loading/supply on methylation is a key uncertainty limiting the ability to predict the effects of changing atmospheric mercury deposition on fish mercury concentrations. As discussed earlier, this topic is being investigated with the METAALICUS project, which includes a component for the testing and improvement of D-MCM. Changes in mercury emissions could be paralleled by changes in emissions and loads of other constituents potentially affecting methylation and fish mercury concentrations, particularly sulfur. A better understanding of the relationship between sulfur cycling and methylmercury production would help address this issue.

D-MCM addresses mercury cycling within the lake system, but does not predict mercury concentrations [Hg(II) or methylmercury] associated with watershed export. Many lakes receive substantial amounts of their inorganic Hg(II) from the watershed, and these loads significantly impact predicted fish mercury concentrations in the receiving lake. A riverine version of MCM, would address the prediction of watershed export of mercury. Such a version of MCM will also provide a tool for examining fish mercury bioaccumulation in rivers.

Finally, an important aspect of any model prediction is the associated confidence limits. D-MCM now has a Monte Carlo capability (Tetra Tech 2002) to help address uncertainty associated with model predictions.

4.3.2 Watershed Mercury Loading Framework

The Watershed Mercury Loading Framework is a Monte-Carlo-based tool developed to estimate inorganic and organic mercury loads to waterbodies (such as reservoirs, lakes, and estuaries) from land-based and atmospheric sources (EPRI 2003b). The Watershed Mercury Loading Framework assumes that mercury can be deposited from the atmosphere as wet and dry deposition, discharged into streams from a variety of land-based sources, and eventually transported to a receiving waterbody.

The framework was developed to allow rapid initial estimates of mercury loads to receiving waterbodies within an uncertainty framework and to assess the effectiveness of controlling specified loads. Loads from atmospheric sources are calculated from regional atmospheric deposition data from the Mercury Deposition Network and the retention of deposited mercury by different land use categories. The model considers loading rates from point sources such as sewage treatment plants or industrial discharges and non-point sources such as mine seepage to waterbodies, methylmercury loads from methylation in wetlands and deposition, and first-order transport loss coefficients in streams, to estimate the total loads delivered to a waterbody. Data

on the watershed characteristics, point sources, and the land uses in a watershed can be obtained from online sources such as from the US EPA's environmental databases. Data on the behavior of mercury in watersheds, such as retention in different land-uses, methylation in wetlands, and uptake/settling in rivers, is more difficult to obtain. However, the framework incorporates the results of EPRI-funded environmental reviews on inputs and outputs of mercury from terrestrial watersheds (Grigal 2002) and mercury sequestration in forests and peatlands (Grigal 2003).

The Watershed Mercury Loading Framework was applied to compute mercury loads to two representative waterbodies, a reservoir with a steep watershed in the Rocky Mountains in Colorado, and a lake surrounded by wetlands in Wisconsin (EPRI 2003b). The loads estimated with consideration of uncertainty showed a wide variation in estimated mercury loading. The range was 0.5 to 3 kg for inorganic mercury in the Rocky Mountain Reservoir, and 0.75 to 3.5 kg of inorganic mercury and 0.01 to 0.06 kg of methylmercury in the Wisconsin lake. The wide range of estimates in the results was driven by several factors. Among these were the range of retention factors in forested land which ranged from 85 to 95%; the loss rate of mercury in streams (0 to 0.04-0.06/mile), and (in the case of the Wisconsin lake) the methylation rate of mercury due to atmospheric deposition in wetlands (0-0.01/yr). These values are consistent with, and indeed, based upon, literature reports. The range of watershed loads that ultimately results from this exercise demonstrates the limited quantitative knowledge of mercury transport, even though there is an abundance of general information on mercury behavior in the environment. The results do not suggest that the mercury loading to watersheds is irresolvable beyond the level presented here, only that the dynamic nature of the loads requires that there be fairly intensive monitoring, inter-annually and intra-annually, to narrow the uncertainty range. Reliable and temporally well-resolved data are also needed before detailed mechanistic modeling of watershed mercury transport is carried out. Complex models, without adequate data for calibration, may not provide load estimates with any greater reliability than the average base-case values computed by the Watershed Mercury Loading Framework.

4.3.3 Watershed Analysis Risk Management Framework (WARMF)

WARMF is a decision support system for watershed analysis as well as TMDL calculation, allocation, and source alteration. WARMF was developed to calculate TMDLs for various pollutants and to conduct watershed management analyses. WARMF has been applied to many river basins in the United States, and has been enhanced to calculate mercury TMDLs.

The WARMF package – containing models, databases, calibrated coefficients, and graphical software – was developed to provide a highly empirical approach involving a large quantity of data and watershed/water quality models to predict the response of aquatic systems to changes in mercury loading. WARMF also extends the TMDL analysis and provides tools to facilitate the stakeholder decision-making process.

4.4 Summary

Based upon research work conducted over the past seven years since EPRI's prior research update (EPRI 1996a), several facts regarding the behavior of mercury in the aquatic environment have become generally accepted. These are summarized below along with identification of additional research and information needed.

- Mercury in various forms enters water bodies from terrestrial, aquatic, and atmospheric sources. A small portion of the total mercury in the aqueous phase is transformed by bacteria in zones of low oxygen (sulfate-reducing bacteria are typically involved) into methylmercury in aquatic systems.
- Sulfate and sulfide are now known to play a complex role in methylation of mercury, with sulfate stimulating MeHg formation at low levels, and sulfide inhibiting formation of MeHg at high sulfide levels. Other abiotic factors of significance in mercury methylation in aquatic environments include dissolved organic carbon and pH.
- Upon uptake by phytoplankton, mercury is initially bio-concentrated by a relatively large factor. From phytoplankton, methylmercury may enter higher trophic levels, including fish, as primarily a function of the food web and not of the aquatic chemistry. Maximum MeHg concentrations have been observed in fish when there is an ample inventory of bioavailable mercury [i.e., Hg(II)], sediment and/or water-column conditions promote methylation (e.g., in wetlands), and a multi-step food-web structure exists.
- The bioaccumulation of MeHg in aquatic organisms, in particular fish, is primarily a function of interacting factors, including the rate of introduction of new inorganic mercury into the system (mercury loading), the net mercury methylation rates (methylation efficiency), food web length, and total mass.
- Improvements are needed in our ability to predict mercury methylation rates: from biotic as well as abiotic methylation, demethylation (by biological photochemical or other processes) and the role of sulfur chemistry. In addition, further work is needed on the likely effects of environmental perturbations on methylation processes in natural systems (EPRI 2003c).
- Changes in mercury emissions might be paralleled by changes in emissions and loads of other constituents, particularly sulfur, potentially affecting methylation and fish mercury concentrations. A better understanding of the relationship between sulfur cycling and methylmercury production would help address this issue, and lend information to update existing models.
- The role in bioaccumulation of newly deposited mercury vs. old mercury, and the time lags between deposition change and biota response, are being addressed by the METAALICUS field study. These issues may require several years of monitoring before they can be adequately answered.
- The role of inorganic mercury loading/supply on methylation is a key uncertainty limiting the ability to predict the effects of changing atmospheric mercury deposition on fish mercury concentrations. This topic is being investigated with the METAALICUS project.
- Speciation, production of methylmercury, and uptake into biological organisms at the primary producer trophic level are fundamental to our understanding of the bioaccumulation

process, since this level appears to represent the largest increase in concentration. Additional information is needed on the kinetics of uptake at the primary producer level.

- Elevated fish mercury concentrations may lead to limits on human consumption and possible impacts on wildlife that consume fish, thus constraining the beneficial uses of water bodies. Elevated mercury in fish may also cause ecotoxicological impacts in related food webs, based upon recent results suggesting that high fish mercury concentrations may also have adverse effects upon fish biology.
- There is a need for the critical examination of the reproductive effects of MeHg on fish, birds, and mammals. Recent evidence suggests that the reproductive success and survival of fish are reduced by dietary exposure to MeHg encountered in waters with contaminated food webs. The further development of toxicological endpoints for the exposure of top predators to MeHg is needed.

References

- Aiken, G. 2003. Personal communication with Dr. Curt Pollman of Tetra Tech, Inc. Discussion on the chemical nature of DOC based on research in the South Florida Everglades.
- Atkeson, T.D. and C.D. Pollman 2002. Trends of mercury in Florida's environment: 1989 - 2001. ACS National Meeting, Orlando, FL, April 7-11, 2002.
- Baldi, F., M. Pepi, and M. Filippelli 1993. Methylmercury resistance in *Desulfovibrio desulfuricans* strains in relation to methylmercury degradation. Applied and Environmental Microbiology. v. 59. no. 8. p. 2479-2485.
- Benoit, J.M., C.C. Gilmour, and R.P. Mason 2001a. The influence of sulfide on solid phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). Env. Sci. Technol. 35:127-132.
- Benoit, J.M., C.C. Gilmour, and R.P. Mason 2001b. Aspects of Bioavailability of Mercury for Methylation in Pure Cultures of *Desulfobulbus propionicus* (1pr3). Applied and Environmental Microbiology, 67(1):51-58.
- Benoit, J.M., C.C. Gilmour, R.P. Mason, and A. Heyes 1999a. Sulfide Controls on Mercury Speciation and Bioavailability to Methylating Bacteria in Sediment Pore Waters. Environ. Sci. Tech. 33: 951-957.
- Benoit, J.M., R.P. Mason, and C.C. Gilmour 1999b. Estimation of Mercury-sulfide Speciation in Sediment Pore Waters using Octanol-Water Partitioning and Implications for Availability to Methylating Bacteria. Environ. Toxicol. Chem. 18: 2138-2141.
- Benoit, J.M., C.C. Gilmour, R.P. Mason, G.F. Riedel, and G.S. Riedel 1998. Behavior of Mercury in the Patuxent River Estuary. Biogeochemistry 80:249-265.

- Bishop, K., Y.H. Lee, C. Pettersson, and B. Allard 1994. Terrestrial Sources of Methylmercury in Surface Waters: the Importance of the Riparian Zone, Abstract from the International Conference on Mercury as a Global Pollutant. Whistler, British Columbia, Canada. July 1994.
- Branfireun, B.A., A. Heyes, and N.T. Roulet 1996. The Hydrology and Methyl Dynamics of a Precambrian Shield Headwater Peatland. *Water Resources Research* 32: 1785-1794.
- Branfireun, B.A., N.T. Roulet, C.A. Kelly, and J.W.M. Rudd 1999. In Situ Sulphate Stimulation of Mercury Methylation in a Boreal Peatland: Toward a Link Between Acid Rain and Methylmercury Contamination in Remote Environments. *Global Biochemical Cycles* 13(3): 743-750.
- Brumbaugh, W. G., D. P. Krabbenhoft, et al. 2001. A National Pilot Study of Mercury Contamination of Aquatic Ecosystems Along Multiple Gradients: Bioaccumulation in Fish, U. S. Geological Survey. USGS/BRD/BSR-2001-0009. iii + 25.
- Choi, S-C., and R. Bartha 1994. Environmental Factors Affecting Mercury Methylation in Estuarine Sediments. *Bull. Environ. Contam. Toxicol.* 53:805-812.
- Compeau, G.C. and R. Bartha 1985. Sulfate reducing bacteria: Principal methylators of mercury in anoxic estuarine sediments. *Appl. Environ. Microbiol.* 50:498-502.
- Compeau, G.C. and R. Bartha 1987. Effect of Salinity on Mercury Methylation Activity of Sulfate-reducing Bacteria in Estuarine Sediments. *Applied and Environ. Microbiol.* 53(2):261-265.
- Driscoll, C.T., V. Blette, C.L. Schofield, R. Munson, and L. Holsapple 1995. The Role of Dissolved Organic Carbon in the Chemistry and Bioavailability of Mercury in Remote Adirondack lakes. *Water, Air, and Soil Pollution* 80: 499-508.
- Engstrom, D.R. and E.B. Swain 1997. Recent declines in atmospheric mercury deposition in the upper Midwest. *Environmental Science & Technology* 31(4): 960-967.
- EPRI 1996a. Mercury in the Environment, A Research Update. Palo Alto, CA. Electric Power Research Institute.
- EPRI 1996b. Regional Mercury Cycling Model: A model for mercury cycling in lakes - R-MCM Version 1.0 Beta - Draft User's Guide and Technical Reference. Palo Alto, CA, Electric Power Research Institute.
- EPRI 2000. Dynamic Mercury Cycling Model for Windows 95/NT - A Model for Mercury Cycling in Lakes - D-MCM Version 1.1 - User's Guide and Technical Reference. Palo Alto, CA, Electric Power Research Institute.
- EPRI 2001a. Controls on fluxes of mercury in aquatic food webs: application of the Dynamic Mercury Cycling Model to four enclosure experiments with additions of stable mercury isotopes. Palo Alto, CA. Electric Power Research Institute. 1005171.

EPRI 2001b. Watershed Analysis Risk Management Framework (WARMF): Update One, A Decision Support System for Watershed Analysis and Total Maximum Daily Load Calculation, Allocation and Implementation. Palo Alto, CA. Electric Power Research Institute.

EPRI 2003a. Watershed Analysis Risk Management Framework (WARMF): Progress Report 4, Mercury TMDL Study for St. Louis River Basin, Nemadji River Basin and North Coast River Basins of Minnesota. Palo Alto, CA. Electric Power Research Institute.

EPRI 2003b. Watershed Mercury Loading Framework. Palo Alto, CA. Electric Power Research Institute.

Frederick, P.C., J.R. Graney, et al. 2001. Wading birds as bioindicators of mercury contamination in Florida: annual and geographic variation.

Gagnon, C., E. Pelletier, and A. Mucci 1997. Behaviour of Anthropogenic Mercury in Coastal Marine Sediments. *Marine Chemistry* 59:159-176.

Gilmour, C.C., E.A. Henry, and R. Mitchell 1992. Sulfate Stimulation of Mercury Methylation in Freshwater Sediments. *Environ. Sci. Tech.* 26: 2281-2287.

Gilmour, C.C. and G.S. Riedel 1995. Measurement of Hg Methylation in Sediments using High Specific-Activity ²⁰³Hg and Ambient Incubation, *Water, Air, and Soil Pollution* 80:747-756.

Gilmour, C.C. 2003. Status Report on the Effect of Water Quantity and Quality on Methylmercury Production. Appendix 2B-2 to 2003 Everglades Consolidated Report for South Florida Water Management District. 21 p.

Golding, G.R., C.A. Kelly, R. Sparling, P.C. Loewen, J.W.M. Rudd, and T. Barkay 2002. Evidence for facilitated uptake of Hg(II) by *Vibrio anguillarum* and *Escherichia coli* under anaerobic and aerobic conditions. *Limnology and Oceanography* 47(4): 967-975.

Gray, J. S. 2002. Biomagnification in marine systems: the perspective of an ecologist. *Marine Pollution Bulletin* 45(1-12): 46-52.

Grigal, D. F. 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. *Environ. Rev.* 10:1-39.

Grigal, D. F. 2003. Mercury sequestration in forests and peatlands: a review. *J. Environ. Qual.* 32: 393-405.

Grippo, M.A. and A.G. Heath. 2003. The effect of mercury on the feeding behavior of fathead minnows (*Pimephales promelas*). *Ecotoxicology and Environmental Safety* 55(2003): 187-198.

Hall, B.D., R.A. Bodaly, R.J.P. Fudge, J.W.M. Rudd and D.M. Rosenberg 1998. Food as the Dominant Pathway of Methylmercury Uptake by Fish. *Water, Air, and Soil Pollution*. 100: 13-24.

- Harris, R.C. and W.J. Snodgrass 1993. Bioenergetics Simulations of Mercury Uptake and Retention in Walleye (*Stizostedion vitreum*) and Yellow Perch (*Perca flavescens*). Water Poll. Res. J. Canada. 28(1): 217-236.
- Harris, R.C. and R.A. Bodaly 1998. Temperature, growth and dietary effects on fish mercury dynamics in Two Ontario Lakes. Biogeochemistry 40(2/3):175-187.
- Hammerschmidt, C.R., M.B. Sandheinrich, et al. 2002. Effects of dietary methylmercury on reproduction of fathead minnows. Abstracts of Papers of the American Chemical Society 223: 182-ENVR.
- Hrabik, T.R. and C.J. Watras 2002. Recent declines in mercury concentration in a freshwater fishery: isolating the effects of de-acidification and decreased atmospheric mercury deposition in Little Rock Lake. Science of the Total Environment 297(1-3): 229-237.
- Hudson R.J.M., S.A. Gherini, C.J. Watras, and D.B. Porcella 1994. Modeling the Biogeochemical Cycle of Mercury in Lakes: The Mercury Cycling Model (MCM) and Its Application to the MTL Study Lakes. In: Mercury Pollution - Integration and Synthesis. C.J. Watras and J.W. Huckabee (Eds.), CRC Press, Inc., Lewis Publishers.
- Hintelmann, H., R. Harris, et al. 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. Environ. Sci. Technol. 36(23): 5034-5040.
- Husar, J.D. and R.B. Husar 2002. Trends of anthropogenic mercury mass flows and emissions in Florida. Clayton, MO, Latern Corporation.
- Jay, J.A., F.M.M. Morel, and H.H. Hemond 2000. Mercury Speciation in the Presence of Polysulfides. Environ. Sci. Tech. 34: 2196-2200.
- Kelly, C.A., J.W.M. Rudd, R.H. Hesslein, D.W. Schindler, P.J. Dillon, C.T. Driscoll, S.A. Gherini, and R.E. Hecky 1987. Prediction of Biological Acid Neutralization in Acid-Sensitive Lakes. Biogeochemistry 3:129-140.
- Kelly, C.A., J.W.M. Rudd, R.A. Bodaly, N.P. Roulet, V.L. St. Louis, A. Heyes, T.R. Moore, S. Schiff, R. Aravena, K.J. Scott, B. Dyck, R. Harris, B. Warner, and G. Edwards 1997. Increases in Fluxes of Greenhouse Gases and Methylmercury following Flooding of an Experimental Reservoir. Environ. Sci. Technol. 31:1334-1344.
- King, J.K., H.E. Kostka, M.E. Frischer, and F.M. Saunders 2000. Sulfate-Reducing Bacteria Methylate Mercury at Variable Rates in Pure Culture and in Marine Sediments. Applied and Environ. Microbiol. 66(6): 2430-2437.
- Krabbenhoft, D. 2003. Personal communication. Discussion of stable isotope addition studies and evidence of rapid uptake of mercury into the food web with Dr. Curt Pollman of Tetra Tech, Inc. based on research in south Florida Everglades.

Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarz, J.P. Hurley, and A.W. Andren 1995. Mercury Cycling in the Allequash Creek Watershed, Northern Wisconsin. *Water, Air, and Soil Pollution* 80: 425-433.

Krabbenhoft, D.P., J.G. Wiener, et al. 1999. A National Pilot Study of Mercury Contamination of Aquatic Ecosystems Along Multiple Gradients. U.S. Geological Survey Toxic Substances Hydrology Program - Proceedings of the technical meeting, Charleston, S. C., March 8 - 12, 1999. U.S.G.S. Water Resources Investigations Report 99-4018B. 2: 147-160.

Latif, M.A., R.A. Bodaly, et al. 2001. Effects of environmental and maternally derived methylmercury on the embryonic and larval stages of walleye (*Stizostedion vitreum*). *Environmental Pollution* 111(1): 139-148.

Langer, C.S., W.F. Fitzgerald, P.T. Visscher, and G.M. Vandal 2001. Biogeochemical Cycling of Methylmercury at Barn Island Salt Marsh, Stonington, CT, USA. *Wetlands Ecology and Management*. 9: 295-310.

Leaner, J.J. and R.P. Mason 2002. Factors controlling the bioavailability of ingested methylmercury to channel catfish and Atlantic sturgeon. *Environ. Sci. Technol.* 36: 5124-5129.

Lindqvist, O., K. Johansson et al. 1991. Mercury in the Swedish Environment - Recent Research on Causes, Consequences and Corrective Methods. *Water Air and Soil Pollution* 55(1-2): R11-&.

Marvin-DiPasquale, M., J. Agee, C. McGowan, R.S. Oremland, M. Thomas, D. Krabbenhoft, and C.C. Gilmour 2000. Methyl-mercury degradation pathways: A Comparison Among Three Mercury-Impacted Ecosystems. *Environ. Sci. Tech.* 34: 4908-4916.

Marvin-DiPasquale, M., J. Agee, and R.S. Oremland 2001. Environmental Controls on Methylmercury Production and Degradation by Bacteria in Florida Everglades Sediments. Report for South Florida Water Management District by US Geological Survey Menlo Park, CA. 47p.

Marvin-DiPasquale, M.C., J.L. Agee, et al. 2003. Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California. *Environmental Geology* 43(3): 260-267.

Mason, R.P., J.R. Reinfelder. et al. 1996. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Environmental Science & Technology* 30(6): 1835-1845.

Morel, F.M.M., A.M.L. Kraepiel, and M. Amyot 1998. The Chemical Cycle and Bioaccumulation of Mercury. *Annu. Rev. Ecol. Syst.* 29: 543-566.

Munthe, J., K. Kindbom, O. Kruger, G. Petersen, J. Pacyna, and A. Iverfeldt 2001. Examining Source-Receptor Relationships for Mercury in Scandinavia, Modelled and Empirical Evidence. *Water, Air, and Soil Pollution*. 1:299-310.

Oremland, R.S., C.W. Culbertson, M.R. Winfrey 1991. Methylmercury Decomposition in Sediments and Bacterial Cultures: Involvement of Methanogens and Sulfate Reducers in Oxidative Demethylation. *Appl. Environ. Microbiol.* 57:130-137.

Rand, G.M. 1995. *Fundamentals of Aquatic Toxicology*. 2nd Edition. Taylor & Francis Publishers.

Ravichandran, M., G.R. Aiken, J.N. Ryan, and M.M. Reddy 1999. Inhibition of precipitation and aggregation of metacinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. *Environ, Sci, Tech.* 33:1418-1423.

RMB Consulting & Research, Inc. 2002. Atmospheric mercury emissions from major point sources - Broward, Dade, and Palm Beach Counties, 1980 - 2000. Raleigh, NC, RMB Consulting & Research, Inc.

Rodgers, D. 1994. You are what you eat and a little bit more: Bioenergetics-based models of methylmercury accumulation revisited. *Mercury Pollution Integration and Synthesis*, C. Watras and J.W. Huckabee Editors. Lewis Publishers. p. 427-440

SFWMD 2003. South Florida Water Management District – Everglades Consolidated Report.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, R.J. Flett, and N.T. Roulet 1996. Production and Loss of Methylmercury and Loss of Total Mercury from Boreal Forest Catchments Containing Different Types of Wetlands. *Environ. Sci. Technol.* 30: 2719-2729.

Tetra Tech Inc. 2002. Dynamic Mercury Cycling Model for Windows 95/NT – A Model for Mercury Cycling in Lakes – D-MCM version 2.0 – User’s Guide and Technical Reference. October 2002. Prepared for EPRI.

Tetra Tech, Inc. 2003. Behavior of mercury in coal ash settings. Draft Report prepared for EPRI. April 2003.

USEPA 1997. *Mercury Study Report to Congress*, Volume I: Executive Summary. Washington, D. C., U. S. Environmental Protection Agency. EPA-452/R-97-003.

USEPA 2001a. Water Quality Criterion of the Protection of Human Health: Methylmercury. Washington, D. C., U. S. Environmental Protection Agency, Office of Science and Technology. EPA-823-R-01-001.

USEPA 2001b. Mercury MAPS. A Quantitative Spatial Link Between Air Deposition and Fish Tissue. Washington, D.C., United States Environmental Protection Agency, Office of Water. EPA-823-R-01-009.

USEPA 2002. Proceedings and Summary Report: Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments, U. S. Environmental Protection Agency. EPA/625/R-02/005. xii + 58

Watras, C.J. and N.S. Bloom 1992. Mercury and methylmercury in individual zooplankton: implications for bioaccumulation. *Limnol. Oceanogr.* 37(6): 1313-1318.

Watras, C.J., K.A. Morrison, et al. 2000. Decreasing mercury in northern Wisconsin: Temporal patterns in bulk precipitation and a precipitation-dominated lake. *Environmental Science & Technology* 34(19): 4051-4057.

Wiener, J.G., D.P. Krabbenhoft, et al. 2002. Ecotoxicology of Mercury. *Handbook of Ecotoxicology*. D. J. Hoffman, B. A. Rattner, G. A. Burton and J. Cairns. New York, Lewis Publishers: 409 - 463.

Wiener, J.G. and P. Shields 2000. Mercury in the Sudbury River (Massachusetts, USA): Pollution History and a Synthesis of Recent Research. *Ca, J, Fish Aquat. Sci.* 57: 1053-1061.

5

ASSESSMENT OF MERCURY EXPOSURE FROM FISH CONSUMPTION

5.1 Introduction

This chapter reviews recent data and analyses regarding MeHg concentrations in fish and fish consumption rates. For the purposes of human exposure assessment, mercury compounds can be considered as 1) elemental mercury vapor 2) other inorganic mercury forms, and 3) monomethylmercury (MeHg).

The average adult's exposure to mercury vapors occurs primarily from dental amalgams. Studies (Weiner and Nylander, 1995) have placed the daily range of exposure from dental amalgams in adults as from 4 to 21 grams per day. For a 100 kg male, this is equivalent to a dose of 40 mg/kg-day.

Exposure to other inorganic mercury compounds occurs primarily from non-fish dietary components, while exposure to methylmercury (MeHg) occurs virtually entirely via consumption of fish (USEPA, 2001a). Levels of MeHg in fish have been found to be 1,000 to 10,000 times as high as those in other foods (USEPA, 2001b). Furthermore, exposure through fish consumption is not geographically isolated. As of December 2000, 41 states had issued 2,242 fish advisories for mercury (USEPA, 2001b). Due to the well-documented susceptibility of humans to the neurotoxic effects of MeHg, and its prevalence in fish, MeHg is the mercury form of greatest concern from a health risk point of view (USEPA, 1997). EPA refers to higher sensitivity in children, while the health literature focuses primarily on *in utero* exposures. This review chapter therefore focuses on MeHg exposure to humans from fish consumption.

The two factors of greatest importance in accurately quantifying human exposure to MeHg via fish consumption are, first, developing representative estimates of MeHg concentrations in fish, and, second, determining accurate fish consumption rates for target demographic groups. Generally, the group of greatest concern is women of childbearing age (due to potential exposure of the fetus) and young children (where relative dose is higher among pre-adolescents than among older children due to lesser body weight). There is as yet no clear evidence of whether post-natal exposure of children is a significant factor in health risk, however.

Concentrations of MeHg in fish vary significantly depending on at least four key factors. The first is the trophic level of the fish (level in the aquatic food web); second, age of the fish; third, whether the fish is wild or farm-raised; and, fourth, whether the fish is a freshwater, marine, or estuarine species (Wiener et al. 2002). Accurate estimation of fish consumption rates is especially important to quantify risks for demographic groups that may consume higher amounts of fish than the average person, such as sports anglers, native cultures, or indigent populations.

In addition, accurate characterization of fish consumption rates in children is especially important due to the presumed greater sensitivity of children to the effects of MeHg. Neurodevelopmental deficits correlated with maternal exposure to methylmercury, as shown by postnatal testing of subject children, indicates that exposure via the mother prior to birth is the time of greatest sensitivity. Therefore, accurate estimates of fish consumption by pregnant women are especially important to quantify *in utero* exposure. These issues will be discussed in further detail in the following chapter on the health effects of MeHg.

There are several dimensions of fish consumption rates that must be considered for quantitative exposure assessment. Exposure is determined by, first, the frequency of consumption of fish meals; second, the type of fish consumed; third, the origin of the fish (whether farmed or wild) and, fourth, the size of the portion.

Estimates of fish mercury concentrations and fish consumption rates can be used to predict likely MeHg exposures, however, actual human exposure to mercury may also be independently corroborated through the use of biomonitoring. Specifically, for mercury, hair and blood may be used to better quantify actual dose of mercury compounds, and converted to exposure rates via bioavailability factors and elimination rates as measured in controlled exposure/dose experiments.

This chapter will first discuss concentrations of methylmercury in fish, fish consumption rates and patterns of fish consumption, current national and state fish advisories, the ambient water quality criterion for methylmercury, and the use of biomonitoring in mercury exposure assessments. The summary at the end of the chapter provides an overview of conclusions and suggestions for further research.

5.2 Concentrations of Methylmercury in Fish

Although the details remain to be clarified, the general mechanism by which mercury enters fish is well-understood. First, inorganic mercury (Hg(II)) enters a water body either by atmospheric deposition from various sources or from point or non-point discharges directly to the water body. A portion of the inorganic mercury (one to three percent) appears to be converted to MeHg, the main form of organic mercury, by microbial activity in the water column, sediments, or water body margins, apparently by sulfate-reducing bacteria. Wetland areas on the margins of water bodies appear to be particularly important in this conversion process (Wiener et al. 2002).

Unlike inorganic forms, the MeHg form of mercury is hydrophobic and therefore is readily absorbed into animal tissues (fat and muscle). Nearly all of the MeHg appears in the consumed portion of the muscle and flesh of fish and marine mammals. MeHg may be taken up by the fish directly from the water column, or by ingestion of food or sediment. At this time we do not know how much fish uptake of mercury is directly from the water column. However, uptake via the ingestion of fish is considered the most important uptake mechanism for mercury. Since MeHg tends to accumulate in animal tissues, fish that consume other fish (piscivores) or animals will tend to accumulate much more MeHg than fish which are primarily herbivores. Further, since MeHg is not readily excreted or metabolized in fish, levels of MeHg in predatory fish will tend to accumulate over the lifetime of the fish. Levels of MeHg in top trophic level predatory fish

such as shark, pike, bass, and swordfish may accumulate MeHg up to 10 million times the concentration in the surrounding water column (USEPA, 2001b)

Some of the mercury depositing to the earth's surface eventually makes its way to water bodies containing sport or food fish. Although most of the mercury that reaches aquatic systems eventually ends up in permanent sediments or is hydrologically flushed from the system, a small fraction is converted to MeHg, which is the form or "species" that is transferred via predation from one trophic level to the next in aquatic food webs. Ecosystems where fish contain elevated levels of methylmercury typically have areas of methylation, such as wetlands or anoxic sediments, where microbial processes convert Hg(II) to methylmercury. In particular, the metabolic activity of sulfate-reducing bacteria in such anoxic zones is recognized as being the most important source of methylmercury in many aquatic systems.

Methylmercury is absorbed from the water by algae and other microorganisms that are consumed by larger organisms (benthic invertebrates, pelagic zooplankton) feeding at the base of the food web. The state of the science is not sufficient to generalize from one system to another as to the relative strength of benthic vs. pelagic routes for the initial entry of methylmercury into the food web. It can, however, be generalized that systems with low pH or with elevated dissolved organic matter concentrations tend to have higher total mercury and methylmercury concentrations in the water column, and higher methylmercury in fish tissues.

Once methylmercury is fixed into biological tissues, grazing and predation transfer it through the food web. Organisms in each successive trophic level can bioconcentrate methylmercury in their tissues at hundreds to thousands times that of the previous level. Even in systems with relatively high mercury loadings, direct exposure of fish (via gills and skin) to methylmercury is not significant – food is the exposure pathway for piscivorous fish. Because of differences in food web structure, pH, dissolved organic matter, life span and size of top piscivorous fish, and many other known and unknown factors, the concept of using a bioaccumulation factor (BAF) to back-calculate a water column methylmercury criterion from methylmercury concentrations in fish tissue is problematic. However, after the science has moved forward, well beyond where it is now, it may be possible to use the BAF approach on a local or regional basis in well-understood systems.

Although fish tissue is usually analyzed for total mercury, studies have shown that virtually all (>90%) of the mercury present in fish is MeHg (Morgan et al., 1994) and located in fish muscle, the portion generally consumed in fish used for human food. Accurate characterization of MeHg concentrations in fish is critical to quantitative assessment of health risk. As stated above, numerous factors affect fish MeHg concentrations, including whether the fish is fresh or processed (canned). The canning process does not affect the fish MeHg content; canned tuna typically have lower MeHg concentrations than fresh tuna because canned tuna comes from younger, smaller fish.

USEPA utilized a mean MeHg concentration in freshwater and estuarine fish of 0.26 mg/kg as the basis for the methylmercury Ambient Water Quality Criterion, setting the criterion at 0.30 mg/kg wet weight (at 17.5 gram fish intake/day) as a fish Tissue Residue Criterion (EPA 2001a). The FAO/WHO Codex Alimentarius guideline levels for fish are 0.5 mg/kg wet weight for non-predators and 1 mg/kg wet weight for predators (such as shark, swordfish, tuna, pike and others) (UNEP 2003) Data submitted to the United Nations Environment Programme for the Global

Mercury Assessment indicated that mercury concentrations in various fish species from numerous locations in the world are generally from about 0.05 to 1.4 mg/kg wet weight (UNEP 2003). Thus, there are many locations around the world where some freshwater and marine fish contain concentrations ranging up to 400 percent greater than the EPA fish tissue residue criterion for MeHg and almost 40 to 300 percent greater than the FAO/WHO guideline.

In contrast, the average concentration of mercury in the types of fish commonly purchased in stores is less than 0.3 ppm, the level of the EPA criterion. Canned tuna has an average mercury concentration of 0.17 ppm, or one half of the US EPA criterion. Certain species of predatory fish such as shark, swordfish, king mackerel, tilefish, and larger tuna typically contain mercury concentrations greater than 1.0 ppm (UNEP 2003), twice the EPA criterion.

5.2.1 Freshwater vs. Marine/Estuarine

Two large studies of mercury in freshwater fish served as the basis for the USEPA ambient water quality criterion for MeHg. These studies included Lowe et al. (1985) and USEPA (1992). The Lowe study reported mercury concentrations in fish collected between 1978 and 1981 at 112 stations throughout the United States. The most common species collected were carp, largemouth bass, and white sucker. The geometric mean concentration was 0.11 µg/g wet weight. The minimum and maximum concentrations were 0.01 and 0.77 µg/g wet weight, respectively. In the USEPA study five bottom-feeding species and five game species were sampled at 314 sampling locations across the United States. It is important to note that these sample locations were selected based on proximity to either a point or non-point pollution source directly to water. The maximum mercury level detected was 1.8 µg/g, and the mean was 0.26 µg/g. The highest concentrations were detected in walleye, largemouth bass, and carp.

Other studies have detected significantly higher concentrations than those reported above with maximum values ranging from 2 to 5.8 ppm reported in some species in New York State (Simonin and Meyer, 1998). The most comprehensive study of mercury in marine fish and shellfish is that conducted in the early 1970's by the National Marine Fisheries Service (NMFS). This study analyzed 5,707 samples of marine fish and shellfish representing more than 200 commercial and recreational seafood species. Average mercury concentrations ranged between 0.009 µg/g wet weight (mullet) to 1.327 µg/g (shark) with most species showing average concentrations of between 0.1 and 0.2 µg/g. No studies focusing exclusively on estuarine fish have been conducted, however, in reviewing the marine fish surveys USEPA concluded that MeHg concentrations in estuarine fish are comparable to freshwater fish (USEPA, 2001a).

A recent study examined heavy metals over a three- year period in farm-raised channel catfish, rainbow trout and red swamp crayfish from facilities across the southern United States. Levels of mercury were on average 2.5% to 1% of the one-part-per-million limit in all farm-raised fish in all samples (Santerre et al. 2001). When compared to captured fish, catfish ranks third in total production, behind Alaskan pollock and Pacific salmon, with Pacific cod ranking fourth. Domestically, catfish is the leading fish grown commercially in the U.S. Catfish represented 70 percent of total fish production in 1998-99, with trout representing 10 percent of U.S. aquaculture output (Santerre et al. 2001).

In a study conducted under the Sea Grant Alaska program from 1999 to 2000, the concentration of mercury in Alaskan fish was evaluated. Tissue from chum, Chinook, Coho, and sockeye salmon taken from four rivers in Alaska was analyzed for total mercury and MeHg. The reported mean concentration of MeHg measured in the muscle tissue of four types of fish, from highest to lowest was Alaskan Pike (8.6 µg/g wet weight), Alaskan Grayling (1.44 µg/g), various Alaskan salmon (0.48 µg/g), and Alaskan whitefish (0.26 µg/g) (Schneider et al. 2001). This pattern of MeHg concentrations reflects the trophic levels of the Alaskan fish types, with the Alaskan pike as the predatory fish with the highest levels.

The levels of mercury in fish for the Great Lakes Region may turn out to be critical to high end consumers. A study of 89 Ojibwa tribal members (Gerstenberger et al 1997) showed that 34.8% ate fish from Lake Superior once or twice a week, while 18.2% ate fish from smaller inland lakes once or twice a week.

5.2.2 Effect of Cooking and Preparation on Methylmercury Levels in Fish

When MeHg is taken up by fish, it is found primarily in the muscle tissue (fillets) bound to proteins. No practical cooking or preparation method, such as skinning or trimming, has been shown to reduce MeHg levels in fish (Chicourel, 2001; EPA, 1999; Morgan, 1997; USEPA 2001b). In fact, because cooking reduces the moisture content of the fish, this actually results in an increased concentration of MeHg in the cooked fish (USEPA 2001b).

5.2.3 Effect of Species and Age on Methylmercury Concentrations

In general, fish species that occupy higher trophic levels (predatory or piscivorous fish) tend to have higher concentrations of mercury (Wiener et al. 2002). This is because of the tendency for MeHg to accumulate in animal tissue rather than in plants. For fish at the fourth or fifth trophic level, the ultimate effect is that methylmercury concentrations in their tissues can be hundreds of thousands to millions of times as great as methylmercury concentrations in the water column. Hence, large predatory fish, such as king mackerel, pike, shark, swordfish, walleye, barracuda, large tuna (as opposed to the small tuna usually used for canned tuna), scabbard, and marlin, as well as seals and toothed whales, contain the highest concentrations. A comparison of MeHg levels in predatory species and bottom-feeding species (carp, catfish, sucker) found that concentrations were significantly higher in predatory species (USEPA, 2001b).

Although fish mercury levels may vary widely across different water bodies, within any given water body fish mercury levels generally increase with age (size) (MacCrimmon et al. 1983 and Mathers et al. 1985, both cited in Wiener et al. 2001). In piscivorous fish species, such as walleye and lake trout, the methylmercury content of the diet and associated rate of accumulation can increase with age, accelerating abruptly when the fish become large enough to shift from a diet of invertebrates to prey fish (MacCrimmon et al. 1983 and Mathers et al. 1985, both cited in Wiener et al. 2001). In adult fish, females have been found to contain higher methylmercury concentrations than males because females must consume more food than males to support the energy requirements of egg production (Nicoletto and Hendricks 1988, and Trudel et al. 2000, both cited in Wiener et al. 2002). The increased feeding rates in females cause greater dietary uptake of methylmercury during this life cycle, and only a small fraction of the accumulated

methylmercury is eliminated during spawning (Hammersmidt et al. 1999, Niimi 1983, and Johnston 2001 cited in Wiener et al. 2002).

Thus, the contamination of fish by MeHg is affected by numerous physical, chemical, and biological processes. That this is a complex process requiring further research is indicated by the fact that two lakes apparently similar physically, chemically and biologically can show very different concentrations of MeHg in their respective fish populations (Grieb et al., 1990; Cope et al., 1990). Within geographic areas of North America, the mean concentrations of methylmercury in same-age fish vary several-fold among lakes that presumably receive similar rates of mercury deposition. Moreover, mean concentrations of mercury in same-age yellow perch are inversely correlated with lake pH and related chemical variables in mid-continent lakes in North America. Similarly, for example, estimated mercury concentrations in 3-year-old largemouth bass from 53 Florida lakes varied over threefold from 0.04 to 1.53 mg/g wet weight and were correlated with lake pH and related chemical factors (Wiener et al. 2002).

5.3 Fish Consumption Rates in the U.S. Population

Fish consumption rates differ significantly in different segments of the population. Accurate estimates of these varying ingestion rates are essential to quantitative risk assessment in sensitive or highly-exposed subpopulations such as children, sport fishers, pregnant women, and native or subsistence cultures. This section first examines fish consumption rates for the general population, followed by rates for pregnant women, children, native or subsistence cultures and sport fishers. This is followed by a discussion of analyses of patterns of fish consumption.

5.3.1 General Population

Food consumption rates of fish for freshwater/estuarine fish, marine and total fish have been found to widely vary in the U.S. by gender, age, region, income level, and whether the individual is a sport fisher or from a native/subsistence culture. Average daily fish consumption rates range from regional rates as high as 50.2 g of total fish in New Jersey (Stern et al. 1996) with a national average of about 15 g per person per day (Jacobs et al. 1998, Gassel 1997).

Jacobs and others performed an analysis of 3 years of recent data from the U.S. Department of Agriculture (USDA) (USDA 1989, 1990, 1991) and estimated food consumption rates for three fish habitats: freshwater/estuarine fish, marine fish, and all fish (Jacobs et al. 1998). The estimated daily fish consumption rates for all fish for the U.S. population was 15.65 g per person, with 4.71 g from freshwater/estuarine sources and 10.94 g from marine sources. The average daily consumption rate for women aged 18-45 years from all sources was found to be 14.25 g.

Gassel conducted a comprehensive review of available literature on fish and shellfish consumption rates (Gassel 1997). The results indicate that the consumption of fish and shellfish by the general population ranged from 12.0 to 17.9 g/day. Gassel also reported that the estimated consumption of fish and shellfish has increased by approximately 25% from the early 1990s. Consumption rates for the sport fishing population ranges up to 4 times as great as the generation population, from 12.3 to 63.2 g/day. Gassel confirmed that consumption rates for subpopulations

by race, age, sex, income, fishing mode, region of the country, and other demographic variables were found to vary.

Another recent study of 1000 randomly selected New Jersey residents (Stern et al. 1996) found the daily fish consumption rates (median) for all adults to be 50.2 g and for women aged 18–40 years to be 41 g. Stern's team also estimated the median methylmercury intake of 7.5 µg/day for all adults and 6.3 µg/day for women (18–40 years).

In a recent survey of both North Dakota and Minnesota, residents' fish consumption rates were analyzed (Benson et al. 2001). Consumption of store-bought fish exceeded sport-caught fish for all populations surveyed. The total median fish consumption rates ranged from 1.4 to 15.1 g/day, and the estimated upper level consumption rate (95th percentile) ranged from 41.5 to 73.6 g/day. The median and upper-level exposure rates (95th percentile) of 62.7 g/day for Minnesota and 64.9 g/day for North Dakota were also within the range of 41 to 78 g/day (95th percentile) determined for national surveys. Seasonal variations in consumption examined for women of childbearing age indicate that the number of meals of fish consumed in June and July was the highest and the level of exposure may be 2 to 3 times higher in the summer.

The relationship between education levels and fish consumption levels indicates no significant differences in fish consumption levels versus education levels. The fish consumption rates and estimated mercury exposure were examined for various income levels of respondents in the North Dakota/Minnesota study (Benson et al. 2001). The highest level of fish consumption was found for North Dakota respondents who have incomes of over \$75,000 per year. The Minnesota data show a bimodal distribution with a peak at \$10,000 to \$15,000 and another at \$50,000 to \$75,000 (Benson et al. 2001).

Comparison with other study results of the age and sex for the selected populations was made. In general, the male populations have a higher fish consumption rate than all the other populations based on other national surveys. Consumption rate data in the Gassel review, discussed above, indicate that males consumed more fish than females especially for sport fishers (Gassel 1997). Benson and others found that the consumption rates for the male population in Minnesota were consistent with the other surveys (Benson et al. 2001). However, in North Dakota, the highest consumption rates were found among women ages 15–44 yrs, and women >44 yrs also had higher consumption rates than the men (Benson et al. 2001).

In 2000, the National Research Council Committee on Toxicological Effects of Methylmercury found that the EPA RfD for human exposure to methylmercury of 0.1 µg/kg-day is scientifically sound for the protection of human health (NRC 2000). The RfD was used in this project as a benchmark for at-risk exposure. In addition, 0.3 µg/kg-day was used to evaluate adult exposure.

Estimates of fish ingestion rates have been reported in the most recent edition of U.S. EPA's Exposure Factors Handbook and Estimated Per Capita Fish Consumption in the United States report (USEPA 1997, 2002). These estimates were developed based on the U.S. Department of Agriculture Continuing Survey of Food Intake for Individuals (CSFII). These estimates include both store-bought and sport-caught consumption and are projected from surveys taken over 3-day periods. For the general population, the mean consumption rate, as indicated in table 10-7 of the Exposure Factors Handbook, of finfish and shellfish from freshwater and estuarine habitats is 6.0 g/day and from marine habitats is 14.1 g/day. The weight uncooked fish tissue is used to

calculate the estimated mean consumption rates for the general population and are based on three year combined survey weights.

The results of these studies were compared to the results of other surveys conducted in the United States to determine if the results obtained in this work are consistent with other surveys conducted and to compare the rates of fish consumption and estimated mercury exposure in Minnesota and North Dakota to other regional and national data. The fish consumption rates in the United States based on national surveys show a range of median fish consumption from 8.1 to 18.7 g/day. In this survey, the median consumption rates were found to be 12.3 and 12.6 g/day for Minnesota and North Dakota, respectively.

5.3.2 Women of Childbearing Age

For women of childbearing age, Tables 10-29 and 10-30 of the Exposure Factors Handbook present estimates of fish consumption rates for women between the ages of 15 and 44. These tables indicate that the estimated mean daily consumption rate of fish and shellfish from fresh water and estuarine habitats is 5.50 g/day and from marine habitats is 12.84 g/day. Similar the general population, these rates were based on the CSFII.

More recently, data concerning fish consumption and blood levels of total mercury for women between the ages of 16 and 49 for about 1700 women were released by the U.S. Centers for Disease Control and Prevention (2002). These data were developed as part of the *National Health and Nutrition Examination Survey* (NHANES) conducted by the National Center for Health Statistics. The recent NHANES data release includes blood Hg concentration data on 1,709 women, including 286 pregnant women, and 1,646 questionnaires on fish consumption over a 30 day period for women with blood Hg data, including 266 of the pregnant women. The NHANES questionnaires asked women how many fish meals, split into twenty-one categories, they had consumed over a thirty day period. Overall, NHANES reported the mean number of fish meals over the 30 day period consumed by pregnant women was essentially identical to the number of meals consumed by women between the ages of 16 and 49. The number of fish meals reported to be consumed by pregnant women was 2.16 and for women between the ages of 16 and 49 the number was 2.15 meals (EPRI 2003).

5.3.3 Children

As indicated in Tables 10-29 and 10-30 of the Exposure Factors Handbook, for the U.S. population under 14 years of age the estimated mean daily consumption rate of fish and shellfish from fresh water and estuarine habitats is 2.35 g/day and from marine habitats 9.02 g/day. The analysis of first year NHANES data base showed that children had about half the blood Hg levels as adult women (EPRI 2003).

Benson and others recently included children in a survey of North Dakota and Minnesota residents' fish consumption and assessment of exposure to methylmercury (Benson et al. 2001). The median values for Minnesota and North Dakota residents showed fish consumption rates for children ranked 4th behind other adult categories for men and women. However, the estimated upper level consumption rates (95th percentile) in Minnesota and North Dakota were found to be

the highest for children. The estimated upper-level fish consumption rates (95th percentile) for children ranked 4th again behind the other categories for adults. Based on the median values, the estimated mercury exposure levels for the Minnesota and North Dakota populations were all below the EPA reference dose for methylmercury of 0.1 µg/kg-day. However, the estimated upper-level exposure (95th percentile) was found to be the highest for children, at levels of 0.297 µg/kg-day in Minnesota and 0.38µg/kg-day in North Dakota. The estimated percentages of children above the EPA reference dose level of 0.1 µg/kg-day are 21% of children (0–14 years) in Minnesota, and 29% of children in North Dakota. The fish consumption rates for children in both states were determined to be consistent with other reported consumption rates. The estimated mercury exposure calculated from the survey information collected in both states was comparable to EPA data (EPA 1997) and found to be very similar to exposures that EPA reported. The results of the comparisons of the estimated mercury exposure for Minnesota children are also very similar, with the results for North Dakota children indicating slightly higher exposures to mercury.

5.3.4 Native Populations and Sport Fishers

Fish consumption studies that provided data for subpopulations of native populations and sport fishers are discussed here. Some studies in the Gassel review mentioned earlier indicated that higher rates of fish consumption were found for certain racial or ethnic subpopulations. Higher consumption rates were found for some Asian, Blacks, Native Americans, and other ethnic groups (Gassel 1997).

The recent survey of North Dakota and Minnesota residents' fish consumption rates and the potential exposure to methylmercury (Benson et al. 2001), included Native American populations from one tribe in Minnesota and two tribes in North Dakota. The Minnesota Bois Forte Tribe had lower median and upper level (95th percentile) consumption rates when compared to the general survey population. Both of North Dakota's two tribes, the Spirit Lake Nation and Three Affiliated Tribes, in general, consume very small quantities of fish as compared to the general population based on median values. However, relatively high upper-level (95th percentile) consumption estimates were found for the two North Dakota tribes. The estimated mercury exposure for the Minnesota-based Bois Forte Tribe population was similar to the other populations surveyed. The estimated mercury exposure for North Dakota-based tribal populations surveyed was lower than the other populations surveyed.

Nonetheless, definitive data for Native Americans, subsistence fish eaters and other consumers with high rates of fish consumption are still lacking.

Sport fishers consumption rate of fish has ranged as low as 1/5 of the national average (3.7 g of freshwater fish) to as high as four times the national average (Ebert et al. 1993, Gassel 1997) of 15.65 g per person (Jacobs et al. 1998). Some evidence indicates that some elderly male sport fish consumers exceed the average consumption rates by two to three times (Gassel 1997). The Santa Monica Bay Seafood Consumption Study showed the consumption of sport-caught fish by populations in California were determined to be up to ten times higher than the national average at 21 g/day, 50 g/day, 107 g/day, and 161 g/day for the median, median, 90th, and 95th percentile rates, respectively (Gassel 1997). Ebert and others (1994) reviewed fish consumption surveys and found the median rates of fish consumption ranged from 2 to 31 g/day on the basis

of surveys of anglers from selected states and river systems and the general U.S. population. Ebert and others (1993) surveyed 2500 licensed resident anglers in Maine; that survey indicated an annual average consumption rate of freshwater river fish of 3.7 g/day.

Sport-caught fish consumption (medians) in Minnesota and North Dakota were found to be 3.9 and 4.5 g/day, respectively (Benson et al. 2001). These rates appear low compared to other surveys and the national average of about 15 g/day. This finding may have resulted from the timing of the survey, an August through September time frame, and may not have been during the time when most of the sport-caught fish are consumed. Seasonal consumption of sport-caught fish was evaluated; the results indicate the highest number of meals per month consumed is in June and July. Based on these results, the exposure may be 2 to 3 times higher in the summer. The upper-level intake rates (95th percentile) for sport-caught fish in Minnesota and North Dakota are 32.1 and 33.9 g/day, respectively. These upper-level consumption rates are similar to sport fisher rates obtained in a Wisconsin study (REF).

Residents with fishing licenses in both Minnesota and North Dakota had higher consumption rates as compared to residents without fishing licenses. Residents with fishing licenses had higher median estimated exposure to mercury as compared to the residents without fishing licenses, but were still well below the EPA reference dosage (Benson et al. 20001).

5.3.5 Patterns of Fish Consumption in the U.S. Population

Patterns of fish consumption refer to the relative types and sources of fish consumed. Since mercury concentrations vary with the type and origin of fish the specific pattern of fish consumption may greatly affect mercury exposure. For example, freshwater fish tend to have higher mercury concentrations than marine fish. Predatory or carnivorous fish tend to have much higher mercury concentrations than herbivorous fish, etc. Thus, it is important for each fish consumption survey to collect adequate information to identify the types and source of fish consumed by respondents.

In the NHANES survey discussed above, the data collected on fish meals consumed cannot be identified as either marine or freshwater fish for three categories that make up slightly over 25% of all responses in the survey. However, several categories – breaded fish, other fish, and unknown fish – cannot be identified as either marine or freshwater fish. Combined, these three categories make up slightly over 25% of all responses in the survey. If “other” and “unknown” are excluded, 384 fish meals were reported for freshwater fish, out of 3,541 total reported meals. Of these 384 meals, 302 were catfish or trout, the two fish species that are most commonly farm-raised. In addition, 341 meals of salmon were reported. Salmon, an estuarine fish, is also increasingly farm-raised. Consequently, these data do not clearly identify the relative fractions of marine and wild freshwater fish (EPRI 2003).

Fish consumption data from a variety of data sources are reported in the EPA’s *Mercury Study Report to Congress*, in a 2002 EPA report, and in EPA’s *Exposure Factors Handbook* (U.S. EPA, 1997b, 2002, and 1997a, respectively). Table 10-7 of the *Exposure Factors Handbook* indicates that the mean consumption rate of finfish (that is, not including shellfish) from freshwater and estuarine habitats is 3.6 grams per day, and from marine habitats 12.5 grams per day (EPRI 2003).

5.4 Current National and State Fish Advisories for Mercury\

Agencies at both of the federal and state levels issue fish advisories regarding concentrations of methylmercury in non-commercial fish.

5.4.1 National Fish Advisories

Fish consumption advisories are issued by the Food and Drug Administration (FDA) for commercial (store-bought) sources of fish and by the USEPA for non-commercial (wild-caught) sources of fish based on analysis of a variety of contaminants, including mercury.

Fish advisories have been issued for mercury in one or more freshwater bodies in 41 states, and 13 states have issued statewide mercury fish advisories. Mercury is the most frequent basis for fish advisories, representing 79 percent of all advisories as of December 2000 (US EPA 2001a).

The US EPA's set of general recommendations for fish consumption are summarized in Table 5-1 below. For example, fish with mercury concentrations ranging from 0.48 -0.97 mg methylmercury/kg wet weight should be eaten no more than once a month and with 0.97 - 1.9 mg/kg wet weight only every second month, whereas fish containing more than 1.9 mg/kg wet weight should not be eaten at all (US EPA, 2001a).

Table 5-1
US EPA's monthly fish consumption limits for methylmercury (US EPA, 2001b).

Max. number of fish meals/month	Fish tissue concentrations (ppm = mg/kg, wet weight)
16	> 0.03–0.06
12	> 0.06–0.08
8	> 0.08–0.12
4	> 0.12–0.24
3	> 0.24–0.32
2	> 0.32–0.48
1	> 0.48–0.97
0.5	> 0.97–1.9
None (<0.5)*	> 1.9

* None = No consumption recommended.

> means "above" (example "> 0.06–0.08" means: "above 0.06 to 0.08")

The FDA has jurisdiction over fish sold in U.S. commerce, and issues action levels for concentration of mercury in fish and shellfish. The current FDA action level (as per 1998) is 1 ppm (1 mg/kg) total mercury based on health impacts. Freshwater fish can have mercury levels which exceed the FDA action limit of 1 ppm. The levels in some marine species such as shark, swordfish, and king mackerel are also typically this high. However, the concentration of methylmercury in commercially important marine species is on average close to ten times lower than the FDA action level. Based upon National Marine Fisheries data, marine fish have shown mercury levels over twenty years to be relatively constant in various species. Comparable trends data for freshwater fish do not exist, although there are data for coastal and estuarine sites (US EPA, 1997).

Using an alternative approach, the US ATSDR developed its current Minimal Risk Level (MRL) of 0.3 µg/kg body weight per day for methylmercury using the Seychelles Child Development Data (US ATSDR, 1999). The MRL is an estimate of the level of human exposure to a chemical that does not entail appreciable risk of adverse non-cancer health effects. They are intended for use by the public health officials as screening tools to determine when further evaluation of potential human exposure at hazardous waste sites is warranted.

In January 2001 the Food and Drug Administration (FDA) Center for Food Safety and Applied Nutrition (CFSAN) issued a consumer advisory for pregnant women and women of childbearing age regarding the risks of mercury in fish (FDA, 2001). This advisory recommends that such women avoid eating shark, swordfish, king mackerel, and tilefish due to the tendency of these fish to contain high levels of MeHg. The advisory suggests that other fish can be consumed but no more than 12 cooked ounces per week.

Also in January 2001, the USEPA issued a mercury-related fish consumption advisory stating that “women who are pregnant or may become pregnant, nursing mothers and young children, limit consumption of such fish [freshwater fish] to one meal per week (six ounces of cooked fish per adult; two ounces of cooked fish per child (USEPA 2001b). Note that the USEPA advisory, which applies mainly to freshwater, sport-caught fish, is more restrictive than the FDA advisory by a factor of two.

5.4.2 State Fish Advisories

MeHg is the leading cause of fish consumption advisories in the United States (Gensberg and Toal, 2000) and, as of December 2000, has been associated with 2,242 fish advisories in 41 states (USEPA, 2001b). As the awareness of the potential health impacts from consuming fish containing MeHg has grown, the number of such advisories has increased 149% from 899 issued in 1993 to 2,242 in 2000. The number of states reporting such advisories has also increased from 27 in 1993 to 41 in 2000.

Because of concern that even a single meal of highly contaminated fish may produce adverse effects in pregnant women, the State of Connecticut recently developed a single-meal fish advisory. Using the same one-compartment pharmacokinetic model used by the USEPA to relate MeHg ingestion rate to maternal hair concentrations, Ginsberg and Toal (2000) estimated that one meal of fish containing 2.0 ppm or more MeHg could result in an expectant mother's

exceedance of the RfD for days to weeks during fetal gestation. The model was validated against blood concentrations in human test subjects who ingested MeHg in fish either as a single meal or multiple meals.

5.5 Ambient Water Quality Criterion for Methylmercury

The USEPA recently issued a national ambient human health water quality criterion for MeHg pursuant to the Clean Water Act section 304(a) (USEPA, 2001a). The MeHg criterion, called a Tissue Residue Criterion (TRC), is 0.3 mg MeHg/kg fish. The criterion was based on the USEPA MeHg Reference Dose (RfD) of 0.1 µg/kg body weight/day. The RfD is an “estimate of daily exposure to the human population (including sensitive subgroups) that is likely to be protective without an appreciable risk of deleterious health effects during a lifetime.” The TRC is the concentration in fish tissue that should not be exceeded based on a total fish and shellfish consumption rate of 17.5 g/day.

Historically, all water quality criteria developed to date under this program have been expressed as water column concentrations. However, for a number of reasons, including the difficulties in extrapolating from water concentrations to fish tissue concentrations, and the importance of fish consumption as the primary source of human exposure to MeHg, USEPA decided to issue the MeHg criterion expressed as a fish tissue concentration. Although USEPA attempted to account for mercury consumed in fish from marine sources, they assumed that marine fish and farmed fish would be unaffected by EPA action to reduce mercury emissions.

5.6 The Use of Biomonitoring in Mercury Exposure Assessment

Biomonitoring may play an important role in quantitatively evaluating actual human exposure to mercury and to help ensure that such exposures remain below safe levels. Blood and hair are the most common tissues used for mercury monitoring.

Mercury levels in hair have been shown to reflect levels in internal organs (Clarkson, 1992; Pfeiffer et al., 1993) and to be significantly positively correlated with fish consumption, the number of dental amalgams, and blood levels of mercury (Airey 1983, Clarkson 1992; Pfeiffer et al., 1993; Babi et al., 2000). Hair is considered to be the best screening indicator for human MeHg exposure (Babi et al., 2000), although commercial laboratories widely vary in the accuracy of their results (Siedel et al. 2001).

The World Health Organization (WHO) expert committee on methylmercury noted that a 5% risk of subtle developmental effects may be associated with maternal hair mercury levels of 10-20 ppm (WHO, 1990). More recently, the USEPA and the National Academy of Sciences recommended that whole blood mercury levels remain less than 5.0 µg/L and hair levels less than 1.0 µg/g (NRC, 2000). These levels, which correspond to the USEPA RfD for MeHg of 0.1 µg/kg/day, are apparently frequently exceeded in the general population.

Next, this section provides a discussion of three recent studies of mercury levels in blood and hair. The first two studies drew upon blood and hair of surveyed individuals from local populations; the third study of blood levels was based upon a more extensive data set. It is

noteworthy that the mercury biomonitoring of hair from women of childbearing age in the first study showed very low mercury levels (from 0.01 to 0.64 µg/g) (Benson et al. 2001), while the second, more localized, study indicated high blood levels of mercury in individuals with a high rate of fish consumption (a mean blood mercury level from 13 to 15 µg/L) (Hightower and Moore 2002).

In the recent survey of North Dakota and Minnesota residents' fish consumption rates described earlier in this chapter, the potential exposure to methylmercury was also analyzed (Benson et al. 2001). Hair donor selection was limited to women of childbearing age. The mercury levels found in the hair samples were very low and ranged from 0.01 to 0.64 µg/g. The estimated mercury exposure was determined from hair samples and compared to fish consumption survey results. The survey-based estimated mercury exposure was, on average, a factor of six higher than the hair-based calculation. These results indicate that a relatively strong correlation exists between the individual mercury exposure estimated from reported fish consumption and mercury level measured in human hair.

In a study of 123 patients visiting a private Internal Medicine practice in San Francisco, California, Hightower and Moore (2002) found a mean blood mercury level in 66 women of 15 µg/L and a mean of 13 µg/L in 23 men. There was no evidence that these patients were subjected to unusual levels or sources of mercury exposure, however, patients were selected for mercury testing based on a dietary history indicating that relatively high fish consumption rates may have existed. Furthermore, patients who ate fish caught out locally were excluded from the survey.

5.6.1 Blood Levels of Methylmercury and Fish Consumption: NHANES 2002 Data

This section provides a detailed discussion of recent analyses of a large data set for human blood levels of methylmercury and national fish consumption (EPRI 2003; Schober et al. 2003). Data from the federal National Health and Nutrition Examination Survey (NHANES), released in June 2002, provided the first opportunity to compare blood levels of total mercury with the amount of fish consumed for a large number of U.S. citizens. The NHANES data make this comparison possible for a large number of U.S. women and children who have participated in the survey. The data include the results of measurements of concentrations of mercury in blood for 1,709 women between the ages of 16 and 49, and for 705 children between the ages of 1 and 5. Weighting factors were provided so that results from the sample population can be adjusted to reflect the age, geographic location, and ethnicity of the U.S. population as a whole.

5.6.1.1 Blood Concentrations

Of the 1,709 women whose blood levels of mercury were measured, 286 were pregnant. Seven more pregnant women participated in the study, but their blood levels of mercury were not measured and their ages fell outside the 16-49 range. Thus, using the 16-49 age group did not eliminate any pregnant women for whom blood mercury data were available.

Analyses of the NHANES data for 2001 indicated that approximately 8 percent of all of the women tested had hair and blood mercury levels exceeding the levels corresponding to the US EPA RfD (CDC, 2001; Schober *et al.*, 2003, both cited in UNEP 2003). These results from the

NHANES data confirm EPA's estimate from national dietary surveys that up to 7 percent of women of childbearing age in the U.S. may exceed the exposure of the EPA RfD (USEPA 1997).

The most recent NHANES results from 2002 report both total and speciated mercury in blood. According to documentation accompanying release of the CDC data files, "speciated" mercury refers to inorganic (elemental and ionic) mercury (EPRI 2003). Thus, total mercury includes these inorganic forms plus organic methylmercury. The NHANES data on blood levels of speciated mercury appear to be unusable, except for the upper tail of the distribution (EPRI 2003). For 97% of all samples the reported blood levels of speciated (i.e., inorganic) mercury were either 0.3 or 0.4 µg/L, with the lowest reported value (or detection limit divided by the square root of two) being 0.3 µg/L. For about 25% of these samples, reported blood levels of speciated mercury exceeded blood levels of total mercury, which could be as low as 0.1 µg/L.

Clearly, the high detection limits for speciated mercury make it impossible to determine what fraction of total mercury is due to speciated (inorganic) forms (EPRI 2003). At the upper end of the total mercury distribution, blood levels were sufficiently high that a meaningful estimate could be made of the distribution of total mercury minus inorganic mercury. However, the problem of high detection limits for inorganic mercury does not permit the calculation of the mean blood concentration of methylmercury.

The data released in 2002 show lower blood levels of total mercury, and suggest lower mercury exposures, than the first-year data reported in 2001. Table 5-2 and Figure 5-1 describe the distribution of the June 2002 results. When these data released in 2002 are weighted to account for U.S. demographic patterns, about 9% of women in the study have blood levels of total mercury above 5.37 ppb. Since the reference dose (RfD) is for methylmercury, not for total mercury, the number of women exposed above the RfD for methylmercury is lower.

Distribution of Top 10% of MeHg Blood Levels, U.S. Women, Ages 16-49, with Demographic Weights Applied

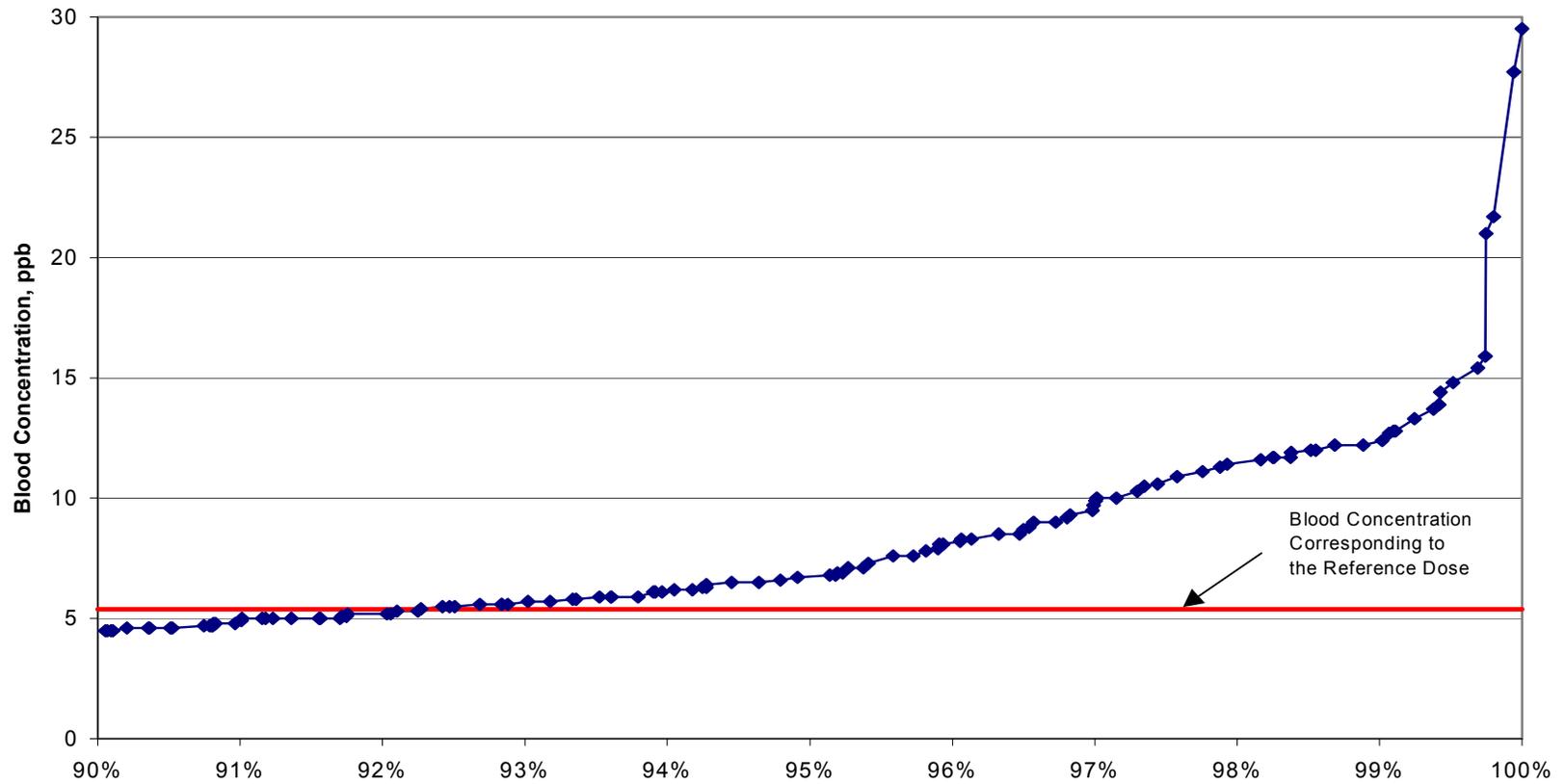


Figure 5-1
Distribution of Top 10% of MeHg Blood Levels, U.S. Women, Ages 16-49, with Demographic Weights Applied (EPRI 2003)

Table 5-2
Blood Mercury Levels of Women Ages 16–49, NHANES data

	All Women in Sample	Pregnant Women
Number of women in sample	1709	286
Geometric mean, total blood Hg	1.02*, 0.92 [†] ppb	0.97*, 0.78 [†] ppb
Arithmetic mean, total blood Hg	2.00*, 1.72 [†] ppb	1.86*, 1.45 [†] ppb
90 th percentile	4.9*, 4.0 [†] ppb	5.0*, 3.1 [†] ppb
75 th percentile	2.1*, 1.9 [†] ppb	2.0*, 1.6 [†] ppb
50 th percentile	1.0*, 0.9 [†] ppb	1.0*, 0.8 [†] ppb
25 th percentile	0.5*, 0.4 [†] ppb	0.4* [†] ppb
10 th percentile	0.2* [†] ppb	0.2* [†] ppb
Exceed RfD blood level of 5.37 ppb [§]	8.7%*, 6.0% [†]	9%*, 4.9% [†]

* Weighted for demographic factors

[†] Unweighted for demographic factors

[§] This compares total mercury blood concentrations with the reference dose (RfD) for methylmercury.

As noted above, the upper tail of the distribution for methylmercury can be calculated, because for the women with the highest blood mercury concentrations, the imprecision in the inorganic mercury measurements do not greatly affect the difference between total mercury and inorganic mercury. When this methylmercury distribution is examined, the data indicated that slightly over 5% of the women in the sample, before demographic weights are applied, have blood methylmercury concentrations above the RfD. After applying the demographic weights, it appears that about 7.7% of the women have blood concentrations above the RfD.

5.6.1.2 Fish Consumption

Data on fish consumption are available for 1,646 of the 1,709 women whose blood levels of mercury were measured, for 277 of the 286 pregnant women in that group, and for 667 of the 705 children. The NHANES data include detailed information on food consumed within the previous 24 hours, and a count of how many times various types of fish were consumed over the previous 30 days. The types of fish in the NHANES dataset include: breaded fish products, bass, catfish, cod, flatfish, haddock, mackerel, perch, pike, pollock, porgy, salmon, sardines, sea bass, shark, swordfish, trout, tuna, walleye, “other” fish, and “unknown” fish. Data for the types of fish consumed is potentially useful for determining patterns of fish consumption among women with the highest measured blood levels of mercury. Conversely, this information can also be used to compare the blood levels of mercury in women who consume fish far more frequently than average (EPRI 2003).

5.6.1.3 Fish Consumption versus Mercury Concentration

Table 5-3 shows the number of fish meals women consumed in the previous 30 days when the women are grouped according to their measured blood levels of total mercury (expressed as blood mercury percentiles). It includes only those women for whom both fish consumption and blood level data are available. From the table, it is clear that blood levels of mercury rise as fish consumption rises (EPRI 2003). This relationship holds for women in the 16–49 age group, and for pregnant women within that group. It is noteworthy that the woman with the highest blood level of mercury (measured at 38.9 ppb; see Figure 5-2) reported eating no fish during the previous 30 days.

Figure 5-2 also illustrates the positive trend observed when the number of fish meals women consumed is compared with their measured blood levels of total mercury. The line on the figure represents the best linear fit to the data. However, it is clear that the data points are widely scattered and that accurate prediction of an individual’s blood level of mercury based on her fish consumption is impossible.

Table 5-3
Fish Consumption (meals in the previous 30 days) versus Blood Mercury Levels, NHANES data (unweighted for demographic factors)

Blood Hg Percentile	Women 16–49	Pregnant Women, 16–49
All	2.15	2.16
Top 90 th percentile	5.41	7.46
Top 75 th percentile	4.08	4.57
Top half of group	3.25	3.27
Lowest 25 th percentile	0.73	0.72
Lowest 10 th percentile	0.54	0.51
Those with blood Hg > RfD level*	6.22	8.92

*Refers to women with blood levels of total mercury exceeding the reference dose (RfD) for methylmercury.

Tables 5-4 and 5-5 show the number of fish meals reported over the previous 30 days for each type of fish. It is important to know how many freshwater fish women in the survey consumed because mercury emissions from U.S. utilities are likely to have a much greater impact on the mercury content within freshwater fish than marine fish. However, it is difficult to get a clear picture of freshwater fish consumption by women in the survey for two reasons. First, the total number of meals reported for “other” or “unknown” fish exceeds the number of meals reported for freshwater fish. Until it is known how many of these other and unknown fish are freshwater species, the actual number of freshwater fish meals consumed by women in the survey remains uncertain (EPRI 2003).

**Blood Mercury Versus Fish Meals
Women Ages 16-49**

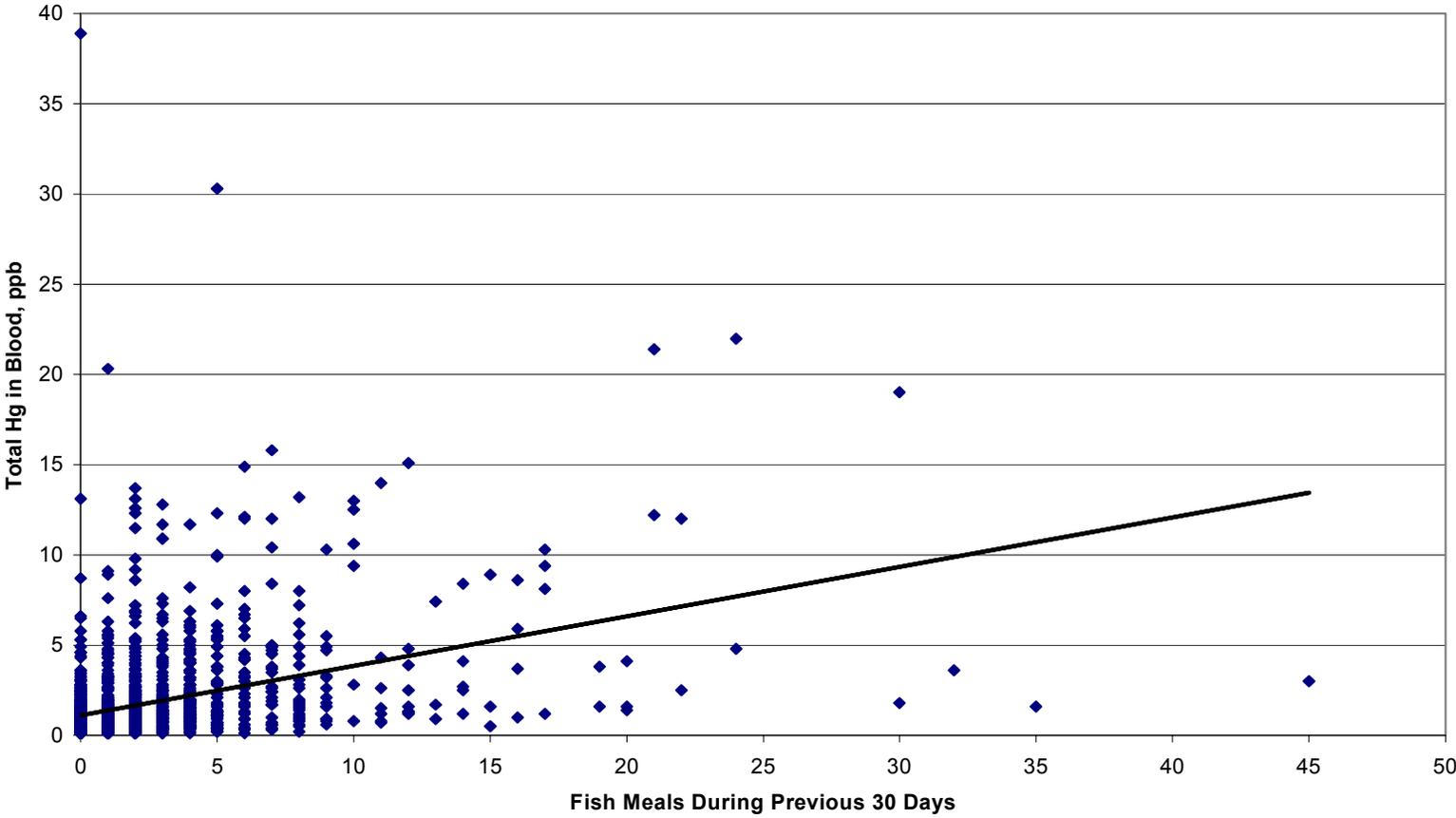


Figure 5-2
Blood Mercury versus Fish Meals, Women Ages 16-49 (EPRI 2003)

Second, catfish and trout make up almost 80% of the freshwater fish meals reported for all women, and more than 90% of such meals for pregnant women and children. Unfortunately, it is impossible to tell from the data whether these catfish and trout meals involve wild or farm-raised fish. The distinction is important because farm-raised catfish and trout have lower methylmercury levels than their wild cousins (Santerre, 2001). This is so because farm-raised fish are housed and cultivated using specialized feed in a way that prevents methylmercury from accumulating in their bodies, as it does in wild fish. For this reason, mercury exposures from consumption of farm-raised catfish and trout are already low, and are unlikely to be affected by changes in U.S. utility mercury emissions.

Table 5-4
Fish Meals Reported for the Previous 30 Days by Women Ages 16–49 and Children Ages 1-5, NHANES data

Fish Type	Meals Reported by all Women (1646 in sample)	Meals Reported by Pregnant Women (277 in sample)	Meals Reported by Children (667 in sample)
Breaded fish	403	48	274
Bass	24	1	5
Catfish	253	44	81
Cod	105	13	17
Flatfish	92	11	51
Haddock	38	6	13
Mackerel	18	1	7
Perch	46	4	0
Pike	1	0	2
Pollock	67	8	9
Porgy	9	0	1
Salmon	341	44	72
Sardines	56	8	24
Sea bass	15	4	2
Shark	4	2	1
Swordfish	28	12	0
Trout	49	8	13
Tuna	1,470	289	460
Walleye	11	0	3
Other fish	385	58	154
Unknown fish	126	37	42
Total fish meals	3,541	598	1,231

The fraction of fish consumed that are wild, freshwater fish is not identified specifically in the NHANES data (EPRI 2003). This fraction depends on the portion of catfish, trout, other, and unknown fish that were consumed were wild freshwater fish. To estimate a total number of fish meals consumed by women ages 16-49 of about 3,000 fish meals, researchers assumed that most of the trout and catfish were farm-raised, some of the breaded fish were catfish, and about half of the salmon were farm-raised. Of this number of fish meals, 84 fish meals were assumed be of species that are almost certain to be wild, freshwater fish, and another 500 or so meals are of “other” and “unknown” fish. This estimate is probably high, but a high estimate was made to avoid underestimating the fraction of wild freshwater fish meals because the effect of mercury emission reductions on the methylmercury content of fish is greatest for such fish. Having selected an estimate of 10% as the fraction of fish meals, excluding farm-raised fish that were wild freshwater fish, researchers assumed that the remaining 90% of fish meals were of marine fish.

5.6.1.4 NHANES Study Conclusions

In summary, the NHANES data released in 2002 provided the first opportunity to compare a biomarker for mercury exposure—blood level of total mercury—with information about fish consumption for a large number of individuals in the U.S. Although the data show that blood levels of mercury rise as fish consumption rises for the sample population as a whole, data variability precludes accurate prediction of an individual’s blood level of mercury based on her fish consumption (EPRI 2003).

When the data are weighted to account for U.S. demographic patterns, about 7.7% of women in the study have blood levels of methylmercury above 5.37 ppb, the blood concentration associated with the reference dose (RfD). Utility emissions of mercury contribute to these exposures primarily by adding mercury to the loading in freshwater fish that are then consumed. About 2.3% of fish meals eaten by women in the survey were estimated to be made up of wild freshwater fish, and 10–25% of the fish meals were of freshwater fish (either wild or farm-raised). These proportions are dependent upon assumptions made about the undefined species in the NHANES survey. It appears that for fish types that would be affected by reductions in mercury emissions (all fish except farm-raised fish), 10% is a conservatively high estimate of the fraction of fish meals that include wild, freshwater fish.

**Table 5-5
Summary of NHANES Data on Fish Meals**

Fish Type	Meals Reported by all Women (1646 in sample)	Meals Reported by Pregnant Women (277 in sample)	Meals Reported by Children (667 in sample)
Total fish meals	3,541	598	1,231
Total freshwater fish*	384	57	104
Total freshwater fish other than trout and catfish*	82	5	10
Catfish and trout meals	302	52	94
Total "other" and "unknown" fish meals	511	95	196

* If "breaded," "other," and "unknown" fish are not included as freshwater fish.

5.7 Summary and Conclusions

- There are many locations around the world where some freshwater and marine fish contain mercury concentrations range up to four times the EPA fish tissue residue criterion for MeHg and almost 40 to 300 percent above the FAO/WHO guideline.
- In contrast, the average concentration of mercury in the types of fish commonly purchased in U.S. stores is less than 0.3 ppm, the level of the EPA criterion. Canned tuna has an average mercury concentration of 0.17 ppm, or one-half of the EPA criterion. However, species of predatory fish typically contain mercury concentrations greater than 1.0 ppm, twice the EPA criterion.
- A substantial body of research work has confirmed that fish species from higher trophic levels (predatory or piscivorous fish) tend to contain higher concentrations of MeHg, due to the bioaccumulation of MeHg in animal tissue. For fish at higher trophic levels, the MeHg concentrations in tissue can be orders of magnitude greater than concentrations in the water column. Thus, large predatory fish, such as king mackerel, pike, shark, swordfish, walleye, barracuda, large tuna, scabbard, and marlin, as well as seals and toothed whales, contain the highest MeHg concentrations.
- Although fish mercury levels may vary widely across water bodies, within any single water body, fish mercury levels generally increase with age (size). In adult fish, females have been found to contain higher MeHg concentrations than males, due to increased feeding rates during egg production by females.
- Recent research has shown that within geographic areas of North America, the mean concentrations of MeHg in same-age fish vary widely among lakes that receive similar rates of mercury deposition. The variability may be explained by the inverse correlation found

with lake pH and related chemical variables in these mid-continent lakes. Additional research work could clarify and quantify these relationships in lakes and rivers.

- Further studies of bioaccumulation and interactions in the food webs for species of food fish would help to better describe, quantitatively, the links between releases of mercury and observed concentration levels and impacts of MeHg upon humans.
- The recent NHANES data set provides the first opportunity to compare a biomarker for exposure—blood level of total mercury—with information about fish consumption for a large number of individuals in the U.S. These data show that blood levels of mercury rise as fish consumption rises for the sample population as a whole.
- When the NHANES data are weighted to account for U.S. demographic patterns, about 7.7% of women in the study have blood levels of methylmercury above 5.37 ppb, the blood concentration associated with the reference dose (RfD). However, NHANES data variability appears to preclude accurate prediction of an individual's blood level of mercury based on fish consumption.
- Coordinated and expanded monitoring of mercury concentrations in human hair blood, and other relevant human samples would be useful in order to allow better definition of populations at risk from increased exposure. Biomarker monitoring may be useful as a tool for prioritizing prevention actions on a local scale.
- Utility emissions of mercury contribute to human exposure primarily by adding mercury to the loading in freshwater fish that are then consumed. Fish that would be affected by reductions in power plant mercury emissions, i.e., wild freshwater fish, were conservatively estimated to be in an average of 10% of the fish meals for women in the NHANES survey.

References

Airey, D. 1983 Mercury in Human Hair Due to Environment and Diet: A Review. *Environ. Health Perspec.* , 52, 303–316.

Babi, D., Vasjari, M., Celu, V. and M. Korovesi. 2000. Some results of Hg content in hair in different populations in Albania. *The Science of the Total Environment* 259:55-60

Benson, S.A., C.R. Crocker, J. Erjavec, R.R. Jensen, C.M. Nyberg, C.Y. Wixom, and J.M. Zola. 2001. *Fish Consumption Survey: Minnesota and North Dakota*, Final Report

For U.S. Department of Energy, National Energy Technology Laboratory. DOE Cooperative Agreement No. DE-FC26-98FT40321. By Energy & Environmental Research Center, University of North Dakota, 2001-EERC-10-01 October 2001

Centers for Disease Control and Prevention, “Blood and hair mercury levels in young children and women of childbearing age—United States, 1999,” *Morbidity and Mortality Weekly Report*, Vol. 50, No. 8, March 2, 2001.

Clarkson, T.W. 1992. Mercury: Major issues in environmental health. *Environmental Health Perspectives* 100:31-38

Ebert, E.S.; Price, P.S.; Keenan, R.E. 1994. Selection of Fish Consumption Estimates for Use in the Regulatory Process. *J. Exposure Anal. Environ. Epidemiol.* 4 (3), 373–393.

Ebert, E.S.; Harrington, N.W.; Boyle, K.J.; Knight, J.W.; Keenan, R.E. 1993. Estimating Consumption of Freshwater Fish Among Maine Anglers. *North Am. J. Fisheries Manage.* 13, 737–745.

EPRI, 2003. A Framework for Assessing the Cost-Effectiveness of Electric Power Sector Mercury Control Policies. Palo Alto, CA. TR-1005224.

FDA. 2001. Consumer Advisory. An Important Message for Pregnant Women and Women of Childbearing Age Who May Become Pregnant About the Risks of Mercury in Fish. Center for Food Safety and Applied Nutrition. Washington, D.C.

Gassel, M. *Chemicals in Fish Report No. 1: Consumption of Fish and Shellfish in California and the United States*; Final Draft Report. Pesticide and Environmental Toxicology Section, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency: Berkeley, CA, 1997.

Gerstenberger, S.L.; Travis, D.R.; Hanson, L.K.; Pratt-Shelley, J.; Dellinger, J.A. 1997. Concentrations of Blood and Hair Mercury in an Ojibwa Population That Consumes Great Lakes Regional Fish. *Clinical Toxicol.* 35 (4), 377–386.

Ginsberg, G.L. and B.F. Toal. 2000. Development of a single-meal fish consumption advisory for methyl mercury. *Risk Analysis* 20: 41-47

Hammerschmidt, C.R., Wiener, J.G., Frazier, B.E., and Rada.R.G., 1999. Methylmercury content of eggs in yellow perch related to maternal exposure in four Wisconsin lakes, *Environ. Sci. Tech.* 33: 999-1003.

Hightower, J.M and D. Moore. 2003. Mercury levels in high-end consumers of fish. *Environmental Health Perspectives* 111:604-608.

Jacobs, H.L.; Kahn, H.D.; Stralka, K.A.; Phan, D.B. 1998. Estimates of per Capita Fish Consumption in the U.S. Based on the Continuing Survey of Food Intake by Individuals (CSFII). *Risk Analysis* 18 (3), 283–291.

MacCrimmon, H.R., Wren, C.D., and Gots, B.L., 1983. Mercury uptake by lake trout, *Salvelinus namaycush*, relative to age, growth, and diet in Tadenac Lake with comparative data from other Precambrian Shield Lakes. *Can. J. Fish. Aquat. Sci.*, 40, 114-120.

Mathers, R.A., and Johansen, P.H. 1985. The effects of feeding ecology on mercury accumulation in walleye and pike in Lake Simcoe, *Can. J. Zool.* 63, 2006-2012.

Morgan, J.N., Berry M.R. and R.L. Graves. 1998. Effects of commonly used cooking practices on total mercury concentration in fish and their impact on exposure assessments. *Journal of Exposure Analysis and Environmental Epidemiology* 7:19-33

National Research Council. *Toxicological Effects of Methylmercury*. National Academy Press: Washington, DC, 2000; pp 306–307.

Nicoletto, P.F. and Hendricks, A.C. 1988. Sexual differences in accumulation of mercury in four species of centrarchid fishes. *Can J. Zool.* 66: 944-949.

Niimi, A.J., Biological and toxicological effects of environmental contaminants in fish and their eggs, *Can. J. Fish. Aquat. Sci.* 40:306-312.

Pfeiffer, W.C., Lacerda, L.D., Salomons, W. and O. Malm. 1993. Environmental fate of mercury from gold mining in the Brazilian Amazon. *Environmental Review* 1:26-37

Phelps, R.W.; Kershaw, T.G. 1980. Interrelationships of Blood and Hair Mercury Concentrations in a North American Population Exposed to Methylmercury. *Archives Environ. Health* 35 (3), 161–168.

Santerre, C.R., P.B. Bush, D.H. Xu, G.W. Lewis, J.T. Davis, R.M. Grodner, R. Ingram, C.I. Wei, and J. Hinshaw, 2001, “Metal Residues in Farm-Raised Channel Catfish, Rainbow Trout and Red Swamp Crayfish from the Southern U.S.,” *Food Science*, (February).

Schnieder, D., Naidu, S., Jewett, S., Zhang, X., Duffy, L., Middaugh, J.P. 2001. Mercury in Pike. *Arctic Science Journeys*. Available at <http://www.uaf.edu/seagrant/NewsMedia/01ASJ/07.27.01mercury.html>

Siedel, S., R. Kruezer, D. Smith, S. McNeel, and D. Gilliss. 2001. Assessment of Commercial Laboratories Performing Hair Mineral Analysis. *Journal of the American Medical Association*. January. **283** (1). 67-72.

Stern, A.H.; Korn, L.R; Ruppel, B.E. 1996. Estimation of Fish Consumption and Methylmercury Intake in the New Jersey Population. *J. Exposure Anal. Environ. Epidemiol.* 6 (4), 503–525.

Trudel, M., Tremblay, Al, Schetagne, R., and Rasmussen, J.B. 2000. Estimating food consumption rates of fish using a mercury mass balance model. *Can. J. Aquat.Sci.* 57: 414-428.

US ATSDR, 1999

U.S. Department of Agriculture (USDA) 1989. *Continuing Survey of Food Intakes by Individuals, Data Set and Documentation*; Agriculture Research Service, Beltsville Human Nutrition Research Center: Beltsville, MD.

U.S. Department of Agriculture (USDA) 1990. *Continuing Survey of Food Intakes by Individuals, Data Set and Documentation*; Agriculture Research Service, Beltsville Human Nutrition Research Center: Beltsville, MD.

U.S. Department of Agriculture (USDA) 1991 *Continuing Survey of Food Intakes by Individuals, Data Set and Documentation*; Agriculture Research Service, Beltsville Human Nutrition Research Center: Beltsville, MD.

U.S. Environmental Protection Agency (USEPA). 1997. *Mercury Study Report to Congress, Volume IV: An Assessment of Exposure to Mercury in the United States*, EPA-452/R-97-006, (December).

USEPA. 2001a. Water Quality Criteria: Notice of Availability of Water Quality Criterion for the Protection of Human Health: Methylmercury. Federal Register January 8, 2001 6:1344-1359

USEPA. 2001b. Mercury Update: Impact on Fish Advisories. Office of Water. Washington, D.C.

USEPA. 2001c. Note to Correspondents. FDA and EPA Issue Advisories on Fish. Released January 12, 2001. Communications, Education and Media Relations. Washington, D.C.

Weiner JA, Nylander M: An estimation of the uptake of mercury from amalgam fillings based on urinary excretion of mercury in Swedish subjects. *Sci Total Environ*, 1995 Jun 30; 168(3): 255-65.

Wiener, J. G., D. P. Krabbenhoft, et al., 2002. Ecotoxicology of Mercury. *Handbook of Ecotoxicology*. D. J. Hoffman, B. A. Rattner, G. A. Burton and J. Cairns. New York, Lewis Publishers: 409 – 463.

WHO (World Health Organization). 1990. Environmental Health Criteria 101: Methylmercury. World Health Organization. Geneva.

6

HEALTH EFFECTS OF MERCURY

6.1 Introduction

The adverse human health effects of methylmercury (MeHg) are well-documented and were comprehensively reviewed in the EPA's *Mercury Study Report to Congress* (USEPA 1997) and by the National Research Council (NRC 2000). MeHg is primarily a neurotoxicant; in this capacity it is also thought to be a neurodevelopmental toxicant when exposure occurs *in utero* to the developing fetus. Typical effects of acute MeHg poisoning in which exposure levels are very high over a relatively short period of time include vision impairment, slurred speech, loss of coordination, loss of feeling in the extremities, and seizures. The neurotoxic effects of MeHg may be especially profound if exposure occurs during prenatal development. Therefore, particular concern is related to prenatal (*in utero*) exposure of children to MeHg. The EPA's approach to managing exposures to methylmercury via the primary pathway, through fish consumption, has taken the form of a criterion for water quality for lakes and rivers that is based upon fish tissue content of methylmercury (USEPA 2001b). Mercury fish advisories reflect this concern by specifically targeting warnings for pregnant women and women of childbearing age. These advisories, issued by states are designed to protect women of childbearing age from too frequently consuming fish that is likely to have methylmercury concentrations above certain levels.

All of these factors have led to efforts to further control mercury releases; thus, decreasing exposures to methylmercury. While the majority of exposures of the U.S. population to methylmercury are due to the consumption of commercially purchased marine fish, U.S. regulatory agencies have little control over the sources that contribute to concentrations in marine fish. The U.S. Food and Drug Administration limits the concentration of methylmercury in marine fish available for sale to 1 mg/kg, and also has issued an advisory to pregnant women (US FDA 2001). This advisory recommends that pregnant women not consume shark, swordfish, king mackerel, and tilefish, and also that consumption of other fish by pregnant women be limited to an average of 12 ounces, cooked weight, per week.

Because the literature regarding the health effects of MeHg is vast and has been extensively reviewed earlier (EPRI 1996; USEPA 1997, 2001a and 2001b; NRC 2002), this update of the health effects of MeHg focuses on key recent studies and research developments. Particular emphasis is placed on 1) recent developmental neurotoxicity studies since such effects are considered to be the most sensitive indicators of MeHg toxicity, 2) physiologically based pharmacokinetic (PBPK) models, which are powerful tools for improving quantitative exposure and risk assessment, 3) the updating of the USEPA benchmark dose, which is the basis for the revised RfD, and 4) the development and updating of the USEPA Reference Dose (RfD) for

MeHg. The RfD and benchmark dose are very important because they serve as the basis for most MeHg regulatory risk assessments.

6.2 Studies Examining the Developmental Toxicity of Methylmercury

Based on their high rates of consumption of fish and marine mammals, populations from both of the Faroe Islands and the Republic of Seychelles have been extensively studied for the potential effects of MeHg exposure. Neurodevelopmental effects, manifesting as very subtle cognitive or behavioral effects have been addressed extensively in these large population studies. These two studies conducted in Faroese and Seychellois populations have found inconsistent results. The results of a cross-sectional study in the Faroe Islands found some neuropsychological deficits in children that appeared to be associated with *in utero* exposure to MeHg, while the long-term prospective study of mercury exposure in the Seychelles did not.

Grandjean and others conducted a large study of children on the Faroe Islands, to follow a birth cohort of 1022 born in 1986-87 (Grandjean et al. 1997; Grandjean et al. 2003). The mothers were exposed mainly from consumption of pilot whale meat and blubber with relatively high concentration of MeHg, an average of 1.6 µg/g in whale meat. The study found that prenatal exposure to MeHg as measured in cord blood mercury levels at birth resulted in some observed neuropsychological deficits when the children were tested at 7 years of age. The brain functions most vulnerable to MeHg exposure appeared to be attention, memory, and language, while motor speed, visual/spatial function, and executive function showed less impairment at increased mercury exposures. The mercury concentration in cord blood appeared to be the best exposure indicator for the adverse effects. Developmental delays were statistically significantly associated with MeHg exposures, even excluding the children whose mothers had hair mercury concentrations above 10 µg/g (Grandjean et al. 2001). Within the low exposure range, each doubling of the prenatal MeHg exposure level was associated with a reported developmental delay of 1 to 2 months. The neurological deficits were associated with ingestion of fish containing 5 to 7 times higher mercury than the mean levels of mercury concentrations found in the fish in the Seychelles study (and in most of the world, as discussed in an earlier chapter). Similar findings of developmental delays were found with dietary consumption of shark muscle (mean MeHg of 2.2 µg/g) and reported from a cohort study of children in New Zealand (Crump et al. 1998). The Crump analysis also found that results were extremely sensitive to one outlier point in the data; inclusion of this point resulted in no significant effects where exclusion resulted in a finding of statistically significant effects for the population.

Myers and colleagues recently reported on the results of the 9-year follow-up from the Seychelles Child Development Study (Myers et al. 2003). A cohort of 779 mother-infant pairs was established, from which 717 were followed up at around their ninth birthday and evaluated with a broad range of cognitive-behavioral assessments. Mothers reported consuming fish on average 12 meals per week. The type of fish consumed and the fish MeHg concentrations in the Seychelles is similar to that of women's diets during pregnancy in most of the world. Prenatal MeHg exposure was determined from maternal hair mercury concentrations in hair segments that grew during pregnancy term. The mean prenatal maternal mercury hair concentration was 6.9 ppm, with a standard deviation of 4.5 ppm. The neurocognitive, language, memory, motor, perceptual-motor, and behavioral functions in the 9 year old children were assessed with tests that were deemed to be sensitive for detection of subtle neurobehavioral MeHg effects. Multiple

linear regression with adjustment for covariates that affect child development was used to investigate the association between prenatal MeHg exposure and the primary endpoints.

After adjusting for covariates, Myers et al. found a weak association between mercury in maternal hair at the end of pregnancy and two endpoints in twenty-one tests. Decreased performance was noted on one test of speed and coordination (non-dominant-hand grooved peg board). A performance improvement in a second test was noted, however; children of mothers with higher levels of MeHg in their hair did better at ratings of hyperactivity than children of mothers with lower concentrations. Further, performance on all other cognitive tests was not associated with MeHg in maternal hair. These findings demonstrate that the association with the non-dominant-hand test is likely a random finding. The study concludes that the data do not indicate that prenatal exposure to MeHg from maternal fish consumption is associated with neurodevelopmental risk from prenatal MeHg exposure resulting solely from ocean fish consumption (Myers et al. 2003). Previous findings from testing of the cohort at 6, 19, 29, and 66 months of age were similarly negative. Secondary analyses of earlier studies with other statistical models have been consistent with conclusions based on the primary analysis (Axtel et al. 1998, 2000).

Existing evidence suggests that MeHg exposure from fish consumption during pregnancy of the level seen on the average does not appear to have measurable cognitive or behavioral effects in later childhood (Myers et al. 2003). The positive findings from the Faroe Islands studies may be related to the fact that pilot whale blubber and shark muscle were consumed in addition to fish and pilot whale meat; the blubber and shark contain 5 to 7 times the concentrations of MeHg as the marine fish consumed in the Seychelles. In addition, whale blubber has high concentrations of polychlorinated biphenyls (PCBs) and other persistent organic pollutant, and the meat has concentrations of inorganic Hg at levels similar to those of MeHg. These factors do not, however, appear to explain the results from New Zealand (Myers 2003). Given the relatively small study population, and outcome dependence on one data point (Crump et al, 1998), these results, however, can be viewed as equivocal. An additional theory proposed to explain why the Faroe and Seychelles studies produced conflicting results was that the exposures via fish consumption in the Seychelles were more uniform over time than the more episodic exposures via to whale consumption in the Faroe Islands. Absent a better mechanistic understanding of how methylmercury affects a developing fetus, the significance of continuous versus more episodic exposures remains speculative (EPRI 2003).

The effects on the human brain of post natal exposure to dietary mercury is still being explored, although early findings suggest it may be associated with subtle neurodevelopmental toxicity (Grandjean et al. 2003). Studies in Japanese infants (Sakamoto et al. 2002) and in rats (Sakamoto et al. 2002) indicate that post-natal exposures to MeHg decline during lactation. The decline in infant levels of MeHg found in both humans and rats during the breast-feeding period is felt to be explained by the low mercury transfer through breast milk and the rapid growth of infants after birth (rapidly increasing brain and body volumes).

Other recent studies have shown that observed early neurodevelopmental effects attributed to exposure to PCBs and MeHg in U.S. infants were not observed when the same children were tested again at about five years of age (Stewart et al. 2003). The researchers suggested that observed neurodevelopmental effects as reflected by test performance may possibly be reversible with increasing age.

6.3 Physiologically Based Pharmacokinetic Models

Physiologically based pharmacokinetic (PBPK) models provide a quantitative framework for determining the kinetic consequences of different dosing patterns and dose levels, in different mammalian species, and for different physiological states (i.e., pregnancy). For MeHg, PBPK modeling in the risk assessment process is used to estimate the relationship between the measure of exposure used in epidemiological studies (mercury in hair and blood) and the daily ingested dose used to determine an RfD. This report provides an update of earlier work in this research area described by EPRI in 1996 (EPRI 1996).

Several PBPK human and animal mercury models have been developed to improve quantitative extrapolation of MeHg disposition between species and to better relate MeHg ingestion to mercury levels in key tissues, for example hair, breast milk, and the kidneys. The EPRI PBPK model includes 10 tissue compartments for MeHg, oxidation of MeHg to inorganic mercury (In-Hg) in liver, gut, and brain (Gearhart et al., 1995; Clewell et al., 1999). The model also includes a placenta and growing fetus compartment to account for exposure of the fetus during pregnancy. Brain mercury compartments included MeHg, inorganic Hg, and mercury incorporated into tissue proteins, which was assumed to be derived from the inorganic Hg pool. To determine the ingested dose that resulted in the Hg concentration in the hair as a biomarker, a back-calculation of the dose (dose reconstruction) was made using a toxicokinetic model of parameters to estimate the tissue MeHg concentration after ingestion of the MeHg dose. Important parameters for mercury are the uptake of MeHg from the gastrointestinal tract, the distribution of MeHg to body tissues (including biomarker tissues), metabolism, and the elimination of MeHg or Hg from those same tissues. PBPK models require a quantitative description of several physiological and toxicokinetic inputs (e.g., body weight, blood volume, and hair-blood partition coefficients).

Understanding the quantitative relationship between MeHg ingestion and hair levels is important because of the key role that hair plays as a biomarker of exposure. Improved understanding of mercury excretion kinetics in breast milk is obviously important for predicting exposure to infants, a sensitive subgroup for MeHg toxicity. Finally, the kidney is one of the important target organs for mercury toxicity.

Gearhart et al. (1995) developed a multi-compartment adult and fetal model to analyze epidemiological data for a methylmercury risk assessment. This model, which consists of a maternal model with a fetal sub-model, was parameterized for human physiology by Clewell et al. (1999) for use in a variability and sensitivity analysis of MeHg. The model estimates changes in maternal and fetal tissues during gestation and in maternal hair and blood concentrations following ingestion of MeHg, as well as the resulting fetal cord blood concentrations. This model was used to address the relationship between mercury in maternal hair and daily ingested dose and was found to be comparable to similar analyses performed using a simple compartmental model (USEPA 2001b). The sensitivity study by Clewell et al. (1999) suggests that the most important determinants of PBPK variability for MeHg are hair, blood partition, body weight and hair growth rate and that inter-individual kinetic variability in this instance differs by a factor of about 1.8 between individuals in contrast to the usual risk assessment default value of 10.

To characterize neurological impairments of prenatal MeHg exposure in children, Gearhart et al. (1995) applied the Hg PBPK model and statistical dose-response analysis to epidemiological data from a large population in New Zealand characterized by relatively constant chronic

exposure to MeHg from dietary consumption of fish. The focus of the effort was to incorporate a fetal model and to create a multi-species model amenable to simulation of the kinetics of MeHg in humans by changing the species-specific parameters. PBPK parameters such as tissue/blood partition coefficients and volume distributions for humans were taken from current literature. A benchmark dose was provided based on the results of 28 neurobehavioral tests in 6-year old children prenatally exposed to MeHg in seafood. The range of benchmark doses calculated was 10 to 31 ppm maternal hair MeHg. Gearhart et al. suggested a NOAEL of 17 ppm Hg in maternal hair for the most sensitive neurological event in children. At a maternal mercury hair concentration of 17 ppm, the PBPK model estimated fetal brain concentrations of MeHg of 50 ppb would result from a maternal dietary intake of MeHg in fish ranging from 0.8 to 2.5 µg/kg/day. The benchmark dose was implicitly defined as the lower 95% confidence interval on the dose associated with a 10% change in the test scores from the New Zealand study.

In work to determine the most relevant dose metric for estimating exposure to the fetus *in utero*, several factors have been found to be important, including the critical period of development of the nervous system in the fetus and ingestion patterns in the mother. In a recent study by Gentry et al. (2001), analyses were conducted using existing biological monitoring data from MeHg exposed Iraqi and Faroese cohorts the PBPK model described above to quantitatively evaluate the impact of dose-rate in assessing exposure *in utero*. Results from an initial analysis, conducted using short-term exposure scenarios reconstructed with the PBPK model from data on the Iraqi cohort, indicated that actual fetal exposure to MeHg during the third trimester could vary by as much as an order of magnitude in that cohort, depending on when exposure to the mother occurred, for acute exposures resulting in the same peak maternal hair concentrations. This result suggested that the dose metric used for assessing exposure to the fetus might also be critical for variable or episodic exposures, such as in the Faroe Islands population. Therefore, a second dose reconstruction study was performed in which the results of a segmental hair analysis for the member of the Faroe Islands cohort who showed the most variability in hair mercury concentration during pregnancy were analyzed with the PBPK model to infer the variation in MeHg ingestion. This ingestion pattern was then used to estimate various dose metrics for a correlation analysis to determine the dose metric that was most closely correlated with fetal exposure during the probable window of susceptibility for the effects of MeHg. The results of the analysis suggest that if the third trimester is the window of susceptibility for MeHg exposure in the fetus and if exposure to MeHg is highly variable over the course of pregnancy, then the maternal hair concentration at the end of pregnancy is a more appropriate measure of exposure than fetal cord blood concentration or peak/average maternal hair concentration during pregnancy (Gentry et al. 2001).

Young et al. (2001) developed a PBPK model using data for 12 animal species including the human. The PBPK model predicted the disposition of both MeHg and its inorganic mercury metabolite. This model predicted that the kidneys can be expected to retain relatively high inorganic mercury levels long after MeHg is no longer detectable in the blood. Human model results were consistent with test animal model results.

Carrier et al. (2001a,b) developed a PBPK model for MeHg in the rat which was validated with independent datasets. The model was then extended to humans. The human model accurately predicted concentrations of mercury and MeHg in important tissues including blood, hair, kidney, and urine.

Breast milk is another important source of exposure to children as well as a potential biomonitoring tissue. Byczkowski and Lipscomb (2001) used a PBPK model to investigate the lactational transfer of MeHg. This model could be used to help quantify exposures and health risks for infants exposed to MeHg in breast milk during the early postnatal period.

6.4 The Current U.S. EPA Methylmercury Reference Dose

For health risks other than cancer, EPA limits exposures to hazardous substances through the use of the RfD, which it defines as “An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.” It can be derived from a [No Observed Adverse Effects Level] NOAEL (the dose level below which no adverse effects were observed), [Lowest Observed Adverse Effects Level] LOAEL (the lowest level at which adverse effects were observed), or benchmark dose (in the case of MeHg, it is the lower 95% confidence limit on the exposure level that would produce a 5% increase in the incidence of abnormal test scores on the Boston Naming Test), with uncertainty factors generally applied to reflect limitations of the data used” (US EPA 2001a). The current MeHg RfD is the first to use a defined increase of 5% over background for adverse effect. All previous RfDs applying the BMD approach have used a default value of 10% which is less conservative.

The premise behind the Reference Dose approach is that it is scientifically inappropriate to assume that risk is proportional to dose at low doses (as is the assumption for carcinogens). Instead, it is assumed that a threshold exists below which toxic effects do not occur. The reference dose is determined by reviewing the literature to determine either a NOAEL, or a LOAEL or by calculating the benchmark response (BMR). Each of these constitutes a “point of departure,” and various safety and uncertainty factors are then applied to derive a reference dose.

EPA published a new Reference Dose (RfD) document for methylmercury in July 2001 (US EPA 2001a). The value of the RfD was unchanged from the previous value of 0.1 µg/kg/day; rather, EPA updated the technical basis for the RfD. The current value is one-third of its prior value, 0.3 µg/kg/day, issued in 1995. The RfD is assumed to be protective of all exposed populations in the U.S. including sensitive subpopulations which are children exposed *in utero*.

6.4.1 Past Methylmercury RfDs

Prior to July 2001, the RfD for MeHg was based on a poisoning event that occurred in Iraq when grain treated with a MeHg fungicide was consumed. The initial analysis of the Iraqi poisoning focused on paresthesia, a neurological disorder that resembles prolonged “pins and needles.” Neurological effects were found in Iraqi children whose mothers had been exposed to MeHg-contaminated grain while pregnant, where these children had been acutely exposed *in utero* (Bakir et al. 1973, Clarkson et al. 1975; Marsh et al. 1980, 1981, 1987). An RfD of 0.3 µg/kg-day was derived based on this health endpoint. Later, EPA revised the RfD downward to 0.1 µg/kg-day based on observed delays in the age of walking and talking in children born to Iraqi mothers exposed to MeHg while pregnant.

For many toxicologists and others concerned with MeHg exposures to the general population, use of the Iraqi poisoning event as the basis for the RfD was unsatisfactory for several reasons (EPRI 2003a). The Iraqi poisoning reflected the short-term exposure to very high levels of MeHg, in comparison to the situation of concern in the U.S. context – chronic exposures to low levels of methylmercury. In addition, there are uncertainties regarding the extent to which the health risks from consuming MeHg in grain are representative of those from fish consumption. In the Iraqi event, the grain had been provided to a rural population experiencing famine. It was suggested that the underlying health status of the Iraqis and their limited dietary protein made this event a poor surrogate for chronic exposures to low levels of MeHg from fish consumption. Finally, the studies in Iraq were retrospective. While maternal exposure could be estimated from measurements of mercury in hair, other records such as the precise age of the children were lacking.

6.4.2 The National Research Council Study

Ongoing debate since 1997 regarding the precise level below which MeHg exposure can be considered to be safe prompted Congress in 1999 to direct a National Research Council (NRC) review of the issue. Specifically, the NRC was directed to focus on pertinent data developed after the EPA 1997 *Mercury Study Report to Congress*. The NRC completed this report in July of 2000 (NRC 2000).

Most of the data reviewed by the NRC were developmental neurotoxicity data. Particular emphasis was placed on three epidemiological studies conducted in the Seychelles Islands, the Faroe Islands, and New Zealand. These subject populations were known to have a diet high in fish and/or marine mammals. All of these studies examined developmental neurotoxicity in children who were considered to have been exposed *in utero*.

The two primary studies reviewed stood out as more informative due to the large number of subjects involved, duration of follow-up, and the controls for confounding. These studies were conducted in the Faroe Islands and in the Seychelles, and produced results that differed from one another. As discussed earlier, the Faroe study indicated a developmental effect from methylmercury to children exposed *in utero*, while the Seychelles study did not.

The NRC also evaluated a study from New Zealand. In comparison to the Faroe Islands and Seychelles studies, the New Zealand study was much smaller. It included 57 sets of mother-child pairs. The study used maternal hair concentration as the exposure metric. The results were positive, but very sensitive to one data point which was a highly exposed child whose test scores were normal. The NRC noted that although this study had received less peer review than the other two, there did not appear to be any serious flaws in the design and conduct of the three studies that would preclude their use in a risk assessment. The NRC concluded that the brain was the most sensitive target organ for methylmercury toxicity and therefore that effects on the brain should serve as the basis for a revised RfD. The NRC concluded that the Faroe Island study was the most appropriate study for deriving an RfD.

The NRC recommended, based on benchmark dose calculations of the Faroe study results, that the exposure metric to be used was cord blood. The basis for this conclusion was that fetal exposures were more closely linked to blood concentration than to maternal hair concentration

and because the observed effect on test scores showed a stronger correlation with cord blood concentrations than with hair concentrations. Based on a 5% benchmark dose limit (that is, the lower 95% confidence limit on the exposure level that would produce a 5% increase in the incidence of abnormal test scores on the Boston Naming Test), a blood concentration of 58 parts per billion (ppb) MeHg in cord blood was recommended. This blood concentration corresponded to a hair concentration of 12 parts per million (ppm). For comparison, the hair concentration previously used by EPA in the Iraqi-based RfD was 11 ppm. Despite the similarity of the calculated hair concentration based on the Faroe study to that from the Iraqi study, the NRC recommended that the Iraqi study no longer be used as the scientific basis for the RfD.

In addition to the recommended 58 ppb cord blood MeHg, the NRC recommended that an uncertainty factor of at least 10 be used, based on individual variability and on other health endpoints that had not been evaluated appropriately. The NRC noted that the application of an uncertainty factor of 10, based on a one-compartment model to convert between blood concentration and methylmercury intake, would produce no change in the RfD, which would remain at 0.1 µg/kg-day.

6.4.3 The Current Reference Dose

In July 2001, EPA arrived at the RfD value that was recommended by the NRC, at 0.1 µg/kg-day, but derived this value by a slightly different analysis from that used by the NRC (USEPA 2001a). There are two major differences between how EPA derived the RfD and the method used by the NRC. The first is that EPA used a qualitative integrative analysis based on an evaluation of multiple test endpoints. While the quantitative test results used came mainly from the Faroe study (specifically its results on the Boston Naming Test) along with other qualitative results from that study, qualitative results from the New Zealand study also were included. EPA's analyses included PCB-adjusted benchmark dose limits, along with the unadjusted results and with results for the lowest PCB group in the Faroe data set. [In this instance, the benchmark dose is the lower 95% confidence limit on the exposure level that would produce a 5% increase in the incidence of abnormal test scores on the Boston Naming Test.] It was EPA's conclusion that no adjustment was required for concomitant exposure to PCBs in this study and that these analyses pointed to an RfD of 0.1 µg/kg/day if an uncertainty factor of 10 is used. The second significant change by EPA, in comparison to the NRC's recommendation, concerns the basis for the uncertainty factor of 10. EPA used two uncertainty factors of 3 (which produce a combined uncertainty factor of 10 after rounding). One factor was to account for uncertainty and variability in estimating the relation between MeHg intake and MeHg in blood; the other was to account for pharmacodynamic variability and uncertainty. EPA did not apply the uncertainty factor for database limitations that had been recommended by the NRC. The full details of the derivation of the RfD are available at EPA's Integrated Risk Information System (IRIS) website.

6.5 The U.S. EPA Benchmark Dose for Methylmercury

The benchmark dose (BMD) approach is used to derive a RfD; its use allows a broader set of response data to be used to derive the point of departure. The BMD method uses the statistical lower confidence limit of the dose that produces a predetermined change in response rate of an adverse effect in comparison to the background rate for the response.

A combined BMD analysis was performed by the NRC for a number of endpoints from all three studies (Faroe and Seychelle Islands and New Zealand) (NRC 2000). A central tendency measure was estimated, equivalent to a BMD, and applied across these studies for all endpoints identified as significant, and for all endpoints at 5.5 years of age in the Seychelles study. The NRC then determined a lower limit equivalent to a BMDL based on a theoretical distribution of BMDs. Using a hierarchical random-effect model, the NRC reduced random variation in the estimate for these same endpoints from all three studies. Additionally, this analysis was used in calculating BMD and BMDLs for the most sensitive and median endpoints from both the Faroe Islands and New Zealand studies. Using this approach allowed an integrative analysis of data from all three studies.

In developing the benchmark dose from the Faroe Islands study, the EPA considered the recommendation from the NRC that effects on the brain are the most sensitive indicator of MeHg toxicity. Thus, a lower limit on the benchmark dose (BMDL) (5% effect level) of 58 ppb in cord blood was developed based on the administration of a single neurobehavioral test, the Boston Naming Test (BNT) to the Faroe Islands children. The use of this BMDL has resulted in some controversy because EPA peer reviewers and others believed that the BNT results were confounded by concomitant PCB exposure, particularly at higher levels of MeHg exposure (Grandjean et al., 2001). Grandjean et al. found that cord blood concentrations of PCBs in Faroese children were correlated with deficits on the BNT, the Continuous Performance Test, and possibly the California Verbal Learning Test. Peer reviewers recommended that a PCB-adjusted BMDL of 71 ppb be used. Shipp et al. (2000) used the Seychelles Island study as the basis for the MeHg RfD and estimated a lowest BMDL of 21 ppm in maternal hair. Despite the lack of any observed adverse effects in the Seychelle Island study group, Shipp et al. used this study for their BMDL calculation citing the careful conduct and analysis of the study, the large number of mother-infant pairs, and the lack of confounding factors. Crump et al. (2000) also used the Seychelles Island study as the basis for an alternate BMDL calculation. These investigators estimated an average BMDL of 25 ppm mercury in maternal hair, with a range of 19 to 30 ppm.

The NRC analyzed the inter-individual variability in the ingested dose of methylmercury corresponding to a given maternal-blood or hair-mercury concentration (NRC 2000). A default value of 10 is usually applied for this factor. Two analyses of the variability and uncertainty in the ingested dose estimates were based on the one-compartment model (Stern 1997; Swartout and Rice 2000) and an analysis based on a PBPK model were reviewed (Clewett et al., 1999). In general, all three analyses were found to indicate similar ranges of variability due to pharmacokinetic factors. The ratios of estimated ingested doses at the 50th percentile/99th percentile ranged from 1.7 to 3.3 (NRC 2000). Using maternal blood as the starting point, results from the three analyses range from 1.7 to 3.0.

Nonetheless, the 58 ppb BMDL was ultimately adopted by EPA as the basis for developing a MeHg RfD. The EPA RfD is qualitatively based on many endpoints, including the Boston Naming Test on which the quantitative results were based. The 58 ppb BMDL was converted to the RfD of 0.1 µg/kg/day using a one-compartment pharmacokinetic model in combination with an uncertainty factor of 10 to reflect primarily the following two sources of uncertainty:

- Pharmacokinetic inter-individual uncertainty (especially the MeHg half-life and the relationship between cord and maternal blood mercury concentrations)

- Pharmacodynamic variability and uncertainty

Each of the above uncertainties was addressed with a separate uncertainty factor of 3.

Additional uncertainties considered included difficulties in quantifying long-term effects, the lack of a two-generation reproductive effects assay and concern regarding the possibility of effects below the BMDL. USEPA considered all of the above uncertainties to be adequately addressed with a single composite uncertainty factor of 10.

6.6 Mutagenicity, Carcinogenicity and Reproductive Toxicity

MeHg has been shown to be clastogenic (causing chromosome damage), however, it does not appear to cause point mutations. USEPA has classified MeHg as being of high concern for human germ cell mutagenicity.

MeHg has not been shown to be carcinogenic in any human study; however, at very high toxic doses MeHg has caused increased incidences of kidney tumors in mice. USEPA considers the evidence for MeHg carcinogenicity in humans to be inadequate and limited in experimental animals. At this time USEPA has not calculated a cancer slope factor for MeHg and concludes that under the typical low-level exposure occurring through fish consumption MeHg is not likely to be a carcinogen.

6.7 Summary and Recommendations

- Brain toxicity, especially neurodevelopmental toxicity manifesting as subtle cognitive or behavioral effects, has been of greatest concern.
- Existing evidence suggests that MeHg exposure from fish consumption during pregnancy at the U.S. average population level does not appear to have measurable cognitive or behavioral effects in later childhood.
- In general, more information is needed to identify the lowest levels of MeHg exposure which may cause even subtle neurotoxicity as the result of long-term exposure. There is no strong evidence of a multigenerational impact of mercury, that is, the unexposed offspring of exposed children evidencing neurodevelopmental deficits due solely to their parents' exposures. Additional studies to clarify this possibility would be useful.
- The research suggested above can be used to address the need for a database uncertainty factor. For example, if a BMD for cardiovascular effects is similar or higher than the BMD for neurological impairment, then the former effect is not likely to be a critical effect, and the need for the database uncertainty factor is correspondingly reduced. Likewise, the immunotoxicity effects should be further studied as to whether they are considered adverse, adaptive, compensatory or beneficial. If both adverse and relevant, then they would likely be used as the critical effect and the RfD for methyl Hg can then be revised accordingly. The need for the database uncertainty factor is then correspondingly reduced.
- The impact of mixed chemical exposures to MeHg and PCBs on childhood subjects in the Faroe Islands is still unclear. In contrast, the Seychelles Island data are from exposures to

primarily one chemical, MeHg. The large PCB exposures to breast-fed infants in the Faroe Islands may be affecting the health of the population independent of any neurological response, or they may be enhancing the toxicity of methyl Hg (Dourson et al. 2001). Studies containing both negative and positive correlations of neurological impairment, PCB exposure information, and PCB levels in cord tissue are available and should be reviewed to develop mixture RfDs. A mixture RfD would reflect the fact that many fish are contaminated with both chemicals.

- Current EPA RfD guidelines could be enhanced with new approaches to uncertainty factors and data unique to MeHg. For example, new research in the area of human variability in toxicokinetics has been incorporated into the recent guidelines of the International Programme on Chemical Safety (Meek et al., 2000) for compound-specific adjustment factors (formerly referred to as data-derived uncertainty factors). This guidance is now undergoing an international review, including review by scientists with ATSDR, EPA and FDA.
- Effects on reproductive function and potential delayed neurotoxicology effects manifested in aging after relatively low exposure early in life can also be addressed.
- Research can also be undertaken to improve the choice of dose-response function for application within the risk assessment process itself. Studies that will result in greater understanding of the sensitivity and specificity of test instruments used in assessing neurobehavioral and neuropsychological function are underway and will provide more information with which to select the most appropriate benchmark level. Experience in the use of biologically relevant models, such as the flexible K-power model, applied to several different data sets may identify a small set of models that have wide applicability. Alternatively, one could hypothesize a dose-response, generate simulated data for this dose-response, and then evaluate alternative models for the simulated data set.
- The objective of conducting these studies is to inform the risk assessment process by reducing uncertainties. The goal is to eventually be able to objectively determine the body of information that is sufficient to reduce uncertainties. This, in turn, will entail leaving behind default assumptions (such as the standard uncertainty factor of 10). The ability to let fall such default assumptions would indicate an appropriately high degree of confidence in the scientific method as well as the quality of information it can bring to the issue of human health risk assessment for low level exposure to methylmercury.
- The determination of the critical effect for MeHg is important. Investigating other potential critical effects will either change the basis of the RfD or reduce the need for uncertainty factors. Specifically, recent recommendations are consistent (Dourson et al 2001; Wyzga and Yager 2001) in suggesting that a review of studies that indicate other potential critical effects of MeHg should be compared to check for possible confounders.

References

- Axtell C.D., Myers G.J., Davidson P.W., et al. 1998. Semiparametric modeling of age at achieving developmental milestones after prenatal exposure to methylmercury in the Seychelles Child Development Study. *Environ Health Perspect.* 106: 559–64.
- Axtell C.D., Cox C., Myers G.J., et al. 2000. The association between methylmercury exposure from fish consumption and child development at five and a half-years of age in the Seychelles Child Development Study: an evaluation of nonlinear relationships. *Environ. Res. Sec. A.* 84: 12–19.
- Babi, D., Vasjari, M., Celo, V. and M. Korovesi. 2000. Some results of Hg content in hair in different populations in Albania. *The Science of the Total Environment* 259:55-60.
- Bakir, F., S. F. Daminji, L. Amin-Zaki, M. Murtadha, A. Khalidi, N. Y. Al-Rawi, S. Tikriti, H. I. Dhahir, T. W. Clarkson, J. C. Smith, and R. A. Doherty. 1973. Methylmercury Poisoning in Iraq. *Science* 181:230-241.
- Byczkowski, J.Z. and J.C. Lipscomb. 2001. Physiologically based pharmacokinetic modeling of the lactational transfer of methylmercury. *Risk Analysis* 21:869-882
- Carrier, G., Brunet, R.C., Caza, M. and M. Bouchard. 2001. A toxicokinetic model for predicting the tissue distribution and elimination of organic and inorganic mercury following exposure to methyl mercury in animals and humans. I. Development and validation of the model using experimental data in rats. *Toxicology and Applied Pharmacology* 171:38-49
- Carrier, G., Brunet, R.C., Caza, M. and M. Bouchard. 2001. A toxicokinetic model for predicting the tissue distribution and elimination of organic and inorganic mercury following exposure to methyl mercury in animals and humans. II. Application and validation of the model in humans. *Toxicology and Applied Pharmacology* 171:50-60
- Clarkson, T. W., L. Amin-Zaki, and S. K. Al-Tikriti 1975. An Outbreak of Mercury Poisoning Due to Consumption of Contaminated Grain. *Fed. Proc.* 34:2395-2399.
- Clewell, H.J., Gearhart, J.M., Gentry, P.R., Covington, T.R., Van Landingham, C.B., Crump, K.S., and A.M. Shipp. 1999. Evaluation of the uncertainty in an oral reference dose for methylmercury due to inter-individual variability in pharmacokinetics. *Risk Analysis* 19:547-558
- Crump, K.S., Van Landingham, C., Shamlaye, C., Cox, C., Davidson, P.W., Myers, G.J. and T.W. Clarkson 2000. Benchmark concentrations for methylmercury obtained from the Seychelles Child Development Study. *Environmental Health Perspectives* 109:257-263
- Crump, K.S., Kjellstrom, T., Shipp, A.M., Silvers, A., and Stewart, A. 1998. Influence of prenatal mercury exposure upon scholastic and psychological test performance benchmark analysis of a New Zealand cohort. *Risk. Anal.* 18:701-13.

Dourson, M.L. et al. 2001. Uncertainties in the reference dose of methylmercury. A Review. *Neurotoxicol.* 22: 677-89

EPRI 2003a. Implementation of the United States Environmental Protection Agency's Methylmercury Criterion for Fish Tissue. Palo Alto, CA. TR-105520.

EPRI, 2003b. A Framework for Assessing the Cost-Effectiveness of Electric Power Sector Mercury Control Policies. Palo Alto, CA. TR-105224.

Gentry, P.R., Clewell, H.J., Shipp, A.M. and Yager, J.W., 2001. Comparison of alternative exposure measures for evaluating the neurological effects of methylmercury in children. *The Toxicologist* 60 1, p. 19.

Grandjean, P., Weihe, R. White, et al., 1997, "Cognitive Deficit in 7-year-old Children with Prenatal Exposure to Methylmercury," *Neurotoxicol. Teratol.* 20:1-12.

Grandjean, P., Weihe, P., Burse, V.W., Needham, L.L., Storr-Hansen, E., Heinzow, B., Debes, F., Murata, K. Simonsen, H., Ellefsen, P., Budtz-Jorgensen, E., Keiding, N. and R.F. White. 2001. Neurobehavioral deficits associated with PCB in 7-year-old children prenatally exposed to seafood neurotoxicants. *Neurotoxicology and Teratology* 23:305-317.

Grandjean, P., White, R.F., Weihe, P. Jorgensen, P.J. 2003. Neurotoxic risk caused by stable and variable exposure to methylmercury from seafood. *Ambul. Pediatr.* 3:18-23.

Jacobson, J.L. 2001. Contending with contradictory data in a risk assessment context: the case of methylmercury. *Neurotoxicology* 22:667-75

Marsh DO, Clarkson TW, Cox C, Myers GJ, Amin-Zaki L, Al-Tikriti S. 1987. Fetal methylmercury poisoning. *Arch Neurol* 44:1017-1022.

Marsh, D. O., G. J. Myers, T. W. Clarkson, L. Amin-Zaki, S. Tikriti, and M. A. Majeed. 1981. Dose-Response Relationship for Human Fetal Exposure to Methylmercury. *Clin. Toxicol.* 18:1311-1318.

Marsh, D. O., G. J. Myers, T. W. Clarkson, L. Amin-Zaki, S. Tikriti, and M. A. Majeed. 1980. Fetal Methylmercury Poisoning: Clinical and Toxicological Data on 29 Cases. *Ann. Neurol.* 7:348-353.

Meek B, A. Renwick, E. Ohanian, M. Dourson, and B. Lake 2000. Guidelines for application of compound-specific adjustment factors (CSAF) in dose/concentration response assessment. *Comments on Toxicology.* Cited in Dourson et al. 2001.

Myers, G.J., Davidson, P.W., Cox, C., Shamlaye, C.F., Palumbo, D., Cernichiari, E., Sloane-Reeves, J., Wilding, G.E., Kost, J., Huang, L.S., Clarkson, T.W. 2003. Prenatal methylmercury exposure from ocean fish consumption in the Seychelles child development study. *Lancet* 361:1686-92

NRC (National Research Council) 2000. Toxicological Effects of Methylmercury. NRC on the Toxicological Effects of Methylmercury. National Academy Press. Washington, D.C.

Ortega HG, Lopez M, Takaki A, Huang QH, Arimura A, Salvaggio JE. 1997. Neuroimmunological effects of exposure to methylmercury forms in the Sprague–Dawley rats. Activation of the hypothalamic–pituitary–adrenal axis and lymphocyte responsiveness. *Toxicol Ind Health* 13(1):57–66. Cited in Dourson et al. 2001.

Sakamoto M., M.Kubota, S. Matsumoto, A. Nakano, and H. Akagi 2002. Declining risk of methylmercury exposure to infants during lactation. *Environ. Res.* 90: 185-189.

Sakamoto M., A. Kakita, K. Wakabayashi, H. Takahasi, A. Nakano, and H. Akagi 2002. Evaluation of changes in methylmercury accumulation in the developing rat brain and its effects: a study with consecutive and moderate dose exposure throughout gestation and lactation periods” *Brain Res.* 949: 51-59.

Salonen, J.T., Seppanen, K., Nyyssonen, K., Korpela, H., Kauhanen, J., Kantola, M., Tuomilehto, J., Esterbauer, H., Tatzber, F. and Salonen, R., 1995. Intake of mercury from fish, lipid peroxidation, and the risk of myocardial infarction and coronary, cardiovascular, and any death in eastern Finnish men. *Circulation* 91, pp. 645–655. Cited in Dourson et al. 2001.

Shipp, A.M., Gentry, P.R., Lawrence, G., Van Landingham, C., Covington, T., Clewell, H.J., Gribben, K. and K. Crump. 2000. Determination of a site-specific reference dose for methylmercury for fish-eating populations. *Toxicology and Industrial Health* 16:335-438

Stewart PW et al. 2003 Cognitive development in preschool children prenatally exposed to PCBs and MeHg. *Neurotoxicol. & Teratol.* 25 (1): 11-22.

Toxicology Excellence for Risk Assessment (TERA) 1999. Comparative dietary risks: balancing the risks and benefits of fish consumption. Cincinnati, Ohio: EPA Office of Water Cooperative Agreement CX825499-01-0, 1999. www.tera.org/pubs/cdrpage.htm. Cited in Dourson et al. 2001

USEPA. 1997. *Mercury Study Report to Congress, Volume IV: An Assessment of Exposure to Mercury in the United States*, EPA-452/R-97-006, (December)

USEPA 2001a. Reference Dose for Chronic Oral Exposure, available online in Integrated Risk Information System (IRIS) - methylmercury, at <http://www.epa.gov/iris/subst/0073.htm>

USEPA 2001b. Methylmercury Water Quality Criterion for Protection of Human Health.

Wild, L.G., Ortega, H.G., Lopez, M. and Salvaggio, J.E., 1997. Immune system alteration in the rat after indirect exposure to methylmercury chloride or methylmercury sulfide. *Environ. Res.* 74 1, pp. 34–42. Cited in Dourson et al. 2001

Wyzga, R. E. and J.W. Yager 2001. Research to Improve Mercury Risk Assessments. Minamata Workshop Proceedings, Minamata Research Institute, Minamata, Japan. March 2001. Young, J.F., Wosilait, W.D. and R.H. Luecke. Analysis of methylmercury disposition in humans utilizing a PBPK model and animal pharmacokinetic data. *Journal of Toxicology and Environmental Health A.* 63:19-52

7

MERCURY EMISSION CONTROL APPROACHES

7.1 Overview

A variety of control approaches that address mercury during pre- and post-combustion can achieve reductions in mercury emissions from power generation facilities fueled by coal. Pre-combustion strategies essentially involve pollution prevention measures, such as fuel management by coal cleaning, or selection of lower mercury content fuels. These measures may achieve reductions in mercury concentrations in the fuel prior to the fuel entering the combustion zone. Post-combustion methodologies are generally absorption or conversion techniques focused on removal of one or more of the mercury species incorporated in the boiler exhaust stream. Many existing controls for gaseous and particulate pollutants can secondarily reduce mercury emissions through simultaneous “co-control” physical and chemical reactions. Currently it appears that the most effective strategies for achieving mercury reductions incorporate multiple control technologies either in series or simultaneously.

The ability of emission control strategies to adequately capture mercury at the typically low concentrations in the various fuels is affected by the high chemical reactivity that allows mercury to be present in multiple forms and/or to convert reversibly from one ionic species into another. Other chemicals within the fuel stream, such as chlorine or fluorine, can affect both the reactivity of a respective mercury species as well as impair the accuracy of certain measurement analyses. Therefore, the chemical reactivity and the specific sensitivity to control strategies of the mercury compounds to be reduced is also considered in the selection of a control strategy.

In the evaluation of controls, it is important to identify what the relative control efficiency is for each form of mercury as well as to consider whether a technique removes single or multiple forms of mercury or only converts one or more into another form. As some mercury techniques have the ability to enhance conversion of one mercury form into another, management strategies for reducing mercury could incorporate existing emission devices along with a species conversion technique as a principal removal strategy.

This chapter will focus on technologies that achieve reductions through actual control whether specifically intended as a primary control or through secondary, or co-control, for other pollutants.

EPRI, the Department of Energy-National Energy Technology Laboratory (DOE NETL), and the U.S. EPA have conducted extensive research and development programs over the past decade with the objective to develop cost-effective methods for reducing power plant mercury emissions, especially from coal-burning facilities in the U.S. EPRI’s program began with research to develop an understanding of the factors that affect the properties of mercury

emissions in flue gas steams, and then progressed to studies of the effectiveness of promising control strategies, including carbon injection. EPRI's program is now at the stage of developing and demonstrating a range of control options.

EPRI issued a report in March 2001 summarizing the known options for controlling power plant mercury emissions (EPRI 2002c). Since that report, additional pilot and full-scale control technology tests were conducted for dry control technologies and investigation of the potential for co-control of mercury from NO_x controls and flue gas conditioning. Mercury control technology development efforts have increased in the past seven years and some promising options have been identified. However, significant uncertainties still exist due to the wide variety of power plant configurations and coals burned as well as the lack of long-term, full-scale test data.

This chapter first discusses the promise of pre-combustion control technologies for mercury. Second, a discussion is provided of results of investigations of the co-control of mercury from particulate, SO₂, NO_x controls and flue gas conditioning. Third, the status of the development of dry mercury control technologies is reported. Fourth, recent results of studies of the effect on trace gases of activated carbon injection are discussed. Fifth, a recent study of the fluxes of mercury from ash is summarized.

7.2 Pre-combustion Control Technologies

Pre-combustion techniques for reducing mercury emissions are focused at lowering mercury concentrations prior to combustion. Pre-combustion approaches are principally fuel cleaning techniques, although fuel-switching or management strategies have also been investigated.

The cleaning techniques normally considered for pre-combustion control reductions are coal washing/cleaning with either an aqueous solution or with a magnetic medium as the separation medium. Other cleaning techniques, such as K-Fuel, have been developed that remove mercury through heat, although data for these non-aqueous cleaning approaches are limited.

7.2.1 Coal Cleaning

Coal cleaning or washing is a physical technique that can remove coal contaminants that are bound with particulates or soils (commonly the pyritic fraction) associated with the coal. The degree of association of coal mercury with the mineral fraction has been estimated by several researchers as up to 50% of the total mercury content. Mercury that is bound organically to the carbon structure or absorbed onto internal carbon structures is little affected by cleaning. Mercury compounds associated with the particulate fraction (Hg(0) and Hg(II)) may be removed; however, a residual mineral content (from 8-15%) is typically retained in the cleaned coal. Cleaned coals also generally lose BTU content with a gain in moisture content. Toole-O'Neil et al. (1999) evaluated the tendency of coal cleaning to preferentially remove mercury. Of the 24 cases of coal cleaning cited, the average decrease in mercury concentration was 37% on an energy basis, ranging from 12% to 78% overall. On a mass basis, the average mercury reduction from coal cleaning was 30%, which indicates a coal cleaning factor of 0.70, a higher rate of mercury removal than that applied by EPA in 1997 (21%) (Brown et al. 1999).

In general, effective removal of coal contaminants can be enhanced when coals are finely ground and subjected to intense agitation. In practice, coal cleaning efficiencies vary considerably with multiple factors such as coal type, rank, ash content and mineral composition. Although these methods appear to reduce mercury, further research is needed to examine the potential impacts on the post-combustion form and control of the remaining mercury. Some additional benefits of coal cleaning include a reduction in the sulfur content, which translates into lower SO₂ emissions, as well as increased heating value which results from reduced ash formation (i.e., less coal must be burned to achieve the same output) and lower disposal costs (SENES 2002).

Coal cleaning is widely used on eastern U.S. coals to reduce ash and sulfur compounds in bituminous and anthracite coals. There is less experience with cleaning in the western U.S. on sub-bituminous coals and North Dakota lignites. This option has traditionally been applied to higher rank coals burned in the east, rather than lower rank western coals.

7.2.2 Fuel management strategies

Mercury emissions can be lowered for a distinct facility by selecting and burning fuels of lower mercury concentration. Within a given coal type, current data suggests that many deposits exhibit a high degree of variability in mercury content on a seam to seam basis. The ability to selectively mine lower mercury concentration seams has not been demonstrated repetitively, nor have the business economics been quantified to encourage such mining efforts. While shifting coal types could impact mercury emissions, the economic and physical impacts of differing fuel types onto generation capabilities and the boiler and fuel handling complex are likely to exceed costs associated with direct controls.

Fuel switching or co-firing with natural gas or fuel oil can lower mercury emissions by displacing coal combustion. Operational capabilities for switching are limited or non-existent for many facilities.

7.3 Post-Combustion Mercury Control Methods

Post-combustion, there are three basic methods of flue gas treatment to capture mercury: first, capture of particulate-bound mercury in particulate matter (PM) control devices; second, adsorption of elemental and oxidized mercury onto sorbents for subsequent capture in PM control devices, and; third, removal of soluble oxidized mercury in wet scrubbers (including processes to convert elemental to oxidized mercury for subsequent capture in wet scrubbers). With regard to mercury emissions reduction, these control methods can be subdivided into three categories of post-combustion flue gas treatment: first, mercury controls designed for capture of air pollutants other than mercury (NO_x, SO₂, and PM); second, new combinations and modifications of traditional control technologies, and; third, control technologies designed for mercury control (or multiple pollutant control).

An overview of the chemical processes, control technologies and removal efficiencies for these are provided in this section.

7.3.1 Mercury Behavior in Flue Gas

Effective removal is dependent on the species of mercury present in the flue gas. As described previously, mercury in flue gas is typically in two chemical forms: elemental (Hg(0)) and ionic (Hg(II)) (How do we know this? I am not aware of any measurement methods that can speciate different forms of flue gas ionic mercury. Also, equilibrium predictions do not give an accurate picture of what the actually ionic species are. Suggest delete). (Not true, reducing temperature does not improve elemental mercury removal in many cases). Oxidized mercury, such as Hg(II) is water soluble and is less volatile compared to Hg(0). Low temperature is important for effective oxidized mercury removal (.

7.3.2 Co-control of Mercury by Particulate and SO₂ Controls

In general, elemental mercury is not readily captured by wet or dry SO₂ scrubber systems while ionic mercury (Hg(II)) compounds are more readily adsorbed or absorbed onto particulate surfaces or SO₂ scrubber systems depending on the temperature, scrubber conditions, and mercury species. (We are not sure all ionic mercury species in flue gas can be scrubbed). .

Measurements from EPA's ICR of coal and flue gas mercury concentrations at a variety of U.S. power plants suggest that existing emission control devices for particulates (fly ash) and sulfur dioxide (SO₂) capture, on average, 40% of the mercury present in the flue gas from burning coal (EPRI 2000). Mercury removal rates, however, varied from 0% to over 90% among power plants tested. DOE/FETC and EPRI studies indicate that mercury removal rates for plants equipped with wet flue gas desulfurization (WFGD) systems are between 50 and 65% of the mercury, which includes the particulate-bound mercury. The vapor phase represents 80-95% of the oxidized mercury in the flue gas prior to scrubbing by the WFGD. The highest concentrations of oxidized mercury occur in the flue gas of plants utilizing WFGD systems (e.g., Ohio Valley plants firing medium- to high-sulfur bituminous coals). Many full-scale characterization studies conducted by DOE/FETC contractors on power plants firing PRB coal indicate between 20 and 30% mercury capture associated with electrostatic precipitators; and on average 50-60% mercury capture at plants equipped with baghouses, with removal rates as high as 90% observed. These results are of interest since, on a mass basis, over one-third of the coal utilized in the U.S. is from the Powder River Basin (PRB) and other subbituminous coals. Particulate mercury can be captured by baghouses or ESPs. As data from EPA's ICR demonstrated, baghouses typically provide higher capture effectiveness for mercury than ESPs, probably due to the longer contact times between the flyash dustcake on the filter surface and mercury vapor than in an ESP.

Additional data for mercury in coal and from combustion in Canadian power generation boilers will soon become available. In June 2003 the Canadian government issued a similar data request to EPA's ICR. To assess mercury emissions from coal fired generation in Canada, the Canadian Council of Ministers of the Environment (for each province) recently agreed to a Uniform Data Collection Program (UDCP) (CCME 2003). Measurements of coal mercury and chlorine content, ash and flue gas measurements are to be collected by plant operators for the UDCP over the next 24 months. The UDCP's goal is to include the development of quality-assured speciated mercury emissions data for every electricity-generating unit in Canada.

Researchers are investigating several potential technologies, including injecting materials into flue gases that can absorb or react with mercury to produce solids that can subsequently be captured by particulate control devices, or that produce compounds of mercury that can be captured by SO₂ controls. These emerging mercury control technologies are discussed further below.

7.3.3. Effect of SCR, SNCR and FGC on Mercury Emissions

To comply with revised PM_{2.5}, ozone, and NO_x standards, a number of generators are either installing or considering installing selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) systems to reduce NO_x emissions. SCR devices for reduction of NO_x emissions have long been expected to enhance mercury capture by particulate collection devices and SO₂ scrubbers through increased oxidation of mercury. Conversion of more of the elemental mercury to Hg(II) would increase the potential removal in a wet FGD, but is not expected to significantly increase removal by precipitators and fabric filters.

EPRI recently evaluated the effect that SCR, SNCR, and flue-gas conditioning (FGC) systems have on total and speciated mercury emissions (EPRI, DOE and EPA 2000, 2002; EPRI 2002a, 2003a). A major portion of this program was co-sponsored by EPRI, the U.S. Department of Energy, and the U.S. Environmental Protection Agency. Previous pilot scale tests indicated that SCR and possibly NH₃ injection for flue gas conditioning might enhance mercury capture, although the effect appears highly coal-specific (EPRI, DOE and EPA 2000).

Full-scale tests were made at six coal-fired power plants to investigate the role that SCR, SNCR, and FGC have on mercury emission speciation. The samples were evaluated using two approaches: the wet-chemistry Ontario Hydro method, and near real-time continuous mercury monitors (CMMs). Additional sampling involved EPA Method 26A to test for chlorides, a selective condensation method to measure SO₃, and EPA Method 27 for NH₃ slip. Fly ash and coal samples also were collected to estimate mercury mass balance across control devices. Figure 2-2 indicates the co-benefits of SCRs and FGDs on mercury emissions. Significant oxidation of mercury was found to occur across the SCR reactor for two of the four plants. The two plants using a flue gas desulfurization (FGD) system showed correspondingly significant mercury removal. Ammonia injection did not appear to significantly affect mercury speciation for any of the units using SCR, SNCR (urea injection), or FGC.

For bituminous coals, the results indicated that SCR systems convert elemental mercury to oxidized mercury, which is more easily captured in downstream air pollution control devices (primarily FGD systems). The extent of oxidation was variable and seemed to be affected by the coal type and catalyst design. Three of the bituminous SCR sites included FGDs, with total mercury removal rates achieved of 85-90 percent. Comparable results without the SCR system on-line ranged from 43% to 51%. These improvements may be due to the combined effects of the SCR system to increase the oxidation of mercury (to Hg(II)) and reduce mercury “re-emissions” in the FGD. The results are also limited – only 3 power plants tested – and the 3 FGDs tested do not present the most common FGD design in the US, which is limestone reagent with forced oxidation. Since the mechanisms for Hg removal and re-emissions are not well understood, additional studies are needed.

For Powder River Basin, or PRB, coals, less oxidation is expected, and catalyst aging may be an issue. This is based on limited measurements made in 2001 at a cyclone-coal-fired power plant burning a PRB coal and employing an SCR. An additional pulverized-coal PRB/SCR site is planned in 2003.

Thus, these studies generally document significant increased mercury oxidation and removal. The extent of oxidation is unclear except for plants with bituminous coals. Oxidation was increased from use of the SCR at most tested sites. The degree of oxidation appears to correlate with catalytic residual exposure time. Some indications that oxidation variances may be subject to the age of the catalyst, the types of catalyst, the catalytic constituents of the SCR catalysts, and to residence time have been theorized, but data are inconclusive. SCR testing on lignite, bituminous, and sub-bituminous coals all showed evidence of oxidation increases; however, oxidation has exhibited ranges from less than 40% to more than 90% effectiveness. Reports of diminished catalytic action, or “poisoning,” of catalysts from mercury reactions are also not clearly documented. Lignite sites have generally shown less enhancement of oxidation than other coals.

Confounding issues that surround SCR usage in quantifying the degree of oxidation are that when SCR is in place, increases of both unburned carbon (LOI in ash, due to low NO_x burner applications) and of excess ammonia (ammonia slip) are both generally present. The increase in unburned carbon may function as a synthetic “activated carbon” that results in direct “carbon” capture of both Hg(0) and Hg(II) species. Un-reacted ammonia (slip) is adsorbed onto particulate surfaces and may also enhance sulfur mercury reactions, again with the result being that Hg(I) bound onto ash particulates is subjected to more effective removal by particulate control devices.

A negative aspect impacting SCR usage is that de-activation, or poisoning, of catalytic function of SCR has been reported associated with lignite coals. The duration or degree of actual impact is unclear at this time. It is also unclear as to degree or the quantity of reaction time for the reduction in oxidation and perhaps SCR catalytic function occurs.

7.3.4 Mercury Control by Emerging Technologies

Post combustion mercury control options are relatively expensive to implement. One reason for the expense is that large flue gas volumes must be treated to capture a very small amount of mercury; typical mercury concentrations in untreated flue gas are in the low parts-per-billion range. At this time, the mercury in the flue gas can be characterized as being primarily in two forms: oxidized or elemental. The ability of systems to capture mercury is dependent, in part, on the species of mercury in the flue gas as discussed in a prior chapter. Several dry control technologies are emerging in their promise for mercury emissions reduction. These include activated carbon, a compact hybrid particulate collector, hybrid combinations of existing control technologies, and advanced design catalysts.

7.3.4.1 Activated Carbon

Beyond capture by existing particulate and SO₂ controls, the approach that would most likely be used in the near-term if additional controls are required would be activated carbon injection

(ACI) upstream of a particulate control device. Under most conditions, if the carbon achieves good contact with the gaseous mercury for a sufficient amount of time, it will adsorb the mercury. The resulting mercury-laden carbon is then collected by the downstream particulate control. The amount of mercury adsorbed is dependant upon the mercury adsorption capacity of the activated carbon and the mass transfer characteristics of the system, where the mercury removal will increase with increasing sorbent capacity up to the mass transfer limit of the system.

Overall, activated carbons can remove both elemental and oxidized mercury. The capacity of activated carbons can be affected by flue gas composition and temperature depending on the mercury species present. For elemental mercury, lack of halides such as chloride/chlorine in the flue gas can reduce the carbon capacity significantly. A temperature effect can be seen when conditions exist where the carbon capacities may decrease below the threshold levels, such as where high levels of oxidized mercury exist and the temperature is significantly greater than 300°F (150°C).

The activated carbon that has been used as the baseline activated carbon for many of the tests to date has been Norit FGD carbon, a brand made from Texas lignite. Norit FGD carbon currently costs 50 cents/lb (\$1.1/kg) delivered. However, it has been shown that activated carbon can be made from different carbonaceous sources such as other coals (ND lignite, eastern bituminous), biomass (wood waste, corn waste, nut shells), waste tires and soot. These alternate types of activated carbon all appear to work as well as the baseline FGD carbon in many cases.

The cost of these alternate activated carbon sources will depend on the value of the starting material and the processing steps needed to make the final product. A very high capacity carbon such as Norit FGD may not be needed for mercury control, as the process is generally mass transfer limited. Thus, simplifying the processing steps or use of a cheaper carbonaceous source may reduce the final cost of the ACI as a control technology for utility boilers. Norit sells a lower grade of activated carbon (FGL) that is about 20% lower cost than FGD carbon and it appears to perform about equal to FGD. Initial projections show that cheaper carbons may be available at 20% to 50% lower cost than Norit FGD carbon. However, projected future costs are difficult to determine without having insight into competing sorbent manufacturers' businesses and what happens when very large quantities of activated carbon may be needed. Until the infrastructure is developed, demand resulting from widespread use of carbon-based sorbents for mercury control on coal-fired power plants may outstrip supply capacity. This may temporarily drive up sorbent prices.

Some biomass may require less processing steps for conversion to activated carbon. However, the carbon yield from biomass may be quite low compared to coal. The inherent unburnt carbon (LOI) in some flashes has been shown to provide reasonable mercury adsorption if concentrated and ground. However, the cost of separating and grinding the LOI carbon may be substantial and it may cost more to recycle and use the LOI carbon than to buy and inject commercial activated carbon. Other researchers have proposed using coal reburn as a method for simultaneous NO_x and mercury reduction by increasing the flyash carbon content through the reburn process.

Iodide activated carbon (IAC) has been shown to be an effective mercury sorbent for flue gas, and may perform better than untreated sorbents in flue gas with high elemental mercury and low chloride concentrations. However, the IAC tested to date costs fourteen times that of Norit FGD

carbon. EPRI is currently conducting research to look at alternate IAC sources and alternate methods for activating the carbon.

Besides activated carbon, other sorbents such as those based on zeolites, clay, amended silicates, flyash, and activated lime are potential candidates for mercury adsorption [5,6,7]. There is very little mercury adsorption performance data for these alternative sorbents, especially under actual flue gas conditions and even less is known about the balance-of-plant impacts and potential cost for commercially prepared quantities. Non-carbon based sorbents have generated significant interest in their potential to overcome use problems associated with activated carbon contaminated flyash.

7.3.4.2 TOXECON™ Activated Carbon Injection

Injection of activated carbon or sorbents into a baghouse after an existing ESP (electrostatic precipitator) is referred to as TOXECON™. The fly ash and carbon are intimately mixed if the carbon is injected upstream of a conventional baghouse. This could make ash use or disposal more difficult. By contrast, with TOXECON™, most of the fly ash will have been removed by the ESP before carbon injection into the baghouse. This reduces the volume of activated carbon-contaminated fly ash to <5% of the total fly ash volume.

7.3.4.3 MerCAP™

The operating concept for MerCAP™ is to place fixed structures into the flue gas stream to adsorb mercury, and then periodically regenerate them and recover mercury. The fixed structures can be made of a sorbent or coated with a sorbent material such as activated carbon or metals such as gold and silver to amalgamate with mercury. As the surfaces of the sorbent structure become saturated, the structure can be heated electrically or by other means such as passing hot flue gas over them.

7.3.5. Evaluation of Mercury Control by Emerging Technologies

Of the mercury control technology options available, three dry technologies were evaluated including ACI, chemical additives, and MerCAP™. ACI refers to the injection of powdered, untreated, activated carbon only (EPRI 2003b). For MerCAP™, a preliminary engineering economic study was conducted.

The two short-term, full-scale tests carried out show that chemical additives injected into the boiler can increase mercury oxidation and potentially enhance mercury capture. The addition of chloride compounds increases mercury oxidation in ND lignite and PRB flue gases; the consequent HCl concentration and mercury oxidation in the flue gas generally increased with the chloride feed rate. Three chloride salt solutions were evaluated; each is a proprietary blend along with sodium chloride. The chloride salt solution was injected into a boiler and did oxidize the elemental mercury; however, the oxidized mercury formed was not removed across the SD-BH or the wet particulate scrubber (WPS). Essentially all of the HCl formed is removed across the SD-BH and the WPS; however, the levels of chloride in stack emissions will increase as the flue gas HCl levels increase. Significant operational impacts were observed during the testing;

longer-term tests of corrosion, slagging, air pollutant emissions and waste disposal will need to be conducted.

ACI is the most-investigated option for mercury removal, for most plants equipped with only an ESP or BH. This approach appears to be effective for removal of all species of mercury and, therefore, is applicable to all coals studied thus far. For plants firing Western coals with low chloride contents (PRB, ND lignite), the study determined that there may be limitations on the maximum mercury removal efficiencies achievable with ACI (located ahead of the ESP and WPS). The effectiveness of ACI may also be significantly reduced with spray dryer baghouses. Chemical additives and chemical impregnation of the activated carbon was found to improve ACI mercury removal across the SD-BH and WPS by a factor of 2 to 4. The potential for these approaches to improve ACI removal across an ESP remains to be determined. Figure 7-1 summarizes the results of pilot and field injection data for ACI before an ESP.

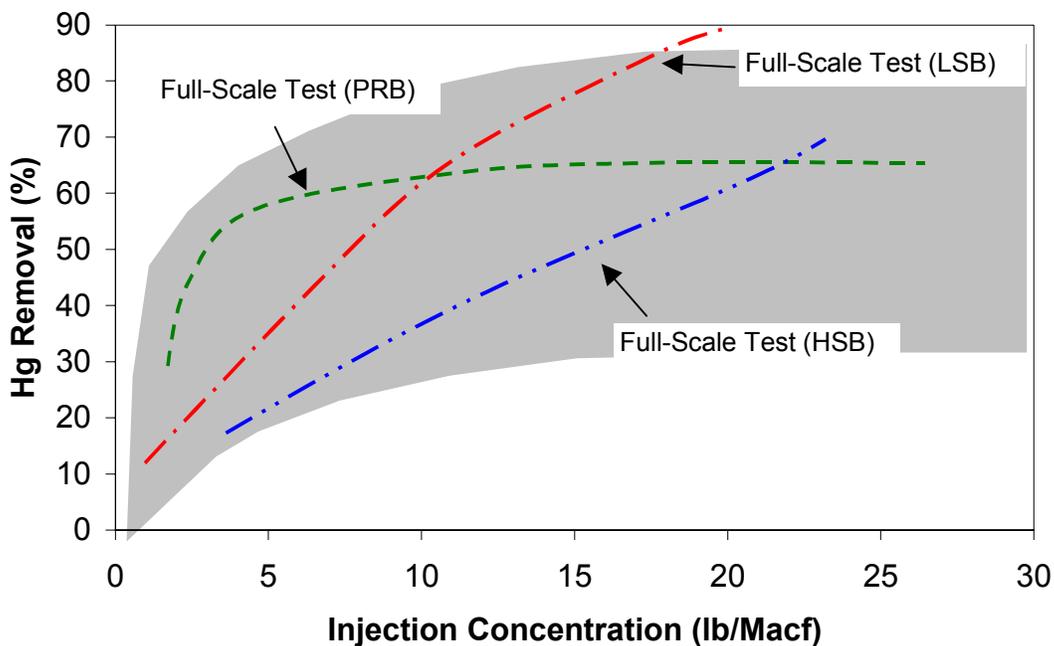


Figure 7-1
Summary of results of pilot and field injection data for ACI before an ESP (EPRI 2003b)

The tests to date indicate that, under the right conditions, MerCAP™ can remove greater than 80% mercury downstream of a SD-BH in ND lignite flue gas. MerCAP™ with gold as the sorbent surface did not perform well in unscrubbed flue gas. It is uncertain whether the low effectiveness is due either to: specific flue gas components (which reduced the capacity of gold for mercury in the gases tested), an effect of temperature, or a combination of both factors. A preliminary engineering economic study shows that MerCAP™ costs can be attractive relative to the use of COHPAC™ ACI for mercury control (Figure 7-2). Further development work is needed to establish a realistic sorbent capacity, regeneration frequency, and sorbent life.

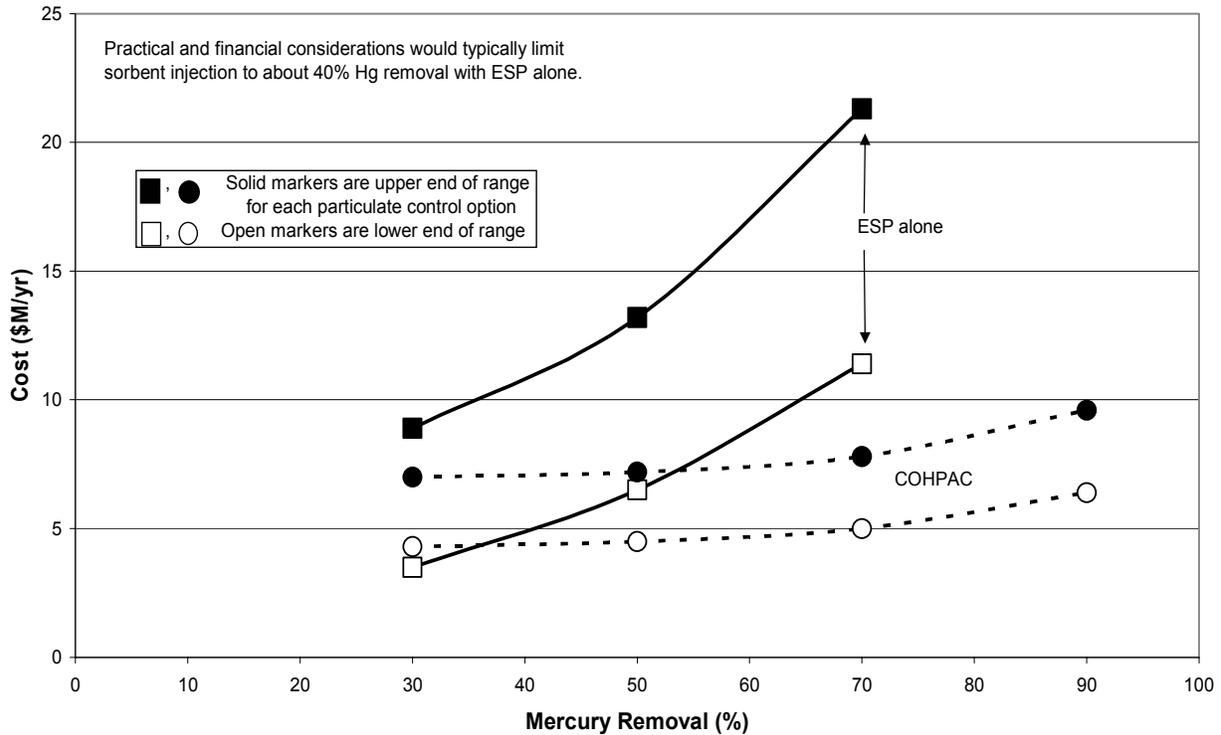


Figure 7-2
Representative Range of Mercury Removal Costs by Sorbent Injection for a 500 MWE Power Plant with an ESP

7.3.6 Other Emerging Control Technologies

Several other emerging control technologies are also reported in other sources (SENES 2002; MDEP 2002). Pulse corona or ultra-high current-impressed electrostatic precipitators have the potential to impose high electronic current fluxes onto mercury vapors passing through such fields. Elemental mercury is subject to oxidation and may result in a partial conversion to oxidized mercury in such areas. Documentation and quantification of the degree of conversion is quite limited, but there are indications that oxidation is likely.

First, PowerSpan Corporation has developed an Electro Catalytic Oxidation (ECO™) process that includes a plasma reactor upstream of a wet electrostatic precipitator augmented with ammonia injection. The proponents have reported significant oxidation of mercury and reportedly a 68.3% removal of mercury across the wet precipitator.

Second, Croll-Reynolds-MSE Technology has developed a Plasma Enhanced Electrostatic Precipitator (PEESP), which also utilizes a plasma technology along with an electrostatic precipitator with reagent gas injection. This concept is in the proof-of-concept stage, but should also show enhancement of the oxidation of the mercury species in a flue gas stream.

7.4 Effects of Activated Carbon Injection on Trace Elements

Extensive field pilot and full-scale testing in the past three years have been conducted to develop and evaluate cost-effective methods for reducing power plant mercury emissions, especially from coal-burning facilities. However, currently, little information is available regarding the impact of mercury control options (e.g., sorbent and chemical injection, catalytic oxidation) on the removal and emissions of other trace toxics (metals and acid gas species such as hydrogen chloride).

At five coal-fired utility boiler sites additional flue gas trace toxics measurements were conducted at the inlet and outlet of each control system during both baseline and mercury control testing (EPRI 2003c). Baseline, full-scale, and pilot-scale mercury control tests were made. The five plants selected for this work were also tested as part of the mercury control by dry technologies described earlier. The primary objective was to determine if the mercury control technologies influence removal and emissions of other trace elements and acid gas species. Trace element and acid gas test data from five test programs were standardized and examined to look for trends within and across sites. Particulate and vapor phase metals that were evaluated include antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, nickel, and selenium. Hydrogen chloride and hydrogen fluoride were also evaluated between chloride injection tests and tests without chloride injection (i.e., baseline and sorbent injection tests). Measurement methods included U.S. EPA Method 29 trace element and Method 26a acid as measurements. Control systems at the test sites included ESPs, SD/FF, WPS, and catalytic oxidation.

For the ten trace elements in the vapor phase tested, no statistically significant difference was observed between the control device outlet concentrations for baseline and mercury control at any of the sites. For selenium, the differences in vapor phase selenium concentrations across the control device at four of the sites are probably due to the differences in both coal selenium levels and flue gas temperature. Complete material balance information for selenium at the test sites, including coal, fly ash, and total Method 29 measurements at the control device outlet locations would be necessary to confirm these possible trends. Based upon inlet and outlet HCl measurements for chemical injection tests at two sites, the removal of HCl across the SD and WPS systems remained relatively constant between baseline and chemical injection tests.

In general, for vapor phase trace elements, no statistically significant difference was observed between control device outlet vapor concentrations for baseline and mercury control at any of the sites. Removal efficiency of HCl was found to be constant for each power plant configuration and independent of the hydrogen chloride concentration at the control device inlet. Chloride injection was found to have no impact on the concentration of the ten vapor phase trace elements tested in the flue gas. Variations in concentrations of vapor phase selenium for outlet flue gas streams are likely due to variations in coal selenium content and flue gas temperature rather than effects of sorbent or chemical injection. Additional test data for mercury control systems, including coal selenium analyses and total Method 29 measurements at the inlet and outlet of the control system, are needed to better understand selenium. Most of the trace metals of interest are present in the particulate phase. Thus future tests should include both particulate and vapor phase samples to provide more comprehensive insights regarding the fate of trace elements.

7.5 By-product and Waste considerations

7.5.1 Mercury Fluxes From Coal Fly Ash

During combustion of coal to produce electricity, the mercury in coal is either emitted to the atmosphere or captured with the coal combustion products (CCPs), principally fly ash and flue gas desulfurization solids. Of the estimated 75 tons of mercury contained in coal burned annually at power plants nationally; about 60 percent is released to the atmosphere industry wide, and the remaining 40 percent is removed by particulate and sulfur dioxide control devices and managed with the CCPs. Previous work in three projects sponsored by EPRI indicated that mercury in existing CCPs is present in relatively low concentrations and is relatively stable, with little evidence of leaching or volatilization (EPRI 2001a, b, c). The amount of mercury captured in CCPs is expected to increase over the next decade due to the implementation of enhanced control technologies for both criteria air pollutants and for mercury.

Preliminary laboratory tests of volatilization and leaching of mercury from 18 fly ash samples were made by using more sensitive analytical techniques than were used in most previous studies (EPRI 2002d). The fly ash samples were derived from combustion of bituminous, subbituminous, and lignite coals, and included fly ash collected from a mercury control demonstration project. Three of the 18 fly ash samples were collected from the demonstration project, in which an activated carbon sorbent was injected upstream of the electrostatic precipitator for enhanced mercury control. Volatilization experiments were performed using a gas exchange chamber under varying light and temperature conditions, and leaching was performed using the Synthetic Precipitation Leaching Procedure (SPLP).

Total mercury concentrations for all fly ash samples are summarized in Figure 7-3. Concentrations ranged from 7 to 913 $\mu\text{g}/\text{kg}$ and were less than 250 $\mu\text{g}/\text{kg}$ in 14 of 18 samples. Concentrations were above 250 $\mu\text{g}/\text{kg}$ in four of the 18 samples. Total mercury concentrations did not appear to be correlated to coal type in this sample set. By type of coal, concentrations of mercury in fly ash ranged from 10 to 163 $\mu\text{g}/\text{kg}$ for lignite, 56 to 92 for subbituminous (excluding carbon injection samples), and 7 to 913 $\mu\text{g}/\text{kg}$ for bituminous. All of the bituminous and subbituminous ash samples exhibited negative mercury vapor flux under dark conditions. One sample of five of lignite-derived ash exhibited deposition of atmospheric mercury while the other four samples exhibited mercury emission.

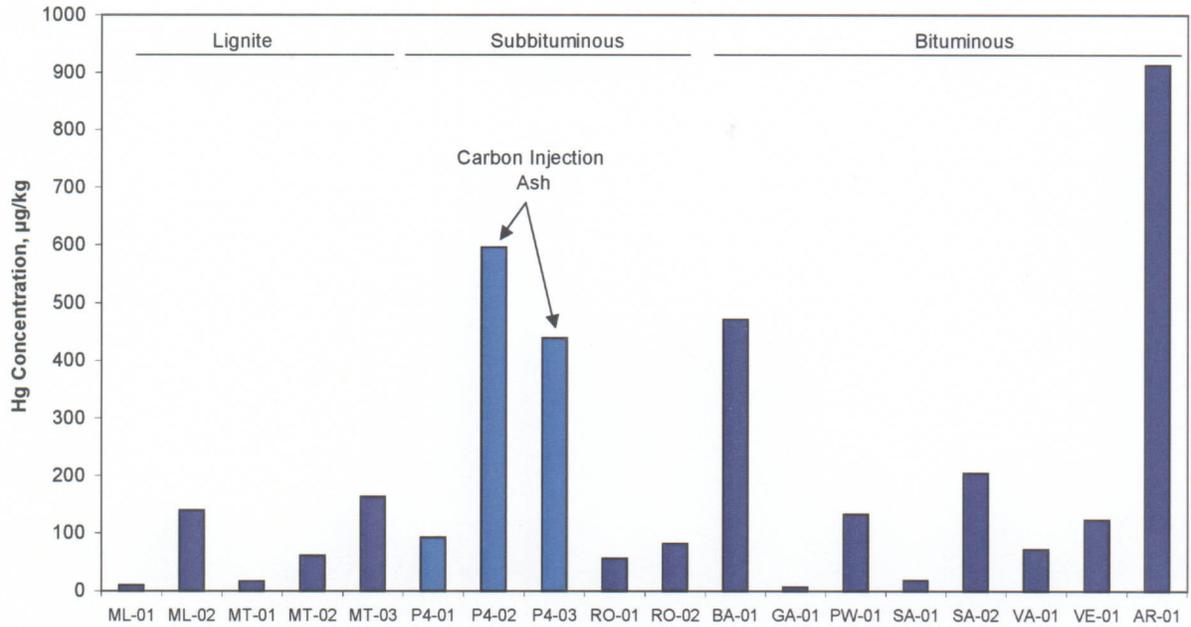


Figure 7-3
Total Mercury Concentration in Fly Ash Samples

Carbon injection did not appear to significantly affect the mercury release behavior of the ash. There was a net deposition of mercury from the ambient air to the fly ash for all three samples from the carbon injection test.

In general, deposition to ash for the dark 25° C exposure was greater than that occurring during light 25° C or dark 45° C exposures. For those samples exhibiting positive flux (mercury emission) at dark 25° C exposure, greater emissions occurred for light 25° C and dark 45° C exposures. Figure 7-4 provides a summary of the mercury flux to air from ash samples under varying conditions of light and temperature. These results are consistent with previous work indicating both light and temperature enhance mercury emissions.

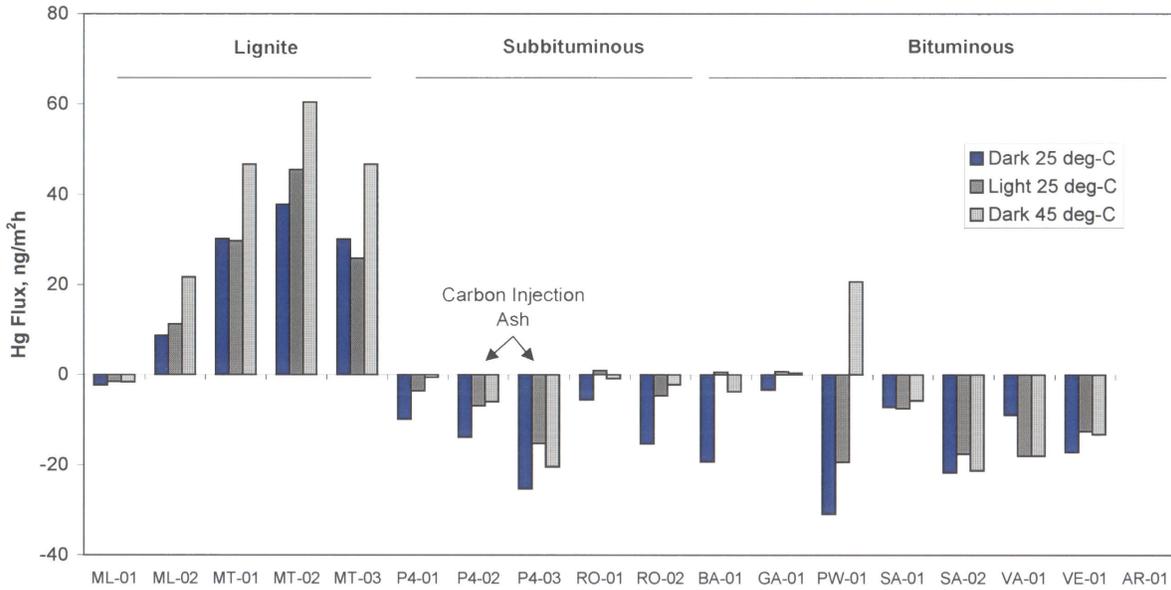


Figure 7-4
Summary of Mercury Flux to Air from Fly Ash Samples Under Varying Conditions of Light and Temperature

In an extended measurement over a period of several weeks, a significant correlation was found between inlet air concentration and mercury deposition to fly ash. Deposition rates increased (flux becoming more negative) as a function of increasing inlet air mercury concentrations (Figure 7-5).

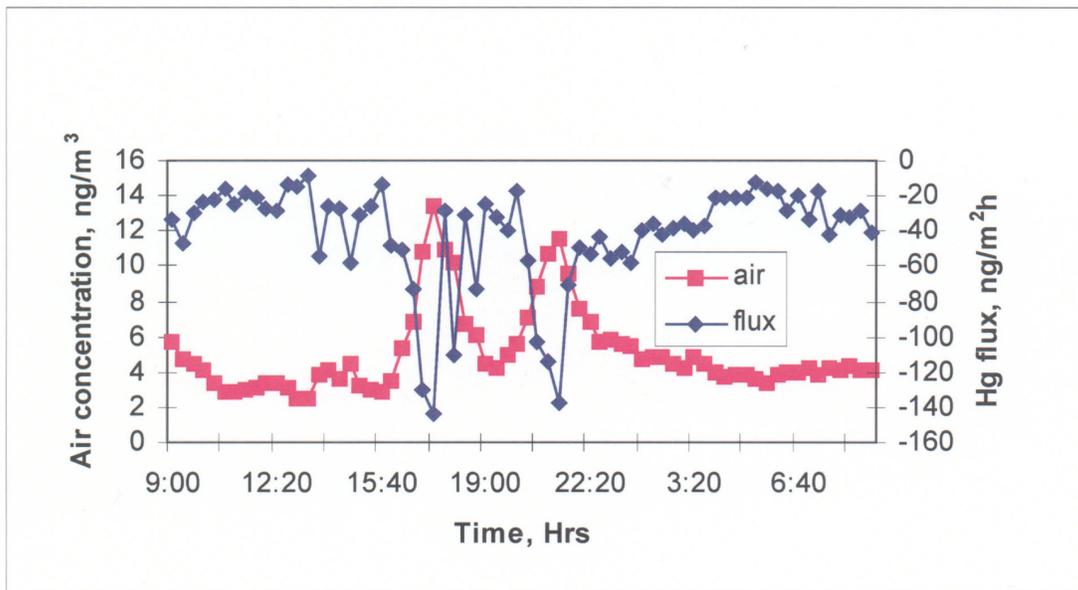


Figure 7-5
Fly Ash Mercury Deposition Rates as a Function of Inlet Air Mercury Concentrations

Mercury concentrations in the leachate extracts were all very low, less than 11 ng/L. These concentrations are more than two orders of magnitude lower than the U.S. EPA maximum contaminant level of 2000 ng/L for mercury in drinking water, and all were below the current U.S. EPA water quality criterion of 12 ng/L (EPA, 1986, Quality Criteria for Water, EPA 440/5-86-001).

There was no apparent correlation between mercury leachate concentration and coal type or total concentration in the fly ash. Mercury leachate concentrations for the carbon injection ashes were slightly higher than the baseline sample, but were still very low at less than 5 ng/L.

This analysis of 18 coal fly ash samples suggests there is little potential for re-release of mercury from coal fly ash or leachate. Bituminous and subbituminous samples of fly ash were sinks for atmospheric mercury, exhibiting negative mercury flux in contact with ambient air. Lignite samples that exhibited net positive emissions were found to release an insignificant amount of the total mercury captured in fly ash to air. Leaching tests yielded very low concentrations of mercury in leachate, less than 11 ng/L for all samples.

While activated carbon may be injected in front of ESPs in the future to capture mercury in response to mercury emission limits on coal fired boilers, the preliminary results presented here suggest that the mercury release from combustion by-products will not be significantly increased. Ash/sorbent samples were sinks for atmospheric mercury, with deposition rates increasing slightly for the ash/sorbent samples. Leachate concentrations from ash collected during the carbon injection project were below 5 ng/L.

Based on these preliminary experiments, mercury re-emission from ash does not appear to occur to a significant extent. Additional work is underway to evaluate the emissions from coal fly ash at field sites to confirm the laboratory results.

**Table 7-1
Projected ACI Mercury Removal Effectiveness for Bituminous Coals (EPRI 2003b)**

Coal Type	Existing Emissions Control	Measured Achievable Mercury Control	Potential options for additional removal	Key Issues and Uncertainties,
Bituminous	ESP (Cold side)*	90% (1 full scale low sulfur bituminous only, Unknown for medium to high sulfur bituminous)	- increase/modify flyash LOI - reduce flue gas temperature - add COHPAC™ downstream of ESP (TOXECON™)	- still requires very high ACI rates and costly - ash use/disposal - limited cooling possible, significant corrosion problems - need more long term data on small (<150 SCA) full-scale ESPs to assess balance-of-plant impacts. - only 1 full-scale + 2 pilot test on TOXECON™ - No long term TOXECON™ data
	ESP+ wetFGD**	No data (>60% baseline without ACI, expect ACI to be same as ESP case)	- same as ESP case - could inject before wet FGD	- same issues as above if ACI before ESP although wet FGD may alleviate any increased ESP emissions - unknown performance ACI before wet FGD and unknown impact on FGD
	SD-ESP	No data	- ACI should work - increase flyash LOI content	- may impact ESP performance
	SD-BH	>90% baseline	- ACI should work if needed	
	BH	No data (75% baseline without ACI)	- ACI should work - increase/modify flyash LOI	- only two pilot test on PRB coal - ash use/disposal.

* It is assumed that ACI before a hot-side ESP will not work. For a hot-side ESP, a COHPAC™ baghouse should be located downstream of the air heater, and activated carbon injected before the baghouse, downstream of the air heater.

** The addition of SCR for NOx control, mercury oxidation catalysts (discussed in more detail in a separate report) or chemical additives may increase oxidized mercury content and improve Hg removal across the wet FGD.

Table 7-2
Projected ACI Mercury Removal Effectiveness for Western Coals (EPRI 2003b)

Coal Type	Existing Emissions Control	Measured Achievable Mercury Control	Potential options for additional removal	Key Issues and Uncertainties,
Sub bituminous and ND lignite (<i>Texas lignite and western bituminous?</i>)	ESP (Cold side)*	60-70% (only 1 full-scale test, + 4 pilots)	<ul style="list-style-type: none"> - alternate sorbents such as IAC (with adequate capacity in low Cl flue gas) - increase flue gas Cl - add COHPAC™ downstream of ESP (TOXECON™) 	<ul style="list-style-type: none"> - ash use/disposal - may be difficult to achieve 90% removal at reasonable cost - May be more cost effective to add COHPAC™ for ash sales - no long term tests with TOXECON™ (ACI into COHPAC™) - Need more long term full-scale data on small ESP(<150 SCA) - high cost of alternate sorbents and their stability - balance-of-plant problems with increased Cl
	ESP+ wetFGD	No data same as ESP case	<ul style="list-style-type: none"> - same as ESP case - MerCAP™ 	<ul style="list-style-type: none"> - same issues as above if ACI before ESP although wet FGD may alleviate any increased ESP emissions
	SD-ESP	No data (see problems with SD-BH below)	<ul style="list-style-type: none"> - alternate sorbents - increase flue gas Cl 	<ul style="list-style-type: none"> - impact on ESP performance - high cost of alternate sorbents and their stability - balance-of-plant problems with increased Cl
	BH	90%(2 pilots only) (67% baseline without ACI)	<ul style="list-style-type: none"> - alternate sorbents - increase flue gas Cl 	<ul style="list-style-type: none"> - ash use/disposal - high cost of alternate sorbents and their stability - balance-of-plant problems with increased Cl
	SD-BH	ACI<70% IAC~90% (only 1 full-scale test, + 2 pilots)	<ul style="list-style-type: none"> - alternate sorbents - increase flue gas Cl - MerCAP™ 	<ul style="list-style-type: none"> - high cost of alternate sorbents and their stability - balance-of-plant problems with increased Cl
	WPS	ACI<15% IAC<55% (only 1 full-scale test)	<ul style="list-style-type: none"> - alternate sorbents - longer sorbent gas contact time - increase flue gas Cl 	<ul style="list-style-type: none"> - only 1 full-scale test - unlikely to achieve >60% removal - high cost of alternate sorbents and their stability - balance-of-plant problems with increased Cl

7.6 Summary

- Coal cleaning may help reduce coal mercury concentration and impact (positively or negatively) flue gas mercury speciation. However, coal cleaning will more likely be used as a supplemental mercury reduction strategy than a primary mercury control option if high mercury control levels are needed.
- Current research results indicate that additional mercury capture may be achieved by the introduction of a sorbent prior to SO₂ and PM control technologies.
- Research results to date indicate that a number of uncertainties create difficulties in quantifying mercury removals and in identifying factors that impact these removals. These uncertainties all originate from the primary fact that we now know that mercury chemistry is highly complex and kinetically dynamic than previously thought by researchers. This is due to both mercury species reactivity and mercury conversion rates.
- There may currently be a widespread misapplication of terminology for reporting on the chemical forms or species of mercury as well as its physical forms. Many reports appear to use the chemical forms interchangeably; a reanalysis of selected original data, results and subsequent citations would be beneficial to ensure appropriate terminology and mercury species identification. This is important since mercury species have been shown to convert from one to another; further, the mixture composition may change from point to point within the combustion system.
- Analytical methods to determine mercury species may not always be reliable. When coupled with exceptionally low concentrations (trace to ppm range) and the ability of mercury compounds to convert from one species to another, chemical analysis may not well represent which mercury compounds are actually being measured. Most test data are still based on manual wet methods which may not facilitate reliable evaluation of the variability of mercury nor the long term evaluations of the application of mercury removal technologies.
- Two considerations are important in the analysis of specific Hg control technology alternatives. First, recognition of the appropriate chemical composition of mercury species at the point of the capture reaction is a key consideration. Second, an understanding of the implications of the chemical analysis methods utilized is necessary to evaluate control test results and to understand the appropriateness of a given technology.
- Control technologies that reduce SO₂, NO_x and PM for coal-fired plants yield levels of mercury control ranging from 0 to over 90%, depending on coal type, boiler design, and emission control equipment. Power plants firing PRB coal indicate between 20 and 30% mercury capture associated with electrostatic precipitators; and on average 50–60% mercury capture at plants equipped with baghouses, with removal rates as high as 90% observed. On average, the lower the coal rank, the lower the mercury emissions reductions; however, mercury emissions reductions may also vary within a given coal rank.
- SCR systems can convert elemental mercury to oxidized mercury, which is more easily captured in downstream air pollution control devices (primarily FGD systems). Oxidation of mercury seemed to be affected by the coal type and catalyst design with the extent of oxidation higher for Eastern bituminous than Western coals.

- Emerging control technologies for mercury are under development and demonstration, but are not commercially deployed. Integrated control methods that target multiple pollutants including SO₂, NO_x, PM, mercury and CO₂ may ultimately be the most a cost-effective approach.
- Activated carbon injection (ACI) is the most investigated option for mercury removal, for most plants equipped with only an ESP or BH. This approach appears to be effective for removal of all species of mercury .. Low ACI mercury removal effectiveness were observed at SD-BH and WPS sites (<70% and <20% respectively at high ACI rates) burning low chloride western coals (ND lignite and PRB). ACI mercury removals measured to date across PRB fired sites equipped with ESPs were also limited to <70%. The tests to date indicate that flue gas chloride and SO₂ content are key components that affect ACI performance. For conditions where activated carbons have lower effectiveness, chemically impregnated activated carbons appear to show promise.
- The tests to date indicate that given the right conditions, MerCAP™ with gold coated plates around 10 ft (3 m) long and spaced 0.5 inches (1.3 cm) apart can remove >80% mercury. In the tests conducted to date, this performance was achieved downstream of a SD-BH and a wet scrubber. It is uncertain at this point whether the low effectiveness is due to specific flue gas components which reduced the gold capacity for mercury in the gases tested, to an effect of temperature, or to a combination of both.
- Tests to determine if the mercury control technologies influence removal and emissions of other trace elements and acid gas species showed no statistically significant difference was observed between the control device outlet concentrations for baseline and mercury control at any of the sites. For selenium, the differences in vapor phase selenium concentrations across the control device are probably due to the differences in both coal selenium levels and flue gas temperature.
- During combustion of coal to produce electricity, the mercury in coal is either emitted to the atmosphere or captured with fly ash and flue gas desulfurization solids. Of the estimated 75 tons of mercury contained in coal burned annually at power plants nationally; about 40 percent is removed by particulate and sulfur dioxide control devices. Current work confirmed previous results indicating that mercury in existing CCBs is present in relatively low concentrations and is relatively stable, with little evidence of leaching or volatilization.
- While mitigating the problem of atmospheric mercury pollution, control strategies for coal-fired power plants will still result in mercury wastes that are potential sources of future re-emissions. These mercury wastes should be disposed of or reused to prevent or minimize re-emission of mercury to the environment.

References

Brown T.D., et al, R.A., . 1999. Mercury Measurement and its Control : What we Know, Have Learned, and Need to Further Investigate, J. Air & Waste Manage. Assoc., pp. 1-9. June.

Canadian Council of Ministers of the Environment (CCME) 2003. Canadian Uniform Data Collection Program (UDCP) for Mercury from Coal-fired Electric Power Generation, A Guidance Document. Mercury Canada-wide Standards Development Committee.

Chu, P., D. Laudal, L. Brickett, C. Lee, 2003. *Power Plant Evaluation of the Effect of SCR Technology on Mercury*. Paper presented at the Combined Power Plant Air Pollutant Control Mega Symposium (MEGA Symposium), May 19-22, 2003. Washington, D.C.

Commonwealth of Massachusetts, Department of Environmental Protection (MDEP) 2002. Evaluation of the Technological and Economic Feasibility of Controlling and Eliminating Mercury Emissions from the Combustion of Solid Fossil Fuel. December.

EPRI, DOE, EPA 2002. Power Plant Evaluation of the Effect of Selective Catalytic Reduction on Mercury. Final Report. TR-1005400.

EPRI, DOE, EPA 2000. Pilot-scale screening evaluation of the Impact of Selective Catalytic Reduction for NO_x on Mercury Speciation. Final Report. TR-1000755. (cited in Laudal et al. 2003.)

EPRI, 2003a. Impact of NO_x Controls on Mercury Controllability: Update 2002. TR-1004268. Technical Update.

EPRI, 2003b. Development and Demonstration of Mercury Control by Dry Technologies. TR 1004261.

EPRI, 2003c. Effects of Mercury Controls on Removal and Emissions of Trace Elements and Acid Gas Species. TR-1004264. Technical Update.

EPRI 2002a. Impacts on NO_x Controls on Mercury Controllability. March. TR-1004000

EPRI 2002b. Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems- Site 3 Topical Report. February, 2002. TR-1004057. R. Rudy

EPRI 2002c. Mercury Removal Options for Power Plants. March 2002. TR-1004072.

EPRI, 2002d. Mercury Releases from Coal Fly Ash. TR-1005259.

EPRI 2001a. Proceedings: 14th International Symposium on Management and Use of Coal Combustion Products (CCPs). TR-101158. DM Golden

EPRI 2001b. Impact of Mercury Controls on Coal Combustion By-Product Utilization. December. TR-1004610.

EPRI 2001c. Occurrence and Fate of Mercury in Coal Ash and Flue Gas Desulfurization Sludge. TR-1005212. December.

EPRI 2001d. Estimation Methodology for Total and Elemental Mercury Emissions from Coal-Fired Power Plants. Palo Alto, CA. TR-1001327.

EPRI 2000. An Assessment of Mercury Emissions from U.S. Coal-Fired Power Plants. Palo Alto, CA. TR-1000608.

Laudal, D.L. J.S. Thompson, J.H. Pavlish, L. Brickett, P. Chu, R.K. Srivastava, C.W. Lee, and J. Kilgroe 2003. Mercury Speciation at Power Plants Using SCR and SNCR Control Technologies. *EM-Environ. Man.* 16-22.

SENES Consultants Ltd. (SENES) 2002. Evaluation of Technologies for Reducing Mercury Emissions from the Electric Power Generation Sector. February. Technical Report prepared for Canadian Council of Ministers of the Environment.

Toole-O'Neil, B. et al, Mercury Concentrations in Coal—Unraveling the Puzzle, *Fuel* 78, p. 47-54, 1999.

UNEP 54790-01 – Global Mercury Assessment. April, 2002

US Department of the Interior, Bureau of Mines Information Circular 9412 – The Materials Flow of Mercury in the United States. 1994. SM Jasinski

US Department of the Interior, US Geological Survey Circular 1197 – The Materials Flow of Mercury in the Economies of the United States and the World. June, 2002. JL Sznoppek, et al.\

8

ANALYSIS OF MERCURY MANAGEMENT STRATEGIES

8.1 Introduction

This chapter will briefly describe the results of an assessment of potential mercury control steps for utility mercury emissions and implications for mercury deposition and exposure; and results of an evaluation of how these scenarios for management might impact both the costs of mercury controls, and the potential for lowered risk to community residents..

8.2 Assessment of Potential Mercury Control Measures and Implications for Deposition and Exposure

Since EPRI's 1996 report on mercury in the environment, atmospheric mercury modeling has become more sophisticated due to advances in data collection techniques, better resolution of mercury emission and deposition data, refinement of kinetic rates and reactions, and a more precise understanding of the factors affecting mercury fate and transport. Researchers have continued to develop and apply models for investigating mercury at local, regional, and global scales. Modeling studies have combined atmospheric and watershed models to evaluate atmospheric mercury deposition into lakes (Seigneur et al. 1997, 2002).

The Trace Elements Analysis Model (TEAM), a three-dimensional Eulerian model originally developed for EPRI for simulation of long-range acid rain processes, has been used in a series of applications investigating atmospheric concentrations and deposition fluxes of mercury in the U.S. Since initial use of the TEAM modeling system with a 100-km grid resolution for simulating regional mercury fate and transport by EPRI, a finer 20-km horizontal grid resolution was embedded (Pai et al 2000) into the eastern half of model domain. This fine grid represented a portion of the northeastern U.S encompassing 50 percent of the largest mercury point sources in the regional inventory.

Because of the great spatial range of mercury deposition, ranging from near-source wet deposition to global wet and dry deposition, it is essential to assess the relative importance of local, regional, continental, and global sources of mercury that may produce deposition in sensitive watersheds. Accomplishing this requires that both global and regional-scale processes be simulated together. The use of a multiscale modeling system has been applied to investigate the contributions of such sources to deposition in the U.S. and smaller geographic regions within the U.S. The modeling system includes a global CTM and a nested continental Eulerian model (TEAM) to simulate transport, transformations, and deposition of mercury (Seigneur et al. 2001). The global CTM provides the boundary conditions (i.e. coarse-resolution ground-level atmospheric concentrations) for TEAM. The global CTM is run until steady state is achieved

between emissions of mercury into the atmosphere and deposition to the surface. Emissions and atmospheric mercury chemistry are the same in both models, but the time and space scales differ. The modeling system was applied to estimate the relative contributions of regional and global sources to mercury deposition across the continental U.S. (EPRI, 2000; Seigneur et al. 2003a), in New York State (Seigneur et al. 2003b), and in Wisconsin (Vijayaraghavan et al., 2002 cited in Seigneur et al. 2003b). Since its initial application, the atmospheric mercury chemistry and depositional processes simulated by CTM have undergone a series of modifications (EPRI 2000, Seigneur et al. 2002).

The multiscale modeling system consisting of the global CTM and TEAM were used to analyze regional and global source contributions to mercury deposition in the contiguous U.S. (Seigneur et al. 2003a). The analysis consisted of a base case scenario in which simulated deposition results based on a 1998 mercury emissions inventory were evaluated and compared with observed data. In addition, sensitivity simulations were run corresponding to mercury emission reduction scenarios. Global simulations were run to estimate relative impacts of global anthropogenic and natural sources on mercury deposition in the U.S. Source-receptor relationships between U.S. power plant emission and mercury deposition at selected locations within the contiguous U.S. were also developed.

The emission inventory used in this study was based on that of Seigneur et al. (2001) and consists of anthropogenic and background mercury emissions into the atmosphere. The inventory of anthropogenic emissions was changed to reflect updates to U.S. anthropogenic emission data (Seigneur et al. 2003a). Important changes were the use of an emission inventory for U.S. coal-fired power plants (EPRI 2002), the addition of a Wisconsin Chloralkali plant, and the inclusion of mobile sources (i.e. passenger vehicles). Total U.S. anthropogenic emissions were calculated to be 133 Mg/yr, approximately six percent of the total global anthropogenic emissions (2127 Mg/yr) used in the model. Background emissions were assumed to amount to 2000 Mg/y from the oceans and 2260 Mg/y from land. Total global emissions from all sources are assumed to be 6386 Mg/yr. Using the emissions inventory described previously, the modeling system was run using output from the global CTM as boundary conditions for the west coast of the U.S. and at the borders with Mexico and Canada. In the global CTM, an average atmospheric lifetime of mercury was calculated to be 1.2 years.

The surface Hg(0) concentrations were found to display a strong latitudinal gradient with background concentrations mostly in the range of 1.2 to 1.6 ng/m³ in the southern hemisphere and mostly in the range of 1.6 to 1.9 ng/m³ in the northern hemisphere. Concentrations above 1.9 ng/m³ are simulated over the large source areas of eastern Europe and eastern Asia. In the southern hemisphere, South Africa shows up as a large source area with Hg(0) concentrations up to 1.7 ng/m³. The Hg(II) concentrations show stronger spatial variations than the Hg(0) concentrations due to their stronger correlations with source areas, such as South Africa, North America, Europe and Asia. The highest Hg(II) concentrations (in the range of 200 to 300 pg/m³) are found over eastern China, due to the fact that Asia accounts for about half of the global anthropogenic emissions. The Hg_p concentrations are solely of anthropogenic origin and, therefore, they provide footprints of the major source areas. Concentrations of Hg_p in eastern Asia are in the range of 100 to 200 pg/m³.

TEAM was then run using the U.S. emissions inventory and output from the global CTM. According to model results, Hg(0) concentrations are higher in the eastern than in the western

United States except for a few isolated grid cells in the West showing concentrations above 1.7 ng/m³. Maximum Hg(0) concentrations reach 2.9 ng/m³. Hg(II) concentrations are mostly below 100 pg/m³, except for a few grid cells that show concentrations in the range of 100 to 191 pg/m³.

Hg_p concentrations reach 120 pg/m³ in some grid cells but are primarily below 50 pg/m³. Wet deposition fluxes are highest on the west coast and in the eastern United States. The high wet deposition fluxes on the west coast are due to the high Hg(II) concentrations at the upwind boundary as well as high precipitation along the mountain ranges of the Cascades and Sierra Nevada. The high wet deposition fluxes in the eastern United States result from the influence of local/regional sources (e.g., in the Northeast) or high precipitation (e.g., Florida). The highest wet deposition flux (46 µg/m²-y) near Baltimore is influenced by emissions from a local municipal waste incinerator; the incinerator has had its own MACT controls put in place since the period represented by the simulation. Dry deposition fluxes are highest in the northeastern United States. High dry deposition fluxes in the Northeast result from the combined impacts of local/regional emission sources. The highest total deposition flux (100 µg/m²-y) occurs near Baltimore and is likely a result of deposition of Hg emitted from the aforementioned waste incineration.

For North America, modeled wet deposition fluxes of mercury were compared to observations available from the Mercury Deposition Network (MDN). The coefficient of determination (r^2) is 0.81, the normalized error is 18%, and the normalized bias is 4%. The coefficient of determination is 0.51, the normalized error is 24%, and the normalized bias is 4%. These results show slightly improved model performance compared to previous modeling efforts (Seigneur et al., 2001, 2003b).

The continental model was applied to simulate the impacts of various power plant emission control scenarios proposed by industry and others for U.S. coal-fired power plants on mercury deposition within the contiguous United States. For each scenario, the reductions were applied as follows: The alternative coal-based and stack-rate mercury limits for pulverized coal plants were applied to each power plant to determine overall annual reductions in mercury emitted for each unit. These overall reductions were used to set the less restrictive of either the specified stack limit or coal-based limit as the new emission rate for the plant. For units already meeting either limit, there was no further control applied.

Five reduction scenarios were applied in the simulations of “illustrative MACT limits.” The overall reductions in coal-fired power plant mercury emissions from the base case amount to 47%, 30%, 16%, 75%, and 83% for Scenarios 1 through 5, respectively. These values correspond to reductions in mercury from the mercury coal content of 68%, 58%, 49%, 85%, and 90% for Scenarios 1 through 5, respectively. The emissions of the continental North American domain were modified accordingly and a TEAM simulation was conducted for each scenario. Reductions in mercury deposition from the base case were less than 10% over most of the United States. The average reductions in mercury deposition over the contiguous United States were 3.4%, 2.7%, 1.2%, 5.9% and 6.2% for Scenarios 1 through 5, respectively. It is important to note that the largest calculated decreases in mercury deposition were predicted to occur in Pennsylvania, downwind of the Ohio Valley. Seigneur et al. (2002b) have shown that TEAM overestimates mercury wet deposition in this area. As discussed by Vijayaraghavan et al. (2002), there is some evidence that reduction of Hg(II) to Hg(0) may occur in power plant plumes, which is not currently accounted for by models such as TEAM. This could explain, at least partially, the

model over-predictions over Pennsylvania since the Hg(0) is less likely to be deposited than the Hg(II).

The global and continental models were used in combination to investigate the relative contributions of major source categories (anthropogenic emissions from individual continents and natural emissions from land and the oceans) to deposition in the U.S. Twenty receptor areas were selected including nineteen individual grid cells and the entire contiguous United States. The contribution of North American sources to deposition ranged from 9 to 86% (Figures 8-1 and 8-2). Asia showed the largest contribution among continents with values ranging from 5 to 32%. Natural emissions contributed from 3 to 38%. With the understanding that the model may overpredict mercury wet deposition in the northeastern U.S., the authors suggest North American contribution estimates should be seen as upper bounds. The estimated contribution of North American emissions to mercury deposition in Everglades National Park, Florida, is 17%; this value is significantly different from previous estimates that ranged from 30 to 70% (Dvonch et al., 1999 and Guentzel et al., 2001 cited in Seigneur et al. 2003a), thereby emphasizing that significant uncertainties remain in understanding of mercury atmospheric fate and transport. These results also suggest that reducing mercury deposition will require a global strategy, particularly for areas such as the Everglades where atmospheric deposition of mercury is dominated by the global background (Seigneur et al. 2003a).

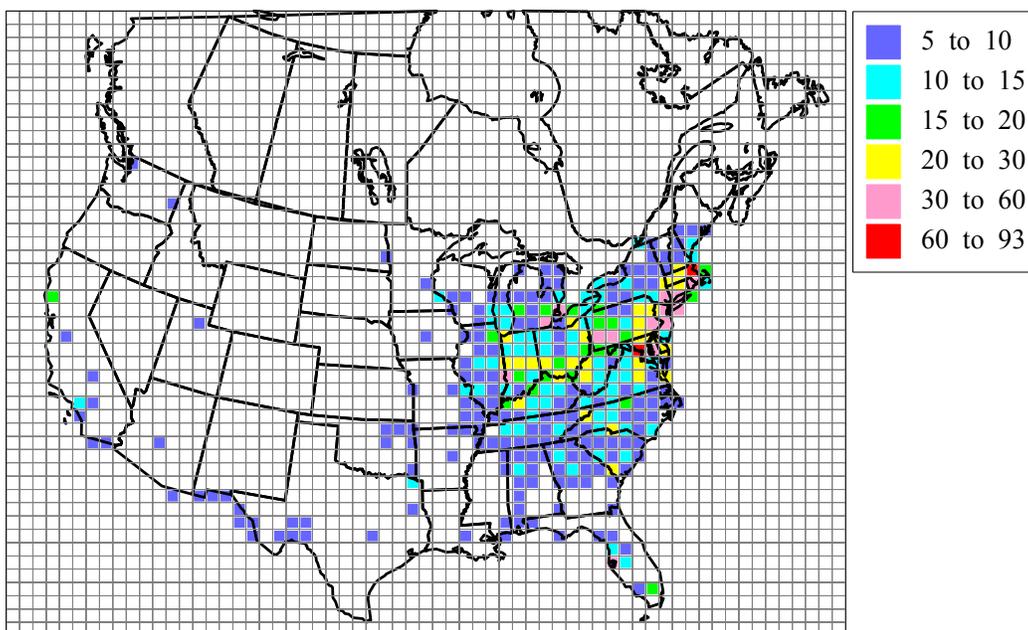
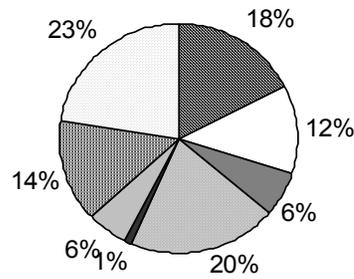


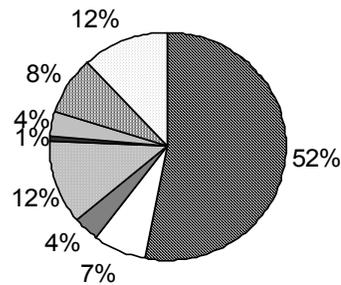
Figure 8-1
Total deposition fluxes of total Hg ($\mu\text{g}/\text{m}^2\text{-y}$): contribution of North American anthropogenic emissions. (Seigneur et al. 2003)

The contribution of mercury emissions from various source areas to mercury deposition at a given receptor depends on a myriad of factors including the speciation of these emissions, the location of the source area with respect to the receptor area, and the atmospheric conditions (i.e., meteorology, chemistry and deposition processes) that affect air parcels transported from the source area to the receptor area.

Wet Deposition to All U.S. Grid Cells



Dry Deposition to All U.S. Grid Cells



Total Deposition to All U.S. Grid Cells

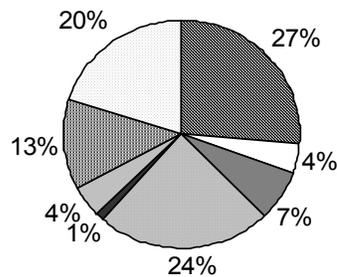


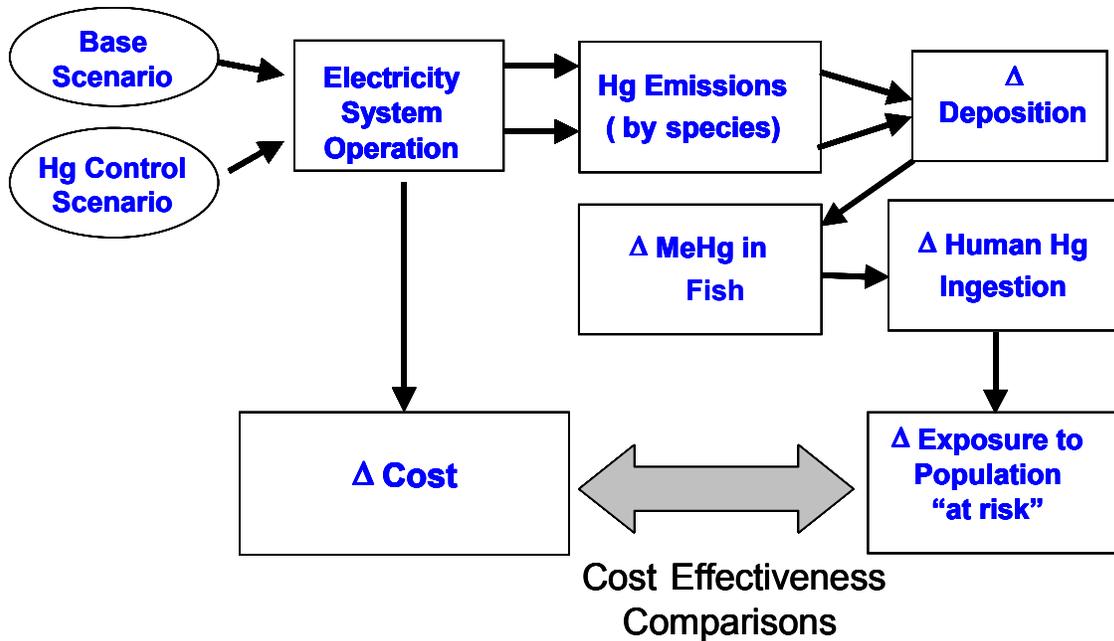
Figure 8-2
Relative contributions (%) of anthropogenic continental emissions and natural emissions from land and oceans to total mercury deposition over the entire contiguous United States (re-emissions were assigned to anthropogenic and natural sources according to their respective emission levels). (Seigneur et al. 2003a)

A simplified version of the continental model (a response-surface model) was developed to represent the impacts of fifteen power plant source areas on twenty receptor areas. Because the atmospheric mercury model is a linear system, the response-surface model provides an accurate representation of the original model. This simplified version of the model was used to develop mercury control costs when used in an associated cost model (Charles River Associates' Electric Power Markets Model, EPMM) and estimate the relative effectiveness of alternative mercury management strategies in the U.S. The results of this EPRI study are described below.

8.4 Controls, Relative Costs and Effectiveness in Altering Exposure to Mercury

An integrated analysis framework was developed to assess the costs of mercury controls on coal-fired steam electricity generating units and the corresponding effectiveness of those controls, measured by the reduction in human exposure to mercury that might be brought about (EPRI 2003). The framework projects emissions of mercury from electricity generation under alternative regulatory regimes at a regional spatial scale, by mercury species. The framework then tracks these emissions through the mercury atmospheric and biogeochemical cycle to uptake and retention by fish and eventual consumption by humans. The framework outputs include measures of effect such as changes in the total cost of producing electricity, changes in speciated mercury emissions, changes in deposition, and the impact of altered environmental mercury levels on exposures of women in the upper end of the distribution of methylmercury (MeHg) levels in blood. The last of these is used to estimate the change that might occur due to mercury controls in the number of women with MeHg blood levels above the EPA-determined reference dose (RfD), and the (lower) number of annual births of children "at risk" due to the consequent drop in mercury levels in fish consumed by these women. Using these measures, one can compare the relative cost-effectiveness of alternative Maximum Achievable Control Technology (MACT) standards, legislation such as the Clear Skies Act, and other policies for controlling utility mercury emissions.

Figure 8-3 depicts the key components of the framework and the connections between them. The basic outputs of the framework are incremental costs and incremental changes in human health risk from one regulatory scenario relative to another. For most of the policy options, "effectiveness" is defined as the increased number of children born each year to mothers with maternal blood MeHg below the EPA RfD, due to the controls on utility mercury emissions, that is, an increase in the number of children not "at risk." Estimation of the incremental human health risk changes requires a sequence of linked computational steps. Starting from estimated emissions changes, the framework estimates the extent to which emissions of the different Hg species are being changed, then converts these speciated emissions changes into projected deposition changes, which are in turn used to estimate changes in human MeHg consumption, and hence, changes in the member of humans that are "at risk."



Note: The **Delta (Δ)** symbolizes a change between the Base and the Hg control policy scenario

Figure 8-3
Computational Elements of Hg Cost-Effectiveness Framework (Smith et al., 2003)

To project the costs and emissions changes expected from regulations, the Electric Power Market Model (EPMM) was used. The EPMM simulates the operation of every electricity-generating unit in the U.S. for each modeled future year, and determines the least-cost operations without exceeding specified limits. System operational decisions include altering the utilization of existing capacity, building new capacity, retiring existing capacity, installing retrofits, and switching the fuel types of existing units. EPMM minimizes costs over all modeled years simultaneously and accounts for synergies in controlling multiple pollutants. The mercury emissions rates for each type of coal are based on EPRI's earlier analysis of the ICR data.

EPMM's outputs include projections of a large number of electricity generating system outcomes for 28 source regions of the continental U.S.; these regions were chosen to be approximately contiguous with boundaries and sub-regions of electric reliability councils in the U.S. Key EPMM results extracted for input into the cost-effectiveness framework include national costs by year and regional total mercury emissions by year. To disaggregate the mercury emissions to individual species, the framework makes use of EPMM output on types of retrofits and types of coals being consumed in each region.

The cost-effectiveness framework's additional computations to speciate the mercury emissions are based on EPRI's analyses of the average speciation observed in emitted mercury for different unit configurations using the ICR data. The inputs to this component of the framework are EPMM's projected regional mercury emissions, and combinations of coal types and control equipment installed in the various units in the region.

Based upon the mercury species involved, the fate and transport step of the framework has a different relationship for each species. These atmospheric fate and transport relationships have been quantified in the TEAM model. TEAM is a three-dimensional Eulerian model that used 1998 and 1999 data to simulate transport, atmospheric specie transformation and wet/dry deposition of mercury over North America. To incorporate the fate and transport relationships of the TEAM model into the cost-effectiveness framework, a linearized version of TEAM was developed; the resulting linear form had a net positive bias of 6% compared to the full nonlinear version. The source-receptor results of the linearized model were used to produce a series of transfer coefficients (TCs). These TCs provide a set of parameters to describe how a unit of change in emissions in each specific ‘source regions’ affects deposition in each specific receptor locations. The TCs summarize atmospheric transformation processes as well as general transport. That is, the emissions may be defined in units of precursor chemical, and the predicted deposition may be defined in units of a chemically transformed species of more direct environmental relevance.

The TEAM model provided a separate set of TCs for emissions of Hg(0), Hg(II), and Hg_p from 15 source regions of the United States (organized roughly into the boundaries of the regional electric reliability councils) for both wet and dry deposition of Hg in 19 specific receptor locations across the United States. There was also a TC for total U.S. deposition changes due to emissions from any one-source region. Figure 8-4 presents a graphical summary of the TCs associated with four of the 19-receptor locations.

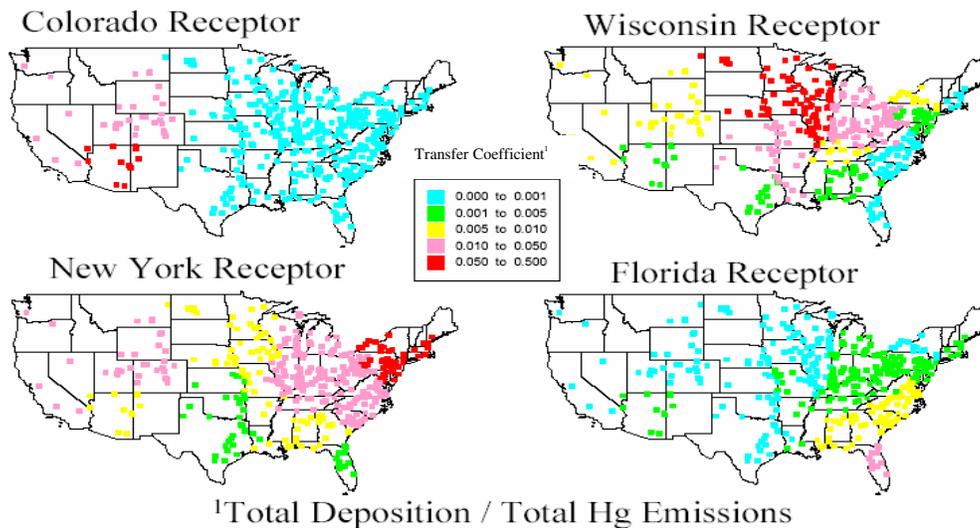


Figure 8-4
Transfer Coefficients for Four Receptor Locations (from Smith et. al)

(TCs are stated in units of total deposition at the designated receptor (in $\mu\text{g}/\text{m}^3$) per Mg of Hg emitted from each source shown as a dot on the map. Color of each dot reflects the magnitude of the impact of Hg emissions from each source on the receptor in question. Blue indicates the least source-receptor impact, and red indicates the highest source-receptor impact.)

The TCs used in the framework are stated as a percentage change in regional deposition per percentage change in 1998/1999 emissions from each source region. Each region's future projected annual emissions of Hg(0) and Hg(II) (i.e., the outputs of the previous framework step, derived from the EPMM model run) are converted into a proportion of 1998/1999 emissions for the same region, then multiplied by the appropriate TC. For the current version of the framework, there is no differentiation between wet and dry deposition. Rather, wet and dry deposition are summed to obtain the total mercury deposition change in each receptor location.

According to the analysis of 1998/1999 data, U.S. electricity generating units were responsible for less than 8% of the total mercury deposited across the United States (total net mercury mass transfer to the surface); thus, the effect of reductions in electricity generation mercury emissions on U.S. mercury deposition was expected to be modest, on average. For example, a 10% reduction in national ionic mercury emissions (Hg(II)) produces only a 0.75% reduction in total U.S. mercury deposition, and a 10% reduction in national elemental mercury emissions lowers U.S. deposition by only 0.03%. Thus, a relatively large percent reduction in national mercury emissions from electricity generation may have a fairly small impact on overall mercury deposition levels. However, the changes can vary more significantly from receptor to receptor, and this variability is retained in the framework's calculations.

No TCs were developed for deposition to ocean areas. Since U.S. utility mercury emissions are a small fraction of total global emissions (46 of 6,000 tons), changes in utility emissions will represent a tiny fraction of distant deposition to ocean waters, and to marine fish species. These small deposition changes are accounted for in the modeling because marine fish make up the largest source of MeHg in the fish portion of a typical U.S. diet. The study assumed that all ocean fish benefit equally from a given percentage reduction in U.S. electricity generating emissions. This simple assumption avoided neglecting the potential additional benefit to U.S. residents from U.S. control actions alone via reductions in mercury in marine fish.

Once estimates of mercury deposition changes in various regions were made, an estimate was made of the change in MeHg exposure to the U.S. population of women of childbearing age. Of interest was the change in exposure to women at the upper end of the MeHg exposure distribution, that is, women who are exposed to MeHg at levels near or above EPA's RfD. The goal was to estimate the effect that reductions in mercury emissions from U.S. coal-fired power plants have upon the exposures of U.S. women to MeHg, including the specific effect of mercury controls in reducing the number of women with exposures above the RfD. Several assumptions were made, as are summarized below.

1. All MeHg exposure occurs through fish and shellfish consumption.
2. The change in MeHg content of all fish and shellfish in a given year is proportional to the change in mercury deposition to the habitat waters in that year.
3. Wild, freshwater fish are assumed to experience reductions in MeHg in proportion to the change in deposition averaged over the lower 48 U.S. states.
4. The MeHg content of marine fish will decline in proportion to the change in total global mercury emissions attributable to just the change in U.S. utility emissions.

5. Farm-raised fish do not contribute to MeHg exposures.
6. MeHg exposures from the consumption of marine and wild, freshwater fish are proportional to the amount consumed.
7. The fish consumption patterns of women of childbearing age are not affected by changes in mercury emissions.

Researchers believe that the available data concerning fish consumption, particularly consumption of wild freshwater fish, are inadequate to support an analysis that takes several distributional patterns into consideration. Estimates of changes in MeHg consumption were not made on a regional basis because data on geographic distribution of consumption of wild freshwater fish is not yet refined enough to attribute specific patterns spatially. In addition, data on the geographic distribution of blood levels of mercury are not available, so it cannot be determined whether women with high blood concentrations live in areas where above-average quantities of wild, freshwater fish are consumed.

Data regarding the relative consumption rates for marine and wild fish for women between the ages of 16 and 49 were taken from the NHANES data set (National Health and Nutrition Examination Survey, Centers for Disease Control and Prevention, U.S. Department of Health and Human Services). The NHANES data set includes blood mercury concentration data on 1,709 women, of whom 286 were pregnant at the time of the survey and blood sampling. Questionnaires were available for 1,646 women with blood mercury data, including 266 pregnant women.

To quantify the effectiveness of mercury exposure reductions, an exploratory measure was applied: the shift in the number of babies born annually in the U.S. to mothers with blood MeHg levels above the RfD, when comparisons are made between the number of mothers above the RfD prior to and following imposition of a mercury control scenario. The RfD for MeHg is 0.1 $\mu\text{g}(\text{MeHg})/\text{kg}(\text{body weight})\text{-day}$.

This is calculated by assuming a percentage shift in the exposure of each individual fish consumer that is equal to the average percentage change in estimated MeHg consumption, reflecting drops in the MeHg in the fish consumed. Then an estimate was developed of the impact of these changes on the distribution of MeHg blood levels for women of childbearing age, focused on the fraction of the relevant population above the RfD that would then fall below the RfD. No attempt is made to quantify or monetize these health benefits.

NHANES provides blood MeHg concentration data for women of childbearing age. When appropriate adjustments are made for demographic factors in the NHANES data (that is, when the data are weighted to make the observations representative of U.S. women in terms of age, race, and geographic location), the cumulative distribution of the blood MeHg levels calculated indicated that 7.7% of women aged 16-49 have blood levels above the RfD.

The estimated change in the number of births per year to women with blood MeHg concentrations above the RfD can be compared to the estimated change in the cost of electricity production due to mercury controls alone, in order to calculate the average cost of reducing the

number of such “at risk” births. One could also consider alternative cost-effectiveness metrics such as dollars per percent change in deposition, or per percent change in total consumption.

The framework was applied to a pair of publicly proposed utility mercury control proposals. These proposals were each advanced in mid-2002, in the U.S. Congress (Clear Skies Act of 2002) and in a public working group convened by the U.S. EPA, respectively. (The Clear Skies Act of 2003 is essentially identical to that of 2002 in the numerical details of mercury controls simulated in the cost-effectiveness study.)

- Hg controls, Clear Skies Act of 2002 (the “CSA” scenario).
 - a. Implements a national cap-and-trade program
 - b. Total mercury emissions capped at 26 tons in 2010, then at 15 tons in 2018.
 - c. Note that the phasing of the CSA mercury cap is in general alignment with the phasing of the Base scenario’s caps on SO₂ and NO_x
- MACT standard: set at 2.2 lbs/10¹² Btu stack limit (the “MACT” scenario)
 - a. Imposes its mercury requirements fully by 2008.
 - b. Example of a MACT used here is a 2.2 lb/10¹² Btu emissions rate limit applied at every unit (without subcategorization).
 - c. No trading or averaging across plants is allowed in this scenario.

This illustrative MACT scenario could be viewed as “less stringent” numerically than the CSA cap, because if each unit were to exactly meet this MACT limit, total emissions would likely be about 24 tons per year, rather than 15 tons as in the second stage of CSA mercury compliance. On the other hand, the MACT is fully implemented in 2008, well ahead of any co-controls by CSA that might be obtained from the need to reduce SO₂ and NO_x emissions as well, while full compliance under CSA falls ten years later. Thus the expenditure rate to reach full compliance is higher under MACT, which leads to additional costs.

The purpose of the calculations was to illustrate the steps in the framework, and to provide a preliminary assessment of several cost-effectiveness measures for the two alternative approaches to utility mercury controls.

Figure 8-5 displays this cost-effectiveness measure for the CSA and MACT for the years 2008 through 2020. It showed that the CSA approach to reducing mercury produces risk reductions at a much lower average cost, generally in the range of \$400,000 per birth to avert an “at-risk” situation for mercury under this scenario. The MACT produced comparable total risk reduction earlier, but at a much greater cost per avoided “at-risk” birth, starting as high as \$1,000,000 per birth in 2008. These cost-effectiveness differences are not a result of cost discounting; the annual costs are not discounted at all in this analysis. Rather, the cost-effectiveness differences occur because the MACT approach does not take advantage of any of the co-controls or “co-benefits” controlling mercury that can be expected from earlier or coincidental SO₂ and NO_x controls required under CSA; it forces the incremental expenditure of over \$4 billion per year to address

mercury alone by the time of the 2008 compliance date. This expenditure is primarily for significant amounts of ACI retrofits that do almost nothing to take advantage of future expenditures that would occur even in the Base case to reduce SO₂ and NO_x.

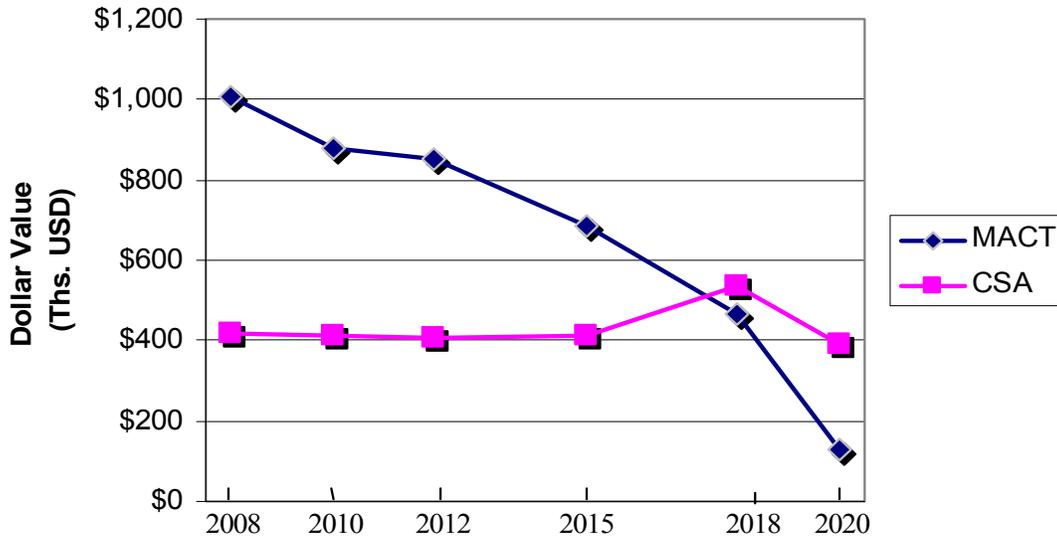


Figure 8-5
Cost per Birth Moved Below the RfD Under CSA and MACT (Smith et. al)

Another comparison of alternative approaches related to the regional differences in mercury deposition changes. By 2020, the CSA and MACT achieve comparable total mercury emissions, 15 and 18 tons per year, respectively. However, this is achieved through different rule provisions. CSA allows great flexibility regarding where the controls occur, since it incorporates a mercury trading allowance, while also allowing better leverage of SO₂ and NO_x co-controls. MACT, on the other hand, imposes mercury emissions limits on each plant in the country, and is met with greater emphasis on the mercury-specific controls of ACI.

8.5 Summary

- Global and continental models were used in combination to estimate the relative contributions of major source categories (anthropogenic emissions from individual continents and natural emissions from land and the oceans) to deposition in the U.S. The contribution of North American sources to deposition ranged from 9 to 86%. Asia showed the largest contribution among other continents with values ranging from 5 to 32%. Natural emissions contributed from 3 to 38%.
- The contribution of mercury emissions from various source areas to mercury deposition at a given receptor depends on a myriad of factors including the speciation of these emissions, the location of the source area with respect to the receptor area, and the atmospheric conditions (i.e., meteorology, chemistry and deposition processes) that affect air parcels transported from the source area to the receptor area.

- Uncertainties associated with long-range simulation of atmospheric fate and transport of atmospheric mercury include speciation of mercury emissions for source categories other than coal-fired power plants and Hg(II) dry deposition fluxes over a variety of Earth surfaces under varying meteorological conditions. Data describing speciation of anthropogenic mercury emissions are also needed, especially for source categories other than power plants.
- Data gaps for model formulation primarily pertain to needs of further field and laboratory experimentation to characterize chemical and physical mercury transformations. More research is needed regarding the completeness of the redox chemical mechanism of aqueous mercury, the kinetics of the reactions that have been identified, the fraction of mercury that can adsorb on airborne particulate matter and whether or not the adsorption is reversible, and the values of reactant concentrations.
- More information is needed regarding removal by wet deposition (hydrometeors) of mercury species and, specifically, the completeness of Hg(II) and Hg_p scavenging below clouds. Direct measurement of the dry deposition velocities of Hg(0), Hg(II), and Hg_p are needed to replace surrogate mechanisms in the models (such as deposition velocities based on other material, e.g., HNO₃). Data for model evaluation needed includes speciated ambient measurements of mercury and fluxes of wet and dry deposition.
- The incremental reduction in the average exposure to MeHg from mercury emissions controls from either CSA or MACT is small. After consideration of the reductions that are estimated to result from SO₂ and NO_x controls, the additional reduction in exposures in the period out to 2020, is, on average, in the range of 0.05-0.75% (one twentieth to three-quarters of a percent).
- After accounting for MeHg exposure reductions due to potential co-controls from future SO₂ and NO_x reductions, the total reduction in average MeHg exposure that is estimated to occur by 2020 is less than 1%. About half of this reduction would occur by 2020 in the absence of any explicit mercury control policy, as a byproduct of projected SO₂ and NO_x controls.
- A portion of the U.S. MeHg exposure reduction is associated with consumption of marine fish with lower mercury levels due to the scenarios, rather than with consumption of freshwater fish from U.S. lakes and streams. This is due to the existing higher U.S. consumption rate of marine fish, which could offset the fact that U.S. electricity generating emissions are responsible for a smaller fraction of deposition to the world ocean than to U.S. inland waters. Thus, the exposure reduction is made up of two key components, a relatively high fraction of fish consumption of marine fish, which will experience a relatively small reduction in fish mercury content due to U.S. emission controls; and a relatively small fraction of consumption of wild freshwater fish, which are more likely to experience a larger reduction in fish mercury content due to controls.
- Cost-effectiveness can vary to a significant degree from one mercury control approach to another, even if the final emissions levels are comparable. The cost-effectiveness of mercury emission controls are limited in part by the significant reductions in emissions that will occur as SO₂ and NO_x controls are implemented.
- Cost-effectiveness can be greatly enhanced by coordinating mercury control requirements with reductions mandated for electricity generating emissions of SO₂ and NO_x, because these measures provide co-control of the most important part of the emissions, the ionic form of mercury (Hg(II)).

References

- Canadian Council of Ministers of the Environment (CCME) 2003. Canadian Uniform Data Collection Program (UDCP) for Mercury from Coal-fired Electric Power Generation, A Guidance Document. Mercury Canada-wide Standards Development Committee.
- Commonwealth of Massachusetts, Department of Environmental Protection (MDEP) 2002. Evaluation of the Technological and Economic Feasibility of Controlling and Eliminating Mercury Emissions from the Combustion of Solid Fossil Fuel. December.
- EPRI 2003. *A Framework for Assessing the Cost-Effectiveness of Electric Power Sector Mercury Control Policies*. Palo Alto, CA. TR-105224.
- Seigneur, C., K. Vijayaraghavan, K. Lohman, P. Karamchandani and C. Scott, 2003a. Modeling Mercury Atmospheric Deposition in the United States. CP142-03-01. Prepared for EPRI.
- Seigneur, C. K. Lohman, K. Vijayaraghavan, and R. Shia, 2003b. Contributions of global and regional sources to mercury deposition in New York State. *Environ. Poll.* 123(3): 365-373.
- Seigneur, C., P. Karamchandani, K. Vijayaraghavan, R. Shia, and L. Levin, 2003c. On the effect of spatial resolution on atmospheric mercury modeling. *Sci. Tot. Environ.* 304: 73-81.
- Seigneur, C., K. Vijayaraghavan, K. Lohman and P. Karamchandani, 2003d. Modeling the atmospheric fate and transport of mercury over North America: Power plant emission scenarios, *Fuel Processing Technol.*, in press.
- Seigneur, C., K. Vijayaraghavan, K. Lohman, P. Karamchandani, C. Scott, and L. Levin, 2002. *Modeling Mercury Atmospheric Deposition in the United States*. Presented at the American Geophysical Union Fall Meeting, San Francisco (December).
- SENES Consultants Ltd. (SENES) 2002. Evaluation of Technologies for Reducing Mercury Emissions from the Electric Power Generation Sector. February. Technical Report prepared for Canadian Council of Ministers of the Environment.
- Smith, A. E., J. L. Rego, B. E. Lonergan, and C. G. Whipple 2003. *A Framework for Assessing the Cost-Effectiveness of Electric Power Sector Mercury Control Policies*. Presented at the EUEC, January 2003. Tucson, AZ.
- UNEP 2002. Global Mercury Assessment. April. Report No. 54790-01.

9

CONCLUSIONS AND RESEARCH RECOMMENDATIONS

9.1 Mercury Sources and Emissions

Conclusions

1. Background mercury sources include such natural categories as mercuriferous crustal formations, wildfires, and volcanic sites, as well as legacy sources (sites of former human activity). The relative amount contributed by background and anthropogenic sources to mercury deposition at local, regional, and global scales is still under active investigation. Recent studies support a developing consensus that the significance of background sources to global levels of mercury is greater than previously thought, particularly contributions due to surface disturbance by human activity.
2. The consensus estimate for the mean residence time of mercury in the atmosphere is about one year, although recent findings on source strengths and possible removal mechanisms of mercury provide evidence for a shorter lifetime period.
3. Current global emissions of mercury amount to 6386 metric tons per year (T/y) with anthropogenic emissions estimated at 2127 T/y and natural emissions totaling 1064 T/y. It is estimated that the U.S. emits 133 T/y of the 193 T/y total mercury (divalent plus gaseous elemental plus particulate-bound) emitted within North America. Of the U.S. portion, electric utilities contribute about 42 T/y, or about 32% of the U.S. total.
4. Significant progress has been made in three important areas of research: methods development for the measurement of mercury emissions, definition of the factors most important in governing mercury emissions, and scaling up emissions from natural source areas. Advances from all three of these areas of research facilitated important advances to refine the understanding of the contribution of sources of mercury to the global budget.

Research Recommendations

To credibly balance the mercury biogeochemical cycle and quantify the impacts of atmospheric mercury, advancement in several areas of research are needed. Continued measurement and speciation estimates of the flux from a variety of settings (the marine boundary layer, soils, geological substrates, volcanoes and forest fires) are needed to verify recent measurements. Emissions from these background sources should be more completely and quantitatively characterized for regional and global scales. In addition, the seasonality of natural and

background mercury emissions in different climatic regimes needs to be established. Techniques need to be developed for distinguishing between primary emissions and re-emissions of earlier deposited mercury from natural surfaces. Additional field measurements and analyses could further characterize the kinetics and dynamics of gas phase oxidation and subsequent condensation in mercury deposition.

9.2 Mercury Emissions from Coal-Fired Power Plants

Conclusions

5. The mercury content of coal and stack emissions at U.S. coal-fired power plants were characterized during EPA's mercury Information Collection Request (ICR) in 1999-2000. Every such plant measured mercury and chlorine in most coal shipments, while roughly 80 units had simultaneous coal and stack gas measurements done. In addition, air quality control device effectiveness was gauged by inlet and outlet measurements.
6. The rate of mercury emission from stacks was found to be dependent on the coal type and the SO₂ and/or particulate control system installed. EPRI studies of ICR data found that the form (valence state or species) of mercury and its removal rate by particular control devices are a function of coal chlorine content. Based upon these data, both EPRI and EPA estimated utility coal-fired emissions to be about 45 metric tons (10⁶ g) in 1999.
7. The percentage of each chemical form or mercury species formed during the coal combustion process and post-combustion conditions varies significantly from one plant to another. The mercury species in emissions governs first, its atmospheric fate and transport, and second, the effectiveness of flue gas control technologies in removing mercury.
8. Mercury measurement technology is advancing. The Ontario Hydro Method has received EPA validation as the preferred method for flue gas mercury speciation. The current generation of continuous mercury monitors (CMMs) provides near real-time results for research applications, but their absolute accuracy and operational reliability are still issues.

Research Recommendations

Continued testing and evaluation of continuous or near-continuous mercury monitoring/sampling methods is required for regulatory compliance, based on EPA proposals of December 2003 and March 2004. In addition, development of fast, precise and accurate speciation methods for flue gas mercury are needed to assist trends analysis for run-up and post-implementation periods of any regulatory steps.

9.3 Atmospheric Mercury: Transport and Fate

Conclusions

9. Improved methods for field measurement and laboratory analysis for mercury have enabled an increase in the understanding of reaction kinetics and characterization of emission sources. Major advances were the development of methods for speciating atmospheric mercury and for measuring concentrations of divalent mercury at low concentrations in ambient air and flue gas. All of these advances have contributed to reducing the uncertainty in understanding atmospheric mercury fate and transport processes.
10. Results from recent studies provide insights into the reaction kinetics of mercury. Reactive gaseous mercury (RGM) represents a few percent of total airborne mercury in ambient air distant from local sources; however, concentrations can be several hundred times higher near anthropogenic point sources directly emitting mercury containing RGM. Aqueous-phase mercury chemistry results in net production of either elemental or oxidized mercury, depending upon the availability of oxidants, particulate-phase components, and reactive halogens including chlorine and bromine. Aqueous-phase oxidation has also been observed in a multitude of settings including the nocturnal marine troposphere, the marine boundary layer, and the Arctic troposphere.
11. Several studies have documented a relationship between the rate of oxidation of elemental mercury and the presence of reactive halogens (in various forms) and increased UV/ambient temperatures in various ocean and near ocean settings (marine boundary layer, marine troposphere, and Arctic troposphere).
12. Local-scale modeling indicates that the rate of Hg(II) deposition is dependent upon the nature of aerosol particles and relative humidity; deposition is increased with increases in relative humidity.

Research Recommendations

Further field and laboratory experiments are needed to enhance our understanding of complex chemical and physical mercury transformations. In addition, model development and evaluation require significant additional process data. Specifically, our understanding would be improved with further research on the net direction and completeness of the aqueous-phase redox mechanism of mercury; the kinetics of the reactions, the fraction of mercury that can adsorb on particulate matter (and whether or not the adsorption is reversible), and the rates of reactions. Additional work is also needed regarding wet removal of mercury species and, specifically, the completeness of Hg(II) and Hg_p scavenging below clouds. Model evaluation would be improved by both speciated ambient measurements of Hg and of fluxes of wet and dry deposition, especially under varying meteorological conditions.

9.4 Mercury in Aquatic Ecosystems

Conclusions

13. Mercury in various forms, and of varying bioavailability, enters water bodies from terrestrial, aquatic, and atmospheric sources. A fraction of the incoming mercury from the atmosphere is methylmercury, of unknown origin. A small portion of the total mercury in the aqueous form is transformed by sulfate-reducing bacteria in aquatic systems into methylmercury (MeHg).
14. Sulfate and sulfide are now known to play a complex role in the methylation of mercury, with sulfate at low concentrations stimulating MeHg formation, and sulfide inhibiting formation of MeHg at high sulfide levels. Other abiotic factors of significance in mercury methylation in aquatic environments include dissolved organic carbon and pH.
15. After uptake by phytoplankton, MeHg is initially bioconcentrated by a relatively large factor, and may enter higher trophic levels, including fish, primarily as a function of food web processes and not of the aquatic chemistry. The bioaccumulation of MeHg in aquatic organisms, particularly fish, is primarily a function of a number of factors, including the rate of introduction of new inorganic mercury into the system (mercury loading), the mercury methylation rates (or methylation efficiency), food web length, and total mass.
16. The role in bioaccumulation of newly deposited mercury vs. old mercury, and the time lags between deposition change and biota response, are addressed in the METAALICUS field study, currently underway, as well as additional studies in the Everglades and elsewhere.
17. The METAALICUS study is examining how increasing or decreasing loadings of inorganic mercury to aquatic systems affects fish tissue concentrations. Several similar studies would help evaluate current assumptions of linearity between changes in inorganic mercury loading to aquatic systems and changes in fish tissue concentrations. METAALICUS studies will also examine the variability of mercury content among species within the same trophic level and adjacent trophic levels to contribute to improving our ability to estimate bioaccumulation factors.

Research Recommendations

Improvements are needed in our ability to predict mercury methylation rates by biological or abiotic processes. More research is also needed to determine the currently unknown enzyme that is active in methylation. Further work would also be useful on the role of sulfur chemistry, the interrelationship between the water/sediment chemistry and microbial activity, and effects of environmental perturbations on methylation processes.

The assessment of the biological and ecotoxicological effects of MeHg exposure to biota in aquatic ecosystems is lagging far behind progress in understanding biogeochemical processes. Increased understanding of the effect of dissolved organic carbon (DOC) on bioaccumulation would help to determine ranges of DOC concentrations that may inhibit or enhance bioaccumulation. Additional information is needed on the kinetics of MeHg uptake to determine whether methylmercury concentrations co-vary with concentrations in primary producers or whether significant lags occur between peak concentrations in water and in primary producers.

Topics pertaining to the ecotoxicology of mercury in aquatic food webs that merit intensive scientific study include the need to critically examine the reproductive effects of MeHg on fish, birds, and mammals, along with the combined effects of MeHg and other co-occurring environmental stressors. Recent evidence suggests that the reproductive success and survival of fish are reduced by dietary exposure to MeHg encountered in waters with contaminated food webs.

To assess the METAALICUS results, an intercomparison of data from other geographical areas should be undertaken to evaluate the relationships between fish mercury concentrations and changes in the mercury loading under varying chemical conditions.

The majority of studies of mercury in the aquatic environment have dealt with freshwater systems. There is need for a better understanding of ocean cycling of mercury, particularly in the flow from tributaries to coastal areas and in estuarine systems. Enhancing our understanding of mercury bioaccumulation under elevated salinity and chlorinity conditions would enable the prediction of bioaccumulation of mercury in estuaries.

9.5 Assessment of Mercury Exposure from Fish Consumption

Conclusions

18. Fish species from higher trophic levels (particularly top-level predatory or piscivorous fish) tend to contain higher concentrations of MeHg, due to bioaccumulation, but varying by waterway chemistry. For fish at higher trophic levels, the MeHg concentrations can be orders of magnitude greater than MeHg concentrations in the water column.
19. The average concentration of mercury in the fish types commonly found in U.S. commerce is less than 0.3 ppm, the level of the EPA fish tissue criterion. Canned tuna has an average mercury concentration of 0.17 ppm, or one-half of the EPA criterion. However, species of predatory fish typically contain mercury concentrations greater than 1.0 ppm, three times the EPA criterion level.
20. The ongoing NHANES program has provided the first opportunity to compare a biomarker for exposure—blood level of total mercury—with information about fish consumption for a large number of U.S. women of childbearing age. These data show that blood levels of mercury rise as fish consumption rises for the sample population as a whole. When the NHANES data are weighted to account for U.S. demographic patterns, about 7.7 percent of women in the study have blood levels of methylmercury above 5.37 ppb, the blood concentration associated with the EPA Reference Dose (RfD). However, NHANES data variability appears to preclude accurate prediction of an individual's blood level of mercury based on fish consumption.
21. Fish that would experience changes in mercury due to reductions in power plant mercury emissions, i.e., primarily U.S. wild freshwater fish, were estimated to make up an average of 8 percent of the fish meals for women in the NHANES survey.

Research Recommendations

Coordinated and expanded monitoring of mercury concentrations in human hair, blood, and other biomarkers for mercury would be useful in order to allow better definition of subpopulations at risk from increased exposure. Biomarker monitoring may be useful as a tool for prioritizing prevention actions on a local scale.

9.6 Health Effects of Mercury

Conclusions

22. Brain toxicity, especially neurodevelopmental toxicity manifesting as subtle cognitive or behavioral effects, have been of greatest concern.
23. Existing evidence suggests that MeHg exposure from fish consumption during pregnancy at the U.S. average population level does not appear to have measurable cognitive or behavioral effects in later childhood.

Research Recommendations

In general, more information is needed to identify the lowest levels of MeHg exposure, which may cause even subtle neurotoxic effects as the result of long-term exposure. In addition, it would be helpful to conduct a 2-generation reproductive toxicity study for MeHg exposure.

Such research could address the need for a database uncertainty factor. For example, if a BMD for cardiovascular effects is similar to or higher than the BMD for neurological impairment, then the former effect is not likely to be a critical effect, and the need for the database uncertainty factor is correspondingly reduced. Likewise, the immunotoxicity effects should be further studied as to whether they are considered adverse, adaptive, compensatory or beneficial. If both adverse and relevant, then they would likely be used as the critical effect and the RfD for methyl Hg can then be revised accordingly. The need for the database uncertainty factor is then correspondingly reduced.

This area of research would benefit from an analysis of the impact of mixed chemical exposures in the Faroe Islands. In contrast, the Seychelles Island data are from exposures to primarily one chemical, MeHg. The large PCB exposures to breast-fed infants in the Faroe Islands may be affecting the health of the population independent of any neurological response, or they may be enhancing the toxicity of methyl Hg (Dourson et al. 2001). Studies containing both negative and positive correlations of neurological impairment, PCB exposure information, and PCB levels in cord tissue are available and should be reviewed to develop mixture RfDs. A mixture RfD would reflect the fact that many fish are contaminated with both chemicals.

Current EPA RfD guidelines could be enhanced with new approaches to uncertainty factors and data unique to MeHg. For example, new research in the area of human variability in toxicokinetics has been incorporated into the recent guidelines of the International Programme on Chemical Safety (Meek et al., 2000) for compound-specific adjustment factors (formerly

referred to as data-derived uncertainty factors). This guidance is now undergoing an international review, including review by scientists with ATSDR, EPA and FDA.

Effects on reproductive function and potential delayed neurotoxicology effects manifested in aging after relatively low exposure early in life should also be addressed.

Research should be undertaken to improve the choice of dose-response function for application within the risk assessment process itself. Studies are underway to improve understanding of the sensitivity and specificity of test instruments used in assessing neurobehavioral and neuropsychological function. These will provide more information with which to select the most appropriate benchmark dose.

The objective of conducting these studies is to inform the risk assessment process by reducing uncertainties. The goal is to eventually be able to objectively determine the body of information that is sufficient to reduce uncertainties. That would imply a high degree of confidence in quantitative approaches as well as in the quality of information it can bring to the issue of human health risk assessment for low level exposures to methylmercury.

The determination of the critical effect for MeHg is important. Investigating other potential critical effects may lead either to a change in the basis of the RfD or reduce the need for uncertainty factors. Specifically, recent recommendations (Dourson et al 2001; Wyzga and Yager 2001) are consistent in suggesting that a review of studies that indicate other potential critical effects of MeHg should be compared to check for possible confounders. First, studies of other fish-eating populations where beneficial effects on cardiovascular performance have been shown (Salonen et al. 1995) should be reviewed. Second, a review is needed of studies where adverse immunological effects occurred (Ortega et al. 1997; Wild et al. 1997). TERA (1999) conducted a study in which a comparative dietary risk framework was developed to compare the possible health risks of consuming contaminated fish, while considering the potential health benefits lost by not eating fish. Depending on qualitative and quantitative aspects of available studies, a BMD for the cardiovascular toxicity of methyl Hg could be determined. Similarly, the immunological effects of MeHg found should be confirmed and their relevance to the choice of critical effect in humans should be studied. Such an analysis would address whether immunotoxicity is a more sensitive effect than neurological impairment.

9.7 Mercury Emission Control Approaches

Conclusions

24. Mercury flue-gas chemistry is complex and dynamic due to both mercury species reactivity and mercury conversion rates. A number of uncertainties still exist in the understanding of mercury's chemical kinetics and thus, creates difficulties in determining how to reduce mercury emissions.
25. Control technologies that reduce SO₂, NO_x and PM emissions for coal-fired plants yield levels of mercury control ranging from 0 to over 90 percent, depending on coal type, boiler design, and emission control equipment. On average, the lower the coal rank (higher heating value), the lower the mercury emissions reductions.

26. The oxidized form of mercury is effectively captured by wet and dry SO₂ scrubbers and also appears to be captured more readily by ESPs. However, there is some evidence that the oxidized mercury captured in a scrubber may be partially re-emitted as elemental mercury. Alternatively, existing SO₂ scrubbers capture virtually no elemental mercury. Particulate-bound mercury, associated with unburned carbon in the fly ash, is generally captured by the particulate control device.
27. SCR systems can convert elemental mercury to oxidized mercury, which is more easily captured in downstream air pollution control devices (primarily FGD systems). Oxidation of mercury seems to be determined by coal type and catalyst design.
28. Two considerations are important in the analysis of specific add-on Hg control technology alternatives. First, understanding the mercury species at the point of the reduction reaction is a key consideration. Second, an understanding of the implications of the mercury analysis methods utilized is necessary in the review of the control test results.
29. Emerging control technologies, such as activated carbon injection, for mercury are under development or in demonstration, but are not commercially deployed yet in utility plants. Integrated control methods that target multiple pollutants including SO₂, NO_x, PM, mercury and CO₂ may ultimately be the most a cost-effective approach.
30. Current research results indicate that additional mercury capture may be achieved by the introduction of a sorbent prior to SO₂ and PM control technologies. Activated carbon injection (ACI) is the best-studied option for mercury removal for most plants equipped with only an ESP or BH. This approach appears to be effective for removal of all species of mercury. The tests to date indicate that flue gas chloride and SO₂ content are key components that affect ACI performance. For conditions where activated carbons have lower effectiveness, chemically impregnated activated carbons appear to show promise. The tests to date indicate that MerCAP™ can remove greater than 80 percent of mercury in emissions.
31. During combustion of coal to produce electricity, the mercury in coal is either emitted to the atmosphere or captured with fly ash and flue gas desulfurization solids. Of the estimated 75 tons of mercury contained in coal burned annually at power plants nationally, about 40 percent is removed by particulate and sulfur dioxide control devices. Current work confirmed previous results indicating that mercury in existing CCBs is present in relatively low concentrations and is relatively stable, with little evidence of leaching or volatilization.

Research Recommendations

Additional studies of alternative control technologies are needed to test the appropriate mercury removal technology for coal-fired plants by coal type, coal mercury content, and existing air pollution control devices.

9.8 Analysis of Mercury Management Strategies

Conclusions

32. A combination of global and continental models were used to estimate the relative contributions of major source categories (anthropogenic emissions from individual continents and natural emissions from land and the oceans) to deposition in the U.S. The contribution of North American sources to deposition ranged from 9 to 86 percent. Asia showed the largest contribution among all other continents with values ranging from 5 to 32 percent. Natural emissions contributed from 3 to 38 percent.
33. The contribution of mercury emissions from various source areas to mercury deposition at a given receptor depends on a myriad of factors including the speciation of these emissions, the location of the source area versus the receptor area, and the atmospheric conditions (i.e., meteorology, chemistry and deposition processes) that affect air parcels transported from the source area to the receptor area.
34. The incremental reduction in the average exposure to MeHg from mercury emissions controls from either CSA or MACT is small. After accounting for MeHg exposure reductions due to potential co-controls from future SO₂ and NO_x reductions, the total reduction in average MeHg exposure that is estimated to occur by 2020 is less than 1 percent. About half of this reduction would occur by 2020 in the absence of any explicit mercury control policy, as a byproduct of projected SO₂ and NO_x controls.
35. Cost-effectiveness can vary to a significant degree from one mercury control approach to another, even if the final emissions levels are comparable. The cost-effectiveness of mercury emission controls are limited in part by the significant reductions in emissions that will occur as SO₂ and NO_x controls are implemented.
36. Cost-effectiveness can be greatly enhanced by coordinating mercury control requirements with reductions mandated for electricity generating emissions of SO₂ and NO_x, because these measures provide co-control of the most important part of the emissions, the ionic form of mercury (Hg[II]).
37. A cap-and-trade approach, which also can improve overall cost-effectiveness, appears not to present any significant potential to create “hot spots” compared to a MACT. In fact, it appears to offer comparable benefits deriving from utility mercury emissions reductions to all the receptor locations modeled.

Research Recommendations

Uncertainties associated with long-range simulation of atmospheric fate and transport of atmospheric mercury include speciation of mercury emissions for source categories other than coal-fired power plants and dry deposition fluxes over a variety of surfaces under varying meteorological conditions. More information is needed for removal by wet deposition of mercury species and, specifically, the completeness of Hg(II) and Hg_p scavenging below clouds. Direct measurement of the dry deposition velocities of Hg(0), Hg(II), and Hg_p are needed to

replace surrogate mechanisms in the models (such as deposition velocities based on other material, e.g., HNO₃).

Program:

Air Toxics Health and Risk Assessment

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