# Introduction

Mercury (Hg) is a naturally occurring element in our environment. It enters the atmosphere as a result of natural events, such as volcanic eruptions, or anthropogenic activities, such as the combustion of fossil fuels, especially coal. Mercury is persistent, bio-accumulative, and toxic. Because of these properties, mercury poses potential human health risks, especially for pregnant women, developing fetuses, and young children. Mercury is also toxic to wildlife, especially fish, birds, and fur-bearing mammals that consume organisms contaminated with mercury. Human exposure to mercury occurs almost exclusively through fish consumption (U.S. EPA, 1997). Because of potential health risks, nearly all states in the United States currently have some form of fish advisory for their water bodies, most of which are based on high levels of mercury (U.S. EPA, 2004). Pennsylvania currently has a statewide advisory for all rivers and lakes that was initiated in 2001 (U.S. EPA, 2004).

Concerned over the toxicity of mercury and its potential impact on humans and the environment, The United States Environmental Protection Agency (U.S. EPA) conducted a detailed assessment of the magnitude of U.S. mercury emissions by source, the health and environmental implications of these emissions and depositions, and the availability and cost of control technologies. This assessment, entitled *Mercury Study Report to Congress* (U.S. EPA, 1997) was required under section 112(n)(1)(B) of the Clean Air Act Amendments of 1990, Public Law No. 101-549, 42 U.S.C. 7412 (U.S. Congress 1990). Information presented in the following paragraphs was obtained from the *Mercury Study Report to Congress* (U.S. EPA, 1997) and EPA's *Mercury Research Strategy* (U.S. EPA, 2000). Information was also obtained from a report on the *Deposition of Air Pollutants to the Great Waters: Third Report to Congress* (U.S. EPA 2000a), an Environmental Protection Agency web site on mercury (http://www.epa.gov/mercury), from the National Research Council's report on *Toxicological Effects of Methylmercury* (National Research Council, 2000), and from the proceedings of the 8th Annual Conference on Air Quality, Global Climate Change, and Renewable Energy (www.EUEC.com) as well as a selection of scientific journal publications. As the state-of-the-science for mercury is continuously changing, these reports and the information presented in them, as well as in this report, represent the current state-of-knowledge on the topic.

## Forms of Mercury

Mercury's toxicity levels in the environment depend on its chemical form. Mercury exists in the atmosphere in primarily four forms: gaseous elemental mercury vapor ($Hg^0$) or metallic or zero valent mercury; gaseous divalent mercury $Hg_2^{2+}$ (mercurous) or $Hg^{2+}$ (mercuric-Hg (II)); particulate-bound mercury ($Hg_p$), both $Hg^0$ and $Hg^{2+}$; and organic mercury (mainly methylmercury (MeHg). Elemental mercury is a heavy, silvery-white liquid metal at typical ambient temperatures and pressures. The vapor pressure of mercury is strongly dependent on temperature, and it vaporizes readily under ambient conditions. Consequently, elemental mercury ($Hg^0$) is not found in nature as a pure, confined liquid, but instead exists as a vapor in the atmosphere. It is insoluble in water and is less chemically active than other forms of mercury. As a result, its removal rate is slow and thus can be transported in the atmosphere thousand of miles from emission sources. Consequently, gaseous elemental mercury vapor ($Hg^0$) is the major component of the global circulation of atmospheric mercury (Schroeder and Munthe, 1998).

Gaseous divalent mercury ($Hg_2^{2+}$ and $Hg^{2+}$), also called reactive gaseous mercury (RGM), can form many inorganic and organic chemical compounds; however, mercurous mercury ($Hg_2^{2+}$) is very unstable under ordinary environmental conditions and therefore is generally not found in the atmosphere. Mercuric mercury ($Hg^{2+}$) is less volatile than $Hg_2^{2+}$ and more water-soluble than $Hg^0$. Mercuric mercury may be found in the gas phase or bound to airborne particles. Both gas-phase and particulate $Hg^{2+}$ are readily removed from the atmosphere by precipitation. Oxidation processes in the atmosphere and in-cloud water can also convert elemental mercury to $Hg^{2+}$. Because of its high solubility, gas-phase $Hg^{2+}$ may be removed from the atmosphere within a few tens to a few hundred miles of its source. Particular-phase mercury may be deposited at intermediate distances from the source depending on the size of the aerosol (Schroeder and Munthe, 1998).

Methylmercury (MeHg) is the most toxic of the organic mercury species. While some MeHg is found in precipitation, most of the MeHg occurring in lakes and other surface waters as well as in soil, sediments, and biota is generated by microbially mediated transformations of $Hg^{2+}$ (Schroeder and Munthe, 1998). These processes seem to be accelerated under acidic conditions (Driscoll et al., 1995). Methylmercury is a neurotoxin and teratogen, which bioaccumulates up the food chain by a factor of a million or more in fish (U.S. EPA, 1997). Other organic mercury compounds that may be found under normal environmental conditions are: mercuric salts ($HgCl_2$, $Hg(OH)_2$, and HgS); methylmercury compounds, methylmercuric chloride ($CH_3HgCl$) and methylmercuric hydroxide ($CH_3HgOH$); and, in small fractions, other organomercurics, such as dimethylmercury and phenylmercury.

## Mercury Emissions

Since the 19th Century, the total amount of mercury in the environment has increased by a factor of two to five above pre-industrial levels (Mason et al., 1994). Over the years, some mercury compounds have been specifically developed as pesticides, fungicides, and germicides to be used to preserve grains, in paints, and with vaccines. Because mercury is an excellent conductor of electricity, it has been widely used in products, such as batteries, electric switches, thermostats, thermometers, and barometers. Because mercury and its compounds are persistent, bioaccumulate in the environment, are toxic to humans, and pose ecosystem risks, the use of mercury in many products, such as paint and batteries, has decreased significantly the past several decades (U.S. EPA, 1997b).

Sources of mercury emissions to the atmosphere in the United States can be broadly classified as natural mercury emissions, anthropogenic mercury emissions and re-emitted mercury. Re-emitted mercury is mercury that was previously deposited on the Earth's surface following either anthropogenic or natural releases and is re-emitted to the atmosphere by natural, biologic or geologic processes. Natural mercury emissions, which are estimated to contribute about one-third of the current worldwide mercury air emissions (www.epa.gov/mercury), occur when geologically-bound mercury is released during natural processes, such as volcanic eruptions, geothermal releases, and from naturally enriched substances. Volcanic eruptions are estimated to contribute approximately 700 Mg/yr of mercury to the atmosphere (Pyle and Mather, 2003), while geothermal emissions are estimated to contribute another 60 Mg/yr (Varenkamp and Busek, 1988). Emissions from naturally enriched substances have been estimated at more than 1500 Mg/yr (EUEC, 2005). However, it should be noted that all estimates of natural mercury emissions are highly uncertain as is the relative proportion of emissions from various sources.

The mobilization and release of mercury by human activities is referred to as anthropogenic mercury emissions. Anthropogenic emissions can be classified as point or area sources. Point sources accounted for all but 2.2% of the 158 tons emitted in the United States in 1994-95 (U.S. EPA, 1997b). The largest point sources of mercury emissions in the United States in 1994-95 were combustion sources which accounted for 87.3% (137.9 tons/year) of the total anthropogenic emissions inventory. The largest single combustion source is coal-fired utility boilers which accounted for 32.7% (51.6 tons/year) of the 1994-95 inventory. Other major contributing point combustion sources include municipal waste incinerators (29.6 tons/year, 18.7%), medical waste incinerators (16.0 tons/year, 10.1%), and hazardous waste combustion (7 tons/year, 4.4%). Manufacturing sources accounted for approximately 10% of the 1994-95 mercury emissions with the majority of these point sources resulting from chlor-alkali production (7 tons/year, 4.4%), Portland cement production, excluding hazardous waste-fired (5 tons/year, 3.2%), and pulp and paper manufacturing (2 tons/year, 1.3%).

Seigneur et al., (2004) estimated that total emissions in the United States in 2004 were 151.9 Mg/yr, with electric utilities, waste incineration, and non-utility coal burning contributing 41.5 Mg/yr (27.3%), 28.8 Mg/yr (19.0%), and 12.8 Mg/yr (8.4%), respectively. Mobile sources were estimated at 24.8 Mg/yr (16.3%), with the rest coming from mining (6.4 Mg/yr, 4.2%), chlor-alkali facilities (6.7 Mg/yr, 4.4%), and other sources (30.9 Mg/yr, 20.3%). Seigneur et al. (2004) also estimate that 50% of mercury emissions in the United States are in the form of elemental mercury ($Hg^o$), 46% are gaseous divalent mercury (Hg II), while only 4% occurs as particulate emissions ($Hg_p$). Total mercury emissions from southern Canada (14.7 Mg/yr) and Northern Mexico (33.5 Mg/yr) bring the total 2004 anthropogenic mercury emissions in North America to approximately 200 Mg/yr (Seigneur et al., 2004).

On a global scale, the amount of mercury released annually from natural sources has been estimated to be between 2000 tons per year (Nriagu and Pacyna, 1988) and 3000 tons per year (Jackson, 1997). Global anthropogenic emissions have been estimated to be between 3560 tons per year (Nriagu and Pacyna, 1988) and 4000 tons per year (Jackson, 1997). The uncertainties associated with these estimates can be significant and are discussed by Schroeder and Munthe (1998).

More recent global mercury balances estimate new anthropogenic emissions at 2160 Mg/yr (Bergan et al., 1999), 2400 Mg/yr (Mason and Sheu, 2002) and 2143 Mg/yr (Seigneur et al., 2003). Re-emitted anthropogenic emissions are estimated to be 2000 Mg/yr by Bergan et al. (1999), 2090 Mg/yr by Mason and Sheu (2002), 4800 Mg/yr by Lamborg et al. (2002) and 2134 Mg/yr (range 1067 Mg/yr to 2670 Mg/yr) by Seigneur et al. (2003). Natural emissions from land

and oceans ranged from 1600 Mg/yr (1000 Mg/yr land, 600 Mg/yr oceans) (Lamborg et al., 2002) to 2134Mg/yr (1180 Mg/yr land, 954 Mg/yr oceans) (Seigneur et al., 2003). Clearly, considerable uncertainty in mercury emission estimates by source exists within the scientific community (Seigneur et al., 1999).

Although the United States is a major source of anthropogenic mercury emissions (151.9 Mg/yr) (Seigneur et al., 2004), its contribution is relatively small on a global scale. Annual (2003) anthropogenic emissions from Asia (1118 Mg), Europe (508 Mg), Africa (246 Mg) and South/Central America (176 Mg) play a much larger role on a global scale. Across the Northern Hemisphere the largest source of emissions occurs in China (EUEC, 2005).

## Mercury Deposition

The deposition of mercury from the atmosphere occurs by two mechanisms: wet deposition and dry deposition. Wet deposition occurs when reactive gaseous mercury (primarily $Hg^{2+}$) dissolved in precipitation is deposited on the surface of the Earth. Particulate-bound mercury is also deposited by this mechanism, but it is a relatively minor component (in most areas) when compared to dissolved $Hg^{2+}$. Dry deposition occurs when both gaseous and particulate forms of mercury are deposition on the Earth's surface. The amount of mercury at any one location is comprised of mercury from the natural global cycle, the global cycle perturbed by anthropogenic activities, as well as regional and local anthropogenic sources. In addition to air emissions, mercury may also enter an ecosystem through direct water discharge of past uses of mercury, such as in paints or fungicide applications to crops. Research results indicate that natural sources, industrial sources, and recycled anthropogenic mercury each contribute to about one-third of the current mercury burden in the global atmosphere (Pirrone et al., 1996). However, more recent measurements suggest that natural mercury emissions may be larger than past estimates (Lindberg et al., 1998) and that mercury may be constantly recycled between terrestrial ecosystems and the atmosphere

Routine monitoring for mercury deposition in precipitation was not initiated in the United States until January 1996 (Lamb and Bowersox, 2000) when the National Atmospheric Deposition Program (NADP) initiated the Mercury Deposition Network (MDN). Consequently, limited data were available to describe spatial and temporal patterns in mercury deposition in the United States at the time EPA undertook the Mercury Study (U.S. EPA, 1997). As a result, in its initial assessment of the fate and transport of mercury in the environment (U.S. EPA, 1997b), EPA relied on computer simulation models to describe the environmental fate of emitted mercury. Two models were used in this analysis: The Regional Lagrangian Model of Air Pollution (RELMAP), for assessing regional scale atmospheric transport and the Industrial Source Code Model (ISC3), for local scale analysis. EPA's ISC3 model was used to predict average annual concentrations as well as wet and dry deposition fluxes that result from emissions within 50 km of a single source. The regional RELMAP (Bullock et al., 1997; Eder et al., 1986) predicts average annual atmospheric mercury concentrations as well as wet and dry deposition fluxes for 40 $km^2$ grids across the continental United States. Model predictions were based on anthropogenic emissions from sources identified in EPA's 1994-95 inventory (U.S. EPA, 1997b). The predicted results from RELMAP were added to a uniform elemental mercury background concentration of 1.6 nanograms per cubic meter (ng/m$^3$) which represents natural and re-emitted anthropogenic sources of mercury worldwide (Fitzgerald and Mason, 1996). The results of these simulations indicate that the highest deposition rates from anthropogenic and global sources of mercury were predicted to occur in the southern Great Lakes and Ohio River Valley, the Northeast (including Pennsylvania) and scattered areas of the south, with the highest deposition in central and south Florida (U.S. EPA, 1997c). The computer simulations also suggest that about one-third of the United States anthropogenic emissions (approximately 52 tons) are deposited on the lower 48 states; an additional 35 tons of mercury from the global reservoir is also deposited on the lower 48 states bringing the total mercury burden to approximately 87 tons annually. For a detailed description of the mercury deposition modeling effort by EPA, readers are referred to the *Mercury Study Report to Congress: Volume III, Fate and Transport of Mercury in the Environment* (U.S. EPA, 1997c).

A more recent model simulation was conducted by the Electric Power Research Institute for 2004 (EUEC, 2005). Model output (Figure 1), which includes estimates of both wet and dry mercury deposition for the continental United States and southern Canada, were for the most part, similar in spatial patterns to the earlier EPA effort, especially for the Ohio River Valley and the Northeast. Modeled results also indicate relatively high levels of mercury deposition in western and eastern Pennsylvania with less deposition occurring across the center region (Figure 1), especially across the north central counties. This spatial pattern is very similar to the distribution of wet mercury deposition results based on data from Mercury Deposition Network sites located in Pennsylvania and discussed in the results section of this report.

## Environmental Concerns

When atmospheric mercury is deposited on aquatic and terrestrial ecosystems, biological transformations can produce methylmercury. The bioaccumulation of methylmercury by aquatic organisms, such as clams, crayfish, plankton, etc., and their consumption by fish and small mammals is the primary mechanism by which methylmercury enters the food web. Because of the bioaccumulation effects of methylmercury, the concentration of methylmercury in fish may be several orders of magnitude higher than the concentrations in the aquatic ecosystem inhabited by the fish. The consumption of contaminated fish by both humans and wildlife (e.g., loons, ducks, eagles, otters, mink, etc.) is the primarily means by which mercury enters organisms at the top of the food chain. For a detailed discussion on the fate and transport of mercury in the environment, readers are referred to the *Mercury Study Report to Congress, Volume III* (U.S. EPA, 1997c); for an assessment of the ecological and human health effects, refer to *Volume V* and *Volume VI* (U.S. EPA, 1997d and 1997e, respectively).

Methylmercury is known to be toxic to humans causing permanent damage to the brain and kidneys. Developing nervous systems in both humans and animals are particularly vulnerable to methylmercury exposure. Consequently, pregnant women and young children are particularly sensitive and are at greatest risk to exposure. Chronic, low-dose prenatal methylmercury exposure from maternal consumption of contaminated fish has been associated with subtle neurotoxicity problems, such as poor performance on neurobehavioral tests, particularly tests of attention, fine-motor function, language, visual-spatial abilities and verbal memory (National

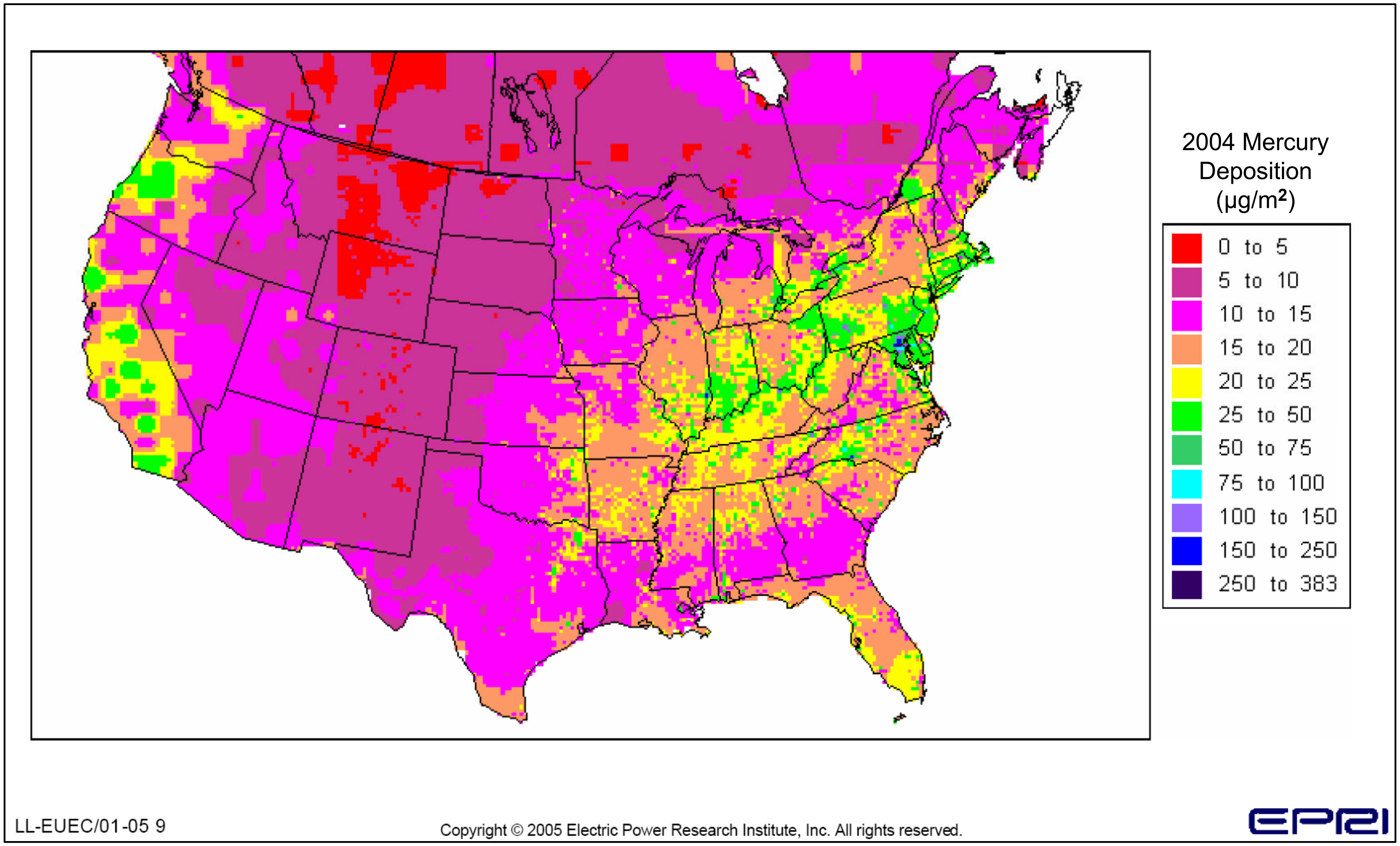
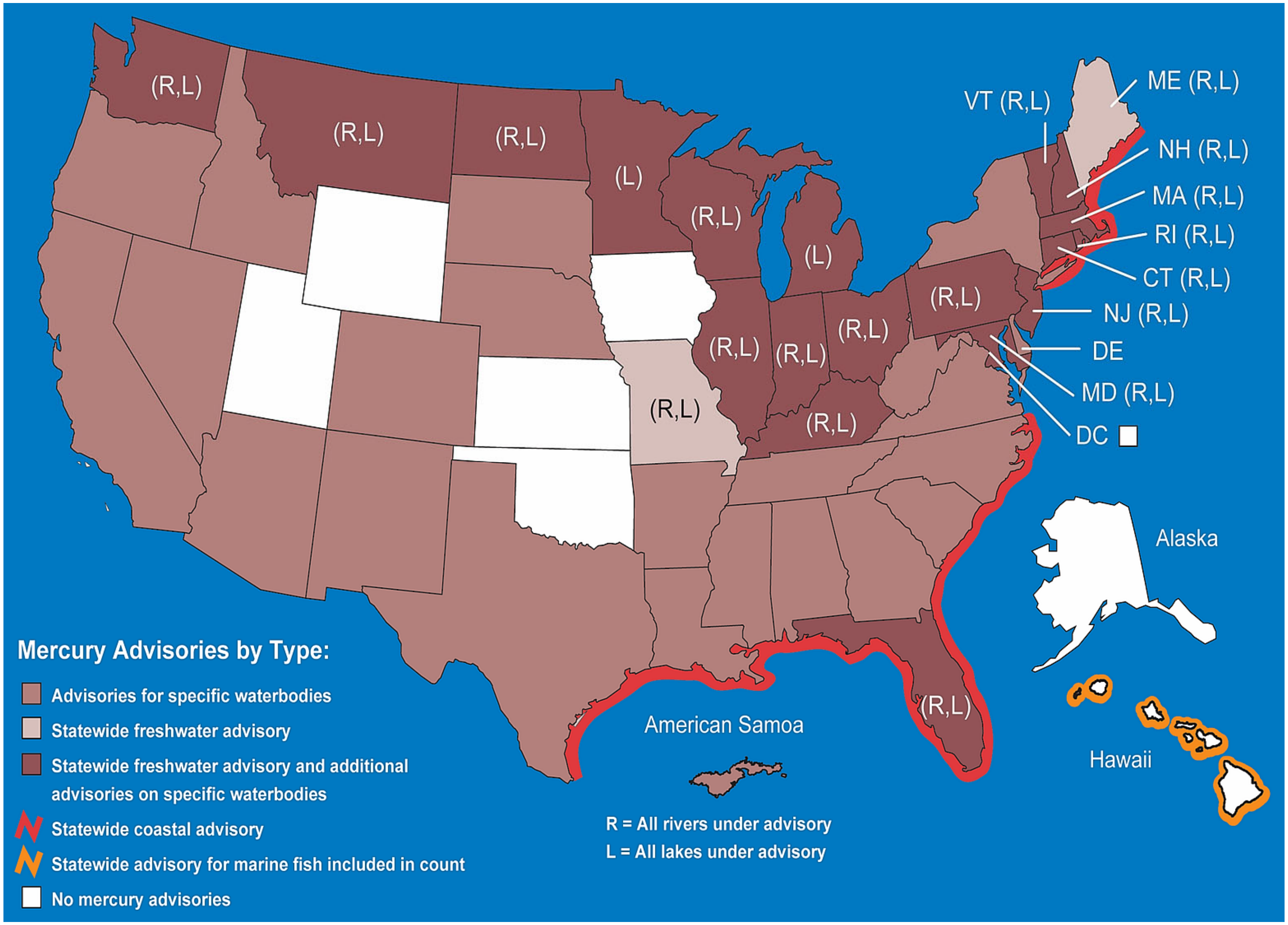


Figure 1. Total mercury deposition simulation for the United States and southern Canada using the Regional Lagrangian Model of Air Pollution (EUEC, 2005).

Research Council, 2000). The most severe effects of mercury contamination reported in adults from high dose exposure in Japan and Iraq include mental retardation, cerebral palsy, deafness, blindness, and dysarthria (National Research Council, 2000). Because of the potential risks to humans, particularly pregnant women and young children, most states in the United States have issued fish advisories for some or all water bodies located in their boundaries including coastal waters in the Gulf of Mexico (U.S. EPA, 2004). Most of these advisories are based on elevated mercury concentrations in fish samples from these waters (Figure 2). A fish advisory for all surface waters in Pennsylvania was issued in 2001 (U.S. EPA, 2004). Despite the number of advisories, an analysis of dietary surveys reported in the *Mercury Study Report to Congress* (U.S. EPA, 1997d), typical fish consumers in the United States are not in danger of ingesting harmful levels of methylmercury as reflected by the relatively low amounts of fish consumed by the typical citizen.

The impacts on wildlife (fish, birds, and fur-bearing mammals) from exposure to methylmercury are described in detail in the *Mercury Study Report to Congress, Volume IV*: *An Assessment of Exposure to Mercury in the United States* (U.S. EPA, 1997d). Like human impacts, mercury toxicity in wildlife is related to the consumption of bioaccumulated mercury in less complex organisms within their food web. Overall, wildlife (e.g., fish, birds, and fur-bearing mammals) appears to be more susceptible to mercury effects when located in ecosystems that experience high levels of deposition, inhabit ecosystems already impacted by acidic deposition or have characteristics other than low pH that result in high levels of mercury bioaccumulation in aquatic biota, and are species that are likely to experience high levels of exposure because of their feeding preferences (U.S. EPA, 2000). Fish toxicity is highly variable and dependent on species, size, life stage, and age along with a number of environmental factors. The effects of methylmercury may result in death, reduced reproduction, impaired growth and development, behavioral abnormalities, altered blood chemistry, reduced feeding rates and predatory success, and altered oxygen exchange. Some signs of acute mercury poisoning are represented by emaciation, brain lesions, cataracts, and an inability to capture food. Evidence suggests that effects can be detected in water concentrations between 0.1 and 1.0 microgram per liter (µg/L) for some species. Symptoms of mercury poisoning in birds include muscular in-coordination, falling, slowness, fluffed feathers, calmness, hyperactivity, hypoactivity, and drooping eyelids. Liver and kidney damage, neurobehavior effects, reduced food consumption, weight loss, spinal cord damage, reduced cardiovascular function, and impaired growth and development have also been reported. Impacts on fur-bearing mammals, such as mink and otter, are less well known due to the limited number of studies and confounding effects of other stressors, such as habitat fragmentation and inbreeding (U.S. EPA, 2000).

In the *Mercury Study Report to Congress,* (U.S. EPA, 1997a) EPA found that "a plausible link exists between past and present, human-induced atmospheric emissions of mercury in the United States and increased concentrations of mercury that have been found in the environment and in freshwater fish". However, EPA goes on to say that an apportionment between mercury sources and mercury in environmental media and biota cannot be described in quantitative terms with the current scientific understanding of the environmental fate and transport of the pollutant. Based on modeled mercury deposition estimates (Figure 1) and the number and location of mercury fish advisories in the United States (Figure 2), the problem appears to be potentially most severe in



Fish Consumption Advisories for Mercury

***NOTE:*** This map depicts the presence and type of fish advisories issued by the states for mercury as of December 2004. Because only selected water bodies are monitored, this map does not reflect the full extent of chemical contamination of fish tissues in each state or province.

Figure 2. Fish consumption advisories due to mercury levels in surface waters of the United States as of December 2004 (U.S. EPA, 2004)

the Great Lakes, the Northeast, in the Gulf States, and in South Florida. Many lakes and streams in these areas contain fish with mercury levels above state (0.5 to 1.0 mg/L) and U.S. Food and Drug Administration action level (1.0 mg/L) for human consumption (U.S. EPA, 1997 and 2004).

## The Mercury Deposition Network

The Mercury Deposition Network (MDN), coordinated through the National Atmospheric Deposition Program (NADP), was designed to study and quantify spatial and temporal trends in the deposition and fate of mercury in the atmosphere. The NADP began monitoring trace chemicals in precipitation at 18 sites in 1978 in order to describe and study "acid rain" related problems. It has since grown to a network of more than 270 sites located throughout the United States and Canada. (More information on the NADP is available at http://nadp.sws.uiuc.edu). In 1995, following a year of field testing (Vermette et al., 1995), the NADP began "transition phase" mercury monitoring at 26 sites in preparation for the acceptance of the MDN into NADP which occurred in January 1996. Since 1996, the MDN has grown to more than 100 active sites in the USA and Canada (Figure 3).

Mercury deposition data from the MDN will be an important input to atmospheric and multi-media models designed to assess the fate and consequences of mercury emissions and will provide feedback to better assess trends in mercury deposition. Thus, the MDN database will be particularly useful in the evaluation of the effectiveness of EPA and/or state mandated controls on mercury emissions to the atmosphere (U.S. EPA, 2000). Summarized in this report are the results of mercury monitoring at eight MDN sites located in Pennsylvania from January 2005 through December 2006. The results are discussed in relationship to similar data collected at sites throughout the United States and southern Canada.

### Network Design and Operation

Both wet and dry depositions are important processes for the movement of mercury from the atmosphere to land and water surfaces. The Mercury Deposition Network (MDN) is a wet deposition network and does not attempt to measure dry deposition of mercury. The main reason for this is that dry deposition methods are based on indirect measurements that are largely experimental and difficult to implement at isolated sites using personnel with a wide variety of backgrounds. Wet deposition measurements, on the other hand, are based on direct collection techniques that use standardized methods and equipment that are relatively easy to implement and operate at remote sites. Although dry deposition of mercury is very important in terrestrial systems (Lindberg et al., 1992) other studies have estimated that wet deposition is the most important atmospheric process for the movement of mercury to water bodies (Lamborg et al., 1995; Mason et al., 1997; Scherbatskoy et al., 1997). Since the primary environmental problems associated with mercury deposition are fish contamination and human health risks associated with the consumption of contaminated fish (U.S. EPA 1997), wet deposition is probably the most