Mercury: From source to sink, considerations for fish consumption advisories in the State of Connecticut

Margaret Lynn

Gaboury Benoit, Advisor
Jay Ague, Second Reader
29 April 2015

A Senior Essay presented to the faculty of the Department of Geology and Geophysics, Yale University, in partial fulfillment of the Bachelor's Degree.

Abstract

Background levels of mercury in the biosphere have increased substantially due to anthropogenic activity. Mercury in its elemental form is easily transformed into its organic form, Methylmercury (MeHg). Methylmercury is classified as a persistent bioaccumulative toxin. As a result of its negative health implications, mercury contamination is a pervasive environmental and public health concern. Connecticut is influenced by mercury contamination from legacy point sources and local, regional, and global atmospheric deposition which has led the state to issue fish consumption advisories for all water bodies due to mercury contamination. While comprehensive scientific information has played an important role in determining advisories and areas of future study in New England, in Connecticut, fish consumption advisories are established on just two studies based on the level of Hg in fish in the state. In addition, Connecticut has the most stringent standard for Hg concentrations in fish tissue. In the future, more comprehensive monitoring would solidify the relationship between atmospheric deposition and subsequent accumulation of mercury in aquatic food webs. In addition, the fish consumption advisory currently in place in Connecticut discourages economic growth from recreational fishing and does not adequately protect the most at-risk populations. Reworking the advisory to include only the water bodies with the highest levels of mercury contamination and making sure that the most susceptible populations are well informed about consumption advisories in Connecticut is essential to the health of the state's population and environment.

1.0 Introduction

Mercury (Hg) is ubiquitous both in the world's ocean and coastal zones as well as freshwater systems. Globally, natural[1] sources account for 70% (5207 Mg) of mercury released annually into the biosphere and anthropogenic sources contribute the rest (2320 Mg of mercury) (Pirrone et al., 2010). It is estimated that over the last century, anthropogenic emissions of mercury have tripled the concentrations of Hg in the atmosphere and on the ocean surface (Mason et al., 1994). Mercury is associated with both atmospheric transport and urban runoff, and is typically connected with industrial and municipal wastewater discharge (Mecray and ten Brink, 2000). Atmospheric deposition has been the primary Hg source responsible for global contamination of both marine and freshwater systems (Mason et al., 1994; USEPA, 1997).

Mercury in its elemental form does not have any significant or widespread health consequences. It is the organic form of mercury, methylmercury (MeHg), which has toxic qualities. Methylmercury is a known developmental neurotoxin and has the potential to bioaccumulate in fish and bioconcentrate through the aquatic food chain (Mergler et al., 2007). Humans are exposed to MeHg through the consumption of fish, making mercury a public health concern worldwide. In order to reduce this threat to public health, fish consumption advisories are often put in place. Understanding the biological and chemical factors that affect the production, transport, and fate of mercury are essential to monitoring and modeling efforts that attempt to mitigate the risk of mercury in the environment and therefore eliminate advisories. The link between atmospheric releases of Hg and fish contamination has resulted in policy development and legislative action in many industrialized countries since the mid 1990's (Swain et al., 2007).

Connecticut exhibits widespread mercury contamination from atmospheric deposition and historical industrial discharges. Mercury contamination began around 1820 in Central and Western parts of the state and around 1840 in eastern Connecticut (Varekamp et al., 2003). In Connecticut, the first fish consumption advisory was established after a report indicated that the mercury concentrations of fish in lakes and streams in Connecticut were above the EPA's recommended level of 0.3 ppm (Neumann, 1996). The advisory has remained in place until today.

[1] In this instance, "natural "mercury includes primary mercury emissions and re-emissions.

Future management of bioaccumulative toxins in coastal waters will need to take into consideration the best ways to protect human and ecological health as well as address the natural and anthropogenic processes that cause high levels of toxins. Particular attention to the fate of mercury from the point of emission to eventual deposition and subsequent contamination of wildlife needs to be taken in order to reduce potential human health hazards. This paper surveys the current status of mercury contamination in Long Island Sound and freshwater bodies in Connecticut. To protect ecological and human health, a better understanding of the relationship between reductions in source emissions of Hg, the transport and transformation of Hg through the biosphere and the response in aquatic systems, and Hg's accumulation in fish is of utmost importance.

In this essay I first present background information on mercury including a discussion on how mercury cycles through freshwater and marine systems. Then I provide information on how atmospheric mercury deposition impacts and present a modeling scenario for predicting this relationship. To focus in on Connecticut, I will review some of the current knowledge about Hg in Long Island Sound as well as the monitoring reports that Connecticut's freshwater fish consumption advisories are based on. Furthermore, I provide evidence of the socioeconomic consequences of Hg pollution and subsequent fish advisories. Finally, I offer recommendations on how Connecticut can improve monitoring efforts and balance human health risks and economic benefits of recreational fishing in the revision of consumption advisories.

2.0 Context and Background

2.1 Sources of Mercury

Sources of mercury released into the atmosphere are characterized in three ways: natural mercury emissions, anthropogenic mercury emissions, and re-emitted mercury emissions (USEPA, 1997). Natural sources of mercury emissions to the atmosphere include volcanoes, forest fires, and volatilization from certain soils and rock weathering (NESCAUM, 1998). Anthropogenic emissions are further categorized by area and point sources. Point sources are fixed to a specific geographical location, such as fossil fuel combustion, manufacturing and other miscellaneous sources while area sources are

"typically small and numerous and usually cannot be readily located geographically" (USEPA, 1997). In addition to releases into the atmosphere, anthropogenic releases of mercury include direct releases to surface water and soils. Another important source of mercury in the environment is the re-release or mercury that was originally deposited on land and in hydrological settings (NESCAUM, 1998).

Anthropogenic releases have dominated discharges into the atmosphere globally. Two-thirds of present Hg fluxes on the land and in the ocean are either directly or indirectly released from anthropogenic activities (Mason et al., 1994). Combustion of fossil fuels, coal in particular, is the largest source of anthropogenic mercury globally (Pacyna et al., 2006). Another major source of mercury is waste incineration. The Hg content of wastes varies greatly and is difficult to quantify (Pacyna et al., 2006). Because the residence time of mercury in the atmosphere is around a year, Hg has sufficient time to circulate the planet before being deposited on water, land or ice (Morel et al., 1998). Other sources of Hg emissions in the United States can be seen in Figure 1.

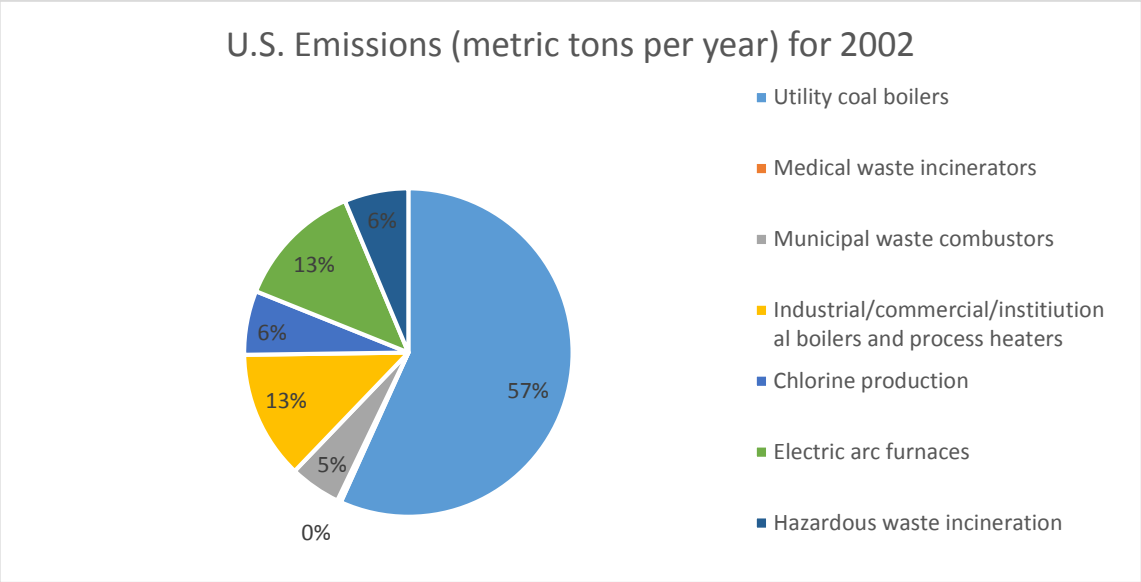


Figure 1.In the United states, utility coal burners contributed the majority of Hg to the atmosphere in the United States. Adapted from (Driscoll et al., 2007).

Over the last quarter of the 19th century and first quarter of the 20th century, mercury concentrations in lake sediments steadily increased, with peak loading occurring during the 1960s and 1970s in the northeastern United States (Kamman and Engstrom, 2002). Mercury emissions in Europe and North America decreased substantially from 1990

through 1995 (Pacyna and Pacyna, 2002). These decreases can be attributed to an overall drop in industrial activities, as well as added installation of emission control technologies on coal-fired power plants and other combustion sources (Pacyna and Pacyna, 2002). Other major reductions of global Hg use have been attributed to (1) the substitution of non-Hg containing products and production processes (2) more efficient use of Hg where Hg is still used in production and (3) a shift away from reliance on coal as an energy source (Swain et al., 2007).

2.2 Chemical Properties

Mercury is a heavy, silvery, chemical element, with atomic number 80. Because of its liquid state at standard conditions for temperature and pressure, Hg is commonly referred to as 'quicksilver.' It exists as a trace metal in the earth's crust, but has become ubiquitous in the biosphere. Mercury is classified as a persistent bioaccumulative toxin (PBT) by the US Environmental Protection Agency (Smith and Trip, 2005). The behavior, fate and health hazard potential of mercury depends directly on its chemical state (Renzoni et al., 1998). Dissolved Hg is found in several forms, summarized in Table 1 below.

Table 1 Source: Morel et al. (1998)

Common Name	**Species**	**Characteristics**
Elemental mercury	Hg^0	Volatile, but relatively unreactive. Gaseous.
Elemental mercury	Hg(II)	Ionic, gaseous.
Methylmercury	MeHg	Organic; ability to bioaccumulate.

Mercury cycles globally in the atmosphere as gaseous Hg^0 (Mason et al., 1994). In marine settings, Hg(II) is reduced to Hg^0 through a series of complex biological and chemical transformations, and returned to the atmosphere in a process often referred to volatilization or gas evasion (Morel et al., 1998). A smaller proportion of Hg is exported to sediments, making coastal and estuarine sediments an important sink for elemental Hg (Mason et al., 1994; Morel et al., 1998). In lakes and other freshwater environments, gas evasion and sedimentation also work as sources and sinks respectively of Hg to and from the atmosphere (Morel et al., 1998). On land, a majority of Hg is permanently buried in soils, with a smaller fraction being reduced back to the atmosphere as Hg^0 (Morel et al., 1998).

Organic mercury, methylmercury (MeHg), is the most toxic form of mercury and the form that is most prevalent in fish and animal tissues (Kidd et al., 2012). After inorganic mercury compounds enter water bodies through various pathways, they undergoes the process of methylation (Renzoni et al., 1998). Sulfur-reducing bacteria located in sediments and anoxic waters are key actors in the methylations process (Morel et al., 1998). Methylation is thought to be enhanced in anoxic waters and sediments, especially in lakes (Morel et al., 1998). The specific cycling and methylation processes, however, are not well understood (Kidd et al., 2012). Key to the properties of MeHg is its ability to bioaccumulate through the food chain. While Hg^0 and Hg(II) have the ability to diffuse through planktonic bacteria and microalgae, MeHg is retained by the bottom dwellers of the food chain (Morel et al., 1998). Organisms at higher trophic levels and concentrations increase as it advances through the food chain subsequently efficiently retain MeHg.

2.3 Cycling of Mercury in the Environment

Overall, the toxicity of Hg is dependent on the physical, chemical and biological factors of the aquatic environment it is deposited in (Ullrich et al., 2001). Mercury cycling and transformation is different in freshwater and marine systems, and will be addressed separately in this section.

2.3.1 Freshwater Environments

Mercury cycles through the air, land and water, "undergoing a number of complex chemical and physical transformations" (NESCAUM, 1998). The physical pathway of mercury is illustrated in Figure 2. Overall, the biggest factor in predicting the MeHg concentration in water and sediments is the amount of elemental Hg loading to the system (Driscoll et al., 2007; Kamman et al., 2005). In addition, chemical thresholds have been identified that predict high levels of Hg in fish. These parameters are as follows: "total phosphorus concentrations of less than 30 μg per L; pH of less than 6.0; ANC of less than 100 μeq per L; and DOC of more than 4 mg carbon per L" (Driscoll et al., 2007).

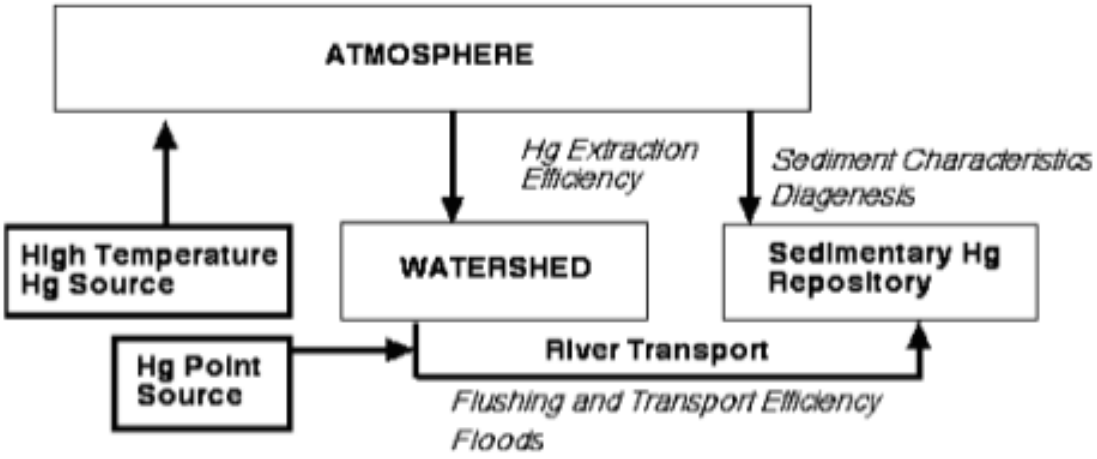


Figure 2 A simplified diagram of the pathways of Hg from source to sink. From (Varekamp et al., 2003).

Methylation of Hg is the key reaction that causes mercury to bioaccumulate in aquatic food webs. In freshwater systems the mercury cycle is composed of a series of source and sink terms. In-lake production is shown to be an environment where methylation occurs (Mason et al., 1994). However, in-lake production of MeHg is not the only source of this toxic element in freshwater systems. It has been shown that wetlands are important sources of MeHg as well (Rudd, 1995). The primary sink for atmospheric Hg is the terrestrial environment (Mason et al., 1994). Two of the factors that are thought to stimulate the conversion of Hg into MeHg in freshwater systems are (1) the acidification of lakes, ponds and streams and (2) higher levels of tropospheric ozone in the summer[2] (NESCAUM, 1998).

The main factor controlling the concentration of MeHg in biota is the MeHg concentration in water (Morel et al., 1998). The concentration of MeHg in aquatic systems is "controlled by the relative efficiency of the methylation and demethylation processes" (Morel et al., 1998). Total Hg concentration in fish has been shown to increase across fish species with both length and age (Neumann and Ward, 1999). Neumann and Ward (1999) suggest that species-specific prey type and availability, changes in trophic position and consumption rates affect the amount of Hg in fish and therefore need to be considered when assessing Hg concentrations of fish in individual water bodies.

[2] Higher levels of ozone are thought to convert Hg to a chemical form that is more susceptible to deposition.

2.3.2 Marine Cycling

Overall, less is known about the biogeochemical cycling of Hg in coastal and estuarine systems than freshwater systems (Rolfhus and Fitzgerald, 2001). The majority of Hg in coastal regions is particle-bound, carried in with fine-grained materials (Varekamp et al., 2003). Hg accumulation rates in coastal marshes are an order of magnitude greater than Hg deposition rates (Varekamp et al., 2003). This is an indication that Hg contaminated sediments are concentrated from watersheds into coastal marshes (Varekamp et al., 2003). For marine fish species, MeHg concentrations were positively correlated to fish length, but large variations in MeHg levels were found among larger individuals (Hammerschmidt and Fitzgerald, 2006).

Methylmercury levels in coastal fish species are directly related to the production of MeHg in the sediments underlying coastal marine habitats (Hammerschmidt and Fitzgerald, 2006). In coastal marine ecosystems like the Connecticut shoreline of Long Island Sound, MeHg concentrations are a result of net sedimentary production and dietary bioaccumulation (Hammerschmidt and Fitzgerald, 2006). Because of the relationship between anthropogenic Hg loadings to the near-shore environment and subsequent bioaccumulation of MeHg, it is reasonable to infer that the MeHg levels in fish have increased relative to pollutant loadings (Hammerschmidt and Fitzgerald, 2006). While MeHg concentrations in migratory fish are not directly dependent on the production of MeHg in LIS, many near-shore fish inhabit embayments and coastal waters such as LIS permanently or seasonally (Hammerschmidt and Fitzgerald, 2006). Therefore, their MeHg content reflects their lifetime exposure in LIS.

Overall, five noteworthy features of mercury cycling in the marine environment have been noted by Fitzgerald et al. (2007):

> "(1) Atmospheric deposition is the dominant input term to the world ocean.
>
> (2) Riverine fluxes, while important at the margins, are a small part of the global budget.
>
> (3) Evasion is a major process whereby Hg leaves the ocean.
>
> (4) Deep sea burial is a relatively small term, which requires that most Hg is removed from participation in the global cycle on century time scales through sequestration on land.

(5) Human activity has likely perturbed the cycle by increasing emissions to the atmosphere (and therefore the rest of the surface environment) by approximately a factor of 3."

2.4 Health Effects

Mercury is in its most toxic state when it is in its organic form, methylmercury (MeHg). Methylmercury has the ability to bioaccumulate in aquatic organisms, making the consumption of fish with high concentrations of MeHg the primary exposure pathway for humans. Chronic, acute, and especially prenatal exposure to MeHg has been linked to neurological damage as a result of human consumption of such aquatic organisms (Harris et al., 2003). Dietary MeHg is almost entirely absorbed by the blood and is carried throughout the body, inundating tissues including the brain (Borum et al., 2001). At the lowest dose, the most severe consequence of MeHg exposure is neurotoxicity, especially in developing individuals (Borum et al., 2001). Beyond effects on humans, MeHg also is toxic to fish, mammals and birds. In both controlled feeding settings and field-based studies, a range of toxic effects were seen in these animals, including neurological, hormonal, behavioral, and reproductive changes (Scheuhammer et al., 2007).

The US EPA and FDA (2004) specifically warn women who may become pregnant to avoid regular consumption of fish that are high in MeHg. This substance has a long residence time in the body; sometimes it may take over a year for levels to drop through natural processes (Borum et al., 2001). In the past, experts have concluded that reducing and eliminating sources of MeHg exposure is key to preserving human health (Mergler et al., 2007). Hg exposure as a result of the consumption of fish varies is a result of the frequency of fish consumption and species of fish or fish-eating mammal (Mergler et al., 2007). In addition to exposure dose, absorption kinetics appears to have an effect on how much MeHg ends up being absorbed by humans and animals (Mergler et al., 2007). Although most studies indicate that approximately 100% of MeHg in fish is absorbed by the gastrointestinal tract (Mergler et al., 2007), other studies suggest that this relationship might not be so simple (Canuel et al., 2006). Government officials often simplify this absorption relationship in order to establish guidelines for fish consumption. They assume a constant and linear relationship between the amount of MeHg consumed and body burden (Canuel et al., 2006).

In 2001, the US EPA set fish tissue criterion for MeHg at 0.3 ppm under section 304(a) of the Clean Water Act in order to protect human health (Borum et al., 2001). Figure 3 shows the equation used by the EPA to set fish tissue criterion.

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI_i}$$

Where:

TRC = Fish tissue residue criterion (mg methylmercury/kg fish) for freshwater and estuarine fish

RfD = Reference dose (based on noncancer human health effects) of 0.0001 mg methylmercury/kg body weight-day

RSC = Relative source contribution (subtracted from the RfD to account for marine fish consumption) estimated to be 2.7×10^{-5} mg methylmercury/kg body weight-day

BW = Human body weight default value of 70 kg (for adults)

FI = Fish intake at trophic level (TL) i (i = 2, 3, 4); total default intake is 0.0175 kg fish/day for general adult population. Trophic level breakouts for the general population are: TL2 = 0.0038 kg fish/day; TL3 = 0.0080 kg fish/day; and TL4 = 0.0057 kg fish/day.

Figure 3 Criterion equation from the 2000 Human Health Methodology, rearranged by EPA to "solve for protective concentration in fish tissue rather than water" (Borum et al., 2001).

In Connecticut, the fish tissue concentration standard set for the basis of fish consumption advisories is 0.1 ppm (NEIWPCC, 2007). This is the most stringent standard among all the New England States (see Table 3). This threshold, set by the USEPA, is meant to be protective of "high risk" consumers, such as women who are pregnant or who are of childbearing age (Ginsberg, 1996)[3]. The reference dose for non-high risk groups is set at 0.3 ppm. It is unclear why, if these are the reference doses set by the EPA, that other states do not have fish tissue Hg concentration advisories in place for 0.1 ppm instead of 0.3 ppm for high-risk consumers (see Table 3). Table 2 displays both chronic and acute concentration limits for high-risk groups and chronic concentration limits for other consumer groups. It is worth noting that Connecticut does not publish the limit for 'other'

[3] This source was accessed courtesy of Brian Toal at the CT Department of Public Health. More recent risk assessments could not be provided.

consumer groups of the EPA's recommended 0.3 ppm. These discrepancies will be discussed further later on.

Table 2 Draft Format for Consumption Limits Applicable to CT Lakes Mercury Data from (Ginsberg, 1996).

Advice	High Risk Group - Chronic Consumer[a]	High Risk Group - Acute (Single Meal)[b]	Other Groups - Chronic Consumer[a]
Do not eat	≥ 0.9 ppm	> 1.5 ppm	> 2.8 ppm
May eat 1x/month	0.5 - 0.8 ppm	Not applicable[c]	1.5- 2.7 ppm
May eat 2x/month	0.3 - 0.4 ppm	Not applicable[c]	0.8- 1.4 ppm
May eat 4x/month	0.1 - 0.2 ppm	Not applicable[c]	0.4 - 0.7 ppm
Unrestricted	<0.1 ppm	Not applicable[c]	≤ 0.3 ppm

[a]Data show the acceptable fish concentrations (ave. or geo.mean) for chronic consumption at the indicated advice level.
[b]Data show the maximum fish concentration acceptable for a single fish meal. Lakes which have higher concentrations in individual fish should be avoided (no consumption) by the high risk group. At lower maximum concentrations (≤ 1.5 ppm) the acute risk is not significant and the chronic advice (1st column) applies.
[c]Not applicable since chronic consumption advice applies.

Table 3 Summary of fish tissue mercury concentration limits for sensitive populations for northeastern states. Source: (Lepak et al., 2009).

State	Sensitive population	Fish tissue mercury concentration (parts per million)
Connecticut	Pregnant and nursing women, women who plan to become pregnant within one year, children under 6	0.1
Massachusetts	Pregnant and nursing women, women of child-bearing age, children under 12	0.2
Maine	Pregnant and nursing women, women who may get pregnant, children under 8	0.3
New Hampshire	Pregnant and nursing women, women who may get pregnant, children under 7	0.3
New York	Women of childbearing age, infants, children under 15	1.0
Rhode Island	Pregnant and nursing women, women who plan to become pregnant within one year, young children	0.3
Vermont	Women of childbearing age (particularly pregnant and nursing women, women planning to get pregnant), children under 6	0.3

Source: NEIWPCC (2007).

In the case of MeHg, fish tissue residue is used as a water quality criterion as opposed to using a water column based water quality criterion (Borum et al., 2001). In general, allowable water column concentration (WCC) can be derived from fish tissue

criterion (FTC) and a bioaccumulation factor (BAF) according to the following equation: FTC = BAF x WCC (NEIWPCC, 2007). Based on this relationship, meeting the criterion for fish tissue concentration for Connecticut ensures that water column criteria will also be met.

3.0 Mercury in the Atmosphere

The relationship between atmospheric mercury deposition and methylmercury contamination of aquatic resources is not a simple one. While the link between atmospheric inputs and wildlife contamination is well established, a comprehensive understanding of the linkages between "atmospheric inputs, atmospheric and depositional processes, watershed biogeochemical processes, and biological uptake of methyl mercury need further study and modeling (VanArsdale et al., 2005).

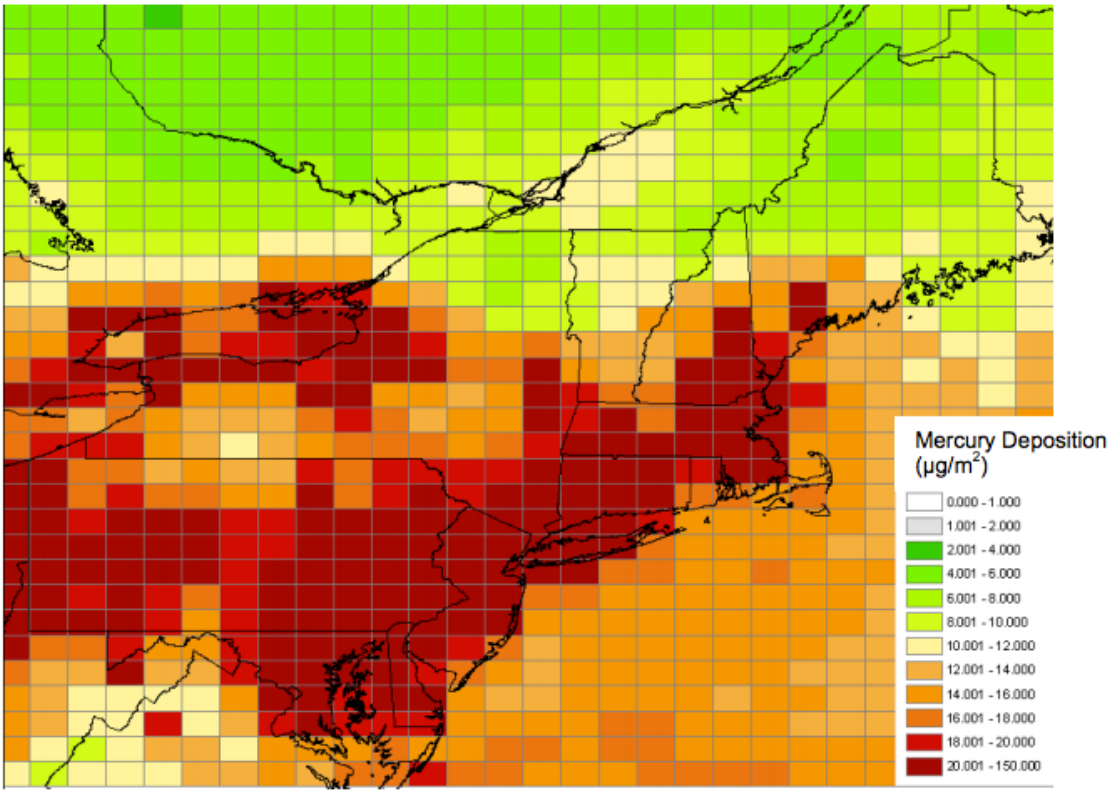
The atmosphere plays a major role in the Hg loading of freshwater ecosystems in the United States (Kamman et al., 2005; USEPA, 1997). In northeastern North America, there is an observed southwest-to-northeast gradient, with higher atmospheric deposition at southern sites (See Figure 4 and Figure 5) (VanArsdale et al., 2005). In addition, seasonal variations have been shown to be important (VanArsdale et al., 2005). Overall, about half of anthropogenic emissions of Hg appear to cycle globally through the atmosphere, while the other half is deposited locally (Mason et al., 1994). An emphasis on the need for better understanding of the relationship between reductions in atmospheric Hg emissions, eventual deposition and the response in Hg concentrations of aquatic systems is made by many scientists (VanArsdale et al., 2005).

3.1 Modeling Atmospheric Deposition and Fish Concentration in the Northeast

The Regional Modeling System for Aerosols and Deposition (REMSAD version 7.13) has been an important tool in predicting how atmospheric mercury travels through the Northeast (Graham et al., 2007). Deposition and atmospheric mercury concentrations were modeled for the years 1996 and 2002 in support of and to update progress on the New England Governors and Eastern Canadian Premiers (NEG-ECP) Mercury Action Plan. The model concluded that substantial reductions of atmospheric mercury in the northeast United States will have benefits at the local level (Graham et al., 2007). The results of REMSAD modeling are shown below in Figure 5. As one can see from these figures,

mercury deposition is heightened, with the highest mercury depositions rates occurring over much of Connecticut in the 1998 model, and high levels of mercury deposition occurring in the southeastern part of the state in the 2002 model.

1998 Modeled Mercury Deposition



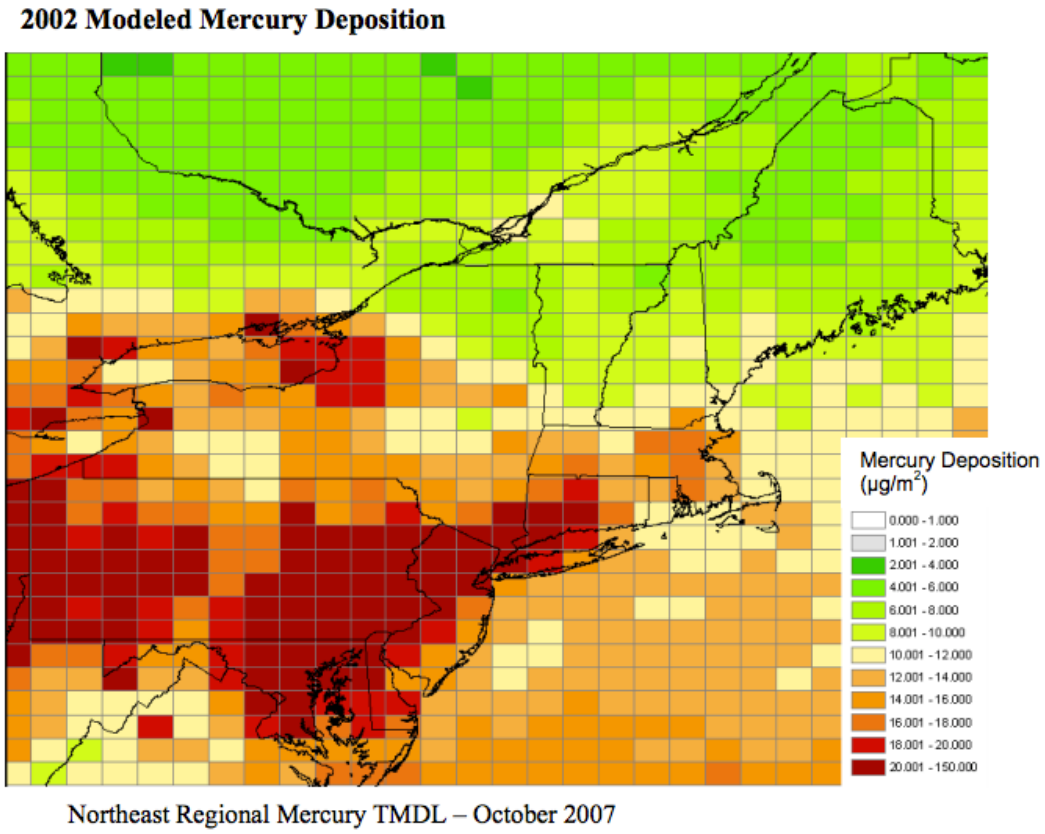


Figure 4 Modeled mercury deposition in the northeastern United States for the years 1998 and 1999. (NEIWPCC, 2007).

To date, on a large spatial scale, there is no precise modeling of the relationship between atmospheric mercury emissions and subsequent bioaccumulation in fish (NEIWPCC, 2007). However, several ecosystem-scale models have been used in order to predict reductions of Hg in fish tissue related to reductions in atmospheric Hg. One such model is the Mercury Cycling Model (MCM). The model predicts that over the long term, reductions in fish tissue mercury concentrations will be achieved proportionally to reductions in emissions and ensuing deposition of Hg (NEIWPCC, 2007).[4] This relationship will not appear over the short-term, as it has been greatly simplified. As the Northeast TMDL (NEIWPCC, 2007) notes, the actual level of Hg in fish "will vary among Northeast water bodies due to different conditions that affect the production of methylmercury and bioaccumulation of methylmercury" (NEIWPCC, 2007). Some of these factors include the

[4] It is important to note that mercury concentrations in fish will be reduced proportionally to reductions in emissions only if atmospheric deposition is the only significant source of Hg to the watershed.

size of the watershed, productivity, acidification status, sulfate loading, and water-level management (NEIWPCC, 2007).

Because these relationships are predicted to appear in the long-term, there is little data available to support modeled predictions. As many authors (Chen et al., 2008; Harris et al., 2007) indicate, a carefully designed monitoring program needs to not only take into account levels of mercury in depositional settings, sediments, fish and wildlife, but also the environmental parameters and controls that affect the complex behavior of mercury in both freshwater and marine environments. Connecticut would benefit from more frequent and expansive monitoring of Hg levels in local freshwater systems in order to assess if and how reductions of Hg emissions have reduced levels of Hg in fish tissue.

4.0 Mercury in Long Island Sound

Connecticut holds an important position as the northern boundary of Long Island Sound. Long Island Sound is "a large, urbanized coastal estuary" and "is among the world's most important commercials and recreational coastal resources" (Balcom et al., 2004). Long Island Sound also has a long history of pollutant loading. Sediments in LIS are contaminated with many different toxic elements and compounds from historic runoff, groundwater discharge, domestic and industrial waste flows, and atmospheric deposition. As Evers et al. (2008) note, LIS is a "strong candidat[e] for the basis of an organized, standardized, monitoring program that tracks estuarine and marine environmental Hg loadings as well as watershed contributions."

4.1 Survey of Hg in Long Island Sound and Coastal Environments

Mercury concentrations of sediments in LIS have been studied extensively. Significant contaminant loading comes from the freshwater inputs from the Connecticut River, Housatonic River, Thames River and the Quinnipiac River along the Connecticut shore and the East River in New York City (Varekamp et al., 2003). Overall, high Hg values are found in the western part of the sound, with lower Hg values found in the eastern part of the Sound (Varekamp et al., 2000). This trend may be the result of two factors, according to Varekamp et al. (2000): "(1) sedimentary processes within LIS; and (2) the regional distribution of Hg contamination sources along the Sound."

My analysis of Long Island Sound as a system stems primarily from one study by Prentiss H. Balcom et al. published in 2004. The study incorporated measurements for the major sources and sinks of elemental mercury and methylated mercury during the years 1995-1997. Balcom et al. (2004) present an assessment on the state of Hg in Long Island Sound and along the Connecticut coast and quantifies the amount of Hg that entered LIS from both localized discharges (including riverine inputs and discharge from water pollution control facilities) and direct and indirect inputs from atmospherically derived Hg. The results of the mass balance for total Hg and MeHg are presented in Figure 3.

In order to discuss the results of the mass balance, it is important to know how the study's authors quantified LIS inputs. Atmospheric deposition estimates were based on measurements made using bulk deposition samplers at four sites along the north shore of the Sound over an 18-month period. These samplers were located (from east to west) in Avery Point, Hammonasset State Park in Madison, CT, the Milford Audubon Center, and the Marshlands in Rye, NY. Four major rivers in CT- the Connecticut, the Housatonic, Thames, and Quinnipiac Rivers- were sampled above salt-intrusion locations. The Connecticut River, because it accounts for the majority (about 70%) of the freshwater inflow into the Sound, was sampled extensively during representative flow regimes over a 15-month period. To quantify the inputs from water treatment facilities, Hg species determinations in effluent from eight WPCF was measured. The major facilities discharging to CTR were sampled more extensively.

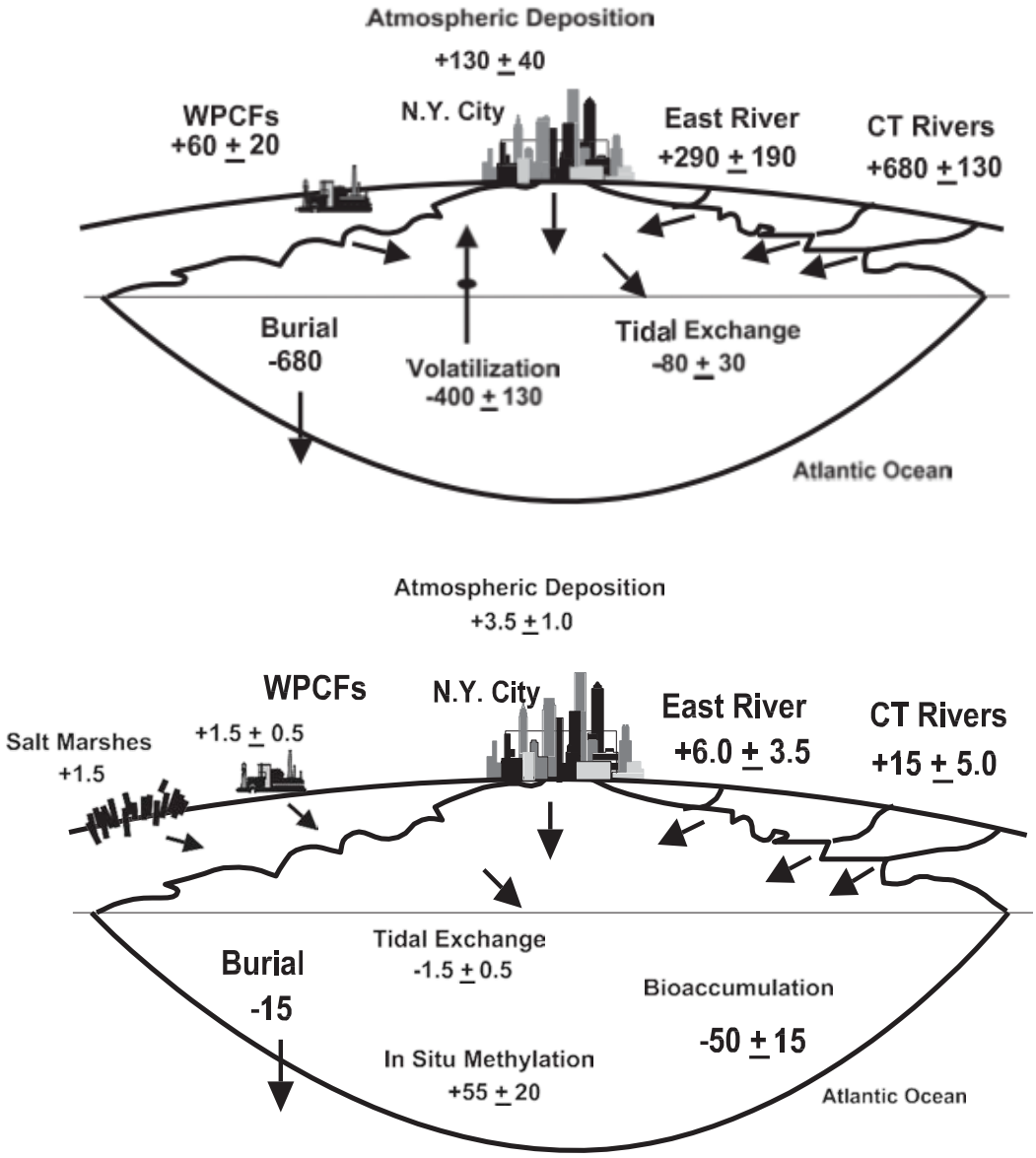


Figure 5 From Balcom et al (2004). (top) mass balance figure for total Hg in Long Island Sound. (below) mass balance figure for MeHg in LIS. All units in (moles year^{-1}).

For the study of atmospheric deposition, Balcom et al. (2004) indicate that the network of four deposition collectors along the CT coastline are representative of the atmospheric flux to LIS (40 ± 10 nmol Hg m^{-2} year^{-1}). The authors found atmospheric deposition rates to be similar to those in more rural areas such as northern Wisconsin and Lake Champlain. The similar deposition rates, they claimed, pointed to the importance of

long-range transport of Hg, as opposed to local and regional emissions around LIS in the amount of Hg that was deposited to LIS. However, other studies indicate that this may not be the case and that local and regional atmospheric releases may be most important. A study (Nadim et al., 2001) conducted from January 1997 through December 1999 collected measurements of atmospheric Hg deposition every week from eight locations around the state of Connecticut: four along the coast of LIS and four at interior locations (Nadim et al., 2001). In addition, four of the sites were classified as urban areas, and four were classified as rural areas in order to determine if urban density and land use was correlated with atmospheric deposition rates.

Overall, Nadim et al. (2001) found significant differences between atmospheric Hg depositions in urban areas from atmospheric deposition at rural sites. Levels of gaseous, particulate, and wet deposition fluxes were higher in Bridgeport, Waterbury, and East Hartford, which are all highly populated, industrial cities in CT. The highest wet-deposition flux of Hg^{2+} among all sites was observed in Bridgeport (1045.47 μg ha^{-1} $week^{-1}$) (Nadim et al., 2001). It is noteworthy that the presence of a solid waste incinerator in Bridgeport is likely a large contributor to this elevated deposition rate because municipal waste combustors are the main source of Hg in the Northeast US. Though the study did not find any statistically significant difference in deposition rates between coastal and non-coastal areas, higher deposition rates in urban areas could affect estimates of fluxes that area made Sound wide. In addition, elevated deposition rates in urban areas could indicate even higher loading of urban watersheds, as well as more rapid response to changes in atmospheric deposition rates. Eckley et al. (2008) conclude that the Hg flux in urban areas respond more rapidly to changes in atmospheric deposition than more rural systems. This rapid response is attributed to the accumulation of Hg on urban windows that is efficiently removed during precipitation events (Eckley et al., 2008). This evidence indicates that monitoring efforts in urban areas might be designed differently than in rural areas in order to capture the variability of Hg concentrations on shorter timescales.

It is worth noting that not all urban estuarine systems have the same flux characteristics. Unlike the conclusion of Balcom et al. (2004), a study on the atmospheric deposition to the Chesapeake Bay found that direct deposition to the bay was the most important contributor (over 50%) to the total Hg levels in the Bay (Mason et al., 1997). The

Chesapeake Bay is a Mason et al. (1997) concluded that regional sources, specifically the Baltimore urban area, had a "marked impact" on the overall atmospheric deposition to the Bay. In addition, unlike the case of LIS and the conclusions of Balcom et al. (2004), the majority (90% or greater) of the Hg deposited to the watershed was retained in the terrestrial domain as opposed to being exported to the Chesapeake Bay.

In Connecticut, historical local point sources are major contributors to the biogeochemical Hg cycle. Multiple studies have documented these contributions (Clark and Benoit, 2009a; Clark and Benoit, 2009b; GOLDOFF et al., 2006; Mecray and ten Brink, 2000; Varekamp et al., 2003; Varekamp et al., 2000). The Housatonic is one river that has experienced historical Hg loading and is subsequently a source of contaminants for LIS. Among other historical industrial pollutants, the Housatonic is contaminated with Hg from the hatting industry in Danbury (Varekamp et al., 2003). Sediments from the Still River basin near Danbury have been found to contain several tens of ppm Hg (Varekamp et al., 2003). These sediments can be suspended and ultimately discharged and deposited in the western section of the Sound (Varekamp et al., 2003).

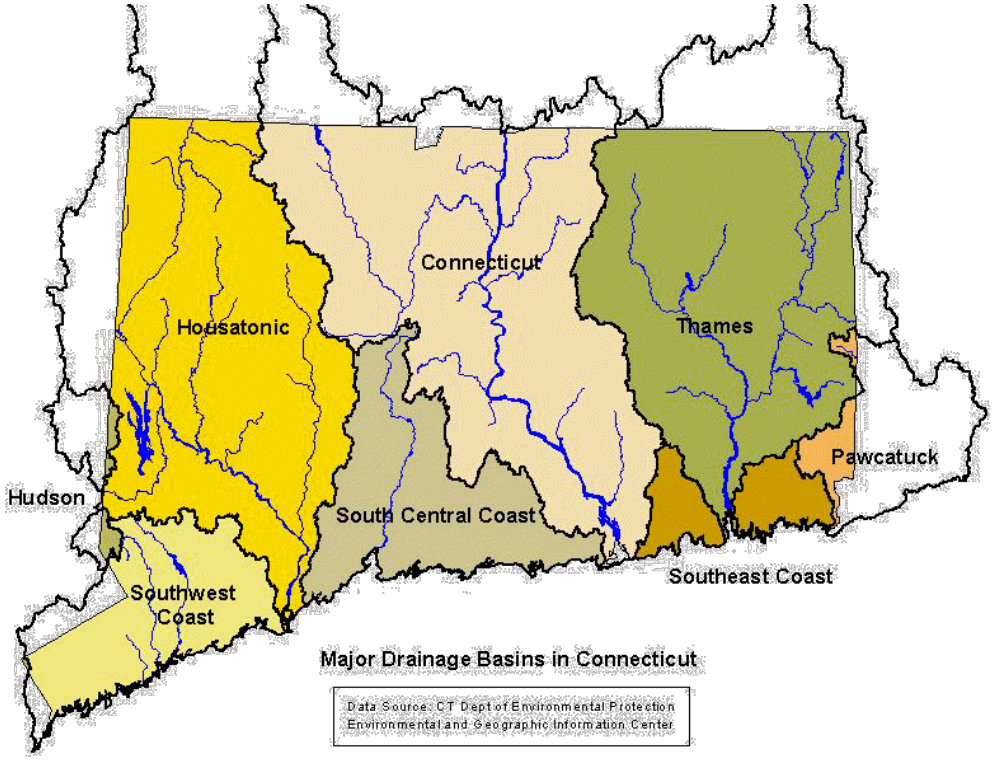


Figure 6. Image of the major drainage basins in Connecticut. The Quinnipiac River is located in the South Central Coast drainage basin.

Further evidence of historic sediment contamination comes from a study by Varekamp et al. (2003). Cores from the area showed a sudden increase in Hg concentration all around the same time, indicating a shift from background concentrations to contaminated concentration levels (Varekamp et al., 2003). Two peaks appear in these cores, one around 1900 and one around 1950-1970 (Varekamp et al., 2003). These two peaks correlate with pulses of Housatonic River sediment that were released into the Sound during unusually wet periods (Varekamp et al., 2003). The 1950-1970 elevated Hg levels are concluded to have been caused by major anthropogenic emissions (Varekamp et al., 2003). The dramatic decrease seen closer to the surface in the core is a result of reduced Hg emissions to the atmosphere (Varekamp et al., 2003).

Not only do these results show the explicit link between human activity (such as coal and fossil fuel combustion) and environmental conditions, they also underscore the potential for Hg from contaminated sediment beds in Connecticut rivers to be released during high flow events. These results have important implications for periods of high rainfall. Not only do high flow events mobilize contaminated sediment, but they also tend to induce higher rates of atmospheric deposition (Nadim et al., 2001; Varekamp et al., 2003). As Varekamp et al. (2003) affirm, even as active Hg loading to watersheds and direct inputs to the sound decrease as a result of new environmental legislation, "the coastal zone will still receive strongly Hg contaminated sediments from the Housatonic River watershed and the Danbury sediment source."

The Quinnipiac River system is another area that has experienced historical point-source Hg loading. In the case of the Quinnipiac River, and specifically the Wharton Brook watershed, elevated Hg levels stem from a silver plating factory located on Wharton Brook (Clark and Benoit, 2009b). While the contribution of freshwater from the Quinnipiac River to LIS is small (<1%), the mean MeHg contribution (dissolved and particulate = 2.5±0.5 pM) from the river was elevated above the Connecticut, Thames, and Housatonic Rivers (Balcom et al., 2004). This study reiterates the conclusion of Balcom et al. (2004), that the primary source of Hg to rivers and LIS is the erosion and disruption of Hg contaminated sediments and tributary loading (Clark and Benoit, 2009b). In addition, this reservoir makes available a hazardous supply of Hg into the future, even as steps are taken to reduce atmospheric Hg fluxes (Varekamp et al., 2003). Again, this means that future sediment-

aided transport of Hg into the coastal zone and faunal contamination from Hg will occur into the future as long as the supply lasts.

It is also important to note that Hg is mobilized in LIS and emitted as Hg^0 back into the atmosphere. It is estimated that 35% of the total inputs into LIS is evaded, or released back to the atmosphere, from the Sound making this coastal system an important part of the geochemical cycling of Hg (Rolfhus and Fitzgerald, 2001). To put the releases from LIS in perspective, over three times the amount of direct deposition to the sound is said to be exported (Rolfhus and Fitzgerald, 2001). This corresponds to the estimates from Balcom et al. (2004) that approximately 400 ± 130 moles $year^{-1}$ are volatized from the sound, and 130 ± 40 moles $year^{-1}$ are a result of direct deposition.

Overall, these studies indicate the unique importance of historical point-source loading and riverine transport of Hg to LIS. The potential to manage these systems include dredging or flood control measures to make sure sediment is not perturbed. However, not all the Hg loading from riverine inputs can be associated with historical, sediment-bound sources. Balcom et al. (2004) conclude their analysis of Hg in LIS with a discussion on the importance of atmospheric deposition to watersheds and subsequent transport to the coastal area. They note that while direct atmospheric inputs to the Sound are a minor component of overall Hg loading (around 11%, see Figure 3), watershed export of initially deposited atmospheric Hg may explain 60-75% (around 680 mol $year^{-1}$) of total riverine Hg inputs to LIS (Balcom et al., 2004). These studies indicate that other rivers, though their freshwater inputs into the sound may be less significant, are a noteworthy source of Hg for LIS. This information provides evidence that watershed-by-watershed analysis of Hg would be the most accurate and comprehensive method for estimating Hg loading to both marine and freshwater systems in CT.

5.0 Mercury in Connecticut's Freshwater Systems

5.1 Advisories and Management

In Connecticut, 2,259[5] lakes, ponds and reservoirs and 5,376 miles of rivers and streams are impaired primarily by atmospheric deposition of Hg (NEIWPCC, 2007). As the CT 2014 Integrated Water Quality Report declares, "All freshwaters of the State have a fish consumption advisory and addressed by a statewide limited consumption advisory for all freshwater fish, except trout, due to atmospheric deposition of mercury" (CTDEEP). Fish consumption advisories are issued by the Connecticut Department of Public Health based on fish tissue contaminant data (CTDEEP, 2014). This data originates from only two studies of the mercury concentration in fish from Connecticut rivers and lakes. The first assessment (Neumann, 1996), conducted on data collected from 1995-1996, resulted in the first statewide advisory being put in place. The follow-up study (Vokoun and Perkins, 2008) found sufficient MeHg concentrations in fish around the state to continue the advisory.

5.2 Review of Connecticut's Hg Monitoring Reports

At the time of the Preliminary Assessment of Total Mercury Concentration in Connecticut (Neumann, 1996), there was limited knowledge about the level of Hg in fish in Connecticut lakes. To date, the only assessment in freshwater systems occurred between 1988 and 1995, when the Department of Environmental Protection and the Department of Public Health did fish monitoring in twelve water bodies. In 1992 and 1993, testing of Hg levels in fish in Connecticut lakes was done as a part of an international mercury monitoring survey. As a result of these monitoring efforts, a fish consumption advisory was established in one Connecticut lake.

The study by Neumann et al. (1996) surveyed levels of mercury in fish tissues from sixty-one lakes and the Connecticut River. Neumann et al. (1996) focused primarily on testing largemouth bass because of its status as a top predator and its popularity among anglers in the state. A lesser focus was placed on testing Hg concentrations in smallmouth bass, bluegills, and yellow perch, which are all popular panfish and occupy a lower trophic

[5] CTDEEP, 2005, Connecticut Comprehensive AMbient Water Quality Monitoring Strategy, *in* Connecticut Department of Environmental Protection, B. o. W. M., ed.: Hartford, CT. reports that there are 2,267 lakes in Connecticut.

level than largemouth bass. In total, the study analyzed a total of 664 fish of 8 species. In addition to fish samples, surficial sediment samples and basic water quality parameters (pH, conductivity, alkalinity, magnesium, calcium, nitrate, nitrite, total dissolved nitrogen, dissolved inorganic phosphorus, particulate phosphorus, total dissolved phosphorus, total suspended solids, temperature, dissolved oxygen, redox potential, and secchi depth) were measured. EPA analytical methods were used on sediment and fish samples.

The data from the study confirmed that Hg concentration increased with the fish species' trophic status. The study also found statistically significant ($p < 0.02$) regional differences in the mean adjusted Hg concentrations of largemouth bass in the state. Mercury concentrations in fish were found to be higher in the southeast region of Connecticut compared to the northwest, southwest, and central lowlands. Regional differences in the pH of lakes were also observed. The southeast region of the state had significantly lower pH than lakes in the northwest, southwest, or central lowlands. However, there was no statistically significant ($p = 0.19$) regional relationship among surficial sediment mercury concentrations. In addition, no significant relationship between sediment Hg concentrations and fish tissue concentrations were found. However, a statistically significant, though not highly correlated ($r = 0.25$, $P<0.001$), relationship between largemouth bass Hg concentration and lake pH was observed. The relationship observed between pH and Hg levels in largemouth bass was an inverse relationship, with largemouth bass concentrations declining as the pH of lakes increased. This relationship highlights the importance of collecting information about water quality as a way of predicting fish tissue concentrations.

The initial report (Neumann et al., 1998) outlines eight recommendations for further study and monitoring efforts. These recommendations are quoted below:

1. Additional monitoring of mercury concentrations in other top-level predators.
2. Determining seasonal trends in fish mercury levels.
3. Quantifying rates of mercury biomagnification among trophic levels.
4. Intensive study of the factors affecting bioavailability in lakes

5. Quantify emissions from specific sources in Connecticut believed to have significant air emissions of mercury.

6. Assess the spatial and seasonal distribution of ambient atmospheric mercury concentration and deposition in Connecticut.

7. Develop a comprehensive model to determine the proportion of mercury deposition from local and regional sources, and to use this as a tool to predict and quantify the effects of processes affecting mercury strategies.

8. Work in progress: investigate further the relationship between fish mercury concentrations in largemouth bass and chemical and physical characteristics of Connecticut lakes.

These trends are explored further in a follow-up report entitled "Relationships Between Large Mouth Bass Mercury Levels and Environmental Characteristics of Connecticut Lakes" published in February 1997 (Hanten Jr et al.). The objectives of this study fall in line with the eighth recommendation of the preliminary assessment: (1) to determine the relationship between mercury concentrations in largemouth bass and environmental characteristics (both chemical and physical) of Connecticut lakes; and (2) to examine environmental characteristics of lakes on a regional scale that may help understand observed regional differences in largemouth bass mercury concentrations" (Hanten Jr et al., 1997). Data from Neumann (1996) was used for this report.

Table 4

Species	**Mean Concentration ug/g wet**	**Max Concentration ug/g wet**	**Source**
Largemouth Bass	0.51	2.65	Neumann, 1996
Largemouth Bass	0.433	1.773	Vokoun & Perkins, 2008

The second monitoring report on the contamination levels of fish tissues in Connecticut was conducted a decade after Neumann (1996). The report, co-authored by J.C. Vokoun and C.R. Perkins (2008), had two main objectives:

"1) update the statewide database on mercury levels in fish tissue

2) compare data with the first assessment conducted in 1995 by sampling many of the same sites." (Vokoun and Perkins, 2008)

The report was intended to provide basic survey information about the concentrations of Hg in fish from Connecticut lakes in order to "inform future discussions regarding modification of the current consumption advisory" (Vokoun and Perkins, 2008). The study analyzed a total of 492 largemouth bass in 51 lakes throughout the state. One of the shortcomings of this study in regards to the recommendations of the Neumann et al. (1996) is that the study only sampled largemouth bass**.** Neumann et al (1996) suggested that other top-level predators be sampled. In addition, in order to fulfill the goal to protect human health, fish that anglers are actually consuming should be targeted for sampling.

Overall, the analysis found that mean Hg concentrations in largemouth bass from Connecticut lakes was significantly lower in the 2005-2006 sampling period than reported in 1995. The authors cautioned that although the concentrations were substantially lower than the decade prior, contamination levels still commonly exceeded threshold levels (0.50 µg/g)[6] and therefore the fish consumption advisory could not be lifted as a result of their findings. They were optimistic that if frequent[7] monitoring continued and it appeared that concentrations kept falling that "the removal of a statewide consumption advisory seems plausible" (Vokoun and Perkins, 2008).

6.0 Monitoring and Management Programs

Concerns over Hg contamination in northeast North America have led to policies that aim to regulate and reduce Hg emissions. Here I present a timeline of major actions taken in Connecticut and New England to reduce local and regional emissions of Hg and better understand its fate in the environment.

In June 1997, the Conference of the New England Governors and Eastern Canadian Premiers, a collaborative organization of the governors of the six New England states and the premiers of the five Eastern Canadian provinces developed a regional Mercury Action Plan (MAP). The plan, finalized in 1998, was formed on the premise that "aggressive and concerted actions are needed to reduce potential health risks attributable to Hg exposures and to expand scientific information on Hg sources, controls and environmental impacts"

[6] It is unclear what 'threshold' Vokoun & Perkins (2008) are making reference to.
[7] Vokoun and Perkins (2008) recommend continuing to monitor at a minimum of every ten years.

(Governors and Premiers, 1998). It was intended to "serve as a first step toward eliminating fish consumption advisories in the Northeast states"(NEIWPCC, 2007).

The Northeast Regional Total Daily Maximum Load (TMDL) was initially established in 1997, with an update in 2007. Total Daily Maximum Load analyses outline the maximum amount of a pollutant that a water body can be subjected to in order to avoid adverse impacts to fish, wildlife, recreation, and other uses, such as fish consumption. The Northeast TMDL attempts to meet the biological water quality standards of 0.3 ppm in fish tissue set by the US EPA. The three phases of the Northeast TMDL are listed below:

> "Phase I, from 1998 to 2003, sets a goal of 50 percent reduction, from in-region and out-of-region sources, from the 1998 baseline. With in-region reductions of 1,549 kg/yr achieved as of 2002, the in-region reduction goal has been exceeded.
>
> Phase II, from 2003 to 2010, sets a goal of 75 percent reduction. This leaves 20 kg/yr for in-region reductions necessary to meet this target. In 2010, mercury emissions, deposition, and fish tissue concentration data will be re-evaluated in order to assess progress and set a timeline and goal for
>
> Phase III to make remaining necessary reductions to meet water quality standards. Not enough data are currently available to accurately assess reductions achieved by out-of-region sources" (NEIWPCC, 2007).

Critical to the removal of fish widespread fish consumption advisories in Connecticut and the Northeast is the reduction of mercury emissions. Regional Hg emissions dropped by 70% between 1998 and 2002 as a result of the Northeast states' commitment to reducing in-state sources of Hg (NEIWPCC, 2007). Legislation addressing the sale and disposal of mercury-containing products, emissions controls on coal-fired power plants, and installation of dental amalgam separators will continue to help states reduce Hg emissions (NEIWPCC, 2007). As the atmospheric deposition numbers begin to fall, regular data on the concentrations of target fish need to be collected. The second state-wide assessment of Hg in fish tissues (Vokoun and Perkins, 2008) serves as potential evidence that these reductions in Hg emissions are having positive affects on the fish tissue levels in freshwater fish. However, further study needs to occur in order to establish long-term trends and directly assess progress.

Applied to the northeastern United States, results of the Regional Lagrarian Model of Air Pollution (RELMAP) suggest that approximately 47 percent of deposition in the Northeast originates from within the area, 30 percent is attributable to sources outside the area, and 23 percent arises from the global atmospheric reservoir (NESCAUM, 1998). Therefore, reducing in-region emission sources of Hg is of great importance. In Connecticut, legislative action has been taken to reduce in-state mercury consumption and emissions. While time lags between decreases in mercury emissions and deposition and subsequent reductions in Hg levels in fish are on the scale of decades have been predicted (Driscoll et al., 2007; Knightes et al., 2009), major reductions in emissions locally are bound to have more immediate, positive effects on the pollution of aquatic systems.

7.0 Fish Consumption Advisories

All of the New England states, as well as New York and New Jersey, have issued health advisories that recommend restrictions on the consumption of fish from fresh water bodies based on measurements showing elevated Hg concentrations in freshwater fish (Graham et al., 2007). Massachusetts has a statewide advisory but only lists waters that have been assessed as impaired waters (NEIWPCC, 2007). New York State does not have a state-wide advisory, but instead lists a number of larger watersheds as impaired for the consumption of fish (NEIWPCC, 2007). In Connecticut, atmospheric deposition of Hg is used as a basis for listing all waters in the state as impaired for the consumption of fish (NEIWPCC, 2007). As mentioned previously, the fish consumption advisory affecting Connecticut is based only on two comprehensive studies published a decade apart (Neumann et al., 1996 and Vokoun and Perkins, 2008). The strategies of Massachusetts and New York, Connecticut's neighbors to the north and west, respectively, offer appropriate opportunities for contrast in how mercury contamination is monitored and addressed.

7.1 Connecticut, Massachusetts, New York

The Massachusetts Department of Environmental Protection has established a network of lakes that are subject to long-term monitoring of two fish species (Graham et al., 2007). Historically, Massachusetts has taken a stronger initiative than Connecticut in addressing the problem of Hg in its freshwater bodies. The state began sampling 189 fresh

water bodies as early as 1983 "as part of a statewide program to identify freshwater fish populations with concentrations of various chemicals, including Hg, that could be harmful to humans" (DEP, 2003). The goals of the 2003 MA DEP report on the levels of Hg included:

> "1) determine if human health fish consumption advisories for mercury were necessary;
>
> 2) examine the relationships between levels of fish tissue total mercury concentrations in the study area and other regions of the State and country; and
>
> 3) examine the possible contribution of local sources of atmospheric mercury to the local fish mercury concentrations" (DEP, 2003)."

As a result of this study, 23 of 24 lakes where largemouth bass were successfully caught were placed under consumption advisories (DEP, 2003). Due to funding and sampling constraints, only placing lakes that are sampled by officials and deemed unsafe under consumption advisories may introduce a higher risk to anglers in Massachusetts. However, a more limited advisory system may be more effective than a blanket advisory for the whole state because it is likely that if only a few advisories exist, fishermen would be more aware of the advisory, and therefore avoid consumption of fish from that source.

In New York State, the New York State Department of Environmental Conservation (NYSDEC) has monitored Hg concentrations in fish since the late 1960's (Simonin et al., 2008). A Statewide Toxic Substances Monitoring Program ran from 1976 until 1993. Since that time, fish monitoring has occurred for research purposes or for specific projects, but no widespread effort has continued (Simonin et al., 2008). One of these efforts was a four-year project initiated in 2003 by the NYSDEC with funding from the New York State Energy Research and Development Authority (NYSERDA). The goals of the project included updating fish tissue concentration data for lakes that had been monitored previously as well as beginning to monitor lakes that had not yet been surveyed (Simonin et al., 2008).

While the study did not intend to "seek to evaluate the rationale or basis for fish consumption advice," the data gathered was provided to the New York State Department of Health (NYSDOH) to assess the necessity of fish consumption advisories for lakes in the state (Simonin et al., 2008). Like in Connecticut, the New York States Department of Health "takes the lead in deriving fish advisories" for the state (Simonin et al., 2008). The report by

Simonin et al. (2008) also developed predictive models, taking lake characteristics in order to "help resource managers identify lakes and fish that may be high in mercury" (p. S-3). The study concluded that the total Hg concentrations in 62% (1,630 fish) of the samples exceeded the U.S. EPA's water quality criterion for MeHg in fish of 300 ng/g. As a result, NYSDOH issued a total of 50 new advisories for specific New York State lakes (Simonin et al., 2008). What is notable about this approach is that instead of providing a blanket advisory for the entire state, the advisories were placed on a lake-by-lake or regional basis. At the end of the report the authors express their hope that this study and others like it that strive for a better understanding of MeHg concentrations in the environment "will lead to policy decisions resulting in lower Hg concentrations in fish and wildlife and fewer numbers of human fish consumption advisories" (Simonin et al., 2008).

7.2 Socioeconomic Consequences of Fish Consumption Advisories

Significant negative health impacts have been felt globally as a result of MeHg consumption. With an assumed Hg emission increase of about 25% between 2005 and 2020, the global assessment for societal damages based solely on loss of IQ caused by the ingestion of MeHg is estimated to be approximately $3.7 billion (2005 dollars) in 2020 (Sundseth et al., 2010). In the case of reduced emissions from the status quo of about 50-60% between 2005 and 2020, the annual benefits of Hg reductions in 2020 are $1.8-2.2 billion (2005 dollars) (Sundseth et al., 2010). An analysis of the prospect of a fish consumption advisory for the Chesapeake Bay estimates annual health benefits to be approximately $14 million (Jakus and Krupnick, 2002). No study of the economic benefits for the establishment of fish advisories in Connecticut or Long Island Sound has been completed.

Fish consumption advisories are the most common way for protecting the public from health dangers associated with MeHg in fish. However, analysis of the effects of fish consumption advisories need to take into consideration that the behavioral adjustments made by anglers may range anywhere from "ignoring the advisory to altogether ceasing trips to the affected water body" (Jakus and Krupnick, 2002). While in the commercial sector the cost of advisories is based on market demand and supply, and shifts in these values can be used to measure market value lost as a result of contamination, impacts on

recreational fishing extend further (Swain et al., 2007). In their Mercury Action Plan (MAP), the NEG-ECP state that beyond the potential negative health effects due to Hg contamination, New England could be subject to "important economic consequences, including reducing the recreational and commercial value of fisheries resources across the region" (Governors and Premiers, 1998). An important aspect of the non-health-related benefits that has not been studied are "the nonuse values associated with benefits to future generations" (Swain et al., 2007). Mercury contamination and the advisories associated with it are likely to affect the quality of current recreational fishing experiences as well as decrease future recreational use in current and future generations (Swain et al., 2007).

Because of these negative socioeconomic consequences, Swain et al. (2007) note that "Fish consumption advisories are considered by many policy makers to be an unfortunate and, hopefully, interim public health necessity." Consumption advisories, though they provide benefits in avoiding health risks due to MeHg consumption, need to be looked at in a critical light.

Swain et al. (2007) make note of an important tension: municipalities are responsible for communicating to people that they should avoid eating highly contaminated fish for the potentially negative health consequences, but fish have a significant nutritional value and associated health benefits. In the past, risk assessments and consumption advisories related to MeHg in fish and shellfish have been criticized for failing to account for the health benefits of fish consumption (Egeland and Middaugh, 1997). The US EPA and FDA have taken steps to remedy this tension.

In 2001 an advisory by the FDA was issued addressed specifically at women who are pregnant or likely to become pregnant. It suggested consumers avoid eating predatory fish and to limit consumption of shellfish, canned tuna and small ocean fish to two or three servings per week (USEPA, 2001). As a result of this advisory, a study conducted in Massachusetts in the years before (1999-2000) and after (2001-2002) observed diminished consumption of all fish (Oken et al., 2003). While the study could not quantify the public health implications of these reductions, it cautioned that a reduction in fish intake could cause more harm than good (Oken et al., 2003). Oken et al. (2003) acknowledge the important health benefits fish provide to people, especially pregnant women, and declared, "it is possible that these benefits could outweigh the harm from

mercury exposure." In 2004 the US EPA and FDA issued a joint statement about Hg in fish and shellfish that emphasized the important nutritional benefits of these goods. Even though the EPA and FDA (2004) warn that "nearly all fish and shellfish contain traces of mercury," they also emphasize that fish and shellfish are part of a healthy diet because they contain "high-quality protein and other essential nutrients, are low in saturated fat, and contain omega-3 fatty acids." After the initial revision in March 2004, in June 2014 they issued draft recommendations on fish consumption for pregnant women and parents (USEPA, 2014).

Swain et al. (2007) claim that policy makers consider fish consumption advisories as 'interim,' with the expectation that measures will be taken in order to reduce fish tissue MeHg concentrations (Swain et al., 2007). This expectation applies to lawmakers in the Northeast. Because Hg pollution in the Northeast is primarily a result of atmospheric deposition, "decreasing its introduction into the environment by limiting mercury emissions to the atmosphere should permit an eventual lifting of the fish consumption warnings." (Graham et al., 2007).

While fish consumption advisories may be adequate for protecting the general population, they may not help the population that is most at risk for experiencing adverse health effects from MeHg consumption. Subsistence fishing, defined by Swain et al. (2007) as "fishing primarily for local distribution and consumption," is a significant pathway of exposure to MeHg in some populations. A significant part of the recreational value of saltwater fishing is dependent on consuming the fish the anglers themselves catch (Rae and Graham, 2004). Being unaware of or failing to conform to posted mercury advisories may result in the consumption of fish with high levels of MeHg and consequently result in health risks (Rae and Graham, 2004). The USEPA and FDA (2004) assert that individuals can "cut back for the next week or two" if they fear they have eaten a lot of fish in a week. While this may be easy for the average population, subsitence fishers do not have the same luxury of getting their food from other sources. In addition, the EPA (2004) advises consumers to check local advisories to learn more about the safety of fish caught in local lakes, rivers, and coastal areas.

A study done on people who fished in the catchment basins of Jamaica Bay Wildlife Refuge in New York City found that only 19% of fishermen believed the fish were

contaminated despite state warnings against about consuming fish in that area (Burger et al., 1993). The authors also found that the fisherman were eating the fish and feeding them to their families on a regular basis. They concluded that most people were unaware or ignoring the health advisories posted by the state because "the fishing situation is familiar, voluntary, pleasurable" and has not resulted in immediate illness. In addition, most of the fishermen believed that they were able to tell when the fish were spoiled, that they could tell from smell and appearance if the fish was good enough to eat.

In Connecticut, protecting subsistence populations is of great importance, especially for low-income individuals. A quote from Dr. Mark Mitchell, the co-chair of the Environmental Health Task force for the National Medical Association Published in a Connecticut Post news article states, "When I asked Latinos, African Americans, Asians -- they all said they ate the fish. Nobody threw the fish back" (Barger, 2013). Mitchell went on to indicate that in his experience, most of the subsistence fisherman were unaware that they required to have a fishing license in order to fish in public waters in Connecticut (Barger, 2013). This lack of awareness is notable because when individuals receive their fishing licenses they are also informed about the state Department of Public Health advisories regarding fish caught in Connecticut waters (Barger, 2013). The department does have a person working to distribute information about fish-consumption advisories to physicians, tackle shop owners, and town halls in order to educate low-income members of the population (Barger, 2013). However, the effort of the health department is restricted by the lack of adequate resources. Brian Toal, an epidemiologist with the state DPH said, "We probably don't do as much as we could" in regards to ensuring that low-income populations are adequately informed about the dangers of consuming fish with high concentrations of Hg (Barger, 2013). This underscores that advisories for the consumption of fish in Connecticut do not protect the populations that are most at risk from contaminants in fish. This lack of protection for low-income and subsistence fishermen populations may ultimately result in increased costs due to health related issues as well as increased loss of IQ and therefore productivity for Connecticut.

8.0 Recommendations

As a result of my analysis, I make recommendations about how the fish advisory decisions should be implemented. The following recommendations address the design of monitoring programs and data collection and future research areas as well as how to make fish consumption advisories sufficiently protective of human health without being detrimental to socioeconomic factors in Connecticut.

1) *Improve sampling procedures*
    a) Sample fish in a way that captures seasonal trends in fish mercury levels (Neumann, 1996) and captures the effects of the reduction of mercury emissions in Connecticut on shorter timescales in urban areas, and longer timescales across the state. While frequent monitoring is more expensive, it keep fish consumption advisories from inhibiting fish consumption and economic opportunities in Connecticut..
    b) Better information is needed on the variability of fish MeHg concentrations (Swain et al., 2007), actual fish consumption patterns of various subpopulations and the toxic effects of low-level chronic exposure (NESCAUM, 1998). The fish species and fish sizes that are representative of actual fish consumption by all population groups, especially subsistence fishermen, should be taken into consideration when designing sampling programs (Lepak et al., 2009; Swain et al., 2007).
2) *Better monitoring and modeling* efforts
    a) Freshwater and coastal systems would be most effectively modeled on a watershed-by-watershed basis. Watershed models for predicting atmospheric deposition-to-fish level models exist and can be used to predict the effects of elevated local Hg emission and deposition rates affect local water bodies. In addition, because Connecticut has many areas with legacy Hg in sediment repositories, a watershed-scale analysis and advisory system would be able to capture sediment-bound sources of mercury as well as atmospheric deposition. In addition, smaller-scale analysis of mercury concentrations in fish would allow for the development of fish consumption advisories to be implemented more accurately.
3) *Evaluate outreach.* Once fish consumption advisories are implemented more frequent evaluation of how advisories are perceived by target audiences- both women of

childbearing age and fishermen. It is important to assess if they even heard about the consumption advisories. A study done on the Savannah River in Georgia and South Carolina found that only half of people had heard of the fish consumption advisories for the area (Burger and Waishwell, 2001). Consistent communication of monitoring results and localized information about which species of fish contain Hg levels above recommended limits.

4) *Restructure Connecticut's blanket fish consumption advisory.* While the simplicity of a blanket advisory may logistically make things easier for the state in terms of communication, it is likely that this type of advisory is inadequate for protecting subsistence populations and discourages recreational fishing activity in Connecticut. While women who are pregnant and may become pregnant are targeted for fish consumption advisories because of the heightened negative health consequences, subsistence fishermen and avid anglers are not. It is likely that subsistence fishermen are equally as susceptible to the negative health effects of MeHg exposure not for biological reasons but because Better communication of fish consumption advisories and an educational program targeted at reaching subsistence fishing populations would be effective at reducing risk.

9.0 Conclusion

Mercury as a contaminant is of particular importance because of its ubiquity in the environment, its toxic effects on the environment and human health, and the global transport potential of mercury in the atmosphere (Pacyna et al., 2006). Overall, understanding the relationship between MeHg concentrations in lakes and fish of various species is essential for issuing fish consumption advisories. Through better, more relevant monitoring programs, relationships between mercury emissions, mercury's cycling in the environment and the subsequent accumulation in freshwater and marine systems can be better understood. In the future, policy makers need to keep in mind the economic benefits that recreational fishing opportunities in the state could generate. While mercury is a persistent threat to human health and will likely not be removed as such in the next 50 years, significant steps can be taken to minimize the risk of mercury exposure to humans.

Acknowledgements

I would like to thank my advisor, Gabe Benoit, for his valuable insights, patient guidance and dedicated attention. I would also like to thank Troy Hill for his much-appreciated direction early on in this process. Brian Toal at the CT Department of Public Health as well as Chris Perkins and Nancy Balcom at the University of Connecticut provided necessary document accessibility. Additional thanks are extended to Dave Evans for academic flexibility and direction over the past four years. Lastly, a huge thanks to the entire geology department for an incredible four years.

References Cited

Balcom, P. H., Fitzgerald, W. F., Vandal, G. M., Lamborg, C. H., Rolfhus, K. R., Langer, C. S., and Hammerschmidt, C. R., 2004, Mercury sources and cycling in the Connecticut River and Long Island Sound: Marine Chemistry, v. 90, no. 1, p. 53-74.

Barger, T. S., 2013, Unhealthy mercury levels persist in fish, Connecticut Post.

Borum, D., Manibusan, M. K., Schoeny, R., and Winchester, E. L., 2001, Water quality criterion for the protection of human health: methylmercury, *in* USEPA, ed.: Washington, DC.

Burger, J., Staine, K., and Gochfeld, M., 1993, Fishing in contaminated waters: Knowledge and risk perception of hazards by fishermen in New York City: Journal of Toxicology and Environmental Health, v. 39, no. 1, p. 95-105.

Burger, J., and Waishwell, L., 2001, Are we reaching the target audience? Evaluation of a fish fact sheet: Science of The Total Environment, v. 277, no. 1–3, p. 77-86.

Canuel, R., Grosbois, S. B. d., Atikessé, L., Lucotte, M., Arp, P., Ritchie, C., Mergler, D., Chan, H. M., Amyot, M., and Anderson, R., 2006, New Evidence on Variations of Human Body Burden of Methylmercury from Fish Consumption: Environmental Health Perspectives, v. 114, no. 2, p. 302-306.

Chen, C. Y., Evers, D. C., Fleishman, B. J., Weiss, J., Mason, R. P., Serrell, N. A., Lambert, K. F., and Bank, M. S., 2008, Meeting report: methylmercury in marine ecosystems—from sources to seafood consumers.

Clark, H. F., and Benoit, G., 2009a, Current and historic mercury deposition to New Haven Harbor (CT, USA): Implications for industrial coastal environments: Science of The Total Environment, v. 407, no. 15, p. 4472-4479.

Clark, H. F., and Benoit, G., 2009b, Legacy sources of mercury in an urbanised watershed: Environmental Chemistry, v. 6, no. 3, p. 235-244.

CTDEEP, 2005, Connecticut Comprehensive AMbient Water Quality Monitoring Strategy, *in* Connecticut Department of Environmental Protection, B. o. W. M., ed.: Hartford, CT.

-, 2014, 2014 State of Connecticut Integrated Water Quality Report, *in* Protection, C. D. o. E., ed.: Hartford, CT.
DEP, M., 2003, Fish Mercury Levels In Northeastern Masachusetts Lakes, *in* DEP, M., ed.: Boston, MA.
Driscoll, C. T., Han, Y.-J., Chen, C. Y., Evers, D. C., Lambert, K. F., Holsen, T. M., Kamman, N. C., and Munson, R. K., 2007, Mercury contamination in forest and freshwater ecosystems in the northeastern United States: BioScience, v. 57, no. 1, p. 17-28.
Eckley, C. S., Branfireun, B., Diamond, M., Van Metre, P. C., and Heitmuller, F., 2008, Atmospheric mercury accumulation and washoff processes on impervious urban surfaces: Atmospheric Environment, v. 42, no. 32, p. 7429-7438.
Egeland, G. M., and Middaugh, J. P., 1997, Balancing Fish Consumption Benefits with Mercury Exposure: Science, v. 278, no. 5345, p. 1904-1905.
Evers, D., Mason, R., Kamman, N., Chen, C., Bogomolni, A., Taylor, D., Hammerschmidt, C., Jones, S., Burgess, N., Munney, K., and Parsons, K., 2008, Integrated Mercury Monitoring Program for Temperate Estuarine and Marine Ecosystems on the North American Atlantic Coast: EcoHealth, v. 5, no. 4, p. 426-441.
FDA, U. a., 2004, What You Need to Know About Mercury in Fish and Shellfish.
Fitzgerald, W. F., Lamborg, C. H., and Hammerschmidt, C. R., 2007, Marine biogeochemical cycling of mercury: Chemical Reviews, v. 107, no. 2, p. 641-662.
Ginsberg, G. R., Hari, 1996, Memorandum: Mercury in Fish Consumption.
GOLDOFF, B., VAREKAMP, J., and NEUPANE, A., MERCURY CONTAMINATION IN W-CONNECTICUT AND LONG ISLAND SOUND FROM HISTORIC HAT-MAKING SOURCES, *in* Proceedings 2006 Philadelphia Annual Meeting2006.
Governors, N. E., and Premiers, E. C., 1998, Mercury Action Plan, Volume 1998: Fredericton, Province of New Brunswick.
Graham, J., Miller, P., Savelli, E., and Woo, J., 2007, Modeling mercury in the Northeast United States, *in* (NESCAUM, N. S. f. C. A. U. M., ed.: Boston, MA.
Hammerschmidt, C. R., and Fitzgerald, W. F., 2006, Bioaccumulation and trophic transfer of methylmercury in Long Island Sound: Archives of Environmental Contamination and Toxicology, v. 51, no. 3, p. 416-424.
Hanten Jr, R. P., Neumann, R. M., Ward, S. M., Carley, R. J., Perkins, C. R., and Pirrie, R., 1997, Relationships between concentrations of mercury in largemouth bass and physical and chemical characteristics of Connecticut lakes.
Harris, H. H., Pickering, I. J., and George, G. N., 2003, The chemical form of mercury in fish: Science, v. 301, no. 5637, p. 1203-1203.
Harris, R., Murray, M. W., Saltman, T., Mason, R., Krabbenhoft, D. P., and Reash, R., 2007, Ecosystem responses to mercury contamination: Indicators of change, CRC Press.
Jakus, P., and Krupnick, A. J., 2002, The benefits and costs of fish consumption advisories for mercury, Resources for the Future.
Kamman, N., Burgess, N., Driscoll, C., Simonin, H., Goodale, W., Linehan, J., Estabrook, R., Hutcheson, M., Major, A., Scheuhammer, A., and Scruton, D., 2005, Mercury in Freshwater Fish of Northeast North America – A Geographic Perspective Based on Fish Tissue Monitoring Databases: Ecotoxicology, v. 14, no. 1-2, p. 163-180.
Kamman, N. C., and Engstrom, D. R., 2002, Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from 210 Pb dated sediment cores: Atmospheric Environment, v. 36, no. 10, p. 1599-1609.

Kidd, K., Clayden, M., and Jardine, T., 2012, Bioaccumulation and biomagnification of mercury through food webs: Environmental Chemistry and Toxicology of Mercur. G. Liu, Y. Cai and N. O'Driscoll, Wiley.

Knightes, C. D., Sunderland, E. M., Barber, M. C., Johnston, J. M., and Ambrose, R. B., 2009, Application of ecosystem-scale fate and bioaccumulation models to predict fish mercury response times to changes in atmospheric deposition: Environmental Toxicology and Chemistry, v. 28, no. 4, p. 881-893.

Lepak, J. M., Shayler, H. A., Kraft, C. E., and Knuth, B. A., 2009, Mercury Contamination in Sport Fish in the Northeastern United States: Considerations for Future Data Collection: BioScience, v. 59, no. 2, p. 174-181.

Mason, R. P., Fitzgerald, W. F., and Morel, F. M., 1994, The biogeochemical cycling of elemental mercury: anthropogenic influences: Geochimica et Cosmochimica Acta, v. 58, no. 15, p. 3191-3198.

Mason, R. P., Lawson, N. M., and Sullivan, K. A., 1997, Atmospheric deposition to the Chesapeake Bay watershed—regional and local sources: Atmospheric Environment, v. 31, no. 21, p. 3531-3540.

Mecray, E. L., and ten Brink, M. R. B., 2000, Contaminant distribution and accumulation in the surface sediments of Long Island Sound: Journal of Coastal Research, p. 575-590.

Mergler, D., Anderson, H. A., Chan, L. H. M., Mahaffey, K. R., Murray, M., Sakamoto, M., and Stern, A. H., 2007, Methylmercury exposure and health effects in humans: a worldwide concern: AMBIO: A Journal of the Human Environment, v. 36, no. 1, p. 3-11.

Morel, F. M. M., Kraepiel, A. M. L., and Amyot, M., 1998, The Chemical Cycle and Bioaccumulation of Mercury: Annual Review of Ecology and Systematics, v. 29, p. 543-566.

Nadim, F., Perkins, C., Liu, S., Carley, R. J., and Hoag, G. E., 2001, Long-term investigation of atmospheric mercury contamination in Connecticut: Chemosphere, v. 45, no. 6–7, p. 1033-1043.

NEIWPCC, 2007, Northeast Regional Mercury Total Maximum Daily Load, *in* Connecticut Department of Environmental Protection, M. D. o. E. P., Massachusetts Department of Environmental Protection, New Hampshire Department of Environmental Services, New York State Department of Environmental Conservation, Rhode Island Department of Environmental Management, Vermont Department of Environmental Conservation, New England Interstate Water Pollution Control Commission, ed.

NESCAUM, 1998, Atmospheric Mercury Emissions in the Northeastern States: Executive Summary.

Neumann, R. M., Carley, Robert J., Perkins, Christopher R., Pirrie, Robert, 1996, Preliminary Assessment of Total Mercury Concentrations in Fishes from Connecticut Water Bodies: Prepared for the Connecticut Department of Environmental Protection: University of Connecticut.

Neumann, R. M., and Ward, S. M., 1999, Bioaccumulation and Biomagnification of Mercury in Two Warmwater Fish Communities: Journal of Freshwater Ecology, v. 14, no. 4, p. 487-497.

Oken, E., Kleinman, K. P., Berland, W. E., Simon, S. R., Rich-Edwards, J. W., and Gillman, M. W., 2003, Decline in fish consumption among pregnant women after a national mercury advisory: Obstetrics & Gynecology, v. 102, no. 2, p. 346-351.

Pacyna, E. G., and Pacyna, J. M., 2002, Global Emission of Mercury from Anthropogenic Sources in 1995: Water, Air, and Soil Pollution, v. 137, no. 1-4, p. 149-165.
Pacyna, E. G., Pacyna, J. M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., and Panasiuk, D., 2006, Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020: Science of the Total Environment, v. 370, no. 1, p. 147-156.
Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R., Friedli, H., Leaner, J., Mason, R., Mukherjee, A., Stracher, G., and Streets, D., 2010, Global mercury emissions to the atmosphere from anthropogenic and natural sources: Atmospheric Chemistry and Physics, v. 10, no. 13, p. 5951-5964.
Rae, D., and Graham, L., 2004, Benefits of reducing mercury in saltwater ecosystems: A case study. Washington, DC, USA: US Environmental Protection Agency.
Renzoni, A., Zino, F., and Franchi, E., 1998, Mercury Levels along the Food Chain and Risk for Exposed Populations: Environmental Research, v. 77, no. 2, p. 68-72.
Rolfhus, K. R., and Fitzgerald, W. F., 2001, The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY: Geochimica et Cosmochimica Acta, v. 65, no. 3, p. 407-418.
Rudd, J. W., 1995, Sources of methyl mercury to freshwater ecosystems: a review: Water, Air, and Soil Pollution, v. 80, no. 1-4, p. 697-713.
Scheuhammer, A. M., Meyer, M. W., Sandheinrich, M. B., and Murray, M. W., 2007, Effects of environmental methylmercury on the health of wild birds, mammals, and fish: AMBIO: A Journal of the Human Environment, v. 36, no. 1, p. 12-19.
Simonin, H., Loukmas, J., Skinner, L., and Roy, K., 2008, Strategic Monitoring of Mercury in New York State Fish: New York State Department of Environmental Protection.
Smith, C. M., and Trip, L. J., 2005, Mercury policy and science in northeastern North America: The mercury action plan of the New England governors and eastern Canadian premiers: Ecotoxicology, v. 14, no. 1-2, p. 19-35.
Sundseth, K., Pacyna, J. M., Pacyna, E. G., Munthe, J., Belhaj, M., and Astrom, S., 2010, Economic benefits from decreased mercury emissions: Projections for 2020: Journal of Cleaner Production, v. 18, no. 4, p. 386-394.
Swain, E. B., Jakus, P. M., Rice, G., Lupi, F., Maxson, P. A., Pacyna, J. M., Penn, A., Spiegel, S. J., and Veiga, M. M., 2007, Socioeconomic consequences of mercury use and pollution: AMBIO: A Journal of the Human Environment, v. 36, no. 1, p. 45-61.
Ullrich, S. M., Tanton, T. W., and Abdrashitova, S. A., 2001, Mercury in the aquatic environment: a review of factors affecting methylation: Critical Reviews in Environmental Science and Technology, v. 31, no. 3, p. 241-293.
USEPA, 1997, Mercury Study Report to Congress, *in* Agency, U. S. E. P., ed., Volume 2.
USEPA, U., 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, Washington: FDA.
-, 2014, Fish: What Pregnant Women and Parents Should Know.
VanArsdale, A., Weiss, J., Keeler, G., Miller, E., Boulet, G., Brulotte, R., and Poissant, L., 2005, Patterns of mercury deposition and concentration in northeastern North America (1996–2002): Ecotoxicology, v. 14, no. 1-2, p. 37-52.

Varekamp, J., Kreulen, B., Buchholtz, M., and Mecray, E., 2003, Mercury contamination chronologies from Connecticut wetlands and Long Island Sound sediments: Environmental Geology, v. 43, no. 3, p. 268-282.
Varekamp, J., ten Brink, M. B., Mecray, E., and Kreulen, B., 2000, Mercury in long island sound sediments: Journal of coastal research, p. 613-626.
Vokoun, J. C., and Perkins, C. R., 2008, SECOND STATEWIDE ASSESSMENT OF MERCURY CONTAMINATION IN FISH TISSUE FROM CONNECTICUT LAKES (2005-2006).