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Investigation of Mercury Use, Release, Deposition, and Exposures in the Tampa Bay Area

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Investigation of Mercury Use, Release, Deposition, and Exposures in the Tampa Bay Area

by

Ryan Michael

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Environmental and Occupational Health
College of Public Health
University of South Florida

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Acknowledgments

The journey to my Ph.D. has been an arduous yet rewarding one. I started this endeavor with great uncertainty about my ability to accomplish such a significant undertaking, and more importantly, greater uncertainty about my ability to shape and determine the trajectory of my life. I stumbled upon three important revelations that have allowed me to overcome these debilitating uncertainties. The first is that it is okay to start over at any time, and make any day a new beginning. If you have been a little bit industrious you never have to start from the bottom. The second is about time. I have had the (mis?)fortune to be awake watching multiple successive days go by in slow increments and have come to the realization that I have been placing importance in days when I should have been treasuring each hour. Time is time, and that block that I constantly mentally dedicate to a particular task only exists when I have just completed that task. The third is about people. I have been extremely lucky to have my life touched by some unbelievably awesome people. These interactions have helped shaped my view of the world, way I interact in it, and the successes I have encountered thus far, and I am forever grateful. The remainder of this missive is dedicated to acknowledging and celebrating these people.

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Abstract

I investigate the links between mercury use, release, deposition, and population exposure in Tampa Bay, with the focus of identifying levers for reducing population mercury exposures. To achieve this, I investigated the trends in mercury use and release by products and processes in the Tampa Bay area using a Material Flow Analysis. Analysis of USEPA National Emissions Inventory data over time (1999 - 2008) identified relevant air source emission categories, and explored and compared state and regional trends in mercury emissions. To understand source contributions to wet deposited mercury in the Tampa Bay area, I analyzed trends in mercury deposition data from the National Atmospheric Deposition Program, Mercury Deposition Network, and the 2001 Bay Regional Atmospheric Chemistry Experiment. I also collected wet deposition samples for mercury and trace metals in the Tampa Bay area during a 6-month campaign at a site at the University of South Florida (USF) campus. Samples were analyzed using Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) for mercury, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for trace metals analysis. Concentration data were analyzed for source contributions using HYSPLIT back-trajectory meteorology-based modeling to assess source locations, and the Positive Matrix Factorization (PMF) statistical receptor model to apportion the deposition data by source type. To explore the factors influencing fish consumption behaviors of the local angler population, I analyzed population surveys collected previously from fisher-folks along the Hillsborough River, in Hillsborough County, Florida. Results from the mercury inventory indicate that mercury releases from industrial sources and dental facilities were the most important sources of mercury to the Tampa Bay area. Furthermore, the solid-waste pool was the most important direct sink in the domain, with air emissions an important indirect sink.

Emissions inventory data indicated that coal-fired power plants were the largest contributors of mercury emissions in the Tampa Bay area. Medical and municipal waste incineration also accounted for significant fractions of total mercury releases to the domain. Emissions from sources in Hillsborough County accounted for a significant portion of mercury emissions in the region and state. Measurement data indicated that event mercury concentration was only very weakly correlated with event precipitation depth, with both studies showing agreement with this phenomenon. Back-trajectory simulations reveal that high mercury concentration events were often from air masses with recent trajectories over Florida land (6 and 24 hr), and with previous high precipitation depth events over the trajectory in the long term (72 hr). The statistical PMF results indicate the importance of coal burning power plant emissions, medical and municipal waste incineration, and agrochemicals on mercury in wet deposition in the Tampa Bay area. Changes were observed between the 2001 and 2012 data, including greater mercury concentrations in 2012, and the removal of medical waste incineration as a mercury source in the 2012 model results. Together with local emissions inventory data, these results suggest that sources local to the Tampa Bay area and in Florida likely contribute substantially to mercury deposition in the region. Finally, population survey data suggests that mercury exposure risks are poorly understood by the fishing population in Hillsborough County. Taken together, these results suggest that policies targeting mercury emissions control, particurlarly for coal-fired power plants and municipal waste processing, and fish consumption education may be instrumental to the protection of susceptible populations.

1. Introduction

1.1. Problem statement

Mercury is a pervasive global pollutant with debilitating health outcomes, and an exposure pathway that transcends social and economic boundaries. Even as the scope and variety of scientific inquiry continues to broaden our understanding of this phenomenon, mercury contamination continues to be a widespread and significant threat to ecosystem and human welfare.

Although mercury exists as many stable complexes, organic mercury species present the greatest risk to human and ecosystem health [Grandjean et al., 1994; Mergler et al., 2007; Clarkson, 1990]. Mercury is the only metal that bioaccumulates, which occurs through its most toxic form, methylmercury. Methylation of mercury species occurs in aquatic environments via biologically mediated reactions occurring in sediments and water columns [Jensen and Jernelov, 1969]. Once absorbed by aquatic fauna, methylmercury is associated with the amino acid component of the muscle tissue, and thus cannot be removed by food preparation or cooking techniques [Morgan et al., 1997]. Fish consumption is therefore a leading route to mercury exposure for vulnerable populations such as women of child-bearing age, the developing fetus, nursing mothers, infants and young children, subsistence fisher folk, and those consuming high seafood diets [Tollefson and Cordle, 1986]. These properties of the metal, combined with its unique exposure route, make mercury pollution an insidious, prevalent, and challenging environmental problem.

Numerous studies of risk assessments for methylmercury by local, regional and international organizations conclude that the developing brain is the main target for methylmercury toxicity [UNEP, 2002; National Research Council, 2000; JECFA, 2004]. Evidence from historical poisoning outbreaks, such as episodes in Japan and Iraq, clearly demonstrates the severe health outcomes in fetal brain development as a result of maternal exposures [D'ltri and D'ltri, 1978; Harada, 1995; Grandjean et al., 2005]. Adverse health effects include mental retardation, cerebellar ataxia, primitive reflexes, dysarthria, and hyperkinesias being observed in infants [Gilbert and Grant-Webster, 1995; Harada, 1995]. More recently, independent prospective cohort studies have associated maternal mercury exposure with decrements in attention, language, verbal memory, motor speed, and visuospatial function in children greater than 7 years after follow-up [Grandjean et al., 1997, 2005; Lindqvist et al., 1991].

Atmospheric deposition processes, specifically wet deposition, are central to the entry of mercury into terrestrial and aquatic ecosystems; Sorenson et al. [1990] estimates that 75% of mercury input to lakes are from direct atmospheric deposition to the surface water. Wet deposition of mercury occurs due to the scavenging of soluble mercury species by liquid and solid phase cloud hydrometeors and their eventual fallout of the atmosphere as rain, hail, snow etc. This process increases the mercury concentrations in soil, water, and vegetation due to direct deposition. Subsequently, efforts to reduce atmospheric mercury deposition have focused on understanding the contributions of various source categories and their associated mercury releases. As demonstrated by several studies, the significance of a particular source to environmental mercury releases may vary markedly by geographic and socioeconomic factors of the particular domain [Lindberg et al., 2007; Mason et al., 1994; Zillioux et al., 1993]. For example, locations with developing economies are predominantly associated with elemental mercury used for metal ore extraction and cultural uses, while those with advanced economies are associated with mercury use as a result of fossil fuel combustion, industrial uses, and consumer products [Pirrone et al., 1996; Veiga and Meech, 1995]. Furthermore, research has demonstrated that waste incineration (medical and consumer), and oil and coal combustion processes account for greater than 70% of mercury wet deposited within relatively short spatial scales [Dvonch et al., 1998, 1999]. This phenomenon is strongly influenced by source emissions profiles and the meteorological characteristics of the domain. These use categories significantly affect the form and species of mercury emitted, the reactivity and transport phenomenon that the species may undergo, and more importantly, the direct local effects resulting from these use categories [Engle et al., 2008; Lindberg et al., 2007; Schroeder et al., 1991]. Specifically, their effect on local population health through interaction with mercury exposure pathways may differ based on their species release profile. Characterization of the influence of local release categories on local environmental mercury is important to the identification of levers for the reduction of population and ecosystem exposures.

Public health endeavors to reduce population mercury exposure have relied on the definition of safe levels of mercury exposure through consumption [Rice et al., 2003; National Research Council, 2000], and establishing and publishing fish consumption advisories to provide guidance to the public regarding consumption of certain species of fish. The aim of these advisories is to inform pregnant and pregnant-aged women, nursing mothers and the parents of young children how to get the positive health benefits from eating fish and shellfish lower in mercury (for example, shrimp, canned light tuna, salmon, pollock, and catfish), while minimizing mercury exposure by avoiding types of fish that are higher in mercury (e.g., shark, swordfish, tile-fish and king mackerel) [USEPA, 2012]. Forty states have issued advisories for methylmercury on selected water-bodies and 13 states have statewide advisories for some or all sport fish from rivers or lakes [USEPA, 2012]. Coastal areas along the Gulf of Mexico, Maine, and the Atlantic Ocean, from Florida through North Carolina, are under advisories for methylmercury for certain fish species [USEPA, 2012]. Additionally, the State of Florida has issued fish consumption advisories due to mercury levels for all of the major rivers in Florida for multiple fish species. However, despite research indicating the occurrence of mercury-contaminated species in most major water bodies, fish and shellfish consumption remains popular and regular part of woman's diets [Anderson et al., 2004]. Additionally, there is an established trend of decreasing awareness prevalence among minorities and underprivileged populations, and the younger age groups [Imm et al., 2005; Karouna-Renier et al., 2008]. Consequently, the distribution of exposures, and the public perception of the risk of exposure to mercury from fish consumption are not well characterized, which may be detrimental to the development of polices that are protective of susceptible populations.

An important question, which arises from the issue of population exposure to environmental contaminants from anthropogenic point sources, is one of environmental inequity. Specifically, this question seeks to determine whether poor and minority communities bear a disproportionate share of the associated environmental risks from mercury emitting facilities. Several studies have found correlations between the siting of municipal landfills, incinerators, coal-fired power plants, and other mercury releasing facilities and their proximity to underprivileged communities [Reams and Templet, 1996; Morell, 1984; USGAO, 1983]. Elucidation of environmental inequity requires characterization of the susceptible populations, and emission sources associated with exposures.

Whilst industrial regulatory measures and public health initiatives have sought to reduce environmental releases and improve public awareness, mercury exposure still presents a significant threat to human and ecosystem health. Current strategies for effectively reducing the health risks posed to vulnerable populations by environmental mercury exposure are deficient. These limitations can be associated with deficits existing in our understanding of the impact of local mercury use and releases on mercury levels in the immediate local environment.

This research investigates the links between mercury use, release and population exposure in Tampa Bay, with the focus of identifying levers for reducing population mercury exposures. Levels of mercury found in fish in the Tampa Bay watershed have been found to be some of the highest in Florida [Kannan et al., 1998], with mercury consumption advisories in place for many fish species in bay area freshwater lakes and streams [Florida Department of Health, 2009]. Additionally, the EPA has identified the Tampa area as having the most elevated levels of mercury deposition in the southern United States [USEPA, 1997]. Atmospheric deposition processes, particularly wet deposition, have been identified as a significant contributor to the high mercury concentration observed in waters in the Tampa Bay area [Atkeson et al., 2007]. The combustion of fossil fuels (primarily coal) in stationary combustion facilities represents the most important anthropogenic source of mercury release in the United States, and may also be true for the Tampa Bay area [Lynam and Keeler, 2006; Pacyna and Pacyna, 2002]. Important environmental mercury sources in the domain include incinerators for urban, medical and industrial wastes, cement plants and chemicals production facilities, and dental facilities. With the decline of mercury used in batteries, mercury-containing lamps and devices are quickly becoming the largest sources of mercury in Tampa Bay's municipal solid waste stream. Mercury is used in many everyday products like fluorescent lamps, thermometers, thermostats and sphygmomanometers. Understanding the impact of each of these source categories on mercury releases to environmental pools is a significant step in identifying levers for reducing population and ecosystem effects of mercury pollution within the domain. Effective strategies for the reduction of mercury exposure to vulnerable populations in Tampa Bay requires elucidation of the relationships existing between local mercury use and release, and observed deposition effects in the domain.

1.2. Research goals, specific aims, and scientific questions

The overarching goal of this research is to identify the most effective levers for reducing mercury exposure to vulnerable populations, with focus on the Tampa Bay area.

The specific aims and associated scientific questions of this research were the following:

- **Aim 1**: To identify the major sectors contributing to mercury use and release in the Tampa Bay area.
  - What are the important release sector(s) (product or process) contributing to environmental mercury releases in the Tampa Bay area?
  - What are the important direct environmental sinks for mercury releases in the Tampa Bay area?
  - What are the important emission source categories contributing to mercury releases in the airshed, and what are the long-term trends in these emissions?
- **Aim 2**: To elucidate the contributions of local emission sources to mercury deposition in the Tampa Bay area.
  - What are the sources contributing to mercury deposition to the Tampa Bay area?

  - How much do local emission sources contribute to local mercury deposition?

- **Aim 3**: To understand the factors determining population vulnerability to mercury exposure in the Tampa Bay area.
  - What is the perception of the angler population in Hillsborough County to mercury exposure from fish consumption behaviors?
  - What characteristics of the fishing population may predispose it to mercury exposure from fish consumption habits?

Understanding the links between mercury release processes and observed deposition phenomenon will result in the identification of levers to mitigate the adverse effect of mercury exposure to vulnerable populations in the Tampa Bay area. Furthermore, an understanding of the factors driving local mercury releases will serve to inform policies that are protective of susceptible populations from environmental mercury exposure.

This body of work seeks to improve upon prior mercury research by combining several different facets of environmental pollution assessment, including mass flux, deposition trends, source apportionment studies, and population survey analysis to inform mitigation strategies for population exposure. A detailed inventory of the products and process contributing to mercury use and release in Tampa Bay is presented. This includes a quantitative assessment of the releases from each sector, and their contributions to environmental pools. I seek to identify which product or process in the domain contributes significantly to mercury releases and the major sink receiving these releases. A seasonal profile of atmospheric mercury deposition was derived from archived regional deposition data, and supplemented by data collected for the Tampa Bay area through a 6-month sampling and analysis campaign. Additionally, I sought to identify the characteristics of the sources contributing significantly to deposition amounts as informed by the wet deposition data, source apportionment analysis and meteorological modeling. The characteristics of vulnerable populations, as well as, the factors affecting exposure was compiled and presented. Overall, this research contributes to an increase of our understanding of mercury use and release in Tampa Bay area, and to the

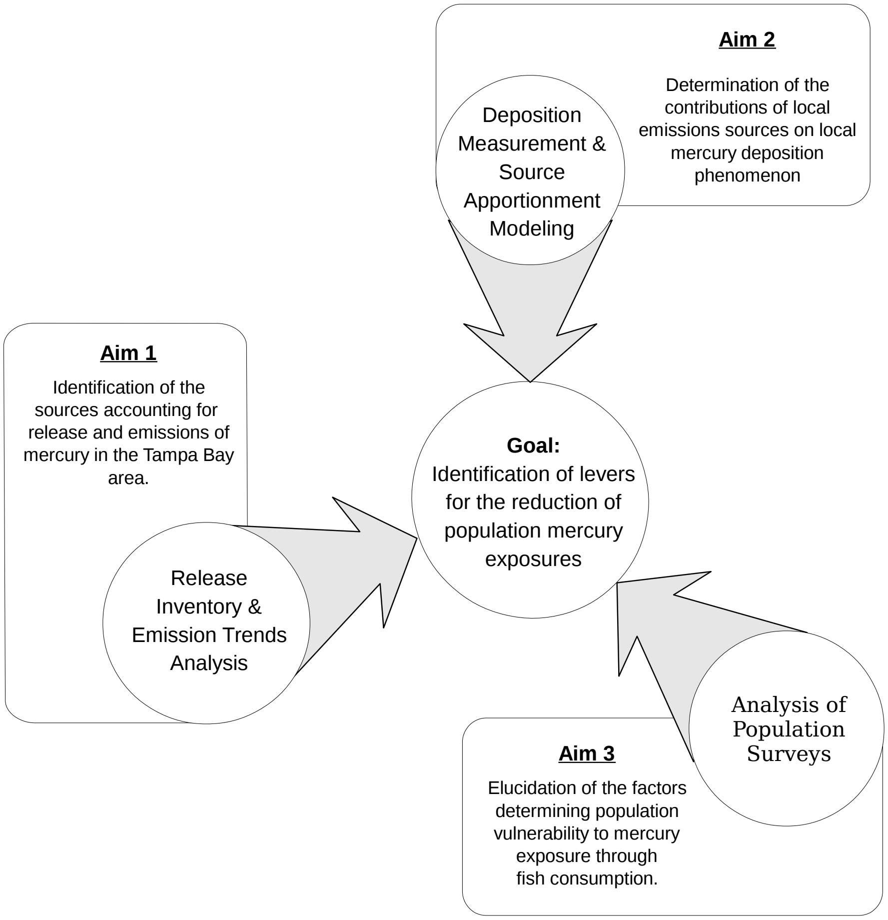


Figure 1.1. Illustrating the relationships between the specific aims, methods, and the overarching goal of this research.

identification specific levers in the mercury system dynamics for Tampa Bay where policy changes can be instituted to reduce mercury use, release, or diminish population exposure.

1.3. Organization of this dissertation

This dissertation is organized and presented in the following five chapters. In Chapter 2, I review the state of the science with respect to mercury use, release, population exposures, environmental cycling, and source apportionment modeling. I also identify research gaps pertinent to this work.

To elucidate the factors contributing to mercury use and release in the Tampa Bay area, a mass-based system inventory was constructed. Methods and results of this analysis are discussed in Chapter 3, with an analysis of EPA's National Emissions Inventory for characterization of local emission source contributions presented in Chapter 4.

Chapters 5 and 6 focuses on trends and source apportionment for wet deposited mercury to the Tampa Bay area. Deposition trends were assessed by an analysis of archived deposition data from the National Atmospheric Deposition Program, Mercury Deposition Network sites. Mercury depositions specific to the Tampa bay area was determined by an analysis of existing data previously collected as part of a special atmospheric deposition experiment in Tampa Bay. This data was supplemented by a wet deposition sampling and analysis campaigns conducted over a six-month period (July 2012 − December 2012) at a site in the Tampa Bay area, for mercury and trace metals. To understand the sources contributing to mercury deposition observed in the domain, a combined meteorological and multivariate statistical approach was employed. Existing and newly collected mercury and trace metals data served as inputs to the models.

Chapter 7 explores the factors determining population exposure to mercury in the Tampa bay area by an analysis of population surveys conducted for the Hillsborough area. The data analyzed was collected as part of a multidisciplinary project to understand the perception of risk to mercury exposure of the local angler population. The data is queried to elucidate the determinants and characteristics of exposure in the local angler population, as well as, to understand risk perception.

Finally, Chapter 8 provides a synthesis of this research, as well as, recommendations for future work.

2. Literature review

2.1. Introduction

Mercury and its compounds are widely recognized as highly toxic to human and ecosystem health. Because of its high mobility and toxicity, small environmental releases can result in significant exposures, emphasizing the importance of understanding the sources of mercury to the environment. Mitigation of the health effects of mercury requires the elucidation and quantification of specific mercury sources contributing to observed exposures. Because of its unique physiochemical properties, mercury is used in a myriad of commercial products and industrial processes, both intentionally, as a reactant, ingredient, or component of a process or product, or indirectly, as an impurity associated with the feed material of industrial processes [Pacyna et al., 2006]. Consequently, the releases of mercury species in a particular domain are dependent on the use categories defining the specific region. Identification of levers to reduce the impact of environmental mercury releases requires an understanding of the contributions of release categories in the domain and the environmental pools that serve as direct receptors for these releases. This requires increasingly detailed mercury inventories at higher resolved spatial scales [Mahaffey and Pirrone, 2005; Mason, 2009].

The importance of atmospheric transport and subsequent deposition of mercury species as a mechanism for the delivery of mercury to Florida has been demonstrated by several authors [Caffrey et al., 2010; Dvonch et al., 2005, 1999, 1995; Guentzel et al., 1995, 2001; Landing et al., 1995]. However, significant uncertainties exist in the attribution of sources contributing to mercury loading to Florida. Studies have demonstrated that the deposition of mercury can be strongly influenced by contributions of aerosol and reactive gaseous mercury from local sources, this being especially true for highly urbanized and industrialized regions [Dvonch et al., 1995], while other authors have concluded that the contributions from long-range sources are more substantial [Guentzel et al., 1995, 2001]. Source attribution for observed mercury deposition is requisite to the identification of levers for the reduction of population mercury exposures.

Because of the generally high rate of seafood consumption among coastal populations, the human population residing along these locations is potentially exposed to elevated levels of mercury [Strom and Graves, 2001]. Studies have shown that public health interventions such as education and fish advisories have limited success in reaching those populations most at risk to mercury exposure from consumption of fish with high levels of mercury, such as pregnant women, and women of childbearing age [Karouna-Renier et al., 2008]. Efforts to protect these populations must not only focus on increasing their awareness of the risks associated with consumption behaviors, but also seek to identify the characteristics of the population predominantly exposed, and the contributing socio-economic determinants of exposure.

An examination of the literature relevant to this research is presented. This includes an examination of the properties of mercury that facilitates its widespread use. Factors accounting for release and entry of mercury species into environmental cycles will be examined, with emphasis on source categories and sinks. The state of the science corresponding to the characterization of environmental mercury concentrations will be assessed. Advances in mass balance, source apportionment, and trajectory modeling for the elucidation of mercury source and source categories contributions will be examined. Finally, I will explore population exposure, the characteristics of local susceptible populations, and their perception of risk from mercury exposure, with emphasis on initiatives that are protective of public health. This review will attempt to highlight areas of uncertainties in the literature where this research will contribute.

2.2. Mercury properties, use categories, and their relation to environmental releases

2.2.1. Physical and chemical properties of mercury

A transition metal, elemental mercury (Hg^0) is a heavy, silvery-white liquid metal at ambient temperatures and pressure. Hg^0 is relatively stable in the environment, volatile, and only sparingly soluble in water. In aqueous solutions, ionic mercury species can exist in monovalent [Hg^+] or divalent [Hg^{2+}] forms [Lin and Pehkonen, 1999]. Of the two oxidized states, monovalent and divalent mercury, the latter is more stable, and thus more common in the environment [Carpi, 1997]. Divalent mercury has been found associated with inorganic molecules such as chlorine [mercury (II) chloride ($HgCl_2$)], sulfur [mercury sulfide (HgS, vermillion, a paint pigment)], and hydroxyl ions [Schroeder and Munthe, 1998; Carpi, 1997]. A number of organic complexes of mercury also exist, including monomethylmercury (MMHg) and dimethylmercury (DMHg). These organic mercury compounds are of greatest concern in the ambient environment due to their significant environmental toxicity. Monomethylmercury compounds are formed by microorganisms in sediments and bioaccumulated and bio-magnified in aquatic food chains, thus resulting in exposures of fish eating wildlife and human populations [Horvat, 2005].

Mercury's ubiquity is largely due to its unique physical properties. Mercury is the only metal that is a liquid at standard temperature and pressure, possesses a high surface tension, high specific gravity, low electrical resistance, a low vapor pressure, and a constant volume of expansion over the entire temperature range of its liquid state [Schroeder and Munthe, 1998]. In addition, mercury's availability, accessibility, and low cost have allowed mercury to play important roles in commerce, industry, mining, metallurgy, manufacturing, medicine, and dentistry [Schroeder and Munthe, 1998; Mahaffey and Pirrone, 2005]. Specific applications and uses of mercury metal includes extraction of gold and silver, catalyst for chlor-alkali production, manometers for measuring pressure, thermometer manufacture, electrical and electronic switches, fluorescent lamps, dental amalgam fillings, pigment and dyes, and pharmaceuticals [Pirrone and Mason, 2009; Mahaffey and Pirrone, 2005].

2.2.2. Mercury consumption

The global supply of mercury comes mainly from primary and secondary sources. Primary sources refers to mining of naturally occurring mercury ore, cinnabar, to produce mercury. This predominantly occurs in Spain, Kyrgyzstan, China, and Algeria [Maxson, 2005; Balistreri and Worley, 2009]. The European Union (EU) passed a trade ban on mercury exports and imports effective in 2010. Similarly, the United States of America (US) passed the Mercury Export Ban Act of 2008 which prohibits the sale of federal stockpiles of elemental mercury, and prohibits the export of elemental mercury from the US, effective January 1, 2013 [Balistreri and Worley, 2009]. The exit of the US and the EU from these markets is hoped to have the impact of increasing mercury scarcity, and encourage the adoption of alternative techniques. Secondary sources may refer to mercury recovered as a by-product of mining or processing other ores (such as mercury recovered from mining gold, silver, copper, zinc, etc.), secondary mercury from recycling or waste processing, residual mercury recovered from decommissioned chlor-alkali facilities, and mercury occasionally released from government or industry inventories [Maxson, 2005].

On January 19, 2013, 147 governments met and agreed to a draft text for the Minamata Convention on Mercury, a formal agreement between nations to protect human and environmental health from anthropogenic mercury emissions and releases [Selin, 2013]. The convention requires participating nations take actions to reduce mercury emissions to the air from power plants and other sources, to reduce the use of mercury in products and industrial processes, especially artisanal gold mining [Kessler, 2013]. The agreement also addresses mercury supply, storage, and waste management, with provisions for technical and financial assistance for member developing member nations. The convention will be open for signature by governments at a Diplomatic Conference in October 2013 in Minamata, Japan, and will be ratified with at least 50 signatures.

Mercury is consumed in a broad range of products and processes around the world. The major categories of demand include industrial processes (chlor-alkali production, catalysis, etc.), medical and industrial measuring devices (fever and other thermometers, measuring and

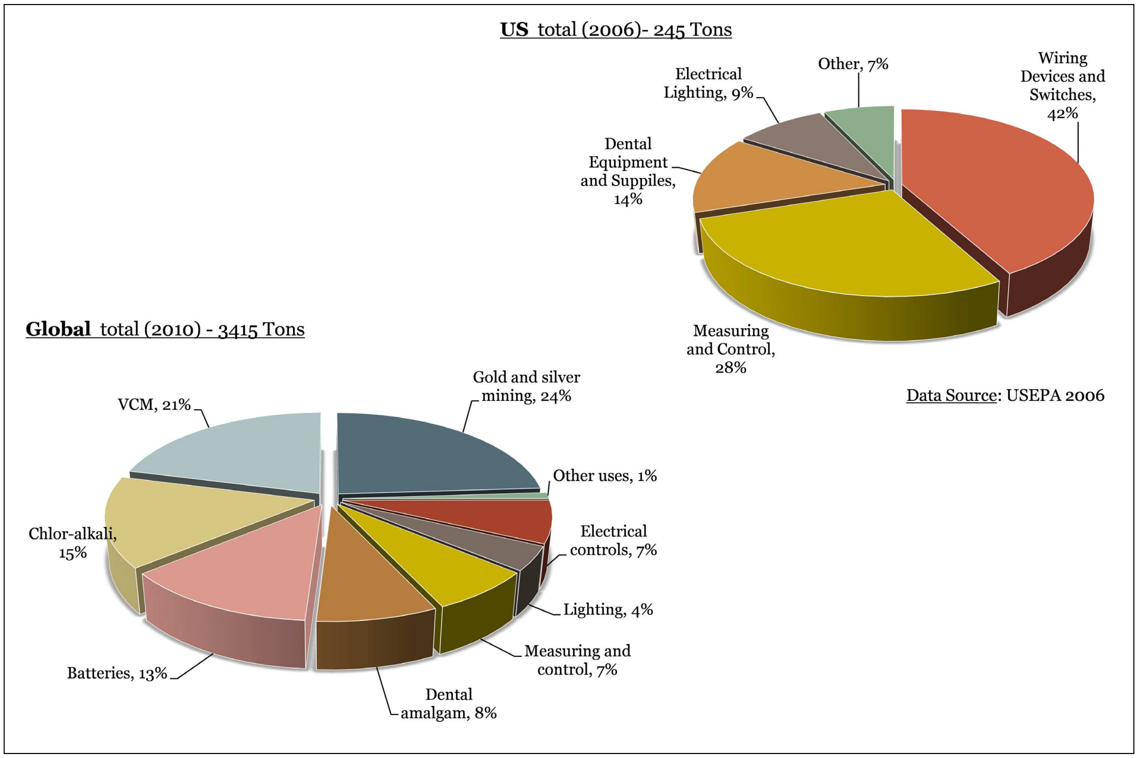


Figure 2.1. Mercury demand by use category for global (bottom-left subplot) and US (top-right subplot) consumption categories. [Compiled from Maxson, 2004; UNEP, 2006, USEPA, 2006]

control devices/equipment), batteries (mercuric oxide and others), lighting (neon, compact fluorescent, high intensity discharge (HID), and other energy efficient lamps), switches (industrial, household, and automotive switches, contacts and relays), laboratory and medical uses (amalgams), pharmaceutical processes, and agricultural products and preservatives [Maxson, 2005]. Additional categories of mercury demand found predominantly, but not exclusively, in developing countries include artisanal gold mining, cosmetics, and cultural uses, such as uses in traditional/alternative medicine. Figure 2.1 compares mercury consumption categories for the US with global estimates using 2006 data [Maxson, 2005; UNEP, 2002]. The plots highlight the significance of various consumption categories as economies vary. Mercury used in gold and silver mining are important consumption categories in developing nations, or nations with economies in transition (artisanal and small scale mining in African and South American countries), while measuring/control devices, and switches represent greater than 70 of mercury consumption in the developed/mature economies. Vinyl chloride monomer (VCM) production uses mercury catalysts, occurs mainly in China, and represents a significant fraction of global mercury consumption totals [Maxson, 2005]. Identifying levers for the reduction of mercury use and release in a domain of interest requires an understanding of the role each use category plays in the environmental, cultural, and socioeconomic dynamics of the system under study.

2.3. Environmental mercury emissions

In an attempt to understand the ecosystem effects of anthropogenic mercury use and release, an extensive amount of research has focused on identifying and estimating the contributions of mercury emission sources; both natural and anthropogenic, towards establishing a global inventory [Ferrara et al., 2000; Friedli et al., 2009; Gustin et al., 2000; Pirrone et al., 2010].

Emission sources of mercury to the environment are twofold. Natural sources include volatilization of mercury from aquatic environments, re-emission from vegetation, volcanic emissions and other geothermal activities, degassing from geological materials, biomass burning, and releases associated with wind-blown dust [Mason et al., 1994; Ferrara et al., 2000]. These processes contribute to a natural cycling of mercury between environmental compartments and are estimated to release annually about 5207 Mg (2008 estimates) of mercury [Pirrone and Mason, 2009]. Mercury emitted from volcanoes, geothermal sources, and topsoil enriched in mercury are categorized as primary natural sources, while the re-emission of previously deposited mercury on vegetation, land or water surfaces can be considered as related to land use changes, biomass burning and other anthropogenic influenced activities [Pirrone et al., 2010, 2001]. Emissions of mercury from surface waters, specifically oceans, is the most important source category for natural releases, accounting for $> 50\%$ of global mercury emissions from naturally sources for 2008 estimates [Pirrone and Mason, 2009]. Other notable contributions from natural source categories include non-vegetated zones ($\sim 10\%$), and biomass burning (13%).

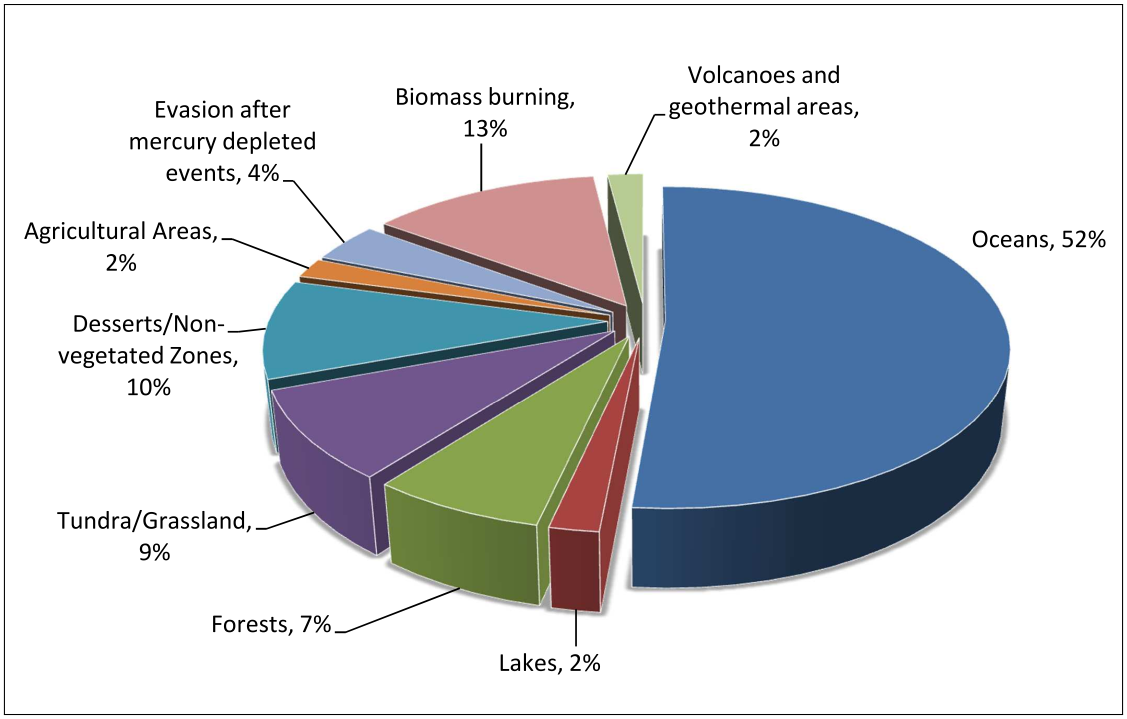


Figure 2.2. Estimates of global mercury emissions from biogenic sources sources (2008). Compiled from Pacyna, [2006], Friedli et al., [2009], and Pirrone et al., [2010].

The second general division of mercury emission sources to the environment involves direct or indirect injection of mercury into the cycle as a result of anthropogenic activities. Though natural sources dominate, the contributions of anthropogenic activities are significant to the global biogeochemical cycling of mercury and the resultant increases in ecosystem mercury concentrations [Pacyna et al., 2006; Pirrone et al., 2010]. Anthropogenic sources are estimated to release approximately 2900 Mg (2008 estimates) of mercury annually with major contributions from fossil fuel-fired power plants, artisanal small scale gold mining, waste disposal, non-ferrous metals manufacturing, and cement production [Pirrone and Mason, 2009]. The significance of a particular industrial source to atmospheric mercury emissions in determined by the bulk material amount, the mercury content of the feed material, and the technology employed to reduce emissions [Pirrone et al., 2010], with the combination of mercury concentration and efficiency of abatement technology being used to derive emission fractions for different source release categories. Figure 2.3 compares the contributions from anthropogenic emission sources to US and global mercury emissions [Maxson, 2005; Pirrone

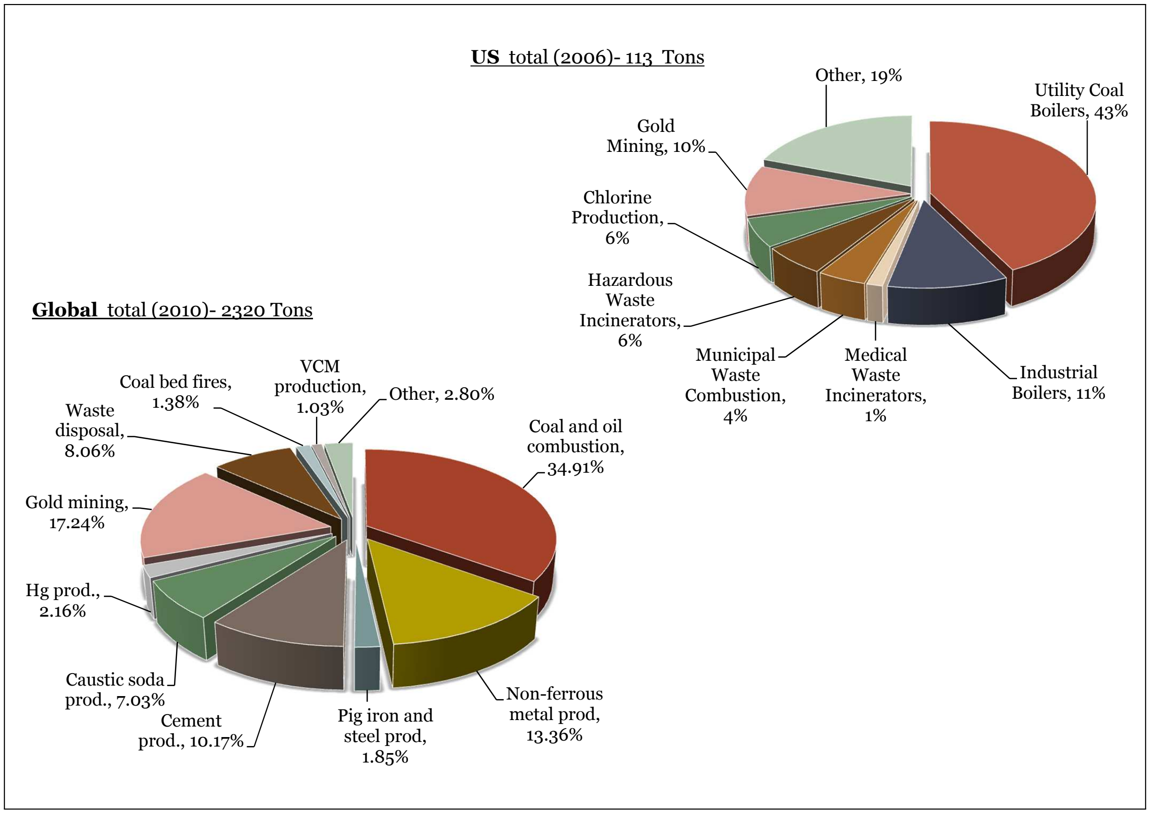


Figure 2.3. Mercury emission estimates for global (bottom-left subplot) and US (top-right subplot) sources. Compiled from Maxson, [2005], UNEP, [2002], EPA [2006], and Pirrone et al., [2010].

and Mason, 2009]. Fossil fuel used in electric power generation, especially those that use coal have been found to be the largest source category of mercury released to the atmosphere for both domains. Concentrations of mercury in coal and natural fuel oils vary substantially, depending on the type of fuel, as well as its origin. Similarly, chemical composition of the input material for incineration is one of the most important factors influencing the quantity of atmospheric emissions of various pollutants from waste incineration processes [Pirrone et al., 1996]. Mercury in industrial wastes mostly originates from the phasing out of mercury from industrial processes and mercury-containing products, with the chlor-alkali industry being one of the most significant sources [Maxson, 2005; Pirrone et al., 2010]. Mercury appears as an impurity associated with the ores of many valuable metals including that of copper, zinc, lead, and nickel ores, as well as in gold ores. Consequently, processes to obtain these metals contribute largely to the release of mercury to the environment, this being especially true in developing countries [Telmer and Veiga, 2009; Veiga et al., 2006]. Anthropogenic releases to land via the application of fertilizers, fungicides, municipal solid waste and the direct discharge of commercial effluent to water bodies also accounts for significant contribution to environmental mercury releases [Stein et al., 1996]. However, similar to the comparison of mercury use estimates, the significance of sources to total emissions varies between domains. Theses differences may increase significantly as the resolution of the domain increases, suggesting that strategies for mitigation of the effects of environmental mercury emissions in a particular domain require an elucidation of the consumption and emission categories defining the specific region.

2.4. The biogeochemical cycling of mercury

The flux of mercury between environmental compartments is dependent on contributions from the natural global cycle, the global cycle influenced by human activities, regional sources, and local sources [Rice et al., 1997]. Whilst a general understanding may exist for the global cycling of mercury [Zillioux et al., 1993; Mason et al., 1994; Lindberg et al., 2007; Engle et al., 2008; Atkeson et al., 2002; Pirrone and Mason, 2009; Pirrone et al., 2010], uncertainties exist about mercury fluxes on a regional or local scale due to the location-specific nature of emission and deposition processes [Rice et al., 1997].

The atmosphere is the most important pathway for the global dispersion and transport of mercury [Mason et al., 1994; Fitzgerald et al., 1998]. Processes accounting for the atmospheric fate and transport of mercury include emissions to the atmosphere, transformation and transport in the atmosphere, deposition from the air, and re-emission to the atmosphere [Rice et al., 1997]. As discussed above, emission of mercury is governed by naturally occurring and anthropogenic processes, with anthropogenic releases being dominated by industrial processes and combustion sources. These sources are thought to emit both gaseous and particulate forms of mercury, with the gaseous forms consisting of both elemental and oxidized chemical forms, and the constitution of particulate forms being dominated by oxidized mercury species [Pirrone and Mason, 2009; Rice et al., 1997].

Atmospheric mercury exists primarily as the inorganic forms; elemental mercury (Hg^0), and gaseous ionic mercury (Hg^{2+}). Due to its relatively low aqueous solubility, and high volatility, elemental mercury is believed to have residence times of between $0.5 - 2$yrs, is distributed fairly evenly in the troposphere, and is thus more susceptible to long range atmospheric transport [Lindqvist and Rodhe, 1985; Rice et al., 1997]. Oxidized and particulate bound Hg species (Reactive Gaseous Mercury, RGM) are easily scavenged by falling rain drops due to their higher solubility, thus Hg^{2+} tend to be found predominantly in the liquid phase of the atmosphere, either dissolved in atmospheric water droplets, or adsorbed onto particles in droplets (Ross and Vermette, 1995). Consequently, Hg^{2+} species tend to have atmospheric lifetimes of a few hours to weeks [Downs et al., 1998; Rice et al., 1997]. Porcella et al., [1996], suggested that the atmospheric residence times of oxidized mercury associated with fine particles [Hg^{2+}(p)] may be longer, approaching that of elemental mercury, Hg^0.

Mercury species are subject to both wet and dry deposition processes. While, divalent mercury species [Hg^{2+}(aq) and Hg^{2+}(p)] undergo both deposition processes, they are shown to undergo faster wet removal rates than elemental mercury. This can be accounted for by the lower Henry's law constants (air-water) they possess which allows the species to partition strongly to the aqueous phase [Rice et al., 1997]. Research shows that due to its high vapor pressure and low water solubility, Hg^0 is not susceptible to any major deposition processes [Seigneur et al., 2004]. However, the transformation of Hg^0 to Hg^{2+}(aq) and Hg^{2+}(p) species in aqueous atmospheric compartments represents an important mechanism by which natural and anthropogenic Hg^0 emission sources can influence the deposition of mercury to terrestrial and aquatic ecosystems [Rice et al., 1997]. These processes represent the most indirect pathways for the removal and subsequent deposition of elemental mercury species. Atmospheric chemical reactions accounting for these transformations include the uptake and oxidation of elemental mercury by O_3, $^{\cdot}OH$, and Cl_2 species in aqueous atmospheric environment [Lin and Pehkonen, 1999]. Hg^{2+} species generated from these reactions may undergo deposition processes, or may be reduced back to Hg^0 by sulfite and other species in the atmosphere [Rice et al., 1997].

Due to the slow rates of uptake of Hg^0 by cloud water, this deposition may occur at distances far removed from the original emission sources [Pirrone et al., 2010; Rice et al., 1997]. Consequently, it has been suggested that this mechanism is significant in the global sense of mercury pollution, while direct deposition of anthropogenically emitted Hg^{2+} species is important for local deposition effects [Seigneur et al., 2001; Schroeder et al., 1991; Rice et al., 1997; Pirrone and Mason, 2009; Mason et al., 1994]. As demonstrated by several studies, the significance of a particular source to environmental mercury releases may vary markedly by geographic and socioeconomic factors of the particular domain [Lindberg et al., 2007; Mason et al., 1994; Zillioux et al., 1993]. For example, locations with developing economies are predominantly associated with elemental mercury used for metal ore extraction and cultural uses; whilst those with advanced economies are associated with mercury use as a result of fossil fuel combustion, industrial uses, and consumer products [Pirrone et al., 1996; Veiga and Meech, 1995]. These use categories significantly affect the form and species of mercury emitted, the reactivity and transport phenomenon that the species may undergo, and more importantly, the direct local effects resulting from these use categories [Engle et al., 2008; Lindberg et al., 2007; Schroeder et al., 1991]. Specifically, their effect on local population health through interaction with mercury exposure pathways may differ based on their species release profile.

The emission profiles of major anthropogenic emission source categories are presented in Figure 2.4. Sources with large Hg^{2+} emission fractions are important for local mercury deposition effects. These include coal-fired power plants and residential heating systems, oil combustion processes, and medical and direct municipal waste incineration facilities [Schroeder et al., 1991; Pirrone et al., 2010; Lindqvist and Rodhe, 1985; Keating, 1997]. Characterization of the influence of local release categories on local environmental mercury is important to the identification of levers for the reduction of population ecosystem exposures.

Once deposited Hg^{2+} species readily partake in a variety of chemical and biological reaction soil sediment and aquatic environments. Hg^{2+} species readily form complexes with soil organic matter, due largely to a high affinity for sulfur-containing functional groups, thus greatly reducing the mobility of mercury in this system [Rice et al., 1997]. As a consequence,

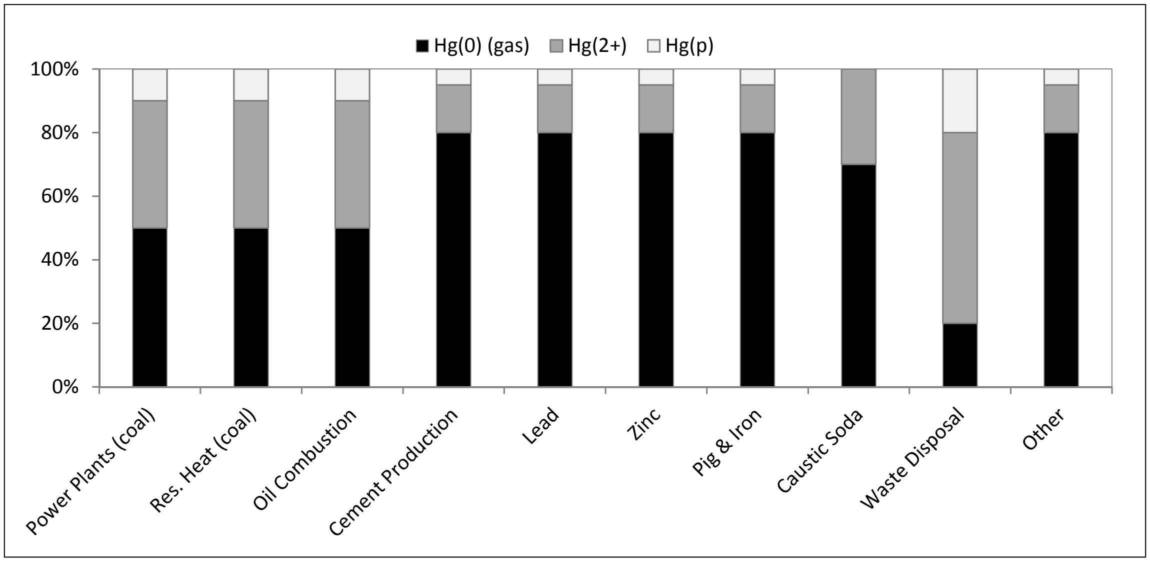


Figure 2.4. Mercury emission profiles from anthropogenic sources. [Compiled from Maxson, 2004; UNEP, 2006, USEPA, 2006, and Pirrone et al.,2010]

the soil is thought to act as a large reservoir for anthropogenic mercury emissions [Morel et al., 1998; Mason et al., 1994; Rice et al., 1997]. However, humic substances have the ability to convert these Hg^{2+} complexes back to Hg^0, thus facilitating the re-emission of to the atmosphere via diffusion through the soil [Morel et al., 1998; Rice et al., 1997].

Remission of deposited mercury also occurs through the evasion of elemental mercury from oceans [Morel et al., 1998]. This process involves the reduction of anthropogenically deposited Hg^{2+} to volatile Hg^0 and subsequent re-emission of the volatile mercury species. Mason et al., [1994], estimates that this process accounts for approximately 30% of total mercury flux to the atmosphere.

Mercury enters aquatic environments via several pathways; wet and dry deposition of atmospheric Hg^{2+}(aq) and Hg^{2+}(p) species, runoff of Hg^{2+}(aq) and methylmercury species, and leaching of Hg^{2+}(aq) and methylmercury from groundwater flow [Rice et al., 1997]. Whilst mercury species may undergo similar aqueous phase reactions as mentioned previously, the most important reaction occurring in aquatic ecosystems is the methylation of mercury species. Methylation reactions are the result of a biologically mediated photochemical reaction involving humic acid and bacterial activity. Methylation of mercury in the water column has been reported by several authors, and is recognized as a potential pathway for the accumulation of mercury in fish [Lindqvist et al., 1991; Rudd et al., 1983; Xun et al., 1987; Sorensen et al., 1990; Parks et al., 1991]. Authors have suggested that suspended particulate matter in the water column can act as sites for methylation/demethylation reactions owing to the presence of attached bacteria [Downs et al., 1998]. Xun et al., [1987], observed that not all mercury compounds entering the aquatic ecosystem are methylated, and demethylation reactions, as well as, volatilization of dimethylmercury may decrease the amount of methylmercury available in the aquatic environment. Moreover, there is a large degree of scientific uncertainty and variability among water bodies concerning the processes that methylate mercury [Rice et al., 1997]. Bacterial methylation rates have been shown to increase under anaerobic conditions, high temperatures, low pH, proper biologic community, adequate suspended solid load and sedimentation rates, and increased quantities of mercury species [Lindqvist et al., 1991; Rudd et al., 1983; Xun et al., 1987; Sorensen et al., 1990; Parks et al., 1991]. Additionally, anthropogenic acidification of lakes appears to increase methylation rates [Rudd et al., 1983].

The bioavailabilty and bioaccumulation of methylmercury in fish and shellfish through the aquatic ecosystem had been well documented [Downs et al., 1998; Guentzel et al., 2007; Morel et al., 1998; Rudd and Turner, 1983; Mason et al., 1995], indicating that nearly 100% of mercury in fish muscle tissue is methylated [Bloom et al., 1991; Rice et al., 1997]. It has also been observed that mercury appears to be passed to planktivorous and piscivorous species via their diets, thus the highest concentrations the highest concentrations of mercury are observed in the larger, longer-lived fish species at the upper end of the food web [Rice et al., 1997]. Being the highest level trophic consumes in the system, humans and wildlife are exposed to methylmercury primarily through fish and shellfish consumption.

There is a general consensus among the research community that anthropogenic mercury releases represent significant contributions to the global cycling of mercury [Mason et al., 1994; Pacyna et al., 2006; Pirrone and Mason, 2009]. It is important to identify regional mercury sources, elucidate their contributions, assess their impacts, and identify sustainable mitigation strategies to reduce population exposure. From a global standpoint, it is important to maintain consistent system inventories to assess the significance of the contributions from these sources to the mercury biogeochemical cycle, and to elicit long term trends [Ebinghaus et al., 2005; Hudson et al., 1995; Lindberg et al., 2007]. From a regional standpoint, understanding the significance of these emission sources to the observed deposition phenomenon at local scales is important to elucidate the contribution of local versus long-range sources for the development of appropriate policies to reduce population exposures [Bookman et al., 2008; Gratz, 2010; Lindberg et al., 2007]. Current research indicates that characterization of sources at the category and facility level is crucial to elucidation of their impact at local scales, and the development of policies that are protective of human and ecosystem health.

2.5. Environmental monitoring and modeling

2.5.1. Environmental monitoring

Trends assessment monitoring and modeling programs are instrumental to the determination of long-term environmental mercury trends, and to measure the effectiveness of risk management programmes. The expected goals of trends monitoring is to find the most efficient points along the mercury transport cycle, to determine trends along that flow, and to determine whether they are responding to control and reduction measures. Based on the previously discussed mercury transport and exposure paths, the most important media of concern are air emissions, ambient air and air deposition, fish tissue, and human tissue [USEPA, 2006]. The United States Environmental Protection Agency (USEPA) has the responsibility of providing information and data that reduces scientific uncertainties, to provide an understanding of the fate and transport of mercury from release to its effects on receptors, and promotes its overall goal of reduction and prevention of mercury releases into the environment[USEPA, 2006]. To this extent, the USEPA has established monitoring and reporting systems to collect data on mercury releases and contamination, including national monitoring of mercury in environmental media, fish tissue, and human blood and hair samples.

Atmospheric transport of mercury is the primary focus from mercury monitoring and modeling due to the significance of the atmosphere in the cycling of mercury from anthropogenic sources to other environmental compartments. Emissions inventories provide information about the sources of mercury, and the relative contributions of those sources to total releases [USEPA, 2006]. The National Emissions Inventory (NEI) and the Toxics Release Inventory (TRI) are two key USEPA reporting efforts for assessment of national mercury emissions. The NEI is a national repository of emissions inventory data for hazardous air pollutants (HAPs). The emissions data and estimates cover major area and mobile sources, and include estimates of emissions at the national, regional, county, and facility specific levels [USEPA, 2006]. The TRI is a compilation of mandatory yearly reports submitted by industrial facilities on the amounts of toxic chemicals, including mercury compounds, released or otherwise managed as waste. Amounts released are reported separately for air, land, water, and off-site disposal [USEPA, 2006].

Monitoring of ambient air and air deposition provide information on mercury once it has been emitted. This monitoring information facilitates the assessment of long-term mercury contamination, and provides input data for mercury modeling activities and other pertinent research activities [USEPA, 2006]. Several major monitoring activities are ongoing for the assessment of mercury in ambient air and air deposition. The Mercury Deposition Network (MDN) is a part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), a nationwide network of over 70 precipitation monitoring sites that collect weekly data on the chemistry of precipitation for monitoring of long-term geographical and temporal trends. Information from MDN is used to develop a national database of weekly concentrations of total mercury in precipitation, and to provide information on the seasonal annual flux of total mercury in wet deposition [USEPA, 2006]. Additionally, the EPA, in collaboration with the United States National Oceanic and Atmospheric (NOAA) Administration is working with other countries as part of the Long Range Transport Monitoring program for the characterization, modeling, and speciation of ambient and source level mercury related to mercury emissions, transport, and deposition on local, regional, and global scales [USEPA, 2006].

Monitoring of fish tissues provides important information about the levels of mercury being consumed by the human population. This information includes geographical and temporal trends in population exposure and fish concentration levels in national water bodies. This information is essential to the evaluation of EPA programs for addressing mercury releases to the environment. This data also serves as input to research and modeling activities for the elucidation of mercury fate and transport in the environment [USEPA, 2006]. The USEPA major monitoring activities on fish tissue include the National Study of Chemical Residues in Lake Fish Tissue, the National Listing of Fish Advisories, and the Ecological Monitoring to Characterize the Condition of U.S. Estuarine Resources [USEPA, 2006]. The National Listing of Fish Advisories is a database that contains all fish advisory information provided to the USEPA by the states, tribes, and Canada. This information details mercury concentration in fish tissue sampled from local and state water-bodies. This data provides guidance for consumption advisories that are issued if elevated concentrations are found.

2.5.2. Modeling mercury releases, cycling, and transport

Atmospheric modeling of mercury is an effective way of understanding the biogeochemical cycling of mercury, and to elucidate the associations between emission sources and subsequent deposition to aquatic ecosystems. Over the last decade, a number of numerical regional and global models have been developed for the transport and transformation of mercury in the atmosphere. These models may track mercury species on a regional scale, or on a global scale. Regional models are useful for investigating episodic situations, while global models are useful for determining mercury budgets, long-range transport, transboundary exchanges, and residences times of mercury in the atmosphere [Dastoor and Larocque, 2004]. Examples of regional scale models include; the Community Multi-scale Air Quality model (CMAQ) [Bullock and Brehme, 2002], a comprehensive air quality model designed to operate on a range of domain sizes, from urban to continental; the Regional Modeling System for Aerosols and Deposition (REMSAD) [ICF, 2002], a three dimensional Eulerian grid model that provides estimates of the concentrations and depositions of the simulated pollutants at each grid location in the modeling domain; the Trace Element Analysis Model (TEAM) model [Pai et al., 1997], a three dimensional model that simulates the transport, chemical and physical transformations, and removal of Hg species [Bullock and Brehme, 2002]. Examples of global models include the Chemical Transport Model for Mercury (CTM-HG) [Seigneur et al., 2001], and the Global/Regional Atmospheric Heavy Metals (GRAHM) model [Dastoor and Larocque, 2004].

The application of receptor models provides another approach to understanding the impacts of Hg sources on specific receptor locations. Receptor models quantify the impact of air pollution sources by using multivariate statistical methods on the sources into specific categories and quantify their relative importance. Researches have utilized source apportionment models as tools in an attempt to re-construct the influence of emissions from different sources of atmospheric pollutants on receptors, and can be placed into three general groups [Hopke et al., 2005; Viana et al., 2008]. Methods that utilize basic monitoring data as a means of identifying sources have been employed by several authors [Hafner and Hites, 2005; Hsu et al., 2003; Kim et al., 2004]. For example, Henry et al., [2002], assessed the concentration of air pollutants by utilizing a nonparametric regression of atmospheric concentration on wind direction. Finally, receptor models based on the statistical evaluation of speciated chemical data acquired at receptor sites have been applied [Dvonch et al., 1999; Keeler et al., 2006; Richards et al., 2008].

The fundamental principle defining these models is the conservation of mass. Several receptor models exist, and they may be defined along the spectrum spanning the degree of knowledge required about pollution sources, as illustrated by Figure 2.5. At one extreme, the Chemical Mass Balance model, CMB, assumes that there is detailed knowledge of the composition of the emissions from all relevant sources, and is thus considered an idealized receptor model. At the other end of the spectrum, approaches such as the Principal Component Analysis (PCA), and Positive Matrix Factorization (PMF), attempt to apportion the sources based on observations at the receptor site alone, thus prior knowledge of sources and source profiles is not required for the quantitative portion of the analysis [Anderson et al., 2002; Dutton et al., 2010; Paterson et al., 1999]. Hybrid models exists where the advantages of both approaches are combined, for example, target transformation factor analysis, in which

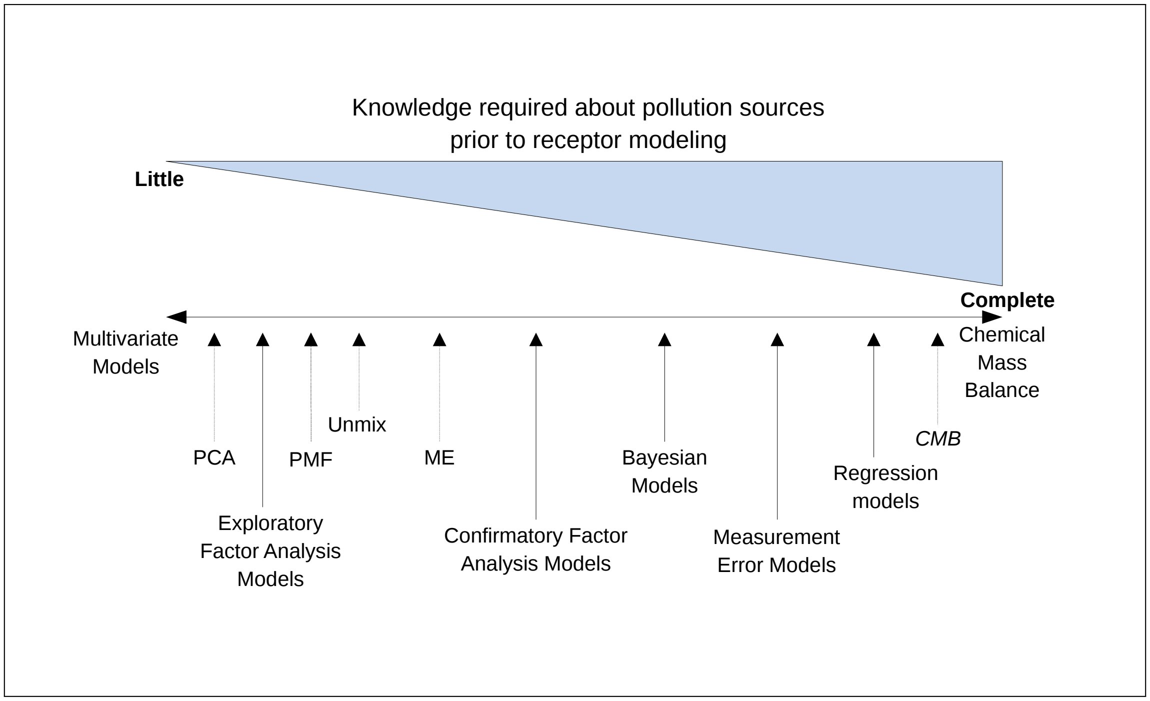


Figure 2.5. An illustration of continuum along which receptor models can be viewed to exist. [Compiled from Maxson, 2004; UNEP, 2006, USEPA, 2006, and Pirrone et al.,2010]

some controls of the solutions is achieved by fixing or freeing specific parameters, which requires prior knowledge of source forms [Viana et al., 2008]. Additionally, researches have sought to leverage the advantages of several approaches by using combinations of the models to identify sources. For example, Keeler et al., [2006], combine multivariate statistical models and meteorological models to understand the factors contributing to mercury observed in wet deposition Ohio. The information provided by receptor models is valuable to the elucidation of sources contributing to atmospheric mercury concentrations, and the development of policies aimed at the mitigation of the effects of the environmental contaminant on human and ecosystem health.

Characterizations of the amounts of mercury that is locally deposited to specific ecosystems and geographical areas, especially locations adjacent to large urban or industrial areas, is important since research shows that a significant portion of total mercury emitted from these sources is of the soluble reactive form [Bullock et al., 1998; Dvonch et al., 1999; Ebinghaus et al., 2005]. This reactive form of mercury is expected to be removed from the atmosphere on a relatively shorter timescale, resulting in deposition processes occurring within 100 km from the source [Dvonch et al., 1999]. It also is important that emphasis be placed on characterizing local releases considering the fact that regardless of form emitted, mercury has the potential to undergo chemical conversions within all domains of the environmental to form species that threaten human and environmental health.

2.6. Characterization of human exposure, health effects, and risk assessment

Human exposure to mercury compounds occurs predominantly through the consumption of aquatic organisms, particularly fish [Tollefson and Cordle, 1986]. The developing brain is the main target for methylmercury toxicity. Evidence from poisoning outbreaks in Japan and Iraq clearly demonstrates the severe health outcomes in fetuses as a result of maternal mercury exposures [D'ltri and D'ltri, 1978; Harada, 1995]. Adverse health effects include mental retardation, cerebellar ataxia, primitive reflexes, dysarthria, and hyperkinesias being observed in infants [Gilbert and Grant-Webster, 1995; Harada, 1995]. Consequently, vulnerable populations include women of child-bearing age, the developing fetus and young children, nursing mothers, and those consuming large amounts of piscivorous fish in their diet [Gilbert and Grant-Webster, 1995; Swain et al., 2007; USEPA, 1997a]

Important differences exist between organic and inorganic forms of mercury with respect to both their exposure pathways. Elemental mercury vapor is rapidly absorbed through the lungs, but poorly in the gastrointestinal tract [Hassett-Sipple et al., 1997]. Once absorbed, elementary mercury is readily distributed throughout the body, having the ability to cross both placental and blood-rain barriers [Hassett-Sipple et al., 1997]. Elimination of elemental mercury occurs via urine, feces, exhaled air, sweat, and saliva [Gochfeld, 2003]. Inorganic mercury has been shown to be weakly absorbed in the gut (7% to 20%), and has a limited capacity for penetrating the blood-brain or placental barriers [Clarkson et al., 2003; Gochfeld, 2003]. Due to its relatively poor absorption tendencies, the majority of ingested inorganic mercury is thought to be excreted through the feces [Hassett-Sipple et al., 1997]. In contrast, methylmercury is rapidly and extensively absorbed through the gastrointestinal tract, with studies indicating that over 98% of the organic mercury is absorbed in the gut of birds and mammals, and can be stored for a significant amount of time [Wolfe et al., 1998]. Due to its lipophillic nature, organic mercury has the ability to cross the blood-brain barrier, where it has been known to produce several neurological effects such as malcoordination and paralysis in human and animals [Gilbert and Grant-Webster, 1995; Myers and Davidson, 1998; Scheuhammer et al., 2007]. These differences have significant implications when considering the routes for population exposure associated with the various mercury species. Elemental and inorganic mercury are mainly associated with occupational exposures, however, it must be noted that some non-occupational exposure may be associated with dental use (fillings), and medical (thermometers) and consumer goods (electronics, switches, light bulbs).

Occupational mercury exposures occur predominantly in the medical sector, specifically in dental offices. Dental amalgams emit mercury vapor that is inhaled and absorbed into the bloodstream [Clarkson et al., 2003]. Although the doses may be small, studies have shown that blood brain and urinary concentrations correlate with the number of amalgam surfaces present, with authors estimating that ten amalgam surfaces would raise urinary concentrations to double the background concentrations [Barregard, 2005; Clarkson et al., 2003; Dye et al., 2005; Kingman et al., 1998]. Household mercury exposures occur predominantly as elemental mercury vapors as a result of broken thermometers. This places infants and young children at highest risk due to their proximity to the floor [Clarkson et al., 2003; Gochfeld, 2003; Zahir et al., 2005].

The use of mercury in cultural and religious practices has been the focus of several studies conducted in the U.S., particularly in cities with large Afro-Caribbean and Latin American populations such as New York City and Miami [Cachada et al., 2009; Riley et al., 2001; Wendroff, 1995]. These activities employ the use of elemental mercury to perform folk medicine and religious practices, with mercury being sourced from religious supply stores called *botanicas* [Riley et al., 2001]. Religious uses includes sprinkling mercury on the floor of a home or car, burning in a candle, mixing with perfume, or being worn around the neck in a vial [Riley et al., 2001; Wendroff, 1995, 1997]. The fact that most of these religious practices are usually preformed in small enclosed spaces, combined with the long residence time of elemental mercury results in potentially high direct mercury exposures to individuals. Understanding the extent of mercury use and the degree of exposure resulting from cultural/religious uses is quite difficult due to the closed nature of these communities, and the secret nature of these practices. Authors have surmised that government intervention would drive the practices further underground and would have no significant effect on mercury use in the community [Riley et al., 2001; Scott, 1974].

Exposure to organic mercury species in the U.S is predominantly associated with the consumption of seafood [Clarkson, 1993; Mahaffey and Pirrone, 2005; Skerfving, 1974; Tollefson and Cordle, 1986]. Because of the generally high rate of seafood consumption among coastal populations, the human population residing along these locations is potentially exposed to elevated levels of mercury [Strom and Graves, 2001]. This may be especially true for the state of Florida, and the Tampa Bay area. Studies have shown that Floridians consume substantially greater quantities of seafood than the average U.S. resident because of the unique geographical characteristics and the presence of very large recreational and commercial fisheries [Degner et al., 1994]. Florida consists of approximately 8,426 statute miles of tidal shoreline, which is the largest for coastal states in the U.S. Additionally; Florida has over 4,500 square miles of inland (fresh) water [Bureau of Economic and Business Research, 2007]. These vast water resources coupled with a favorable climate have resulted in a substantial recreational fishing and commercial seafood industry [Degner et al., 1994]. Degner et al., [1994] estimated that the average Florida adult consumes approximately 46 $\mathrm{g\,d^{-1}}$ of seafood, which contrasts significantly with an estimate of 4.5 $\mathrm{g\,d^{-1}}$ for the general U.S. population, and 17.5 $\mathrm{g\,d^{-1}}$ from recreational fishers. Moreover, Moya et al., [2008], estimated fish consumption rates for consumers of bought and self-caught fish in Connecticut, Florida, Minnesota, and North Dakota, and observed the highest values in Florida for children 1 – 6 years of age. Overall, for the state of Florida, fish consumption ranged from 0.7 – 2.3 $\mathrm{g\,kg^{-1}_{body\ weight}\,d^{-1}}$. The authors also reported a statistically significant increase in the percentage of the population reporting fish and shellfish consumption with an increase in household income and education for the state of Florida, which was not observed in other states [Moya et al., 2008]. Recreational and subsistence anglers may be subject to increased health risks likely due to greater frequency of consumption, and larger total quantities consumed relative to the overall population, thus placing them among that sector of the population most vulnerable to mercury exposure.

Reducing mercury exposure among at-risk groups requires reduced fish consumption, since mercury persists in the environment and this is the predominant exposure pathway. Women of child-bearing age and young children are especially vulnerable to mercury exposure from fish consumption The National Health and Nutrition Examination Survey (NHANES) reported that hair mercury levels in frequent fish consumers were three-fold higher for women and two-fold higher for children compared with non-consumers [McDowell et al., 2004]. Additionally, sensitivity of the fetal nervous system to methylmercury exposure has been well documented [Amin-Zaki et al., 1978; Gilbert and Grant-Webster, 1995; Myers and Davidson, 1998; Schober et al., 2003] with several studies establishing other effects, such as a relationship between elevated mercury levels in pregnant women and pre-term delivery [Mahaffey and Pirrone, 2005].

Public health endeavors to reduce population mercury exposure include establishing fish consumption advisories. The aim of these advisories is to inform pregnant and pregnant aged women, nursing mothers and the parents of young children how to get the positive health benefits from eating fish and shellfish lower in mercury (for example, shrimp, canned light tuna, salmon, pollock, and catfish), while minimizing mercury exposure by avoiding types of fish that are higher in mercury (e.g., shark, swordfish, tile-fish and king mackerel) [USEPA, 2012]. Forty states have issued advisories for methylmercury on selected water-bodies and 13 states have statewide advisories for some or all sport fish from rivers or lakes [USEPA, 2012]. Coastal areas along the Gulf of Mexico, Maine, and the Atlantic Ocean from Florida through North Carolina are under advisories for methylmercury for certain fish [USEPA, 2012]. Additionally, the State of Florida has issued fish consumption advisories due to mercury levels for all of the major rivers in Florida for multiple fish species [USEPA, 2012].

Studies have shown that public health interventions such as education and fish advisories have limited success in reaching those populations most at risk to mercury exposure from consumption of fish with high levels of mercury, such as pregnant and women of child-bearing age [Karouna-Renier et al., 2008]. Barriers to advisory compliance include deficiencies in knowledge of existing advisories, education level, income, and cultural factors. Characterization of the population exposed, and the factors influencing exposure is a needed step in order to mitigate adverse health effects associated with mercury exposure. Efforts to protect these populations must not only focus on increasing their awareness of the risks associated with consumption behaviors, but to also assess the factors that may present barriers to advisory compliance, and influence consumption behaviors.

2.7. Florida's mercury problem

Initial queries to determine the source of mercury pollution to Florida waters identified the state's many garbage incinerators, waste burning furnaces operated by large cities and hospitals, and landfills as potentially responsible. Many authors have established that municipal solid waste combustion, and medical waste incinerators are significant anthropogenic sources of mercury to Florida [Dvonch et al., 1999; Lindberg and Price, 1999; Lindberg et al., 2001]. Mercury associated with the waste input in these facilities, is subject to volatilization at ambient temperatures. Lindberg and Price, [1999], assessed the airborne emissions from municipal landfill operations, by sampling mercury concentrations in the air, measuring mercury flux from passive landfill gas vents, and measuring mercury concentrations over cover material at municipal landfill operations. However, the emissions were determined to be less than 1% of the total anthropogenic mercury releases in the region [Lindberg and Price, 1999]. Thus, the study failed to establish a tidy link between mercury levels in fish and their proximity to local mercury emission sources, such as landfills and solid waste incinerators. The discovery of fish samples in the same system with vastly differing levels of mercury in their flesh led to further uncertainty regarding linking sources to the levels observed [Stephenson, 2001].

Further attempts to reduce uncertainties in the pathways, and mass balance of mercury from waste disposal resulted in additional studies in the south Florida metropolitan area [Atkeson et al., 2002; Lindberg and Price, 1999; Lindberg et al., 2001]. Lindberg et al.,

[2001] identified significant concentrations of total gaseous mercury, monomethylmercury, and dimethylmercury in municipal landfill gas, thus identifying these facilities as significant sources of atmospheric mercury emissions. Considering the chemical properties of the various species of mercury, their different emission profiles, as well as, their susceptibility to chemical inter-conversion via atmospheric reactions, it was postulated that deposition of atmospheric mercury species may play a significant role in mercury loading to Florida.

The importance of atmospheric transport and subsequent deposition of mercury species as a mechanism for the delivery of mercury to remote locations has been demonstrated by several authors [Dvonch et al., 1995; Lindberg et al., 2001; Pirrone et al., 1995; Seigneur et al., 1994]. Studies have demonstrated that the deposition of mercury can be strongly influenced by contributions of aerosol and reactive gaseous mercury form local sources, this being especially true for highly urbanized and industrialized regions [Iverfeldt, 1991; Lee and Iverfeldt, 1991; Lindqvist et al., 1991]. Comparatively, mercury deposition in rural areas was shown to be significantly lower, as a result of attenuation by deposition and dilution processes as distances from the emission sources increases [Guentzel, 1997; Iverfeldt and Lindqvist, 1986; Pirrone and Keeler, 1993]. Elucidation of the influence of atmospheric mercury deposition process to mercury loading to Florida was a necessary step towards understanding its cycling in its ecosystems.

Initial studies for the apportionment of atmospheric mercury deposition to Florida identified local sources as being responsible for mercury loading to the domain. Analyzing daily event precipitation samples collected from multiple sites across Florida, Dvonch et al., [1998], discovered significant site to site and event variations in mercury concentrations that could not be accounted for by rainfall amounts alone. Based on the spatial and temporal patterns observed; the authors postulated that local sources strongly influence atmospheric wet deposition of mercury to Florida, whilst acknowledging that mesoscale meteorological transport conditions may also play a role. As an extension to this study, the authors investigated the source-receptor relationships for mercury and other species deposited in rainfall in south Florida, and concluded that municipal waste incineration and oil combustion account for around 70% of mercury wet deposited at five Florida Everglades sites [Dvonch et al., 1999]. Models results were found to agree closely with stack measurements at local point sources.

Contrasting conclusions were formed by Guentzel et al., [2001], as they also sought to identify the processes influencing rainfall deposition of mercury in Florida, and concluded that processes other than particulate mercury transport and scavenging govern rainfall mercury deposition in Florida. The researchers hypothesized that long-range transport of reactive gaseous mercury species, coupled with strong convective thunderstorm activity during the summertime represents greater than 50% of mercury deposition in southern Florida. Additionally, they concluded that local anthropogenic particulate and reactive gaseous mercury emissions account for only 30 to 46% of the summertime rainfall mercury deposition across Florida [Guentzel et al., 2001]

The current research underscores the level of uncertainty currently associated with our understanding of mercury deposition phenomenon in Florida. Reduction of any uncertainties regarding the magnitude of effect anthropogenic emission may have on mercury biogeochemical cycling, and ultimately human and environmental health is an important step in closing the existing gap in our understanding of this phenomenon. More importantly, there still remains a need to determine the relative importance of local atmospheric sources on ecosystem mercury concentrations. It can be achieved by taking detailed inventories, characterizing the importance of local mercury releases, and improving our characterization of population exposure.

This body of work contributes to our understanding of the local mercury source categories, major sources influencing local mercury deposition. The reduction of uncertainties regarding the magnitude of effect local anthropogenic emission may have on local mercury loading is an important step in closing the existing gap in our understanding of this phenomenon, and will serve to inform policies for the mitigation of human and environmental health effects from mercury exposure.

3. Tampa Bay mercury release inventory

3.1. Introduction

Mercury and its compounds are widely recognized as highly toxic to human and ecosystem health. Because of its high mobility and toxicity, small environmental mercury releases can result in significant exposures, which emphasizes the importance of understanding the sources of mercury to the environment. Mitigation of the health effects of mercury requires the elucidation and quantification of specific mercury sources contributing to observed exposures.

In the United States, population mercury exposure occurs predominantly through fish and seafood consumption [O'Neill, 2004; Tollefson and Cordle, 1986]. The high levels of mercury observed in the tissues of predatory fishes are as a result of the bioaccumulation and biomagnification of methylated mercury species entering the aquatic system predominantly via atmospheric deposition processes [Engstrom et al., 1994; Anderson and Bigler, 2005; Tollefson and Cordle, 1986]. Although natural processes contribute Gustin et al. [2000]; Lindqvist and Rodhe [1985]; Mason and Pirrone [2009], anthropogenic sources constitute a significant to source of atmospheric mercury emissions [Mason, 2009; Friedli et al., 2009; Murray and Holmes, 2004; Pacyna and Pacyna, 2001]. Direct water discharges (predominantly from mining activities) [de Lacerda, 2003; Porcella et al., 1997] and leachate from landfills [USGAO, 1983; Lindberg and Price, 1999] also constitute important routes for the entry of mercury in also the environment.

Anthropogenic mercury releases can be divided in those occurring due to indirect mercury use, such as processing of gold ore, and combustion of fossil fuels, or those releases resulting from the deliberate use of mercury in products. Due to its unique physical and chemical properties, as well as, its availability, accessibility, and low cost, mercury species play important roles in commerce, industry, mining, metallurgy, manufacturing, medicine, and dentistry [Schroeder and Munthe, 1998; Mahaffey and Pirrone, 2005]. Mercury is consumed in a broad range of products and processes in the United States. The major categories of demand include industrial processes (chlor-alkali production, catalysis, etc.), medical and industrial measuring devices (fever and other thermometers, measuring and control devices/equipment) batteries (mercuric oxide and others), lighting (neon, compact fluorescent, high intensity discharge (HID), and other energy efficient lamps), switches (industrial, household, and automotive switches, contacts and relays), laboratory and medical uses (amalgams), pharmaceutical processes, and agricultural products and preservatives [Maxson, 2005]. Understanding the impact of each of these source categories on mercury releases is a significant step in identifying levers for reducing population and ecosystem effects of mercury pollution within the domain.

Government and state agencies have made significant efforts to reduce the environmental impacts of mercury products through legislations, regulations, and consumption guidelines [Wood, 1971; Anderson et al., 2004; Cunningham et al., 1994; Hassett-Sipple et al., 1997; Mahaffey et al., 1997; Ebinghaus et al., 2005]. These efforts seek to reduce the use of mercury and mercury containing products, manage mercury waste, and reduce population exposure to mercury. However, little information exists about the impacts of these efforts on environmental mercury releases, especially at the local and sub-regional level. These deficiencies may exist due to uncertainties arising from a lack of detailed information about mercury releases from the various source types [Cain et al., 2007]. Moreover, the Mercury Study Report to Congress [Keating, 1997], identified the characterization of source contributions to environmental mercury releases at sub-regional and local scales as important uncertainty to be addressed. Here, we try to derive estimates of mercury releases in the Tampa Bay area.

The overarching goal of this chapter is to investigate and describe the links between mercury use and release in the Tampa Bay area. Specifically, I seek to identify which product or process in the domain contributes significantly to mercury releases and the major sinks receiving these releases. Identifying levers for the reduction of mercury use and release in a domain of interest requires an understanding of the role each use category plays in the environmental, cultural, and socioeconomic dynamics of the system under study. Specifically, the results generated from this inventory can be applied to understand the benefits that may be achieved by adopting a particular reduction strategy, thus prioritizing agency efforts to reduce mercury environmental releases

This analysis quantifies the releases and distribution of mercury in products and processes to environmental compartments (air, water, and solid-waste), as these products/processes are used. This is accomplished by building a mercury release inventory for the Tampa bay area. The inventory considered mercury containing products such as clinical thermometers, sphygmomanometers, and switches contained in household appliances and automobiles. The inventory also considered processes contribution to mercury release in the Tampa Bay area, such as, cremations, industrial mercury emissions, and fossil fuel combustion.

3.2. Methods

3.2.1. Substance flow analysis

To determine mercury mass flow rates to environmental pools in the Tampa Bay area, I utilized a hybrid Substance Flow Analysis (SFA) - Industrial Ecology (IE) approach [Allenby et al., 1999; Van der Voet, 2002]. SFA is concerned with analyzing the societal metabolism of substances by evaluating how products and processes affect the flow of that material or substance in a well-defined system.

The Swedish National Chemicals Inspectorate (KEMI) initially utilized a substance flow analysis to estimate mercury releases from batteries, fluorescent lamps, and sewerage sludge, considering their contributions to environmental pollution via incineration, breakage, and land filling [Swedish National Chemicals Inspectorate, 1997]. This method was adopted by Barr ,[2001], in their study of mercury releases related to products in Minnesota [Barr Engineering Company, 2001; Cain et al., 2007], and Obenauf and Skavroneck, [1997], in their mercury source assessment for mercury in the Greater Milwaukee area. The latter studies adopted additional pathway, including assessing the fate of mercury in waste treatment facilities. Spreadsheets were utilized as tools to understand mercury fate during product use, disposal, to track its entry into environmental pools, and to assess waste management strategies. This concept was further extended by de Cerreno et al., [2002], by combining a substance flow analysis with industrial ecology to understand mercury releases to the New York - New Jersey harbor [de Cerreno et al., 2002]. The study sought to develop pollution prevention strategies for the harbor, and included an analysis of the costs associated with the introduction of technologies to reduce the use and release of mercury in the study area. This study adopts some of the methods and parameters developed in previous studies [Obenauf and Skavroneck, 1997; Swedish National Chemicals Inspectorate, 1997; Barr Engineering Company, 2001], especially the work of de Cerreno et al., [2002], and applies them to estimate the release of mercury from sources in the Tampa Bay area.

This approach is applied here to identify the major sources contributing to the use and release of mercury in the Tampa Bay area, and the determination of the distribution of the released mercury between air, water, and solid waste as major environmental compartments. To develop the system, I collected information from various sources including peer-reviewed scientific publications, research reports and white papers, industry association data repositories, and expert reports. This information was then tabulated in a spreadsheet model which allowed for inputs, distribution factors, and release factors to be varied to evaluate multiple scenarios. This analysis considered three scenarios; mercury releases in 2000, 2006, and 2011.

A combination of a 'top-down' and 'bottom-up' system analysis approaches was utilized to determine the contributions of mercury sources to sinks in the domain. The top-down method utilizes macroscopic data to define the overall system before refining sub-components, as the resolution of the data permits. In this way, an overview of the system is formulated without the need to define subsystem components. Conversely, the bottom-up approach requires the definition of all subsystems, which allows for the definition of grander components, until a complete top level system is formed. The approach that was adopted at each level of the system varied depending on the availability and resolution of data defining each source

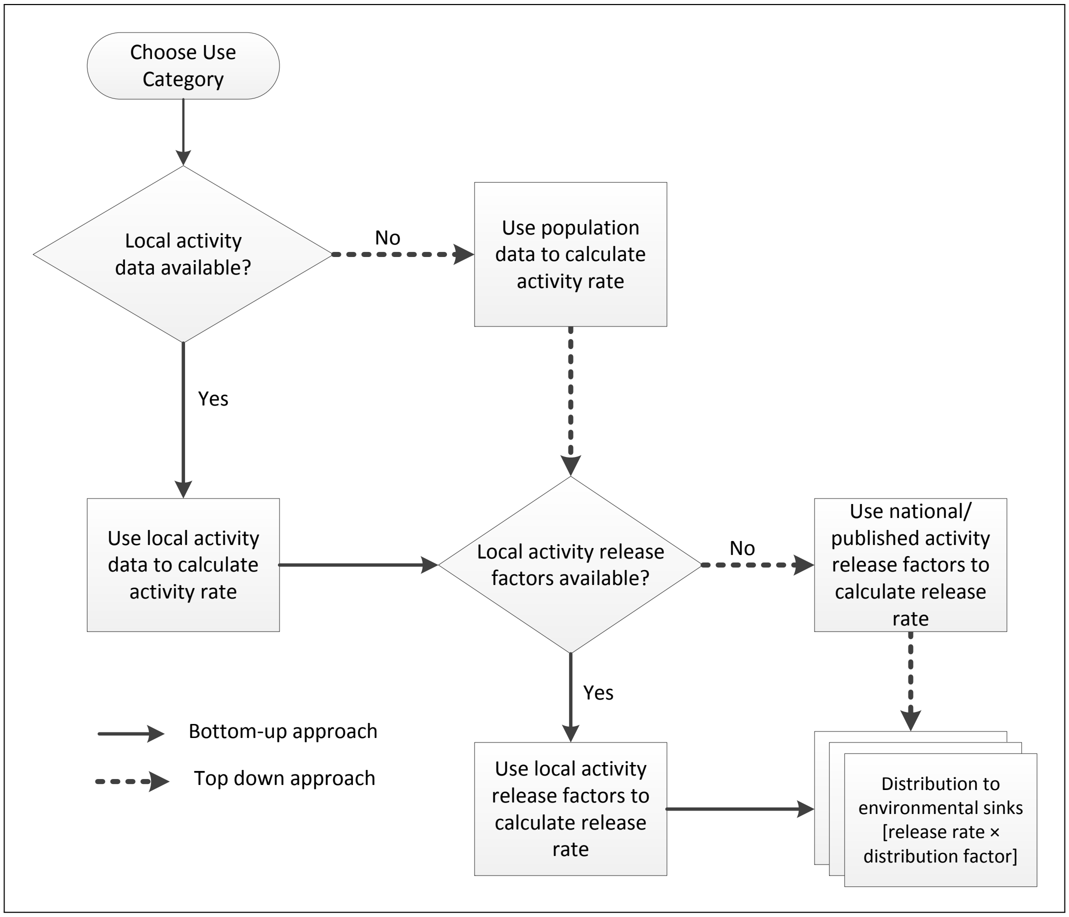


Figure 3.1. Flow diagram for decision process determining inventory calculations

category. Higher resolution, local activity specific data facilitated a more precise bottom-up approach, however as the resolution of the data decreased, a top-down, population driven approach was utilized. Figure 3.1 gives an overview of the decision process involved in this analysis.

Mercury mass releases were based on estimates or measurements conducted for release sectors in the study area (bottom-up approach), or were derived from national estimates and scaled to the domain by a factor that accounts for the relative differences in population (top-down approach). Mercury use and release sources were categorized as products or processes as determined by the activity being studied. For example, residential heating and power generation facilities were considered as mercury release processes, while switches and thermostats contribute to mercury release as derivative products. The quantity of mercury consumed by some use categories can be estimated as directly proportional to the population in the study area, for example, health care activities, and consumption and disposal of consumer goods. These uses depend predominantly upon the demand for goods and services by the domain population, and hence are relatively proportional to population size [Barr Engineering Company, 2001; de Cerreno et al., 2002].

Microsoft Excel® software was used to build the inventory and perform calculations to determine mercury releases from the source categories, and the distribution of these releases into the environmental pools defined. Mercury releases from a specific source category were determined by the use of published release factors, or factors calculated from mass-balance based estimations of the release process. Generally, contribution of each sector to the total mercury releases to a specific pool was determined by multiplying the activity rate (e.g. cremations, vehicles, or thermometers used per year) by the specific mercury release factor for that activity (mass of Hg released/unit activity) to determine a mass release rate ($\mathrm{kg\,yr^{-1}}$). Activity rates were based on local data, when available, or scaled from national data based on population fraction when no local activity data were available. Equation (3.2.1b) describes this approach. Alternatively, a mass release rate was used for some categories, scaled by population fraction, where required, as shown in Equation (3.2.1a)

$$R = f_p \times F_b \times D \times (1 - C) \tag{3.2.1a}$$

$$R = A \times F_a \times D \times (1 - C) \tag{3.2.1b}$$

Here, R is the mass rate of mercury released to a particular sink in $\mathrm{kg_{Hg}\,yr^{-1}}$, f_p is the population scaling factor (regional population/national population) , F_b is the national mass release rate for the source category or product being assessed in $\mathrm{kg\,yr^{-1}}$, F_a is the activity release factor in $\mathrm{kg_{Hg}\,activity^{-1}}$, A is the activity rate of the process or product being assessed in $\mathrm{activity\,yr^{-1}}$, D is the distribution factor to a particular sink (fraction of total mass distributed to air, solid-waste, or waste-water). Where relevant, the recycling or release control of mercury in a particular sector is accounted for by assigning an appropriate recycle or control efficiency factor, given by C. Recycle or control efficiency factors were sourced from published literature [Asari et al., 2008; Hagreen and Lourie, 2004; Sznopek and Goonan, 2000; Jasinski, 1995].

3.2.2. Release parameter data

Relevant data for this inventory was obtained from federal and state data portals including the U.S Census Bureau for national, state and regional population data, and statistics concerning medical facilities [United States Census Bureau, 2010], the Department of Transportation, Federal Highway Association, and the Florida Department of Transportation for regional traffic data [Florida Department of Transportation, 1996], and the U.S EPA for data pertaining to facility and source category mercury releases. Additionally, some use-specific data such as medical and household uses were sourced from regional governing bodies and civic associations, such as the Florida Cremation Association, and Dental Association for medical/cremation statistics.

This study considers the fate of mercury in products and processes utilized in the domain, with particular interest in the role of each environmental compartment (air, waste-water, and solid-waste) as a direct sink for these releases. Release factors consider the mass of mercury generated per unit activity in the domain, and may be specific to a product or process category, such as release factors for fuel combustion, while others may be general, such as releases from the disposal of household waste. The quality of release factors varies greatly. For example, little information may be available on how much mercury is released from products due to breakages and spills, and thus the release factors used to determine mass rates may be highly uncertain. Conversely, release factors derived for waste combustion processes are based on stack measurements and are relatively more accurate. The release factors used in this study were sourced from peer reviewed literature, technical reports, and conference proceedings. A summary of the release rates and release factors used in this analysis, sources, and associated qualitative confidence are presented in Table 3.2.

Ultimately, the allocation of mercury mass among these environmental pools were determined by using distribution factors (fraction of mercury mass released to each environ-

Table 3.1. Distribution factors used to determine mercury releases to environmental pools

	Distribution factors[a]		
Sector	Air	Waste-water	Solid-waste
Transportation	1.00	-	-
Crematoria	1.00	-	-
Dental	-	0.25	0.75
Industry	0.48	-	0.52
Laboratories	0.02	0.67	0.31
Batteries	-	-	1.00
Lamps	0.25	-	0.75
Thermostats	-	-	1.00
Hospitals			
Thermometers	0.12	0.22	0.66
Sphygmomanometers	0.12	0.22	0.66
Dental	-	0.25	0.75
Laboratory	0.25	0.70	0.05
Households			
Furnaces	-	-	1.00
Thermometers	0.10	0.20	0.70
Sewerage	-	1.00	-
Switches			
Appliances	0.28	-	0.72
Automobile	0.33	-	0.67
Lighting	-	-	1.00

[a] Distribution factors were compiled from de Cerreno et al. [2002], Barr Engineering Company [2001], and Cain et al. [2007] .

mental pool). Distribution factors are used to indicate the likelihood that a product, and mercury contained in that product will follow a given pathway by assigning a fraction of the total mass released to that specific pathway. Releases considered in this analysis included atmospheric releases, releases to solid-waste, and releases to waste-water pools. Distribution factors used in this study were derived predominantly from published literature such as peer reviewed studies and reports from professional organizations, or calculated. Table 3.1 summarizes the distribution factors used in this study.

3.2.3. Estimating mercury releases

The following section describes the estimation of total mercury releases from each sector in the Tampa Bay area, and how they were distributed among air, water, and solid waste. This includes the estimation of activity amounts for each category and inventory

Table 3.2. Release rates and factors used to determine mercury releases in the Tampa Bay area

	Activity release factor (F_a)[a]					
Sector[a]	2000	2006	2011	Units	Confidence[b]	Reference
Transportation	2.1×10^{-9}	2.1×10^{-9}	2.1×10^{-9}	kg_{Hg} mile^{-1}	High	Hoyer et al. [2004]
Crematoria	1.5×10^{-3}	1.5×10^{-3}	1.5×10^{-3}	kg_{Hg} cremation^{-1}	High	USEPA [1997b]
Dental Facilities	4.8×10^{-1}	4.7×10^{-1}	4.7×10^{-1}	kg_{Hg} dentist^{-1}	Medium	Adegbembo et al. [2002]
Thermostats	3.0×10^{-3}	3.0×10^{-3}	3.0×10^{-3}	kg_{Hg} thermostat^{-1}	Medium	NEWMOA [2010]
Hospitals						
Thermometers	7.0×10^{-4}	7.0×10^{-4}	7.0×10^{-4}	kg_{Hg} thermometer^{-1}	Medium	de Cerreno et al. [2002]
Sphygmomanometers	9.0×10^{-2}	9.0×10^{-2}	9.0×10^{-2}	kg_{Hg} $\text{sphygmomanometers}^{-1}$	Medium	de Cerreno et al. [2002]
Dental	6.5×10^{-1}	6.5×10^{-1}	6.5×10^{-1}	kg_{Hg} facility^{-1}	Medium	de Cerreno et al. [2002]
Laboratory	2.9	1.64	8.0×10^{-1}	kg_{Hg} laboratory^{-1}	Low	Sznopek and Goonan [2000]
Households						
Furnaces	1.4×10^{-4}	7.8×10^{-5}	5.2×10^{-5}	kg_{Hg} household^{-1}	Low	Cain et al. [2007]
Thermometers	7.0×10^{-4}	7.0×10^{-4}	7.0×10^{-4}	kg_{Hg} thermometer^{-1}	Low	de Cerreno et al. [2002]
Sewerage	1.4×10^{-10}	1.4×10^{-10}	1.4×10^{-10}	kg_{Hg} $\text{L}_{\text{sewerage}}^{-1}$	Low	AMSA [2000]
Switches						
Appliances	1.4×10^{-3}	1.4×10^{-3}	1.4×10^{-3}	kg_{Hg} switch^{-1}	Medium	Obenauf and Skavroneck [1997]
Automobile	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	kg_{Hg} switch^{-1}	Low	de Cerreno et al. [2002]
	Mass release rate (F_b)[c]					
Lighting (switch)	1.6×10^{1}	1.7×10^{1}	1.8×10^{1}	kg_{Hg} yr^{-1}	Low	Obenauf and Skavroneck [1997]
Industry	3.4×10^{2}	5.0×10^{2}	1.1×10^{3}	kg_{Hg} yr^{-1}	High	USEPA [2013]
Laboratories	1.4×10^{2}	9.0×10^{1}	4.5×10^{1}	kg_{Hg} yr^{-1}	Low	Sznopek and Goonan [2000]
Batteries	2.3×10^{1}	1.9×10^{1}	1.4×10^{1}	kg_{Hg} yr^{-1}	Low	NEWMOA [2010]
Lamps	6.4×10^{1}	5.3×10^{1}	3.7×10^{1}	kg_{Hg} yr^{-1}	Low	Obenauf and Skavroneck [1997]

[a] Denotes *bottom-up* method was used to determine mass release rate

[b] Confidence is based on how many independent estimates were available, and rigorousness of the data collection.

[c] Denotes *top-down* method was used to estimate regional mass release rates.

period, and the consideration of qualitative confidence category for products and processes in each sector. As mentioned previously, this analysis compares the periods 2000, 2006, and 2011, thus the method discussed for each sector was repeated across all inventory years, accounting for changes in release factors and activity rates. For sections of the inventory driven by summary national data, US Census data corresponding to inventory years was used. The distribution factors applied are listed in Table 3.1.

3.2.3.1. Automobiles/fuel consumption

Mercury releases from the automobile/fuel use sector were based on daily vehicle miles of travel (DVMT) in the region, sourced from the Florida Department of Transportation (FDOT), Highway Mileage Reports for the four counties in the region [Florida Department of Transportation, 1996]. DVMT data was converted to a yearly amount, and then multiplied by an estimate of mercury released per mile. I used the EPA estimate of $2.9 \times 10^{-9}\,\mathrm{kg\,mile^{-1}}$, assuming a vehicle distribution of 85% gasoline vehicles and 15% for the region [Hoyer et al., 2004]. All mercury released from this sector was assumed to be emitted directly to the air.

3.2.3.2. Cremations

Estimations of mercury release from cremations was derived by multiplying the number of cremations in the region by a release factor. The number of cremations was established by applying a cremation rate [CANA, 2000]) to the number of deaths [FDOH, 2013] in the region over the analysis periods. Mercury release rates from cremations were reported as $1.5 \times 10^{-3}\,\mathrm{kg\,cremation^{-1}}$ [USEPA, 1997b]. Since there are no controls for mercury at crematoria, and no current estimates for how much mercury remains in the ashes, all releases were assumed to be directly released into the airshed.

3.2.3.3. Dental facilities

Release of mercury from dental facilities (dental offices and laboratories) considered two sources; the application of new mercury fillings, and the removal of old fillings both contribute to mercury releases. The estimations were based on the number of dental facilities in the region which was scaled from national data (US Census Bureau [United States Census Bureau, 2010]). Specific amalgam release rates used were $4.5 \times 10^{-4}\,\mathrm{kg\,amalgam}^{-1}$ (application) and $3.6 \times 10^{-4}\,\mathrm{kg\,amalgam}^{-1}$(removal) [de Cerreno et al., 2002]. It was assumed that an equal amount of dentists are using amalgams as are involved in amalgam removal. Additionally, an annual amalgamation application rate of 768 amalgams applied per dentist per year (16 removals per week by 48 weeks [DelConte, 2000]), and an annual removal rate of 816 amalgams removed per dentist per year [de Cerreno et al., 2002] is assumed. Summary amount was then estimated by the number of dentists in the region, the fraction of those dentists applying/removing amalgams, the rate at which application/removal occurs, and the specific application/removal release rates. Cerreno et al., [2002] reported a recycling rate of 10% which was adopted here. Partitioning of mercury in dental waste assumes two pathways, waste-water (25%) and solid-waste (75%).

3.2.3.4. Industrial releases

Data for releases from the industrial sector was determined by querying the USEPA's Toxic Release Inventory (TRI). The TRI is a reporting requirement under the US Emergency Planning and Community Right-to-Know Act of 1986 by industrial facilities having ≥ 10 employees, manufacturing a chemical in excess of 25,000 lbs/year, or otherwise using a chemical in excess of 10,000 lb/year. Industrial mercury releases in the domain was determined from querying the EPA Toxic Release Inventory at the county levels and summing to determine regional contributions. Distribution factors were not calculated since the TRI data was already grouped by category (accounting for releases to air, waste-water, and solid-waste).

3.2.3.5. Laboratories (non-hospital)

The contributions of non-hospital laboratories to mercury releases was estimated from published literature. Sznopek and Goonan, [2000], estimated the contributions of laboratories to mercury releases in the US from industrial sources in 1996, assuming decreases of 1 ton per year starting at an initial value of 20tonnes(1996). This rate of change was adopted here to determine release rates for analysis periods in this study. Summary amount was adjusted for regional contributions by a population scaling factor, and adjusted for the contributions from in-hospital laboratories to prevent double counting. Distribution factors for mercury releases from non-hospital laboratories were reported as 2.5% to air, 67% to waste-water, and 31% to solid-waste.

3.2.3.6. Batteries

The Northeast Waste Management Officials' Association (NEWMOA) and the Interstate Mercury Education and Reduction Clearinghouse (IMERC) commissioned a study that summarized mercury use in products sold in the United States in 2001 and 2004. This data was derived from information submitted by hundreds of manufacturers of switches and relays, dental amalgam, thermostats, lamps, thermometers and other measuring devices, batteries, and chemicals. The contribution of battery use to mercury releases in the domain was calculated by using this national data [NEWMOA, 2010], and adjusting for regional contributions. Extrapolation were made to account for later inventory years. A recycling amount of 10% was assessed [de Cerreno et al., 2002]. Mercury releases from batteries were all distributed to the solid-waste environmental pool [de Cerreno et al., 2002].

3.2.3.7. Fluorescent lamps

Mercury releases from fluorescent lamps was derived from 2000 national data as reported by the Northeast Waste Management Officials Association's Trends in Mercury Use Report [NEWMOA, 2010]. This data was adjusted for regional population by a scaling factor. NEWMOA, [2010], reported data for the periods 2000 and 2004, thus extrapolations were made to derive values for the accounting periods used in this study (2000, 2006, 2011). Recycling rate for fluorescent lamps vary regionally. Since no data could be found on actual rates for the region a value of 20% was used [de Cerreno et al., 2002]. 25% of mercury released from this sector is assumed to volatilize directly to the air compartment, while the remaining 75% goes directly to the solid-waste environmental pool [de Cerreno et al., 2002].

3.2.3.8. Thermostats

The USEPA estimates that the 2619000 thermostats are disposed of nationally every year, with 83% of these thermostats containing mercury [Obenauf and Skavroneck, 1997; USEPA, 1992]. Using a reported value of 3 grams of mercury per thermostat [WDNR, 1997], this amount was adjusted for the regional population by a scaling factor. A recycling rate of 2% was applied to the amount derived [de Cerreno et al., 2002]. All releases from this sector was assumed to partition to the solid-waste pool [de Cerreno et al., 2002].

3.2.3.9. Hospitals

Mercury releases from hospitals included thermometers, sphygmomanometers, dental facilities, and hospital laboratories as contributing sources. The mercury release from each of these sub-sectors were calculated individually and summed to derive the total releases from the hospital sector.

Mercury releases from thermometers considered one thermometer per bed per hospital. Hospital bed-count data in the region were obtained from state hospitals report from the Florida Agency for Health Care Administration. A 10% breakage rate was applied, and the average mercury concentration per thermometer was set at 0.7 grams/thermometer [de Cerreno et al., 2002]. After applying a 10% recycling fraction, mercury release were distributed as follows: Air (12%), waste-water (22%), and solid-waste (66%) [de Cerreno et al., 2002].

Similar assumptions were made to determine the contributions from sphygmomanometers to hospital mercury releases. A one-to-one sphygmomanometers-to-bed ratio was used, however, it was assumed that of the total amount, 90% were wall-mounted, and the remaining were mobile units [de Cerreno et al., 2002]. The mercury content of sphygmomanometers were reported as 90 grams/sphygmomanometer, and breakage fractions of 0.04 and 0.1 were assigned to the wall-mounted and mobile units respectively [de Cerreno et al., 2002]. After accounting for recycling (10%), the similar distribution pattern to thermometers was applied.

The contribution of dental facilities in hospitals were calculated assuming 60% of hospitals in the region had dental facilities on the premises [de Cerreno et al., 2002]. Similar to the estimation for stand alone dental facilities above, amalgam removal and application were calculated separately and summed to derive the total contributions (similar application rates and amalgam mercury concentrations were considered). A recycling rate of 10% was also applied. Mercury distribution from this sub-sector assumed partitioning fractions of 25% to waste-water, and 75% to solid-waste.

The contributions of hospital laboratories were derived by using the national estimates of mercury releases from medical laboratories, dividing by the total number of medical laboratories in the nation to derive an average specific laboratory release factor, and adjusting this amount for the number of regional medical laboratories [Sznopek and Goonan, 2000]. A 5% recycling factor was applied and the releases were distributed to air (24%), waste-water (70%), and solid-waste (5%).

3.2.3.10. Households

Household mercury use and subsequent releases include contributions from residential furnaces, fever thermometers, and household products/waste-water releases. The mercury release from each of these sub-sectors were calculated individually and summed to derive the total releases from the household sector. All calculations were based on household number generated from US Census data corresponding to the analysis period, adjusted for the region.

Releases of mercury from household thermometers were estimated on the assumption of a household consumption rate of 0.24 thermometers sold per household per year, an assumed replacement fraction of 50% (half of the thermometers sold are replacing broken units), and a specific mercury content per thermometer of 0.7 grams [de Cerreno et al., 2002]. 70% of the mercury mass released from this sub-sector is assumed to partition directly to the solid-waste pool, 20% to waste-water, and 10% volatilizes directly to the air.

Releases from household furnaces considered the mercury content of switches contained in the furnaces. Activity from this sector was derived from national estimates of mercury releases from switches, and assuming that household furnaces account for 30% of all mercury releases from switches [Barr Engineering Company, 2001]. The activity derived was then adjusted to account for regional population. All mercury releases from this sub-sector was assumed to partition to the solid-waste pool.

Mercury releases from household products and waste-water discharges was estimated based on the average discharge of mercury per household [AMSA, 2000], and an estimate of yearly regional domestic waste-water treatment (adjusted from state data to account for population of the study domain) [FDEP, 2013]. All discharges were to the waste-water environmental pool.

3.2.3.11. Switches

Mercury releases from switches include contributions from lighting, appliances, and automobile switches.The mercury release from each of these sub-sectors were calculated individually and summed to derive the total releases for the sector.

Estimates of mercury releases from lighting switches in the region were derived from national estimates for lighting switches [Obenauf and Skavroneck, 1997], and scaled to account for regional population. All releases from this sub-sector was assumed to partition to the solid-waste pool [de Cerreno et al., 2002].

The contributions of household appliances to mercury releases from this sector was based on a national average disposal rate of 0.35 appliance per household per year, 0.01 switch per appliance, and 1.4 grams of mercury per switch, accounting for regional population [Obenauf and Skavroneck, 1997]. Distribution of mercury releases from this sub-sector consisted of 28% to air and 72% to solid-waste environmental pools [de Cerreno et al., 2002].

Mercury releases from automobile switches were estimated by counting vehicle ownership in the region via state motor registration data [Florida Department of Transportation (FDOT), Florida Department of Highway Safety and Motor Vehicle (FLHSMV)], and assuming a yearly average automobile disposal rate of 10% [de Cerreno et al., 2002]. Each vehicle was assumed to carry 1.6 switches, with each switch having a mercury mass of 1 gram. A recycling fraction of 6% was applied, and the resulting releases were distributed to the air (33%) and solid-waste (67%) environmental pools.

3.3. Results

Table 3.3 summarizes mercury releases by products and processes in the Tampa Bay area as estimated by the inventory for the periods 2000, 2006, and 2011. Total mercury releases displayed an increasing trend over the period surveyed. Contributions from dental facilities, industrial sources, and mercury containing switches were the most significant source categories accounting for total mercury releases in the Tampa Bay area over all inventory periods. Contributions from the industrial sector displayed the largest rate increases per study interval, and accounted for approximately 20% of total mercury releases over all inventory years. In 2000 and 2006, dental facilities were the most significant category contributing to mercury releases in the Tampa Bay area. In 2011, industrial releases became the highest mercury source category across all sectors, showing a 14% increase in releases over the previous period. Sector specific trends varied, with product sectors such as batteries, lamps, and switches showing trends of decreasing or stable releases over the period, while process sectors such as cremations, dental, and industrial processes displayed trend of increasing mercury releases over the period. Fever thermometers were the largest contributors to mercury releases from households, accounting for approximately 30 - 50% of total mercury releases from the sector. Similarly, mercury releases from automobile switches accounted for greater than 90% of total mercury release from switches in the study domain. Mercury recycling occurred mainly in dental facilities and fluorescent lamp use, and accounted for less than 5% of total mercury released across all inventory years.

Figure 3.2 shows summary mercury releases as estimated by the inventory. The subplots describes the contributions of release sectors for each analysis year (top-left, top-right, and bottom-left subplots), and allocation of summary releases to environmental pool by analysis year (bottom-right subplot). The solid-waste pool served as the largest receptor of mercury releases in the Tampa Bay area, with releases increasing over the study period (2000 - 2011). Similar trends were observed for the waste-water pools. Releases to the air pool demonstrated an initial increase over the first period, 2000 - 2006, before decreasing over the period 2006 - 2011. Contributions from stand-alone dental offices, industrial releases, household releases,

Table 3.3. Summary of Tampa Bay mercury releases to air, waste-water, and solid-waste for mercury containing products and processes (Kg)

	Total			Air			Waste-water			Solid-waste			Recycled[a]		
	2000	2006	2011	2000	2006	2011	2000	2006	2011	2000	2006	2011	2000	2006	2011
Automobiles	41	58	54	41	58	54	0	0	0	0	0	0	0	0	0
Batteries	20	17	12	0	0	0	0	0	0	20	17	12	2	2	1
Crematoria	11	22	24	11	22	24	0	0	0	0	0	0	0	0	0
Dental Facilities	508	572	830	0	0	0	127	143	207	381	429	622	56	71	113
Fluorescent Lamps	51	42	30	13	11	7	0	0	0	38	32	22	13	11	7
Hospitals	167	119	91	33	21	14	94	60	38	39	39	40	5	6	6
Household Releases	234	202	184	7	8	9	57	59	60	169	135	115	0	0	0
Industrial Releases	340	501	1054	161	158	106	1	1	1	178	342	947	0	0	0
Laboratories	18	22	9	0	0	0	12	15	6	6	7	3	0	0	0
Switches	302	413	376	95	131	119	0	0	0	207	281	257	0	0	0
Thermostats	67	71	71	0	0	0	0	0	0	67	71	71	0	0	0
TOTAL	**1760**	**2038**	**2735**	**362**	**410**	**334**	**291**	**277**	**312**	**1106**	**1352**	**2089**	**77**	**89**	**128**
							Products that are included above[b]								
Hosp: Thermometers	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
Hosp: Sphyg[c]	32	34	37	4	4	4	7	8	8	21	23	24	4	4	4
Hosp: Dental Facilities	16	16	17	0	0	0	4	4	4	12	12	13	2	2	2
Hosp: Laboratories	118	68	36	29	17	9	83	48	25	6	3	2	0	0	0
House: Furnaces	118	77	54	0	0	0	0	0	0	118	77	54	0	0	0
House: Thermometers	74	82	87	7	8	9	15	16	17	52	58	61	0	0	0
House: Products/waste	43	43	42	0	0	0	43	43	42	0	0	0	0	0	0
Switch: Lighting	16	17	17	0	0	0	0	0	0	16	17	17	0	0	0
Switch: Appliances	4	5	5	1	1	1	0	0	0	3	3	4	0	0	0
Switch: Vehicles	281	390	353	94	130	118	0	0	0	187	260	235	0	0	0

Due to rounding, row and column values may not add up to summary value displayed.

[a] Not added to total. Recycled mercury from products and processes are considered still in the system and thus not subject to partitioning to distribution pathways.

[b] Subsets of mercury releases from Hospitals, Households, and Switches. Hosp=Hospitals, House=Households.

[c] Sphygmomanometers

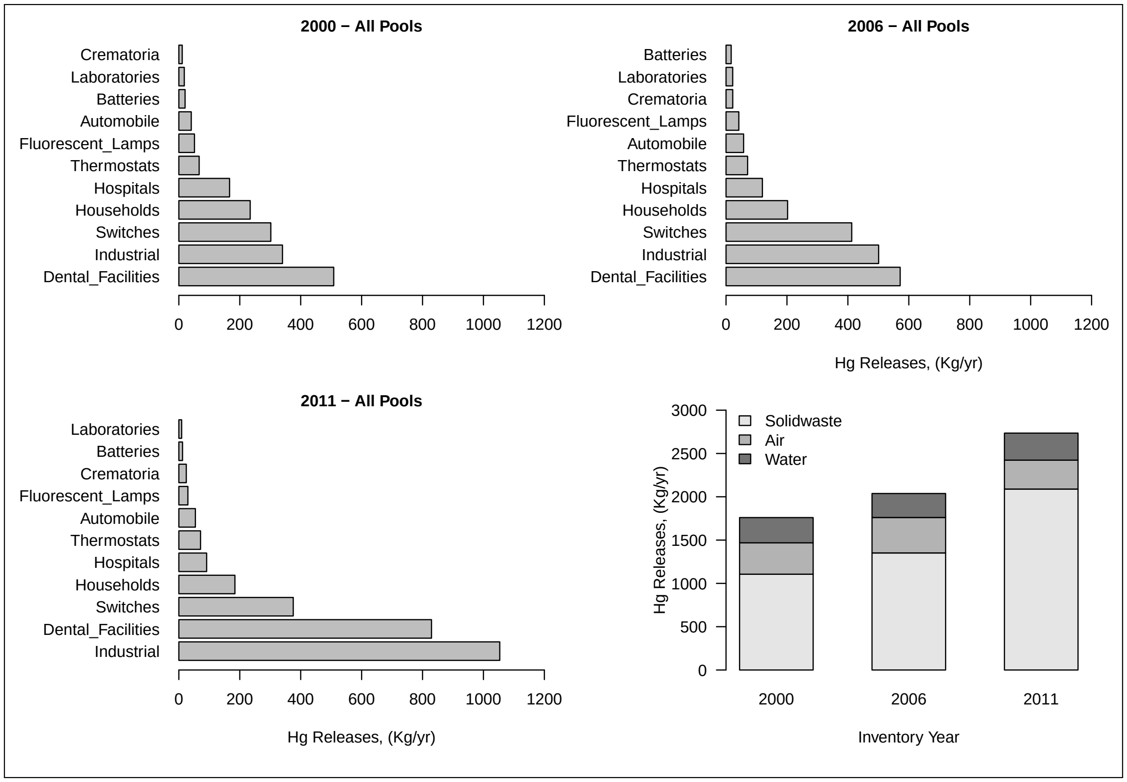


Figure 3.2. Estimations of source contributions to mercury releases to all environmental pools. Reseuts are shown for the inventory periods 2000, (top-left subplot), 2006 (top-right subplot), and 2011 (bottom-left subplot), respectively. Summary releases for all sectors grouped by inventory period is shown by the bottom-right subplot.

and switches were important to this environmental pool, with contributions from industrial releases showing the greatest rate of change over the period (see Table 3.3). Additionally, contributions from mercury containing processes (dental works, industrial processes) were more significant to the solid-waste pool than mercury containing products in the domain.

Figure 3.3 shows the contributions of sectors in the domain to atmospheric mercury releases as estimated by the inventory. Atmospheric mercury releases increased slightly over the period 2000 - 2006, and decreased over the period 2006 - 2011. Industrial emissions and disposal of switches (specifically from automotive switches) dominated atmospheric mercury releases from all sectors, over all inventory periods. Both of these sectors displayed decreases in emissions over the 2006 - 2011 period, which accounted for the decreasing trend observed for summary releases to the pool over the 2006 - 2011 inventory period. There were also notable contributions from the automobile/fuel use sector to this environmental pool, with

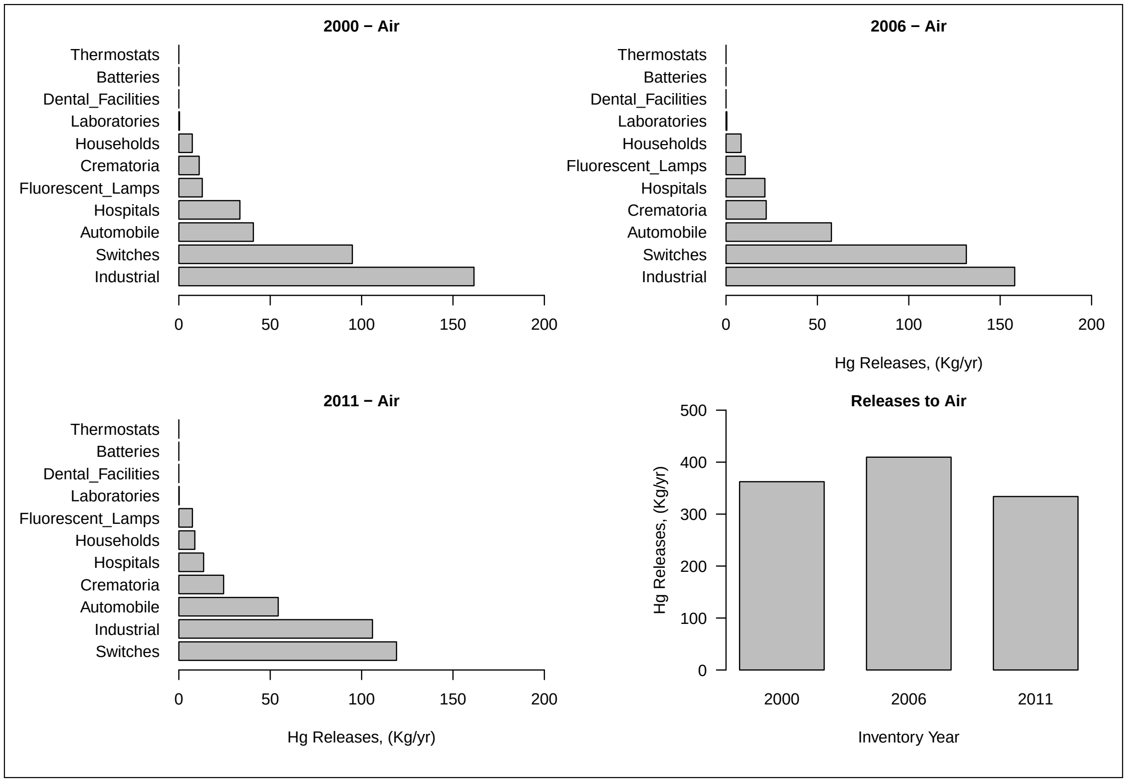


Figure 3.3. Estimates of source contributions to atmospheric mercury releases. Results shown are for the inventory periods 2000, (top-left subplot), 2006 (top-right subplot), and 2011 (bottom-left subplot), respectively. Summary releases for all sectors grouped by inventory period is shown by the bottom-right subplot.

emissions increasing slightly over the 2000 - 2006 interval, and then decreasing over the 2006 - 2011 interval (Table 3.3).

Figure 3.4 shows the contributions of sectors in the domain to mercury releases to the waste-water pool as estimated by the inventory. Mercury releases to the waste-water pool was dominated by releases from dental facilities in the region, accounting for between 45-65% of total releases across all inventory years, with an increasing trend over the period. Additionally, notable contributions were observed for the hospital (laboratories) and household (products/waste) sectors. Overall, an increasing trend in releases to the waste-water pool was observed. Releases to this environmental pool were dominated by contributions from the processes sector, while contributions from products were smaller.

Figure 3.5 shows the releases of mercury to the solid-waste pool by products and processes in the Tampa Bay. Mercury releases to the solid-waste sector included contributions

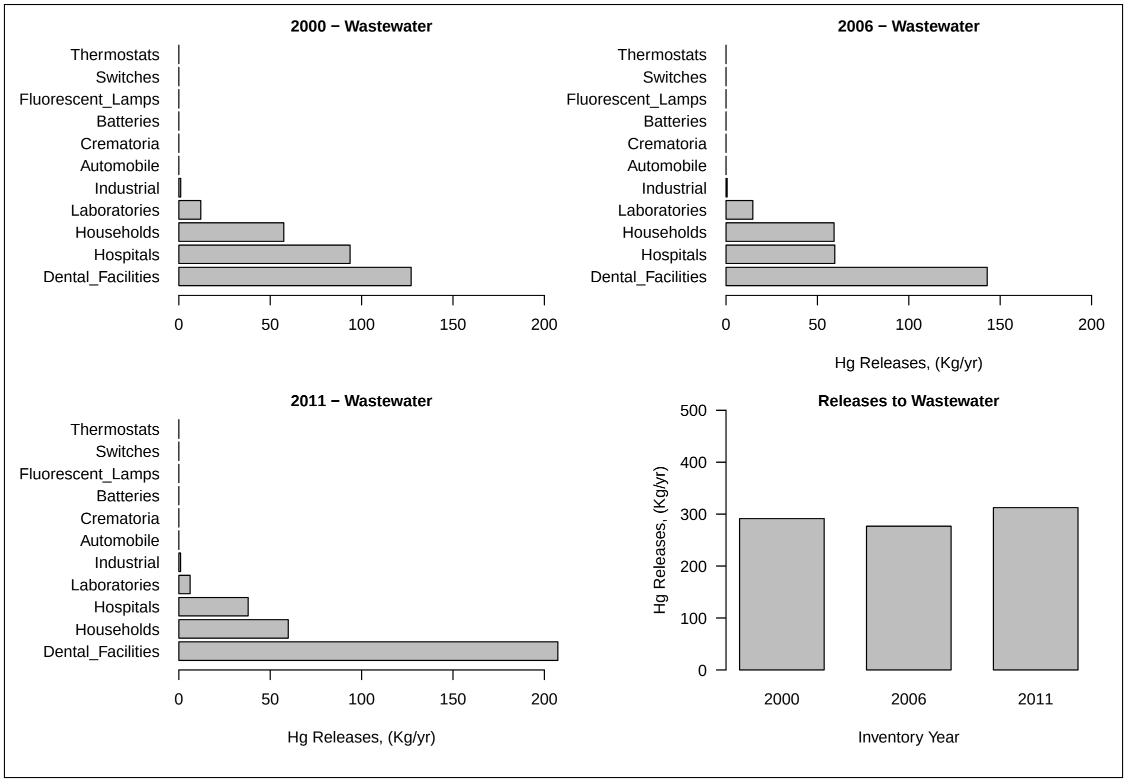


Figure 3.4. Estimates of source contributions to mercury releases to the waste water pool. Results shown are for the inventory periods 2000, (top-left subplot), 2006 (top-right subplot), and 2011 (bottom-left subplot), respectively. Summary releases for all sectors grouped by inventory period is shown by the bottom-right subplot.

from dental and industrial facilities, household products and waste, and switches (vehicles and furnaces). Releases to the solid-waste pool showed an increasing trend over the period, with 2006 - 2011 releases showing the largest growth over the period. The significant increase in contributions to the solid-waste pool from the industrial sector in 2011 was responsible for this trend, accounting for approximately 45% of total releases. Contributions from dental facilities oscillated around 30% over the entire survey period. Releases from automobile switches accounted for approximately 20% of mercury released to the solid waste sector in 2000 and 2006, but contributions decreased by 10% in 2011.

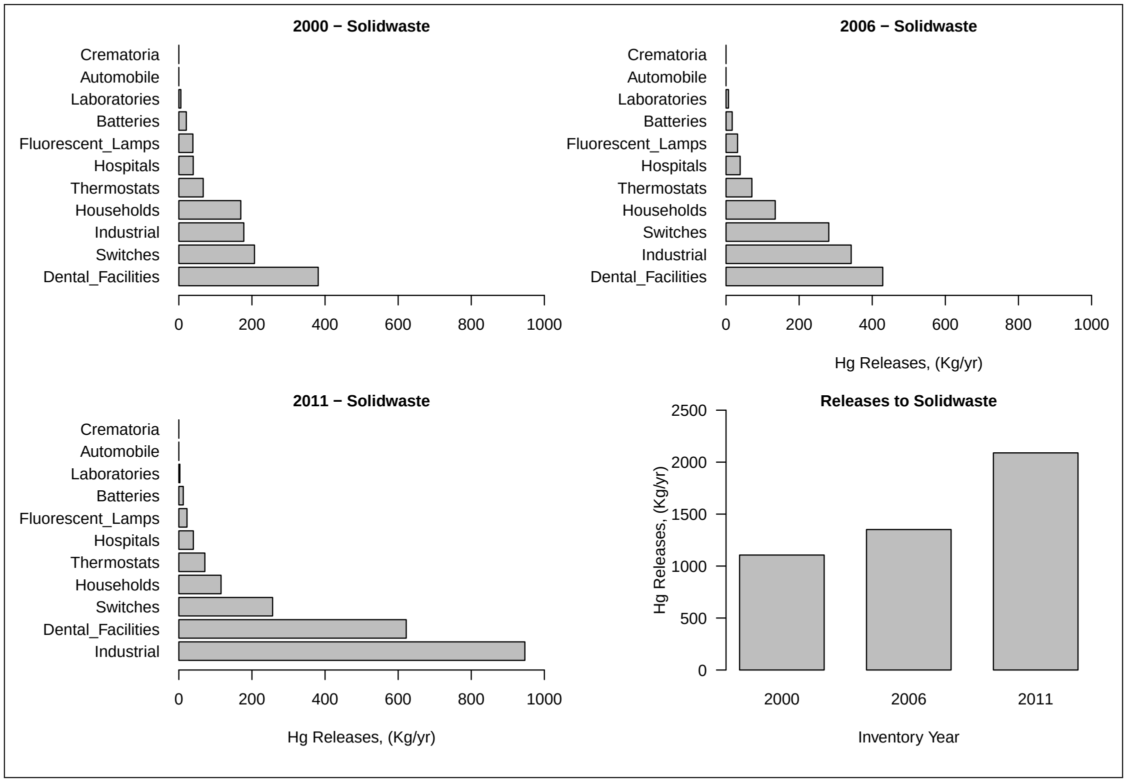


Figure 3.5. Estimates of source contributions to mercury releases to the solid-waste pool. Results shown are for the inventory periods 2000, (top-left subplot), 2006 (top-right subplot), and 2011 (bottom-left subplot), respectively. Summary releases for all sectors grouped by inventory period is shown by the bottom-right subplot.

3.4. Discussion

Results from the inventory shows that industrial releases was the one of most important sources of mercury to the Tampa Bay area. Industrial releases accounted 20% of total releases in 2000, 25% in 2006, and 39% in 2011, with the releases to air and solid-waste pools. As mentioned in the method development section, releases from industrial sources in the domain was derived from USEPA's Toxic release inventory, and was reported as direct emissions to environmental pools. Mercury release from industrial sources were distributed primarily to the air and solid-waste pools. We observe a decrease in fractional distribution to the atmospheric pool across inventory years, with air distribution factors of 0.47, 0.31, and 0.1 for the 2000, 2006, and 2011 inventory years respectively. Conversely, we observe and opposite trend in the distribution factor for the solid-waste pool, which showed an increasing trend of

0.52, 0.68, and 0.9, for the 2000, 2006, and 2011 inventory years respectively. These trends also coincided with an increase in releases from the sector and demonstrates a shift of the source sink that may be a response of increased emissions regulations.

It must be noted that incineration in waste-to-energy (WTE) facilities is the predominant method of solid waste treatment in Florida. The Florida Department of Environmental Protection has identified Florida as having the largest capacity to burn MSW of any state in the US. Consequently, much of the mercury associated with solid waste pools are ultimately released to the air via these processes. Thus, the air may ultimately play a much more significant role as a sink for mercury releases than estimated by this inventory.

Releases to the solid-waste pool increased at a significantly higher rate than that to the waste-water pool, however, it was difficult to discern the source category accounting for these increases. The source of data for industrial mercury releases in the Tampa Bay area consisted of mercury release data from industries such as coal mining, metal mining, electric utilities, food/beverages/tobacco, textiles, paper and printing, wood and leather products, cement industries, stone/glass/clay industries, primary metals, computers and electronics, transportation equipment, and the hazardous waste and chemicals industry. The larger fraction of total mercury releases allotted to this sector contrasts with the relative distribution of mercury releases among source categories from similar studies. In de Cerrano et al., [2002], study of mercury in the New York/New Jersey Harbor, the authors only counted the contributions from industrial furnaces which accounted for as little as 3% of total mercury release in the domain. This may be an attribute of the domain since the geographic and economic characteristics of the New York/New Jersey area differs from the location of this study. Other studies used in this analysis did not assess mercury releases from industrial processes, but rather focused in product categories [Barr Engineering Company, 2001; Cain et al., 2007; Sznopek and Goonan, 2000; NEWMOA, 2010].

Table 3.4 compare the fractional contributions of selected source categories to total mercury concentration as calculated by several similar inventories. There is good agreement in mercury release from dental facilities (stand-alone). In this study dental facilities accounted

Table 3.4. Comparisons of fractional contributions of selected mercury release sectors from similar studies

	Tampa Bay		Minnesota[a]		NY/NJ[b]	US[c]	
	2000	2006	2000	2005	2000	2000	2005
Dental facilities	29%	28%	27%	33%	39%	21%	28%
Switches[d]	17%	20%	16%	19%	16%	31%	28%
Batteries	1%	1%	1%	2%	1%	16%	12%
Fluorescent lamps	3%	2%	11%	7%	7%	10%	7%
Industrial sources	19%	25%	-	-	3%	-	-
Total (kg/yr)	**1,760**	**2,038**	**2,524**	**1,648**	**10,250**	**148k**	**102k**

[a] Substance Flow Analysis of of Mercury in Products, Minnesota Pollution Control Agency.
[b] Pollution Prevention and Management Strategies for Mercury in the New York/New Jersey Harbor.
[c] Substance Flow Analysis of Mercury Intentionally Used in Products in the United States.
[d] Includes releases from lighting, appliances, vehicles, and thermostats.

for 29% of regional total in 2000, 28% in 2006, and 30% in 2011. This distribution compares favorably with the contributions of dental facilities in the New York/New Jersey mercury inventory which accounted for approximately 39% (2000) of total mercury releases. Similarly, Barr, [2001], in their research in support of the Minnesota Mercury Emissions Inventory, reported that dental facilities accounted for approximately 27% of total mercury releases in 2000, and 32% in 2005 [Barr Engineering Company, 2001]. There was also good agreement with fractional distribution of dental sources to total US releases (Table 3.4). Comparative fractional contributions for batteries and switches also show good agreement between the regional inventories, whilst the differences were much larger for the national data. This suggests variations of contributions of sources at different geographic levels which may be important for resolving local deposition phenomenon.

Several limitations exist in the development of this inventory that must be addressed. The mercury mass releases allocated to several categories were not based on specific source emission data, but was derived from bulk regional data and factored based on relative population of the region (top-down approach). This reduces the accuracy of the values allocated to these release sectors. This includes releases from thermostats, fluorescent lighting, batteries, and non-hospital laboratories. Additionally, some distribution and emission factors used were not specific to release activities in the Tampa Bay area, by was adopted from similar peer-reviewed mercury inventory studies [de Cerreno et al., 2002; Barr Engineering

Company, 2001; Sznopek and Goonan, 2000; Cain et al., 2007; NEWMOA, 2010]. Thus there may be some inherent limitations associated with their use for the Tampa area.

Overall, this inventory seeks to understand mercury use in products and process in the Tampa Bay area, and to understand their contributions to environmental mercury releases, with the emphasis of identifying changes in mercury release trends, and areas where pollution prevention strategies can be leveraged to reduce these releases. Estimates on mercury releases to the three key environmental pools indicate that pollution prevention strategies should target solid waste releases. This pool served as a direct receptor for mercury releases from industrial releases, dental facilities, household fever thermometers, and automotive switches, with these sectors accounting for almost 75% of mercury release to this pool. Strategies existing for these sectors include recycling and adopting non-mercury alternatives.

As mentioned previously, secondary treatment of mercury products released to this sink consists predominantly of incineration processes, thus resulting in eventual mercury releases to the atmosphere. Management strategies for the sector should consider removal of mercury from products before secondary treatment processes (waste-to-energe (WTE), incineration, and gasification).

The most significant sector contributing to direct atmospheric mercury emissions is industrial releases. This inventory was not able to tease out individual emission source categories, however, research indicates that fossil fuel combustion, particularly coal, is the most important mercury emission source sector. Understanding the specific source categories contributing to mercury release from industrial sources is an area of this research that will be explored in future work.

Methods are still being debated to address mercury emissions from industrial sources. Many states in the US have adopted mercury programs that seek to address mercury pollution. The State of Florida has developed an inventory of mercury air emission sources, developed mercury consumption advisories for fish species, developed and instituted mercury dental programs, and is a participant in the national program to recover mercury from switches in vehicles.

4. Analysis of regional and local mercury emission trends

4.1. Introduction

Mercury and its compounds are widely recognized as highly toxic to human and ecosystem health. Because of its high mobility and toxicity, small environmental releases can result in significant exposures, and emphasize the importance of understanding the sources of mercury to the environment. Mitigation of the health effects of mercury requires the elucidation and quantification of specific mercury sources contributing to observed exposures.

Mercury is used in a myriad of commercial products and industrial processes, both intentionally, as a reactant, ingredient, or component of a process or product, or indirectly; as an impurity associated with the feed material of an industrial process [Pacyna et al., 2006]. Consequently, the releases of mercury species in a particular domain are dependent on the use categories defining the specific region. Identification of levers to reduce the impact of environmental mercury releases requires an understanding of the contributions of release categories in the domain and the environmental pools that serve as direct receptors for these releases. This requires increasingly detailed mercury inventories at higher resolved spatial scales [Mahaffey and Pirrone, 2005; Mason, 2009].

The atmosphere is the most important pathway for the global dispersion and transport of mercury [Mason et al., 1994; Fitzgerald et al., 1998]. Processes accounting for the atmospheric fate and transport of mercury include emissions to the atmosphere, transformation and transport in the atmosphere, deposition from the air, and re-emission to the atmosphere [Rice et al., 1997]. As mentioned previously, emission of mercury is governed by naturally occurring and anthropogenic processes, with anthropogenic releases being dominated by industrial processes and combustion sources [Pirrone et al., 2010].

Anthropogenic sources are estimated to release approximately 2900 Mg (2008 estimates) of mercury annually with major contributions from fossil fuel-fired power plants, artisanal small scale gold mining, waste disposal, non-ferrous metals manufacturing, and cement production [Pirrone and Mason, 2009]. The significance of a particular industrial source to atmospheric mercury emissions is determined by the bulk material amount, the mercury content of the feed material, and the technology employed to reduce emissions [Pirrone et al., 2010], with the combination of mercury concentration and efficiency of abatement technology being used to derive emission factors for different source release categories. Fossil fuel used in electric power generation, especially those that use coal have been found to be the largest source category of mercury released to the atmosphere for both domains. Concentrations of mercury in coal and natural fuel oils vary substantially, depending on the type of fuel, as well as its origin. Similarly, chemical composition of the input material for incineration is one of the most important factors influencing the quantity of atmospheric emissions of various pollutants from waste incineration processes [Pirrone et al., 1996].

However, similar to the comparison of mercury use estimates, the significance of sources to total emissions vary between domains. These differences may increase significantly as the resolution of the domain increases, suggesting that strategies for mitigation of the effects of environmental mercury emissions in a particular domain requires an elucidation of the consumption and emission categories defining the specific region.

The objective of this chapter is to explore the trends in mercury emissions from point sources and source categories within the Tampa Bay area. The focus here is to identify emissions sources in the domain that contribute significantly to local mercury emissions and subsequent deposition. We also seek to explore whether significant changes have occurred across reporting periods for specific source categories. We seek to compare the differences in mercury emissions from sources in the Tampa Bay area with statewide emissions. Here we analyze and compare mercury emissions inventory data from the EPA National Emissions Inventory for the reporting years 1999, 2002, 2005, and 2008.

4.2. Methods

Anthropogenic releases of mercury to the atmosphere by sources in the Tampa Bay area was assessed by querying the emissions inventories compiled by the U.S Environmental Protection Agency (EPA), National Emissions Inventory (NEI) database. The NEI is an effort by the USEPA to establish a comprehensive inventory of both criteria and hazardous air pollutants (HAPs), with the intended purpose of providing support for risk analysis and atmospheric transport modeling efforts [Murray and Holmes, 2004].

The inventory is made up of point source, non-point source, and mobile source data, for sources in the US, and contains emissions estimates for major sources, area source, mobile sources, and other sources that do not readily fall into these categories. The EPA defines point sources in the NEI as sources for which the specific location is known, and may be either major sources or area sources. The Clean Air Act (CAA) defines major sources as those stationary sources with the potential to emit between 10 $\text{tons}\,\text{yr}^{-1}$ (one HAP) to ≥ 25 $\text{tons}\,\text{yr}^{-1}$ (combination of HAPs) of HAPs. Facilities whose annual emissions falls below this threshold are considered area sources [Murray and Holmes, 2004]. Non-point sources consists of area sources with smaller or more diffuse emissions, or whose specific location cannot be identified. Data for the inventory is derived from a number of sources including state, local and tribal agencies, and EPA regulated industrial source categories through Maximum Achievable Control Technology (MACT) standards.

NEI point source and non-point source data files for the inventory years 1999, 2002, 2005, and 2008 were downloaded (in MS Access format) for EPA Region 4, which serves Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee and 6 Tribes. Summary files provided by these databases include county emission summaries, source category summaries, point source facility summary, and point source stack summary.

I used R [R Core Team, 2013] to write queries, which were then applied to each database file to identify state and county, point and non-point source, and source category and facility emissions data for mercury compounds reported for each inventory period. This process is illustrated in Figure 4.1. State summaries of point and non-point data for the

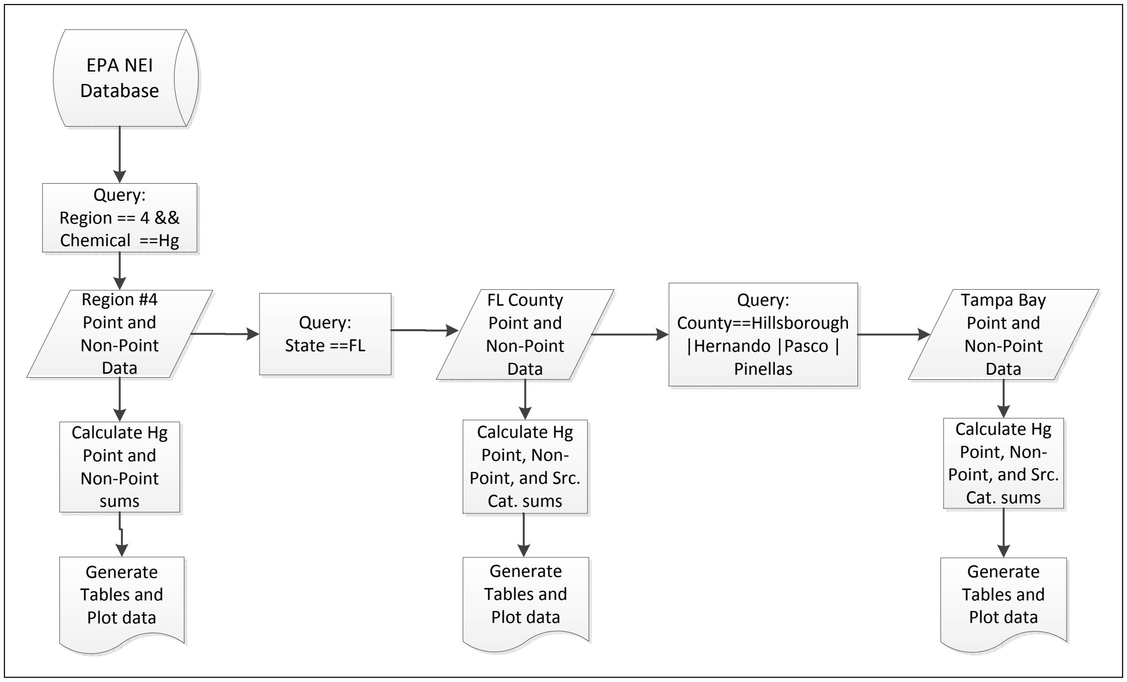


Figure 4.1. Flow diagram describing the process used to analyze EPA NEI mercury emissions data.

region for all inventory years were compared. Data specific to the state of Florida was queried to determine county specific point, non-point, and source category summary emissions, and to gain information about specific emissions and sources near the Tampa Bay area. Source Classification Codes (SCCs) and MACT codes, obtained from NEI look-up databases, were used to group and compare mercury emissions from individual facilities and sectors, and across inventory years.

4.3. Results and discussion

4.3.1. Regional and state level emissions

Figure 4.2 gives total mercury emissions from EPA Region 4 states as a summary of contributions from point and non-point sources. Overall, mercury emissions showed a decreasing trend across inventory years for all states, with the exception of Alabama, which showed a peak of around 5 tonnes in the 2002 inventory year before decreasing over the following periods. Contributions from point sources dominated state releases, accounting

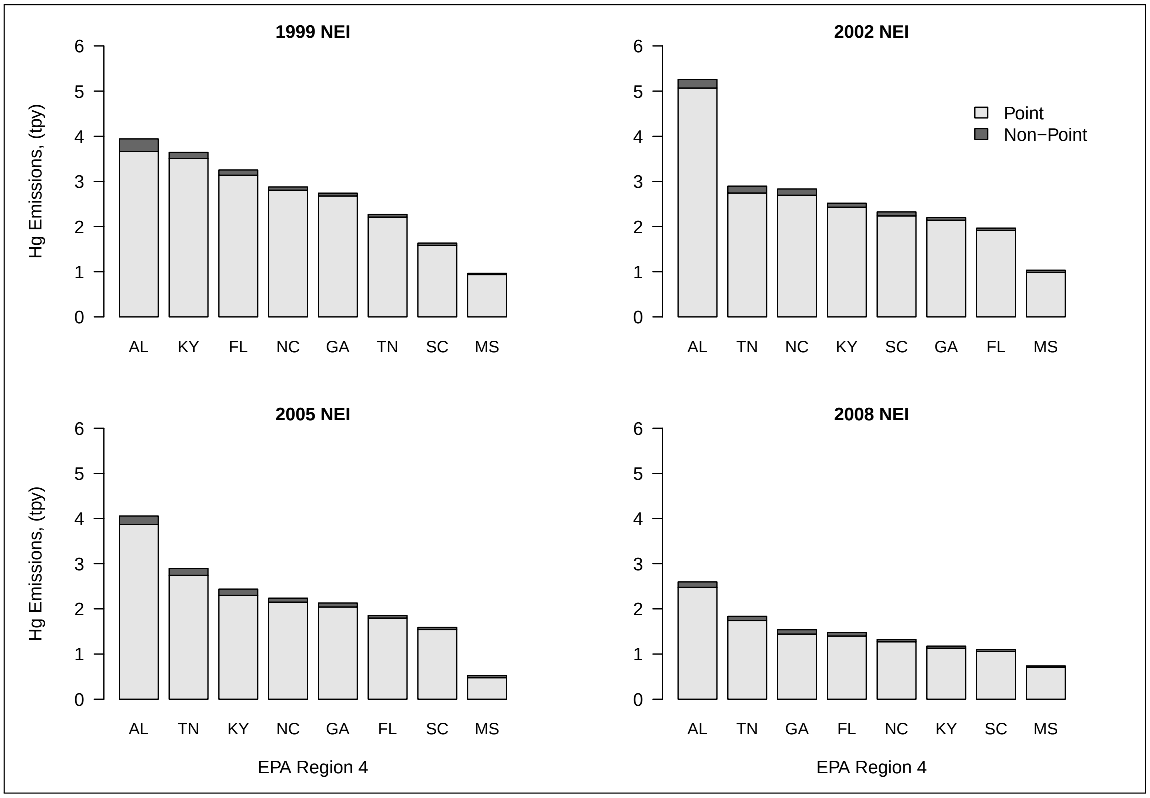


Figure 4.2. Emission summaries for EPA Region 4 states as compiled by the National Emission Inventories (NEI). Contributions from point and non-point sources are compared. The plot details summary NEI data from the 1999 (top-left subplot), 2002 (top-right subplot), 2005 (bottom-left subplot), and 2011 (bottom-right subplot) inventory years.

for greater than 90% of mercury emissions over all states and for all inventory periods. Emissions from Florida were highest in the 1999 inventory (the third highest across all states at approximately 3.5 tonnes) and demonstrated a decreasing trend over the other inventory years.

Figure 4.3 compares the contributions of the top 10 counties to mercury emissions in Florida across inventory years. Emission summaries indicate that the top 10 counties in Florida accounted for 83%, 80%, 80%, and 81% of total mercury emissions from the state over the 1999, 2002, 2005, and 2008 NEI periods, respectively. County summaries displayed a similar trend of decreasing emissions over all inventory years. Contributions from Tampa Bay area counties (Figure 4.3, dark bars), especially Hillsborough County, were significant to total mercury mass emitted in the state for all inventory years. The 1999 inventory shows that mercury emissions from Hillsborough County accounted for approximately 40% of total

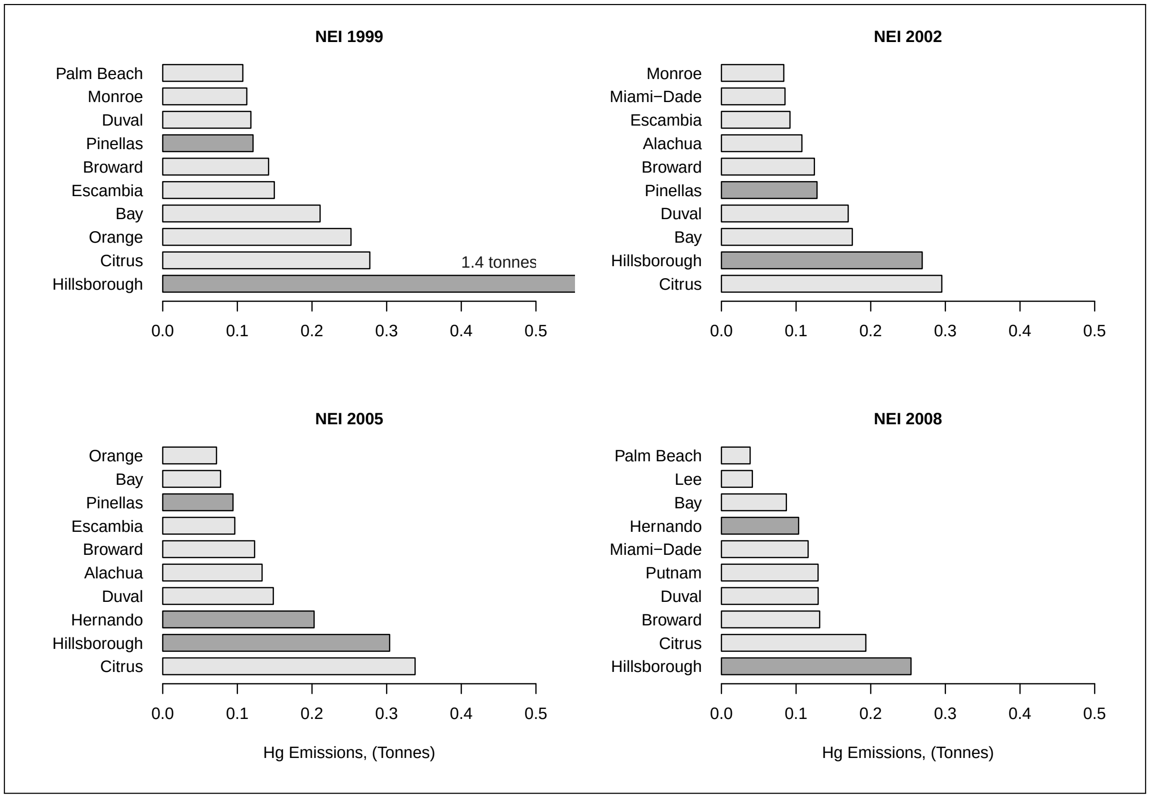


Figure 4.3. Emission summaries for Florida counties as compiled by the National Emission Inventories (NEI). Summary contributions from top 10 counties are compared. The plot details Florida NEI data from the 1999 (top-left subplot), 2002 (top-right subplot), 2005 (bottom-left subplot), and 2011 (bottom-right subplot) inventory years. Dark bars indicate counties in the Tampa Bay area

mercury emitted by the state. Hillsborough County also accounted for the highest statewide mercury emissions in 2008, and the second highest in 2002 and 2005. This disparity cannot be explained by accounting for relative differences in population. Similar to distributions at the state level, mercury emissions from point sources were significantly more than non-point sources, accounting for greater than 90% of total county emissions (see Table 4.2).

Figure 4.4 gives the contributions of the top 10 source categories to mercury emissions in the state. Source categories are summed as classified in the inventory by Standard Industry Classification (SIC) codes, MACT categories, or by North American Industry Classification System (NAICS) codes, depending on availability. The top 10 emission source categories accounted for approximately 94%, 98%, 99%, and 95% of total mercury emissions in the state as reported by the 1999, 2002, 2005, and 2008 inventory years, respectively. Specific

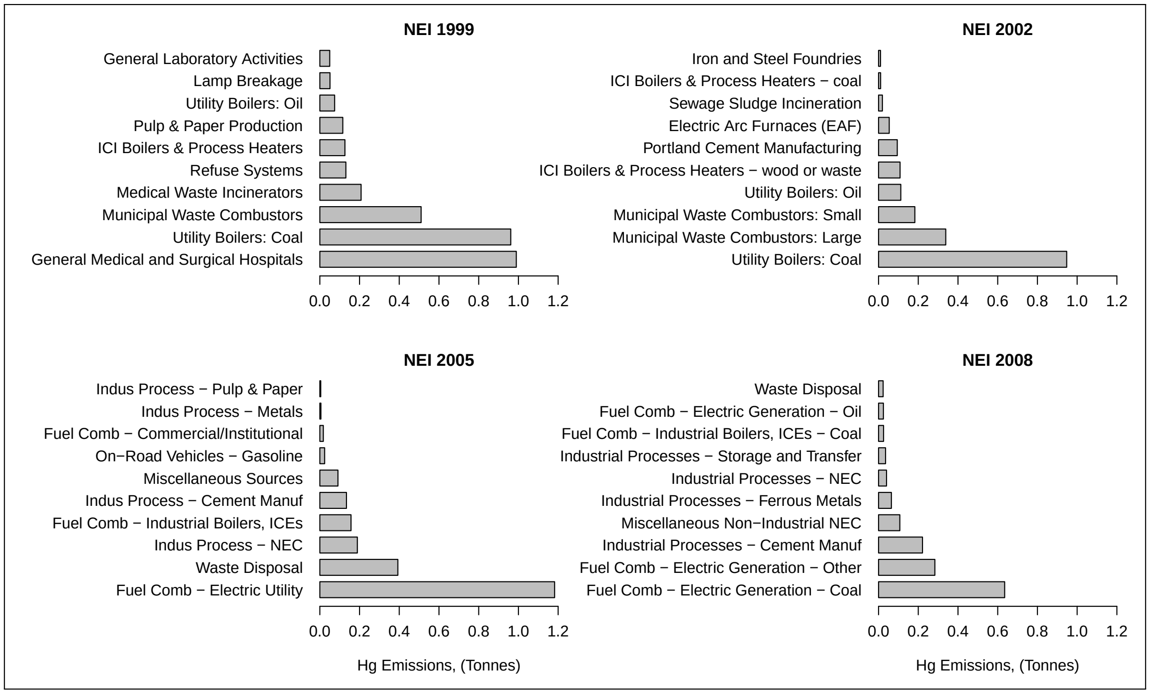


Figure 4.4. Source category emission summaries for Florida counties as compiled by the National Emission Inventories (NEI). Summary contributions from top 10 source categories are compared. The plot details Florida NEI data from the 1999 (top-left subplot), 2002 (top-right subplot), 2005 (bottom-left subplot), and 2011 (bottom-right subplot) inventory years. NEC - National Electrical Code

mass and fractional contributions of the top ten emission source categories for all inventory years are given in Table 4.1.

Utility boilers, specifically coal-fueled facilities, was consistently the largest state-wide emitter of mercury across all source categories, and inventory years. Coal combustion accounted for 28% (1999), 50% (2002), 54% (2005), and 41% (2008) of total mercury emitted in the state. Contributions from oil-fired utilities were less significant, with emissions varying between 2% and 6% across all inventory years (Table 4.1). Municipal waste incinerators also demonstrated significant contributions that was consistent across the inventory years 1999, 2002, and 2005, with emissions varying between 15% and 18%. Contributions from industrial, commercial, and institutional (ICI) boilers varied between 2% and 8%. ICI boilers involve controlled flame combustion and provide thermal energy to run processes, machinery, or to provide electricity [Murray and Holmes, 2004]. These boilers can use coal, oil, natural gas, or other fuels as energy sources. Mercury occurs naturally as trace constituent of theses

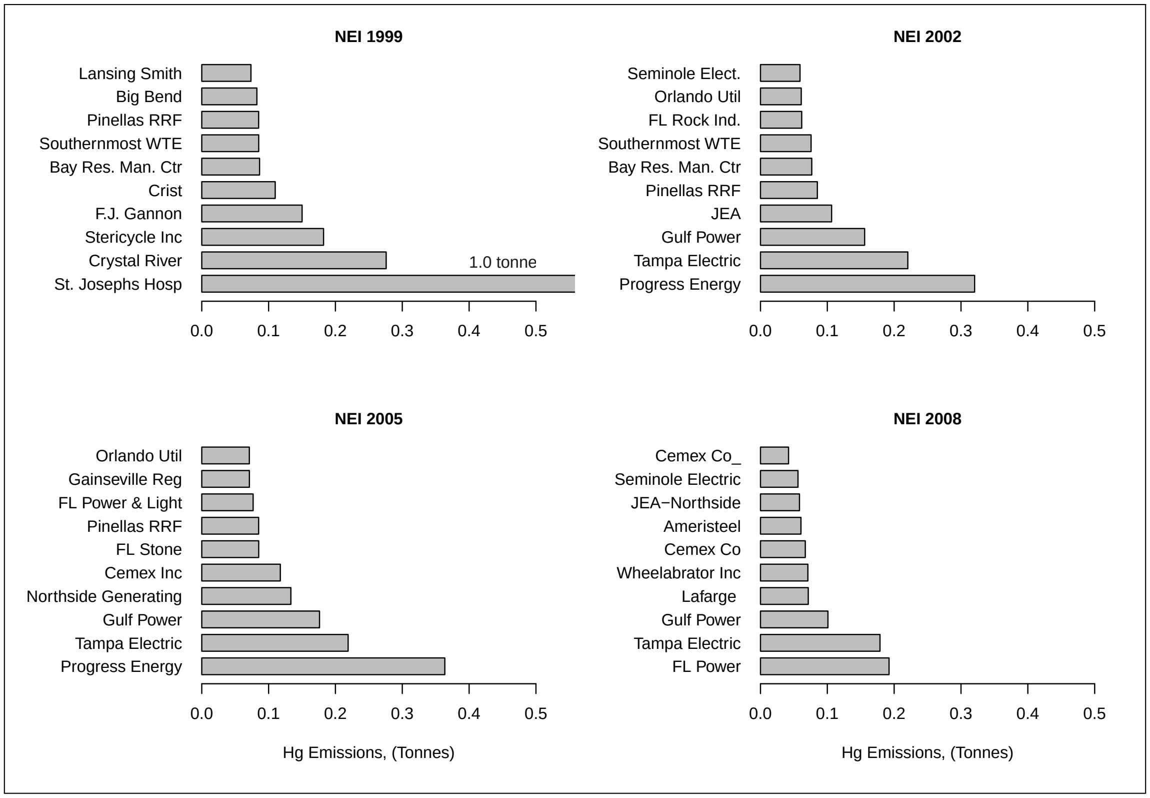


Figure 4.5. Contributions of mercury emitting facilities for Florida counties as compiled by the National Emission Inventories (NEI). Summary contributions from top 10 facilities are compared. The plot details NEI data from the 1999 (top-left subplot), 2002 (top-right subplot), 2005 (bottom-left subplot), and 2011 (bottom-right subplot) inventory years. See Appendix for facility descriptions

fuels, and is released as these fuels are combusted. These units are commonly used in a variety of industries including chemical manufacturing, primary metals industries, health services institutions, and educational institutions [Murray and Holmes, 2004]. Emission from cement manufacture industries displayed a consistent trend of increasing contributions to total releases, accounting for 5%, 6%, and 14% over the 2002, 2005, and 2008 inventory years, respectively.

The 1999 inventory reported a significant contribution from medical and surgical facilities in the state that was not repeated over subsequent inventory years. Interrogation of NEI facility emissions data, as shown by Figure 4.5 revealed the source to be the St. Joseph Hospital located in Hillsborough County. Emissions from this facility accounted for approximately 29% of state total, and 73% of county total for the 1999 inventory year. Mercury emissions from medical facilities may occur as a result of poorly controlled incineration of medical waste including discarded thermometers, sphygmomanometers, esophageal dilators, feeding tubes, and other devices may use mercury as a weight. The facility sums highlight the significant influence of power generating facilities on mercury emissions in the state as shown in Figure 4.5. This trend was consistent across all inventory years. Notable contributions were also observed from waste-to-energy (WTE/RRF) facilities.

4.3.2. Tampa Bay emissions

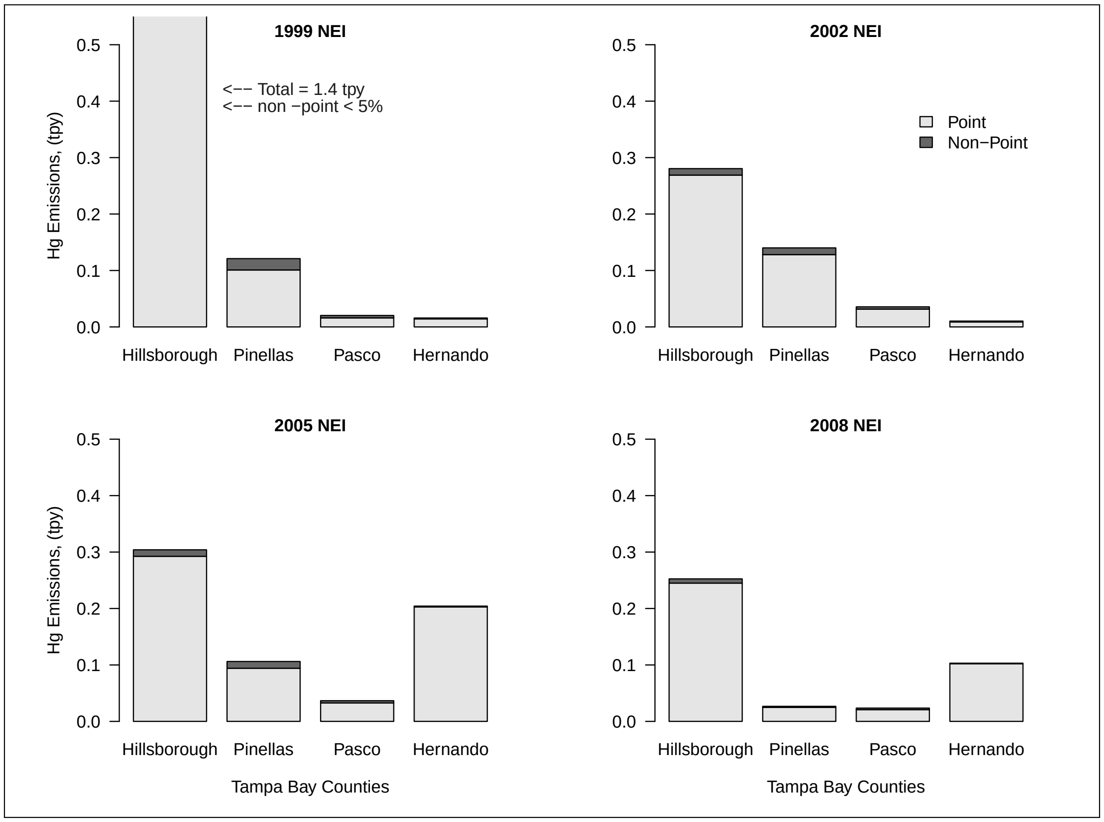


Figure 4.6. Point and non-point emission summaries for Tampa Bay counties as compiled by the National Emission Inventories (NEI). The plot details NEI data from the 1999 (top-left subplot), 2002 (top-right subplot), 2005 (bottom-left subplot), and 2011 (bottom-right subplot) inventory years.

Summary mercury emissions from point and non-point sources in the Tampa Bay area is graphed in Figure 4.6. Additionally, comparative summary of mercury emissions from point and non-point sources in Florida and the Tampa Bay area counties is given in Table 4.2.

Table 4.1. Comparisons of source category mercury emissions to Florida for inventory years 1999, 2002, 2005, and 2008. Top 10 categories are featured.

Source Category	Hg Emissions (tpy)	%
EPA NEI 1999		
General Medical and Surgical Hospitals	9.9E-01	29.0
Utility Boilers: Coal	9.6E-01	28.2
Municipal Waste Combustors	5.1E-01	14.9
Medical Waste Incinerators	2.1E-01	6.1
Refuse Systems	1.3E-01	3.8
ICI Boilers & Process Heaters	1.3E-01	3.7
Pulp & Paper Production	1.2E-01	3.4
Utility Boilers: Oil	7.5E-02	2.2
Lamp Breakage	5.1E-02	1.5
General Laboratory Activities	5.0E-02	1.5
EPA NEI 2002		
Utility Boilers: Coal	9.5E-01	49.5
Municipal Waste Combustors: Large	3.4E-01	17.7
Municipal Waste Combustors: Small	1.8E-01	9.5
Utility Boilers: Oil	1.1E-01	5.9
ICI Boilers & Process Heaters - wood or waste	1.1E-01	5.7
Portland Cement Manufacturing	9.4E-02	4.9
Electric Arc Furnaces (EAF)	5.4E-02	2.8
Sewage Sludge Incineration	1.9E-02	1.0
ICI Boilers & Process Heaters - coal	1.0E-02	0.5
Iron and Steel Foundries	9.9E-03	0.5
EPA NEI 2005		
Fuel Comb - Electric Utility	1.2E+00	53.7
Waste Disposal	3.9E-01	17.8
Indus Process - NEC	1.9E-01	8.6
Fuel Comb - Industrial Boilers, ICEs	1.6E-01	7.1
Indus Process - Cement Manuf	1.3E-01	6.1
Miscellaneous Sources	9.1E-02	4.1
On-Road Vehicles - Gasoline	2.4E-02	1.1
Fuel Comb - Commercial/Institutional	1.8E-02	0.8
Indus Process - Metals	5.5E-03	0.2
Indus Process - Pulp & Paper	4.6E-03	0.2
EPA NEI 2008		
Fuel Comb - Electric Generation - Coal	6.3E-01	41.2
Fuel Comb - Electric Generation - Other	2.8E-01	18.4
Industrial Processes - Cement Manuf	2.2E-01	14.3
Miscellaneous Non-Industrial NEC	1.1E-01	6.9
Industrial Processes - Ferrous Metals	6.5E-02	4.2
Industrial Processes - NEC	4.0E-02	2.6
Industrial Processes - Storage and Transfer	3.5E-02	2.3
Fuel Comb - Industrial Boilers, ICEs - Coal	2.5E-02	1.6
Fuel Comb - Electric Generation - Oil	2.4E-02	1.6
Waste Disposal	2.3E-02	1.5

Source classifications were based on SCC/MACT source category definitions as published in the NEI for each inventory. This accounts for the nominal differences in source categories across inventory years.

ICI = Industrial/Commercial/Institutional
Comb = Combustion
Indus = Industrial

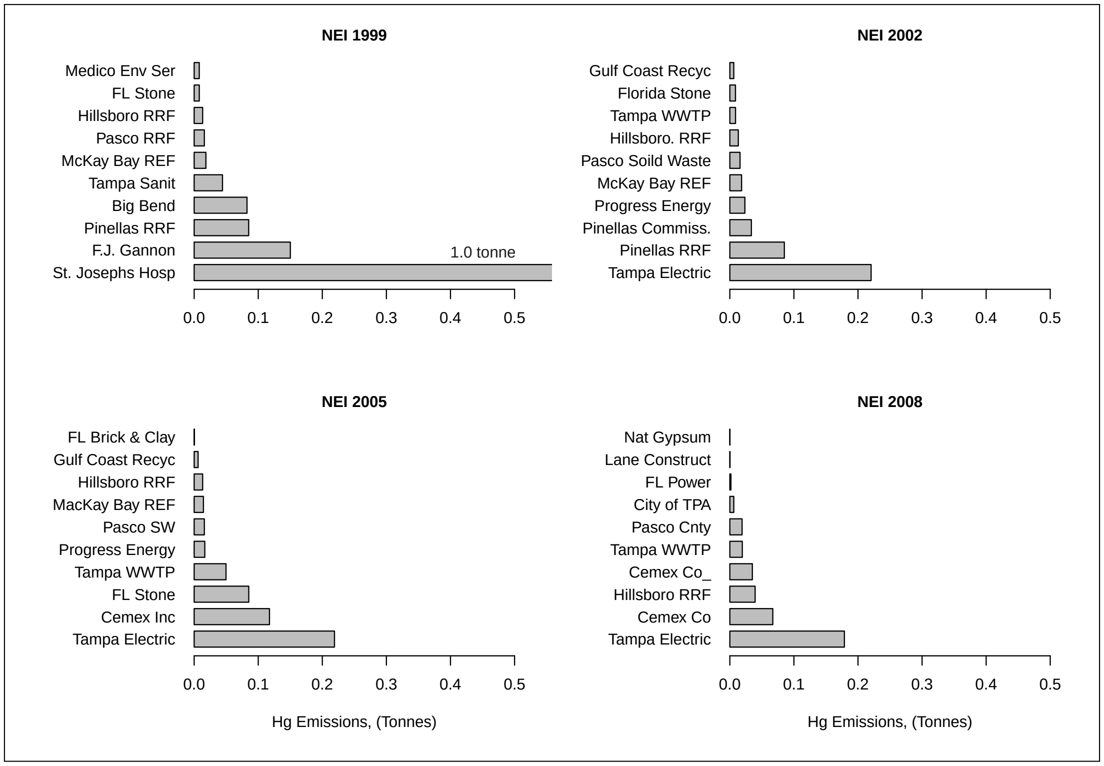


Figure 4.7. Contributions of mercury emitting facilities in the Tampa Bay area as compiled from NEI data. Summary contributions from top 10 facilities are compared. The plot details NEI facility data from the 1999 (top-left subplot), 2002 (top-right subplot), 2005 (bottom-left subplot), and 2011 (bottom-right subplot) inventory years.

Mercury emission in the Tampa Bay area did not display a particular trends, with emissions from the region accounting for 44%, 23%, 32%, and 27% of total emissions in the state over the 1999, 2002, 2005, and 2008 inventory years, respectively. As, discussed previously, mercury emissions for the 1999 inventory year was exceptionally large due to contributions from the medical/surgical hospital sector (single facility).

Similar to regional and state emissions trends, point source contributions dominated, contributing to larger than 93% of mercury emissions to all regional counties, across all inventory years Table 4.2. Emissions from Hillsborough County were the highest across the region for all inventory years, and displayed an overall decreasing trend over the period (1999 - 2008). The other counties displayed significant variations in emissions over the inventory years.

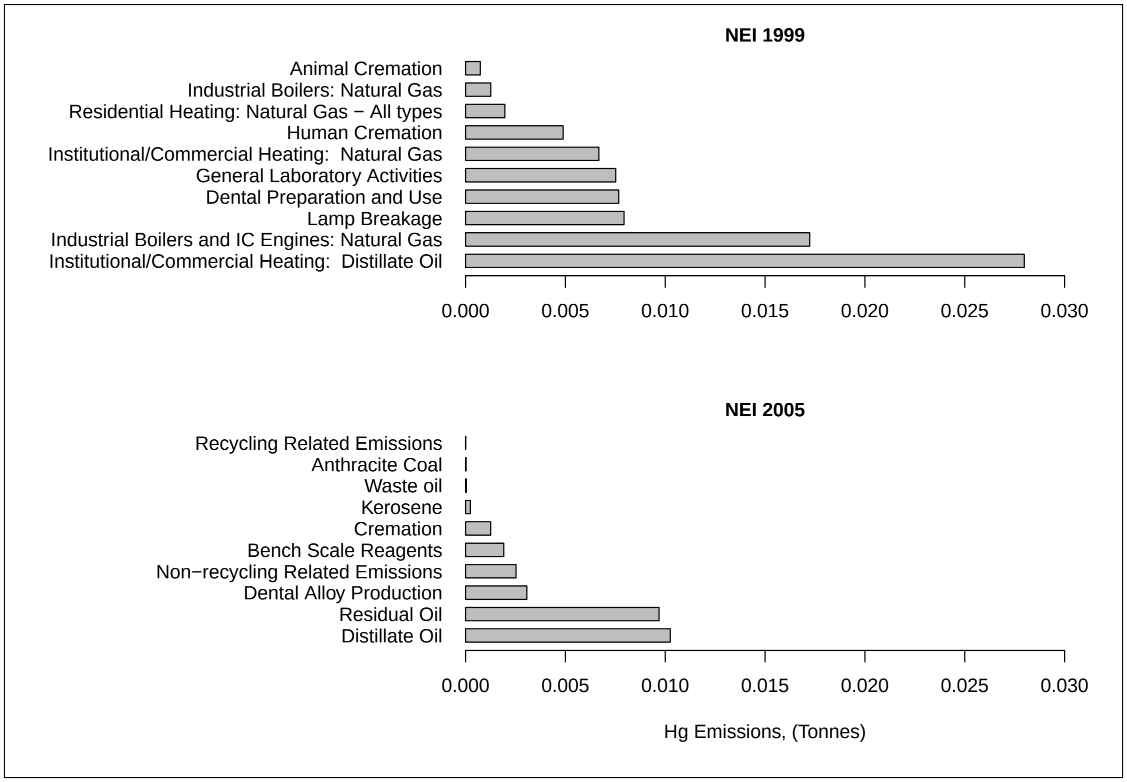


Figure 4.8. Contributions of non-point source categories to mercury emissions in the Tampa Bay area as compiled from NEI data. Summary contributions from top 10 source categories are compared. The plot details NEI facility data from the 1999 (top-left subplot), 2002 (top-right subplot), 2005 (bottom-left subplot), and 2011 (bottom-right subplot) inventory years.

Table 4.3 compares source category contributions to regional mercury emissions across all inventory years. The relative significance of source categories contributing to regional mercury emissions were similar to that observed in the state summaries. With the exception of the 1999 inventory year (previously discussed) utility boilers utilizing coal fuel accounted for the largest fraction of mercury emissions in the region across all inventory years. This source category contributed approximately 28% of regional mercury emissions in the 1999 inventory year, 50% in the 2002 inventory year, 54% in 2005, and 41% in the 2008 inventory year. Municipal and medical waste disposal accounted for approximately 30% of regional mercury emissions in 1999, 36% in 2002, and 18% in 2005, before showing a marked reduction in 2008 with a fraction of 1.5% of regional total. Smaller contributions from utility boilers utilizing oil as their primary fuel source were observed.

Table 4.2. Mercury emissions from point and non-point sources in Florida and the Tampa Bay area for inventory years 1999, 2002, 2005, and 2008 (tpy).

	1999 NEI	2002 NEI	2005 NEI	2008 NEI
Point Source				
Florida	3.1E+00	1.7E+00	1.8E+00	1.4E+00
Tampa Bay[a]	1.4E+00	4.1E-01	6.2E-01	3.9E-01
Hillsborough County	1.3E+00	2.6E-01	2.9E-01	2.4E-01
Pinellas County	1.0E-01	1.2E-01	9.4E-02	2.5E-02
Pasco County	1.6E-02	2.7E-02	3.3E-02	2.1E-02
Hernando County	1.4E-02	7.4E-03	2.0E-01	1.0E-01
Non-Point Source				
Florida	2.8E-01	1.9E-01	1.9E-01	1.2E-01
Tampa Bay	8.6E-02	2.9E-02	2.9E-02	1.3E-02
Hillsborough County	6.0E-02	1.2E-02	1.2E-02	7.6E-03
Pinellas County	2.0E-02	1.2E-02	1.2E-02	1.7E-03
Pasco County	4.3E-03	4.1E-03	4.1E-03	2.8E-03
Hernando County	1.6E-03	1.5E-03	1.5E-03	9.5E-04
Total				
Florida	3.4E+00	1.9E+00	2.0E+00	1.5E+00
Tampa Bay	1.5E+00	4.4E-01	6.3E-01	4.1E-01
Hillsborough County	1.4E+00	2.7E-01	3.0E-01	2.5E-01
Pinellas County	1.2E-01	1.3E-01	9.4E-02	2.8E-02
Pasco County	2.0E-02	3.2E-02	3.3E-02	2.4E-02
Hernando County	1.6E-02	8.9E-03	2.0E-01	1.0E-01

[a] Tampa Bay emissions is the sum of the counties Hillsborough, Pinellas, Pasco, and Hernando.

Figure 4.7 compiles the top ten mercury emitting facilities in the Tampa Bay region, comparing their summary contributions across the inventory years 1999, 2002, 2005, and 2008. As mentioned in the discussion of regional and state totals, the St. Joseph Hospital, located in Hillsborough County accounted for a substantial portion of mercury emissions in the region in during the 1999 inventory year. Similar to observations made at the regional and state level, power generation facilities dominated contributions across all inventory years, though no distinct trend is observed. Notable contributions were also observed from waste-to-energy, recycling, and waste treatment facilities in the region.

Figure 4.8 shows the contributions from non-point source categories to mercury emissions in the Tampa Bay area. Non-point sources of mercury to the region show a decreasing trend in emissions over the inventory years assessed. Non-point emissions were highest in Hillsborough County and lowest in Hernando County. Due to unavailability of data, non-point source category comparisons were made between 1999 and 2008 NEI years only.

Dominant area source contributing to mercury releases in the region were industrial, commercial, and institutional heating equipment utilizing distillate oil, residual oil, and natural gas as fuel sources. Contributions from breakage of mercury containing lamps were also among the highest non-point source categories. It is estimated that approximately 620 million fluorescent bulbs are discarded annually [Aucott et al., 2003]. Despite the existence of recycling programs, it is estimated that, nationally, only about 20% of discarded bulbs are recycled [Aucott et al., 2003]. It is expected that most of the bulbs that are not recycled are likely broken during disposal. Contributions from human and animal cremation facilities in the region were also significant non-point source categories. Mercury releases from cremations occur as a result of mercury amalgams in the body with readily vaporizes during the process.

4.4. Conclusion

The overall goal of this chapter was to assess mercury emissions and trends in mercury emissions from sources in the Tampa Bay area. Trends in the NEI indicate that electric utilities, especially coal-fired power-plants, are the largest contributors to mercury emissions in the Tampa Bay area, and the state. This finding is echoed at the national level with coal combustion accounting for a significant fraction of mercury released to regional and global cycles [Carpi, 1997; Pacyna and Pacyna, 2002; Seigneur et al., 2007]. More importantly, emissions from coal combustion utilities is consistent across all inventory years, second only to emissions from medical facilities in the 1999 inventory year. The trend is true both at the state, and regional (Tampa Bay) level.

The amount of mercury released by coal combustion processes is impacted by coal rank, combustion conditions including flue gas temperature, fly ash properties, and the concentrations of other constituents of the coal, particularly chlorine [Murray and Holmes, 2004]. Particulate matter is suggested to have a major impact on mercury emissions, thus pollution control after combustion is the predominant option for mercury control. Fabric filters are usually employed but are shown to be generally ineffective at controlling elemental mercury [Murray and Holmes, 2004]. Legislations to develop and implement appropriate

Table 4.3. Comparisons of source category mercury emissions to the Tampa Bay area counties for inventory years 1999, 2002, 2005, and 2008. Top 10 source categories for each period are featured.

Source Category	Hg Emissions (tpy)	%
EPA NEI 1999		
General Medical and Surgical Hospitals	9.8E-01	65.1
Utility Boilers: Coal	2.3E-01	15.4
Municipal Waste Combustors	1.3E-01	8.8
ICI Boilers & Process Heaters	5.5E-02	3.6
Refuse Systems	4.4E-02	2.9
Cement, Hydraulic	8.0E-03	0.5
Medical Waste Incinerators	8.0E-03	0.5
Lamp Breakage	7.9E-03	0.5
Offices and Clinics of Dentists	7.7E-03	0.5
General Laboratory Activities	7.5E-03	0.5
EPA NEI 2002		
Utility Boilers: Coal	2.2E-01	50.3
Municipal Waste Combustors: Large	1.3E-01	30.3
ICI Boilers & Process Heaters - wood or waste	3.4E-02	7.7
Utility Boilers: Oil	2.4E-02	5.5
Sewage Sludge Incineration	8.9E-03	2.0
Portland Cement Manufacturing	8.3E-03	1.9
Secondary Lead Smelting	6.2E-03	1.4
Publicly Owned Treatment Works (POTWs)	8.7E-04	0.2
Asphalt Processing and Asphalt Roofing Manufacturing	8.5E-04	0.2
Medical Waste Incinerators	5.3E-04	0.1
EPA NEI 2005		
Fuel Comb - Electric Utility: Coal	1.2E+00	53.7
Waste Disposal	3.9E-01	17.8
Industrial Processes - NEC	1.9E-01	8.6
Fuel Combustion - Industrial Boilers, ICEs	1.6E-01	7.1
Indus Process - Cement Manufacture	1.3E-01	6.1
Miscellaneous Sources	9.1E-02	4.1
On-Road Vehicles - Gasoline	2.4E-02	1.1
Fuel Comb - Commercial/Institutional	1.8E-02	0.8
Indus Process - Metals	5.5E-03	0.2
Indus Process - Pulp & Paper	4.6E-03	0.2
EPA NEI 2008		
Fuel Comb - Electric Generation - Coal	1.8E-01	43.7
Industrial Processes - Cement Manuf	1.0E-01	24.9
Fuel Comb - Electric Generation - Other	8.3E-02	20.2
Waste Disposal	2.0E-02	5.0
Miscellaneous Non-Industrial NEC	1.2E-02	2.9
Fuel Comb - Electric Generation - Oil	7.6E-03	1.9
Mobile - On-Road Gasoline Light Duty Vehicles	3.2E-03	0.8
Mobile - Locomotives	6.8E-04	0.2
Industrial Processes - NEC	5.8E-04	0.1
Fuel Comb - Residential - Oil	2.3E-04	0.1

Source classifications were based on SCC/MACT source category definitions as published in the NEI for each inventory. This accounts for the nominal differences in source categories across inventory years.
ICI = Industrial/Commercial/Institutional
Comb = combustion
Indus = Industrial

frameworks and technologies for the reduction of mercury emissions from fossil fuel power generation facilities are still being debated.

Emissions from medical waste facilities were significant in the 1999 inventory year. In 1999 emissions from general medical and surgical hospitals accounted for 29% of mercury emissions in the state, and 65% of mercury emissions in the region. A single facility in Hillsborough County was shown to account for this spike in emissions in the 1999 inventory year. The medical waste category did not feature in the top 10 emissions source categories in the following inventory years (2002, 2005, and 2008).

Municipal waste incineration were also important sources of mercury to the atmosphere. Waste incineration accounted for approximately 15% to 30% of mercury emissions in the region. Additionally, ICI boilers and process heaters, and cement manufacture were relatively less significant.

There were not substantial variations in emission trends between the regional (Tampa Bay area) and state profiles and summaries. Emissions from Tampa Bay area source categories and facilities contribute significantly to the total mercury emissions in the state. Hillsborough County accounted for a significant fraction of mercury emissions in the region and state.

5. Source apportionment of deposited mercury to Tampa Bay: 2001 BRACE data analysis

Note: This is a draft of a multi-author manuscript in preparation for journal publication for which I am first author. My role in this research was the analysis of deposition data for source identification, specifically HYSPLIT back-trajectory modeling, and PMF receptor modeling and data analysis.

5.1. Background

Mercury is a persistent environmental contaminant whose most toxic form, methyl mercury, is found at high levels in fish present in water bodies throughout the world [Downs et al., 1998]. Methyl mercury strongly bioaccumulates and biomagnifies in aquatic ecosystems, making consumption of predatory fish the leading route to toxic human exposures [Tollefson and Cordle, 1986]. Deleterious human health effects include impaired mental function, neurological disorders, cardiovascular effects, and kidney damage [Tchounwou et al., 2003]. Adverse effects on other species, including piscivorous birds and mammals, have also been documented [Scheuhammer et al., 2007; Wolfe et al., 1998]. In order to mitigate these effects, attribution of observed levels of mercury (Hg) in the environment to Hg sources is needed.

Sources of Hg released to the environmental are numerous, but emission to the atmosphere and subsequent surface deposition is a primary source pathway leading to levels currently observed in water bodies [USEPA, 1997a]. Anthropogenic emissions come from combustion of fossil fuels (largely at coal- and oil-fired power plants), incineration (largely at medical and municipal waste facilities and crematoriums), and volatilization during production and use of mercury-containing products (fluorescent light bulbs, measurement instruments, and switches) [Pacyna et al., 2006; Pirrone et al., 2010]. Volatilization of Hg used for goal and silver mining is also an important source globally [de Lacerda, 2003; Porcella et al., 1997]. Once emitted, Hg can be transported long distances or be deposited locally, depending on chemical speciation and meteorological phenomena [Engle et al., 2008; Gratz, 2010; Seigneur et al., 2001]. Oxidized mercury in gaseous species (categorized as reactive gaseous mercury, RGM) and mercury in particulate matter (categorized as particulate mercury, HgP) are readily deposited near to sources, through collection during rain events. Gaseous elemental mercury (Hg0) is much less soluble and can persist over long distances and timescales before oxidizing to more soluble forms [Lindberg and Stratton, 1998; Seigneur et al., 2001; Shia et al., 1999]. Due to limited characterization of speciated source emissions profiles, dry deposition, and aqueous Hg chemistry, substantial uncertainties exist in connecting specific sources of Hg emissions to measured levels of mercury deposition [Lindberg et al., 2007].

Of particular interest is identifying the relative contributions to deposition to sensitive watersheds of local anthropogenic sources versus distant sources. The level of uncertainty in the scientific literature on the point is detrimental to adequate control at all management levels, from international to local. For example, a substantial aspect of the controversy concerning the now-vacated Clean Air Mercury Rule in the United States centered on whether its cap and trade approach would lead to higher levels of mercury deposition and pollution in areas near poorly controlled sources [O'Neill, 2004]. Previous research specifically addressing the relative contributions is somewhat contradictory. Large-scale photochemical modeling studies suggest a substantial contribution to mercury wet deposition is due to photochemical conversion of Hg^0 from distant sources [Seigneur et al., 2004; Selin et al., 2007; Sillman et al., 2007]. Conversely, deposition measurement analysis case studies in eastern Ohio and southeastern Florida suggest a dominant role for contribution of local and regional sources [Dvonch et al., 1999; Keeler et al., 2006; White et al., 2009]. However, recent work of Caffrey et al. [2010] in northwest Florida does not support differences in deposition at local spatial scales, suggesting that the relative contributions of local versus long-range sources could be substantially location dependent.

In this chapter, we investigate deposition and sources of mercury in the Tampa Bay region. Levels of mercury found in fish in the Tampa Bay watershed have been found to be some of the highest in Florida [Kannan et al., 1998], with mercury consumption advisories in place for many fish species in bay area freshwater lakes and streams [USEPA, 2012]. To investigate atmospheric mercury sources to the Tampa region, we analyzed trends in mercury deposition data, performed back trajectory modeling, and applied statistical receptor modeling based on Tampa special-site metals deposition data. Methods, results, and potential implications for local versus long-range source influences are discussed in the following sections.

5.2. Methods

5.2.1. Deposition network data

Measurement data potentially relevant to mercury deposition in the Tampa Bay area were identified and investigated. Data sources include wet deposition data collected through the Mercury Deposition Network, mercury concentrations from the PM2.5 speciation network, and precipitation event mercury data from a special-study monitoring site in Tampa.

The Mercury Deposition Network is the mercury deposition arm of the National Atmospheric Deposition Program, a cooperative monitoring program comprised of federal and state agencies, academic institutions, Native American tribal governments, and private organizations. The network consists of more than 100 active sites throughout the United States, Canada and Mexico that measure mercury deposition in precipitation [NADP, 2007]. These sites measure long-term trends in wet deposition of total mercury through automated collectors and precipitation gauges, and provides nationally consistent surveys of mercury wet-deposition concentrations and fluxes for regional and international deposition patterns. For this study, the trends and annual cycles in precipitation and mercury deposition at the five Mercury Deposition Network sites in Florida were plotted and compared for discussion of implications for Tampa area deposition.

At the time of this study, there were no available network sites for dry deposition or atmospheric concentrations of mercury in Florida. However, the US Environmental Protection Agency was measuring mercury collected in fine particulate matter (PM2.5) through its PM2.5 Speciation Trends Network [USEPA, 1998; NRC, 2004]. These sites are a part of the national air quality monitoring system and include seven speciation sites in Florida. Multi-year trends in the annual summary data on mercury concentrations from the sites in Florida were analyzed for discussion of implications for dry deposition.

5.2.2. Special site data from the Bay Regional Atmospheric Chemistry Experiment

Trace metals deposition data was measured at one monitoring site in Tampa through the Bay Regional Atmospheric Chemistry Experiment [Atkeson et al., 2007]. This site (AirMon FL18) is located on the Tampa side of the Gandy Bridge that connects the south Tampa peninsula with St. Petersburg. Keeler et al. [2006] describes the collection and chemical analysis methods used. Notably, samples were collected every 24 hours when precipitation occurred. Hence, individual sample data on trace metals and precipitation amounts are available for each day when precipitation occurred. Each day with precipitation is referred here to as a precipitation event day. This analysis employs data collected between March 2000 and March 2001 (provided by the Florida Department of Environmental Protection). This data is utilized to compare temporal trends in precipitation depths and mercury concentrations, and is also used in combination with back trajectory and receptor modeling, described below, to understand source contributions.

5.2.3. Back trajectory modeling

5.2.3.1. Background and model parameters

Meteorological trajectories are defined as the paths traversed by infinitesimally small particles of air [Dutton, 1986; Stohl et al., 2002]. Perceived as a fluid, these particles, marked at a certain point in space, at a given time, can be traced forward and backward in space along its trajectory [Stohl et al., 2002]. In trajectory models, this is achieved by integrating the trajectory equation:

$$\Delta x_i = v_i \Delta t \tag{5.2.1}$$

where Δx is the position increment during a time step Δt resulting from the wind v. The index i runs from 1 to 3 and denotes the 3 dimensions of space, and the mean (non-turbulent) horizontal and vertical winds, derived from a meteorological model, are used [see Stohl, 1998, for a discussion on the computation and use of meteorological trajectories]. While forward trajectories describe where a particle will go, backward trajectories indicate where they came from. Thus, meteorological trajectories are often applied to interpret measurements of atmospheric trace substances, in order to establish relationships between their sources and their receptors [Hoyer et al., 1995; Louis et al., 1995; Han et al., 2005].

To investigate potential source influences on the Tampa special site data, back trajectory modeling was performed to determine air mass trajectories corresponding to specific mercury wet deposition event days. First, to help reduce confounding associated with precipitation amount, the Tampa deposition event day data were grouped by similar precipitation level, with natural divisions in the rain depth distribution defining the group bins. The eight groups with the highest precipitation levels (and generally higher mercury deposition levels) were then selected for back trajectory analysis, for a total of 23 event days analyzed. After back trajectory modeling of each selected event day (described below), back trajectory characteristics for event days within each precipitation group that had comparatively higher mercury concentrations in the deposited water were compared with those having lower mercury concentrations. Specifically, short-term (6 hr), intermediate term (24 hr), and long-term (72 hr) back trajectory locations and previous precipitation amounts (along the trajectory) were compared. By comparing these characteristics, potential source influences that led to comparatively high mercury concentrations at similar rain levels were identified.

For this analysis we applied the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT, Version 4) model developed by the National Oceanic and Atmospheric

Administration (NOAA) [Draxler and Hess, 1997, 1998]. HYSPLIT is hybrid between Eulerian and Lagrangian model approaches, in which advection and diffusion are made in a Langrangian framework, while concentrations are calculated on a fixed grid [see Draxler and Hess, 1998, for the description and development of this modeling approach].

After initial exploration of back trajectories initiated for several hours throughout precipitation events, the hour with the highest precipitation amount for each event day was selected to initialize back trajectory modeling. Hourly precipitation data collected at Tampa international airport (NOAA, 2000) were used to determine the highest precipitation hour. Back trajectories were initiated at three heights, 250, 500, and 1000 m, in order to span the vertical space through which precipitation may have fallen. To drive the HYSPLIT model, meteorological data from the National Centers for Environmental Prediction (NCEP) model output were used. Specifically, the EDAS (Eta Data Assimilation model) data (with 80 km horizontal resolution, 23 vertical levels, and 3 hr temporal resolution) was used for timeframes with available data. GDAS FNL archive data (the NCEP Global Data Assimilation System model final run data) was used instead for two events (June 25 and March 27, 2000) for which runs with EDAS data did not go to completion. These data have a 190 km grid resolution, 13 vertical layers, and 6 hr temporal resolution.

5.2.4. PMF analysis

5.2.4.1. Model description

Receptor models allow the estimation of the contributions of different primary emission sources to the ambient concentrations of species collected at a receptor [Ogulei et al., 2005; Xie et al., 1999; Reff et al., 2007]. To apportion mercury deposited in Tampa to sources, we applied multivariate statistical receptor analysis on the BRACE deposition data, using the Positive Matrix Factorization (PMF) package, Version 3.0 [Norris et al., 2008].

PMF is a multivariate receptor modeling technique that calculates site-specific source profiles with time variations of these sources based on correlations embedded in ambient data. Simply, PMF decomposes a matrix of ambient data into two matrices that must be interpreted to determine which source types are represented. PMF uses time series data on simultaneously measured concentrations of multiple chemical species to determine species composition profiles for independent factors such that the sum of the profiles multiplied by the contributions of each factor over time gives the overall observed time variances in the data. In PMF, a data matrix C, consisting of m chemical species, from p number of sources, measured over n sampling events, is factored to generate G, a $n \times p$ matrix of fractional source contributions to each sample (time variations), and F, a $p \times m$ matrix of source compositions (profiles)[Paatero and Tapper, 1994; Hopke, 2000]. The factor model can be expressed as [Paatero and Tapper, 1994; Hopke, 2000]:

$$C_{(n\times m)} = G_{(n\times p)} \cdot F_{(p\times m)} + E_{(n\times m)} \tag{5.2.2}$$

where E represent a matrix of residuals. The concentration of a specie, x_{ij}, at a receptor is given by:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{5.2.3}$$

where x_{ij} refers to the observed concentration of the j^{th} species for the i^{th} (measurement) event, g_{ik} is the contribution of the k^{th} factor for the i^{th} event, f_{kj} is the fraction of the k^{th} factor that is species j. The model assumes that only the x_{ij}'s are known, and the goal is to estimate the contributions (g_{ik}), and the fractions (or profiles/factors) (f_{kj}). The residual matrix **E** is defined as the difference between the measurement **X** and the model **Y** as a function of factor **G** and **F**. The residual, e_{ij} is given by:

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \tag{5.2.4}$$

The general receptor modeling problem is solved by using a constrained, weighted, least squares approximation. PMF allows each data point to be individually weighed, based its associated uncertainty. This feature allows for adjustment of the influence of each data point, depending on the confidence in the measurement. Additionally, it is assumed that the contributions and mass fractions are all non-negative, hence the "constrained" part of the least squares. PMF operates by minimizing the sum (called Q) of the squared weighted residuals, e_{ij}, between modeled and measured species concentrations, weighted inversely by the variation of the data points, s_{ij}, according to the constrained, weighted least squares model:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{s_{ij}} \right]^2 = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{e_{ij}^2}{s_{ij}^2} \tag{5.2.5}$$

where s_{ij} represents the uncertainties in collection and determination of the j^{th} species for the i^{th} event. The objective is to determine the matrices **G** and **F**, by minimizing Q. The equation is solved using an iterative algorithm in which the matrices **G** and **F** vary simultaneously at each iteration step [Paatero and Tapper, 1994]. **F** and **G** are both forced to be non-negative in order to make physical sense (i.e., factors cannot have negative species concentrations and ambient samples cannot have a negative factor contribution). Theoretically, if the uncertainties correctly characterize the data and every point is perfectly modeled, Q should be approximately the number of species multiplied by the number of observations (i.e., the degrees of freedom). The modeled Q is required to be within 50% of the theoretical Q to ensure a reasonable fit for all observations. Model generated factor profiles are then mapped to known emissions profiles for source identification [Hopke, 2000; Reff et al., 2007].

The PMF model is designed to describe the average behavior of the dataset, and can thus be disturbed by atypical measurements present in the data and uncertainty matrices [Reff et al., 2007; Paatero and Tapper, 1994]. These extreme measurements may not be outliers, and may inform about events (such as forest fires) impacting the data, however, they may have undesirable influences on the least-squares model solution. The influences of such data on PMF solutions can be diminished by using an adjusted minimum Q function, called *robust mode.* When robust mode is used, the uncertainties of measurements for which the scaled residuals (e_{ij}/s_{ij} in Eqn. 5.2.5) are greater than the parameter, called the outlier distance, α, are increased to down-weight their influence on the PMF solution [Reff et al., 2007]. Most researchers that utilize this method uses a value of $\alpha = 4$ [Alleman et al., 2010; Kim et al., 2004; Hopke, 2000; Paatero and Tapper, 1994]. In robust mode, the PMF algorithm attempts to minimize Q_{Robust} rather than the Q defined in Eqn. 5.2.5, where Q_{Robust} is defined as:

$$Q_{Robust} = \sum_{i=1}^{n}\sum_{j=1}^{m} \frac{e_{ij}^2}{h_{ij}^2 s_{ij}^2} \tag{5.2.6}$$

$$h_{ij} = \left\{ \begin{array}{ll} 1 & \text{for } |e_{ij}/s_{ij}| \leq \alpha \\ \\ |e_{ij}/s_{ij}|/\alpha & \text{for } |e_{ij}/s_{ij}| > \alpha \end{array} \right\} \tag{5.2.7}$$

This mode of the model was used for all factor profile and contributions generated in this study. Factors are not always associated with a single source and are often difficult to interpret because the sources associated with each factor must be identified by the user based on the composition of the source profiles. Figure 5.1 illustrates the steps and decisions required for source characterization using PMF.

5.2.4.2. Characterization of input data

Species concentrations from the 48 wet event day samples measured at the special study Tampa site were used as input to derive potential source profiles with PMF. Chemical elements measured at the Tampa monitoring site for each event day were Hg, Na, Ag, Cs, Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Sb, Ba, La, Ce, and Pb. Reported uncertainties (U) for each data point included the sample collection uncertainty (SC = 10%), precipitation depth measurement uncertainty (PD = 5%), the element-specific analytical method detection limits (MDL), and analytical measurement precision uncertainties (AM)

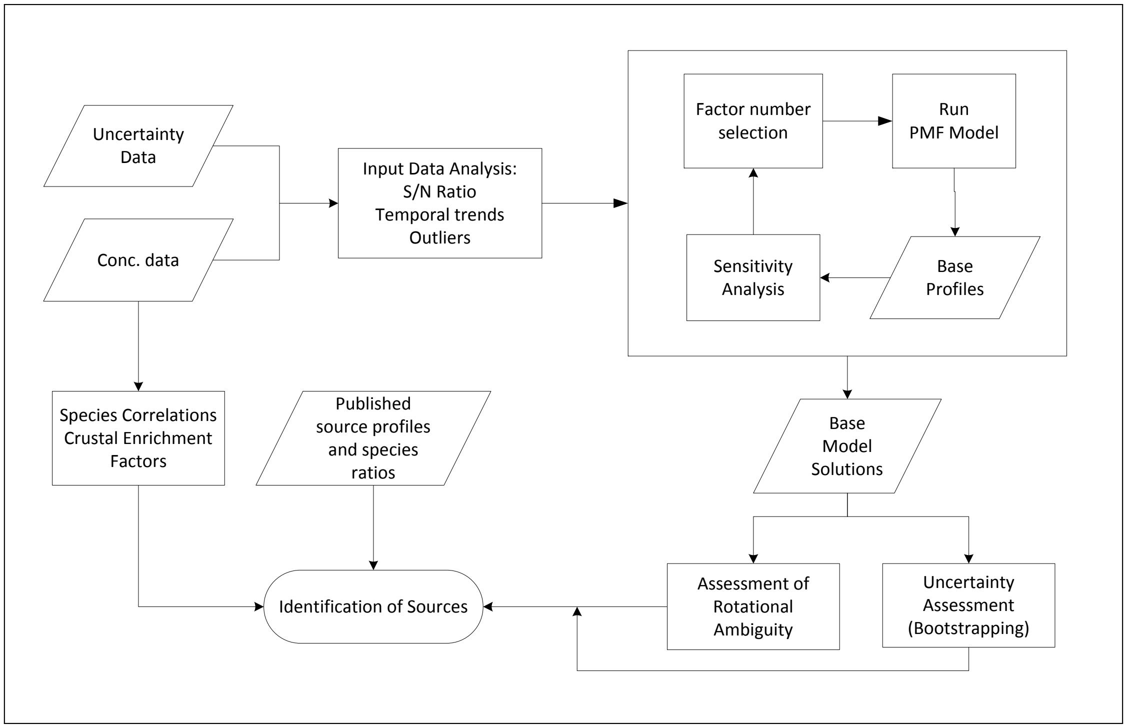


Figure 5.1. Flowchart illustrating the steps involved in source characterization using PMF model.

[see Keeler et al., 2006, Supplemental Information]. Species uncertainties were determined as Norris et al. [2008]:

$$U = (MDL) + \sqrt{(SC)^2 + (AM)^2 + (PD)^2} \tag{5.2.8}$$

All species with reported uncertainty characteristics had more than 80% of observations greater than their respective MDLs. One missing observation (for mercury species) was replaced by the arithmetic mean of the species concentration, and one half of the species detection limit was used to determine the uncertainty associated with this observation [see Paatero and Hopke, 2003, for a discussion of this approach]. A sample-specific uncertainty matrix was used for model runs, determined by the method of Polissar et al. [2001], for species with reported MDLs, and the method of Chueinta et al. [2000] for species with unreported MDLs (Na, Ag, Cs) [See Reff et al., 2007, for a discussion on PMF uncertainty estimation approaches]. The influence of the applied uncertainties on species concentrations was assessed by calculation of the species-specific signal-to-noise ratios [Paatero and Hopke, 2003]. All species were included in the analysis, and no additional uncertainty was applied to species in the model.

5.2.4.3. Model application

To perform PMF analysis, the number of independent factors, *(p)*, influencing the variability in the deposited concentration profiles must be set *a priori*. To determine p, we performed sensitivity analysis on the mean percent error between the theoretical and model generated Q-value for model runs, with p ranging from 5 to 15. The mean percent error is defined as $|Q_{th} - Q_r|/Q_{th}$, where Q_{th} and Q_r are the theoretical and modeled Q-values, respectively [see Hopke, 2000; Eberly, 2005; Reff et al., 2007, for discussion of this factor selection approach]. Twenty random starting points with non-random seeds were used for our analyses, to ensure a reproducible global minimum solution was achieved. Since the optimum number of factors for resolving the uncertainty in the dataset occurred in the range of $10 \leq \text{p} \leq 13$, subsequent simulations considered 10-, 11-, and 12-factor models runs.

Additional sensitivity analysis for factor selection employed the use of model residuals to reduce selection uncertainty. Lee et al. [1999] suggested the use of the information from the scaled residual matrix (R) in PMF to determine the optimal number of factors and reduce ambiguity due to manual judgment. Each column in R represents the quality of the fitting of each species to the product of the G and F matrices as defined in Equation (5.2.5). For a specific number of factors, two parameters are obtained from R: *IM*, the maximum individual column mean, and *IS*, the maximum individual column standard deviation, where:

$$IM = \underset{j=1\cdots m}{max}\left(\frac{1}{n}\sum_{i=1}^{n} r_{ij}\right) \qquad (5.2.9)$$

and

$$IS = \underset{j=1\cdots m}{max}\left(\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(r_{ij} - \bar{r_j})^2}\right) \qquad (5.2.10)$$

The *IM* and *IS* parameters serve as indicators to identify the species having the least fit and the most imprecise fit, respectively [Lee et al., 1999]. When the number of factors increases to a critical value, *IM* and *IS* should demonstrate a corresponding change of decreasing uncertainty, reflecting an appropriate resolution of data variability for the number of sources modeled. To reduce the risk of overfitting, this approach is used in conjunction with sensitivity analysis for factor number selection.

5.2.4.4. Model verification

Residual analysis was also performed to assess model fit. Examination of the distribution of the scaled residuals is useful to determine how well the model fit each species, where the scaled residuals are defined as $r_{ij} = e_{ij}/s_{ij}$ (see Equation (5.2.5)). For a model with appropriate fit, the residuals, e_{ij}, and the error estimates, s_{ij}, should be similar to each other, and the scaled residual should occur in the range of ±3 [Paatero and Tapper, 1994; Norris et al., 2008; Chueinta et al., 2000]. Species with many large scaled residuals, or non-normal residual distributions are indicative of a poor model fit. Assessment of model fit was also performed by examination of the observed/predicted (O/P) scatter plots, and associated correlation coefficients for individual species. Species with coefficients of determination below 0.9 were examined for extreme events that may be accounting for the poor model fit. For example, *Co* (r^2=0.54) and *Ni* (r^2=0.29) both had observations that were greater than ten times the value of their respective means. The model was recalculated with events corresponding to extreme species concentrations omitted from the analysis (3 events based on extreme observations for *Ni*, *Co*, *Sb* and *Ag* species). The recalculated coefficient of determination varied between 0.999 and 0.9 for all species reflecting an improved model fit. Subsequently, final analysis was conducted with these events omitted from model input data.

Bootstrapping was performed on the selected base solution to assess variability and uncertainty in the solution. Uncertainty analyses consisted of 100 runs of the bootstrapped factor, with a minimum correlation coefficient of 0.6, and a block size of 2. A 95% confidence cutoff was applied to determine significance of each contribution. (Contributions were considered significant if the fifth percentile of the distribution was greater than 0). Once factor profiles were predicted with PMF, these profiles were compared to available information on dominant species, and species ratios emitted from particular industries and activities to correlate factors with source categories occurring in the domain.

Rotational ambiguity in model solutions was assessed by use of the FPEAK parameter in PMF. Positive and negative values (from -0.5 to 0.5, in 0.1 increments) of the FPEAK parameter were examined for their effect on the Q values, G-space plots, factor contributions, and factor profiles of the base model solution [see Paatero, 1997; Paatero et al., 2002, for a discussion of this approach]. A value of 0.3 was chosen to determine final model solutions, as it helped to resolve some of the slight interdependence of factors observed, and was found to resolve some of the dominant species for each factor without increasing non-dominant ones.

We ultimately selected a p of 11 as it resulted in the minimum difference between the model-calculated value of Q and the number of degrees of freedom in the data set (the theoretical Q_{th}), and generated factors that were resolved to sources in the domain with the least uncertainty.

5.2.4.5. Initial analysis of source influences on species concentrations

Initial explorations of relative contributions of biogenic and anthropogenic emission sources on species concentrations was achieved by calculating crustal Enrichment Factors (cEF) for each species. Enrichment factors are a means of identifying and quantifying anthropogenic influences on global element cycles by normalizing observed element concentrations to that of a "conservative" naturally occurring element [Zoller et al., 1974; Duce et al., 1975]. Enrichment factors were estimated using the generalized formula from Chester and Stoner [1973]:

$$cEF = \frac{\left(\frac{[X]}{[A]}\right)_{sample}}{\left(\frac{[X]}{[A]}\right)_{crust}} \tag{5.2.11}$$

where [X] and [A] refer to the concentration respectively of a given element X, and of the reference element A. For cEF $>$ 1, X is considered enriched in the atmosphere relative to its concentration in the earth's crust, and for cEF ≈ 1, the source in not enriched in the atmosphere, implying minimal anthropogenic contributions to species concentrations [Galloway et al., 1982]. Using Al as the reference element, calculations were based on the average upper crust elemental compositions published by McLennan [2001]. Aluminum is considered a good reference element to normalize metal concentrations due to its crustal abundance, and the relatively constant metal to aluminum crustal ratios [Turekian and Wedepohl, 1961; Taylor, 1964]. Additionally, studies have suggested that aluminum concentrations are not likely to be significantly affected by anthropogenic aluminum sources [Windom et al., 1989; Schropp et al., 1990]. We account for the inherent uncertainties associated with the choice of reference element, and composition of reference soil by considering larger differences in calculated cEF than those standardized in the literature [Galloway et al., 1982; Chester and Stoner, 1974; Duce et al., 1975]

Likely contributions of specific emission source categories to observed species concentrations were explored by examining statistical correlations between species pairs. A good correlation between species indicates a similar source or source type [Norris et al., 2008]. Associations between species were explored using scatter plots and Pearson correlation coefficients. Additionally, analysis of time series of species concentration observations were used to elucidate temporal patterns in the data, and to assess the occurrence of unusual events that may have contributed to significant departures from normal species emission trends.

Several authors have attempted to relate elemental concentration ratios of trace species in deposition samples to specific emission sources [Dvonch et al., 1998, 1999; Gratz, 2010; Alleman et al., 2010; Olmez et al., 1998; Polissar et al., 2001]. For example, Hg/Pb ratios from stack measurements preformed in South Florida were used to define the signatures for medical (Hg/Pb = 8.08) and municipal (Hg/Pb = 0.06 ±0.02) waste incineration [Dvonch et al., 1999; Gratz, 2010]. Published species ratios were compared to those calculated for the BRACE data to deduce likely source contributions.

Ultimately, identification of model predicted factors was an iterative process of exploring statistical correlations between species concentrations, analysis of profiles and species contributions of predicted factors, confidence of generated factors as assessed by bootstrapping, and comparison of elemental ratios with published literature. Confidence in source identification was also informed by interrogation of emissions inventory data from the NEI.

5.3. Results and discussion

5.3.1. Trends and cycles in the deposition network data

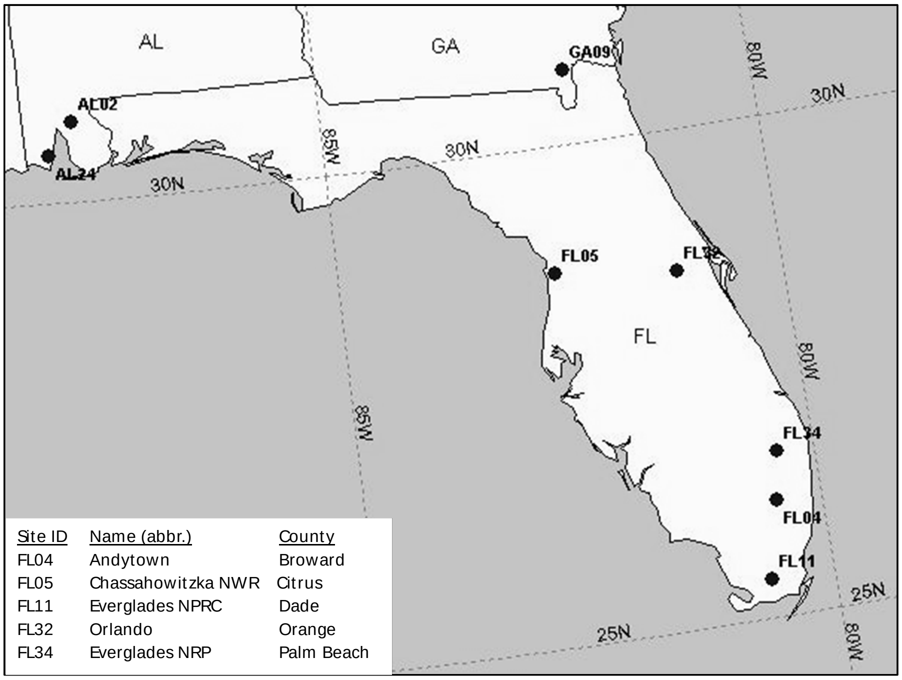


Figure 5.2. Mercury Deposition Network site locations in Florida from 1996 – 2008. Abbreviations used in the legend are: NWR is National Wildlife Refuge, NPRC is National Park Research Center, and NRP is Nutrient Removal Project. Sites FL04 and FL32 are now inactive. Map source: National Atmospheric Deposition Program.

Weekly total mercury wet deposition data are available for Florida for the years 1996-2009 from the Mercury Deposition Network. There are five Mercury Deposition Network sites in Florida that were active during some part of this period, as shown in Figure 5.2. There is no site in the Tampa Bay area. The two closest sites (FL05 and FL32) are located to the North and Northeast of Tampa in Citrus and Orange counties, respectively. The multi-year trend in total mercury deposition at the Mercury Deposition Network sites in Florida is

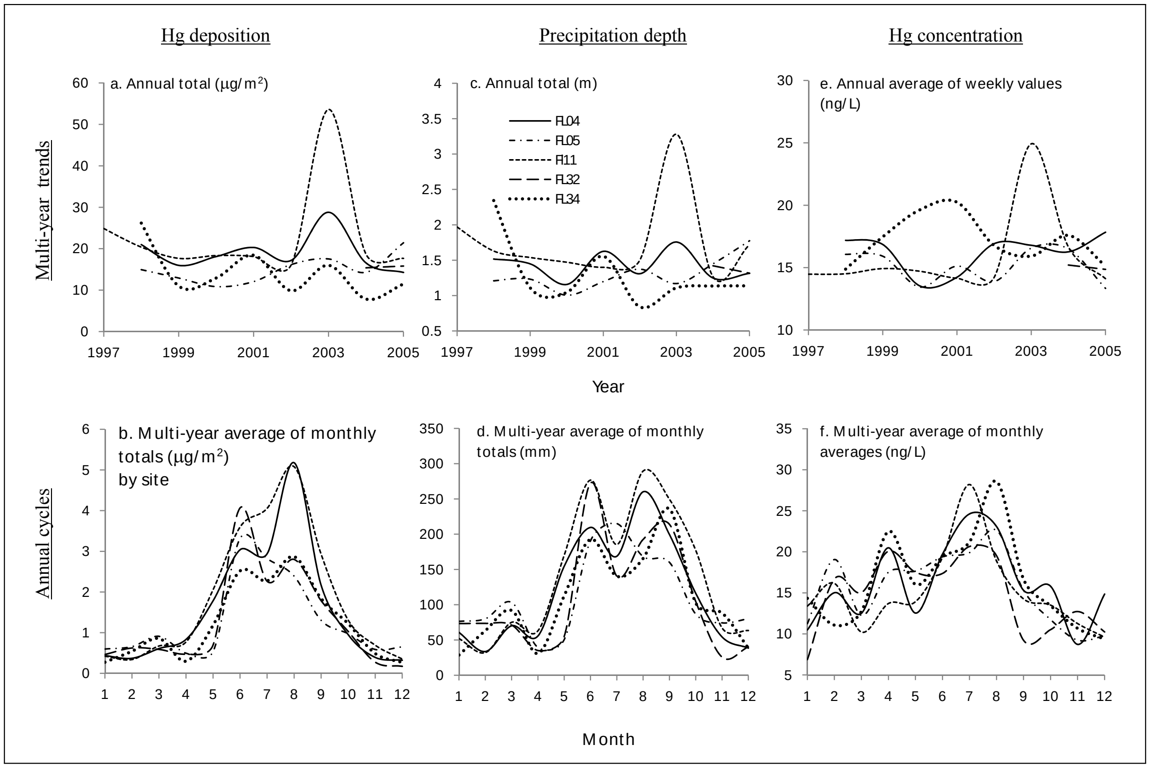


Figure 5.3. Investigation of MDN data for cycles and trends. The figure gives annual cycles and multi-year trends in mercury deposition (a, b), mercury concentration (c,d), and precipitation depth (e, f) respectively, for each Mercury Deposition Network site. (Site IDs used in the legend are identified in the legend of Figure 5.2)

provided in Figure 5.3a. No long-term trend is evident in the data. However, mercury wet deposition appears to fluctuate from year to year. The annual cycle of deposition at each site is provided in Figure 5.3b. Mercury wet deposition is seen to be highest during the summer months, from about June to September, at all sites in all years. This is likely due in part to increased precipitation amounts during the summer, as Florida has considerable convective storm activity during the summer. Figure 5.3 (c and d) shows the corresponding precipitation depth, which displays a similar annual cycle to mercury deposition. Measured mercury concentration, shown in Figure 5.3 (e and f), appears to exhibits less similarity to mercury deposition (or precipitation amount). Although concentrations are larger during the summer months, the difference between summer and winter months is not as large or abrupt as for either precipitation amount of mercury deposition amount. The multi-year trend also exhibits somewhat different fluctuations and an additional substantial peak in 2001 at one site.

5.3.2. Wet deposition at the Tampa special site

Figure 5.4, left subplot, provides the temporal trends in mercury wet deposition, precipitation depth, and mercury concentrations in the collected rain at the Tampa special site, for the time period of the data. The figure indicates similar trends to that seen at the Mercury Deposition Network sites. These include higher wet mercury deposition during summer months and higher deposition is months with higher precipitation. However, the trend in monthly average mercury concentrations does not correspond well to trends in either precipitation depth or mercury deposition. Looking at individual event data, as shown by scatter plots in Figure 5.4, right subplot, it is observed that mercury deposition increases as precipitation depth increases. However, mercury concentrations are largely uncorrelated with rain depth. (A slightly decreasing regression slope is found (not shown) that could possibly be due to dilution effects). A closer look at the event data indicates that for relatively constant precipitation depth, some events have high mercury concentrations, while others have low concentrations.

5.3.3. Back trajectories from the Tampa special site

The occurrence of events with relatively high or low mercury concentrations for similar precipitation levels suggests the potential importance of source emissions or other air mass influences on mercury deposition level (as discussed in Section 5.2.3). Back trajectories are presented for events with relatively high and relatively low mercury concentrations data, grouped by similar precipitation level.

Back trajectory simulation results for the highest precipitation level (Group 1) are shown in Figure 5.5. Group 1 is characterized by precipitation depth at the special site in the range of 5.30 to 5.78 cm. Two events (6/25/2000 and 7/26/2000) in this group had high measured mercury concentrations at about 31 $\mathrm{ng\,L^{-1}}$ and the other two events (8/12/2000 and 3/29/2001) had comparatively low mercury concentrations of 5.6 $\mathrm{ng\,L^{-1}}$ and 9.7 $\mathrm{ng\,L^{-1}}$,

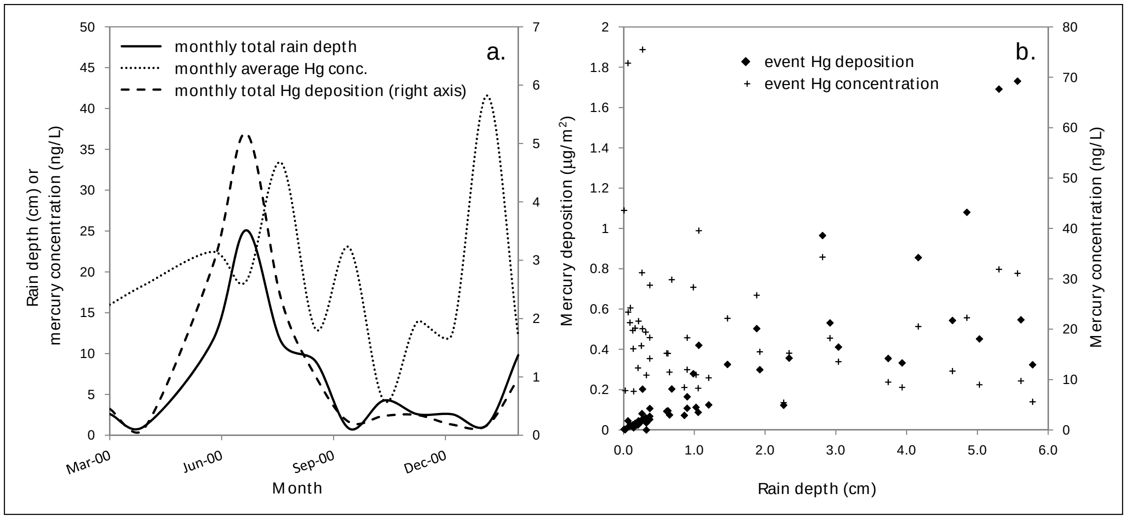
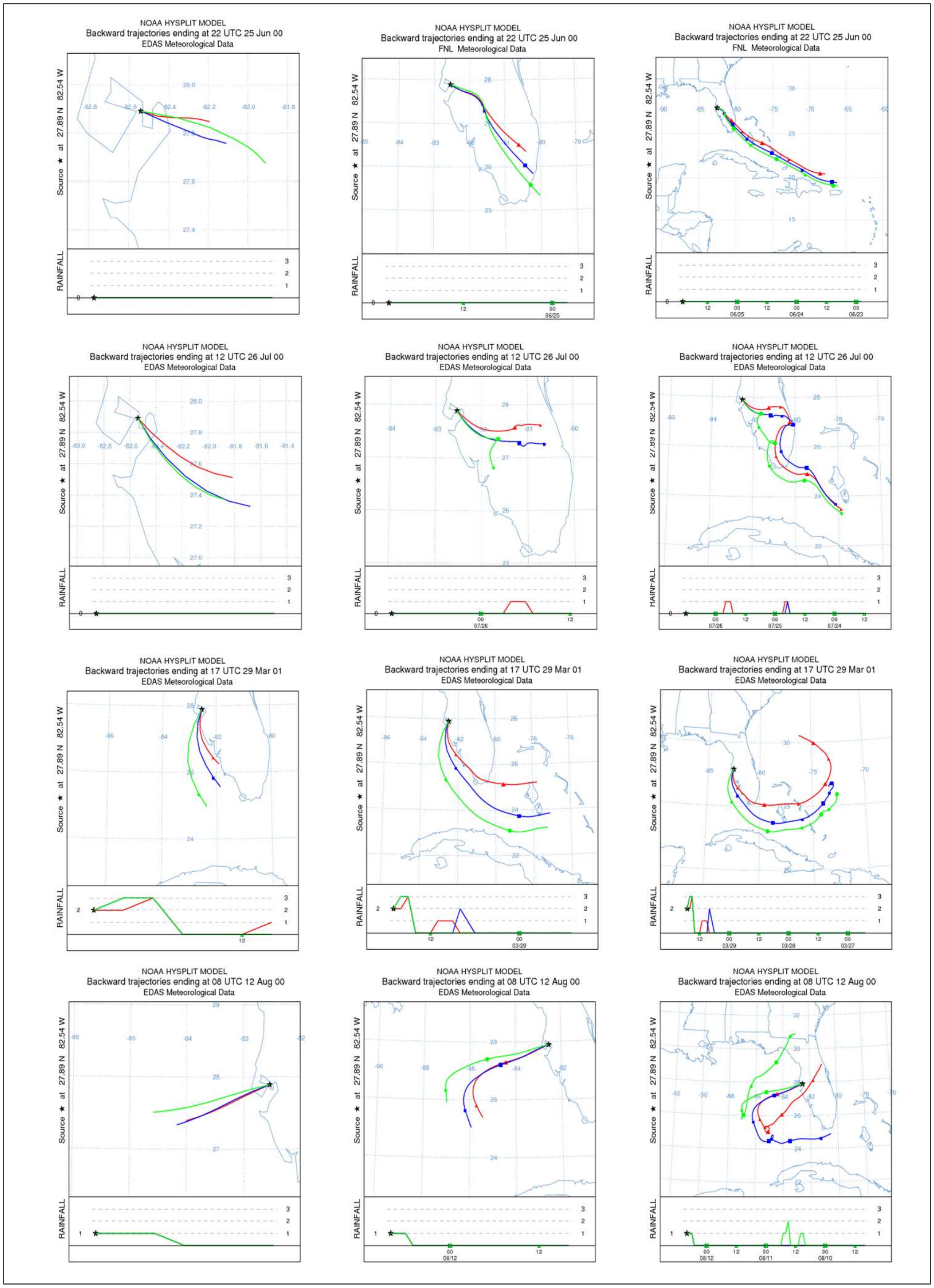


Figure 5.4. Analysis of 2001 Tampa special site data. The figure gives mercury wet deposition, rain depth, and mercury concentration in collected rain for the special event wet deposition monitoring site in Tampa from March 2000 to March 2001. The left sub-plot (a) provides monthly values, while the right sub-plot (b) is a scatter plot of rain depth versus both Hg deposition and Hg concentration for each event. Linear correlations (r values) for each comparison are 0.79 and 0.17, respectively

respectively. Back trajectory result show that the high mercury concentration events had short-term (6 hr) air mass backward trajectories coming from the south and east of the monitoring site, primarily over nearby land. The low mercury concentration events had short-term trajectories from a more southerly and westerly origin, primarily passing over the Gulf of Mexico. For the intermediate (24 hr) trajectories, the high mercury concentration event air masses traveled primarily over Florida land, while the low mercury concentration event air masses traveled mainly over Gulf and Caribbean waters. The longer-term (72 hr) trajectory locations show fewer overall differences, with all four event trajectories traveling primarily over water (in the Caribbean, Gulf, and Atlantic Ocean) during their initial 48 hr (with a few hours of overland travel). With regard to precipitation along the trajectory, the first event (6/25/2000) had no occurrence of previous precipitation while the other events exhibited some previous precipitation, with the highest previous precipitation in the low concentration events.

Table 5.1 provides a summary of the trajectory characteristics (trajectory location and previous precipitation level) for all similar precipitation depth groups analyzed using



NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 25 Jun 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 25 Jun 00
FNL Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 25 Jun 00
FNL Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 26 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 26 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 26 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 29 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 29 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 29 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 12 Aug 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 12 Aug 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 12 Aug 00
EDAS Meteorological Data

Figure 5.5. HYSPLIT Back trajectories for the highest precipitation level group (Group 1). The top two rows are trajectories for the high concentration events. The bottom two rows are for the low concentrations events. The columns provide 6 hr, 24 hr, and 72 hr back trajectories, from left to right, respectively. The red, blue, and green lines provide trajectories initiated at 250m, 500m, and 1000m heights, respectively

Table 5.1. Characteristics of back trajectories for the 2001 BRACE deposition data. Events are grouped by similar precipitation level.

Grp	Date	Depth	Hg Level	Trajectory Location and Amount of Precipitation[b]		
		(cm)	(ng L^{-1})[a]	0 – 6 hrs	6 – 24 hrs	24 – 72 hrs
1	25.Jun.2000	5.30	31.9 (H)	E: Fl (N)	SE: Fl (N)	SE: Bahamas (N)
	26.Jul.2000	5.57	31.1 (H)	SE: Fl (N)	E: Fl (VL)	SE: Bahamas (VL)
	29.Mar.2001	5.61	9.7 (L)	S: Gulf (L)	SE: Bahamas (VL)	E: Atlantic (N)
	12.Aug.2000	5.78	5.6 (L)	W: Gulf (VL)	SW: Gulf (N)	Gulf & Fl (L)
2	24.Jul.2000	4.85	22.3 (H)	SW: Gulf (N)	W: Gulf (L)	W: Gulf (VL)
	14.Jul.2000	4.65	11.7 (L)	W: Gulf (N)	W: Gulf (VL)	NW: Gulf (N)
	16.Sept.2000	5.03	9.0 (L)	SW: Gulf (N)	S: Gulf (H)	SE: Gulf & Fl (L)
3	9.Jul.2000	4.16	20.5 (H)	NE: Fl (N)	E: Fl (N)	W, NW: Fl, Gulf, Al (VL)
	4.Mar.2001	3.74	9.5 (L)	SW: Gulf (VL)	S, SW: Gulf, Car. (I)	S,SW: Gulf,Caribbean (N)
	25.Nov.2000	3.94	8.5 (L)	SW: Gulf (I)	S: Gulf, Car. (I)	S, E:Car.,Bah.,Atlantic (N)
4	23.Aug.2000	2.81	34.3 (H)	NE: Fl(N)	E: Fl,Atlantic (N)	E,NE: Atlantic (VL)
	4.Jul.2000	2.92	18.2 (I)	Tampa Bay[c](VL)	SE: Fl (L)	SE: Bahamas (H)
	17.Sept.2000	3.04	13.6 (L)	S, SW: Gulf (VH)	S: Gulf (VH)	S, SW: Caribbean (H)
5	17. Jun. 2000	2.34	15.3 (I)	E, SE: Fl (VL)	SE, Fl (VL)	E: Bahamas, Atlantic (N)
	8.Jan.2001	2.26	5.4 (L)	SW: Gulf (N)	S: Gulf (L)	W: Gulf (N)
6	20. Jun. 2000	1.88	26.7 (H)	W: Fl, Gulf (N)	W: Gulf (N)	E, SE: Fl, Bahamas (N)
	8.Jul.2000	1.93	15.5 (I)	SW: Fl, Gulf (N)	W: Gulf (N)	NW: Gulf, SE U.S. (N)
7	27. Mar. 2000	1.47	22.2 (H)	SW: Gulf (N)	SW: Gulf (N)	E: Gulf (N)
	1.Feb.2001	1.20	10.4 (L)	SW: Gulf (N)	S: Gulf (N)	S: Car. (N)
8	31. Aug. 2000	1.06	39.6 (H)	SW, S: Gulf (VL)	SW: Gulf (VL)	NW, SW, S: Al, Gulf, Car. (VL)
	29.Aug.2000	0.99	28.3 (H)	NW: Gulf (N)	NW: Gulf, Fl, Al (VL)	L: SE US (N)
	11.Jun.2000	1.02	11.0 (L)	E: Fl (VL)	E: Atlantic (H)	NE: Atlantic (N)
	28.Dec.2000	1.06	8.3 (L)	S, SW: Gulf (H)	SE: Gulf (H)	NE: Atlantic, NE U.S. (N)

[a] Characters H, I, or L indicate whether the event mercury concentration was relatively high, intermediate, or low (respectively) within the group. [b] The directional location of the trajectory relative to the Tampa special site is given first, with the qualitative level of precipitation along the trajectory indicated in parentheses. For location, standard compass direction and state acronyms are used. For previous precipitation, N, VL, L, I, H, and VH signify the following, respectively: none, very low, low, intermediate, high, and very high. Grp = precipitation group bins, Depth = precipitation depth, and Car. and Bah. are short for Caribbean and Bahamas, respectively. [c] Lingering over the bay area.

back trajectory modeling. Note that each event has been characterized as a high (H), intermediate (I), or low (L) mercury concentration event with respect to other events within each precipitation group. Results indicate that both the trajectory location and the amount of previous precipitation appear to be important to mercury concentration in the collected sample. Although results are mixed, for most of the higher precipitation depth groups (Groups 1, and 3 - 5), air masses from an easterly direction, over Florida land in the short- and intermediate-term (6 hrs and 24 hrs), resulted in comparably higher mercury concentrations in collected samples within a similar precipitation group than those from a westerly direction over water. (For Group 2, all the trajectories were primarily from over Gulf waters.) The long-term (24 to 72 hr) trajectory location does not appear to impact the mercury concentration in collected samples. Additionally, air masses with little or no previous precipitation often resulted in the higher mercury concentrations within each group, though many low concentration events also had little or no previous precipitation. Together, these results suggest that mercury sources in Florida and local to the Tampa Bay region may have an influence on the total mercury wet deposition in the area.

5.3.4. Statistical factors from PMF modeling

5.3.4.1. Analysis of input data

Summary statistics for the BRACE deposition data is shown in Table 5.2. Average species concentrations ranged from a high of 10 $\mathrm{mg\,L^{-1}}$ (Na) to a low of 6 $\mathrm{ng\,L^{-1}}$ (Ag). Mean species concentrations are comparable to measurements performed within the region during a shorter campaign with fewer elements [Graney et al., 2004]. A notable exception is the mean concentration of Pb species which were an order of magnitude greater in the BRACE data, but still relatively high here. The elevated Pb species suggests a lead source (battery cycling), or a metals processing/smelting source with significant lead mass fraction in the region. The influence of marine aerosols, indicative of the local bay area meteorology, is observed in the significantly higher mean concentrations of Na and Mg species in the data.

Species signal-to-noise (S/N) ratios varied from 7.7 to 2.4. All were above the limit considered to be acceptable for inclusion in the model for factor identification [Paatero and Hopke, 2003; Norris et al., 2008]. Results from residual analysis showed all species scaled residuals followed a normal distribution, and 85% of species had residuals between ±3 standard deviations. The coefficient of determination for predicted species concentrations varied between 0.999 and 0.9 for 80% of the species modeled. Species with coefficients of determination below 0.9 included *Cu* (0.86), *Ag* (0.76), *Ag* (0.69), *Co* (0.54), and *Ni* (0.29). Examination of observed/predicted (O/P) scatter plots for poorly modeled species indicated that extreme observations were accounting for the low r^2 values. *Co* (0.54) and *Ni* (0.29) both had observations that were ten times the value of their respective means. The recalculated model with events corresponding to extreme species concentrations omitted from the input dataset (3 events based on extreme observations for *Ni*, *Co*, *Sb* and *Ag* species) showed good improvement, with the recalculated coefficient of determination varying between 0.999 and 0.9 for all species.

5.3.4.2. Factor number selection

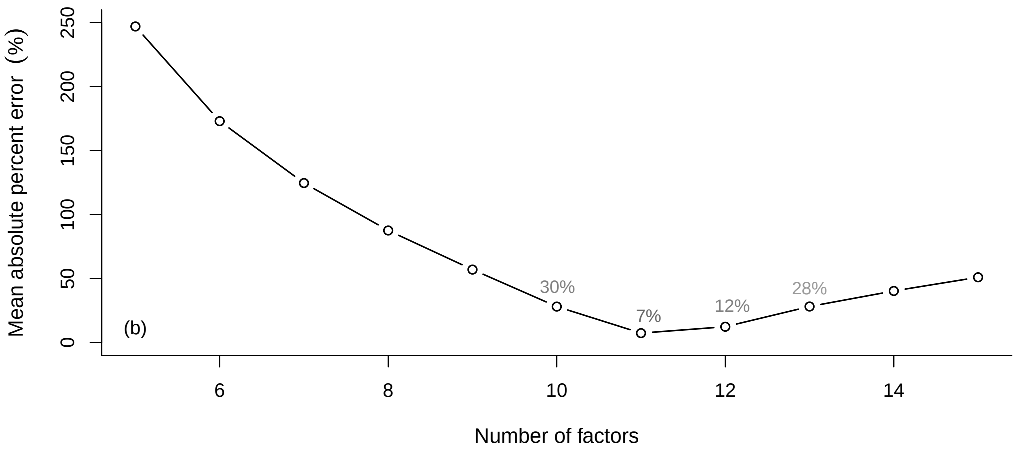
Figure 5.6 shows the results of the sensitivity analysis for factor number determination. Subplot (a) shows the variation in the maximum individual column mean, IM, and the maximum column standard deviation, of the scaled residuals with changes in the number of factors modeled. *IS* and *IM* mirrors a similar trend of decreasing variability as the number of factors increases, indicating that the optimal number of factors for resolving the variability in the dataset occurs when p $\geq$ 10. Subplot (b) plot shows the variation in the absolute percent error between the theoretical Q value, Q_{th}, and the mean model generated value, Q_r for model runs as the number of factors varies between $5 \leq$ p ≤ 15. A steep decline in the absolute percent error is observed as the number of factors modeled, p, increased, with Q_r approaching Q_{th} to a minimum absolute difference of approximately 7%, corresponding to an 11-factor model. For eleven factors, the calculated minimum robust Q value, Q_r, of 1282, was within 7% of the theoretical Q value, Q_{th} of 1200 (n=48, m=25, $Q_{th} = n \times m$).

Table 5.2. Species summary statistics and investigation of source influences for 2001 BRACE deposition data.

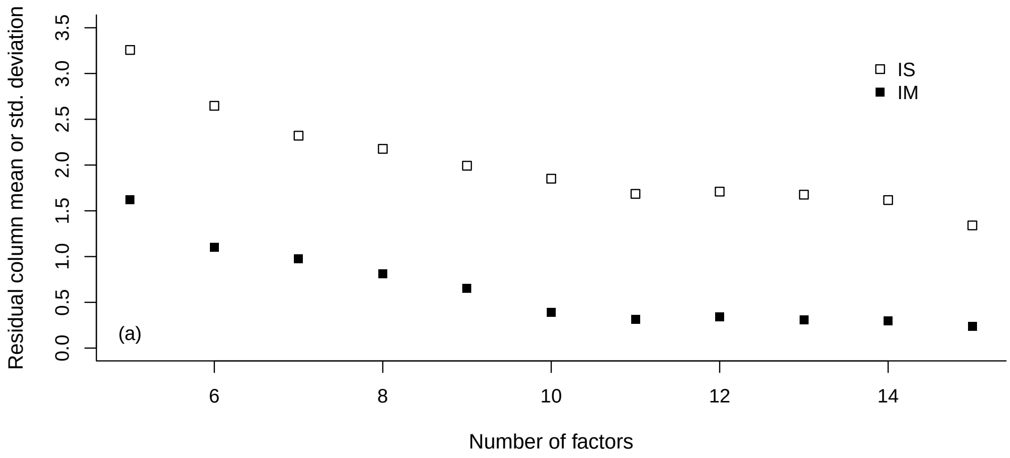
Species	Mean	Min	25th	Median	75th	Max	S/N	Crust[a]	cEF[b]
				($\mathrm{ng\,L^{-1}}$)				wt (%)	
Ag	6.2	1.0	2.0	3.6	6.3	4.6×10^{1}	5.4	5.0×10^{-3}	1.7×10^{-1}
Al	6.0×10^{4}	5.8×10^{3}	2.2×10^{4}	3.0×10^{4}	6.3×10^{4}	4.9×10^{5}	6.4	8.0	1.0
As	3.2×10^{2}	1.8×10^{1}	9.5×10^{1}	2.0×10^{2}	3.2×10^{2}	3.1×10^{3}	5.8	1.5×10^{-4}	2.9×10^{2}
Ba	1.5×10^{3}	4.5×10^{2}	6.4×10^{2}	1.1×10^{3}	2.0×10^{3}	8.3×10^{3}	5.6	5.5×10^{-2}	3.8
Cd	1.2×10^{2}	2.1×10^{1}	5.0×10^{1}	6.8×10^{1}	1.2×10^{2}	8.8×10^{2}	4.7	9.8×10^{-6}	1.6×10^{3}
Ce	2.0×10^{2}	1.2×10^{1}	5.1×10^{1}	9.3×10^{1}	1.9×10^{2}	1.6×10^{3}	7.6	6.4×10^{-3}	4.1
Co	5.7×10^{1}	1.2×10^{1}	2.2×10^{1}	3.3×10^{1}	6.2×10^{1}	2.8×10^{2}	6.9	1.7×10^{-3}	4.5
Cr	3.6×10^{2}	3.0×10^{1}	9.6×10^{1}	1.7×10^{2}	2.9×10^{2}	3.2×10^{3}	7.6	8.3×10^{-3}	5.7
Cs	1.0×10^{1}	1.0	3.5	9.6	1.3×10^{1}	3.6×10^{1}	5.5	4.6×10^{-4}	3.1
Cu	3.7×10^{3}	4.0×10^{2}	1.7×10^{3}	2.8×10^{3}	3.8×10^{3}	2.0×10^{4}	2.4	2.5×10^{-3}	2.0×10^{2}
Fe	5.0×10^{4}	4.7×10^{3}	1.6×10^{4}	2.7×10^{4}	5.6×10^{4}	4.5×10^{5}	6.7	3.5	1.9
Hg	1.9×10^{1}	5.4	1.1×10^{1}	1.8×10^{1}	2.3×10^{1}	7.6×10^{1}	6.2		
La	2.2×10^{2}	1.1×10^{1}	4.2×10^{1}	9.7×10^{1}	2.1×10^{2}	3.0×10^{3}	7.6	3.0×10^{-3}	1.0×10^{1}
Mg	2.3×10^{5}	2.1×10^{4}	1.0×10^{5}	1.8×10^{5}	2.6×10^{5}	1.3×10^{6}	7.5	1.3	2.3×10^{1}
Mn	2.1×10^{3}	1.6×10^{2}	6.4×10^{2}	1.2×10^{3}	2.2×10^{3}	1.5×10^{4}	7.1	6.0×10^{-2}	4.7
Na	1.6×10^{6}	1.8×10^{3}	7.5×10^{5}	1.2×10^{6}	1.7×10^{6}	1.0×10^{7}	5.7	2.9	7.6×10^{1}
Ni	9.2×10^{2}	1.1×10^{2}	3.6×10^{2}	7.0×10^{2}	1.1×10^{3}	3.2×10^{3}	6.1	4.4×10^{-3}	2.8×10^{1}
P	1.1×10^{5}	3.3×10^{3}	9.9×10^{3}	1.5×10^{4}	4.8×10^{4}	2.9×10^{6}	7.2	7.0×10^{-2}	2.1×10^{2}
Pb	9.8×10^{2}	1.6×10^{2}	4.6×10^{2}	6.3×10^{2}	1.2×10^{3}	5.1×10^{3}	7.5	1.7×10^{-3}	7.8×10^{1}
S	1.0×10^{6}	1.7×10^{5}	5.7×10^{5}	8.7×10^{5}	1.5×10^{6}	4.2×10^{6}	7.5		
Sb	3.8×10^{2}	4.0	6.4×10^{1}	2.8×10^{2}	5.7×10^{2}	1.3×10^{3}	5.2	2.0×10^{-6}	2.5×10^{4}
Sr	3.0×10^{3}	4.9×10^{2}	1.0×10^{3}	1.6×10^{3}	3.1×10^{3}	2.2×10^{4}	7.5	3.5×10^{-2}	1.1×10^{1}
Ti	7.8×10^{2}	1.0×10^{2}	2.7×10^{2}	5.2×10^{2}	7.8×10^{2}	3.6×10^{3}	6.2	4.1×10^{-1}	2.5×10^{-1}
V	1.7×10^{3}	1.5×10^{2}	6.6×10^{2}	1.0×10^{3}	1.9×10^{3}	1.1×10^{4}	7.7	1.1×10^{-2}	2.1×10^{1}
Zn	2.6×10^{4}	3.9×10^{3}	1.0×10^{4}	1.8×10^{4}	2.4×10^{4}	2.8×10^{5}	7.3	7.1×10^{-3}	5.0×10^{2}

[b] Composition of upper continental crust for deposited species [McLennan, 2001].

[c] Upper crustal enrichment factors calculated with Al as the reference element.



(a) Trend in mean absolute percent error with change in number of modeled factors



(b) Trend in maximum column mean, *IM*, and column standard deviation, *IS*, of standardized residuals with changes in the number of factors modeled

Figure 5.6. Sensitivity analysis for factor number selection.

The results associated with the minimum Q_r (i.e. the global minimum) are used for further analysis on source identification.

Analysis of variability in model solution indicated good stability in model results. For the selected base solution, all bootstrapped runs converged. Mapping of bootstrapped factors to base factors varied from 49% to 94% across factors. Unmapped factors varied between 4% and 30% indicating some uncertainty in the stability of model results. Assessment of rotational ambiguity of derived factors via sensitivity analysis of the FPEAK parameter indicted no distinct interdependence (presence of "edges" in G-Space plots) for any factor pair. A modest increase in the Q_r for rotated solutions (less than 2 times the base Q) was observed as the FPEAK parameter was applied, well within the recommended range of a factor of ten for a dataset of this size [see Norris et al., 2008].

5.3.4.3. Initial analysis of source contributions

Mean crustal Enrichment Factors (cEF) are reported in Table 5.2. Elements with cEF ≤ 5, considered indicative of biogenic influences, included Ag, Ba, Ce, Co, Cs, Fe, Mn, and Ti species. Elements with intermediate enrichment ($5 \leq$ cEF ≤ 100) assumed indicative of anthropogenic sources included Mg, Na, Ni, Pb, Sr, and V. Elements with cEF ≥ 100, highly enriched and likely influenced by anthropogenic emissions, included Sb, Cd, Zn, As, P, and Cu in decreasing order of value of cEF. Results for enriched species show good agreement with published data for the enrichment of metals by anthropogenic emissions in the United States, which have been found to follow a relative order of Se > Pb > Sb > Cd > Cu > Zn > Cr > V > Co [Galloway and Whelpdale, 1980].

Figures 5.7 and 5.8 shows correlation plots and Pearson correlation coefficients for species pairs in the dataset. Strong positive correlations (r ≥ 0.8) are observed among the heavy metal species: Al, Fe, Mn, Ba, Cr, Ce, Cs, Cd, Pb, La and As. Taken in the context of high enrichment factors observed for several of these species, these correlations suggests contributions from anthropogenic sources. Oil burning (Cd, Pb, Cr, Fe, Cu, V, Ni, Mn), diesel vehicles (Pb, Cd, Cu, Fe, Mn), road dust (Cr, Fe, Mn, Cd, Pb), and metal industries (Cd, Pb, Cr, Fe, Mn) have been shown to account for a significant fraction of atmospheric emissions of these species [Samara et al., 2003; Arditsoglou and Samara, 2005; Voutsa et al., 2002]. Na and Mg species correlated well ($r = 0.97$) with studies suggesting the concentrations and correlations observed being indicative of the influence of marine aerosols [Dvonch et al., 1998]. This is reinforced by the significantly higher mean concentrations of Na and Mg species in the data, and the combination of sampling location and local meteorology. Additionally, notable correlations existed between *Al-Fe* ($r^2 = 0.95$) and *Al-Mn* ($r^2 = 0.92$) species pairs, being indicative of influences from metal smelting and municipal waste combustion sources, respectively [Dvonch et al., 1998; White et al., 2009; Polissar et al., 2001].

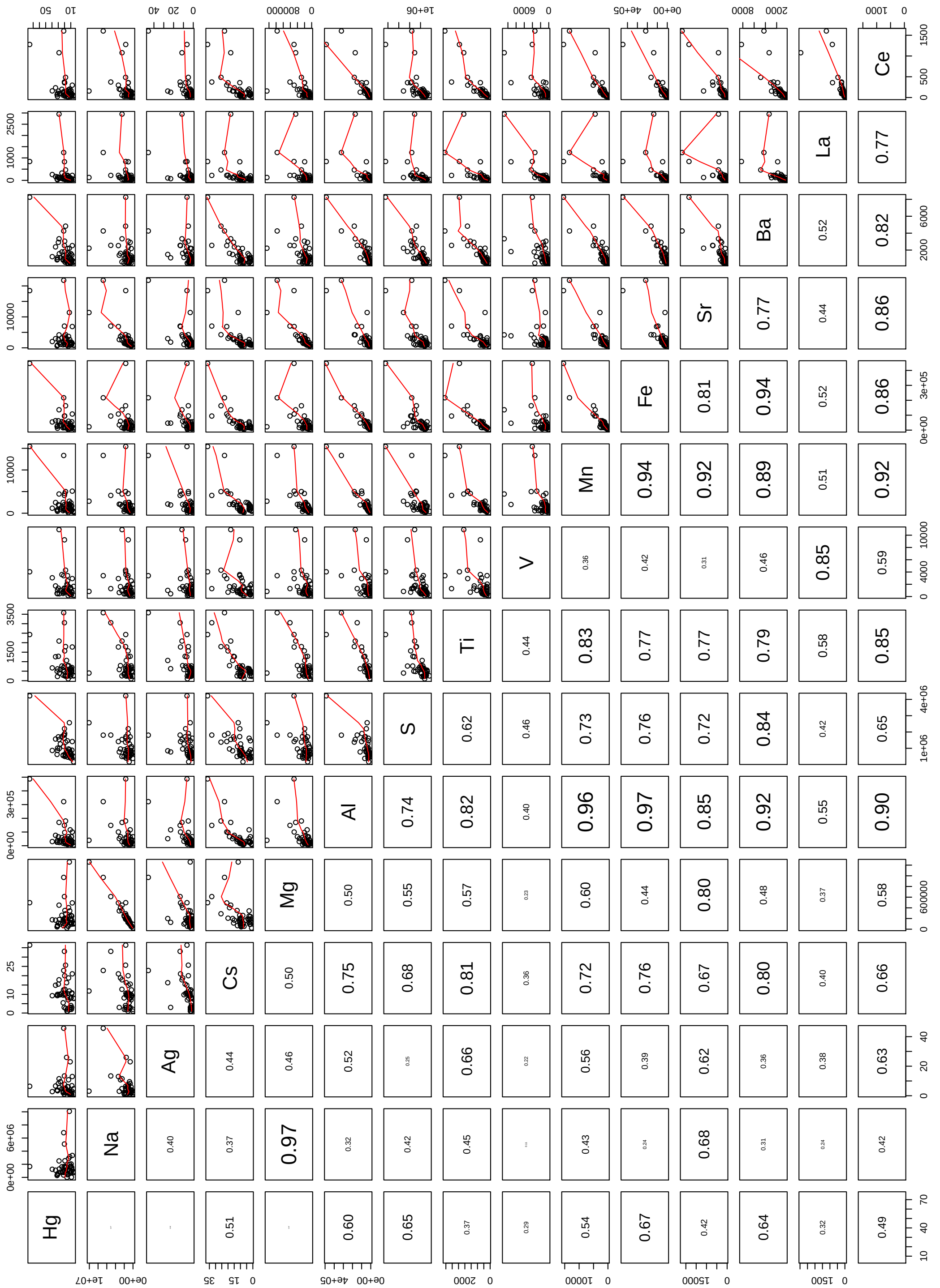


Figure 5.7. Correlation matrix of select species for preliminary source identification. Species plotted shown on the diagonal. Panel below diagonal gives the Pearson's correlation coefficient of species pairs as a function of goodness of fit (species pairs with poor fitting are shown at relatively reduced font size). The upper panel plots a smoothing scatterplots (locally weighted regression) of the species pairs. Correlation coefficients corresponding to a species pair is found at the intersection of the column and row from the diagonal.

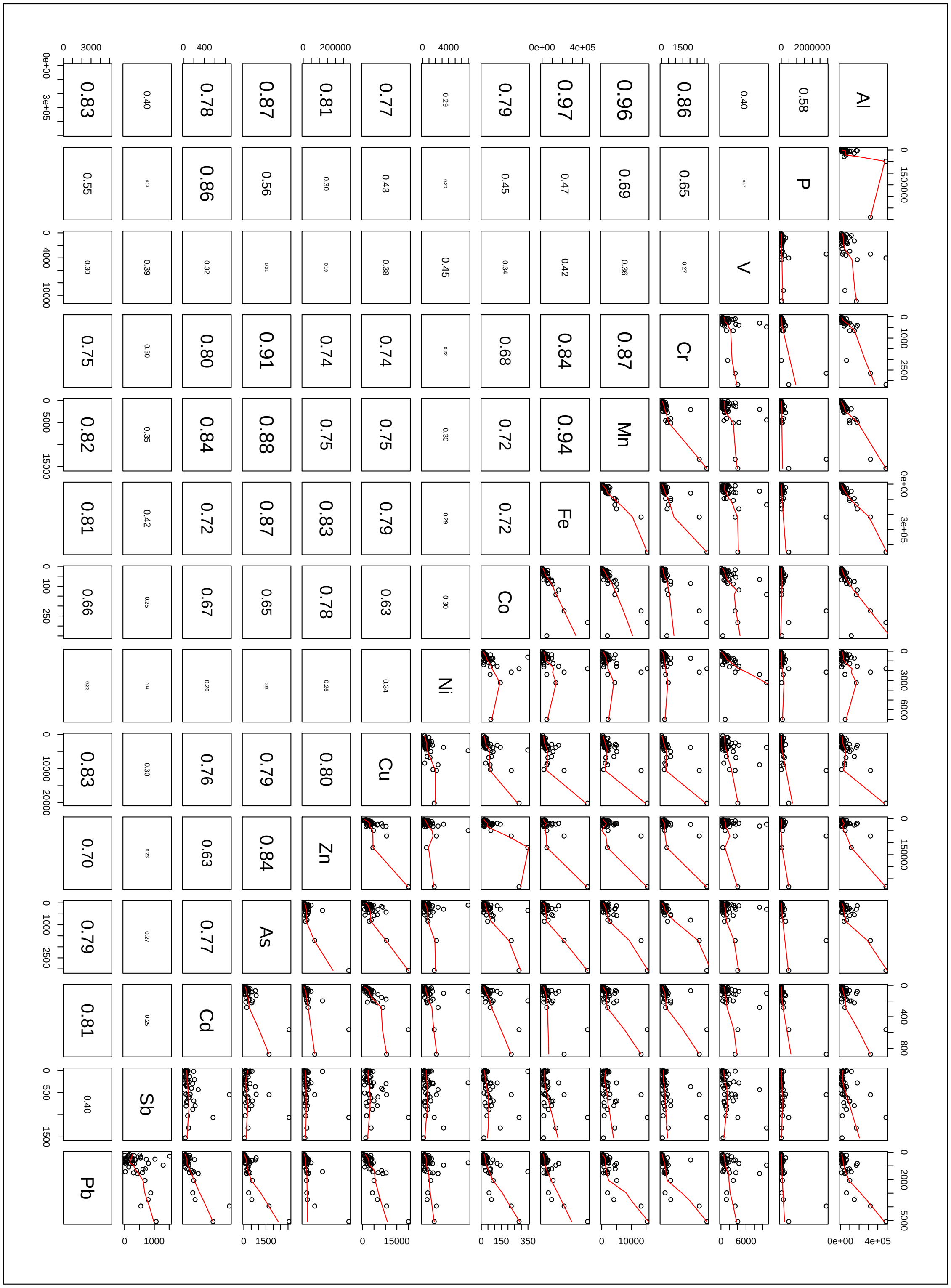


Figure 5.8. Correlation matrix of select species for preliminary source identification. Species plotted shown on the diagonal. Panel below diagonal gives the Pearson's correlation coefficient of species pairs as a function of goodness of fit (species pairs with poor fitting are shown at relatively reduced font size). The upper panel plots a smoothing scatterplots (locally weighted regression) of the species pairs. Correlation coefficients corresponding to a species pair is found at the intersection of the column and row from the diagonal.

5.3.4.4. Factor identification

Figure 5.9 gives the contributions, and compositions of the 11 factors resolved by PMF, along with probable source types. Elemental ratios calculated from mean species concentrations are compared with published data in Table 5.3. Each factor and the rationale for its identification is discussed below.

5.3.4.5. Agrochemicals

The profile and species contributions for this factor is shown in Figure 5.9, subplot (a). The factor profile was defined by a dominant phosphorus signal, contributing 85% factor total mass, with smaller contributions from Na (6%), Mg (4%), and Al (4%). The factor contributed 91% of total phosphorous species mass observed in the data, as well as, Sr (23%), Cd (21%), and Ag (17%) total species masses. High phosphorus and potassium loadings have been used to identify emissions from agrochemical sources in source apportionment studies [Keeler et al., 2006; Gratz and Keeler, 2011]. Lee et al. [2000] used elemental concentration ratios of tracer species to identify contributions from agricultural soils in trace metal data. Table 5.3 compares the ratios with those calculated in this study. We see good agreement for V/Ni and Zn/Cd concentration ration for the resolved factor. Additionally, good correlations are observed between species pair that are indicative of this source. These include Pb-Cd (r^2 = 0.81), Cu-Pb (r^2 = 0.83), Zn-Pb (r^2 = 0.7), and Zn-Cd (r^2 = 0.63) (see Table 5.3). This factor was resolved with the little uncertainty, having 94% of bootstrapped factors mapping back to the base factor. Studies have shown that the atmospheric deposition of phosphorus is a significant nutrient source to water bodies in the Tampa Bay area [Pribble and Janicki, 1999; Grimshaw and Dolske, 2002].Additionally, we observe that P is highly enriched in the dataset as shown in Table 5.2. Land application of phosphorus-based chemicals as fertilizers for crops, and subsequent adsorption to soil particles is significant route to atmospheric loading of phosphorus. Additionally, organic and inorganic phosphorus is an important component of animal waste. Taking into consideration the substantial contributions to phosphorus

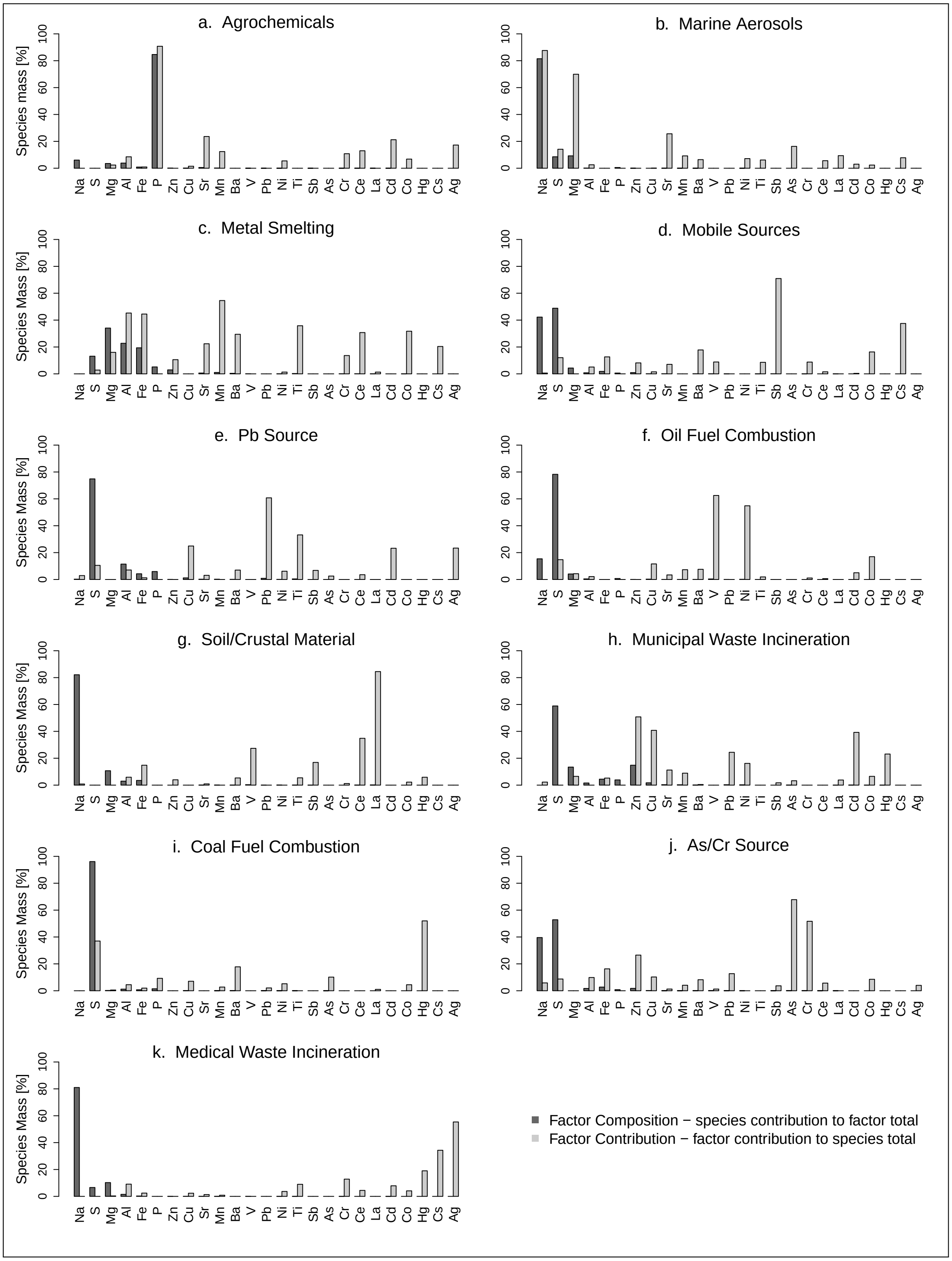


Figure 5.9. Source identification for an 11-factor PMF simulation. The plots shows the factor fractional contributions to total species mass (dark bars) and the factor profiles (species fractional contributions to factor total, light bars) for each source identified.

Table 5.3. Comparison of trace element concentration ratios for source identification.

Source	Reference	Pb/Cd	V/Ni	Cr/Fe	Cu/Sb	Mn/Fe	As/V	Pb/Cu	Zn/Pb	Pb/Mn	Zn/Cd	La/Ce
Agrochemicals	This study	5.5E-1	4.1E-1	2.6E-2	5.1E+0	2.1E-1	-	2.2E-1	1.1E+1	6.2E-2	6.0E+0	5.6E-1
	Agricultural soil[d]	-	6.5E+0	-	-	-	1.0E-1	-	4.0E+0	-	5.3E+0	
	Soil[c]	-	8.3E+0	-	3.0E-1	-	1.0E-1	-	3.1E+0	-	9.4E+0	
Coal Combustion	This study	-	-	-	7.9E+1	3.7E-2	-	3.2E-1	-	1.2E+0	-	1.4E+0
	Coal combustion[c]	-	7.0E-1	-	5.0E-1	-	4.8E+0	-	1.9E+0	-	1.7E+1	
Municipal Waste	This study	5.6E+0	-	-	-	5.9E-2	-	1.7E-1	5.1E+1	1.1E+0	2.8E+2	-
	Metal Incineration[a]	9.5E+1	1.7E-1	6.0E-3	1.0E+1	1.5E-2	3.1E-1	3.9E+1	8.4E+0	5.3E+0	8.0E+2	
	Steel Manufacture[b]	6.4E+1	6.7E-1	9.0E-3	-	5.0E-3	-	4.1E-1	-	2.2E+0	-	
Metal Smelting	This study	-	3.0E+0	2.2E-3	-	5.4E-2	-	-	-	-	1.2E+3	4.8E-1
	Metal Incineration[a]	9.5E+1	1.7E-1	6.0E-3	1.0E+1	1.5E-2	3.1E-1	3.9E+1	8.4E+0	5.3E+0	8.0E+2	
	Steel Manufacture[b]	6.4E+1	6.7E-1	9.0E-3	-	5.0E-3	-	4.1E-1	-	2.2E+0	-	
Oil Combustion	This study	8.8E+0	2.8E+0	-	3.3E+1	-	3.5E-3	1.9E-1	9.3E-1	1.4E+0	8.2E+0	2.5E+0
	Oil Burning[a]	1.6E+2	2.5E+0	1.1E-2	7.1E+1	4.3E-2	2.0E-2	8.7E-1	1.2E+0	2.8E+0	1.9E+2	1 - 2
	Oil combustion[d]	-	2.4E+0	-	1.6E+0	-	3.0E-3	-	7.2E+0	-	3.3E+0	
Mobile Sources	This study	2.4E+0	-	3.7E-3	9.0E-1	-	-	7.5E-2	2.0E+2	-	4.8E+2	2.3E+0
	Catalytic cars[b]	9.1E+1	2.2E+0	1.0E-3	3.2E+2	5.0E-3	1.1E+0	1.1E+0	3.4E+0	1.1E+1	5.6E+1	3.0E-1
	Gasoline vehicles[a]	-	2.0E-2	-	3.2E+2	-	1.1E+0	-	3.4E+0	-	5.6E+1	
	Diesel vehicles[a]	-	1.5E-1	1.0E-2	7.0E+2	5.0E-2	7.0E-3	3.0E-1	7.6E+0	2.0E+0	4.1E+2	3.0E-1
Crustal Material	This study	1.3E+1	5.9E+0	-	-	1.5E-2	1.9E-3	-	-	1.4E-1	-	2.6E+0
	Crustal Material[e]	-	1.8E+0	-	2.8E+2	-	1.0E-2	-	5.4E+0	-	3.5E+2	5.0E-1
As/Cr Source	This study	-	9.8E+0	2.8E-2	1.2E+1	5.4E-3	9.5E-1	2.8E-1	3.9E+1	3.1E+0	-	1.5E+0
	Cement Production[a]	4.7E+0	9.0E-2	6.0E-3	7.4E+0	2.1E-2	3.0E-2	6.7E-1	4.2E+1	4.0E-2	2.0E+2	3.0E-1
Lead Sources	This study	2.1E+1	-	3.9E-4	-	5.0E-2	-	7.3E-1	7.8E-2	4.1E+0	1.6E+0	4.3E-3
	Metal Incineration[a]	9.5E+1	1.7E-1	6.0E-3	1.0E+1	1.5E-2	3.1E-1	3.9E+1	8.4E+0	5.3E+0	8.0E+2	
	Steel Manufacture[b]	6.4E+1	6.7E-1	9.0E-3	-	5.0E-3	-	4.1E-1	-	2.2E+0	-	

[a]Samara et al.,[2003]; [b]Arditsoglou and Samara, [2005]; [c]Watson et al., [2001]; [d]Lee et al., [2000]; [e]Mason and Moore, [1982]

species mass attributed to this factor, it is likely that chemical cycling of phosphorus from agricultural industries may be responsible species concentrations observed.

5.3.4.6. Marine aerosols

The profile and species contributions for this factor is shown in Figure 5.9, subplot (b). This factor was identified by its significant contributions to sodium and magnesium species in the deposition dataset. The factor accounted for 70% of all Mg species, and 80% of all Na species in the dataset. The factor profile (species contribution to factor total) showed predominant sodium species mass >80%, with some contributions from magnesium (10%), and sulfur (10%). Sodium and magnesium are major components of sea salt. Dvonch et al. [1998], identified Na, Cl, and Mg species as tracers for contributions from the marine environment to species mass in deposition studies. The mean Na/Mg concentration ratio of this data set (8.8) compared well with values from other similar studies, Alleman et al. [2010] (8.4), and Yuan et al. [2006] (8.5). Additionally, sodium and magnesium displays a strong positive correlation, with a Na-Mg correlation coefficient of 0.97 as shown in Figure 5.7. Considering our sampling and model domain, this factor likely highlights contributions of the nearby Tampa Bay and the Gulf of Mexico. The factor solution stability was demonstrated by a relatively high bootstrap remapping fraction (∼80%) for factor uncertainty analysis.

5.3.4.7. Metal smelting

This factor is characterized by significant contributions to heavy metal species; Mn (50%), Al (45%), Fe (44%), Ti (35%), Co (30%), Ba (30%), Ce (30%), Sr (22%), and Cs (20%), with some minor contributions to several other metal such as Cr, La, and Zn (Figure 5.9, subplot (c)). The factor profile indicated significant fractional contributions from Mg (34%), Al (23%), Fe (19%), and S (13%) species to total factor mass. Table 5.2 indicates that most of the heavy metal species loaded in this factor show high enrichment, suggesting anthropogenic influences. Olmez et al. [1998], suggested a As/Se ratio of <1 to be indicative of emissions from smelters. This comparison could not be made since Se was not a part of the suite of metals in this dataset. Individual metals indicative of emissions from metal smelting processes include Ni, Ti, Cu, Mn, Co, As, Cd, Cr, Sn, Sb, and Pb [White et al., 2009; Olmez et al., 1998], some of which are prominent in the factor contribution matrix here (Figure 5.9, subplot (c), light bars). Species pairs relevant to metal smelting sources show strong positive correlations (shown in Figures 5.7 and 5.8). These include Mn-Fe (r^2 = 0.94), Al-Fe (r^2 = 0.97), Ti-Mn (r^2 = 0.83), Cr-As (r^2 = 0.91), Pb-Cu (r^2 = 0.83) and Al-Mn (r^2 = 0.96) among selected species pairs. Table 5.3 compares calculated elemental concentration ratios for signature species in this study with available literature values. We compared the values calculated here with those for scrap metal incineration [Samara et al., 2003], and steel manufacture [Arditsoglou and Samara, 2005]. The Zn/Cd (800, 1200 this study), Cr/Fe (0.006, 0.002 this study), and Mn/Fe (0.02, 0.05 this study) elemental ratios showed good agreement. This also factor displayed a high bootstrap remapping fraction (∼80%) and good stability in model solutions. Considering the high loading of the heavy metal species, their strong correlations, and the close agreement with elemental concentration ratios, this factor suggest contributions from a metal smelting/processing facility in the region.

5.3.4.8. Mobile sources

A source accounting for approximately 71% of overall antimony species mass was resolved by PMF. The factor also made significant contributions to Cs (37%), Ba (20%), and Co (16%) Figure 5.9, subplot (d). Examination of the factor profile (species contributions to factor total mass) indicated that it consisted predominantly of S (49%) and Na (42%). Anthropogenic antimony sources include both domestic and industrial coal and fuel combustion, pyrometallurgical non-ferrous Cu-Ni-based metal production, incinerators, and road traffic [Gomez et al., 2005; Cal-Prieto et al., 2001]. Gomez et al. [2005] identified vehicular traffic as one of the main sources contribution to high levels of antimony in highly populated areas, as result of brake dust. Species indicative of motor vehicle emissions include Si, S, Ce, Ca, Fe, Cu, Zn, and Ba [Dvonch et al., 1998; Landis et al., 2007]. Comparison of selected species ratios for the factor with similar studies (see Table 5.3) shows some agreement in the Cr/Fe (0.001, 0.004 this study) ratios with those corresponding to emissions from catalytic cars. Metal species corresponding to mobile source emissions showed good correlations as shown by

Figures 5.7 and 5.8. These include Cu-Fe ($r^2 = 0.79$), S-Ba ($r^2 = 0.84$), Fe-Ba ($r^2 = 0.94$), Fe-Zn ($r^2 = 0.83$), Ba-Ce ($r^2 = 0.82$), and Cu-Zn ($r^2 = 0.80$). The factor also showed low variability in percentage of species and concentration of species, and a bootstrap remapping fraction of 75%. Being the single largest antimony contributing factor, and considering the traces of barium, cesium and other earth metals comprising this factor, this is most likely a traffic related source.

5.3.4.9. Lead sources

PMF resolved a significant lead contributing source as shown by Figure 5.9, subplot (e). This factor accounted for 60% of the Pb species observed in the dataset. It also accounted for a significant percentage of Ti (33%), Cu (25%), Ag (23%), and Cd (23%) species in the dataset. The factor profile indicated substantial contributions from S (75%) and Al (11%) to total species mass. The factor also had high variability in percentage of species for all model runs. Interrogation of trace elements ratios hints at influences from heavy metals processing industries (steel manufacturing industries), with evidence form close agreements with Pb/Cd (64, 21 this study), Mn/Fe (0.02, 0.05 this study), Pb/Cu (0.4, 0.7 this study), and Pb/Mn (5.3, 4.1 this study) species ratios Table 5.3. We observe good correlations between the principal species of this factor (relative % contribution) as shown by Figures 5.7 and 5.8. Pb-Cd ($r^2 = 0.81$), Pb-As ($r^2 = 0.79$), Pb-Zn ($r^2 = 0.70$), Pb-Cu ($r^2 = 0.83$), and Pb-Mn ($r^2 = 0.82$) all show good agreement. The high mercury loading, and strong correlations between lead and other heavy metals, especially cadmium, copper and zinc, and high enrichment factors, suggest contributions from lead processing facilities, such as battery recycling or waste incineration.

5.3.4.10. Oil combustion

PMF resolved a factor which accounted for ∼60% of V species and 55% of Ni species, with minor contributions to Co (17%), S (15%), and Cu (12%) (Figure 5.9, subplot (f)). The largest contributions to factor mass came from S species (78%), with smaller contributions from Na and Mg species. Loading of Ni and V species are indicative of emissions from oil combustion processes [Olmez and Gordon, 1985]. Tracers for oil combustion sources have been identified as S, V, Ni, Al, Ca, Fe, Mo, and La [Dvonch et al., 1998; Kim et al., 2004; Keeler et al., 2006]. Comparisons of selected elemental concentration rations reveal good agreement with published data. Specifically, a La/V ratio of 0.45 (0.15 this study) has been identified as a signature of oil-fired power-plants [Olmez and Gordon, 1985]. Similarly, a La/Ce ratio of 1-2 (2.54 this study), and a V/Ni ratio of 2.7 (2.76 this study) were used to identify oil combustion sources in metals deposition studies [Dvonch et al., 1998; Landis et al., 2007; Kitto, 1993]. Correlations between species pairs with large contributions show strong associations (see Figures 5.7 and 5.8). Species pairs with strong positive correlations include La-Ce ($r^2 = 0.77$), and La-V ($r^2 = 0.85$). The significant loading of V and Ni species, both with high enrichment factors (see Table 5.2), suggests the influence of oil combustion processes on species in the deposition data. Oil combustion emission categories may include contributions from oil fired power generating facilities, and industrial and residential heating equipment in the domain.

5.3.4.11. Soil/Crustal material

A source with significant contributions to the La (85%), Ce (35%), and V (27%) species masses in the dataset was identified by PMF (Figure 5.9, subplot (g)). Factor profile consisted predominantly of Na (82%), with some contribution from Mg (11%) species. Taylor and McLennan (1985), suggested a La/Ce ratio of 0.6 (2.6 this study) is indicative of average continental crustal material. Similarly, Fe/Al rations of 0.4 (1.2 this study), Mg/Al ratios of 0.2-0.3 (3.6 this study), and V/Ni of 1.8 (5.9 this study) have been used to identify soil/crustal dust as a PMF source [Keeler et al., 2006; Olmez and Gordon, 1985]. Other tracers for soil/crustal emission sources include Ti, Mn, Sr, La, and Mn. This source showed good stability and little variation between model runs. Correlation plots of species pairs associated with this factor also indicated strong associations. These included Ce-Mn ($r^2 = 0.92$), Fe-Al ($r^2 = 0.97$), and La-Ce ($r^2 = 0.77$), see Figures 5.7 and 5.8). The loading of La and Ce species, which are predominantly of biogenic origin, suggests the influence of crustal material on this factor.

5.3.4.12. Municipal waste incineration

A source was resolved that contributed substantially to Zn (50%), Cu (40%), Cd (40%), Pb (24%), Hg (23), and Ni (16%) loading (see Figure 5.9, subplot (h)). The factor profile indicated a significant S (60%) and Zn (15%) species contributions. The factor had a bootstrap remapping fraction of 57%, and also indicated some instability in model solutions. Zn, Cu, Cd and Ni showed high enrichment in the dataset, indicating proboble anthropogenic origin (see Table 5.2). Polissar et al. [2001] identified the emissions from municipal waste incineration by comparing the Zn/Pb and Hg/Pb species concentration ratios. A Zn/Pb ratio of 1.8 (8.4 this study) and a Hg/Pb ratio of 0.06 (0.03 this study) were used to identify contributions from municipal waste incineration for PMF analysis [Polissar et al., 2001; Olmez et al., 1998; Dvonch et al., 1998, 1999]. Incineration, medical and municipal, may also be associated with the species that observed high loading from this factor [Polissar et al., 2001; Olmez et al., 1998; Dvonch et al., 1998]. We observe strong correlations between the following species pairs; Zn-Cu ($r^2 = 0.80$), Zn-Cd ($r^2 = 0.63$), Zn-Pb ($r^2 = 0.70$), Cu-Pb ($r^2 = 0.83$), and Cd-Pb ($r^2 = 0.81$). The high loading of this factor to several metal species, high enrichment factors for those species, and string positive correlations between species pairs hints at contributions metals processing source. The relatively insignificant contributions to biogenic species (La, Ce) but relatively high contribution to mercury species suggests that this factor may be due to the processing bulk consumer waste products. The overwhelming presence of sulphur species in the factor profile also hints at combustion processing.

5.3.4.13. Coal-fuel combustion

A factor was identified which contributed to the largest fraction of mercury species, in the data (52%) as shown by Figure 5.9, subplot (i). It also contributed to about a quarter of sulfur species, and substantial amounts of As (12%) and Ba (20%) species. Analysis of the factor profile revealed that it consisted almost completely of sulfur species (>95%), being consistent across model runs. There was some variation in the model solution for this factor, with only 54% of bootstrapped factors mapping back to the original factor. The presence of large percentages of sulfur species has been used to identify the contributions of coal-fuel combustion sources by several authors. Specifically S/Se [White et al., 2009], and As/Se [Tuncel et al., 1985] species ratios have been used to identify coal combustion sources contributing to sulfur species mass. Unfortunately, Se was not a species that was part of the species dataset, thus these ratios cannot be determined. We observe positive correlations between Ba-Ce (r^2 = 0.82), Hg-S (r^2 = 0.65), and Hg-Ba (r^2 = 0.64) species pairs. Based on the significant sulfur contributions and its consistent correlation with mercury species there is a high degree of confidence in associating this factor with coal-fuel combustion sources.

5.3.4.14. Arsenic/Chromium source

A heavy metals factor with significant contributions to As (68%) and Cr (52%) was resolved by the model. Other significant species included Zn, Fe, Pb and Cu (see Figure 5.9, subplot (j)). The factor profile consisted predominantly of S (53%) and Na (40%) species. The factor species concentrations ratio were compared to those for cement manufacturing, however large differences were observed (see Table 5.3). Cr species serve as tracer species for iron/steel production sources [White et al., 2009]. Additionally, As-Cr (r^2 = 0.91), As-Zn (r^2 = 0.84), As-Fe (r^2 = 0.87), and Cr-Zn (r^2 = 0.74) species show strong positive correlations. However, a lack of additional source identification information resulted in this factor being unresolved for a local emission category.

5.3.4.15. Medical waste combustion

PMF resolved a factor that was characterized by significant contributions to several species. These include Hg (20%), Ag (55%), Cs (35%), and Cr (13%), with smaller contributions to Al, Ti, and Cd species (see Figure 5.9, subplot (k)). Factor profile indicated contributions from Na (80%) and Mg (10%) species to factor mass. This factor had a remapping fraction of 0.49, with percentage contribution for the base solution within bootstrap IQR for all species. Note the relatively high mercury loading observed here. To help identify this factor we compared it to the municipal waste incineration factor identified previously (Figure 5.9, subplot (h)). Both factors had high mercury loading but we observe lower contributions to a smaller subset of metals here. We do not observe to loading of metals typical of consumer products (Pb, Zn, Cu, Ni). Here we see Cr, Ti, Cd, Cs and Ag loadings. Polissar et al. [2001] and Dvonch et al. [1998] have suggested a Hg/Pb species ration of ∼8 to be indicative of emission from medical waste facilities. Whilst this ratio was not observed, due to the high Hg and other heavy metals loading, and the presence of S species in the factor profile we suggest that emissions from the incineration of medical products make be influencing this factor.

In summary, seven probable factors were resolved by PMF modeling on the deposition dataset, and were identified as coal fuel combustion, medical waste incineration, municipal waste incineration, oil combustion, traffic-related emissions, a soil/crustal material source, marine aerosols, metal smelting, agro-chemical emissions, a lead signal, and a chromium signal.

5.3.5. Factor contributions to mercury species mass

Figure 5.10 shows the model resolved factors contributing to mercury species mass observed in the dataset. Four sources were identified as the major contributors to mercury species mass. Coal fuel combustion sources were found to be the largest mercury contributing factor, accounting for approximately 52% of mercury species in the dataset. This makes sense when we examine emissions inventory for the period (1999 NEI, discussed in Chapter 6. Coal fired combustion has been shown to account for greater than 50% of mercury mass in Florida, and the Tampa Bay area specifically. Municipal waste incineration sources were identified as the second largest mercury-contributing source, accounting for approximately 23% of mercury species in the dataset. Medical waste combustion sources were identified as the third highest mercury contributing source. The emissions inventory identifies a medical waste facility as being a significant contributor to local mercury emissions (ST. Joseph's Hospital in Tampa). Finally, the crustal material source contributed about 6% of the mercury species observed in the deposition data.

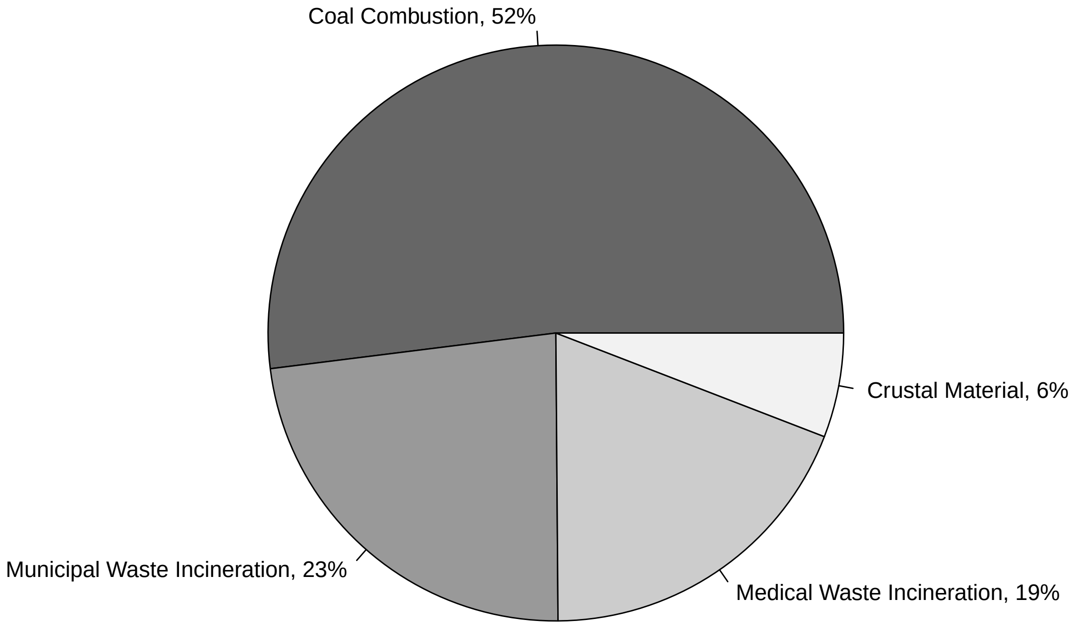


Figure 5.10. Mercury contributing factors from 2001 BRACE deposition data. PMF model solution showing factor fractional contributions to mercury species in the deposition data

The regression results of the PMF predicted versus measured Hg concentrations had slope of 0.93, an intercept of 0.48, and a coefficient of determination (r^2) of 0.89, indicating an excellent fit to the data.

5.4. Conclusion

Results from analysis of the network data indicate no long-term trend in wet deposition of mercury in Florida over the decade of available data. However, concentrations of mercury in the PM2.5 data suggest the possibility of increasing dry deposition of mercury. Additionally, the annual cycle of wet deposition shows that mercury deposition amount closely follows precipitation amount (with abruptly higher amounts in summer months), but mercury concentrations in deposited rain exhibit different peaks and smaller relative differences between seasons. In the special event data studied here, the mercury concentration was largely uncorrelated with the rain depth while the mercury deposition amount was highly correlated with rain depth. These results indicate that rainfall in the area scavenges mercury with little dilution effect, suggesting a large (or quickly replenished) reservoir of oxidized mercury in the local atmosphere. Additionally, fluctuations in measured concentrations suggest differences in sources of mercury to each air mass through which scavenging occurs.

Results from backward trajectory modeling of the event data suggest the likely influence of Florida sources on high mercury concentration events studied here, while the PMF analysis indicates influences on mercury deposition from medical and municipal waste incinerators and utility coal boilers. These results are interesting when compared with emissions inventory data. In the 1999 National Emission Inventory [USEPA, 2012], the most recent inventory prior to the collection of the event data, the St. Joseph's hospital medical waste incinerator was the largest Hg source in Florida and in Hillsborough County (which contains Tampa). It contributed 75% of the inventoried emissions in the county and 30% of that in Florida. For readily deposited Hg alone (RGM plus HgP), the medical waste incinerator category accounted for about 50% of inventoried emissions in Florida. Emissions from coal-fired power plants contributed 21% of the readily deposited Hg emissions in Florida, and the 2nd and 3rd largest individual stationary sources of mercury in Hillsborough County were coal-fired power plants in or near Tampa (the Gannon and Big Bend plants). Finally, the phosphate rock industry (rock mining, fertilizer production, cement and asphalt manufacturing) is substantial in the study area. Mercury emissions from several related facilities (Coronet Industries, National Gypsum Co., Cargill Fertilizer, James Hardie Buliding Products) in the county are inventoried, but at much lower emission rates than the above sources. Municipal waste incineration is also a substantial mercury source type in the county, emitting the third largest inventoried amount after coal combustion. Note that in the 2002 National Emissions Inventory [USEPA, 2008], the contribution of St. Joseph's hospital (and medical waste incineration generally) decreased substantially, due to controls implemented there.

Taken in the context of area emission inventories, the analysis results here point towards substantial contributions to Tampa mercury deposition from local and regional Florida sources. However, contributions from distant sources cannot be precluded since incinerators have large mercury emissions globally. Further work is needed, combining modeling and event data, for quantitative assessment of the contributions of local versus distant sources of mercury deposition.

6. Mercury deposition to the Tampa Bay area: Source influences from the 2012 USF deposition experiment

6.1. Introduction

Mercury is a persistent environmental contaminant whose most toxic form, methyl mercury, is found at high levels in fish present in water bodies throughout the world [Downs et al., 1998]. Methyl mercury strongly bioaccumulates and biomagnifies in aquatic ecosystems, making consumption of predatory fish the leading route to toxic human exposures [Tollefson and Cordle, 1986]. Deleterious human health effects include impaired mental function, neurological disorders, cardiovascular effects, and kidney damage [Tchounwou et al., 2003]. Adverse effects on other species, including piscivorous birds and mammals, have also been documented [Scheuhammer et al., 2007; Wolfe et al., 1998].

In order to mitigate these effects, attribution of observed levels of mercury (Hg) in the environment to Hg sources is needed. Of particular interest is identifying the relative contributions to deposition to sensitive watersheds of local anthropogenic sources versus distant sources. The level of uncertainty in the scientific literature on the point is detrimental to adequate control at all management levels, from international to local. Previous research specifically addressing the relative contributions is somewhat contradictory. The objective of this focus area is to assess the contribution of local emission sources on the loading of mercury to the Tampa Bay area through wet deposition phenomenon, and to identify the source categories and facilities contributing to significant atmospheric mercury deposition.

In a previous chapter I investigated the deposition and sources of mercury in the Tampa Bay region utilizing previously collected data from the Bay Regional Atmospheric Chemistry Experiment (BRACE) [Atkeson et al., 2007]. This data was utilized to compare temporal trends in precipitation depths and mercury concentrations, and was also used in combination with back trajectory and receptor modeling to understand source contributions. Some uncertainties existed with the trace metals deposition data measured through the BRACE study. Several species that are instrumental to the characterization of emissions sources were not available in the BRACE dataset. These included selenium, which in combination with sulfur species is used to identify source contributions from coal combustion facilities. Additionally, measurement uncertainties associated with key several species were not reported in the BRACE dataset, and were estimated for use in PMF receptor modeling. Finally, the data used in this study was collected during the period March 2000 to March 2001, and may not be able to accurately develop a profile of current emission sources. Collection of new speciated data allows for a more accurate description of current emission sources influencing deposition phenomenon in the Tampa Bay area, and allow for comparisons of sources influencing mercury deposition over the periods.

In this chapter, I investigate the deposition and sources of mercury in the Tampa Bay region utilizing new measurement data collected in the Tampa Bay area. This data, consisting of mercury and trace metals concentration data, along with deposition data will inform mercury deposition trends in the Tampa Bay area. Trace metal data were used as input for source apportionment modeling efforts. I also performed meteorological trajectory simulations to determine the pathway traversed by air masses influencing deposition events in the domain. Identification of emission sources will be informed by querying the EPA's National Emissions Inventory for contributions of emission sources native to the Tampa Bay area. Sample collection and analysis methods, deposition, back-trajectory, and receptor modeling results, and potential implications for local versus long-range source influences are discussed in the following sections.

6.2. Materials and methods

6.2.1. Study site description

The sampling site was located on the grounds of the University of South Florida campus (28.056,-82.422). Sampler location was based on guidelines from the NADP/MDN Site Selection and Installation manual [NADP, 2007]. The site was at least 140m from the nearest high volume roadway (Fowler Avenue), and 180m from USF Pine Drive, a well used arterial road on the campus. The site was also close to the laboratory facilities. A meteorological station for synchronization of environmental variables was also nearby. Figure 6.1 depicts the site location, as well as, its proximity to major roads, the meteorological station, and laboratory facilities. The site was approximately 300m northwest of the meteorological station (ID:KFLTAMPA78, [28.057, -82.425], Elevation: 40ft) located in the USF Botanical Gardens at the intersection of Pine and Alumni Drive, USF (see Figure 6.1). Additionally, the sampler was located approximately 600m from the laboratory facilities located at the Interdisciplinary Research Building (IDRB), on the USF campus, thus enabling easy monitoring of equipment and minimal commute for deposition samples.

6.2.2. Event wet deposition sampling

6.2.2.1. Sample collection

A 6-month sampling campaign, covering the period July 2012 to December 2012, was conducted for the collection of wet-only deposition samples. Collection of event-based precipitation samples was achieved using an automated precipitation sampler, similar to those in use by the National Atmospheric Deposition Program, Mercury Deposition Network (NADP/MDN) sample collection sites. The collector, referred to as MDN Mercury Deposition Sampler (N-CON Systems Company, Inc), samples continuously, by opening automatically during wet weather. An infrared, optical sensor detects the onset of precipitation and uncovers the sample container within five drops (Figure 6.2). The sensor also detects drizzle or heavy fog, any of which may carry significant amounts of deposition. Within two minutes

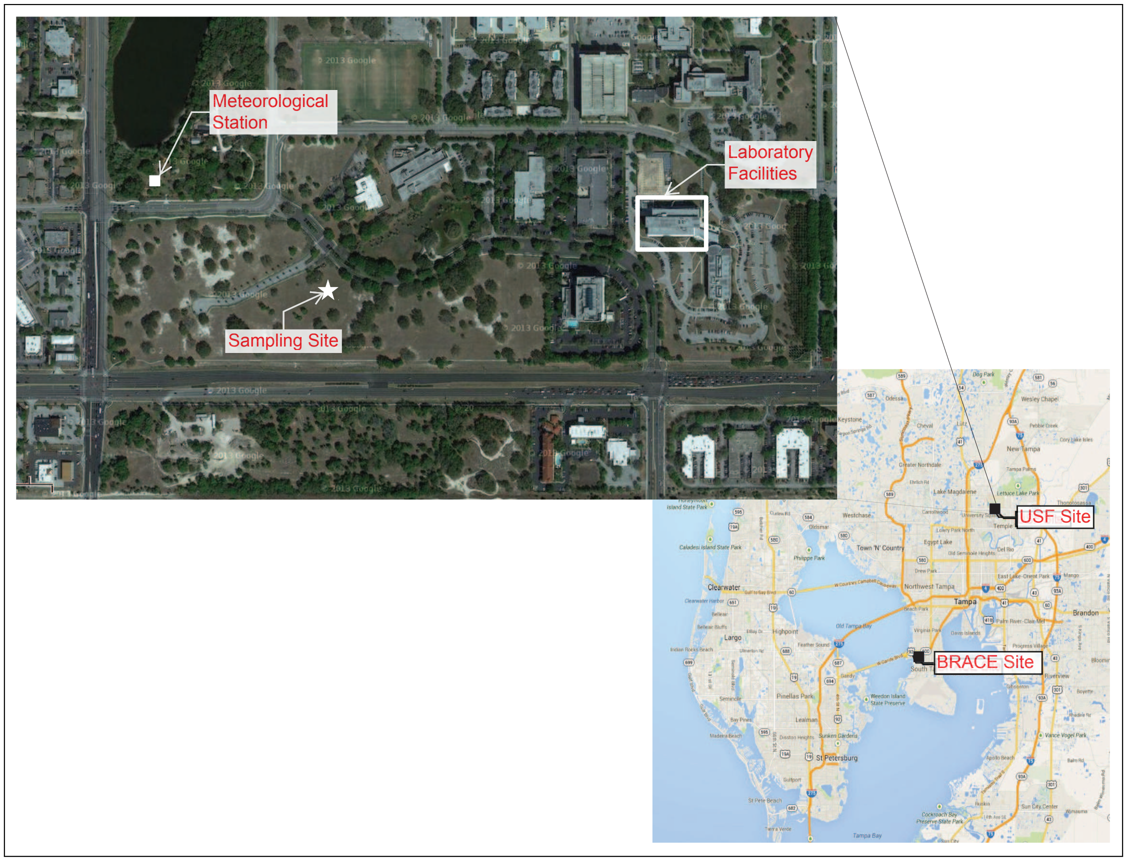


Figure 6.1. USF deposition sampling site map. The topographical map illustrates the locations of the sampling site, the meteorological station, and the laboratory facilities. The relative proximity of the 2001 BRACE and the 2012 USF study sites are also displayed.

after precipitation stops, the cover returns to seal the collector funnel and minimize exposure to dry deposition. The sampling train consists of a high density polyethylene (HDPE) funnel (average collection area 126 cm^2), and a 1L HDPE sample bottle. The stem of the funnel was molded to the cap of the sample bottle allowing for maintenance of sample integrity during sample collection. The sampler was mounted atop an 8ft NPS pipe set into the ground. Electrical power was supplied by a deep discharge marine battery that was recharged by a solar panel during daylight hours.

All field and analytical supplies were subjected to an eleven-day acid-cleaning procedure using the method described by Landis and Keeler [1997], originally developed by Rossmann and Barres [1992]. Supplies to be cleaned included standard laboratory glassware, HDPE sampling trains, Teflon® bottles for trace metal samples, and borosilicate glass bottles for

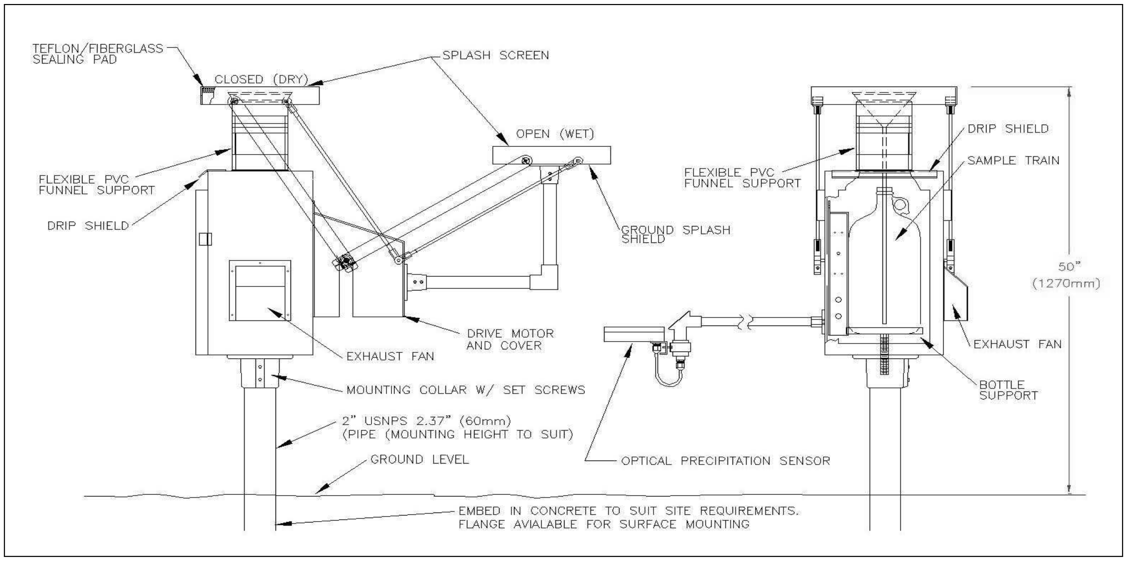


Figure 6.2. Schematic of wet deposition sampler showing opening mechanism, sensor and sampling train. Reprinted with permission from supplementary materials and manuals (Vendor, N-CON Systems Company, Inc).

mercury samples. Supplies to be acid cleaned were first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox®. Supplies were then rinsed with reagent water (18-MΩ minimum, ultrapure deionized water) and then heated in 3M hydrochloric acid (EM Science Tracepure® HCl in reagent water) for six hours at 80°C.

The supplies were then placed in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO_3 in Milli-Q water) for 3-5 hours at room temperature. At the end of the seven day acid soak inside the clean room, the supplies were rinsed five times with Milli-Q water and allowed to air dry on a clean surface in a clean room. The dried supplies were triple bagged in new polyethylene bags and stored in the clean room, until ready to be deployed in the field. The Teflon® precipitation sampling bottles were not allowed to dry. After the seven day $\mathrm{HNO_3}$ soak, the Teflon® bottles were rinsed three times with Milli-Q water and were filled with a 5% Bromine Monochloride (BrCl) solution and allowed to soak in the clean room until needed.

The sampler was checked once per day between 10:00am and 11:00am for the duration of the 24hr sampling period. If a precipitation event had occurred over the period, the sampling train was removed and a clean sampling train installed. The sample bottle was capped and triple bagged and transported to the laboratory in a covered HDPE bin. Sample date, time, and other environmental variables were recorded in a field logbook. Specific deposition event time period was determined from the USF Botanical gardens meteorological station located about 300 m from the sampling site (ID:KFLTAMPA78, [28.057, -82.425], Elevation:40ft). If no event had occurred for 3 consecutive sampling periods, an equipment blank was collected by rinsing the sampling train with reagent water (18-MΩ minimum, ultrapure deionized water), the sample bottle capped, triple bagged and transported to the laboratory.

Upon receipt at the laboratory, the event precipitation volume was determined gravimetrically. Precipitation depth was determined as the captured sample volume divided by the measured funnel area. Mercury deposition amounts were calculated as the measured concentration multiplied by the calculated precipitation depth. Aliquots were reserved and preserved separately for the determination of total mercury and trace metal concentrations. Trace metal samples were given priority for samples with low precipitation depth. This was due to the higher number of trace metal event samples required for high confidence in receptor modeling.

A 60 ml aliquot was reserved for determination of trace metal concentration. Trace metal samples were preserved in 5% HNO_3 and stored in pre-cleaned Teflon sample bottles at $4 \pm 2°C$. The maximum holding time for trace metals samples was 120 days from time of collection to analysis [USEPA, 2002].

Samples for determination of total mercury were placed in pre-cleaned borosilicate glass bottles with Teflon®-lined caps, and preserved with 5% $KBr/KBrO_3$. Samples were stored in a cleanroom at $\pm 2°C$. The maximum sample holding time for mercury was 60 days from the time of collection (BrCl preservation allows for a 90-day stability for determination of total mercury in deposition samples) [USEPA, 2002].

Integrity of sampling supplies was assessed by systematic sampling of bottle blanks and field blanks. Bottle blanks were collected one every three samples by filling a sample bottle with a 5% BrCl solution for 24 hr and assessing the total mercury content of the solution. Field blanks assessed the integrity of the sample container as it travels from the lab to the field, and as it resides in the sampler in the absence of an event. At the previously defined interval without a sample, a field blank is captured by rinsing the sampling train with ultrapure water, and retaining this sample for analysis of total mercury concentrations [USEPA, 2002].

6.2.3. Precipitation sample analysis

6.2.3.1. Total mercury analysis

Total mercury concentration was measured using EPA's Method 1631, Revision E (see Appendix D), for the determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). The method is applicable for the determination of Hg in the range of 0.5 – 100 $\mathrm{ng\,L^{-1}}$. A method detection limit (MDL; EPA 40 CFR 136, Appendix D) of 0.2 $\mathrm{ng\,L^{-1}}$, and a minimum level of quantitation (ML) of 0.5 $\mathrm{ng\,L^{-1}}$ has been established in the absence of interference. NIST Standard Reference Material 3133 was analyzed for quality control and instrument calibration. Figure 6.3 gives a schematic diagram of the CVAFS system. A summary of the method is presented here.

Prior to analysis, all Hg in a previously preserved 50-mL sample aliquot is oxidized to $\mathrm{Hg^{2+}}$ with BrCl. After oxidation the sample is sequentially reduced with $\mathrm{NH_2OH{\cdot}HCl}$ to destroy the free halogens, then reduced with stannous chloride ($\mathrm{SnCl_2}$) to convert $\mathrm{Hg^{2+}}$ to $\mathrm{Hg^{\circ}}$. The $\mathrm{Hg^{\circ}}$ is separated from solution by purging with ultra-high purity (UHP) argon gas. The $\mathrm{Hg^{\circ}}$ is collected onto an initial gold trap (sampling trap). The Hg is thermally desorbed from the first gold trap into an inert (UHP Argon) gas stream which carries the released $\mathrm{Hg^{\circ}}$ to a second gold (analytical) trap. The Hg is desorbed from the analytical trap into the inert gas stream that carries it into the cell of a cold vapor atomic fluorescence spectrometer (CVAFS) for detection.

Quality was assured through calibration and testing of the oxidation, purging, and detection systems. Specifically, analytical runs were validated by instrument, system, and reagent blanks, with a level less than the Practical Limit of Quantitation (PQL) used as

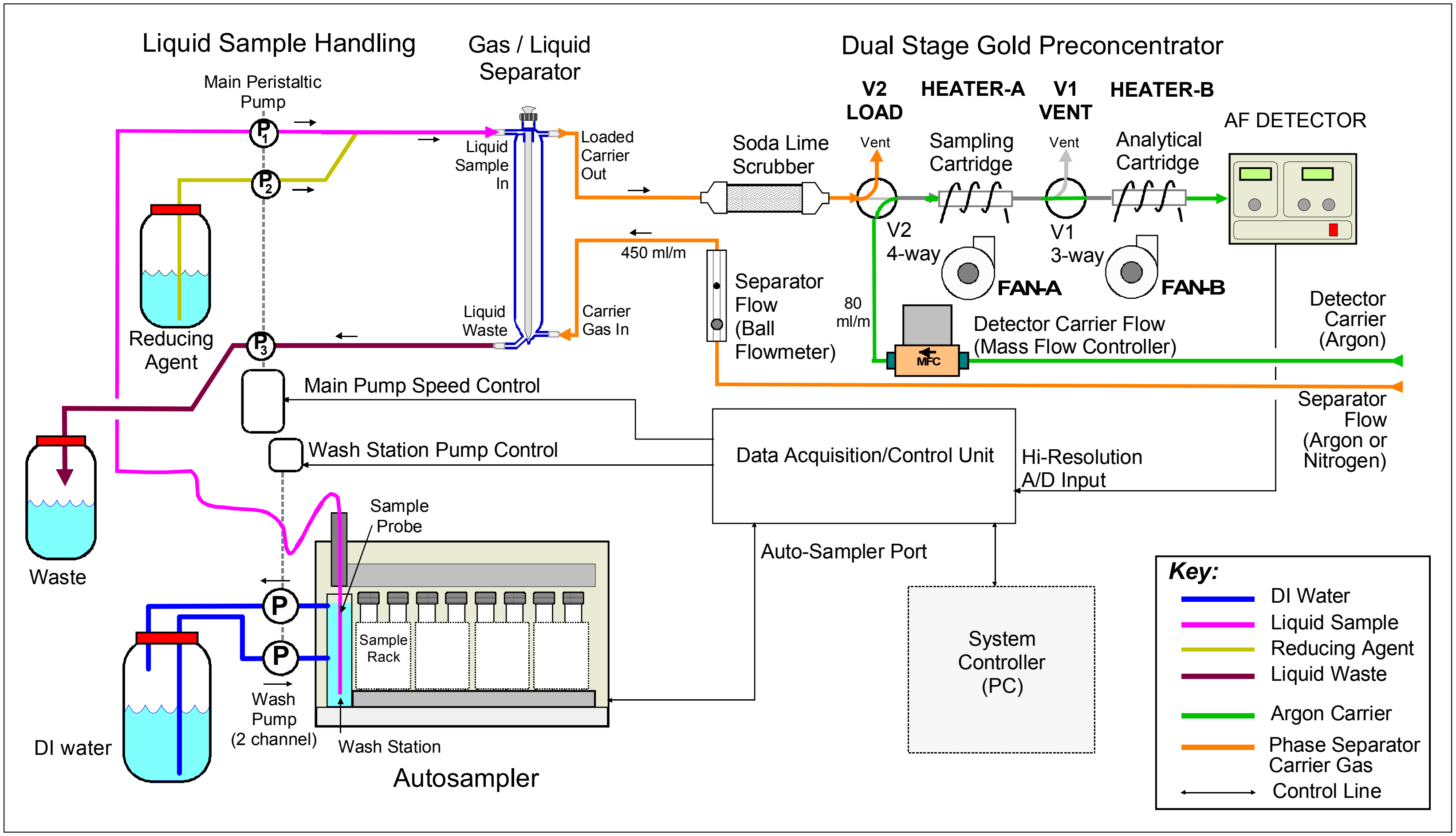


Figure 6.3. Schematic diagram for the Flow-Injection, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System.

the QA/QC standard. Initial and ongoing precision and recovery (IPR/OPR) and recovery duplicate samples were assessed at the 5 $\mathrm{ng\,L^{-1}}$ level (equal to the PQL) throughout the duration of an analytical run at an average of every 8 samples. IPR/OPR recoveries were accepted between the range of 79 - 120%, relative standard deviation (RSD) $\leq$ 21%, and relative percent difference (RPD) $\leq$ 24%. Method accuracy was assessed by sequential matrix spikes (MS) and matrix spike duplicates (MSD) at a level of 3 times the sample concentration. MS/MSD acceptance criteria was a percent recovery range of 71 - 125%, and a RPD of $\leq$24%.

The instrument was calibrated to range of 1.0 to 100$\mathrm{ng\,L^{-1}}$ using calibration points of 1.0, 5.0, 10, 20, 50, and 100 $\mathrm{ng\,L^{-1}}$. Instrument signal derived from mercury concentrations in calibration standards in the standards were used calculate a mean calibration factor given by the following:

$$CF_m = \frac{\sum \frac{(A_x - \bar{A}_{SB})}{C_x}}{N_{std}} \tag{6.2.1}$$

where CF_m is the mean calibration factor, A_x is the peak height or area for Hg in calibration standard x, $\bar{A}_{SB}$ is the mean peak height or area for Hg in calibration blanks (minimum = 5), C_x is the concentration of calibration standard x, and N_{std} is the total number of calibration standards used. The acceptance criteria for CF_m was RSD $\leq$ 15% or the recovery of the lowest standard within the range 75 - 125%.

Determination of mercury concentration in standards and sample was derived by dividing the blank-adjusted peak area for samples and standards by the calibration factor such that:

$$[Hg](\mathrm{ng\,L^{-1}}) = \frac{(A_s - \bar{A}_{SB})}{CF_m} \times \frac{V_{std}}{V_{sample}} \tag{6.2.2}$$

where A_s is the peak height or area for Hg in sample, $\bar{A}_{SB}$ is the mean peak height or area for Hg in system blanks (minimum = 3), CF_m is the mean calibration factor, V_{std} is the volume (mL) used for standards – volume (mL) reagent used in standards, and V_{sample} is the volume (mL) of sample – volume (mL) reagent used in sample.

6.2.3.2. Trace element analysis

To quantify the trace metals concentration in the deposition samples we applied EPA Method 200.8 [Brockhoff et al., 1999]. Trace metal samples were acidified with concentrated Trace Metal Grade (TMG) Nitric acid (HNO_3) to a 5% solution (V/V) in a Teflon®R 60 mL sample bottle. Sample were stored for a minimum of 30 days to provide adequate time for trace element desorption off particles, and the walls of the sample bottle. Samples were analyzed using a Perkin Elmer Elan II DRC quadrupole inductively coupled plasma mass spectrometer (ICP-MS).

The method describes the multi-element determination of trace elements by ICP-MS. In summary, sample material in solution is introduced by pneumatic nebulization into a radio-frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width, at 5% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier or Faraday detector and the ion information processed by a data handling system [Brockhoff et al., 1999].

Calibration curves were determined using multi-element High Purity®R trace element standards in 5% TMG HNO_3 that was matched to the sample composition. NIST Standard Reference Material 1640a was analyzed for quality control of the instrument calibration. All samples were analyzed in triplicate, and the resulting concentration was determined from the mean of the replicate analyses. MDLs for the trace elements analyzed in this study was assessed by the standard deviation of nine replicates of the instrument blank for each species. Selected samples (assigned randomly) were assessed in duplicate to estimate method precision. Analytical uncertainties were determined as the average relative standard deviation for each species, across all observations. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix was corrected for by the use of internal standards. Acceptance criteria for quality control metrics were followed as defined in EPA Method 200.8 [Brockhoff et al., 1999].

6.2.4. Back trajectory modeling

6.2.4.1. Background and model parameters

Back trajectory modeling background and development is described in the previous chapter. For this analysis I applied the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT, Version 4) model developed by the National Oceanic and Atmospheric Administration (NOAA) [Draxler and Hess, 1997, 1998]. HYSPLIT is hybrid between Eulerian and Lagrangian model approaches, in which advection and diffusion are made in a Langrangian framework, while concentrations are calculated on a fixed grid [see Draxler and Hess, 1998, for the description and development of this modeling approach]. HYSPLIT4 requires gridded meteorological data from weather prediction models or archived data, which it linearly interpolates to a terrain-following coordinate system. To drive the HYSPLIT model, meteorological data from the National Centers for Environmental Prediction (NCEP) model output were used. Specifically, the EDAS (Eta Data Assimilation model) data (with 80 km horizontal resolution, 23 vertical levels, and 3 hr temporal resolution) was used for time frames that coincided with event precipitation data.

6.2.4.2. Model application

Back trajectories were initiated from the hour that coincided with the hour of maximum precipitation throughout the duration of each event. Hourly precipitation data collected from the USF Botanical gardens meteorological station (ID:KFLTAMPA78, [28.057, -82.425], Elevation:40ft) were used to determine the highest precipitation hour. Back trajectories were initiated at three heights, 250, 500, and 1000 m, in order to span the vertical space through which precipitation may have fallen.

To investigate potential source influences on event mercury concentrations observed at the USF site, back trajectory modeling was performed to determine air mass trajectories corresponding to specific mercury wet deposition event days. Back-trajectory simulations were performed for all precipitation event days (30 events were recorded over the duration of this study). After back trajectory modeling of each precipitation event day, back trajectory characteristics for event days that had comparatively higher mercury concentrations in the deposited water were compared with those having lower mercury concentrations. Specifically, short-term (6 hr), intermediate term (24 hr), and long-term (72 hr) back trajectory locations and previous precipitation amounts (along the trajectory) were compared. By comparing these characteristics, potential source influences that led to comparatively high mercury concentrations were identified.

6.2.5. PMF analysis

6.2.5.1. Background

Receptor models allow the estimation of the contributions of different primary emission sources to the ambient concentrations of species collected at a receptor [Ogulei et al., 2005; Xie et al., 1999; Reff et al., 2007]. To apportion mercury deposited in Tampa to sources, I applied multivariate statistical receptor analysis on the BRACE deposition data, using the Positive Matrix Factorization (PMF) package, Version 3.0 [Norris et al., 2008]. PMF model background and development is described in the previous chapter.

6.2.5.2. Characterization of input data

Trace metal data measured at the USF site was used as input to derive potential source profiles with PMF. The data consisted of 23 trace metal species, collected over 30 event days. Chemical elements measured at the Tampa monitoring site for each event day were Li, P, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, Ba, La, Ce, Hg, Pb, Na, Mg, Al, K, Ca, Mn, and Fe. Estimated uncertainties for each data point included the sample collection uncertainty (SC, 10%), precipitation depth measurement uncertainty (PD, 5%), the element-specific analytical method detection limits (MDL), and analytical measurement precision uncertainties (AM). There were seven missing observation for mercury species due to inadequate collection volume

(08/06/2012, 08/14/2012, 08/17/2012/, 08/18/2012, 09/18/2012, 09/22/2012, 12/11/2012). These missing values were replaced by the arithmetic mean of the species concentration, and one half of the species detection limit was used to determine the uncertainty associated with these observations [see Paatero and Hopke, 2003, for a discussion of this approach]. Mo, Ag, and U were discarded from the final input data since greater than 60% of observations were less than their specific MDLs (see Table 6.3). For samples with species concentrations less than their respective MDLs, the observations were replaced with half of the species MDL. The sample sample-specific uncertainty matrix was used for model runs, determined by the method of Polissar et al. [2001]. The influence of the applied uncertainties on species concentrations was assessed by calculation of the species-specific signal-to-noise ratios [Paatero and Hopke, 2003].

6.2.5.3. Model application

To perform PMF analysis, the number of independent factors, *(p)*, influencing the variability in the deposited concentration profiles must be set *a priori*. Sensitivity analysis methods for factor selection were discussed in the previous chapter, and are applied here. Twenty random starting points with non-random seeds were used for our analyses, to ensure a reproducible global minimum solution was achieved. The results indicated that the optimum number of factors for resolving the uncertainty in the dataset occurred in the range of $7 \leq$ p ≤ 9. Subsequent simulations considered 7-, 8-, and 9-factor models runs. Residual analysis was employed to reduce factor selection uncertainty employing the method of Lee et al. [1999] as discussed previously.

We ultimately selected a p of 7 as it resulted in the minimum difference between the model-calculated value of Q and the number of degrees of freedom in the data set (the theoretical Q_{th}), and generated factors were resolved to sources with the least uncertainty.

Residual analysis was also performed to assess model fit. Examination of the distribution of the scaled residuals is useful to determine how well the model fit each species, where the scaled residuals are defined as $r_{ij} = e_{ij}/s_{ij}$, s_{ij} represents the uncertainties in collection, and e_{ij} is the residual. For a model with appropriate fit, the residuals, e_{ij}, and the error estimates,

s_{ij}, should be similar, and the scaled residual should fluctuate between ±3 [Paatero and Tapper, 1994; Norris et al., 2008; Chueinta et al., 2000]. Species with many large scaled residuals, or non-normal residual distributions may indicate poor model fit. Species with coefficients of determination below 0.9 included *Pb* (0.84), *Cu* (0.81), *Ni* (0.74), *Ba* (0.69), *K* (0.57), *Li* (0.51), *As* (0.48), *Se* (0.26), and *Cd* (0.05). Examination of observed/predicted (O/P) scatter plots for some poorly modeled species indicated that extreme observations were accounting for the low r^2 values. For example, *Cd* (0.05) species had an observation that was greater than ten times the value of the species mean. The model was recalculated with events corresponding to extreme species concentrations omitted from the analysis (an extreme event at 9/18/2012). The recalculated coefficient of determination increased from 0.05 to 0.73 reflecting an improved model fit. Consequently, sensitivity analysis was conducted on extreme observations to characterize their effect on model fit.

To assess sources of uncertainty and characterize variability in model solutions bootstrapping was performed on the selected base solution. Uncertainty analyses consisted of 100 runs of the bootstrapped factor, with a minimum correlation coefficient of 0.6, and a block size of 2. A 95% confidence cutoff was applied to determine significance of each contribution. (Contributions were considered significant if the fifth percentile of the distribution was greater than 0).

Rotational ambiguity in model solutions was assessed by use of the FPEAK parameter in PMF. Positive and negative values of the FPEAK parameter (from -0.5 to 0.5 in 0.1 increments) were examined for their effect on the Q values, G-space plots, factor contributions, and factor profiles of the base model solution [see Paatero, 1997; Paatero et al., 2002, for a discussion of this approach]. A value of 0.1 was chosen to generate model predictions as it helped to resolve some of the slight interdependence of factors observed, and was found to resolve some of the dominant species for each factor without increasing non-dominant ones.

6.2.5.4. Analysis of source influences on species concentration

Initial explorations of relative contributions of biogenic and anthropogenic emission sources on species concentrations was achieved by calculating crustal Enrichment Factors (cEF) for each species. Enrichment factors are a means of identifying and quantifying anthropogenic influences on global element cycles by normalizing observed element concentrations to that of a "conservative" naturally occurring element [Zoller et al., 1974; Duce et al., 1975]. Enrichment factors were estimated using the generalized formula from Chester and Stoner [1973]:

$$cEF = \frac{\left(\frac{[X]}{[A]}\right)_{sample}}{\left(\frac{[X]}{[A]}\right)_{crust}} \tag{6.2.3}$$

where [X] and [A] refer to the concentration respectively of a given element X, and of the reference element A. For cEF > 1, X is considered enriched in the atmosphere relative to its concentration in the earth's crust, and for cEF ≈ 1, the source in not enriched in the atmosphere, implying minimal anthropogenic contributions to species concentrations [Galloway et al., 1982]. Using Al as the reference element, calculations were based on the average upper crust elemental compositions published by McLennan [2001]. Aluminium is considered a good reference element to normalize metal concentrations due to its crustal abundance, and the relatively constant metal to aluminum crustal ratios [Turekian and Wedepohl, 1961; Taylor, 1964]. Additionally, studies have suggested that aluminum concentrations are not likely to be significantly affected by anthropogenic aluminum sources [Windom et al., 1989; Schropp et al., 1990]. We account for the inherent uncertainties associated with the choice of reference element, and composition of reference soil by considering larger differences in calculated cEF than those standardized in the literature [Galloway et al., 1982; Chester and Stoner, 1974; Duce et al., 1975].

Likely contributions of specific emission source categories to observed species concentrations were explored by examining statistical correlations between species pairs. A good correlation between species indicates a similar source or source type [Norris et al., 2008]. Associations between species were explored by calculating Pearson correlation coefficients.

Several authors have attempted to relate elemental concentration ratios of trace species in deposition samples to specific emission sources [Dvonch et al., 1998, 1999; Gratz, 2010;

Alleman et al., 2010; Olmez et al., 1998; Polissar et al., 2001]. For example, Hg/Pb ratios from stack measurements preformed in South Florida were used to define the signatures for medical (Hg/Pb = 8.08) and municipal (Hg/Pb = 0.06 ±0.02) waste incineration [Dvonch et al., 1999; Gratz, 2010]. Published species ratios were compared to those calculated for the BRACE data to deduce likely source contributions.

Once factor profiles were predicted with PMF, these profiles were compared to available information on dominant species, and species ratios emitted from particular industries and activities to match factors with source categories occurring in the domain. This is an iterative process of examining statistical correlations between species concentrations, analysis of the profiles and species contributions of predicted factors, confidence of generated factors as assessed by bootstrapping, and comparison of elemental ratios with published literature.

6.3. Results and discussion

6.3.1. Hg concentration and deposition

The sampling campaign yielded 23 precipitation event samples over the period July 2012 - December 2012 (30 total samples, but 7 samples were of insufficient volume for determination of total mercury concentration.). Precipitation depth ranged from 0.7 - 6.6 cm. High precipitation depth events coincided with usual precipitation trends for the region, occurring over the initial two months (summer) of the campaign before tapering off for the fall/winter period.

The Method Detection Limit (MDL) for total mercury in this study was 1.8 $\mathrm{ng\,L^{-1}}$ (using EPA method 1631, revision E). A minimum quantitation limit (MQL) of 5.0 $\mathrm{ng\,L^{-1}}$ was established for reporting Hg concentrations in this study. This was determined as the lowest calibration standard with recovery within the range of 75 - 125%, and relative standard deviation (RSD) $\leq$15%. The analytical precision of replicate Hg analysis was 6.2 ± 1.6% (n = 8). Bottle blank determinations resulted in a mean value of 0.5 ± 0.4 $\mathrm{ng\,L^{-1}}$ (n = 11), and was reported as below detection limit. Field blanks were shown to contain mercury concentrations below the MQL ($\leq$5 $\mathrm{ng\,L^{-1}}$, n = 26). Duplicate sample pairs give

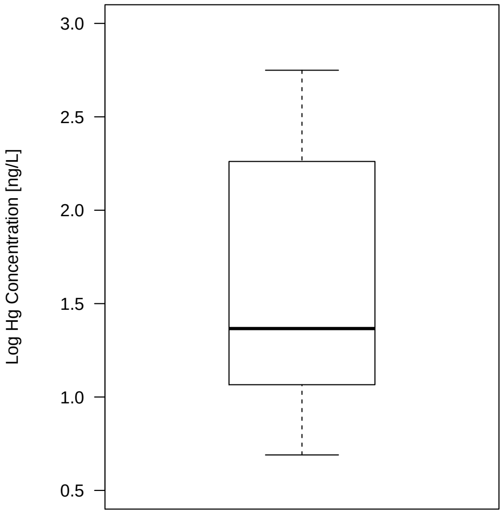


Figure 6.4. Variability in event mercury concentration as observed in 2012 USF deposition data. The boxplot shows the variability in event mercury concentration observed at the USF site from July 2012 to December 2012. The upper and lower whiskers represent the locations of the maximum and minimum and maximum event concentrations respectively. The box spans the interquartile range, and the segment depicts the location of the median.

an absolute mean difference of 6.2% ± 1.6%. Recoveries of quality control samples (NIST SRM 3133) showed an absolute mean of 109.4 ± 6.2% (n = 12, level = 5 ng L^{-1}. Matrix spike recoveries showed a mean recovery of 96.4% (RSD = 10%, n = 8), with a mean relative percent difference between matrix spike duplicates of 9.4 ± 8.3%.

Figure 6.4 show the variability in mercury concentration measured during this study. Mercury concentration ranged from 5 - 562 ng L^{-1}, with a median concentration of 23 ng L^{-1}. Figure 6.5 shows the variability in precipitation depth and event mercury concentration. Several high mercury concentration events were observed over the period. Higher mercury concentration events occurred over the period 07/22/2012 to 08/13/2012. Event mercury concentration did not correspond with precipitation depth. This relationship was further explored by a regression between event precipitation depth and event mercury concentrations to explore the effect of concentration dilution during precipitation events. As shown by Figure 6.6, event precipitation depth explained less than 1% of the variation observed in event mercury concentration. This result correlates with the relationship observed between event precipitation depth and mercury concentration in the BRACE data analysis

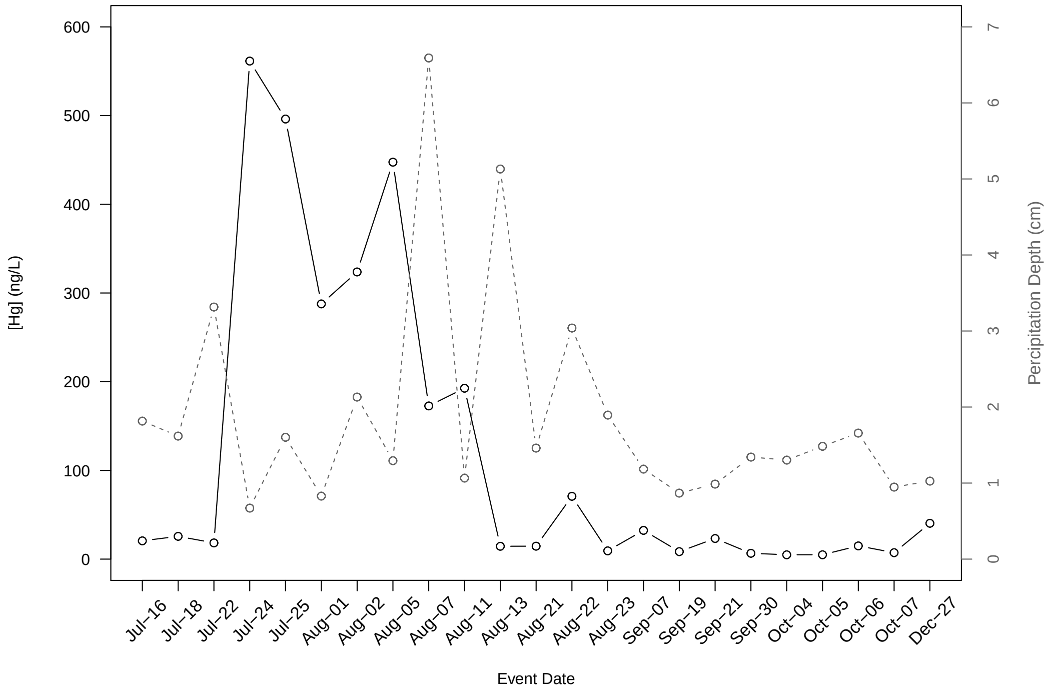


Figure 6.5. Variability in event precipitation depth and event mercury concentration in 2012 USF deposition data. The plot shows temporal variability in event precipitation depth (solid lines, left axis), and event mercury concentration (dashed line, right axis) observed at the USF site from July 2012 to December 2012.

discussed previously (see Figure 6.4). The extremely weak relationship observed suggests that the dilution of mercury concentrations during high volume precipitation events, or the enhancement of mercury concentrations during smaller (volume) precipitation events cannot account for the large observed ranges in event mercury concentration. Factors that may be contributing to the large range of event mercury concentrations observed include atmospheric transport, chemical cycling, and/or contributions from nearby mercury emitting sources [Gratz et al., 2013; White et al., 2009; Dvonch et al., 1999].

Figure 6.7 shows the temporal variability in event mercury deposition and precipitation depth over the period. Similar to the relationship observed with event concentration, event mercury deposition did not correlate well with precipitation depth. We observe high deposition events occurring with both low and high precipitation depth events. Event deposition ranged from 0.1 - 11.4 $\mu g\,m^{-2}$, with a median of 0.4 $\mu g\,m^{-2}$. Event mercury deposition observed in this study was compared with event deposition observed at the National Atmospheric

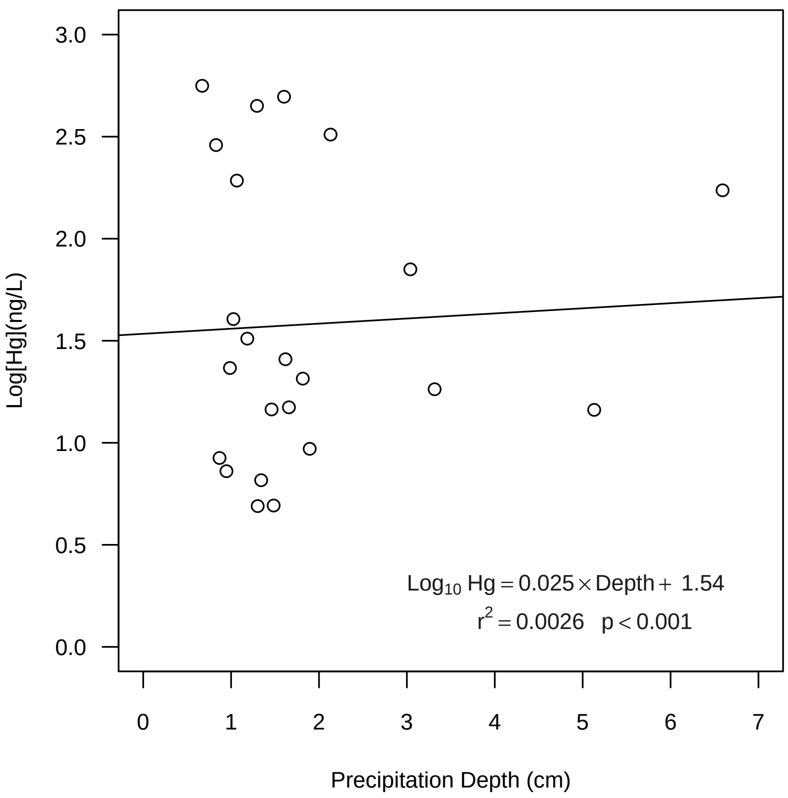


Figure 6.6. Regression of event mercury concentration versus event precipitation depth observed in 2012 USF deposition data.

Table 6.1. Comparison of event precipitation, concentration, and deposition between the USF site and NADP/MDN FL05 site.

	USF	FL05
Total event samples (N)	23	17
Total precipitation depth (cm)	43.3	58.3
Volume-weighted mean concentration (ng L^{-1})	107.6	13.6
Concentration Range (ng L^{-1})	4.9 - 561.5	2.6 - 28.4
Total Deposition (µg m^{-2})	46.6	7.9
Mean event deposition (µg m^{-2})	2	0.5
Maximum event deposition (µg m^{-2})	11.38	2

Deposition Program, Mercury Deposition Network MDN Chassahowitzka Site (NADP/MDN FL05), and is shown in Table 6.1. The NADP/MDN site in located 58 miles north of the USF site in Citrus County (28.7486, -82.5551). FL05 observed 15 cm greater total precipitation depth over the 6-month period. However, large differences were observed in the volume weighted mean mercury concentration (VWM), and total and mean mercury deposition, with

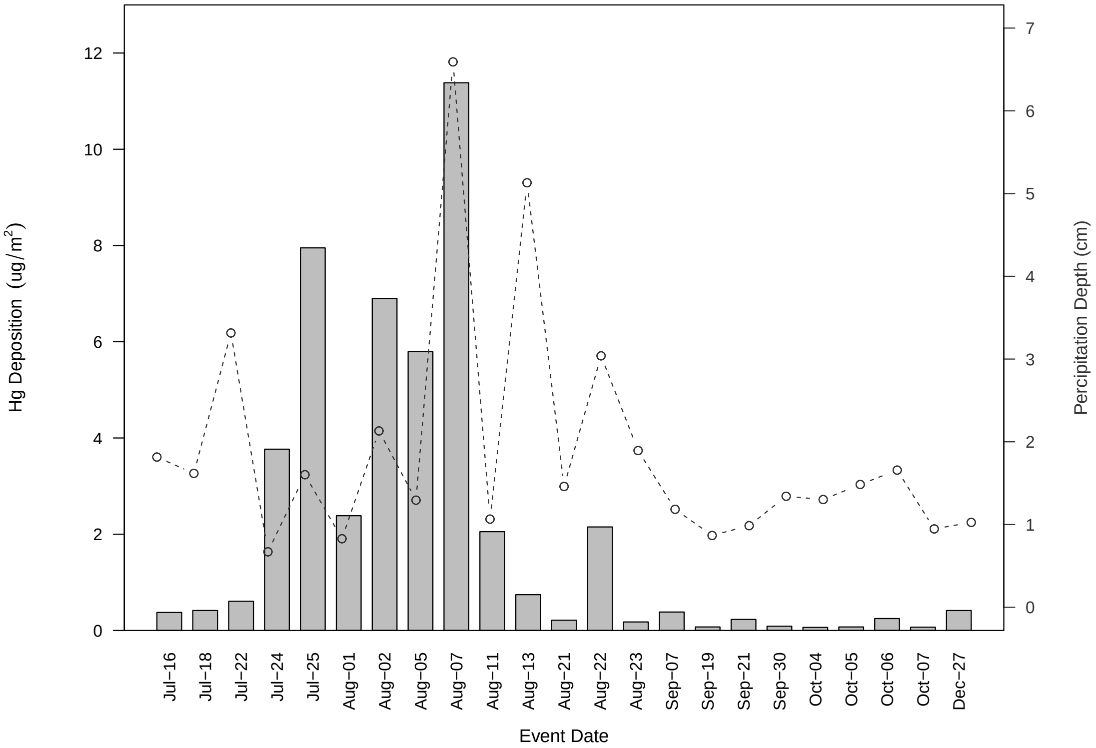


Figure 6.7. Comparison of temporal variation of event deposition and event precipitation depth in 2012 USF deposition data. The plot shows temporal variation of event deposition (solid bars, right axis) and event precipitation depth observed at the USF site.

substantially greater values observed at the USF site. This difference can be attributed to contributions from multiple high concentration events observed at the USF site, contributing to the elevation of the average event concentration and deposition. These differences observed in volume weighted mean concentration and event deposition between the receptors suggests substantial contributions from source(s) that may be local for the USF receptor.

6.3.2. Event back trajectories

The occurrence of events with relatively high or low mercury concentrations for similar precipitation levels suggests the potential importance of local emissions sources or other air mass influences on local mercury deposition. To better understand these influences, the data was grouped into quintiles by event mercury concentration, and sorted from highest to lowest. Back-trajectories were then examined for events within the groups with air mass originating over Florida at least in the short or intermediate term, and with previous precipitation occurring over the trajectory in the intermediate to long term. The occurrence of high or intermediate precipitation events over the trajectory suggests an increased likelihood of the washing out of soluble mercury species associated with the air mass prior to arrival at the USF receptor in the long or intermediate term [Slemr et al., 1985; Guentzel et al., 1995]. Therefore, for these events, mercury species observed at the receptor is assumed to be a result of local emission sources influencing the tracked air mass, and allows us to elucidate the significance of these sources to local wet deposition phenomenon. Table 6.2 gives the back-trajectories associated with each deposition event, and describes the mean direction of trajectory origin, and the level of precipitation. We discuss the trends in these concentration quintiles next.

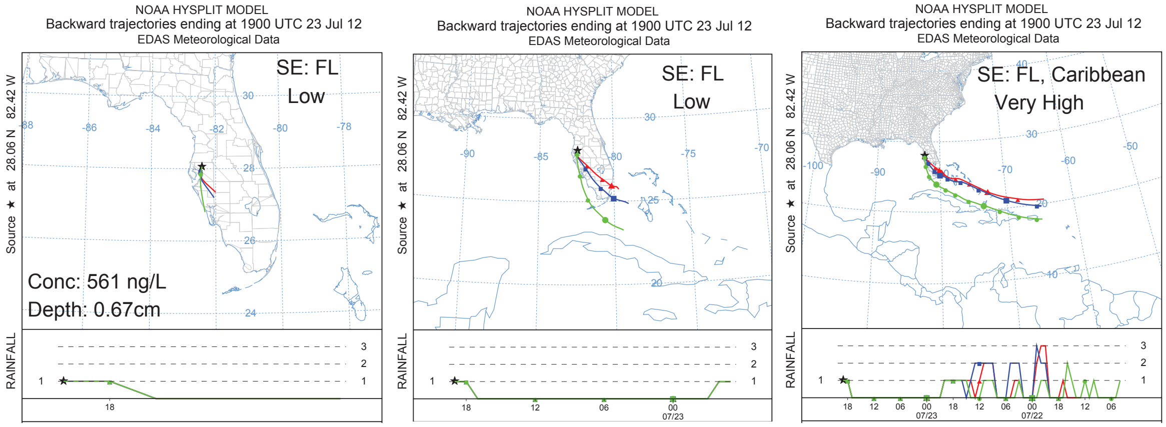
Back-trajectory simulation results for the highest concentration quintile (Group 5) are shown in Table 6.2. Event precipitation depth in this group ranged from 0.83 - 2.13 cm, and event mercury concentration ranged from 561 - 193 $\mathrm{ng\,L^{-1}}$. Figure 6.8 [(a) - (f)] shows the back-trajectory result for the two highest mercury concentration events in the quintile. The highest concentration events in this quintile had their trajectory originating over Florida land in the short- and intermediate-term. Short-term back-trajectories (6hr) showed air mass impacting the receptor predominantly from the south and southeast, and lingering over Florida land. More importantly, we observe intermediate to very high precipitation levels over the path of the trajectory in the long-term (3 day) trajectories, suggesting that mercury mass observed at the receptor may have origins over Florida land. Long term trajectories in this group did not display any trend in the origins of air masses, varying from the Gulf of Mexico to the North Atlantic. Considering the high event mercury concentration observed and the high occurrence of trajectories that originated over Florida land, it's likely that sources in the Tampa Bay county, or nearby counties may be contributing substantially to the mercury mass observed.

The 4th quintile had the highest precipitation depth event of 6.59 cm. Event mercury concentration corresponding to this depth was 173 $\mathrm{ng\,L^{-1}}$ and highlights the lack of dilution effect at play, which would suggest a finite, or easily washed mercury pool contributing to

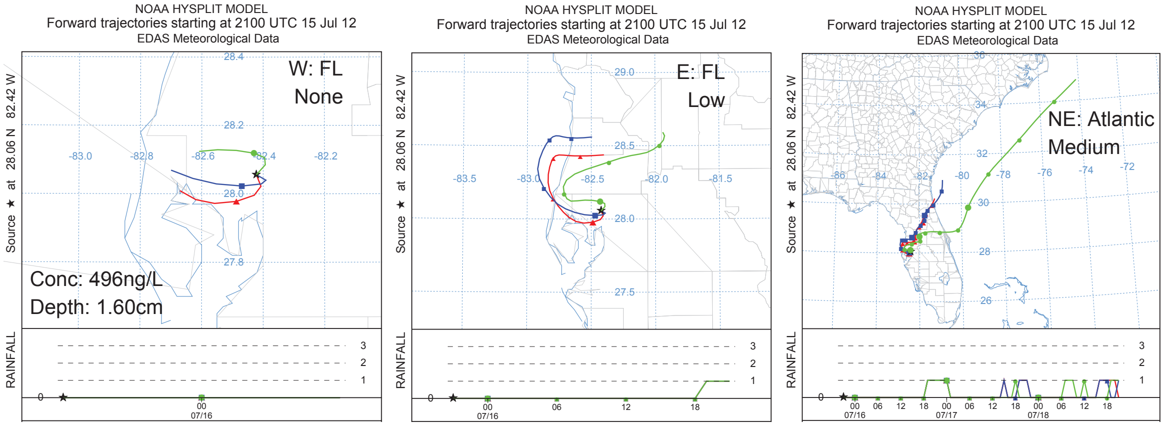
Table 6.2. Characteristics of event back trajectories for the 2012 USF deposition data. Events are grouped by quintiles of mercury concentration level.

Grp	Date	Depth	Hg Level	Trajectory Location (Amount of Precipitation)[a]		
		(cm)	($\mathrm{ng\,L^{-1}}$)	0 – 6 hr	6 – 24 hr	24 – 72 hr
5	24.Jul.2012	0.67	561.46	SE: Fl (L)	SE: Fl(L)	SE: Fl,Caribbean (VH)
	16.Jul.2012	1.60	496.15	W: Fl (N)	E: Fl (L)	NE: Atlantic (I)
	5.Aug.2012	1.29	447.51	N: Fl (N)	E: Fl (N)	W,S: Gulf/Atlantic(I)
	6.Oct.2012	2.13	323.74	W: Gulf (I)	W: Gulf (H)	NW: US (VH)
	1.Aug.2012	0.83	287.7	W: Gulf (N)	W,SW: Gulf (VL)	W:Gulf (I)
	7.Oct.2012	1.07	192.65	SW: Fl Gulf (N)	S: Fl (N)	SE: Bahamas (N)
4	22.Aug.2012	6.59	172.67	S: Fl (N)	SE: Bahamas (N)	E: Caribbean (N)
	22.Jun.2012	3.04	70.78	SW: Gulf (N)	S: Gulf (N)	S: Caribbean (L)
	21.Sept.2012	1.03	40.38	NW: Gulf Coast (N)	NW: Gulf Coast (N)	N,W: Gulf Coast (VH)
	27.Dec.2012	1.18	32.40	S: Gulf (N)	S: Gulf (L)	S: Caribbean (L)
	18.Jul.2012	1.62	25.67	SW: Fl Gulf (N)	SW: Gulf (L)	S: Cuba (L)
	19.Sept.2012	0.99	23.25	W: Gulf (I)	W: Gulf (L)	W:Gulf,(M)
3	2.Aug.2012	1.82	20.63	E: Fl (N)	W : Fl (L)	NW: Fl,Atlantic (L)
	7.Aug.2012	3.32	18.30	S: Fl (N)	SW: Fl (N)	SE: Caribbean (N)
	25.Jul.2012	1.66	14.92	NE: Fl (L)	E: Atlantic (I)	SE: Atlantic (L)
	4.Oct.2012	1.46	14.57	SW: Gulf (L)	SW: Gulf (L)	SE: Caribbean (L)
	13.Aug.2012	5.13	14.50	W: Gulf (N)	S: Gulf (N)	SE: Caribbean (L)
	23.Aug.2012	1.89	9.34	W: Gulf (N)	SW:Gulf (L)	S: Caribbean (L)
2	11.Aug.2012	0.87	8.43	SW: Gulf (I)	SW: Gulf (L)	S: Caribbean,(L)
	7.Sept.2012	0.95	7.26	NE: Fl (L)	E: Fl (I)	SE: Atlantic (VH)
	30.Sept.2012	1.34	6.56	N,NE: Fl (N)	NE: Fl (N)	E: Atlantic (VL)
	5.Oct.2012	1.48	4.93	SE: Fl (I)	SE: Bahamas (H)	SE: Atlantic (I)
	21.Aug.2012	1.30	4.90	S,SW: Gulf (L)	S: Cuba (L)	S: Caribbean (H)
	18.Sept.2012	0.36	-	SE: Fl (N)	E: Atlantic (I)	NE: Atlantic (L)
1	14.Aug.2012	0.47	-	S,W: Gulf (N)	S,W Gulf (L)	S: Cuba Fl (L)
	17.Aug.2012	0.47	-	NW: Gulf (N)	SW: Gulf (N)	S: Gulf (N)
	18.Aug.2012	0.47	-	SW: Gulf (L)	SW: Gulf (L)	SE: Cuba,Carib (L)
	22.Sept.2012	0.47	-	N: Fl (N)	SW: Gulf (I)	W,SW: Gulf (L)
	11.Dec.2012	0.47	-	S: Gulf (N)	S: Cuba (N)	SE: Atlantic (L)
	6.Aug.2012	0.50	-	S: Fl (N)	S: Fl (L)	SE: Caribbean (VH)

[a] The directional location of the trajectory relative to the USF sampling site is given first, with the qualitative level of precipitation along the trajectory indicated in parentheses. For location, standard compass direction and state acronyms are used. For previous precipitation, N, VL, L, I, H, and VH signify the following, respectively: none, very low, low, intermediate, high, and very high. Grp = concentration group bins, Depth = precipitation depth. [c] Lingering over the Tampa Bay area.

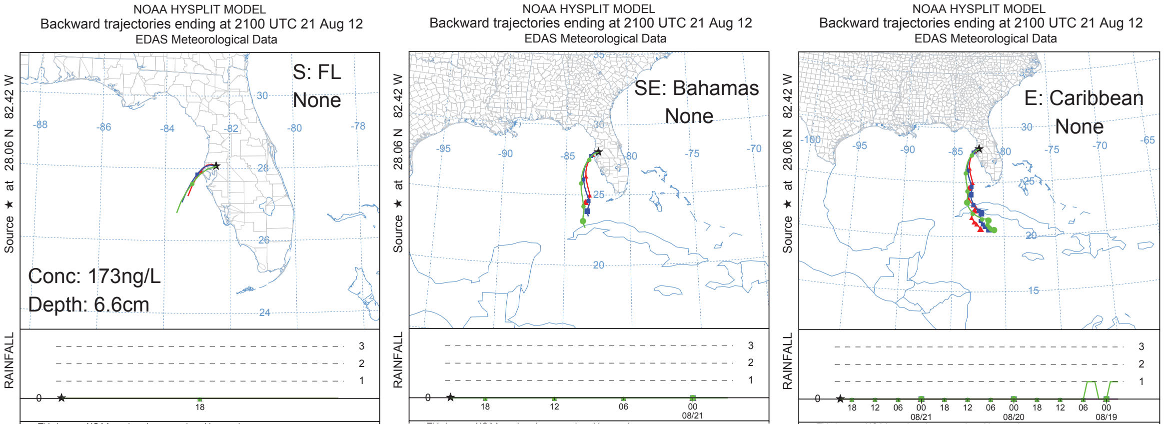


(a) 6 hour trajectory **(b)** 24 hour trajectory **(c)** 3 day trajectory

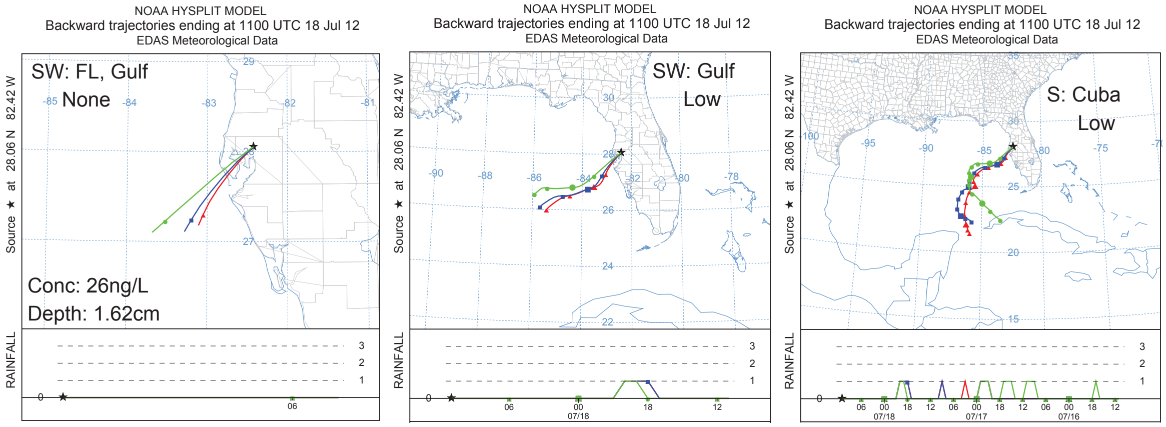


(d) 6 hour trajectory **(e)** 24 hour trajectory **(f)** 3 day trajectory

Figure 6.8. Back trajectories for the highest concentration quintile, Group 5. The plot shows trajectories for selected events in the group for which the air mass originated over Florida land, and with high or intermediate precipitation occurring along the path in the long or intermediate term. Event mercury concentration and precipitation depth is given in the first subplot for each group. For location, standard compass direction and state acronyms are used. Precipitation along the trajectory is classified as none, very low, low, intermediate, high, and very high. The red, blue, and green lines provide trajectories initiated at 250m, 500m, and 1000m heights above ground level, respectively.



(a) 6 hour trajectory **(b)** 24 hour trajectory **(c)** 3 day trajectory



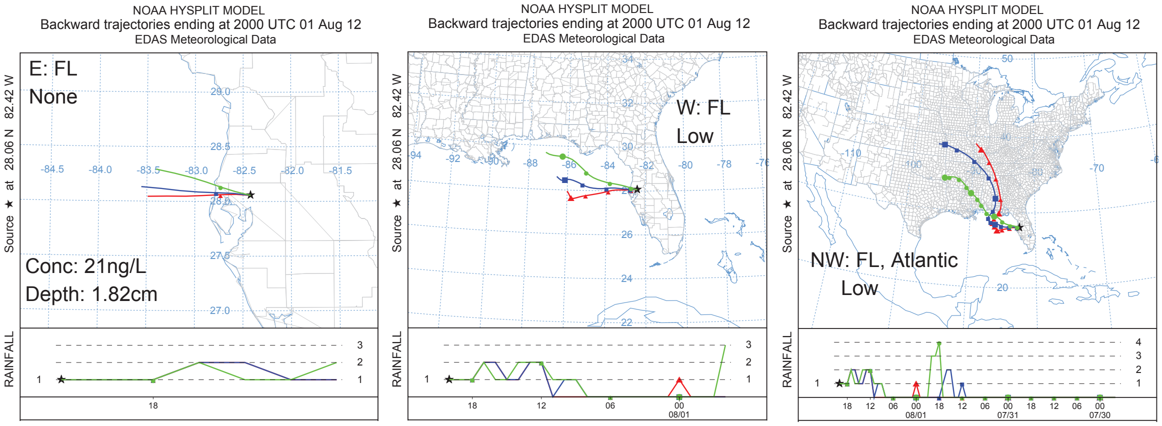
(d) 6 hour trajectory **(e)** 24 hour trajectory **(f)** 3 day trajectory

Figure 6.9. Back trajectories for the second highest concentration quintile, Group 4. The plot shows trajectories for selected events in the group for which the air mass originated over Florida land, and with high or intermediate precipitation occurring along the path in the long or intermediate term. Event mercury concentration and precipitation depth is given in the first subplot for each group. For location, standard compass direction and state acronyms are used. Precipitation along the trajectory is classified as none, very low, low, intermediate, high, and very high. The red, blue, and green lines provide trajectories initiated at 250m, 500m, and 1000m heights above ground level, respectively.

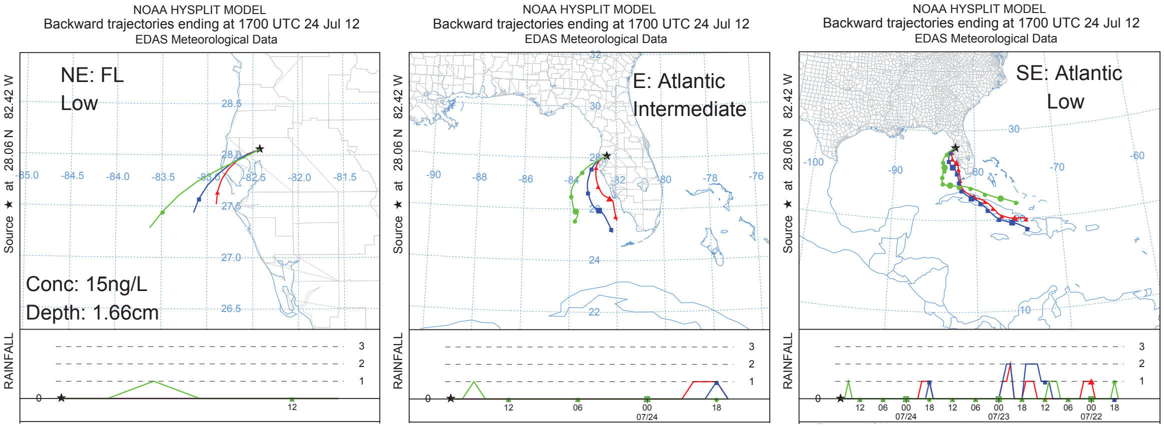
mercury deposition observed. Event mercury concentration within the quintile ranged from 23.4 - 172.7 ng L^{-1}, while event precipitation depth ranged from 1 cm - 6.59cm (Table 6.2, Group 4). The highest mercury concentration event of this quintile had back-trajectories that originated over Florida land in the short-term Figure 6.9 [(a) - (c)]. No previous precipitation was observed along the path of this trajectory. Figure 6.9 [(d) - (f)] shows the other event in this quintile that traversed over Florida land. Here we observe some previous precipitation, albeit at low levels. Overall, we observe trajectories originating predominantly from the south and southwest over the Gulf of Mexico and the Caribbean.

Event mercury concentration and precipitation depth for the third quintile ranged from 9 - 21 ng L^{-1} and 1.46 - 5.13 cm, respectively. The top 3 event mercury concentration values in this group had trajectories that traversed over Florida land in the short- and intermediate-term. For these events, two had long term trajectories with rainfall occurring over their path, albeit at low levels, shown in Figure 6.10 [(a) - (c)]. Trajectories for this group originated predominantly from the south and southwest in the short-term, traveling over the Tampa Bay area. Long term trajectories demonstrated some variation in origins, varying between the Atlantic and the Caribbean. Overall, rainfall along the trajectory pathway was low.

The second quintile consisted of events with precipitation depths and mercury concentrations ranging from 1.46 - 5.13 cm and 5 – 8 ng L^{-1}, respectively. Here, we also observe the underlying trend of high mercury concentration events have trajectories in the short- and intermediate-term that traversed over Florida land. All events that traveled over Florida land had previous precipitation events occurring along the trajectory in the long term, with depths ranging from low to very high. Figure 6.11 [(a) - (c)] gives the trajectories of 2 events with high mercury concentrations within the group, trajectories that traversed primarily over Florida land, and relatively high precipitation depth events occurring over the path of the trajectory in the long term. Overall, trajectories originated from over the Gulf of Mexico or Florida land in the short and intermediate terms, and originated over the Caribbean or the Atlantic in the long term.

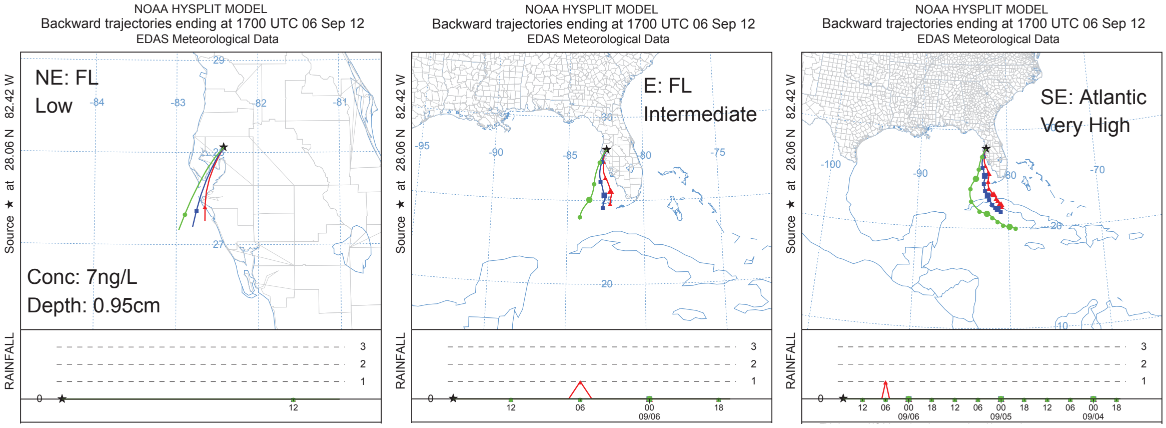


(a) 6 hour trajectory (b) 24 hour trajectory (c) 3 day trajectory

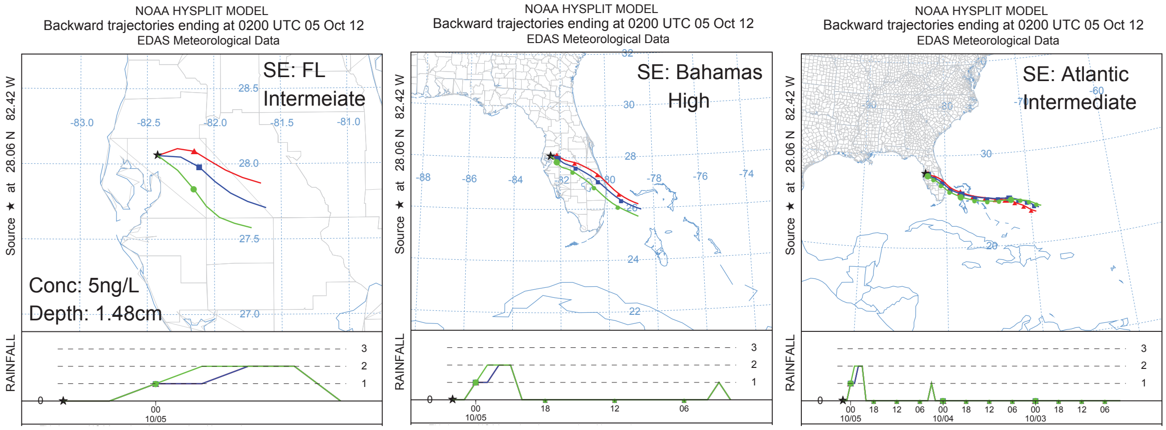


(d) 6 hour trajectory (e) 24 hour trajectory (f) 3 day trajectory

Figure 6.10. Back trajectories for the third concentration quintile, Group 3. The plot shows trajectories for selected events in the group for which the air mass originated over Florida land, and with high or intermediate precipitation occurring along the path in the long or intermediate term. Event mercury concentration and precipitation depth is given in the first subplot for each group. For location, standard compass direction and state acronyms are used. Precipitation along the trajectory is classified as none, very low, low, intermediate, high, and very high. The red, blue, and green lines provide trajectories initiated at 250m, 500m, and 1000m heights above ground level, respectively.



(a) 6 hour trajectory **(b)** 24 hour trajectory **(c)** 3 day trajectory



(d) 6 hour trajectory **(e)** 24 hour trajectory **(f)** 3 day trajectory

Figure 6.11. Back trajectories for the second concentration quintile, Group 2. The plot shows trajectories for selected events in the group for which the air mass originated over Florida land, and with high or intermediate precipitation occurring along the path in the long or intermediate term. Event mercury concentration and precipitation depth is given in the first subplot for each group. For location, standard compass direction and state acronyms are used. Precipitation along the trajectory is classified as none, very low, low, intermediate, high, and very high. The red, blue, and green lines provide trajectories initiated at 250m, 500m, and 1000m heights above ground level, respectively.

In summary, we see that high mercury concentration events of each group had trajectories that originated predominantly over Florida land in the 6 hr and 24 hr prior to the precipitation event at the receptor. Long term trajectories for high mercury concentration events showed some variation, originating over the Atlantic, Caribbean Sea, and the Gulf of Mexico. Low mercury concentration events had a strong trend of trajectories originating over the Gulf of Mexico in the short-term. Some variations were observed in the intermediate term. The longer-term trajectories showed fewer variations, with origins occurring over the Caribbean and Atlantic. Overall, the trajectories suggests that the air mass reaching the receptor during these high mercury concentration events may be influenced by emission sources local to Florida and the receptor. This result agrees with findings from previous analysis of data from the region (see Chapter 5).

We observed the occurrence of high or intermediate precipitation depth events over the trajectory pathways for events with high mercury concentrations. This also agrees with observation from the BRACE data analysis where we found that both the trajectory location and the amount of previous precipitation appear to be important to mercury concentration in the collected sample. This suggests an increased likelihood of mercury mass impacting the receptor, originating over Florida land, and/or localized to the receptor.

6.3.3. Trace metals concentration

The sampling campaign yielded 30 precipitation samples for trace metals assay. Analysis of bottle blanks, field blanks, and funnel rinses were shown to contain trace metal concentrations below the MDLs. Duplicate sample pairs give an absolute mean difference of 9.4 ± 2.7%.. Recoveries of quality control samples (NIST-1640a) returned an absolute mean recovery of 111.6 ±2.5%. Table 6.3 reports the trace element MDLs, and the average analytical uncertainties for each element.

Summary statistics for the trace metals deposition data collected that the site is plotted in Figure 6.12. Average species concentrations ranged from a high of $1.7 \times 10^6\ \mathrm{ng\,L^{-1}}$ (Na) to a low of $1.1 \times 10^1\ \mathrm{ng\,L^{-1}}$ (La). Mean species concentrations are comparable to measurements performed within the region during a shorter campaign with fewer elements [Graney et al., 2004], and the BRACE data (previous chapter), although lower mean concentrations were observed in this study. Comparison of mean species concentrations between this study and the BRACE data showed that the 2001 BRACE data was generally higher, with the exception of mercury, which is higher in the 2012 USF deposition data. Species signal-to-noise (S/N) ratios, shown in Table 6.4, varied from 7.9 to 0.2. The S/N ratio for Se (0.2) and As (0.5) were below the limit considered acceptable for factor identification [Norris et al., 2008]. Arsenic was flagged as a weak species , which tripled the uncertainties associated with the species for model prediction, and Selenium was discarded from the final dataset used for model prediction.

Mean crustal Enrichment Factors (cEF) are reported in Table 6.4. Elements with cEF ≤ 5, considered indicative of biogenic influences, included Ba, Ce, Co, Cs, Fe, K, La, Mn, and Sr species. Elements with intermediate enrichment ($5 \leq$ cEF ≤ 100), assumed indicative of anthropogenic sources included As, Ca, Li, Mg, Na, Ni, Pb, and Se. Elements with cEF ≥ 100, highly enriched and likely influenced by anthropogenic emissions, included Cd, Sb, P, Cu and Zn, in decreasing order of value of cEF. Results for enriched species show good agreement with published data for the enrichment of metals by anthropogenic emissions in the United States, which have been found to follow a relative order of Se > Pb > Sb > Cd > Cu > Zn > Cr > V > Co [Galloway and Whelpdale, 1980].

Figure 6.13 shows correlation plots and Pearson correlation coefficients for selected species pairs. Similar to observations in the BRACE data, Na and Mg species correlate well ($r = 0.92$), with studies suggesting the concentrations and correlations observed being indicative of the influence of marine aerosols [Dvonch et al., 1998]. This is reinforced by the significantly higher mean concentrations of Na and Mg species in the data, and the combination of sampling location and local meteorology. Strong positive correlations were observed between La and Ce (r = 0.99), Al - Fe (0.97), and Al - Mn (0.97). Correlations between these species have been found to be indicative of contributions from crustal material [Mason and Moore, 1982; Olmez and Gordon, 1985]. Additionally Al-Fe and Al-Mn species pairs, have also been associated with influences from metal smelting and municipal waste combustion sources, respectively [Dvonch et al., 1998; White et al., 2009; Polissar et al.,

Table 6.3. Quality control variables for trace metals species in the 2012 USF deposition data.

Species	MDL[a] (μg/L)	Below MDL (%)	AM (%)[b]
Li	4.0×10^{-2}	0	2.9
P	8.3	0	5.1
Co	9.7×10^{-3}	50	13.1
Ni	2.1×10^{-1}	0	1.8
Cu	2.3×10^{-1}	7	1.6
Zn	2.4×10^{-1}	7	1.5
As	4.3×10^{-2}	47	18.5
Se	1.0×10^{-1}	13	75.9
Sr	5.3×10^{-2}	7	4.0
Mo	5.5×10^{-2}	100	4.4
Ag	4.8×10^{-1}	100	11.2
Cd	3.4×10^{-3}	7	11.9
Sb	1.2×10^{-2}	7	1.5
Ba	1.3×10^{-2}	7	0.7
La	1.2×10^{-3}	17	20.1
Ce	9.7×10^{-4}	7	8.7
Pb	6.7×10^{-3}	7	1.1
U	9.7×10^{-3}	93	20.2
Na	2.3	0	1.1
Mg	7.3×10^{-1}	0	0.7
Al	9.3	7	21.8
K	8.8×10^{-1}	0	5.1
Ca	4.1	0	1.5
Mn	1.6×10^{-2}	0	1.0
Fe	9.4×10^{-2}	0	8.1

[a] Analytical method detection limit. [b] Analytical measurement uncertainties determined as the average relative standard deviation (RSD) for each element.

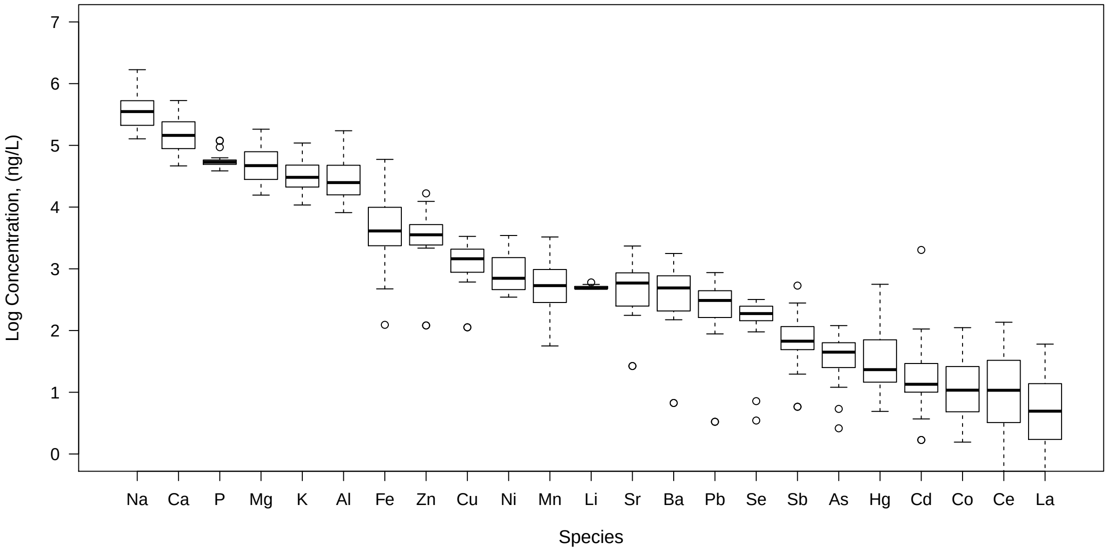


Figure 6.12. Summary statistics for 2012 USF deposition data.

Table 6.4. Element statistics and Crustal Enrichment Factors for USF deposition data.

Species	Mean[a]	Min	25th	Median	75th	Max	S/N[b]	Crust[c]	cEF[d]
Al	4.1×10^{4}	8.1×10^{3}	1.6×10^{4}	2.5×10^{4}	5.2×10^{4}	1.7×10^{5}	2.4	8.04	1.0
As	4.7×10^{1}	2.6	2.5×10^{1}	4.5×10^{1}	6.4×10^{1}	1.2×10^{2}	0.6	1.50×10^{-4}	6.1×10^{1}
Ba	6.0×10^{2}	6.7	2.0×10^{2}	4.9×10^{2}	8.2×10^{2}	1.8×10^{3}	7.8	5.50×10^{-2}	2.1
Ca	1.9×10^{5}	4.6×10^{4}	8.8×10^{4}	1.5×10^{5}	2.6×10^{5}	5.3×10^{5}	7.8	3.00	1.2×10^{1}
Cd	9.0×10^{1}	1.7	9.3	1.3×10^{1}	3.0×10^{1}	2.0×10^{3}	5.1	9.80×10^{-6}	1.8×10^{3}
Ce	2.4×10^{1}	4.8×10^{-1}	3.2	1.1×10^{1}	3.7×10^{1}	1.4×10^{2}	6.0	6.40×10^{-3}	7.4×10^{-1}
Co	2.1×10^{1}	1.6	4.8	1.1×10^{1}	2.8×10^{1}	1.1×10^{2}	2.3	1.70×10^{-3}	2.4
Cu	1.6×10^{3}	1.1×10^{2}	8.7×10^{2}	1.5×10^{3}	2.1×10^{3}	3.4×10^{3}	5.0	2.50×10^{-3}	1.2×10^{2}
Fe	9.0×10^{3}	1.2×10^{2}	2.2×10^{3}	4.1×10^{3}	1.1×10^{4}	5.9×10^{4}	6.2	3.50	5.0×10^{-1}
Hg	9.9×10^{1}	4.9	1.5×10^{1}	2.3×10^{1}	9.6×10^{1}	5.6×10^{2}	7.7	-	-
K	3.8×10^{4}	1.1×10^{4}	2.1×10^{4}	3.0×10^{4}	4.9×10^{4}	1.1×10^{5}	7.0	2.80	2.7
La	1.1×10^{1}	1.4×10^{-1}	1.7	4.9	1.6×10^{1}	6.0×10^{1}	3.2	3.00×10^{-3}	7.2×10^{-1}
Li	5.0×10^{2}	4.7×10^{2}	4.8×10^{2}	4.8×10^{2}	5.2×10^{2}	6.0×10^{2}	6.1	2.00×10^{-3}	4.9×10^{1}
Mg	5.6×10^{4}	1.6×10^{4}	2.8×10^{4}	4.7×10^{4}	7.9×10^{4}	1.8×10^{5}	7.9	1.33	8.2
Mn	8.2×10^{2}	5.6×10^{1}	2.7×10^{2}	5.3×10^{2}	1.0×10^{3}	3.3×10^{3}	7.8	6.00×10^{-2}	2.7
Na	4.1×10^{5}	1.3×10^{5}	2.1×10^{5}	3.5×10^{5}	5.3×10^{5}	1.7×10^{6}	7.9	2.90	2.8×10^{1}
Ni	1.1×10^{3}	3.5×10^{2}	4.5×10^{2}	7.1×10^{2}	1.6×10^{3}	3.5×10^{3}	4.5	4.40×10^{-3}	5.1×10^{1}
P	5.8×10^{4}	3.9×10^{4}	4.9×10^{4}	5.4×10^{4}	5.8×10^{4}	1.2×10^{5}	4.5	7.00×10^{-2}	1.6×10^{2}
Pb	3.2×10^{2}	3.3	1.6×10^{2}	3.1×10^{2}	4.4×10^{2}	8.7×10^{2}	7.8	1.70×10^{-3}	3.7×10^{1}
Sb	1.0×10^{2}	5.8	4.8×10^{1}	6.7×10^{1}	1.2×10^{2}	5.3×10^{2}	6.3	2.00×10^{-5}	9.8×10^{2}
Se	1.9×10^{2}	3.5	1.4×10^{2}	1.9×10^{2}	2.5×10^{2}	3.2×10^{2}	0.2	5.00×10^{-3}	7.5
Sr	6.6×10^{2}	2.7×10^{1}	2.5×10^{2}	5.9×10^{2}	8.7×10^{2}	2.3×10^{3}	6.5	3.50×10^{-2}	3.7
Zn	4.5×10^{3}	1.2×10^{2}	2.4×10^{3}	3.6×10^{3}	5.2×10^{3}	1.7×10^{4}	7.3	7.10×10^{-3}	1.2×10^{2}

[a] Concentration of species observed in wet deposition data in $\mathrm{ng\,L^{-1}}$.

[b] Signal-to-noise ratio

[c] Composition of upper continental crust for deposited species in wt(%)[From McLennan [2001]].

[d] Upper crustal enrichment factors calculated with *Al* as the reference element.

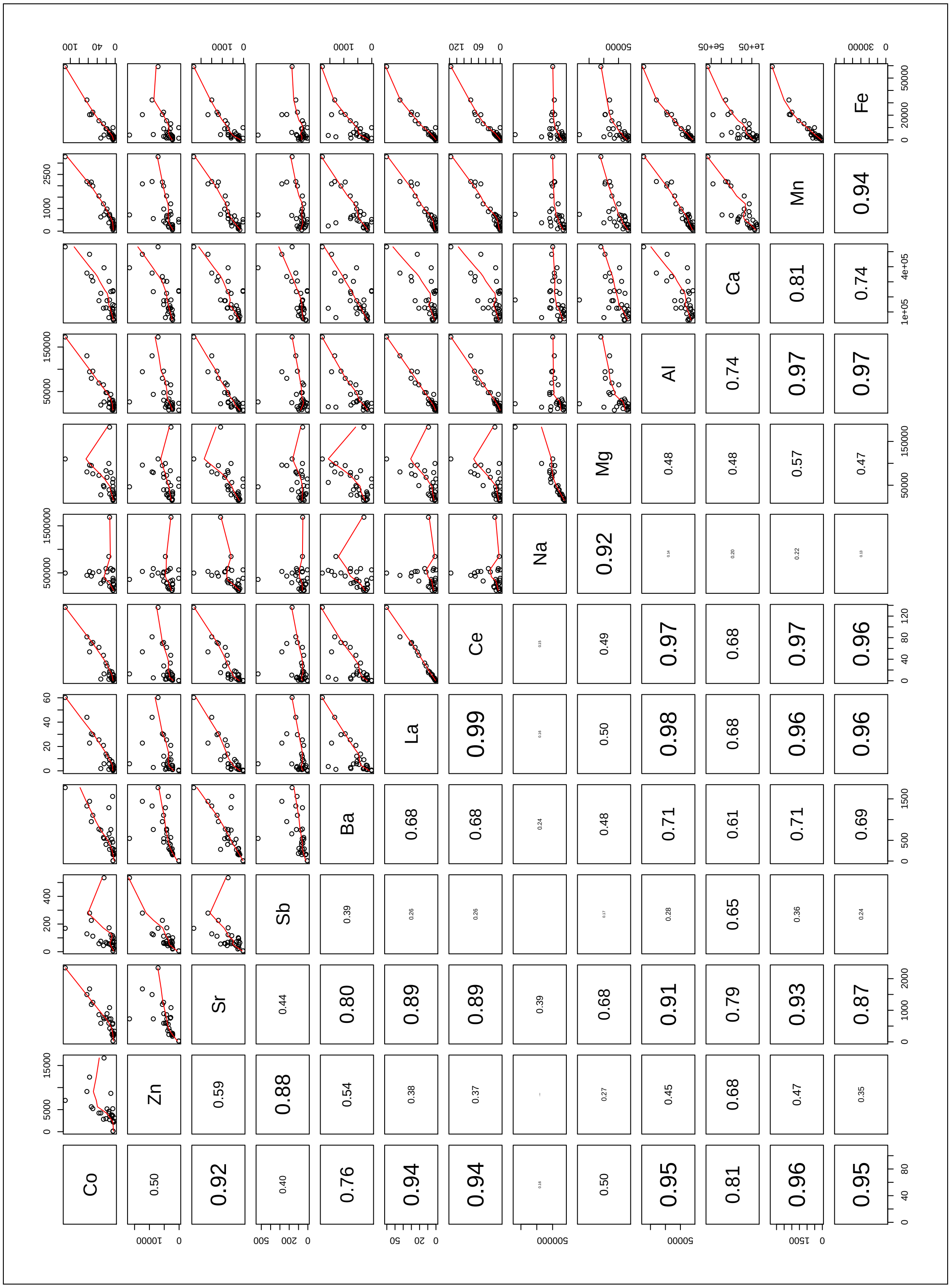


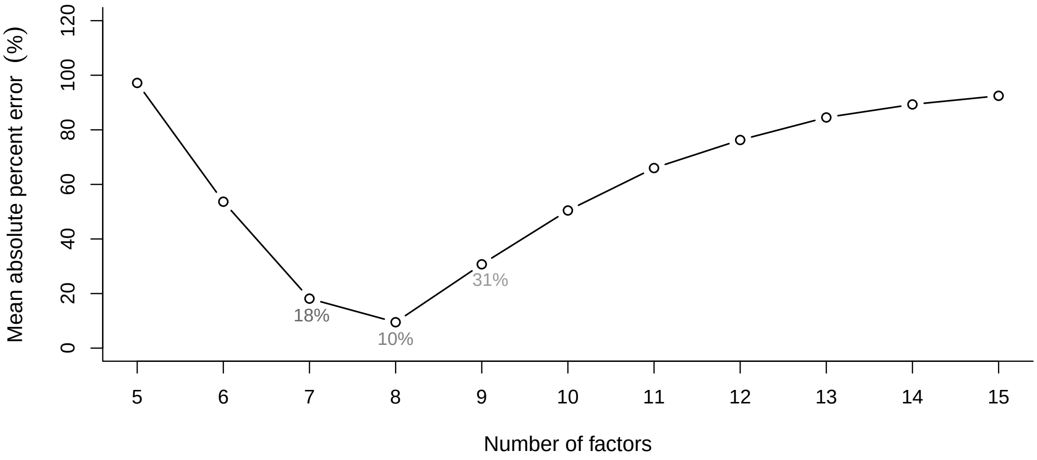
Figure 6.13. Correlation matrix of select species for preliminary source identification. Species plotted shown on the diagonal. Panel below diagonal gives the Pearson's correlation coefficient of species pairs as a function of goodness of fit (species pairs with poor fitting are shown at relatively reduced font size). The upper panel plots a smoothing scatterplots (locally weighted regression) of the species pairs. Correlation coefficients corresponding to a species pair is found at the intersection of the column and row from the diagonal.

2001]. Sb - Zn (0.88), Ce - Fe (0.96) and Ba - Fe (0.69) correlations have been used to identify contributions from road transport sources [Alleman et al., 2010]. La - Co (0.94) correlations are linked to contributions from petrochemistry [Alleman et al., 2010]. Strontium correlations has been associated with resuspension dust [Alleman et al., 2010]. Here we see it correlate well with several species (Ba, La, Ce, Al, Ca, Mn, Fe, and Co). Additionally, several species groups (not necessarily measured here) are known to be indicative of contribution from anthropogenic sources. These include oil burning (Cd, Pb, Cr, Fe, Cu, V, Ni, Mn), diesel vehicles (Pb, Cd, Cu, Fe, Mn), road dust (Cr, Fe, Mn, Cd, Pb), and metal industries (Cd, Pb, Cr, Fe, Mn) [Samara et al., 2003; Arditsoglou and Samara, 2005; Voutsa et al., 2002]. Taken in the context of high enrichment factors observed for several of these species, these correlations suggests contributions from anthropogenic sources may be influencing the species masses observed.

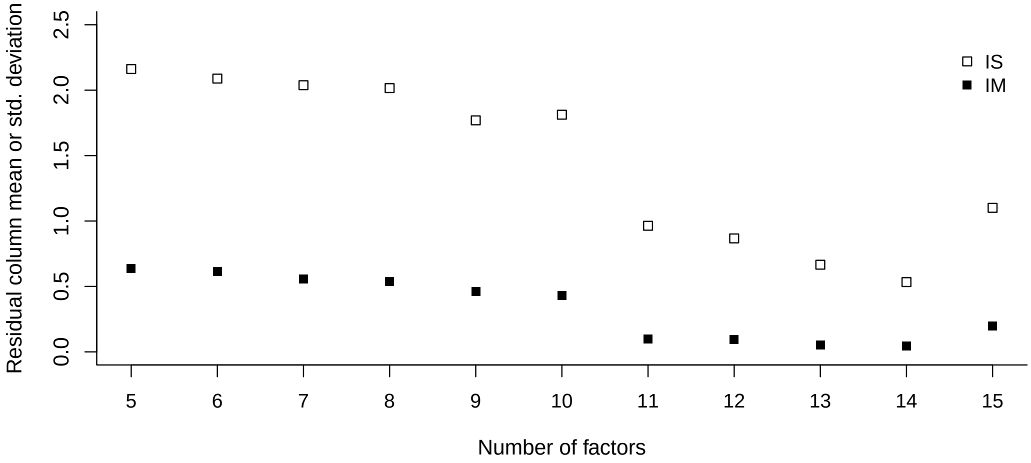
6.3.4. Statistical factors from PMF modeling

6.3.4.1. Factor number selection

Figure 6.14 shows the results of the sensitivity analysis for factor number determination. Figure 6.14(a) gives the variation in the absolute percent error between the theoretical Q value, Q_{th}, and the mean model generated value, Q_r for model runs as the number of factors varies between $5 \leq \text{p} \leq 15$ (mean absolute percent error ≤ 10). A steep decline in the absolute percent error is observed as the number of factors modeled, p, increased, with Q_r approaching Q_{th} to a minimum absolute difference of approximately 10%, corresponding to an 8-factor model. For 8 factors, the calculated minimum robust Q value, Q_r, of 596, was within 10% of the theoretical Q value, Q_{th} of 630 ($n = 30$, $m = 22$, $Q_{th} = n \times m$). Figure 6.14(b) shows the variation in *IM*, the maximum individual column mean, and *IS*, the maximum individual column standard deviation, with changes in the number of factors modeled. *IS* and *IM* mirrors a similar trend of decreasing variability as the number of factors increases, approaching an inflection point at p = 14. Comparison of the results generated from the sensitivity analysis for factor selection indicates some degree of over-fitting as the



(a) Variation in mean absolute percent error with change in number of modeled factors.



(b) Variation in maximum column mean, *IM*, and column standard deviation, *IS*, of standardized residuals with changes in the number of factors modeled.

Figure 6.14. Sensitivity analysis for factor number selection.

number of model factors increases beyond p $\geq$ 10. Further sensitivity analysis conducted with p = (7, 8) indicated that the dataset was better resolved using a 7-factor model. This was based on comparisons of variability of model predicted profiles and contribution matrices using both p-values. A 7-factor model had less variability in predicted profiles, as well as, a relatively greater remapping fraction for uncertainty analysis.

Results from residual analysis for assessment of model fit indicated that all species had scaled residuals that followed a normal distribution, and 85% of species had residuals between ±3 standard deviations. The coefficient of determination for predicted species concentrations varied between 0.999 and 0.9 for 80% of the species modeled. For a 7-factor model, all bootstrapped runs converged. Mapping of bootstrapped factors to base factors varied from 32% to 99% across factors. Unmapped factors varied between 0% and 63% indicating some uncertainty in the stability of model results. A modest increase in the Q_r for rotated solutions (less than 2 times the base Q) was observed as the FPEAK parameter was applied, well within the recommended range of a factor of ten for a dataset of this size [see Norris et al., 2008]. No distinct interdependence of factors (presence of "edges" in G-Space plots) was observed for any factor pair. The results associated with the minimum Q_r (i.e. the global minimum), individual factor stability and species variability is discussed next.

6.3.5. Factor identification

The dataset was ultimately resolved for 7 factors. Figure 6.15 gives the contributions, and compositions of the resolved factors along with probable source types. Each factor and the rationale for its identification is discussed below.

6.3.5.1. Crustal material

This factor was identified by its contributions to the La (70%), Ce (73%), and Fe (68%) species masses in the dataset (Figure 6.15, (a)). Taylor and McLennan [1985] suggested a La/Ce ratio of 0.6 (0.4, this study) is indicative of average continental crustal material. Similarly, Fe/Al ration of 0.4 (0.2, this study), and Mg/Al ratios of 0.2-0.3 (0.7, this study) have been used to identify soil/crustal dust as a PMF source [Keeler et al., 2006; Olmez and Gordon, 1985]. Other tracers for soil/crustal emission sources include Ti, and Sr. Sr species correlated well with other crustal material indicators such as Ce, Fe, and La species (see Figure 6.13). The factor profile consisted predominantly of Na (55%), with some contribution from Mg (11%) species, which is common for ubiquitous species at high relative concentrations. Correlation plots of species pairs associated with this factor also show good agreement (Ce-Mn ($r^2 = 0.97$), Fe-Al ($r^2 = 0.97$), and La-Ce ($r^2 = 0.99$), see Figure 6.13). Additionally, we observe low cEF for the key species identifying this factor, Ce (0.7), La (0.7), and Fe (0.5) (see Table 6.4). A low cEF (≤ 5) is indicative of biogenic influences [Galloway

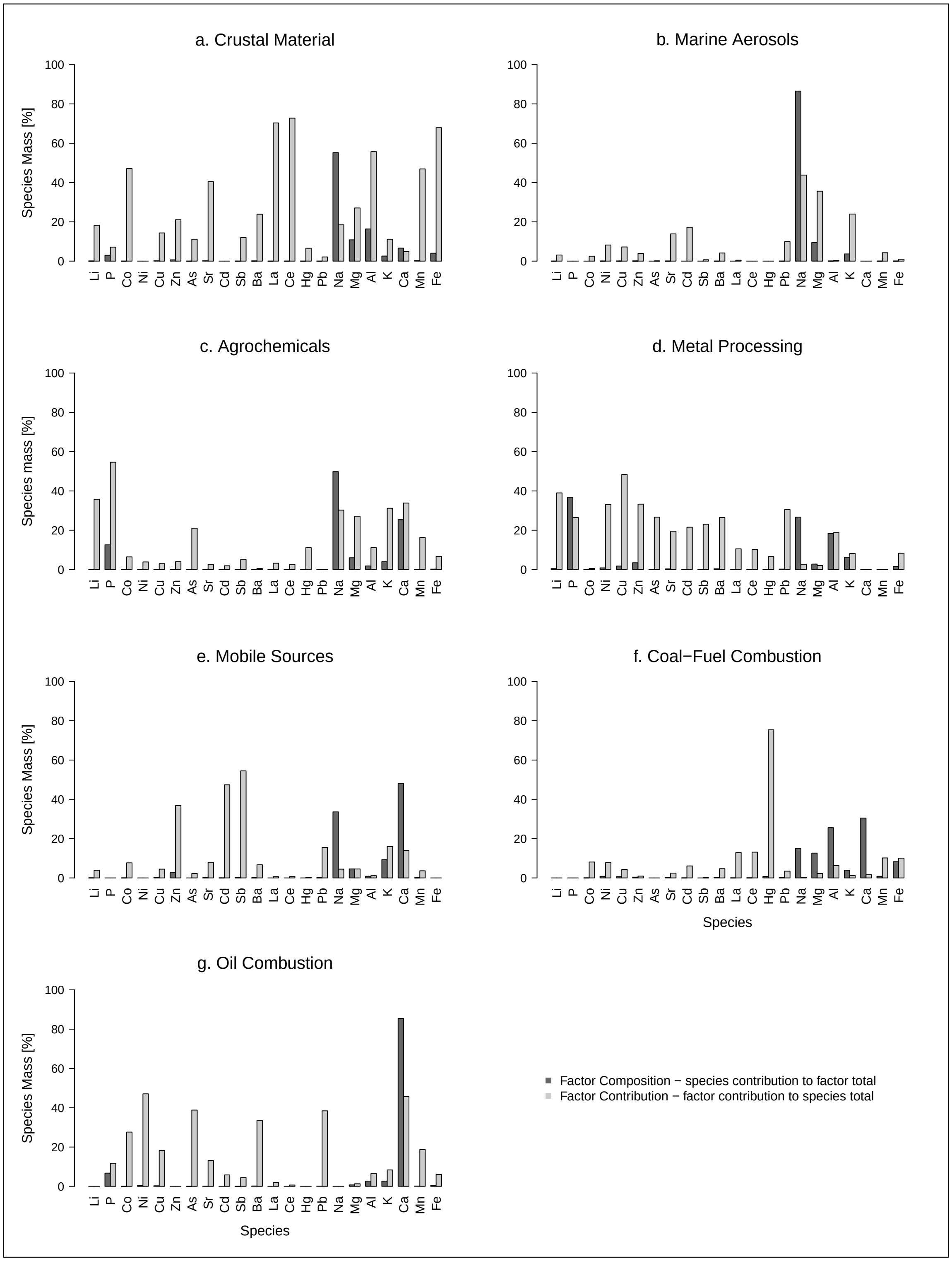


Figure 6.15. Source identification for an 7-factor PMF simulation. The plots shows the fractional contributions to total species mass (dark bars) and the source profiles (species fractional contributions to factor total, light bars) for each source identified.

and Whelpdale, 1980]. The factor solution was robust, with a bootstrap remapping fraction of 0.99 indicating low variability in model solution. The species mass attributed to this factor by the model, and the distribution of those species, indicates the likely identification of this factor as crustal material.

6.3.5.2. Marine aerosol

This factor accounted for significant contributions to sodium, magnesium, and calcium species in the deposition dataset, Figure 6.15, subplot (b). Sodium and magnesium are a major component of sea salt. The factor accounted for 36% of all Mg species, and 44% of all Na species in the dataset. The factor profile (species contribution to factor total) showed predominant sodium species mass >80%, with some contributions from magnesium (10%). Dvonch et al. [1998], identified Na, Cl, and Mg species as tracers for contributions from the marine environment of species mass in deposition studies. The mean Na/Mg ratio of this data set (9.2) compared well with values from other similar studies, Alleman et al. [2010] (8.4), and Yuan et al. [2006] (8.5). Additionally, sodium and magnesium displays a strong positive correlation ($r^2 = 0.94$), as shown in Figure 6.13. The factor solution stability was demonstrated by a relatively high bootstrap remapping fraction (∼80%) for factor uncertainty analysis. Considering our sampling and model domain, this factor likely highlights contributions of the nearby Tampa Bay and Gulf of Mexico.

6.3.5.3. Agrochemicals

A factor, defined predominantly by a substantial phosphorus signal was resolved by the model, contributing 55% of phosphorus and substantial amounts of Li (36%), Na (30%), Mg (27%), K (31%), and Ca (34%) species in the data set Figure 6.15, subplot (c). The factor profile indicated that phosphorus accounted for 13% of the factor total. Recent source apportionment studies in Steubenville, OH, and Underhill, VT, have identified phosphorus sources via its contributions to P and K elevated loadings [Keeler et al., 2006; Gratz and Keeler, 2011]. Interestingly, this factor was associated with minor contributions of Hg mass in deposition data. We see some agreement in our generated factor with 11% of mercury mass being accounted for by this factor in our model results. Phosphorus is an important component of animal waste, and a significant component of the agriculture industry, which accounts for greater than 25% of land uses in the Tampa Bay area. Additionally, one of the largest phosphate mines are located in the state [Cathcart, 1980]. Overall, regression diagnostics indicated a good fit for modeled phosphorus species in the dataset, giving $r^2 = 0.9$ and a slope of 0.8. Additionally, the factor had little uncertainty, with a bootstrap remapping fraction of 0.87. Another factor (identified as metal processing) indicated a higher profile mass for phosphorus (see Figure 6.15, subplot f), however, indicator species such as K and Li at relatively higher concentrations in this factor lends confidence in its identification as indicative of contributions from an agrochemical source or sources in the region.

6.3.5.4. Coal-fuel combustion

This factor contributed to the largest fraction of mercury species, in the data (75%) Figure 6.15, subplot (d). It also contributed to Ce (13%), La (13%), Mn (10%), Fe (10%), Co, (8%), and Ni (8%) loadings. The factor displayed good stability with a remapping fraction of 0.83. Typically, S/Se [White et al., 2009], and As/Se [Tuncel et al., 1985] species ratios have been used to identify coal combustion sources contributing to deposition data. Unfortunately, Se and S species were not part of this dataset, thus these ratios and their contributions cannot be determined. The low Ni loadings also indicates less influences from oil fuel combustion, which can also contribute to Hg deposition albeit at lower levels. Similarly, relatively low contributions from the heavy metals Ni, Cu, As, Pb, indicates little influences from smelters or metal waste combustion facilities in the region.The attribution of greater than 50% of Hg wet deposition to coal combustion is consistent with findings in the USEPA source category emissions inventory for the state and region (see Chapter 4). Due to the high mercury loading, this factor is attributed to influences from coal fuel combustion.

6.3.5.5. Mobile sources

A source accounting for approximately 54% of overall antimony species mass was resolved by PMF. The factor also made significant contributions to Zn (37%), Cd (47%), and Pb (16%) species masses Figure 6.15, subplot (e). The factor also showed low variability in percentage of species and concentration of species apportioned, and a good bootstrap remapping fraction of 75%. Anthropogenic antimony sources include both domestic and industrial coal and fuel combustion, pyrometallurgical non-ferrous Cu-Ni-based metal production, incinerators, and road traffic [Gomez et al., 2005; Cal-Prieto et al., 2001]. Gomez et al. [2005] identified vehicular traffic as one of the main sources contribution to high levels of antimony in highly populated areas, as result of brake dust. Comparison of selected species ratios for the factor with similar studies shows good agreement with emissions from catalytic cars, La/Ce - 0.3 [Samara et al., 2003], this study, 0.43. Additionally, La/Ce species show extremely strong correlations here ($r^2 = 0.99$) (see Figure 6.13). The Cu/Sb ratio is often used to fingerprint road traffic sources with a value 4.6 commonly used [Weckwerth, 2001; Sternbeck et al., 2002]. Calculated Cu/Sb ratio for this study was of the same order of magnitude at 1.3. Additionally, cEF factors indicate that Antimony was highly enriched in the dataset (cEF = 980). Being the single largest antimony contributing factor, and considering the traces of barium, cesium and other earth metals comprising this factor, this is most likely a traffic related source.

6.3.5.6. Metal processing

This factor is characterized by significant contributions to heavy metal species; Ni (33%), Cu (48%), Zn (33%), As (27%), Co (30%), Ba (27%), Ce (30%), Sb (23%), and Pb (31%), with some minor contributions to several other metal such as La, Ce, and Al (Figure 6.15, subplot (f). Here we see influences from both highly enriched anthropogenic (Pb, Cd, Cu, As) sources and crustal elements (La, Ce). There is inherent difficulty in separating the source signatures for metal smelting and waste incineration due to common elements in their emissions (Pb, Zn, [Polissar et al., 2001]). Olmez et al. [1998], suggested a As/Se ratio of <1 to be indicative of emissions from smelters (we could not calculate this since this element was not evaluated in this dataset). Several species pairs relevant to metal smelting sources show strong positive correlations (Figure 6.13). These include Mn-Fe ($r^2 = 0.94$), Al-Fe ($r^2 = 0.97$), and Al-Mn ($r^2 = 0.97$) species pairs [Polissar et al., 2001]. The Zn/Cd elemental ratio observed in this study (344) showed some agreement with the literature value of 803 for metal smelting [Samara et al., 2003; Arditsoglou and Samara, 2005]. Polissar et al. [2001] identified the emissions from municipal waste incineration by comparing the Zn/Pb and Hg/Pb species mass ratios. A Zn/Pb ratio of 1.8 (15.8, this study), and a Hg/Pb ratio of 0.06 (0.07, this study) were used to identify contributions from municipal waste incineration for PMF analysis [Polissar et al., 2001; Olmez et al., 1998; Dvonch et al., 1998, 1999]. Uncertainty estimations for this factor revealed high variability in model results, and a bootstrap remapping fraction of only 0.32. The relatively large contributions to several heavy metal species masses suggests that metal processing facilities, incinerating or smelting may be the origin of this factor.

6.3.5.7. Oil combustion

PMF resolved a source that accounted for the highest contributions of Ni (47%), As (39%), Ba (34%), Pb (38%), and Ca (46%) species in the dataset, as shown by Figure 6.15, subplot (g). Table 6.4 shows that all major species contributed by the factor were enriched. Trace element concentration ratios indicate good agreement for oil fuel combustion as a likely influence on the species contribution profile observed. These included Cd/Pb (160, 101 this study), Cu/Sb (71, 64 this study), Mn/Fe (0.04, 0.3 this study), Pb/Cu (0.9, 0.4 this study), and La/Ce (1-2, 1.3 this study) species ratios [Arditsoglou and Samara, 2005; Samara et al., 2003]. V and Ni are the common indicator species for oil combustion, with a V/Ni ratio of 2.46 [Samara et al., 2003], and 2.4 [Arditsoglou and Samara, 2005] being used to indicate source influences. However, V species were not available in this dataset. Considering the good agreement with the concentration ratios for the species observed in the factor, this is likely an oil burning facility or facilities. Oil combustion emission categories include oil fired power generating facilities, and industrial and residential heating equipment.

In summary, seven probable sources were resolved by PMF modeling on the deposition dataset, and were identified as agrochemicals (P, K, Ca), coal fuel combustion (Hg, Co, Ni, Cd, Mn), traffic related emissions (Sb, Cd, Pb, Zn), crustal material (La, Ce, Mn, Fe), marine aerosols (Na, Mg, K), metal processing (Ni, Cu, Zn, Cd, Sb, Ba, Sr, As) and oil combustion (Pb, Co, Ni, Cu, As).

6.3.6. Factor contributions to mercury species mass

Figure 6.16 shows the model resolved factors contributing to mercury species mass observed in the dataset. The regression results of the PMF predicted versus measured Hg concentrations had slope of 1.01, an intercept of 0.97, and a coefficient of determination (r^2) of 0.99, indicating an excellent fit to the data. Most of the scaled residuals were between ±3.0, with a random distribution of positive and negative values indicating good model fit.

Four sources were identified as the major contributors to mercury species mass. Coal fuel combustion was identified as the largest mercury contributing factor, accounting for approximately 75% of mercury species in the dataset. The fractional allocation of mercury species to coal combustion sources here is approximately 20% higher than that reported for the BRACE data analysis (see Figure 5.9), but consistent with changes in the local emissions inventory (see Chapter 4).

Agrochemical sources were identified as the second largest mercury-contributing source, accounting for approximately 11% of mercury species in the dataset. This result differs from the results of the BRACE data, where this source was not resolved as a mercury emission source. The role of agricultural soils in the environmental cycling of mercury has been well documented [Schroeder and Munthe, 1998; Zhang et al., 1999; Lindberg et al., 1979]. Agrochemical industries (especially phosphate mining) are major part of the industrial landscape in the Tampa Bay area, with notable contributions to mercury emissions as shown by our results.

Metal processing was identified as the third highest mercury contributing factor, accounting for 7% of Hg species mass. Finally, the crustal material source also contributed about 7% of the mercury species observed in the deposition data.

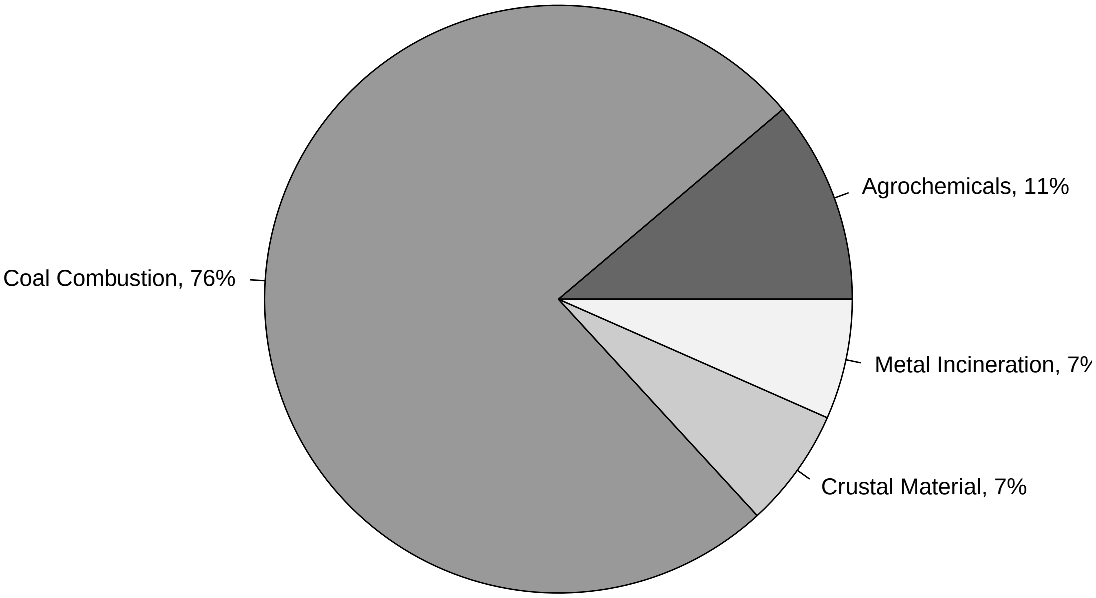


Figure 6.16. Mercury contributing factors from 2012 USF deposition data. The plot shows model predicted factor fractional contributions to mercury species in the deposition data

6.4. Summary

We performed wet deposition sampling at a site on the USF campus for 6 months to capture mercury and trace metals data. The data was used to drive receptor modeling efforts to understand the influence of local emission sources on mercury deposition phenomenon in Tampa Bay area, and compare with similar studies previously conducted in the area.

Results from mercury event sampling indicates an extremely weak relationship between event precipitation depth and event mercury concentration. Event precipitation depth explained less than 1% of the variation observed in event mercury concentration. Event mercury deposition mirrored this trend. This suggests the dilution/concentration effects do not play a role on the concentrations observed, and a large, or readily replenished source, local to the receptor may be responsible for the variations observed.

Results from back-trajectory modeling indicated that high mercury concentration events coincided with air mass trajectories that consistently tracked over Florida landmass in the short and intermediate term. Additionally, we observed high mercury concentration events with trajectory over Florida landmass, with high precipitation depth events over the course of the trajectory in the 2 days before reaching the receptor. This may possibly result in the washout of mercury species close to the origin of the trajectory in the long term. This suggests that mercury species reaching the receptor are often from air masses over Florida land, and possibly local to the receptor. This suggest the likely influences of Florida sources on high mercury concentration events studied here.

Additionally, PMF results indicate that coal-fired power generation, agrochemical and metal processing facilities may be influencing mercury deposition in the Tampa Bay area. These results agree well with analysis of the National Emission Inventory (NEI) across the 1999, 2002, 2005, and 2008 inventory years, which showed that coal-fired power facilities accounted for greater than 50% of mercury emissions in the Tampa Bay area (Hillsborough, Pinellas, Pasco, and Hernando Counties) for every inventory year except 1999 (65% attributed to medical facilities). Taken in the context of area emission inventories, the analysis results here point towards substantial contributions to Tampa mercury deposition from local and regional Florida sources.

7. Population vulnerability to mercury exposure in the Tampa Bay area

7.1. Background

Fish are an important source of proteins among many sectors of the population in the US, being important not only in rural regions, but for subsistence and recreation fishers in urban areas [Ramos and Crain, 2001; Burger and Campbell, 2004; Burger, 2005; Burger et al., 2004].The many benefits to fish consumption has been much heralded by public health institutions and researchers. A consistent fish diet of approximately 1-2 meals per week has been associated with a substantial reduction in the risk of cardiovascular disease and deaths from heart attacks, reduction of cholesterol levels, enhancement of cognitive development, and the promotion of good health [Daviglus et al., 1997, 2002; Albert et al., 2002; Burger and Gochfeld, 2009]. The American Heart Association has assessed the health benefits of fish and its associated omega-3 fatty acids, and have promoted a balanced diet of two meals of fish per week [Krauss et al., 2000; Anderson et al., 2004]. Additionally, trends have shown that the consumption of fish and shellfish as a dietary source of protein has surpassed that of other animal sources [Anderson and Bigler, 2005]. However, unlike domesticated animals, the majority of fish consumed by the general population is harvested from the wild (saltwater oceans, and freshwater rivers and lakes). The combination of free range of movement, an opportunistic diet, and the fact that most of the sought after fish species are top level predators in aquatic food systems, makes wild fish species vulnerable to accumulating bio-persistent pollutants circulating in the environment [Anderson and Bigler, 2005]. Mercury, specifically methylmercury, is one such pollutant. Methylmercury have been found in sufficiently high levels in the some fish and seafood to pose a health risk to consumers [Clarkson, 1990; Gochfeld and Burger, 2005; Mahaffey and Pirrone, 2005; Zahir et al., 2005; Hightower and Moore, 2003]. Moreover, it has been shown that methylmercury counteracts the cardio-protective effects of omega-3 fatty acids [Guallar et al., 2002; Gochfeld and Burger, 2005]. Human exposure to mercury compounds occurs predominantly through the consumption of aquatic organisms, particularly fish [Tollefson and Cordle, 1986; Rice et al., 2000].

The developing brain is the main target for methylmercury toxicity with evidence from poisoning outbreaks in Japan clearly demonstrating the severe health outcomes in fetuses as a result of maternal exposures [D'ltri and D'ltri, 1978; Harada, 1995]. Adverse health effects include mental retardation, cerebellar ataxia, primitive reflexes, dysarthria, and hyperkinesias being observed in infants [Gilbert and Grant-Webster, 1995; Harada, 1995]. Consequently, vulnerable populations include women of child-bearing age, the developing fetus and young children, nursing mothers, and those consuming large amounts of piscivorous fish in their diet [Gilbert and Grant-Webster, 1995; Swain et al., 2007; Hightower and Moore, 2003].

In 2004 the USEPA and FDA issued a joint consumer advisory about methylmercury in fish and shellfish [Shimshack et al., 2007a]. This advisory was aimed at the most susceptible population for mercury exposure; women who might become pregnant, women who were pregnant, nursing mothers and young children. The aim was to provide recommendations for selecting and eating fish to maximize the benefits of fish consumption, whilst minimizing the harmful effects of methylmercury. Since the consumption of fish with high methylmercury levels can lead to elevated levels of mercury in the blood of unborn babies and young children, a Reference Dose (RfD) for methylmercury was calculated to protect the developing nervous system. Currently, U.S. EPA uses a RfD of $0.1\ \mu\mathrm{g}\,\mathrm{kg}^{-1}_{\text{body-weight}}\,\mathrm{d}^{-1}$ as an exposure without recognized adverse effects [Rice et al., 2000, 2003].

Forty states have since issued advisories for methylmercury on selected water-bodies and 13 states have statewide advisories for some or all sport fish from rivers or lakes [USEPA, 2012]. Coastal areas along the Gulf of Mexico, Maine, and the Atlantic Ocean from Florida through North Carolina are under advisories for methylmercury for certain fish [USEPA, 2012]. Additionally, the State of Florida has issued fish consumption advisories due to mercury levels for all of the major rivers in Florida for multiple fish species [USEPA, 2012]. Studies have shown that Floridians consume substantially greater quantities of seafood than the average U.S. resident because of the unique geographical characteristics and the presence of very large recreational and commercial fisheries [Degner et al., 1994]. Moreover, Moya et al., [2008], estimated fish consumption rates for consumers of bought and self-caught fish in Connecticut, Florida, Minnesota, and North Dakota, and observed the highest values in Florida for children 1 to 6 years of age. Overall, for the state of Florida, fish consumption ranged from 0.7 - 2.3 $\mathrm{g\,kg^{-1}_{body\text{-}weight}\,d^{-1}}$. In comparison, fish consumption from the other states surveyed were Connecticut 0.23 - 0.84 $\mathrm{g\,kg^{-1}_{body\text{-}weight}\,d^{-1}}$, Minnesota 0.11 - 0.69 $\mathrm{g\,kg^{-1}_{body\text{-}weight}\,d^{-1}}$, and North Dakota 0.70 - 2.3 $\mathrm{g\,kg^{-1}_{body\text{-}weight}\,d^{-1}}$. Recreational and subsistence fisher-folk may be subject to increased health risks likely due to greater frequency of consumption, and larger total quantities consumed relative to the overall population, thus placing them among that sector of the population most vulnerable to mercury exposure.

Research suggest that the decision to consume fish and shellfish is a case of risk balancing (comparing alternative risks and benefits [Burger and Gochfeld, 2009]), involving not only those risks posed by fish consumption, but the health risks posed by alternative protein sources such as red meat [McMichael and Butler, 2005]. Therefore, the ability to make informed dietary decisions requires access to information on the risks and benefits of particular fish species, as well as, alternative protein sources. However, studies have shown that public health interventions such as educational outreach and fish consumption advisories have limited success in reaching those populations most at risk to mercury exposure from consumption of fish with high levels of mercury, such as pregnant and women of child-bearing age [Karouna-Renier et al., 2008]. Barriers to advisory compliance include deficiencies in knowledge of existing advisories, education level, income, and other cultural factors [Anderson et al., 2004; Burger and Gochfeld, 2008; Park and Johnson, 2006; Shimshack, 2004; Shimshack et al., 2007b; Teisl et al., 2011]. Several studies have focused on understanding the role of risk communication [Morgan et al., 1997; Park and Johnson, 2006; Shimshack, 2004], and risk perception [Anderson et al., 2004; Kingman et al., 1998; Burger et al., 1998] on consumption behavior among fish eating populations. Burger [1998], examined fishing behavior, consumption patterns, and risk perception for people fishing and crabbing in New

Jersey. The study revealed that overall, women fished in significantly larger groups than men, and that their groups included more children. Subjects reported catching fish on most of their outings, and consumed as much as 80% of their catch [Burger et al., 1998]. Approximately 90% of the respondents believed that fish caught in the area was safe to eat although around 40% of them had heard some warning about their safety. The authors concluded that there was inadequate understanding about the relationship between contaminants, fish size, and trophic level, thus more risk communication is needed. Understanding population perception to risk from consumption activities, and the factors determining mercury exposures will serve to inform policies that are protective of population health.

In this study we explore the factors determining population vulnerability to mercury exposure from fish consumption in the Tampa Bay area. Specifically, I seek to understand the factors influencing fish consumption behaviors of the angler population in the Tampa Bay area, to elucidate population perception to mercury exposure from fish consumption, and to identify barriers to mercury health advisory compliance among the fishing population. These goals were achieved by the analysis of survey data collected in Hillsborough County, Florida, with emphasis on the fishing population, to understand the relationships between mercury awareness and fish consumption practices.

7.2. Methods

The data used in this study was collected as part of a larger interdisciplinary research project to understand the dynamics of mercury use and community sustainability. This research was conducted by students and professors at the University of South Florida over the course of a semester. The overarching project focused on the concept of environmental sustainability with an emphasis on pollution prevention, and specifically considered the social, economic, and environmental consequences of mercury use. Three principal tasks were defined in this research: social analysis and population risk perception to mercury exposure, understanding environmental mercury concentrations, and characterization of the fate and transport of mercury in different environmental media. Students were responsible for all aspects of the project, including the sampling of environmental media (water, sediment, and fish tissue), conducting population surveys for risk analysis efforts, and construction, testing and application of models. My role in this research project included collection of environmental media for mercury analysis, conducting population surveys, and modeling mercury fate and transport in the Tampa Bay area. The survey data collected in the study is used here to understand population mercury vulnerability and susceptibility to exposure through population fish consumption practices. Here, I describe the data collection and the survey instrument utilized in this study.

7.2.1. Data collection

The study targeted anglers along the Hillsborough River and other fishing locations in Tampa Bay, and was conducted over the spring of 2008. The objectives of the study were to determine the influence of social (educational level, gender, ethnicity), and economic factors on risk perception, fish mercury awareness, and consumption behavior in the sample population.

Sampling was conducted in areas frequented by anglers and fisher-folk in the Bay area, specifically along the Hillsborough River. The surveys were conducted at 19 sites over the period February to March, 2008 and was conducted under approval by the University of South Florida Institutional Review Board (IRB/Pro No. 106211). Individuals were approached whilst they were conducting fishing activities and asked to participate in the study. Surveyors identified themselves as affiliated with the University of South Florida, and described the aims and objectives of the study to participants. The survey was designed and administered. The survey took approximately 15 to 20 minutes, and once completed another person was approached for interview.

Demographic and socio-economic data gathered included age distribution, ethnicity, occupation, place of residence, home ownership, household income and family size, and education level. To elucidate behavior characteristics contributing to mercury exposure from fish consumption habits, the respondents were queried on fishing regularity, daily, weekly, and seasonal fishing patterns. Questions were also structured to determine fishing methods, preferred fishing locations in the sample domain, preferred fish species, and factors determining consumption practices. Population perception to risk from mercury exposure was assessed by querying respondent's awareness of mercury in fish tissue and its impacts. Participants were questioned on their knowledge of fish species containing significantly high levels of mercury, fish consumption advisories, and sources of public health information regarding fish-mercury issues. Finally, the respondents were queried on the impact of their awareness of the threat posed by mercury in fish on their consumption habits (see Appendix E for a copy the survey instrument used in this study)

The data was coded in Microsoft Excel® to generate frequency and summary tables, which was then imported into R® [R Core Team, 2013] for statistical analysis. Non-parametric statistical analysis was performed using the Pearson's Chi-squared test of independence between the categorical variables. For small expected values, we applied Pearson's Chi-squared test with Yates' continuity correction or Fisher's exact test of independence as applicable. A probability level of $P < 0.05$ was accepted as significant and the null hypothesis that all answers have an equal probability of occurring was tested.

7.3. Results

7.3.1. Demographic data

Figure 7.1 gives the distribution of demographic variables among survey respondents. A total of 35 persons completed the survey. Males accounted for a larger fraction (67%) of the survey population than females (33%). This varies from population distribution of Hillsborough County, for which females represent 51% [United States Census Bureau, 2010], and indicates less women in the population partake in fishing activities. The mean age of respondents was within the range 26-35 years with significant differences between the groups for gender ($\chi^2 = 10.1$, $P = 0.017$). Male respondents ranged between 18 - 65 years, whilst female respondents ranged from 26 - 50 years. Caucasians accounted for 54% of the survey population, African Americans accounted for 29%, Hispanics 9%, and Native American 6%.

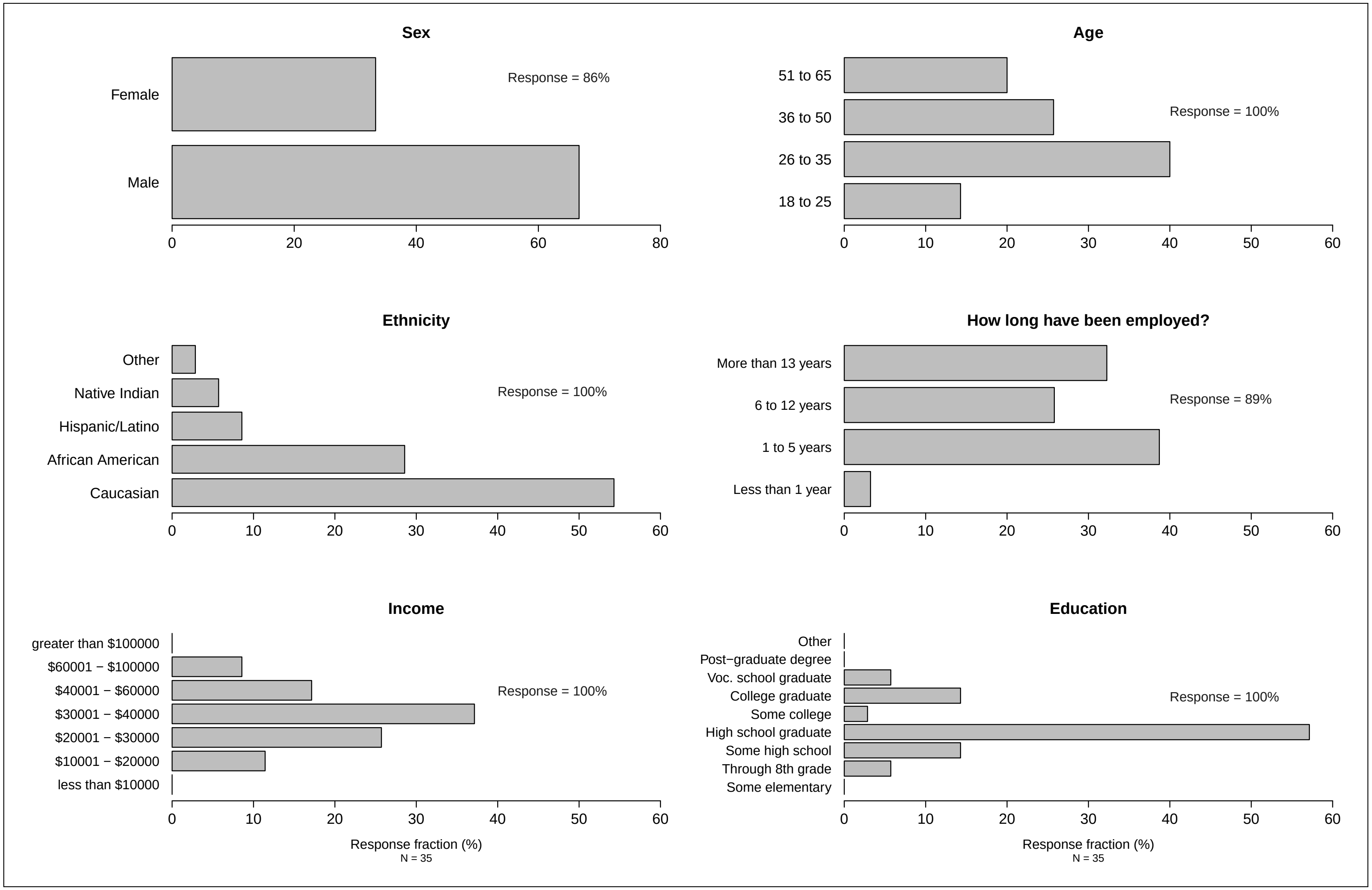


Figure 7.1. Distribution of demographic variables among survey participants.

This distribution differs slightly from the county distribution for race, where Caucasians account for 75%, African American account for 17%, and Native Indians account for 0.5%.

Responses for survey questions pertaining to occupations held by survey participants revealed that 20% of respondents held white collar jobs (insurance agents, office managers, teachers), 17% were unemployed (accounting for retired persons, and housewives), and the larger remainder (67%) held blue collar jobs (contractors and construction workers, mechanics and heavy equipment operators, and other skilled workers). The length of employment of respondents ranged from 1 year to greater than 13 years with an average of 6 to 12 years. Average income ranged between $30,000-40$,000. The average education level was a high school graduate, however, education level ranged from through 8th grade to vocational school graduate. High school graduates accounted for approximately 60% of respondents, which was higher than the Hillsborough County average of 30%.

Figure 7.2 describes the distribution of residential variables among respondents. A larger fraction (87%) of the respondents lived in the Hillsborough County area, with the city of Tampa being most frequent among responses. Other cities mentioned included Plant City, Brandon and St. Petersburg. Respondents who were not from the Hillsborough county area (11%) did not spend much time in the area, and were predominantly in the area for the purpose of fishing ($>$90%). 71% of respondents rented their home as compared to a 29% home ownership fraction. The average size of residence among participants was 3 bedrooms.

Household demographics are given by Figure 7.3. The average household occupancy was 4 persons, and ranged from 1 to 6 among respondents. 49% of households had at least 2 adults in the household (persons greater than 18). 21% of respondents reported having at least one person in the range 3 – 10 years living in the household. None of the respondents reported having infants (less than 2 years old). Only 3% of households reported having a pregnant woman residing there.

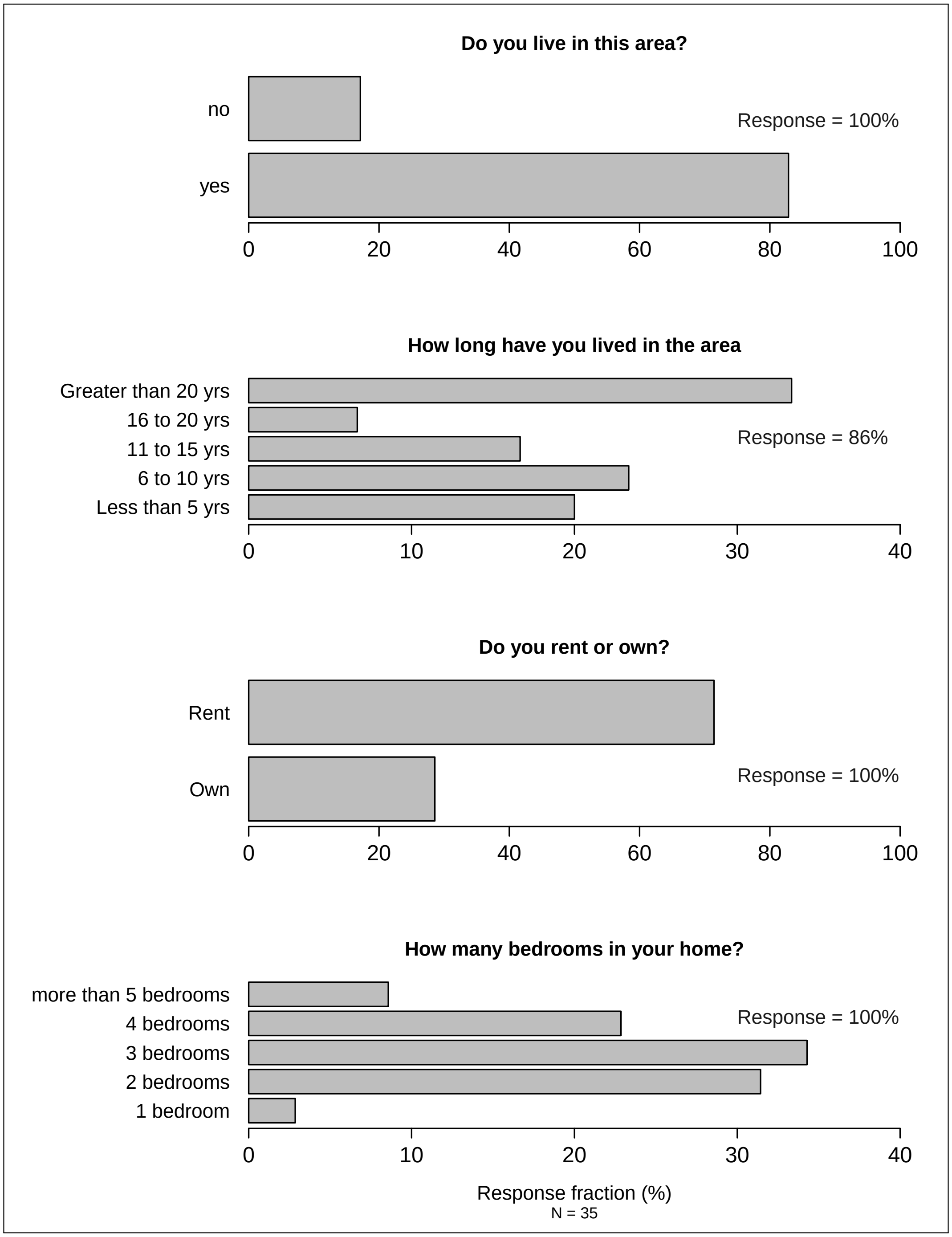


Figure 7.2. Distribution of residential variables among survey participants.

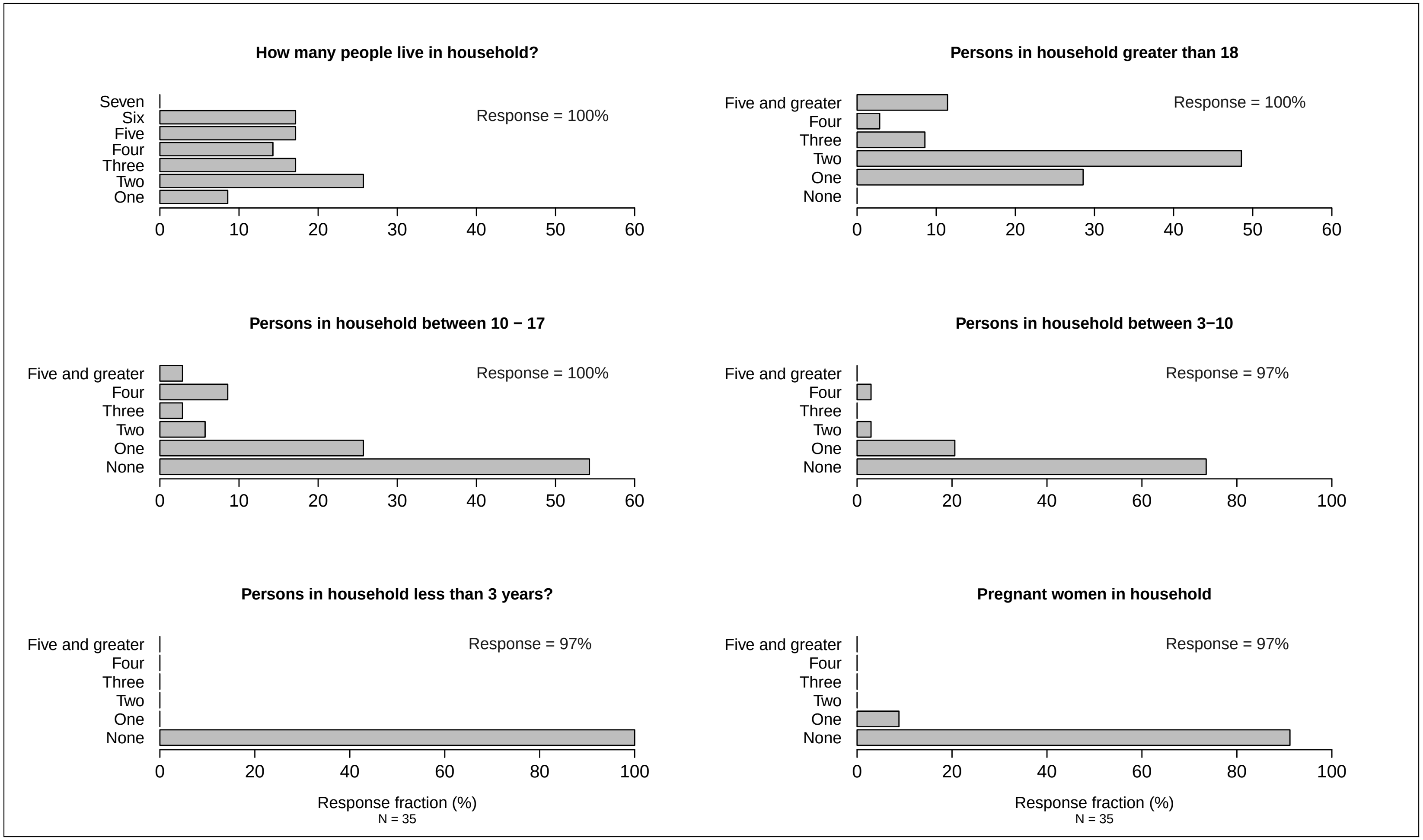


Figure 7.3. Examination of household characteristics among survey participants.

7.3.2. Exploring population fishing habits

Figure 7.4 describes the fishing habits of respondents in the survey. Participants reported fishing at an average frequency of once per week (49%). There was no preference for a particular season, with most participants reporting that they fished all year round (94%). Most participants preferred to fish in the morning (49%). Only 11% did not have a preference for fishing time. A large fraction of (91%) of respondents utilized bait and hook as their principal method of catching fish. Net and traps (6%) and multiple methods (3%) were are also reported.

Whilst most of the surveys were conducted along the Hillsborough River, many of the survey respondents reported regularly fishing at different locations. These included Gandy Bridge, Trout Creek, Ballast Point, and the Skyway Bridge. Reasons for fishing in a particular location were much more diverse. Reasons included ease of accessibility to the site, reputation and experience of good fishing (high fish population), reduced crowding and serenity. Participants also tended to fish in location where they are able to partake in multiple outdoor activities such as boating/canoeing. Similar diversity was demonstrated by fish species caught by survey participants. Species included Largemouth Bass (*Micropterus salmoides*), Bluegill (*Lepomis macrochirus*), Catfish (*Siluriformes*), Brim (*Abramis brama*), Flounder (*Paralichthys albigutta*), Gar (*Lepisosteus oculatus*) and Tuna (*Thunnini allothunnus*). Most participants list 2 – 4 species as frequently caught with Largemouth Bass and Catfish having the most frequent mentions.

Recreational purposes was the dominant answer given for reasons for fishing, accounting for 77% of participant responses. A combination of food and recreation accounted for 20% of the responses, whilst only 3% of survey participants fished solely for consumption purposes. 94% of the population confirmed that they do not sell any of the fish caught, which agrees well with the trend of recreational purposes being the dominant reason for participant fishing activities.

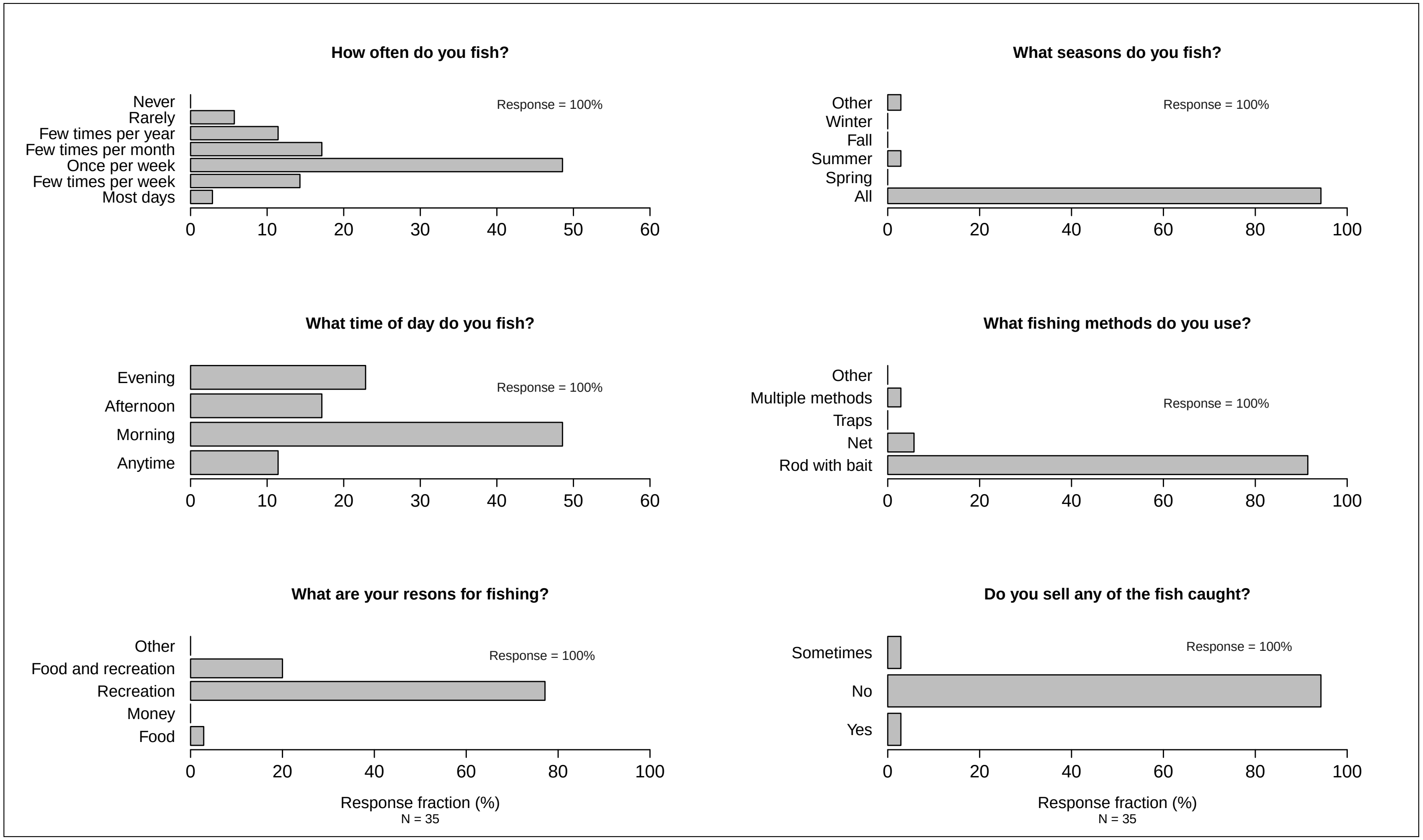


Figure 7.4. Examination of fishing habits among survey participants.

7.3.3. Fish consumption practices

Figure 7.6 describes the fish consumption habits and decisions among survey participants. A large majority (86%) of survey participants reported that they consume their catch. Consumption frequency varied, ranging from rarely to a several times per year. However, we observe an average consumption frequency of once per week for caught fish. Catch consumption decisions were found to be independent of income ($\chi^2 = 3.03$, P = 0.55), and education ($\chi^2 = 10.5$, P = 0.06) (Figure 7.5). Specific catch retention decisions were based predominantly on size (50%), while 25% of the population considered the species of fish. A quarter of the respondent reported that they consume whatever was caught.

General fish consumption (store/restaurant bought fish) displayed a similar trend to consumptions patterns for caught fish. Consumption ranged from several times per week to rarely. Average consumption frequency was once per week. General fish consumption practices was found to be independent of income ($\chi^2 = 8.65$, P = 0.07) and sex ($\chi^2 = 7.3$, P = 0.29) (Figure 7.5). People cited taste and the promotion of health as the most important reasons for choosing to eat fish, these reasons accounting each accounting for 34% of responses. Cultural reasons accounted for 9% of responses, while multiple reasons (a combination of taste, healthier and cultural reasons) accounted for 16% of responses. Most persons surveyed also consumed other types of meat as a source of proteins (97%).

7.3.4. Risk perception to mercury exposure from fish consumption

Participants were queried on their most common source of public health information. Television usage accounted for the largest fraction (39%) of responses. 33% of respondents identified that they used multiple methods to access public health information including Internet usage, television, and radio broadcasts. 11% specifically identified newspapers as a means of obtaining public heath information. Municipal billboards only account for 3% responses.

Figure 7.7 describes the surveyed population's knowledge about and perception of risk of exposure to mercury from fish consumption practices. 73% of survey participants professed

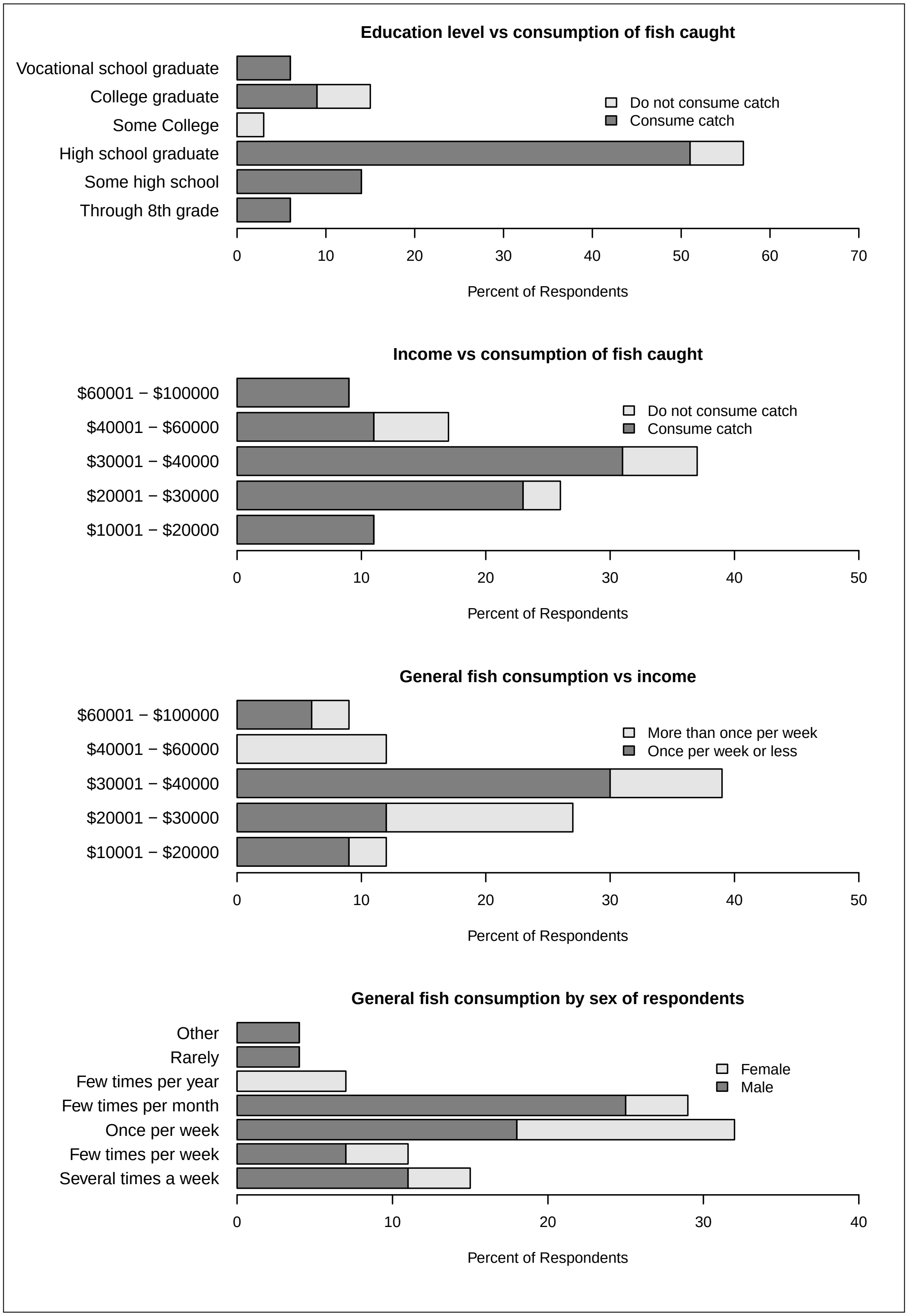


Figure 7.5. Variation of consumption of caught and purchased fish with education level, income and sex.

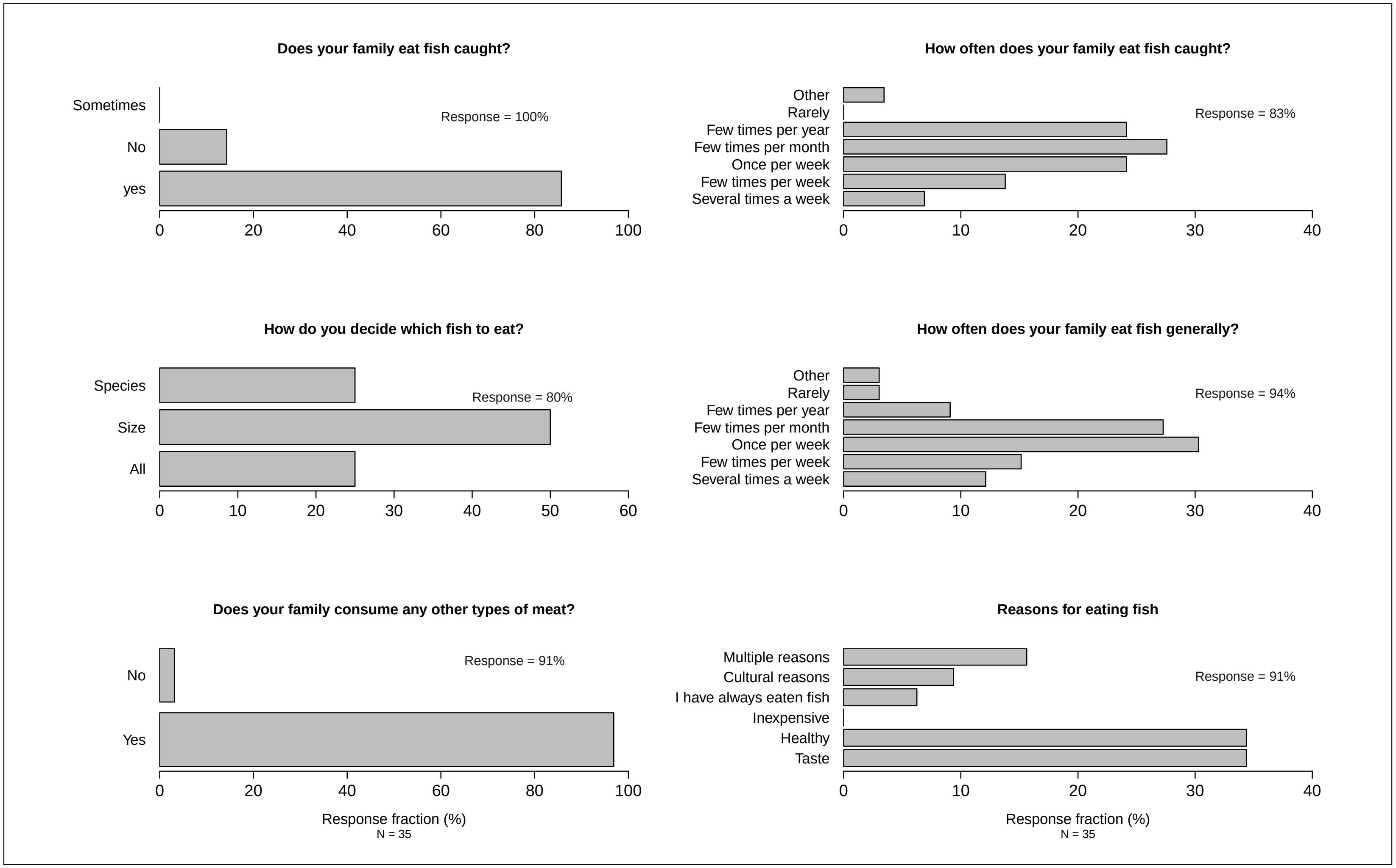


Figure 7.6. Examination of fish consumption habits among survey participants.

an awareness of the risk of exposure to mercury from consuming some species of fish, while the remainder were unaware. Awareness of exposure to mercury from fish consumption was found to be independent of income ($\chi^2 = 8.22$, P = 0.08), sex ($\chi^2 = 0.5$, P = 0.5) and education ($\chi^2 = 2.75$, P = 0.6).

When asked if they had seen informational guidelines/brochures pertaining to fish consumption, fish species, and mercury exposure 66% of the population surveyed said they had not seen any information, while the remainder (34%) said they saw informational guidelines. While a larger fraction of males (40%) reported seeing informational guidelines than females (20%), access to informational guidelines was found to be independent of sex ($\chi^2 = 0.47$, P = 0.5).

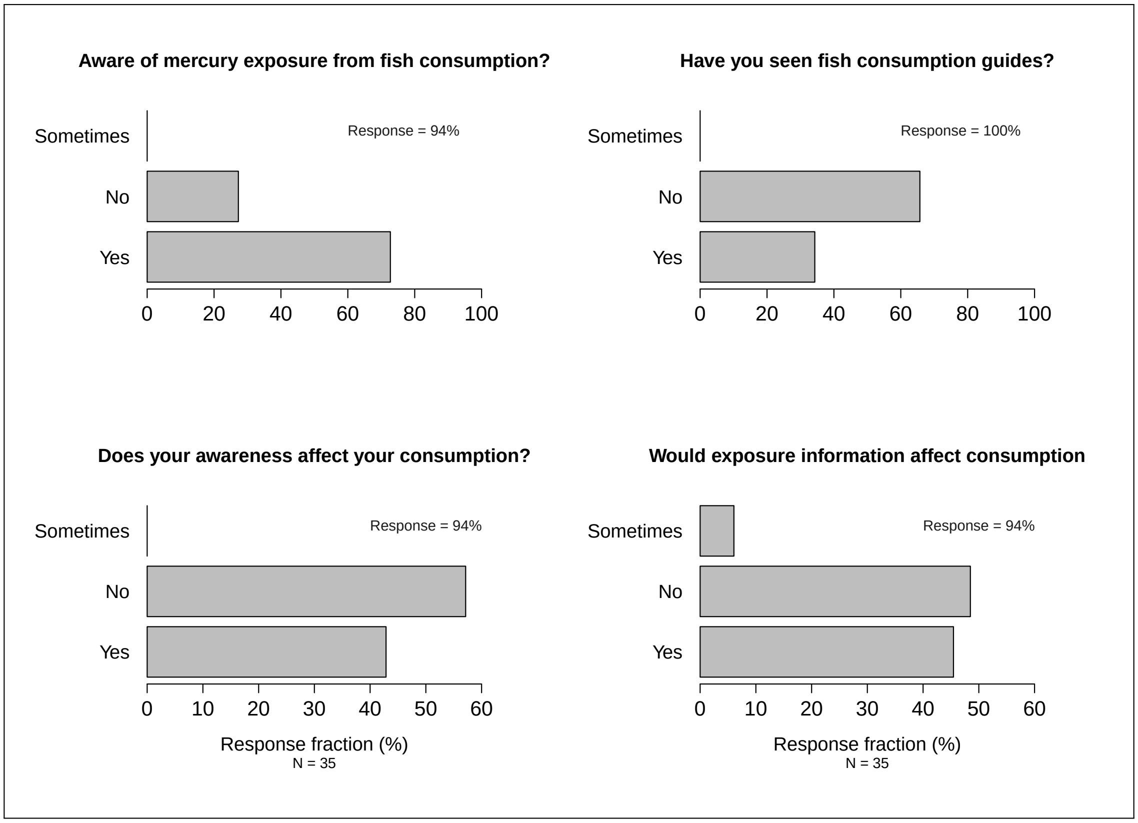


Figure 7.7. Risk perception and awareness of mercury exposure from fish consumption in the survey population.

Population perception of risk to exposure to mercury from consumption of fish was assessed by inquiring whether participants who were aware of the risk of exposure to mercury from fish consumption practices changed their consumption habits, or, for those who did not have access to informational guidelines or exposure information, whether information about the risk of exposure would affect their consumption practices.

For the fraction of the surveyed population who had encountered guidelines or information about the risk of exposure to mercury from consumption of certain fish species, when queried about whether their awareness had affected their consumption practices, 57% reported it did not affect their consumption practices, while 43% said it did. Most of the participants who acknowledged a change in consumption behavior indicated that they had reduced their consumption of certain species of fish as they became more aware of the associated risks.

For the fraction of the surveyed population who had not encountered guidelines or information about the risk of exposure, when queried whether information about exposure would affect their consumption, 45% acknowledged that exposure information would affect their consumption habits, whilst 48% said that information about exposure risks would not affect their habits. 6% percent of the population were unsure if information would affection their consumption habits. Participant perception of exposure to mercury from fish consumption was independent of sex ($\chi^2 = 0.03$, P = 0.86), however, significant differences were found for the responses at different educational levels ($\chi^2 = 10.5$, P = 0.03), suggesting that risk perception to mercury exposure was associated with education level.

7.3.5. Re-examining gender influences

Figure 7.8 compares the gender differences in demographic variables, fishing frequency, and perception of risk of exposure to mercury from fish consumption in the survey population. While the age range of men partaking in fishing activities were wider, spanning 18 to 65 years, most of the women fishing were younger. Of the 36% of survey participants in the 26 – 35 years age bracket, 23% were women, accounting for 70% of women in the survey population. This difference between the genders was significant ($\chi^2 = 10.1$, P = 0.02). This is important when we consider that women of this age group are particularly vulnerable to mercury exposure, and subsequent effects on the fetus, and infants.

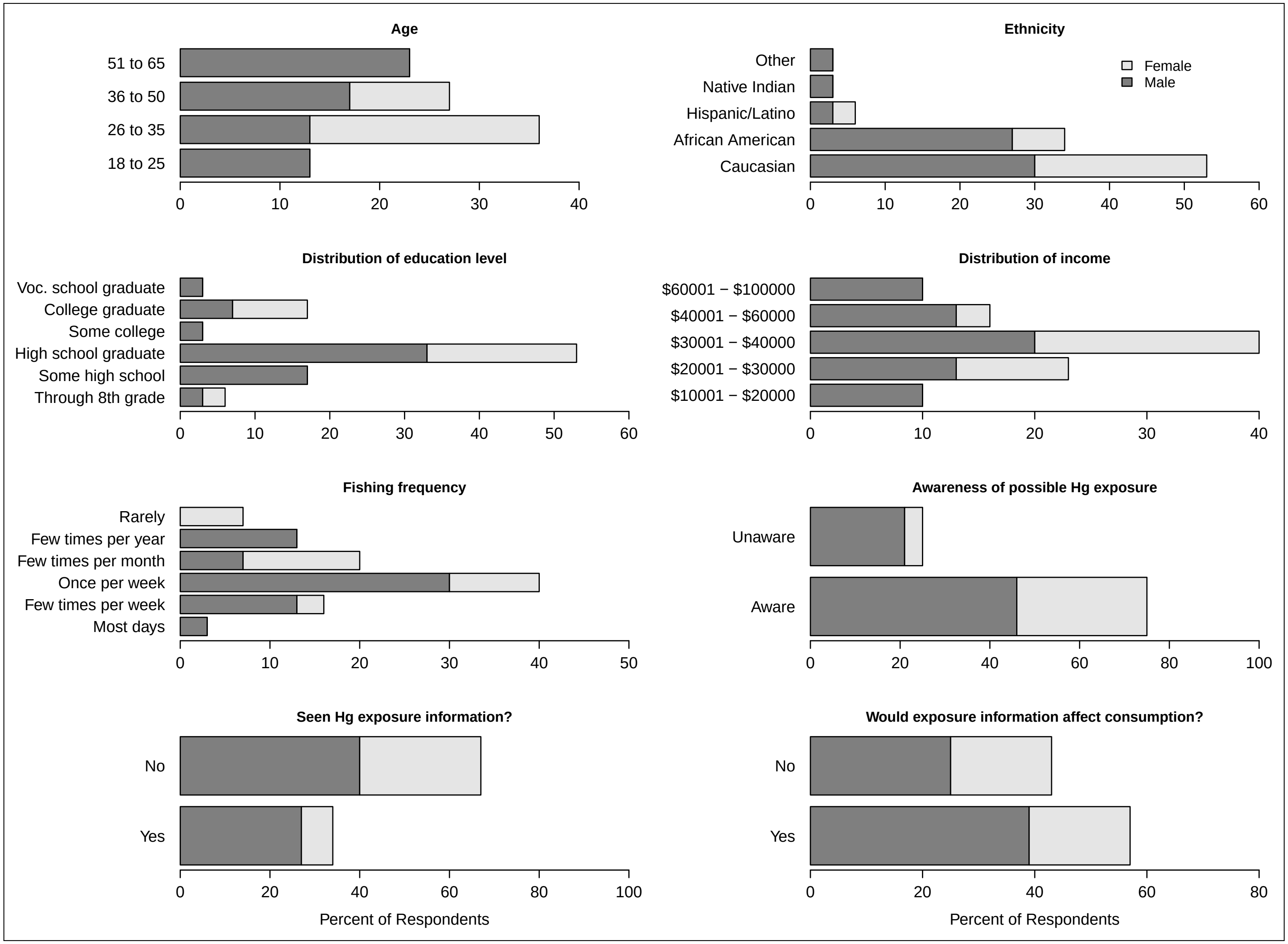


Figure 7.8. Gender differences in demographic variables, fishing frequency, risk awareness, and risk perception in the survey population.

More white women fished than all the other ethnicities combined, however no significant differences were observed between ethnicity and gender. The distribution of education level indicated that, on average, women in the study tended to have a higher level of education than men. A larger fraction of women were college educated when compared with men of the same educational bracket. Additionally, 90% of women in the study had high school education or higher as compared to less than 70% of men. Women reported a narrower income range ($20,000 – $60,000) than men, with 70% of the female population earning in the higher range of this bracket. Overall, average income for women was not significantly different than that for men.

Men tended to fish more often than women overall. 40% of the women interviewed reported fishing once per week or more frequently, with the remainder reportedly fishing as little as a few times per month or rarely. Conversely, 70% of the male fishing population fished as frequently as once per week or more. However, gender specific differences in fishing frequency were not revealed in statistical tests ($\chi^2 = 10.3$, $P = 0.06$).

Larger fractions of both genders expressed awareness of possible mercury exposure from consumption of certain fish species, however, more women were aware of the risk of exposure than men were. 88% of women said they were aware of possible exposure as compared to 68% of men, not accounting for sample size. No gender difference was found in the population awareness of possible exposure to mercury from consumption of certain fish species. The gender differences observed in awareness to exposure from consumption is puzzling when we look at responses from population when asked if they had seen informational guidelines on fish consumption and the risk of mercury exposure. While both genders had greater fractions of their respective populations reporting not seeing any information, less women reported seeing exposure risk information than men. This seems counter to the trend observed in gender differences for population awareness.

Examination of gender differences for population perception of risk of exposure to mercury from fish consumption revealed that males perceived a greater risk of exposure than females. 61% of males revealed that knowledge of the risk provided by fish consumption effected a change in their consumption behaviors, while 39% said they instituted no change

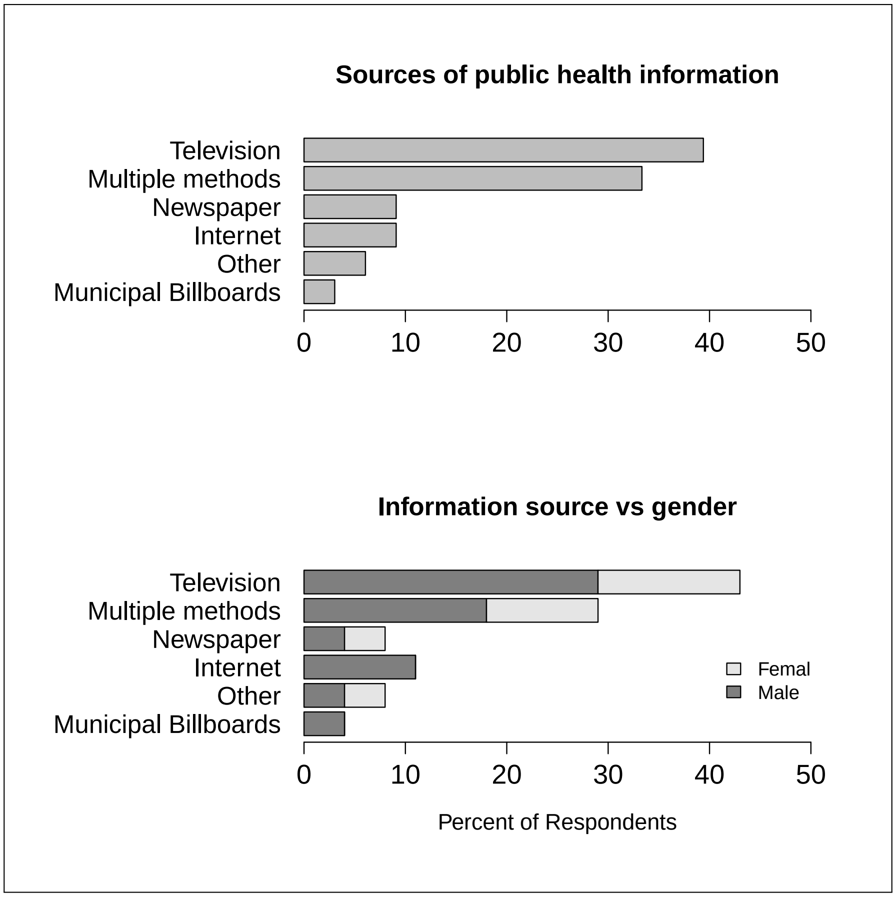


Figure 7.9. Distribution of public health information sources utilized by the population.

in consumption behavior. Conversely, 50% of women said knowledge about exposure would change consumption behaviors while the other half said it would not. No significant difference was observed in risk perception to exposure between genders in the survey population.

Figure 7.9 gives the distribution of sources utilized by the population to access public health information. The most popular means of access to public health information was television broadcasts, while the least popular municipal billboards. There were no significant differences in source of public health information between genders.

7.4. Discussion

The data presented here suggests that the fishing public in Tampa Bay area recognizes that there are risks and benefits of consuming fish. However, little is known about their knowledge of the specific risks and benefits. For instance, whether information about portion sizes and consumption frequencies of specific species, and whether the risks associated with specific locations are known. It must be recognized that the survey administered was part of an exploratory study to understand population perception and did not attempt to quantify public knowledge of specific fish species likely to increase exposure, specific consumption guidelines, and water bodies under advisory.

It was interesting to note the responses from participants who were aware of the risks associated with consumption practices but did not report a change or adjustment of consumption behaviors. Respondents suggested that since they have been fishing and consuming fish for a long time (3 respondents suggested 10+ years), the benefits of fish consumption far outweighs the perceived risks. Additionally, participants suggested that the levels in fish were not sufficiently high enough to be harmful. This suggests that a gap exists between fisherfolk and the scientific community with respect to the scientific knowledge about fish consumption safety. As researchers have suggested [Kasperson et al., 1988; Slovic et al., 1979], this gap may be due to differences in the perception of the risk associated with consumption behavior rather than knowledge of the associated risks.

The results suggest that most of the survey respondents did not understand that mercury levels vary in fish as a function of size, age, and trophic level, such that older predatory fish are likely to contain higher levels of mercury than smaller non-predatory species. This is demonstrated by the fact that 50% of respondents make catch consumption choices based on the size of the catch, where there is preference for larger fish. Another 25% of respondents had no preference, consuming whatever is caught. This suggests that there is a need for public health policies aimed at educating the public about the relationship between mercury exposure, fish size, age, and trophic levels. It's important to communicate that reducing the risk of mercury exposure from fish consumption practices does not necessarily require a reduction in consumption rate of all fish, but rather a change in the fish species and sizes consumed [Burger et al., 1998; Burger and Waishwell, 2001].

While a larger fraction of the population may have been aware of the likelihood of mercury exposure from consumption of fish (57%), a relatively smaller fraction have seen informational guides about fish consumption and mercury, with only 34% reporting that they did. This suggests that there is room for improvement in public health programs that address population assess to health information. Consumption advisories generally target women of child-bearing age because of the developing fetus, however, it was observed that fewer women have seen mercury exposure literature such as advisories and other public health consumption guidelines.

8. Summary and Recommendations

8.1. Summary

Through this dissertation I explored the relationships between mercury use and release in the Tampa Bay area, atmospheric mercury deposition phenomenon, and population susceptibility to mercury from fish consumption practices. The overarching goal of this research was to identify areas in the mercury use, release, and exposure cycle that may be leveraged to inform mitigation strategies for the reduction of population mercury exposures in the Tampa Bay area. To achieve this goal a multifaceted approach was employed by combining methods of environmental pollution assessment, including estimation of mass release rates, estimation of mercury mass deposition, source apportionments studies for source identification, and population survey analysis for susceptibility exploration.

For the first aim of this research, I investigated the trends in mercury use and release in the Tampa Bay area. This analysis was divided into two sections. First, I quantified the releases, and the distribution of the released mercury derived from products and process used in the Tampa Bay area. This was accomplished by building a spreadsheet-based mercury use and release inventory utilizing a hybrid Systems Flow Analysis - Industrial Ecology approach. Mercury mass flow rates and distributions amounts were based on published release rates and distribution factors, or calculated from bulk data, and apportioned for the domain. The inventory compared mercury releases for the inventory years 2000, 2006, and 2011. Results indicated that mercury releases from dental facilities and industrial sources may be the most important sources of mercury to the Tampa Bay area. Furthermore, the solid-waste pool was the most important sink in the domain. The inventory compared well with similar studies for most of the release categories compared.

As releases to air had previously been found to contribute substantially to overall releases, I also focused on investigating trends in regional and local mercury emissions, by analyzing the USEPA National Emissions Inventory. The focus of this was to explore whether significant changes had occurred across reporting periods for several emissions categories, and to identify the major source categories or facilities contributing to mercury emissions in the Tampa Bay area. Results indicate that coal-fired power-plants were the largest contributors of mercury emissions in the Tampa Bay area. Medical and municipal waste incineration also accounted for substantial fractions of total mercury releases to the domain. Emissions from sources in Hillsborough County accounted for a substantial portion of mercury emissions in the region and state.

For the second aim of this research I investigated the sources accounting for mercury deposition to the Tampa bay area. Characterizations of the amounts of mercury that is locally deposited to specific ecosystems and geographical areas, especially locations adjacent to large urban or industrial areas, is important since research shows that a significant portion of total mercury emitted from these sources is of the soluble reactive form . This reactive form of mercury is expected to be removed from the atmosphere on a relatively shorter timescale, resulting in deposition processes occurring within 100 km from the source, characterized here as *local scale* effects. It also is important that emphasis be placed on characterizing local releases considering the fact that regardless of form emitted, mercury has the potential to undergo chemical conversions within all domains of the environmental to form species that threaten human and environmental health.

Source apportionment for atmospheric mercury deposition in Florida is poorly resolved, with conflicting accounts in the scientific literature, and may be detrimental to adequate control at all management levels. To understand source contributions to wet deposited mercury in the Tampa bay area, I analyzed trends in mercury deposition data, collected wet deposition samples for mercury and trace metals determination in the Tampa Bay area, performed back-trajectory meteorological modeling, and applied statistical receptor modeling based on a Tampa special-site metals deposition data, and on the data collected by the wet deposition campaign.

This analysis was divided into two parts. First, I analyzed measurement data relevant to the Tampa Bay area through the Mercury Deposition Network air quality monitoring sites for multi-year trends in mercury deposition. Additionally, mercury and trace metals data, measured through the Bay Regional Atmospheric Mercury Experiment (BRACE) in 2001, at a site in Tampa, was analyzed to investigate source influences on the special site data. Specifically, I performed back-trajectory modeling to determine air mass trajectories corresponding to specific mercury wet deposition event days. Statistical receptor modeling, utilizing the Positive Matrix Factorization model, was also performed on this special site data to explore source influences on mercury deposition events.

In the second part of this analysis, I investigated the deposition and sources of mercury to the Tampa Bay area utilizing new measurement data I collected in the Tampa Bay area in 2012. The collection of new speciated data was done to investigate differences in time in emission sources influencing mercury deposition to the Tampa Bay area. This was achieved by the collection of wet-only deposition samples over the period July to December, 2012, for the determination of mercury and trace metal amounts. Similar analyses were performed for this data.

Results from the analysis of wet deposition data indicated that event mercury concentration was weakly correlated with event precipitation depth for both studies. This suggest that dilution/concentration effects may not play a role on the event mercury concentrations observed, and suggests a large or quickly replenished reservoir of oxidized mercury in the local atmosphere. Results from back-trajectory also showed good agreement between the two studies. The results indicated that high mercury concentration events had air mass with trajectories consistently over Florida land, with previous high precipitation depth events over the trajectory. This suggest the likely influence of Florida sources on high mercury deposition events observed here. Results from statistical receptor modeling differed between the measurement periods. The 2001 BRACE data was resolved to 11 sources, of which four were shown to account for mercury species mass in the deposition data, and included coal combustion (52%), municipal waste incineration (23%), medical waste incineration (19%), and crustal material (6%). Contribution from the medical waste sector was found to be consistent with the data from the EPA National Emissions Inventory, which indicated elevated mercury emissions from medical sources in the region for the period. The 2012 USF data was resolved to 7 sources, of which four were shown to account for mercury species mass in the deposition data. The sources were identified as coal combustion (76%), agrochemicals (11%), metal smelting (7%), and crustal material (7%). The medical waste signature was not present here, consistent with the substantial decrease in emissions as reported by the NEI for the medical sector for the period. Overall, coal combustion processes were found to be the most important emission sources contributing to mercury in wet deposition in the Tampa Bay area, with both measurement periods showing good agreement.

The third aim this dissertation was to understand the factors determining population vulnerability to mercury exposure from fish consumption practices by fisher-folk in the Tampa Bay area. To elucidate the factors influencing fish consumption behaviors of the local angler population I analyzed population surveys collected from fisher-folks along the Hillsborough River, in Hillsborough County, Florida. Results from the survey analysis suggests that while the fishing public recognizes that there are risks of mercury exposure associated with fish consumption, little is known about the specific risk associated with portion sizes, consumption frequencies, and fishing location for various fish species. Furthermore, the results suggests that survey respondents may not understand the underlying theory of bioaccumulation and biomagnification with respect to the concentration of mercury in fish tissues since most respondents considered catch size (larger being better) as the predominant factor determining consumption decisions. Finally, a relatively small portion of the population reported seeing informational guide about fish consumption and mercury exposure, suggesting that deficiencies exist in current public health initiatives to inform the public about likely exposures to mercury from fish consumption practices.

8.2. Answers to scientific questions

Here I recap the scientific questions presented at the beginning of this dissertation, and discuss how the results of my work contributed to answering each.

- What are the important release sector(s) (product or process) contributing to environmental mercury releases in the Tampa Bay area?

Results from the mercury release inventory indicates that industrial releases and dental facilities were the largest sources of mercury to the Tampa Bay area. The greatest rate increase over the inventory years was seen for industrial sources, going from 340 $\mathrm{kg\,yr^{-1}}$ in 2000 to 1054 $\mathrm{kg\,yr^{-1}}$ in 2006. Industrial releases from sources in the domain was derived from USEPA's Toxic release inventory, and was reported as direct releases to environmental pools. Facilities that report to TRI are typically larger facilities involved in manufacturing, metal mining, electric power generation, chemical manufacturing and hazardous waste treatment. Substantial contributions to mercury mass were also observed from dental facilities, and households in the region.

- What are the important direct environmental sinks for mercury releases in the Tampa Bay area?

Results from the mercury release inventory identified the solid-waste pools as the largest sink for direct mercury releases in the region. We observe a decrease in fractional distribution to the atmospheric pool across inventory years, with air distribution factors of 0.47, 0.31, and 0.1 for the 2000, 2006, and 2011 inventory years respectively. Conversely, we observe and opposite trend in the distribution factor for the solid-waste pool, which showed an increasing trend of 0.52, 0.68, and 0.9, for the 2000, 2006, and 2011 inventory years respectively. These trends also coincided with an increase in releases from the sector and demonstrates a shift of the source sink that may be a response of increased emissions regulations. Secondary processing of solid waste represents a substantial source of atmospheric mercury emissions, thus the fraction of releases to the solid waste pool may be overestimated.

- What are the important emission source categories contributing to mercury releases in the air-shed, and what are the long term trends in these emissions?

From my analysis of the EPA National Emissions Inventory, mercury emissions trends indicate that electric utilities, especially coal-fired power-plants, are the largest contributors to mercury emissions in the Tampa Bay area, and the state. Mercury emissions from coal-fired power plants accounted for 28% (1999), 50% (2002), 54% (2005), and 41% (2008) of total mercury emitted in the state. This trend was repeated at the regional level where this source category contributed approximately 28% of regional mercury emissions in the 1999 inventory year, 50% in the 2002 inventory year, 54% in 2005, and 41% in the 2008 inventory year. Additionally, contributions from point sources dominated state and regional releases, accounting for greater than 90% of mercury emissions over all states and for all inventory periods.

- What are the sources contributing to mercury deposition to the Tampa Bay area?

Results from wet deposition studies, and statistical receptor modeling indicate that coal-fired power generation facilities accounts for a substantial fraction of mercury (50% to 75%) in wet deposition impacting the Tampa Bay area. Emissions from medical waste combustion facilities were significant in the BRACE data analysis (19%, 2001 data), but did not show up in the USF data analysis (2012 data). Municipal waste incineration, agrochemicals, and crustal material were as resolved as significant mercury emissions sources.

- What is the significance of local emission sources to local mercury deposition events?

Results from the analysis of wet deposition data indicated that event mercury concentration was weakly correlated with event precipitation depth, with both studies showing agreement with this phenomenon. This suggest that dilution/concentration effects did not play a role on the event mercury concentrations observed, and suggests a large or quickly replenished reservoir of oxidized mercury in the local atmosphere. Results from backward trajectory modeling of the event data suggest the likely influence of Florida sources on high mercury concentration events studied here. Both datasets analyzed here show good agreement. We observed that high mercury concentration events coincided with air mass trajectories that consistently tracked over Florida landmass. Additionally, we observed high mercury concentration events with trajectory over Florida landmass, with high precipitation depth events over the course of the trajectory, suggesting that mercury species reaching the receptor are likely from air masses over Florida land, and possibly local to the receptor.

- What is the perception of the angler population in Hillsborough County to mercury exposure from fish consumption behaviors?

Results from the survey of the local angler population along the Hillsborough River suggests that the fishing public in Tampa Bay area recognizes that there are risks and benefits of consuming fish from the Hillsborough River and other fishing locations. A significant fraction of the population expressed being aware of likely risk of mercury exposure from fish consumption practices. However, a larger fraction expressed that awareness does not affect their consumption habits. The perception of risk to mercury exposure from fish consumption was found to be statistically associated with education level.

- What characteristics of the fishing population may predispose it to mercury exposure from fish consumption habits?

Results from the population survey indicated that the perception of risk to mercury exposure from fish consumption was found to be statistically associated with education level. Awareness of the function of size, and trophic level on fish tissue mercury concentration was not demonstrated among the population. This was revealed by the fact that 50% of respondents make catch consumption choices based on the size of the catch, where there is preference for larger fish. Cultural factors seems to be at play here. Respondents suggested that since they have been fishing and consuming fish for a long time the benefits of fish consumption far outweighs the perceived risks. Additionally, participants suggested that the levels in fish were not sufficiently high enough to be harmful based on their knowledge of fish species.

8.3. Recommendations for future work

Through this dissertation, I have studied the relationships between mercury use, release, and population exposure in the Tampa Bay area. I have identified the sources accounting for significant mercury releases in the region, and have compiled substantial evidence implicating local emission sources in local mercury deposition phenomenon. Additionally, I have explored the factors affecting population mercury exposure through fish consumption practices. Here I discuss additional work that may be needed to improve the findings discussed previously.

I quantified mercury releases in the region by implementation a spreadsheet-based mercury use and release inventory. Several uncertainties exists in the development of this inventory. The mercury mass releases allocated to several categories were not based on source emission data specific to the Tampa bay area, but was derived from bulk regional data and factored based on relative population of the region (top-down approach). This reduces the accuracy of the values allocated to these release sectors. Additionally, some distribution and emission factors used were not specific to release activities in the Tampa Bay area, but was adopted from similar peer-reviewed mercury inventory studies. Thus there may be some inherent uncertainties associated with their use. Improvement of quantification of mercury releases from sources in the Tampa Bay area requires a more detailed approach and an increase in the quality of mercury use data. Release and distribution factors need to be improved to reflect the activities of the region. Additionally, I had little information about recycling efforts in the region, thus the amount of mercury apportioned to recycling efforts in the region may be underestimated.

We combined meteorological back-trajectory modeling with source apportionment modeling, via PMF, to assess source contributions to locally deposited mercury. This work can be improved by applying hybrid receptor models to better elucidate source influences. Hybrid receptor models combines statistical receptor models with meteorological models to resolve types and geographical location of sources. One such model is the Quantitative Transport Bias Analysis model [Keeler and Samson, 1989]. QTBA utilizes air mass back trajectories and observed meteorological data along with measured pollutant concentrations to identify sources. Gratz et al. [2013] recently applied QTBA to assess emission sources of atmospheric mercury in wet deposition across Illinois.

The population data analyzed to understand the factors determining population mercury exposure was derived from a survey administered as part of an exploratory study to understand population perception. Thus it did not seek to interrogate respondents of specific consumption characteristics and fish species awareness. Specifically the instrument did not attempt to quantify public knowledge of specific fish species likely to increase exposure, specific consumption guidelines for different fish species, and water bodies under advisory. This data is needed for assessment of deficiencies in current public programs to improve population awareness to mercury exposure from fish consumption practices.

8.4. Levers for reducing population exposures

We can apply the results and data generated here to identify levers for the reduction of mercury exposure of the population in the domain. Figure 8.1 simplifies the relationships between anthropogenic mercury use, release, and population mercury exposure as investigated by this study, highlighting areas of leverage for the reduction of population mercury exposure. I posit that the most significant areas to influence change in the mercury *use-release-exposure* dynamics is influencing initial mercury use, controlling anthropogenic releases, and reducing consumption behaviors.

The consumption of fish is the primary route of exposure to mercury, thus, the most important lever to reduce population exposure is to adjust consumption behavior of the population. Results here show that deficiencies exist within the population with respect knowledge of species, portion, frequency, and locations that safe for fish consumption behavior. There are inherent difficulties in communicating mercury exposure risks to the population due to socioeconomic and cultural variables.

As discussed in Chapter 3 mercury is consumed in a wide variety of products and processes in the Tampa bay area. Use of mercury in products consists of measuring and control equipment, electrical switches and relays, dental amalgams, light bulbs, batteries, and industrial processes. Measuring and control equipment, electrical switches and relays, light bulbs, and batteries are not considered to release mercury until they are disposed, except under circumstances where their integrity becomes compromised due to misuse. Therefore, their entry into the pathway is most often as a result of method of disposal. This significantly

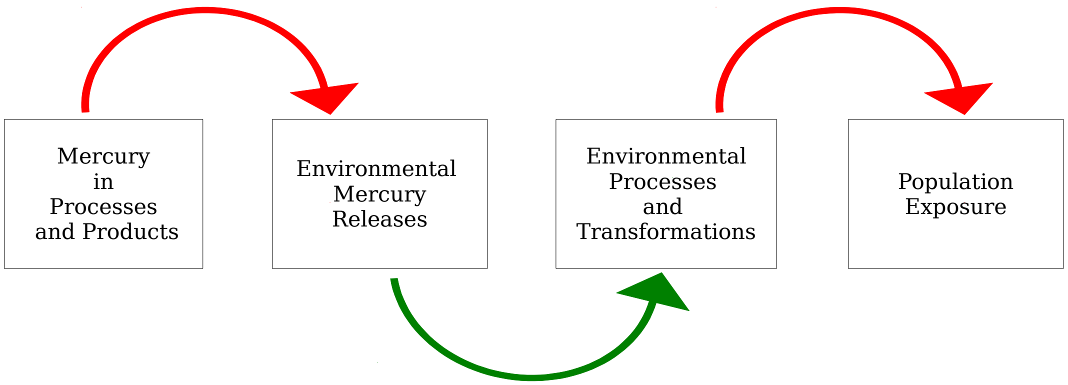


Figure 8.1. Simplified linear representation of the population mercury exposure pathway. The red arrows highlights areas of leverage for the reduction of population mercury exposure.

impacts the solid-waste and air environmental pools. Retrieval and recycling or proper disposal of mercury containing components in these product categories presents a significant barrier to entry into environmental cycles and subsequent population exposures.

The use of mercury in dental processes also presents a substantial contribution to environmental mercury releases in the Tampa Bay area, being significant for solid-waste and wastewater pools. Steps to reduce mercury releases from dental facilities include amalgam substitution, recycling of un-spilled amalgam fraction.

Industrial releases are derived substantially from the combustion of fossil fuels (coal, oil, and natural gas), with coal being the most significant contributor. Emissions from coal-fired was the single most important emission source in the region for the last decade, accounting for 50% of total mercury emissions. Reducing emissions from this sector would result in a significant reduction of mercury entering the exposure pathway. Current emission strategies include electrostatic precipitators (ESPs), fabric filters, and flue gas desulfurization (FGD) technologies, and primarily target divalent and particulate mercury species. Several policy options may be used to reduce mercury emissions from industrial processes, and include technology requirements emission performance standards, and emissions taxes.

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Appendix A.

Mercury inventory supplementary figures

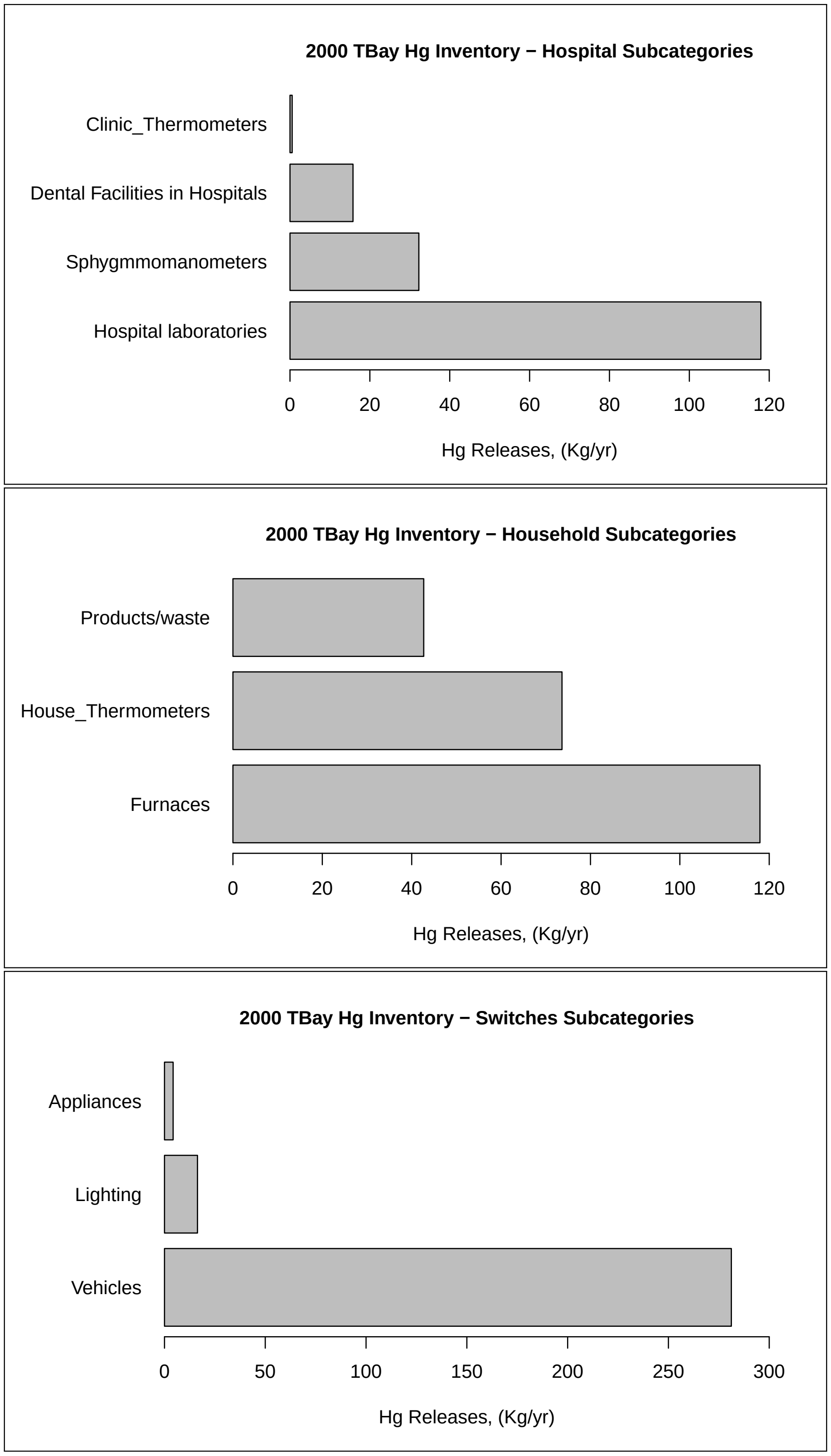


Figure A.1. Estimations of summary mercury releases by products and processes subcategories for the 2000 inventory period. The plot shows subcategories within Hospitals (top subplot), Households (middle subplot), and Switches (bottom subplot), respectively.

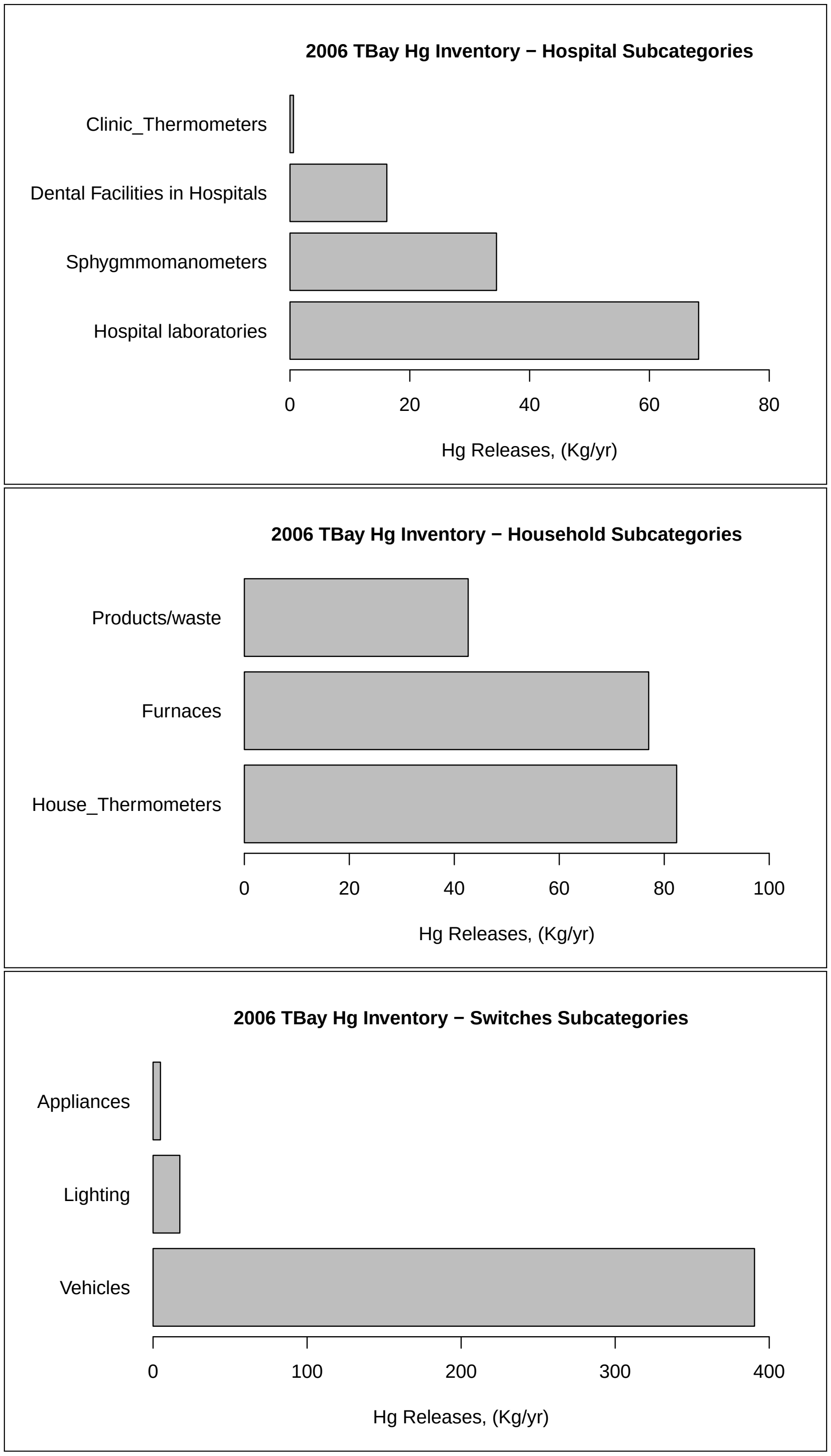


Figure A.2. Estimations of summary mercury releases by products and processes subcategories for the 2006 inventory period. The plot shows subcategories within Hospitals (top subplot), Households (middle subplot), and Switches (bottom subplot), respectively.

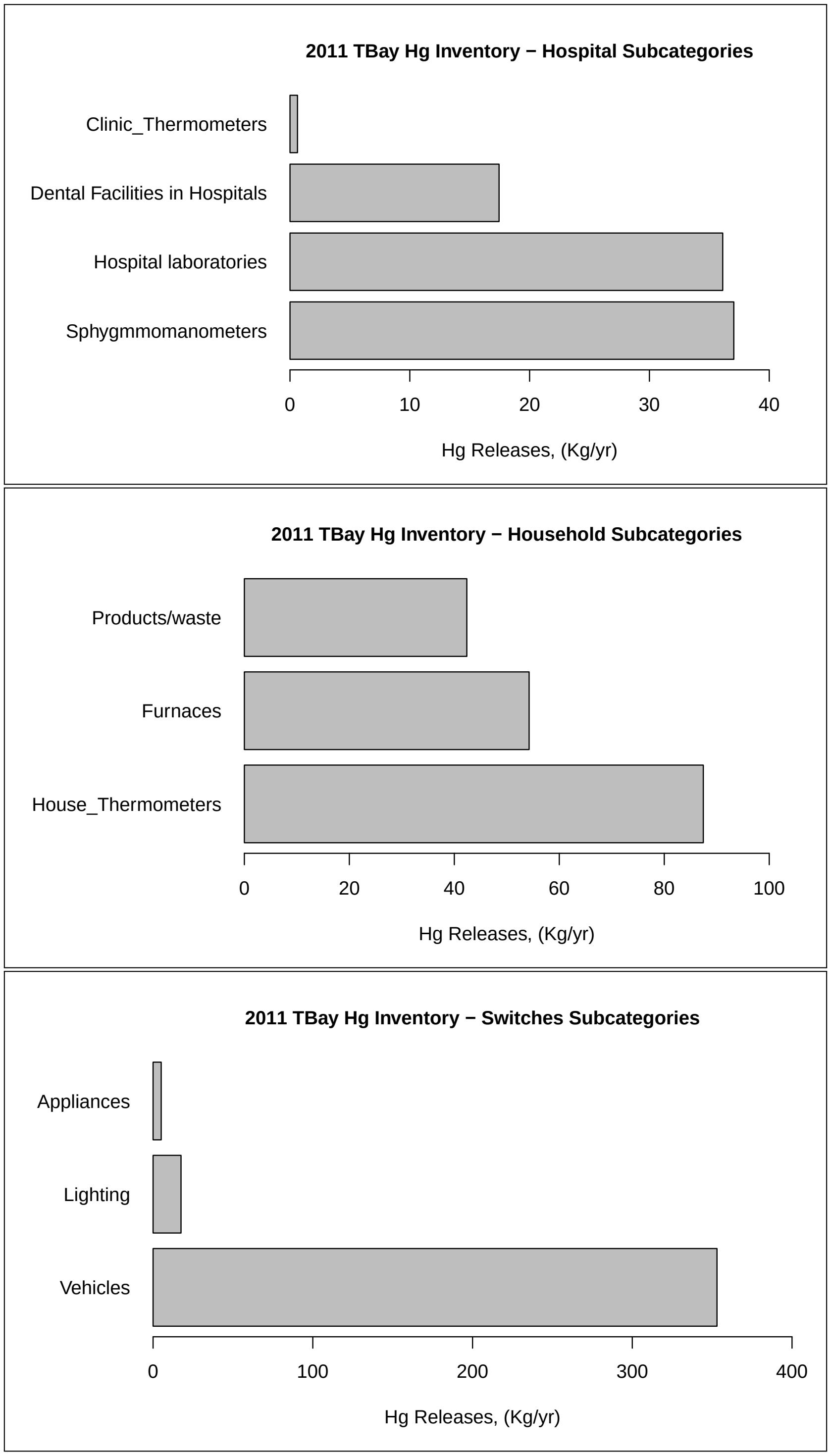


Figure A.3. Estimations of summary mercury releases by products and processes subcategories for the 2011 inventory period. The plot shows subcategories within Hospitals (top subplot), Households (middle subplot), and Switches (bottom subplot), respectively.

Appendix B.

Emissions trends analysis supplementary figures

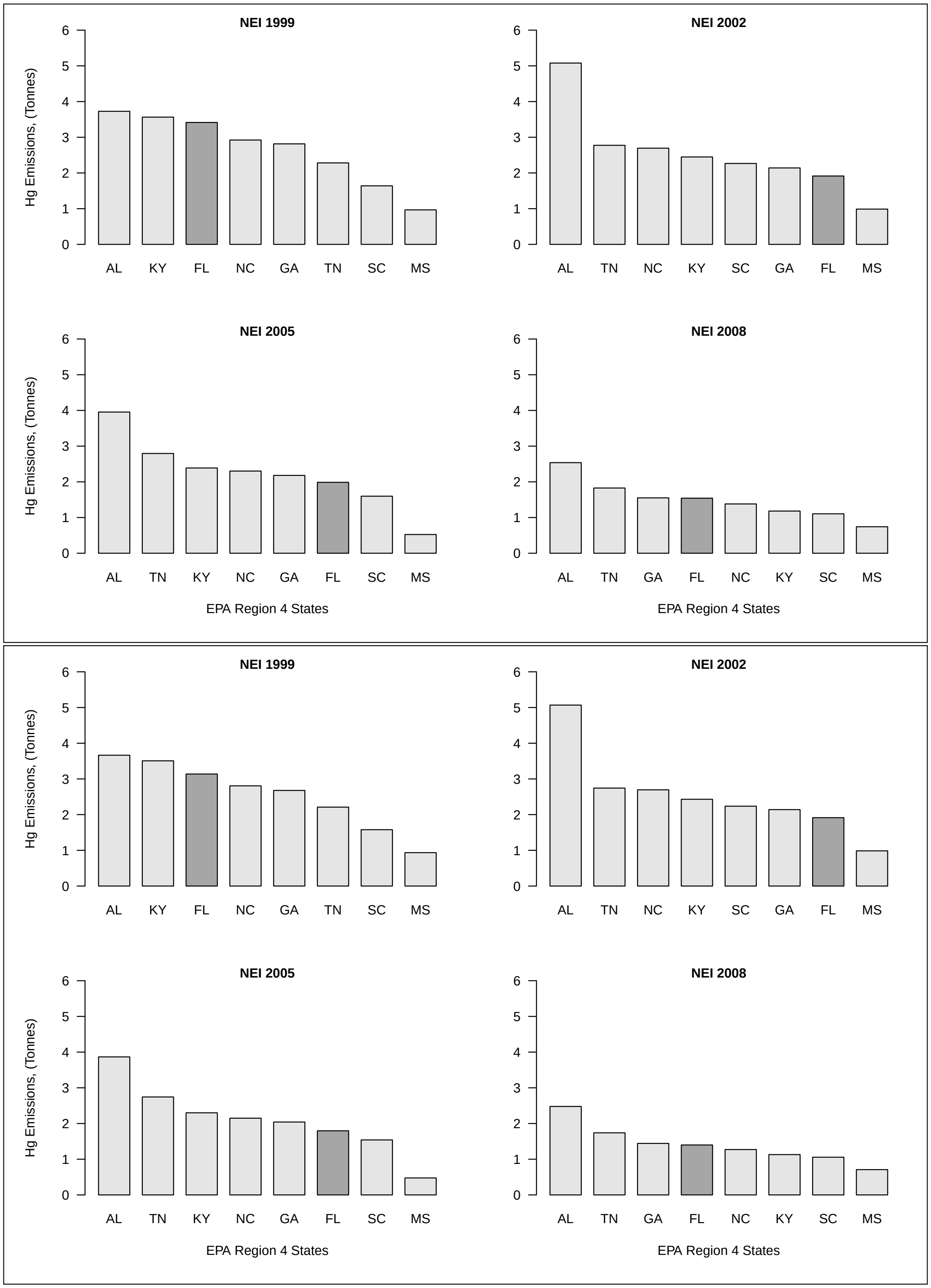


Figure B.1. Total (top subplot) and Point (bottom subplot) source emission summaries for EPA Region 4 states as compiled by the National Emission Inventories (NEI). The plot details NEI data from the 1999, 2002, 2005, and 2011 inventory years.

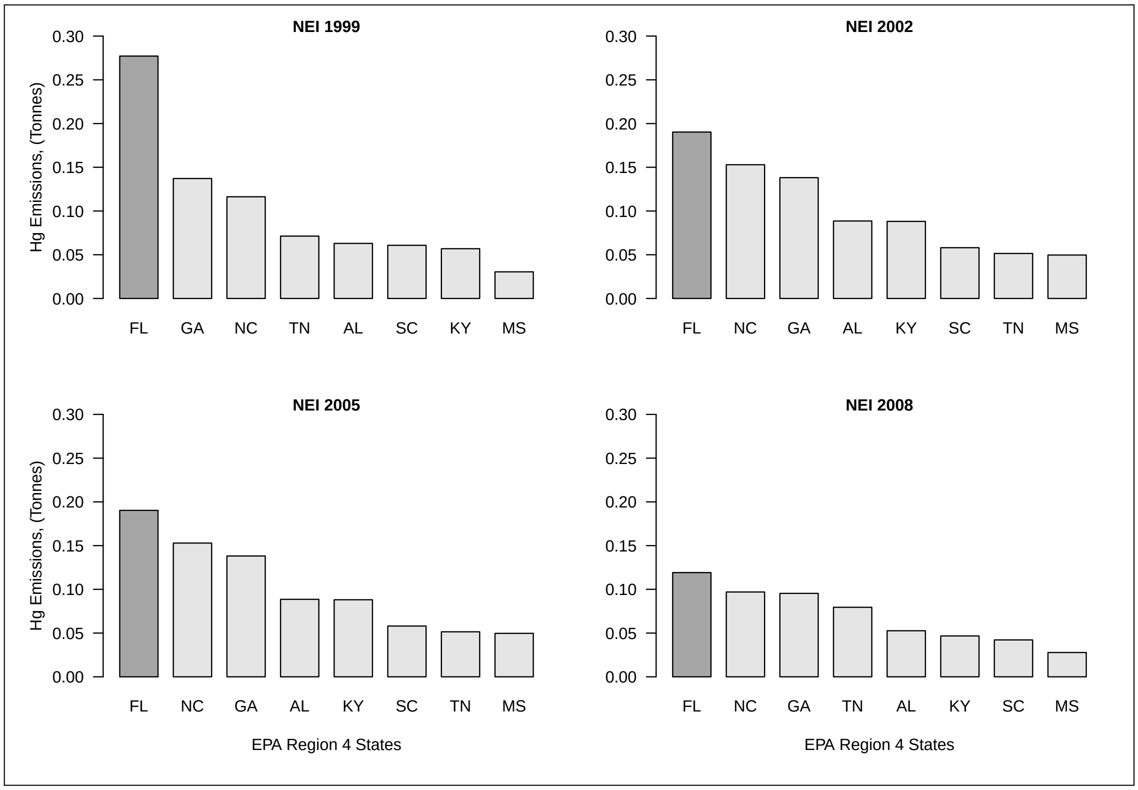


Figure B.2. Non-point source emission summaries for EPA Region 4 states as compiled by the National Emission Inventories (NEI). The plot details NEI data from the 1999, 2002, 2005, and 2011 inventory years.

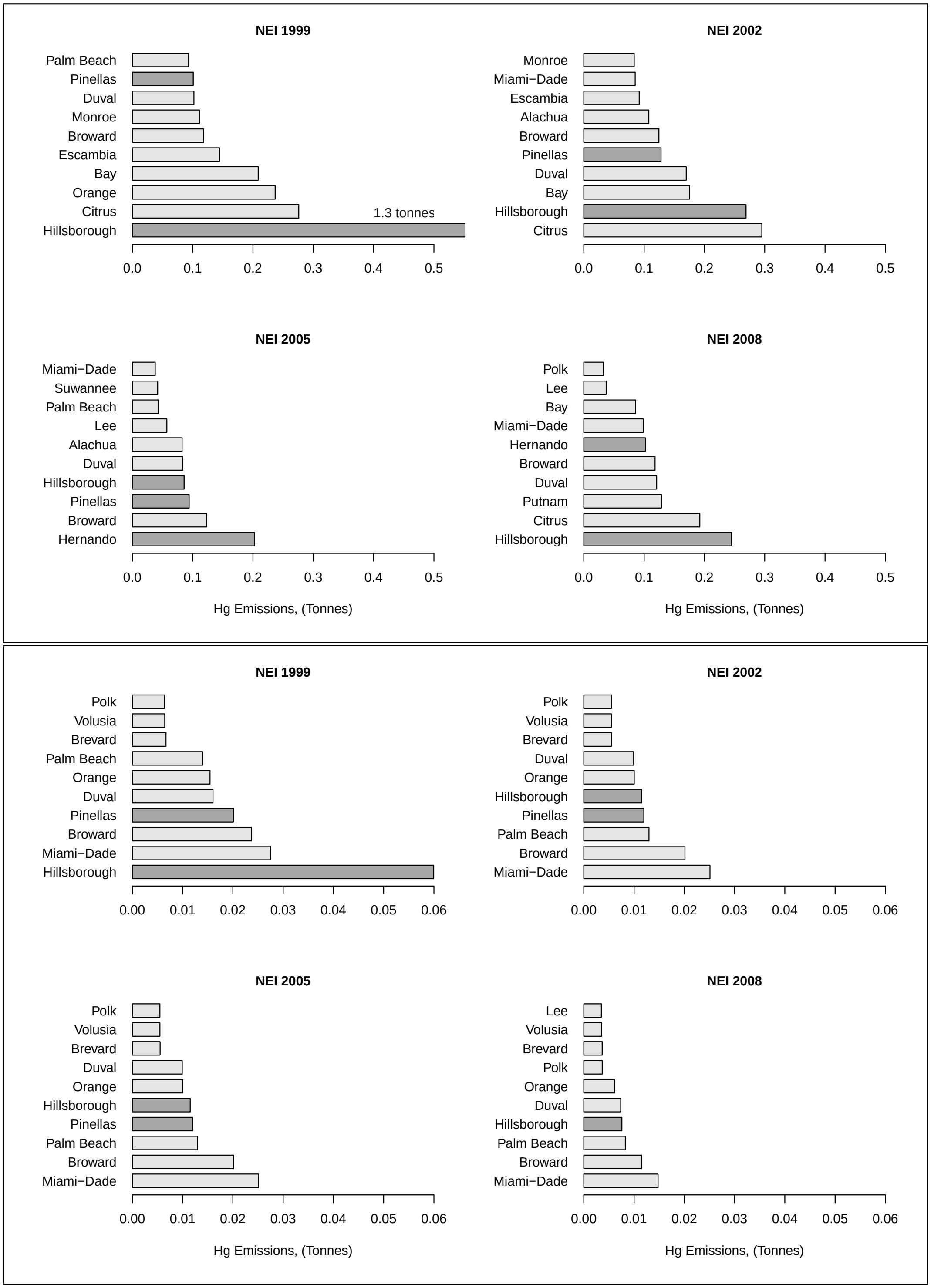


Figure B.3. Point (top sub-plot) and non-point (bottom sub-plot) source emission summaries for Florida counties as compiled by the National Emission Inventories (NEI). The plot details NEI data from the 1999, 2002, 2005, and 2011 inventory years.

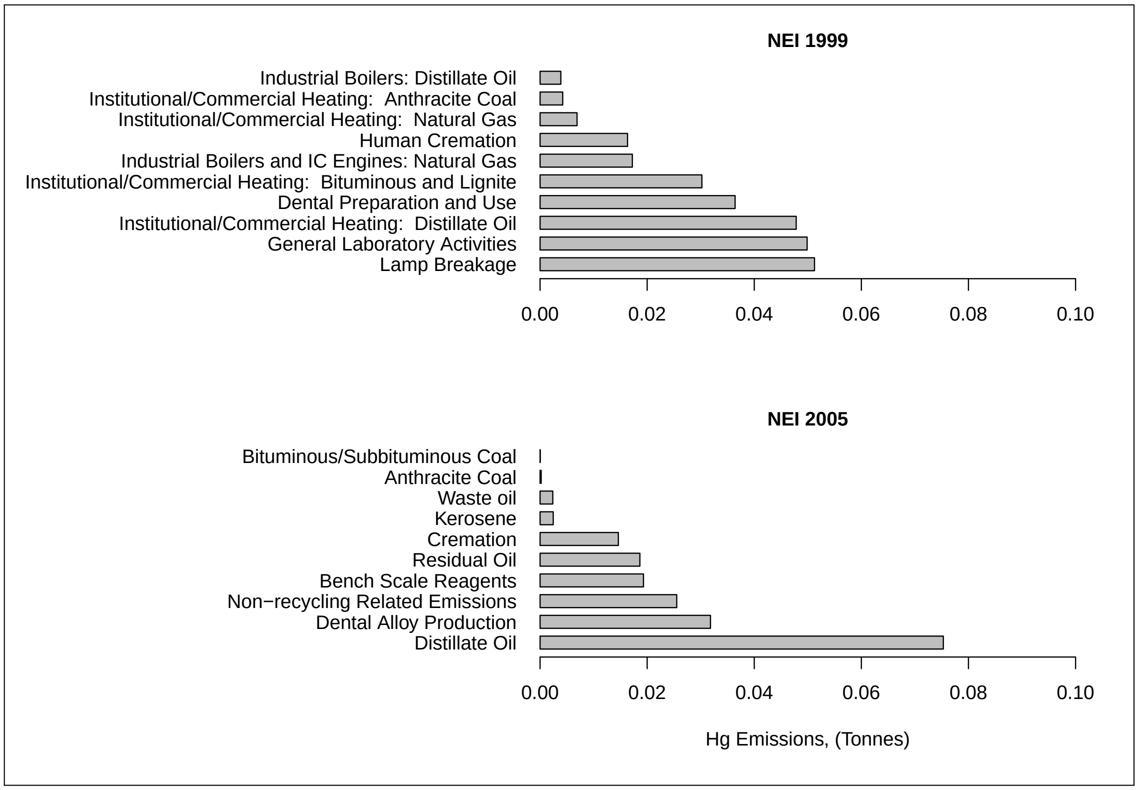


Figure B.4. Non-point source category emission summaries for Florida counties as compiled by the National Emission Inventories (NEI). The plot details NEI data from the 1999 and 2005 inventory years.

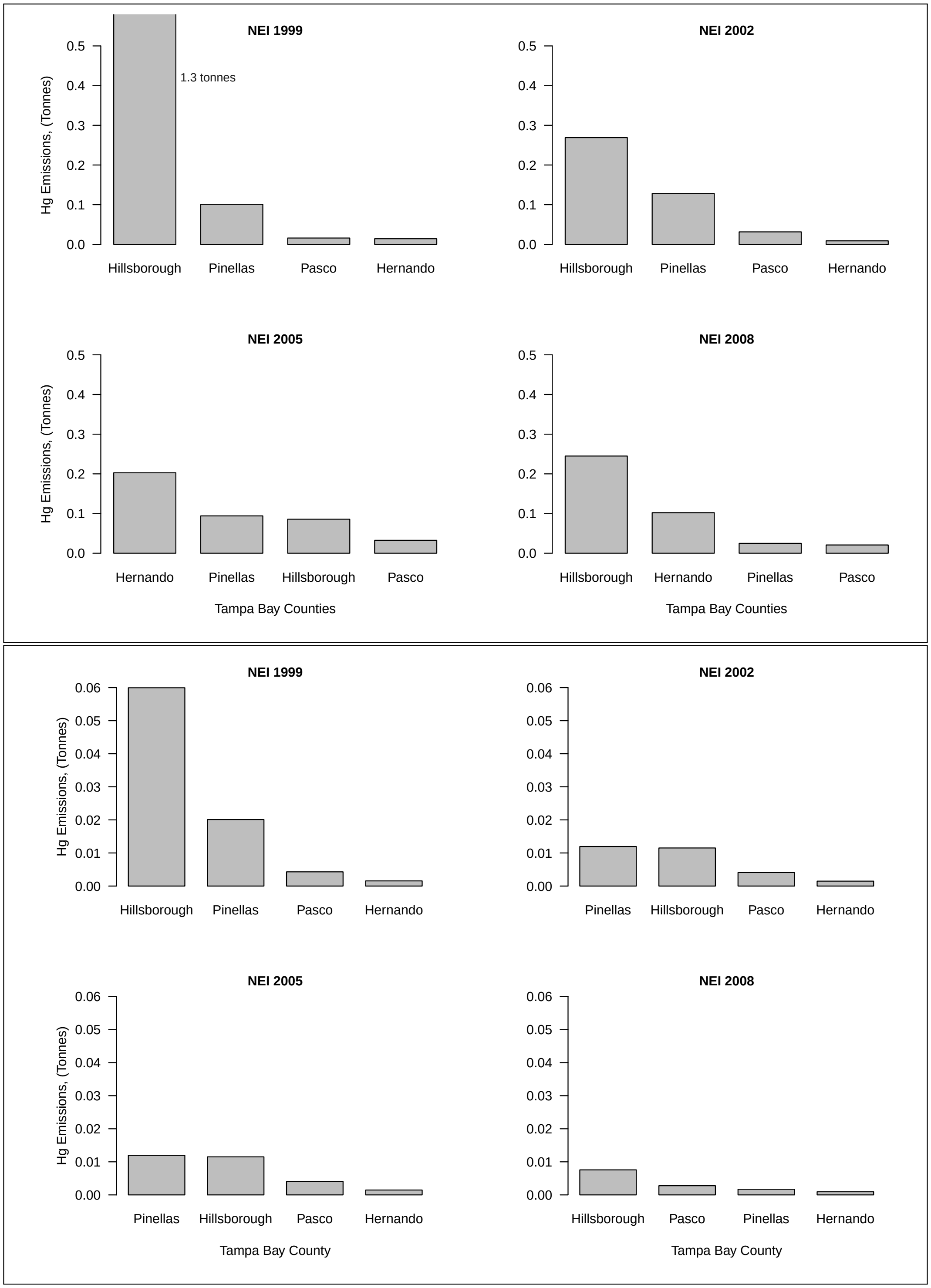


Figure B.5. Point (top sub-plot) and non-point (bottom sub-plot) source emission summaries for Tampa Bay counties as compiled by the National Emission Inventories (NEI). The plot details NEI data from the 1999, 2002, 2005, and 2011 inventory years.

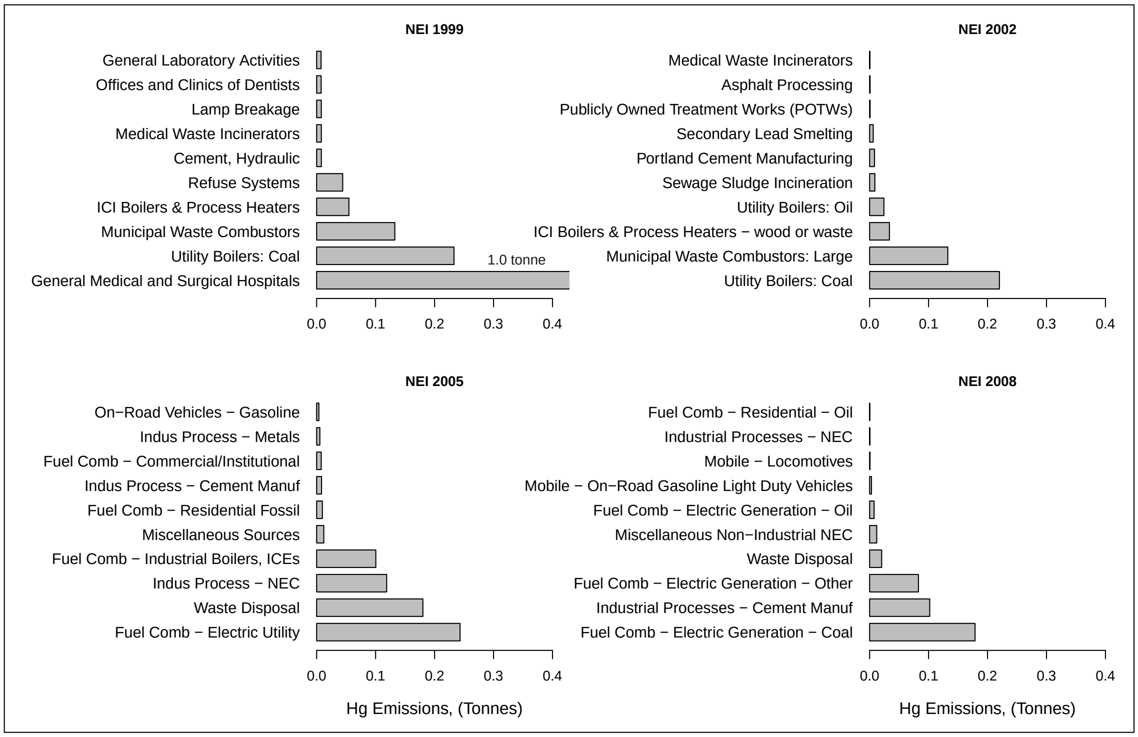


Figure B.6. Source category emission summaries for Florida counties as compiled by the National Emission Inventories (NEI). The plot details NEI data from the 1999, 2002, 2005, and 2011 inventory years.

Appendix C.

BRACE data analysis supplementary figures and tables

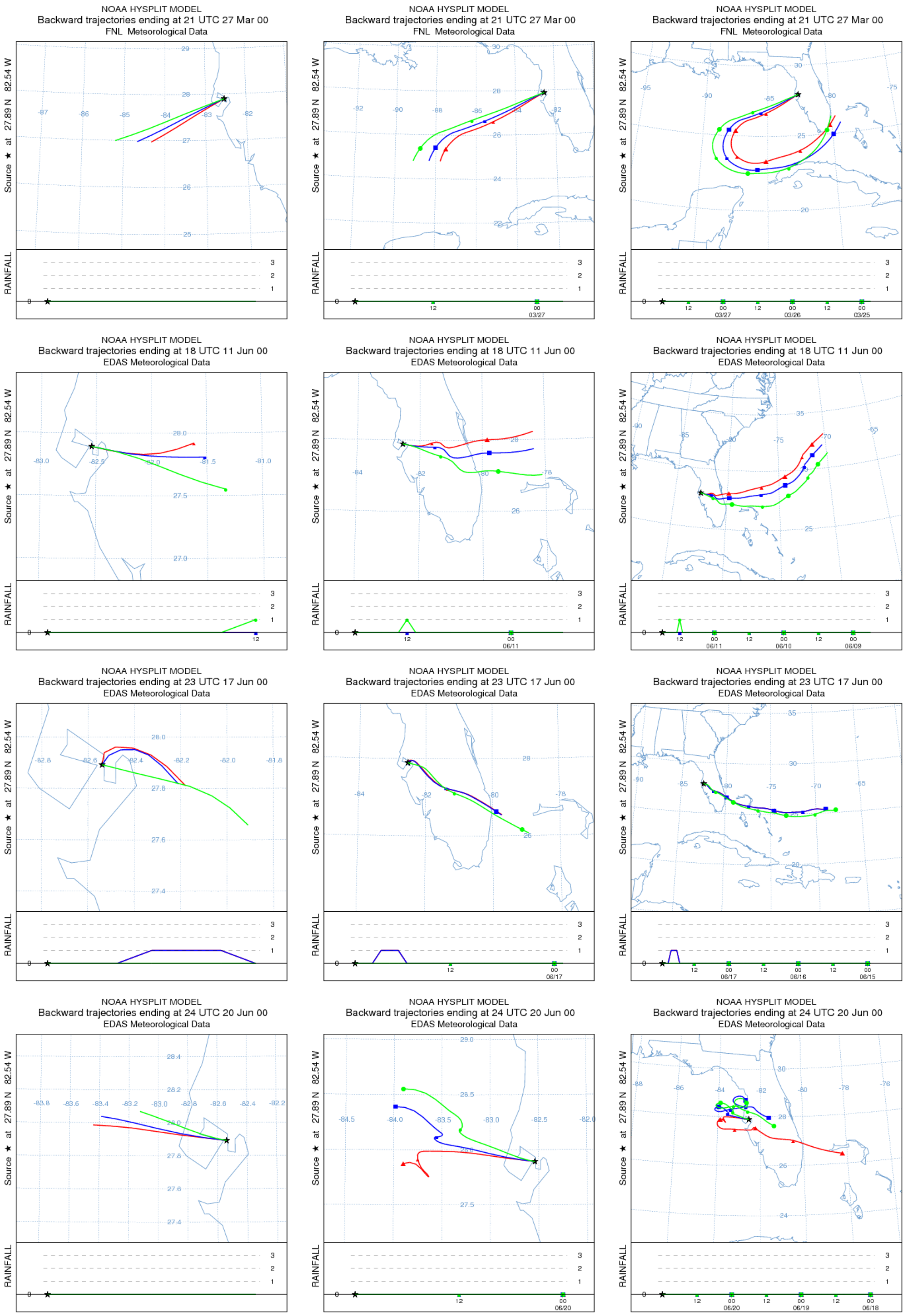
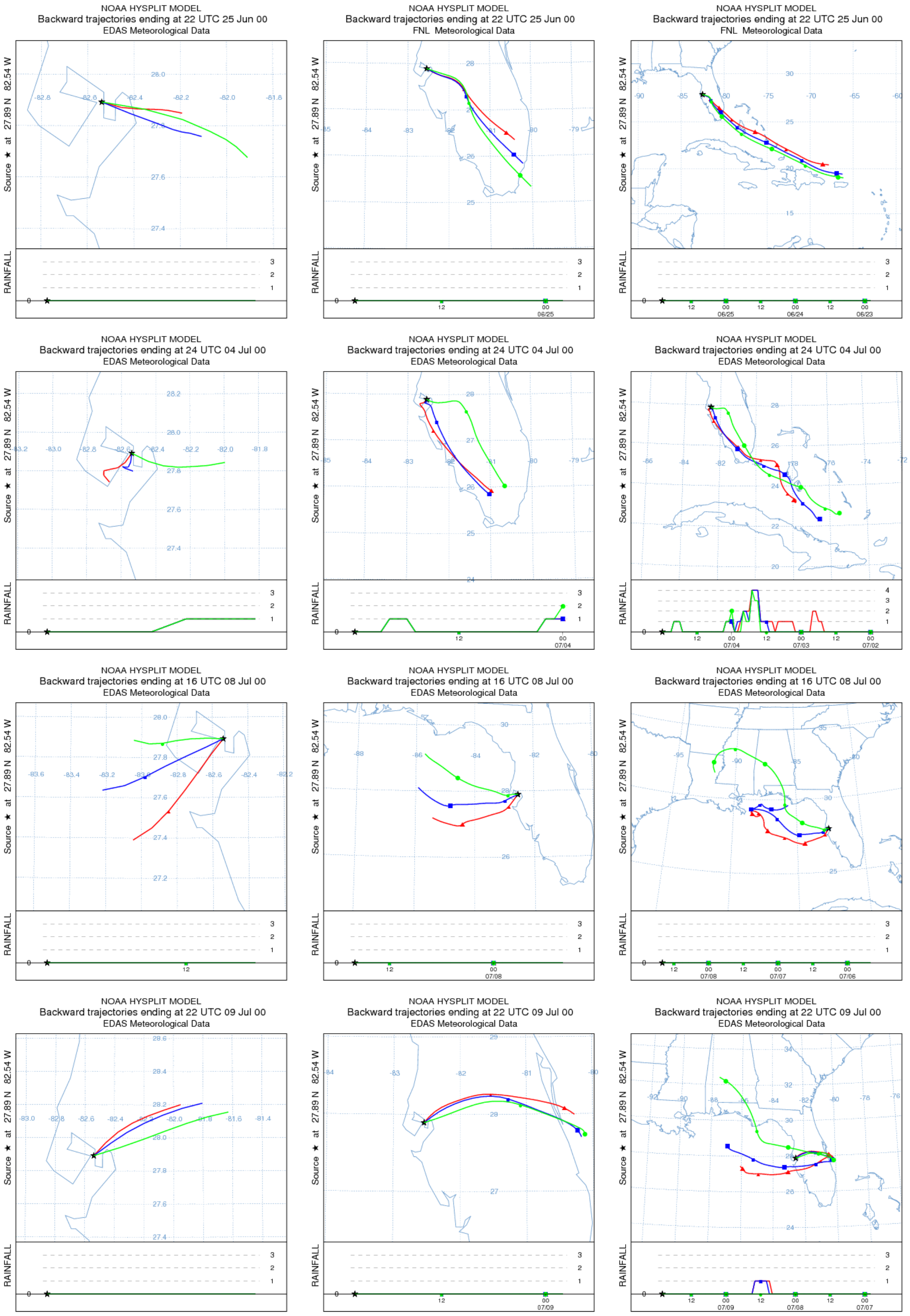


Figure C.1. Back trajectories for the BRACE deposition data for events occuring over the period March, 2000 – June, 2000. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).



NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 25 Jun 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 25 Jun 00
FNL Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 25 Jun 00
FNL Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 24 UTC 04 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 24 UTC 04 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 24 UTC 04 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 08 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 08 Jul 00
EDAS Meteorological Data

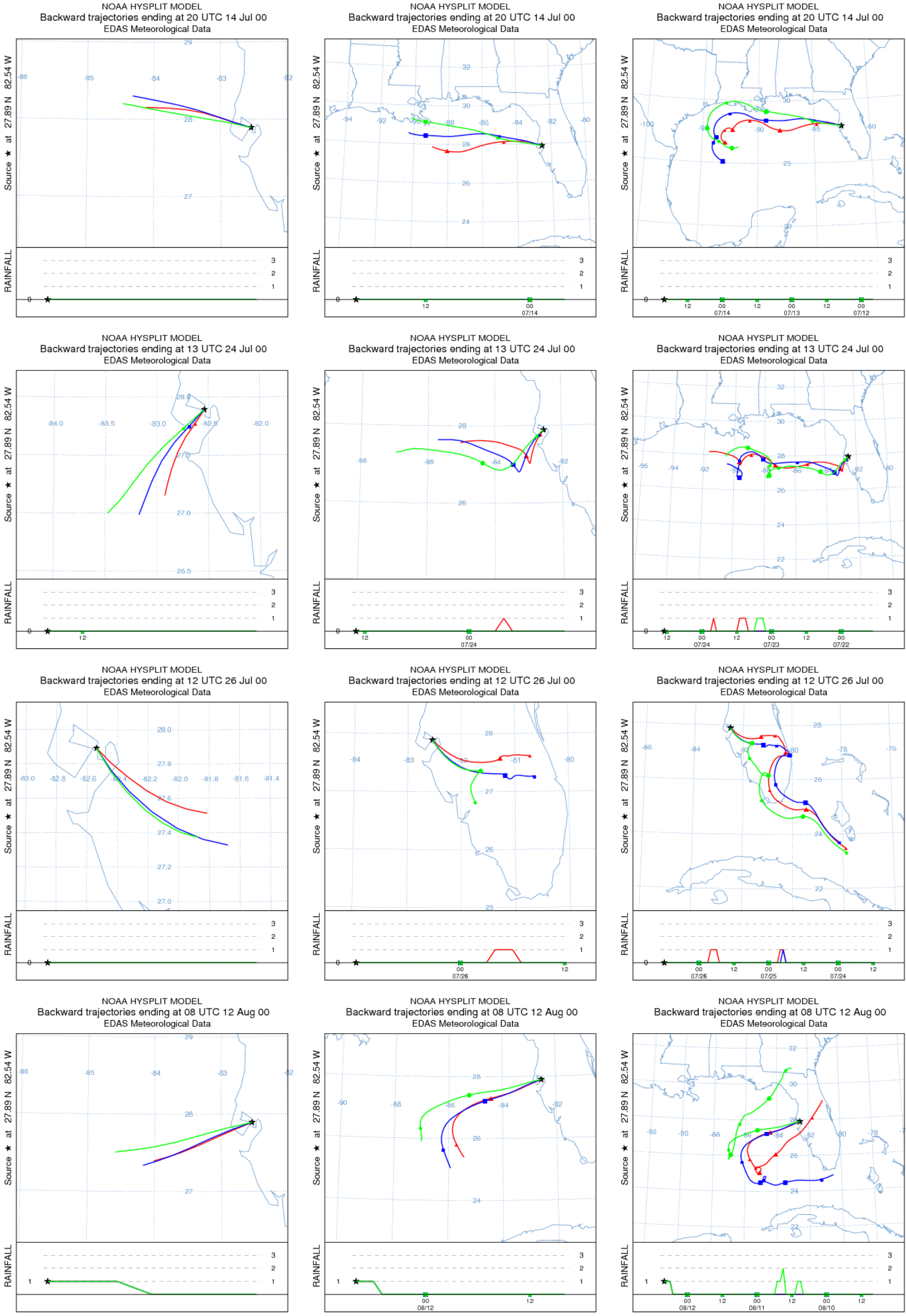
NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 08 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 09 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 09 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 09 Jul 00
EDAS Meteorological Data

Figure C.2. Back trajectories for the BRACE deposition events occuring over the period June, 2000 – July, 2000. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).



NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 14 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 14 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 20 UTC 14 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 13 UTC 24 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 13 UTC 24 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 13 UTC 24 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 26 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 26 Jul 00
EDAS Meteorological Data

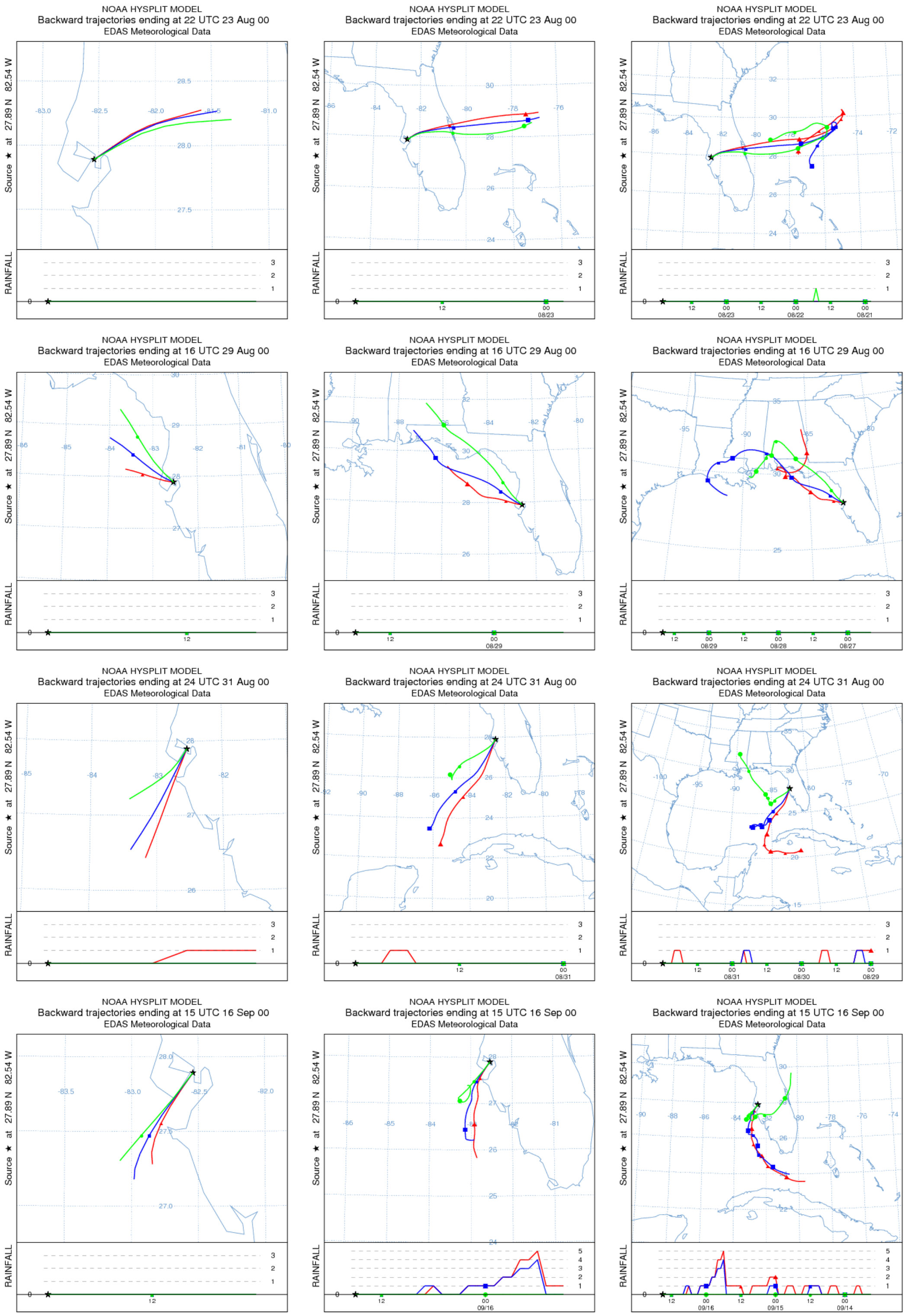
NOAA HYSPLIT MODEL
Backward trajectories ending at 12 UTC 26 Jul 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 12 Aug 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 12 Aug 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 08 UTC 12 Aug 00
EDAS Meteorological Data

Figure C.3. Back trajectories for the BRACE deposition events occuring over the period July, 2000 – August, 2000. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).



NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 23 Aug 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 29 Aug 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 24 UTC 31 Aug 00
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 15 UTC 16 Sep 00
EDAS Meteorological Data

Figure C.4. Back trajectories for the BRACE deposition events occuring over the period August, 2000 – September, 2000. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

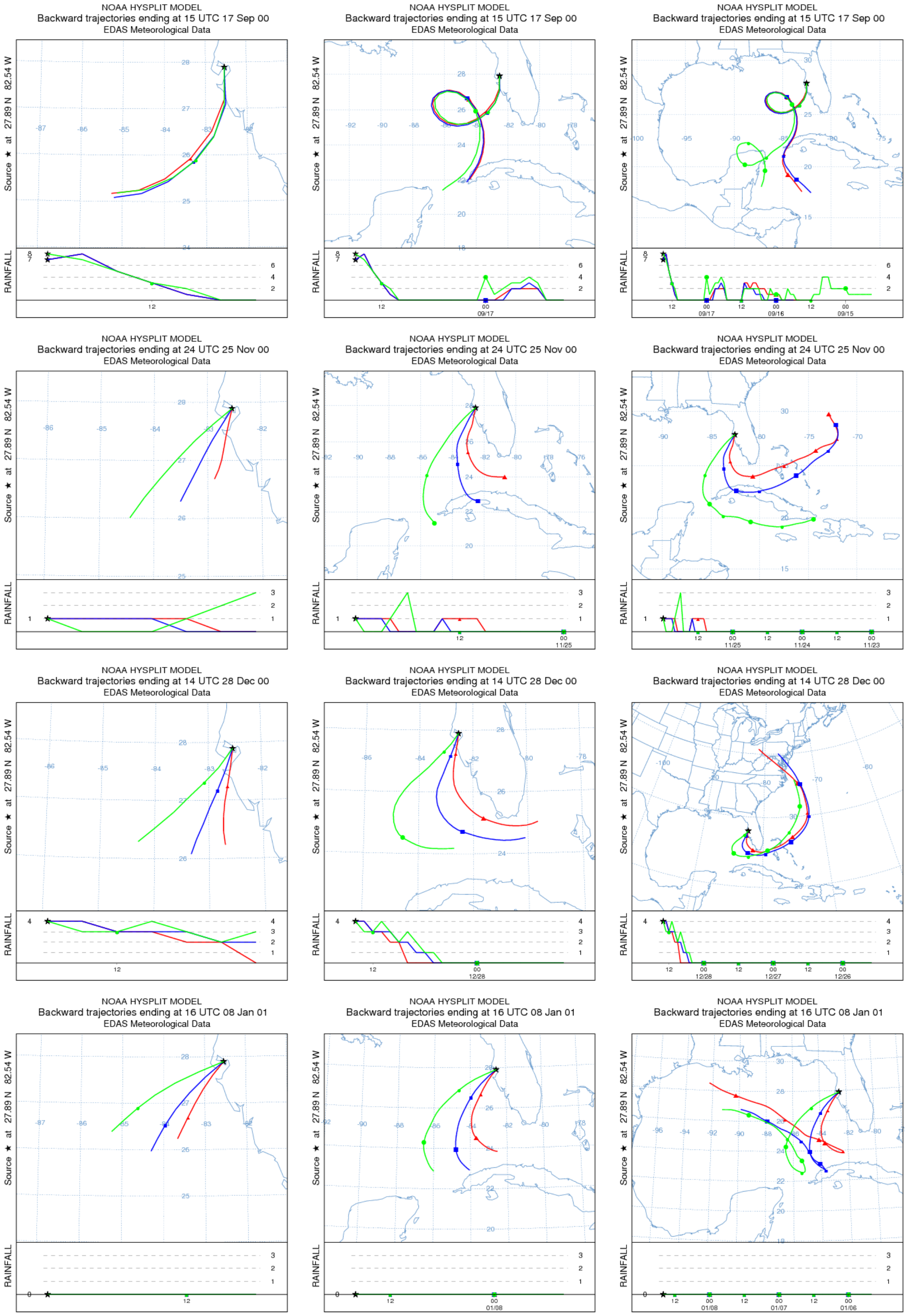
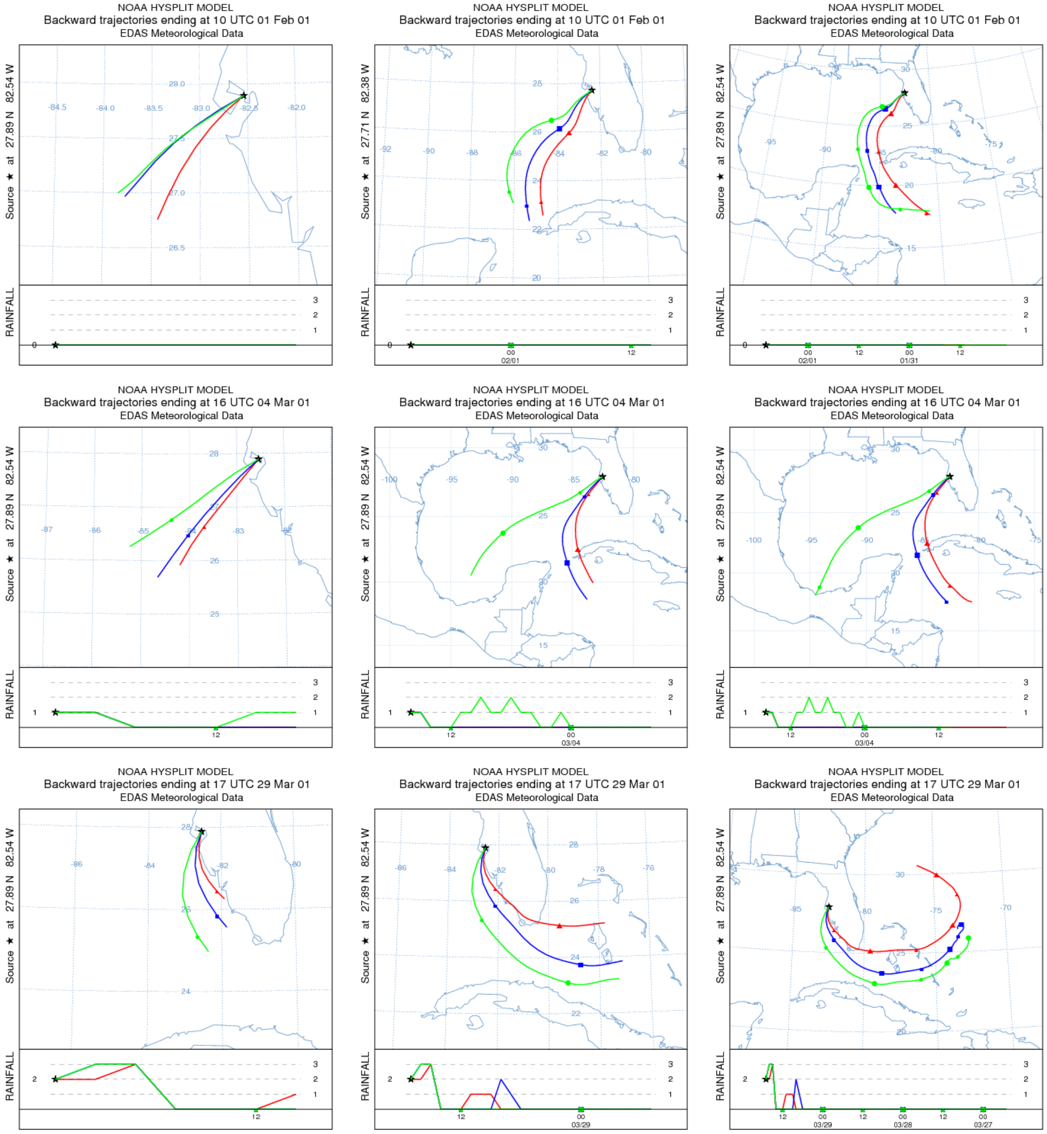


Figure C.5. Back trajectories for the BRACE deposition events occuring over the period September, 2000 – January, 2001. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).



NOAA HYSPLIT MODEL
Backward trajectories ending at 10 UTC 01 Feb 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 10 UTC 01 Feb 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 10 UTC 01 Feb 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 04 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 04 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 16 UTC 04 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 29 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 29 Mar 01
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 29 Mar 01
EDAS Meteorological Data

Figure C.6. Back trajectories for the BRACE deposition events occurring over the period February, 2000 – March, 2001. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

Appendix D.

USF data analysis supplementary data, figures and tables

Table D.1. Analysis data for the estimation of method detection limit . 2012 USF mercury deposition study

Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
Clean		0.00	0.20		1:33:05	48.58
Clean					1:35:56	0.00
Sample1					1:40:05	0.00
Sample2		149.07	0.00		1:44:15	3.46
Sample3					1:48:24	0.00
Sample4		149.07	0.00		1:52:33	84.42
Sample5		149.07	0.00		1:56:42	35.87
Sample6		149.07	0.00		2:00:50	61.62
Sample7		149.07	0.00		2:04:59	19.21
Sample8		149.07	0.00		2:09:12	43.90
Sample9		149.07	2.71		2:13:21	801.88
Sample10		149.07	1.90		2:17:30	607.12
Sample11		149.07	1.18		2:21:39	432.84
Sample12		149.07	0.91		2:25:48	367.43
Sample13		149.07	2.69		2:38:47	796.43
Sample14		149.07	0.86		2:42:56	357.05
Sample15		149.07	0.81		2:47:04	343.22
Sample16		149.07	0.77		2:51:13	333.50
Sample17		149.07	0.73		2:55:22	323.51
Sample18		149.07	0.62		2:59:30	298.69
Sample19		149.07	0.49		3:03:39	266.94
Sample20		149.07	0.30		3:07:48	220.28
Sample21		149.07	0.41		3:11:57	248.00
Sample22		149.07	0.59		3:16:06	290.00
Sample23		149.07	0.33		3:20:15	227.69
Sample24		149.07	0.32		3:24:24	226.59
Sample25		149.07	0.00		3:28:32	54.14
Sample26		149.07	0.00		3:32:41	65.02
Sample27		149.07	0.00		3:36:50	61.15
Sample28		149.07	0.00		3:40:59	59.87
Sample29		149.07	0.00		3:45:08	62.41
Sample1		149.07	0.00		3:49:17	67.47
Sample2		149.07	0.00		3:53:25	64.06
Sample3		149.07	0.00		3:57:34	59.75
Sample4		149.07	0.00		4:01:43	67.22

Table D.1 – continued on next page

Table D.1 – continued from previous page

Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
Calblank		0.00	3.10		4:05:52	744.69
Calblank		0.00	3.23		4:10:01	777.61
Calblank		0.00	2.18		4:14:10	524.92
Calblank		0.00	0.35		4:18:19	83.38
Calblank		0.00	0.32		4:22:28	77.86
Calblank		0.00	0.32		4:26:37	76.56
Calblank		0.00	0.32		4:30:46	77.42
Calblank		0.00	0.28		4:34:55	67.90
Calblank		0.00	0.27		4:39:04	64.95
Calblank		0.00	0.27		4:43:13	65.75
Calblank		0.00	0.39		4:47:22	93.50
Calblank		0.00	0.32		4:51:31	78.12
Calblank		0.00	0.34		4:55:40	81.20
Calblank		0.00	0.78		4:59:49	187.85
Calblank		0.00	0.40		5:03:58	96.65
Calblank		0.00	0.39		5:08:07	94.95
Calblank		0.00	0.38		5:12:16	92.01
Calblank		0.00	0.32		5:16:25	77.56
Calblank		0.00	0.25		5:20:34	59.62
Calblank		0.00	0.26		5:24:43	63.28
Calblank		0.00	0.24		5:28:52	58.82
Calblank		0.00	0.28		5:33:01	67.57
Calblank		0.00	0.28		5:37:10	68.03
Calblank		0.00	0.25		5:41:19	60.68
Calblank		0.00	0.28		5:45:28	66.62
Calblank		0.00	0.28		5:49:39	68.42
Std_100.0	B1	149.07	100.36	91.26	5:53:48	24285.71
Std_50.0	B2	149.07	50.03	91.52	5:57:56	12180.10
Std_20.0	B3	149.07	21.19	97.77	6:02:05	5244.65
Std_10.0	B4	149.07	10.39	97.38	6:06:14	2646.71
Std_5.0	B5	149.07	5.17	99.93	6:10:23	1391.74
Std_1.0	B6	149.07	1.08	128.00	6:14:31	408.18
Flush		149.07	0.00		6:20:06	69.61
Sample11		149.07	0.00		6:24:15	62.47
Sample12		149.07	0.00		6:28:24	63.35
Std_1.0	B1	149.07	0.98	122.58	6:32:33	385.95
Std5.0	B2	149.07	5.03	100.64	6:36:42	1359.28
Std10.0	B3	149.07	10.21	102.05	6:40:51	2603.33
Std20.0	B4	149.07	20.26	101.31	6:45:00	5021.99
Std50.0	B5	149.07	49.40	98.80	6:49:09	12029.60
Std100.0	B6	149.07	97.19	97.19	6:53:18	23522.97
Flush		149.07	0.00		6:58:54	111.48
Method Blank		149.07	0.00		7:03:04	76.19
Method Blank		149.07	0.00		7:07:12	69.83
MDL1	A1	149.07	10.35		7:11:21	2638.36
MDL2	A2	149.07	4.61		7:15:30	1257.04
MDL3	A3	149.07	1.54		7:19:39	519.19
MDL4	A4	149.07	1.01		7:23:48	391.16
MDL5	A5	149.07	0.83		7:27:57	347.57
MDL6	A6	149.07	1.01		7:32:06	392.74
MDL7	A7	149.07	0.77		7:36:15	334.18
MDL8	A8	149.07	2.79		7:40:24	820.31

Table D.1 – continued on next page

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Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
MDL9	A9	149.07	2.48		7:44:33	744.96
MDL10	A10	149.07	0.75		7:48:43	328.79
Method Blank		149.07	0.00		7:52:51	60.60
Method Blank		149.07	0.00		7:57:00	60.07
Method Blank		149.07	0.00		8:01:09	53.21

Table D.2. Analysis data for the estimation of total mercury in diluted samples. 2012 USF mercury deposition study

Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
Clean		0.00	0.03		16:48:52	5.99
Clean					16:51:44	0.00
Sample1		35.72	0.00		16:55:53	4.00
Sample2		35.72	0.00		17:00:02	4.26
Sample3		35.72	0.02		17:04:10	39.70
Sample4		35.72	0.01		17:08:19	37.74
Sample5		35.72	0.10		17:12:28	58.12
Sample6		35.72	0.51		17:16:37	150.38
Sample7		35.72	0.45		17:20:46	136.10
Sample8		35.72	0.34		17:24:55	110.76
Sample9		35.72	0.28		17:29:04	98.16
Sample10		35.72	0.80		17:33:12	213.25
Sample11		35.72	0.93		17:37:21	243.30
Sample12		35.72	0.76		17:41:30	206.43
Sample13		35.72	0.24		17:45:39	89.87
Sample14		35.72	0.18		17:49:48	74.97
Sample15		35.72	0.20		17:53:57	79.50
Sample16		35.72	0.20		17:58:06	79.90
Sample17		35.72	0.18		18:02:15	76.18
Sample18		35.72	0.19		18:06:24	78.32
Sample19		35.72	0.46		18:10:33	137.40
Sample20		35.72	0.14		18:14:42	66.62
Sample21		35.72	0.47		18:18:51	141.21
Sample22		35.72	0.46		18:23:39	138.78
Sample23		35.72	0.45		18:31:13	135.13
Cal_blank		35.72	0.14		18:35:22	66.64
Cal_blank		35.72	0.06		18:39:31	49.42
Cal_blank		35.72	0.05		18:43:40	46.09
Calblank		0.00	0.17		18:47:49	37.14
Cal_blank		35.72	0.05		18:51:58	46.32
Calblank		0.00	0.16		18:56:07	36.48
Calblank		0.00	0.17		19:00:16	36.91
Calblank		0.00	0.18		19:04:25	39.97
Calblank		0.00	0.18		19:08:34	39.36
Calblank		0.00	0.15		19:12:43	34.39
Calblank		0.00	0.17		19:16:52	38.87
Calblank		0.00	0.16		19:21:01	36.59
Calblank		0.00	0.15		19:25:10	34.59

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Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
Calblank		0.00	0.14		19:29:19	31.91
Calblank		0.00	0.17		19:33:28	36.87
Calblank		0.00	0.15		19:37:37	32.89
Calblank		0.00	0.15		19:41:45	34.37
Calblank		0.00	0.13		19:45:54	30.00
Std_1.0	A1	35.72	1.70	148.44	19:50:03	415.32
Std_5.0	A2	35.72	6.27	121.25	19:54:12	1435.93
Std_10.0	A3	35.72	10.07	97.34	19:58:21	2283.82
Std_20.0	A4	35.72	19.45	93.99	20:02:31	4377.41
Std_50.0	A5	35.72	49.35	95.39	20:06:40	11051.29
Std_100.0	A6	35.72	95.23	95.23	20:10:50	21290.33
Flush		35.72	0.48		20:16:25	142.50
Sample24		35.72	0.45		18:31:13	135.13
7-25		35.72	51.38		20:24:44	11902.20
8-01		0.00	30.26		20:28:54	7025.74
IPR5	A7	35.72	5.80	115.93	20:33:03	1329.57
MDL_Blank	A8	35.72	0.11		20:37:12	59.82
MDL_Blank	A9	35.72	0.00		20:41:21	30.00
MDL_Blank	A10	35.72	0.00		20:45:30	32.31
MDL_Blank	A11	35.72	0.04		20:49:39	43.56
MDL_Blank	A12	35.72	0.00		20:53:48	35.89
MDL_Blank	B1	35.72	0.00		20:57:57	29.49
MDL_Blank	B2	35.72	0.00		21:02:06	34.06
OPR5	B3	35.72	5.74	114.76	21:06:15	1316.49
spike	B4	35.72	9.31	119.14	21:10:24	2113.33
spike	B5	35.72	9.79	124.49	21:14:33	2220.66
8-02		35.72	33.80		21:18:42	7842.72
8-05		35.72	48.05		21:22:50	11133.66
8-07		35.72	19.53		21:26:59	4545.48
8-11		35.72	22.10		21:31:08	5140.74
Std5.0	A2	35.72	5.84	116.77	21:35:17	1338.88
Std_1.0	A1	35.72	1.51	134.38	21:39:26	372.45
Std10.0	A3	35.72	9.51	95.05	21:43:35	2157.37
Std20.0	A4	35.72	19.55	97.76	21:47:44	4399.91
Std50.0	A5	35.72	49.42	98.83	21:51:53	11065.30
Std100.0	A6	35.72	96.36	96.36	21:56:02	21543.12
Flush		35.72	0.83		22:01:40	221.48
Sample30		35.72	0.43		22:05:48	131.11
Sample31		35.72	0.36		22:09:58	115.23
Sample32		35.72	0.28		22:14:07	97.61
Sample33		35.72	0.23		22:18:15	87.44

Table D.3. Analysis data for the estimation of total mercury in deposition samples (Batch 1)– 2012 USF mercury deposition study

Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
Clean		0.00	0.00		1:26:37	0.55
Clean					1:29:29	0.00
Clean					1:32:21	0.00
Sample1		27.09	0.00		1:36:30	0.26
Sample2		27.09	0.00		1:40:39	4.70
Sample3					1:44:48	0.00
Sample4		27.09	0.00		1:48:57	6.37
Sample5		27.09	0.28		1:53:06	103.39
Sample6		27.09	0.23		1:57:15	89.07
Sample7		27.09	0.13		2:01:24	63.31
Sample8		27.09	0.15		2:05:33	66.05
Sample9		27.09	0.11		2:09:43	56.20
Sample10		27.09	0.22		2:13:52	87.35
Sample11		27.09	0.12		2:18:01	59.14
Sample12		27.09	0.13		2:22:10	62.79
Sample13		27.09	0.15		2:26:19	66.69
Sample14		27.09	0.07		2:30:28	46.62
System_blank	A7	27.09	0.18		2:34:37	74.44
System_blank	A8	27.09	0.27		2:38:46	98.33
System_blank	A9	27.09	0.20		2:42:55	81.68
System_blank	A10	27.09	0.24		2:47:04	90.20
System_blank	A11	27.09	0.21		2:51:13	83.66
System_blank	A12	27.09	0.18		2:55:22	74.39
System_blank	B1	27.09	0.18		2:59:31	76.42
Cal_blank		27.09	0.16		3:03:40	70.23
Cal_blank		27.09	0.17		3:07:49	73.22
Cal_blank		27.09	0.10		3:11:58	53.60
Cal_blank		27.09	0.07		3:16:07	47.03
Calblank		0.00	0.11		3:20:16	30.59
Calblank		0.00	0.12		3:24:25	31.59
Calblank		0.00	0.11		3:28:34	28.67
Calblank		0.00	0.10		3:32:43	26.42
Calblank		0.00	0.10		3:36:52	25.68
Calblank		0.00	0.11		3:41:01	29.07
Calblank		0.00	0.09		3:45:10	25.06
Calblank		0.00	0.10		3:49:19	27.44
Calblank		0.00	0.09		3:53:28	24.63
Calblank		0.00	0.10		3:57:37	26.00
Calblank		0.00	0.08		4:01:46	22.81
Std1.0	A1	27.09	1.45	145.34	4:05:55	417.27
Std5.0	A2	27.09	5.05	100.93	4:10:04	1381.91
Std10.0	A3	27.09	9.01	90.13	4:14:13	2446.68
Std20.0	A4	27.09	18.06	90.28	4:18:22	4874.58
Std50.0	A5	27.09	43.83	87.67	4:22:31	11794.90
Std100.0	A6	27.09	85.64	85.64	4:26:40	23018.07
Flush		27.09	0.19		4:32:15	77.29
Method_Blank	D1	27.09	0.07		4:36:24	45.46
Method_Blank	D2	27.09	0.07		4:40:33	47.09
Method_Blank	D3	27.09	0.06		4:44:42	43.65
IPR5	A7	27.09	4.73	94.66	4:48:51	1297.75

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Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
FB_07-04	B1	27.09	1.44		4:53:00	412.67
16.07.2012	B2	27.09	20.61		4:57:09	5558.66
18.07.2012	B3	27.09	25.15		5:01:18	6777.82
22.07.2012	B4	27.09	17.22		5:05:27	4648.62
24.07.2012	B5	27.09	510.55		5:09:36	137087.73
25.07.2012	B6	27.09	480.50		5:19:20	129022.04
OPR5	A8	27.09	5.32	106.35	5:29:05	1454.59
22.07.2012-MS15	C3	27.09	41.49	128.78	5:37:23	11164.61
22.07.2012-MSD	C4	27.09	49.41		5:41:33	13291.85
01.08.2012	B8	27.09	261.61		5:45:41	70257.37
02.08.2012	B9	27.09	314.39		5:55:26	84427.23
05.08.2012	B10	27.09	418.35		6:05:10	112336.61
07.08.2012	B11	27.09	165.49		6:15:04	44454.77
OPR5	C7	27.09	5.79	115.72	6:19:13	1580.32
11.08.2012	C1	27.09	191.39		6:33:07	51407.40
OPR5	C8	27.09	5.07	101.42	6:42:52	1388.42
FB_07-09	D4	27.09	0.55		6:47:02	175.46
FB_07-13	D5	27.09	0.48		6:51:11	155.22
FB_07-21	D6	27.09	0.44		6:55:20	144.02
FB_07-28	D7	27.09	0.38		6:59:29	128.91
FB_07-31	D8	27.09	0.35		7:03:38	122.24
FB_08-10	D9	27.09	0.33		7:07:47	115.50
Std_1.0	A1	27.09	1.70	166.34	7:11:56	484.08
Std_5.0	A2	27.09	5.16	100.75	7:16:05	1411.06
Std_10.0	A3	27.09	9.56	93.44	7:20:14	2594.12
Std_20.0	A4	27.09	17.58	85.89	7:24:23	4746.36
Std_50.0	A5	27.09	43.49	84.98	7:28:32	11701.11
Std_100.0	A6	27.09	84.25	82.32	7:32:41	22643.83
IPR5	A7	27.09	5.16	103.22	7:36:51	1412.54
IPR5	A8	27.09	5.12	102.49	7:40:59	1402.82
FB_08-26	D10	27.09	0.20		7:45:08	80.81
Method_Blank		27.09	0.16		7:49:17	68.75
FB_08-29	D11	27.09	0.24		7:53:26	92.40
FB_09-01		27.09	0.21		7:57:35	83.36
FB_09-04		27.09	0.20		8:02:01	80.10
Sample31		27.09	0.18		8:06:10	74.23
Sample32		27.09	0.23		8:14:20	87.93
Sample33		27.09	0.16		8:18:29	69.19
Sample34					8:22:38	68.29

Table D.4. Analysis data for the estimation of total mercury in deposition samples (Batch 2)– 2012 USF mercury deposition study

Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
Clean		0.00	0.43		11:12:57	102.32
Clean					11:15:49	0.00
Clean					11:18:41	0.00
Sample1		46.37	0.11		11:22:50	73.00
Sample2		46.37	0.09		11:26:59	67.24
Sample3		46.37	0.05		11:31:08	58.97
Sample4		46.37	0.24		11:35:17	102.35
Sample5		46.37	0.17		11:39:26	87.31
Sample6		46.37	0.15		11:43:35	80.96
Sample7		46.37	0.11		11:47:44	73.21
Sample8		46.37	0.11		11:51:53	72.66
Sample9		46.37	0.12		11:56:02	75.77
Sample10		46.37	0.06		12:00:11	59.75
Sample11		46.37	0.05		12:04:20	57.92
Sample12		46.37	0.04		12:08:29	56.93
Sample13		46.37	0.04		12:12:38	55.96
Sample14		46.37	0.03		12:16:47	53.55
Sample15		46.37	0.03		12:20:56	54.17
Sample26		46.37	0.04		12:25:06	55.13
Sample17		46.37	0.03		12:29:14	54.61
Sample18		46.37	0.06		12:33:23	59.80
Sample19		46.37	0.03		12:37:32	53.15
Sample20		46.37	0.00		12:41:41	43.65
Sample21		46.37	0.05		12:45:50	57.18
Sample22		46.37	0.02		12:49:59	51.24
Calblank		0.00	0.19		12:54:08	44.85
Calblank		0.00	0.15		12:58:17	35.58
Sample25		46.37	0.13		13:02:26	75.85
Sample27		46.37	0.00		13:06:36	28.28
Sample28		46.37	0.00		13:10:45	41.22
Sample29		46.37	0.00		13:14:54	36.29
Sample30		46.37	0.13		13:19:03	76.71
Sample31		46.37	0.11		13:23:12	71.79
Sample32		46.37	0.11		13:27:21	72.01
Sample33		46.37	0.09		13:31:30	67.01
Sample34		46.37	0.11		13:35:39	72.80
Sample35		46.37	0.13		13:39:48	77.95
System_blank		46.37	0.20		13:43:57	92.34
System_blank		46.37	0.16		13:48:06	84.14
System_blank		46.37	0.15		13:52:14	80.65
System_blank		46.37	0.11		13:56:23	71.82
System_blank		46.37	0.08		14:00:32	65.84
System_blank		46.37	0.10		14:04:41	68.82
System_blank		46.37	0.10		14:08:50	70.30
Cal_blank		46.37	0.10		14:12:59	69.48
Cal_blank		46.37	0.67		14:17:08	204.27
Cal_blank		46.37	0.02		14:21:17	50.50
Calblank		0.00	0.21		14:25:26	49.49
Calblank		0.00	0.19		14:29:34	45.27
Calblank		0.00	0.19		14:33:43	45.81

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Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
Calblank		0.00	0.19		14:37:52	44.27
Calblank		0.00	0.17		14:42:01	41.13
Calblank		0.00	0.19		14:46:09	43.84
Calblank		0.00	0.17		14:50:18	39.44
Calblank		0.00	0.17		14:54:27	39.02
Calblank		0.00	0.15		14:58:36	36.36
Calblank		0.00	0.17		15:02:45	40.27
Calblank		0.00	0.17		15:06:54	39.63
Std_1.0	A1	46.37	4.84	243.14	15:11:03	1186.27
Std_5.0	A2	46.37	6.17	127.02	15:15:12	1498.46
Std_10.0	A3	46.37	9.36	96.44	15:19:22	2249.80
Std_20.0	A4	46.37	19.07	98.34	15:23:30	4537.01
Std_50.0	A5	46.37	43.38	89.52	15:27:39	10262.45
Std_100.0	A6	46.37	97.69	100.82	15:31:48	23053.60
Cal_blank		46.37	0.15		15:35:57	80.79
Calblank		0.00	0.25		15:40:06	58.26
IPR5.0	A7	46.37	6.95	139.08	15:44:15	1684.23
Method Blank		46.37	0.07		15:48:24	62.21
FB_09-10		46.37	0.14		15:52:33	80.47
Std_1.0	A1	46.37	4.81	334.70	15:56:42	1179.81
Std5.0	A2	46.37	6.20	124.03	16:00:51	1506.90
Std10.0	A3	46.37	9.50	95.00	16:05:00	2283.91
Std20.0	A4	46.37	19.04	95.22	16:09:09	4531.71
Std50.0	A5	46.37	43.66	87.32	16:13:18	10329.07
Std100.0	A6	46.37	98.43	98.43	16:17:28	23228.98
FB_09-13		46.37	0.20		16:21:37	94.50
FB_09-15		46.37	0.10		16:25:47	70.79
Method Blank		46.37	0.05		16:29:57	58.90
OPR5.0	A8	46.37	5.15	103.07	16:34:06	1260.07
FB_9-25		46.37	0.15		16:47:18	81.57
FB_9-28	B1	46.37	1.14		16:51:28	313.97
120716	B2	46.37	20.64		16:55:37	4906.59
120718	B3	46.37	25.69		16:59:45	6096.96
120722	B4	46.37	18.31		17:03:54	4358.31
120725	B5	46.37	496.80		17:08:03	117053.32
OPR5.0	A9	46.37	5.14	102.71	17:21:57	1255.85
120716_MS	D1	46.37	50.06		17:26:06	11836.37
120716_MSD	D2	46.37	51.56		17:30:15	12190.14
120802	B7	46.37	324.16		17:34:35	76392.10
120805	B8	46.37	448.09		17:44:19	105580.62
120807	B9	46.37	172.89		17:54:04	40765.00
120811	B11	46.37	192.89		18:07:57	45476.22
120813	B12	46.37	14.50		18:12:06	3461.84
OPR5.0	A10	46.37	5.04	100.76	18:16:15	1232.87
120821	C1	46.37	14.58		18:20:24	3479.24
120822	C2	46.37	70.86		18:24:33	16735.45
120823	C3	46.37	9.34		18:28:42	2245.60
120907	C4	46.37	32.42		18:32:51	7682.61
120919	C5	46.37	8.42		18:37:00	2029.65
120921	C6	46.37	23.27		18:49:27	5526.58
OPR5.0	A11	46.37	5.22	104.31	18:53:36	1274.71
FB_10-10		46.37	0.18		18:57:45	88.65

Table D.4 – continued on next page

Table D.4 – continued from previous page

Sample_ID	Location	Blank	Conc (ppt)	Recovery(%)	Run_End	Peak (raw)
FB_10-13		46.37	0.13		19:01:55	75.92
120930	C7	46.37	6.55		19:06:06	1588.79
121004	C8	46.37	4.89		19:10:14	1197.23
121005	C9	46.37	4.92		19:14:24	1204.63
121006	C10	46.37	14.92		19:18:32	3561.36
121007	C11	46.37	7.25		19:22:41	1754.25
121227	C12	46.37	40.42		19:26:50	9566.02
OPR5.0	A12	46.37	5.14	102.86	19:30:59	1257.67
121006_MS	D1	46.37	53.14		19:35:08	12562.64
121006_MSD	D2	46.37	39.42		19:39:17	9331.28
FB_10-17		46.37	0.14		19:43:26	79.88
FB_10-21		46.37	0.10		19:47:36	69.73
Method Blank		46.37	0.07		19:51:46	63.20
FB_10-24		46.37	0.10		19:55:56	70.54
121006_MS	D1	46.37	52.27		20:00:07	12357.92
121006_MSD	D2	46.37	39.44		20:04:15	9334.89
OPR5.0	A12	46.37	4.97	99.41	20:08:24	1217.03
FB_10-27		46.37	0.12		20:12:33	75.81
FB_10-30		46.37	0.10		20:16:42	70.81
FB_11-03		46.37	0.09		20:20:51	68.23
FB_11-09		46.37	0.09		20:25:00	68.12
FB_12-10		46.37	0.08		20:29:09	65.59
Sample56					20:33:18	69.38
Sample57					20:37:27	22.38

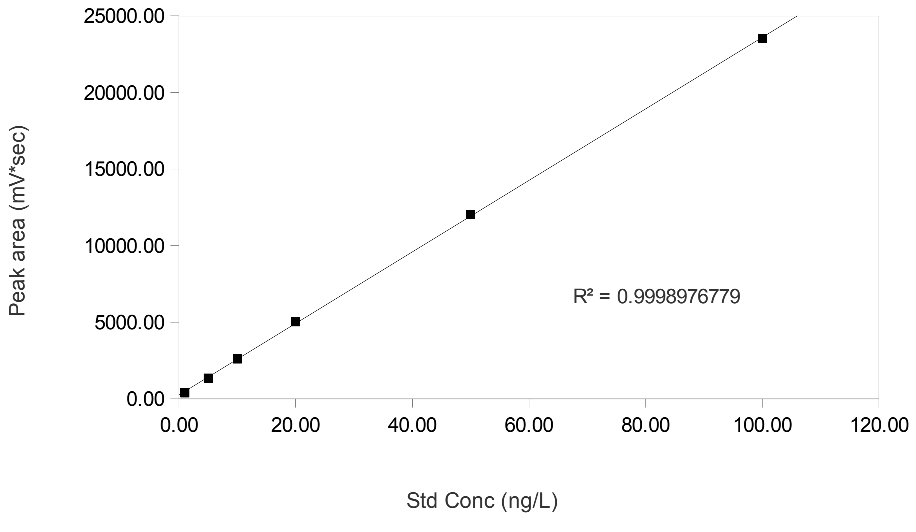


Figure D.1. Standard curve for the determination of total mercury in MDL samples. 2012 USF mercury deposition study

Table D.5. Quality assurance and quality control data for total mercury analysis – Blanks and quality control standards – 2012 USF mercury deposition study

Precision and Recovery

Standard	Mass	Blank	Peak	Calc Concentration	% Recovery
IPR5.0	5	46.37	1684.23	6.96	139.25%
OPR5.0	5	46.37	1260.07	5.16	103.28%
OPR5.0	5	46.37	1255.85	5.15	102.92%
OPR5.0	5	46.37	1232.87	5.05	100.97%
OPR5.0	5	46.37	1274.71	5.23	104.52%
OPR5.0	5	46.37	1257.67	5.15	103.07%
OPR5.0	5	46.37	1217.03	4.98	99.63%
IPR5	5	27.09	1297.75	5.21	104.10%
OPR5	5	27.09	1454.59	5.85	116.95%
OPR5	5	27.09	1388.42	5.58	111.53%
IPR5	5	27.09	1412.54	5.68	113.51%
IPR5	5	27.09	1402.82	5.64	112.71%
				Mean	109.37%
				SD	10.95%
				Upper recovery interval	87.48%
				Lower recovery interval	131.27%
				Confidence	6.19%

Field Blanks

Sample	Mass	Blank	Peak	Calc Concentration
FB_07-04		27.09	412.67	1.58
FB_07-09		27.09	175.46	0.61
FB_07-13		27.09	155.22	0.52
FB_07-21		27.09	144.02	0.48
FB_07-28		27.09	128.91	0.42
FB_07-31		27.09	122.24	0.39
FB_08-10		27.09	115.50	0.36
FB_08-26		27.09	80.81	0.22
FB_08-29		27.09	92.40	0.27
FB_09-01		27.09	83.36	0.23
FB_09-04		27.09	80.10	0.22
FB_09-10		46.37	80.47	0.16
FB_09-13		46.37	94.50	0.22
FB_09-15		46.37	70.79	0.12
FB_9-25		46.37	81.57	0.17
FB_9-28		46.37	313.97	1.15
FB_10-10		46.37	88.65	0.20
FB_10-13		46.37	75.92	0.14
FB_10-17		46.37	79.88	0.16
FB_10-21		46.37	69.73	0.12
FB_10-24		46.37	70.54	0.12
FB_10-27		46.37	75.81	0.14
FB_10-30		46.37	70.81	0.12
FB_11-03		46.37	68.23	0.11
FB_11-09		46.37	68.12	0.11
FB_12-10		46.37	65.59	0.10
			Mean	0.32
			SD	0.34
			Confidence	0.13

Table D.6. Calibration, recovery, and sample data for the estimation of total mercury in diluted samples. 2012 USF mercury deposition study

Calibration

STD Mass	Calib. Factors	Blank	Peak	Calc Conc.	% Recovery
1.00	379.69	27.09	415.32	1.64	164.39%
5.00	280.06	27.09	1435.93	6.06	121.26%
10.00	224.82	27.09	2283.82	9.73	97.34%
20.00	217.09	27.09	4377.41	18.80	93.99%
50.00	220.31	27.09	11051.29	47.69	95.39%
100.00	212.55	27.09	21290.33	92.03	92.03%
Mean Calblank	35.63				
CF_Mean	230.97				
CF_SD	27.81				
CF_RSD	0.12	Acceptable (< 15%)			

Precision and Recovery

Standard	Mass	Blank	Peak	Calc Conc.	% Recovery
IPR5	5.00	27.09	1329.57	5.60	112.05%
OPR5	5.00	27.09	1316.49	5.55	110.91%
Mean	111.48%				
SD	0.80%				
Upper recovery interval	109.88%				
Lower recovery interval	113.08%				
Confidence	1.11%				

Sample Concentrations

Sample ID	Mass	Blank	Peak	Calc Conc.	Ad. Conc.
25.07.2012	–	27.09	11902.20	51.38	513.78
01.08.2012	–	27.09	7025.74	30.26	302.65
02.08.2012	–	27.09	7842.72	33.80	338.02
05.08.2012	–	27.09	11133.66	48.05	480.51
07.08.2012	–	27.09	4545.48	19.53	195.26
11.08.2012	–	27.09	5140.74	22.10	221.03

Table D.7. Calibration, recovery, and sample data for the estimation of total mercury in deposition samples (Batch 1). 2012 USF mercury deposition study

Calibration

STD Mass	Calib. Factors	Blank	Peak	Calc Conc.	% Recovery
1.00	390.18	27.09	417.27	1.60	159.84%
5.00	270.96	27.09	1381.91	5.55	111.00%
10.00	241.96	27.09	2446.68	9.91	99.12%
20.00	242.37	27.09	4874.58	19.86	99.29%
50.00	235.36	27.09	11794.90	48.21	96.41%
100.00	229.91	27.09	23018.07	94.18	94.18%
Mean Calblank	27.09				
CF_Mean	244.11				
CF_SD	15.87				
CF_RSD	0.06	Acceptable ($< 15\%$)			

Precision and Recovery

Standard	Mass	Blank	Peak	Calc Conc.	% Recovery
IPR5	5.00	27.09	1297.75	5.21	104.10%
OPR5	5.00	27.09	1454.59	5.85	116.95%
OPR5	5.00	27.09	1388.42	5.58	111.53%
IPR5	5.00	27.09	1412.54	5.68	113.51%
IPR5	5.00	27.09	1402.82	5.64	112.71%
Mean	111.76%				
SD	4.73%				
Upper recovery interval	102.30%				
Lower recovery interval	121.23%				
Confidence	4.15%				

Sample Concentrations

Sample ID	Mass	Blank	Peak	Calc Conc.
16.07.2012		27.09	5558.66	22.66
18.07.2012		27.09	6777.82	27.65
22.07.2012		27.09	4648.62	18.93
24.07.2012		27.09	137087.73	561.46
25.07.2012		27.09	129022.04	528.42
01.08.2012		27.09	70257.37	287.70
02.08.2012		27.09	84427.23	345.74
05.08.2012		27.09	112336.61	460.07
07.08.2012		27.09	44454.77	182.00
11.08.2012		27.09	51407.40	210.48

Table D.8. Calibration, recovery, and sample data for the estimation of total mercury in deposition samples (Batch 2). 2012 USF mercury deposition study

Calibration

STD Mass	Calib. Factors	Blank	Peak	Calc Conc.	% Recovery
1	1137.58	46.37	1186.27	4.82	482.36%
5	292.93	46.37	1498.46	6.21	124.21%
10	224.17	46.37	2249.80	9.51	95.05%
20	224.47	46.37	4537.01	19.04	95.18%
50	205.74	46.37	10262.45	43.62	87.24%
100	231.87	46.37	23053.60	98.32	98.32%
Mean Calblank	42.23				
CF_Mean	235.84				
CF_SD	33.344	Acceptable ($< 15\%$)			

Precision and Recovery

Standard	Mass	Blank	Peak	Calc Conc.	% Recovery
IPR5.0	5	46.37	1684.23	6.9625	139.25%
OPR5.0	5	46.37	1260.07	5.1639	103.28%
OPR5.0	5	46.37	1255.85	5.1460	102.92%
OPR5.0	5	46.37	1232.87	5.0486	100.97%
OPR5.0	5	46.37	1274.71	5.2260	104.52%
OPR5.0	5	46.37	1257.67	5.1537	103.07%
OPR5.0	5	46.37	1217.03	4.9814	99.63%
Mean	102.40%				
SD	1.77%				
Upper recovery interval	98.85%				
Lower recovery interval	105.94%				
Confidence	1.31%				

Sample Concentrations

Sample ID	Mass	Blank	Peak	Calc Conc.
120716		46.37	4906.59	20.63
120718		46.37	6096.96	25.67
120722		46.37	4358.31	18.30
120725		46.37	117053.32	496.15
120802		46.37	76392.10	323.74
120805		46.37	105580.62	447.51
120807		46.37	40765.00	172.67
120811		46.37	45476.22	192.65
120813		46.37	3461.84	14.50
120821		46.37	3479.24	14.57
120822		46.37	16735.45	70.78
120823		46.37	2245.60	9.34
120907		46.37	7682.61	32.40
120919		46.37	2029.65	8.43
120921		46.37	5526.58	23.25
120930		46.37	1588.79	6.56
121004		46.37	1197.23	4.90
121005		46.37	1204.63	4.93
121006		46.37	3561.36	14.92
121007		46.37	1754.25	7.26
121227		46.37	9566.02	40.38

Table D.9. Calibration, recovery, and sample data for the estimation of total mercury in diluted samples. 2012 USF mercury deposition study

Calibration

STD Mass	Calib. Factors	Blank	Peak	Calc Conc.	% Recovery
1.00	379.69	27.09	415.32	1.64	164.39%
5.00	280.06	27.09	1435.93	6.06	121.26%
10.00	224.82	27.09	2283.82	9.73	97.34%
20.00	217.09	27.09	4377.41	18.80	93.99%
50.00	220.31	27.09	11051.29	47.69	95.39%
100.00	212.55	27.09	21290.33	92.03	92.03%
Mean Calblank	35.63				
CF_Mean	230.97				
CF_SD	27.81				
CF_RSD	0.12	Acceptable (< 15%)			

Precision and Recovery

Standard	Mass	Blank	Peak	Calc Conc.	% Recovery
IPR5	5.00	27.09	1329.57	5.60	112.05%
OPR5	5.00	27.09	1316.49	5.55	110.91%
Mean	111.48%				
SD	0.80%				
Upper recovery interval	109.88%				
Lower recovery interval	113.08%				
Confidence	1.11%				

Sample Concentrations

Sample ID	Mass	Blank	Peak	Calc Conc.	Ad. Conc.
25.07.2012	–	27.09	11902.20	51.38	513.78
01.08.2012	–	27.09	7025.74	30.26	302.65
02.08.2012	–	27.09	7842.72	33.80	338.02
05.08.2012	–	27.09	11133.66	48.05	480.51
07.08.2012	–	27.09	4545.48	19.53	195.26
11.08.2012	–	27.09	5140.74	22.10	221.03

Table D.10. Determination of method detection limit (MDL). 2012 USF mercury deposition study

Calibration

STD Mass	Peak	Calib. Factors (CF)	STD Conc	% Recvry
1.00	385.95	306.44	1.20	1.20
5.00	1359.28	255.95	5.00	1.00
10.00	2603.33	252.38	9.86	0.99
20.00	5021.99	247.12	19.31	0.97
50.00	12029.60	239.00	46.70	0.93
100.00	23522.97	234.43	91.62	0.92
Mean Calibration Blank		79.51		
Mean CF		255.89		
Std. Dev. - CF		26.04		
Relative Std. Dev.		0.10	Acceptable (< 15%)	

Estimating MDL

Sample_ID	Peak	Calc Conc
MDL3	519.19	1.72
MDL4	391.16	1.22
MDL5	347.57	1.05
MDL6	392.74	1.22
MDL7	334.18	1.00
MDL9	744.96	2.60
MDL10	328.79	0.97
Mean		1.40
Std. Dev.		0.59
MDL		1.85

Table D.11. Quality assurance and quality control data for total mercury analysis – Duplicate samples – 2012 USF mercury deposition study

Duplicates

Sample ID	D1	D2	RPD
120716	20.63	22.66	9.40%
120718	25.67	27.65	7.43%
120722	18.30	18.93	3.39%
120725	496.15	528.42	6.30%
120802	323.74	345.74	6.57%
120805	447.51	460.07	2.77%
120807	172.67	182.00	5.26%
120811	192.65	210.48	8.84%
		Average	6.24%
		Stdev	2.37%
		Confidence	1.64%

Table D.12. Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631

Metal	Lowest Ambient Water Quality Criterion $^{(1)}$	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL$^{(2)}$	ML$^{(3)}$
Mercury (Hg)	1.3 ng L^{-1}	0.2 ng L^{-1}	0.5 ng L^{-1}

^{1}Lowest water quality criterion for the Great Lakes System (Table 4, 40 CFR 132.6). The lowest Nationwide criterion is 12 ng/L (40 CFR 131.36).
^{2}Method detection limit (40 CFR 136)
^{3}Minimum level of quantitation

Table D.13. Quality Control Acceptance Criteria for Performance Tests in EPA Method 1631

Acceptance Criteria	Limit (%)
Initial Precision and Recovery (IPR)	
Precision (RSD)	21
Recovery (X)	79 – 121
Ongoing Precision and Recovery (OPR)	77 – 123
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	
Recovery	71 – 125
Relative Percent Difference (RPD)	24

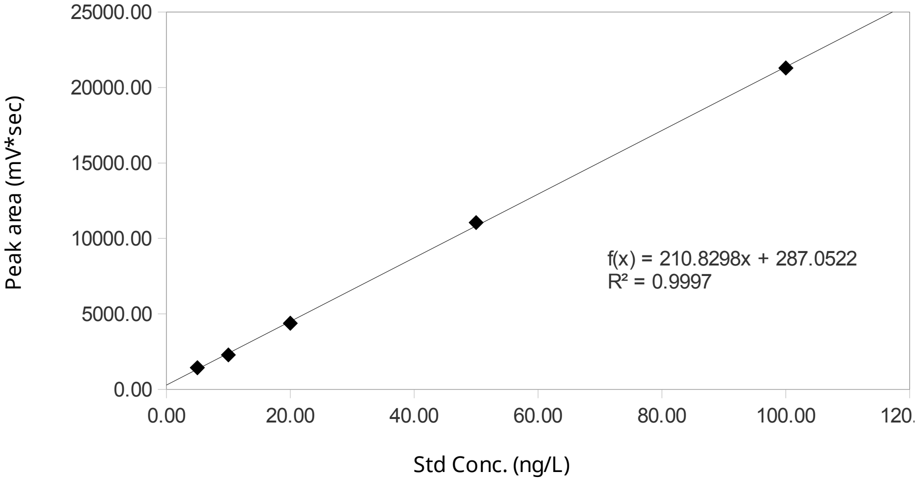


Figure D.2. Standard curve for the determination of total mercury in diluted samples. 2012 USF mercury deposition study

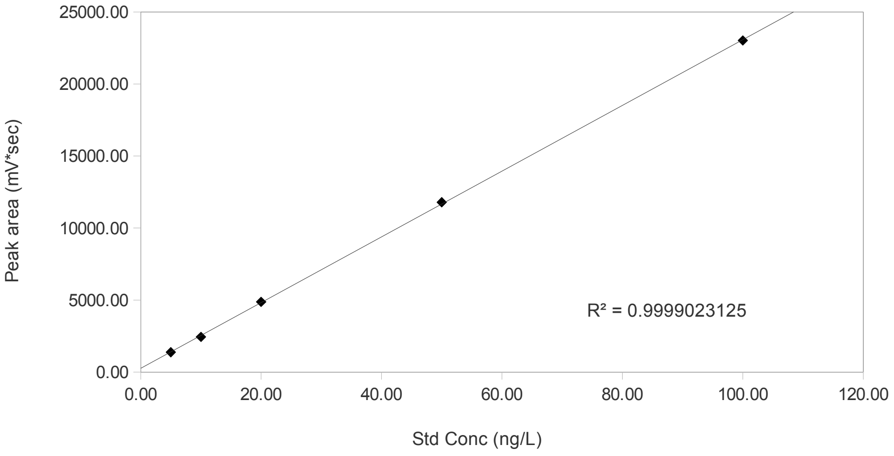


Figure D.3. Standard curve for the determination of total mercury in in deposition samples (Batch 1). 2012 USF mercury deposition study

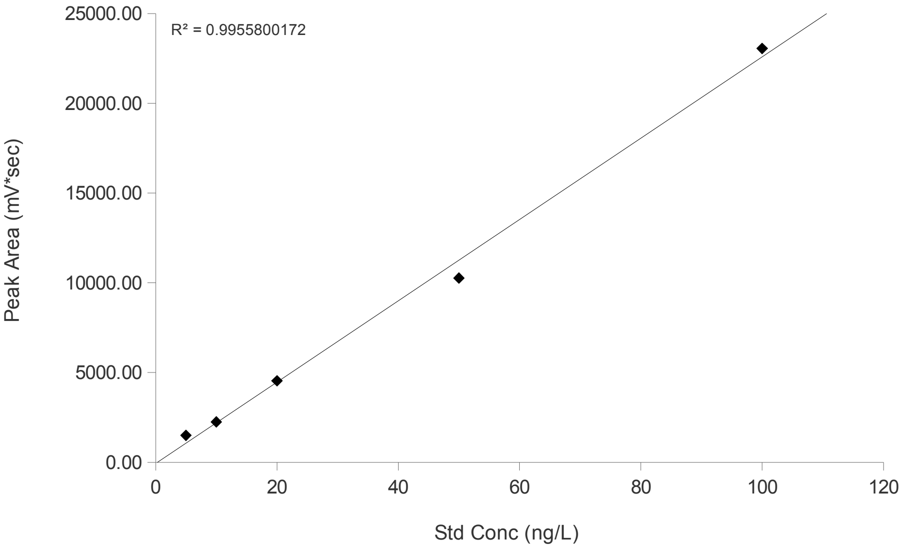


Figure D.4. Standard curve for the determination of total mercury in in deposition samples (Batch 2). 2012 USF mercury deposition study

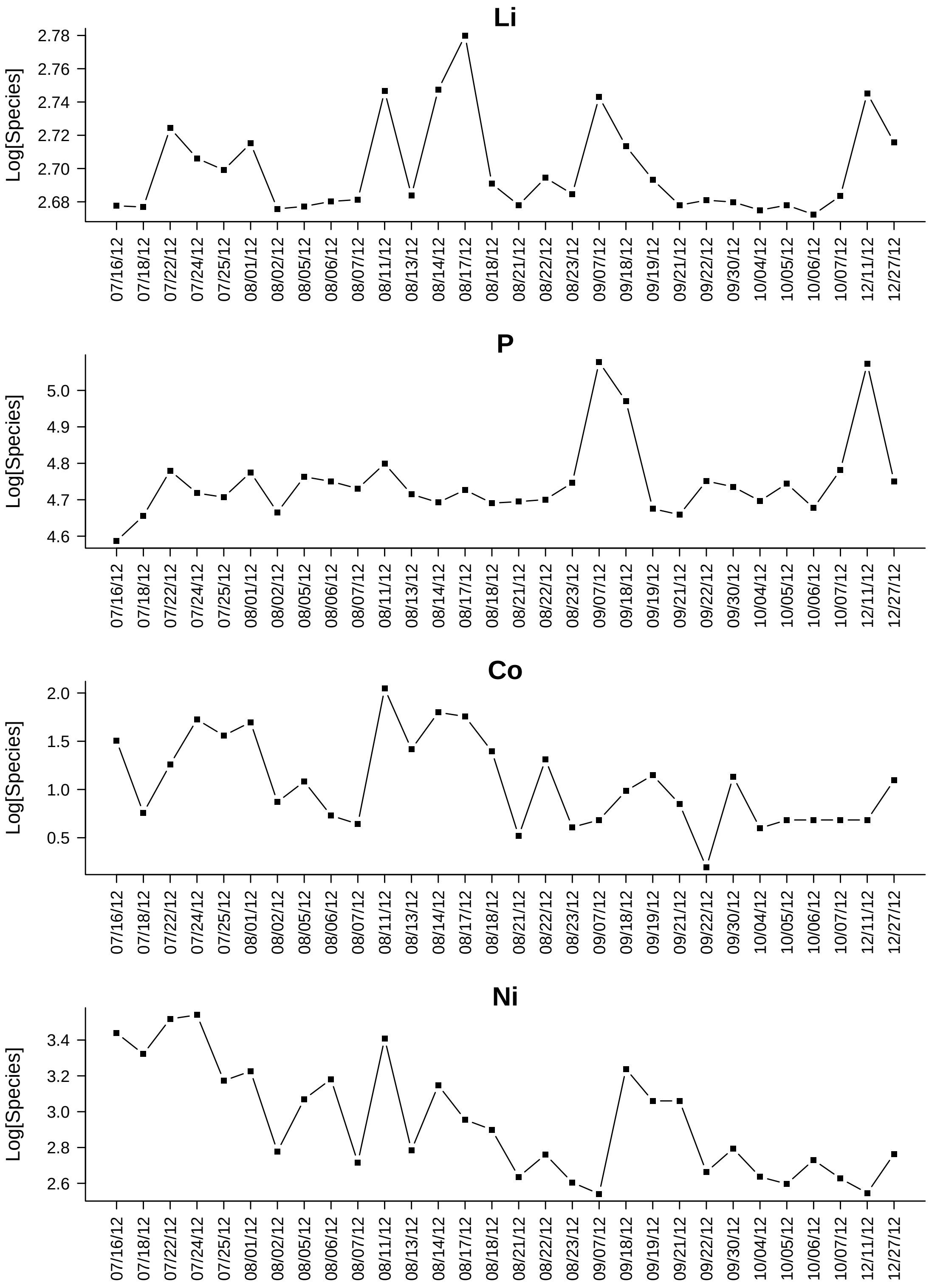


Figure D.5. Temporal profiles for trace metals deposition data. 2012 USF mercury deposition study

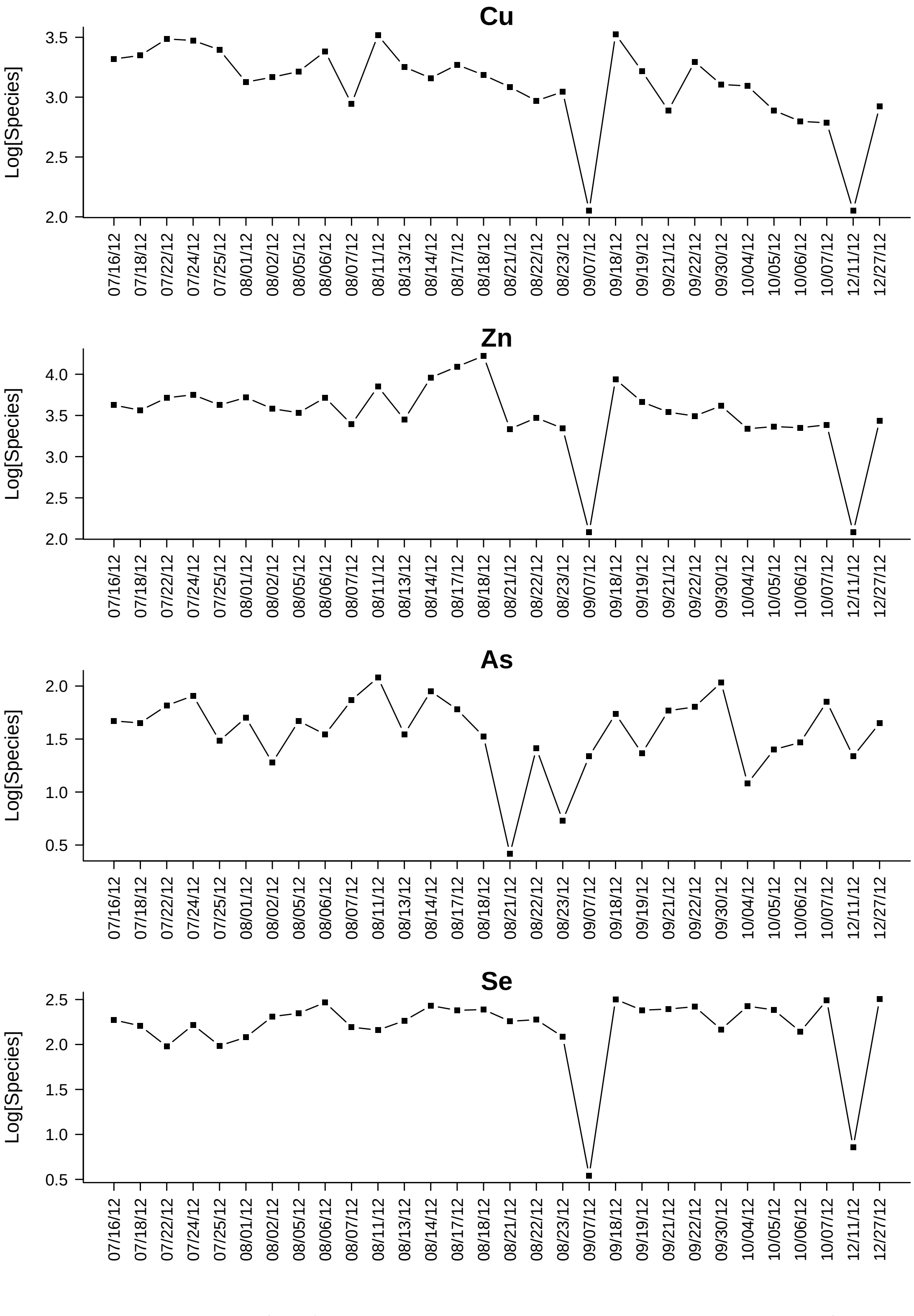


Figure D.6. Temporal profiles for trace metals deposition data continued. 2012 USF mercury deposition study

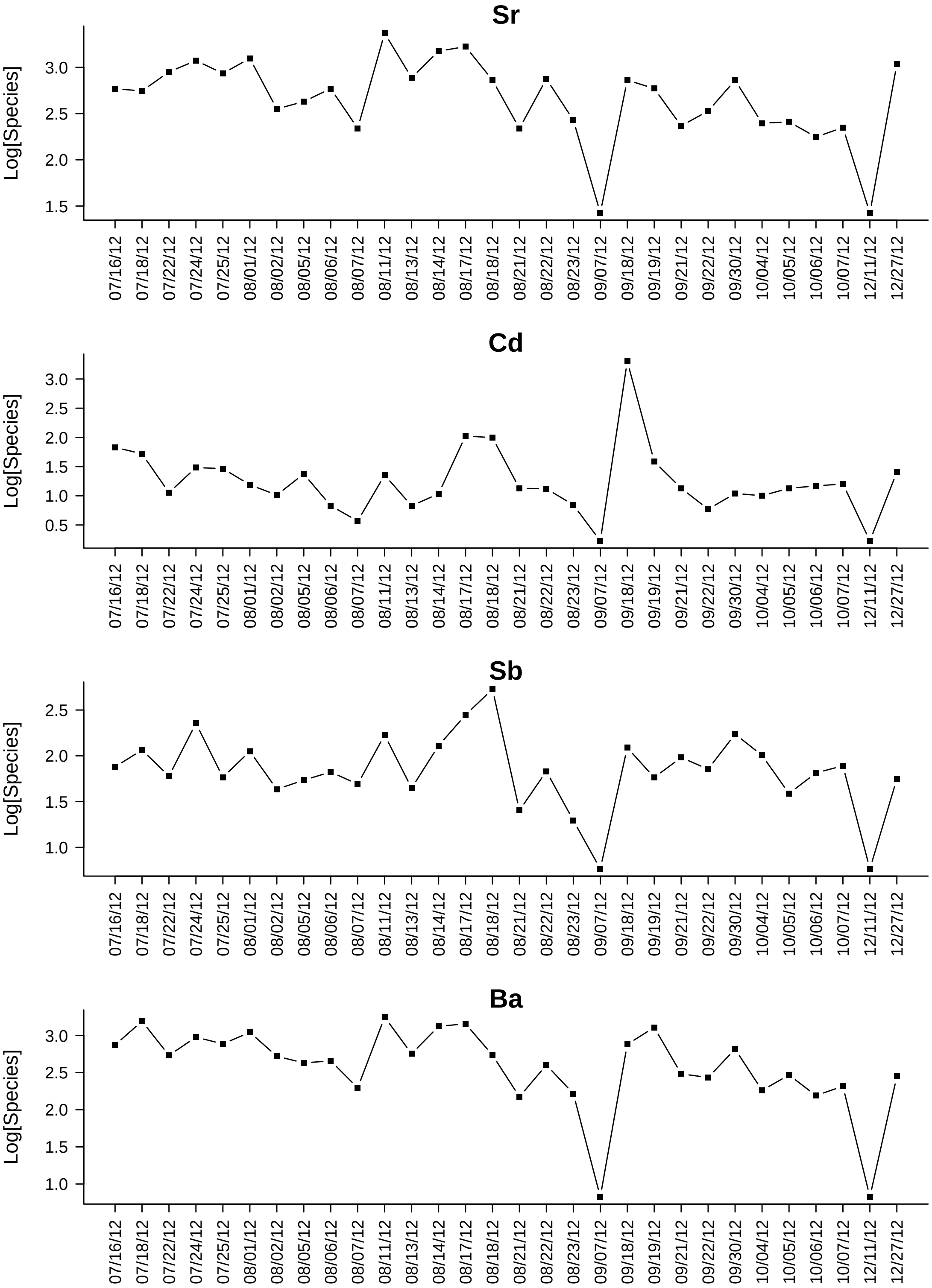


Figure D.7. Temporal profiles for trace metals deposition data continued. 2012 USF mercury deposition study

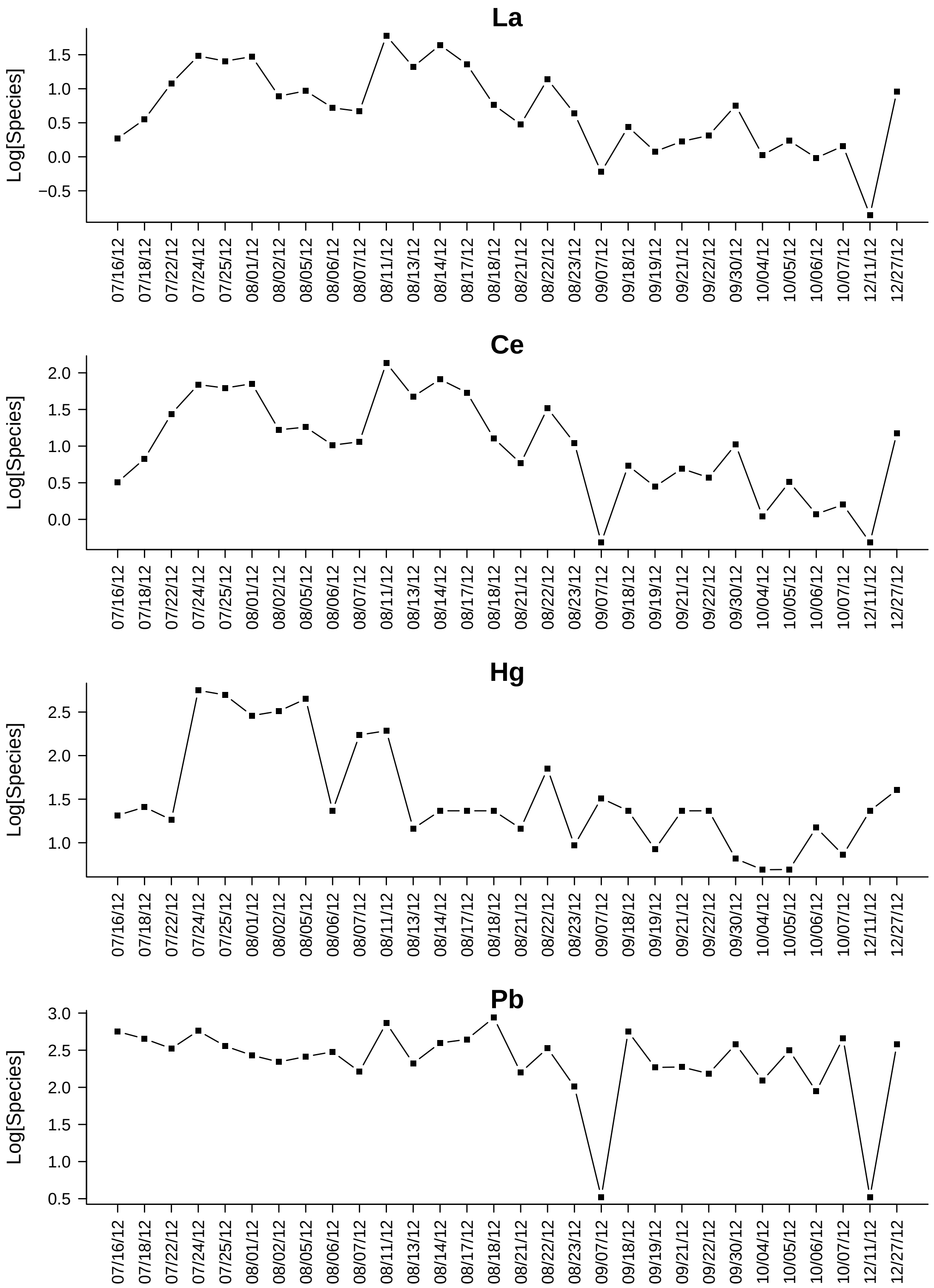


Figure D.8. Temporal profiles for trace metals deposition data continued. 2012 USF mercury deposition study

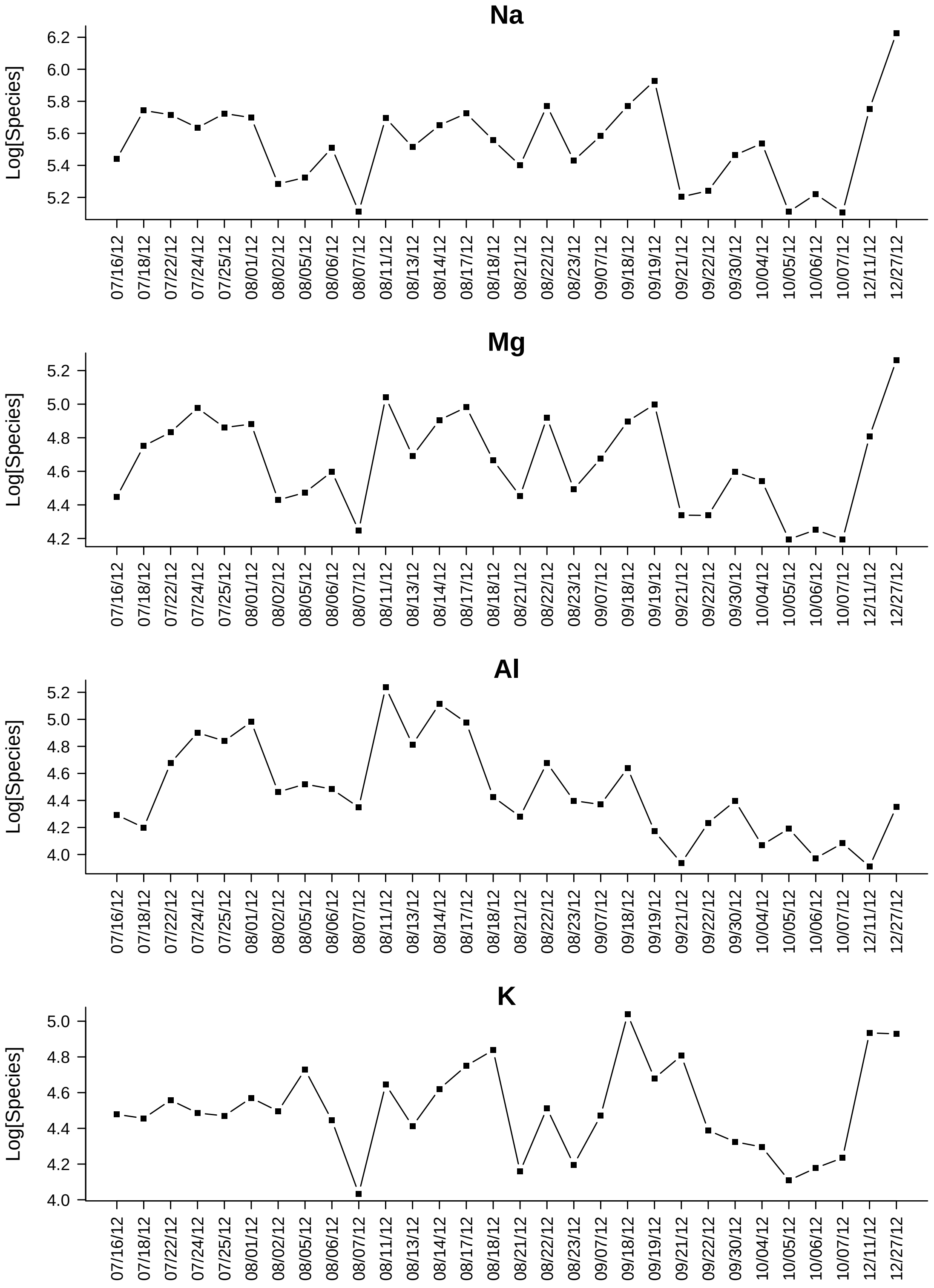


Figure D.9. Temporal profiles for trace metals deposition data continued. 2012 USF mercury deposition study

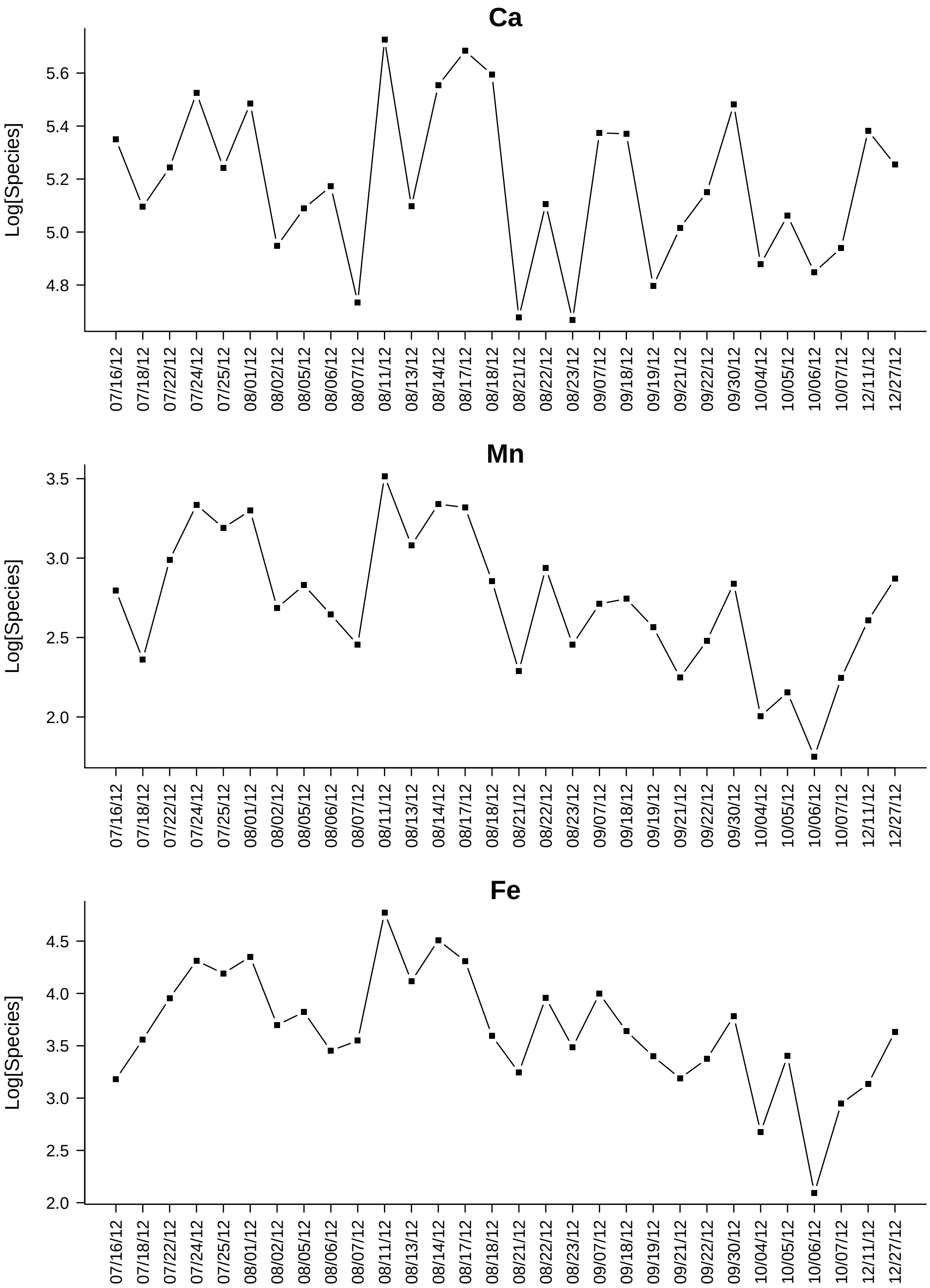


Figure D.10. Temporal profiles for trace metals deposition data continued. 2012 USF mercury deposition study

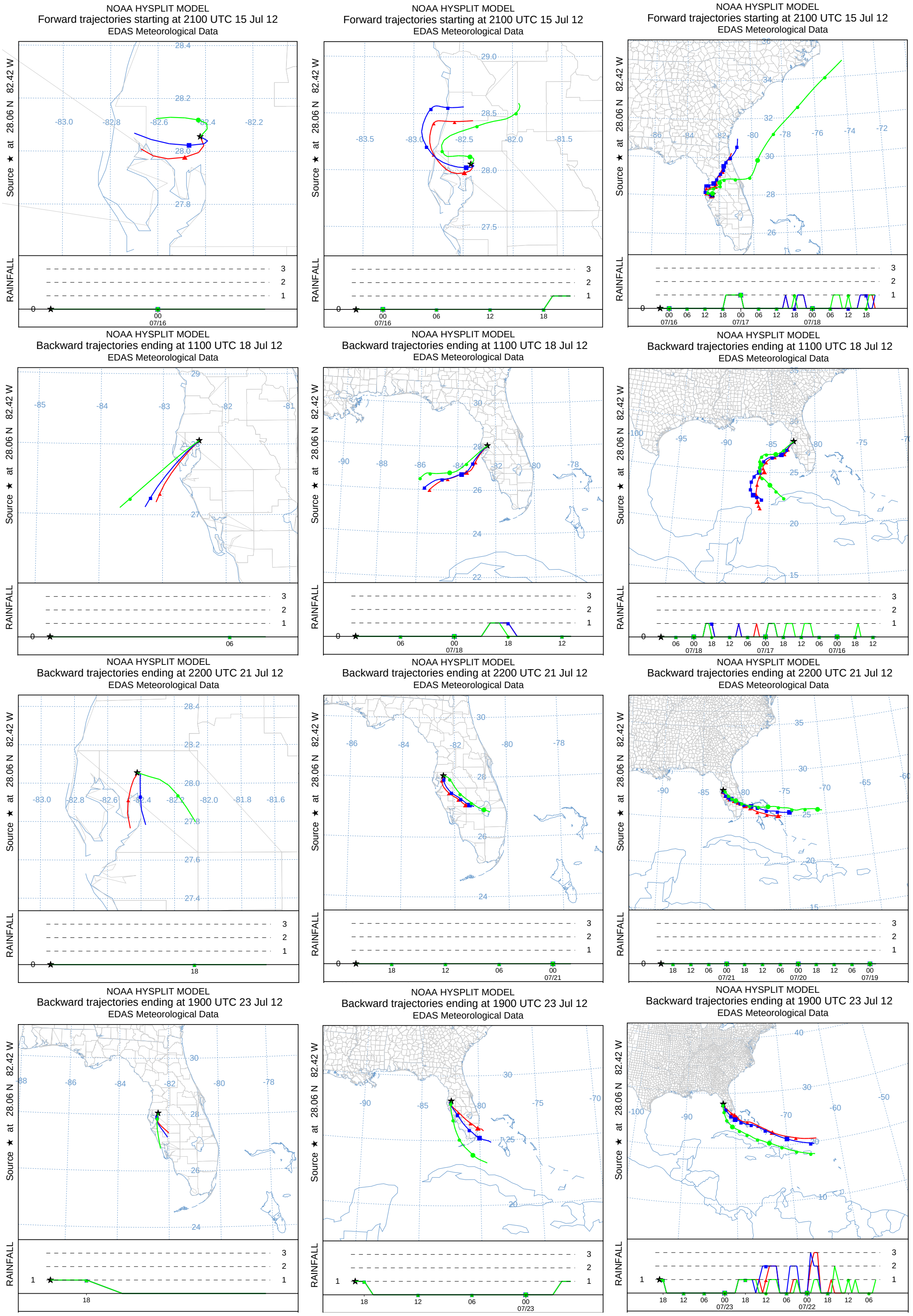


Figure D.11. Back trajectories for the BRACE deposition events occurring over the period July, 2012. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

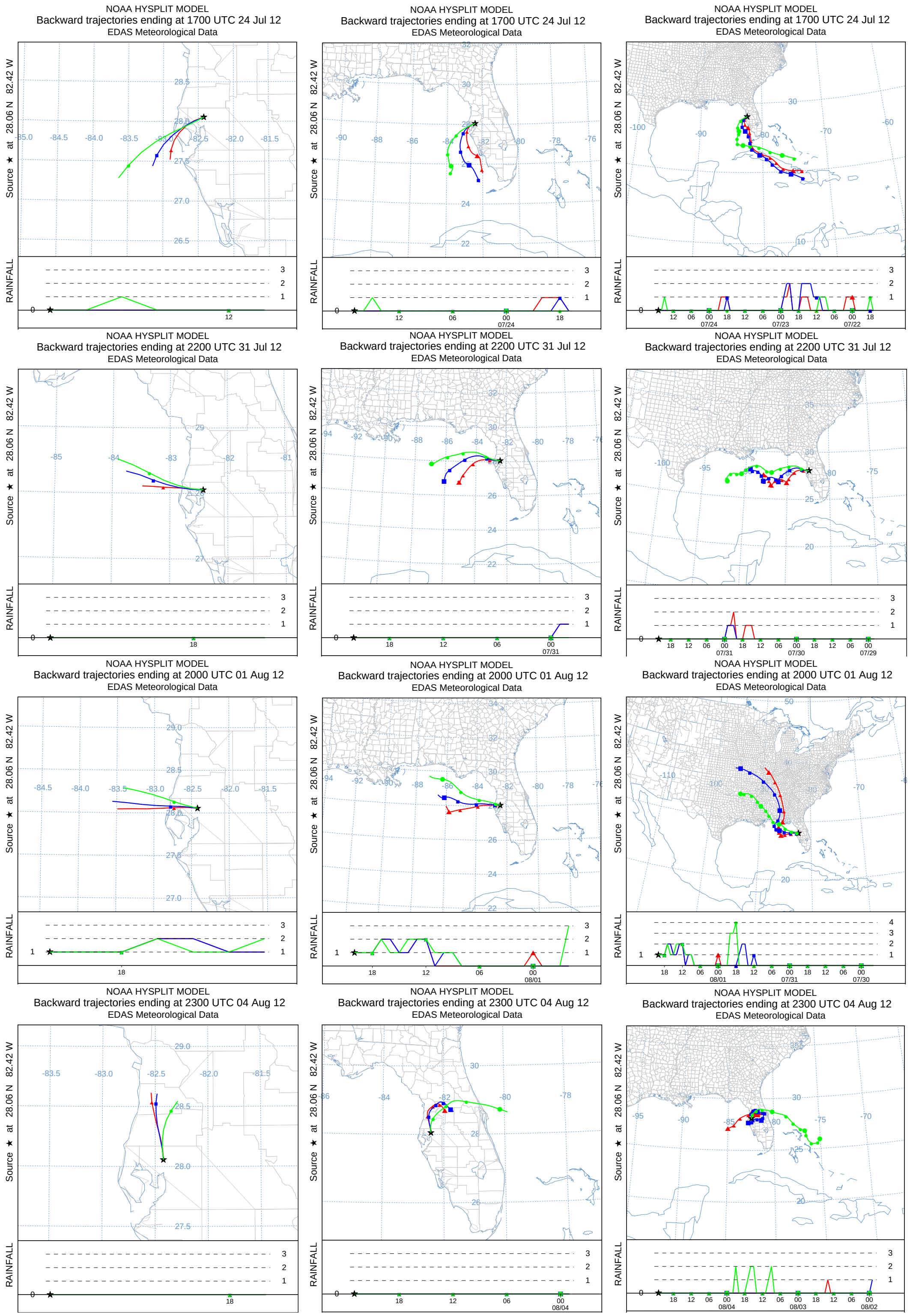


Figure D.12. Back trajectories for the BRACE deposition events occurring over the period July, 2012 – August, 2012. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

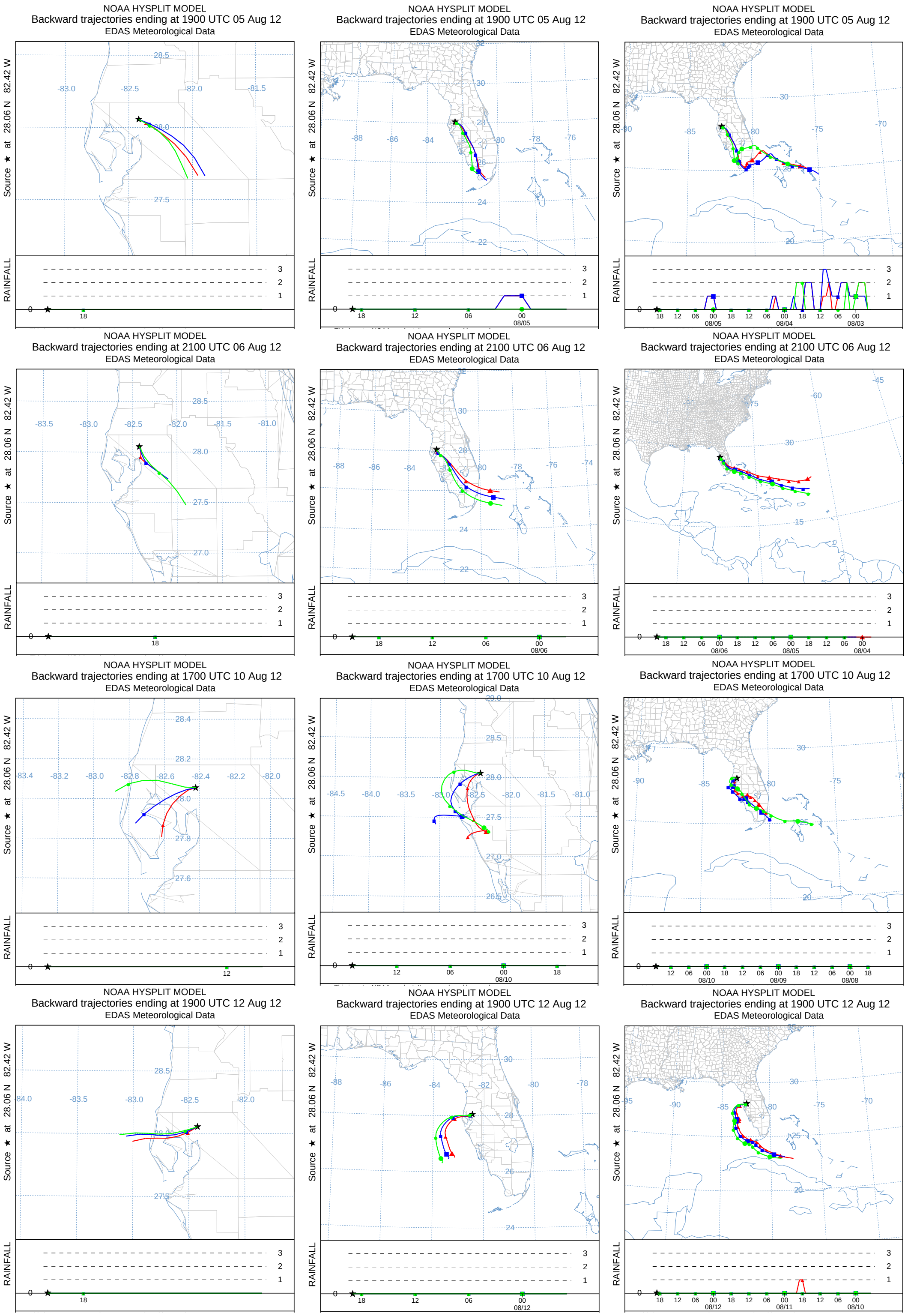
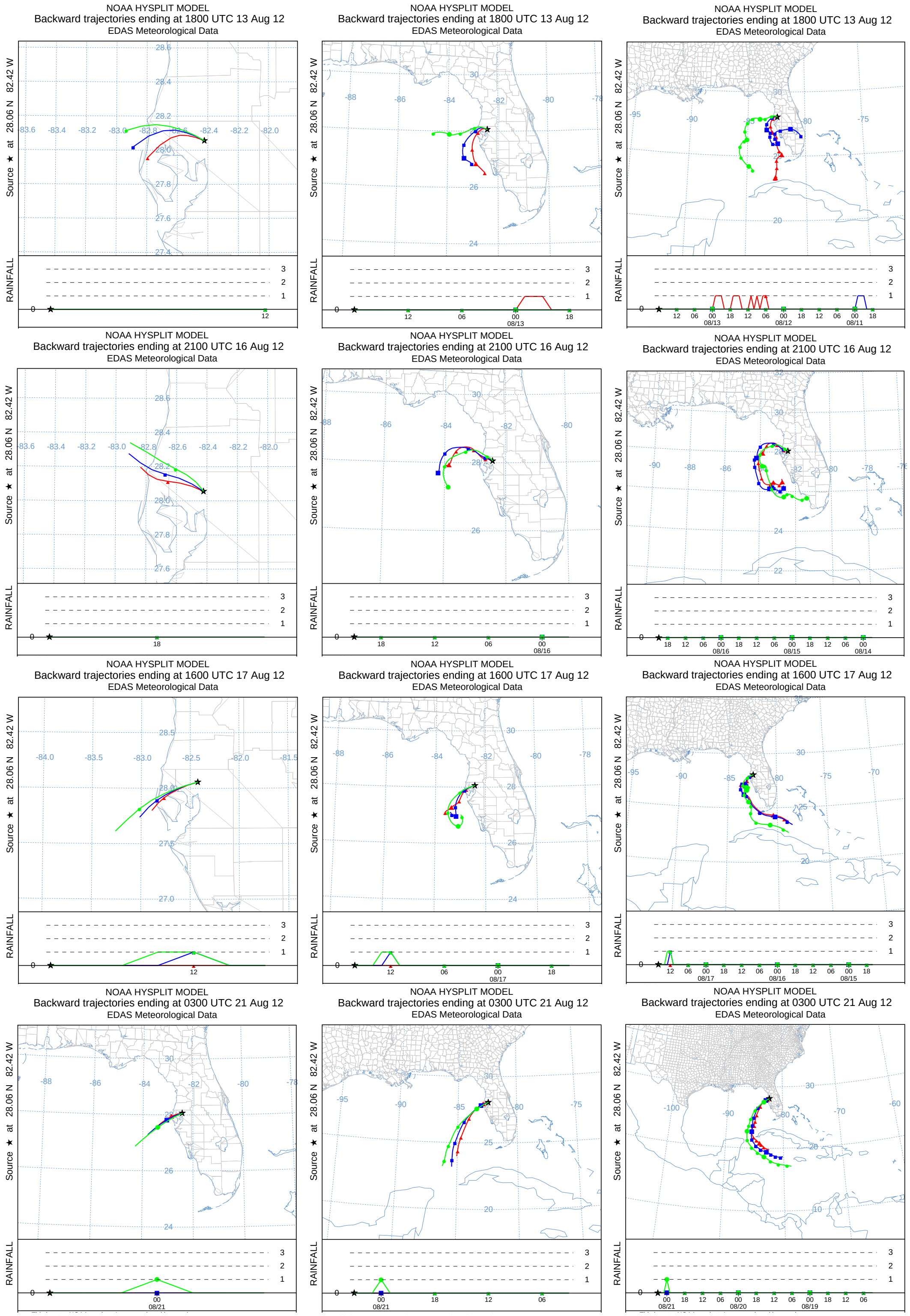


Figure D.13. Back trajectories for the BRACE deposition events occurring over the period August, 2012, continued. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).


NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 13 Aug 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 2100 UTC 16 Aug 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1600 UTC 17 Aug 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0300 UTC 21 Aug 12
EDAS Meteorological Data

Figure D.14. Back trajectories for the BRACE deposition events occurring over the period August, 2012, continued. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

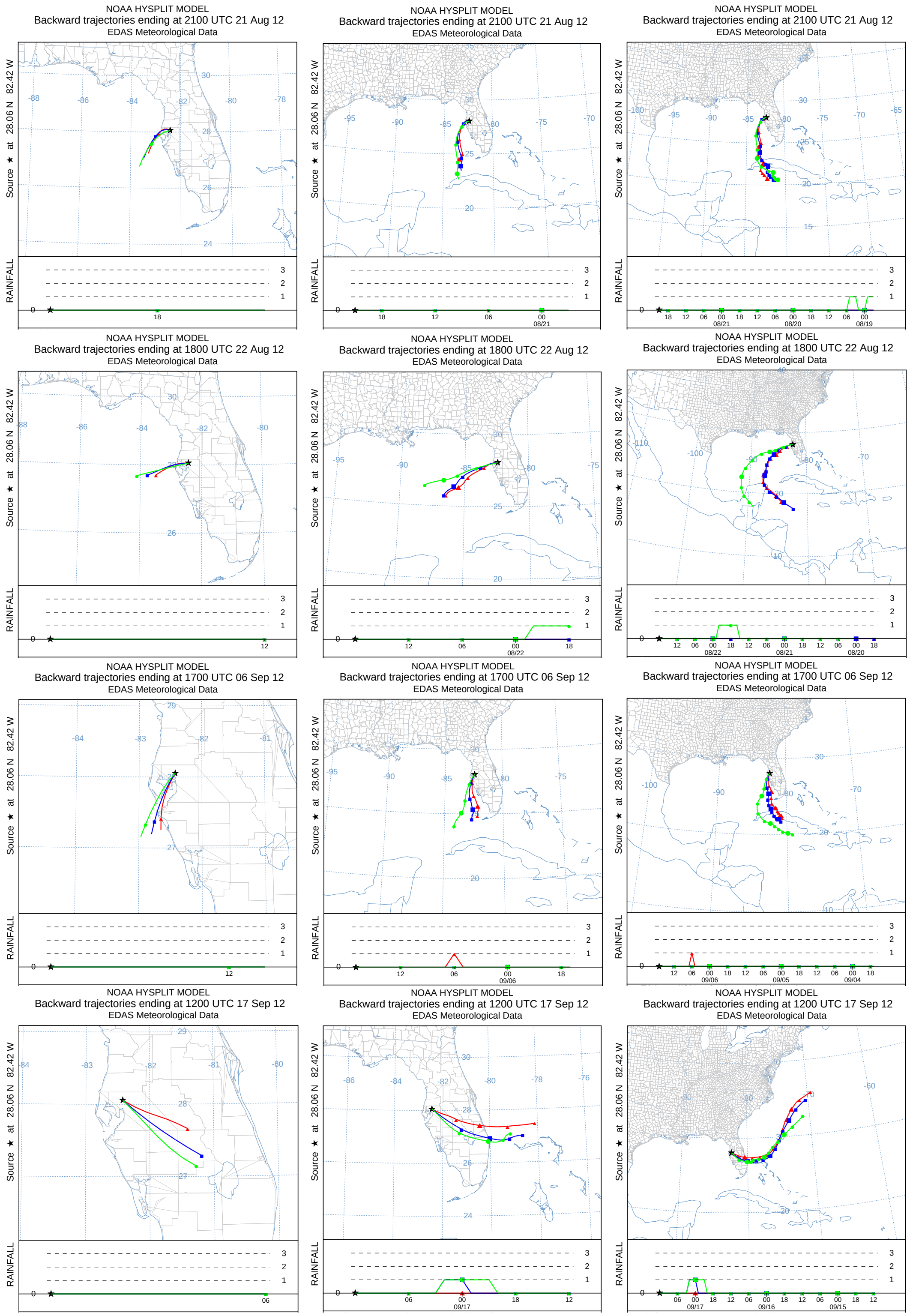


Figure D.15. Back trajectories for the BRACE deposition events occurring over the period August, 2012 – September, 2012. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

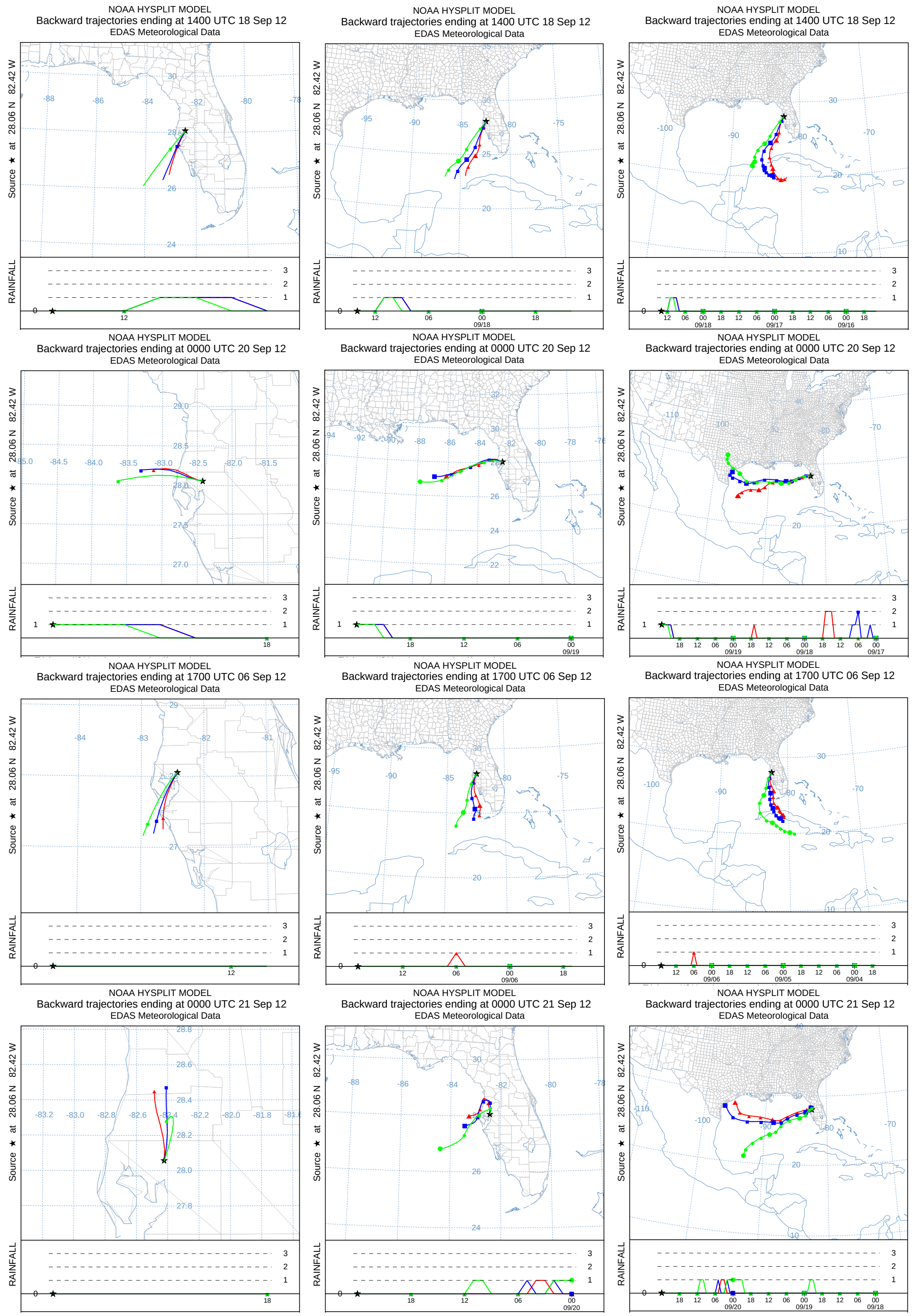
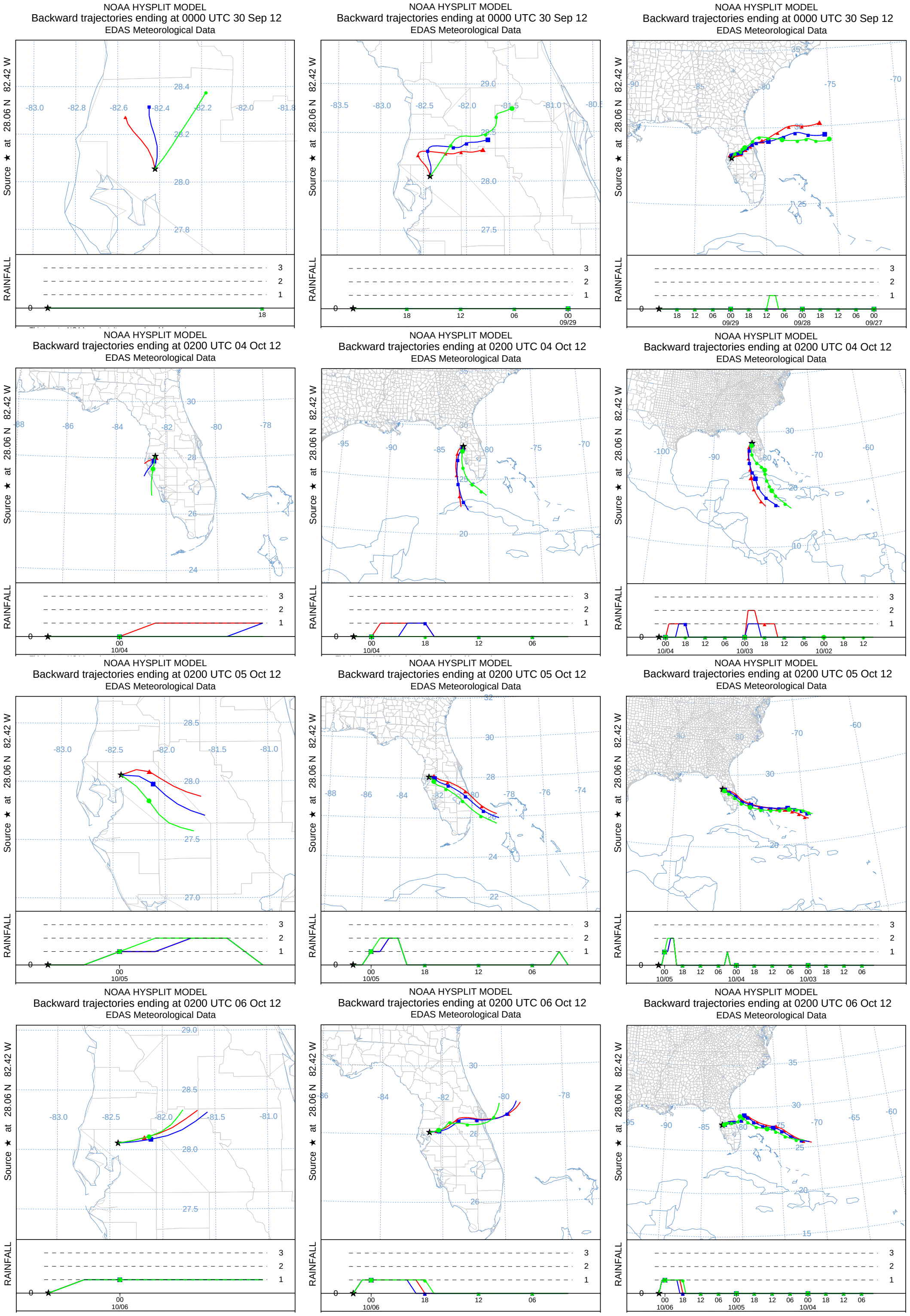


Figure D.16. Back trajectories for the BRACE deposition events occurring over the period September, 2012. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).



NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 30 Sep 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 30 Sep 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 30 Sep 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 04 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 04 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 04 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 05 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 05 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 05 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 06 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 06 Oct 12
EDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 0200 UTC 06 Oct 12
EDAS Meteorological Data

Figure D.17. Back trajectories for the BRACE deposition events occurring over the period September, 2012 – October, 2012. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

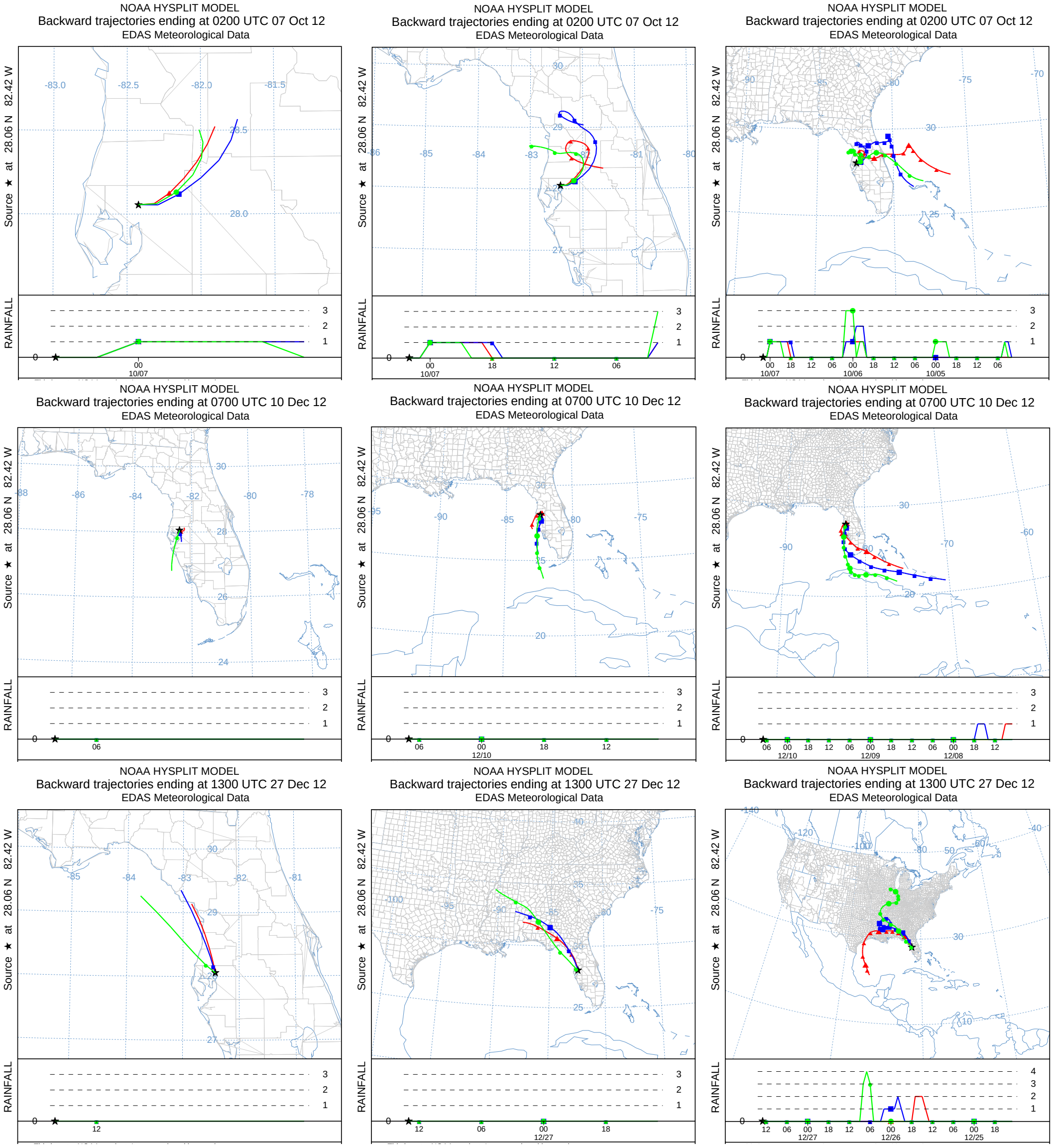
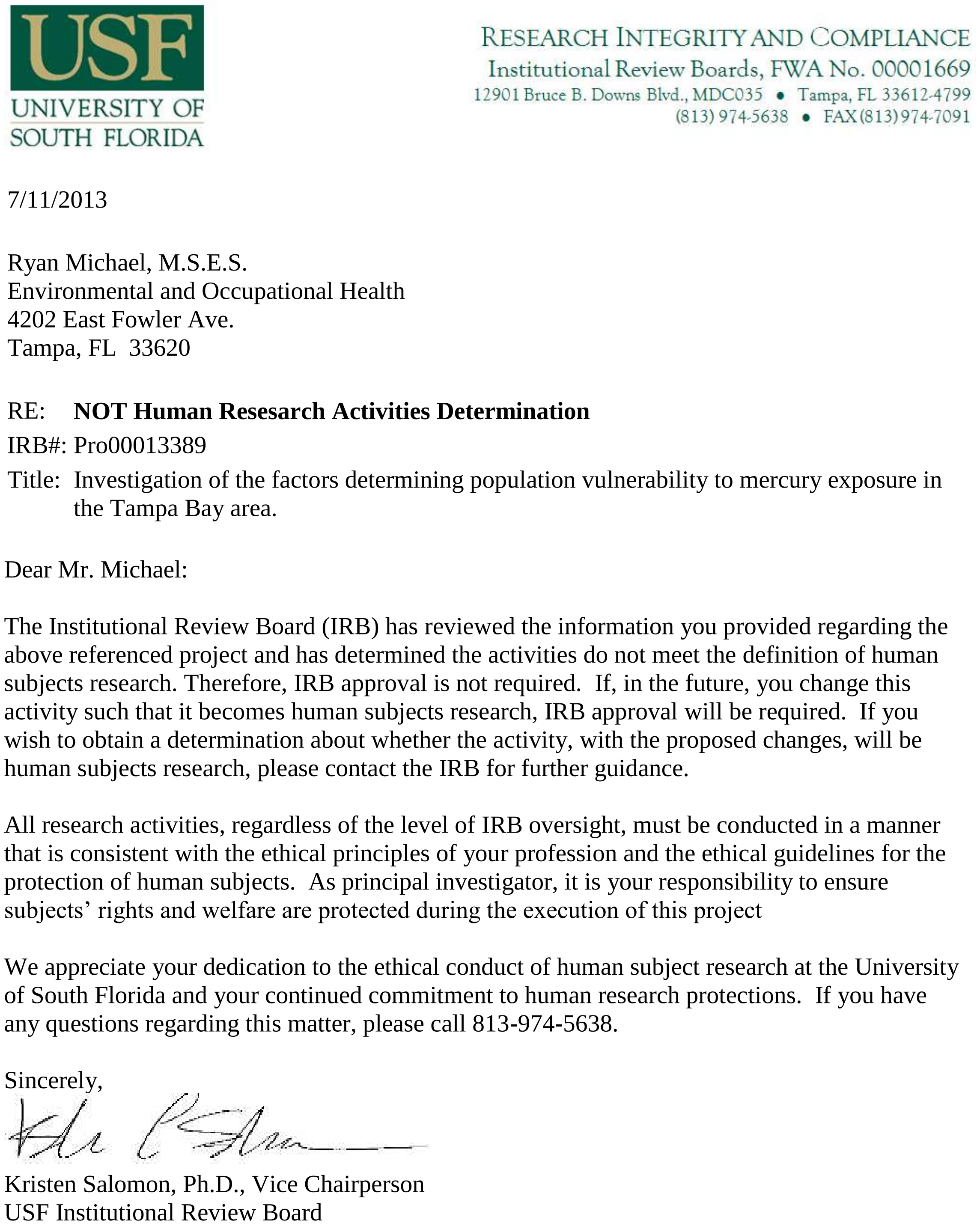


Figure D.18. Back trajectories for the BRACE deposition events occurring over the period October, 2012 – December, 2012. Trajectories are sorted chronologically by event days(top to bottom), with increasing duration from left to right (6hr, 24hr, and 72 hr).

Appendix E.

Population survey data



USF
UNIVERSITY OF
SOUTH FLORIDA

RESEARCH INTEGRITY AND COMPLIANCE
Institutional Review Boards, FWA No. 00001669
12901 Bruce B. Downs Blvd., MDC035 • Tampa, FL 33612-4799
(813) 974-5638 • FAX (813) 974-7091

7/11/2013

Ryan Michael, M.S.E.S.
Environmental and Occupational Health
4202 East Fowler Ave.
Tampa, FL 33620

RE: **NOT Human Resesarch Activities Determination**
IRB#: Pro00013389
Title: Investigation of the factors determining population vulnerability to mercury exposure in the Tampa Bay area.

Dear Mr. Michael:

The Institutional Review Board (IRB) has reviewed the information you provided regarding the above referenced project and has determined the activities do not meet the definition of human subjects research. Therefore, IRB approval is not required. If, in the future, you change this activity such that it becomes human subjects research, IRB approval will be required. If you wish to obtain a determination about whether the activity, with the proposed changes, will be human subjects research, please contact the IRB for further guidance.

All research activities, regardless of the level of IRB oversight, must be conducted in a manner that is consistent with the ethical principles of your profession and the ethical guidelines for the protection of human subjects. As principal investigator, it is your responsibility to ensure subjects' rights and welfare are protected during the execution of this project

We appreciate your dedication to the ethical conduct of human subject research at the University of South Florida and your continued commitment to human research protections. If you have any questions regarding this matter, please call 813-974-5638.

Sincerely,

Kristen Salomon, Ph.D., Vice Chairperson
USF Institutional Review Board

Survey Number:

II) Questionnaire

Questions to be asked of the subject are provided in italics. When choices are given in the questionnaire, circle the answer provided by the respondent, or write in answers not listed.

Complete the following information first:

Date: ____________________

Site Name: ____________________

GPS Location (if available): ______________________

Sex of Respondent: Male, Female, Unknown

Observer notes on the interview, subject, and/or location

____

____

Demographic Information:

1. *What is your age? less than 18 yrs, 18 to 25, 26 to 35, 36 to 50, 51 to 65, over 65,*
   Other: ___________

If the subject answers < 18 yrs, indicate that the survey is for subjects > 18 yrs and end the survey as discussed on Page 1.

2. *How would you identify your race or ethnicity? Some possible choices are:*
   Caucasian, African American, Hispanic or Latino, Native American, Asian, East Indian,
   Afro Caribbean, Afro Amerindian, Mixed European Caribbean (specify) _________________,
   *Other (please specify):*______________________________, *Prefer not to answer*

3. *Do you live in this area?* Yes, No
   If yes: *In which city do you live?*____________________
   How long have you lived in the area?
   Born here, < 5 yrs, 6 to 10 yrs, 11 to 15 yrs, 16 to 20 yrs, over 20 yrs, _________
   If no: *How much time per year do you spend in this area?*______________________
   What is the reason for your visits? Work, Family, Vacation, Other (specify)___________

4. *Do you own your home or rent it?* Own, Rent, Other, (pls. specify)___________

5. *How many bedrooms are in your home?* ________________

Survey Number:

6. *What is your occupation?* ___________________________

7. *How many years have you been in that occupation?*
   less than 1 year, 1 to 5 years, 6 to 12 years, 13+ years, _______________

8. *What is your highest level of formal education?:*
   some elementary, through 8th grade, some high school, high school graduate, some college, college graduate, vocational school graduate, post-graduate degree, other (pls. specify)
   ____

9. *What is your annual household income in US dollars?*
   less than 10,000; 10,001 to 20,000; 20,001 to 30,000; 30,001 to 40,000;
   40,001 to 60,000; 60,001 to 100,000; above 100,000

10. *How many people live in your household (including yourself)?* ___________

11. *How many people in your household are in the following age groups?*
    Adults > 18 yrs (___); Children 10-18 (___) below 10 (___) Infants (___)
    Pregnant women (____)

Fishing and Fish Consumption

12. *How often do you fish? Most days, A few times a week, Once per week, 1 to 2 times per month, A few times a year, Rarely, Never*

13. *Do you fish year round?* Yes, No. *If no, which seasons do you fish?*_______________

14. *What time of the day do you normally begin fishing?*
    Morning, Afternoon, Evening, _____________

15. *What fishing methods do you use?*
    *Rod with bait. Net, Traps, Other (pls. specify)*____

If traps, then what time do you set and retrieve traps?
Set Time: __________________________
Retrieve Time: ______________________

Survey Number:

16. *Where do you normally fish?* ____________________________________

17. *Why do you choose to fish there?*____

18. *What types of fish do you usually catch? If it differs by season, please note the season applicable to each.*

    1.
    2.
    3.
    4.
    5.
    6.
    7.
    8.
    9.
    10.

19. *What are your reasons for fishing? For food, For money, For recreation, Other*___________

    (Circle all that apply)

20. *Do you sell any fish you catch?* Yes, No, ____________

    If so, how much do you earn from fish sales per week?

    <=$50, $51 to $100, $101-$500, more than $500

21. *Is fishing profitable?* Yes, No

    *Why or why not?*____

22. *Do you or your family ever eat the fish you catch?* Yes, No

    *If yes, how often do you or your family eat the fish you catch? Several times a week, A few times a week, Once per week, 1 to 2 times per month, A few times a year, Rarely, Other*_______

    If yes, how do you decide which fish to eat? __________________________________

    ____

23. *How often do you eat fish generally? Several times a week, A few times a week, Once per week, 1 to 2 times per month, A few times a year, Rarely, Other*__________

Survey Number:

24. *Do you and your family eat other types of meat or other proteins?* Yes, No

25. *What are your reasons for eating fish?*
It tastes good, It's healthier than other meats, It's inexpensive, I've always eaten fish,
*For cultural reasons, Other*____

26. *From what sources do you get public health information, in general?*
Radio, Newspaper, Television, Mailings, Email, Internet, Schools, Neighbor,
Municipal billboards, Public meetings, Church/religious organization, Employer, Doctor,
Other, (pls. specify) ____________________

27. *Are you aware that some types of fish can contain levels of mercury that may be harmful to some people?* Yes, No

28. *Have you seen informational guides on fish consumption and mercury?* Yes, No

29. *If yes to either of the above, how has it affected your family's fish consumption?*
____

30. *If no, would such information likely affect your family's fish consumption?*
Yes, No, Why or why not?____

The survey is complete. Go back to page 1 and follow the instructions.

Table E.1. Codes for the analysis of Hillsborough County mercury risk perception survey.

Question #	Question	Value	Code
Sex	Sex of respondent	Male	1
		Female	2
1	What is your age?	less than 18	1
		18 to 25	2
		26 to 35	3
		36 to 50	4
		51 to 65	5
		over 65	6
2	How would you identify your ethnicity	Caucasian	1
		African American	2
		Hispanic/Latino	3
		Native Indian	4
		Asian	5
		East Indian	6
		Afro Caribbean	7
		Mixed European Caribbean	8
		Other	9
3	Do you live in this area (Hillsborough County)	yes	1
		no	2
3b	What city do you live in	value	Null
3c	How long have you lived in the area	less than 5 yrs	1
		6 to 10 yrs	2
		11 to 15 yrs	3
		16 to 20 yrs	4
		greater than 20 yrs	5
3d	How much time per year do you spend in the area	more than once per week	1
		Once per week	2
		few times per month	3

Table E.1 – continued on next page

Table E.1 – continued from previous page

Question #	Question	Value	Code
		few times per year	4
3e	What is the reason for your visit	Work	1
		Family	2
		Vacation	3
		Fishing	4
		Other	5
4	Do you own your home or rent?	Own	1
		Rent	2
		Other	3
5	How many bedrooms in your home	1 bedroom	1
		2 bedrooms	2
		3 bedrooms	3
		4 bedrooms	4
		more than 5 bedrooms	5
6	What is your occupation	value	Null
7	How many years have you been in that occupation	Less than 1 year	1
		1 to 5 years	2
		6 to 12 years	3
		more than 13 years	4
8	What is your highest level of education	some elementary	1
		through 8th grade	2
		some high school	3
		high school graduate	4
		some college	5
		college graduate	6
		vocational school graduate	7
		Post-graduate degree	8
		other	9

Table E.1 – continued on next page

Table E.1 – continued from previous page

Question #	Question	Value	Code
9	What is your annual income in US dollars	less than 10,000	1
		10001 – 20000	2
		20001 – 30000	3
		30001 – 40000	4
		40001 – 60000	5
		60001 – 100000	6
		greater than 100000	7
10	How many people live in you household	1	1
		2	2
		3	3
		4	4
		5	5
		6	6
		7	7
11	How many people in household older than 18 years	1	1
		2	2
		3	3
		4	4
		>5	5
11b	How many people in household between 10 âĂŞ 17 years	None	1
		1	2
		2	3
		3	4
		4	5
		>5	6
11c	How many persons in household below 3 - 10 years	None	1
		1	2
		2	3
		3	4
		4	5
		>5	6

Table E.1 – continued on next page

Table E.1 – continued from previous page

Question #	Question	Value	Code
11d	How many infants in the household (less than 2)	None	1
		1	2
		2	3
		3	4
		4	5
		>5	6
11e	How many pregnant women in household	None	1
		1	2
		2	3
		3	4
		4	5
		>5	6
12	How often do you fish	Most days	1
		A few times per week	2
		Once per week	3
		1 to 2 times per month	4
		A few times per year	5
		Rarely	6
		Never	7
13	What seasons do you fish	All	1
		Spring	2
		Summer	3
		Fall	4
		Winter	5
		Other	6
14	What time of the day do you normally begin fishing	Anytime	1
		Morning	2
		Afternoon	3
		Evening	4

Table E.1 – continued on next page

Table E.1 – continued from previous page

Question #	Question	Value	Code
15	What fishing methods do you use	Rod with bait	1
		Net	2
		Traps	3
		Multiple methods	4
		Other	5
16	Where do you normally fish	Value	Null
17	Why do you choose to fish there	Value	Null
18	What types of fish do you usually catch	Value	Null
19	What are your reasons for fishing	food	1
		money	2
		recreation	3
		food and recreation	4
		other	5
20	Do you sell any of the fish caught	yes	1
		No	2
		Sometimes	3
20b	How much do you earn from fish sales per week	<\$50	1
		\$51 – \$100	2
		\$100 – \$500	3
		>\$500	4
21	Is fishing profitable	yes	1
		no	2
		Sometimes	3
22	Do you or your family ever eat the fish you catch	yes	1
		no	2
		sometimes	3

Table E.1 – continued on next page

Table E.1 – continued from previous page

Question #	Question	Value	Code
22b	How often do you or your family eat the fish you catch	Several times a week	1
		A few times per week	2
		Once per week	3
		1 to 2 times per month	4
		A few times per year	5
		Rarely	6
		Other	7
22c	How do you decide which fish to eat	whatever is caught is eaten	1
		size- large	2
		species of fish	3
23	How often do you eat fish generally	Several times a week	1
		A few times per week	2
		Once per week	3
		1 to 2 times per month	4
		A few times per year	5
		Rarely	6
		Other	7
24	Do you and you family eat other types of meat or protiens?	yes	1
		no	2
25	what are your reasons for eating fish	Taste	1
		healthy	2
		inexpensive	3
		I have always eaten fish	4
		Cultural reasons	5
		Multiple reasons	6
26	From what sources do you get public health information in general	Radio	1
		Newspaper	2
		Television	3
		Mailings	4
		Email	5

Table E.1 – continued on next page

Table E.1 – continued from previous page

Question #	Question	Value	Code
		Internet	6
		Schools	7
		Neighbor	8
		Municipal Billboards	9
		Public meetings	10
		Church/religious organizations	11
		Employer	12
		Doctor	13
		Multiple methods	14
		Other	15
27	Are you aware that some types of fish can contain levels of mercury that may be harmful to some people	yes	1
		no	2
28	Have you seen informational guides on fish consumption and mercury	yes	1
		no	2
29	How has your awareness of mercury exposure affected your family's fish consumption	yes	1
		no	2
		maybe	3
30	Would information about mercury exposure from fish affect you family fish consumption.	yes	1
		No	2
		maybe	3

Table E.2. Response frequencies for Hillsborough County mercury risk perception survey data.

Question	Response	Frequency
Sex	Male	20
Sex	Female	10
Q1	less than 18	0
Q1	18 to 25	5
Q1	26 to 35	14
Q1	36 to 50	9
Q1	51 to 65	7
Q1	over 65	0
Q2	Caucasian	19
Q2	African American	10
Q2	Hispanic/Latino	3
Q2	Native Indian	2
Q2	Other	1
Q3	yes	29
Q3	no	6
Q3c	less than 5 yrs	6
Q3c	6 to 10 yrs	7
Q3c	11 to 15 yrs	5
Q3c	16 to 20 yrs	2
Q3c	greater than 20 yrs	10
Q4	Own	10
Q4	Rent	25
Q5	1 bedroom	1
Q5	2 bedrooms	11
Q5	3 bedrooms	12
Q5	4 bedrooms	8
Q5	more than 5 bedrooms	3
Q7	Less than 1 year	1
Q7	1 to 5 years	12
Q7	6 to 12 years	8
Q7	more than 13 years	10
Q8	some elementary	0
Q8	through 8th grade	2
Q8	some high school	5
Q8	high school graduate	20
Q8	some college	1
Q8	college graduate	5
Q8	vocational school graduate	2
Q8	Post-graduate degree	0
Q8	other	0
Q9	less than 10,000	0
Q9	10001 – 20000	4
Q9	20001 – 30000	9
Q9	30001 – 40000	13
Q9	40001 – 60000	6
Q9	60001 – 100000	3
Q9	greater than 100000	0
Q10	One	3
Q10	Two	9
Q10	Three	6
Q10	Four	5

Table E.2 – continued on next page

Table E.2 – continued from previous page

Question	Response	Frequency
Q10	Five	6
Q10	Six	6
Q10	Seven	0
Q11	None	0
Q11	One	10
Q11	Two	17
Q11	Three	3
Q11	Four	1
Q11	Five and greater	4
Q11b	None	19
Q11b	One	9
Q11b	Two	2
Q11b	Three	1
Q11b	Four	3
Q11b	Five and greater	1
Q11c	None	25
Q11c	One	7
Q11c	Two	1
Q11c	Three	0
Q11c	Four	1
Q11c	Five and greater	0
Q11d	None	34
Q11d	One	0
Q11d	Two	0
Q11d	Three	0
Q11d	Four	0
Q11d	Five and greater	0
Q11e	None	31
Q11e	One	3
Q11e	Two	0
Q11e	Three	0
Q11e	Four	0
Q11e	Five and greater	0
Q12	Most days	1
Q12	A few times per week	5
Q12	Once per week	17
Q12	1 to 2 times per month	6
Q12	A few times per year	4
Q12	Rarely	2
Q12	Never	0
Q13	All	33
Q13	Spring	0
Q13	Summer	1
Q13	Fall	0
Q13	Winter	0
Q13	Other	1
Q14	Anytime	4
Q14	Morning	17
Q14	Afternoon	6
Q14	Evening	8
Q15	Rod with bait	32
Q15	Net	2

Table E.2 – continued on next page

Table E.2 – continued from previous page

Question	Response	Frequency
Q15	Traps	0
Q15	Multiple methods	1
Q15	Other	0
Q19	food	1
Q19	money	0
Q19	recreation	27
Q19	food and recreation	7
Q19	other	0
Q20	yes	1
Q20	No	33
Q20	Sometimes	1
Q22	yes	30
Q22	No	5
Q22	Sometimes	0
Q22b	Several times a week	2
Q22b	A few times per week	4
Q22b	Once per week	7
Q22b	1 to 2 times per month	8
Q22b	A few times per year	7
Q22b	Rarely	0
Q22b	Other	1
Q22c	whatever is caught is eaten	7
Q22c	size- large	14
Q22c	species of fish	7
Q23	Several times a week	4
Q23	A few times per week	5
Q23	Once per week	10
Q23	1 to 2 times per month	9
Q23	A few times per year	3
Q23	Rarely	1
Q23	Other	1
Q24	Yes	31
Q24	No	1
Q25	Taste	11
Q25	healthy	11
Q25	inexpensive	0
Q25	I have always eaten fish	2
Q25	Cultural reasons	3
Q25	Multiple reasons	5
Q26	Radio	0
Q26	Newspaper	3
Q26	Television	13
Q26	Mailings	0
Q26	Email	0
Q26	Internet	3
Q26	Schools	0
Q26	Neighbor	0
Q26	Municipal Billboards	1
Q26	Public meetings	0
Q26	Church/religious organizations	0
Q26	Employer	0
Q26	Doctor	0

Table E.2 – continued on next page

Table E.2 – continued from previous page

Question	Response	Frequency
Q26	Multiple methods	11
Q26	Other	2
Q27	yes	24
Q27	No	9
Q27	Sometimes	0
Q28	yes	12
Q28	No	23
Q28	Sometimes	0
Q29	yes	6
Q29	No	8
Q29	Sometimes	0
Q30	yes	15
Q30	No	16
Q30	Sometimes	2