FIELD MEASUREMENTS OF MERCURY DEPOSITION IN PULLMAN AND PUYALLUP, WA

By

LANKA DESILVA

A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTERS OF SCIENCE IN ENVIRONMENTAL ENGINEERING

WASHINGTON STATE UNIVERSITY
Department of Civil and Environmental Engineering

DECEMBER 2011

To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of LANKA DESILVA find it satisfactory and recommend that it be accepted.

_____

Marc W. Beutel, Ph.D., Chair

_____

Brian K. Lamb, Ph.D.

_____

Jennifer C. Adam, Ph.D.

ACKNOWLEDGEMENT

The completion of this thesis would not have been possible without the knowledge and guidance of my advisors, professors, and fellow graduate students with whom I have worked alongside over the past year and half. I would like to thank Dr. Marc Beutel for his encouragement and direction during my graduate school career. I would also like to thank Dr. Brian Lamb, Dr. Jennifer Adam, Dr. Joseph Vaughn, and the research faculty in the Laboratory for Atmospheric Research (LAR) for providing instruction and financial support. This project was also partly funded by the National Science Foundation. A very special thank you to Mr. Dory Clausnitzer and Dr. John Stark at the WSU Puyallup Research and Extension Center. I would also like to thank Ms. Melanie Marshall for allowing me to have a place to stay while conducting my research on the Westside. The dry deposition wet sampler and precipitation collector could not have been completed without the hard work and dedication of Mr. Gary Held and the other members of the WSU Engineering Machine Shop. I would especially like to thank Stephen Dent for inspiring me to become a more meticulous researcher. A special thank you to my research group, Seyoum Gebremariam, Piper Marshall, Suzanne Cox, and Ricardi Duvil, for their motivation. My friends back home in Alabama have always pushed me to never give up on my dreams and I thank them with all my heart. No words can express how my family has supported me through my master's degree. I want to thank them for all their love and support that they have given me.

FIELD MEASUREMENTS OF MERCURY DEPOSITION IN

WESTERN AND EASTERN WASHINGTON

Abstract

by Lanka DeSilva, M.S.
Washington State University
December 2011

Chair: Marc W. Beutel

The overarching objective of this study was to evaluate mercury deposition in two locations in Washington State: Pullman, WA in the rural east side of the state and Puyallup, WA on the populated west side of the state. Measurements were made from late summer to early fall of 2011 using a wet surface sampler for dry deposition and a precipitation collector for wet deposition. Puyallup was hypothesized to have higher rates of mercury deposition due to its proximity to substantial anthropogenic sources including intensive urban activities and atmospheric influxes from Asia. Dry deposition fluxes were 55.0 ± 34.5 ng/m^2/d (average plus/minus standard deviation; n = 4) in Pullman and 29.7 ± 7.0 ng/m^2/d in Puyallup (n = 6). Wet deposition fluxes were 166 ± 112 ng/m^2/d (n = 4) in Pullman and 25.3 ± 5.1 ng/m^2/d in Puyallup (n = 3). In contrast to our hypothesis, deposition levels were higher in Pullman, particularly during one dry deposition sampling event in late August (103 ng/m^2/d) and three wet deposition sampling events in late June (303 ng/m^2/d) and mid July (112 and 206 ng/m^2/d). The high deposition rates in Pullman were likely a result of local anthropogenic activities that enhance mercury depositing including summertime agricultural harvesting and field burning. Field results

were also compared to mercury depositional fluxes predicted by the numerical air quality forecast system AIRPACT-3. Modeled deposition results were lower than measured deposition results for both Pullman and Puyallup during the comparable sampling duration. A likely reason for lower modeled deposition rates compared to measured deposition rates is the lack of agricultural field burning emissions data available for the AIRPACT-3 model. This study, while limited in its scope, adds to the data set of mercury deposition in Washington, which has little data for the east side of the state and mainly consists of wet deposition on the west side of the state.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

1.1 Background

Atmospheric mercury deposition is a worldwide health concern due to its transportability and strong tendency to methylate and bioaccumulate up the aquatic food webs (Lin and Pehkonen, 1999). This issue is of great importance since biota in water bodies around the world have high concentrations of mercury. There are a number of natural sources of atmospheric mercury such as volcanic eruptions and forest fires, but some of the most important sources are from anthropogenic activities including metal production, coal fired power plants, waste treatment and incineration, and pulp industries (Morel et al., 1998). Many recent studies have indicated that biomass burning has significantly increased rates of mercury deposition. As the soil is heated due to biomass burning, mercury that was originally deposited to the soil is remitted back into the atmosphere as gaseous elemental mercury. As detailed by Biswas et al. (2004), soil burning contributes approximately 100 Mg/yr of mercury re-emissions in the US. These anthropogenic sources that contribute to atmospheric mercury deposition have significant effects on the delicate environment of the Pacific Northwest. This region includes alpine meadows and forests, rare ecosystems that are sensitive to atmospheric pollutants (Rattray and Sievering, 2001). Due to their obscure locations, atmospheric mercury deposition is a major route to these ecosystems (Fritsche, 2008). As of 2000, industrial processes contributed ~30% of the total mercury emissions globally; whereas natural sources accounted for ~60% of the total (Pacyna et al., 2006; Pirrone et al., 2001). Some the significant natural sources of atmospheric mercury emissions are the volatilization from water bodies and re-emissions from the top soil

surface and vegetation. Mercury emissions from natural and anthropogenic sources worldwide are detailed in Tables 1 and 2.

Table 1. Studies Examining Mercury Emissions from Natural Sources

Natural Sources	Hg Emissions ($ng/m^2/h$)	Reference
Water Surface		
North-Western Mediterranean Sea	1.16	Cossa et al., 1996
Scheldt Estuary, Belgium	5.8	Cossa et al., 1996
Lake Ontario, North America	0-9	Poissant et al., 2000
Vegetation		
Walker Branch Forest, TN, USA	10-300	Linberg et al., 1998
Forest near Lake Gardsjon, Sweden	1-4	Lindberg et al., 1998
Soil		
Shaded Forest, Sweden	0.3	Xiao et al., 1991
Shaded Forest, TN, USA	2-7	Carpi and Lindberg, 1998

Table 2. Anthropogenic Sources Contributing to Mercury Emissions

Anthropogenic Sources	Hg Emission (tons/yr)	Reference
Gold Mining		
Amazon, Brazil since 1979	180	Lacerda, 1997
USA since 1969	6	Lacerda, 1997
Dixing region, China since 1992	120	Lacerda, 1997
Coal Combustion		
North America since 1992	81	Pirrone et al., 1996
Eastern Europe since 1992	114	Pirrone et al., 1996
Asia since 1992	420	Pirrone et al., 1996
Waste Treatment and Incineration		
North America since 1992	130	Pirrone et al., 1996
South America since1992	25	Pirrone et al., 1996
Asia since 1992	300	Pirrone et al., 1996

Mercury in the atmosphere mainly exists in the gaseous elemental form, Hg(0), and less than 5% of the total is typically present as gaseous divalent mercury, Hg(II), and particulate mercury, Hg(p) (Sakata and Marumoto, 2004). The atmospheric lifetime of Hg(II) and Hg(p) are much shorter than Hg(0) (USEPA, 1997). Due to their short lifetime, both Hg(II) and Hg(p) have been observed to be the two main forms of mercury deposited to the earth's surface. Hg(0) has a residence time of a year in the atmosphere, which allows it to be transported globally. While industrial areas contribute a majority of the mercury emissions into the atmosphere, some of the most remote regions of the world can be affected by atmospheric transport. Hg(0) can oxidize to Hg(II) in the atmosphere by the presence of ozone (O_3), chlorine (Cl_2), and hydrogen peroxide (H_2O_2) (Morel et al., 1998). Ozone pollution has increased in the past few years, therefore it is possible to observe higher levels of Hg(II) in the atmosphere. Hg(II) and Hg(p) are the main forms of mercury deposited from the atmosphere through both wet and dry deposition (Sakata and Marumoto, 2004). One of the dominate forms of mercury present in dry deposition is Hg(II) due to its high deposition velocity (Zhang et al., 2009), which may explain why it is the main form of mercury deposited to the earth's surface. The dry deposition process involves atmospheric gaseous and particulate-bond chemicals settling to a surface by turbulent diffusion, whereas wet deposition is the removal of gaseous and particulate-bond chemicals from the atmosphere by precipitation scavenging.

Industrial development in the US has contributed greatly to mercury deposition. As part of the National Atmospheric Deposition Program (NADP), the Mercury Deposition Network (MDN) has over 100 monitoring stations in the US and Canada. These sites only measure for wet mercury deposition. Currently, the MDN does not provide dry mercury deposition measurements through the program's website. In Washington State, there are only two MDN monitoring

stations: Station Seattle/NOAA WA18 (King County) and Station Makah National Fish Hatchery WA03 (Clallam County), which are both located in Western Washington. This program allows state regulators, educators and the public to view past and current mercury deposition data in rural and urban areas of the US and Canada. In the US Environmental Protection Agency (USEPA) Mercury Report to Congress (1997), total atmospheric mercury concentrations in rural areas were 1-4 ng/m^3, whereas observed concentrations in urban areas were much higher, approximately 10-170 ng/m^3. However, these levels have increased since the publication of this report (Figure 1.3). Dry deposition in industrialized areas contribute about 50% of the total deposition, while wet deposition rates are observed to be higher usually in rural areas (Sakata et al., 2008; Era-Miller, 2011). The total dry and wet mercury deposition for the US are summarized in Figure 1.1 and 1.2.

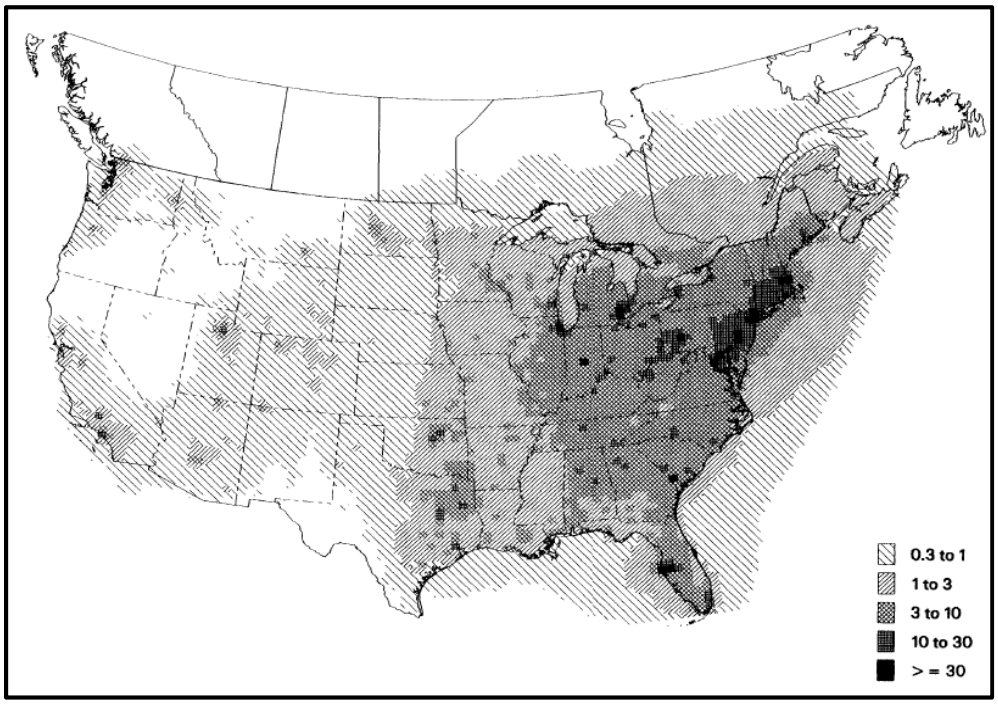

Figure 1.1. US total mercury dry deposition for 1989, µg/m^2/yr (USEPA, 1997).

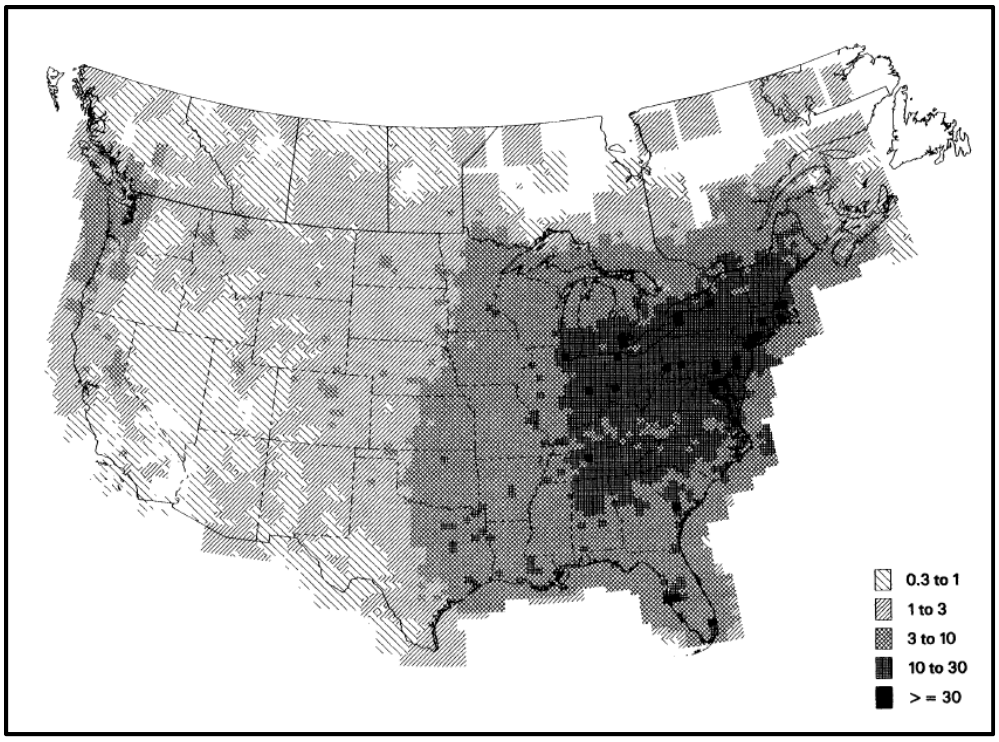

Figure 1.2. US total mercury wet deposition for 1989, µg/m^2/yr (USEPA, 1997).

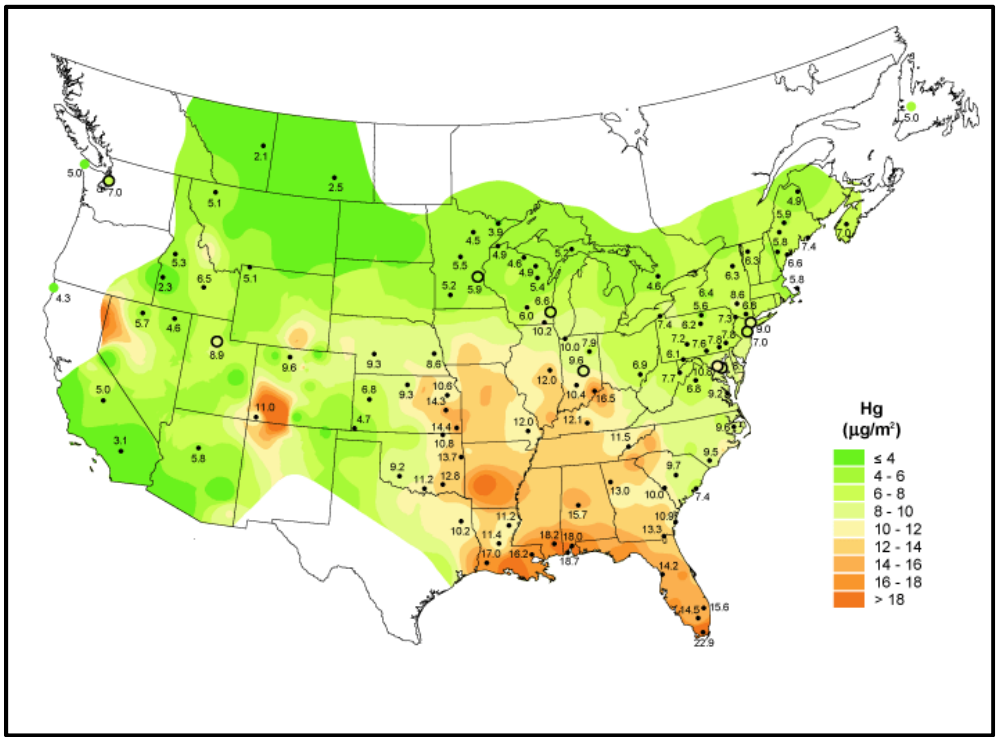

Figure 1.3. Annual US total mercury wet deposition for 2009 (NADP/MDN, 2011).

Seasonality plays a major role in atmospheric mercury concentrations and deposition. As detailed by Lamborg et al. (1995), mercury concentrations in precipitation and wet deposition fluxes are higher during summer than in winter in the US. Research has indicated that the conversion of Hg(0) to Hg(II) is accelerated with increasing air temperature (Era-Miller, 2011). While temperatures are typically higher during the summer, Hg(II) concentrations tend to be elevated. Hg(II) is water soluble, which can easily accumulate in precipitation. Concentrations of Hg(p) have been observed to be higher during winter conditions (Iverfeldt, 1991; Keeler et al, 1995; Schroeder and Munthe, 1998).

Once Hg(II) or Hg(p) are deposited onto the landscape and transported into aquatic systems, they can be bought to the sediments by particle settling, and then later released by diffusion or resuspension (Watras and Huckabee, 1994). If Hg(0) is deposited into the water, it has limited solubility, and thus is unavailable to living organisms. However, Hg(II) is highly soluble in water and is the main form of mercury that is present in biota. Hg(II) may also transform back and forth to Hg(0) by redox and oxidation reactions. These reactions can be observed in both the oxic surface water and anoxic bottom water (Morel et al., 1998). Deposited Hg(II) can be converted into toxic methylmercury (CH_3Hg^+) by the activity of sulfate-reducing bacteria found in the anoxic bottom water and sediments (Benoit et al., 2003). As methylmercury forms within the aquatic ecosystem, it may enter the food chain via phytoplankton or bacteria and eventually bioaccumulate within fish (Figure 1.4) (Watras et al., 1998). Methylmercury can cause severe and chronic neuorotoxicological effects in both mammals and birds (Ullrich et al., 2001). Such severity in mammals can deteriorate reproduction and fetal development (Megler et al., 2007).

Methylmercury can also be buried in the sediments and eventually released by diffusion or resusupension. Sedimented Hg(II) and methylmercury can be released from sediments under some circumstances, particularly anaerobic sulfide rich conditions. Sunlight exposure to methylmercury and Hg(II) has a general detoxifying effect. Methylmercury can break down to Hg(II) or Hg(0) by sunlight exposure, also known as demethylation, and can leave the aquatic ecosystem as a gaseous Hg(0) via volatilization (Swain et al, 1992). As stated by the US Geological Survey (USGS, 2009), nearly one third of the US water bodies are listed with mercury-related fish consumption advisories. The USEPA (2004) has listed a statewide fish consumption advisory for all lakes and rivers in state of Washington.

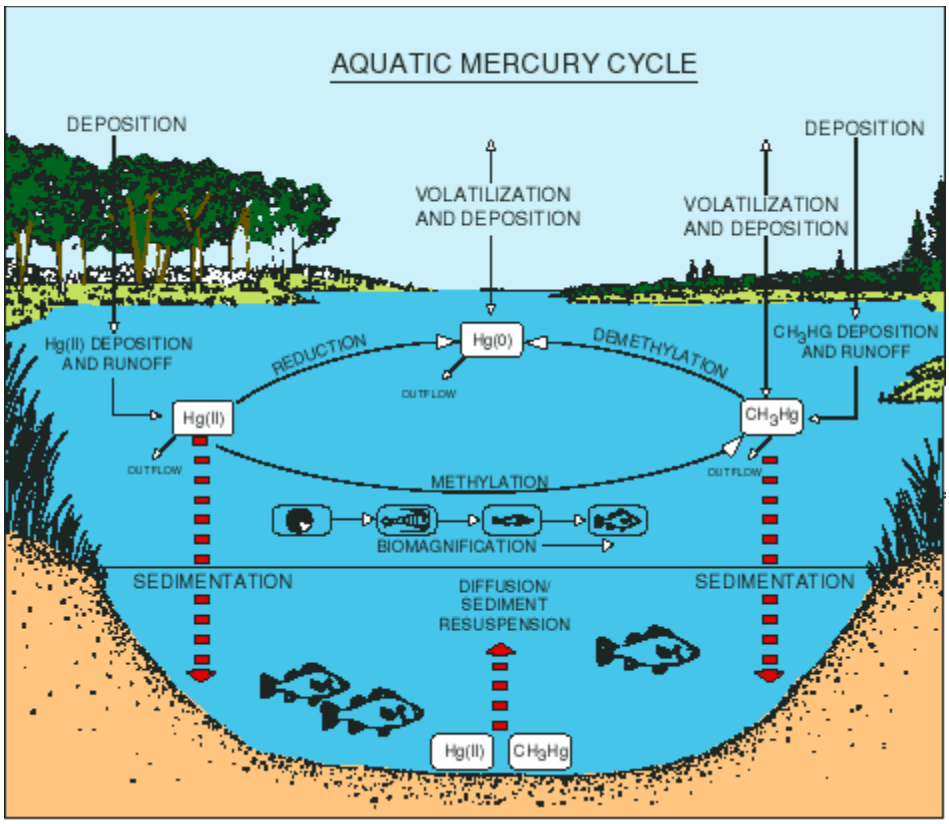

Figure 1.4. The mercury cycle in aquatic environments (Watras and Huckabee, 1994).

1.2 Air Quality Modeling

The Air Indicator Report for Public Access and Community Tracking (AIRPACT) is a numerical air quality forecast system that operates daily for the Pacific Northwest (Chen et al., 2008). This system employs the Community Multi-scale Air Quality (CMAQ) model and simulates ozone, $PM_{2.5}$, mercury deposition and other pollutant species on a gridded basis (12 km grid cells) with an hourly time step. AIRPACT was developed by the Laboratory for Atmospheric Research (LAR) at Washington State University (WSU). The newly developed system, AIRPACT-3, covers a larger region, which includes Washington, Oregon, Idaho, and boarding areas. In the system, the region consists of 95 by 95 horizontal grids in 21 vertical layers. With the use of this system, state and local air quality managers can monitor pollutants in the region, which will allow them to administer warnings to the public (Chen et al., 2008). The framework of AIRPACT-3 integrates the CMAQ Chemical Transport Model, the Mesoscale Meteorological/Weather Research Forecast model (MM5/WRF), Sparse Matrix Operator Kernel Emissions (SMOKE), initial conditions, and boundary conditions.

Researchers at the University of Washington manage the MM5/WRF model system, which is implemented into CMAQ's Meteorology-Chemistry Interface Processor (MCIP). The MM5/WRF system provides hourly weather forecasts for the Pacific Northwest. As detailed by Pleim et al. (1996 and 1997), dry deposition velocity can be estimated by the dry deposition subsection of the MCIP configuration. These results are then applied to AIRPACT-3. The SMOKE system (version 2.1) integrates anthropogenic and biogenic emissions as well as real-time wildfire emission estimates from various emission inventory databases (Chen et al., 2008). Generated emission data from SMOKE is then incorporated into CMAQ where it is finally outputted from AIRPACT-3. Emissions from agricultural field burning, which occur in Eastern

Washington and Northern Idaho, are monitored by the ClearSky smoke dispersion forecast system. AIRPACT-3 does not account for these types of emissions (Chen et al., 2008). The initial conditions are determined from results of the last model hour for the forecast from the day before. As stated by Chen et al. (2008), boundary conditions implemented into AIRPACT-3 are derived from MOZART-2, which is a global chemical model that analyzes yearly seasonal variability of chemical species. Parameters for both initial and boundary conditions are then applied to CMAQ. The framework of AIRPACT-3 is summarized in Figure 1.5.

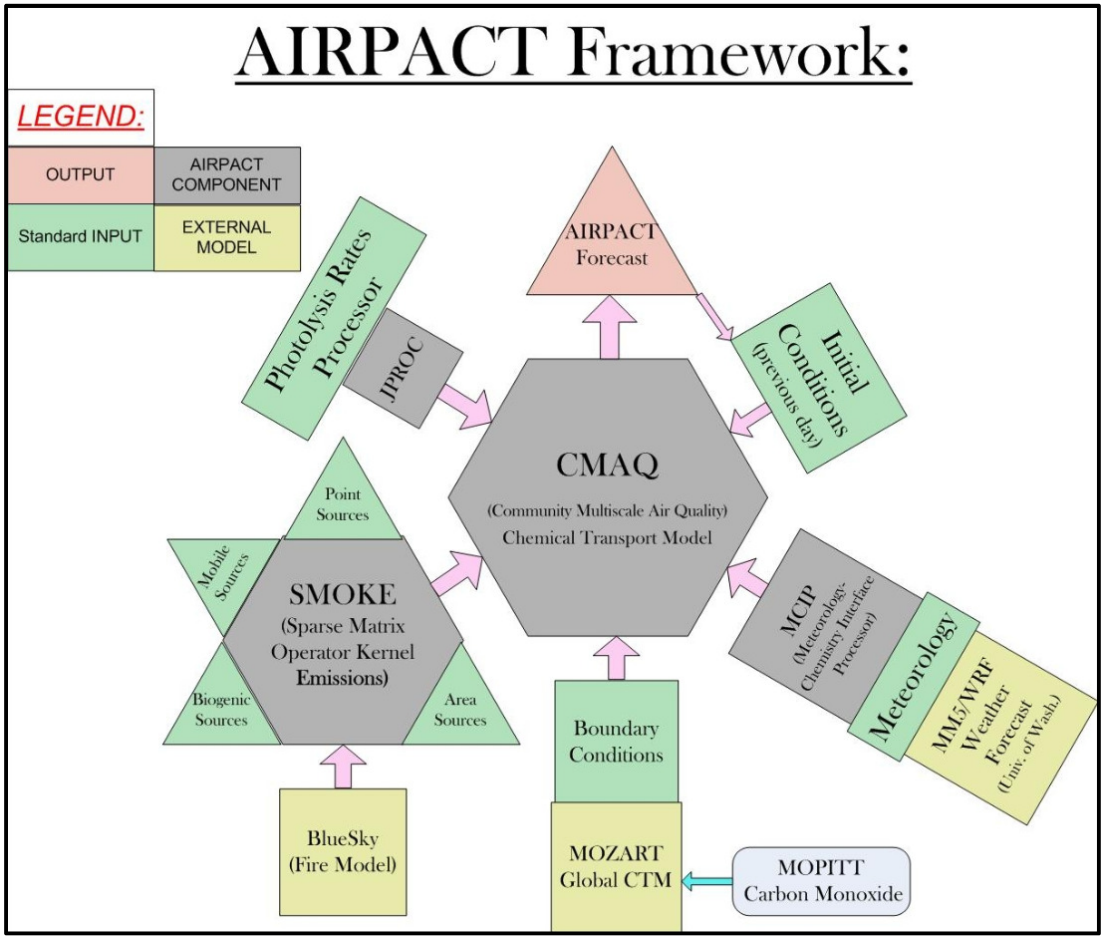

Figure 1.5. The contributing systems to the AIRPACT-3 framework (LAR, 2010).

As detailed by Bullock and Brehme (2002, 2006), mercury chemical reactions were added to the CMAQ Chemical Transport Model, version 4.6. The CMAQ Chemical Transport Model utilizes the SAPRC99 chemical mechanism (Carter et al., 2000), which holds the basis of the following mercury reactions:

$$\mathrm{Hg} + \mathrm{O_3} = 0.5(\mathrm{HgIIAer}) + 0.5(\mathrm{HgIIGas}) \quad \mathrm{k} = 2.11 \times 10^{-18}\ {}^{\mathrm{cm}^3}/_{\mathrm{molecule} \cdot \mathrm{s}} \text{ at } 1256.5\ \mathrm{K}$$

$$\mathrm{Hg} + \mathrm{Cl_2} = \mathrm{HgIIGas} \quad \mathrm{k} = 2.6 \times 10^{-18}\ {}^{\mathrm{cm}^3}/_{\mathrm{molecule} \cdot \mathrm{s}}$$

$$\mathrm{Hg} + \mathrm{H_2O_2} = \mathrm{HgIIGas} \quad \mathrm{k} = 8.5 \times 10^{-19}\ {}^{\mathrm{cm}^3}/_{\mathrm{molecule} \cdot \mathrm{s}}$$

$$\mathrm{Hg} + \mathrm{OH} = 0.5(\mathrm{HgIIAer}) + 0.5(\mathrm{HgIIGas}) \quad \mathrm{k} = 7.7 \times 10^{-14}\ {}^{\mathrm{cm}^3}/_{\mathrm{molecule} \cdot \mathrm{s}}$$

where elemental mercury (Hg) reacts with ozone (O_3) to form 50% aerosol mercury (HgIIAer) and 50% gaseous divalent mercury (HgIIGas); elemental mercury reacts with chlorine (Cl_2) to form 100% gaseous divalent mercury; elemental mercury reacts with hydrogen peroxide (H_2O_2) to form 100% gaseous divalent mercury; and elemental mercury reacts with hydroxyl radical (OH) to form 50% aerosol mercury and 50% gaseous divalent mercury. For each chemical reaction, a specific constant reaction rate (k) is utilized to determine the final concentration of the species at a given time.

The CMAQ system handles parameters such as gaseous and aqueous chemical transformations, aerosol behavior involving vertical and horizontal diffusion and advection, and deposition, which can all be specifically oriented to model mercury. As SMOKE is gathering the

mercury concentration emissions inventory data, the system converts the values to gridded, hourly resolution and speciates the various forms of mercury (Lin et al., 2005). This specific conversion is needed to initialize the simulation of mercury in CMAQ. As stated above, dry deposition is determined from the estimated dry deposition velocity values obtained from the MCIP configuration. CMAQ also incorporates a cloud chemistry component, which determines in-cloud and below-cloud processes related to wet deposition (AQCHEM; Byun and Ching, 1999; Bullock and Brehme, 2006). Wet deposition rates are determined for both convective and non-convective storms.

Boundary conditions for mercury have been determined from historical and local research studies. Boundary conditions for the north, east, and west are set to 1.7 ng/m^3, which is included for each of the model layers (Bullock et al., 2002; Jaffee et al., 2005). To account for high mercury emissions from Nevada, mainly due to smeltering of ore from gold mines, the south boundary conditions are set to 2.3 ng/m^3 (Gustin et al., 1996; Engle et al., 2001). With the combination of the above reaction equations, the chemical parameters found in CMAQ, the generated mercury concentration emission values from SMOKE, the deposition velocities from MCIP, and the addition of initial and boundary conditions, a final generated dry and wet mercury deposition is outputted from AIRPACT-3. An output file displays the hourly timestamps (Universal Zulu Greenwich) for the given grid cell, which reflects the end of the hour for which that deposition was calculated. At each hourly timestamp, a generated deposition rate is given for each of the four mercury species. The species are reported as follows: Hg (gaseous elemental mercury), HgII (gaseous divalent mercury), APHGJ (> 1 micron aerosol particulate mercury), and APHGI (.1 – 1 micron aerosol particulate mercury). The deposition rate is reported in

kg/ha/hr. To determine a total mercury deposition flux, the deposition rate generated for all four species were totaled and then divided by the duration of the sampling period.

1.3. Project Objectives

The overarching objective in this study was to evaluate dry and wet deposition in two locations in Washington State with anticipated differences in rates of mercury deposition: Pullman with its rural settings was expected to observe low concentrations of mercury deposition, and Puyallup with its industrial surroundings was hypothesized to have higher rates of mercury deposition. According to dialog with state regulators, there is a lack of mercury deposition data in the eastern part of the state (Era-Miller, 2011). In addition, we found no data on dry deposition in the western part of Washington State. This effort will partly address this knowledge gap. An additional goal of this project was to compare field monitoring results with modeled results of mercury deposition from the AIRPACT-3 model. The purpose of this comparison was to inform development of the mercury component of this model, which is operated by the Laboratory for Atmospheric Research at Washington State University.

To achieve the objective outlined above, I first developed an apparatus to measure real-time mercury deposition based on the analytical mercury capabilities at hand at the WSU mercury laboratory. Based on an extensive review of the literature, I developed a wet surface sampler similar to that used by Yi et al. (1997) and Sakata and Marumoto (2004) in order to measure dry deposition. To minimize contamination, virgin grade Teflon was used to make the sampler. It took several weeks to find an affordable distributor that sold specific sized Teflon sheets. Two large sheets of Teflon were needed in order to construct the holder and plate of the wet surface sampler. The development of the complete set-up of the apparatus took two months

to finalize materials, appropriate dimensions, and construction, with a final cost of $3,000. A design similar to Landis and Keeler (1997) was used to measure wet deposition. The system consisted of a borosilicate glass funnel attached to a Teflon sampling bottle, which was used for rain water collection.

1.4. Previous Work

Work conducted by Matt Porter, a M.S. graduate from Washington State University, examined numerical model experiments of mercury atmospheric chemical transport and deposition. The scope of his project focused on the comparison of the AIRPACT-3 model results with observations, which would determine relative confidence in model performance. Observations of ambient concentration measurements of mercury were administered in southern Idaho. Additional comparisons were also made with the wet deposition measurements from the EPA National Acid Deposition Program Mercury Deposition Network. One of the major focal points in his research was to fill the knowledge gap with regards to dry deposition estimates within the model. Some of the recommended improvements to the model include mercury emissions from vegetation and soil surfaces, which could support more accurate estimates of dry deposition. The project also detailed on many types of anthropogenic and natural mercury sources which provided an excellent background to atmospheric mercury pollution. The work conducted by Matt Porter has provided this project with a better understanding of the AIRPACT-3 model components and the specific types of emissions that contribute to mercury deposition.

2. STUDY SITE

2.1 Pullman Sampling Site

The dry deposition wet sampler and wet deposition precipitation collector were assembled on the rooftop of Dana Hall, a three-story building (9.8 m height), located on the campus of Washington State University (WSU) in the city of Pullman. The campus is situated in Eastern Washington in Whitman County and mainly surrounded by agricultural wheat, barley, lentil, and pea fields. Based on meteorological data from 1940-2006, the National Oceanic and Atmospheric Administration (NOAA) and the Western Regional Climate Center (WRCC), describes the climate of Pullman as semi-arid with hot, dry summers and cold, wet winters (WRCC, 2005). An overview of the climate in Pullman is summarized in Table 3.

Table 3. Average Monthly Climate Data (1981–2010) in Pullman, WA

Month	Maximum Temperature (°F)	Minimum Temperature (°F)	Precipitation (in)	Snowfall (in)
January	36.7	25.7	2.55	10.1
February	41.2	27.2	1.81	4.6
March	49.2	31.8	2.05	2.9
April	56.6	35.8	1.75	0.6
May	65.0	41.8	1.77	0.1
June	71.7	46.5	1.31	0.0
July	82.4	50.3	0.65	0.0
August	83.6	50.3	0.66	0.0
September	73.9	43.8	0.77	0.0
October	60.2	36.3	1.58	0.1
November	44.0	30.8	2.91	3.9
December	35.2	24.0	2.56	9.8
Annual	58.3	37.0	20.38	32.0

*Data obtained from NOAA (2006).

Surrounding the site are campus buildings and parking lots. A bus service and other local traffic to the campus are within the vicinity of the study site. The Palouse River and Coulee City Railroad runs once or twice a week through the city of Pullman. The railroad track is approximately 0.21 km from Dana Hall. The Pullman Wastewater Treatment Plant is located 1.81 km northwest and the Pullman-Moscow Regional Airport is approximately 5 km northeast of the study site. The Port of Whitman County Industrial Park is 3.2 km northeast of the site and home to Schweitzer Engineering Laboratories, Inc. Schweitzer produces an electrical power line and transformer fault locator, which is sold and serviced worldwide (City of Pullman, 2011). The Whitman County Agricultural Department (WSU Whitman County Extension, 2011) notes that typical wheat harvesting periods are between July and August. Natural occurring fires along the agricultural fields are usually during the months of August and September. It is common to also observe scheduled burning of crop fields during these months. As detailed by Givelet et al. (2003), atmospheric mercury contamination began during the late 15th century, primarily as a result of the burning of crop fields, a practice of Native North Americans. Such occurrences may still have a significant effect on mercury deposition.

2.2 Puyallup Monitoring Site

Dry and wet deposition measurements were taken on the rooftop of the Avian Health and Food Safety Laboratory (4 m height) at the WSU Puyallup Research and Extension Center. The site, which is located in Western Washington, is mainly surrounded by agricultural land, residential houses, and urban development. Climate date obtained from NOAA and WRCC depicts Puyallup as having cool and comparatively dry summers and mild, wet, and cloudy winters (WRCC, 2005). Monthly averages for Puyallup are displayed in Table 4.

Table 4. Average Monthly Climate Data (1981–2010) in Puyallup, WA

Month	Maximum Temperature (°F)	Minimum Temperature (°F)	Precipitation (in)	Snowfall (in)
January	47.9	33.2	4.80	3.10
February	51.6	34.8	4.97	1.48
March	56.7	36.6	4.15	0.38
April	61.6	39.5	3.14	0.0
May	67.6	44.7	2.21	0.0
June	72.8	49.0	1.91	0.0
July	78.0	52.1	0.90	0.0
August	79.2	51.9	0.74	0.0
September	73.2	47.1	1.37	0.0
October	62.6	42.1	3.47	0.03
November	50.4	36.1	6.21	0.64
December	45.8	32.4	5.01	1.23
Annual	62.4	41.7	38.86	6.86

*Data obtained from WRCC (2005).

The Puyallup Wastewater Treatment Plant is located 1.45 km northeast of the study site. Some of the surrounding industry consists of food production, manufacturing of aircrafts, electronics, cargo and freight companies, and lumber production (City of Puyallup, 2005). Two heavily industrialized cities in Washington are Seattle and Tacoma, both which are located in the western region of the state. The city of Seattle is approximately 46 km north of the study site and includes industrial manufacturing of transportation equipment, computer software and electronics, biotechnology, and lumber processing (City of Seattle, 1995). Major commerce in Tacoma includes production of lumber, pulp, paper, chemicals, and food products (City of Tacoma, 2010). An oil refinery is also located in the Port of Tacoma where 39,000 barrels of petroleum are refined per day (US Oil and Refining, 2011). The city of Tacoma is approximately 11 km northwest of the site. The Centralia Power Plant, which is 73 km southwest of the study site, is the only operating coal fire power plant in Washington. The power plant is considered one

of the major sources of mercury deposition to Western Washington. In 2002, the city Puyallup opened the Puyallup Sound Transit Commuter Rail Station, which makes connections to some of the larger cities such as Tacoma, Seattle, and Everett. The railroad tracks are roughly 0.63 km north of the site. Puyallup also serves as a major crossroad for some of the state's main freeways in the Central Puget Sound area (City of Puyallup, 2005). There are many outside sources of mercury pollution entering the state of Washington. Such sources are several different rivers that enter Washington from Oregon, Idaho, and Canada. Some of the more significant rivers are the Columbia and Spokane River (WSDE/WSDH, 2003). A unique source of mercury deposition to Washington State is from long range atmospheric transport from Asia due to coal burning plants (Era-Miller, 2011). Though research has indicated global transport of mercury from Asia to the western coast of the US, these affirmations could not be confirmed (WSDE/WSDH, 2003). The locations of the two study sites are displayed in Figure 2.1.

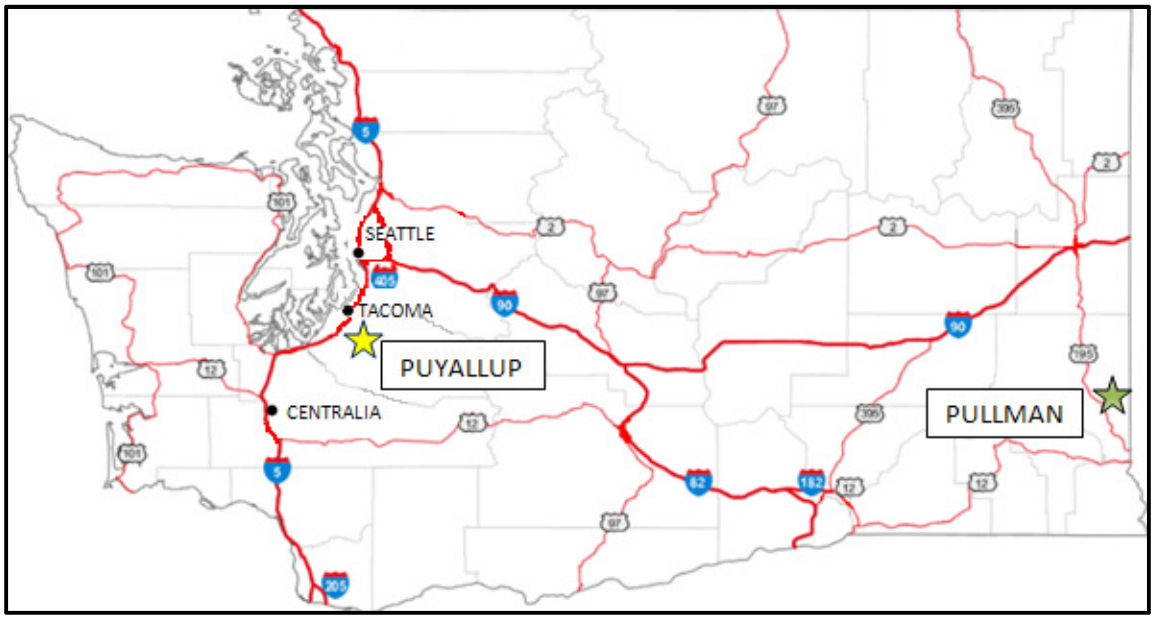

Figure 2.1. The location of sample sites in Washington (Modified from WSM, 2005).

3. METHODS

3.1 Dry Deposition Sampling

Dry deposition samples were collected at both study sites utilizing a wet sampler based on Yi et al. (1997) and Sakata and Marumoto (2004). This unique type of sampler was developed to collect dry deposition in an aqueous matrix, which was then conductive to analytical evaluation of total mercury. The method has only recently been developed and applied to mercury deposition; as far as we know no mercury deposition measurements using this apparatus have been performed in Washington State. Because the apparatus has a water surface and is acidic, it has a high affinity for mercury species and may represent an upper bound for mercury deposition. An illustration and photograph of the wet sampler are shown in Figure 3.1 and 3.2.

Three separate experiments were conducted at each sample site. Meteorological data were obtained for each sample period from Mesowest, which is an online service provided by the National Weather Service and the University of Utah that observes current weather conditions for the western United States (Mesowest, 2002). Mesowest is utilized by LAR, which provides weather data from its station located on the rooftop of Dana Hall (Station W7YH-2 Pullman). For the study site in Puyallup, WA, data were obtained from Mesowest at Station Puyallup South Hill. Table 5 and 6 displays a summary of the meteorological data taken concurrently with the sampling periods at both sites.

The dry deposition wet sampler consists of a holder, plate, pump, and water storage system (3 gallon glass carboy). The water surface holder and plate were made of Teflon. A similar airfoil shape in the Yi et al. (1997) study was used for the holder. It consisted of a leading edge angle of approximately 10°, which minimized the air flow disturbance over the water

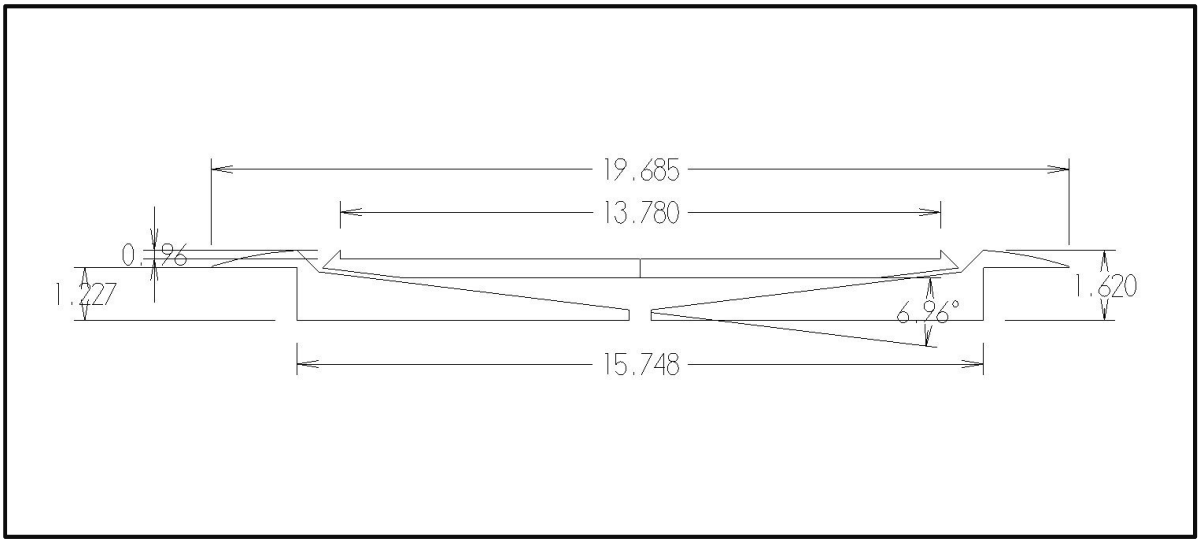

Figure 3.1. A diagram of the dry deposition wet sampler (dimensions in inches).

Figure 3.2. A complete setup and top view of the dry deposition wet sampler.

Table 5. Meteorological Data for Dry Deposition Sampling Periods in Pullman

Sampling Period	Date	Mean Temperature (°F)	Mean Relative Humidity (%)	Mean Wind Speed (mph)	Wind Direction
1	Aug 15, 2011[a]	67	46	5.7	Southwest
	Aug 16, 2011	59	45	2.0	Southwest
	Aug 17, 2011	61	38	2.6	Southwest
	Aug 18, 2011[a]	68	31	3.8	Southwest
	Aug 19, 2011	62	40	2.4	Southwest
	Aug 20, 2011	63	38	2.0	West
	Aug 21, 2011	66	35	2.0	Southeast
	Aug 22, 2011[a]	71	34	4.5	Southwest
2	Aug 23, 2011[a]	72	40	3.7	West
	Aug 24, 2011	67	45	2.0	Southeast
	Aug 25, 2011	75	38	3.3	West
	Aug 26, 2011	72	38	2.5	Southeast
	Aug 27, 2011	73	40	1.8	Southwest
	Aug 28, 2011[a]	74	36	3.6	Southeast
3	Aug 29, 2011[a]	79	37	4.5	Southwest
	Aug 30, 2011	70	45	4.9	Southwest
	Aug 31, 2011	58	51	4.6	Southwest
	Sept 1, 2011	54	54	7.0	West
	Sept 2, 2011	59	40	4.2	Southwest
	Sept 3, 2011	54	40	2.5	East
	Sept 4, 2011	59	35	3.8	East
	Sept 5, 2011[a]	66	36	3.0	Southwest

[*]Data obtained from Mesowest (2002).
[a]Indicates when a sample was collected.

Table 6. Meteorological Data for Dry Deposition Sampling Periods in Puyallup

Sampling Period	Date	Mean Temperature (°F)	Mean Relative Humidity (%)	Mean Wind Speed (mph)	Wind Direction
1	Sept 12, 2011[a]	61	77	0	-
	Sept 13, 2011	59	80	0	-
	Sept 14, 2011	60	75	0	-
	Sept 15, 2011[a]	58	75	0	-
	Sept 16, 2011	55	69	0	-
	Sept 17, 2011[a]	54	79	0	-
2	Sept 21, 2011[a]	64	72	0	-
	Sept 22, 2011	66	73	0	-
	Sept 23, 2011[a]	72	66	0	-
	Sept 24, 2011	72	66	0	-
	Sept 25, 2011[a]	65	70	1.3	Southeast
3	Sept 27, 2011[a]	57	78	0.8	Southwest
	Sept 28, 2011	54	75	0.5	West
	Sept 29, 2011[a]	57	73	1	Northeast
	Sept 30, 2011	55	83	1.2	Northeast
	Oct 1, 2011	52	88	0.7	Southwest
	Oct 2, 2011[a]	54	88	0.5	North

[*]Data obtained from Mesowest (2002).
[a]Indicates when a sample was collected.

surface by producing a boundary layer. In view of a rain event, a Plexiglas cover was placed over the dry deposition wet sampler to minimize the amount of precipitation collection on the apparatus. Water from the storage system was circulated to the water surface plate by the utilization of a tubing pump. Due to four weirs on the outer edge of the plate, water was recycled throughout the system. All tubing and fittings were entirely made of Teflon. A refrigeration unit kept the water storage system at a temperature of approximately 10°C, which was usually 5-10 degrees lower than the air temperature. The purpose of the refrigeration system was to reduce water evaporation, prevent mercury volatilization, and to allow for continuous deposition sampling without the addition of water to the system during a 1 week period (Sakata and Marumoto, 2004). Due to the cooler climate and low relative humidity in Western Washington, dew condensed on the water surface and evaporation was minimal. A similar study conducted by Sakata and Marumoto (2004) explains that water evaporation is lowered with decreasing atmospheric water vapor saturation deficit, which is ultimately related to air temperature, relative humidity, and wind speed. To limit the interaction of birds with the wet sampler, a statue of an owl was placed in close proximity to the apparatus.

Dry deposition experiments in Pullman, WA were conducted for 5-7 day periods. Sampling intervals in Puyallup, WA were administered for 3-4 days. Due to rain events and the end of the dry season, shorter dry periods were expected in Western Washington. Before each experiment, the water surface holder, plate, tubing, Teflon fittings, and glass carboy were cleaned thoroughly with a 25% nitric acid solution. Each material was then triple rinsed with deionized reagent grade water (DI) and placed to dry in a Class 100 clean hood. For minimal contamination and easy transport to study sites, the holder, plate, tubing, and Teflon fittings were bagged in polyethylene plastic. Five liters of 0.5 mol/L HCl receiving solution was contained in

the water storage system for collection of dry deposition. Stratton et al. (2001) states that the main forms of mercury in the hydrochloric acid solution are $HgCl_4^{2-}$ and $HgCl_3^-$. With the use of a mist chamber, their research tested the creation of Hg (II) using 0.25 mol/L HCl by oxidation of Hg(0), thus specifying that after collection mercury is stabilized without adsorption or volatilization (Stratton et al., 2001; Sakata and Marumoto, 2004). Therefore, deposited mercury is contained in a soluble form within the receiving solution.

Once the water surface sampler was assembled, the sampling solution was pumped to the water surface plate at a rate of 200 mL/min for approximately 30 min. This allowed for all five liters to completely cycle through the system. Next, two 125 mL samples were taken from the water surface and noted as time zero. The system was then permitted to run for several days. In some experiments, two samples were collected, one mid-way through the collection period and another at the end of the period. After each sampling period was completed, the residual water was extracted and weighed. Based on EPA Method 1631 (USEPA, 2002), all water samples were preserved with 1% BrCl solution (v/v), which oxidizes all mercury in the sample to Hg(II). Two bottle blanks were collected for each experiment, one containing only DI water and the other containing the 0.5 mol/L HCl receiving solution. Both blanks were preserved in the same manner as the water samples. The purpose of these blanks was to determine the background concentrations of mercury in reagent water and sampling system receiving solution. All samples were bagged and kept in a clean laboratory until analysis.

3.2 Wet Precipitation Collector

The precipitation collector that was utilized to collect wet deposition is similar to that of Landis and Keeler (1997). A schematic and photograph of the instrument are displayed in Figure

3.3 and 3.4. There are four major parts to the wet deposition precipitation collector: a borosilicate glass funnel (1,251 cm^2 collection area), a Teflon adaptor, a Teflon sampling bottle (1 liter), and a Plexiglas holder. The Plexiglas holder was designed in order to support the borosilicate glass funnel when attached to the Teflon adaptor and sampling bottle. For minimal contamination, the adaptor and sampling bottle were made of Teflon. At the Pullman study site, four experiments were performed during separate rain events; whereas three experiments were conducted in Puyallup. For each sampling experiment, meteorological data, including the amount of precipitation per day were obtained from NOAA and Mesowest. A summary of these data is reported in Table 7 and 8.

Wet deposition experiments in Pullman, WA were conducted for the full duration of a rain event. Collected water was minimal during these experiments since the wet season was coming to a closure in Pullman, WA. Each sampling period conducted in Puyallup, WA usually lasted for two or three days. Rain water that was collected during these experiments was substantially larger due to the normal wet conditions found in Western Washington. Prior to each sampling experiment, the borosilicate glass funnel, adaptor, and sampling bottle were cleaned and stored in the same manner as the dry deposition wet sampler. Twenty milliliters of 0.08 mol/L HCl receiving solution was contained in the sample bottle. The purpose of this process, as mentioned in the dry deposition procedure, was to stabilize mercury without volatilization after collection (Stratton et al., 2001; Sakata and Marumoto, 2004; Landis and Keeler, 1997).

A subsample of the receiving solution was collected prior to the sampling event. After each sampling period, the rain water was collected and weighed. Bottle blanks were also collected. All samples were preserved and stored in the same method as the dry deposition samples.

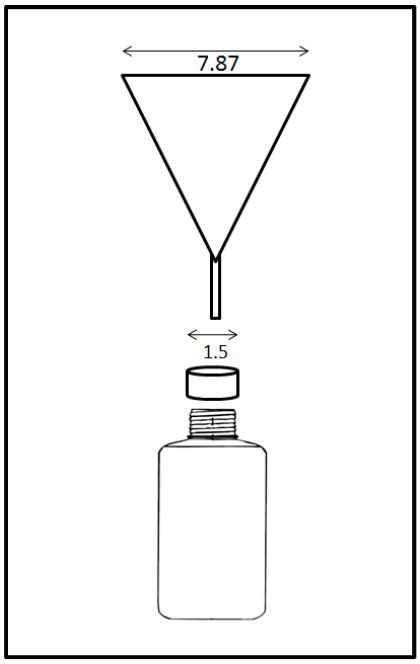

Figure 3.3. A schematic of the wet deposition precipitation collector (dimensions in inches) (Modefied from Landis and Keeler, 1997).

Figure 3.4. Photograph of an assembled wet deposition precipitation collector.

Table 7. Meteorological Data for Wet Deposition Sampling Periods in Pullman

Sampling Period	Date	Mean Temperature (°F)	Mean Relative Humidity (%)	Mean Wind Speed (mph)	Wind Direction	Rain Fall (in)
1	June 28, 2011	68	52	5	West	0.01
	June 29, 2011[a]	63	61	11	Southwest	Trace
2	July 12, 2011	68	59	5	Northwest	0.01
	July 13, 2011[a]	57	70	4	Northwest	0.01
3	July 14, 2011[a]	56	64	4	Southwest	Trace
4	Oct 10, 2011	50	67	9	Southeast	0.13
	Oct 11, 2011[a]	53	69	15	Southwest	0.14

[*]Data obtained from NOAA (2006) and Mesowest (2002).
[a]Indicates when sample was collected.

Table 8. Meteorological Data for Wet Deposition Sampling Periods in Puyallup

Sampling Period	Date	Mean Temperature (°F)	Mean Relative Humidity (%)	Mean Wind Speed (mph)	Wind Direction	Rain Fall (in)
1	Sept 17, 2011	53	79	0	-	0.21
	Sept 18, 2011	58	89	0	-	0.30
	Sept 19, 2011[a]	59	76	0	-	0
2	Sept 25, 2011	65	70	1.3	Southeast	0.21
	Sept 26, 2011	55	81	1.4	Southeast	0.27
	Sept 27, 2011[a]	57	78	0.8	Southwest	0.01
3	Oct 2, 2011	54	88	0.5	North	0.3
	Oct 3, 2011[a]	55	80	0	-	0.09

[*]Data obtained from NOAA (2006) and Mesowest (2002).
[a]Indicates when sample was collected.

3.3 Mercury Analysis

Mercury samples were analyzed based on EPA Method 1631 (USEPA, 2002) on a Brooks Rand MERX-T auto analyzer. Analyses were run in triplicate, accept for the June and July precipitation events in Pullman which yielded enough volume for only one analysis. 25 mL of the sample was put into an autosampler vial for analysis. To eliminate excess BrCl in the sample, 100 µL of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) was added to each vial. Then, for the reduction of Hg(II) to Hg(0), 100 µL of stannous chloride ($SnCl_2$) was also added to each sample vial. Vials were loaded on the autosampler. Nitrogen gas was used to purge the samples in the vials in order to volatilize Hg(0) to the gold amalgamation traps. Total mercury concentrations in the samples were then measured with a cold-vapor atomic fluorescence spectrometry. All cleaning procedures and analytical processes were administered in a clean laboratory. The method detection limit (MDL) for total mercury on the Brooks Rand MERX-T is 0.02 ng/L. Standard quality control procedures for total mercury included matrix spikes (71-125% recovery) and method blanks.

3.4 Flux Estimates

The deposition flux for total mercury for both dry and wet deposition was calculated by the following equation:

$$\text{Deposition Flux} = \frac{(\mathrm{M_F} - \mathrm{M_I})}{\mathrm{D_S} \times \mathrm{A}}$$

where M_F (ng) and M_I (ng) is the mass of the final and initial solution in the sampling apparatus, respectively; D_S (days) is the duration of the sampling period, and A (m^2) is the surface area of the sampler (0.096 m^2 for the dry deposition sampler; 0.031 m^2 for the wet deposition sampler).

Mass was calculated as concentration times volume. Wet deposition was also reported as the concentration of mercury averaged over the precipitation (ng/L) and as the mass of deposited mercury normalized to precipitation during the sampling period (ng/mm).

4. RESULTS

4.1 Dry Mercury Deposition

In Pullman, atmospheric dry mercury deposition was measured for five to seven day periods: August 15-22, 2011; August 23-28, 2011; and August 29-September 5, 2011. During August 15-22, 2011, a sample was taken during the middle of the sampling period, which resulted in determining two dry depositional fluxes for this specific experiment. Deposition fluxes ranged from 24 to 103 ng/m^2/d and averaged 55 ng/m^2/d (Table 9). The highest flux corresponded with smoky conditions in the area resulting from agricultural burning. Based on the loss of water mass over the course of sampling, evaporation rate were consistently around 0.5 L/d, which corresponds with relatively low levels of relative humidity and high wind velocities (31-54% and 1.8-15 mph; Table 5 and Mesowest, 2002).

Sampling intervals in Puyallup were administered for only three or four days due to the presence of frequent precipitation events: September 12-17, 2011; September 21-25, 2011; and September 27-October 2, 2011. For each of these experiments, a sample was collected in the middle of the sampling period. This allowed for the calculation of two dry mercury deposition fluxes within a sampling period. Deposition fluxes ranged from 20 to 37 ng/m^2/d and averaged 29.7 ng/m^2/d (Table 10). Relative to Pullman, dry mercury depositions in Puyallup were lower in magnitude and less variable. Based on the loss of water mass over the course of sampling, evaporation rates were also lower, and ranged from 0.03-0.19 L/d, which corresponds with relatively high levels of relative humidity and low wind velocities (66-88% and 0-1.3 mph; Table 6 and Mesowest, 2002).

The method to calculate a dry depositional flux for the experiments conducted in Pullman was implemented for the Puyallup studies. The initial volumes for these events averaged about 4.75 L. An evaporation rate calculated for these experiments ranged from 0.03 to 0.19 L/d, resulting in an average final volume of approximately 4 L. The initial concentrations of the samples taken at time zero varied from 0.68 to 1.37 ng/L, whereas final samples taken at the end of the sampling periods ranged from 3.45 to 5.14 ng/L. The averaged final dry deposition flux for the three sampling periods conducted in Puyallup was 29.7 ng/m^2/d. The data for the measurements of dry deposition at the two study sites are summarized in Table 9 and 10.

4.2 Wet Mercury Deposition

In Pullman, sampling periods ranged from 2 to 21 hours, one in June, two in July, and one in October. Monitored rain events ranged from low intensity (below around 0.2 mm/hr) in June and July to moderate intensity in July and October (above around 0.3 mm/hr). Wet deposition results were variable for the four monitoring events (Table 11). The mercury concentration of the rainwater ranged from 55-75 ng/L in the low intensity events to 6-15 ng/L in the moderate intensity events. Wet deposition fluxes were around 100-300 ng/m^2/d for the three June-July events and 44 ng/m^2/d for the October event. Precipitation-normalized wet deposition was around 2 ng/mm for the two low intensity events and less than 0.5 for the medium intensity events.

In Puyallup, sampling events included two in September and one in October. The duration of the sampling events ranged from 16-55 hours, but precipitation intensity was fairly consistent ranging from approximately 0.3-0.4 mm/hr. Wet deposition results were very similar

for the three monitoring events (Table 12). The mercury concentration of the rainwater was around 3 ng/L, wet deposition fluxes were around 25 ng/m^2/d, and precipitation-normalized wet deposition was around 0.1 ng/mm. All these measurements of wet mercury deposition were low relative to measurements in Pullman.

Table 9. Dry Deposition of Total Mercury in Pullman, WA

Date	Duration (days)	Initial Volume (L)	Final Volume (L)	Evaporation Rate (L/d)	Initial Total [Hg][a] (ng/L)	Final Total [Hg][a] (ng/L)	Dry Hg Deposition[b] (ng/m^2/d)
Aug 15-18, 2011	2.77	4.87	3.28	0.57	1.57 ± 0.26	7.12 ± 0.28	58
Aug 18-22, 2011	3.96	3.02	0.75	0.57	7.12 ± 0.28	41.1 ± 0.85	24
Aug 23-28, 2011	5.04	4.74	1.96	0.55	1.43 ± 0.18	28.9 ± 0.26	103
Aug 29-Sept 5, 2011	7.11	4.74	1.02	0.52	1.26 ± 0.28	30.8 ± 0.74	37
Average ± Standard Deviation							55.0 ± 34.5

[a]Average ± Standard Deviation of triplicate analysis.
[b]Deposition based on dry deposition wet sampler surface area of 0.096 m^2

Table 10. Dry Deposition of Total Mercury in Puyallup, WA

Date	Duration (days)	Initial Volume (L)	Final Volume (L)	Evaporation Rate (L/d)	Initial Total [Hg][a] (ng/L)	Final Total [Hg][a] (ng/L)	Dry Hg Deposition[b] (ng/m^2/d)
Sept 12-15, 2011	3.03	4.75	4.26	0.16	1.37 ± 0.03	4.01 ± 0.12	36
Sept 15-17, 2011	1.64	4.01	3.74	0.16	4.01 ± 0.12	5.14 ± 0.26	20
Sept 21-23, 2011	2.05	4.75	4.69	0.03	0.79 ± 0.10	2.37 ± 0.03	37
Sept 23-25, 2011	1.74	4.43	4.38	0.03	2.37 ± 0.03	3.45 ± 0.15	28
Sept 27-29, 2011	2.00	4.75	4.37	0.19	0.68 ± 0.08	2.21 ± 0.04	33
Sept 29-Oct 2, 2011	2.97	4.11	3.55	0.19	2.21 ± 0.04	4.48 ± 0.34	24
Average ± Standard Deviation							29.7 ± 7.03

[a]Average ± Standard Deviation of triplicate analysis.
[b]Deposition based on dry deposition wet sampler surface area of 0.096 m^2

Table 11. Wet Deposition of Total Mercury in Pullman, WA

Date	Duration (hr)	Initial Volume (mL)	Final Volume (mL)	Precip. (mm/hr)	Initial Total [Hg][a] (ng/L)	Final Total [Hg] (ng/L)	Rainfall [Hg] (ng/L)	Wet Hg Deposition[c] (ng/m^2/d)	Wet Hg Deposition (ng/mm)
June 28-29, 2011	3.50	20	38.9	0.17	0.81 ± 0.11	36.1[b]	73.4	303	2.30
July 12-13, 2011	11.0	20	48.5	0.08	0.90 ± 0.04	33.8[b]	56.8	112	1.78
July 14, 2011	2.17	20	61.2	0.60	0.88 ± 0.15	9.84[b]	14.2	206	0.45
Oct 10-11, 2011	21.0	20	210	0.29	0.27 ± 0.05	5.74 ± 0.51[a]	6.32	44	0.20
Average ± Standard Deviation							37.6 ± 32.5	166 ± 112	1.17 ± 1.03

[a]Average ± Standard Deviation of triplicate analysis.
[b]Final precipitation volume allowed for only single analysis.
[c]Deposition based on funnel surface area of 0.031 m^2.

Table 12. Wet Deposition of Total Mercury in Puyallup

Date	Duration (hr)	Initial Volume (mL)	Final Volume (mL)	Precip. (mm/hr)	Initial Total [Hg][a] (ng/L)	Final Total [Hg][a] (ng/L)	Rainfall [Hg] (ng/L)	Wet Hg Deposition[b] (ng/m^2/d)	Wet Hg Deposition (ng/mm)
Sept 17-19, 2011	37.9	20	467	0.38	0.71 ± 0.11	2.27 ± 0.10	2.34	21	0.07
Sept 25-27, 2011	55.4	20	533	0.29	0.86 ± 0.09	3.28 ± 0.11	3.38	24	0.11
Oct 2-3, 2011	16.1	20	209	0.38	0.62 ± 0.35	3.18 ± 0.10	3.45	31	0.11
Average ± Standard Deviation							3.05 ± 0.62	25.3 ± 5.1	0.10 ± 0.02

[a]Average ± Standard Deviation of triplicate analysis.
[b]Deposition based on funnel surface area of 0.031 m^2.

5. DISCUSSION

5.1 Dry Mercury Deposition

The accumulation of mercury over time is seen in both the Pullman and Puyallup field efforts. During the August 15-22, 2011 sampling period in Pullman, mercury concentration increased from 1.6 ng/L to 7.1 ng/L within 3 days, and then gradually elevated from 7.1 ng/L to 41 ng/L within the next four days. Much of the increase in concentration was a result of the high rates of evaporation, around 0.5 L/d, which concentrated deposited mercury into an ever smaller amount of receiving solution. The relatively high rate of loss of receiving solution in Pullman also meant that measurements could be conducted for only five to seven days. In Puyallup for the sampling period of September 21-25, 2011, mercury concentrations increased from 0.79 ng/L to 2.37 ng/L within 2 days and then increased from 2.37 ng/L to 3.45 ng/L within the next day and a half. A similar occurrence is also seen in the other sampling intervals. In contrast to Pullman, relatively low evaporation rates of around 0.03 to 0.20 L/d in Puyallup had minor effects on concentrating mercury into receiving solution. The measured values of mercury concentration reveal the success in the development of the wet sampler apparatus to measure dry deposition. Of particular note are the low standard deviations associated with triplicate total mercury analyses (Table 9 and 10). Relative standard deviations were low and typically ranged from 2-16%, confirming the precision of the mercury analytical method.

When converted to fluxes, the average dry deposition flux measured for each sampling period in Pullman ranged from 24 to 103 ng/m^2/d and averaged 55 ng/m^2/d for four sampling periods. Fluxes measured in Puyallup ranged from 20 to 37 ng/m^2/d and averaged 30 ng/m^2/d for

six sampling periods. As noted by Sakata and Marumoto (2004), mercury concentrations in the atmosphere and mercury depositional fluxes are highly variable. Their study of mercury dry deposition in Japan, using a wet sampler similar to the one used in this study, showed high variability. Our study displayed some variability. For example, mercury dry deposition in Pullman was highly variable with a relative low standard deviation of 63% (n = 4). But dry deposition in Puyallup was fairly steady with a relative standard deviation of 24% (n = 6).

The magnitude of dry mercury deposition measured in this study in both Pullman and Puyallup were comparable to values reported in other locations and summarized in Table 13. Literature values ranged from 1.5 to 269 ng/m^2/d and had a median value of 38 ng/m^2/d. An important factor that affects mercury deposition is location. Urban areas and areas downwind of large sources of mercury emissions, such as metropolitan areas in the Western US, typically have elevated levels of mercury deposition (Pirrone et al., 1998) (see Figure 1.1). However, some researchers have found that because of the extreme transportability of mercury by various weather conditions, rural areas can also high levels of mercury deposition (Miller et al., 2005). In the case of our study sites, the magnitude of mercury deposition measured in rural Pullman (max of 103 ng/m^2/d) corresponded with levels measured in rural New York (142 ng/m^2/d) by Huang et al. (2010). The magnitude of dry deposition at the urban site in Puyallup (around 30 ng/m^2/d) corresponded closely with levels measured in urban Japan (29 ng/m^2/d) by Sakata and Marumoto (2004).

In contrast to expectations, rates of mercury dry deposition were higher in Pullman compared to Puyallup. Of particular note is the extreme deposition event of 103 ng/m^2/d in Pullman during the August 23-28 sampling event, which is two to four times higher than all

Table 13. Comparison of Dry Mercury Deposition Fluxes from Various Locations

Location	Reference	Dry Hg Deposition ($ng/m^2/d$)[a]	Land Description	Collection Dates
Pullman, WA	This study	24-103	Rural	Aug-Sept, 2011
Puyallup, WA	This study	20-37	Urban	Sept-Oct, 2011
Komae, Japan	Sakata and Marumoto, 2004	29	Urban	May-Dec, 2002
Connecticut, US	Miller et al., 2005	33	N/A	MDN data, 2002-2004
Massachusetts, US	Miller et al., 2005	33	N/A	MDN data, 2002-2004
Maine, US	Miller et al., 2005	42	N/A	MDN data, 2002-2004
New York, US	Huang et al., 2010	142	Rural	2007-2009
Moss Landing, CA	Gill, 2008	1.4	Coastal/Urban	2004-2005
Illinois, US	Lombard et al., 2011	142	N/A	2004
Nevada, US	Weiss-Penzias, et al., 2009	269	Residential/Urban	June-Aug, 2007

[a]Values given as an average total dry mercury deposition flux.

other events at both sites. A probable reason for higher deposition rates in Pullman compared to Puyallup, and the extreme rate in Pullman noted above, is the time of sampling, which coincided with a number of agricultural activities and meteorological characteristics that could enhance mercury deposition.

Agricultural harvest activities can enhance mercury emissions and deposition. A study conducted in southern Ontario, Canada indicates that corn harvesting events result in high concentrations of Hg(0) and Hg(p) re-emissions to the atmosphere (Cobbett and Van Heyst, 2007). Measured concentrations ranged from 22.4 to 77.3 pg/m^3. Once crops are planted for the season, atmospheric mercury will deposit to the soil and vegetation. Because fields are not harvested for several months, plant and soil surfaces accumulate Hg(p) and Hg(II). As crops are harvested, the accumulated mercury is dispersed back up into the atmosphere, where wind and rain events can transport and deposit the mercury back to the landscape. In Pullman, agricultural fields are typically harvested from late June to mid September, which corresponds to our monitoring timing. In addition, some of the highest detected wind speeds, ranging from 7-15 mph, where detected during these sampling periods (Table 5 and Mesowest, 2002). Agricultural harvesting combined with high winds likely exacerbated mercury emissions and deposition.

Fires and agricultural field burning can significantly contribute to mercury re-emissions and subsequent deposition. Biswas et al. (2004) showed that in the US, biomass/soil burning (e.g. vegetation, vegetation stock, and top soil surface) emits roughly 100 Mg annual mercury flux into the atmosphere. The Biswas et al. (2004) study may explain why we observed high mercury concentration in Pullman since the majority of the land surrounding the area is agricultural fields. A majority of the land in Eastern Washington is used for agricultural purposes, especially the surrounding areas of Pullman. Andreae and Merlet (2001) report that

approximately 540 million tons/yr of agricultural waste (e.g. vegetation and stock, top soil surface) is burned worldwide, resulting in 100 tons/yr of mercury emissions. A study conducted by Friedli et al. (2003) examined mercury emissions from large wildfires in temperate and boreal forests in Washington State and agricultural waste fire in Oregon. The results indicated that mercury emissions from agricultural waste fire are significantly higher than wildfires from temperate or boreal forests. Fires can also enhance mercury deposition (Era-Miller, 2011). As elemental mercury is remitted back into the atmosphere by agricultural burning, the conversion of Hg(0) to Hg(II) is amplified by the high air temperatures associated with the fires. With its relatively high deposition velocity, Hg(II) can then deposit out of the lower air column relatively quickly (Zhang et al., 2009).

In the Pullman area, agricultural fields are commonly burned after harvesting periods to reduce crop residue (WSU Whitman County Extension, 2011). Typical timing of field burning in Pullman is August and September, however as stated by the Department of Ecology for Washington State, the majority of the burning for this year occurred in September and October in Whitman County. At the Department of Ecology in Spokane, Washington, I reviewed burn permits for all farms in Whitman and Walla Walla County. Of particular note, a large majority of fields in Walla Walla County were being burning in mid August, which correlates with the time we were sampling for dry deposition. As stated by the Department of Ecology, typical wind movement from Walla Walla County is NE, which is directly towards Pullman and the Whitman County area. As field burnings were occurring in Walla Walla County, a majority of the fields in Whitman County were being harvested, which may explain why we detected higher levels during the Pullman sampling periods. Table 14 shows specific dates when agricultural fields were

burned in both Whitman and Walla Walla County compared to our dry deposition sampling events.

Table 14. Agricultural Field Burning Data for Whitman and Walla Walla County

County	Burn Date	Acres	Dry Deposition Sampling Date
Whitman	Aug 15, 2011	140	Aug 15-22, 2011
Whitman	Aug 15, 2011	Bale	Aug 15-22, 2011
Whitman	September 1, 2011	130	Aug 29-Sept 5, 2011
Walla Walla	Aug 15, 2011	70	Aug 15-22, 2011
Walla Walla	Aug 15, 2011	200	Aug 15-22, 2011
Walla Walla	Aug 15, 2011	50	Aug 15-22, 2011
Walla Walla	Aug 15, 2011	103	Aug 15-22, 2011
Walla Walla	Aug 15, 2011	100	Aug 15-22, 2011
Walla Walla	Aug 16, 2011	26	Aug 15-22, 2011
Walla Walla	Aug 17, 2011	120	Aug 15-22, 2011
Walla Walla	Aug 18, 2011	133	Aug 15-22, 2011
Walla Walla	Aug 18, 2011	162	Aug 15-22, 2011
Walla Walla	Aug 22, 2011	18	Aug 15-22, 2011
Walla Walla	Aug 27, 2011	26	Aug 23-28, 2011

*Data obtained from Department of Ecology for Washington State (2011).

As noted above, higher air temperatures enhance the conversion of elemental mercury to Hg(II), which can then deposit out of the atmosphere. In Pullman, air temperatures were relatively high during the sampling events, and this may also have enhanced mercury deposition. Some of the highest air temperatures detected in Pullman in August and September ranged from 70 to 97 °F (Mesowest, 2002). These were the highest temperatures observed for the summer

season in Pullman. In comparison, during the sampling periods in Puyallup, which were from mid September to early October, summer conditions in this region of the state were ending. Daily mean temperature observed during these sampling events was around 58 °F (Table 6). Most of the time there was no wind detected and the highest reported value throughout the events was 1 mph. With low air temperatures and no significant amount of wind speed, and no local source of mercury emissions such as agricultural harvesting or field burning, dry deposition in Puyallup was relatively low during the sampling period.

5.2 Wet Mercury Deposition

The average wet deposition flux measured for each sampling period in Pullman ranged from 44 to 303 ng/m^2/d and averaged 166 ng/m^2/d for four sampling periods. High deposition correlated with high average concentrations of mercury in rainfall (6-36 ng/L). The two low intensity precipitation events in June and July had especially high deposition rates when normalized to precipitation (2.3 and 1.8 ng/mm). Fluxes measured in Puyallup were lower and ranged from 21 to 31 ng/m^2/d and averaged 25 ng/m^2/d for three sampling periods. Concentrations in precipitation were also lower and less variable at around 3 ng/L. The magnitude of wet mercury deposition measured in this study in both Pullman and Puyallup were comparable to values reported in other locations and summarized in Table 15. Literature values ranged from 6 to 172 ng/m^2/d and had a median value of 52 ng/m^2/d. The concentration of mercury in the longer-duration storms of the Puyallup site, 3 ng/L, also compared to those reported by Iverfeldt (1991) for a 24 hour storm which were around 5 ng/L.

There are several explanations for why the wet deposition rates were higher in Pullman than in Puyallup. The June and July rain events in Pullman corresponded with the start of the harvesting period and the first scheduled agricultural field burnings for the season. As described above, agricultural harvesting and field burning contributes greatly to mercury re-emissions to the lower atmosphere and subsequent deposition of Hg(II), which is highly water soluble and can easily accumulate in and deposit out in precipitation (Era-Miller, 2011). Another factor to take into account is the duration and intensity of the rain events. The first three experiments administered in Pullman, June 28-29 (3.5 hrs and 0.6 mm), July 12-13 (11 hrs and 0.9 mm), and July 14 (2.2 hrs and 1.3 mm), were the shortest and least intense rain events captured from all the sampling events from both Pullman and Puyallup. A significant study performed by Iverfeldt (1991) explains that mercury concentration in precipitation is lower in long-duration rain events; whereas short-duration storms will result in higher concentrations of mercury in the rainwater. This implies that a washout or first-flush mechanism can strip mercury out of the atmosphere at the beginning of a rain event. As detailed by Ferrara et al. (1986), mercury concentration in rain is time dependent. The study reveals that an atmospheric washout mechanism is observed during the beginning of a storm and higher mercury concentrations are detected in rainfall after a long duration of dry weather. This is significant since the June 28-29 sampling period was one of the first rain events we had observed after a few weeks of dry conditions. So relative to short storms, long storms can exhibit lower overall mercury deposition since they dilute a given mercury mass washed out of the atmosphere with more water. The Oct 10-11 (21 hrs and 6.1 mm) sample period in Pullman and the three events conducted in Puyallup (16-55 hrs and 6.1-16.1 mm) were relatively long rain events. These rain events resulted in substantially lower mercury deposition rates (21-44 ng/m^2/d) and average concentrations (2-6 ng/L) than the short-duration low-intensity

events. Therefore, with agricultural harvesting and short duration rain events, rates of wet mercury deposition can be extremely high, and this was observed during June and July in Pullman when wet deposition rates were around 100-300 ng/m^2/d.

As stated by Iverfeldt (1991), evaporation/condensation processes in clouds, movement of air masses, and the number of rain events can affect the mercury concentration in rainwater. Studies indicate that mercury concentrations are higher in precipitation, and that wet deposition fluxes are higher, during the summer than in winter (Lamborg et al., 1995). This is akin to the high rate of wet deposition observed in Pullman in June and July (100-300 ng/m^2/d) compared to low rates observed in Pullman and Puyallup in October (31-44 ng/m^2/d). High temperatures during the summer enhance the conversion from Hg(0) to Hg(II), and Hg(II) is highly water soluble, resulting in accumulation within precipitation.

Table 15. Comparison of Wet Mercury Deposition Fluxes from Various Locations

Location	Reference	Wet Hg Deposition ($ng/m^2/d$)	Land Description	Collection Dates
Pullman, WA	This study	44-303	Rural	June-Oct, 2011
Puyallup, WA	This study	21-31	Urban	Sept-Oct, 2011
Alabama, USA	Engle et al., 2010	36	Rural	April 2005-April 2006
Puerto Rico, USA	Engle et al., 2010	82	N/A	2006
Massachusetts, USA	Engle et al., 2010	11	Rural	Feb 2008-Feb 2009
Illinois, USA	Engle et al., 2010	172	Urban	2004
Seattle, WA[a]	MDN, 2011	32	Urban	Aug 2010
Tokyo Bay, Japan	Sakata et al., 2008	49	Urban	2003-2005
Nevada, USA[b]	Lyman et al., 2007	6-20	N/A	2005-2006
Chesapeake Bay, MD	Mason et al., 2000	38-82	N/A	1997-1998

[a]MDN site WA18, value given in ng/m^2 from August 17-24 (not a daily rate)
[b]MDN site NV99

5.3 Measured Versus Modeled Mercury Deposition Rates

For the four dry deposition sampling events in Pullman, modeled dry mercury deposition was outputted from the AIRPACT-3 model. Modeled dry deposition fluxes ranged from 0.80 to 2.22 ng/m^2/d. Deposition fluxes were also determined for the three sampling periods in Puyallup. These modeled deposition fluxes ranged from 3.71 to 5.94 ng/m^2/d. Relative to Pullman, modeled dry mercury deposition in Puyallup was observed to be slightly higher. The modeled values for dry mercury deposition fluxes are lower than the measured mercury deposition fluxes for the corresponding sampling periods for both Pullman and Puyallup (Table 16). A probable reason for lower modeled deposition rates in Pullman compared to measured deposition rates is the lack of agricultural field burning emissions data available for the AIRPACT-3 model. This component is not part of the model, but LAR utilizes the ClearSky model to monitor these types of emissions.

Modeled wet mercury deposition was generated for the four sample periods in Pullman and three events in Puyallup. Non-convective and convective (Wet1) wet deposition fluxes ranged from 0 to 8.21 ng/m^2/d, and convective (Wet2) deposition fluxes ranged from 0.80 to 2.22 ng/m^2/d in Pullman. Modeled Wet1 fluxes in Puyallup were higher and ranged from 1.47 to 9.26 ng/m^2/d; whereas Wet2 fluxes were lower and ranged from 0.02 to 0.84 ng/m^2/d. The Wet1 and Wet2 simulated fluxes for the first three sampling events in Pullman were similar; whereas the Oct 10-11 sampling period had a higher Wet1 flux compared to the Wet2 flux. Thunderstorms dominate Wet2 flux and since these storms rarely occur in Pullman a low Wet2 flux was observed during these sampling events. Measured wet deposition fluxes in Pullman and Puyallup were higher in magnitude than the modeled wet deposition flux values (Table 17). Of particular note, the AIRPACT-3 model was unable to detect wet deposition during the June 28-

29 and July 14 sampling periods, thus showing that the model may not properly estimate mercury deposition. Generated deposition values are given for the entire 12 by 12 km grid cell, while mercury deposition sampling was at a signal point within the cell. This could have led to a discrepancy in the modeled versus measured rates. Another possible reason for the disconnect between model deposition data and measured deposition data may be due to the emission rates inputted to AIRPACT-3. Emissions data are based on past studies and historical data archived from various databases. To achieve a more accurate deposition rate from the model, additional measurement studies should be conducted in order to obtain an average dry and wet deposition rate for a specific location. In addition, a higher grid resolution (e.g. 4 by 4 km) would also achieve more accurate values.

Table 16. Comparison of Measured and Modeled Dry Mercury Deposition

Location	Date	Measured Dry Hg Deposition ($ng/m^2/d$)	Modeled Dry Hg Deposition ($ng/m^2/d$)
Pullman	Aug 15-18, 2011	58	2.22
	Aug 18-22, 2011	24	0.80[a]
	Aug 23-28, 2011	103	0.96[b]
	Aug 29-Sept 5, 2011	37	1.09
Puyallup	Sept 12-15, 2011	36	3.71
	Sept 15-17, 2011	20	2.61
	Sept 21-23, 2011	37	5.94
	Sept 23-25, 2011	28	7.03
	Sept 27-29, 2011	33	2.93
	Sept 29-Oct 2, 2011	24	3.80

[a]Model value based on measurements from Aug 18-20, 2011.
[b]Model value based on measurements from Aug 24-28, 2011.

Table 17. Comparison of Measured and Modeled Wet Mercury Deposition

Location	Date	Measured Wet Hg Deposition ($ng/m^2/d$)	Modeled Wet1 Hg Deposition ($ng/m^2/d$)[a]	Modeled Wet2 Hg Deposition ($ng/m^2/d$)[b]
Pullman	June 28-29, 2011	303	0	0
	June 12-13, 2011	112	3.29	3.28
	July 14, 2011	206	0	0
	Oct 10-11, 2011	44	8.21	0.98
Puyallup	Sept 17-19, 2011	21	1.47	0.02
	Sept 25-27, 2011	24	3.71	0.08
	Oct 2-3, 2011	31	9.26	0.84

[a]Deposition rate determined for convective and non-convective rain events.
[b]Depositon rate determined for convective rain events.

6. CONCLUSION

The overarching objective in this study was to evaluate dry and wet deposition in a rural and urban setting in Washington State with anticipated differences in rates of mercury deposition. In this project, I developed an apparatus to measure real-time mercury deposition, evaluate wet and dry deposition in Pullman and Puyallup, WA, and compare field monitoring results with modeled results of mercury deposition from the AIRPACT-3 model. Measured dry and wet depositions were higher in Pullman than in Puyallup, which was not expected. A probable reason for higher deposition rates in Pullman compared to Puyallup is the time of sampling, which coincided with a number of agricultural activities and meteorological characteristics that could enhance mercury deposition. Due to a time constraint and the scope of this study, temporal variability between the two locations was not included.

Agricultural activities such as harvesting and crop field burning can enhance mercury re-emissions and deposition. During the majority of the dry deposition sampling events, it was observed that agricultural fields near the Pullman area were being harvested; whereas fields in Walla Walla County were being burned for the season. Due to movement of air masses, a smoky haze from the agricultural fields in Walla Walla County was observed in Pullman. Higher air temperatures enhance the conversion of elemental mercury to Hg(II), which can then deposit out of the atmosphere. Relatively high air temperatures were detected during the dry deposition sampling periods, thus enhancing mercury deposition.

The duration and intensity of a rain event contribute significantly to wet mercury deposition. The majority of the rain events captured in Pullman were short-duration storms signifying high concentrations of mercury in the rainwater due to atmospheric washout

mechanism. Rain events observed in the last sampling period in Pullman and the three in Puyallup, were long-duration storm events resulting in a lower mercury concentration in the precipitation. Therefore, with agricultural harvesting, short-duration rain events, and high air temperatures during the Pullman sampling periods, rates of wet mercury deposition can be extremely high.

Modeled deposition data obtained from the AIRPACT-3 model were lower than dry and wet deposition rates measured in the field. A likely reason for lower modeled deposition rates compared to measured deposition rates is the lack of agricultural field burning emissions data available for the AIRPACT-3 model and a majority of the emissions inputted into the model are historical data obtained from various databases. To achieve a more accurate deposition rate from the model, additional measurement studies should be conducted in order to obtain an average dry and wet deposition rate for a location.

A limitation of this study included how long monitoring was allowed for dry deposition. Partial seasons were studied due to time constraints. It would be interesting to monitor dry deposition for a full year to see how seasonal variability affects the rates of mercury deposition between the two locations. Other considerations could include the placement of the apparatus at other locations around the state to monitor for longer durations, sampling of agricultural top soil for total mercury concentrations, and filtered versus non-filtered water samples to separate particulates in the collected water sample. Continued sampling of Eastern and Western Washington will offer a more conclusive study of the rates of atmospheric dry mercury deposition.

7. REFERENCES

Andreae, M.O. and P. Merlet. 2001. Emission of trace gases and aerosols from biomass burning. Global Biogeochemical Cycles. 15: 955-966.

Benoit, J.M., C.C. Gilmour, A. Heyes, R.P. Mason and C. Miller. 2003. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In: Cai, Y., Braids, O.C. (Eds.), Biogeochemistry of Environmentally Important Trace Element. American Chemical Society. Washington, D.C., pp. 262-297.

Biswas, A., B. Klaue, G.J. Keeler, and J.D. Blum. 2004. Forest fire effects on mercury concentrations in a rocky mountain forest ecosystem. RMZ Mater. Geoenviron. 51(1):830.

Bullock, R.O. and K.A. Brehme. 2002. Atmospheric mercury simulation using the CMAQ model: formulation description and analysis of wet deposition results. Atmospheric Environment. 36: 2135-2146.

Bullock, R.O. and K.A. Brehme. 2006. CMAS paper: atmospheric mercury simulation with

Byun, D.W. and J.K.S Ching. 1999. Science algorithms of the EPA models-3 community multiscale air quality (CMAQ) modeling system. EPA-600/R-99/030. US Environmental Protection Agency. US Government Printing Office, Washington, DC. CMAQ version 4.5.1. Retrieved from http://www.cmascenter.org/conference/2006/abstracts.

Carpi, A., S.E. Lindberg. 1998. Application of a teflon^{TM} dynamic flux chamber for quantifying soil mercury flux: Tests and results over background soil. Atmospheric Environment. 32(5): 873-882.

Carter, W. P. L. 2000. Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment. Final Report to California Air Resources Board Contract No. 92-329, and 95-308. May (2000).

Chen, J., J. Vaughan, J. Avise, S. O'Neill, and B. Lamb. 2008. Enhancement and evaluation of the AIRPACT ozone and $PM_{2.5}$ forecast system for the Pacific Northwest. Journal of Geophysical Research. 113, D14305, doi:10.1029/2007JD009554.

City of Pullman. 2011. Departments. Available from http://www.pullman-wa.gov.

City of Puyallup. 2005. Business – Economic Development. Available from http://www.cityofpuyallup.org.

City of Seattle. 1995. Business in Seattle. Available from http://www.seattle.gov.

City of Tacoma. 2010. Community and Economic Development Department. Available from http://www.cityoftacoma.org.

Cobbett, F.D. and B.J. Van Heyst. 2007. Measurements of GEM fluxes and atmospheric mercury concentrations (GEM, RGM, and Hg^P) from an agricultural field amended with biosolids in Southern Ont., Canada (October 2004-November 2004). Atmospheric Environment. 41(11): 2270-2282.

Cossa, D., M. Conquery, C. Gobeil, and J.-M. Martin. 1996. Mercury fluxes at the ocean margins. In: Watras, C.J., J.W. Huckabee (Eds.). Mercury as a Global Pollutatn: Towards Integration and Synthesis. Lewis Publishers. Boca Raton, FL. pp. 229-247.

Engle, M.A., M.S. Gustin, and H. Zhang. 2001. Quantifying natural source mercury emissions from the Ivanhoe Mining District, north-central Nevada, USA. Atmospheric Environment. 35: 3987-3997.

Engle, M.A., M.T. Tate, D.P. Krabbenhoft, J.J. Schauser, A. Kolker, J.B. Shanley, and M.H. Bothner. 2010. Comparison of atmospheric mercury speciation and deposition at nine sites across central and eastern North America. Journal of Geophysical Research. 115. D18306. doi: 10.1029/2010JD014064.

Era-Miller, B. 2011. Toxics atmospheric deposition in Eastern Washington State – literature review. Washington State Department of Ecology. EA Project Code: 10-124. Unpublished.

Ferrara, R., B. Maserti, A. Petrosino, and R. Bargagli. 1986. Mercury levels in rain and air and the subsequent washout mechanism in a central Italian rgion. Atmospheric Environment. 20: 125-128.

Friedli, H.R., L.F. Radke, R. Prescott, P.V. Hobbs, and P. Sinha. 2003. Mercury emissions from the August 2001 wildfires in Washington State and an agricultural waste fire in Oregon and atmospheric mercury budget estimates. Global Biogeochemical Cycles. 17(2): 1039, doi:10.1029/2002GB001972.

Fritsche, J., D. Obrist, M.J. Zeeman, F. Conen, W. Eugster, and C. Alewell. 2008. Elemental mercury fluxes over a sub-alpine grassland determined with two micrometeorological methods. Atmospheric Environment. 42: 2922-2933.

Gill, G. 2008. Task 3 – Atmospheric mercury deposition studies. Calfed Mercury Project. Available at http://mercury.mlml.calstate.edu/wp-content/uploads/2008/10/06_task3.final.pdf.

Givelet, N., F. Roos-Barraclough, and W. Shotyk. 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural “background” values (past 8000 years). Journal of Environmental Monitoring. 5: 935-949.

Gustin, M.S., G.E. Taylor, and T.L. Leonard. 1996. Atmospheric mercury concentrations associated with geologically and anthropogenically enriched sites in central western Nevada. Environmental Science and Technology. 30: 2572-2579.

Huang, J., H. Choi, P. Hopke, and T. Holsen. 2010. Ambient mercury sources in Rochester, NY: results from principle components analysis (PCA) of mercury monitoring network data. Environmental Science and Technology. 44: 8441-8445.

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

Keeler, G., G. Glinsorn, and N. Pirrone. 1995. Particulate mercury in the atmosphere: its significance, transport, transformations, and sources. Water, Air, and Soil Pollution. 80: 159-168.

Laboratory for Atmospheric Research (LAR), Department of Civil and Environmental Engineering, Washington State University. 2010. AIRPACT-3 framework diagram.

Lacerda, L.D. 1997. Global mercury emissions from gold and silver mining. Water, Air, and Soil Pollution. 97: 209-221.

Lamborg, C.H., W.F. Fitzgerald, G.M. Vandal, and K.R. Rolfhus. 1995. Atmospheric mercury in northern Wisconsin: sources and species. Water, Air, and Soil Pollution. 80: 189-198.

Landis, M.S. and G.J. Keeler. 1997. Critical evaluation of a modified automatic wet-only precipitation collector for mercury and trace element determinations. Environmental Science and Technology. 31: 2610-2615.

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

Lin, C.J. and S.O. Pehkonen. 1999. The chemistry of atmospheric mercury: a review. Atmospheric Environment. 33: 2067-2079.

Lin, C.J., S.E. Lindberg, T.C. Ho, and C. Jang. 2005. Development of a processor in BEIS3 for estimating vegetative mercury emissions in the continental United States. Atmospheric Environment. 39: 7529-7540.

Lombard, M., J. Bryce, H. Mao, and R. Talbot. 2011. Mercury deposition in southern New Hampshire, 2006-2009. Atmospheric Chemistry and Physics Discussions. 11: 4569-4598.

Lyman, S.N., M.S. Gustin, E.M. Prestbo, and F.J. Marsik. 2007. Estimation of dry deposition of atmospheric mercury in Nevada by direct and indirect methods. Environmental Science and Technology. 41(6): 1970-1976.

Mason, R.P., N.M. Lawson, and G.R. Sheu. 2000. Annual and seasonal trends in mercury deposition in Maryland. Atmospheric Environment. 34(11): 1691-1701.

Meglar, D., H.A. Anderson, L.H.M Chan, K.R. Mahaffey, M. Murry, M. Sakamoto, and A.H. Stern. 2007. Methylmercury exposure and health effects in humans: a worldwide concern. Ambio. 36(1): 3-11.

Mesowest. 2002. Available from http://mesowest.utah.edu/index.html.

Miller, E.K., A. Vanarsdale, G.J. Keeler, A. Chalmers, L. Poissant, N.C. Kamman, R. Brulotte. 2005. Estimation and mapping of wet and dry mercury deposition across northeastern North America. Ecotoxicology. 14: 53-70.

Morel, F.M., A.L. Kraepiel, and M. Amyot. 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics. 29: 543-566.

National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN). 2011. Mercury deposition network maps. Retrieved from http://nadp.sws.uiuc.edu/MDN/maps.aspx.

National Oceanic and Atmospheric Adminstration (NOAA). 2006. NOWData – NOAA online weather data. Retrieved from http://www.weather.gov/climate/xmacis.php?wfo=otx.

Pacyna, E.G., J.M. Pacyna, F. Steenhuisen, and S. Wilson. 2006. Global anthropogenic mercury emission inventory for 2000. Atmospheric Environment. 40: 4048-4063.

Pirrone, N., G.J. Keeler, and J.O. Nriagu. 1996. Regional differences in worldwide emissions of of mercury to the atmosphere. Atmospheric Environment. 30: 2981-2987.

Pirrone, N., I. Allegrini, G.J. Keeler, J.O. Nriagu, R. Rossmann, and J.A. Robbins. 1998. Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records. Atmospheric Environment. 32(5): 929-940.

Pirrone, N., P. Costa, J.M. Pacyna, and R. Ferrara. 2001. Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. Atmospheric Environment. 35: 2997-3006.

Pleim, J.E., J.F. Clarke, P.L. Finkelstein, E.J. Cooter, T.G. Ellestad, A. Xiu, and W.M. Angevine. 1996. Comparison of measured and modeled surface fluxes of heat, moisture and 12-77 chemical dry deposition. In: Air Pollution Modeling and its Application XI. Gryning and Schiermeier (Eds). Plenum Press, New York.

Pleim, J.E., A. Xiu, P.L. Finkelstein, and J.F. Clarke. 1997. Evaluation of a coupled landsurface and dry deposition model through comparison to field measurements of surface heat, moisture, and ozone fluxes. Proceedings of the 12th Symposium on Boundary Layers and Turbulence, July 28-August 1, 1997. Vancouver, BC.

Poissant, L., M. Amyot, M. Pilote, and D. Lean. 2000. Mercury water-air exchange over the upper St. Lawrence River and Lake Ontario. Environmental Science and Technology. 34: 3069-3078.

Porter, M. K.2007. Regional modeling of nitrogen, sulfur, and mercury atmospheric deposition in the Pacific Northwest. MS Thesis. Washington State University.

Rattray, G. and H. Sievering. 2001. Dry deposition of ammonia, nitric acid, ammonium, and nitrate to alpine tundra at Niwot Ridge, Colorado. Atmospheric Environment. 35:1105-1109.

Sakata, M. and K. Marumoto. 2004. Dry deposition fluxes and deposition velocities of trace metals in the Tokyo metropolitan area measured with a water surface sampler. Environmental Science and Technology. 38: 2190-2197.

Sakata, M., Y. Tani, and T. Takagi. 2008. Wet and dry deposition fluxes of trace elements in Tokyo, Bay. Atmospheric Environment. 42:5913-5922.

Schroeder, W.H. and J. Munthe. 1998. Atmospheric mercury – an overview. Atmospheric Environment. 32: 809-822.

Stratton, W.J., S.E. Lindberg, and C.J. Perry. 2001. Atmospheric mercury speciation: critical Evaluation of a mist chamber method for measuring reactive gaseous mercury. Environmental Science and Technology. 35: 170-177.

Swain, E.B, D.R. Engstrom, M.E. Brigham, T.A. Henning, and P.L. Brezonik. 1992. Increasing rates of atmospheric mercury deposition in midcontinental North America. Science. 257: 784-787.

Ullrich, S.M., T.W. Tanton, and S.A. Abdrashitova. 2001. Mercury in the aquatic environment: a review of factors affecting methylation. Environmental Science and Technology. 31(3): 241-293.

United State Environmental Protection Agency (USEPA). 1997. Mercury Study Report to Congress. Fate and transport of mercury in the environment, Vol. III. EPA-452/R-97-005, USEPA,US Government Printing Office, Washington, D.C.

United State Environmental Protection Agency (USEPA). 2002. Method 1631, revision E: mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. EPA-821-R-02-019.USEPA, Washington, D.C.

United States Environmental Protection Agency (USEPA). 2004. National listing of fish advisories. EPA-823-F-04-016. USEPA. Washington, D.C.

United States Geological Survey (USGS). 2009. USGS contributes to the design of a proposed national mercury monitoring network (MercNet). USGS Toxic Substances Hydrology Program. June 2009. Available from http://toxics.usgs.gov/highlights/mercnet.html.

United States Oil and Refining. 2011. Available from http://www.usor.com.

Washington State Department of Ecology and Department of Health (WSDE/WSDH). 2003. Washington State mercury chemical action plan. Available from http://www.ecy.wa.gov/biblio/0303001.html.

Washington State Map (WSM). 2005. Available from http://geology.com.

Washington State University (WSU) Whitman County Extension. 2011. County Resources Agriculture. Available from http://www.whitman.wsu.edu/countyag.htm.

Watras, C.J. and J.W. Huckabee, editors. 1994. Mercury pollution: Integration and synthesis. Ann Arbor, MI: Lewis Publishers.

Watras, C.J., R. Back, S. Halvorsen, R. Hudson, K. Morrison, and S. Wente. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Science of the Total Environment. 219: 183-208.

Weiss-Penzias, P., M. Gustin, and S. Lyman. 2009. Observations of speciated atmospheric mercury at three sites in Nevada: evidence for a free tropospheric source of reactive gaseous mercury. Journal of Geophysical Research. 114: D14302.

Western Regional Climate Center (WRCC). 2005. Available from http://www.wrcc.dri.edu.

Xiao, Z.F., J. Munthe, W.H. Schroeder, and O. Lindqvist. 1991. Vertical fluxes of volatile Mercury over forest soil and lake surfaces in Sweden. Tellus. 43B: 267-279.

Yi, S.M., T.M. Holsen, and K.E. Noll. 1997. Comparison of dry deposition predicted from models and measured with a water surface sampler. Environmental Science and Technology. 31: 272-278.

Zhang, L., L. Wright, P. Blanchard. 2009. A review of current knowledge concerning dry deposition of atmospheric mercury. Atmospheric Environment. 43: 5853-5864.