Analysis of Temporal Variance of Mercury Wet Deposition at a Rural Ohio River Valley Site

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the Russ College of Engineering and Technology of Ohio University

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This thesis titled
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ABSTRACT

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Mercury (Hg) is identified as a Hazardous Air Pollutants (HAP’s), among the 189 present in the environment. Coal fired power plants are identified to be the major anthropogenic sources of mercury emissions in the atmosphere. Athens is located in the center of the Ohio River Valley region, which is surrounded by a number of coal fired power plants, chemical plants and manufacturing industries. Ambient mercury data is monitored and the mercury wet deposition samples are collected at the Athens Surface Air Monitoring (SAM) station. The primary objective of this study is to see the temporal variance in the mercury data observed at the Athens SAM station. Also, the study compares the mercury wet deposition data with the data from the other Mercury Deposition Network (MDN) sites across the United States. The study also aims at finding out the potential source regions for the wet deposited mercury, observed at the Athens SAM station.

Approved: _____________________________________________________________

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CHAPTER 1: INTRODUCTION

Mercury is introduced into the environment by anthropogenic sources such as coal fired power plants, mining activities, fossil fuel combustion, waste incineration, iron-steel production, coke and lime production, hazardous waste recycling, non-ferrous metal smelting, petroleum refining, mercury cell chlor-alkali plants, (Keeler et al. 2006) and natural sources such as volcanic eruptions, the weathering of soils and rocks and vaporization from oceans (Schroeder and Munthe 1998). Scientists today believe that more than half, (i.e. 50-75%), of the mercury in the environment is from anthropogenic sources (Keeler et al. 2006).

Mercury is emitted in the environment mainly in three distinct forms. The first form is a gaseous and volatile elemental form, Hg (0). The other two forms are semi volatile oxidized form, Hg (II); and non volatile particulate form, Hg (p) (Selin et al. 2006). Elemental mercury is very volatile and chemically inert. It has an atmospheric life time of 6-24 months which is considered to be relatively high (Schroeder and Munthe 1998). It is oxidized by species such as Ozone (O₃), Hydrochloric acid (HCl), Hydrogen Peroxide (H₂O₂), Hydroxide radical (OH), Chlorine (Cl₂), etc, to semi volatile reactive gaseous mercury i.e. Hg(II) (Ryaboshapko et al. 2002). Divalent mercury Hg (II) and particulate mercury Hg (p) have a short residence time and undergo wet and dry deposition to the earth’s surface (Mercury.Utah.Gov 2008). The fate and transport of the mercury species are later discussed in the background chapter. A fraction of the deposited mercury is converted into methyl mercury by the bacteria present in the sediments of
water bodies and bio-accumulates up the food chain, causing serious threats to the environmental health (Yatavelli et al. 2006). Consumption of methyl mercury contaminated fish is the primary source of mercury exposure in human beings.

The Environment Protection Agency (EPA) has labeled mercury as a human toxicant and methyl-mercury as a neurotoxin because of their adverse effects to the ecosystem. Various rules and regulations have been implemented by the United States EPA to control mercury emissions. Two of these are the Clean Air Mercury Rule (CAMR) & Clean Air Interstate Rule (CAIR). The Clean Air Mercury Rule (CAMR) and The Clean Air Interstate Rule (CAIR) aim at reducing anthropogenic mercury emissions in the United States by significant amounts.

The CAMR was promulgated in the year 2005 by the EPA to regulate Hg emissions directly from the coal fired power plants (USEPA Clean Air Mercury Rule 2008). The CAIR mainly addresses the transport of pollution across state borders in the Eastern part of the United States. CAIR regulates the emissions of SO$_2$ and NO$_x$ from power plants. Thus, CAMR and CAIR have joined forces to provide a multi pollutant approach to reduce Hg, SO$_2$ & NOx emissions from power plants (USEPA Clean Air Mercury Rule 2008). Later in this study, I will discuss the objectives and the targets of these two rules.

The Ohio River Valley region (ORV) is considered as one of the major pollutant source regions to the Eastern part of the United States of America. It is surrounded by a high number of coal fired power plants, mining activities, and industrial plants including
chemical, metal smelting and manufacturing activities (Yatavelli et al. 2006). A surface air monitoring (SAM) station is located in Athens, Ohio and is in close proximity to a number of coal fired power plants as seen in Figure 1. Coal combustion is one of the major contributors of mercury wet deposition, approximately 70%. (Keeler et al. 2006). The Athens SAM site is described later in the Methods & Instrumentation chapter. The data collected at the Athens SAM site is used for this study. The objectives of the study are described in Chapter 3: Research Objectives.

Figure 1. Location map with sampling site, study area, and numerous point sources in the Ohio River Valley Region (Yatavelli et al. 2006).
CHAPTER 2: BACKGROUND

Mercury is a unique metal that exists as a silver liquid at room temperature. Even though it is extremely toxic in nature, it does have useful characteristics. It can be found in different mediums, such as air, water and soil in the environment. Its movement between those various sections of the environment is commonly referred to as fluxes and its quantities in those sections are called pools (Mercury and the Environment 2004). Mercury fluxes and pools contribute to the global mercury budget. The global mercury budget includes emissions and re-emissions from both human and natural sources. The current ambient levels of elemental mercury are 1.6ng m\(^{-3}\), which are significantly higher from those which were estimated to be around 0.5-0.8ng m\(^{-3}\), before the start of the industrial revolution (Mercury.Utah.gov 2008). Figure 2 shows the amount of mercury emitted from different sources and re-emitted from land and ocean across the different states of United States.

Taking into account the re-emissions of the deposited mercury, differentiating and quantifying the amount of mercury deposited by the human and natural sources are difficult tasks. To predict the potential source regions of mercury emissions, it is important to understand its transport and the local, regional and global fluxes apart from the biogeochemical reactions. This chapter provides an overview on the fate and transport of mercury, oxidation and depletion, its adverse effects on the health of the general population and different laws and regulations that have been proposed to control mercury emissions.
2.1 Fate & Transport

Mercury is released in the environment as elemental mercury Hg(0), reactive gaseous mercury Hg(II) or particulate mercury Hg(p) by anthropogenic sources (Selin et al, 2008). More than 95 percent of the mercury in air is in its elemental form, Hg(0) (Ryaboshapko et al. 2002), mainly emitted mercury from natural sources. With a residence time of about 1-2 years, elemental mercury is more stable compared to the other two forms of mercury (Schroeder and Munthe 1998). Due to its stability and high residence time it can be circulated and transported from its source of emission to
anywhere in the world, which is why mercury is found even in pristine places like the Arctic where there are no sources (Mercury – a priority pollutant, 2005).

Hg(0) is first oxidized by O$_3$, HCl, H$_2$O$_2$, Cl$_2$, to divalent mercury (Ryaboshapko et al. 2002). Then it is deposited to the surface of the earth via dry and wet deposition. Once the mercury is emitted to the atmosphere, depending upon its physical and chemical form, it could be transported larger distances via atmospheric transport or deposited locally to the emission source (Mercury.utah.gov 2008). Hg(II) and Hg(p) have a shorter residence time period, ranging from a few hours to several days. Hg(II) is much more soluble in water than Hg(0) and has an atmospheric life of 5-14 days before being deposited on the earth’s surface due to precipitation (Mercury.utah.gov 2008). Particulate bound mercury Hg(p) (mercury adsorbed onto the particulate matter) is generally deposited near the source of emission, with larger particles falling closer to the source of emission than the smaller particulates (Mercury.utah.gov 2008). Generally, the deposited mercury is re-emitted from the land, air and soil surfaces and undergoes long range atmospheric transport before being re-deposited somewhere else.

2.2. Biogeochemical Interactions

Mercury exists in various physical states and chemical forms. To better understand its atmospheric transport and effects due to anthropogenic sources, its biogeochemical interactions must be studied thoroughly. Figure 3 describes the biogeochemical cycle.
Since mercury has a different residence time period, lifetime of a species, associated with it in its different physical states, it is important to study its transformations into different physical states and chemical forms. The Hg(II) form of mercury is responsible for its deposition on land and water, whereas, the Hg(0) form is transported in the atmosphere from one place to the other via air masses before it is deposited to the land or water by its oxidation into Hg (II). Therefore, to better estimate the sources of its emissions, it is important to study its transformation into different physical states and chemical forms via oxidation and reduction reactions.

\[\text{Figure 3. Describes the biogeochemical cycle of mercury. (Mercury and the Environment 2004).}\]
2.2.1 Oxidation

More than 95 percent of mercury present in the air is in its elemental form, Hg(0) (Tracy et al. 1998). Elemental mercury is chemically inert and oxidation of Hg(0) results in its wet or dry deposition. Hg(0) is oxidized to Hg(II) by species such as O₃, H₂O₂, Cl₂ present in the atmosphere. Hg(II) can be easily adsorbed by particulates present in the atmosphere, resulting in dry deposition, or by water droplets, resulting in wet deposition. Mercury oxidation can occur in both gaseous and aqueous phases. Oxidation with ozone is one of the most important gas phase reaction (Hall 1995). As suggested by B. Hall, the reaction rate of oxidation of mercury by ozone in the gaseous phase is \((3 \pm 2) \times 10^{-20} \text{ Cm}^3 \cdot \text{Molec}^{-1} \cdot \text{S}^{-1}\) at 20°C and the reaction is:

\[
\text{Hg}(0)_{(g)} + \text{O}_3_{(g)} \rightarrow \text{HgO}_{(g)} + \text{O}_2_{(g)}
\]  

(1)

The reaction rate of oxidation of elemental mercury by ozone in aqueous phases is higher than the gaseous phase reaction. The aqueous phase reaction takes place with species such as Hg(0) and O₃ dissolved in cloud droplets. As suggested by Munthe et al. 1991, the reaction rate of oxidation of mercury by ozone in an aqueous phase (1995) is \((4.7 \pm 2.2) \times 10^{-7} \text{ M}^{-1} \cdot \text{S}^{-1}\) and the reaction is:

\[
\text{Hg}(0)_{(aq)} + \text{O}_3_{(aq)} \rightarrow \text{HgO}_{(aq)} + \text{O}_2_{(aq)}
\]  

(2)

The reaction rate of oxidation of elemental mercury by Cl₂ was found to be \((2.6 \pm 0.2) \times 10^{-18} \text{ C m}^3 \cdot \text{Molec}^{-1} \cdot \text{S}^{-1}\) (Ariya et al. 2002). The reaction is:
Hg(0)(g) + Cl₂(g) → HgCl₂(g)       (3)

The upper limit of the reaction rate of oxidation of elemental mercury by H₂O₂ was determined to be 8.5 * 10¹⁹ Cm³.molec⁻¹.S⁻¹ (Tokos et al. 1998). The reaction is:

Hg(0)(g) + H₂O₂(g) → Hg(OH)₂(g) . (4)

Other aqueous phase oxidation pathways of Hg(0) occur due to hypochlorine Acid (HOCl) and hypochlorite ion (OCl⁻). The oxidation reactions of mercury with Cl₂, HOCl, OCl⁻, generally occur in the absence of sunlight near water surfaces like oceans; that is they occur during the night due to decomposition of Cl₂ and its compounds in presence of light (physical-chemical properties of Mercury and selected POPs). Pehkonen and Lin (1998) studied the oxidation of Hg(0) by species HOCl and OCl⁻.

HOCl(aq) + Hg(0)(aq) → Hg(II)(aq) + Cl⁻(aq) + OH⁻(aq)  (5)

With the reaction rate = (2.09 ± 0.06) * 10⁶ M⁻¹.S⁻¹.

OCl⁻(aq) + Hg(0)(aq) → → Hg(II)(aq)) + Cl⁻(aq) + OH⁻(aq). (6)

With the reaction rate = (1.99± 0.05)* 10⁶ M⁻¹.S⁻¹.

Thus, the Hg(0) is transformed in to Hg(II) by various species in the air.
2.2.2 Reduction

Reduction is a transformation process where divalent mercury, Hg(II), is converted into elemental mercury, Hg(0). Munthe et al, 1991 studied the reduction of Hg(II) to Hg (O) in the presence of sulphite. According to their study, the transformation of Hg(II) to Hg(0) involved formation of an unstable intermediate HgSo₃, which decomposes to Hg⁺, which in turn resulted in the formation of Hg(0). The reduction reaction takes place in an aqueous medium. Few studies (Constantinou et al. 1995, Pehkonen and Lin 1998) have discussed the reduction of Hg(II) into Hg(0) using sulphite.

Reduction reactions of Hg(II) into Hg(0) as studied by Munthe et al, 1991 are:

\[
\text{Hg(II)_{(aq)}} + \text{SO}_3^{2-}_{(aq)} \rightarrow \text{HgSO}_3_{(aq)}
\]  

(7)

With reaction rate = 2 * 10⁻¹³ M

\[
\text{HgSO}_3_{(aq)} + \text{SO}_3^{2-}_{(aq)} \rightarrow \text{Hg(SO}_3)^{2-}_{(aq)}
\]  

(8)

With reaction rate = 4* 10⁻¹² M

\[
\text{HgSO}_3_{(aq)} \rightarrow \text{Hg(0)} + \text{SO}_3^{2-} + \text{H}^+
\]  

(9)

With reaction rate = 0.6 S⁻¹. (Pleijel and Munthe 1995).

Pleijel and Munthe (1995) discussed the reduction mechanism of Hg(OH)₂ to Hg(0) by photolysis. The reaction is:

\[
\text{Hg(OH)}_2_{(aq)} \rightarrow \text{Hg(0)}_{(aq)} + \text{products}
\]  

(10)
The other reduction agent is the hydro peroxide radical. Lin and Pehkonen (1999) discussed the reduction of Hg(II) by HO$_2$ radical. The reduction reactions involved are:

\[
\text{HO}_2(\text{aq}) + \text{Hg (II)}(\text{aq}) \rightarrow \text{Hg (I)}(\text{aq}) + \text{O}_2(\text{aq}) + \text{H}^+(\text{aq}) \quad (11)
\]

\[
\text{HO}_2(\text{aq}) + \text{Hg (I)}(\text{aq}) \rightarrow \text{Hg(0)}(\text{aq}) + \text{O}_2(\text{aq}) + \text{H}^+(\text{aq}) \quad (12)
\]

A detailed description of chemistry of ambient mercury is discussed by Lin and Pehkonen (1999) in their article “The Chemistry of Atmospheric Mercury: A Review”.

2.3. Effects on Health

People are mainly affected by the organic form of mercury, i.e., methyl mercury. The primary source of exposure to human beings is the consumption of fish contaminated with methyl mercury. A number of factors such as dose, age, or duration determine the magnitude of harm that mercury can have on a person’s health. In adults, there is a blood brain barrier that is responsible for protecting the brain from harmful toxins. However, every now and then, there could be an opening in this barrier and this allows for toxins that are already present in the blood to reach the brain. Hence, fish consumption warnings are often targeted to pregnant women.

The exposure of methyl mercury to fetuses, infants & children can cause impairments to neurological development. There is no blood brain barrier present in fetus and a baby does not have a fully developed barrier until it is at least six months old. Some of the common adverse effects observed in children who were exposed to methyl...
mercury were impacts on cognitive thinking, memory, language or visual spatial skills (USEPA Mercury Health Effects 2008).

2.4. Rules & Regulations

The EPA issued two reports to the U.S. congress stating the adverse effects of Hg on public health. The first report, *The Mercury study Report to congress* (USEPA 1997a, b, c) emphasized on the source and amount of mercury emissions in the U.S. and, the adverse effects of mercury and mercury compounds on humans and wildlife. In 1998, the second report, *The Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units* (USEPA 1998) mainly emphasized on the emissions from the utility companies and stated Hg as one of the major pollutants from coal-fired power plants.

The Clean Air Mercury Rule (CAMR) (USEPA Clean Air Mercury Rule 2008) was the first federal rule that was issued by the EPA to reduce mercury emissions from coal-fired power plants. At present, the CAMR builds on the EPA’s Clean Air Interstate Rule (CAIR) to reduce emissions from the power plants. When fully implemented, the EPA aims to reduce the Hg emission from the 1999 baseline of 48 tons/year to 15 tons/year by the end of 2018, a reduction of nearly 70%. This will be challenging to protect public health and the environment without affecting the generation of affordable energy and reducing the mercury, SO₂ and NOₓ emissions simultaneously through CAMR & CAIR. CAMR uses a market based cap-and-trade program to reduce Hg emissions in two distinct phases. The first cap phase, due in 2010 sets a goal of reducing Hg emissions
to 38tons/year. This can be achieved by taking co-benefits from CAIR to reduce Hg emissions by reducing SO\textsubscript{2} and NO\textsubscript{x} emissions. The second cap phase, due in 2018, aims at reducing Hg emissions to 15tons/year. According to EPA’s modeling, CAIR will be significant in reducing the Hg emissions from coal-fired power plants and CAMR is expected to reduce emissions that contribute to atmospheric mercury worldwide. (USEPA Clean air Mercury rule 2008).
CHAPTER 3: RESEARCH OBJECTIVES

This study aims at:

A. Evaluating mercury wet deposition data at the Athens site and comparing it with other MDN sites in the United States.

B. Analyzing the temporal variance of mercury wet deposition data recorded at the Athens site.

C. Identifying the potential source regions of mercury wet deposition at the Athens site using Potential Source Contribution Function (PSCF) and Residence Time Weighted Concentration (RTWC).

In addition to the above tasks, this study also involves continuous monitoring and maintenance of the SAM station at Athens, Ohio.
CHAPTER 4: METHODOLOGY AND INSTRUMENTATION

4.1. Athens Surface Air Monitoring Station Description

Taking into perspectives a large geographic area, Athens is located at the heart of a heavily polluted region, the Ohio River Valley, which is home to a number of coal-fired power plants and other industrial facilities, including coke plants, metal smelting and processing plants and chemical plants. The Ohio River Valley encompasses a vast area which centers along the Ohio River. The land use pattern is diversified within the region since urban, semi-rural and rural areas co-exist.

This advantageous location of Athens allowed for The Center of Air Quality at Ohio University, along with generous funding from the Department of Energy National Technology Laboratory (DEO NETL), to establish the surface air monitoring (SAM) site in the winter of 2004. The site has been continuously operating since it was first activated. It is situated at 7760 North Blackburn Road, (39°18’ N Latitude & 82°7’ W longitude) in a rural area approximately 3.5 km southwest of downtown, Athens. The site is stationed at a height of 330 m (1000 ft) above mean sea level and is the highest point in its surrounding area. The site is nestled in agricultural and residential settlement, with threads of scattered forest around it.

The SAM is equipped with instruments to measure ambient concentrations of various atmospheric pollutants. Apart from atmospheric and wet deposited mercury species, the monitoring site also continuously measures a wide range of co-pollutants
such as particulate matter, NOₓ, SO₂, O₃, CO & meteorological data. The center is responsible for monitoring and examining the impacts of mercury in the Ohio River Valley, that are mainly the contributions of coal-fired power plants and various other anthropogenic sources in the region. Table 1 shows the data recorded and monitored at the Athens SAM station (Fahrni 2005).

Table 1

**Summary of Data with the Appropriate Units Monitored at the Site**

<table>
<thead>
<tr>
<th>Species</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>Ppb</td>
</tr>
<tr>
<td>Nitrogen Oxides (NOₓ)</td>
<td>Ppb</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>Ppm</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>Ppb</td>
</tr>
<tr>
<td>Fine Particulate Matter (PM₂.₅)</td>
<td>µg m⁻³</td>
</tr>
<tr>
<td>Elemental mercury (Hg₀)</td>
<td>ng m⁻³</td>
</tr>
<tr>
<td>Reactive gaseous mercury (RGM)</td>
<td>pg m⁻³</td>
</tr>
<tr>
<td>Particulate mercury (Hgₚ)</td>
<td>pg m⁻³</td>
</tr>
<tr>
<td>Wet Deposited mercury concentration</td>
<td>ng l⁻¹</td>
</tr>
<tr>
<td>PM2.5 – Federal Reference Method</td>
<td>µg m⁻³</td>
</tr>
<tr>
<td>PM2.5 – Chemical Speciation</td>
<td>µg m⁻³</td>
</tr>
<tr>
<td>Barometric Pressure</td>
<td>mm Hg</td>
</tr>
<tr>
<td>Solar Radiation</td>
<td>watt / m²</td>
</tr>
<tr>
<td>Wind Speed (at 25 ft agl)</td>
<td>Mph</td>
</tr>
<tr>
<td>Wind Direction (at 25 ft agl)</td>
<td>Degrees</td>
</tr>
<tr>
<td>Wind Speed (at 375 ft agl)</td>
<td>Mph</td>
</tr>
<tr>
<td>Wind Direction (at 375 ft agl)</td>
<td>Degrees</td>
</tr>
<tr>
<td>Rainfall</td>
<td>Inches</td>
</tr>
</tbody>
</table>
As seen in Figure 4, the Belfort Rain gauge and the Aerochem Metrics Precipitation sampler (wet deposition collector) are located outside the fence. The Belfort rain gauge was replaced by NOAA rain gauge as directed by the MDN in July 2008 (Figure 5). Also, seen in the site are two sheds and a trailer. The shed 1 holds TEKRA

Figure 4. A picture of Athens SAM Station-Belfort rain gauge.
Figure 5. A picture of Athens Sam station- NOAA IV rain gauge.

4.2. Monitoring Methods

4.2.1. TEKRAN Mercury Vapor Analyzer

The schematic diagram of the TEKRAN Mercury Vapor Analyzer is shown in Figure 6. The TEKRAN Mercury Vapor Analyzer consists of three major components:

1. Mercury Speciation and Pump Unit (model 1130)
2. Mercury particulate unit (model 1135) and
3. Ambient mercury vapor analyzer (model 2537 A).
Under the guidance of USEPA research and development office and Florida State Department of Environmental Protection, the mercury monitoring system was developed and its performance tested to measure the ambient mercury (Landis et al. 2002). The TEKRAN detects elemental mercury, divalent mercury and particulate mercury by using automated pure gold cartridge pre-concentration system coupled with cold vapor atomic fluorescence spectroscopy (CVAFS) technique. This method is well described in Landis et al (2002).

The 2537 A analyzer, 1130 pump unit and the data acquiring computer are placed inside shed 1 (can be seen in Figures 4 & 5), whereas the 1130 speciation unit and 1135 particulate unit are placed on a deck behind the shed at a distance of 2 meters (Fahrni...
2005). Figure 7 shows the 2537A analyzer with the pump placed inside the shed. Figure 8 shows the 1130 speciation unit below the 1135 particulate unit at the Athens SAM station.

*Figure 7. TEKRAN 2537A analyzer with Model 1130 pump unit inside the field shelter.*

*Figure 8. The 1130 Speciation unit & the 1135 Particulate unit.*

Ambient air at a flow rate of 10 L Min\(^{-1}\) (2537A pulls 1.0 L Min\(^{-1}\) & 1130 pump module unit pulls 9 L Min\(^{-1}\)) is passed through the heated impactor cyclone inlet to avoid particulate matter greater than 2.5 µm to enter the KCL coated denuder. Smaller
particles (< 2.5 µm) pass through the KCL coated quartz denuder placed inside the 1130 speciation unit without being adsorbed on it due to laminar flow conditions (Sheu and Mason 2001). The KCL coated quartz annular denuder selectively adsorbs GOM, and then the air stream free from GOM passes through the Regenerable Particulate Filter (RPF) placed inside the 1135 particulate unit. The RPF captures the particulate mercury and then the remaining mercury fraction in the air stream, GEM, passes through and is trapped onto the pure cold cartridges to measure the GEM using CVAFS technique.

The TEKRAN mercury vapor analyzer is programmed for a 3 hour cycle. In the first two hours of the cycle, the 2537 A analyzer measures ambient elemental mercury in twenty four 5 minutes increments, meanwhile, the Hg(II) & the Hg(p) are being adsorbed on the denuder and RPF simultaneously. After completion of two hour Hg(0) sampling, one hour of desorbed cycle was initiated to analyze Hg(p) and Hg (II). The Hg(p) and the Hg(II) are decomposed to Hg(0) from the RPF and denuder by heating the 1135 particulate unit and 1130 speciation unit to 800°C and 500°C respectively. Hg(0) is then carried into the 2537 A analyzer by passing zero air for measuring the amounts of Hg(II) and Hg(p) in the air. After the heating cycle, the zero air was passed through the system to remove the traces of mercury and to cool down the system to 50°C. The 2537 A analyzer consists of two alternating gold cartridges to sample the air and to analyze the mercury fraction using Cold vapor atomic fluorescence spectrophotometry (CVAFS) technique. The 2537 A unit pulls 1.0 LMin⁻¹ for analysis, and passes the sample air over one of the cartridges where mercury amalgamation occurs over the gold surface. The ultra high pure argon stream then carries thermally decomposed Hg(0) from the other
gold cartridge into the cell of CVAFS to quantify the amount of mercury at a wavelength of 253.7nm (Poissant 1997).

Regular maintenance of TEKRAN is required for its proper working. The maintenance is done on weekly, biweekly, monthly, quarterly, semi annually, annually or whenever if a problem rises. The weekly maintenance comprises of regular data monitoring, checking Argon pressure in the cylinder, keeping an eye whether the desired temperatures of 500°C and 800°C are achieved in model 1130 & 1135 respectively.

Apart from the regular maintenance, the TEKRAN analyzer was calibrated bi-weekly using its internal Hg(0) permeation tube source and monthly by using manual Hg(0) injections. The manual Hg(0) injection calibrations are accomplished by using the TEKRAN model 2505 saturated mercury vapor calibration unit. If the internal Hg(0) permeation tube source calibrations and manual Hg(0) injection calibrations were off by 5%, then the systems permeation rate was calibrated again (Landis et al. 2002).

TEKRAN analyzer used to measure ambient mercury, reported Hg(0) in units of ng m$^{-3}$ and Hg(II) & Hg(p) in units of pg m$^{-3}$. Ambient mercury data collected at the Athens SAM station is monitored continuously. If the zero air concentrations is greater than 1.5 pg m$^{-3}$ then the data is marked as invalid. If the zero air concentration lies between 0.75 to 1.5 pg m$^{-3}$, then it is flagged. The flagged data may be used in the analysis if no other problems occurred along with it. If the zero air concentrations are below 0.75 pg m$^{-3}$, then the data is marked as valid (Yatavelli et al. 2006).
4.2.2. Aerochem Metrics Wet Deposition Collector

The MDN collector used at the Athens SAM station is a Model 301, wet precipitation Collector manufactured by Aerochem Metrics Inc., Bushnell, Florida. The MDN Collector is coupled with a rain gauge to measure and record the timing and length of the rainfall (precipitation event). The MDN collector was coupled with Belfort Instrument Company (Baltimore, Maryland) precipitation event recorder. The Belfort rain gauge can be seen in Figure 10. According to the mercury Deposition Network’s Protocol, the Belfort rain gauge was replaced by a NOAA IV All-weather precipitation gauge in July 2008. The Aerochem Metrics wet precipitation collector and the NOAA IV All-weather precipitation gauge are shown in Figures 9 and 11.

Figure 9 shows the Aerochem wet precipitation collector and is well described in Vermette et al. (1995) and Sweet and Prestbo (1999). The precipitation samples are collected on weekly basis and shipped to Frontier Geosciences, Inc., Seattle, Washington for total mercury analysis. The collector has two sides, the wet side and the dry side. It is a dual orifice that can be used to measure mercury as well as other metals in precipitation. At the Athens SAM station, the precipitation is collected only for mercury analysis. The unit has a polycarbonate lid coated with Teflon that opens and rests on the dry bucket during precipitation event and closes to protect the orifice glass inlet from dry particulates. During winter, a thermostat is operated to melt snow and prevent coagulation in the funnel. Every week, generally on Tuesday’s, all the glassware are exchanged and the MDN collector is cleaned in accordance with the MDN’s protocol.
An electric connection exists between the MDN collector and the rain gauge. The Belfort rain gauge consists of a bucket for storing rain water during precipitation event, weight scale, winding clock and two recorder ink pens. The winding clock makes the recorder pens record the information of precipitation events on a Belfort chart. The second recorder pen is connected with the weight scale and records the amount of rainfall that occurred during a precipitation event. The Belfort chart is sent along with the sample and is replaced every week with a new chart. Figure 10 shows a photograph of Belfort rain gauge that was used at the Athens SAM station.
Figure 10. A photograph of Belfort rain gauge.

Figure 11 shows the NOAA IV All-weather precipitation gauge used at the monitoring site. It consists of the ETI’s infrared onset precipitation detector, collection chamber and windscreen. This gauge provides an accurate measurement of snow and rain precipitation. The measurement is carried out using the onset precipitation detector’s infrared sensors that detect the rain or snow during the precipitation event and the advanced “weigh-it-all” measures the precipitation adhered to the walls of the collection chamber. The windscreen increases the efficiency of detection of the gauge during windy conditions.
4.2.2.1. Sampling Analysis

After collection, the samples are sent via courier services to Frontier Geosciences Inc, Seattle, Washington laboratory for analysis which is carried out in a class 100 clean room. The concentration of Hg in the precipitation sample is determined by employing a pure gold cartridge coupled with cold vapor atomic fluorescence spectroscopy (CVAFS) technique. Prior to purging the Mercury sample onto the gold cartridge trapped by nitrogen gas free of mercury, BrCl solution is added to the sample to oxidize the mercury compounds to divalent mercury. The bottle is then stored in a dark room for several hours before being analyzed (Lin and Pehkonen 1999). NH2OH.HCl solution is added to eradicate the sample of free halogens and then the sample is treated with SnCl2 to reduce all the Mercury to elemental mercury. Total Hg was quantified by employing its
amalgamation property and CVAFS technique. The analysis of the precipitation samples to determine the Mercury concentration is well described in Keeler et al., 2005 and Vermette et al., 1995.

4.3. Source Apportionment Methods

Source Apportionment is defined as the process of allocating the pollutant measured at the receptor site (here Athens SAM station) to a potential source. Source apportionment techniques are usually carried out by using the trajectory statistics methods. These methods are designed to find the source of emissions of different pollutants and to trace their transport in the atmosphere (Ashbaugh et al. 1985, Stohl 1996). There are many ways of finding out the sources of pollutant emissions. A few of them used in this study are discussed in the following paragraphs.

4.3.1. Potential Source Contribution Function

Potential Source Contribution Function is a statistical tool developed by Ashbaugh et al. (1985) and is the conditional probability that an air parcel with a certain level of pollutant concentration above a criteria value arrives at the receptor site after travelling across a geographical area. This method is used to trace back mercury wet deposition geographical source origins based on the concentration measurements recorded at the SAM site. This method of analysis is widely used in many studies to find the potential source regions of the pollutants. Few of the studies that used this method are Lucey et al. 2001, Gao et al. 1996, Cheng et al. 1996. This method requires both the
meteorological data, which can be obtained at the National Oceanic and Atmospheric Administration (NOAA) website, and the pollutant species concentration data to trace back the origin of the pollutant. The result of this model is a back trajectory of the pollutant for a desired period of time.

This method is used to find the potential source regions of the particles that are measured at the monitoring site. However, this method cannot tell us the “emission inventory” of the particular pollutant (Lucey et al. 2001.) To find the source regions of these pollutants, they can be considered as air Parcels. The result of this model is a back trajectory and these air parcels travel along the trajectory backwards in time (Lucey et al. 2001). The geographic region around the monitoring site is divided into grid cells and each grid cell is assigned an address \((i, j)\). Let \(N\) be the total number of trajectory endpoints that occurred during the period being studied and \(n_{ij}\) be the total number of trajectory endpoints falling in a particular grid cell \((i, j)\). Let the probability of the occurrence of this event be denoted by \(P(A_{ij})\) and defined as: \(P(A_{ij}) = \frac{n_{ij}}{N}\). Let \(m_{ij}\) be the number of end points among the \(n_{ij}\), that have a concentration value higher than the expected “criterion” value measured at the receptor site. Let the probability of occurrence of this event be denoted by \(P(B_{ij})\) and defined as: \(P(B_{ij}) = \frac{m_{ij}}{N}\). (Lucey et al. 2001.)

The PSCF value is defined in terms of conditional probability as:

\[
PSCF_{ij} = \frac{P(B_{ij})}{P(A_{ij})} = \frac{(m_{ij}/N)/(n_{ij}/N)} = \frac{m_{ij}}{n_{ij}} \tag{13}
\]
Therefore, \[ \text{PSCF}_{ij} = \frac{m_{ij}}{n_{ij}}. \] (14)

Where, \( m_{ij} \) is the number of the trajectories having higher concentration of mercury recorded at the monitoring site than the criterion value.

\( n_{ij} \) is the total number of trajectories passing through the cell(i,j).

Cells that have a higher \( \text{PSCF}_{ij} \) Value, i.e., if their values are closer to unity, then the probability of those grid cells having the source is higher or it suggests that the cell is located in the pathway of a regularly occurring trajectory (Deshpande 2007).

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) 4 model, developed by Air Resource Laboratory of NOAA, is used to run back trajectories at different heights for any desired time period for carrying out the PSCF analysis. To identify high emission sources, an arbitrary criteria value is chosen and this can be the median (Poissant 1999) or the mean (Begum et al, 2005), or any other value of the data (Gao, 2007). For the purpose of this study, the 25\(^{th}\) percentile is chosen as the criterion value. Since even a small exposure of mercury is considered to be harmful to humans, we chose this value of 2.5 ng/m\(^2\). The trajectory endpoints are calculated using the global Data Assimilation System (GDAS) meteorological data.

4.3.2. Residence Time Weighted Concentration

Seibert developed Concentration Weighted Trajectory method (Seibert et al. 1994) to overcome the drawbacks of the PSCF method of determining the “statistical
significance of its outcome” (Stohl 1996). This method was designed to find the potential source location of pollutants. The approach of this method imposes weighted concentrations onto each grid cell bearing the address \((i,j)\) and the mean concentration of the cells are calculated as:

\[
C_{ij} = \frac{1}{\sum_{l=1}^{m} T_{ijkl}} \sum_{l=1}^{m} C_l T_{ijkl}
\]  

(15)

Where, \(C_{ij}\) is the average weighted concentration in the grid cell \((i,j)\).

\(C_i\) is the measured concentration on the arrival of the trajectory.

\(T_{ijkl}\) is time spent by the trajectory \(l\) in the grid cell \((i,j)\)

\(m\) is the total number of trajectory end points in the grid cell \((i,j)\).

\(l\) is the index of the trajectory.

It is obvious that the “sources of air pollutants are often concentrated in ‘hot spots’” (Stohl 1996) and the main drawback of this method is that it could not relate the measured concentration data to the corresponding section of the trajectory. Instead, this method attributed the data equally to all the section of the trajectory.

Stohl improvised seibert’s CWT method to Residence Time Weight Concentration (Hsu et al. 2003). This method uses the \(C_{ij}\) value calculated from the CWT method as the first guess value to do the redistribution of the concentration along
the back trajectory. The first guess $C_{ij}$ value is calculated using the equation similar to that developed by Seibert.

$$\tilde{C}_{ij} = \frac{1}{\sum_{l=1}^{m} T_{ijl}} \sum_{l=1}^{m} \log (C_l) T_{ijl}$$  \hspace{1cm} (16)

Since the concentration field follows the log normal distribution, the above equation has a logarithmic term. Also, the concentrations are smoothed “within 95% confidence interval of the mean concentration” in each and every grid cell by using a 9-point operator (Hsu et al. 2003).

The equation for redistribution of concentration is:

$$C_{kl} = C_l \frac{x_{klN_l}}{\sum_{j=1}^{N_l} x_{jl}} = C_l \frac{x_{kl}}{\bar{x}_l}, \ j = 1, N_l$$  \hspace{1cm} (17)

Where, $X_{kl}$, are the mean concentrations of the grid cells.

$K=1, N_l$ are the segments of the trajectory, $l$.

$l$ is the index of the trajectory.

$$\bar{x}_l = \frac{(\sum_{j=1}^{N_l} X_{jl})}{N_l}$$ is the average of the mean concentrations of the grid cells.

After the redistribution is done to all the individual trajectories, a new concentration field is computed using the equation given below:
\[
\overline{C}_{ij} = \frac{1}{\sum_{l=1}^{m} \sum_{k=1}^{N_l} T_{ijkl}} \sum_{l=1}^{m} \sum_{k=1}^{N_l} \log(C_{kl}) T_{ijkl}.
\]  

(18)

Where, \(T_{ijkl}\) is the residence time of segment \(k\) of trajectory \(l\) in grid cell \((i,j)\).

A new concentration field is obtained with the above equation. This new concentration field is used to do the second redistribution. The process is continued or repeated until the average difference between the two successive iterations becomes less than 0.5%. The description of this method is described in Stohl (1996).
CHAPTER 5: RESULTS AND DISCUSSION

5.1 Baseline

The Mercury Wet Deposition data used for this study was collected at the Athens rural supersite, established in the winter of 2004, and analyzed at the Frontier Geosciences in Seattle. The Athens site has been continuously operational since spring 2004 to collect weekly precipitation samples to analyze mercury. This study analyzes weekly samples data from 05/12/2004 to 09/30/2008. For the purposes of the study, weekly samples with a quality grading of ‘C’ were discarded except for the weekly sample collected from 09/05/2007 to 09/11/2007. Typically, the Athens supersite experiences plume hits during the months of April and September. Therefore, the records of mercury deposition at the site during these months are high when compared to other months. Taking into consideration that this was the only week with precipitation during September 2007, eliminating this sample would result in no mercury wet deposition during the month of September. This is rather unusual, when compared to the characteristics of the Athens site.

The individual mercury concentrations recorded at the site were within the range of 0.9 ng/L to 64.1 ng/L with an average value of 12.86 ng/L for the N=221 weekly samples. The average amount of precipitation observed in Athens was 0.88 inches with a maximum depth of 9.18 inches. Mercury wet deposition was calculated by taking the product of mercury concentration and the precipitation depth. The unit of concentration is ng/l and that of precipitation is inches. Hence, the unit of wet deposition is ng/m². The
individual mercury deposition samples collected at Athens supersite ranged anywhere between 4.3 ng/m² to 1752.8 ng/m² with an average deposition of 233.09 ng/m².

The mercury concentrations and mercury wet deposition at the Athens supersite for the years 2004-2008 are shown in figures 12 and 13 respectively.

Figure 12. Weekly sample events of mercury concentration collected at Athens supersite from May 2004 to September 2008.
The highest values for rainfall and deposition were recorded at the Athens site during the month of September. The weekly sample collected on 09/10/2004 recorded the highest amount of precipitation, 9.18 inches, with mercury wet deposition of 629.6 ng/m$^2$. The following sample collected on 09/21/2004 recorded the highest mercury deposition amount of 1752.8 ng/m$^2$, with precipitation of 8.52 inches. The remnants of the hurricanes Frances and Ivan caused these unconventional precipitation events associated with the low pressure system over the site (Yatavelli et al, 2006).

Table 2 depicts the year to year number of events collected, total precipitation, the total and average mercury deposition and concentration recorded at the Athens supersite, Athens, Ohio.
Table 2.

Mercury Concentration and Wet Deposition from Weekly Samples Collected at Athens, Ohio from May 2004 to September 2008

<table>
<thead>
<tr>
<th>Year</th>
<th>Number of Weekly Sample</th>
<th>Total Precipitation (inches)</th>
<th>Total Hg Wet Deposition (ng/m²)</th>
<th>Average Hg Wet Deposition (ng/m²)</th>
<th>Average Hg Concentration (ng/L)</th>
<th>Maximum Hg Concentration (ng/L)</th>
<th>Maximum Hg Wet Deposition (ng/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>32</td>
<td>44.84</td>
<td>8287</td>
<td>295.96</td>
<td>15.06</td>
<td>62.1</td>
<td>1752.8</td>
</tr>
<tr>
<td>2005</td>
<td>52</td>
<td>32.94</td>
<td>9104.6</td>
<td>206.92</td>
<td>14.37</td>
<td>64.1</td>
<td>1059.2</td>
</tr>
<tr>
<td>2006</td>
<td>49</td>
<td>43.50</td>
<td>10440</td>
<td>232.00</td>
<td>10.60</td>
<td>23.6</td>
<td>804.5</td>
</tr>
<tr>
<td>2007</td>
<td>50</td>
<td>35.27</td>
<td>9037.5</td>
<td>200.83</td>
<td>11.92</td>
<td>39.17</td>
<td>769.1</td>
</tr>
<tr>
<td>2008</td>
<td>38</td>
<td>31.83</td>
<td>8272.30</td>
<td>229.786</td>
<td>12.36</td>
<td>33.70</td>
<td>1060.3</td>
</tr>
<tr>
<td>Sum</td>
<td>221</td>
<td>188.38</td>
<td>45141.40</td>
<td>1165.50</td>
<td>64.31</td>
<td>222.67</td>
<td>5445.9</td>
</tr>
<tr>
<td>Mean</td>
<td>44.2</td>
<td>37.676</td>
<td>9028.28</td>
<td>233.099</td>
<td>12.862</td>
<td>44.534</td>
<td>1089.18</td>
</tr>
</tbody>
</table>

5.2 Comparison of Athens Site with the Other MDN Sites

The magnitudes of wet deposition of mercury vary significantly throughout the United States of America. Global modeling studies indicate that this heterogeneous nature of mercury wet deposition in the United States can be attributed to various spatial and temporal factors. This section of the study intends to evaluate mercury wet deposition at the Athens SAM site and to characterize and compare this data with that of the other MDN sites in the country. For the purpose of this study, we downloaded data from the National Mercury Deposition Network (NADP) website and abstracted a total of 112 sites that included appropriate data for the years 2004-2007.
Situated in the mid-Atlantic region (36 – 40 °N), Athens (36°18‘ N, 82°7‘ W) experiences a relatively moderate level of wet deposition of mercury. According to the Mercury Deposition Network (MDN), the amount of total mercury deposition in Athens for the years 2005, 2006 and 2007 were 9.8 µg/m², 10.2 µg/m² and 8.7 µg/m² respectively. These are relatively higher values than that of other MDN sites in the country. It was observed that the mercury wet deposition at the Athens SAM site ranked 25th among the 70 MDN sites, which has ample data that were equivalent to the data gathered at the Athens site. This is demonstrated in the Table that can be found in the Appendix A. In order to carry out a spatial-temporal analysis of mercury wet deposition, the data was plotted and devised into maps using the Arc GIS software. These maps provided lucid results that indicated clear spatial and temporal trends.

An obvious trend that can be inferred from these maps was the higher precipitation in Eastern United States than the Western regions. This trend was in accordance with the typical weather pattern in Northeast United States. The figures for precipitation and deposition also demonstrated that precipitation and wet deposition were highly related. The data demonstrated higher precipitation in the East than in the West and also higher values of wet deposition in the East. Precipitation and mercury wet deposition can thus, be rendered to be complementary in nature in that they both are dependent on each other. Higher wet deposition is observed in regions with higher precipitation. Thus, precipitation can be rendered to be a crucial determinant of mercury wet deposition.
Figure 14. Average precipitation in the United States observed during the years, 2004-2007.

Another deduction made from the maps was that the amount of mercury wet deposition was observed to be more in Southeast United States than the Northeast region. It can be inferred that at lower latitudes wet deposition of mercury is higher by significant amounts which proposes an inverse correlation between latitude and mercury wet deposition. This can be attributed to a number of factors including precipitation, scavenging efficiency, and extreme weather events such as hurricanes. As stated above, precipitation is an important determinant of mercury deposition. Considering its susceptibility to be hit by hurricanes, the area encompassed in Southeast United States has more precipitation which in turn leads to more wet deposition of mercury.
Figure 15. Average mercury deposition in the United States observed during the years, 2004-2007.

It was also relevant from the data that there were strong seasonal variations of wet deposition, with a maximum in summer and minimum in winter. These seasonal variations are clearly depicted in the ARC GIS monthly mappings that are included in the Appendix B. These variations can be accounted for by more precipitation in the summer and precipitation scavenging efficiency (rain vs. snow). Another justification for the variations is the enhanced Hg (0) oxidation to Hg (II) during summer (Mason et al. 2000). The summer maximum of mercury wet deposition in Southeast is due to the deep convective scavenging of Hg (II) from high altitudes (Guentzel et al. 2001) and that of the Northeast can be accounted for by the Hg (0) photochemical oxidation. It has also been suggested that warmer temperatures could allow for atmospheric reactions that
fabricate RGM from elemental mercury and could therefore, potentially increase the probability of wet deposition (Mason et al. 2000). In Eastern United States, precipitation is concentrated in the warmer months, April-September, which indicates higher quantities of mercury wet deposition. Similar results were observed by Selin and Daniel, 2008 which were that the summer maxima was 119 ngm$^{-2}$ d$^{-1}$ at 28$^0$–32$^0$N, 40 ngm$^{-2}$ d$^{-1}$ at 36$^0$–40$^0$N, and 25 ngm$^{-2}$ d$^{-1}$ at 44$^0$–48$^0$N. The study also observed the decline in the winter minima of mercury wet deposition; 18 ngm$^{-2}$ d$^{-1}$ at 28$^0$–32$^0$N, 16 ngm$^{-2}$ d$^{-1}$ at 36$^0$–40$^0$N, and 5 ngm$^{-2}$ d$^{-1}$ at 44$^0$–48$^0$N.

Another meaningful observation from the data plotted, shown in Figure 16, was the independent nature of concentration with regards to precipitation and wet deposition. In the maps plotted, it was clearly revealed that concentration was autonomous and was not related to precipitation or mercury wet deposition. The largest magnitudes of wet deposition of mercury were observed to be in Eastern United States, in contrast with concentration which was more in the Southwest regions. In terms of mercury wet deposition, the states with relatively high averages for the year 2004-2007 were Florida, Arkansas, Tennessee, Indiana, Ohio, Texas, Louisiana, Alabama, Kentucky, Missouri, Nebraska and South Dakota whereas states with the highest average concentrations were Arizona, New Mexico, Nevada and some parts of California. This discrepancy emphasizes the dissociation between concentration and mercury wet deposition.
5.3 Temporal Analysis

A clear seasonal trend was observed in the wet deposition of mercury at the Athens supersite. From figure 24, it can be derived that the warmer months experience more mercury wet deposition than winter months. High deposition of mercury during warmer months could be a potential outcome of atmospheric chemistry of mercury, its source emissions and meteorology, precipitation, wind direction and speed, etc. (Keeler et. al)

RGM dissolves efficiently in rainwater, resulting in wet deposition. During warmer months, the concentration of RGM species is higher because of oxidation of elemental mercury to RGM aided by oxidizing agents such as O₃, H₂O₂, Cl₂, etc., that are
present in the atmosphere (Lin & Pehkonen, 1999). Scavenging of RGM species during summer precipitation is much more effective than the winter precipitation. This is because of the high concentration of oxidizing agents such O$_3$, OH radicals in the atmosphere during the warmer months. (Lin & Pehkonen., 1999, Schroeder & Munthe., 1998, Keeler et al., 2005).

In a study describing long term atmospheric mercury wet deposition from 1993 to 2003, Keeler et al (2005), observed that temperature is a substantial factor influencing mercury deposition at the receptor site. Previous studies have documented seasonal trends of mercury concentrations and wet deposition, with maximum and minimum levels during summer and winter respectively (Keeler et al., 2005, Burke et al., 1995, Selin & Daniel, 2008). Several studies have attributed various reasons for such a trend; scavenging of RGM by rain water to be more efficient than snow (Selin & Daniel, 2008, Glass and Sorensen, 1999), more precipitation in summer (Glass and Sorensen, 1999) and improved oxidation of elemental mercury to RGM by various oxidants during summer (Selin & Daniel, 2008, Mason et al., 2000). This study also yielded similar results. However, the Athens site records frequent plume hits from the regional industrial point sources that result in elevated levels of mercury wet deposition at the receptor site during the months of April and September. Selin and Daniel (2008) have identified the maximum occurrence of mercury wet deposition to be in the industrial Midwest and Northeast regions owing to the contributions of domestic sources.

The elevated levels of mercury wet deposition experienced at the Athens site ($39^\circ18' \text{N} 87^\circ17' \text{W}$) during warmer months compared to the colder months can be
accounted for by both qualitative and quantitative approaches. The qualitative investigation can be explained on the basis of the meteorological conditions over the Ohio River valley (ORV). The ORV has an oxidizing environment (Kimm et al. 2009) which enhances the capability of oxidation of elemental mercury to RGM. At northern latitudes (36-48°N), the oxidation is improved by a factor of 3-5 during the summer compared to the winter (Selin & Daniel, 2008). In addition to scavenging of RGM from local and regional sources, the Hg wet deposition is increased by the oxidation of elemental mercury from the global pool to RGM. Selin & Daniel (2008) stated that, 60 percent of mercury wet deposition in the United States is the result of scavenging of RGM produced from the oxidation of elemental mercury from the global pool in the troposphere. High deposition of mercury during warmer months can also be attributed to the inefficient scavenging of RGM by snow when compared to rain.

The quantitative approach can be explained by the amount of rainfall recorded during the warmer months. The Athens site experiences high amount of rainfall during the months of April and September resulting in high mercury wet deposition. Also, the site records frequent plume hits during these months suggesting the availability of large amount of RGM in the environment to be scavenged by precipitation resulting in mercury wet deposition. Seasonal trends have also been reported in various previous studies in the United States (Hoyer et al., 1995, Burke et al., 1995, Keeler et al., 2005).

To gain a better understanding of the seasonal trend, a graph was plotted depicting concentration and deposition across the different seasons. The seasons were divided according to the following months, winter – December, January and February,
spring - March, April and May, summer - June, July and August, fall - September, October and November. The frequency distribution of mercury concentration is shown in Figure 17. The weekly samples were divided over a range of their concentrations and then distributed across the seasons. The highest number of samples were found to be in the range of 5-10 ng/L followed by 10-15 ng/L and 0-5 ng/L. Summer months had the highest percentage of weekly samples that fell in >40, 30-35, 25-30 ng/L range. It is clearly evident that the mercury concentration was more in the warmer month’s (spring and summer) than the winter. Most of the winter weekly samples fell in the lower range values. The higher concentration during warmer months when compared to that of colder months can be a result of increased convection of air parcels during warmer months. The transport of mercury via air parcels over long distances and high concentrations of oxidants such as O₃, OH radicals during warmer months causes the deposition of aged RGM onto the earth’s surface.
Figure 17. Frequency distribution of seasonal Hg concentration in weekly precipitation samples at Athens supersite from May 2004 – Sept 2008.

The frequency distributions of mercury deposition of the weekly samples collected from May 2004 to September 2008 are shown in Figure 18. It is evident that the samples collected during the winter months were more frequent in the lower ranges. Summer and spring months had high percentages of weekly samples falling in the higher ranges. Fall months had moderate percentage of the samples falling in all the ranges. The highest number of weekly samples were observed to be in 0-50 ng/m² range i.e. approximately 27 percent (N=59) of all the weekly samples. Winter season weekly samples were the highest in this range (i.e. 0-50 ng/m²) accounting for about 34% of the samples followed by the fall season (30%). The spring season had the least amount of percentage of samples falling in this range (13%). About 15% (N= 33) of the total weekly samples fell in >400 ng/m² range. Among these, the summer season had the
highest percentage (45%), followed by spring (30%) and followed by fall (22%). The winter season had just one weekly sample that fell in this range. This indicates that all the high amount of mercury wet deposition is associated with the rain form. Therefore, understanding the microphysical properties of clouds can give us a better understanding in the seasonal trends of mercury deposition.

Figure 18. Frequency distribution of seasonal Hg deposition in weekly precipitation samples at Athens supersite from May 2004 – Sept 2008.

5.4 Meteorological Effect

In order to investigate the impact of the variation of temperature across different months on mercury wet deposition, the monthly averages of mercury wet deposition and temperature were calculated. Figure 19 demonstrates the comparison of these monthly
averages of temperature (line) and mercury wet deposition (bars) for the time period of 2004 through 2008. Keeler et al, 2005 had observed a significant \( (r^2=0.67) \) effect of temperature on mercury wet deposition at the Vermont site while Athens site experienced less significant \( (R= 0.25) \) correlation with temperature. Elevated levels of mercury wet deposition were observed during the months of April and September. This can be explained by the number of plume events recorded during these months and clockwise advection of air parcel associated with precipitation events.

Figure 19. Average monthly temperature and Hg wet deposition observed at the Athens site.

RGM concentrations recorded above 35 pg/m\(^3\) were classified as plume hits. The number of plume hits recorded during these months was much higher compared to the other months (Figure 20). Higher concentrations of RGM are observed during the plume
events suggesting a contribution from local anthropogenic sources. Several coal fired power plants are located at a moderate distance from the Ohio River Valley spanning from the southeast through southwest to Athens and are believed to be responsible for plume episodes at the Athens site. During the warmer months, the southeasterly, southerly, and southwesterly winds are associated with high concentrations of RGM that are attributed to local industrial sources. This is due to the typical synoptic weather pattern observed over the Northeast United States (Figure 21) by the sequence of continental and maritime tropical air parcels moving out from Canada into upper Midwest (Wolff et al., 1982). Figure 21 shows that the mean paths of 5-day back trajectory air parcel movement that are associated with precipitation follow a synoptic weather pattern.

![Figure 20](image)

*Figure 20. Total number of plume hits every month observed at Athens site.*
Figure 21. Synoptic weather pattern of air parcel movement.
A surface high pressure region was observed over the eastern United States, with clockwise circulation of winds around the high. Also, a surface low pressure region can be associated with upper Midwest, with counterclockwise wind circulation around the high. This results in the advection of air parcels from the south to north to the east of low pressure regions towards high pressure regions (Sandstorm and Changnon, 2007). Low pressure regions have rising air patterns that cause cloudy and rainy weather. These regions are located at the South of Athens and precipitation is caused by southerly winds that flow into Athens as a result of synoptic weather patterns. Precipitation has a high significant correlation (R=0.70, p<0.0001) with mercury wet deposition at the Athens site. This relation is clearly depicted in Figure 22 which shows a clear frequency trend between mercury wet deposition and precipitation. From tables 3 and 4 we can infer that there is a higher correlation between meteorology factors and mercury wet deposition than that between ambient gaseous mercury and co-pollutants. This suggests a dominant influence of meteorology on mercury wet deposition at the Athens site.
Figure 22. Monthly distribution of the MDN, precipitation and ambient mercury data for the time period from August 2004- June 2006.
Figure 23 and 24 demonstrates the average and total monthly mercury wet deposition measured at the Athens supersite from May 2004 to Sept 2008. The figure illustrates a clear trend between the warmer and colder months, with warmer months experiencing higher levels of deposition compared to the colder ones. This can be attributed to the combined result of turbulent mixing and convective transport of mercury species to the receptor site during the warmer months. Also, the concentrations of O$_3$, OH radicals that oxidize elemental mercury to RGM are high during the warmer months resulting in high concentrations of RGM. Scavenging of RGM is high during warmer months because of the solubility characteristics of RGM species in rain water and snow (Hoyer et al, 1995, Keeler et al, 1997, Keeler et al, 2005).

![Graph of average monthly mercury wet deposition](image)

*Figure 23. Average monthly mercury wet deposition observed at Athens, Ohio.*
5.5 Wet & Dry Deposition

A comparison was carried out between wet and ambient gas data to investigate the correlation between the two. Taking into account the fact that plume events lead to higher levels of RGM at the Athens site when compared to non-plume events, the data generated does not follow a normal distribution. Hence, Spearman’s coefficient correlation is used to determine the statistical significance, probability and level of correlation between this non-parametric data.

Tables 3 and 4 portray the correlation coefficient of mercury wet deposition with the meteorology parameters as well as gaseous mercury species and co-pollutants. Table
suggests that the correlation between ambient gaseous mercury, SO₂ and NOₓ are statistically significant with mercury wet deposition (P<0.05). Among the various ambient gaseous mercury species, SO₂, NOₓ and O₃, RGM was the most substantial determinant in the mercury wet deposition during warmer months, April through September (R= -0.2). During the warmer months, Ozone was significant (P=0.024) with the mercury wet deposition, insinuating its influence by the oxidation of Hg⁰ to RGM. High concentration of RGM associated with the plume episodes and low R values suggests the contribution of RGM from local, regional and global sources at the Athens site.

Table 3.

*Non Parametric Significance Test Correlation Coefficients for MDN vs. Gas Data*

<table>
<thead>
<tr>
<th></th>
<th>Hg(0)</th>
<th>Hg(p)</th>
<th>RGM</th>
<th>SO₂</th>
<th>NOX</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>-0.15926</td>
<td>-0.19137</td>
<td>-0.18328</td>
<td>-0.17782</td>
<td>-0.19681</td>
<td>-0.04665</td>
</tr>
<tr>
<td>P</td>
<td>0.02034</td>
<td>0.00586</td>
<td>0.00775</td>
<td>0.00724</td>
<td>0.00296</td>
<td>0.53172</td>
</tr>
<tr>
<td>Intercept</td>
<td>1.164968</td>
<td>5.99419</td>
<td>10.53961</td>
<td>10.53961</td>
<td>6.47724</td>
<td>32.3006</td>
</tr>
<tr>
<td>Slope</td>
<td>-0.5826</td>
<td>-0.56725</td>
<td>-1.12128</td>
<td>-1.12128</td>
<td>-0.42971</td>
<td>-0.31846</td>
</tr>
<tr>
<td>#</td>
<td>212</td>
<td>206</td>
<td>210</td>
<td>227</td>
<td>226</td>
<td>182</td>
</tr>
</tbody>
</table>
Table 4.

Non Parametric Significance Test Correlation Coefficients for MDN vs. Meteorology Data

<table>
<thead>
<tr>
<th></th>
<th>Precipitation</th>
<th>Temperature</th>
<th>Wind Speed</th>
<th>Wind Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>0.70231</td>
<td>0.24723</td>
<td>0.08167</td>
<td>-0.10875</td>
</tr>
<tr>
<td>P</td>
<td>&lt;0.0001</td>
<td>0.00016</td>
<td>0.22027</td>
<td>0.10221</td>
</tr>
<tr>
<td>Intercept</td>
<td>1.90E-04</td>
<td>11.28646</td>
<td>5.52248</td>
<td>184.9442</td>
</tr>
<tr>
<td>Slope</td>
<td>0.00498</td>
<td>1.49531</td>
<td>0.075</td>
<td>-3.01543</td>
</tr>
<tr>
<td>#</td>
<td>227</td>
<td>227</td>
<td>227</td>
<td>227</td>
</tr>
</tbody>
</table>

Figure 22 portrays the monthly averages of mercury wet deposition and ambient mercury data between August 2004 and June 2006. The frequency trend between the divalent mercury and the mercury in wet deposition are similar to each other. There is a moderate correlation between the mercury in wet deposition and the RGM concentrations. Figure 22 also reveals that RGM concentrations and mercury wet deposition are high during April and September months. Thus, the high concentrations of mercury wet deposition and RGM in air during April and September can be justified by several plume hits recorded at the Athens SAM station in these months.

Figure 22 pointed out that there is no relationship trend between the mercury in wet deposition and elemental mercury. The average elemental mercury value observed at the Athens SAM station was among the global elemental mercury range of 1.4ng/ m$^3$ to 1.6ng/ m$^3$. In Figure 22 it is illustrated that there exists a weak correlation between the mercury concentrations in precipitation and particulate mercury concentration. Also, the particulate mercury concentrations are higher during the winter months i.e. December
through March. The higher concentrations of particulate mercury during winter may be due to the vertical temperature inversion. This generally occurs during a winter morning (7AM – 12 PM), when the surface air is colder than the air at the tropospheric level. At this point of time there is no turbulent mixing. This results in higher particulate concentrations. However, during summer the particulate concentrations are lower because of turbulent mixing between the troposphere level air and surface level air.

5.6 Multiple Linear Regression

Spearman’s Correlation Coefficient indicated a significant correlation between mercury wet deposition and gaseous pollutant species such as ambient mercury species, \( \text{SO}_2 \), \( \text{NO}_x \) and \( \text{O}_3 \). These ambient mercury species, \( \text{SO}_2 \) and \( \text{NO}_x \), are primarily emitted from industrial facilities such as coal-fired power plants. In addition, some meteorological parameters such as precipitation and temperature were also found to be significant. Therefore, in order to determine the percentage contribution of meteorological impacts vs. emission impacts Multiple Linear Regression was conducted. Mercury wet deposition was the dependent variable. As a result of the multiple linear regression analysis, precipitation was found to be significant (\( p<0.01, \beta=0.819 \)) and showed a very high correlation with mercury wet deposition. Considering its substantial influence on wet deposition of mercury, the other factors had minimal impact and no significant correlation was observed. Thus, we could not quantify the contributions of meteorological and emission impacts on mercury wet deposition. These results can be found in Appendix C.
5.7 Source Apportionment

The mercury wet deposition data from May 2004 to September 2008, collected at the Athens supersite, was used to determine the potential source regions. It was clearly evident from the results stated above that mercury wet deposition was strongly associated with precipitation. Therefore, mercury wet deposition was distributed in accordance with precipitation periods, i.e. on an hourly basis.

PSCF and RTWC were employed to identify the potential source regions affecting the mercury wet deposition in Athens. Air parcel back trajectories for different starting heights from the Athens monitoring station were generated using the HYSPLIT4 model. The National Center for Environmental Prediction (NCEP) / National Center for Atmospheric Research (NCAR) Reanalysis data were used as meteorological input for HYSPLIT 4. When the reanalysis data was not available, the NCEP’s EDAS (Eta Data Assimilation System) 40Km data was used instead.

Since precipitation formation occurs at higher altitudes and is a factor influencing mercury wet deposition, the starting heights of different back trajectories were set at 500m, 1000m, 1500m, 2000m, 3000m and 4000m. The geographic area surrounding Athens site was divided into $0.5^\circ \times 0.5^\circ$ latitude and longitude grid cells. The PSCF and RTWC values of mercury wet deposition were calculated based on a 5-day backward trajectory.

5.7.1 Potential Source Contribution Function

Since the mercury wet deposition data does not follow a normal distribution, as seen in figure 25, 2.5 ng/m$^2$ (25$^{th}$ percentile) was set as an arbitrary criterion value to
carry out the PSCF analysis. This provided a benchmark against which higher and lower trajectory values could be compared.

Figure 25. Frequency distribution of mercury wet deposition.

In order to reduce the uncertainty associated with the grid cells having less number of endpoints, an arbitrary down weight function $W_{ij}$ was applied. Table 5 demonstrates the total number of endpoints, grid cells, average number of endpoints, and across different starting heights employed in this study.
Table 5.

*Arbitrary Down Weight Functions for PSCF Analysis*

<table>
<thead>
<tr>
<th>Starting Height (m)</th>
<th>Total number of end points</th>
<th>Total number of cells</th>
<th>Average number of endpoints</th>
<th>1</th>
<th>0.7</th>
<th>0.5</th>
<th>0.3</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>304556</td>
<td>4226</td>
<td>72</td>
<td>360&lt;n_ij≤360</td>
<td>72&lt;n_ij≤145</td>
<td>36&lt;n_ij≤72</td>
<td>n_ij≤36</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>294471</td>
<td>4348</td>
<td>68</td>
<td>271&lt;n_ij≤360</td>
<td>136&lt;n_ij≤271</td>
<td>68&lt;n_ij≤136</td>
<td>33&lt;n_ij≤68</td>
<td>n_ij≤33</td>
</tr>
<tr>
<td>1500</td>
<td>281137</td>
<td>4363</td>
<td>65</td>
<td>194&lt;n_ij≤360</td>
<td>129&lt;n_ij≤194</td>
<td>65&lt;n_ij≤129</td>
<td>33&lt;n_ij≤65</td>
<td>n_ij≤33</td>
</tr>
<tr>
<td>2000</td>
<td>262441</td>
<td>4317</td>
<td>61</td>
<td>183&lt;n_ij≤360</td>
<td>122&lt;n_ij≤183</td>
<td>61&lt;n_ij≤122</td>
<td>31&lt;n_ij≤61</td>
<td>n_ij≤31</td>
</tr>
<tr>
<td>3000</td>
<td>225846</td>
<td>4257</td>
<td>54</td>
<td>107&lt;n_ij≤360</td>
<td>54&lt;n_ij≤107</td>
<td>27&lt;n_ij≤54</td>
<td>14&lt;n_ij≤27</td>
<td>n_ij≤14</td>
</tr>
<tr>
<td>4000</td>
<td>194890</td>
<td>4016</td>
<td>49</td>
<td>98&lt;n_ij≤360</td>
<td>49&lt;n_ij≤98</td>
<td>25&lt;n_ij≤49</td>
<td>13&lt;n_ij≤25</td>
<td>n_ij≤13</td>
</tr>
</tbody>
</table>

Figures 26 through 31 portray the PSCF results at an altitude of 500m, 1000m, 1500m, 2000m, 3000m and 4000m for a 5-day back trajectory. These maps indicate that the potential source directions and locations are situated southwest of Athens. The probable potential source regions also overlapped with the RGM point sources which were obtained from the 2002 National Emission Inventory and are located southwest of Athens. The RGM point sources from other directions are not major contributors of mercury wet deposition analyzed at the Athens supersite. It was also observed that the source inventories located at east end of Athens did not have a substantial effect on the magnitude of mercury wet deposition at the site. These results can also be found in studies carried out by Keeler et al., (2005) and Lai et al., (2007). This trend can be explained by the clockwise flow of air parcels that prevail over northeast United States, as represented in Figure 21. This also implies that the parcels that bring precipitation are likely to have originated from the southwest and are affected by synoptic weather...
patterns. The PSCF results suggested that the largest potential source areas included Gulf of Mexico, Eastern Texas, Arkansas, Louisiana, Southern Missouri, Tennessee, Kentucky, Southern Illinois, Southern Indianapolis, Northern Alabama, North East Oklahoma, Northern Mississippi, and South East Kansas. These areas had a PSCF value ranging from 0.71 to 1.

Figure 26. PSCF based on a 5-day back trajectory with a starting height of 500m.
Figure 27. PSCF based on a 5-day back trajectory with a starting height of 1000m.

Figure 28. PSCF based on a 5-day back trajectory with a starting height of 1500m.
Figure 29. PSCF based on a 5-day back trajectory with a starting height of 2000m.

Figure 30. PSCF based on a 5-day back trajectory with a starting height of 3000m.
Selin and Daniel (2008) stated that the North American anthropogenic source emissions of mercury wet deposition extend over a broad area ranging from East Texas through Midwest to Pennsylvania. The results of Selin and Daniel (2008) confirmed with the findings of this study. Coal fired power plants are the largest emission sources in these areas except for the Gulf of Mexico. Gulf of Mexico is identified as a potential source even though there were no emission sources around the area. The Atlantic Ocean near the eastern United States coast was also observed to be a potential source with a PSCF value ranging from 0.2 to 0.5. The re-emission of mercury from the oceanic water bodies and its oxidation to RGM by various marine derived halogen radicals and compounds causes it to be identified as a potential source (Lai et al. 2007, Sheu and
Mason, 2001). The re-emitted mercury is oxidized, transported to receptor site via the air parcels and finally scavenged through precipitation.

With an increasing altitude, the potential source regions were observed to be more widespread. Lower altitudes of 500m and 1000m mainly indicated local and regional contributions to mercury wet deposition at Athens. At these altitudes, lower parts of the Ohio River Valley had significant contributions to mercury deposition and this can be justified by the presence of industrial facilities in these regions. Selin et al. 2007 proposed the industrial Midwest to be a region of high mercury wet deposition indicating the local emissions of RGM and particulate mercury. As shown in Figure 32, adapted from Selin et al. 2007, the territory Southwest of Athens has high magnitudes of mercury emissions primarily from anthropogenic sources and the PSCF results of this study indicate air parcel movements towards Athens travelled over these high concentration regions.

Figure 32. “Percentage contributions from North American primary anthropogenic sources to total (wet plus dry) annual mercury deposition simulated in the model for 2003. North America is defined as the geographical domain shown in the figure.” (Adapted from Selin et al., 2007.)
Higher altitudes of 3000m and 4000m indicated the contributions from global sources, besides that of local and regional sources. Even though there was a lack of emission sources in the area, Gulf of Mexico was found to be a potential source region. This can be attributed to the oxidation of elemental mercury from the global pool by various oxidants such as \( \text{O}_3 \) and OH radicals (Selin et al. 2007). The mercury is also emitted from oceanic water bodies and is oxidized by marine derived halogens (Lai et al. 2007, Sheu and Mason, 2001) and transported.

5.7.1.1 Weighted Overlay PSCF

The typical PSCF analysis points out the potential sources of a particular pollutant corresponding to the ambient concentration in that layer related to the starting height. The PSCF has been widely used to trace the source locations and probable transport pathways of various pollutants (Deshpande2007, Gao et al. 1996). Lai et al. 2007), employed the PSCF technique to investigate the potential source locations for mercury wet deposition. The PSCF observation represents the ambient concentration of the particular pollutant pertaining to that given layer. Considering its association with precipitation, mercury wet deposition cannot be explained by the PSCF results of just one layer.

Since RGM is easily soluble in water, it is scavenged by precipitation and affects the magnitude of mercury wet deposition recorded at the receptor site. It was observed that the RGM concentration increased with altitude, beginning at surface level, suggesting its presence in all the layers. The RGM data was obtained from Mozart chemical transport model using Streets emissions estimates for all the layers (Streets et al,
2005). Figure 33 represents the increasing magnitudes of RGM concentration with rising altitude for the year 2004. It can be deduced from Figure 32 that the RGM concentration increases initially until 700m, suggesting the contributions from the local and regional emission inventories. Between 700m and 4500m, the RGM concentration shows a decreasing trend that can be attributed to the scavenging nature of precipitation.

![Figure 33. Vertical profile of RGM for the year 2004, error bars represent ±1σ. (L): Shows the RGM concentration up to 32000m altitude. (R): Shows the RGM concentration up to 6000m.](image)

As stated above, since the nature of mercury wet deposition sampling is associated with precipitation scavenging of RGM from all the layers, it is necessary to integrate all the PSCF results. This was done by overlaying all the layers into one layer
in order to indicate the potential source directions and locations. The weighted overlay technique from ArcGIS made it possible to superimpose these layers. Rather than assigning equal importance to each layer, the layers were weighted in order to reflect their relative importance. These layers were weighted in proportion to their respective RGM concentrations, which are depicted in Figure 33. Figure 34 gives a pictorial representation of the weighted overlay that was allocated to the layers.

![Weighted overlay model showing percentage contributions from different layer heights.](image)

Figure 35 represents the weighted overlay PSCF map pointing out the potential direction and source locations affecting the mercury wet deposition at the Athens site.
This weighted overlay map indicated lower Ohio River Valley, upper Mississippi River, Kentucky, Tennessee, and Northern Alabama to be potential sources with a high probability to contribute towards the mercury wet deposition at the Athens site. These territories are illustrated in the figure by the darkest shade, i.e. weighted overlay region with PSCF values ranging from 0.71 - 1. This could be explained by the local and regional emission from the industrial facilities, oxidation of global and emitted elemental mercury. This region is similar to PSCF map plotted at lower altitudes of 500m and 1000m emphasizing on the contribution from local sources.

Contributions from the oxidation from the global pool are evident in both regions with PSCF values 0.21 - 0.5 (Region 2) and 0.51 – 0.7 (Region 3) in the map. Additionally, region 3 also reveals contributions from emission inventories, whereas, region 2 denotes those from the evasion of mercury from oceans. Regions 2 and 3 are comparable to the PSCF maps plotted at higher altitudes of 3000m and 4000m.

Therefore, the results from the PSCF analysis bring to light the probability that mercury wet deposition at Athens site is affected not only by local and regional, but also global background mercury.
Figure 35. Weighted overlay PSCF map.

5.7.2 Residence Time Weighted Concentration

The results derived from the RTWC analysis were highly similar to those observed from the PSCF analysis. Potential pathways of air parcels were pointed out via the RTWC analysis and the results also indicated that a majority of the source locations were concentrated southwest of Athens. Figures 36 through 41 represent the RTWC results observed at 500m, 1000m, 1500m, 2000m, 3000m, and 4000m respectively. These maps indicated Ohio River Valley, Mississippi River Valley, Southern Illinois, Southern Indiana, Kentucky, Tennessee, Mississippi, Alabama, Louisiana, and Arkansas to be potential source regions that contribute towards mercury wet deposition. It is clearly evident from the results that overlapping occurs between regions with high RTWC values and the RGM inventories.
Maps that were plotted at altitudes of 500m and 1000m suggested contributions from the local and regional sources. Apart from these sources, the maps plotted at higher altitudes (>1000m) indicated global sources to be contributors as well. Gulf of Mexico and Atlantic Ocean were also demonstrated to be potential source regions. It can also be concluded that with increasing altitudes, potential source regions progressed and extended more towards the Southwest areas.

Figure 36. RTWC based on a 5-day back trajectory with a starting height of 500m.
**Figure 37.** RTWC based on a 5-day back trajectory with a starting height of 1000m.

**Figure 38.** RTWC based on a 5-day back trajectory with a starting height of 1500m.
Figure 39. RTWC based on a 5-day back trajectory with a starting height of 2000m.

Figure 40. RTWC based on a 5-day back trajectory with a starting height of 3000m.
Figure 41. RTWC based on a 5-day back trajectory with a starting height of 4000m.

RTWC results at lower altitudes of 500m – 2000m estimated the potential sources to be more widespread when compared to the PSCF results. However, a RTWC analysis at higher altitudes (>2000m) revealed that the potential source regions were more constricted and narrow in contrast with the PSCF results. This can be based on the premises that PSCF employs a threshold value to differentiate between high concentration and low concentration related trajectories, whereas, RTWC assigns a weighted measured concentration not only on the trajectories but also on the segment of the trajectories. However, the weighted overlay maps of RTWC pinpointed similar source regions as that of the PSCF analysis. Lower Ohio River Valley, upper Mississippi River Valley, Kentucky, Tennessee, Northern Alabama and Mississippi, Southern Indiana and Illinois were pointed out to be to be potential source contributors as depicted.
in figure 42. By and large, the results of PSCF and RTWC are congruent in nature and the overarching views of both these analyses suggest contributions from local, regional and global sources of mercury wet deposition.

*Figure 42. Weighted overlay RTWC map.*
CHAPTER 6: SUMMARY

For thousands of years, mercury has proven to be useful to mankind in a number of fields including industries, mining activities, manufacturing, etc. The emissions of mercury as a result of these activities and also due to power generation have increased the concentrations of mercury in the atmosphere. However, attributing to its adverse effects on human health, there is a need to control the magnitudes of mercury in the environment. The Center of Air Quality at Ohio University is greatly interested and effectively executes the examination of the impacts of mercury, PM$_{2.5}$ and co-pollutants in the Ohio River Valley as contributed by the coal-fired power plants and other anthropogenic sources. Therefore, this study aims at investigating the concentrations of mercury in the atmosphere, the amounts of mercury wet deposition, particularly that in Athens, Ohio and the sources of wet deposition. The results derived from this study are matters of interest not only to academic institutions but also policy makers and regulatory authorities.

The first objective was to evaluate the mercury wet deposition data observed at the Athens site and compare it the other MDN sites in the United States. With relatively moderate levels of mercury wet deposition, Athens ranked 25$^{th}$ among the other 70 MDN sites that were used to compare and characterize the data of the Athens SAM site and also to investigate the overall trends of mercury wet deposition and concentrations. The mercury wet deposition data required for this study was obtained from the Athens Surface Air Monitoring site for the time period beginning May 2004 through September 2008. The data that was collected at the site was then evaluated and interpreted to yield
results that demonstrated the existence of temporal trends in the wet deposition of mercury and the factors that contribute to it. The second objective was to analyze the temporal variance in the mercury wet deposition data observed at the Athens site. The temporal analysis of mercury followed seasonal trends, with elevated levels of wet deposition during the months of April and September, attributing to the number of plume events recorded during these months and clockwise advection of air parcel associated with precipitation events. A major factor determining the rise and fall in levels of mercury wet deposition across different seasons and its asymmetrical distribution over the United States was found to be precipitation. The data demonstrated higher precipitation in the East than in the West and these exact same trends were shown by wet deposition. Higher wet deposition is observed in regions with higher precipitation.

Wet deposition was also found to be relatively low in the north and the west, and the highest in the southeast. This reflects a fusion of high OH concentrations and perpetual precipitation events, and origins from the global pool of the elemental form of mercury that is transformed into reactive gaseous mercury and eventually deposited. RGM was more closely tied to mercury wet deposition than elemental mercury, which fell in the global range of 1.4-1.6 ng/m³ and particulate mercury, which was found to be higher in winter due to vertical temperature inversion. As stated above precipitation was a major factor in mercury wet deposition and its influence was so substantial that other factors had minimal impact and no significant correlation. Hence, we could not quantify the contributions of meteorological and emission impacts on mercury wet deposition. The final objective of the study was to find out the potential source regions contributing to the
mercury wet deposition observed at the Athens site. Results from the PSCF and RTWC analysis showed that mercury wet deposition at Athens site was not only from local and regional sources but also from the global background mercury. These conclusions were made on the premises that at higher altitudes PSCF suggested certain potential source locations even though there was a deficit of source inventories.

In conclusion, this thesis presented the temporal trends of mercury wet deposition encompassing the factors that contribute to these variations and the source-receptor relationship.
CHAPTER 7: FUTURE WORK

This study estimated the temporal variance in the mercury wet deposition data recorded at the Athens supersite and found out that it displayed seasonal trends with higher mercury wet deposition in warmer months compared to colder. This trend was attributed to various reasons such as precipitation, oxidation, plume events, and predominantly due to rain. Understanding the micro physics of solubility of mercury in the snow is important to know why mercury wet deposition was low in the colder months. Furthermore, higher oxidation levels are most likely accountable for elevated levels of mercury wet deposition during warmer months. Thus, quantifying the amount of elemental mercury both from emission inventories and global background that oxidizes into RGM and affects the mercury wet deposition is a difficult task to achieve.

In addition, the studies utilized various receptor modeling methods, such as PSCF and RTWC to determine the potential pathways and directions of the air parcels that contribute to mercury wet deposition at the Athens site. A multivariate factor analysis method such as Positive Matrix Factorization (PMF) can be employed to determine specific source types that influences mercury wet deposition. PSCF and PMF together would then be more robust in pointing out the sources that affect mercury wet deposition at the Athens site. However, to perform source apportionment, analysis of precipitation samples should include the composition of trace elements, since currently only mercury concentration is examined. In order to minimize the uncertainty of the data collected to carry out source apportionment, event based samples should be collected instead of weekly ones.
Further, this study also suggests that the contributions from the local, regional and global sources affect the levels of mercury wet deposition at the Athens site. Therefore, quantifying the contribution from the local and global sources would be useful to policy makers in formulating regulations related to emissions. This can be achieved by employing global modeling methods such as GEOS CHEM, which is “a global 3-D model of composition driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office (GMAO) (Harvard University Atmospheric Chemistry Modeling Group, 2009) or Model of Ozone and Related Chemical Tracers (MOZART) “a global three-dimensional chemical transport model which can easily be driven with various meteorological inputs and model resolutions” (Horowitz et al, 2003). These are some areas that could be investigated to gain a better understanding on sources that contribute to mercury wet deposition.
REFERENCES


APPENDIX A: RANKING OF ATHENS SAM SITE WHEN COMPARED TO MDN SITES BASED ON MERCURY WET DEPOSITION FOR THE YEARS 2005-2007

<table>
<thead>
<tr>
<th>Rank</th>
<th>Site_ID</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevation (meters)</th>
<th>Precipitation(mm)</th>
<th>Hg Concentration (µg/L)</th>
<th>Hg Wet Deposition (µg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FL11</td>
<td>25.39</td>
<td>-80.68</td>
<td>2</td>
<td>5080.745</td>
<td>1.66675</td>
<td>57.56777</td>
</tr>
<tr>
<td>2</td>
<td>FL05</td>
<td>28.7486</td>
<td>-82.5551</td>
<td>3</td>
<td>4392.948</td>
<td>1.59873</td>
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</tr>
<tr>
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<td>AL02</td>
<td>30.7905</td>
<td>-87.8497</td>
<td>46</td>
<td>4654.192</td>
<td>1.62327</td>
<td>46.01479</td>
</tr>
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### APPENDIX A: RANKING OF ATHENS SAM SITE WHEN COMPARED TO MDN BASED ON MERCURY WET DEPOSITION FOR THE YEARS 2005-2007 CONTINUED

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APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)

Average Precipitation in the United States Observed During April for the Years, 2004-2007

Average Mercury Wet Deposition in the United States Observed During April for the Years, 2004-2007

Average Mercury Concentration in the United States Observed During April for the Years, 2004-2007
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
APPENDIX B: ARC GIS MONTHLY MAPS REPRESENTING MERCURY DEPOSITION, MERCURY CONCENTRATION AND PRECIPITATION IN THE UNITED STATES FOR 2004-2007 (CONTINUED)
## APPENDIX C: MULTIPLE LINEAR REGRESSION

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* Dependent Variable: Mercury Wet Deposition.