A Comprehensive Investigation Of Ambient Mercury In The Ohio River Valley: Source-Receptor Relationship And Meteorological Impact

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Fei Gao
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by

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ABSTRACT

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The study characterized the temporal variation of the ambient mercury species (GEM, RGM, and Hgp) measured at a rural site in the Ohio River Valley area from July 2004 to May 2006. Source-receptor relationships of the mercury species were evaluated by utilizing principal component analysis (PCA). The influence of meteorological parameters (temperature, wind speed, relative humidity, barometric pressure, and solar radiation flux) on mercury concentration was studied statistically. Three patterns of mixing height change and the mercury concentration variation were identified and elaborated. Multiple linear regression was used to quantify the collective impacts of meteorological conditions on mercury concentration. The ratio of RGM /Hgp was investigated in relation to the mercury transport. Conditional probability function (CPF) was applied to evaluate the directional contributions of possible mercury sources. Potential source contribution function (PSCF) was employed to identify the potential RGM source regions. The results of CPF and PSCF were found to be in relatively good agreement.

Approved: _____________________________________________________________

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<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>BP</td>
<td>Barometric Pressure</td>
</tr>
<tr>
<td>CAQ</td>
<td>Center for Air Quality</td>
</tr>
<tr>
<td>CPF</td>
<td>Conditional Probability Function</td>
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<tr>
<td>GEM</td>
<td>Gaseous Elemental Mercury</td>
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<tr>
<td>Hgp</td>
<td>Particulate Mercury</td>
</tr>
<tr>
<td>HYSPLIT</td>
<td>Hybrid Single-Particle Lagrangian Integrated Trajectory</td>
</tr>
<tr>
<td>MH</td>
<td>Mixing Height</td>
</tr>
<tr>
<td>PR</td>
<td>Precipitation</td>
</tr>
<tr>
<td>PSCF</td>
<td>Potential Source Contribution Function</td>
</tr>
<tr>
<td>PT</td>
<td>Potential Temperature</td>
</tr>
<tr>
<td>RfC</td>
<td>Reference Concentration</td>
</tr>
<tr>
<td>RfD</td>
<td>Reference Dose</td>
</tr>
<tr>
<td>RGM</td>
<td>Reactive Gaseous Mercury</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>RPF</td>
<td>Regenerative Particulate Filter</td>
</tr>
<tr>
<td>SF</td>
<td>Solar Radiation Flux</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TGM</td>
<td>Total Gaseous Mercury</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environment Programme</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>WS</td>
<td>Wind Speed</td>
</tr>
</tbody>
</table>
CHAPTER 1: INTRODUCTION

Mercury (Hg) is a metallic element, existing in the earth crust, soil, water, and air (United States Environmental Protection Agency (USEPA), 2007 a). Human activities have greatly altered the mercury cycle (Lynam & Keeler, 2006). An increasing amount of mercury emissions have entered into the atmosphere. Mercury has increased approximately 3 fold since the pre-industrialization era (Fitzgerald, 1995). Figure 1 illustrates the disturbance of mercury cycle by anthropogenic emissions.

Ambient mercury is listed as one of the 189 hazardous air pollutants in the Clean Air Act Amendments of 1990 and is one of the 33 air toxics included in USEPA’s National-Scale Air Toxics Assessment Study 1996 conducted. The inhalation reference concentration (RfC) for mercury is set at 300 ng/m³ by USEPA (1997), whereas the generally accepted background concentration of ambient mercury is in the range of 1.5-2.5 ng/m³ (Temme, Slemr, Ebinghaus, & Einax, 2003), far lower than the RfC, inhalation of ambient air is not likely to pose a serious threat to human health.

However, mercury can become a potential public health hazard after it is deposited in a water body. The atmospheric deposition of mercury is a significant mercury loading mechanism for aquatic ecosystem (Landis & Keeler, 2002; Wiener, Krabbenhoft, Heinz, & Scheuhammer, 2003). There are two pathways of mercury deposition: wet deposition and dry deposition. The relative importance of the two deposition venues considerably depends on the location of interest (Lindberg, Meyers, Taylor, Turner, & Schroeder, 1992; Munthe, Hultberg, & Iverfeldt, 1995; Rea, Keeler, & Scherbatskoy, 1996; Marsik, Keeler, & Landis, 2007).
Figure 1. The disturbance of mercury cycle by anthropogenic activities\(^1\). From United Nations Environment Programme (UNEP) (2002), adapted from Lamborg, Fitzgerald, O’Donnell, and Torgersen (2002).

\(^1\) All fluxes (arrows) and pools (in frames) in metric tons. “Pre-industrial” refers to the time before ca. 1870.
Significant amounts of methyl-mercury can be produced via in-situ methylation after mercury is deposited (Rolfhus et al., 2003). The conversion of deposited inorganic mercury is carried out primarily by sulfate-reducing bacteria living in anoxic environments through complex biochemical reactions (United States Geological Survey, 1997). Methyl-mercury is a strong toxin, and can accumulate along food chains (USEPA, 2007 b). Bioaccumulation of methyl-mercury can lead to magnified concentration in fish and shellfish (USEPA, 2007 a), which can pose a potential threat to the public health when they are ingested. Consuming mercury-loaded fish is deemed as the primary avenue of methyl-mercury exposure to the general public (UNEP, 2002). After the ingestion, methyl-mercury can pass through the blood-brain barrier and damage the central nervous system (UNEP, 2002). This process is well illustrated by Levin (2003) in Figure 2.

Methyl-mercury can cause a wide range of health issues. The main effects of methyl-mercury exposure are neurological and cardiovascular related (USEPA, 1997). The oral reference dose (RfD) of methyl-mercury is set at 0.0001 mg/kg-day by USEPA (1997) to prevent such effects.

As methyl-mercury can readily be passed through the placenta, it is of pronounced concern to pregnant women and fetus (USEPA, 1997; UNEP, 2002). As a result of prenatal exposure, children may encounter difficulty with vocabulary, verbal learning, attention, motor functions, and other neurological related symptoms (National Research Council, 2000). In the U.S., about 6% of women of childbearing age experience blood mercury level at or higher than the RfD, equivalent to 5.8 µg/L (Jones,
Sinks, Schober, & Pickett, 2004). In light of this, USEPA and U.S. Food and Drug Administration have issued fish consumption advisories for certain water bodies to warn of the excessive fish consumption (USEPA, 2007a), especially for pregnant women, and hence to reduce the opportunity for overdosed exposure.

Figure 2. The mercury exposure pathways. From Levin (2003).

A variety of sources both natural and anthropogenic can emit mercury into the atmosphere (Lin & Pehkonen, 1999). The estimated amount of mercury entering into the global atmospheric pool is in the range of 4400-7500 metric tons annually (Lindquist et al., 1991; Lamborg et al., 2002). The anthropogenic emissions, composed of direct emissions and reemissions of the previous deposition, are believed to be the dominant, accounting for approximately two thirds of the total emissions (USEPA, 2007c). Figure
Figure 3 shows the estimated global anthropogenic mercury emissions in 2000, based on the data from Pacyna, Pacyna, Steenhuisen, and Wilson (2006) (China emission excluded), and from National Argonne Laboratory (updated emission in China) (Streets et al., 2005). As seen in the graph, Asia is the region where most mercury is emitted. Country wise, China is indisputably one of the most significant mercury emission sources.

![Image of global mercury emissions map](image.png)

**Figure 3.** Global anthropogenic mercury emissions in 2000. Courtesy of Myoungwoo Kim, Center for Air Quality, Ohio University.

Mercury exists in three forms in the atmosphere: gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), and particulate mercury (Hgᵣ). GEM is the
most dominant specie and generally accounts for more than 95% of the atmospheric mercury composition (Munthe & McElroy, 1992; Lindberg & Stratton, 1998; Lindberg, Stratton, Pai, & Allan, 2000; Landis, Keeler, Al-Wali, & Stevens, 2004). The residence time of GEM in the atmosphere is estimated to be between 0.5 and 2 years (Munthe & McElroy, 1992; Schroeder & Munthe, 1998), which enables its transport to long distances, even on a global scale.

The residence time of RGM is much shorter than that of GEM ranging from a few hours to a few days (Lindberg & Stratton, 1998; Lin & Pehkonen, 1999; Calvert & Lindberg, 2005). Hgp exists associated with airborne particulates and deposits slightly slower than RGM. The deposition rates of RGM and Hgp are at 0.14-0.24 cm/s and 0-1.6 cm/s, respectively (Malcolm & Keeler, 2002).

The transformation between mercury species with different oxidation states (0 and +2) is complex (Poissant, 1997). GEM (0) can be oxidized to RGM (+2) mainly in cloud droplets (aqueous phase) by ozone (O₃), hydroxyl radical (OH), chlorine (HOCl/OCl⁻), or in gaseous phase by O₃ (Lindberg & Stratton, 1998). In gaseous phase, oxidation of mercury is quite slow (Iverfeldt & Linqvist, 1986; Hall, 1995). RGM on the other hand, can be reduced back to elemental mercury by SO₂ or SO₃²⁻ in aqueous phase (Lindberg & Stratton, 1998). Table 1 presents the major reaction pathways of mercury species.
Table 1

**Selected Mercury Reactions and Rate Constants**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reference^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Hg}_0^0 + O_3(g) \rightarrow \text{HgO}(g) + O_2(g))</td>
<td>((3 \pm 2) \times 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})</td>
<td>1</td>
</tr>
<tr>
<td>(\text{Hg}_0^0 + O_3(aq) + 2H^+ \rightarrow \text{Hg}_2^{2+} + H_2O + O_2(aq))</td>
<td>((4.7 \pm 2.2) \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1})</td>
<td>2</td>
</tr>
<tr>
<td>(\text{Hg}_0^0 + OH \rightarrow H_2^+(aq) + OH^-)</td>
<td>(2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})</td>
<td>3</td>
</tr>
<tr>
<td>(\text{Hg}_0^+ + OH^- \rightarrow \text{Hg}_2^{2+} + OH^-)</td>
<td>(10^{10} \text{ M}^{-1} \text{ s}^{-1})</td>
<td>4</td>
</tr>
<tr>
<td>(\text{HOCl}_0(aq) + \text{Hg}_0^0 \rightarrow \text{Hg}_2^{2+} + \text{Cl}^- + OH^-)</td>
<td>((2.09 \pm 0.06) \times 10^6 \text{ M}^{-1} \text{ s}^{-1})</td>
<td>5</td>
</tr>
<tr>
<td>(\text{OCI}_0^- + \text{Hg}_0^0 \rightarrow \text{Hg}_2^{2+} + \text{Cl}^- + OH^-)</td>
<td>((1.99 \pm 0.05) \times 10^6 \text{ M}^{-1} \text{ s}^{-1})</td>
<td>5</td>
</tr>
<tr>
<td>(\text{Hg}_0^0 + H_2O_2(g) \rightarrow \text{Hg(OH)}_2(g.s))</td>
<td>(8.5 \times 10^{-19} \text{ cm}^{-3} \text{ molec}^{-3} \text{ s}^{-1})</td>
<td>1</td>
</tr>
<tr>
<td>(\text{HgSO}_3(aq) \rightarrow \text{Hg}_0(aq) + \text{products})</td>
<td>(0.6 \text{ s}^{-1})</td>
<td>6</td>
</tr>
</tbody>
</table>

CHAPTER 2: METHODOLOGY

2.1 Surface Air Monitoring Site

Athens is located within the boundary of the Ohio River Valley, where more than a dozen of coal-fired power plants and other industrial facilities are located. The Ohio River Valley encompasses a vast area which expands along the Ohio River. It expands to the southwestern Pennsylvania, northwestern West Virginia, southern Ohio, and along the northern border of Kentucky (Figure 4).

The land use pattern is diversified within the region: urban, semi-rural, and rural areas. Besides coal-fired power plants, a variety of industrial facilities including coke plants, metal smelting and processing plants, and chemical plants are also present in the valley. In 2004, the Center for Air Quality at Ohio University established the surface air monitoring site in the rural area of Athens with funding from the Department of Energy National Energy Technology Laboratory. The site has been under continuous operation since its inception. The Center undertakes the monitoring and modeling responsibilities to examine the impacts of mercury and PM$_{2.5}$ in the Ohio River Valley as contributed by the coal-fired power plants and other anthropogenic sources.

Ambient mercury measurements at the site started in July, 2004. The thesis presents parts of the results yielded by the ongoing research dedicated to ambient mercury conducted at the Center. The objective of the research is to account for the temporal variation of ambient mercury species measured at the site by evaluating the sources-receptor relationship and meteorological influence, and by analyzing the mercury transport.
The surface air monitoring site is located in a rural setting about 3.5 kilometers southwest of downtown Athens, at 7760 North Blackburn Road (82.118° W, 39.308° N). The elevation of the station is about 330 meters above mean sea level, and it is arguably the highest point in the region, south to Ohio River and southwest to Cincinnati (Fahrni, 2005). As noted by Fahrni (2005), the surrounding area features agriculture lands, dispersed houses, and fragmented forest patches. No industries are in the immediate proximity. U.S. Route 50 is approximately 347 m away. Within 150 km radius of the site, eleven coal-fired power plants and a number of other industrial and chemical premises exist. Yet, local emissions from Athens are negligible. The unique location (also seen in Figure 4) of the site offers a good opportunity to capture transport of air pollutants in the Ohio River Valley airshed.
2.2 Instrumentation

Tekran® automated mercury monitoring components were used for continuous mercury measurement in this study. This set of instruments (Figure 5) include a mercury speciation and pump unit (Tekran® model 1130), a mercury particulate unit (Tekran® model 1135), and a mercury vapor analyzer (Tekran® model 2537A).

The 1130 and 1135 units were mounted on a vertical manifold attached to a deck built within the monitoring site; the air inlet is 2 m above ground level. The 2537A
analyzer, the 1130 pump unit and the data acquisition computer were housed in a shelter close to the vertical manifold.

Figure 5. The Tekran® mercury monitoring instrument set.

The speciation units were programmed to sample the ambient air at a flow rate of 10 L min⁻¹ in a 1-hour interval every second hour. During sampling, air was drawn through an impactor inlet into the speciation units, first through the 1130 then the 1135. The KCl-coated quartz annular denuder in the model 1130 captured RGM while the regenerative particulate filter (RPF) in the 1135 was collecting Hg_p. A fraction (1 L min⁻¹) of the air stream was drawn into the 2537A, where GEM was measured continuously in two alternating cartridges in twelve 5-min sampling intervals using cold vapor atomic
fluorescence spectrophotometry (CVAFS). After the one hour GEM sampling, the pump first flushed the system with 7 L min\(^{-1}\) zero air in preparation of the following process. The RPF was heated to 800 °C to convert Hg\(_n\) into GEM which was then flushed to 2537A for measurement; the denuder was then heated to 500 °C to desorb RGM which was also measured as GEM in 2537A. After this, the system cooled down and was purged by zero air again. This whole process lasted another hour. More detailed description on the system can be found in Landis, Stevens, Schaedlich, and Prestbo (2002). Data quality control and assurance procedures were discussed by Fahrni (2005). Figure 6 gives the schematic diagram illustrating how Tekran monitoring components function systematically.

Along with ambient mercury concentration, gaseous pollutants (SO\(_2\), CO, NO\(_x\), and O\(_3\)), PM\(_{2.5}\) mass, and meteorological parameters (wind speed/direction, surface air temperature, barometric pressure, precipitation, and relative humidity) were also acquired at the site during the mercury monitoring. Fahrni (2005) and Yatavelli et al. (2006) noted all the instrumentations deployed for the data acquisition in greater details.
2.3 Data Analysis Tools

The speciated mercury concentrations, along with the co-pollutants, and the meteorological data, collected at the site were later analyzed statistically in order to establish the source-receptor relationships of mercury species; to evaluate how meteorological parameters affected the mercury concentration variations, and to investigate mercury transport in the Ohio River Valley. Three major statistical
approaches were employed, including principal component analysis, conditional probability function, and potential source contribution function.

2.3.1 Principal Component Analysis (PCA)

PCA is the most common type of factor analysis. The common objective of applying PCA is to reduce the dimensionality of a dataset by extracting a fewer number of uncorrelated factors from it. Such factors are also termed as principal components and are expected to explain the maximum possible variance of the entire dataset.

A typical algorithm of PCA can be described as follows (Dong & McAvoy, 1995). For a random \( n \)-dimension dataset \( X = [x_1, x_2, \ldots, x_n] \) with each column representing a variable, \( m \) principal components can be derived as \([f_1, f_2, \ldots, f_m]\). The first principal component \( f_1 \) can be written as \( f_1 = Xp_1 \), where \( p_1 \) is an eigenvector of the covariance matrix of dataset \( X \) corresponding to the highest eigenvalue. \( p_1 \) defines the direction in the \( m \) dimension data space on which the greatest data variability is found. Thus \( f_1 \) is the projection of each of the \( n \) vectors onto that direction. The second principal component \( f_2 \), is to explain the maximal amount of the variability of the residual data, thus \( f_2 = R_1p_2 \), where \( R_1 \) denotes the remnant data, given as \( R_1 = X - f_1p_1^T \), and \( p_2 \) is also an eigenvector of the covariance matrix of \( X \) corresponding to the second highest eigenvalue. With the same principle, desired \( m \) total principal components can be extracted, which altogether can explain the majority of the data variability. If the \( n \) data vectors are correlated, then \( m < n \). Based on the description above, the following equation
is true: $X = f_1 p_1^T + f_2 p_2^T + \ldots + f_n p_n^T + E$, where $E$ represents residual, composed of little data variance.

PCA has been employed in a number of research endeavors to study the source-receptor relationship of mercury (Ames, Gullu, & Olmez, 1998; Kim & Kim, 2001; Blanchard et al., 2002; Liu et al., 2007). Appendix A summarizes the identified principal components (factors) with relevance to mercury from each of the research activities.

Lynam and Keeler (2006) applied PCA to investigate the potential sources of mercury species measured at an urban site in Detroit, MI. The extracted factors were identified as specific source types based on the association of indicative pollutants with the factor and the inter-correlation between different variables within the same factor. In their study, RGM was found to be associated with two main factors: photochemistry and coal combustion. They argued that the air masses that contained photochemical oxidants were likely to go through regional transport. The study also confirmed the impacts of automobile emissions on GEM as GEM was found in a factor representing automobile engine combustion.

PCA analysis in this research is of significance since it was the first attempt to investigate the source-receptor relationship of mercury based on the speciated mercury data measured at a rural site. It was able to reveal comprehensive information on the source contributions to all mercury species in a rural setting. Meaningful comparisons were made to other relevant work to further establish its validity.
2.3.2 Conditional Probability Function (CPF)

First introduced by Ashbaugh, Malm, and Sadeh (1985), CPF tests the probability that an air mass from a certain wind direction will result in an elevated concentration of the pollutant at the receptor site. A higher CPF value corresponds to a higher probability that the source region lies in the given direction. The CPF can be formulated mathematically as follows (Kim & Hopke, 2004):

\[
CPF_{\Delta \theta} = \frac{m_{\Delta \theta}}{n_{\Delta \theta}},
\]

where \( m_{\Delta \theta} \) represents the number of measurements exceeding the designated threshold concentration value and are associated with the wind direction within the sector \( \Delta \theta \) during the entire measurement period. \( n_{\Delta \theta} \) denotes the total number of measurements from that wind direction (\( \Delta \theta \)).

2.3.3 Potential Source Contribution Function (PSCF)

PSCF was initially developed by Ashbaugh et al. (1985) and Malm et al. (1986). Gao, Cheng, & Hopke (1993) defined PSCF as the conditional probability that an air parcel with a certain level of pollutant concentration above a criterion value arrives at the receptor after traveling across a geographical area. The criterion value for PSCF calculation can be set arbitrarily, e.g., at median (Poissant, 1999) or mean (Begum, Kim, Jeong, Lee, & Hopke, 2005) value of the dataset, or at other selected value. A number of studies have employed PSCF for identifying the geographical source regions of air pollutants. (Zeng & Hopke, 1989; Gao et al., 1994, 1996)
To calculate PSCF, the first step is to identify the endpoints of the back trajectories. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) 4 model (Draxler & Hess, 1998) developed by Air Resource Laboratory of National Oceanic and Atmospheric Administration can be used to compute the back trajectories of air parcels. The whole geographical region where back trajectories transverse then should be divided into an array of grid cells whose size is dependent on the geographical scale of the problem of interest (Hopke, 2003). Figure 7 displays an area overlaid by a 0.2°x0.2° grid system. If a back trajectory endpoint of an air parcel falls into a cell, the trajectory is assumed to transport the pollutants emitted from that cell all the way to the receptor site (Hopke, Zeng, & Cheng, 1990; Cheng et al., 1993).
Figure 7. The 0.2°x0.2° grid system covering Ohio and the neighboring states.

The following passages describe the algorithm of PSCF. Let $N$ denote the total number of trajectory segment endpoints during the study. If $n$ segment trajectory endpoints fall into the $ij$th cell (represented by $n_{ij}$), then the probability of this event $A_{ij}$ is given by

$$P[A_{ij}] = \frac{n_{ij}}{N}$$
In the same \( ij \)th cell, if there are \( m \) segment endpoints which are associated with the trajectories that arrive at the receptor site causing higher measured value than the criterion value (represented by \( m_{ij} \)), then the probability of the high concentration event \( B_{ij} \) is given by

\[
P[B_{ij}] = \frac{m_{ij}}{N}
\]

The PSCF value for that cell is defined as follows:

\[
PSCF_{ij} = \frac{P[B_{ij}]}{P[A_{ij}]} = \frac{m_{ij}}{n_{ij}}
\]

PSCF value represents the conditional probability that an air parcel passing through the \( ij \)th cell can result in elevated concentration at the receptor site (Hopke, 2003). A high PSCF value indicates a high possibility of the cell being the source of pollutant emission. In this way, a PSCF value filed can show the possible locations of the pollutant emission sources (Cheng et al., 1993).

The trajectory endpoints bear uncertainties. Such uncertainties increase as the distance from the receptor site increases (or the time of back trajectories lengthens) (Stohl, 1996). Since the PSCF value is statistically calculated, if the errors of trajectory endpoints are random and not systematic, increased number of endpoints can reduce the uncertainty and make the PSCF approach the true values (Begum, Kim, Jeong, Lee, & Hopke, 2005). Previous studies show that the error is most probably random (Poissant, 1999).
When only small numbers of back trajectory endpoints are available in a cell, the calculated PSCF value should be treated differently than the PSCF value calculated from a large number of endpoints. A weight function can be used to give a weighted PSCF value for the cell calculated from a small number of endpoints (Poissant, 1999). Zeng and Hopke (1989) propose that when the number of end points in a particular cell is less than about three times of the average number of the end points for all cells, the weight function should apply. The ranges and corresponding weighing factors are determined empirically based on the problem of interest (Owega, Evans, Khan, Jervis, & Fila, 2006).
CHAPTER 3: DATA PRESENTATION

3.1 Speciated Mercury Dataset Summary

Table 2 summarizes the mercury measurements made between July 27\textsuperscript{th}, 2004 and May 31\textsuperscript{st}, 2006. The mean (± SD) concentration of GEM was 1.60± 0.24 ng/m\textsuperscript{3}. It was the predominant mercury form and accounted for a little over 99\% of the total mercury composition. The measured GEM level was in general agreement with the background GEM level (1.7 ng/m\textsuperscript{3}) in the Northern Hemisphere (Ebinghaus et al., 2003; Slemr et al., 2003; Kim et al., 2005). The average concentrations of H\textsubscript{g}p\textsubscript{o} and RGM were 5.03 ± 5.44 pg/m\textsuperscript{3} and 10.78 ± 22.02 pg/m\textsuperscript{3}, respectively. The two mercury species, H\textsubscript{g}p\textsubscript{o} and RGM each comprised approximately 0.3\% and 0.7\% of the total ambient mercury, respectively.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>GEM (ng/m\textsuperscript{3})</th>
<th>H\textsubscript{g}p\textsubscript{o} (pg/m\textsuperscript{3})</th>
<th>RGM (pg/m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (N)</td>
<td>7459</td>
<td>6953</td>
<td>7418</td>
</tr>
<tr>
<td>Mean</td>
<td>1.60</td>
<td>5.03</td>
<td>10.78</td>
</tr>
<tr>
<td>SD</td>
<td>0.24</td>
<td>5.44</td>
<td>22.02</td>
</tr>
<tr>
<td>Min</td>
<td>0.69</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Max</td>
<td>5.43</td>
<td>76.82</td>
<td>461.59</td>
</tr>
<tr>
<td>25\textsuperscript{th} percentile</td>
<td>1.46</td>
<td>1.83</td>
<td>1.12</td>
</tr>
<tr>
<td>50\textsuperscript{th} percentile</td>
<td>1.58</td>
<td>3.59</td>
<td>3.21</td>
</tr>
<tr>
<td>75\textsuperscript{th} percentile</td>
<td>1.70</td>
<td>6.31</td>
<td>10.05</td>
</tr>
<tr>
<td>90\textsuperscript{th} percentile</td>
<td>1.85</td>
<td>10.65</td>
<td>28.51</td>
</tr>
</tbody>
</table>
3.2 Temporal Variability of Mercury Species

All mercury species displayed an apparent seasonal variation over the entire measurement time period. The seasonal trends of GEM, Hgp, and RGM have been depicted in Figure 8, 9, 10, respectively.

Figure 8. Seasonal variation of GEM.3

3 The median is marked by a horizontal line in the box. The lower hinge (score at the 25th percentile) and upper hinge (score at the 75th percentile) comprise the edges of the box. The box range is the inter-quartile range (IQR); the whiskers denote the range of values that fall within 1.5 IQR; values plotted with dots are more than 1.5 IQR outside the box. The average mercury concentrations by season are shown in the line graph below. Figure 10-13 follow the same symbology.
Figure 9. Seasonal variation of Hg$_{p}$.

Figure 10. Seasonal variation of RGM.
As shown in the graphs, the lowest average GEM concentrations were observed in summer (June to August) and fall (September to November), while winter (December to February) experienced the highest GEM levels. Similarly, the mean Hg₂ values reached a peak in winter and the lowest concentration was measured in summer or fall. For RGM, the spring concentration was consistently higher than its winter counterpart and the same was true of the fall concentration as compared to the summer level. Spring (March to May) 2005 saw the highest RGM concentration over the entire time period. The total gaseous mercury (TGM) concentration, consisting of GEM and RGM, tended to be higher in the colder seasons relative to the warmer seasons.

Similar seasonal pattern of TGM variation was also reported by other researchers (Slemr & Scheel, 1998; Ames et al., 1998; Blanchard et al., 2002; Poissant, Pilote, Beauvais, Constant, & Zhang, 2005). Blanchard et al. (2002) proposed a number of factors that could potentially explain the seasonality exhibited by TGM, including differences in meteorological conditions between the cold and warm seasons, such as mixing height, wind speeds, dry and wet deposition rates; the use of coal as a fuel for domestic heating (Rotty, 1987) between the warm and cold seasons, and the seasonal cycle of atmospheric oxidants (e.g. O₃). Liu et al. (2007) attributed the elevation in winter Hg₂ concentration to the enhanced gas-to-particle conversion of RGM due to lower temperatures and reduced UV radiation resulting in the increased feasibility of condensation of mercury compounds onto atmospheric particles. However, the underlying model of gas-to-particle conversion was not well established.
Figures 11, 12 and 13 shows the overall diurnal trends of GEM, Hg$_p$, and RGM during the sampling time period.

*Figure 11. Diurnal trend of GEM.*
Figure 12. Diurnal trend of HgP.

Figure 13. Diurnal trend of RGM.
GEM experienced the lowest average concentration in the early morning and the 
highest around noon. Poissant et al. (2005) reported a similar diurnal cycle and suggested 
that this could be linked to many parameters such as sources, chemicals and meteorology. 
Yatavelli et al. (2006) argued that the high concentrations around mid-day could be the 
result of turbulent mixing caused by the boundary layer dynamics. Detailed discussion 
will be presented in the later part of the thesis. The daytime concentration of RGM was 
higher than its nighttime level. It peaked in the early afternoon. This is in good 
agreement with the RGM diurnal trends reported in several other studies (Poissant et al., 
2005, Gabriel, Williamson, Brooks, & Lindberg, 2005; Liu et al., 2007). The 
enhancement of RGM levels during the day implied the contribution of photochemical 
production e.g. oxidization of GEM by ozone (Poissant et al., 2005; Liu et al., 2007), and 
the nighttime decrease of RGM could be related to the removal of RGM through 
nocturnal dry deposition (Liu et al., 2007). \( \text{Hg}_0 \) showed a similar variability as RGM did. 
Its concentration in the daytime was higher than that in the nighttime. This is consistent 
with the results reported by Poissant et al. (2005), yet contradicts the findings of Liu et al. 
(2007).

3.3 Air Pollutants and Meteorological Data

The air pollutants, \( \text{SO}_2 \), \( \text{CO} \), \( \text{O}_3 \), \( \text{NO}_x \), and \( \text{PM}_{2.5} \) (mass), as well as the 
meteorological parameters, including relative humidity (RH), temperature (T), wind 
speed (WS), wind direction (WD), precipitation (PR), and barometric pressure (BP) were 
monitored while the ambient mercury was sampled. Their values were averaged in 1-
hour interval to match the time resolution of mercury concentrations. Table 3 presents
the statistical summary of the available data of air pollutants, temperature, and relative humidity measured during the sampling period time.

Potential temperature (PT), mixing height (MH), and solar radiation flux (SF) were obtained from the HYSPLIT 4 model with the Global Reanalysis meteorological database.

Table 3

<table>
<thead>
<tr>
<th></th>
<th>O₃ (ppb)</th>
<th>NOₓ (ppb)</th>
<th>SO₂ (ppb)</th>
<th>CO (ppm)</th>
<th>PM₂.₅ (μg/m³)</th>
<th>RH (%)</th>
<th>T (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size(N)</td>
<td>4766</td>
<td>6693</td>
<td>6654</td>
<td>6891</td>
<td>7312</td>
<td>7040</td>
<td>7037</td>
</tr>
<tr>
<td>Mean</td>
<td>29.06</td>
<td>5.78</td>
<td>4.08</td>
<td>0.20</td>
<td>15.21</td>
<td>75.19</td>
<td>54.07</td>
</tr>
<tr>
<td>Min</td>
<td>7.10</td>
<td>11.28</td>
<td>2.71</td>
<td>0.43</td>
<td>37.68</td>
<td>1.59</td>
<td>2.84</td>
</tr>
<tr>
<td>Max</td>
<td>97.99</td>
<td>25.97</td>
<td>22.88</td>
<td>1.45</td>
<td>121.98</td>
<td>99.69</td>
<td>94.24</td>
</tr>
<tr>
<td>SD</td>
<td>17.18</td>
<td>4.91</td>
<td>4.20</td>
<td>0.23</td>
<td>10.70</td>
<td>18.83</td>
<td>17.74</td>
</tr>
<tr>
<td>25th percentile</td>
<td>16.41</td>
<td>2.29</td>
<td>1.14</td>
<td>0.02</td>
<td>8.42</td>
<td>61.36</td>
<td>40.32</td>
</tr>
<tr>
<td>50th percentile</td>
<td>28.13</td>
<td>4.11</td>
<td>2.67</td>
<td>0.16</td>
<td>12.90</td>
<td>77.92</td>
<td>55.34</td>
</tr>
<tr>
<td>75th percentile</td>
<td>40.00</td>
<td>7.78</td>
<td>5.50</td>
<td>0.39</td>
<td>19.48</td>
<td>91.64</td>
<td>68.67</td>
</tr>
<tr>
<td>90th percentile</td>
<td>52.57</td>
<td>12.78</td>
<td>9.90</td>
<td>0.55</td>
<td>29.62</td>
<td>98.73</td>
<td>76.57</td>
</tr>
</tbody>
</table>
CHAPTER 4: SOURCE-RECEPTOR RELATIONSHIP

Concentrations of mercury species together with air pollutants including CO, NO\textsubscript{x}, O\textsubscript{3}, SO\textsubscript{2}, and PM\textsubscript{2.5} mass were used as the input components for PCA analysis. PCA was performed using the statistical software package STATISTICA. Two principal components (PC), with eigenvalues greater than 1 were extracted (see Table 4). The two factors together could explain about 50% of the total variance of the dataset.

Table 4

*Extracted Factors, Variable Factor Loadings, and Variance Explained by Each Factor*

<table>
<thead>
<tr>
<th>Variables</th>
<th>PC 1</th>
<th>PC 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEM</td>
<td>0.41</td>
<td>-0.52</td>
</tr>
<tr>
<td>Hg\textsubscript{p}</td>
<td><strong>0.56</strong>\textsuperscript{4}</td>
<td>-0.14</td>
</tr>
<tr>
<td>RGM</td>
<td><strong>0.70</strong></td>
<td>0.20</td>
</tr>
<tr>
<td>CO</td>
<td>0.11</td>
<td>-0.61</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>0.46</td>
<td>-0.65</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>0.18</td>
<td><strong>0.81</strong></td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td><strong>0.85</strong></td>
<td>0.00</td>
</tr>
<tr>
<td>PM\textsubscript{2.5}</td>
<td>0.19</td>
<td>0.38</td>
</tr>
</tbody>
</table>

| Eigenvalue | 2.26 | 1.66 |
| Variance explained | 25% | 24% |

\textsuperscript{4} Factor loadings above 0.5 are marked with bold.
Factor 1 was able to explain approximately 25% of the data variance. RGM, Hg\textsubscript{p}, and SO\textsubscript{2} scored high factor loadings (0.70, 0.56, and 0.85, respectively) in this factor. As suggested by Lynam and Keeler (2006), grouping mercury species (RGM, Hg\textsubscript{p}) and SO\textsubscript{2} in the same factor indicates a common emission source for these pollutants. Electrical utilities burning fossil fuels, especially coal, are the primary source of SO\textsubscript{2}, and release more than 65% of the total emissions (USEPA, 2000). Coal-fired power plants are also the single largest anthropogenic sources of mercury in the U.S. (USEPA, 2007 a). The 1999 Information Collection Request data showed that mercury emissions from coal-fired power plants comprised approximately 43% of the total domestic anthropogenic mercury emissions (USEPA, 2007 d). More recent research (USEPA, 2006) showed approximately 40% to 80% of mercury emissions from these plants were in the form of RGM. There are 11 coal-fired power plants present within a radius of 150 km of Athens. Mercury emissions from these plants around Athens could potentially contribute to the RGM level observed in Athens. Thus it is reasonable to designate this factor as the impact of coal-fired power plants.

The Spearman correlation coefficient (in Table 5) between RGM and SO\textsubscript{2} ($r_s = 0.61$, $p<0.0001$) also supported that RGM and SO\textsubscript{2} were highly correlated. Figure 14 illustrates the covariance of RGM and SO\textsubscript{2} in a plume episode observed at the site. GEM exhibited moderate factor loading (0.41) in factor 1, suggesting that the coal-fired power plants emissions also had an impact on GEM concentration measured at the Athens site.
Table 5

*Spearmen Correlation Coefficients for Mercury Species and Criteria Pollutants*\(^5\)

<table>
<thead>
<tr>
<th></th>
<th>GEM</th>
<th>Hg(_0)</th>
<th>RGM</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEM</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(_0)</td>
<td>0.20</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>RGM</td>
<td>0.21</td>
<td>0.44</td>
<td>1</td>
</tr>
<tr>
<td>CO</td>
<td>0.31</td>
<td>0.19</td>
<td>0.12</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>0.37</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>O(_3)</td>
<td>-0.21</td>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>0.29</td>
<td>0.34</td>
<td>0.61</td>
</tr>
<tr>
<td>PM(_{2.5})</td>
<td>0.03</td>
<td>0.10</td>
<td>0.08</td>
</tr>
</tbody>
</table>

*Figure 14. Correlation between RGM and SO\(_2\) (from Jan 30, 05 1:00 to Jan 31, 05 23:00).*

\(^5\) All \(p\) values are below 0.0001 (\(p<0.0001\)).
The variance explained by factor 2 comprised 24% of the total dataset variance. In this factor, O₃ showed a high positive factor loading (0.81), while NOₓ had a negative factor loading (-0.65). The high factor loading of O₃ suggested a factor representing photochemistry (Lynam & Keeler, 2006), for O₃ is a well-known photochemical oxidant. The anti-correlation between NOₓ and O₃ \((r_s = 0.49, p<0.0001)\) was again indicative of photochemical activity (Liu et al., 2007). A factor loading of 0.2 for RGM was seen in factor 2, indicating that RGM was not highly associated with photochemistry overall. The low Spearman correlation coefficient between RGM and O₃ \((r_s = 0.16, p<0.0001)\) also substantiated this argument.

PCA was also utilized to analyze the season stratified data. A comparison was made between the principal components derived from the data of winter 2005 and that of summer 2005 (Table 6).

Two principal components were identified for the winter dataset: a combustion factor (PC I) and a factor of coal-fired power plants (PC II). PC I featured high scores for NOₓ and CO, which are pollutants resulting from combustion processes (Lynam & Keeler, 2006), and thus was recognized as a factor representing combustion. PC II contained high factor loadings for RGM (0.91) and SO₂ (0.72), hence considered as a factor indicating the impact of coal-fired power plants. These two factors could collectively explain ~61% of the total data variance. The summer PCs were characterized as a composite factor of coal-fired power plants and photochemistry (PC I), and a combustion factor (PC II). The two factors together accounted for ~47% of the data variance. Notably O₃ did not exhibit a high factor loading in the factors extracted
from the winter dataset, whereas O₃ was seen to be associated with RGM in PC I derived for the summer months. This suggested the enhanced photochemical activities during summer and the subsequent formation of RGM attributable to oxidation of GEM. The non-parametric correlation coefficient between RGM and O₃ was also significantly higher for the summer time than the winter counterpart. The unexplained data variance for the summer data was considerably higher, suggesting the meteorological influence might play a greater role in affecting the mercury variability in summer.

Table 6

**A Comparison of PCA Results Derived from Winter and Summer Data in 2005**

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th></th>
<th>Summer</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC I</td>
<td>PC II</td>
<td>PC I</td>
<td>PC II</td>
</tr>
<tr>
<td>GEM</td>
<td>0.62⁶</td>
<td>0.36</td>
<td>-0.00</td>
<td>0.65</td>
</tr>
<tr>
<td>Hgₚ</td>
<td>0.53</td>
<td>0.51</td>
<td>0.56</td>
<td>0.10</td>
</tr>
<tr>
<td>RGM</td>
<td>-0.07</td>
<td>0.91</td>
<td>0.80</td>
<td>0.00</td>
</tr>
<tr>
<td>CO</td>
<td>0.56</td>
<td>0.00</td>
<td>0.07</td>
<td>0.58</td>
</tr>
<tr>
<td>NOₓ</td>
<td>0.85</td>
<td>0.28</td>
<td>-0.10</td>
<td>0.74</td>
</tr>
<tr>
<td>O₃</td>
<td>-0.79</td>
<td>0.11</td>
<td>0.68</td>
<td>-0.19</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.48</td>
<td>0.72</td>
<td>0.80</td>
<td>0.26</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>0.67</td>
<td>0.12</td>
<td>0.29</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>3.70</td>
<td>1.19</td>
<td>2.26</td>
<td>1.64</td>
</tr>
<tr>
<td>Variance explained</td>
<td>37%</td>
<td>24%</td>
<td>27%</td>
<td>20%</td>
</tr>
</tbody>
</table>

---

⁶ Factor loadings above 0.5 are marked with bold.
High factor loadings of RGM and Hg$_p$ were seen to cluster in the same factor, which was valid for the data of winter and summer in 2005, and that of the entire measurement period. This was consistent with Lynam and Keeler’s finding (2006). According to this study, the gas-to-particle transformation processes between the two mercury species could help explain the correlation ($r_s=0.44$, $p<0.0001$).
CHAPTER 5: METEOROLOGICAL PARAMETERS AND MERCURY CONCENTRATION VARIATION

5.1 Surface Meteorological Parameters and Mercury Concentration Variation

Previous studies (Blanchard et al., 2002; Han et al., 2004; Gabriel et al., 2005) have shown meteorological conditions can impact mercury concentrations. In this section, meteorological variables including temperature (T), wind speed (WS), relative humidity (RH), barometric pressure (BP), and solar radiation flux (SF) are analyzed with respect to the change in mercury concentrations, respectively.

Figure 15 examines the statistical correlations of surface air temperature, wind speed, and relative humidity with mercury species. Appendix B further investigates the seasonal correlation of mercury species with all the 5 meteorological parameters.

5.1.1 Temperature

As shown in Figure 15, the Spearman correlation coefficient for GEM vs. temperature was -0.25 for the sampling period. The non-parametric correlation coefficient for TGM vs. temperature was also calculated at -0.25. Similar negative correlations between TGM and temperature ($r_s = -0.22$ and $r_s = -0.26$) were reported by Han et al. (2004) based on the measurements made at the rural sites located in Stockton and Sterling, New York.

The statistically significant relationship ($p<0.0001$) between GEM and temperature suggests that colder air resulted in the prevention of GEM dispersion and the subsequent increase of GEM concentration. The weak negative correlation coefficient ($r_s = -0.25$), however, suggests the involvement of large-scale dynamics of
meteorological conditions including mixing height, wind speed, dry and wet deposition (Han et al., 2004; Blanchard et al., 2002).

Figure 15. Relationship between surface temperature, wind speed, and relative humidity with mercury.
A negative correlation was observed for \( \text{Hgp} \) with temperature \( (r_s =-0.22) \). The inverse relationship between \( \text{Hgp} \) and temperature might be due to the fact that \( \text{Hgp} \) concentration is affected by adsorption or condensation of gaseous mercury onto ambient particles, which is dependent on ambient temperature (Sakata & Marumoto, 2002; Liu et al., 2007). This inverse correlation was more pronounced in winter as Appendix B shows. Similar temperature dependency of \( \text{Hgp} \) concentration has been observed in other areas (Iverfeldt, 1991; Keeler, Glinsorn, & Pirrone, 1995; Sakata & Marumoto, 2002).

On the other hand, weak positive correlation \( (r_s = 0.11) \) between RGM and temperature was observed for the entire sampling period. This is consistent with the observation made at the three sites in Potsdam, Stockton, and Sterling, New York (Han et al., 2004). During the study, a weak positive relationship between RGM concentration and temperature was seen at all sites. This might reflect the temperature dependency of photochemical oxidation of GEM to RGM (elevated oxidation induced by higher temperature). Han et al. (2004) also suggested the higher concentrations of oxidants in warmer seasons (Lee, Dollard, & Pepler, 1998) facilitated the oxidation of GEM, resulting higher RGM concentration.

5.1.2 Wind Speed

A statistically significant \( (p<0.0001) \) correlation between \( \text{Hgp} \) and wind speed was observed for the sampling period (Figure 15). The negative correlation \( (r_s =0.13) \) might be due to greater dispersion of \( \text{Hgp} \) with higher wind speed and subsequent concentration decrease. In contrast, weak positive correlations of GEM and RGM with wind speed \( (r_s =0.09, r_s =0.05, \) respectively) were observed. This result contradicted what reported
by Gabriel et al. (2005). They observed the GEM concentration correlated inversely with wind speed both in Tuscaloosa, AL (urban site) and Cove Mountain, TN (rural site).

5.1.3 Relative Humidity

Figure 15 also illustrates the relationship between the mercury concentrations with relative humidity. There was no statistically significant relationship between RH and GEM. Yet, negative correlation of Hg$_p$ and RGM with RH were observed. Seasonal correlations between RH and all three mercury species were statistically significant ($p<0.0001$), as seen in Appendix B. A negative correlation between GEM and RH was seen in summer; however, the correlations between GEM and RH in the rest of seasons were positive.

There were negative correlations for RGM vs. RH and Hg$_p$ vs. RH for all the seasons. The negative correlation between RGM and RH might be attributed to the elevated chemical reduction of RGM back to GEM with higher humidity. Munthe, Xiao, and Lindqvist (1991) found that conditions of high humidity could act as potential reactors for oxidation-reduction reactions between GEM and RGM. In such an open aqueous system, oxidation and reduction mercury can take place simultaneously, yet reduction prevails, especially under windy conditions, for the accelerated removal of dissolved GEM from the aqueous system (Zhang & Lindberg, 2001; Fitzgerald et al., 1991). Han et al. (2004) reported significant positive correlations between water vapor mixing ratio with GEM in the three New York sites and suggested the reduction of Hg$^{2+}$ to GEM took place in the liquid water droplets in clouds and fogs.
As for the negative correlation between $H_{g_p}$ and RH, it contradicts what Lynam and Keeler (2005) concluded after comparing the data obtained in Detroit and in Tuscaloosa, AL (Lynam & Keeler, 2002). They suggested that higher humidity could facilitate gas to particle conversion of RGM to $H_{g_p}$, resulting in elevated $H_{g_p}$ concentration.

### 5.1.4 Barometric Pressure

$H_{g_p}$ was found to consistently display positive correlation with atmospheric pressure through the seasons. This is in good agreement with Keeler and Dvonch’s (2005) finding that synoptic-scale meteorological conditions characterized by high pressure (>1020 mbar) systems were associated with the elevated (above-average) $H_{g_p}$ concentrations during the fall and winter months at the sites located in the eastern and southern portions of the Great Lakes region. Keeler and Dvonch (2005) also observed the lower atmospheric pressure (1015 mbar) during the spring and summer time was associated with above average gas-phase mercury concentrations (TGM). However, only weak negative correlation of GEM with pressure ($r_s = -0.07$) in summer was observed at the Athens site. The rest could not be verified here.

### 5.1.5 Solar Radiation Flux

There were positive correlations between RGM and solar radiation flux observed during all seasons. And the correlation was the most prominent in the summer months. This could be attributed again to the seasonal cycle of oxidants (e.g. ozone) that the oxidants are at higher concentrations under higher solar radiation flux in summer (Lee, Dollard, & Pepler, 1998), and consequently the oxidization of GEM to RGM can be
enhanced. Lynam and Keeler (2005) also noted in one study in Detroit, MI, that RGM and ozone were both at elevated concentrations coinciding with the peak solar radiation.

5.2 Mixing Height and Mercury Concentration

The fluctuation of the atmospheric boundary layer is considered to be an important factor affecting mercury concentrations (Blanchard et al., 2002; Han et al., 2004; Gabriel et al., 2005). Episodes of mixing height change and mercury species variation were observed at the Athens sites. Three major patterns of mixing height shift and the subsequent mercury concentration variation were identified. The following passages elaborate such correlation. For each pattern, one representative episode is illustrated. The mixing height was calculated using the HYSPLIT 4 model.

5.2.1 Pattern 1

Figure 16 shows the positive correlation between GEM and mixing height observed in August of 2004. The drastic decrease of the boundary layer during the night (nocturnal boundary layer) suppressed convective mixing between low level air and the lower level of free troposphere. GEM in the free troposphere is subject to long-range transport (Swartendruber et al., 2006) and thus free troposphere is recognized as a well known global mercury pool.

The increased solar radiation in the early morning broke up the nocturnal boundary layer. The drastic rise of the boundary layer resulted in the convective and turbulent mixing between boundary layer and the free troposphere. GEM was brought down from the lower free troposphere and the measured GEM concentration was consequently increased. A study conducted in Bush Estate, Scotland (Moxley & Cape,
1997) also observed a similar phenomenon: the elevated concentration of CO in the morning due to air mixing with troposphere as the nocturnal boundary layer broke. Notably, good association of CO and GEM in the free troposphere has also been reported (Jaffe et al., 2005).

As for the observed RGM spike, it was due to the increased turbulent mixing in the morning allowing emitted RGM to be advected over the Ohio River valley airshed reaching the Athens site as well as the oxidation occurring in the plume. As depicted in Figure 17, the increased concentration of SO₂ indicated the advected plume. Ozone spike and the simultaneous NO₃ decrease were seen during the same period of time. The elevated RGM and ozone concentrations indicated the oxidation of GEM to RGM (Lynam & Keeler, 2005).

![Figure 16. Relationship between mixing height and GEM concentrations: pattern 1.](image)
Figure 17. Co-pollutants concentrations during the episode in August 2004. From Fahrni et al. (2007).

5.2.2 Pattern 2

Figure 18 shows the inverse correlation between mixing height and GEM during an episode event in March of 2005. The observed high pressure system (see Figure 19) stagnated the surface air and provided weak mixing. During this episode, the increase of the mixing boundary layer under such a stable atmosphere enhanced the convective and turbulent mixing at 200 to 500 m level. GEM dispersion occurred due to the elevation of the mixing height which resulted in the decrease of GEM concentration. During the same time period, the SO$_2$ and NO$_x$ increased drastically as shown in Figure 20, indicating the arrival of a plume from the anthropogenic emission source (such as coal-fired power plants, waste incinerators, and steel production). The drop of GEM was also attributed to
the oxidation of GEM, causing the simultaneous spike of RGM, in spite of the decrease of ozone concentration. The similar mercury depletion events were also observed elsewhere during spring time in Arctic (Lindberg et al., 2001). The oxidation of GEM and the loss of ozone were most probably due to the chlorine and bromine compounds according to Lindberg et al. (2001).

Figure 18. Relationship between mixing height and GEM concentrations: pattern 2.
Figure 19. Synoptic weather condition on March 29, 2005 (19:00 EST). From Unisys (2005).

Figure 20. Co-pollutants concentrations during the episode in March 2005. From Fahrni et al. (2007).
5.2.3 Pattern 3

This pattern is characterized with the increase of mixing height with the ensuing elevation of both GEM and RGM concentrations. The representative episode took place in October 2004 (Figure 21). Under the stable condition, increasing of the mixing height provided enhancement of turbulent mixing and hence facilitated the advection. During this episode, primary emissions of GEM and RGM from nearby anthropogenic emission sources (coal-fired power plants) were advected to the Athens site. Thus GEM and RGM were both seen to increase. This argument was substantiated by the observed increase of SO$_2$ and NO$_x$ concentrations during the event, suggesting the arrival of a plume, as shown in Figure 22. The decrease of ozone during the plume event could be attributed to the NO$_x$ titration effect (Sillman, 1999).

![Figure 21.](image.png)
Figure 22. Co-pollutants concentrations during the episode in October 2004. From Fahrni et al. (2007).

5.3 Multiple Linear Regression

Multiple linear regression analysis of speciated mercury concentrations against meteorological parameters was performed to determine the collective impacts of meteorological variables controlling temporal variations of mercury species. Hien, Bae, Tham, Nhan, and Vinh (2002) utilized multiple linear regression to investigate the meteorological impacts on the particulate matter during the monsoon season in Hanoi, Vietnam and found the meteorological parameters could explain a considerable portion (~60% - ~74%) of particulate concentration variations.

The independent variables used in this study include temperature (T), relative humidity (RH), solar radiation flux (SF), atmospheric pressure (BP), wind speed (WS),
and precipitation (PR) for surface meteorological parameters and potential temperature (PT) and mixing height (MH) for vertical atmospheric turbulence parameters. A delayed impact of the meteorological conditions on mercury species was observed. To take into consideration of this impact, the meteorological data with three hours lag time was incorporated in the dataset as independent variables. Thus 16 independent variables were used as descriptors for this analysis. A stepwise multiple regression was conducted for season and direction and determinants with statistical significance \( (p<0.05) \) were selected. Henceforth, northeast, east and southeast directions will be designated as the eastern cluster and northwest, west and southwest directions as the western cluster.

Appendix C, D, and E present the multiple linear regression results for GEM, Hgp, and RGM, respectively, arranged by season as well as by wind direction. The symbols marked with subscript “P” denote the parameters that have 3-hour delayed effects. Figure 23 illustrates the result in a more visual manner: the distance to the center corresponds to \( R^2 \) value in that direction.

GEM during the cooler seasons (spring and winter), the major determinants explaining the variance of mercury for the eastern cluster were T, BP, PT, delayed PT and MH while WS, delayed MH, delayed RH and PT were the determinants for the western cluster for the same period. However, for the warmer seasons (summer and fall), T and PT were the determinants for the eastern cluster, whereas T, BP and RH were the determinants for the western cluster. For Hgp during summer and fall, BP, RH, PT and T were the main determinants for the eastern cluster while the same for the western cluster were RH, MH, and PT. During the cooler months, T, PT, and RH were the major
determinants for both the clusters that affect Hg_p. The variance in RGM during the warmer seasons was mainly explained by T, BP, RH and SF for the eastern cluster and by PT, MH and BP for the western cluster. The determinants for the western cluster were MH, BP and PT. For the cooler seasons, the determinants for the eastern cluster were T and RH while those for the western cluster were T, PT, and RH. As Figure 23 shows, the contribution of meteorological conditions to RGM variation from the eastern cluster was greater than that from the western cluster.

Overall, the results showed that meteorological parameters could explain 25-31% of the variation in GEM, 39-47% of the variation in Hg_p, and 26-33% of the variation in RGM from the western cluster and 38-52% of GEM, 42-55% of Hg_p, and 44-48% of RGM variation from the eastern cluster.
Figure 23. Meteorological conditions’ governing on RGM, GEM, and Hgₚ at the Athens site from the different wind directions.
CHAPTER 6: MERCURY TRANSPORT ANALYSIS

6.1 RGM/Hg\textsubscript{p} Ratio Analysis

RGM is known to possess a higher deposition rate than Hg\textsubscript{p} (Malcolm & Keeler, 2002), and the gas-to-particulate conversion of RGM to Hg\textsubscript{p} is an ongoing process. Thus, the higher RGM/Hg\textsubscript{p} ratio might indicate a shorter range of transport of the time, whereas a lower ratio would reflect a longer residence time (Lynam & Keeler, 2005). Lynam and Keeler (2005) argued that RGM/Hg\textsubscript{p} ratio determination could be used as an effective tool to estimate the age of RGM. Values of RGM/Hg\textsubscript{p} ratio were averaged for a given sector and plotted as a function of wind direction with the results displayed in Figure 24.

For the given study period, high (≥0.4) RGM/Hg\textsubscript{p} ratios were observed from the directions ranging from northeast to southeast direction (~20° - ~170°). This might suggest that the emissions coming from these directions were most probably local in nature. The RGM/Hg\textsubscript{p} ratio from the remaining directions was much lower suggesting that the mercury from these directions was most likely aged and the low ratio could be the result of deposition of RGM and/or the conversion of RGM to particulate form.

This finding was also in good agreement with the results of the source apportionment study for PM\textsubscript{2.5} conducted in Athens (Kim, Deshpande, & Crist, 2007). According to this study, the northwest and the southwest directions were seen to contribute to the pool of secondary particulate matter (secondary nitrate and organics) in Athens while the eastern directions primarily brought in local particulates.
Figure 24. RGM/Hgₚ ratio in relation to different directions.

6.2 Conditional Probability Function

The transport of mercury from different wind directions was evaluated by applying the conditional probability function analysis. 10° of direction interval was used in the calculation to achieve a more resolved CPF result. The median values of each mercury species were set as each threshold values. The CPF results were plotted in polar charts (see Figure 25).

As shown in the Figure 21, the GEM attribution was evenly distributed among all directions, indicating that global background was predominant source of GEM at the Athens site. High CPF values of RGM were associated with winds from the northeast, east, and southeast to Athens, suggesting that the sources were possibly located in those
directions. $\text{Hg}_p$ attribution was also equally distributed among all directions. This might indicate that $\text{Hg}_p$ concentrations from the southwest to north directions resulted from gas-particle conversion of RGM associated with regional flow while $\text{Hg}_p$ concentration from the northeast to southeast directions originated from primary influence from local sources. This result is comparable to that found at the rural site in Cove Mountain, TN (Gabriel et al., 2005). Gabriel et al. (2005) reported that GEM and $\text{Hg}_p$ did not display apparent concentration variation in relation to wind direction, whereas RGM did.

Figure 25. CPF results for GEM, RGM, and $\text{Hg}_p$. 
6.3 PSCF Analysis

PSCF was utilized to identify the potential source regions of RGM. Back trajectories starting from the surface monitoring site were calculated using HYSLPLIT 4 model. The National Center for Environmental Prediction (NCEP)/National Center for Atmospheric Research (NCAR) Reanalysis data was used as meteorological input for HYSLPIT 4. When the reanalysis data was not available, the NCEP’s EDAS (Eta Data Assimilation System) data was used instead. The starting height of all back trajectories was set at 500 m, which is approximately the average height of the mixing layer (Gao, Cheng, & Hopke, 1993). By selecting 500 m as the starting height, the impact of surface friction could be diminished and the winds in the lower boundary layer could be clearly represented (Begum, Kim, Jeong, Lee, & Hopke, 2005).

The PSCF value of RGM was calculated first based on 48 hour back trajectories. Han, Holsen, Hopke, and Yi (2005) used the same resolution (48 hour based PSCF) to identify the potential source regions of RGM measured at three rural sites (Potsdam, Stockton, and Sterling) in New York. For this research, median value of the RGM concentration at 3.21 ng/m³ was used as the criterion value to separate the “clean” and “polluted” trajectories.

In order to reduce the uncertainty of PSCF value in grid cells with a small number of endpoints, an arbitrary down weight function $W_{ij}$ was applied when the endpoints in a cell were less than 3 times of the average number of endpoints per cell (Zeng and Hopke, 1989; Han et al., 2005). The total number of endpoints was 254854 and 3849 cells were involved. Thus it gave the average endpoints per single cell at approximately 66. The
following down weight function was integrated in calculating the PSCF values in each grid cell. \( n \) denotes the number of endpoints that fall into a single cell, while \( W_{ij} \) represents the weighting factor:

\[
W_{ij} = \begin{cases} 
0.7 & 90 < n \leq 199 \\
0.5 & 45 < n \leq 90 \\
0.3 & 20 < n \leq 45 \\
0.1 & n \leq 20 
\end{cases}
\]

The grid system covering Ohio and neighboring states was consisted of \( 0.2^\circ \times 0.2^\circ \) cells. Figure 26 shows the calculated PSCF values and the distribution of anthropogenic RGM emission sources in the year of 2002 (USEPA, 2007 e). As it shows, the regions with the highest PSCF values (0.6-0.8) were predominantly located east of Athens. Away from Athens, the PSCF values tended to decline. The majority of anthropogenic RGM emission sources are included in the region with relatively high PSCF values. This result is in good agreement with the CPF result mentioned before, indicating the regions east to Athens are a potential source region contributing to the RGM measured at the Athens site.

In order to test the robustness of the PSCF result, 72 hour back trajectory based PSCF was also calculated. The criterion value and the grid cell dimension remains the same. The average number of endpoints per cell was approximately 80. Thus the following down weight function was applied:

\[
W_{ij} = \begin{cases} 
0.7 & 120 < n \leq 240 \\
0.5 & 60 < n \leq 120 \\
0.3 & 25 < n \leq 60 \\
0.1 & n \leq 25 
\end{cases}
\]
Figure 27 presents the PSCF result. A comparison between the two PSCF runs show that the two PSCF results were in reasonably good agreement (Figure 22 and 23). The PSCF result was thus deemed robust.

Figure 26. PSCF based on 48 hour back trajectory, with a starting height at 500 m.
Figure 27. PSCF based on 72 hour back trajectory, with a starting height at 500 m.
CHAPTER 7: SUMMARY

The understanding of ambient mercury characteristics is an essential basis for imposing sound and effective mercury emission control regulation. However, unknowns remain as to the factors that contribute to the temporal variation of ambient mercury concentration as well as the underlying mechanisms. Thus it is of great interest to the academic community as well as to the regulation authority to investigate such issues. The Center for Air Quality at Ohio University is committed to the ambient mercury research in the Ohio River Valley. The thesis presents parts of the mercury research conducted at the Center,

The ambient mercury concentrations, the air pollutants concentrations, and the surface meteorological data for the research were acquired at the Center’s surface air monitoring site. The unique location of site enables it capture the potential regional transport of air pollutants in the Ohio River Valley. The collected data was then statistically analyzed in terms of source-receptor relationship, meteorological impacts, and transport, for the variation of ambient mercury concentration has been considered as a result of influences of a combination of emission strength, chemistry, and meteorological conditions. An analysis of their temporal variability showed that the concentrations of mercury species displayed clear seasonal and diurnal trends with higher concentrations being observed in the cool seasons (winter and spring) as against the warm seasons (summer and fall). As regard to the diurnal trends, GEM experienced its lowest concentrations in the early morning, and it is the highest around noon. The RGM and Hgp both displayed higher concentrations during the daytime than in the nighttime
The PCA results revealed that the emissions from coal-fired power plants and oxidation were the main sources of RGM. Emissions from coal-fired power plants also contributed to a part of the variation in GEM. The individual effects of meteorological parameters (temperature, relative humidity, wind speed, barometric pressure, and solar radiation) on mercury variation were also evaluated. Three mechanisms of mixing boundary layer shift and mercury concentration change were identified and elaborated. The three patterns are: (1) decrease of GEM concentration during night as a result of nocturnal boundary layer and the rise of GEM concentration in the morning due to the mixing with lower free troposphere; (2) the mixing height increase and GEM drop coupled with oxidation of GEM to RGM; and (3) the rise of mixing height and the simultaneous increase of GEM and RGM concentrations.

Multiple linear regression analysis between the mercury species and (surface and vertical) meteorological parameters revealed that a greater fraction of the mercury variance could be explained by meteorology for the eastern directions than for the western directions. Analyzing the RGM/H$_{g_p}$ ratio with respect to the wind direction further found that the RGM sources affecting Athens in the east were most probably local in nature.

The CPF analysis identified the possible source directions of the mercury species. It appeared that RGM was mostly transported from the northeast, east and southeast of Athens, whereas GEM and H$_{g_p}$ appeared to be impacting Athens from all directions.
PSCF was used to identify the possible source regions of RGM measured at the site. The result shows the high PSCF regions predominantly located in the eastern direction. This is consistent with the CPF result.

Therefore, this thesis provided a comprehensive account that explained the temporal variation of ambient mercury concentration in terms of source-receptor relationship, meteorological impacts, and the transport pattern of mercury. Such results do not warrant a direct order for mercury control over specific mercury emission sources. Yet it suggests possible mercury reduction could be achieved by reducing the mercury emission from the anthropogenic emission sources including coal-fired power plants located in the regions flagged with high PSCF value, which are mostly located in the eastern directions to Athens.
CHAPTER 8: FUTURE WORK

The thesis evaluated the source-receptor relationship of mercury species, and meteorological impacts, as well as the atmospheric transport pattern; however, the chemical transformation of mercury was not discussed in great detail. Episodes of RGM spikes and simultaneous depletion of GEM were observed at the site (see Figure 18) frequently and mercury chemistry was believed to play an important role in this process. The preliminary work on two-phase box modeling was able to simulate such dynamics, and showed the involvement of redox chemistry of halogen, ozone, and OH radicals during such plume events. A more refined and robust research is needed to better understand the mercury chemistry. Two-phase box modeling thus should be an indispensable part of future research work.

The future research will also need to focus on mercury wet deposition. One of the most important aspects of the research work is to identify the sources for mercury wet deposition. The source apportionment research requires precipitation-event-based sampling apparatus which is capable of capturing highly time-resolved data and advanced analytic techniques that can quantify the dissolved chemical species, including trace metals. An enhanced multivariate source apportionment technique such as positive matrix factorization (PMF) then can apply to apportion sources of wet deposited mercury.
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### APPENDIX A: SELECTED LITERATURE REVIEW ON MERCURY STUDIES INVOLVING PCA

<table>
<thead>
<tr>
<th>Literature</th>
<th>Site Details</th>
<th>Study duration</th>
<th>Mean Concentration</th>
<th>Principal Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames et al., 1998</td>
<td>Remote site in upper state, Peach River, New York</td>
<td>Hg$_{g}$: October, 1991–September, 1993; Gaseous mercury: July, 1992–September, 1994.</td>
<td>Mean vapor phase mercury $\sim$ 2.5 ng/m$^3$; mean particulate mercury $\sim$ 0.09 ng/m$^3$</td>
<td>Fine Hg$<em>{g}$: factor of regional, and copper smelter; coarse Hg$</em>{g}$: Al processing factor</td>
</tr>
<tr>
<td>Kim and Kim, 2001</td>
<td>Dense residential area surrounded by parks, Seoul, Korea</td>
<td>September 1997; May-June 1998</td>
<td>Mean TGM for two campaigns: 3.94 and 3.43 ng/m$^3$</td>
<td>Fall daytime: TGM, meteorological parameters, and ozone in factor 2; the rest of time: TGM and criteria pollutants in factor 1</td>
</tr>
<tr>
<td>Blanchard et al., 2002</td>
<td>Three rural sites around the Great Lakes</td>
<td>1997-2001</td>
<td>Mean TGM: 1.5 -2 ng/m$^3$</td>
<td>Point Petre: mercury in factor 3 of general anthropogenic/coal combustion; Egbert: mercury in factor 2 of general anthropogenic activities</td>
</tr>
<tr>
<td>Lynam and Keeler, 2006</td>
<td>Urban site with industrial facilities and highway nearby, Detroit, Michigan</td>
<td>July, Sep 2000; July 2001; Jul-02</td>
<td>GEM: between 1.8 ng/m$^3$ for July 2000, 1.7 ng/m$^3$ for September 2000; 2.0 ng/m$^3$ for July 2001; 3.1 ng/m$^3$ for July 2002</td>
<td>July 2000: RGM in photochemistry factor and combustion factor; Sept 2000: all mercury species in coal combustion factor; July 2001: RGM in factor of photochemistry plus combustion, GEM in combustion factor; July 2002: GEM in combustion factor</td>
</tr>
<tr>
<td>Swartzendruber et al., 2006</td>
<td>No local source influence, 2.7km asl, Portland, Washington</td>
<td>May-August, 2005</td>
<td>Mean GEM, Hg$_{p}$, RGM concentrations were 1.54 ng/m$^3$, 5.2 pg/m$^3$, 43 pg/m$^3$</td>
<td>RGM in factor 1 of free troposphere influence</td>
</tr>
<tr>
<td>Liu et al., 2007</td>
<td>Urban site with industrial facilities and highway nearby, Detroit, Michigan</td>
<td>Entire year 2003</td>
<td>Mean GEM, Hg$_{p}$, RGM concentrations were 2.2±1.3 ng/m$^3$, 20.8±30.0, and 17.7±28.9 pg/m$^3$</td>
<td>Mercury species in factor 2, anthropogenic sources particularly coal combustion; GEM also in factor 2, climatological influence</td>
</tr>
</tbody>
</table>
APPENDIX B: SEASONAL SPEARMAN CORRELATION COEFFICIENTS FOR MERCURY SPECIES AND METEOROLOGICAL PARAMETERS

<table>
<thead>
<tr>
<th>Variables</th>
<th>T</th>
<th>RH</th>
<th>BP</th>
<th>WS</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEM</td>
<td>-0.17***</td>
<td>0.11***</td>
<td>0.00</td>
<td>0.05**</td>
<td>-0.05**</td>
</tr>
<tr>
<td>Hg</td>
<td>-0.18***</td>
<td><strong>-0.35</strong>*</td>
<td>0.27***</td>
<td>-0.16***</td>
<td>0.06**</td>
</tr>
<tr>
<td>RGM</td>
<td><strong>0.35</strong>*</td>
<td><strong>-0.59</strong>*</td>
<td>0.27***</td>
<td>0.05**</td>
<td>0.17***</td>
</tr>
</tbody>
</table>

Spring

| GEM       | 0.22*** | -0.16** | -0.07** | -0.01** | 0.07** |
| Hg       | 0.10**  | **-0.57*** | 0.24*** | -0.08** | **0.33*** |
| RGM       | 0.16*** | **-0.48*** | 0.20*** | 0.16*** | **0.30*** |

Summer

| GEM       | 0.05**  | 0.12*** | -0.06** | 0.03** | -0.06** |
| Hg       | 0.15*** | **-0.25*** | **0.34*** | -0.18*** | 0.19*** |
| RGM       | **0.30*** | **-0.43*** | **0.31*** | -0.05** | **0.23*** |

Fall

| GEM       | 0.18*** | 0.25*** | 0.07** | -0.09** | 0.07** |
| Hg       | **-0.35*** | **-0.24*** | **0.31*** | -0.27*** | 0.07** |
| RGM       | **0.17*** | **-0.37*** | 0.11*** | 0.03** | **0.10*** |

Note:
Values denote Spearman coefficient of correlation ($r_s$). *** Very significant correlations ($p<0.0001$). ** Significant correlations ($0.0001 \leq p < 0.05$). $r_s \geq 0.3$ are marked bold. MH: mixing height; T: temperature; RH: relative humidity; BP: barometric pressure; WS: wind speed; SF: solar radiation flux
### APPENDIX C: RESULTS OF MULTIPLE LINEAR REGRESSION FOR GEM

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>NE</th>
<th>E</th>
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<th>S</th>
<th>SW</th>
<th>W</th>
<th>NW</th>
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</thead>
<tbody>
<tr>
<td>$R^2$ (p)</td>
<td>0.16</td>
<td>0.38</td>
<td>0.41</td>
<td>0.27</td>
<td>0.29</td>
<td>0.25</td>
<td>0.14</td>
<td>0.24</td>
</tr>
</tbody>
</table>

#### Spring

<table>
<thead>
<tr>
<th>$D$ ($\beta$)</th>
<th>PT(+1.3), T(0.88), MH(-0.23), WS(-0.18)</th>
<th>BP(-0.74), T(+1.11), MH(-0.51), WS(-0.31)</th>
<th>PT(-1.2), T(-0.51), MH(-0.51), MH(-0.18)</th>
<th>MH(-0.37), T(+0.33), RH(0.25)</th>
<th>T(+1.41), PT(-0.25), RH(0.16)</th>
<th>MH(-0.39), BP(0.62), T(+0.88)</th>
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</thead>
</table>

#### Summer

<table>
<thead>
<tr>
<th>$D$ ($\beta$)</th>
<th>SF(0.51), SF(-0.38), WS(-0.26)</th>
<th>PT(-1.8), T(0.89), MH(0.51)</th>
<th>PT(1.09), RH(0.66), SF(0.57)</th>
<th>PT(1.44), RH(0.61)</th>
<th>RH(-0.61), RH(0.54)</th>
<th>BP(-1.4), RH(0.45)</th>
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</thead>
</table>

#### Fall

<table>
<thead>
<tr>
<th>$D$ ($\beta$)</th>
<th>T(1.65), PT(-0.69), RH(0.68), SF(-0.34), MH(-0.33), SF(-0.28)</th>
<th>T(1.49), RH(0.61), MH(-0.53), MH(-0.38), SF(-0.24)</th>
<th>PT(-1.0), T(0.90), BP(0.90), RH(0.51), SF(-0.3)</th>
<th>T(1.87), PT(-1.3), BP(0.73), RH(0.70), SF(-0.22)</th>
<th>T(1.49), T(-1.1), T(0.73), RH(0.39), SF(-0.18)</th>
<th>BP(0.24), T(0.56), PT(-0.2)</th>
</tr>
</thead>
</table>

#### Winter

<table>
<thead>
<tr>
<th>$D$ ($\beta$)</th>
<th>PT(+1.11), T(-0.49), BP(0.30), RH(0.28), MH(-0.23)</th>
<th>PT(-0.83), T(0.80), Solar(-0.41), MH(-0.38), RH(0.36), R(-0.37)</th>
<th>T(1.14), PT(-0.85), Solar(-0.41), MH(-0.38), RH(0.36), R(-0.37)</th>
<th>RH(0.37), PT(0.24), W(0.24)</th>
<th>RH(0.40), T(-0.53), BP(0.37), RH(0.25), WS(-0.20)</th>
<th>PT(-1.1), T(0.56), MH(-0.45), WS(-0.31), SF(-0.28), R(0.15)</th>
</tr>
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</table>

**Note:**
Statistical Significance of Determinants: p<0.05.

*D ($\beta$) is determinants with standardized coefficients, $\beta$. 

Statistical Significance of Determinants: p<0.05.
APPENDIX D: RESULTS OF MULTIPLE LINEAR REGRESSION FOR HgP

<table>
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<tr>
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<td>R² (p)</td>
<td></td>
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</tr>
<tr>
<td>Spring</td>
<td>0.34</td>
<td>0.56</td>
<td>0.52</td>
<td>0.49</td>
<td>0.57</td>
<td>0.31</td>
<td>0.35</td>
<td>0.32</td>
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<tr>
<td>D (β)</td>
<td>T(-0.50), PT(-0.50), RH(-0.26), MH(0.20), WS(-0.19),</td>
<td>T(-1.29), RH(-0.81), SF(0.45), WS(-0.30), BP(-0.26),</td>
<td>T(-1.0), RH(-0.81), SF(0.45), WS(-0.30), BP(-0.26),</td>
<td>T(-1.9), PT(-0.50), RH(-0.26), MH(0.20), WS(-0.19),</td>
<td>T(-1.9), PT(-0.50), RH(-0.26), MH(0.20), WS(-0.19),</td>
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<td>T(-1.9), PT(-0.50), RH(-0.26), MH(0.20), WS(-0.19),</td>
<td>T(-1.4), PT(-0.50), RH(-0.26), MH(0.20), WS(-0.19),</td>
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<tr>
<td>Summer</td>
<td>0.58</td>
<td>0.47</td>
<td>0.79</td>
<td>0.77</td>
<td>0.79</td>
<td>0.69</td>
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<tr>
<td>D (β)</td>
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<td>RH(-0.89), MH(0.88), BP(0.77), MH(0.55), RH(-0.34), BP(0.21),</td>
<td>RH(-0.93), MH(-0.61), RH(-0.55), BP(0.21),</td>
<td>RH(-0.55), T(-0.40), BP(0.28), MH(0.23), WS(-0.19),</td>
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<td>RH(-0.40), BP(0.40), MH(0.23), WS(-0.19),</td>
<td>RH(-0.40), BP(0.40), MH(0.23), WS(-0.19),</td>
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<tr>
<td>Fall</td>
<td>0.29</td>
<td>0.16</td>
<td>0.20</td>
<td>0.24</td>
<td>0.46</td>
<td>0.28</td>
<td>0.36</td>
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<tr>
<td>D (β)</td>
<td>T(-1.5), PT(1.08), RH(-0.64), RH(0.55), SF(-0.32), MH(0.28),</td>
<td>RH(-0.29), BP(-0.23), T(-0.15), RH(-0.31),</td>
<td>PT(0.46), SF(0.38), BP(0.34), PT(1.48), SF(-0.29), FP(0.34),</td>
<td>MN(0.276), RH(-0.44), MH(-0.17), WP(0.194), SF(-0.29), FP(0.34),</td>
<td>MN(0.276), RH(-0.44), MH(-0.17), WP(0.194), SF(-0.29), FP(0.34),</td>
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<tr>
<td>Winter</td>
<td>0.37</td>
<td>0.47</td>
<td>0.59</td>
<td>0.65</td>
<td>0.38</td>
<td>0.35</td>
<td>0.12</td>
<td>0.22</td>
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<tr>
<td>D (β)</td>
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<td>RH(-0.65), WS(-0.43), BP(-0.29),</td>
<td>PT(-0.99), WS(-0.43), BP(-0.29),</td>
<td>PR(0.27), BP(0.38), MH(-0.17),</td>
<td>PR(0.27), BP(0.38), MH(-0.17),</td>
<td>PR(0.27), BP(0.38), MH(-0.17),</td>
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Note:
Statistical Significance of Determinants: p<0.05.
'D (β) is determinants with standardized coefficients, β.
### APPENDIX E: RESULTS OF MULTIPLE LINEAR REGRESSION FOR RGM

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<tr>
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<th>NE</th>
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<th>SW</th>
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<tr>
<td>R² (p)</td>
<td>0.40</td>
<td>0.51</td>
<td>0.61</td>
<td>0.47</td>
<td>0.30</td>
<td>0.40</td>
<td>0.27</td>
<td>0.24</td>
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<tr>
<td>D (β)</td>
<td>PT (0.64), T (0.62), Td (-0.59), RH (-0.44), WS (0.17), MH (-0.15)</td>
<td>T (0.61), Td (0.53), MH (0.19), WS (-0.15), SF (-0.48), MH (0.46), SF (-0.39)</td>
<td>T (0.98), Td (-0.90), RH (-0.65), SF (-0.24),</td>
<td>PT (1.41), PT (-1.0), RH (-0.53), SF (-0.24),</td>
<td>BP (0.37), PR (0.31), RH (-0.66), MH (-0.19), WS (-0.17)</td>
<td>T (0.95), Td (-0.66), RH (-0.25), SF (-0.24), WS (-0.22), BP (-0.17)</td>
<td>RH (-0.36), WS (-0.29), SF (0.17)</td>
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**Spring**

<table>
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<tr>
<th>R² (p)</th>
<th>0.23</th>
<th>0.29</th>
<th>0.39</th>
<th>0.49</th>
<th>0.25</th>
<th>0.23</th>
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<th>0.63</th>
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<tbody>
<tr>
<td>D (β)</td>
<td>WS (0.37), BP (0.27)</td>
<td>T (0.78), Td (-0.69), RH (-0.51), MH (-0.26)</td>
<td>BP (1.54), BP (-1.1)</td>
<td>BP (1.51), Td (-1.5), BP (-1.4), MH (-0.67), T (0.571)</td>
<td>BP (0.70), RH (-0.52), MH (-0.31)</td>
<td>BP (0.38), BP (0.22), MH (-0.19)</td>
<td>BP (0.58), WS (0.40), RH (-0.32), MH (0.29)</td>
<td>BP (1.35), BP (-0.86), MH (0.43)</td>
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**Summer**

<table>
<thead>
<tr>
<th>R² (p)</th>
<th>0.18</th>
<th>0.51</th>
<th>0.45</th>
<th>0.43</th>
<th>0.38</th>
<th>0.35</th>
<th>0.21</th>
<th>0.30</th>
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<tbody>
<tr>
<td>D (β)</td>
<td>BP (0.37), T (0.34)</td>
<td>PT (0.88), PT (-0.69), RH (-0.51), MH (-0.26)</td>
<td>RH (-0.49)</td>
<td>SF (0.28), RH (-0.25), SF (0.23)</td>
<td>RH (-0.40), SF (0.25),</td>
<td>PT (1.91), Td (-0.96), PT (-0.84), RH (0.49), WS (-0.23)</td>
<td>BP (0.8), RH (0.34), RH (-0.29), BP (0.37), PR (0.31)</td>
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**Fall**

<table>
<thead>
<tr>
<th>R² (p)</th>
<th>0.30</th>
<th>0.61</th>
<th>0.35</th>
<th>0.37</th>
<th>0.26</th>
<th>0.18</th>
<th>0.19</th>
<th>0.16</th>
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<tbody>
<tr>
<td>D (β)</td>
<td>BP (1.34), BP (-1.2), WS (0.40), MH (0.30), MH (-0.26), Solar (-0.23)</td>
<td>RH (-0.58), T (0.74)</td>
<td>RH (-0.42)</td>
<td>RH (-0.34), WS (0.34), SF (0.30), SF (0.30)</td>
<td>RH (-0.36), WS (-0.24), T (0.17)</td>
<td>RH (-0.29), RH (-0.37), PR (0.27), MH (-0.17)</td>
<td>PT (0.98), PT (-0.62), SF (0.24), SF (0.20)</td>
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</tbody>
</table>

Note:
- Statistical Significance of Determinants: p<0.05.
- D (β) is determinants with standardized coefficients, β.