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Atmospheric Total Gaseous Mercury (TGM) Concentration Measurement in Windsor: A study of Variability and Potential Sources

By

Umme Salma Akhtar

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ABSTRACT

A study was conducted in Windsor to investigate the spatial and temporal variability and potential regional sources of total gaseous mercury (TGM). In 2007, TGM concentration was measured using a mercury vapor analyzer at University of Windsor campus. An annual mean of 2.02±1.63 ng/m^3 was observed with higher concentrations in summer and winter, lower in spring and fall. An annual diurnal pattern was observed: high at night and in the early morning and low in the afternoon. A different diurnal pattern was observed in summer. Pearson correlation and Principal Component Analysis of TGM with meteorological parameters and other air pollutants indicate meteorological parameters, photochemical reactions, and fuel combustion are the major factors influencing TGM temporal variability. Hybrid receptor modeling identified significant potential sources in the south-west of Windsor. A spatial study conducted in October, 2006 using a mobile lab that identified intra-city variability of TGM due to local anthropogenic sources.

DEDICATION

To my parents, husband, and teachers for enthusiastic support

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CHAPTER 1: INTRODUCTION

1.1 Background

Mercury (Hg) is a naturally occurring metallic element, one of the twenty trace elements found in the Earth's crust. Hg is usually found in compounds in Earth's crust rather than in elemental form. The International Mineralogical Association (IMA) has approved the existence of more than a hundred Hg-containing minerals. The most common compounds of Hg are compounds of sulfur as sulfur forms stable complexes with Hg (Parsons and Percival, 2005). The principle ore of commercial Hg production is cinnabar (HgS). Major mineral Hg deposits as HgS are in Almadén (Spain), Idria (Slovenia), Monte Amiata (Italy), California (Coastal Range) and British Columbia (Pinchi Lake) (Rytoba, 2005).

Although Hg is an extremely toxic substance, human beings have extensively used Hg since ancient times in different medical, agricultural, industrial, and scientific purposes because of its unique chemical and physical properties (Poissant et al., 2002). The extensive use of Hg over last several centuries resulted in an increase in the atmospheric Hg concentration and consequent depositions by a factor of three to five compared with preindustrial periods (Krabbenhoft et al., 2005). The Hg pollution problem first drew world's attention after in situ methylmercury (MeHg) poisoning in Minamata Bay and Niigata regions of Japan in 1956 (Appendix A) causing death and long-term health problems (Gupta et al., 2005). After the Minamata incidence, change in policies for Hg uses and emission strategies by different countries resulted in decreases in Hg emissions into the environment (Pacyna and Pacyna, 2005).

Mercury is emitted into the atmosphere from different natural and anthropogenic sources. Once released into the environment, Hg can travel over long distances and consequently deposits onto land and aquatic bodies. Thus, Hg is considered as 'global pollutant' because of its mobility in the environment, affecting regions far from sources (Poissant et al., 2002). Highly toxic organic compounds e.g. MeHg are produced in the aquatic system by naturally occurring biological process and it can bio-accumulate in aquatic food chains (Schroeder and Munthe, 1998). Consumption of fish containing high levels of MeHg can cause neurological damages, kidney effects, delayed development, and cognitive changes in children (HC, 2004). The U.S. Environmental Protection Agency (EPA) lists Hg compounds as "hazardous air pollutants". The EPA issued the Clean Air Mercury Rule on March 2005 to reduce the Hg emissions from coal-fired power plants (USEPA, 2008). Hg has been identified as one of the Tier I substances in the Canada-Ontario Agreement (COA) in this agreement with the International Joint Commission (IJC) targets for the ban or phase out of these substances were initiated (Sang and Lourie, 1997; Green Ontario Provincial Strategy, 2008).

Current background atmospheric Hg concentrations range between 1.5-1.7 ng/m^3 in the Northern Hemisphere (Lindberg et al., 2007). Atmospheric Hg concentrations at these levels are not likely to affect human health (HC, 2004). However, deposition of atmospheric Hg to aquatic surfaces and consequent bioaccumulation of Hg compounds in aquatic food webs at high concentration are a great concern. The rate of accumulation of Hg in an aquatic system is believed to be proportional to the atmospheric Hg concentration (Swain et al., 2007).

Study of atmospheric Hg concentration is important to better understand the Hg chemistry and deposition. A number of studies have been performed on atmospheric Hg concentrations in different rural (Nadim et al., 2001; Han et al., 2004; Lynam and Keeler, 2005; Temme et al., 2007) and urban (Nadim et al., 2001; Capri and Chen, 2002; Denis et al., 2006; Liu et al., 2007) sites. Results of these studies indicate elevated Hg concentration and deposition in urban sites compared to the rural sites. Different temporal variability patterns, i.e. seasonal and diurnal variability, were also observed at urban sites. Temporal variability in urban sites was site specific whereas most of the rural areas had a general pattern. The differences in concentration and variability between urban and rural sites observed could be due to differences in local sources, surface characteristics, meteorological conditions and presence of other pollutants in urban and rural sites (Liu et al., 2007). Thus, more studies in urban areas are recommended to understand Hg emission and deposition processes.

Windsor is an industrial city, located along the Canada-USA border. It is located downwind of several industrial states e.g. Michigan, Ohio, Indiana and experiences transboundary air pollution. The combined effects from local anthropogenic sources and trans-boundary pollution have resulted in poor air quality in Windsor (Ontario Ministry of Environment, 2005). So far, very little research has been conducted on atmospheric Hg concentrations in Windsor. Specifically no significant work was done in Windsor regarding the investigation of temporal variability or identification of contributing factors e.g. potential sources and regional effects.

1.2 Objectives

This research work was aimed at determining temporal and spatial variability of airborne Hg along with identifying potential regional sources of atmospheric mercury. To determine the temporal variability of total gaseous mercury (TGM) concentration, an automatic analyzer Tekran® Model 2537A (Tekran Inc., Toronto, ON, Canada) was set up in a lab at University of Windsor sampling ambient air during the study period of 2007. Other air pollutant concentrations, e.g. ozone, sulfur dioxide were measured at the same location. To determine the spatial variability of TGM concentration in Windsor, the analyzer was set up in Environment Canada's mobile lab during October 2006. Potential regional sources were identified using hybrid receptor modeling. Therefore, the specific objectives of this research are to:

- To investigate the effects of emission and deposition processes on temporal variability of TGM concentration by analyzing
    - ➢ Diurnal, seasonal variability of TGM concentration
    - ➢ Correlation of TGM with meteorological parameters and other pollutants
- To identify source-receptor relationship between the Hg sources and TGM concentration in Windsor by analyzing
    - ➢ Inter-relationships of TGM with meteorological parameters and other pollutants categorizing major factors affecting TGM concentration
    - ➢ Air mass trajectories reaching Windsor identifying potential regional sources
- To determine spatial variability of TGM concentration within Windsor

CHAPTER 2: LITERATURE REVIEW

2.1 Physical and Chemical Properties of Mercury

Mercury is the only metallic element that exists as liquid under standard temperature and pressure. It is dense, metallic shiny silver white in color and odorless. Mercury is highly volatile and some metallic Hg can evaporate forming colorless and odorless Hg vapour at room temperature (Poissant et al., 2002). It has high surface tension that accounts for its high adsorptive properties on solids. Hg expands and contracts uniformly as a function of temperature when heated and cooled. It conducts electricity well but has high thermal conductivity (Schroeder and Munthe, 1998). Mercury readily combines with most of the metals, except iron and platinum, to form amalgams (Parsons and Percival, 2005).

Mercury vapour is sparingly soluble in water and relatively stable at normal temperature. Hg vapour does not react noticeably with air (oxygen and nitrogen), ammonia, carbon dioxide, nitrous oxide, or oxygen but combines readily with halogens, sulfur, selenium, and phosphorous (McCorquodale et al., 1992). Important physical and chemical properties of Hg are listed in Table 2.1. These unique physical and chemical properties of Hg lead to its extensive use in industry. Over 3000 distinct industrial applications of Hg have been identified (McCorquodale et al., 1992). Since the industrialization period, Hg has been used in different applications such as chlor-alkali industries, electrical equipment (batteries, fluorescent lamps, switches), measuring devices (thermometers, barometers), as preservatives, pharmaceuticals, fungicides and antiseptics, and in dental amalgams (Parsons and Percival, 2005).

Table 2.1: Physical and chemical properties of mercury (Parsons and Percival, 2005)

Parameter	Value
Atomic number	80
Atomic weight	200.59 amu
Atomic radius	150 pm
Oxidation states	0, +1, +2, +3
Specific Gravity	13.5
Melting point	-38.9°C
Boiling Point	356.58°C
Vapour pressure	0.0002 Pa (234 K)

Mercury can exist in several forms in the atmosphere, such as elemental, inorganic, or organic forms, because of its unusual inter-conversion properties. These different forms are also different in terms of properties and toxicities (Sang and Lourie, 1997). In the atmosphere, Hg can occur in three different oxidation states: 0, +1, and +2. Gaseous elemental mercury (GEM) in the zero oxidation state (Hg^0) constitutes more than 97-99% of the total Hg found in the atmosphere while the remainder is comprised of Hg (II), either as reactive gaseous mercury (RGM) or as particulate mercury (Hg_p) (Fitzgerald et al., 1991; Poissant et al., 2002). Total gaseous mercury is the combination of the three species GEM, RGM and particulate mercury. Organo-mercury compounds, e.g. monomethyl and dimethyl mercury, in small amounts can also be present in the atmosphere (Lindberg and Stratton, 1998). The presence of Hg(I) in the atmosphere is very unusual (Schroeder & Munthe, 1998). The fraction of different species in the atmosphere depends on the meteorological conditions, presence of oxidants and reductants in the atmosphere, and local sources (Liu et al., 2007).

Hg^0 is chemically inert, exhibits high volatility and low solubility in water. These properties result in high residence time of Hg^0 in the atmosphere, about 0.5-2 years. Therefore, Hg^0 can be transported over long distances (Poissant et al., 2002). RGM has a higher solubility in water, i.e. 10^5 times more soluble than Hg^0, and has an atmospheric residence time of a few days to a few weeks (Lin and Pehkonen, 1999). Gaseous Hg (II) is removed from air by wet deposition, i.e. rain, snow. Oxidized Hg (II) associated with particles (Hg_p) is deposited by both wet and dry deposition (by gravity) (Poissant, 2000). Thus, Hg_p has different residence time in the atmosphere depending on particle sizes and meteorological conditions (Sang & Lourie, 1997). Typically, the deposition rate of Hg_p is higher than the other two species (Hg^0 and gaseous Hg (II)).

2.2 Health Concerns of Mercury Pollution

The Extent of Hg toxicity depends on some factors including the route of exposure, forms, and concentration of Hg in the media. The major pathway of Hg exposure is the consumption of aquatic foods containing high concentration of MeHg (EC, 2008a). When aquatic food containing MeHg is consumed, approximately 95% of the MeHg is absorbed through the stomach and intestinal tract. MeHg can be transferred to the blood stream and pass through the blood-brain barrier (Gupta et al., 2005). Toxic effects of MeHg could range from itchiness of the skin, numbness, tremor, tunnel vision, loss of hearing, slurred speech, abnormal behaviour, to cerebral palsy, coma and death depending on the level of exposure (EC, 2008a). Exposure to Hg is more risky for pregnant women, because exposure to lower level MeHg may damage a developing baby's brain and other tissues adversely affecting the development of the central nervous system and may cause psychomotor retardation (HC, 2004; EC, 2008a).

GEM can enter the human body by inhalation or absorption through the skin if the concentration is very high in the atmosphere. If inhaled, approximately 80% enters the blood stream and consequently spreads to all other parts of the body affecting mostly the brain and the kidney. Once accumulated in the kidney and brain, it is readily converted to inorganic forms and can exist there for a long time (HC, 2004). Ingestion is the major pathway of inorganic mercury entering the body. Most of the inorganic mercury accumulates in the kidney, and might cause kidney failure. Other effects could be tremors, loss of co-ordination, slower physical and mental responses, vomiting, bloody diarrhea and gingivitis (Gupta et al., 2005; EC, 2008a).

2.3 Sources, Sink and Fate of Mercury

Based on the Hg emission to the atmosphere, sources can be categorized into: natural sources, anthropogenic releases, and re-emission of Hg (Banic et al., 2005). Annual global input of Hg from all sources including natural, anthropogenic, and re-emission from water surfaces into the atmosphere is about 5500-6000 tons (Moore, 2003). Due to lack of data, the relative contribution from each source could not be identified. However, a study based on modeling of the global Hg cycle suggested a proportion of 40%, 40% and 20% from natural, anthropogenic, re-emitted anthropogenic Hg sources respectively (Hudson et al., 1995).

Major natural sources of Hg emissions are soil and crustal degassing, erosion, vegetation respiration, aquatic evaporation, volcanic and other geothermal activities (McCorquodale et al., 1992). Anthropogenic sources are alternation of earth's crust, mining and base metal smelting, burning of fossil fuels containing Hg, industrial processes using Hg directly or indirectly, municipal and medical waste incinerators, and the use and disposal of compounds containing Hg (McCorquodale et al., 1992; HC 2004; Pacyna and Pacyna, 2005). Total global anthropogenic Hg emission for the year 2000 was 2269 tons. About 65% of global anthropogenic Hg emission comes from stationary combustion of fossil fuels, especially coal (Pacyna and Pacyna, 2005). Another significant anthropogenic source revealed from recent research is the emission of Hg from automobiles. A pilot study (Hoyer et al., 2004) conducted in Michigan indicate that automobile emissions could contribute significantly towards atmospheric Hg. Significant amounts of vapour and particulate phase Hg emission from vehicular exhaust were measured in this study. Emission factors for light-duty gasoline vehicles ranged 0.193 – 0.87 ng/km and for diesel vehicle 3.92 – 6.84 ng/km.

Most of the Hg emitted into the atmosphere from various natural and anthropogenic sources is ultimately deposited onto land and aquatic surfaces. Re-emission of Hg is the emission of previously deposited Hg from these surfaces. Approximately 200,000 tons Hg were emitted into the atmosphere from anthropogenic sources since 19th century and about 95% of it exists in terrestrial soils, and 3% in ocean surface waters (Moore, 2003).

Once emitted into the atmosphere, atmospheric Hg can undergo various physical and chemical transformations before being deposited back to the Earth's surface. These chemical reactions can affect the speciation, deposition and concentrations of atmospheric Hg (Poissant et al., 2002). Lin and Pehkonen (1999) have summarized the important chemical reactions involved in the atmosphere. Photochemical processes may be an important pathway for the oxidation of Hg^0, which is enhanced in the presence of water. Important oxidation reactions of Hg^0 involved in the atmosphere are gaseous and aqueous phase oxidation by ozone (O_3), aqueous phase oxidation by hydroxyl radicals (OH°), chlorine ($HOCL/OCL^-$), gaseous phase oxidation by the nitrate radical ($NO^\circ{}_3$). Oxidation of Hg^0 leads to production of Hg (II). Reduction reactions occurring simultaneously in the atmosphere transform some Hg (II) to Hg^0. Important reduction reactions occur in the aqueous phase with the reductants being by sulfite (SO_3^{2-}) and hydroperoxyl radicals (HO_2°). Photo-reduction of Hg (II) can also produce Hg^0 at a significant rate.

Figure 2.1 shows the major pathways of Hg in the environment. The cycle is described here based on studies by Morel et al., 1998; Poissant et al., 2002; EC, 2008b. Mercury is generally emitted as Hg^0, Hg (II) and Hg_p from different anthropogenic and natural sources, whereas re-emission from soil, water and plants occurs mostly in gaseous forms (Hg^0, Hg (II)). Inorganic Hg is also released from anthropogenic sources to aquatic surfaces. Runoff, soils, or litterfall also contribute Hg to aquatic surfaces. In the atmosphere, inter-conversion of Hg^0 and Hg (II) occurs in the presence of oxidants and reductants or other factors as described earlier. Most of the oxidation and reduction reactions occur at a solid-liquid interface in fog and cloud droplets. Oxidation of Hg^0 leads to production of Hg (II), which is highly soluble in water, thus being deposited easily by wet deposition (rain and snow). Hg (II) can be adsorbed on soot particles in the atmosphere forming Hg_p especially in industrialized areas and is removed from the atmosphere to land or water surface by dry and wet deposition.

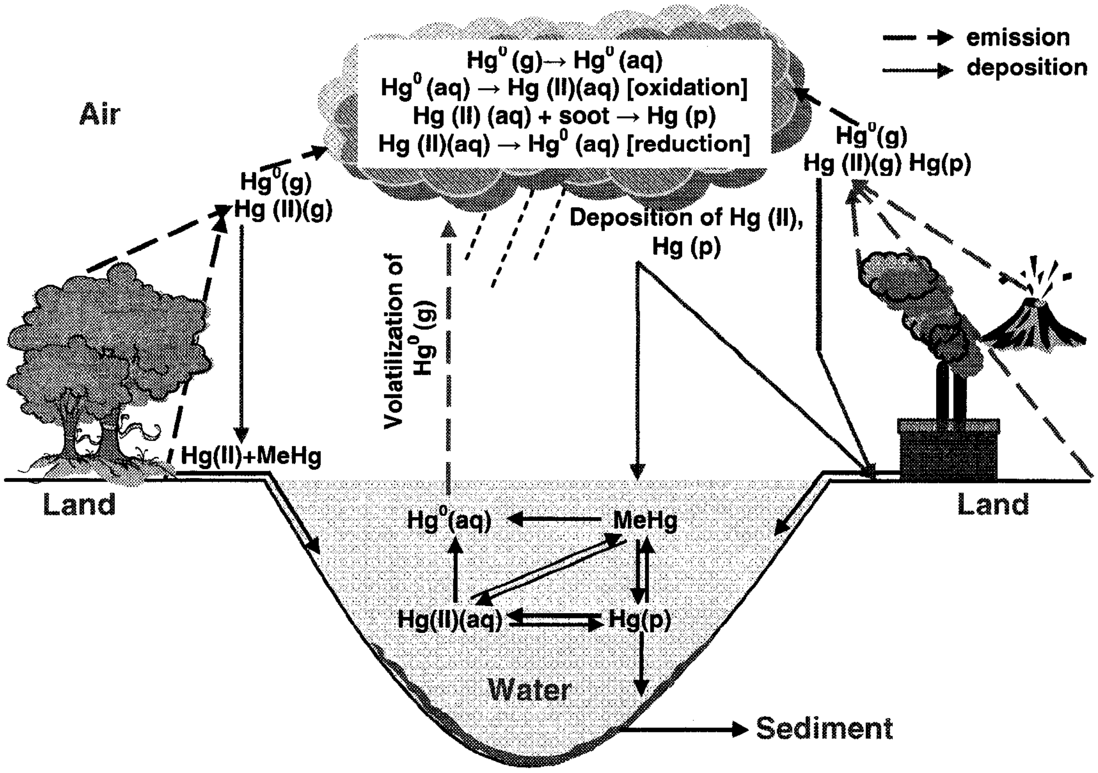

Figure 2.1: Mercury cycle in the environment

In the water, nearly 95% of the Hg (II) forms organic complexes with humic acids. It may also form inorganic complexes with hydroxide, chloride, sulphides. In the presence of methanogenic and sulphate reducing bacteria and high concentration of organic compounds, Hg (II) complexes are converted into highly toxic and bioaccumulative MeHg. Small organisms and plants take up MeHg as they feed and this Hg tends to accumulate in their tissues. MeHg is bio-accumulated at a high concentration level as larger species consume the small organisms and plants. This process continues up in the food chain. Human and other living animals consuming the predatory species are directly affected by bioaccumulation of MeHg. Demethylation of Hg complexes and reduction of Hg (II) may produce Hg^0, which evaporates back to the atmosphere as Hg^0.

Hg emission from both natural and anthropogenic sources contributes to the global Hg atmosphere. Hg can travel over long distances once released into the atmosphere, before deposition. As described earlier, oxidation of Hg^0 in the presence of oxidants transforms it into Hg (II), which is relatively immobile. Wet and dry depositions of Hg (II) onto terrestrial surfaces cause removal of atmospheric Hg. Chemical, photolytic, or biological reduction of Hg (II) to Hg^0 can enhance the mobility of Hg into the atmosphere (Poissant et al., 2002). Elevated Hg concentrations were observed at remote lake regions far from the anthropogenic sources (Swain et al., 1992; Kellerhals et al., 2003). This indicates the transportation of Hg from sources and the consequent deposition is the major pathway of contamination in remote locations. Thus, the emission of Hg from local sources affects not only the local area; it enters in the global troposphere.

2.4 Measurement of Ambient Mercury

2.4.1 Canadian Atmospheric Mercury Measurement Network (CAMNet)

Environment Canada established the Canadian Atmospheric Mercury Measurement Network (CAMNet) in 1995 at 11 rural sites across Canada to provide long-term monitoring of TGM concentration. The location of the monitoring sites ranged from approximately 43° to 82° N latitude and 62° to 123° W longitude across Canada as shown in Figure 2.2. The objectives of CAMNet were to measure TGM concentration throughout the year with the aim to improve the current understanding of the atmospheric transport, transformation and removal processes of Hg^0. This network works to provide information on the occurrence, pathways, behavior and fate of Hg emitted into the atmosphere from sources (EC, 2002). Other studies on CAMNet sites data were conducted by Poissant (1999 and 2000); Blanchard et al., (2002).

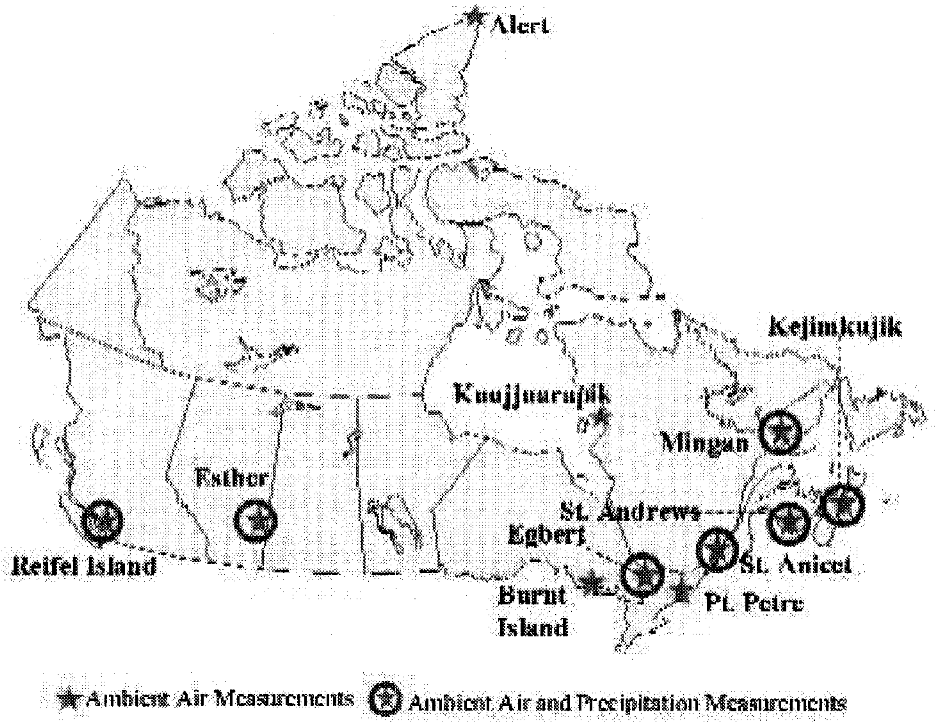

Figure 2.2: Location map of CAMNet sites (EC, 2008c)

An overall average concentration of 1.58 ± 0.17 (ng/m^3) was calculated for 11 rural CAMNet sites during 1995-2005 (Temme et al., 2007). Among these sites, the highest overall average TGM concentrations were observed at the rural affected areas compared to the remote sites. Higher variability was also observed in these areas over the entire period. Exposure to anthropogenic sources near these sites resulted in higher concentrations of Hg. The highest and the lowest concentrations were observed in late winter and fall respectively in most of the sites. Another study conducted on 10 sites of

CAMNet (Kellerhals et al., 2003) observed diurnal variations of maximum concentration around solar noon and minimum just before sunrise.

2.4.2 Mercury Studies in Rural and Urban Sites

Several studies conducted in rural and urban sites in North America measuring atmospheric Hg are presented in Table 2.2 and Table 2.3, respectively. Average concentrations observed in most of the rural sites were close to the currently accepted background concentration of 1.5-1.7 ng/m^3 for elemental mercury in the Northern Hemisphere (Lindberg et al., 2007). Recent studies conducted in urban areas reported higher Hg concentrations compared to the rural sites and the background concentration. A comparative study (Nadim et al., 2001) conducted in Connecticut at four rural and four urban sites reported overall 3-year mean and average seasonal TGM concentrations were significantly higher in urban sites than the rural sites during 1997-1999. Mercury measurement in Toronto (Denis et al., 2006) showed higher concentration than all the CAMNet sites in Canada.

Table 2.2: Selected mercury studies in rural sites in North America

Location	Study Period	Average conc. (ng/m^3)	Reference
Connecticut (4 sites) USA	1997-1999	1.68	Nadim et al., (2001)
New York (3 sites) USA	2000-2001 (summer only)	2.23	Han et al., (2004)
Dexter, MI, USA	1997-1998	1.5	Lynam and Keeler, (2005)
CAMNet Sites, (11 sites) Canada	1995-2005	1.58±0.17	Temme et al., (2007)

Table 2.3: Selected mercury studies in urban sites in North America

Location	Study Period	Average conc. ± SD (ng/m^3)	Reference
Connecticut (4 sites), USA	1997-1999	2.5±0.9	Nadim et al., (2001)
New York (6 sites), USA	2000 (Jun-Nov)	3.8±0.1	Capri and Chen (2002)
Toronto, Canada	2001-2002	2.5±2.2	Denis et al., (2006)
Detroit, USA	2003	2.2±1.3	Liu et al., (2007)

2.4.3 Comparison of Rural and Urban Sites' Temporal Variability

In terms of seasonal variability, general pattern of higher winter and lower summer TGM concentrations were observed in rural sites (Nadim et al., 2001; Temme et al., 2007). On the contrary, the maximum average concentration was observed in summer in the urban sites. Low concentrations were observed in winter in the Connecticut and New York sites. For diurnal modulation, studies in rural sites have reported high concentrations in daytime and low at nighttime. Diurnal variability in urban areas was site specific. Some studies have found higher daytime and lower nighttime concentrations (Denis et al., 2006) whereas few studies have reported the opposite trend of higher nighttime and lower daytime concentrations (e.g., Liu et al., 2007). Differences in urban and rural TGM concentrations and temporal variability depend on presence of mercury sources, surfaces characteristics, presence of other pollutants and different meteorological conditions at urban sites (Liu et al., 2007). Industrial and commercial activities, i.e. municipal and medical waste incineration, emissions from vehicles, medical and dental operations acts as local sources of in urban areas (Capri and Chen, 2001).

Table 2.4: Summary of comparison in rural and urban studies

Variable	Rural	Urban
Average	Low	High
SD	Low	High
Seasonal variability	High- Winter Low- Summer	High- Summer Low- Winter/Spring/Fall
Diurnal variability	High- Midday Low- Night	Site specific

2.4.4 Correlation of TGM with Meteorological Parameters and Other Pollutants

Study of the relationships between TGM concentration and meteorological parameters as well as other air pollutants supports in understanding the TGM concentration variation and chemical reactions involved. Several studies have conducted correlation analyses for metrological parameters including temperature, relative humidity and other air pollutants i.e., ozone (O_3), sulfur dioxide (SO_2) for different study period (Schroeder and Markes, 1994; Lamborg et al., 1995; Poissant, 1997; Kim and Kim, 2001, Han et al., 2004). Some studies found positive correlation of TGM with ambient temperature (e.g., Kim and Kim, 2001), while some reported negative correlation (e.g., Han et al., 2004). Correlation with relative humidity was negative in both of the studies. In the case of O_3, positive correlation with TGM indicated similar emission regions and transportation for both Hg and O_3 (Lamborg et al., 1995) while negative correlation indicated the occurrence of an oxidation reaction of Hg^0 by O_3 (Schroeder and Markes, 1994). Positive correlation between TGM and SO_2 observed in few studies (e.g. Han et al., 2004) indicates both of the pollutants may have sources in common likely coal combustion. A short term study showed that correlations with some pollutants i.e., NOx and PM_{10} could be different between the two seasons (Kim and Kim, 2001). Thus, variation in correlation of TGM concentration with meteorological parameters and other pollutants could be influenced by different factors including the presence of local sources and local environmental condition as well as study period.

2.4.5 Studies of Source-Receptor Relationships of Mercury

Identification of anthropogenic mercury sources and measurement of Hg emission rates at the sources is very important for Hg pollution management. However, Hg emission measurement at the sources is very costly and challenging. For example, to measure mercury emission from power plant stacks, placement of heavy measurement equipment at a high elevation is required. Source-receptor relationships can be used to estimate contributions from different Hg sources based on observations made at the receptor site. The advantage of this approach is that Hg concentration at the receptor site is required for calculation, while emission data from individual sources are not essential (Lynam and Keeler, 2006).

2.4.5.1 Principal Component Analysis

Principal Component Analysis (PCA) is the most common form of multivariate factor analysis (FA). This statistical approach can be applied to reduce the dimensionality of the data by explaining a large set of variables to a more meaningful and smaller set of variables with a minimum loss of information (Natural Resource Canada, 2005). Several studies have used PCA on urban ambient Hg concentrations (Kim and Kim, 2001; Lynam and Keeler, 2006; Liu et al., 2007) to study source-receptor relationships of atmospheric Hg at urban sites. In these source-receptor studies, analysis was conducted on TGM and other air pollutant concentrations along with current meteorological parameters. Based on this analysis major factors affecting Hg concentrations at urban sites were identified as local urban/industrial sources which included combustion of fossil fuel in power plants, regionally transported Hg, photochemical reactions and seasonal meteorological conditions (Kim and Kim, 2001; Liu et al., 2007). A principal advantage of this method is that PCA also provides the extent of variations explained by each factor in terms of percentage.

2.4.5.2 Potential Source Contribution Function (PSCF)

Another approach of determining source-receptor relationships is the use of the Potential Source Contribution Function (PSCF) (Hopke et al., 1990) model. This hybrid receptor modeling technique uses backward trajectories and measures of Hg concentration at the receptor site. Results of PSCF provide possible potential regions that are related to high concentrations experienced at the receptor site (Han et al., 2007). The basic concept of PSCF is that when a trajectory passes over a region, the air parcel is assumed to collect pollutants emitted in that region and once the pollutant is integrated in the air parcel, the loss of the pollutants is negligible between the source and the receptor site (Polissar et al., 2001). It is assumed that there is no physical or chemical change of the pollutant. The potential source region is divided in small grids. The probability of affecting the sampling site by each grid cell is related to the number of back-trajectory endpoints in that cell during higher concentration as compared to a criteria value in the receptor site. The PSCF model helps to create a map showing the potential sources. The mathematical expression of the PSCF is described here (as in Han et al., 2007): Let n_{ij} be the total numbers of back-trajectory segment endpoints that fall into the specific (i, j) grid cell. m_{ij} are the numbers of trajectory segment endpoints for the same cell while the concentrations at the receptor site are higher than the criteria value. The PSCF value for the (i, j) cell is then defined as

$$\mathrm{PSCF}\,(i, j) = m_{ij}/n_{ij} \tag{2.1}$$

PSCF value for each cell is calculated as the ratio of the numbers of high concentration occurrences (m_{ij}) to the total numbers of both high and low concentration occurrences. Small n_{ij} values can produce high PSCF values, but a high n_{ij} value means that there are more trajectory endpoints in that cell, resulting in higher probability that this cell will affect the receptor site if Hg is emitted from that cell. Thus, Zeng and Hopke (1989) proposed multiplying the PSCF values by an empirical weight function W (n_{ij}) to minimize the error of smaller n_{ij}s from the larger ones. For this study, method 2 from the PSCF Calculation Procedure (Appendix B) was applied to calculate the weight function values (Hopke et al., 2007).

It can be expressed as follows:

$$W_{ij} = \begin{cases} 1.0 & n_{ij} > 2 \cdot avg. \\ 0.75 & ave < n_{ij} \leq 2 \cdot avg. \\ 0.5 & 0.5 \cdot ave < n_{ij} \leq avg. \\ 0.15 & 0 < n_{ij} \leq 0.5 \cdot avg. \end{cases} \tag{2.2}$$

where avg. is the average number of trajectory segment endpoints in each cell.

This method has been used successfully for potential source identification of both rural and urban areas (Poissant, 1999; Han et al., 2007). PSCF modeling identifies large source areas instead of individual sources (Han et al., 2007). This model does not determine the extent of various factors affecting receptor site Hg concentrations as the PCA source-receptor relationships but delivers useful results in terms of geographical location of potential source areas. Thus, both these methods should be applied together to determine the major sources of TGM concentrations.

2.5 Mercury Pollution Issues from Canadians Perspective

2.5.1 Mercury Sources in Canada

Major anthropogenic sources of Hg emissions in Canada are smelting of metals, municipal, sewage, and medical waste incineration, coal combustion and cement manufacturing. Canadian anthropogenic Hg emissions for the year 2003 are shown by sectors in Figure 2.3. Combustion of fossil fuel, primarily coal combustion, for electricity generation is the major source of Hg emissions in Canada. The miscellaneous emissions contributing 4% includes emissions from sources like residential and commercial fuel combustion, the asphalt paving industry, crematoria, the chemicals industry and landfill sites. Emissions from vehicles could be another potential anthropogenic source. Annual average emission of Hg from natural sources in Canada was estimated as 1.1×10^6 kg. This total amount is comprised of emission from wind erosion of soil, sea salt spray, forest and brush fires, along with re-emission of Hg vapour from terrestrial vegetation, soil, ocean surfaces (within territorial limits) and lakes and rivers (Richardson et al., 2003).

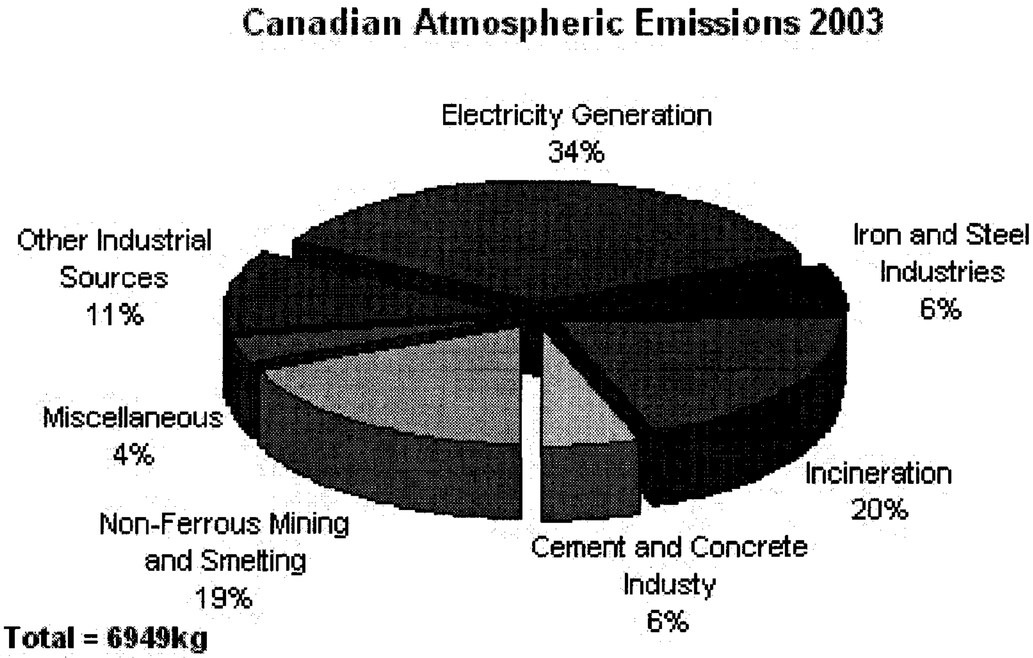

Figure 2.3: Canadian Mercury Emissions by sector for 2003 (EC, 2008a)

2.5.2 Mercury Management

As the awareness of Hg toxicity has increased, the Government of Canada has taken several initiatives to reduce the use of Hg and its emission to the environment, and the risks associated with exposure to Hg (HC, 2004). In the process of Hg management, Canada is involved in development and implementation of regulations and Canada-wide Standards (CWS). Since 2000, the Canadian Council of Ministers of the Environment (CCME) developed several CWS for mercury-containing lamps, dental amalgam waste, and emissions from base metal smelting and incinerators. The CCME is also working to develop a CWS for the coal fired electric power generation sector by the year 2005 for implementation by 2010 (Howland et al., 2005). Different provinces have undertaken additional acts, regulations and guidelines regarding liquid effluent, drinking water and emission from industrial sources along with the federal regulations (EC, 2000).

The release of Hg into the environment from anthropogenic sources in Canada is reported to the National Pollutant Release Inventory (NPRI). Under the authority of Canadian Environmental Protection Act (CEPA), owners or operators of facilities that process or otherwise use Hg and meet reporting thresholds and other requirements are required to report their pollutant releases, disposals and transfers for recycling annually to the NPRI (NPRI, 2008). In Table 2.5, Hg emissions in total and to different media (air, water, land) from different facilities reported to NPRI in Canada for the year 2000 to 2006 are listed. Seen in Table 2.5, nationwide decrease in total emission is observed since 2003 whereas atmospheric emission has decreased since 2004 (Figure 2.4). Approximately 40% of the Hg deposited annually in Canada may come from foreign sources (Howland et al., 2005). In order to reduce Hg release in a domestic and global perspective, Canada is working with United States and Mexico through the North American Commission for Environmental Co-operation (NACEC) (HC, 2004).

Table 2.5: Mercury and mercury compounds emission Canada from 2000 to 2006 (Data source: NPRI, 2008)

Year	No. of Facility	Emission to			Total (Kg)
		Air (Kg)	Water (Kg)	Land (Kg)	
2000	199	5975	231	41	6248
2001	247	6027	489	349	6865
2002	308	5498	283	56	5837
2003	310	5336	1329	50	6715
2004	293	5707	338	13	6058
2005	279	5156	533	3.4	5693
2006	277	4598	341	14	4954

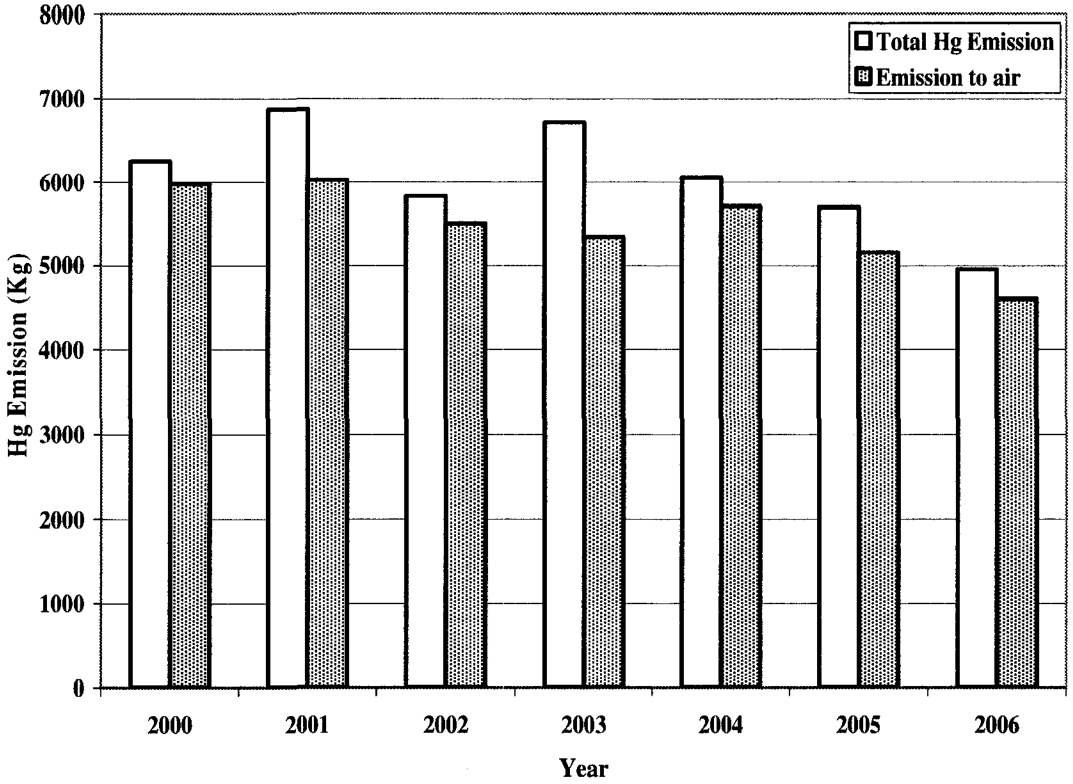

Figure 2.4: Total and atmospheric mercury emission since 2000 to 2006 in Canada (Data source: NPRI, 2008)

2.6 Mercury Study in Windsor

Windsor is the southernmost border city of Canada. The city is connected with the USA by the Ambassador Bridge. This is the busiest international border crossing in North America with an average of 330 commercial truck crossings per hour. Windsor is also connected with the USA by a tunnel which is the busiest passenger border crossing in North America. In 2001, an average of 1,747 vehicles per hour crossed the border via the Bridge and the Tunnel (Ontario Chamber of Commerce, 2004).

Air Quality in Ontario Report for the year 2005 has reported that the Windsor Downtown Site had experienced the highest number of days (37) with at least one hour of poor Air Quality Index (AQI). The predominant wind direction in Windsor was from south west (SW) to south-southwest (SSW) indicating transportation of pollution from the USA. Major potential local sources of air pollution in Windsor are industrial facilities and traffics leading to and from the Bridge and the Tunnel. Potential local sources of Hg in Windsor are two local companies: City of Windsor - Lou Romano Water Reclamation Plant and Aramco Management Ltd. (NPRI, 2008). Other potential sources include automobile industries, dental clinics, municipal and medical incinerators, and vehicular emissions. Detroit, the neighbor city of Windsor has many industrial facilities including iron/steel manufacturing, refineries, sewage sludge incineration, automobile industries, and coal fired utilities (Liu et al., 2007). However, information on Hg concentration levels in Windsor is very limited. A short-term study performed at the University of Windsor conducted from February 9 to March 10, 2004 has reported a high average concentration of 5.9 ng/m^3 (Banik, 2004). Thus, a long-term study of atmospheric Hg in Windsor will provide valuable information in terms of atmospheric Hg concentration and temporal variation along with any regional affect, as this is an urban industrial site with strong transboundary pollution.

CHAPTER 3: MATERIALS AND METHODS

3.1 Sampling Sites

3.1.1 Sampling Site of Temporal Variability Study

The sampling site was located in the University of Windsor, Ontario, Canada (Figure 3.1). The latitude and longitude of the sampling site are 42°18.27′ N and 83°3.98′ W, respectively. All air quality monitoring instruments measuring total gaseous mercury (TGM), black carbon (BC), particulate mass ($PM_{2.5}$), ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO, NO_2), total volatile organic compounds (VOCs) were set up in Room 112, at the south end of Essex Hall, University of Windsor. Ambient air was collected through sample lines hung out of the window at a height of 5 meters above ground. In front of Essex Hall, there is a grass area of about 60 m × 24 m. The site is in the north of Wyandotte St. West (27 m) and opposite to the entrance/exit roadway of the Ambassador Bridge. The site is also close to the Huron Church Road (app. 200 m west) which is the major roadway for the trucks entering/exiting from the Ambassador Bridge. Heavy local traffic in the nearby area of the sampling site is experienced because of the entrance and exit of traffic to the Bridge as well as traffic of University of Windsor.

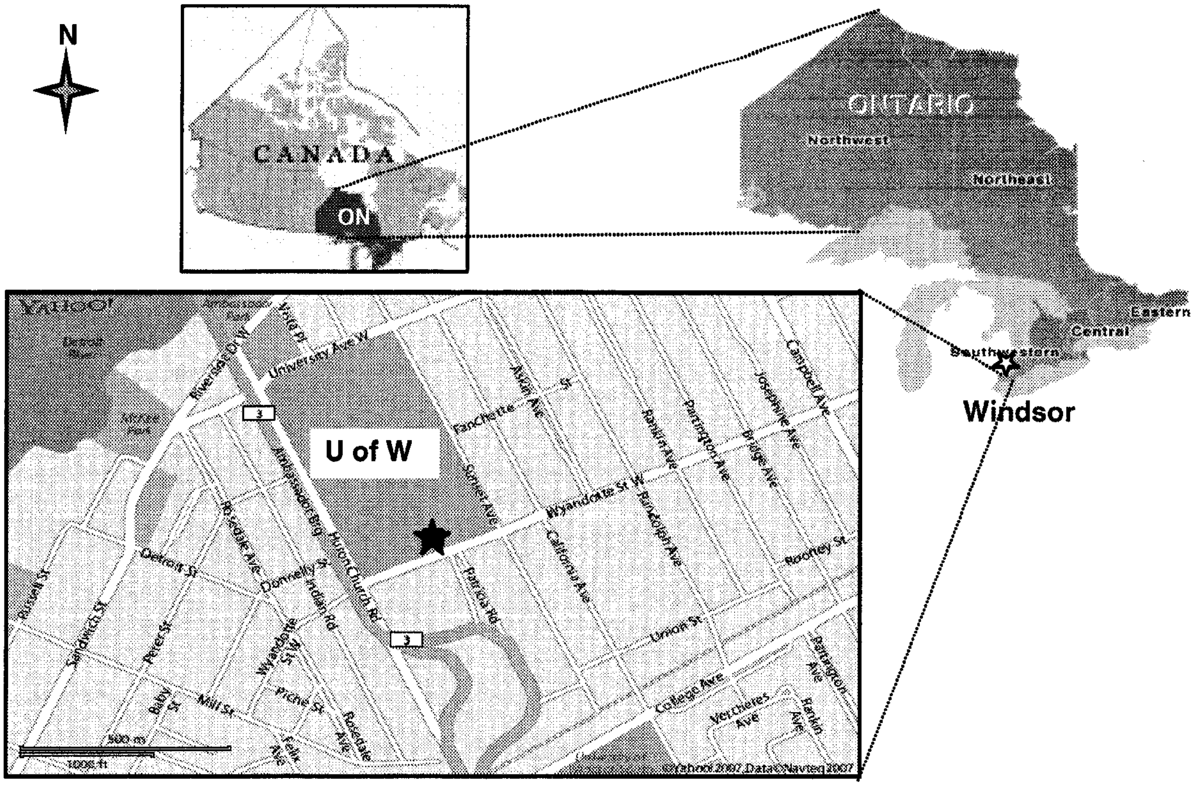

Figure 3.1: Map of sampling location in University of Windsor, Windsor, ON, Canada (Black star in the figure indicates the sampling site. Base maps adapted from Yahoo Local Maps, 2008 and Google Map Image of Canada, 2008)

3.1.2 Sampling Sites of Spatial Variability Study

A mercury analyzer was placed in Environment Canada's CRUISER (Canadian Regional and Urban Investigation System for Environmental Research) to determine the spatial variability of TGM concentrations in Windsor. Measurements were conducted by sampling ambient air from 13 predetermined sites in Windsor. The sampling sites are indicated in Figure 3.2. The latitude and longitude of these sites ranged from 42°13'39" to 42°20'36" N ~~and~~ from 83°06'14" to 82°53'35" W respectively as listed in Table 3.1. The CRUISER drove for 9 to 10 hours everyday. The sequence of sites were chosen randomly everyday. The CRUISER was parked in Windsor Lou Romano Water Reclamation Plant at night (Site 1).

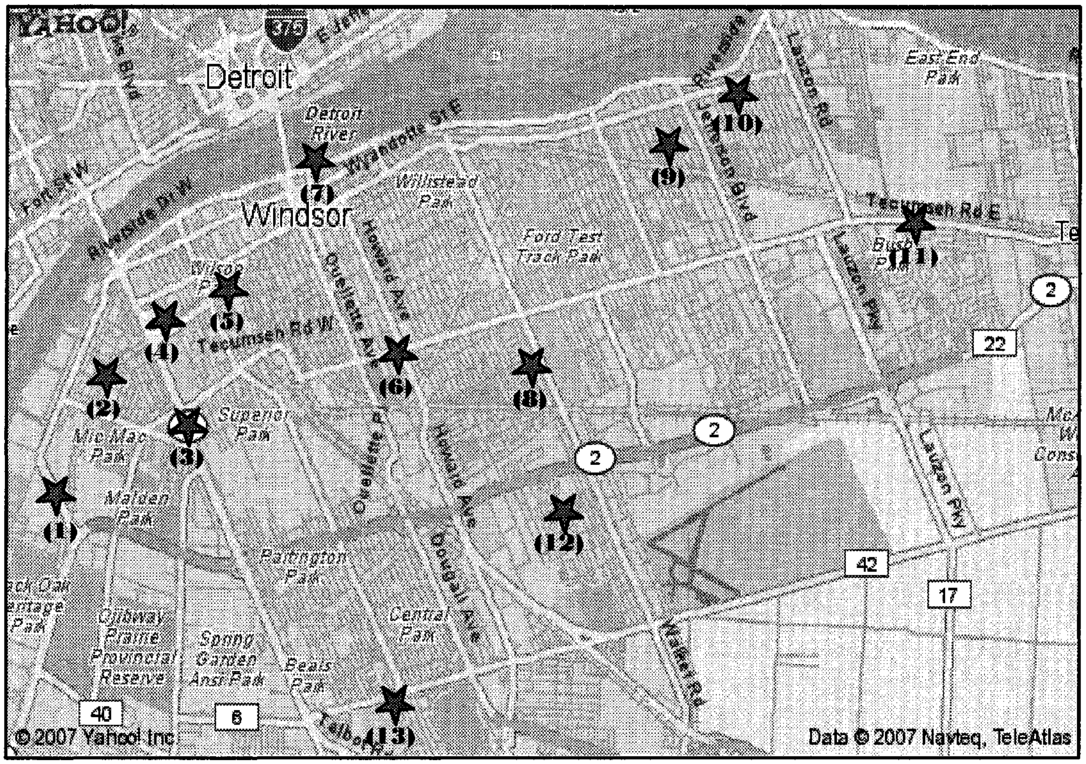

Figure 3.2: Map of sampling sites of spatial variability study in Windsor, 2006

★ Indicates the sampling sites (Base map adapted from **Yahoo Local Maps, 2008**)

Table 3.1: Location of the 13 spatial sites in Windsor

Site	Address	Latitude	Longitude
1	4155 Ojibway Pky (Windsor Lou Romano Water Reclamation Plant)	42° 16' 41"	-83° 4' 56"
2	College/South St	42° 17' 35"	-83° 4' 23"
3	1611 Felix Avenue	42° 17' 12"	-83° 3' 33"
4	2601 Union St	42° 18' 7"	-83° 3' 41"
5	944 Mackay Ave	42° 18' 13"	-83° 2' 59"
6	469 Hyde St	42° 17' 48"	-83° 1' 1"
7	Riverside Parking Lot	42° 19' 18"	-83° 1' 58"
8	2574 Turner Rd	42° 17' 36"	-82° 59' 24"
9	1192 Prado Pl	42° 19' 15"	-82° 57' 56"
10	7055 St. Rose St	42° 19' 49"	-82° 57' 9"
11	9805 Asgrad Rd	42° 18' 39"	-82° 55' 8"
12	1368 Hansen Cr	42° 16' 35"	-82° 59' 13"
13	1538 Villa Maria Boulevard N	42° 15' 1"	-83° 0' 59"

3.2 Operation of Instruments

3.2.1 Mercury Analyzer

An automatic analyzer, Tekran® 2537A mercury vapor analyzer (Tekran Inc., Toronto, ON, Canada) was used to measure TGM concentration in the ambient air (Table 3.2). The analyzer provides nearly continuous analysis of TGM at sub-ng/m^3 levels. The instrument samples air and trap mercury vapor into a cartridge containing an ultra-pure gold adsorbent. The amalgamated mercury is thermally desorbed and detected using Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS). A dual cartridge arrangement allows continuous sampling of the air stream. While one cartridge is sampling ambient air, the other is being analyzed. Particulate matter is removed from the sample air before entering the analyzer by a 47 mm diameter Teflon filter (0.45 μm). An internal permeation source allows the instrument to recalibrate itself automatically. At the outset of a calibration sequence the traps are cleaned by thermally desorbing any residual mercury and cartridge zeros are obtained with a stream of clean zero air. As well, the internal permeation source is triggered to deliver a programmed amount of elemental mercury vapor during the calibration span which produces a second calibration point (Tekran Inc., 2006).

3.2.2 Other Air Monitoring Instruments

A Magee Scientific Aethalometer® (Magee Scientific Company, Berkeley, CA, USA) was used to measure black carbon concentration in ambient air (Table 3.2) using a continuous filtration and optical transmission technique. The principle of the Aethalometer is to measure the attenuation of a beam of light (880 nm) transmitted through a filter, while the filter is continuously collecting the aerosol sample.

Measurements are made at successive regular intervals of a time base period. The increase in optical attenuation from one period to the next is due to the increment of aerosol black carbon collected from the air stream during the period. BC concentration in the sampled air stream during the period is calculated by dividing this increment by the volume of air sampled during that time (Hansen, 2005).

Model 8520 DUSTTRAK™ Aerosol Monitor (TSI Incorporated, Shoreview, MN, USA) were used to measure $PM_{2.5}$ (Table 3.2). The instrument uses light scattering technology to determine mass concentration in real-time. An aerosol sample is drawn into the sensing chamber in a continuous stream. One section of the aerosol stream is illuminated with a small beam of laser light. Particles in the aerosol stream scatter light in all directions. A lens at 90° to both the aerosol stream and laser beam collects some of the scattered light and focuses it onto a photodetector. The detection circuit converts the light into a voltage. This voltage is proportional to the amount of light scattered which is, in-turn, proportional to the mass concentration of the aerosol. The voltage is read by the processor and is multiplied by an internal calibration constant to yield mass concentration (TSI Inc., 2006).

In the Airpointer (recordum® Messtechnik GmbH, Mödling, Austria), several air pollutants measurement modules including O_3, SO_2, NO, NO_2, NO_x, CO, and total VOCs are integrated (Table 3.2). The sample ambient air flows directly to the modules. Airpointer measures the amount of sulfur dioxide in a sample by exciting the SO_2 molecules by ultraviolet (UV) light with a wavelength of 214 nm and then measuring their fluorescence with a detector. As the excited SO_2 molecules decay to lower energy states they emit UV light that is proportional to the SO_2 concentration. The NO_x module measures the concentration of NO_x and NO in a gas sample and also calculates the concentration of NO_2. The analyzer measures the chemiluminescence of nitrogen monoxide when it reacts with ozone and produces exited NO_2 molecule, which emits energy as a light pulse. The intensity of the light can be measured with a photomultiplier and so the concentration can be calculated. Any NO_2 contained in the gas is not detected in the above process. In order to measure the NO_x which is regarded as the sum of NO and NO_2 in the sample gas, the device periodically switches the sample gas stream through a converter cartridge filled with molybdenum chips. The heated molybdenum reacts with NO_2 in the sample gas and produces NO. This NO is routed to the reaction cell where it undergoes the chemiluminescence reaction described earlier. By converting the NO_2 in the sample gas into NO, the analyzer can measure the total NO_x content of the sample gas. Finally, the NO_2 concentration is calculated by simply subtracting the known NO content from the known NO_x content.

The CO module uses a high-energy heated element to generate a beam of board-band IR light. This beam is directed through multi-pass cell filled with sample gas. Upon exiting the sample cell, the beam passes through a band-pass filter that allows only light at a wavelength of 4.7 μm to pass. Finally, the beam strikes a solid-state photo detector that converts the light signal into a modulated voltage signal representing the attenuated intensity of the beam. In the O_3 module, a high-energy Hg vapor lamp is used to generate a beam of UV light. This beam passes through an absorption tube filled with sample gas and at the exit is detected by vacuum diode that only detects radiation at a wavelength of 254 nm. The detector output is a voltage that varies with the light's intensity. The concentration of O_3 in the absorption tube is calculated using the voltage value. The VOC module uses the photo-ionization detection method. Non methane total VOCs are ionized using a UV lamp. The ions migrate into an electric field to discharge electrodes. By discharging, an electric current is produced which is used as a measurement signal (recordum® Messtechnik GmbH, 2005).

3.3 Sample Collection Procedure

3.3.1 Sample Collection for Temporal Variability Study

The collection of ambient air was performed by setting all the instruments inside the lab and the inlet lines were then extended outside the window. The window was about 5 meters high above the ground. To minimize adsorption in the lines, the shortest possible inlet lines were used for all instruments. The sampling time was logged as the Daylight Saving Time (DST) from March 11 to November 4, 2007 in Tekran, Aethalometer, and DUSTTRAK while for the Airpointer data was logged in Eastern Standard Time (EST) during this period. All the instruments were synchronized in time every week. Operation was interrupted for the instruments several times for instruments' maintenance and repairing. Table 3.2 summarizes set up parameters of different instruments.

Hourly averaged meteorological parameters for the year 2007 were collected from Environment Canada Climate website (EC, 2008d). The parameters were measured at Windsor International Airport, located about 10 km south-east of the sampling site. Meteorological parameters considered in this study were surface air temperature (Temp), relative humidity (RH), wind speed (WS) and wind direction (WD).

Table 3.2: Summary of the instruments used for temporal variability study

Name of equipment	Pollutants	Sampling interval	Length of sample line	Flow rate (L/min)
Tekran 2537A	TGM	5 min	1.5 m	1.5
Aethalometer	BC	3 min	1.5 m	4
DUSTTRAK	$PM_{2.5}$	1 min	1.2 m	1.7
Airpointer	O_3, SO_2, NO_2, NO, CO, total VOCs	1 min	3 m	4.35

3.3.2 Sample Collection for Spatial Variability Study

TGM measurements were conducted in two stages: one from October 16 to 19 2006, and another from October 24 to 26 2006. The Tekran analyzer was housed in air-conditioned environment (20°C) of the mobile lab. Ambient air was collected through 5.5 m long Teflon tubing from 4 m above the ground. The analyzer was programmed to collect air at a flow rate of 1 L/min for 5 minute sampling intervals. It was calibrated automatically using internal permeation source at an interval of 24 hrs during the study period. For each visit, the mobile lab collected ambient air at each site for approximately 15 to 30 minutes. TGM concentrations during mobile sampling driving sessions as well as stationary sampling were measured along with the measurement in the 13 sites. Readings from a GPS unit located in the CRUISER were used to identify the sites and this was used to process the mercury concentrations according to the sites. Table C.1 (Appendix C) provides the time duration spent and the number of measurements collected at each site.

3.4 QA/QC

3.4.1 Tekran 2537A Mercury Vapor Analyzer

The analyzer was calibrated automatically through the built-in permeation mercury source at 23 hour intervals. The filter paper in the sample line was replaced every month. An argon gas cylinder was replaced with a new one if the gas pressure dropped below 200 psi. Weekly routine checks were conducted to ensure the accuracy and precision of the measurement data throughout the study period. Any data that failed to fulfill the requirements were rejected from analysis.

Data Quality Control Checks- The TGM mean values and standard deviations of at least five consecutive results from Cartridge A and Cartridge B were compared to ensure that there was no bias between the cartridges. The averages of the two cartridges should agree within 10-15 percent.

Analyzer Status and Baseline Checks- On the Tekran 2537A LCD screen, baseline reading (in between 0.1-0.3 V), and baseline deviation (less than 0.1 mV) was checked.
Calibration Checks- The response factors were recorded for each cartridge. If the response factor decreased by more than 10%, lamp voltage was adjusted. The zero air calibration area (less than 5000) and the area of the SPAN results (within 10 percent) were checked.

3.4.2 Other Instruments

Flow rate, free disk space and amount of tape left in the Aethalometer were checked and the diskette was changed weekly. For the DUSTTRAK, flow rate and zero checking along with re-greasing of the impactor plate were performed weekly. The sample particulate filter of the Airpointer was changed biweekly. Automatic time synchronization of the Airpointer's local time was performed at midnight (12:00) everyday using the Eastern Standard Time (EST) server via the internet. Data download for all of the instruments were done every week.

3.5 Data Analysis

The measuring time intervals for the instruments were different from each other, as shown in Table 3.3. The meteorological parameters were reported as hourly averaged data in Environment Canada's website. All recorded data for different pollutants from different instruments were converted to hourly average concentrations for the convenience of data analysis. All time are reported in Eastern Standard Time (EST) in this study. The available number of hourly averaged pollutant concentration and meteorological parameters for this study are listed in Table 3.3. All statistical analyses in this study were performed using statistical software MINITAB (Release 14, State College, Pennsylvania, USA), except for the Scheffé test, for which SPSS (Release 16 for Windows, Chicago, Illinois, USA) was used. Distribution of all data was checked using probability distribution plot. Parametric statistical analysis was used through out the data analysis according to the Central Limit Theory (Appendix D) as the sample number was large enough for each parameter (Table 3.3). All the statistical analysis were performed at the confidence interval of 95% ($\alpha = 0.05$).

Table 3.3: Available data for each pollutants and meteorological parameters

Pollutants/others	Time period	Number of hourly mean
TGM	Jan 1 to Dec 31, 2007	6659
BC	Jan 1 to Dec 31, 2007	7034
$PM_{2.5}$	Jun 16 to Dec 31, 2007	3230
O_3, SO_2, NO_2, NO, CO, total VOCs	Aug 8 to Oct 30, 2007	1951
Temp, RH, WS and WD	Jan 1 to Dec 31, 2007	8748

3.5.1 Seasonal and Diurnal Variability of TGM

The study period (2007) was divided into four seasons for seasonal distribution analysis. The seasons are winter- January, February, and December, spring- March, April, and May, summer- June, July, and August, and fall- September, October, and November. For comparability with other studies, four seasons were considered in this study as most of the studies have considered the same seasonal division. For diurnal distribution analysis, any hourly averaged concentration greater than the overall mean+4×SD value were omitted from the analysis to minimize the effect of unusual high concentration on diurnal pattern. Afterwards, average concentrations for each hour of the day were calculated to determine the diurnal variability of TGM concentration for the year 2007. Diurnal variability was also determined seasonally. The analysis of variance (ANOVA) was used to check the statistical difference in mean concentration between the hours of a day and seasons. Multivariate comparison tests, i.e. Tukey's and Scheffe's tests, were used for further analysis for seasonal and diurnal variability respectively.

Equality of variance test was calculated using Bartlett's and Levene's tests and a Bonferroni plot for both seasonal and diurnal variability.

3.5.2 Correlation of TGM with Meteorological Parameters and Other Pollutants

Pearson correlation coefficients were calculated annually and seasonally between hourly averaged TGM concentrations and meteorological parameters including temperature, relative humidity, and wind speed. For the correlation study between TGM and other pollutants, the time duration of available data for different pollutants was different from each other (Table 3.3). Pearson correlation analysis was performed on the data when all pollutants concentration was available, between August 8 to October 30, 2007. Wind Rose plot was generated to identify prevailing wind directions at Windsor for the whole year using WRPLOT View (Lakes Environmental, 2006). Pollution Rose plot was also generated to identify the wind directions associated with high TGM concentration in Windsor using Matlab®Version 6.5, (The Mathworks Inc., 2002).

3.5.3 Principal Component Analysis

The objectives of PCA are to reduce the dimensionality of the data set consisting of a large number of inter-related variables and derive a new set of variables that could explain most of the variation present in the original data (Jolliffe, 2002). PCA with varimax rotation was used with the aim to identify the factors affecting TGM concentration and the reasons of variation in concentrations. The components considered for PCA were TGM, O_3, NO, NO_2, SO_2, CO, total VOCs, $PM_{2.5}$, BC, Temp, RH, and WS from August 8 to October 30, 2007. Based on the loadings on the variables, the factors affecting TGM concentration in Windsor was identified.

3.5.4 Identification of Potential Regional Sources

The Hybrid receptor model PSCF (Hopke et al., 1990) was used to identify potential regional sources of TGM concentration in Windsor. The analysis was performed based on backward trajectories and the measured TGM concentrations in Windsor in order to identify potential regional sources of TGM at the receptor site.

3.5.4.1 Backward Trajectory Analysis

HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model 4 (NOAA, 2008) was used in this study to construct the backward trajectories from the sampling site. Modeling of backward trajectory generates a map and a text file. The map generated shows the regions over which the trajectories traveled before reaching the receptor site. This is done by drawing a line extended from the receptor site. The output text file delivers endpoints in terms of latitude, longitude and altitude for each hour back in time (NOAA, 2008). Figure 3.3 is a 72 hour backward trajectory simulation modeled by HYSPLIT. It displays the air mass vector and the regions that the air mass traveled during the simulation period.

Backward trajectories for a 72 hour simulation period were modeled for each day in 2007 for which days daily averaged TGM concentrations were available. It was assumed that daily averaged concentration was affected by the air mass coming to Windsor for the last 72 hour period. Mercury has high residence time in air and can be carried over for longer than 72 hour. However, 72 hour was chosen to identify the regions of North America that could affect Windsor TGM concentration in this simulation time. An archived meteorological dataset of EDAS (Eta Data Assimilation System, NOAA, 2008) at a horizontal resolution of 40 km for 2007 was used to run the model.

Trajectories were modeled using local zero hour (5:00 UTC) as the start time. Emissions from local sources and surface were expected to be minimal at night. Therefore, start time was used as zero hour local time was used as start time to minimize the effect of local sources and emphasize on effect of regional sources. The start height was chosen as 500 m above ground level (AGL) as in other PSCF studies (Gao et al., 1993; Hafner and Hites, 2003; Begum et al., 2005). This height is approximately the height of the air mixing layer (Gao et al., 1993) and the effects of surface friction is small at this height (Begum et al., 2005). Model simulation parameters used in this study are listed in Table 3.4.

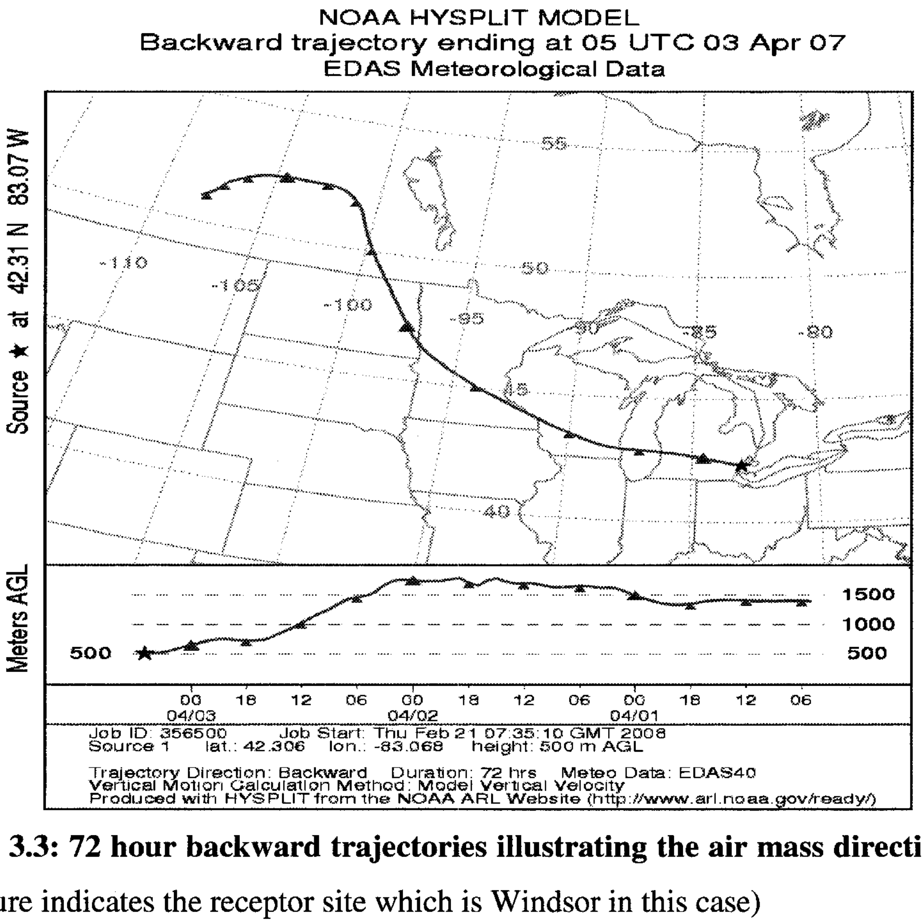

Figure 3.3: 72 hour backward trajectories illustrating the air mass direction (Star in the figure indicates the receptor site which is Windsor in this case)

Table 3.4: Model parameters used for HYSPLIT trajectories

Model Parameter	Setting
Meteorological dataset	EDAS 40km, 2007
Trajectory direction	Backward
Total run time (trajectory duration)	72 hr
Start point	42°18.27´ N and 83°3.98´ W
Start time	5:00 UTC
Start height	500 m AGL

3.5.4.2 Potential Source Contribution Function (PSCF)

The potential source region for this study was identified by the geophysical region covered by the 72 hour trajectories which is calculated from trajectory endpoint files. The potential source region is 24° to 61° N in latitude (south to north) and 51° to 143° W in longitude (east to west). For the PSCF model, the region was divided into girded array of cells, each the size of 1°×1° in latitude and longitude; thus there were 3,404 grid cells. Total endpoints for 293 days (x approx. 72 hour) modeled were 20,510. Thus, there were (20,510 endpoints /3,404 cells) or 6 endpoints per cell on average.

Daily averaged concentrations were calculated for 293 days (for which days TGM data was available) and one trajectory was modeled for each day. Thus, each trajectory represents one daily averaged concentration value. For example, the 24 hour averaged concentration on August 30, 2007 of 2.72 ng/m^3 is assumed to be affected by the trajectory that started at 01:00 August 27 (from a definite location) and reached at Windsor at 0:00, August 30. PSCF values were calculated for annual as well as for each season as the meteorological conditions and TGM concentrations are significantly different among the seasons. For annual potential source identification, annual mean concentration value was considered as the criteria value. For seasonal modulation, both the annual and individual seasonal mean concentration values were used as the criteria values. The reasons for using both values were to identify the seasonal features of potential source regions as well as to compare among the seasons.

The counting of n_{ij}s and m_{ij}s for each cell was conducted by a C++, program written for this project. The steps followed for the program derivation is attached in Appendix B. The program tracks the number of endpoints in each cell and whether or not they are above or below the criteria value. The total number of endpoints and PSCF values for each grid were plotted in a North American map to identify potential regional sources. From the plot it can be suggested that, regions having high PSCF values would be potential sources for Windsor if there was significant mercury emission. To identify regions with high mercury emissions in air, annual mercury emission into air for different regions of USA and Canada were collected from the Toxic Release Inventory (TRI, USEPA, 2008) and National Pollutants Release Inventory (NPRI, 2008) and were plotted on a map. All maps were plotted using ArcGIS 9 Version 9.2 (ESRI, 2006).

3.5.5 Spatial Variability

Statistical summary and Box-Whisker plots of 5 minute TGM concentrations were generated for each of the 13 sites in Windsor to study the spatial variability. ANOVA and Tukey's test were performed to check the difference in means among the sites whereas equality of variances was conducted using Bartlett's and Levene's tests and a Bonferroni plot. The TGM concentration observed at each site was also analyzed to identify the effects of local sources on spatial variability of TGM concentration.

A set of 24 correction factors (CF), one for each hour in the day were derived to eliminate the effect of difference in measurement hours regardless of the locations. First, average concentration for each hour (i.e. 0:00 to 23:00) and also the overall 24 hour average concentration were calculated. Then factors were calculated for each hour as the ratio of 24 hour mean and respective hourly mean. Consequently, the 5 minute TGM concentrations were multiplied by its corresponding hour's CF. This was aimed at reducing the impact of difference in measurement time on spatial variability. Later, both data sets, before and after correction were compared to verify the methodology of sampling (i.e., random sequence of the sampling sites) did not affect the spatial variability.

3.5.6 Data Analysis for Comparison of Two Year's Data

TGM concentrations available for 7 day of October for 2006 and 2007 obtained from spatial variability and temporal variability studies respectively were compared to study any differences between these two consecutive years ANOVA and two sample t-test analyses were conducted to determine the statistical difference between the data sets.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Summary of TGM Concentration and Meteorological Parameters

The descriptive statistics for hourly TGM concentration and meteorological parameters, including temperature, relative humidity, and wind speed are summarized in Table 4.1. A total number of 6659 hourly TGM concentrations were collected for 293 days in 2007. The concentrations were in the range of 0.83 to 40.9 ng/m^3. The overall average concentration was 2.02 ng/m^3 with a standard deviation of 1.63 ng/m^3. This concentration was higher than the reported background concentration of 1.5-1.7 ng/m^3 for Hg^0 in the Northern Hemisphere which constitutes almost 97% of TGM (Lindberg et al., 2007). The observed concentration was also higher than the average concentration of 1.58 ng/m^3 observed at all CAMNet rural sites during 1995-2005 (Temme et al., 2007; also see Table 2.2). However, it was close to 2.2 -2.5 ng/m^3 observed in other urban sites, e.g., Toronto, Detroit, Connecticut (Nadim et al., 2001; Denis et al., 2006; Liu et al., 2007). It is noteworthy that the average concentration was lower than that of 5.9 ng/m^3 measured at the same location during February 9 to March 10 in 2004 (Banik, 2004). This difference in concentration between 2004 and 2007 studies could be largely because of difference in sampling heights, which were at 0.076 m and 5 m respectively. At lower height, higher concentrations were observed due to the canopy effect (re-emission from plants and soil) compared to the higher height measurements (Denis et al., 2006). In addition to this, difference in study year and duration also could lead to the difference in concentrations. Figure 4.1 shows the histogram of hourly TGM concentration and its right-skewed probability distribution. Most of the data (71.7%) was in the 2 to 3 ng/m^3

range while 11% of data was higher than 3 ng/m^3, which also can be seen in the mid-second panel.

Table 4.1: Statistical summary of hourly averaged TGM concentration and meteorological parameters in Windsor, 2007

Variable	Unit	N	Min	Median	Max	Mean	SD
TGM	ng/m^3	6659	0.83	1.73	40.9	2.02	1.63
Temp	°C	8748	-19.6	11.7	35.1	10.8	11.6
RH	%	8748	21	69	100	68.3	16.2
WS	km/hr	8748	0	15	57	15.4	9.2

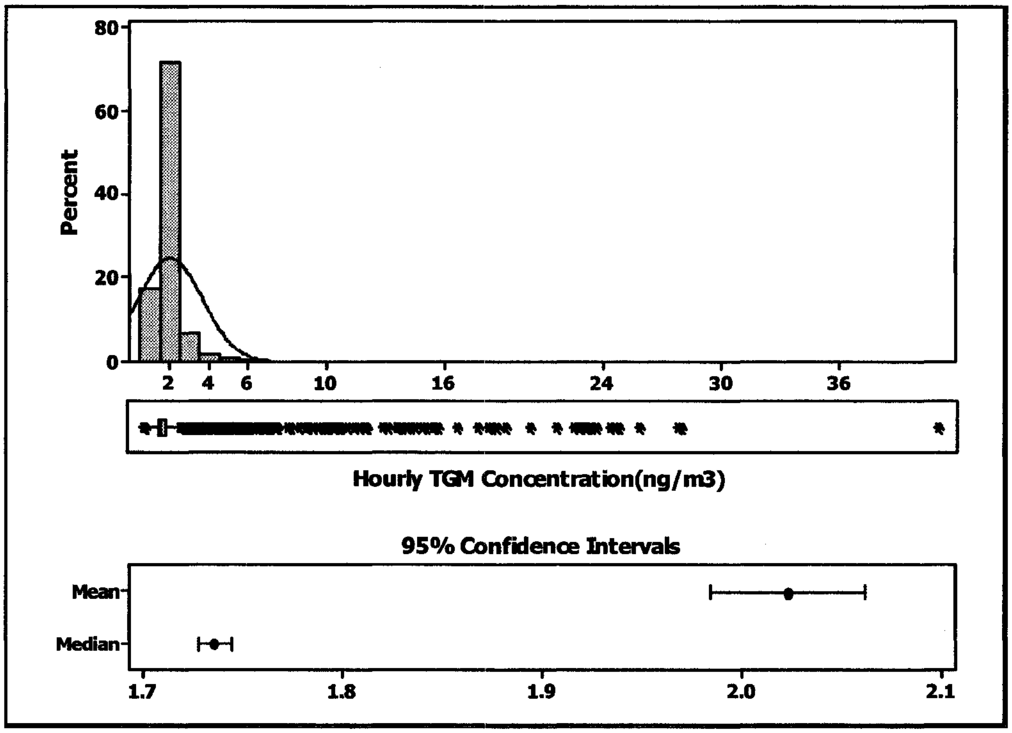

Figure 4.1: Distribution of hourly TGM concentrations in Windsor, 2007

Figure 4.2 shows the time series of hourly TGM concentration for 2007. Frequent occurrences of concentrations higher than the average were observed. TGM concentration exceedences of the overall mean+4×SD value of 8.54 ng/m^3 were observed ten times during the study period, five times in summer, three in winter and only once in spring and fall each. In winter, all three exceedences occurred in January. In most of the cases exceedence were observed in between 9:00 to 16:00 (EST) except for August. Further investigation of these high concentration episodes should be conducted.

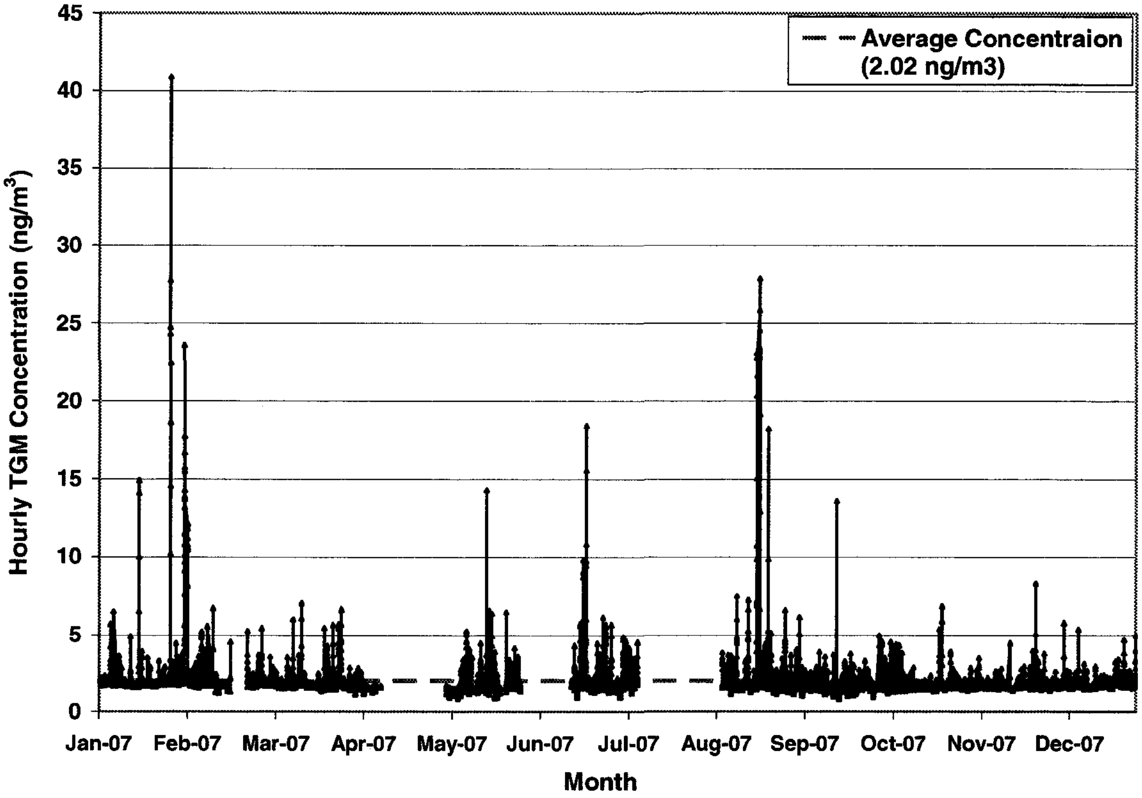

Figure 4.2: Time series plot of hourly TGM concentration in Windsor, 2007

4.2 Temporal Variability of TGM Concentration in Windsor, 2007

4.2.1 Seasonal Variability of TGM and Meteorological Parameters

Statistical summary of seasonal TGM concentration and meteorological parameters are presented in Table 4.2 and Table 4.3. Variability in Hg concentration was observed between different seasons. The highest average TGM concentration of 2.48

ng/m^3 was observed in summer. The average value for winter was also high (2.17 ng/m^3) whereas the low seasonal averages of 1.88 ng/m^3 and 1.76 ng/m^3 were observed in spring and fall respectively. Higher variabilities, i.e. standard deviations, were observed in summer and winter, and low in spring and fall. Statistical summary of meteorological parameters shows temperature was the highest in summer (22.8°C) and the lowest in winter (-2.9°C), as expected. Relative humidity of 75.3% was the highest in winter. The wind speed was high in winter and low in summer.

Table 4.2: Statistical summary of seasonal TGM concentration (ng/m^3) in Windsor

Season	N	Min	Median	Max	Mean	SD
Winter	1962	1.19	1.81	40.90	2.17	2.01
Spring	1478	0.85	1.71	14.25	1.88	0.78
Summer	1062	0.92	1.85	27.91	2.48	2.68
Fall	2157	0.83	1.63	13.60	1.76	0.58

Table 4.3: Statistical summary of seasonal meteorological parameters in Windsor

Variable	Unit	Winter		Spring		Summer		Fall	
		Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
Tem	^0C	-2.9	5.6	9.8	8.8	22.8	4.5	13.3	8.2
RH	%	75.3	12.6	63.1	16.7	64.4	15.5	70.6	16.4
WS	km/hr	18.1	9.5	17.6	9.7	12.0	7.3	13.9	8.5

Figure 4.3 demonstrates the seasonal variability of TGM concentration. It appears that hourly TGM concentrations for all seasons showed right skewed distribution. Results of all statistical analysis for seasonal variability are presented in Appendix E. A low *p*-

value (<0.05) from ANOVA indicates statistically significant differences in the mean concentrations among the seasons. Results of Tukey's test indicate mean concentrations for winter and summer were statistically different from each other. Both mean concentrations were also different from spring and fall; however, mean concentrations of spring and fall were statistically similar. The results from equality of variances test i.e. Bartlett's and Levene's test (Figure E.1) specify that the variances among the seasons were significantly different. The highest variability was observed in summer whereas the lowest was observed in fall.

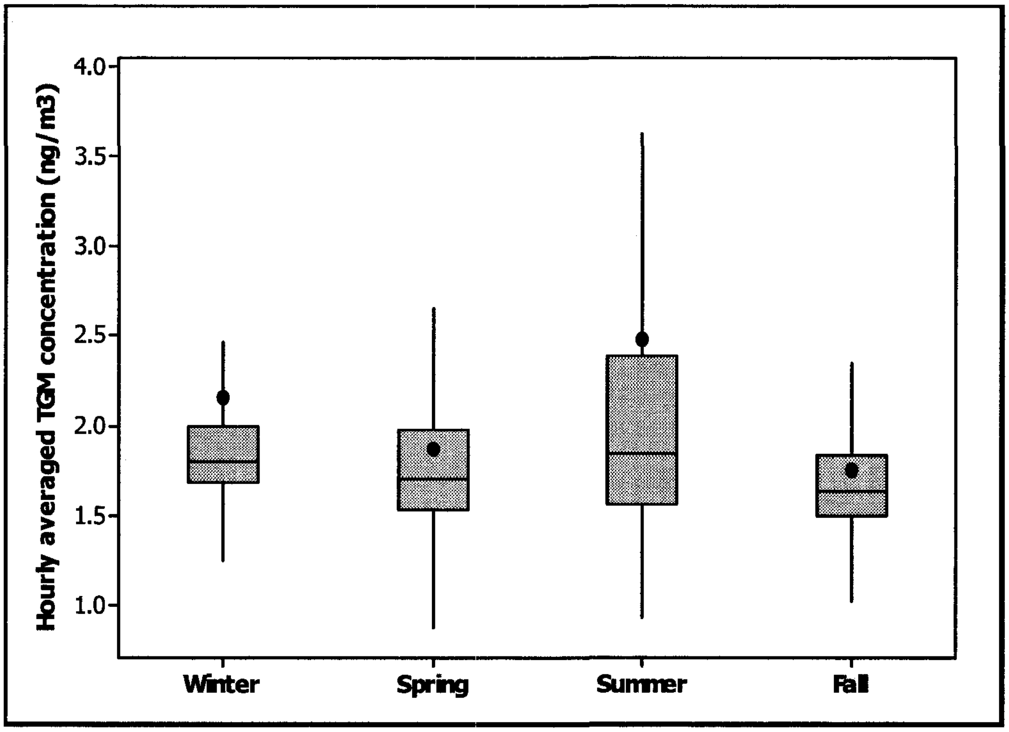

Figure 4.3: Box plot of seasonal variation of TGM concentration in Windsor

(The line inside the box indicates the median and ● indicate the means of TGM concentration. The lower and upper boundaries of the box indicate the 25th and the 75th percentile values, respectively. Whisks above and below the box indicate the 90th and 10th percentile. Same legends were used for other Box Plot through the thesis)

The seasonal pattern of higher summer concentration in comparison with other seasons observed in this study is quite similar to most of the studies conducted in urban sites in North America (Nadim et al., 2001; Denis et al., 2006; Liu et al., 2007). Winter TGM concentration in Windsor was also high as observed in Toronto, Canada (Denis et al., 2006). However, the pattern in Windsor was different from the seasonal pattern observed in North American rural sites (Nadim et al., 2001; Temme et al., 2007). Difference in meteorological conditions as well as atmospheric chemistry between urban and rural sites could lead to elevated TGM concentrations in summer (Liu et al., 2007). A study conducted in several urban sites in New York (Capri & Chen, 2002) suggested that the emissions from urban surfaces could elevate urban mercury concentration. For example, Gabriel et al. (2006) observed higher mercury fluxes during summer from soil, grass, and pavement in an urban site. In addition to higher emissions, lower wind speeds during the summer causes less dilution of atmospheric mercury, resulting in build up of high mercury concentrations.

A possible reason of high concentrations in winter could be the increased heating demand resulting in more coal combustion (Denis et al., 2006). Though there is no coal fired power plant in Windsor, US states to the south and west of Windsor e.g., Indiana, Illinois, Ohio, and Michigan are the largest mercury point sources in North America (Keating, 2003). Five coal fired power plants located in Ontario, Canada also emit one third of the total mercury emission in Ontario (Ontario Clean Air Alliance, 2007). Thus, transportation of airborne mercury from regional sources could affect winter TGM concentrations. Low atmospheric oxidant (ozone) concentration and low removal rate of atmospheric Hg in winter could also result in high concentrations (Stamenkovic et al., 2007). For spring and fall, the low ambient temperature compared to the summer and less power consumption than in winter may lead to lower concentrations and less variability.

4.2.2 Diurnal Variability of TGM Concentration

Figure 4.4 shows the diurnal distribution of hourly TGM concentration on an annual basis. The highest concentration (2.04 ng/m^3) was observed at 03:00 while the lowest (1.70 ng/m^3) was observed during the evening at 16:00 and 18:00. A gradual decrease in concentration was observed from the morning until noon and a comparatively steep decrease was observed right after noon, i.e. 13:00. Then a gradual increase was observed in the evening and over-night. Results of ANOVA indicate that there was significant difference in means among the hours. However, all 24 hours' mean concentrations were found in the same group in Scheffé test (Appendix F).

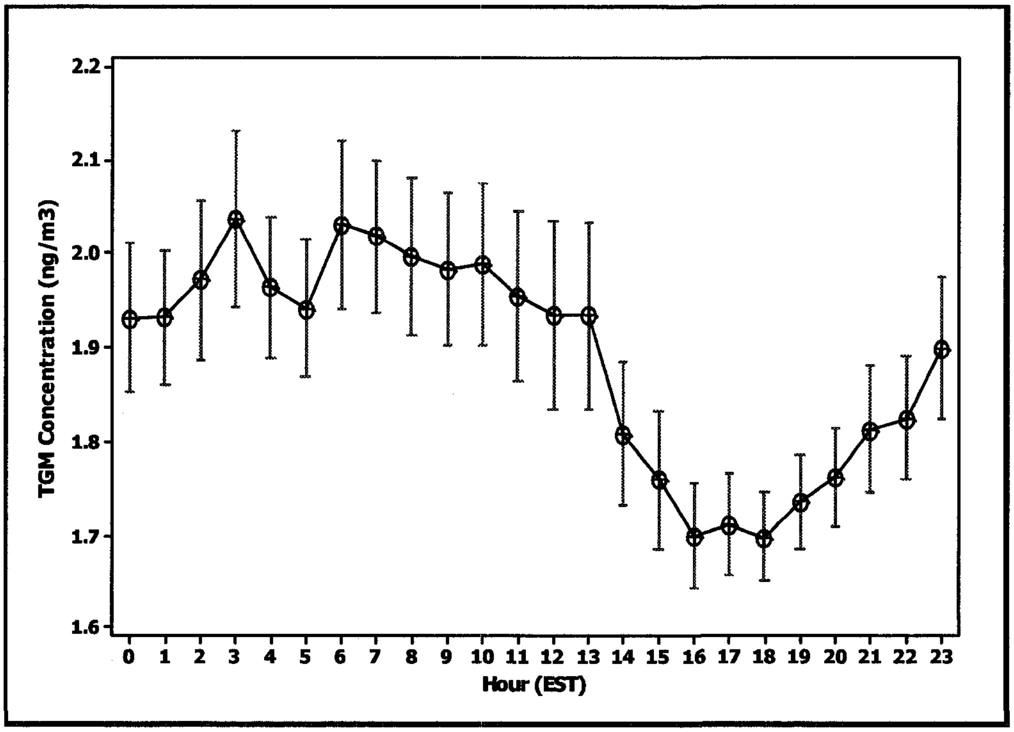

Figure 4.4: Diurnal variability of TGM concentration on annual basis

(The circles and the bars represent the hourly mean and 95% confidence intervals)

After reviewing a number of studies reporting an urban TGM diurnal cycles, it was found that each study had reported a specific diurnal trend (Denis et al., 2006; Liu et al., 2007; Stamenkovic et al., 2007). However, the diurnal cycle observed in this study is similar to that reported in Detroit (Liu et al., 2007). In our study, decreasing concentration from morning to afternoon followed by increasing concentration at night was observed. This similarity in concentrations is likely because of similar emissions and meteorological characteristics in these two studies as these two cities are next to each other.

The diurnal cycle was analyzed for each season to study the diurnal variability more specifically. As shown in Figure 4.5, in winter, spring and fall the diurnal pattern was similar as the diurnal pattern on an annual basis (Figure 4.4). The peak in morning after sunrise could be because of the breakdown of nocturnal inversion (Kellerhals et al., 2003) while the depletion from morning continued till afternoon because of increased vertical mixing and oxidation of Hg^0 resulting overall decrease in atmospheric Hg concentration. The diurnal pattern was significantly different in summer compared to other seasons. TGM concentration increased from early morning reaching a peak concentration at mid morning (10:00). The concentration decreased in the afternoon followed by a gradual increase from the evening until morning. The rate of increase from evening to morning and the rate of decrease in afternoon were greater in summer compared to other seasons. The large variability in the summer could be due to stronger diurnal variations in temperature and mixing height, a higher rate of uptake/emission by vegetation, increased surface emissions, and enhanced oxidation in summer (Kellerhals et al., 2003).

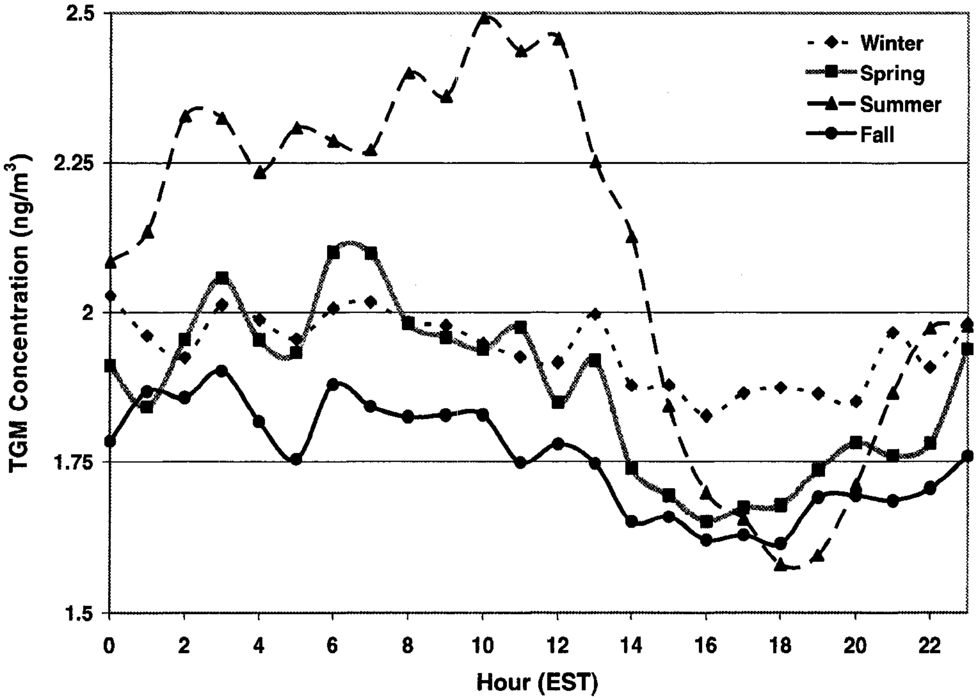

Figure 4.5: Seasonal diurnal variability of TGM concentration in Windsor

From the temporal variability analysis, it can be proposed that the seasonal and diurnal variability could be influence by environmental conditions, such as meteorological parameters, atmospheric chemistry, presence of oxidants, and local/regional sources. To understand the temporal variability more specifically, relationships between TGM concentration and meteorological parameters as well as other pollutants are investigated in the following sections.

4.3 Correlation of TGM Concentration with Meteorological Parameters

Correlations of TGM concentration with meteorological parameters including temperature, relative humidity and wind speed were investigated both annually and seasonally. Pearson correlation coefficients (r-value) along with *p*-values for TGM concentration and meteorological parameters are presented in Table 4.4. No significant relationships between TGM and temperature as well as with wind speed were observed annually as the *p*-values were greater than 0.05 at 95% confidence interval. A weak positive relationship was found with relative humidity (0.111).

Table 4.4: Correlation of TGM concentration (r value) with meteorological parameters (r-values in bold phase represent significant correlation at p-value <0.05)

Meteorological Property	Annual	Winter	Spring	Summer	Fall
Temp	-0.006	**-0.087**	**0.152**	**-0.094**	-0.012
RH	**0.111**	0.010	**0.246**	**0.203**	**0.203**
WS	0.000	0.038	**-0.186**	**0.125**	**-0.114**

Correlation analysis on the seasonal basis found TGM concentration and temperature had significant but a very weak negative relationships in winter and summer (-0.087 and -0.094 respectively) while a weak positive correlation was observed in spring. Based on the correlations, it is very hard to explain the effect of temperature on TGM. To study the effect of temperature on TGM concentration, diurnal cycles of TGM concentration and ambient temperature were plotted together for each season in Figure 4.6. It shows that a decrease in concentration was observed from the morning with increasing temperature in winter, spring, and fall. Decrease in concentration in the afternoon was observed irrespective of the seasons when temperature was the highest. Increased photo-chemically originated oxidants (e.g., O_3) in early afternoon could lead to oxidation of Hg^0 to Hg (II) which is then rapidly deposited resulting in an overall decrease in atmospheric TGM concentration (Stamenkovic et al., 2007). Several studies (Lindberg and Stratton, 1998; Lynam and Keeler, 2005) in urban sites had reported high

RGM concentrations between solar noon and late evening hours causing overall decrease in TGM concentration similar to this study. In summer, the TGM concentration followed the diurnal temperature trend from morning till noon. In this period, the increase in concentration could be governed by temperature driven surface emissions and enhanced biological activities i.e., foliar emission (Denis et al., 2006).

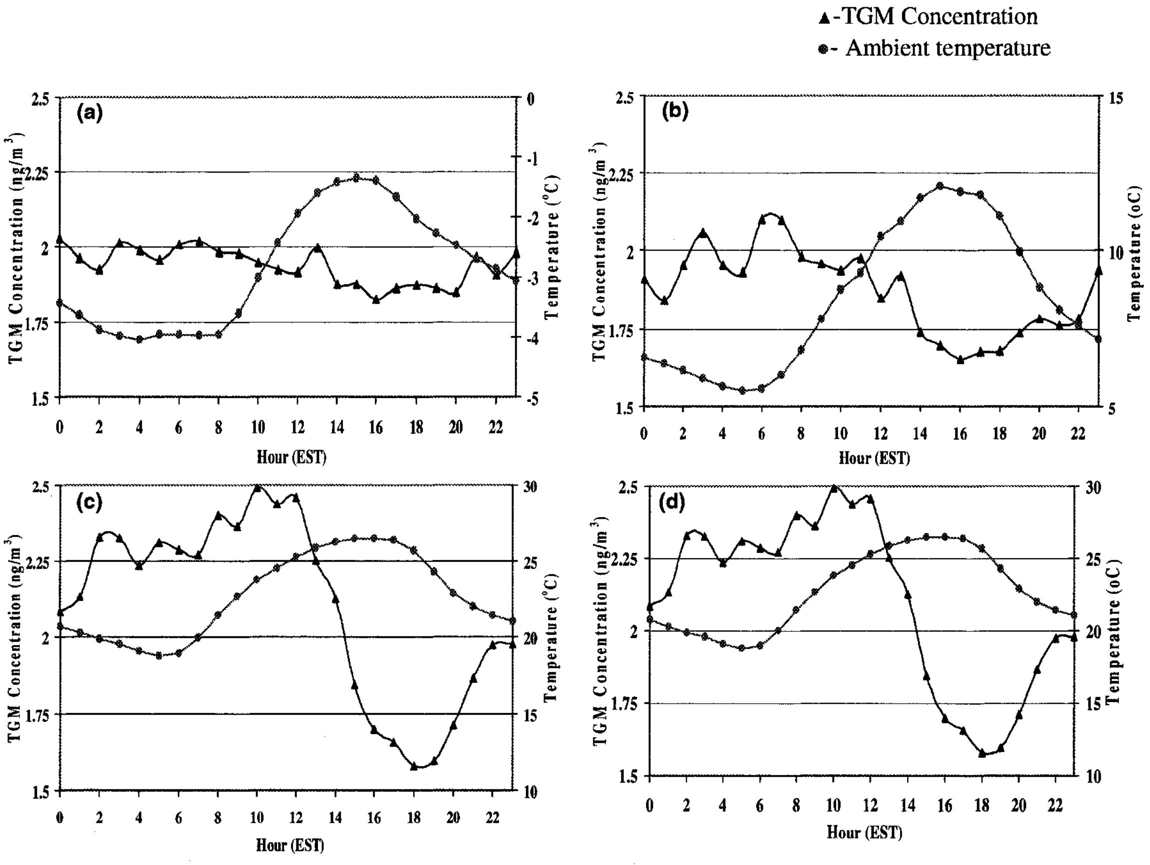

Figure 4.6: Seasonal diurnal variability of TGM concentration and temperature (a) winter, (b) spring, (c) summer, and (d) fall

According to Air Quality in Ontario (2006), higher O_3 concentrations (>50ppb) were observed between 12:00 to 20:00 hours in 2005. This supports the mechanism of depletion observed in TGM concentrations by oxidation in the afternoon in this study. O_3 formation in presence of high temperature is the highest in the summer which could lead to the enhanced oxidation observed in afternoon during this season. In spite of depletion in concentration in the afternoon, significant surface emissions and other factors may lead to the overall higher TGM concentration in summer as observed in seasonal variability.

Significant positive correlations were observed between TGM concentration and relative humidity in summer, fall and spring (Table 4.4). No reason could be identified for such correlations. However, removal of gaseous mercury from the atmosphere is enhanced due to rapid oxidation of elemental mercury in the aqueous phase (Poissant, 1997). High relative humidity (>95%) in air leads to condensation of water vapor. To investigate the effect of higher relative humidity on TGM concentration, TGM concentration was divided in two data sets based on RH $\geq$ 95% and RH $<$ 95%. Correlation analyses for both data sets found significant correlations between TGM and RH. A negative correlation coefficient of -0.094 was found between TGM and RH for RH $\geq$ 95% whereas a positive correlation (0.095) exists for RH $<$ 95%. The r-values were not high, but showed opposite correlations. Thus, high RH could lead to enhanced oxidation resulting in deposition of atmospheric mercury. Significant negative correlations in spring and fall between TGM and wind speed indicate a decrease in concentration at high wind speed because of dilution of air pollutants including mercury while a positive correlation in summer indicate an increase in concentration at higher wind speed. Thus, correlation analysis with meteorological parameters suggests that the temporal variability were affected by surface emissions, condensation of water vapour, and atmospheric reactions Onsite measurement of mercury species, solar radiation, mercury fluxes, and potential oxidant/reductant concentrations will provide more information..

4.4 Correlation with Other Pollutants

Descriptive statistics of several air pollutants measured at the same location for August 8 to October 30, 2007 are presented in Table 4.5. A summary of TGM concentration and meteorological parameters for these 83 days is also included. Relationships between TGM concentration with meteorological parameters as well as other pollutants were determined with the aim to identify the effect of these variables on temporal variability. As pollutants' concentration were data was available only for three months, investigation of seasonal variation in the relationships was not possible. For the correlation analyses, the total number of matching pairs was 1363 observations; other cases were omitted due to missing values.

Table 4.5: Statistical summary of TGM, other air pollutants concentrations and meteorological parameters

Variable	Unit	N	Min	Median	Max	Mean	SD
TGM	ng/m^3	1798	0.83	1.65	26.84	2.01	2.00
O_3	ppb	1815	1.87	22.29	88.66	23.85	15.48
NO_2	ppb	1816	2.13	15.25	57.18	16.27	7.84
NO	ppb	1816	0.33	5.48	377.11	10.93	20.31
SO_2	ppb	1786	0	2.41	69.90	5.57	8.11
CO	ppm	1803	0.09	0.33	2.03	0.38	0.19
VOCs	ppm	1821	0.17	1.03	5.76	1.34	1.06
$PM_{2.5}$	~~mg/m^3~~	1831	0	0.02	0.16	0.03	0.03
BC	µg/m^3	1535	0.13	1.47	20.10	1.85	1.54
Tem	^{0}C	1848	2	18.90	32.00	18.67	5.87
RH	%	1848	25	73	98.00	71.54	16.53
WS	km/hr	1848	0	11	43.00	12.37	7.27

Results of Pearson correlation analysis of TGM with other parameters in Table 4.6 show significant relationships with O_3, NO_2, NO, VOCs CO, and BC. The TGM was negatively correlated with O_3 whereas positively correlated with NO_2, NO, CO, VOCs, and BC. A significant positive relationship between O_3 and temperature indicated the formation of O_3 at high temperature. At the same time, a negative correlation between TGM and O_3 indicated the possible oxidation reaction of Hg^0 into Hg (II). This supports the depletion phenomenon observed in diurnal variability, especially during summer (Table 4.6). NO_2, NO, CO, total VOCs, and BC all have one source in common: combustion of fossil fuels (Hopkins et al., 2007; USEPA, 2008b). Thus, positive correlations of TGM with these pollutants suggest that the source of the Hg is combustion of fossil fuels in different applications, such as power plants and automobiles. Other studies have found a positive correlation between TGM and SO_2, and identified coal fired power plants as the major source for both (Kim and Kim, 2001; Lynam and Keeler, 2006). However, a significant correlation between TGM and SO_2 was absent in this study. This could be due to the period of this study. Our study period could be characterized as late summer (August) and fall (September, October). In fall, power consumption rate is comparatively lower than summer and winter. Thus, Hg and SO_2 emission during this season was low.

Thus, oxidation of Hg^0 resulting in depletion of TGM concentration observed in the diurnal variability is supported by the results of this correlation analyses. This short term study also identified combustion of fossil fuels as the common source of several air contaminants. However, this analysis explained the relationships between TGM and other variables only for the study period of August 8 to October 30, 2007.

Table 4.6: Inter-relationships among hourly TGM, other pollutants concentration, and meteorological parameters

(r-values in bold phase represent significant correlation at *p*-value <0.05)

Variable	TGM	O_3	NO_2	NO	SO_2	CO	VOCs	$PM_{2.5}$	BC	Tem	RH
O_3	**-0.21**										
NO_2	**0.227**	**-0.407**									
NO	**0.171**	**-0.363**	**0.952**								
SO_2	0.004	**0.114**	0.082	0.021							
CO	**0.239**	**-0.295**	**0.741**	**0.684**	**0.187**						
VOCs	**0.146**	**0.148**	0.04	-0.063	**0.34**	**0.129**					
$PM_{2.5}$	0.087	**0.198**	**0.224**	0.073	**0.172**	**0.256**	**0.583**				
BC	**0.215**	**-0.236**	**0.852**	**0.746**	**0.134**	**0.665**	**0.342**	**0.588**			
Tem	**0.104**	**0.66**	**-0.175**	**-0.25**	**0.23**	**-0.109**	**0.554**	**0.432**	**0.103**		
RH	**0.183**	**-0.525**	**0.227**	**0.182**	**-0.149**	**0.117**	**0.239**	**0.253**	**0.279**	**-0.332**	
WS	-0.059	**0.257**	**-0.303**	**-0.23**	**0.203**	**-0.306**	-0.009	**-0.22**	**-0.315**	**0.131**	**-0.38**

4.5 Source Receptor Relationship

4.5.1 Factor Analysis- A Short Term Study

Pearson correlation analysis for the study period of August 8 to October 30, 2007 only determined the one-on-one linear relationship among the variables. Therefore, PCA was conducted with the aim to determine the major factors affecting temporal variability of TGM concentrations during the study period. A total of twelve factors were obtained from the analysis. Factors for which Eigen Values were greater than 1 are presented in Table 4.7 and used for further analysis. As can be seen, four principal factors explain 77% of the total variances. The remaining eight components were not considered further because they explain a very small proportion of the variability (Figure H.1).

Table 4.7: Results of PCA with varimax rotation (N = 1363, bold numbers indicated loadings ≥±0.5)

Variable	Factor 1	Factor 2	Factor 3	Factor 4
TGM	0.16	0.14	**-0.55**	0.30
O_3	-0.29	0.40	**0.74**	0.15
NO_2	**0.96**	-0.01	-0.16	-0.05
NO	**0.93**	-0.15	-0.10	-0.04
SO_2	0.15	0.29	-0.03	**0.69**
CO	**0.84**	0.08	-0.13	0.05
VOC	0.01	**0.85**	-0.23	0.18
$PM_{2.5}$	0.24	**0.84**	-0.03	-0.18
BC	**0.85**	0.40	-0.14	-0.11
Temp	-0.12	**0.75**	0.42	0.24
RH	0.06	0.17	**-0.78**	-0.43
WS	-0.29	-0.15	0.18	**0.71**
Eigen value	4.05	2.38	1.96	1.25
% Var	0.29	0.21	0.15	0.12

Analytically, a factor is the linear combination of the variables defined in terms of factor loading which defines the correlation between a factor and a variable. The Eigen Value gives a measure of the amount of variation in all variables accounted for by the factor. For example, the first factor in our study has a variance (Eigen value) of 4.05. The coefficients of the variables listed under Factor 1 can be expressed as follows::

Factor 1 = 0.96 NO_2 + 0.93 NO + 0.84 CO + 0.85 BC +0.16 TGM+0.15 SO_2 ....

The identification of the factors is subjective. The major four factors affecting TGM concentration variations were identified in this study based on the loadings of the variables for each factor and also comparing the outcome of the analysis with other studies' results (Kim and Kim, 2001; Lynam and Keeler, 2006; Liu et al., 2007).

Factor 1 that explains 29% of total variance had strong positive loadings for NO_2, NO, CO, BC. A weak positive loading (0.15) was also observed for TGM concentration. All these pollutants have a common source, which is the combustion of fossil fuels. Thus, this factor suggests the effects of combustion of fossil fuels on TGM concentration. Factor 2 suggests the effects of the meteorological conditions, which explains 21% of the variance. This factor had strong positive loading for temperature while moderate loadings for TGM and O_3. High temperature could lead to surface emissions as well as foliar emission of Hg^0. Positive loading on O_3 signifies the formation of ozone at high temperature. Factor 2 also had high positive loadings for VOC and $PM_{2.5}$, which could not be explained.

Factor 3 had strong and moderate positive loadings for O_3 and temperature, respectively along with negative loadings on TGM, NO_2, and NO. Formation of O_3 at high temperature consequently oxidizes Hg^0 resulting in decreases in atmospheric mercury concentration. The negative loadings on NO_x also support the possible formation of O_3. Thus, potential photochemical reactions could be identified as Factor 3. Factor 4 had significant positive loadings on SO_2 concentration and wind speed and a moderate positive loading on TGM. As coal combustion is the major source for both SO_2 and Hg, effects of coal combustion were considered as Factor 4. This factor supports transportation of Hg from coal fired power plants located to the south of Windsor as mentioned previously. Detroit, the neighbor city of Windsor, was reported to be affected by regional mercury sources (Liu et al., 2007). Windsor, located downwind to Detroit, is expected to be affected by the same regional sources. A positive loading on wind speed also suggests transportation of Hg from regional sources at high wind speeds.

Results of the PCA suggest combustion of fossil fuels, meteorological conditions, photochemical process, and regionally transported mercury have major significant influence on the temporal variability of TGM concentrations in Windsor. However, this PCA was based on data collected during 83 days. Therefore, the factors identified may not represent long-term factors affecting seasonal and diurnal variability. It is recommended to repeat the PCA, once more data becomes available.

4.5.2 Potential Regional Source Identification

Figure 4.7 (a) shows a Wind Rose plot using hourly wind directions (EC, 2008d) for year 2007. It was found that the predominant wind directions for the study period were between the south and the west. Pollution rose plot in Figure 4.7 (b) shows that high TGM concentrations in Windsor were associated mostly with the wind coming from the south-west of Windsor. However, wind direction at the receptor site does not describe the air mass path before reaching Windsor. The presence of mercury sources along the air mass path could affect TGM concentration in Windsor as Hg^0 can be transported over a long distance (Poissant et al., 2002), as identified by PCA in this study.

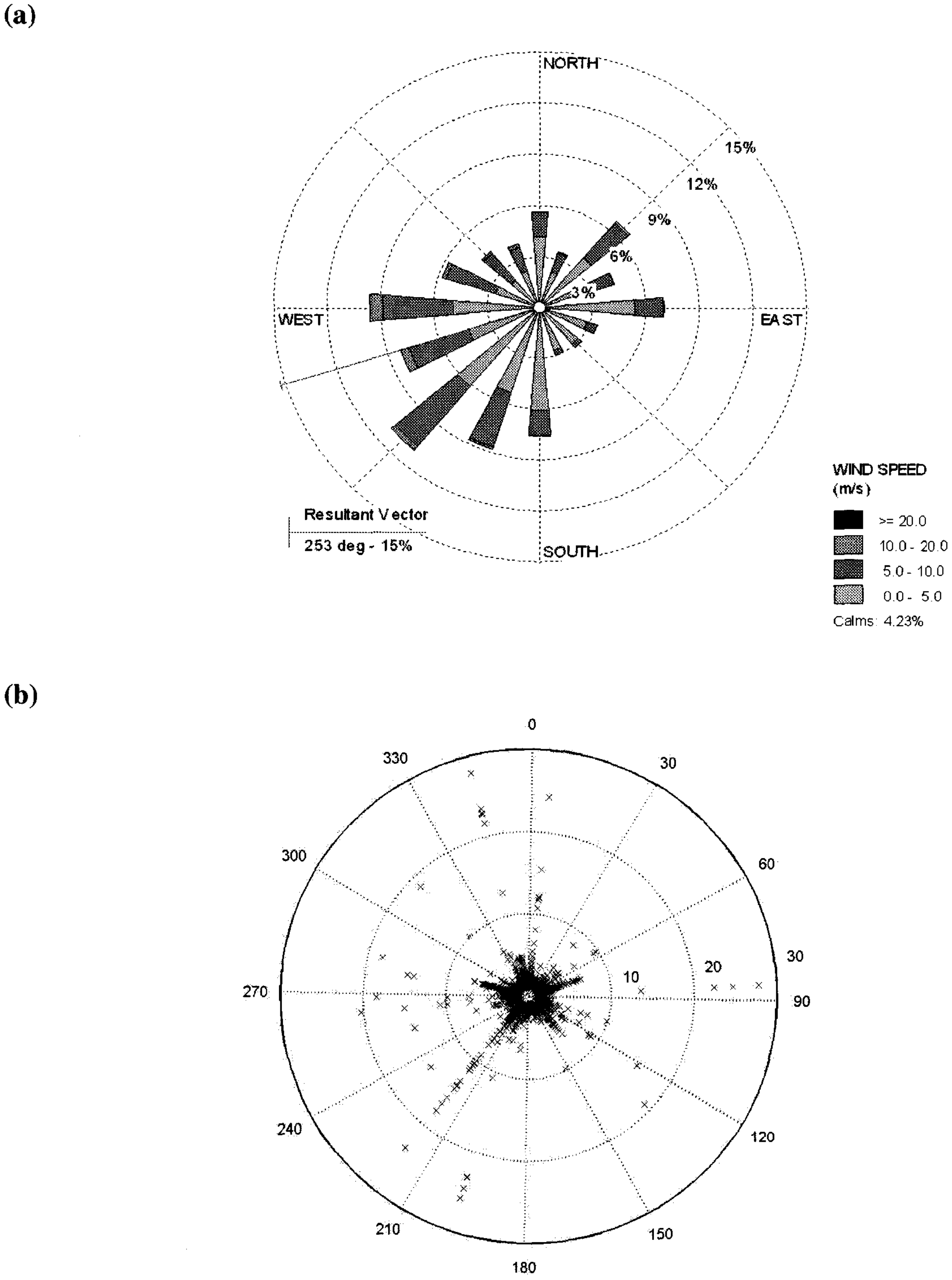

Figure 4.7: Wind Rose (a) and Pollution Rose (b) Plots for Windsor, 2007

In order to determine the geographical location of potential regional sources related to high TGM concentrations in Windsor, the PSCF model (Han et al., 2007) was used. In Figure 4.8, the total number of endpoints for each grid (1°×1°) from HYSPLIT simulation were plotted to determine the regions that could affect Windsor. It shows that air mass traversed mostly over MI, WI, IL, IN, OH and ON before reaching Windsor indicating the prevailing wind direction was between the north-west and the south-west as in the Wind Rose (Figure 4.7 (a)). Fewer grid endpoints were found in the south, the east, and the north-east as in the Wind Rose. However, the north-west direction was not prominent in the Wind Rose. In the 3 day simulation time, a few trajectories had travelled from long distances including Oregon in the west and Newfoundland and Labrador in the east.

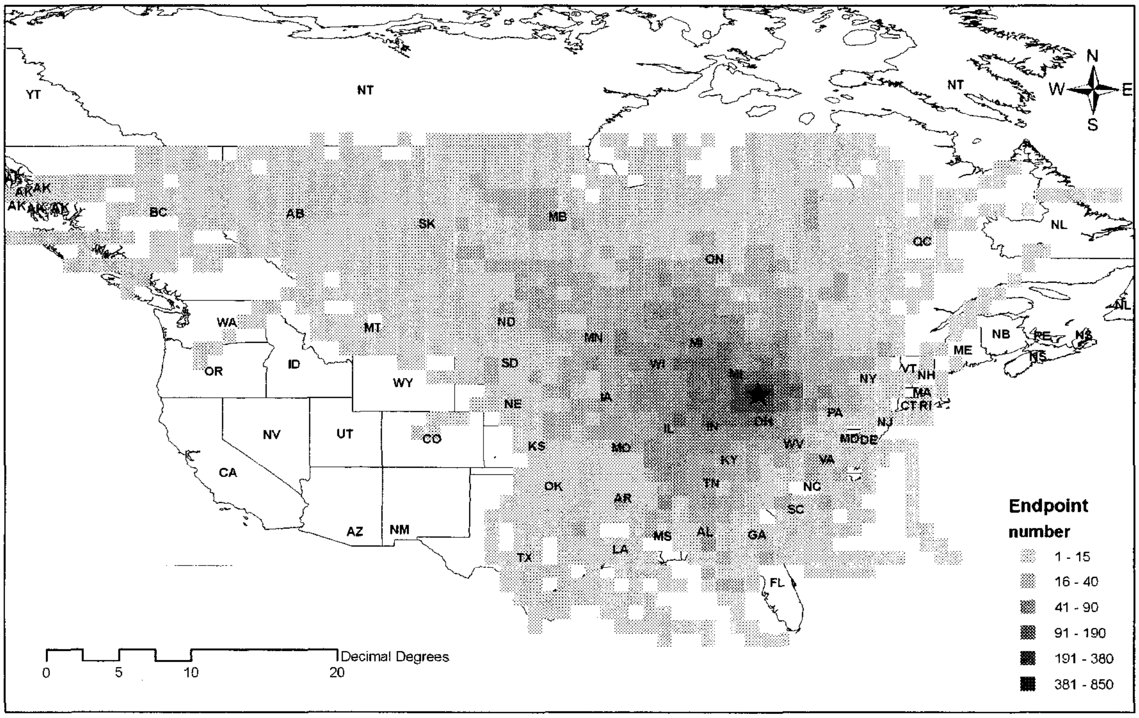

Figure 4.8: Total number of end points for each grid cell (Star indicates Windsor)

As discussed previously the Wind Rose and Pollution Rose were plotted using receptor site wind direction measurements. The results are not extendable as air mass path can change its direction significantly before reaching Windsor. However, the plots are informative as they give a glimpse of wind directions connected with high concentrations and are easy to plot. The endpoint calculation based on trajectory analysis is more informative in terms of air mass path direction, but requires a sophisticated model for simulation. Therefore, these two methods should be used in conjunction with one another to determine potential sources as both of them provide valuable information.

4.5.2.1 Results for Annual PSCF modeling

For annual PSCF modeling, the annual mean concentration of 2.02 ng/m^3 was considered as the criteria value. Thus, days with the daily average concentration greater than the criteria value were considered as high mercury concentration days (Figure 4.9), which was 88 days out of 293 available days in this study. The average number of endpoints (6 per grid) was used in Equation 2.2 to calculate the weight functions. The PSCF modeling results are plotted in Figure 4.10. Highly weighted PSCF values observed in areas indicate Ohio, Indiana, Illinois, Missouri, Kentucky, and Tennessee in the south-west as the potential regions, as well as Iowa in the west and Michigan, Wisconsin, Minnesota up to Manitoba in the north-west. The Gulf of Mexico in the south was also identified as a potential source area. No adjacent grids with high PSCF values in the east, therefore no potential sources were identified in this area. Overall, the major source locations lay to the south-west of Windsor, stretching from Ohio to Texas, also shown in the Pollution Rose (Figure 4.7 (b)). The potential regions identified from this study are similar to the potential regions reported affecting New York (Han et al., 2007).

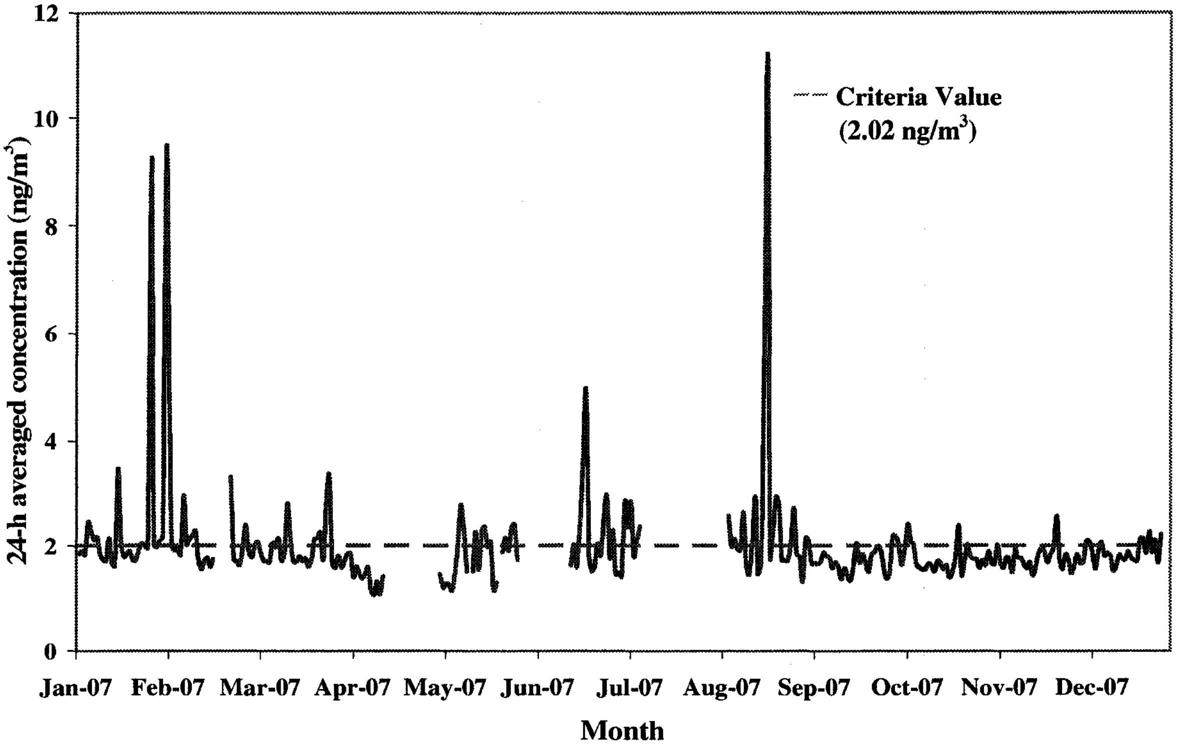

Figure 4.9: Time Series Plot of Daily average TGM concentration in Windsor, 2007

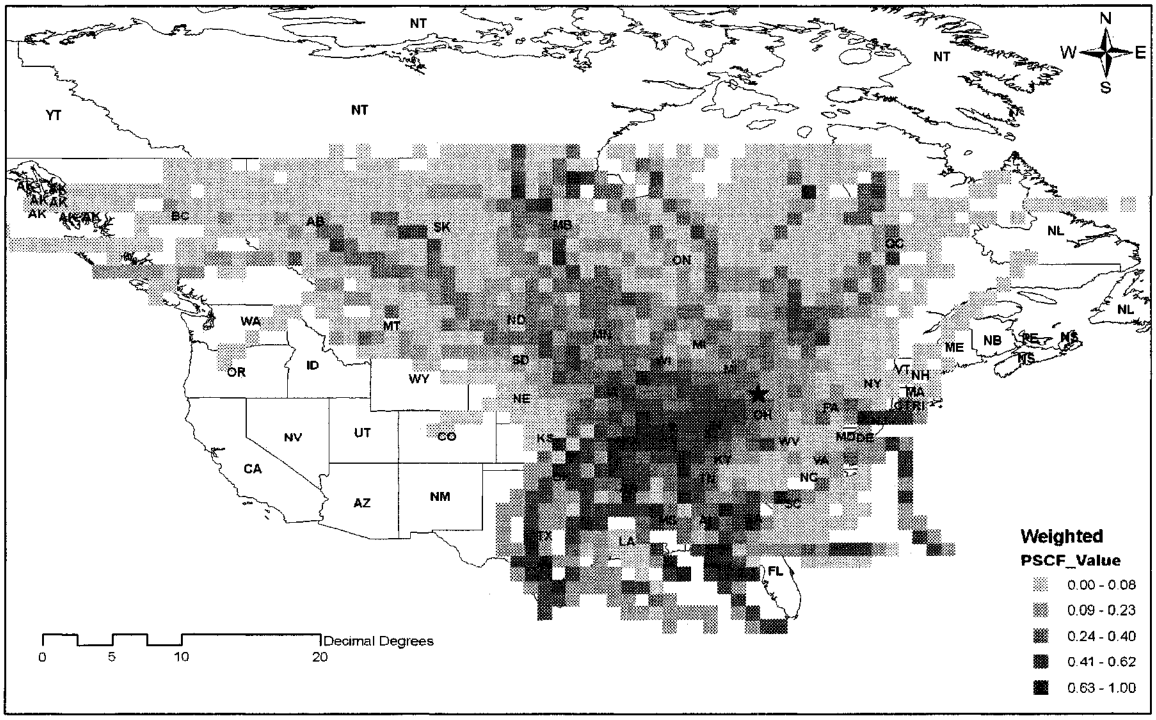

Figure 4.10: Map of Weighted PSCF Value for Windsor (star indicates Windsor)

To verify the potentiality of these regions affecting the Windsor TGM concentration, an air emission inventory of total mercury including all mercury compounds for North America for the year 2006 (Appendix I, Table I.1 and Table I.2), is displayed in Figure 4.11, while Figure 4.12 shows the emission rate (g/km^2) for each state/province calculated by dividing the total mercury emission by the respective state/province area. Overall mercury emission rate was higher in the USA (6.18 g/km^2) compared to in Canada (0.76 g/km^2). The higher mercury emission rates of 33 to 51 gm/km^2 were observed in Indiana, Ohio, Pennsylvania, West Virginia, and Alabama. Other high mercury emitting states were Illinois, Kentucky, Tennessee, Louisiana, and Georgia. Thus, states in the south-west, the south and the southeast of Windsor indeed have high mercury releasing sources. In Figure 4.10, the Gulf of Mexico was identified as source of mercury. Annual atmospheric deposition, including both wet and dry, was 25 tons to the surface water of the Gulf of Mexico and an additional 22 tons of mercury discharged into the Gulf from the Mississippi River according to EPA (Neff, 2008). Although air emissions from oceans were not included in Figure 4.11, re-emission of mercury from Gulf of Mexico could be a potential source of Hg in Windsor. Results obtained from the emission inventory analysis supports the findings of the PSCF modeling (Figure 4.10) that regions located in the south-west affect significantly Windsor TGM concentrations.

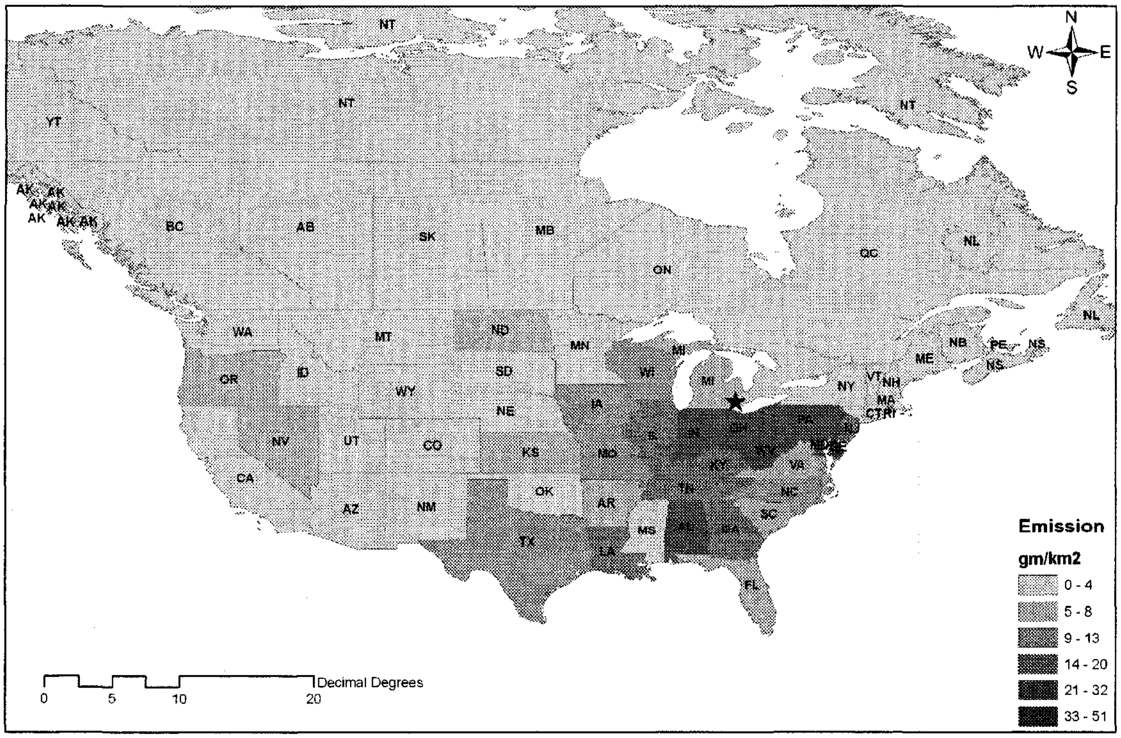

Figure 4.11: Emission of total mercury and mercury compounds (kg)

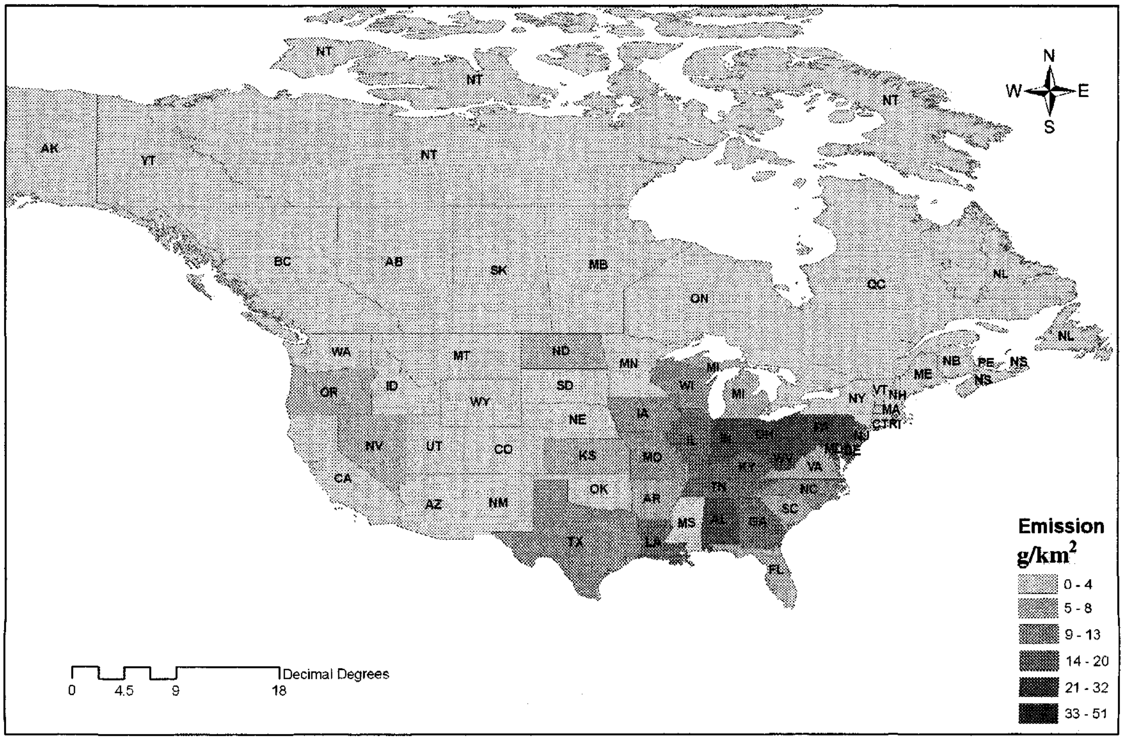

Figure 4.12: Emission rate (g/km^2) of mercury and mercury compounds

4.5.2.2 Results of Seasonal PSCF Modeling

Annual weighted PSCF modeling identified the potential source areas for the entire study year (2007). Seasonal modeling was also conducted to identify seasonality in the potential source areas. For seasonal modeling, both annual mean and respective seasonal means (Table 4.2) were used for each season as the criteria value. The same weight function was used for all four seasons as in annual modeling. For comparison of potential regions among the seasons, the same color scheme for weighted PSCF values was used in the plots for all four seasons (Figure 4.13 to Figure 4.20). As seen in Table 4.8, the maximum number of exceedences over the criteria value was observed in winter (30 day). In summer, spring, and fall the exceedences were for 25, 20, and 13 days respectively.

Results of seasonal PSCF modeling using annual mean as the criteria value are presented in Figure 4.13 to Figure 4.16. In summer, significant source areas were identified in the south-west of Windsor, from Ohio to Texas as in Figure 4.13. The potential sources were located in MI, OH, IN, IL, MO, KS, OK, and TX. No regional influence from the southeast regions was observed. Presence of potential sources over a wide range of areas was observed in winter, between the south-west to the north-west regions, also in the north (Ontario) and in the south (Gulf of Mexico) (Figure 4.14). In spring, significant source areas were identified in the south-west (Figure 4.15) as in summer. The potential sources for these periods were located in OH, IN, KY, and TN. Sources were also identified in the north-east, along Ontario to Quebec. In fall, no significant (except a few grids in the south-west) regional sources were identified (Figure 4.16).

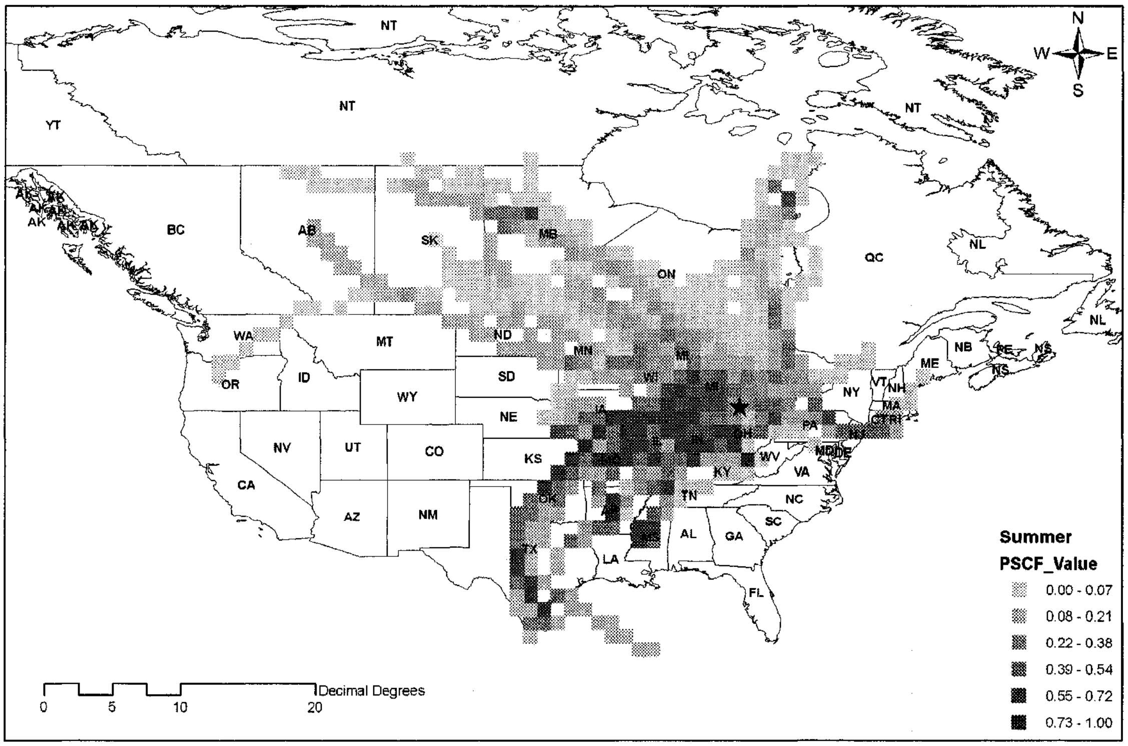

Figure 4.13: Weighted PSCF for Windsor in summer (Criteria value was 2.02 ng/m^3)

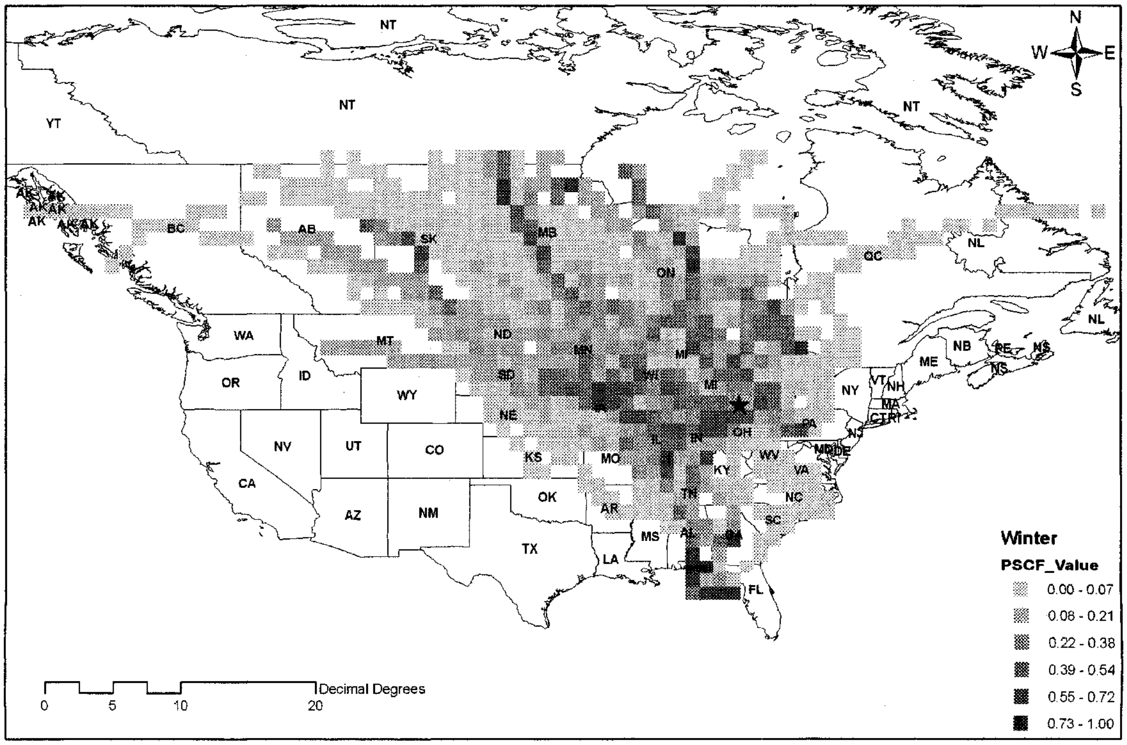

Figure 4.14: Weighted PSCF for Windsor in winter (Criteria value was 2.02 ng/m^3)

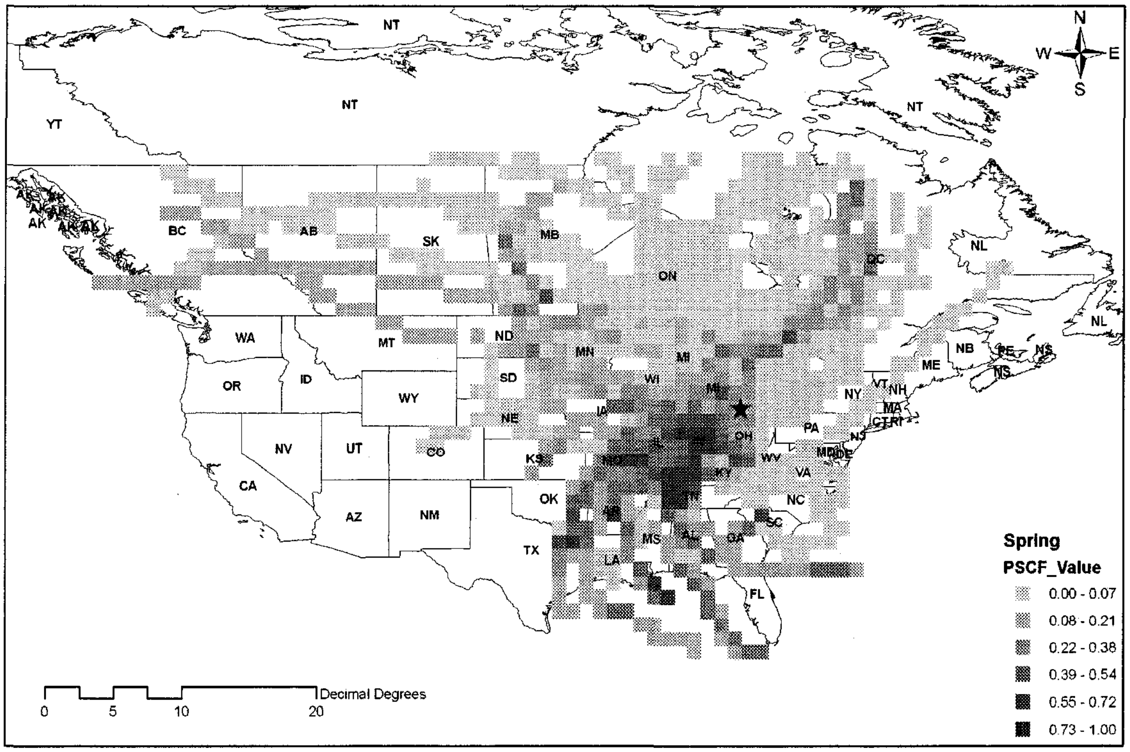

Figure 4.15: Weighted PSCF for Windsor in spring (Criteria value was 2.02 ng/m^3)

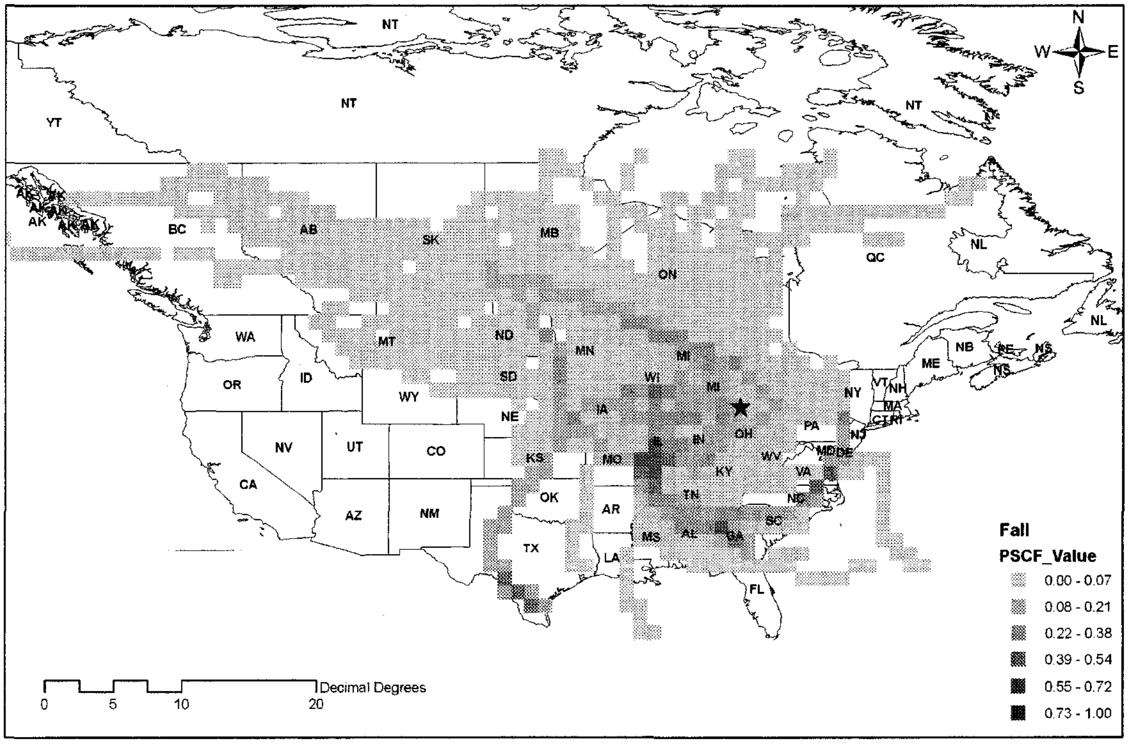

Figure 4.16: Weighted PSCF for Windsor in fall (Criteria value was 2.02 ng/m^3)

In comparison with the annual modeling, the seasonal modeling depicts the seasonal features of potential source areas. Significant source areas were identified in specific directions for each season. More potential source regions were identified in winter and summer as the number of concentration exceedences above the annual mean were higher in these two seasons compared to in spring and fall (Table 4.8). Therefore, this method may not be well suited for comparison among the four seasons.

Figure 4.17 to Figure 4.20 display the seasonality in potential sources using respective seasonal mean. The maximum number of exceedences over the criteria value was observed in fall (36 day). There were 15 days of exceedences over the criteria value in both winter and summer for each, while there were 27 days for spring, as shown in Table 4.8. As expected, more potential source areas were identified than with an annual mean (Figure 4.13 to Figure 4.16) in winter and summer, while less occurred in spring and fall. This is because, for example, less days were modeled in summer (Figure 4.17) using the seasonal mean (2.48 ng/m^3) as opposed to the annual mean (2.02 ng/m^3). MI, OH, IN, IL, AR, MS were identified as significantly responsible for concentration higher than 2.48 ng/m^3 in summer. Similarly, Figure 4.18 shows the potential sources in the south and in the west are responsible for high concentrations (>2.17 ng/m^3) in winter.

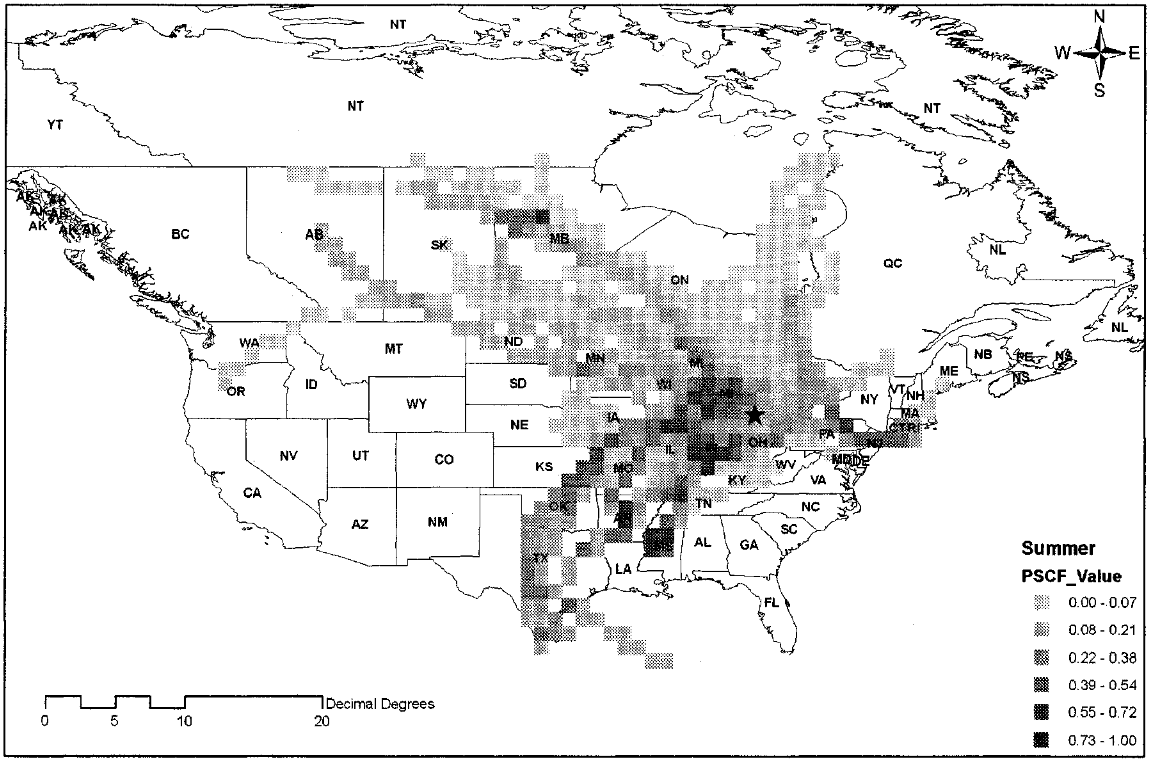

Figure 4.17: Weighted PSCF for Windsor in summer (Criteria value 2.48 ng/m^3)

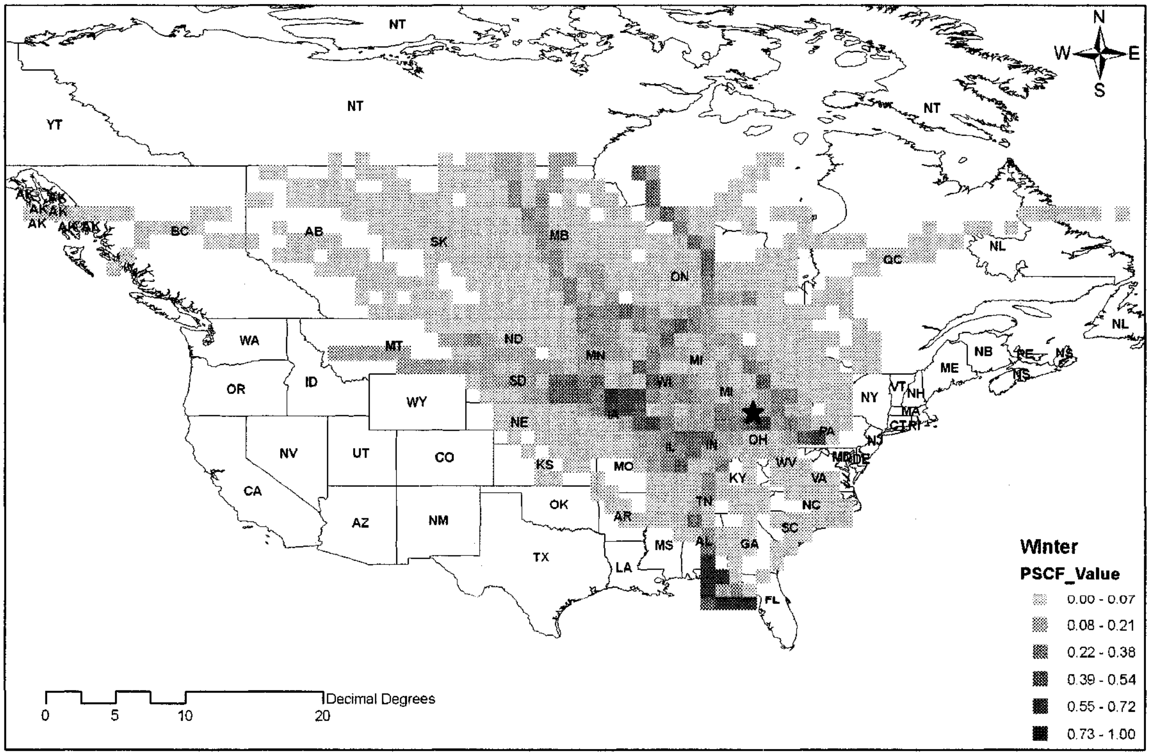

Figure 4.18: Weighted PSCF for Windsor in winter (Criteria value 2.17 ng/m^3)

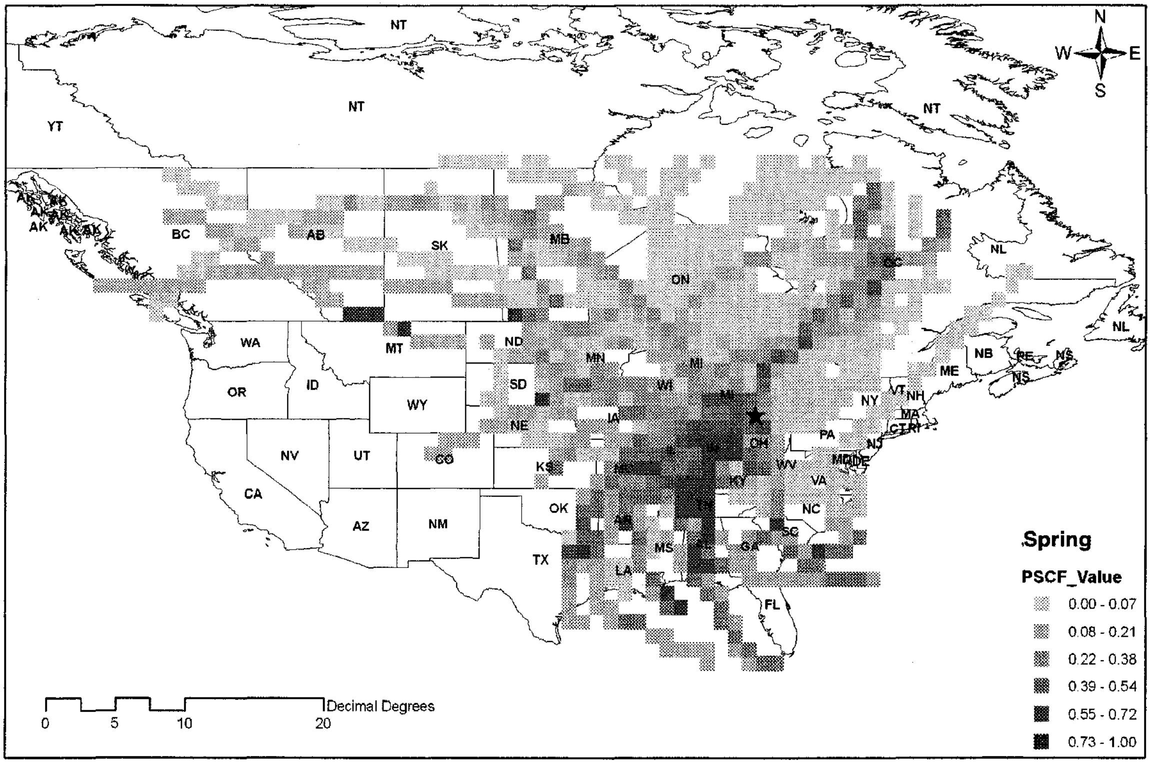

Figure 4.19: Weighted PSCF for Windsor in spring (Criteria value was 1.88 ng/m^3)

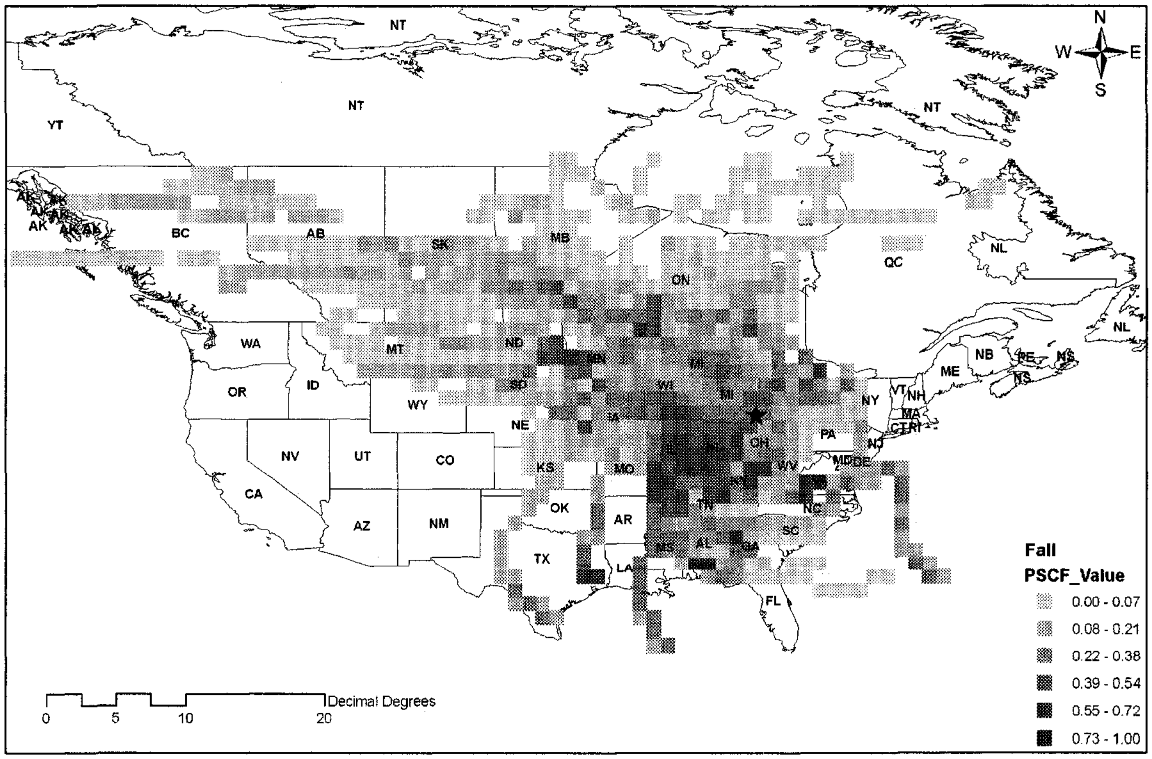

Figure 4.20: Weighted PSCF for Windsor in fall (Criteria value was 1.76 ng/m^3)

To further identify the regions responsible for high concentration days for each season, states/provinces with weighted PSCF values > 0.73 (in at least with two consecutive grids for one state/province) for both criteria values, annual and seasonal means are presented in Table 4.8. Some regions show up consistently at higher criteria value. From the analysis it can be concluded that high Hg concentration days in summer, fall and spring were affected mostly by the south-west regions of Windsor while high concentrations in winter were affected by regions in the west (e.g., Iowa) and some remote sources in the south (AL, Gulf of Mexico).

Table 4.8: Identification of regional sources responsible for high concentration (N= number of days modeled, i.e., exceeding criteria value)

Season	Using Annual Mean	N	Using Seasonal Mean	N
Summer	MI, OH, IN, IL, IA, MO, MS, KS, AR, TX	25	MI , IN, IL, MS, AR	15
Winter	OH, IN, IL, AL, IA, WI, MB, SK, Gulf of Mexico, ON	30	OH, IL, IA, AL, Gulf of Mexico, ON	15
Spring	IN, IL, KY, TN, MO	20	MI, OH, IN, IL, KY, TN, AL, MO, TX, AR, QC, ON	27
Fall	---	13	IN, IL, OH, KY, MO, AL, TX, MN VA, ON, WI, MB, ND	36

Between the two schemes of seasonal PSCF modeling, results using the annual mean identify the seasonality of potential sources since the same criteria value was applied. This method reveals seasonal features, which could be otherwise unavailable from the annual modeling alone. The use of respective seasonal means enables the identification of potential sources responsible for high concentration days in each season therefore a comparison among the four seasons is possible. Therefore, for identification of potential sources, the application of both annual and seasonal means was useful for seasonal PSCF modeling. It was recommended using both methods in the seasonal modeling. If the resources are limited, however the use of seasonal means is preferred. As the annual and seasonal TGM concentrations distributions were right skewed (Figure 4.1 and Figure 4.3), the use of median concentration as the criteria value would be more representative of the TGM concentration.

The seasonal analysis also identify that in each season, the regional influences, in terms of emissions and meteorology, affect Windsor Hg concentration by slightly different mechanisms. Atmospheric depositions are high in summer. As seen in Figure 4.5, the summer diurnal trend is a steep decrease in concentration implying high deposition in afternoon hours. However, surface emission is also the highest in summer as the ambient and soil/water temperatures are both high. Along with the surface emission, regional sources also affect the high concentrations as observed in summer. High power consumption in summer results in more Hg emissions from the coal fired power plants. A number of coal fired power plants are located in the south-west region of Windsor. This region was also identified as potential source region in seasonal PSCF modeling. Thus air masses coming from south west of Windsor at low wind speed (causing less dilution of Hg) could carry over Hg contributing to elevated concentrations in Windsor, In winter, wind speeds are high which leads to more dispersion. On the other hand, anthropogenic emissions are also high in winter due to high energy consumption for heating. Also, there are less chemical transformation and deposition in winter due to low temperature. The net effect of these major factors leads to elevated TGM concentrations in winter. In spring and fall though the air mass came from mostly the south-west regions, average TGM concentration in Windsor was low. It is likely due to relatively low mercury emissions from surfaces and low anthropogenic sources compared to summer and winter.

4.6 Spatial variability of TGM Concentration in Windsor, 2006

4.6.1 Statistical Summary

A summary of the descriptive statistics of 5-min TGM concentrations at the 13 sites in Windsor for a 7-day period (October 16 to 26, 2006) is presented in Table 4.9. An overall average concentration of 2.60±0.37 ng/m^3 was calculated for the 7-day period considering all measurements. Among the 13 sites, a maximum average concentration of 3.64 ng/m^3 was measured at Site 7 (Riverside Parking Lot) whereas a minimum average concentration of 2.23 ng/m^3 was recorded at Site 6 (Hyde St, near Jackson Park). As shown in Figure 4.21, TGM concentrations at Site 13 were more variable (SD 1.69 ng/m^3).

Table 4.9: Statistical summary of TGM concentrations at 13 Windsor sites, L and H in parenthesis stands for lowest for highest concentration

Site	N	Min	Median	Max	Mean	SD	CV
1	934	1.65	2.33	7.5	2.41	0.64	
2	11	1.79	2.6	3.5	2.54	0.6	
3	18	1.59	2.75	3.76	2.57	0.81	
4	22	1.74	2.11	3.58	2.45	0.7	
5	14	1.6	2.07	4.28	2.47	0.91	
6	20	1.49	2.23	3.2	2.23 (L)	0.59	
7	17	1.83	4.39	4.81	3.64 (H)	1.3	
8	22	1.68	2.16	3.65	2.42	0.61	
9	25	1.76	1.95	4.24	2.38	0.83	
10	22	1.77	1.98	4.1	2.54	0.89	
11	22	1.65	1.97	3.72	2.37	0.74	
12	22	1.64	2.06	4.87	2.6	1.13	
13	23	1.64	2.16	7.75	3.02	1.69	

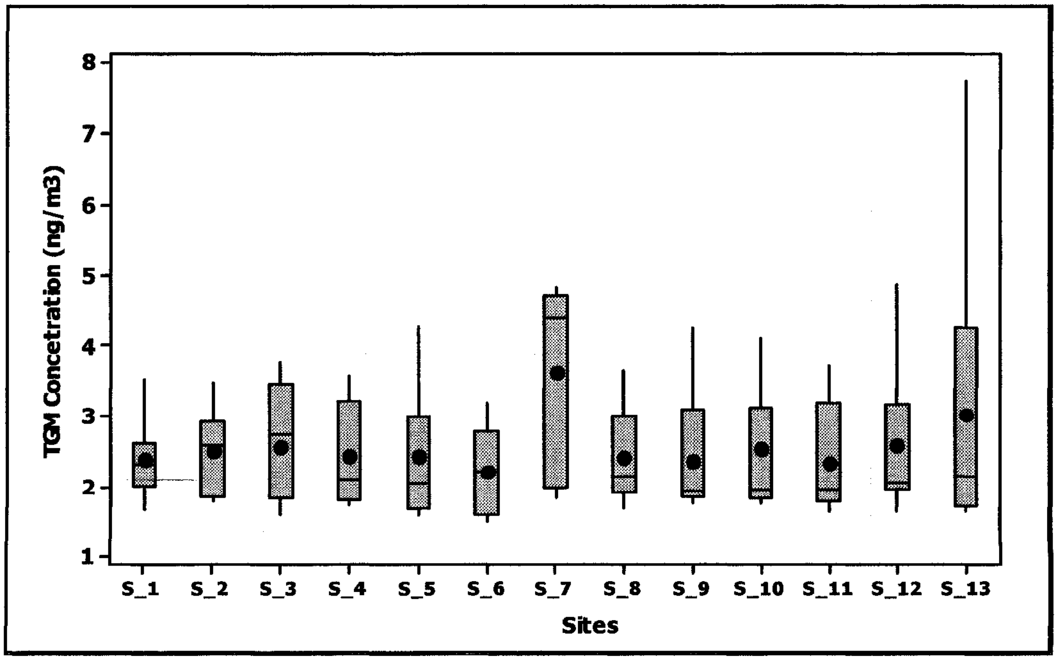

Figure 4.21: Box-Whisker Plot of TGM Concentrations at 13 Sites for 7 day

Results of ANOVA, Tukey's test and equal variance test for this spatial variability study are presented in Appendix J.1. Results of ANOVA indicate statistically significant difference in the mean concentrations among the 13 sites. Results of multiple comparisons using Tukey's test specified that the mean concentration at Site 7 was statistically different from other sites, except Site 13. The Site 1 and Site 6 mean concentrations was statistically different from Site 13 too while statistically similar with others. Other sites mean concentrations were statistically similar. The results from equal variances tests, i.e. Bartlett's and Levene's, showed that the variances among the sites were significantly different, higher variability was observed in Site 13 and Site 7 while the least variability was observed in Site 1. Thus, the statistical analysis indicates that among the 13 sites, Site 7 and Site 13 needs further analysis to identify the reasons for high concentration observed at these two sites.

4.6.2 Effect of Local Sources on TGM Concentration

Two local facilities namely the City of Windsor - Lou Romano Water Reclamation Plant and Aramco Management Ltd. in Windsor reported mercury emission to NPRI in 2006 (NPRI, 2008). The total release of Hg compounds to air and water was 16.002 kg from these two companies. Mercury release data was not available in the inventory for the scrap metal recycling plant and the automobile assembly plants in Windsor, which could also release mercury. Monitoring sites close to these anthropogenic sources may experience high mercury concentrations. The time series of TGM concentrations for each of the 13 sites are presented in Figure 4.22. Concentration measurements in these sites were conducted between 10:00 to 19:00 except for Site 1 for which concentrations were mostly monitored at night-time and early morning.

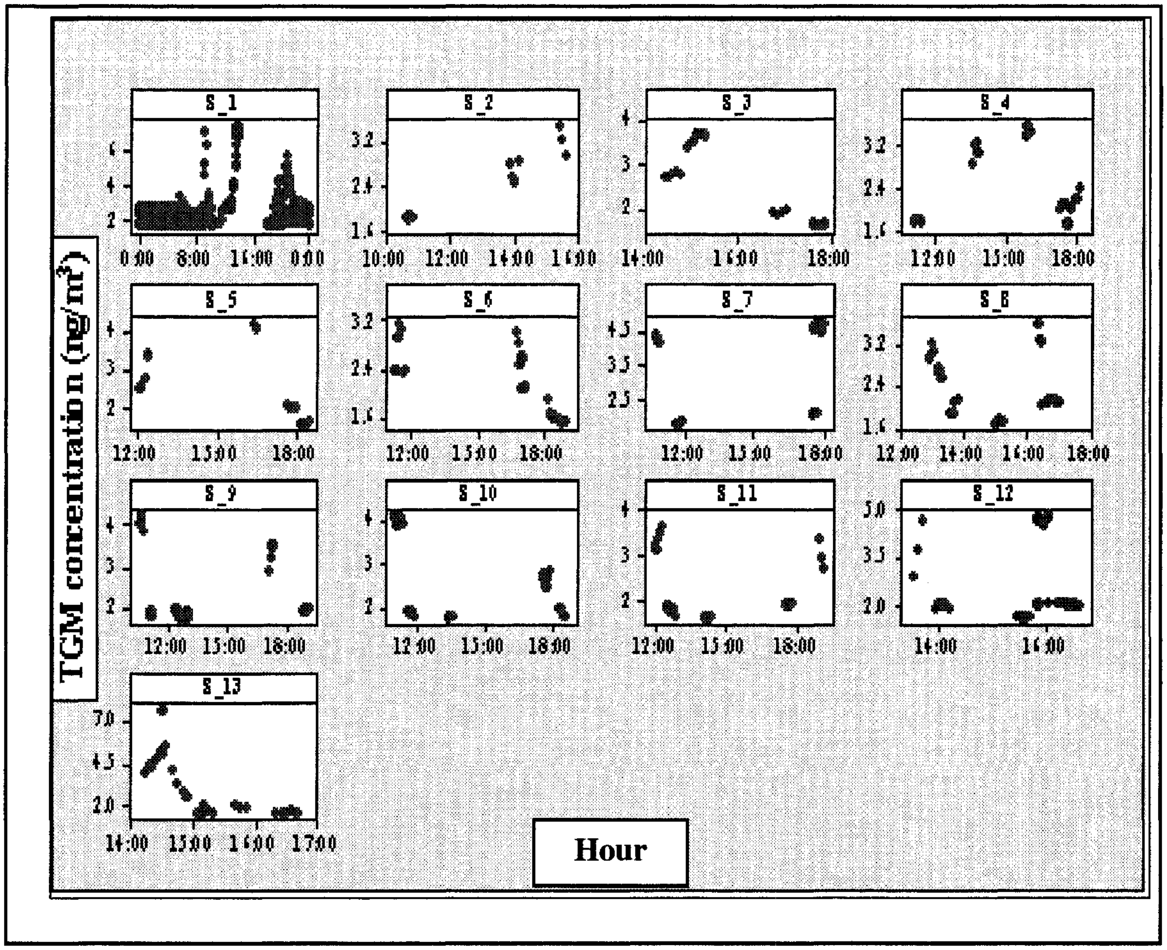

Figure 4.22: Individual TGM concentration at 13 Sites in Windsor

Each day, 3 sites with the highest overall concentrations were identified. Site 1, 7, 9, 12, and 13 were identified at least twice out of the seven days. The reason for high concentrations at these sites could be that Sites 1, 7, 9 are located adjacent to Detroit. Thus, these 3 sites are affected by anthropogenic sources of Detroit. Site 7, close to the Ambassador Bridge can be affected by automobile emissions. The Windsor-Lou Romano Water Reclamation Plant discharging mercury compounds to the Detroit River possibly caused high TGM concentrations observed at Site 1 in the evening. Site 12 was close to the Windsor Airport, the Walker Industrial Park, and Aramco Management Ltd. (a NPRI Hg facility). The reasons for high concentrations and higher variability monitored at Site

13 could not be identified. For each monitoring site, a few data was available, except for Site 1 (Table 4.9). The measurement was conducted at the 12 sites only during daytime and each day the sequence of monitoring sites was chosen randomly. Thus, in addition to the local source, measurement hours could also affect the observed spatial variability.

Figure 4.23 presents the overall diurnal pattern during the study period of October 16 to October 26, 2006 based on TGM concentration measured at the 13 sites and also during driving around Windsor. It shows that daytime TGM concentrations were higher than at night-time, which is different from the 2007 fall pattern of decreasing concentration from morning till afternoon (Figure 4.5). Two peak concentrations were observed, one in mid morning, i.e. 10:00, and another at afternoon, 14:00. In other words, concentration measurements during daytime at different sites, especially between 10:00 to 17:00 had higher concentrations irrespective of location. Similarly, concentration at night time was low which was mostly measured at Site 1.

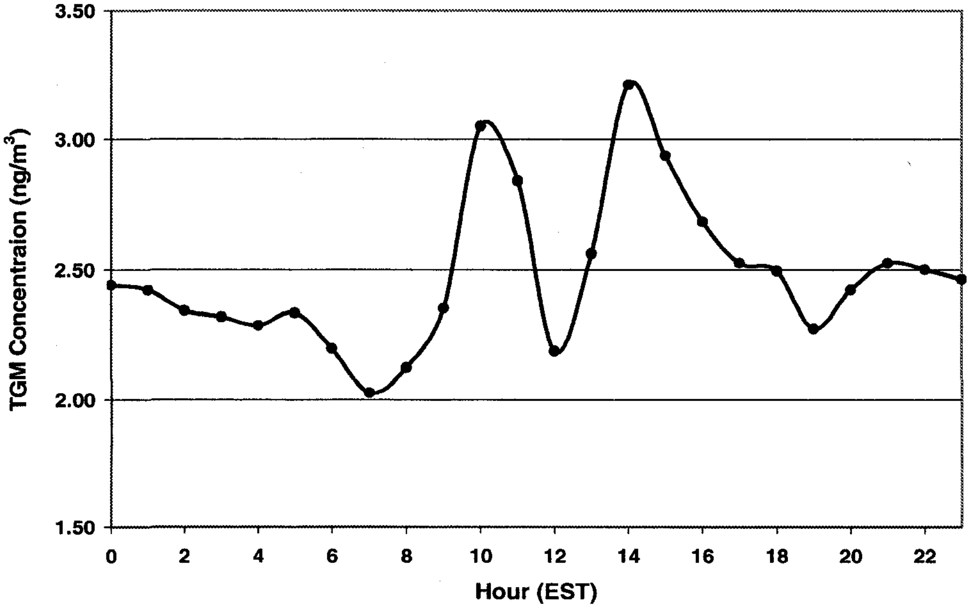

Figure 4.23: Diurnal variability of TGM concentration in Windsor, 2006

The observed diurnal variability might affect the average concentration by sites since the measurement was conducted at different hours of the day. Thus, in order to minimize the effect of hour of the measurement, a set of 24 correction factors (CF) was derived using hourly and daily average concentrations from Figure 4.23. Those factors were applied to the 5 minute TGM concentrations respective to their hour of measurement. Then, the mean concentration was calculated for each site using the corrected concentrations. As presented in Table 4.10, after correction, maximum and minimum average concentration was still observed in Site 7 and Site 6 respectively.

Table 4.10: Comparison of TGM concentration data before and after correction

Site	**Before Correction**		**After Correction**	
	Mean	**SD**	**Mean**	**SD**
1	2.41	0.64	2.53	0.64
2	2.54	0.6	2.10	0.56
3	2.57	0.81	2.19	0.58
4	2.45	0.7	2.29	0.64
5	2.47	0.91	2.51	0.91
6	2.23 **(L)**	0.59	2.05 **(L)**	0.44
7	3.64 **(H)**	1.3	3.34 **(H)**	1.25
8	2.42	0.61	2.31	0.69
9	2.38	0.83	2.34	0.64
10	2.54	0.89	2.30	0.70
11	2.37	0.74	2.46	0.94
12	2.6	1.13	2.32	1.06
13	3.02	1.69	2.44	1.23

Results of ANOVA after correction show statistically significant difference among the means (Appendix J.2), as before. However, Tukey's test found the mean TGM concentration of Site 7 was significantly different from other sites while other sites had statistically similar concentrations. Site 13 was no longer similar to Site 7, and the difference in means between Site 13 and Site 1 was no longer significant. Overall, application of the CFs did not change the spatial variability significantly.

In comparison with multiple sites monitoring by placing one set of the instruments at each site, this study was the first attempt to determine short-term spatial variability of Hg within a city using a mobile lab. The former approach is limited to a few sites because of the high cost of the instruments. The latter method has the advantage of using only one set of instrument in a mobile platform. Therefore, it can visit a large number of sites to determine spatial variability. In this study 13 sites were monitored. From the analysis, it can be concluded that the methodology of choosing monitoring hours randomly for the sites was effective in minimizing the effect of temporal variability. As shown in Table 4.10, the highest and the lowest concentrations were observed at the same locations before and after the correction. This method is potentially applicable to other cities and other air pollutants in estimating spatial variability. To investigate long-term spatial variability, the TGM concentration measured in 2007 can be compared with the TGM data measured at West Windsor by the Ministry of Environment (MOE) for the same year.

4.7 Comparison of TGM Concentration between 2006 and 2007

The result of ANOVA analysis of TGM concentration for the study period of October 19 to 26, 2006 and the same period in 2007 showed significant difference in mean concentrations (Appendix K). Overall averages of TGM concentration were 2.60 ng/m^3 and 1.63 ng/m^3 in 2006 and 2007, respectively. Site averaged concentrations at all

13 locations were higher than the average concentration of 2007. The difference in concentration between the two years could be due to the difference in locations. In 2006, TGM concentration was measured at 13 different sites. Some of them were close to local sources, leading to high concentrations observed. While in 2007, TGM concentration was measured only at one location at the University of Windsor. Based on these small data sets, it can not be concluded whether TGM concentration in 2006 was greater than 2007. However, a nationwide decreasing trend in TGM concentration emission was recognized from 2003 to 2006 (NPRI, 2008; Table 2.4). To investigate the inter-year variability in Windsor, TGM data from the West Windsor MOE station can be analyzed.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study, conducted at the University of Windsor campus measuring TGM concentrations for 2007, has reported an annual TGM concentration of 2.02±1.63 ng/m^3. The total number of available hourly averaged concentrations was 6659 out of a possible 8700. The annual concentration was higher than the concentration observed in all CAMNet sites in Canada (1995 to 2005) but close to the concentrations observed in urban sites in North America during 1997-2003. Different temporal aspects of TGM concentration were investigated. The average TGM concentration was the highest in summer. The concentrations were also high in winter and low in spring and fall. High surface emissions in summer and elevated mercury release due to increased power consumption from regional sources in summer and winter probably resulted in the elevated TGM concentrations in these two seasons compared to spring and fall. On an annual basis, a distinctive diurnal pattern was observed. TGM concentration was high over-night followed by a decrease in concentration from morning till afternoon. An increase in concentration was observed in the afternoon. The over-night high concentrations could result due to build up of a nocturnal inversion layer. The concentration decreased from morning due to the breakdown of the layer. The depletion continued till afternoon due to increased vertical mixing and oxidation and subsequent deposition of Hg resulting in an overall decrease in atmospheric Hg concentration. Diurnal patterns in winter, spring, and fall were similar to the annual pattern. However, summer diurnal pattern was different, with an increasing concentration from morning until noon followed by a steep decrease in the afternoon.

Meteorological parameters and other air pollutants, especially O_3 influence temporal variability of Hg significantly. Results of Pearson correlation analysis on an annual data set found no significant relationships between TGM and temperature or wind speed while a weak positive relationship with relative humidity was found. Correlation analysis was also conducted on seasonal basis. There was a weak relationship between seasonal TGM and temperature which was hard to explain. However, plots of TGM concentration and temperature diurnal cycles for each season identify a decrease in concentration observed in the afternoon when ambient temperature was the highest suggesting oxidation of Hg^0 at high temperature. Temperature driven surface emission during daytime and photochemical reactions in the afternoon explain the higher variability in the summer diurnal pattern, in comparison to other seasons. Apparently, no reason could be identified for the positive correlations between TGM and RH in spring, summer, and fall. High wind speeds leading to dilution of mercury might lead to the significant negative correlation between TGM and wind speed in spring and fall.

Significant relationships were found between TGM and other pollutant concentrations using the short-term measurements during August 8 to October 30, 2007. Negative correlation with ozone supports oxidation of Hg^0 to Hg (II) resulting in subsequent deposition. Other air pollutants (i.e. NO_2, NO, CO, total VOCs, and BC) were all positively correlated with TGM concentration indicating emission of these pollutants including mercury from the same source, likely combustion of fossil fuels. However, no correlations were observed between TGM and SO_2 as well as $PM_{2.5}$.

Four major factors were identified from PCA for the short-term period (August 8 to October 30, 2007) that could potentially affect TGM concentration variations. The factors were fossil fuel combustion products, meteorological conditions including temperature and RH, photochemical reactions and the influence of regional sources. These four factors explained a total of 77% variability existed within the data set. Hybrid receptor modeling using HYSPLIT and PSCF was analyzed in conjunction the Hg emission inventory of North America, to identify the potential source regions affecting Windsor's TGM concentration. From the annual PSCF modeling, the major sources were identified in the south-west of Windsor stretching from Ohio to Texas. Some potential sources in the north-west (Michigan to Manitoba), the west (Iowa) and the south (the Gulf of Mexico) were also identified. In comparison with the annual modeling, seasonal modeling identified potential source regions in specific directions for each season. High Hg concentration days in summer, fall and spring were affected mostly by the regions south-west of Windsor. In winter high concentrations were affected by regions in the west (e.g., Iowa) and some remote sources in the south (AL, Gulf of Mexico). In determining seasonal potential sources, application of both annual mean and seasonal means as criteria value is recommended.

Overall, from the correlation and source-receptor identification analyses, it can be suggested that temporal variability of TGM concentration is affected by a number of factors including variation of meteorological conditions (seasonal as well as diurnal), local sources, photochemical reactions, and influence of regional sources. In each season, the high or low concentrations observed in Windsor were effected by these factors to a greater or lesser extend thus leading to the seasonal variability in concentration.

A short term spatial variability study was conducted in October (2006), by setting up the Hg analyzer in a mobile lab. Among the 13 sites monitored, locations close to the local anthropogenic sources experienced high concentrations. Concentrations were relatively high at sites close to the Detroit River, likely affected by Hg emissions from anthropogenic sources in Detroit. The site close to the Ambassador Bridge was also affected by automobile emissions. Correction factors were applied to minimize effect of difference in measurement hours. Results of spatial variability, before and after correction, indicate that the methodology of randomly selecting the sequence of sites every day for monitoring TGM concentration minimized the effect of temporal variability on the spatial variability.

For 7 days in October, the overall averages of TGM concentration were 2.60 ng/m^3 and 1.63 ng/m^3 in 2006 and 2007, respectively. The difference in concentration was likely due to location dissimilarity. In 2006, concentrations were measured at 13 sites, some of them were close to local sources and Detroit, while in 2007 concentrations were measured was in a single location.

5.2 Recommendations

From the results and analysis obtained from this study it is recommended that

- Further investigations be conducted on periods where high mercury concentration > (mean + 4×SD) episodes were shown in this study to identify the reasons of elevated concentrations.
- Mercury speciation studies along with onsite measurements of solar radiation, wet and dry deposition, and mercury fluxes be conducted to understand the physical and chemical processes affecting the temporal variability of Hg concentrations.

- Factor analysis of TGM concentration using meteorological parameters and other pollutant concentrations be conducted for a longer time period, i.e. at least for one year, to identify major factors affecting variability in Hg concentrations.
- Factor analysis for different seasons and diurnal aspects (e.g. day and night) be conducted to identify factors affecting the seasonal and diurnal variability.
- TGM concentration analysis based on weekday/weekend time period to investigate the potentiality of vehicular emissions as a source of TGM.
- The annual and seasonal modeling be conducted using median values (annual and seasonal) as criteria value
- Conduct several backward trajectories on a daily basis at different timing instead of relying on one per day as the air mass direction can change significantly within a day.
- Trajectory simulation for more than 3 day be conducted to identify potential regional sources in remote regions, which would provide information for policy making of mercury management.
- Comparison of results of annual and seasonal modeling with an emission inventory prepared for using the same grid as the modeling
- Comparison of with another set of TGM measurements at the West Windsor Station (MOE) for the same period to investigate long term spatial variability of TGM concentration in Windsor.
- TGM concentrations in this study should be compared with the TGM measurement of upwind stations, for example at Detroit, MI, to further investigate the regional source influence in terms of a concentration gradient.

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APPENDIX A: MINAMATA DISEASE

Minamata Disease was discovered for the first time in the world at Minamata City Japan in 1956 and for the next time at Niigata City Niigata Prefecture Japan in 1965. The both cases were attributed to the methyl mercury that was generated in the process for producing acetaldehyde using mercury as catalyst. Methyl mercury had accumulated in fishes and shellfishes and those who ate them had been poisoned with it. These cases of poisoning with organic mercury were the first to take place in the world through the food chain transfer of its environmental pollution. The Minamata Disease patients officially recognized at Minamata and Niigata amount to a population of 2,200 or 800, respectively. In addition, those who are suspected of suffering from Minamata Disease (with chronic and mild symptoms) amount to a population of 12 000. The production of factories' methyl mercury containing wastewater was discontinued after the processes that produced methyl mercury were disused in 1968. The mercury discharged into the Minamata Bay still remained there and for its removal, reclamation and dredging were carried out as late as 15 years after its discovery. If the discharge of methyl mercury containing wastewater were discontinued earlier, not so many patients would have been affected by serious Minamata Disease symptoms.

Source: Harada, M. Minamata Disease and the Mercury Pollution of the Globe. http://www.einap.org/envdis/Minamata.html (Accessed March 24, 2008)

APPENDIX B: PROCEDURE FOR PSCF CALCULATION

This is a standalone program for running Potential Source Contribution Function (PSCF). It performs the calculation for each source (factor species ...) individually because the parameters for different sources (factors species ...) could be different.

Inputs:

The only input for this program is a so-called configure file, which requires the following information.

As indicated in the sample_configure file the easiest way to run the demo is to create a 'c:\zzzz' folder unzip the 'PSCF_release.zip' in this folder and then click the executable file in the "release" folder.

1) Path and name of source contribution file (or species concentration file).

The following three numbers on the same line are:

- Number of samples
- Number of sources (species)
- Index of a selected source (species) i.e. column index

2) The threshold value to determine if a sample is valid or not. The judgment is based on the mean contribution (concentration) of all samples. If this threshold value is set to be 1 the mean contribution (concentration) is used as a criterion.

3) Path and name of the file listing all trajectory names. The following number is the number of trajectories listed in this file. This trajectory-list file shows the name of each trajectory and the order index of the corresponding concentration sample. For example, "xxxxxxxx.xxx 6" means the trajectory xxxxxxxx.xxx corresponds to the 6th sample in the contribution (concentration) file.

4) Path of each trajectory. Please do NOT forget “\\” at end of this string. Program will connect this path with the name of each trajectory for reading.

5) Resolution of grid cell.

6) Weighting Methods: (1 or 2).

PSCF value of a cell is the ratio of the # of effective end-points in this cell to the # of the total endpoints in the cell. In general, a weight for one cell is determined by the # of the total endpoints in this cell.

7) Number of weighting intervals. The maximal value is 10.

8) Interval boundaries and corresponding weights

Given the number of weighting intervals (say n) this section provides the boundaries of n intervals (column 1) and their corresponding weights (column 2).

If the weighting method = 1 column 1 (boundary values) is based on the ratio of the ending point # in an observed cell to the average ending point # of all cells. If the weighting method = 2 column 1 is based on the direct ending point number.

Here is a demo sample for method 1. Assuming the interval parameters are:

0.0	0.15
0.5	0.5
1.0	0.75
2.0	1.0

The weighting process can be expressed by

$$W_{ij} = \begin{cases} 1.0 & n_{ij} > 2 \cdot ave \\ 0.75 & ave < n_{ij} \le 2 \cdot ave \\ 0.5 & 0.5 \cdot ave < n_{ij} \le ave \\ 0.15 & 0 < n_{ij} \le 0.5 \cdot ave \end{cases}$$

Where *ave* is the average number of the endpoints in each cell which is automatically calculated by this program and np_{ij} is the number of the end points that fall in cell *ij*. This method could be easier to be generalized for various cases.

Foe method 2 column 1 should be filled with direct boundary values (rather than a ratio value). This program provides the following information that could help users decide interval boundaries i) the average # of the end points of top 10 percents of non-empty cells ii) the average # of the end points of all non-empty cells and iii) the average # of the end points of bottom 10 percents of non-empty cells.

In summary this program provides a friendly interface so users can arbitrarily change the weighting method weighting interval boundaries and weights in the configure file and rerun the model until they get a good result.

9) Path and name of the result file.

Outputs:

The output file of this program contains three columns:

- Latitude of each cell
- Longitude of each cell
- PSCF value of each cell

Notes:

1) As the input of this program the configure file can be put into any directory but you should type complete and correct path and name when you are required to do it on the screen.

2) A friendly reminder. Please use "\\" not "\" to indicate a file path for C language.

3) Please be sure that the contribution (concentration) file and the trajectory list file are put in the directories indicated in the configure file.

4) The "Release" folder that contains the executable file can be put into any directory. After running this program there will be a file containing all the trajectories created in this fold. If not interesting it can be deleted.

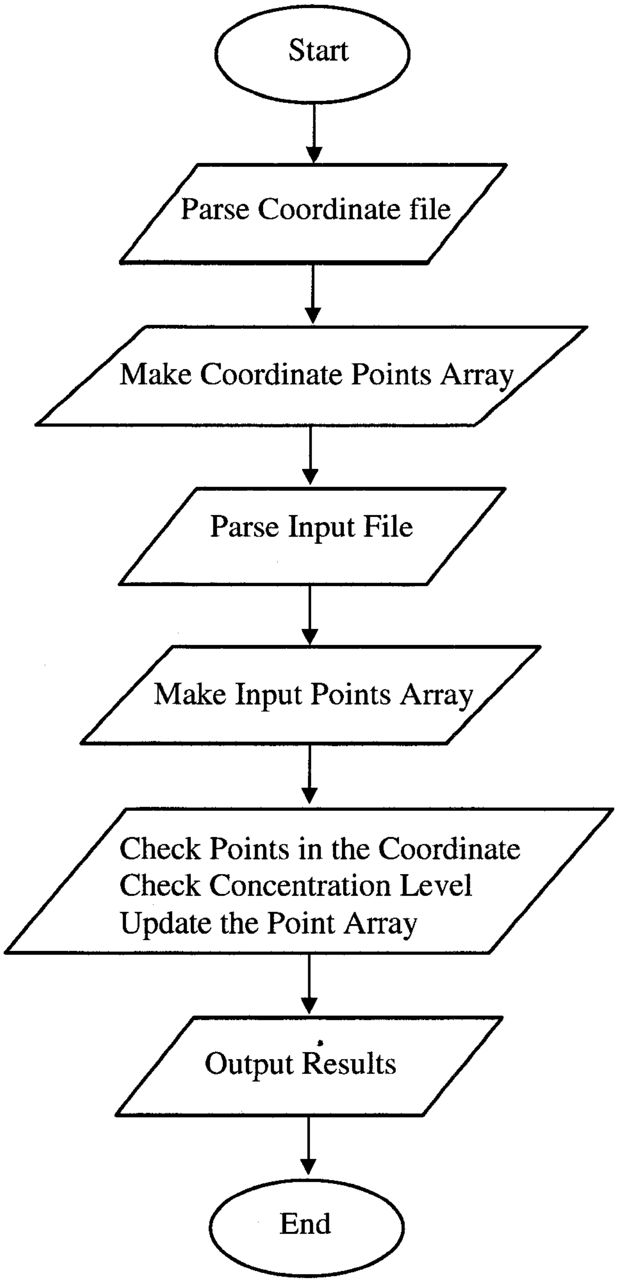
Copyright:

This release-version program is created by Weixiang Zhao, Philip K. Hopke and Eugene Kim in Clarkson University.

Reference:

The original code is available from Weixiang Zhao in Clarkson University by sending an email to wzhao@clarkson.edu.

Flowchart for PSCF Program



APPENDIX C: TGM MEASUREMENT FOR SPATIAL VARIABILITY STUDY, 2006

Table C.1: Time interval of TGM concentration measurement at 13 sites in Windsor (number of 5 minute readings in the parenthesis for each site)

Site	16th Oct	17th Oct	18th Oct	19th Oct	24th Oct	25th Oct	26th Oct
1	11:16-13:50 (31)	00:46-09:20 (100)	00:41-10:00 (112)	00;41-10:15 (115)	-	00:41-08:30 (94)	00:41-09:25 (105)
	20:16-00:00 (45)	19:11-00:00 (58)	19:36-00:00 (53)	19:31-00:00 (54)	18:21-00:00 (34)	18:01-00:00 (72)	18:56-00:00 (61)
2	-	15:26-15:40 (3)	13:51-14:10 (4)	10:31-10:50 (4)	-	-	-
3	-	14:51-15:15 (5)	14:21-14:45 (5)	17:31-17:50 (4)	-	-	16:41-17:00 (4)
4	-	15:46-16:05 (4)	13:26-13:45 (4)	10:56-11:20 (5)	17:56-18:10 (2)	17:36-17:45 (3)	17:11-17:30 (4)
5	-	16:16-16:25 (2)	12:01-12:20 (4)	18:06-18:25 (4)	-	-	17:36-17:55 (4)
6	-	16:41-17:00 (4)	11:16-11:45 (6)	18:41-19:00 (4)	16:56-17:10 (2)	-	18:11-18:30 (4)
7	-	17:26-18:00 (7)	10:36-10:55 (4)	11:31-11:50 (4)	17:21-17:40 (2)	-	-
8	16:16-16:30 (3)	12:46-13:15 (6)	16:46-17:00 (4)	14:51-15:10 (4)	16:21-16:40 (2)	-	13:26-13:45 (4)
9	17:01-17:20 (4)	10:31-10:45 (3)	18:46-19:05 (4)	12:16-13:00 (10)	-	-	10:56-11:15 (4)
10	17:31-17:55 (5)	10:56-11:20 (5)	18:16-18:35 (4)	13:16-13:35 (4)	-	-	11:31-11:50 (4)
11	18:56-19:10 (3)	11:51-12:15 (5)	17:31-17:50 (5)	14:01-14:20 (4)	-	-	12:21-12:50 (6)
12	15:46-16:00 (3)	13:26-13:40 (3)	16:11-16:35 (5)	15:21-15:40 (4)	15:46-16:10 (3)	-	13:51-14:10 (4)
13	14:26-14:55 (6)	14:11-14:30 (4)	15:36-15:50 (3)	16:16-16:40 (5)	15:01-15:15 (1)	-	15:01-15:20 (4)

APPENDIX D: DESCRIPTION OF STATISTICAL METHODS USED IN THIS STUDY

Central Limit Theorem

The Central Limit Theorem states that whenever a random sample of size n is taken from any distribution with mean μ and variance σ^2 then the sample mean will be approximately normally distributed with mean μ and variance σ^2/n. The larger the value of the sample size n, the better the approximation to the normal. This is very useful when it comes to inference. For example it allows (if the sample size is large) to use hypothesis tests which assume normality even if our data appear non-normal.

Pearson's correlation coefficient

Pearson's correlation coefficient is a measure of the linear association between two variables that have been measured on interval or ratio scales. However, it can be misleadingly sometimes when there is a non-linear relationship between the variables.

Analysis of variance (ANOVA)

Analysis of variance (ANOVA) tests the hypothesis that the means of two or more populations are equal. ANOVA determines the importance of one or more factors by comparing the means of the response variable at different factor levels. There should be a continuous response variable and at least one independent variable with two or more levels to run an ANOVA. If a variable is found significant in ANOVA multiple comparison tests can be employed to identify the levels of the factor that are different.

Multiple Comparisons

An ANOVA test is used to find out significant difference between three or more group means. However, the ANOVA simply indicates there is a difference between two or more group means; but it does not tell which means are different. **Tukey's test** is a statistical test generally used in conjunction with an ANOVA to find which means are significantly different from one another. It compares all possible pairs of means and is based on a studentized range distribution q. The test compares the means of every treatment to the means of every other treatment and identifies where the difference between two means is greater than the standard error.

The **Scheffe's test** is one of the most flexible conservative and robust data snooping procedures available. If the overall F statistic is significant Scheffe's procedure can be used to evaluate all a posterior contrast among means not just the pair-wise comparisons. In addition, it can be used with unequal sample sizes. Since an experimenter always evaluates a subset of the possible contrasts Scheffe's procedure tends to be conservative. It is much less powerful than Tukey's HSD procedure for evaluating pair wise comparisons. Scheffe's procedure uses the F sampling distribution and like ANOVA is robust with respect to non-normality and heterogeneity of variance.

Equality of Variance Test

Many statistical procedures assume that although different samples may come from populations with different means they have the same variance. The effect of unequal variances upon inferences depends in part upon whether the model includes fixed or random effects disparities in sample sizes and the choice of multiple comparison procedure. The ANOVA F-test is slightly affected by inequality of variance if the model contains fixed factors only and has equal or nearly equal sample sizes. The equal variance test is used to test the validity of the equal variance assumption. Bartlett's test is a statistical procedure to test the equality of variances. Bartlett's test is suitable for normally distributed data. Levene's test is used when the data come from continuous but not necessarily normal distributions. This method considers the distances of the observations from their sample median rather than their sample mean makes the test more robust for smaller samples.

Two Sample t Test

Two Sample t Test computes a confidence interval and performs a hypothesis test of the difference between two population means when σ's are unknown and samples are drawn independently from each other. This procedure is based upon the t-distribution, and for small samples it works best if data were drawn from distributions that are normal or close to normal.

Reference:

MINITAB Inc. 2006. Statguide: Minitab release 14. State College, Pennsylvania, USA.

SPSS Inc. 2007. SPSS 16 for Windsows, Chicago Illinois USA.

APPENDIX E: RESULTS FOR SEASONAL VARIABILITY, 2007

One-way ANOVA: Winter Spring Summer Fall

```
Source    DF        SS      MS       F      P
Factor     3    442.51  147.50  57.09  0.000
Error   6655  17195.45    2.58
Total   6658  17637.96

S = 1.607   R-Sq = 2.51%   R-Sq(adj) = 2.46%
```

Results of Tukey's Test

```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.97%

Winter subtracted from:
         Lower  Center   Upper  -------+---------+---------+---------+-
Spring  -0.434  -0.292  -0.150          (--*--)
Summer   0.153   0.311   0.468                      (--*--)
Fall    -0.537  -0.408  -0.279        (--*-)
                                -------+---------+---------+---------+-
                                    -0.50      0.00      0.50      1.00
Spring subtracted from:
         Lower  Center  Upper  -------+---------+---------+---------+--
Summer   0.436   0.602  0.768                            (--*--)
Fall    -0.256  -0.116  0.023              (--*-)
                               -------+---------+---------+---------+--
                                   -0.50      0.00      0.50      1.00
Summer subtracted from:
       Lower  Center   Upper  -------+---------+---------+---------+--
Fall  -0.873  -0.718  -0.564  (--*--)
                              -------+---------+---------+---------+--
                                  -0.50      0.00      0.50      1.00
```

Results of Test of Equal Variances

```
95% Bonferroni confidence intervals for standard deviation
            N    Lower    StDev    Upper
  Winter  1962  1.93349  2.01078  2.09409
  Spring  1478  0.74629  0.78068  0.81817
  Summer  1062  2.54507  2.68349  2.83677
  Fall    2157  0.55904  0.58035  0.60324
Bartlett's Test (normal distribution)
Test statistic = 4559.56  p-value = 0.000
Levene's Test (any continuous distribution)
Test statistic = 42.57  p-value = 0.000
```

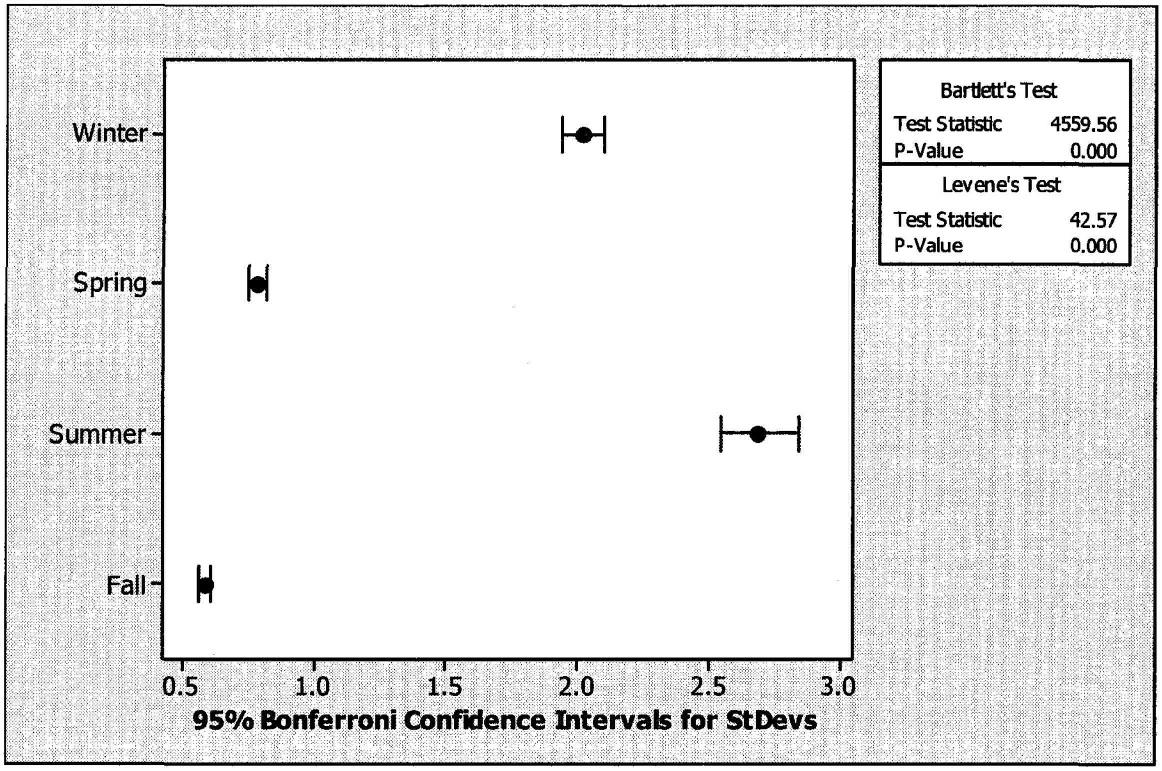


Figure E.1: Plot of standard deviations for four seasons at 95% confidence intervals

APPENDIX F: RESULTS FOR DIURNAL VARIABILITY, 2007

Table F.1: Statistical summary of diurnal variability of TGM concentration

Hour	N	Min	Median	Max	Mean	SD
0	276	0.95	1.75	6.49	1.93	0.67
1	276	0.95	1.76	4.46	1.93	0.60
2	275	1.06	1.77	7.01	1.97	0.72
3	276	1.09	1.79	6.81	2.04	0.80
4	277	1.18	1.78	5.26	1.96	0.64
5	276	1.28	1.78	5.98	1.94	0.62
6	276	1.32	1.79	6.69	2.03	0.76
7	275	1.15	1.79	5.68	2.02	0.68
8	273	0.95	1.78	6.55	2.00	0.71
9	271	0.95	1.78	5.62	1.98	0.68
10	267	0.96	1.76	5.93	1.99	0.71
11	266	0.93	1.79	6.55	1.95	0.75
12	264	0.93	1.72	6.62	1.94	0.83
13	269	0.94	1.72	7.20	1.93	0.83
14	273	0.87	1.71	7.46	1.81	0.64
15	272	0.83	1.68	8.26	1.76	0.61
16	273	0.90	1.64	5.05	1.70	0.46
17	274	0.87	1.65	4.45	1.71	0.46
18	274	0.88	1.66	5.36	1.70	0.40
19	275	0.85	1.69	4.48	1.74	0.42
20	276	1.04	1.70	5.68	1.76	0.44
21	276	1.07	1.70	5.43	1.81	0.56
22	277	1.01	1.69	6.11	1.83	0.55
23	277	0.95	1.73	5.45	1.90	0.64

Table F.2: Sunrise and solar noon time for four seasons in Windsor, 2007 (Time and date .com, 2008)

Season	Sunrise time a.m. (EST)	Solar Noon p.m. (EST)
Winter	7:09 – 8:01	12:21 - 12:46
Spring	4:59 – 7:08	12:29 - 12:44
Summer	4:58 – 5:56	12:30 - 12:38
Fall	5:57 – 7:40	12:16 - 12:36

Results of ANOVA test for diurnal variability

```
Source     DF        SS     MS     F      P
Factor     23    79.990  3.478  8.40  0.000
Error    6540  2708.585  0.414
Total    6563  2788.576

S = 0.6436   R-Sq = 2.87%   R-Sq(adj) = 2.53%
```

Table F.3: Results of Scheffé Test for diurnal variability

Hour	N	Subset for alpha = 0.05
		1
16	275	1.7
18	275	1.7
17	275	1.71
19	276	1.74
15	277	1.76
20	277	1.76
14	275	1.81
21	275	1.81
22	278	1.83
23	277	1.9
0	277	1.93
1	277	1.93
13	278	1.93
5	277	1.94
12	274	1.94
11	277	1.95
4	276	1.96
2	277	1.97
9	274	1.98
10	277	1.99
8	273	2
7	269	2.02
6	271	2.03
3	270	2.04
Sig.		.508

APPENDIX G: CONCENTRATIONS OF OTHER AIR POLLUTANTS

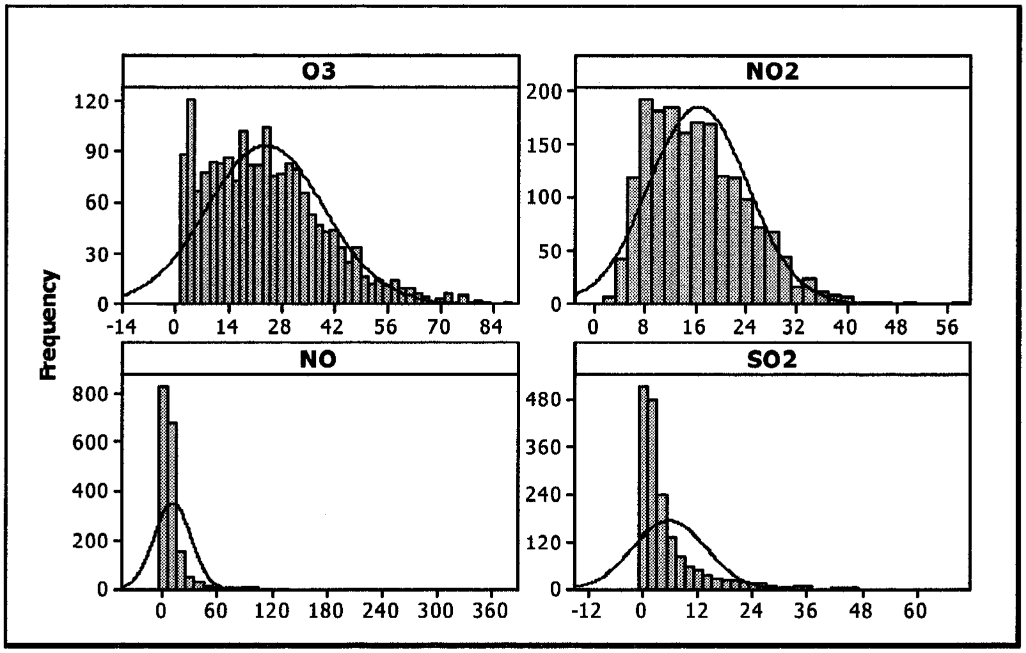


Figure G.1: Histogram of hourly averaged O_3, NO_2, NO, and SO_2 concentrations

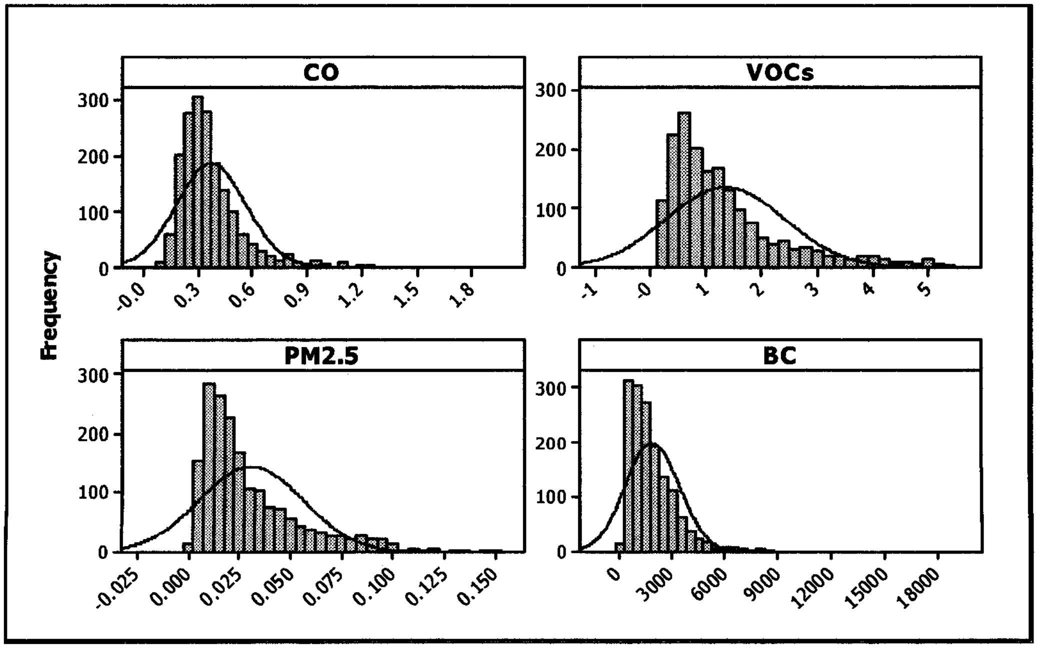


Figure G.2: Histogram of hourly averaged CO, VOCs, $PM_{2.5}$ and BC concentrations

APPENDIX H: PRINCIPAL COMPONENT ANALYSIS

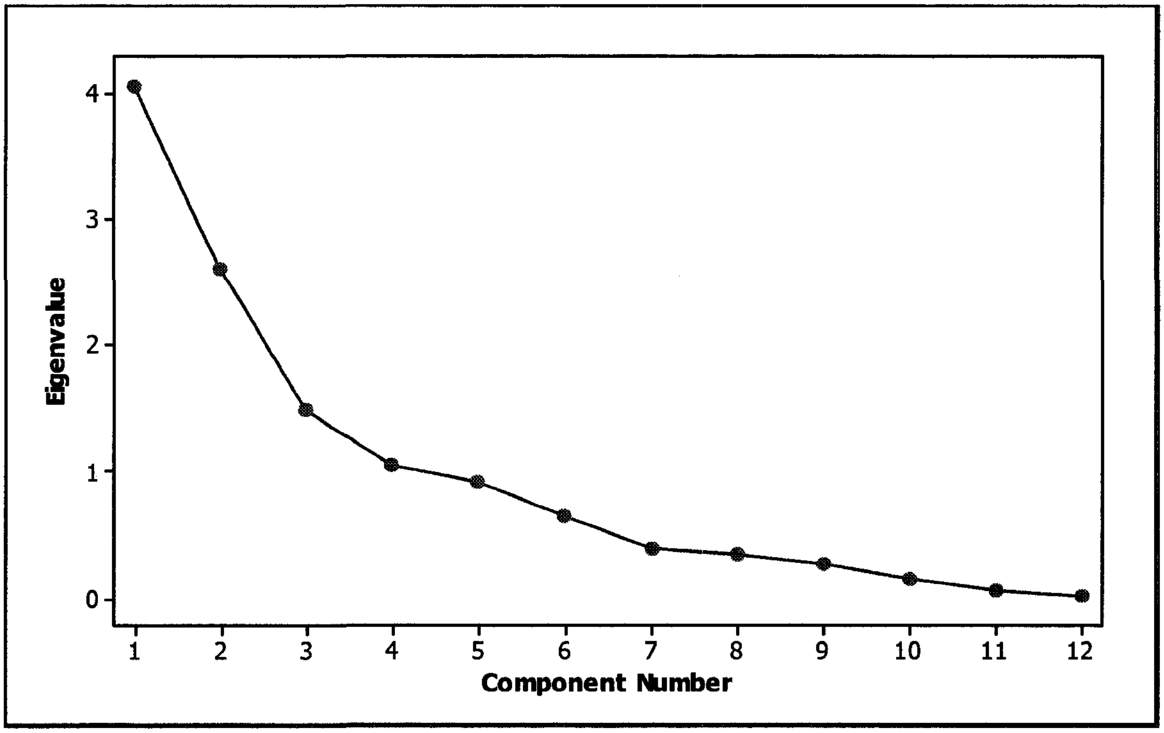


Figure H.1: Scree plot of Principal Component Analysis for all variables

APPENDIX I: MERCURY EMISSION INVENTORY

Table I.1: Total mercury and mercury compounds emission inventory of US, 2006
(Source for area: Wikipedia, 2008a)

State	Short name	Mercury emission (kg)	Area (km^2)	Mercury emission rate (g/km^2)
Alabama	AL	3443.54	135765	25.36
Alaska	AK	34.92	1717854	0.02
Arizona	AZ	704.31	295254	2.39
Arkansas	AR	995.92	137732	7.23
California	CA	1122.00	423970	2.65
Colorado	CO	767.35	269601	2.85
Connecticut	CT	58.05	14357	4.04
Delaware	DE	330.61	6447	51.28
Florida	FL	1059.86	170304	6.22
Georgia	GA	2335.15	153909	15.17
Hawaii	HI	30.84	28311	1.09
Idaho	ID	310.20	216446	1.43
Illinois	IL	2127.44	149998	14.18
Indiana	IN	2793.65	94321	29.62
Iowa	IA	1395.92	145743	9.58
Kansas	KS	1421.32	213096	6.67
Kentucky	KY	1678.00	104659	16.03
Louisiana	LA	1990.02	134264	14.82
Maine	ME	25.85	91646	0.28
Maryland	MD	821.32	32133	25.56
Massachusetts	MA	81.18	27336	2.97
Michigan	MI	1821.32	253266	7.19
Minnesota	MN	821.32	225365	3.64
Mississippi	MS	409.07	125434	3.26
Missouri	MO	2098.41	180533	11.62
Montana	MT	478.91	380838	1.26
Nebraska	NE	540.59	200345	2.70

Nevada	NV	1996.37	286351	6.97
New Hampshire	NH	64.40	24216	2.66
New Jersey	NJ	321.54	22588	14.24
New Mexico	NM	492.52	314915	1.56
New York	NY	602.72	141299	4.27
North Carolina	NC	1822.22	139389	13.07
North Dakota	ND	1178.23	183112	6.43
Ohio	OH	3667.12	116096	31.59
Oklahoma	OK	749.21	181035	4.14
Oregon	OR	1417.23	254805	5.56
Pennsylvania	PA	3012.70	119283	25.26
South Carolina	SC	653.06	82932	7.87
South Dakota	SD	89.80	199731	0.45
Tennessee	TN	1737.41	109151	15.92
Texas	TX	7038.55	695621	10.12
Utah	UT	497.51	219887	2.26
Vermont	VT	0.00	24901	0.00
Virginia	VA	819.50	910	7.40
Washington	WA	177.32	110785	0.96
West Virginia	WV	1913.83	184665	30.50
Wisconsin	WI	1815.87	62755	10.70
Wyoming	WY	760.54	169639	3
Total		**60884.81**		**6.18**

Table I.2: Total mercury and mercury compounds emission inventory of Canada, 2006 (Source for area: Wikipedia, 2008b)

Provinces	Short name	Mercury emission (kg)	Area (km^2)	Mercury emission rate (g/km^2)
Alberta	AB	924	661848	1.40
British Columbia	BC	198	944735	0.21
Manitoba	MB	946	647797	1.46
New Brunswick	NB	138	72908	1.89
Newfoundland & Labrador	NL	45	405212	0.11
Nova Scotia	NS	177	55284	3.20
Ontario	ON	853	1 076395	0.79
Prince Edward Island	PE	5.5	5660	0.97
Quebec	QC	502	1 542056	0.33
Saskatchewan	SK	810	651036	1.24
Total		**4598.5**		**0.76**

APPENDIX J: RESULTS FOR SPATIAL VARIABILITY, 2006

J.1 Results of statistical analysis of TGM concentration (original data)

Results of ANOVA test for spatial variability

```
Source    DF       SS     MS     F      P
Factor    12   35.519  2.960  5.79  0.000
Error   1159  592.304  0.511
Total   1171  627.823

S = 0.7149   R-Sq = 5.66%   R-Sq(adj) = 4.68%
```

Results of Tukey's test

```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.91%

S_1 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_2   -0.5900   0.1291  0.8481               (-----*-----)
S_3   -0.3977   0.1665  0.7306                 (---*----)
S_4   -0.4698   0.0416  0.5530                (---*----)
S_5   -0.5791   0.0593  0.6976               (----*-----)
S_6   -0.7136  -0.1778  0.3579              (----*---)
S_7    0.6505   1.2307  1.8109                         (----*----)
S_8   -0.4985   0.0128  0.5242                (---*---)
S_9   -0.5023  -0.0219  0.4586                (---*---)
S_10  -0.3784   0.1330  0.6444                 (---*---)
S_11  -0.5523  -0.0409  0.4704               (----*---)
S_12  -0.3165   0.1949  0.7063                 (----*---)
S_13   0.1155   0.6159  1.1163                     (---*---)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_2 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_3   -0.8699   0.0374  0.9447             (------*-------)
S_4   -0.9629  -0.0875  0.7880            (------*-------)
S_5   -1.0250  -0.0698  0.8854           (-------*-------)
S_6   -1.1968  -0.3069  0.5831          (------*-------)
S_7    0.1843   1.1016  2.0190                      (------*-------)
S_8   -0.9917  -0.1162  0.7592            (------*------)
S_9   -1.0087  -0.1509  0.7068            (------*------)
S_10  -0.8715   0.0040  0.8794             (------*------)
S_11  -1.0455  -0.1700  0.7055           (-------*------)
S_12  -0.8096   0.0659  0.9413             (-------*------)
S_13  -0.3823   0.4868  1.3559                 (------*------)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_3 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
```

```
S_4   -0.8784  -0.1249  0.6286             (-----*-----)
S_5   -0.9521  -0.1072  0.7376            (------*------)
S_6   -1.1146  -0.3443  0.4259           (-----*------)
S_7    0.2624   1.0642  1.8660                      (------*------)
S_8   -0.9071  -0.1537  0.5998            (------*-----)
S_9   -0.9212  -0.1884  0.5445            (-----*------)
S_10  -0.7870  -0.0335  0.7200             (------*-----)
S_11  -0.9609  -0.2074  0.5460            (-----*------)
S_12  -0.7251   0.0284  0.7819              (-----*------)
S_13  -0.2967   0.4494  1.1955                  (-----*-----)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_4 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_5   -0.7929   0.0177  0.8282             (------*------)
S_6   -0.9519  -0.2194  0.5130            (-----*-----)
S_7    0.4235   1.1891  1.9547                        (-----*-----)
S_8   -0.7436  -0.0288  0.6860              (-----*-----)
S_9   -0.7565  -0.0635  0.6296              (----*-----)
S_10  -0.6234   0.0914  0.8062               (-----*-----)
S_11  -0.7974  -0.0825  0.6323             (-----*-----)
S_12  -0.5615   0.1533  0.8681               (-----*-----)
S_13  -0.1327   0.5743  1.2813                   (-----*-----)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_5 subtracted from:
        Lower   Center   Upper  --------+---------+---------+---------
+-
S_6   -1.0632  -0.2371  0.5891           (------*------)
S_7    0.3158   1.1714  2.0270                       (------*------)
S_8   -0.8569  -0.0464  0.7641             (------*-----)
S_9   -0.8725  -0.0811  0.7103             (-----*------)
S_10  -0.7368   0.0738  0.8843              (------*-----)
S_11  -0.9107  -0.1002  0.7103            (------*------)
S_12  -0.6749   0.1357  0.9462              (------*------)
S_13  -0.2470   0.5566  1.3603                  (------*-----)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_6 subtracted from:
        Lower  Center   Upper  --------+---------+---------+---------+-
S_7    0.6264  1.4085  2.1906                         (------*-----)
S_8   -0.5418  0.1906  0.9231               (------*-----)
S_9   -0.5553  0.1559  0.8672               (-----*-----)
S_10  -0.4216  0.3108  1.0433                (------*-----)
S_11  -0.5956  0.1369  0.8693               (-----*-----)
S_12  -0.3597  0.3727  1.1052                 (-----*-----)
S_13   0.0689  0.7937  1.5186                     (-----*-----)
                               --------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4

S_7 subtracted from:
        Lower   Center    Upper -------+---------+---------+---------+-
S_8   -1.9834  -1.2179  -0.4523   (------*-----)
S_9   -1.9978  -1.2526  -0.5073   (------*-----)
```

```
S_10  -1.8632  -1.0977  -0.3321    (------*-----)
S_11  -2.0372  -1.2716  -0.5061   (-----*------)
S_12  -1.8013  -1.0358  -0.2702     (-----*------)
S_13  -1.3731  -0.6148   0.1435         (-----*-----)
                                 ------+---------+---------+---------+-
                                      -1.2       0.0       1.2

2.4

S_8 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_9   -0.7277  -0.0347  0.6583              (-----*----)
S_10  -0.5946   0.1202  0.8350               (-----*-----)
S_11  -0.7686  -0.0538  0.6610              (-----*-----)
S_12  -0.5327   0.1821  0.8969                (-----*----)
S_13  -0.1039   0.6031  1.3101                   (-----*-----)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_9 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_10  -0.5382   0.1549  0.8479                (----*-----)
S_11  -0.7121  -0.0191  0.6740              (-----*-----)
S_12  -0.4762   0.2168  0.9098                (-----*-----)
S_13  -0.0472   0.6378  1.3227                    (----*-----)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_10 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_11  -0.8888  -0.1740  0.5409             (-----*-----)
S_12  -0.6529   0.0619  0.7767               (-----*----)
S_13  -0.2241   0.4829  1.1899                  (-----*-----)
                                --------+---------+---------+---------+
                                     -1.2       0.0       1.2       2.4

S_11 subtracted from:
        Lower  Center   Upper  --------+---------+---------+---------+-
S_12  -0.4789  0.2359  0.9507                (-----*-----)
S_13  -0.0502  0.6568  1.3638                    (----*-----)
                               --------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4

S_12 subtracted from:
        Lower  Center   Upper  --------+---------+---------+---------+-
S_13  -0.2860  0.4210  1.1280                  (-----*----)
                               --------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4
```

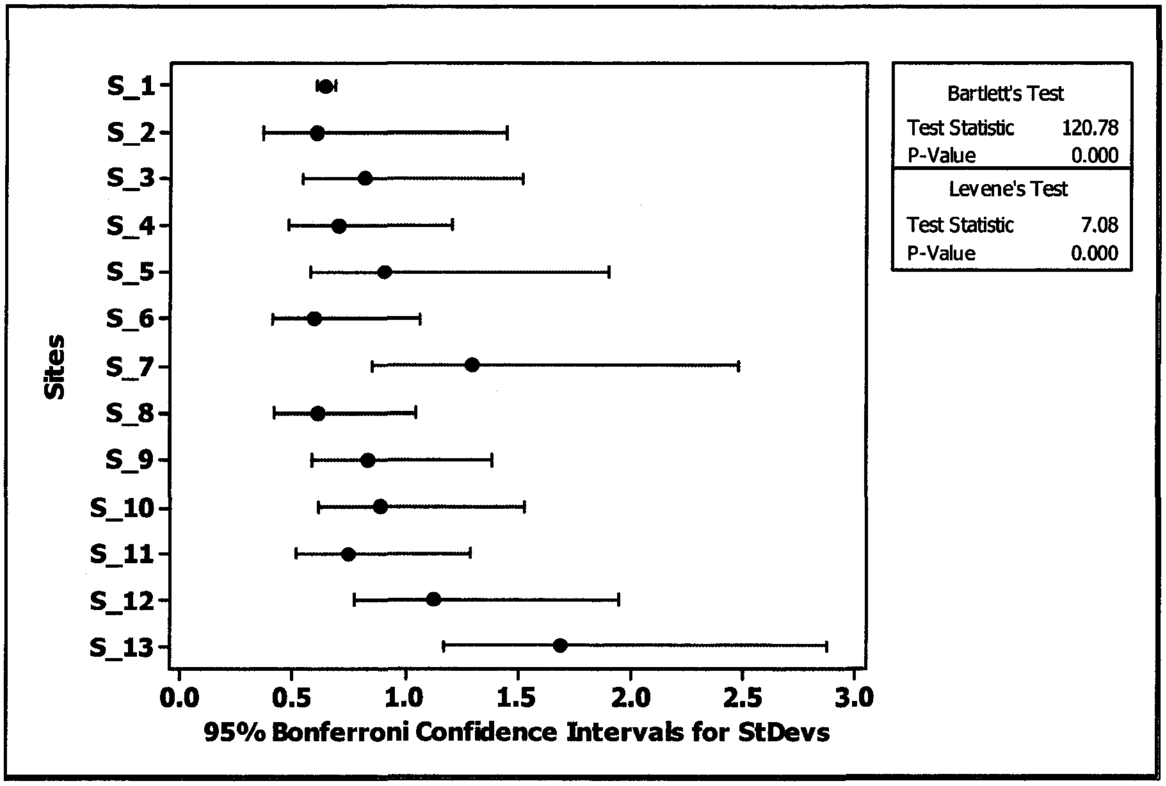


Figure J.1: Plot of standard deviations for 13 Sites at 95% Confidence Intervals

J.2 Results of statistical analysis of TGM concentration after correction

Results of ANOVA test for spatial variability

```
Source    DF       SS     MS     F      P
Factor    12   25.254  2.105  4.51  0.000
Error   1157  540.258  0.467
Total   1169  565.513

S = 0.6833   R-Sq = 4.47%   R-Sq(adj) = 3.47%
```

Results of Tukey's test

```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 99.91%
S_1 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_2   -1.1215  -0.4342  0.2531           (----*-----)
S_3   -0.8802  -0.3409  0.1984             (---*----)
S_4   -0.7308  -0.2420  0.2468              (---*---)
S_5   -0.6299  -0.0197  0.5905               (----*----)
S_6   -1.0068  -0.4816  0.0435            (---*---)
```

```
S_7    0.2734   0.8127  1.3519                      (----*---)
S_8   -0.7124  -0.2236  0.2652              (---*---)
S_9   -0.6522  -0.1930  0.2663               (--*---)
S_10  -0.7362  -0.2361  0.2639              (---*---)
S_11  -0.5660  -0.0772  0.4116               (---*---)
S_12  -0.6978  -0.2090  0.2798              (---*---)
S_13  -0.5730  -0.0947  0.3836               (---*---)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_2 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_3   -0.7740   0.0932  0.9605              (------*------)
S_4   -0.6447   0.1922  1.0290               (------*------)
S_5   -0.4986   0.4145  1.3275                (------*-------)
S_6   -0.9061  -0.0475  0.8111          (-------*------)
S_7    0.3796   1.2468  2.1141                       (------*-------)
S_8   -0.6263   0.2106  1.0474               (------*------)
S_9   -0.5787   0.2412  1.0611               (------*------)
S_10  -0.6454   0.1980  1.0415               (------*------)
S_11  -0.4798   0.3570  1.1938                (------*------)
S_12  -0.6117   0.2252  1.0620               (------*------)
S_13  -0.4913   0.3395  1.1702                (------*------)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_3 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_4   -0.6213   0.0989  0.8192               (-----*-----)
S_5   -0.4863   0.3212  1.1288                (------*-----)
S_6   -0.8861  -0.1407  0.6047             (-----*-----)
S_7    0.3982   1.1536  1.9090                       (------*-----)
S_8   -0.6029   0.1173  0.8376               (-----*-----)
S_9   -0.5526   0.1479  0.8485               (-----*-----)
S_10  -0.6231   0.1048  0.8327               (-----*-----)
S_11  -0.4565   0.2637  0.9840                (-----*-----)
S_12  -0.5883   0.1319  0.8521               (-----*-----)
S_13  -0.4669   0.2462  0.9594                (-----*-----)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_4 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
S_5   -0.5525   0.2223  0.9970               (------*-----)
S_6   -0.9494  -0.2397  0.4701          (-----*-----)
S_7    0.3344   1.0547  1.7749                       (-----*-----)
S_8   -0.6649   0.0184  0.7017              (-----*-----)
S_9   -0.6134   0.0490  0.7115               (----*-----)
S_10  -0.6855   0.0059  0.6972              (-----*-----)
S_11  -0.5185   0.1648  0.8481                (----*-----)
S_12  -0.6503   0.0330  0.7162               (----*-----)
S_13  -0.5285   0.1473  0.8231                (----*-----)
                                -------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_5 subtracted from:
        Lower   Center   Upper  -------+---------+---------+---------+-
```

```
S_6   -1.2601  -0.4619  0.3363         (------*------)
S_7    0.0248   0.8324  1.6399                    (------*------)
S_8   -0.9786  -0.2039  0.5709            (-----*------)
S_9   -0.9297  -0.1733  0.5832            (------*-----)
S_10  -0.9983  -0.2164  0.5655            (-----*------)
S_11  -0.8322  -0.0575  0.7173             (------*-----)
S_12  -0.9641  -0.1893  0.5855            (-----*------)
S_13  -0.8432  -0.0750  0.6932             (-----*------)
                                ------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4

S_6 subtracted from:
        Lower  Center   Upper  -------+---------+---------+---------+-
S_7    0.5489  1.2943  2.0397                       (-----*-----)
S_8   -0.4517  0.2581  0.9678            (-----*-----)
S_9   -0.4010  0.2887  0.9784             (----*-----)
S_10  -0.4720  0.2455  0.9630            (-----*-----)
S_11  -0.3053  0.4045  1.1142             (-----*-----)
S_12  -0.4371  0.2726  0.9824            (-----*-----)
S_13  -0.3156  0.3870  1.0895             (-----*-----)
                               -------+---------+---------+---------+-
                                   -1.2       0.0       1.2       2.4

S_7 subtracted from:
        Lower   Center    Upper  --------+---------+---------+---------
S_8   -1.7565  -1.0363  -0.3160   (-----*-----)
S_9   -1.7062  -1.0056  -0.3051    (-----*----)
S_10  -1.7767  -1.0488  -0.3209   (-----*-----)
S_11  -1.6101  -0.8898  -0.1696     (-----*-----)
S_12  -1.7419  -1.0217  -0.3014   (-----*-----)
S_13  -1.6205  -0.9074  -0.1942    (-----*-----)
                                 ------+---------+---------+---------+-
                                     -1.2       0.0       1.2       2.4

S_8 subtracted from:
        Lower   Center  Upper  -------+---------+---------+---------+-
S_9   -0.6318   0.0306  0.6931            (----*-----)
S_10  -0.7039  -0.0125  0.6788           (-----*-----)
S_11  -0.5369   0.1464  0.8297             (----*-----)
S_12  -0.6687   0.0146  0.6979           (-----*-----)
S_13  -0.5469   0.1289  0.8047            (-----*-----)
                               -------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4

S_9 subtracted from:
        Lower   Center  Upper  -------+---------+---------+---------+-
S_10  -0.7140  -0.0432  0.6276           (-----*----)
S_11  -0.5467   0.1158  0.7783            (-----*----)
S_12  -0.6785  -0.0160  0.6464           (-----*----)
S_13  -0.5565   0.0983  0.7530            (-----*----)
                               -------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4

S_10 subtracted from:
        Lower  Center   Upper  --------+---------+---------+---------+-
S_11  -0.5324  0.1590  0.8503             (----*-----)
S_12  -0.6642  0.0271  0.7185           (-----*-----)
```

```
S_13  -0.5425  0.1414  0.8254               (-----*-----)
                               --------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4

S_11 subtracted from:
        Lower   Center   Upper  --------+---------+---------+---------+
S_12  -0.8151  -0.1318  0.5514             (-----*-----)
S_13  -0.6933  -0.0175  0.6583              (-----*----)
                                --------+---------+---------+---------+
                                     -1.2       0.0       1.2       2.4

S_12 subtracted from:
        Lower  Center   Upper  --------+---------+---------+---------+-
S_13  -0.5615  0.1143  0.7901               (-----*-----)
                               --------+---------+---------+---------+-
                                    -1.2       0.0       1.2       2.4
```

APPENDIX K: RESULTS OF COMPARISON BETWEEN 2006 AND 2007 (October 16 to October 24)

Results of ANOVA: TGM Concentration versus Year

```
Source    DF       SS      MS       F      P
Year       1   697.98  697.98  498.52  0.000
Error   2817  3944.06    1.40
Total   2818  4642.04

S = 1.183   R-Sq = 15.04%   R-Sq(adj) = 15.01%
```

Two-Sample T-Test and CI: TGM Concentration, Year

```
Two-sample T for TGM Concentration

Year     N   Mean  StDev  SE Mean
2006  1406   2.63   1.67    0.044
2007  1413  1.631  0.183   0.0049

Difference = mu (2006) - mu (2007)
Estimate for difference:  0.995189
95% CI for difference:  (0.907792, 1.082586)
T-Test of difference = 0 (vs not =): T-Value = 22.33  P-Value = 0.000
DF = 2817
Both use Pooled StDev = 1.1833
```

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