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# Studies of mercury species in the atomosphere in downtown Toronto

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# **STUDIES OF MERCURY SPECIES IN THE ATMOSPHERE IN DOWNTOWN TORONTO**

**By**

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**A thesis**

**Presented to Ryerson University**

**in partial fulfillment of the**

**Requirements for the degree of**

**Master of Applied Science**

**in the program of**

**Chemical Engineering**

**Toronto, Ontario, Canada, 2005**

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## **Abstract**

### **Studies of mercury species in the atmosphere in downtown Toronto**

Xinjie Song

MASc, Chemical Engineering, Ryerson University, 2005

This study had been carried out in downtown Toronto from December 2003 to November 2004. Gaseous elemental mercury (GEM), reactive gaseous mercury (RGM, also called gaseous oxidized inorganic mercury, GOIM) and mercury associated with particles having size  $<2.5\ \mu\text{m}$  ( $\text{PM}<2.5$ ) were simultaneously measured using Tekran mercury speciation unit. Mean concentration, standard deviation and distribution of GEM,  $\text{PM}<2.5$  and RGM were  $4.52 \pm 3.13\ \text{ng m}^{-3}$  (98.7%),  $21.51 \pm 16.35\ \text{pg m}^{-3}$  (0.5%) and  $14.19 \pm 13.24\ \text{pg m}^{-3}$  (0.3%), respectively. Local and regional anthropogenic sources are believed to contribute the elevated value and high temporal variations. Overall, the mercury species concentrations are lower in winter than in the other three seasons. Nighttime GEM,  $\text{PM}<2.5$  and RGM concentrations are higher than those of daytime. Correlation analysis was conducted between each mercury species and the meteorological parameters (i.e. surface ambient air temperature, relative humidity, wind direction), as well as among the mercury species in this study.

## Acknowledgements

I would like to express my special gratitude to Dr. Julia Lu, my supervisor, for her support, patience, encouragement and understanding throughout my graduate studies. Her constant and invaluable guidance was essential to the completion of this thesis and other conference achievements. Furthermore, I appreciate my co-supervisor, Dr. Jiangning Wu, for her logistic support and inspiring advice. Moreover, I want to thank Mr. Peter Scharping and Mr. Ali Hemmati from the Department of Chemical Engineering for their engineering support during my graduate study. I also acknowledge the help from Dr. James Lu, Ms. Hui Zhou and Dr. Zia Siddiqi.

I thank my family and my friends for the joyful love and continuous support, not only in the study but also in my life.

This work was supported partially by Natural Science and Engineering Research Council of Canada (NSERC), Canadian Foundation of Innovation (CFI), Premier's Research Excellent Awards Program (PREAP) and Ryerson University.

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## **Chapter 1      Introduction**

Among many heavy metal pollutants, mercury is distinctive because of its bioaccumulation and long-term effects to the environment (Song and Lu, 2004). Although the use of mercury and its emissions has been controlled by regulations in the past five decades (Hylander, 2001), continuing increase of the amount of mercury over Atlantic Ocean has been reported between 1977 and 1990 (Slemr and Langer, 1992). Marine mammals such as dolphins, seals and polar bears have continued to show increasing amounts of mercury in their bodies- with some increasing two- or threefold since 1970s (Wittnich and Michael, 2004). The United States Food and Drug Administration (FDA) and Environmental Protection Agency (EPA) (Wittnich and Michael, 2004) have recently announced stringent warnings concerning mercury, which ensured the hazard to youngsters and pregnant women. Increasing concerns were emerged during the last decade especially after the discovery of the atmospheric mercury depletion/oxidation events (MDEs) in the Polar regions each year after polar sunrise (Schroeder et al., 1998).

Both natural and man-made activities contribute to the mercury distribution in the environment (Mason et al., 1994; Schroeder and Munthe, 1998) and the long-range atmospheric circulation plays an important role in mercury transport, deposition and re-emission around the world . Researches have been done and are being done to understand the transport, transformation and fate of mercury in the environment.

Mercury measurements in urban environment are quite limited although a lot of studies were done in the remote and rural areas (Carpi and Chen, 2002; Dvonch et al., 1995; Fang et al., 2004, 2003; Kim and Kim, 2000, 2001, 2002; Liu et al., 2002; Lynam and Keeler, 2004; Nadim et al., 2001; Sakata and Marumoto, 2002; Banic et al., 2003; Blanchard et al., 2002; Chen et al., 2004; Iverfeldt et al., 1995; Kellerhals et al., 2003; Lee et al., 1998; Poissant, 2000; Schmolke et al., 1999; Slemr and Scheel, 1998; Berg et al., 2003; Golubeva et al., 2003; Poissant and Pilote, 2003; Schroeder et al., 1998; Gardfeldt et al., 2001; Iverfeldt et al., 1995; Lamborg et al., 1999; Lee et al., 2000; Slemr and Langer, 1992; Temme et al., 2003; Weiss-Penzias et al., 2003). Mercury speciation studies were even less in the last few years.

## **1.1 Scope of the study**

In this study, mercury species had been monitored from December 23, 2003 to December 2, 2004 at Ryerson University in downtown Toronto using the Tekran mercury speciation system. This system is based on mercury pre-concentration on gold, thermal desorption and cold vapor atomic fluorescence spectrometry (CVAFS) detection. Operation, maintenance and calibration of the system were carried out according to the operation manual. Data were retrieved from the unit to a computer and treated with Excel. The temporal and diurnal variability were analyzed.

## **1.2 Objective and contribution**

The main objectives of the thesis are as follows:

- (1) To measure the concentrations of mercury species in downtown Toronto;
- (2) To measure the meteorological parameters at the same site (e.g. ambient air temperature, relative humidity, rain, wind direction, wind speed and solar radiation);
- (3) To study the factors that affect the fate, transport, transformation of Hg in the urban environment;
- (4) To compare our results with the urban and other sites in the literature.

## **1.3 Thesis organization**

Chapter 2 gives a literature review on the mercury sources, the environment impacts and health effect. The research achievements on the environmental measurement as well as the urban atmospheric speciation studies are summarized. This part gives a clear overview on the atmospheric mercury research status and improvements.

Chapter 3 provides a detailed description for the sampling site, instruments, sampling cycles, mercury detection theory and data analysis.

Chapter 4 presents results and discussion on the atmospheric mercury speciation studies. The monthly and seasonal variability are firstly presented followed by diurnal pattern studies. Statistical analysis, divided into several parts categorized as concentration comparison, speciation constitution, relative frequency analysis and relationship analysis, were performed and summed up in this section. The effects from meteorological parameters including air temperature, relative humidity and wind direction are discussed. As a comparison, anthropogenic effects were also summarized.

Based on the discussion, study summary were presented in Chapter 5. Recommendations on the future work can be found in this chapter as well.



## **Chapter 2      Literature Review**

### **2.1    Mercury in the environment: properties, source, usage, species and fate**

Mercury (Hg) is a natural occurring element known as a “heavy metal” that cycles between the atmosphere, land and water (Butler and Harrod, 1989; Cox, 1989). Mercury is unique, as it is the only metal that is liquid at room temperature having a melting point of  $-38.83\text{ }^{\circ}\text{C}$  and a boiling point of  $356.6\text{ }^{\circ}\text{C}$  (Greenwood and Earnshaw, 1997). It is very dense with the specific gravity 13.5 times that of water and an atomic weight of  $200.59\text{ g mol}^{-1}$ . Droplets of liquid mercury are shiny and silver-white with a high surface tension, appearing rounded when on flat surfaces (Porterfield, 1984). The liquid is highly mobile and droplets combine easily due to low viscosity. Mercury has a relatively high vapour pressure and the highest volatility of any metal, vapourizing to become a colourless, odourless gas. The metal is a good conductor of electricity, but a poor conductor of heat. The detailed chemical and physical properties are listed in Table 1 (Huheey et al., 1993; James and Lord, 1992; Kaye and Laby, 1993).

**Table 1      Physical and chemical properties of mercury**

<b>Items</b>	<b>Description</b>	<b>Items</b>	<b>Description</b>
<b>Name</b>	Mercury	<b>Atomic number</b>	80
<b>Chemical Symbol</b>	Hg	<b>Atomic Mass</b>	200.59
<b>Origin</b>	Natural	<b>Earth Abundance</b>	0.05 ppm
<b>Physical State</b>	Liquid	<b>Common Ions</b>	Hg <sup>+</sup> , Hg <sup>2+</sup>
<b>Density [298K]</b>	13546 kg m <sup>-3</sup>	<b>Heat of Fusion</b>	2.331 kJ mol <sup>-1</sup>
<b>Electron Affinity</b>	-18 kJ mol <sup>-1</sup>	<b>Heat of Vaporization</b>	59.15 kJ mol <sup>-1</sup>
<b>Melting Point</b>	-38.83 °C	<b>Heat of Atomization</b>	61 kJ mol <sup>-1</sup>
<b>Polarizability</b>	5.4 Å <sup>3</sup>	<b>Radius of Covalent</b>	144 pm
<b>Boiling Point</b>	356.73 °C	<b>Electronic Configuration</b>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>
<b>Radius of Hg<sup>1+</sup></b>	127 pm	<b>Electrical Conductivity [298K]</b>	1.06x10 <sup>6</sup> Ohm <sup>-1</sup> m <sup>-1</sup>
<b>Radius of Hg<sup>2+</sup></b>	112 pm	<b>Thermal Conductivity [300K]</b>	8.34 W m <sup>-1</sup> K <sup>-1</sup>
<b>Radius of Atomic</b>	160 pm		

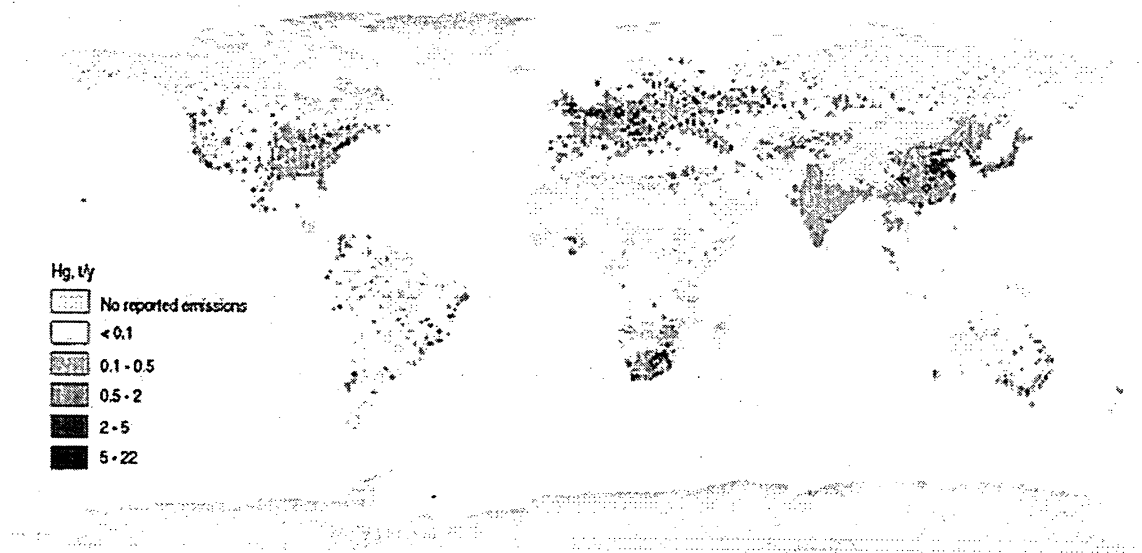
1 pm = 1 x 10<sup>-12</sup> metre

Mercury and its compounds are widely distributed in the environment because of both natural and man-made activities. Mercury rarely occurs free in nature, and is found mainly in cinnabar ore (HgS) (Winter, 2002). Other occurrence in the crust is described in Table 2. Mercury enters the environment cycles (chemical and biological) as a result of normal breakdown of minerals in rocks and soil through exposure to wind and water. Naturally, mercury can enter the atmosphere from volcanoes, wild fires, mercury rich soils, and water surfaces (Lee et al., 1998). It is estimated that, however, annual, natural emissions from continental sources are approximately 1,000 tonnes. In pre-industrial times, evasion from the oceans is thought to have been 600 tonnes. Today, however, evasion from the oceans has increased to approximately 2,000 tonnes due to the re-emission of mercury deposited as a result of human activities (Environment Canada, 2005).

**Table 2      Occurrence of Hg in nature**

<b>Name of Occurrence</b>	<b>Chemical Description</b>
<b>Amalgamate of Hg</b>	Hg, Ag
<b>Calomel</b>	Hg <sub>2</sub> Cl <sub>2</sub>
<b>Cinnabar</b>	HgS
<b>Coloradoite</b>	HgTe
<b>Livingstonite</b>	HgSb <sub>4</sub> S <sub>8</sub>
<b>Metacinnabar</b>	HgS
<b>Tetrahedrite</b>	(Cu,Hg) <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>
<b>Tiemannite</b>	HgSe

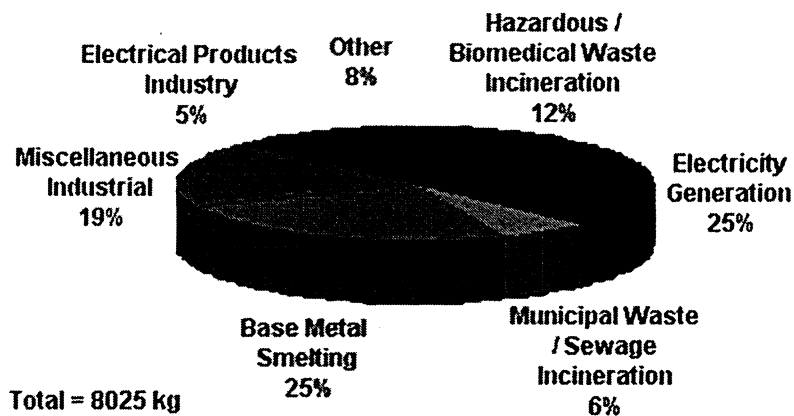
Since the advent of industrialization, the amount of mercury mobilized and released to the environment has increased significantly due to human activities (Environment Canada, 2005; USEPA, 2005). Anthropogenic sources of mercury include fossil fuel combustion, metal smelting, refining and manufacturing, waste incineration, gold mining, thermometers, electrical switches, paintings, batteries, chloro-alkali plants, medicinal, agricultural compounds and fluorescent lamps. Figure 2-1 depicts the global total Hg emission in 1990 (CGEIC, 1996).



**Figure 2-1 Spatial distribution of global emissions of mercury to air within a  $1 \times 1$  grid in 1990**

In Canada, the largest anthropogenic source of mercury until the 1980s was the chloralkali industry. Although mercury is still employed in this industry to manufacture chlorine and sodium hydroxide, emissions have now declined due to pollution control, conversion to non-

mercury processes and plant closures (Environment Canada, 2005). It is estimated that total annual natural source emissions of Hg averages at  $1.1 \times 10^6$  kg in 1989 (Richardson et al., 2003). Between 1990 and 1995, Canadian anthropogenic mercury emissions dropped from approximately 32 to 11 tonnes primarily as a result of process improvements in the base metal mining industry. From 1995 to 2000, Canadian anthropogenic mercury emissions dropped to a total of just over 8 tonnes. Figure 2-2 shows the Canadian anthropogenic atmospheric mercury emissions from various sectors for the year 2000 (Environment Canada, 2005).



**Figure 2-2 Canadian anthropogenic emission of mercury from various sectors to the atmosphere in 2000**

Mercury combines with all the common metals, except iron and platinum, to form alloys that are called amalgams. Because of its unique properties, Mercury has been used in a variety of consumer products. Table 3 (Galligan et al., 2002) lists some of the mercury-containing products and the normal Hg content range. Mercury forms monovalent and divalent

compounds. The commercially important compounds of mercury are mercurous chloride,  $\text{Hg}_2\text{Cl}_2$  or calomel, which is a white, relatively insoluble salt that is used in calomel electrodes. Mercuric chloride,  $\text{HgCl}_2$ , or corrosive sublimate, is highly poisonous because it has a high solubility. It is used as a disinfectant, in preparing other mercury compounds,

**Table 3      Some mercury-containing products**

<b>Products</b>	<b>Usage</b>	<b>Hg Content</b>
<b>Barometer and vacuum gauge</b>	Measure atmospheric pressure	300 to 600 g
<b>Batteries</b>	Button cell type	5 and 25 mg
<b>Dental amalgam</b>	Fabricate a hard durable tooth filling	50%
<b>Flame sensors</b>	Open or shut off gas, in fire detection systems to activate alarms	1 g
<b>Flowmeters</b>	Measure the rate of flow of gas, water, air and streams	up to 5000 g
<b>Hydrometers</b>	Measure the specific gravity and density of a liquid	0.002 g to 1 g
<b>Hygrometers/ Psychrometer</b>	Measure the moisture content in air	3 to 7 g
<b>Lamps</b>	Essential component for more energy efficient than incandescent lights, high intensity discharge (HID) or bright lamp,	1 to 225 mg
<b>Manometers</b>	Measure air, water and gas pressure	340 g

**Table 3      Mercury-containing products (Cont'd)**

<b>Products</b>	<b>Usage</b>	<b>Hg Content</b>
<b>Medical devices</b>	Dilate the esophagus of a patient during thoracic surgery, otolaryngology; extraction of intestinal obstructions; measure human blood pressure	20 to >1000 g
<b>Mercury compounds</b>	Laboratory and industrial	varies
<b>Pyrometers</b>	Measure extremely hot materials in foundry applications and exhaust temperatures for large engines	5 to 10 g
<b>Relay</b>	Capable of opening a normally-closed circuit or closing a normally-open circuit	1- 150 g
<b>Switches</b>	Regulate the flow of electricity	0.4-71 g
<b>Thermometer</b>	Measure temperature	0.5-5 g
<b>Thermostats</b>	Heating and cooling systems in residential, medical, commercial and industrial settings	3 g
<b>Thermostat probes</b>	Prevent gas from flowing when the pilot light of the appliance is off	1 g

and in antifungal skin ointments. Mercuric sulfide,  $\text{HgS}$ , occurs in a red form and an amorphous black form. The red form (vermilion) is used as a coloring material.

Mercurochrome is an organic mercury compound that is used on wounds as an antibacterial agent (Tekran, 2005). Mercury fulminate ( $\text{Hg}(\text{ONC})_2$ ), is a detonator used in explosives.

Organic mercury compounds are the most toxic and dangerous. Methyl mercury is a lethal pollutant found in rivers and lakes. The main source of pollution is industrial wastes settling to the river and lake bottoms, which later were converted to organic mercury in the nature environment.

Natural transformations and environmental pathways of mercury are very complex and are greatly affected by local conditions (Environment Canada, 2005). Understanding the relationships between local conditions and mercury levels in various environmental media and living organisms is critical to predicting changes in concentration and form. There are two main types of reactions in the mercury cycle that convert mercury through its various forms: oxidation-reduction and methylation-demethylation. In oxidation-reduction reactions, mercury is either oxidized to a higher valence state (e.g. from relatively inert  $\text{Hg}^0$  to the more reactive  $\text{Hg}^{2+}$ ) through the loss of electrons, or mercury is reduced, the reverse of being oxidized, to a lower valence state (Environment Canada, 2005). In the environment, mercury is transformed into methylmercury when the oxidized, or mercuric species ( $\text{Hg}^{2+}$ ), gains a methyl group ( $\text{CH}_3$ ).

Due to the volatility of elemental mercury ( $\text{Hg}^0$ ), and the fact that  $\text{Hg}^0$  has atmospheric residence time of up to 2 years, mercury can travel in a multi-step sequence of emission to the



atmosphere, transportation, deposition and re-emission. As a result, mercury from point source emissions may remain localized in the environment, or may be transported regionally and even globally. Atmospheric transport is then likely the primary mechanism by which  $\text{Hg}^0$  is distributed throughout the environment, unlike many pollutants that follow erosion or leaching pathways. Mercury can enter the atmosphere as a gas or bound to other airborne particles and circulates until removal. Removal occurs primarily through the "wet" deposition of  $\text{Hg}^{2+}$  in rainfall, however it can also occur in the presence of snow, fog, or through direct, or "dry", deposition. Approximately 98% of the estimated 5,000 tonnes of mercury in the lower atmosphere is gaseous elemental mercury (GEM). This gas is readily transported by atmospheric circulation and has a mean atmospheric residence time of about one year to one and a half years. GEM is relatively unreactive, it deposits directly to the earth's surface at a very low rate, it is very insoluble in water and therefore is not removed efficiently in precipitation, and thus has a long atmospheric resistance time and can travel far away from the sources of emission (Lee et al., 1998). The features of Hg mobilization processes classify mercury not only as a pollutant of local interest but of global interest as well (Poissant et al., 2002). The transformation of insoluble  $\text{Hg}^0$  to its more reactive and water-soluble form,  $\text{Hg}^{2+}$  or reactive gaseous mercury (RGM, also called GOIM, gaseous oxidized inorganic mercury), is thought to provide the mechanism for the deposition of  $\text{Hg}^0$  to land and water.  $\text{Hg}^0$  oxidation may also be affected by concentrations of other atmospheric pollutants such as ozone, sulphur dioxide and soot. Another small part of the mercury burden is associated with particles (PM). Particulate Hg originates from direct emissions or from oxidation of  $\text{Hg}^0$ . These species have relatively short residence times in the atmosphere ranging from hours to months. RGM has a residence time of just 5 to 14 days in the atmosphere, and may travel tens

to hundreds of kilometers. PM tend to fall out closer to the source of emissions, with larger particles falling out faster than smaller ones. The site-specific deposition of mercury is variable, and is affected by conditions like meteorology, temperature and humidity, solar radiation and emission characteristics (speciation, source, stack height, etc.) (Poissant, 2000). During MDEs, atmospheric  $\text{Hg}^0$  can be rapidly oxidized to the reactive and water soluble form of  $\text{Hg}^{2+}$ , and deposited on snow and ice surfaces. This reaction is thought to occur photochemically (in the presence of sunlight) and in the presence of chemicals released from sea salt (for example, bromine and chlorine ions). As a result, a pulse of reactive mercury enters the Arctic environment at the beginning of the short lived growing season. Mercury can undergo transformation by bacteria through chemical and biological processes in the natural environment from less toxic inorganic forms to extremely toxic methylated species, such as mono- or dimethyl mercury (Kim and Kim, 2002).

## **2.2 Health effect of mercury**

Almost all mercury compounds are toxic and can be dangerous at very low levels in both aquatic and terrestrial ecosystems (Sigel and Sigel, 1997). It can be bioaccumulated and biomagnified in the food chain up to  $10^7$  bioaccumulation factors (Clarkson, 1997). The highly toxic, organic compound methylmercury, which is absorbed into the body about six times more easily than inorganic mercury, can migrate through cells that normally form a barrier to toxins (Clarkson, 1997, 1998, 2002). It can cross the blood-brain and placental barriers, allowing it to react directly with brain and fetal cells. Mercury contamination causes a wide range of symptoms in organisms, and affects the kidneys and neurological systems in

particular. While low levels may not be directly lethal for individual organisms, toxicological effects like impaired reproduction, growth, neuro-development, and learning ability, in addition to behavioral changes, can lead to increases in mortality and the risk of predation for some wildlife.

The main effects of mercury exposure to humans are understood to be neurological, renal (kidney), cardiovascular and immunological impacts (WHO, 1976; WHO, 1989; WHO, 1990). Chronic exposure to mercury can cause damage to the brain, spinal cord, kidneys, liver and developing fetus. Exposure to mercury while in the womb can lead to neurodevelopmental problems in children. Mercury can impair the ability to feel, see, move and taste, and can cause numbness and tunnel vision. Long-term exposure can lead to progressively worse symptoms and ultimately personality changes, stupor, and in extreme cases, coma or death. Recent findings have described adverse cardiovascular and immune system effects at very low levels (WHO, 1991). Symptoms of methylmercury toxicity, also known as Minamata disease (Weiss, 1996), range from tingling of the skin, numbness, lack of muscle coordination, tremor, tunnel vision, loss of hearing, slurred speech, skin rashes, abnormal behaviour (such as fits of laughter), intellectual impairment, to cerebral palsy, coma and death, depending on the level of exposure. In addition, methylmercury has been classified as a possible human carcinogen by the U.S. Environmental Protection Agency (USEPA, 1995; USEPA, 2005).

Most people are exposed to mercury as a result of normal activities such as the inhalation of air, contact with water and soil and/or exposure to substances or products containing mercury such as dental amalgam. The main pathways for mercury intake in humans are through the

consumption of food, especially fish, and the application of dental amalgams as a tooth restorative. Recent research has indicated that exposure to mercury vapour resulting from past spills of liquid mercury in the home may also be an important pathway (Environment Canada, 2004).

The exposure limits for workers exposed to mercury vary with the governmental jurisdiction (USOSHA, 2005). A typical value was set up at  $50 \mu\text{g m}^{-3}$  average air concentration for an 8 hour shift by National Institute of Occupational Safety & Health (NIOSH). In 1994, the WHO (World Health Organization) reduced their exposure limit for total inorganic mercury (including elemental mercury) from 50 to  $25 \mu\text{g m}^{-3}$  (WHO, 2005). Ambient air standard has not been developed by most jurisdictions based on the fact that firstly, There was no practical way to measure these small concentrations until recently, and secondly, the deleterious effects of low levels of mercury on the environment have only recently become known. However, few jurisdictions set the criteria many years ago in response to the potential health problems of high level emissions from industrial sources. For example, the Ontario ambient air standard is  $5 \mu\text{g m}^{-3}$  ( $5000 \text{ ng m}^{-3}$ ) for an hour average (Tekran, 2005).

### **2.3 Atmospheric mercury measurement**

Research on the concentration status of elemental mercury in the atmosphere is important in understanding the fate of this element in the environment as the atmosphere is the major pathway of transporting mercury from sources of emission and distributing it in the environment. It is also fundamental for predicting ambient concentrations of mercury species formed through certain atmospheric chemical mechanisms. The ability of mercury to

accumulate has resulted in a need to measure extremely low levels in a convenient and accurate manner.

Many researches were conducted around the world on the atmospheric mercury measurements. They can be divided into four categories depending on the sampling site classification: remote, rural, marine/coastal and urban. In this section, all the categories will be reviewed.

The Canadian Atmospheric Mercury Measurement Network (CAMNet) was established in 1994 by Environment Canada. It consists of 11 sites across Canada territory and provides valuable rural and background data ever since. The Alert site in CAMNet is one of the first attempts to unveil atmospheric mercury concentration secrets in the Polar regions. The mean total gaseous mercury concentration during 1997-1999 was  $1.55 \pm 0.39 \text{ ng m}^{-3}$  (Kellerhals et al., 2003). The GEM concentration in Canadian urban atmosphere, on the other hand, is less-known throughout all these years, because there is no urban site in the CAMNet.

For the atmospheric mercury measurements in rural areas around the world, Banic et al. reported the vertical distribution of GEM in Canada (Banic et al., 2003). Blanchard et al. conducted the 4 years continuous total gaseous mercury (TGM) measurement in Ontario, Canada (Blanchard et al., 2002), while Kellerhals et al. (2003) summarized the 10 CAMNet sites' mean GEM at  $1.60 \pm 0.15 \text{ ng m}^{-3}$ . Poissant (Poissant, 1997, 2000; Poissant et al., 1995) observed the atmospheric mercury in Quebec, Canada. Lee et al. (2001) and other scientist in United States contribute their work to the atmospheric mercury in North America as well.

Among them, Lindberg and Stratton (Lindberg et al., 1998; Lindberg and Stratton, 1998) measured the TGM at  $3.46 \pm 1.7 \text{ ng m}^{-3}$  at sites in Tennessee and Indiana, USA over a 4-year period and RGM in the range of 50-200  $\text{pg m}^{-3}$ . Chen et al. (2004) and Lee et al. (2000) did the TGM in the state of Connecticut, USA during 1997-1999. In Europe, Iverfeldt et al. (1995) provided the yearly average TGM concentrations from 3.3 (1980) to 2.6 (1992)  $\text{ng m}^{-3}$  over Scandinavia, Sweden. Schmolke et al. (1999) carried out the simultaneous measurement of TGM at four sites on a 800 km transect in central Europe and gave the rural TGM concentration result at 1.53-1.93  $\text{ng m}^{-3}$ . A decreasing trend in atmospheric mercury in 1990s was revealed (Slemr et al., 2003). Overall, complicated rural mercury concentration distributions were present around the world.

It is an important milestone in atmospheric mercury study that scientists discovered the MDEs. The rapid decrease of atmospheric TGM in the Arctic spring was first observed in Alert, Canada (Schroeder et al., 1998). This phenomenon was confirmed in European arctic sites Svalbard, Norway in 2001 (Berg et al., 2003b) and Station Nord, Greenland in 2002 (Ferrari et al., 2003). Lindberg's subsequent field study in Barrow, USA employed speciation measurements and obtained same result (Lindberg et al., 2002). Subarctic site in Quebec, Canada (Dommergue et al., 2003; Ferrari et al., 2003) was also in the area list where the MDEs occur. Recent study revealed that MDEs also happened in Antarctic areas during polar summer (Temme et al., 2003a).

These findings ignited significant increasing interests on the atmospheric behavior of mercury in the polar regions. The mechanisms leading to the arctic MDEs and the fate of the mercury

entering to the ecosystems became hot topics in these years. The strong relationship between GEM and ozone was showed initially (Schroeder et al., 1998). It is reported later that MDEs are a result of oxidation of gaseous elemental mercury to form particulate mercury (Lu et al., 2001) and RGM species (Lindberg et al., 2002). It is proposed that the halogenated compounds may be involved in the destruction as active oxidation agents. Ariya et al. (Ariya and Ryzhkov, 2003) suggested that Br atoms and BrO radicals are the most effective halogens driving mercury oxidation based on their own kinetic data and modeling. Ferrari et al. (Ferrari et al., 2004) indicated the snow pack as the main pathway for the oxidized mercury from interstitial air to the ecosystem. Hence, the arctic may become a big sink for mercury. The particular chemical(s), reaction(s) and mechanisms behind this whole scene, however, remain unclear. Identifying the nature of the oxidized RGM will be continued in various measurements, modeling, approaches and efforts in the coming relatively long time period.

As for the determination of atmospheric mercury in other Arctic areas, Berg et al. reported the Svalbard site measurement in European Arctic (Berg et al., 2001). Gaseous elemental mercury (GEM), total particulate mercury (TPM), reactive gaseous mercury (RGM) and total mercury in surface snow have been measured at the Zeppelin mountain during 2000 and 1.47 ng m<sup>-3</sup> for GEM, 2-12 pg m<sup>-3</sup> for RGM, 1- 46.8 pg m<sup>-3</sup> for TPM and 2 g L<sup>-1</sup> for total mercury in surface snow were found in that study. Golubeva et al. studied the Russian Arctic GEM measurement (Golubeva et al., 2003). A series of measurements of gaseous elemental mercury concentrations in near-surface air of the Russian Arctic Region were carried out from 1994 to 1997. Mean of 1.7 ng m<sup>-3</sup> for Kola Bay, 1.6 ng m<sup>-3</sup> for Motovsky Bay, 1.1 ng m<sup>-3</sup> for

the eastern part of the Barents Sea and  $0.7 \text{ ng m}^{-3}$  for the western part of the Kara Sea were found in their study.

## **2.4 Urban atmospheric mercury speciation studies**

Urban environment plays an important role in the fate of atmospheric mercury cycle (Song and Lu, 2004; Zhou et al., 2004). It is emission sources because of the condensed human activities like municipal waste/sewage incineration, electrical products industry, hazardous/biomedical waste incineration, heating/cooling system operation and usage of mercury-containing products. Further more, it is also the main place where people are in the exposure of atmospheric mercury. Table 4 shows the summary of the GEM results from large cities(Song and Lu, 2005). To my knowledge, there is no report on the mercury speciation study in urban environment up to now. For better understanding of the transport, transformation, deposition and health effect of mercury in urban areas, mercury speciation studies are urgently needed.



**Table 4. Comparison of GEM concentrations among urban cities**

Area	Country	City	Study Year	Average <sup>a</sup> (ng m <sup>-3</sup> )	Std. Dev. (ng m <sup>-3</sup> )	Reference
Asia	China	Beijing	1998	8.3-24.7	3.1-24.8	(Liu et al., 2002)
	China	Changchun	1999-2000	18.4	/	(Fang et al., 2004)
	China	Guiyang	2001-2002	8.40	/	(Feng et al., 2004a)
	Korea	Seoul	1987-1988	14.4	9.56	(Kim and Kim, 2002)
			1999-2000	5.34	3.92	
	Japan	Tokyo	2000-2001	2.70	3.59	(Sakata and Marumoto, 2002)
Europe	France	Bordeaux <sup>b</sup>	1995-1996	2.7	/	Pecheyran, et al., 2000
North America	USA	4 sites in Connecticut <sup>c</sup>	1997-1999	2.19-2.69	0.66-1.72	Nadim et al., 2001
	USA	Broward County	1993	2.8-3.3	/	Dvonch et al., 1995
	USA	Chicago	1994-1995	3.6	2.9	Landis et al., 2002
	USA	Detroit	1999-2002	1.17-40.33	/	(Lynam and Keeler, 2004)
	USA	New York	2000	3.84	/	(Carpi and Chen, 2002)
	Canada	Toronto	2001-2002	2.48	2.22	Our previous study
	Canada	Toronto	2003-2004	4.52	3.13	This study

## Chapter 3 Experimental

Monitoring of atmospheric mercury species was conducted from December 23, 2003 to December 2, 2005 at Ryerson University campus in downtown Toronto (pop.: ~3,000,000), Canada. A meteorological station was set up on May 3, 2004 at the same location.

### 3.1 Sampling site description

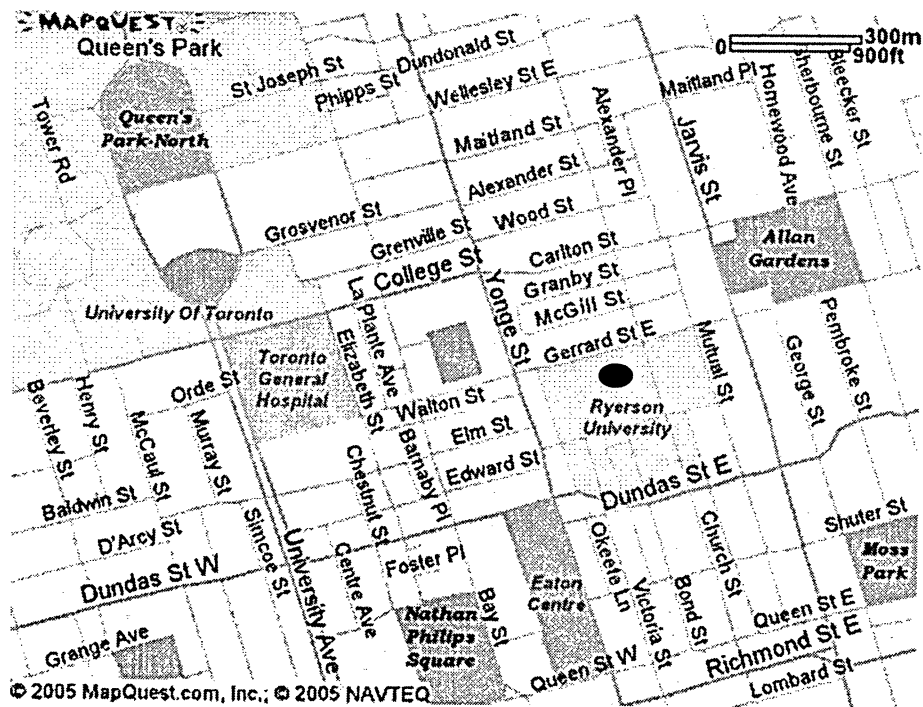
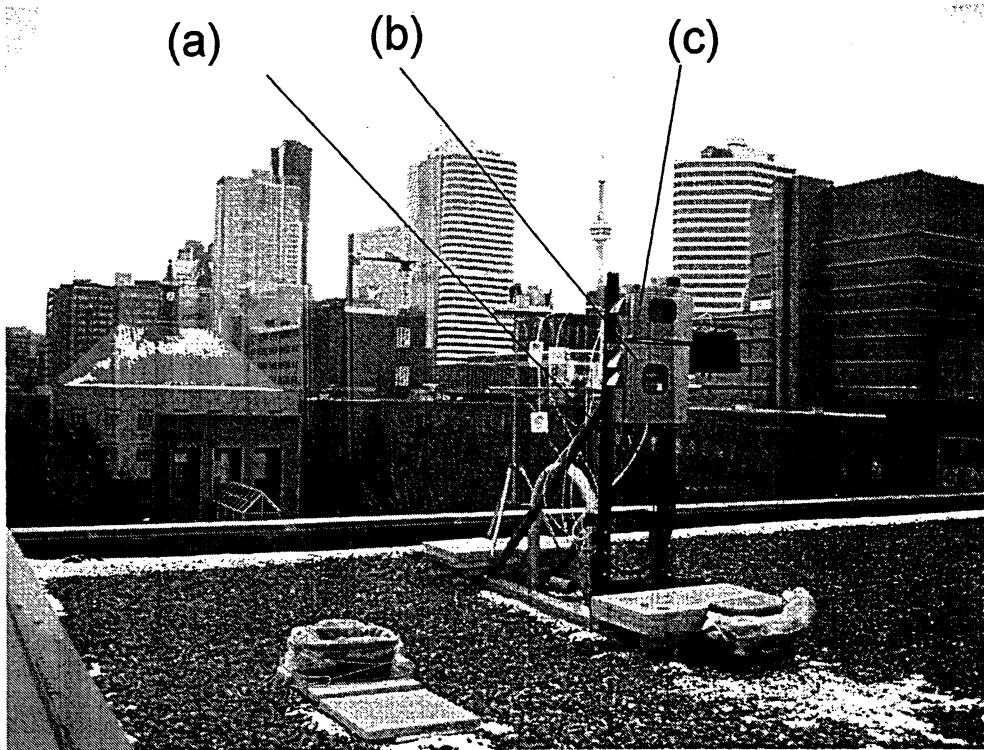


Figure 3-1 Sampling site (●) map in Toronto, Ontario, Canada

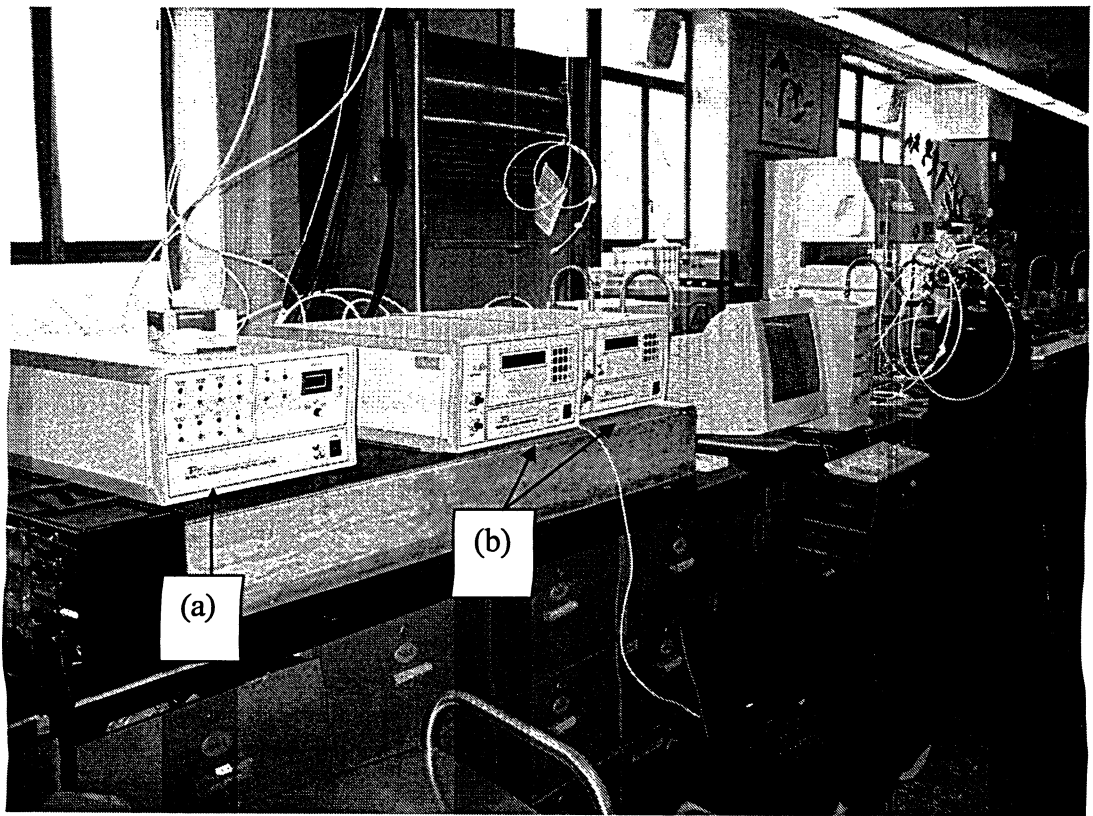
The sampling site is surrounded by commercial, public and private buildings. The latitude and longitude of the sampling site are 43° 40' N and 79° 24' W, respectively. The air sampling system was mounted on the rooftop of the 3-story science building. Sampling site map is shown in Figure 3-1.

## 3.2 Instruments

A mercury speciation system was used for the study (Figure 3-2 and Figure 3-3).



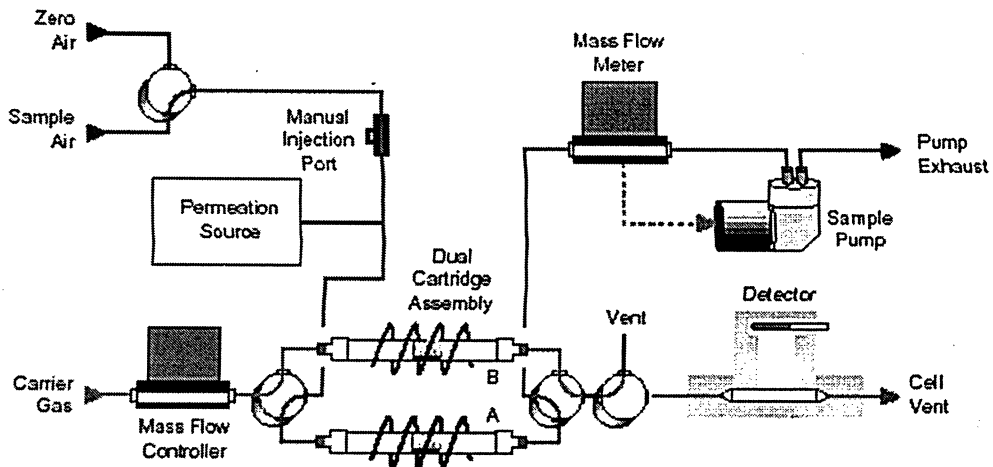
**Figure 3-2** Mercury speciation system - sampling units: (a) air inlet; (b) RGM – denuder sampling unit; and (c) PM unit



**Figure 3-3     Mercury speciation system – pump module (a) and mercury vapor analyzer (b)**

The system consists of a RGM sampling unit (Tekran, model 1130, Toronto), PM sampling unit (Tekran, model 1135, Toronto), a pump module and a mercury vapor analyzer (Tekran, model 2537A, Toronto). The speciation units were installed on the rooftop of the science building. A heated line (50 °C) is used to carry sample air and zero air between the sampling units at the rooftop and the analyzer that located in the lab. The research lab is on the third floor of the building, just underneath the speciation unit. The pump module contains an air pump, a flow meter and a two-stage zero air cartridges system. Air is pulled in from the inlet

(Figure 3-2 (a)). A front-end inline impactor excludes all the particles  $> 2.5 \mu\text{m}$ . RGM is taken up by the KCl-coated denuder when the air stream is flowing through the 1130 unit.  $\text{PM}_{<2.5}$  is collected in the 1135 unit downstream. GEM in the air sample is pre-concentrated on the gold trap and analyzed through thermal desorption and cold vapor atomic fluorescence spectrometry (CVAFS) in the 2537A analyzer. The RGM and  $\text{PM}_{<2.5}$  are thermally converted to  $\text{Hg}^0$  and analyzed in sequence using the 2537A analyzer.



**Figure 3-4 Tekran ambient air mercury analyzer 2537A flow diagram**

The flow diagram of the ambient air mercury analyzer is displayed in Figure 3-4. The analytical train of the Tekran 2537A instrument is based on the amalgamation of mercury onto a pure gold beads followed by a thermal desorption and analysis by cold vapor atomic fluorescence spectrometry (CVAFS) ( $\lambda = 253.7 \text{ nm}$ ). The analyzer provides analysis of GEM in the air at sub-ng  $\text{m}^{-3}$  levels. The dual cartridge design allows alternate sampling and

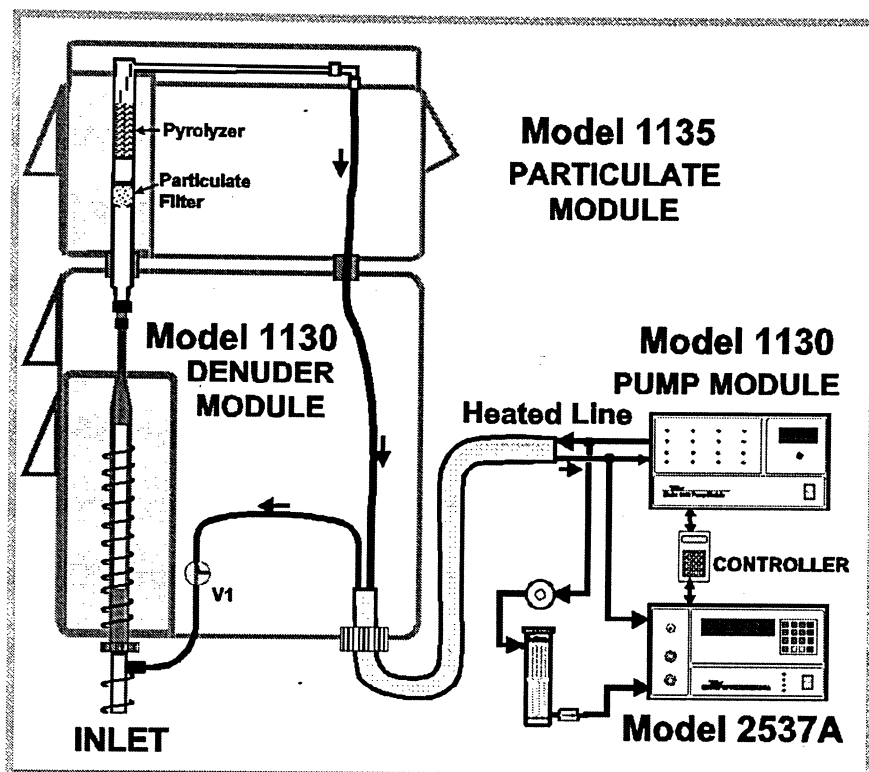
desorption, resulting in continuous measurement of mercury in the air stream. The analyzer was programmed to sample the air at a flow of  $1 \text{ L min}^{-1}$  at 5 min sampling intervals.

The analyzer has two options for calibration: internal elemental mercury permeation tube and manual  $\text{Hg}^0$  injections. The internal permeation source provides approximately  $1 \text{ pg s}^{-1}$  of  $\text{Hg}^0$  at  $50^\circ\text{C}$  into a zero stream whereas the manual injections use a certain volume of air saturated with mercury vapour at a known temperature from a mercury vapor calibration unit (Tekran 2505). The analyzer was calibrated by automatic permeation source every 24 hours. Manual injection calibration was used once every three months or whenever it is needed in order to verify the permeation source rate. With the precision of the Tekran 2537A  $< 2\%$ , the average detection limit is about  $0.1 \text{ ng m}^{-3}$  for GEM (Poissant et al., 2005; Poissant et al., 2004).

A direct primary calibration method for RGM and  $\text{PM}_{<2.5}$  measurements with the Tekran speciation unit does not yet exist, as presently there exist no certified reference material for RGM and PM. The measurements of these species are operationally defined.

A WeatherHawk weather station system was installed at the south site of Tekran speciation unit in May 2004. Virtual Weather Station (VWS) software was used to obtain and download high time resolved (every 1 minute) meteorological parameters such as ambient air temperature, wind direction, wind speed, humidity, rain and solar radiation.

### 3.3 Sampling cycles and species differentiation



**Figure 3-5 Schematic diagram of the Tekran speciation system: Tekran 2537A ambient air mercury analyzer with the 1130 (RGM) and 1135 (PM<2.5) speciation units**

Figure 3-5 shows the Schematic diagram of the Tekran speciation system. In the first hour (sampling phase) of the 2-hour analyzing cycle, ambient air was pulled by the air pump in the pump module through the impactor at  $10 \text{ L min}^{-1}$ . The KCl-coated quartz annular denuder in Model 1130 captures RGM while allowing GEM and PM<2.5 to pass through. PM<2.5 is trapped onto a unique quartz regenerable filter located within the Model 1135 unit. The air in

the downstream of the 1135 unit is pulled by the mercury analyzer (2537A) at  $1 \text{ L min}^{-1}$  (Figure 3-5) and GEM in the air stream is analyzed in 5 min intervals. The  $\text{PM}_{<2.5}$  and RGM were then sequentially flushed with zero air, thermally converted to  $\text{Hg}^0$  and analyzed by Tekran 2537A during the desorption phase – the second hour of analyzing cycle. More specifically in desorption phase, 3 steps (15 min) of flushing zero air were introduced through the speciation unit and 4 steps (20 min) of  $\text{PM}_{<2.5}$  heating at  $800^\circ\text{C}$  were followed. Then 3 steps (15 min) of RGM heating at  $600^\circ\text{C}$  finalized with 2 more zero air flushing (10 min) made up the whole procedure. Each step took 5 minutes to finish. A Teflon coated membrane filter with  $0.2 \mu\text{m}$  pore size and 47mm diameter was placed upstream of the pump module and was replaced every two weeks to generate zero air for flushing and calibration. The system was programmed so that the GEM determinations were reported in units of  $\text{ng m}^{-3}$  and the purge and heat cycles were reported in unit of  $\text{pg m}^{-3}$ . The denuders (RGM collector) and the regenerable particulate filter (RPF,  $\text{PM}_{<2.5}$  collector) were reconditioned and changed every week according to the Tekran protocol (Tekran, 2001). This speciation system was maintained and operated according to the manual, while the system check protocol (Appendix A) was followed during the study.

### **3.4 Data handling and analysis**

Data files, in text format, are generated daily and automatically saved on a computer. A Windows based application, Combine, was used to pre-treat the data. This program separates readings for RGM, GEM and  $\text{PM}_{<2.5}$  and places the data for each species into separate columns. It also provides proper time alignment for data readings, leaving appropriate gaps



during periods of no data and combining results from several capture files. Meteorological data from December 2003 to May 2004 were downloaded from Environment Canada website and were collected on site after our weather station was set up in May 2004. The data downloaded from the Environment Canada website are hourly measurements of temperature, dew point temperature, relative humidity, wind direction, wind speed, air pressure, etc. at Toronto Lester B. Pearson airport weather station. The data from Ryerson University station were collected at 1 min intervals and hourly averages were calculated using a self-constructed working sheet/procedure (see Appendix B). Microsoft Excel was subsequently used to analyze both the mercury speciation and weather data. Data regression and other statistical analysis were employed. Samples of calculation and data analysis are listed in Appendix C. Error analysis and calibration data can be referred in Appendix D.

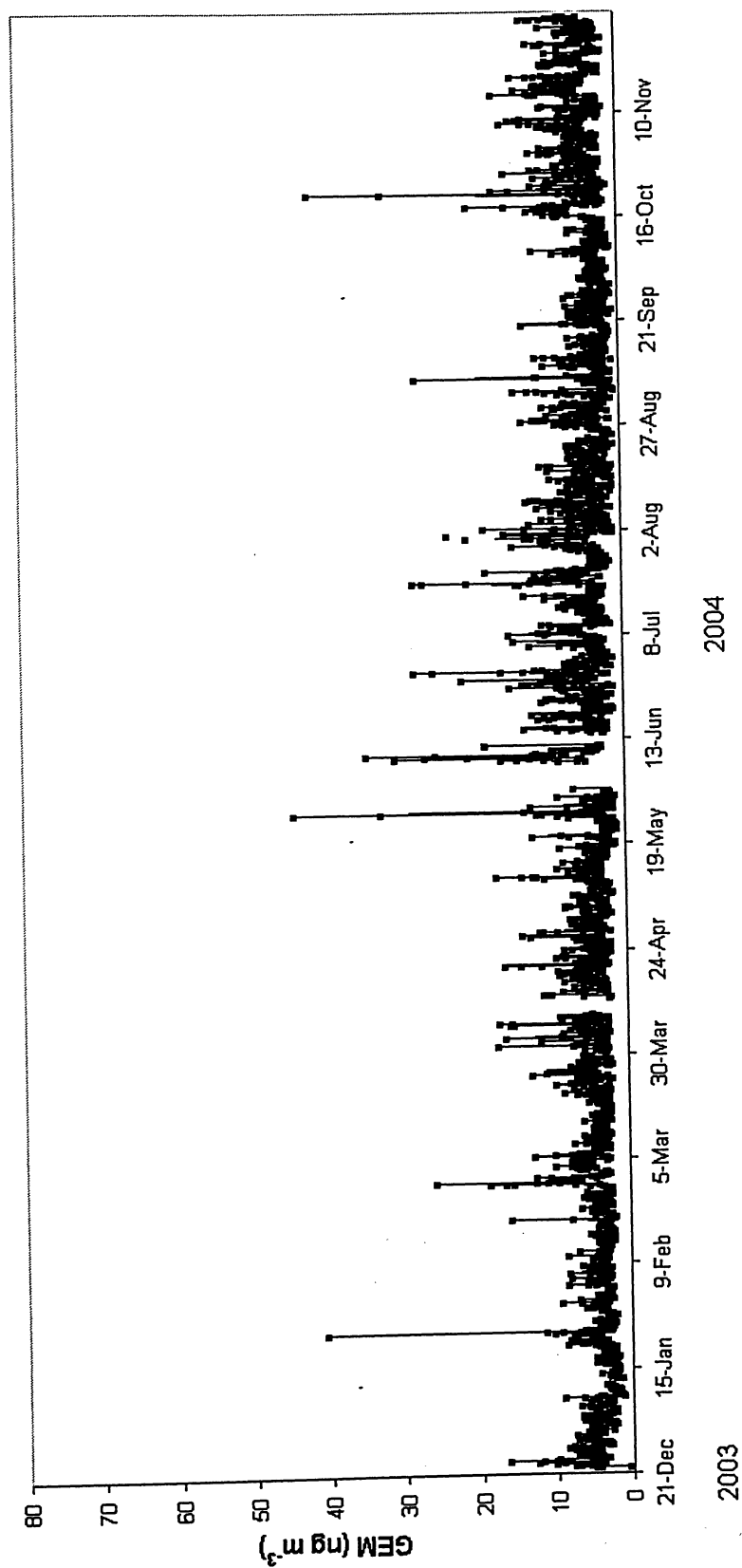
## **Chapter 4      Results and discussion**

### **4.1    Temporal variability: Overall and seasonal analysis**

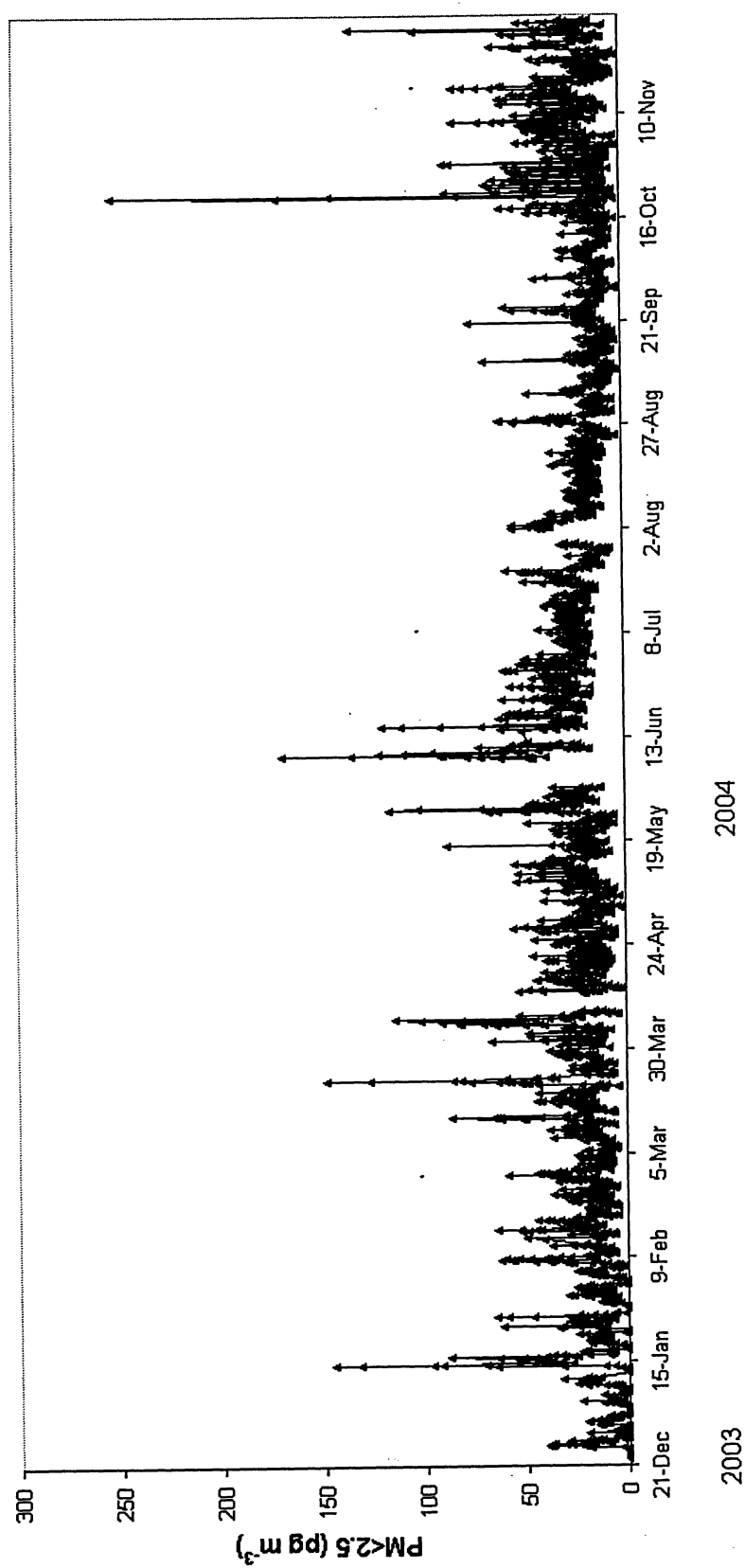
Figure 4-1 to Figure 4-3 show the time series of GEM, RGM and PM<sub><2.5</sub>, respectively. The interruptions occurred during certain periods due to instrument maintenance.

Large variability and numinous spikes of GEM were observed as shown in Figure 4-1. GEM has large variability from March to October 2004. Frequent and high spikes indicate the effect of anthropogenic sources at the sampling site and leading to high standard deviation values. This phenomenon was previously observed in other studies (Carpi and Chen, 2002; Dommergue et al., 2002; Kim and Kim, 2000, 2002).

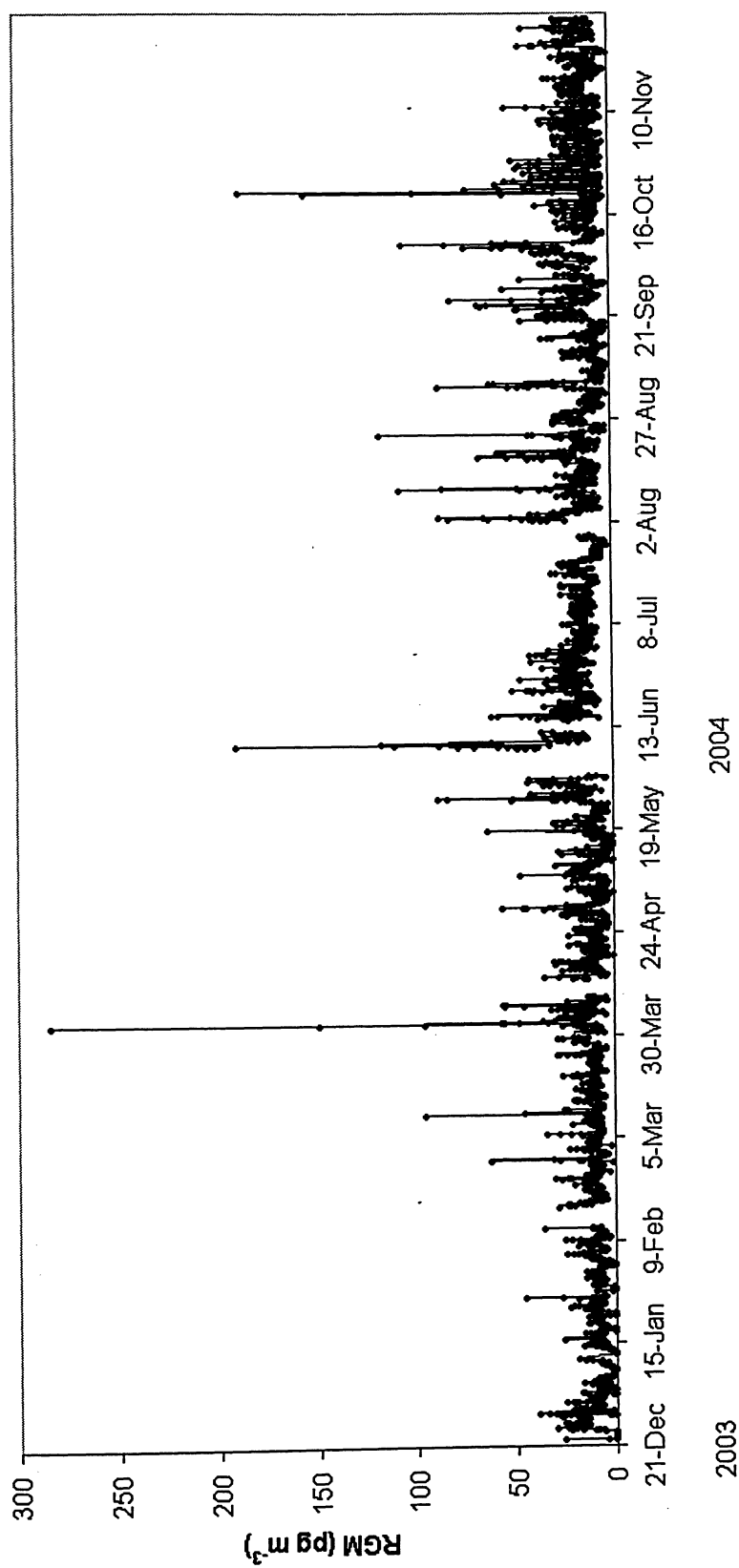
Similar trends were seen for the PM<sub><2.5</sub> (Figure 4-2) and RGM (Figure 4-3) time series. While RGM has large variability during March to October 2004, PM<sub><2.5</sub> showed less variability from June to September 2004. Because of the possibility of transformation among the species, the relationship and mechanism behind this is very important to understand the pollutant. These two species may directly come from the same sources of GEM or transformed from GEM. Of course, RGM and PM can also be turned to GEM.



**Figure 4-1** Time series of GEM in downtown Toronto from December 2003 to November 2004



**Figure 4-2** Time series of PM<sub><2.5</sub> in downtown Toronto from December 2003 to November 2004



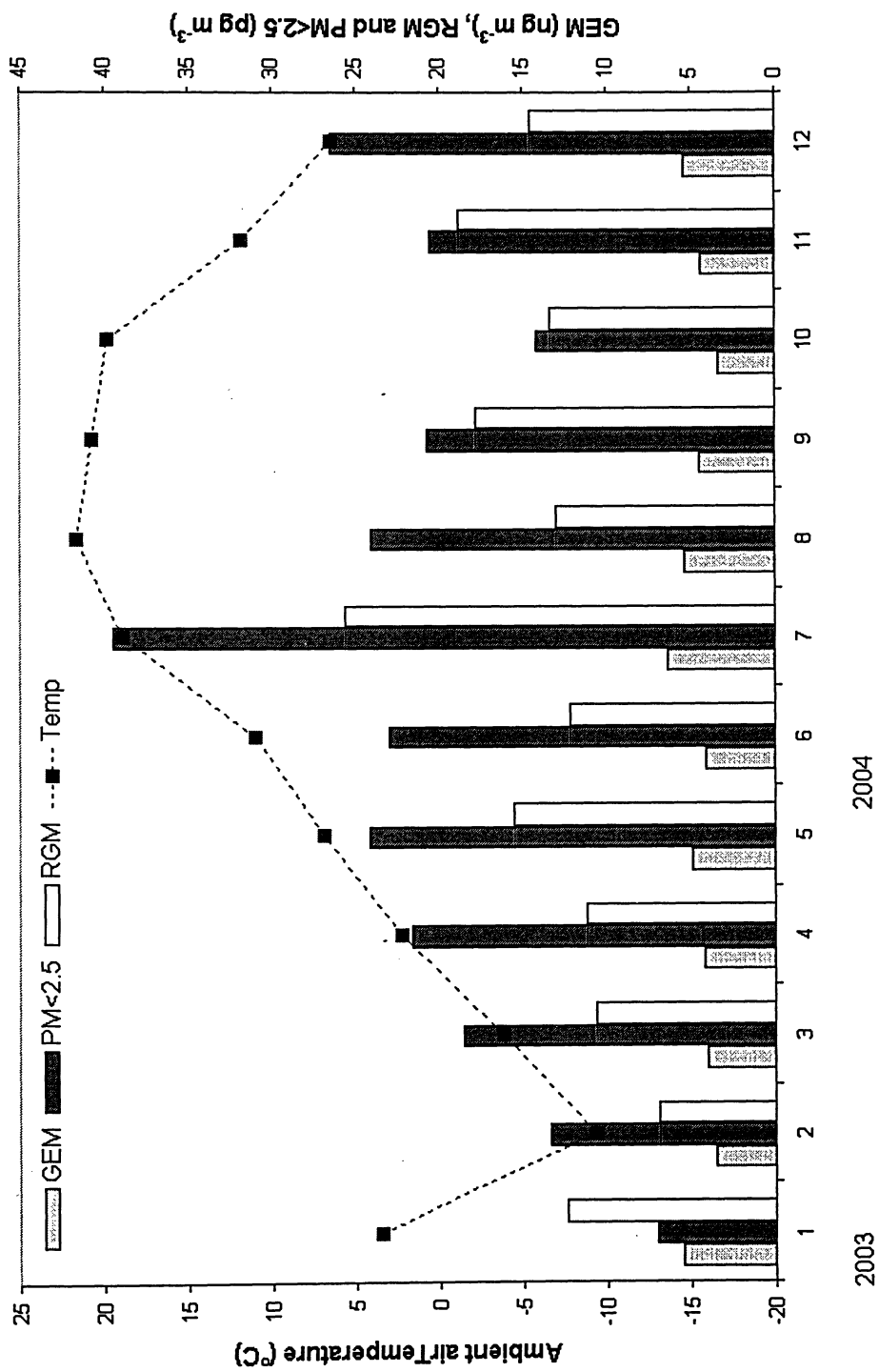
**Figure 4-3** Time series of RGM in downtown Toronto from December 2003 to November 2004

To investigate seasonal variability of the species concentrations, monthly average concentrations were calculated for each species. These data are shown in Figure 4-4. The trend for this can be described as follow: higher concentrations observed in summer especially in June and lower values in winter for all three mercury species.

## **4.2 Diurnal variability**

Annual hourly median atmospheric mercury species are shown in Figure 4-5. All species showed some evidence of a diel cycle with the higher nighttime concentrations and drop in the early morning. For GEM, there were no significant peaks during the daytime but a broad peak showed up from 22:00 to 07:00 (local standard time) the next morning. The mean amplitude of the GEM diel cycle was 24% of the mean concentration. RGM had the minimum at 11:00 and reached to the daytime peak at 16:00. Then the trend went slightly upwards from 19:00 and reached to the nighttime peak at 03:00. The mean amplitude of the RGM diel cycle was 14% of mean concentration. PM<sub>2.5</sub> had the overall lowest concentration at 09:00 and plateau area from 12:00 to 23:00 with small drops. The relative higher concentrations happened from 24:00 to 07:00. The mean amplitude of the PM<sub>2.5</sub> diel cycle was also 14% of mean concentration.

The GEM diel cycle observed at our sampling site is similar with those at several European rural sites (Lee et al., 1998; Schmolke et al., 1999) and Asian rural sites (Feng et al., 2003) but contrast with other studies (Poissant, 2005; Kellerhals et al., 2003). It was proposed at the



**Figure 4-4 Monthly variability of the species concentrations**

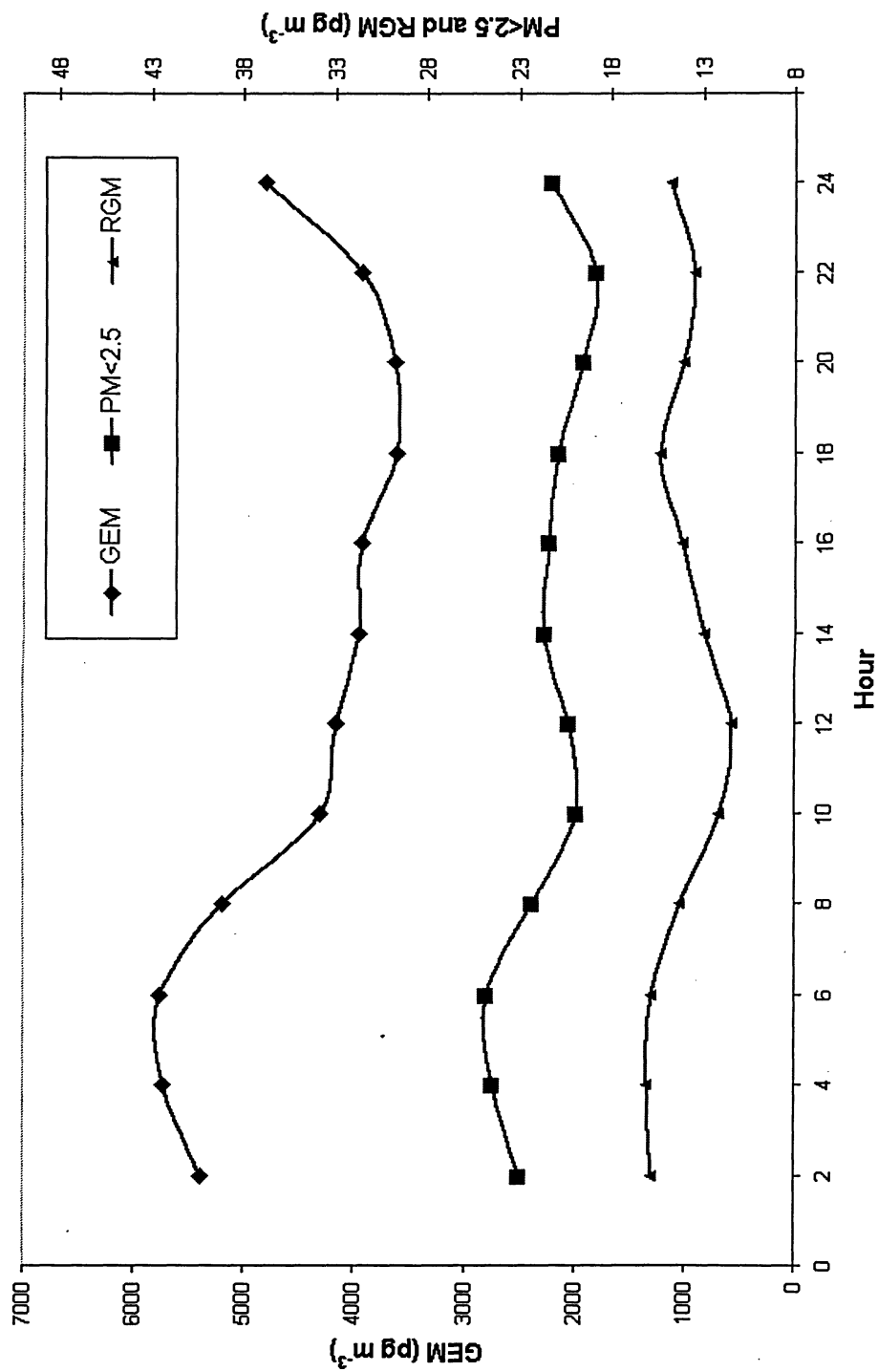


Figure 4-5 Diel cycle of the annual average mercury species concentrations



European sites that the nighttime peak was attributed to soil mercury emissions building up under the nocturnal inversion. It is not the case at our sampling site, however. Firstly, the European sites were intensively focused on the rural and remote environment while ours in the heart of the metropolis. Secondly, our instruments were mounted on the rooftop of a building, which is about 15 meters above the ground. Kellerhals et al. (2003) discussed the diel cycle at the CAMNet sites as the result of nighttime depletion of TGM in the lowest atmosphere. The strong nocturnal depletion of TGM occurred at eight CAMNet sites supported their argument. Poissant et al. (2005) reported that their hourly pattern of GEM concentrations might be related to the convolution of many processes such as sources, chemicals and meteorology.

Our result didn't reveal any GEM nocturnal depletion event or any daytime peak phenomena. It is suggested that, however, the anthropogenic effects may be much stronger than the local soil emission and meteorological factors at our sampling site. The building is ventilated all the time to keep the room temperature and to limit the indoor CO<sub>2</sub> concentration (Ngam, 2005). To save the energy, big fans (located 30 m away from the sampling site on the rooftop) were shut down from 22:00 to 06:00 the next morning. During the nighttime, the ventilation was controlled by computer program at the minimum requirement. It is possible that potential local sources were naturally diffused to the monitoring location, which caused the higher GEM concentration. After 06:00 each morning, the air were circulated and diluted by the powerful fans and the GEM concentration was reduced accordingly. Chemistry labs and chemical storage room locate just underneath the sampling site, along with the campus planning maintenance facilities. GEM concentration was detected as high as 200 ng m<sup>-3</sup> in the

research lab, which may contribute in part to the phenomena. Simple calculation indicated that a stronger mercury source exist around and need to be further investigated. The reason for the high GEM concentration in the research lab also need further study.

### **4.3 Statistical analysis**

Table 5 and Table 6 provide some of the various meteorological parameters during the study period. The data from Pearson airport weather station, Environment Canada (December 2003-April 2004) and from Ryerson station (May 2004- December 2004) were used in this study. Figure 4-6 compares the surface temperatures measured at the two stations from May 2004 to December 2004, showing that the temperatures are comparable at both sites. Thus the daily surface air temperatures measured at the Pearson station can be used for analyzing the data from Ryerson sampling site all year round.

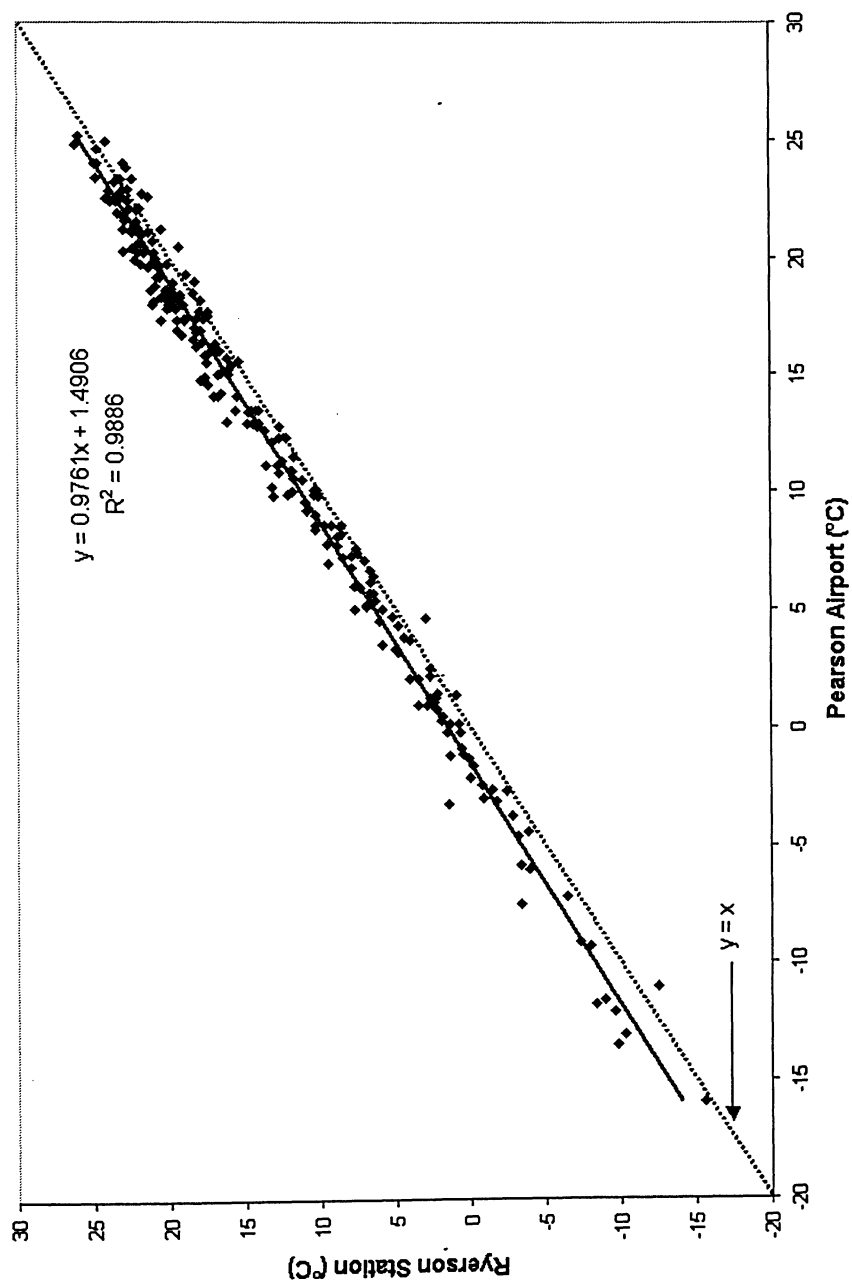
Other meteorological parameters, such as wind direction, wind speed, relative humidity, however, are not comparable between the two stations. The downtown structure, highrises and urban heat island effect caused the differences for the weather parameters other than surface temperature.

**Table 5      Statistical summary of some meteorological parameters around the sampling site: Toronto Lester B. Pearson international airport station data from December 23, 2003 to May 3, 2004**

	Surface Air	Relative	Wind	Wind Speed	Daily Rain
	Temperature (°C)	Humidity (%)	Direction (°)	(km/h)	(mm)
<b>Number of values</b>	3192	3192	3098	3192	132
<b>Mean</b>	-0.38	72.2	223	18.2	1.32
<b>Median</b>	0.2	73	250	17	0
<b>Min</b>	-23.8	28	10	0	0
<b>Max</b>	24.4	100	360	63	16.4
<b>SD</b>	8.25	15.45	103.2	11.0	3.17

**Table 6** Statistical summary of some meteorological parameters at the sampling site: Toronto Ryerson University station data from May 3, 2004 to November 30, 2004

	Surface Air	Relative	Wind	Wind Speed	Daily Rain	Solar Radiation
	Temperature (°C)	Humidity (%)	Direction (°)	(km/h)	(mm)	(W m <sup>-2</sup> )
<b>Number of values</b>	4916	4916	4916	4944	4916	4916
<b>Mean</b>	16.30	58.91	158	3.99	0.08	162.42
<b>Median</b>	17.39	57.86	170	3.72	0	16.48
<b>Min</b>	-3.24	7.63	4	0	0	0
<b>Max</b>	34.99	100	313	15.22	14	975.5
<b>SD</b>	6.68	22.03	62.61	2.60	0.58	243.4



**Figure 4-6 The comparison of the surface temperature from Pearson airport and Ryerson University from May 2004 to December 2004**

Table 7 displays the statistical summary for the measured atmospheric mercury species and seasonal distribution. Hourly averaged GEM data were used in this summary. High standard deviations for GEM (69% of the mean concentration), RGM (76%) and PM<sub><2.5</sub> (93%) are shown in the table, which indicated the effect of the anthropogenic sources at the sampling site. Poissant et al. (2005) stated the reason for the larger standard deviation of their rural RGM and PM<sub><2.5</sub> as the faster reactivity and lower residence time of these mercury species. As discussed above, our sampling site was affected by local sources besides the reactivity reason, if there is any. Poissant's data demonstrated that standard deviation of PM<sub><2.5</sub> is 208% of mean PM<sub><2.5</sub> concentration and standard deviation of RGM is 367% of mean RGM concentration while standard deviation of GEM is only 25% of mean GEM concentration.

Elevated GEM concentration (annual mean 4.52 ng m<sup>-3</sup>) was detected in this study compared to our previous effort. The three-season mean GEM concentration was found at 2.48 ng m<sup>-3</sup> during June 2001 and February 2002. If calculated according to the same three seasons as previous one, the mean GEM concentration from this study is 4.46 ng m<sup>-3</sup>. The possible reasons for this are as follows. (1) Different sampling site. Canopy shaded building side was chosen for the study in 2001-2002. The sampling inlets were 3.5 m and 7.0 m above the ground, right beside the street sidewalk. Building effects and other human activities sources may contribute less to that measurement. (2) Different meteorological effects. With the building shaded area, less sunshine during the most time of the day will drive less GEM from potential soil sources. Wind direction and wind speed were also affected by the sampling area's setup.

**Table 7      Seasonal statistical summary of atmospheric mercury species ( $\text{pg m}^{-3}$ ) in downtown Toronto from December 2003 to November 2004**

		Mean	Stdev.	Median	Min	Max	N
<b>Winter 04</b>	<b>GEM</b>	$4.04 \times 10^3$	$2.33 \times 10^3$	$3.47 \times 10^3$	$0.51 \times 10^3$	$40.44 \times 10^3$	1000
<b>Dec. 23 03</b>	<b>PM&lt;2.5</b>	15.89	14.79	13.13	<0.5	144.84	994
<b>Mar. 19 04</b>	<b>RGM</b>	9.55	6.98	8.59	<0.5	95.32	950
<b>Spring 04</b>	<b>GEM</b>	$4.77 \times 10^3$	$3.60 \times 10^3$	$3.81 \times 10^3$	$1.04 \times 10^3$	$44.10 \times 10^3$	889
<b>Mar. 20 04</b>	<b>PM&lt;2.5</b>	26.84	19.39	21.88	2.39	169.14	890
<b>Jun. 19 04</b>	<b>RGM</b>	15.45	17.47	11.32	<0.5	283.51	890
<b>Summer 04</b>	<b>GEM</b>	$4.69 \times 10^3$	$3.34 \times 10^3$	$3.72 \times 10^3$	$0.59 \times 10^3$	$27.77 \times 10^3$	1064
<b>Jun. 20 04</b>	<b>PM&lt;2.5</b>	21.52	10.32	19.84	1.64	68.35	1032
<b>Sep. 19 04</b>	<b>RGM</b>	15.08	11.18	12.83	0.85	116.26	1032
<b>Fall 04</b>	<b>GEM</b>	$4.67 \times 10^3$	$3.26 \times 10^3$	$3.87 \times 10^3$	$0.66 \times 10^3$	$40.97 \times 10^3$	836
<b>Sep. 20 04</b>	<b>PM&lt;2.5</b>	22.94	19.99	17.56	1.75	251.90	835
<b>Nov. 30 04</b>	<b>RGM</b>	17.25	14.84	13.82	<0.5	186.87	826
<b>All</b>	<b>GEM</b>	$4.52 \times 10^3$	$3.13 \times 10^3$	$3.66 \times 10^3$	$0.51 \times 10^3$	$44.10 \times 10^3$	3782
<b>Dec. 03</b>	<b>PM&lt;2.5</b>	21.51	16.35	18.59	<0.5	251.90	3743
<b>Nov. 04</b>	<b>RGM</b>	14.19	13.24	11.20	<0.5	283.51	3690

The GEM concentrations from the CAMNet-Alert station in the Arctic are considered as background values and the mean concentration was reported as  $1.55 \pm 0.39 \text{ ng m}^{-3}$  (Kellerhals et al., 2003). The GEM concentration in downtown Toronto is much higher than that from Alert and the average value ( $1.60 \text{ ng m}^{-3}$ ) of the rural sites in CAMNet (1997-1998). It is worth to note that standard deviation was much higher for the measurements in Toronto, compared with those for the sites in the CAMNet.

Compared with other urban environmental GEM studies (Table 4), the mean value from this study is slightly higher than those from other urban cities in North America. Data from Asian area, especially from China, are even significantly higher. It is good to see the decrease of mercury in some Asian area, such as Seoul, during the last decade (Kim and Kim, 2002). Intense campaigns were carried out across Europe during the past years (Munthe et al., 2003; Schmolke et al., 1999) to estimate the overall distribution of mercury species across Europe. Only few data, however, were reported on mercury concentrations in urban environment in Europe. The results in Table 4 show that the GEM concentrations in the urban atmosphere are characterized by high standard deviations. This statistical parameter basically shows the effects from human activities rather than poor reproducibility of the analytical instrument thus can be considered as a unique characteristic of urban atmospheric mercury concentrations.

RGM concentration in urban atmosphere had not been reported by other researchers. Poissant et al. (2005) illustrated  $3 \pm 11 \text{ pg m}^{-3}$  in 2003 in St. Anicet (Quebec) rural site and  $3.63 \pm 4.07 \text{ pg m}^{-3}$  in 2002 in the Bay St. Francois remote wetlands, which were far less than our mean

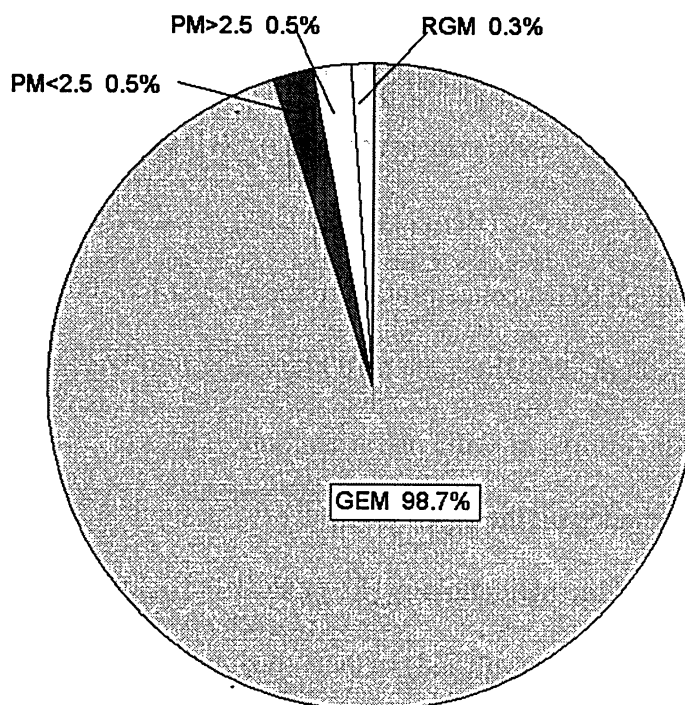


RGM concentration ( $14.19 \pm 13.24 \text{ pg m}^{-3}$ ). Scientists from Environment Canada presented the RGM concentration during MDEs in the Arctic area in recently years (Environment Canada, 2004). Lindberg and Stratton (1998) from United States measured RGM on the order of  $50\text{-}200 \text{ pg m}^{-3}$  in ambient air rural sites in Tennessee and Indiana over a 4-yr period (August 1992 to October 1995). RGM at Rural European site showed average concentrations of  $5\text{-}90 \text{ pg m}^{-3}$  (Ryaboshapko, 2001). Measurement of RGM during a spring MDEs campaign at Svalbard in the European arctic (Berg et al., 2003a) gave the range of  $<2\text{-}12 \text{ pg m}^{-3}$ . Temme et al. reported the RGM concentration in the range of  $5\text{-}300 \text{ pg m}^{-3}$  at a coastal site in the Antarctic (Temme et al., 2003b).

Few studies were conducted on the urban atmospheric particulate mercury using the widely accepted development of the methodology (Lu et al., 1998). Lu's method was used to determine total filterable mercury (TFM) in the atmosphere and proved to be precise and reproducible (Siddiqi et al., 2005; Zhou et al., 2004). Similar technology was applied in Tekran speciation to measure  $\text{PM}_{<2.5}$ . The comparison with the atmospheric mercury speciation study in rural Canada (Poissant et al, 2005) revealed that the  $\text{PM}_{<2.5}$  concentrations from our study and theirs are at the same level regardless the environmental setting.

Lu's method and recent development were employed in another project in our research group and obtained weekly mean TFM concentrations throughout the year 2004 (Siddiqi et al., 2005).  $\text{PM}_{>2.5}$  concentrations were gained by subtract the  $\text{PM}_{<2.5}$  value from the TFM value. Mean results from simple calculation demonstrated that the  $\text{PM}_{<2.5}$  takes about half of

the TFM. The whole distribution of the atmospheric mercury in Toronto thus can be pictured in Figure 4-7.



**Figure 4-7    Distribution of the atmospheric mercury in Toronto**

The majority of the species is GEM, which is well-known (Fitzgerald, 1995; Hall et al., 1995; Poissant et al., 2004) and well-documented (Dommergue et al., 2002; Feng et al., 2003; Gustin et al., 1997; Poissant, 1997; Poissant, 2000). This constitution is the first complete understanding of the distribution of atmospheric inorganic mercury species, compared the previous attempt as GEM (98.4%) > PM<2.5 (1.4%) > RGM (0.2%) (Poissant et al., 2005) that did not measure PM>2.5. Another difference between our data and Poissant's is that

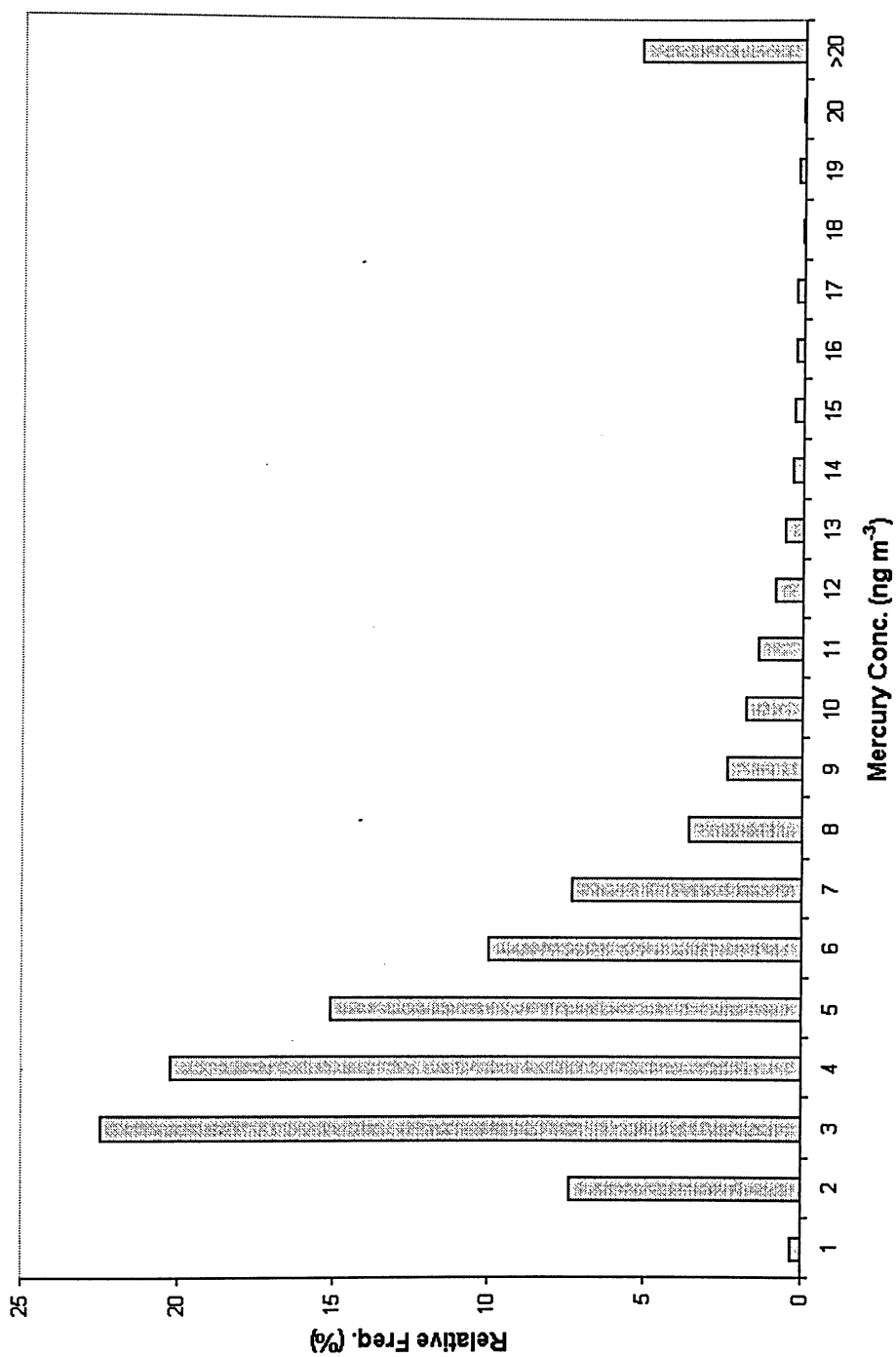
RGM concentration at our sampling site takes larger portion. It should be point out that our composition is verified and valid under normal atmospheric conditions only. But in the polar region after polar sunrise, the distribution of mercury species may be reversed (Lu et al., 2001), enhancing the depletion of RGM and PM on the snow surface. Subsequently, more oxidized inorganic mercury species can be readily assimilated by polar ecosystems, thus transferring potentially toxic mercury to flora and fauna just as biota are preparing for peak summertime activity (Schroeder et al., 1998).

Frequency distributions of these three species are shown in Figure 4-8 to Figure 4- 10. Apparently, GEM (Figure 4-8) and RGM (Figure 4-10) follow the typical log normal distribution pattern while the PM<sub><2.5</sub> (Figure 4-9) is closer to a normal distribution pattern. The majorities of each species in terms of concentration distribution from all experiment period are 2-7 ng m<sup>-3</sup> for GEM, 4-18 pg m<sup>-3</sup> for RGM and 10-24 pg m<sup>-3</sup> for PM<sub><2.5</sub>, respectively. This log normal distribution matches the theoretical distribution of pollutant concentrations for a passive pollutant that is emitted and then subjected to successive random dilutions (Ott, 1995). This pattern is observed in our study, suggesting GEM as a passive pollutant at our monitoring site with the effect of nearby anthropogenic sources by means of air mixing. Similar discussion about the log normal distribution as the result of the passive pollutant can also be found in CAMNet reports (Kellerhals et al., 2003). As for the PM<sub><2.5</sub> normal distribution pattern, it seems that physical adsorption equilibrium of Hg<sup>0</sup> between gas and particle phased dominated by the air temperature (will be discussed below) plays an important role. Thus the distribution is not governed by the pollutant itself but by the particulate characteristics at the sampling site.

The correlations among the species are analyzed and listed in Table 8. Regression (Excel function) analysis was applied to check the statistical significance of the relationship (correlation coefficient) and denoted as P-value in Table 8. The lower the P-value, the higher the statistical significance of the correlation is. Statistical significance can be concluded if the P-value is less than 0.001. With the huge sampling number, the relationship is always statistically significant although the relationship is not much strong (based on r value). The relationship is important for later modeling and predicting the urban atmospheric mercury. It is also a good source for global inventory study on mercury distribution.

**Table 8      Correlation and statistical significance among the atmospheric mercury species in downtown Toronto from December 2003 to November 2004**

Correlation Equation (items unit in $\text{pg m}^{-3}$ )	Sample pairs	r value	t-value	P-value
$[\text{PM}_{<2.5}] = 2.54 \times 10^{-3} [\text{GEM}] + 10.02$	3684	0.4829	33.46	<0.00001
$[\text{RGM}] = 1.59 \times 10^{-3} [\text{GEM}] + 6.95$	3684	0.3810	25.00	<0.00001
$[\text{PM}_{<2.5}] = 0.706 [\text{RGM}] + 11.50$	3684	0.5622	41.26	<0.00001



**Figure 4-8** Relative frequency distribution of GEM in downtown Toronto from December 2003 to November 2004

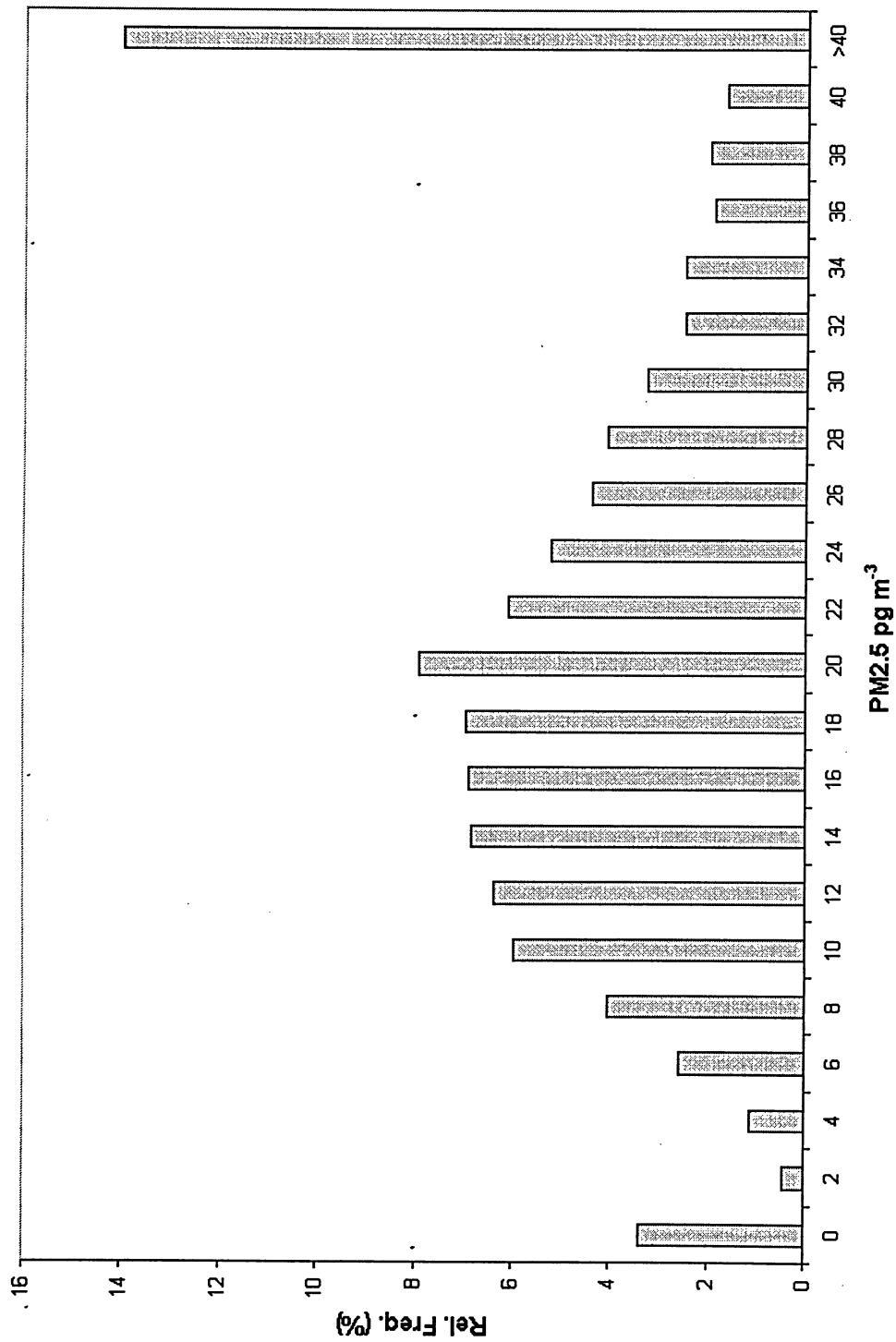
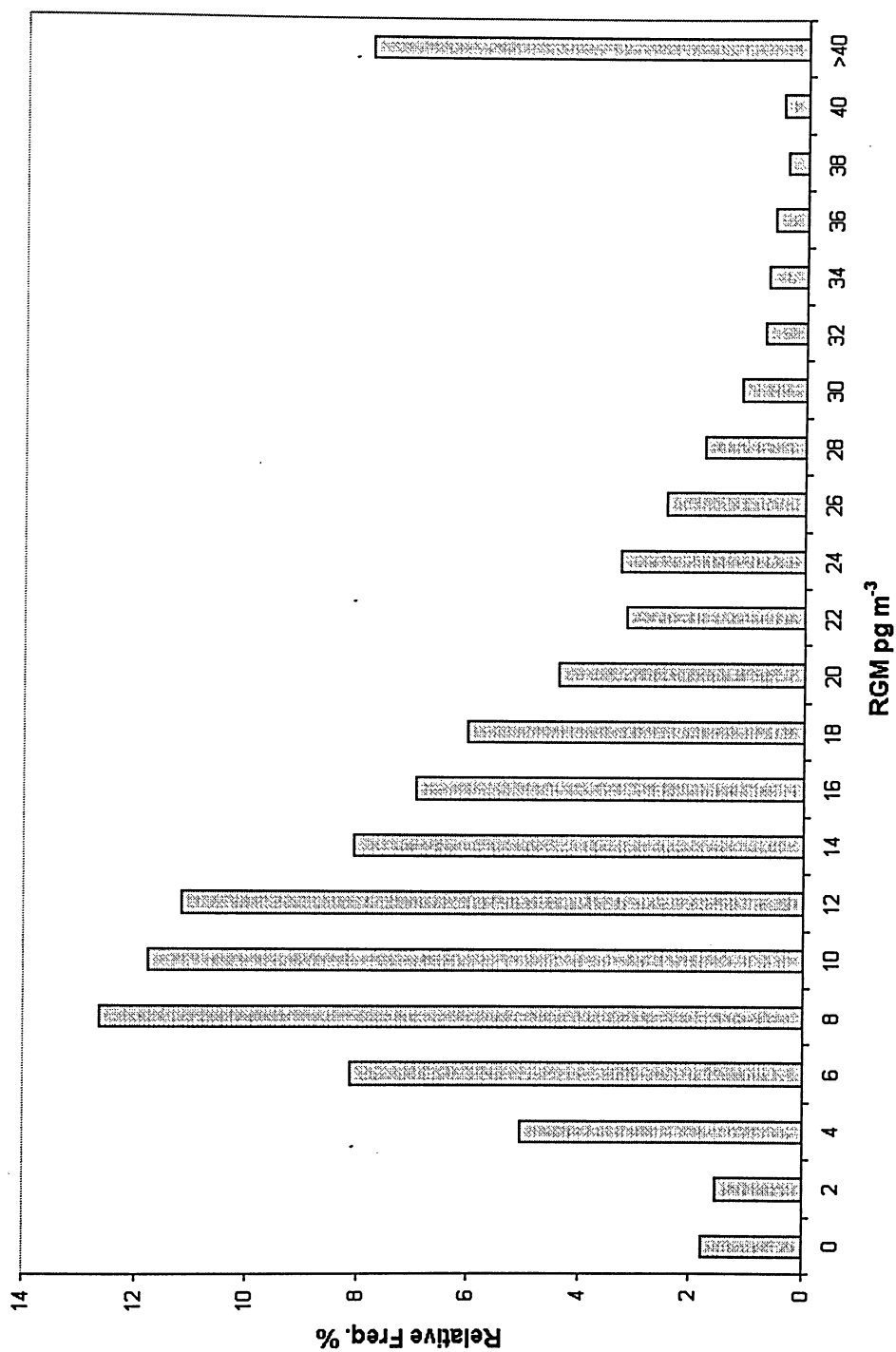


Figure 4-9 Relative frequency distribution of PM<sub>2.5</sub> in downtown Toronto from December 2003 to November 2004



**Figure 4-10 Relative frequency distribution of RGM in downtown Toronto from December 2003 to November 2004**

## **4.4. Effects of meteorological parameters**

Not all of the meteorological parameters are relating the atmospheric mercury species significantly. Ambient air temperature and wind direction/speed, however, are observed to play interesting roles and are discussed in this thesis.

### **4.4.1 Ambient surface air temperature**

Although presented elsewhere (Carpi and Chen, 2002, Poissant, 1995, 2005) that GEM is highly correlated with air temperature, it is not true for our data. Possible reasons for this are different sampling site conditions and different sampling time period. Poissant carried the experiment in rural area where the GEM is mainly came from soil and less affect by anthropogenic sources. Temperature change or solar radiation can enhance the emission in this case. Carpi and Chen (2002) did the experiment from October 20 to November 3. However, only 2 weeks data from their study may not represent the whole year status of atmospheric mercury concentration distribution.

RGM is highly reactive and has short resident time in the atmosphere. Hence the relationship between RGM and air temperature is not obvious and less discussed. No obvious correlation between the temperature and RGM concentration in our study.



Figure 4-11 and Figure 4-12 show the time series of  $PM_{<2.5}$  concentrations and surface air temperatures (daily averages) from our study. A negative correlation between the concentration of  $PM_{<2.5}$  and the surface air temperature were observed when the temperature is below 5 °C during the period of January 2004 to the end of April 2004 (Figure 4-11), while a positive correlation between the concentration of  $PM_{<2.5}$  and the surface air temperature were appeared after May 2004 (Figure 4-12) when the ambient air surface temperatures are normally higher than 10 °C. This can be explained when the formation of PM in urban area is governed by the physical adsorption equilibrium of  $Hg^0$  and  $Hg(II)$  between gas and particle phases: the lower the temperature, the higher the  $[Hg]_p$  will be (Sakata and Marumoto, 2002). Mercury condenses to the surface of the existing particles in the atmosphere when the air temperature drops, leading to the increase in the concentration of  $PM_{<2.5}$ . After May 10, 2004, when the surface air temperatures exceeded 10 °C, a positive correlation was observed in our study (Figure 4-12). Because of the lack of the local particulate data, it is hard to estimate the air temperature effect on the distribution of ambient air particles. It was demonstrated, however, that both situations (positive and negative correlation between ambient particulate concentration and temperature) existed during the period of 1993–1999 in the Czech Republic (Branis, 2003). It was further confirmed that while in the winter the correlation between ambient total suspended particulates (TSP) and temperature was negative, in summer the correlation between the two variables was positive (Branis, 2003). It is possible that, with the more fine particles suspending in the ambient air during warm seasons, more  $PM_{<2.5}$  would be formed by physical adsorption. The positive correlation thus appears in such situations.

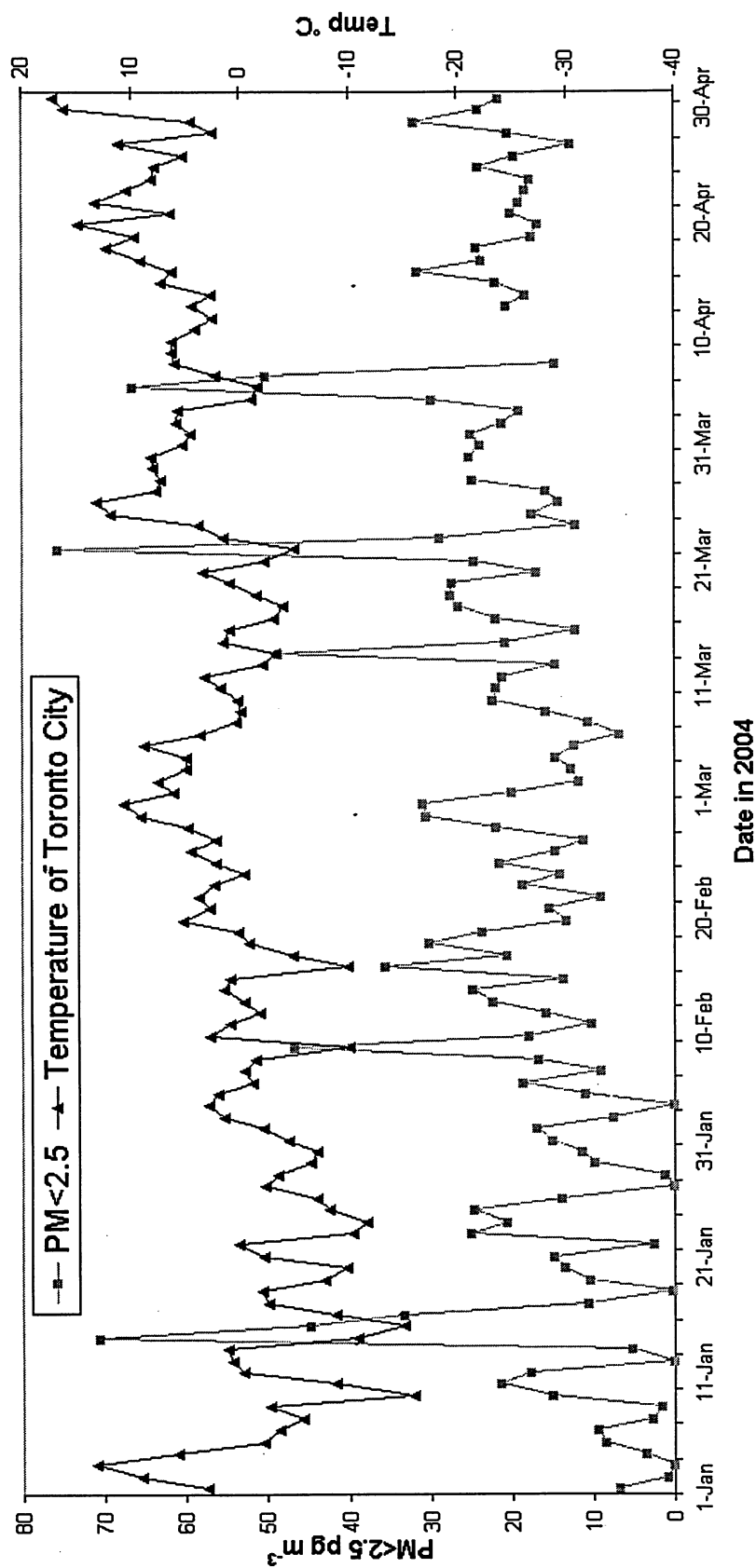


Figure 4-11 Negative correlation trend of PM<sub><2.5</sub> and ambient air temperature (<5 °C) from December 2003 to April 2004

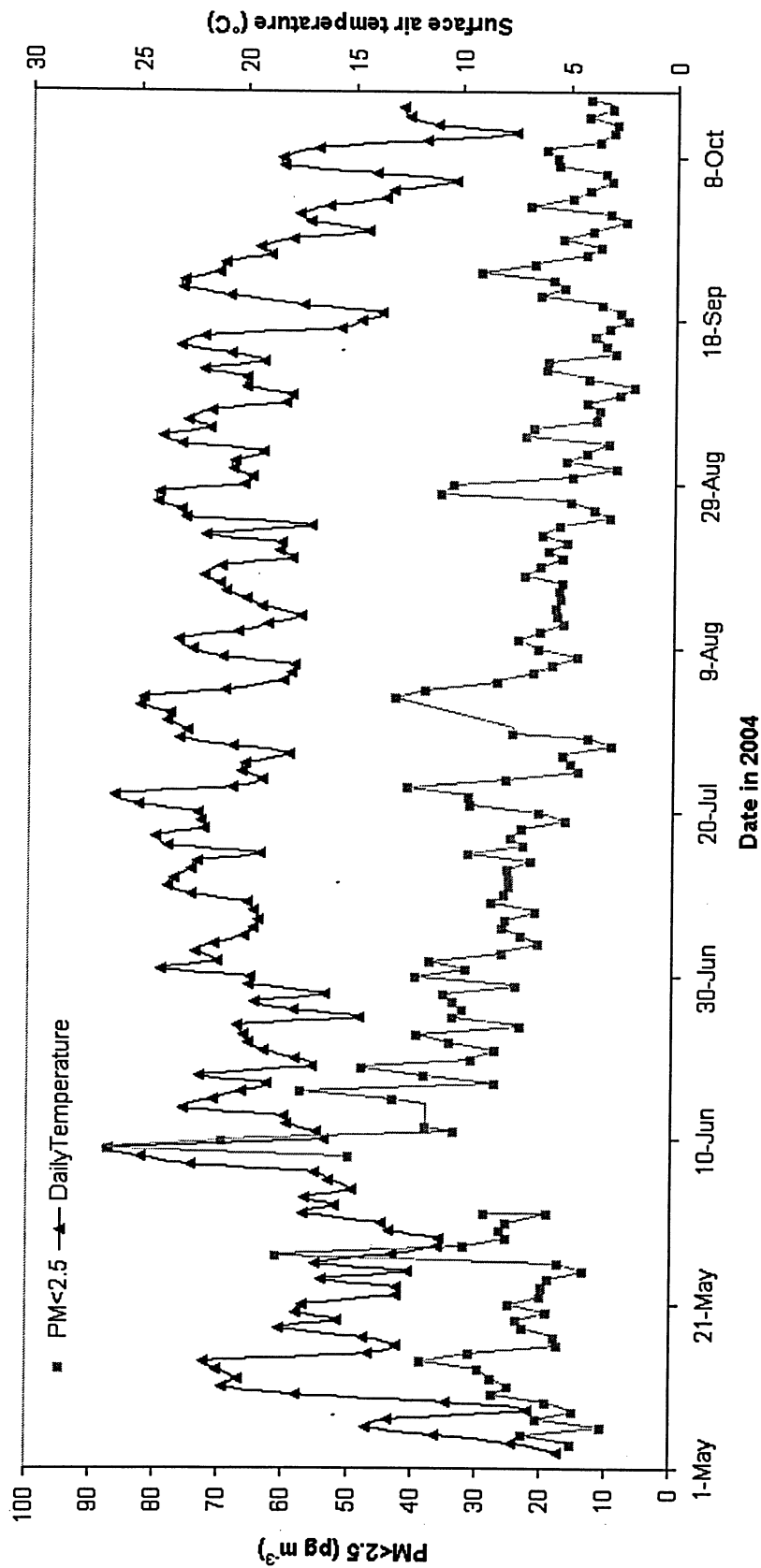


Figure 4-12 Positive correlation trend of PM<sub><2.5</sub> and ambient air temperature (>10 °C) from May 2004 to October 2004

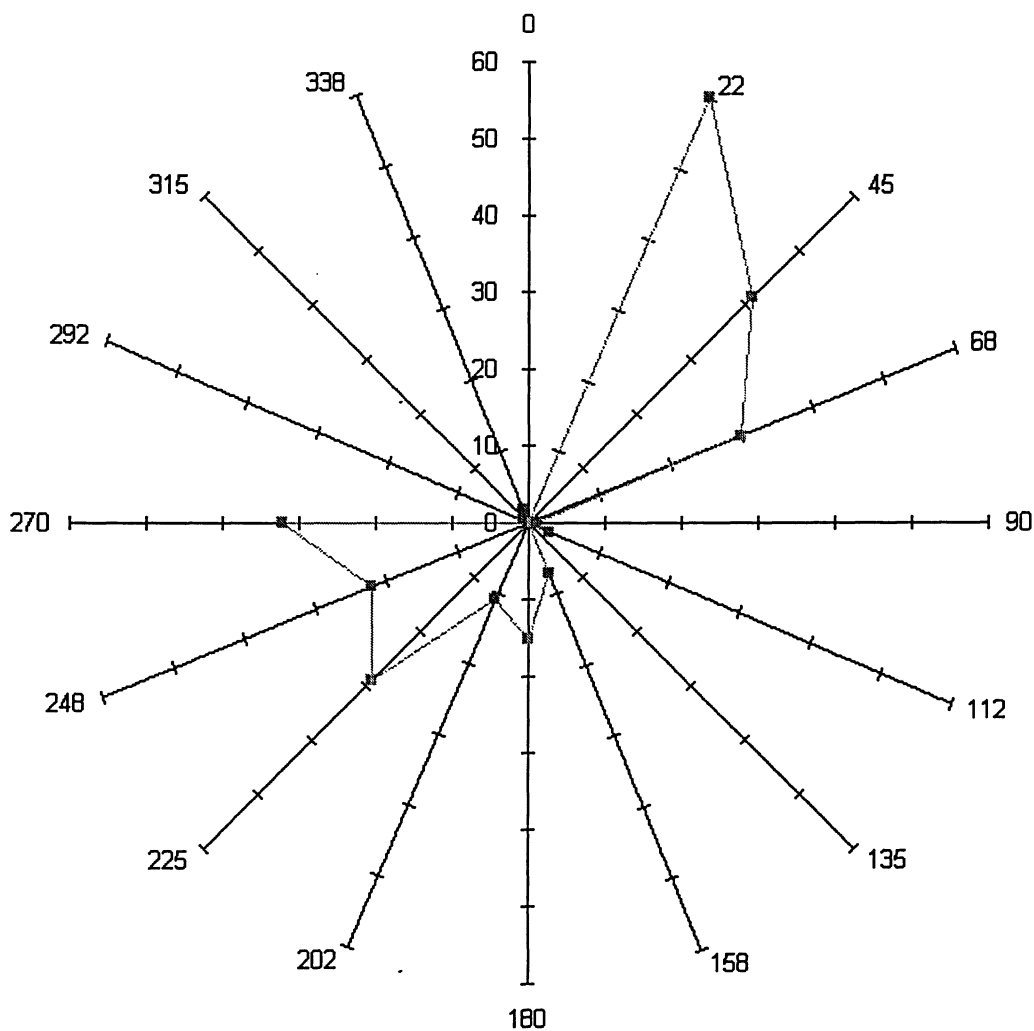
#### **4.4.2 Relative humidity**

Relative humidity is supposed to affect the RGM more than other two species because of its high solubility. Both Poissant and coworkers (2005) and Nacht et al. (2004) reported the anti-correlation between RGM and relative humidity at about  $R^2 = 0.60$ . Our data didn't give obvious indication on how the relative humidity would affect the distribution of any mercury species.

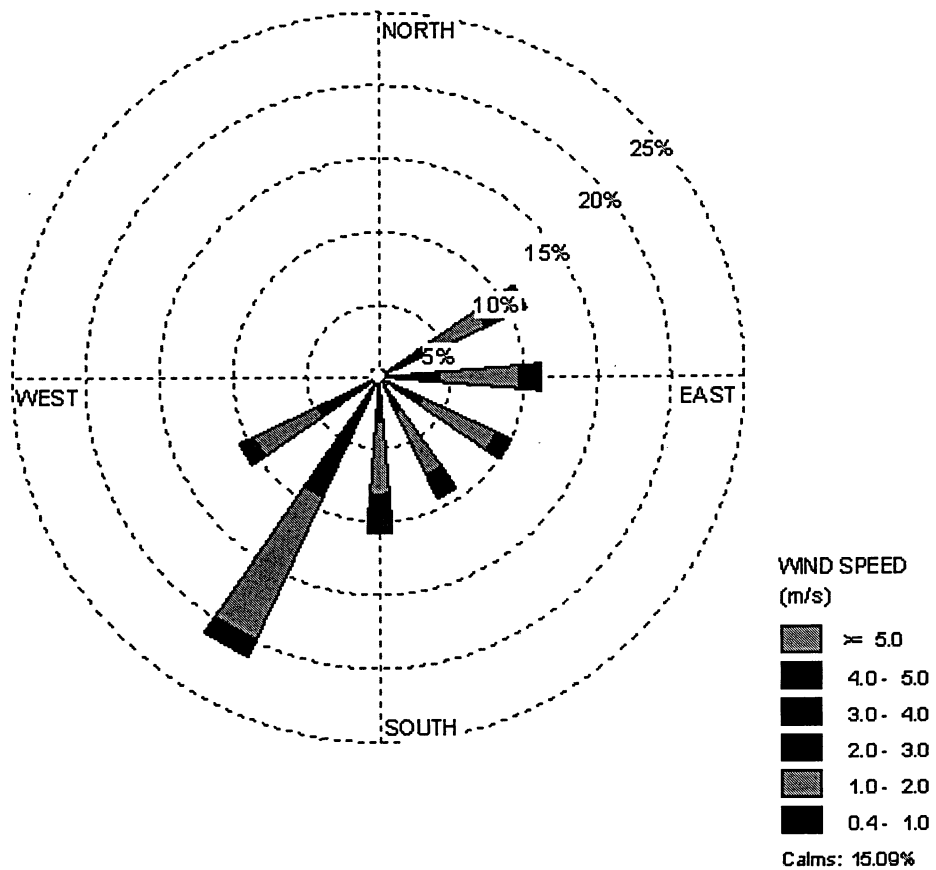
#### **4.4.3 Wind direction and wind speed**

Windrose was constructed by sorting all the wind direction data in 12 sectors, such that the wind frequency was represented to each sector. The wind speeds less than  $0.4 \text{ km h}^{-1}$  are considered calm condition. Dependence of mercury species concentration on wind direction was constructed by averaging the mercury species concentration values that was simultaneously associated with each sorted wind sector. The overall daily windrose pattern (Figure 4-13) shows that northeasterly and southwesterly wind are predominant during the sampling time. The Toronto normal wind direction is Northwest year-round (Environment Canada, 2005). But our sampling site is largely affected by the local buildings, with a 15-story office building to the west and a 30-story resident building to the north in 50-meter's range. The wind would change the directions because of the air moving hydrodynamics. The strongest wind gust came from the southwest (Figure 4-14). Wind dependence of GEM,  $\text{PM}_{<2.5}$  and RGM are displayed in Figure 4-15 to Figure 4-17, respectively. It is clearly demonstrated that the southwesterly winds always carry significantly higher mercury species.

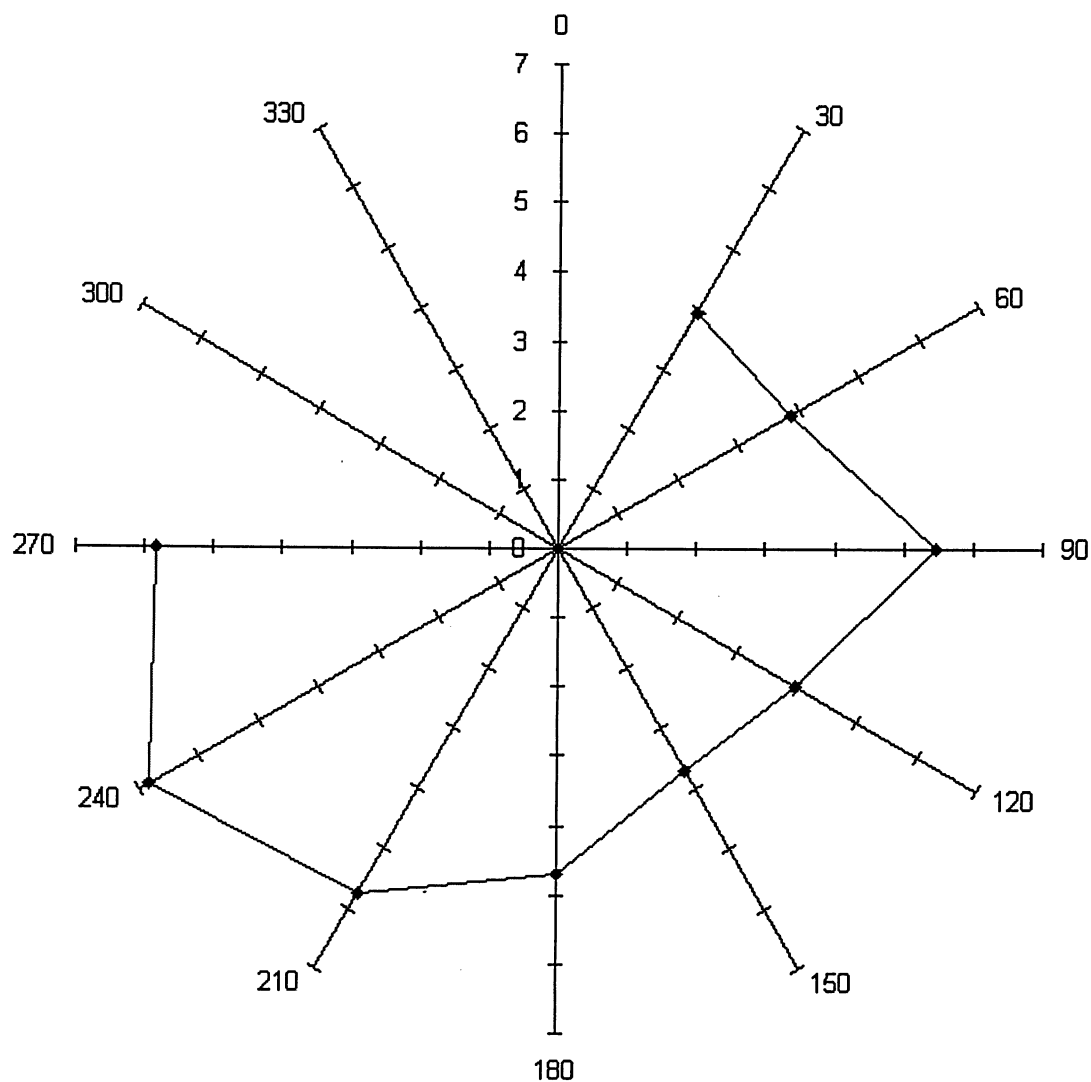
To the southwest of the sampling site, downtown core and a big shopping center lie one block away. It may provide significant mercury sources.



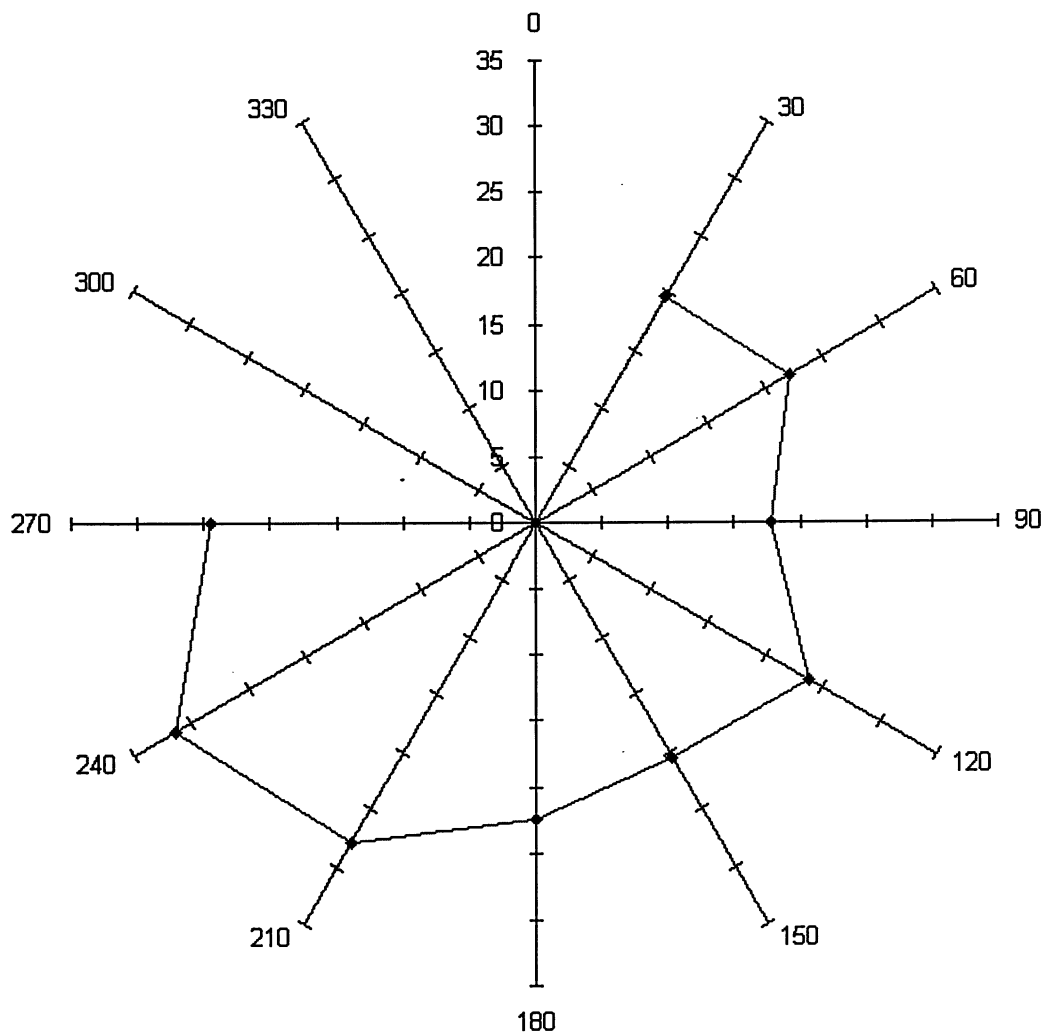
**Figure 4-13 Wind frequent rose for May – December 2004 from Ryerson station**



**Figure 4-14** Wind speed rose for May – December 2004 from Ryerson station

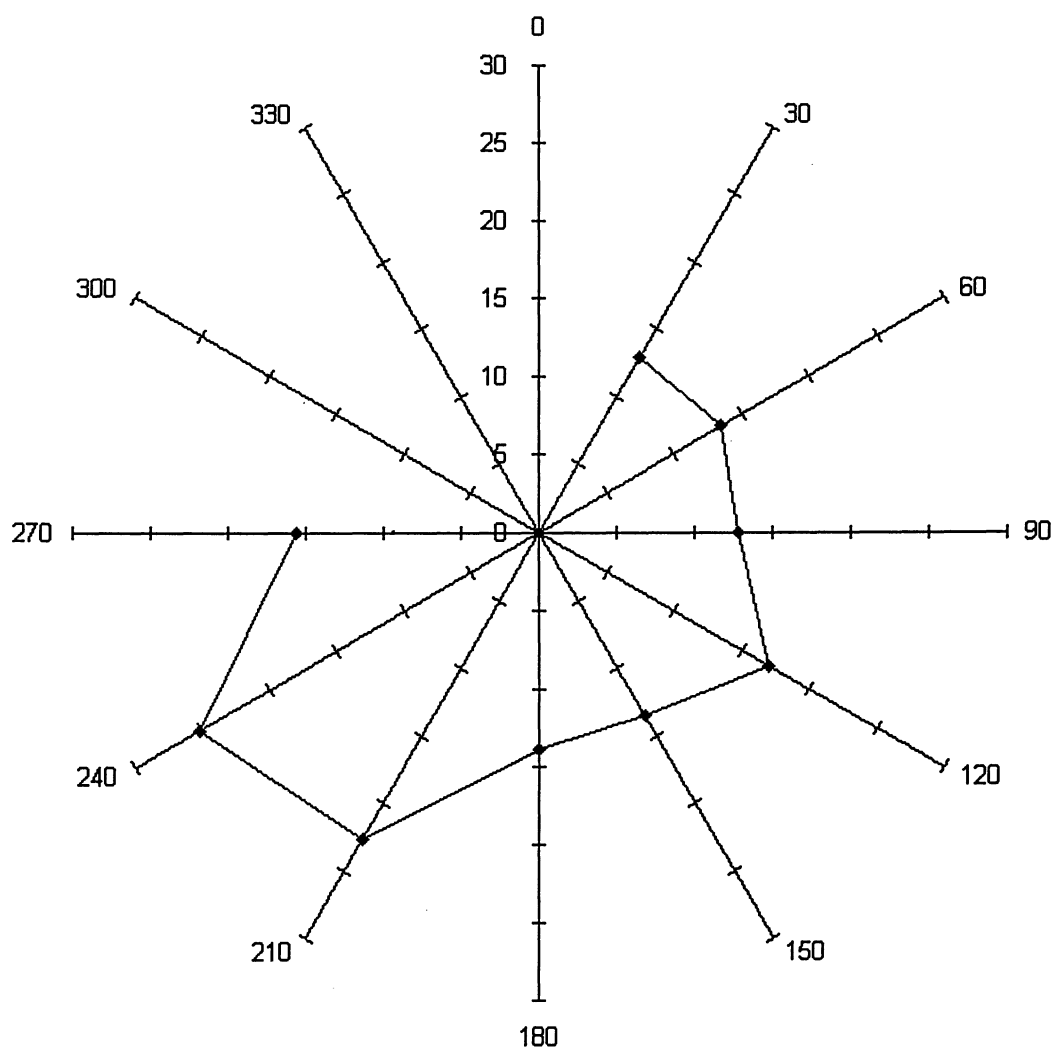


**Figure 4-15 Pollution rose for GEM (ng m<sup>-3</sup>) at Ryerson from May to December 2004**



**Figure 4-16 Pollution rose for PM<sub><2.5</sub> (pg m<sup>-3</sup>) at Ryerson from May to December 2004**





**Figure 4-17 Pollution rose for RGM ( $\text{pg m}^{-3}$ ) at Ryerson from May to December 2004**

#### **4.4.4 Effects of meteorological parameters on hourly average concentrations of mercury species**

The meteorological parameters have weak correlations with the mercury species in terms of hourly average in our study.

By comparing the hourly concentrations of mercury species and meteorological parameters in a flat grassy rural area in southern Quebec, Poissant et al. (2005) found the strong correlation of RGM concentrations with wind speed and solar radiation. An anti-correlation between RGM concentrations and relative humidity was also found in hourly variations analysis. Hourly PM<sub><2.5</sub> concentration exhibited a similar correlations to RGM in their study. There are no more year-long studies on the atmospheric mercury speciation to compare other than the above one. Hence, we only present the diurnal pattern of RGM and PM<sub><2.5</sub> as well as GEM from our sampling site as mentioned in Diurnal variability section. No further discussion would be presented here.

#### **4.5 Anthropogenic effects on the distribution**

Anthropogenic influences on the mercury species were discussed before and are summarized in below:

- (1) The high variability in the concentration of the mercury species is the first clear evidence of the influence of local anthropogenic sources. Frequent spikes and large standard deviation values are the representative characteristics.
- (2) The elevated GEM concentration, compared with CAMNet data and with other rural and remote studies, means the strong link to the urban environment.
- (3) The distinguish diurnal pattern proves the effects of local processes.
- (4) The weak relationship between the meteorological conditions (air temperature, solar radiation, precipitation) and the GEM concentration further confirmed that natural effects contribute less to the pollutant distribution.
- (5) Consistently high concentrations of the mercury species occurring at the same wind direction, indicate the regional anthropogenic sources.

## Chapter 5      Conclusions

### 5.1 Research results summary

Urban environment is an important link in the global mercury cycle. These regional atmospheric mercury releases (highly elevated mercury concentrations from local anthropogenic sources) will provide significant atmospheric mercury loading to the environment.

This study firstly presents the most extensive atmospheric mercury speciation data in urban environment in Canada. The results revealed that the GEM concentration is averaged at  $4.52 \pm 3.13 \text{ ng m}^{-3}$  from December 2003 to November 2004. The mean  $\text{PM}_{<2.5}$  concentration is  $21.51 \pm 16.35 \text{ pg m}^{-3}$  while the RGM is  $14.19 \pm 13.24 \text{ pg m}^{-3}$  during the same sampling period. Elevated GEM concentration and high level of standard deviations demonstrated the effects of human activities.

Large seasonality of GEM,  $\text{PM}_{<2.5}$  and RGM (GEM: 3.34-6.37  $\text{ng m}^{-3}$ ,  $\text{PM}_{<2.5}$ : 6.96-39.46  $\text{pg m}^{-3}$  and RGM: 6.89-25.65  $\text{pg m}^{-3}$ ) were observed in this study. And the seasonal variations in the concentrations of each species are: spring > summer > fall > winter for GEM, spring > fall > summer > winter for  $\text{PM}_{<2.5}$ , fall > spring > summer > winter for RGM. Diurnal

pattern showed that the nighttime concentrations of all three atmospheric species are higher than daytime ones.

Statistical analysis of the data gave a whole picture of the atmospheric mercury distribution as: GEM (98.7%), PM<sub><2.5</sub> (0.5%), PM<sub>>2.5</sub> (0.5%) and RGM (0.3%).

Relative frequency studies show log normal distribution for GEM and RGM concentrations, with 58% measurements of GEM falling between 3-5 ng m<sup>-3</sup> and 59% of RGM between 6-16 pg m<sup>-3</sup>, respectively. PM<sub><2.5</sub> showed the 11-24 ng m<sup>-3</sup> majority (52%) with a Gaussian shape distribution.

Correlation analysis revealed that PM<sub><2.5</sub> and RGM have the highest correlation coefficient followed by the PM<sub><2.5</sub>/GEM pair. RGM and GEM have the weakest relationship based on the analyzed data.

The meteorological parameters play some roles in the distributions of the mercury species. The most obvious effects were the ambient air temperature on the PM<sub><2.5</sub> and the wind direction on the all mercury species. Physical adsorption is believed to control the formation of PM<sub><2.5</sub> onto atmospheric particulate matter. The effect of wind on the mercury distribution suggests local and regional anthropogenic sources.

## 5.2 Future work and recommendation

### (1) Identification of the sources

Local and regional specific anthropogenic sources are urgent to be identified. We are sure there are certain emission sources other than natural processes near our sampling site. Based on our understanding of the urban mercury usage (see literature review part) and possible contamination sources (Dommergue et al., 2002), it is essential to estimate the atmospheric loadings from urban emission sources. The existing mercury-used facilities (lamp, switch etc.) and possible leakage is the threaten scenario in metropolis. Municipal waste incinerating may be considered as public emission source with varied contribution factors because of the chemical composition and the emission control technique. Further more, the mercury concentrations in medical wastes may be 10-15-fold higher than that of municipal waste (Pirrone et al., 1996). Ideally, portable mercury analyzer (sniffer) with high resolution level ( $\sim 0.0001 \text{ mg/m}^3$ ) should be used for local mapping of mercury sources.

The relationship between local  $\text{SO}_2$  data and mercury species, especially GEM was proposed to be another link to the anthropogenic sources (Dommergue et al., 2002). It might suggest the fuel combustion's contribution. Because of the lack of the  $\text{SO}_2$  data, such analysis was not carried out in this study.

Another approach to prove the anthropogenic source is the relationship between Pb and Hg concentrations (Sakata and Marumoto, 2002). This method, nevertheless, need more works and cooperation to finish, thus didn't cover in this thesis. The two ideas, however, remain further consideration.

## (2) Calibration of RGM and PM<sub><2.5</sub> measurements

Calibration of RGM and other methodology developed (PM<sub><2.5</sub> calibration) in our lab should be applied in future studies.

## (3) Further data analysis

More detailed and extended analysis are required to assess the valuable data set. Cross-correlation (Feng et al., 2004b; O'Driscoll et al., 2003) are useful for time series analysis to determine affecting factors and time shifting phenomena such as solar radiation versus GEM. Back trajectories (Han et al., 2005; Han et al., 2004; Poissant et al., 2005) analysis can be used for the transport study. High time resolved parameters, measured at the same time as our mercury speciation data, need to be purchased for further analysis. Considered parameters include ozone concentrations, SO<sub>2</sub> concentrations etc. As most of the studies were done by using Microsoft Excel, more advanced software applications are necessary to perform future analysis. For example, MATLAB is recommended for trend and statistical analysis.

## (4) Flux measurements and other types of monitoring

Atmospheric mercury is only a part of the environmental mercury cycle. The flux (air-surface exchange) is in highly demand (Mason et al., 2005). The mercury speciation in soil, precipitation, and other medias are required for the whole picture of the fate, transport and transformation. Some parts of this consideration are undergoing in our research group for the time being.

Long-term trend analysis and predicting need several year's data. This work, unfortunately, largely depends on the project funding and skilled technician.

Mercury speciation in other urban setting across Canada is another interesting topic. Spatial variability is helpful to the research field. Again, this idea can't be realized without sufficient financial supports. Co-operating with Environment Canada could be a better way to conduct.

#### (5) Modeling and chemistry study

Modeling and chemistry study is the next task to approach. The problem is the extreme complicated chemical reactions involved in the mercury speciation and atmospheric radicals. Lindberg and other researchers (Calvert and Lindberg, 2003; Calvert and Lindberg, 2004) did constructive works, trying to find inherit reasons for MDEs and mercury distribution. With the valuable data from our urban sampling site and the understanding of the mercury chemistry, marvellous achievements could be reached later. But black box method and simple modelling are recommended to start first.



## (6) Recommendation

Tekran speciation unit is a highly automated system, which also need extra care. Ultra low concentration measurements are always deserved to remind along the project. Cross-contamination or improper handling of the instruments will cause severe operating problem and maintain difficulties. Fatal error would lose the data and waste the efforts in the project. Appendix A provides the simple checking instructions on the normal running system. It is considered the start step to develop a complete operation and maintenance protocol.

## **Appendix A     Tekran speciation system check procedure**

This protocol is used to check the instruments (speciation unit and analyzer) on a daily basis to ensure the system is running well. Or take any action if some problems happen.

**Listen**     Under normal situations, the pump and the analyzer is almost noise-free with little comes from pump motor. If the pump or analyzer is racing, which means it can't maintain the flow rate, something must be wrong with the system. In this case, it should be shut down. See below for shutting down procedures.

**Look**     The system is highly auto-ed unless the function keys are not properly pressed. It is easy to check whether the analyzer is running or not from the screen. It will record data to computers every five minutes. One can read the data and judge if the software is functioning. The carrier gas pressure should be checked if the first stage of regulator is bigger than 100 psi and the second stage of it is at 40 psi. If the second stage can't reach 40 psi, the cylinder should be replaced.

**Back up data**     It is important to save data to external floppy disk as backup upon each arrival. Detailed steps for this are provided below.

### **Back up data procedure:**

There are two types of software for collecting data: Window-based (1) and DOS-based (2).

(1), for window-based speciation unit data acquiring program:

1. Minimize (**Not close**) the program (RS232 data capture program) window;
2. Use My computer or window explorer to locate the file location: C:\Tekran/Tekran data/
3. Find and select data files then copy and save them to A: disk (selected file and send to ... A:). The data file is formatted as Rs0405\*\*.dat, where 0405\*\* is the current date.  
There should have one file each day.
4. Release A disk from computer several seconds after copy.
5. Close the explorer window; (If the explorer window is not closed, it will not update the files in the window, which may cause invalid backup data)
6. Maximize the data collecting window. (only this window is open in the computer)
7. Check the data collecting program, the cursor should be flashing at the end of the screen and will have a new line every five minutes. If the current line reflects the current time, it indicates that the program is running well.

(2), for DOS-based data acquiring program:

1. Press Alt + J to Jump into DOS Shell: C:\Tekran>\_
2. Use DOS command to list the data files: Dir. If not in the right folder, use command:  
cd C:\Tekran and then dir

3. Copy each file to A: copy tk040521.tek A: (an example, have to change file name when copy other files: tk040522.tek)
4. Copy all other files to A in the same way, each file each time. There should have one file every 2 days.
5. If asked overwrite the existing one, type Y and enter;
6. **Type “exit” to go back the program from DOS Shell interface. Otherwise, no more data collecting!**
7. In program mode, check the data collecting program, the cursor should be flashing at the end of the screen and will have a new line every five minutes. If the current line reflects the current time, it indicates that the program is running well.
8. In program mode, Alt +Z is used for commands list and instruction. After each use of DOS keys, ESCape key should be used to go back program, or type “exit” from DOS interface.

If the instrument runs well but there is no data collected to the computer, check the computer and may restart the data collecting program as follows:

For (1) speciation unit,

1. Close the current dead program;
2. Find the program: Rs232 data capture program, from the desktop screen and double click it to start.
3. Check the new data line coming out every five minutes.
4. May require to restart the computer and do the steps

For (2) analyzer only:

1. Press Alt+X and reply Yes for closing the current program and wait the computer switch to window;
2. Restart the computer, and the program will automatically restart itself, to DOS mode.
3. Check the new data line coming out every five minutes.

### **Shut down procedure:**

If the system is not running well, for example, pump racing very hard, data number is meaningless, physical broken, other emergencies like blackout, the instruments should be shut down as follows:

1. Press 2 times of ESCape key quickly (like mouse's double click) on the analyzer control panel beside the screen, the system then transfers to idle, the pump moves in zero flushing (7L/min) mode. Then the power switches on analyzer and pump can be turned off.
2. Leave the computers alone.
3. Leave other control stuffs alone.

If blackout, turn off the power switches on analyzers and pump. Don't restart the instruments when powers back as calibration and checks should be applied before start for actual measurements.

**Notes:**

1. Three instruments on the bench in the lab while the other 2 lie on the rooftop. No need to go to rooftop for check during this week.
2. The 3 instruments in the lab are (from left to right): Pump for speciation, analyzer associated with the speciation, another analyzer (stand alone).
3. The laptop computer is used for speciation unit data collecting, while the big desktop computer is used for the analyzer alone.

## **Appendix B      Instruction for Excel formula: Transfer 1min weather station file to 5min and hourly data**

### **Introduction:**

This formula is used for transfer our weather station data (1 set /min) to 5min data set and hourly data on specific day file. The source file is daily saved weather station .cvs or .txt file, for the .txt file, it should be opened and made to excel file first. Output file is excel worksheet file in proper folder with original, 5min data and 1hr data at different sheets.

### **Steps:**

1. Open formula.
2. Open cvs (or Excel) source file, check if it is fully saved by the computer. (some points may be missing): Total rows:1443.

2.1. How to spot the missing points (1/2 regression process):      The row number and the time (increases in 1 min step) column should be match, Say, every five minute data 10:05 or 10:15 should always match the row number that ends with 9 (19, 29, 39..).

Move the mouse cursor to the middle ( $\sim 1/2$ ) of the scrolling zone (right hand side), check the row number and time: if any time end with 5 goes with the row number end with 9,

**YES**, then the missing point must be at the second half of the data, go to 3/4 of the data length, (1/2 of current position to the end) to find;  
**NO**, missing point lies in the first half area, go to 1/4 of the scrolling area. Thus continue to do to find the specific row which is missing.

(Here, 1/2, 1/4 position is somewhere at estimate, not an exact number.)

2.2. Insert a blank line for the missing point, type in the total rain number which should be the same as previous one.

2.3. Save the change to the source file !! (careful at the step, not suppose to change anything in source file, as I only save this to the cvs file and leave the txt file untouched.)

3. Select all (Ctrl+A) of the source file data, copy them (Ctrl +C).

4. Go to formula's original sheet, press on A1 cell using mouse left click, paste whole data here (Ctrl +V).

5. Change A1's format to dd/mm/yyyy to get correct output (check in "5min data" and "1hr data" sheet) if needed (most of the time, depending on the format when it is saved).

6. Check the Rain column data, make up missing point if needed.

6.1. Negative rain number may appear if not properly did in step 2.2, because the output 5min data is rain instead of total rain in original sheet. When a new blank line was inserted because of data missing, the value in "Total Rain" cell is 0, thus make negative after possible subtract if the new line happened to be the cut-off 5min point.

6.2. If not go back to step 2.2, enter 0 at the negative value cell in 5min sheet now. It would be fine for the hourly data then. Sum function is used for the column



“Rain” in the hourly sheet.

7. Check the data for validation if wanted.

8. **Save As** the new file according to the date involved (e.g. 20040902.exl in output folder).

9. Close the output and source excel file.

## Appendix C      Sample of calculation and data analysis

### 1. Unit convert

$$1 \text{ ng} = 10^{-9} \text{ g}$$

$$1 \text{ pg} = 10^{-12} \text{ g} = 10^{-3} \text{ ng}$$

### 2. Constitution of the atmospheric mercury

$$[\text{PM}<2.5] = [\text{PM}>2.5]$$

$$[\text{GEM}] = 4.52 \text{ ng m}^{-3} = 4.52 \times 10^3 \text{ pg m}^{-3}$$

$$[\text{PM}<2.5] = 21.51 \text{ pg m}^{-3}$$

$$[\text{RGM}] = 14.19 \text{ pg m}^{-3}$$

$$\text{Total} = [\text{GEM}] + [\text{PM}<2.5] + [\text{PM}>2.5] + [\text{RGM}]$$

$$= 4577.21 \text{ pg m}^{-3}$$

$$[\text{GEM}] / \text{Total} = 98.7\%$$

$$[\text{PM}<2.5] / \text{Total} = 0.5\%$$

$$[\text{PM}>2.5] / \text{Total} = 0.5\%$$

$$[\text{RGM}] / \text{Total} = 0.3\%$$

### 3. Wind rose and pollution rose

- (1). Align the wind direction data and speciation data to the same time period;
- (2). Select all data columns and sort (Excel function) by wind direction;

(3). Average the speciation data that fall in each wind direction range (12 even ranges in 0-360°, e.g., 15°-45° as 30° sector)

**Appendix Table 1 Data for pollution rose**

<b>Wind Direction Range (°)</b>	<b>Wind Direction (°)</b>	<b>Average GEM (ng m<sup>-3</sup>)</b>
345-15	0	0
15-45	30	3.926
45-75	60	3.851
75-105	90	5.440
105-135	120	3.973
135-165	150	3.672
165-195	180	4.688
195-225	210	5.728
225-255	240	6.803
255-285	270	5.81311
285-315	300	0
315-345	330	0

(4). Draw a chart using Radar type in Excel with the wind direction as X and speciation data as Y.

#### 4. Data analysis

- (1). Time series      Combine date and time to a new column. Format this column to mm/dd/yyyy hh:mm. Select this column and speciation data for a chart using XY(Scatter) type. Add trend line and modify the appearance as needed.
- (2). Diel pattern      Sort data by time. Average data regarding to each hour. Display the diel cycle in Excel chart.
- (3). Statistical analysis      Generate statistical summary using Excel functions, such as Average, Sum, Stdev, etc., by choosing proper data range.
- (4). Correlation and regression      Perform proper analysis by selecting Data Analysis.. function in Tools in Excel function bar. It requires to install Add-Ins packages from Microsoft Office installation disk.

Appendix Table 2    Summary report of Regression data analysis on the correlation of RGM and PM<2.5

Regression Statistics	
Multiple R	0.562248
R Square	0.316123
Adjusted R Square	0.315937
Standard Error	13.56147
Observations	3684

ANOVA				
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i> <i>Significance F</i>
Regression	1	313022.6	313022.6	1702.01    3.7E-306
Residual	3682	677169.5	183.9135	
Total	3683	990192.1		

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 99.0%</i>	<i>Upper 99.0%</i>
Intercept	11.50187	0.329645	34.89169	1.1E-230	10.85556	12.14817	10.65232	12.35141
X Variable 1	0.706016	0.017113	41.25542	3.7E-306	0.672464	0.739568	0.661912	0.75012

## **Appendix D      Error analysis and Calibration data**

For instrumental measurements, the errors in experimental Data lie in two parts: random errors and systematic errors. In general, the random error in a measurement is reflected by its precision. As we monitored the concentration of the atmospheric mercury species, it is impossible to have replicate ambient air data to judge the precision. This can be achieved by evaluating the calibration data. Hence systematic errors are mainly discussed in this part.

There are three types of systematic errors: (1) Instrument errors caused by imperfections in measuring devices and instabilities in their power supplies. (2) Method errors arise from nonideal chemical or physical behavior of analytical systems. (3) Personal errors result from the carelessness, inattention, or personal limitations of the experimenter.

All measuring device, especially electronic instruments, are sources of systematic errors. While errors from electronic field (e.g., temperature changes cause the voltage baseline, current board stabilizer problems) were relied on the improvement of technology, calibration is widely used to eliminate most instrument errors. Our internal calibrations resulted <2% difference between the two cartridges and the manual calibrations revealed <5% difference of actual concentration and output concentration, which are quite acceptable for such kind of atmospheric monitoring study.

**Appendix Table 3    Mercury analyzer calibration summary**

<b>Calibration Type</b>	<b>Gold cartridge and status</b>	<b>Area</b>	<b>Conc. ng m<sup>-3</sup></b>	<b>Response Factor</b>	<b>Difference A and B</b>
<b>Auto Calibration</b>	Zero A	5613	0	/	/
	Zero B	4286	0	/	
	Span A	638674	29.967	4220000	1.6%
	Span B	626133	29.967	4150000	
<b>Manual Calibration</b>	Zero A	2364	0	/	/
	Zero B	0	0	/	
	Span A	464536	20.52	4500000	2.4%
	Span B	450756	20.52	4390000	

**Appendix Table 4    Mercury analyzer manual calibration summary**

<b>Gold cartridge</b>	<b>Actual Conc. ng m<sup>-3</sup></b>	<b>Output Conc. ng m<sup>-3</sup></b>	<b>Difference %</b>
<b>Zero air to A</b>	0	0	0
<b>Zero air to B</b>	0	0	0
<b>A1 (first time)</b>	20.52	19.67	-4.1
<b>B1 (first time)</b>	20.52	20.99	+2.3
<b>A2 (second time)</b>	20.52	20.36	-0.8
<b>B2 (second time)</b>	20.52	20.45	-0.3
<b>A3 (Third time)</b>	20.52	20.56	+0.2
<b>B3 (second time)</b>	20.52	20.30	-1.1

**Appendix Table 5 Mercury analyzer internal calibration example**

Date	Time	Typ	C	Stat	AdTim	Vol	Bl	BlDev	MaxV	Area	ng/m3
04/03/01	23:40:49	CLN	A	NP	0	0	0	0.136	0.041	0	0
04/03/01	23:44:23	CLN	B	OK	1	214	3.63	0.136	0.039	0.137	2916
04/03/01	23:47:09	ZERO	A	OK	1	300	4.99	0.136	0.038	0.137	1770
04/03/01	23:52:09	ZERO	B	OK	1	300	4.99	0.136	0.037	0.137	1810
04/03/01	23:57:09	SPAN	A	OK	1	300	4.99	0.136	0.054	0.507	1275506
04/03/02	0:02:09	SPAN	B	OK	1	300	4.99	0.135	0.04	0.521	1276917

**CALIBRATION:**

S/N: 0147

04-03-02

**ZERO: A**

Sample: 300 sec      BlArea: 1770  
Volume: 4.99 l      BlCorr: 354/l  
Baseline: 0.136 V      PkMax: 0.137 V  
Bl StDev: .04 mv      PkWid: 3.5 sec  
Start: 04-03-01      23:47:09

**ZERO: B**

Sample: 300 sec      BlArea: 1810  
Volume: 4.99 l      BlCorr: 362/l  
Baseline: 0.136 V      PkMax: 0.137 V  
Bl StDev: .04 mv      PkWid: 3.5 sec  
Start: 04-03-01      23:52:09

**SPAN: A SOURCE**

Sample: 300 sec      Area: 1275506  
Volume: 4.99 l      AdjAr: 1273736  
HgAmt: 153.6pg      RespFctr 8292549



Baseline:	0.136 V	PkMax:	0.507 V
Bl StDev:	.05 mv	PkWid:	18.7 sec
Start:	04-03-01		23:57:09

SPAN: B SOURCE

Sample:	300 sec	Area:	1276917
Volume:	4.99 l	AdjAr:	1275107
HgAmt:	153.6pg	RespFctr	8301477
Baseline:	0.135 V	PkMax:	0.521 V
Bl StDev:	.04 mv	PkWid:	19.2 sec
Start:	04-03-02		00:02:09

---

Method errors are difficult to identify and correct. Method inter-comparison is suggested to use for verification of certain method. In our case, there are more to conduct as discussed in the future work part in Chapter 5. The confidences are given by several indications in our study:

1. Low and Zero blanks in calibration.
2. The concentration value decreased to normal (base value) after major spikes.
3. Results from other researcher revealed the comparable range.

Personal judgments are less in our study thus less personal errors were introduced. Digital readouts helped the elimination of number bias.

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