EFFECT OF SOURCES AND METEOROLOGICAL CONDITIONS ON THE CONCENTRATION AND DISTRIBUTION OF
GASEOUS ELEMENTAL MERCURY IN THE URBAN ATMOSPHERE

by

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ABSTRACT

EFFECT OF SOURCES, AND METEOROLOGICAL CONDITIONS ON THE CONCENTRATION AND DISTRIBUTION OF
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Atmospheric gaseous elemental mercury (GEM) and meteorological parameters were monitored at two sites in downtown Toronto, Canada from Oct. 2015 to Oct. 2016 using Tekran 2537A mercury vapour analyzers. The average concentration was found to be $1.78 \pm 0.89 \text{ ng/m}^3$ for Kerr Hall North (KHN) and $1.46 \pm 0.54 \text{ ng/m}^3$ for Jorgenson Hall (JOR) site. Analysis of the data reveals that sporadic events of high mercury concentration are related to local sources.

Comparing this data set with that collected in 2004 revealed that the average atmospheric GEM concentration in downtown Toronto dropped from 4.5 ng/m^3 to 1.78 ng/m^3 . Decreases in GEM were also observed over the same period in rural areas as measured by CAMNet. The decrease might be a result of policy change, as three key national and provincial environmental policies have been enacted since 2004.

The data collected in Toronto suggest GEM concentration and distribution are influenced by local and regional sources, meteorological conditions, and changes in environmental policy.

Keywords: gaseous elemental mercury, Hg^0 , urban pollution, air quality, troposphere

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TABLE OF CONTENTS

ABSTRACT.....	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES	vii
LIST OF FIGURES.....	viii
LIST OF ABBREVIATIONS	ix
1.0 INTRODUCTION	1
1.1 THE RESEARCH PROBLEM	1
1.2 MERCURY: PHYSICAL AND CHEMICAL PROPERTIES	2
1.3 SOURCES OF MERCURY IN THE ENVIRONMENT	3
1.3.1 <i>Natural Sources</i>	4
1.3.2 <i>Anthropogenic Sources</i>	5
1.3.3 <i>Legacy sources / reemissions</i>	6
1.4 MERCURY SPECIATION IN THE ATMOSPHERE	6
1.5 TRANSPORT	7
1.6 TRANSFORMATIONS AND REMOVAL MECHANISMS	9
1.7 HEALTH EFFECTS	10
1.8 GLOBAL MERCURY EMISSION AND TRENDS.....	12
1.9 CANADA’S ROLE IN MERCURY RESEARCH AND EMISSION CONTROL.....	13
1.9.1 <i>Monitoring networks</i>	13
1.9.2 <i>Latest Canadian emissions estimates</i>	13
1.9.3 <i>Health Canada guidelines for mercury exposure</i>	14
1.9.3.1 Canadian Environmental Protection Act	15
1.9.3.2 Mercury legislation in Ontario and Canada	15
1.9.3.3 Products Containing Mercury Regulations	16
1.10 TRENDS IN ATMOSPHERIC MERCURY FROM NORTH AMERICAN CITIES.....	16
2.0 MATERIALS AND METHODS	19
2.1 SITE AND EXPERIMENTAL SETUP.....	19
2.2 INSTRUMENTATION	21
2.2.1 <i>Mercury Vapour Analyzers</i>	21
2.2.2 <i>Cleaning and storage of PTFE components</i>	21
2.2.3 <i>Line setup & generation of zero air</i>	22
2.2.4 <i>Ambient line setup</i>	22
2.2.5 <i>Calibration</i>	23
2.2.6 <i>Validation</i>	23
2.2.7 <i>Tekran model 2537A maintenance and operation</i>	24
2.3 WEATHER STATION SETUP.....	25
2.4 MATCHING THE ANALYZERS.....	25

2.5	DATA HANDLING	27
2.5.1	<i>Mercury data</i>	27
2.5.2	<i>Weather station data</i>	28
2.5.3	<i>Combining Hg & weather data</i>	28
2.6	POST PROCESSING & QUALITY CONTROL	28
2.7	DATA TREATMENT AND ANALYSIS	29
2.7.1	<i>OpenAir package for R</i>	29
2.7.2	<i>Data from CAMNet</i>	30
2.8	STATISTICAL ANALYSIS	31
3.0	RESULTS AND DISCUSSION.....	33
3.1	TEMPORAL TRENDS	33
3.1.1	<i>Annual Trends</i>	33
3.1.2	<i>Seasonal Trends</i>	36
3.1.3	<i>Weekly Trend</i>	37
3.1.4	<i>Diurnal Trend</i>	38
3.2	SPATIAL DISTRIBUTION	39
3.2.1	<i>Annual - mean of GEM by site</i>	39
3.2.2	<i>Annual – weighted mean of GEM by site</i>	40
3.2.3	<i>Regional Source Attribution</i>	41
3.3	COMPARISON OF AVERAGE GEM VALUES AT KHN WITH 2004	43
3.4	PEAK EVENT ANALYSIS	45
3.4.1	<i>Identifying peak events using maxima polar plots</i>	49
3.4.2	<i>Diurnal maxima and weighted average GEM by site and daylight</i>	50
3.4.3	<i>Weighted mean GEM by site and daylight</i>	51
3.5	COMPARISON OF GEM AT URBAN VS. RURAL/REMOTE SITES AND OF CURRENT & HISTORICAL DATA COLLECTED IN CANADA	52
3.6	EFFECT OF AURA BUILDING	53
4.0	CONCLUSION	56
APPENDIX A		57
	<i>Example of Tekran 2537A analyzer output</i>	57
APPENDIX B		58
	<i>Data aggregation and quality control</i>	58
	<i>Cartridge test for agreeability</i>	61
	<i>Peak analysis and correlation tables</i>	62
APPENDIX C		65
i)	<i>Shapiro-Wilk</i>	65
ii)	<i>Quantile-Quantile plots</i>	65
iii)	<i>Kolmogorov-Smirnov test</i>	66
iv)	<i>Kruskal-Wallis & Mann-Whitney U tests</i>	67
REFERENCES		68

LIST OF TABLES

TABLE 1: PROPERTIES OF ELEMENTAL MERCURY	2
TABLE 2: POTENTIAL GAS-PHASE MERCURY REACTIONS.....	9
TABLE 3: HEALTH CANADA GUIDELINES FOR MERCURY EXPOSURE	14
TABLE 4: NOTEWORTHY MERCURY LEGISLATION IN ONTARIO AND CANADA.....	15
TABLE 5: SUMMARY OF GEM CONCENTRATIONS IN URBAN AIR FROM CITIES IN THE NORTHERN HEMISPHERE.....	17
TABLE 6: SITE DETAILS	20
TABLE 7: MODIFIED RESEARCH DATA MANAGEMENT QUALITY (RDMQ) FOR GEM	29
TABLE 8: SUMMARY OF STATISTICS FOR GEM (IN NG/M ³) AT THE EXPERIMENT SITES.	35
TABLE 9: SPEARMAN’S RANK CORRELATION FOR KERR HALL	47
TABLE 10: SPEARMAN’S RANK CORRELATION FOR JORGENSON HALL	48

LIST OF FIGURES

FIGURE 1: BIOGEOCHEMICAL CYCLING OF MERCURY IN THE ENVIRONMENT	4
FIGURE 2: MAP OF SAMPLING SITES IN DOWNTOWN TORONTO	19
FIGURE 3: SCHEMATIC DIAGRAM FOR PRODUCING ZERO AIR FROM THE COMPRESSED AIR IN THE LAB	22
FIGURE 4: PAIRED-MACHINE SAMPLING FOR AN OVERNIGHT PERIOD IN 2015 BEFORE SAMPLING CAMPAIGN.	26
FIGURE 5: PAIRED-MACHINE SAMPLING FOR AN OVERNIGHT PERIOD IN 2016 AFTER SAMPLING CAMPAIGN.	26
FIGURE 6: WORKFLOW FOR COLLECTING, ORGANIZING, COMBINING AND ANALYZING GEM AND WEATHER DATA	27
FIGURE 7: MAP OF CANADA DEPICTING CAMNET (CANADIAN ATMOSPHERIC MERCURY MEASUREMENT NETWORK) AND MDN (MERCURY DEPOSITION NETWORK).	30
FIGURE 8: 1 HOUR AVERAGE TIME SERIES FOR (A) KHN AND (B) JOR FROM OCT 2015 TO OCT 2016	34
FIGURE 9: TIME VARIATION OF GEM OVER A 12 MONTH PERIOD FOR KERR HALL NORTH AND JORGENSON HALL. (A) IS THE VARIATION PER HOUR OVER THE WEEK; (B) MEAN HOURLY GEM; AND (C) MEAN MONTHLY GEM.	35
FIGURE 10: BOXPLOT OF GEM BY SITE AND SEASON FOR SPRING (MAM), SUMMER (JJA), AUTUMN (SON), AND WINTER (DJF) WHERE THE THREE LETTERS REPRESENT THE NAMES OF THREE CONSECUTIVE MONTHS WHICH CONSTITUTE A SEASON.	37
FIGURE 11: BOXPLOT OF GEM BY SITE AND DAY OF THE WEEK. DATA COLLECTION BEGAN IN OCTOBER 2015 AND FINISHED IN SEPTEMBER 2016.	38
FIGURE 12: POLAR PLOT OF THE MEAN GEM CONCENTRATION BY WIND DIRECTION, SPEED AND SITE FOR 2015/2016. CELLS ARE SEPARATED INTO 1 M/S WIND SPEED INCREMENTS AND 10° WIND DIRECTION INCREMENTS. WIND SPEED < 0.5 M/S ARE NOT SHOWN. ARITHMETIC MEAN IS REPRESENTED BY CELL COLOUR.	40
FIGURE 13: ANNUAL WEIGHTED MEAN PLOT FOR BOTH SITES	41
FIGURE 14: REGIONAL POLLUTANTS TO THE RECEPTOR SITES IN 2016 AND 2004.	42
FIGURE 15: WIND ROSE PLOT SHOWING THE FREQUENCY OF WIND DIRECTION AND SPEED AT THE KHN SITE OVER BOTH OF THE SAMPLING CAMPAIGNS.	44
FIGURE 16: ANNUAL WEIGHTED MEAN OF GEM AT KHN FOR 2004 AND 2015/16	43
FIGURE 17: PROBABILITY DISTRIBUTION OF GEM MEASUREMENTS MADE AT KHN AND JOR IN 2015/2016 COPLOTTED WITH GAUSSIAN CURVES	45
FIGURE 18: PLOT OF GEM MAXIMA FOR JOR AND KHN FROM 2015/2016	50
FIGURE 19: GEM MAXIMA FOR KHN AND JOR SEPARATED BY DAY (6 AM - 6 PM) AND NIGHT (6 PM - 6 AM)	51
FIGURE 20: GEM WEIGHTED MEAN SEPARATED BY DAY (6 AM - 6 PM) AND NIGHT (6 PM - 6 AM)	51
FIGURE 21: BOXPLOT OF ANNUAL GEM COLLECTED FROM A REMOTE (ALERT, NUNAVUT) AND RURAL (EGBERT, ONTARIO) SITES FOR 2004 AND 2010 AND AN URBAN (KHN) SITE FOR 2004 AND 2015/2016.	52
FIGURE 22: HISTOGRAMS FOR GEM MEASURED AT KHN FROM THE 265-295° DIRECTION FROM A) 2004 AND B) 2015/2016; C) BOXPLOT OF GEM MEASUREMENTS COMPARING KHN 2004 TO 2015/2016 FOR WIND DIRECTION 265-295°	55

LIST OF ABBREVIATIONS

AMNet	Atmospheric Mercury Network
ASGM	artisanal and small-scale gold mining
CAMNet	Canadian Atmospheric Mercury Measurement Network
CAPMoN	Canadian Air and Precipitation Monitoring Network
CEPA	Canadian environmental protection act
CFPP	coal-fired power plant
CVAFS	cold vapour atomic fluorescence spectroscopy
GEM	gaseous elemental mercury
GEOS	Goddard Earth Observing System
Hg	mercury
MeHg	methylmercury
PMT	photomultiplier tube
PTFE	Polytetrafluoroethylene (Teflon)
RDMQ™	research data management and quality assurance system™
GOM	gaseous oxidized mercury
TGM	total gaseous mercury
UNEP	United Nations Environment Programme
VOC	volatile organic compound

1.0 INTRODUCTION

1.1 The Research Problem

Toronto is the country's largest metropolis with an urban population of 2.6 million people. That number grows to 6 million when the surrounding metropolitan area is included (Statistics Canada, 2011). As the population of the city climbs, so too does population density. Urban sprawl combined with the replacement of buildings with taller ones change the topography of the cityscape, which in turn may affect the air flow pattern in the city canopy hence the concentration and distribution of pollutants. This also means the volume of indoor air also increases. It is known that Hg concentrations in indoor air are higher than outdoor air. These factors together may influence the mercury concentration of outdoor ambient air by the movement of contaminated air from indoors to outside. Outdoor GEM concentrations are also influenced by expanding industries to meet increased demands from a growing population. Fortunately technological advancements in power generation, waste management, materials manufacture, and chemical & ore processing have come a long way in mitigating Hg emissions.

Meteorology plays a key role in the distribution and cycling of mercury in urban, rural and remote settings although perhaps to different extents. In a rural or remote context, away from the effect of anthropogenic influence, meteorology might have a stronger effect compared to an urban environment because meteorology is the governing factor while in an urban environment, GEM concentration and distribution might be more heavily weighted towards point and regional sources. However, this is not to say that meteorology does not play a role in an urban environment. This study will attempt to characterize the effect of meteorological parameters on the concentration and distribution of elemental mercury within the urban atmosphere.

Policies to control the harmful effects of mercury emissions have been in place at the provincial and national level since 1999 and a measurable decrease in global and national atmospheric mercury levels have been independently verified by various groups, both governmental and academic agencies (NADP, ECCO, UNEP, and others (Butler et al., 2007; Temme et al., 2007; UNEP, 2013). These measurements, however, are usually made in rural and/or remote regions, far from point source emissions in order to obtain a better idea of the global background levels. In an urban atmosphere the background Hg levels are quickly surpassed by anthropogenic emissions from local and regional sources. It has been reported that indoor

environments might be contributing to the increase in atmospheric Hg (Cairns et al., 2011), and that the changing topography of the cityscape may influence the concentration and distribution of Hg within the city.

Mercury is a heavy metal naturally occurring in the environment. Its presence in the environment poses a complicated problem because of its persistent nature. Being an element, it does not break down or become benign after any amount of time. Once it enters into the environment, it can cycle indefinitely between air, soil and water. Mercury can travel long distances by air because of its long atmospheric residence time, deposit to far-off remote and isolated regions, and collect in bodies of water where it undergoes transformation to form more toxic Hg species. In preindustrial times mercury was not an environmental concern but since its widespread use during the industrial revolution and global transport due to its long atmospheric residence time, it has become a global problem that science and government have been trying to rectify since the 1950s.

In this experiment, outdoor ambient air is sampled from two locations on the Ryerson University campus. Sampling stations are on the top floors of Kerr Hall North (43°39'33.68" N, 79°22'45.33" W, elevation 30 m) and Jorgensen Hall (43°39'32.53" N, 79°22'51.17" W, elevation 60 m) with air inlets situated 1.5 m above the roofs. The objectives of this study are to (1) determine spatial and temporal variability trends of Hg in ambient air from an urban environment by continuously sampling air for a 12 month period; (2) investigate if topographical changes in the urban landscape affected the concentration and distribution of mercury compared to past studies; (3) and evaluate if mercury policy is effective in mitigating or lowering urban atmospheric elemental mercury.

1.2 Mercury: physical and chemical properties

Table 1 lists some properties relevant to mercury.

Table 1: Properties of elemental mercury

Property	Value
Average Molecular Weight	200.592(3)
Vapour pressure	42°C at 1.0 Pa 175.6°C at 1 kPa
Melting Point	234.3210 K

Boiling Point	629.769 K		
Heat Capacity at 25°C	27.983 J mol ⁻¹ K ⁻¹		
Density at 273K	13.59508 g cm ⁻¹		
Specific Gravity at 273K	73.5560 cm ³ kg ⁻¹		
Aqueous Solubility ^a	49.4 µg/litre at 20°C		
Electron Configuration	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²		
Ground State Energy Level	¹ S ₀		
1 st Ionization Potential	10.4375 eV		
Common Oxidation States	Hg ⁰ , Hg ^I , Hg ^{II}		
Type of bonds formed	Ionic, covalent, Van der Waals		
Atomic Radius	1.50 Å		
Specific Heat	0.138 J/g mol at 20°C		
Henry's Law constant ^b	8.7 x 10 ⁻⁴ to 1.1 x 10 ⁻³ mol/(m ³ Pa)		
Relative Abundance of Hg Isotopes	¹⁹⁶ Hg	195.965807(5)	0.15(1)
	¹⁹⁸ Hg	197.966743(4)	9.97(20)
	¹⁹⁹ Hg	198.968254(4)	16.87(22)
	²⁰⁰ Hg	199.968300(4)	23.10(19)
	²⁰¹ Hg	200.970277(4)	13.18(9)
	²⁰² Hg	201.970617(4)	29.86(26)
	²⁰⁴ Hg	203.973467(5)	6.87(15)

Sources:(Haynes, 2016)

^a (Schroeder et al., 1998)

^b (Sander, 2015)

1.3 Sources of mercury in the environment

The global atmospheric mercury budget is governed by anthropogenic emissions, natural emission sources, and re-emissions from aquatic and terrestrial surfaces otherwise known as legacy emissions. These each contribute approximately 30%, 10% and 60% of the mercury to the atmosphere annually (UNEP, 2013). It is important to understand these sources, quantify their emissions and build inventories of mercury polluters in order to gauge the ecological costs associated with mercury pollution. Once in the atmosphere, elemental mercury undergoes oxidative processes whereby it converts to an oxidized form (Hg²⁺), usually taking the form of salts. The oxidized Hg species are much more soluble than the elemental form, allowing for easy removal from the atmosphere via precipitation. Hg in soils generally gets taken up by vegetation or re-emitted as mercury vapour. Hg in water generally gets sequestered in sediments where it

may remain for thousands of years, or be converted by bacteria into an organic form which bioaccumulates up the food chain. Expansion upon these concepts follows in the rest of the section.

1.3.1 Natural Sources

Mercury is a rare heavy metal found in the crust. It exists naturally in ores such as cinnabar and corderite and is found concentrated in geological structures called veins. Cinnabar may contain between 0.1% and 2.5% Hg by mass (Rytuba, 2003), compared with a crustal abundance of only 0.08ppm Hg (or 0.000008%) by mass (Ehrlich et al., 2009).

Mercury may naturally enter the environment by the weathering of rocks, volcanic eruptions, biomass burning / forest fires, and surface water-to-air transfers (**Figure 1**). Settled mercury may also remobilize from soils, vegetation and surface waters and enter the atmosphere once again (Pirrone et al., 2009).

Figure 1: Biogeochemical cycling of mercury in the environment

1.3.2 Anthropogenic Sources

Sources here include burning fossil fuels from coal fired power plants (CFPPs), burning waste, ferrous and non-ferrous metals manufacturing, chemical production (chlor-alkali plants), explicit mining for Hg, ore processing, cement plants, and artisanal and small-scale gold mining (ASGM) (Pirrone, 2009; UNEP, 2013).

The world's supply of mercury comes from mining, or recovery as a byproduct from various industries, for example mining, smelting and production of other metals (Fe, Al, Cu, Pb, Zn), reprocessing of mine tailings, recycling from consumer products, and private stocks (such as mercury used in chlor-alkali plants) (UNEP, 2002). Typically Canada and the United States do not mine for Hg as a principal commodity but recover it through recycling programs or import it from mercury-producing nations such as China, Russia, Kyrgyzstan, Mexico and Peru (George, 2015; UNEP, 2002).

The United Nations Environment Programme (UNEP) estimates the largest mercury pollution sources on a global level are associated with ASGM and coal burning. Together they account for about 62% of the annual total anthropogenic emissions to air (62% of the estimated 1960 t in 2010) (UNEP, 2013). It is notable that ASGM is not a common practice in modern countries. Also some high-throughput power-producing countries are moving away from coal burning as a means of power generation in favour of renewables. Both practices are being phased out albeit by different motivating factors.

Mercury tends to be higher in an urban environment due in part to some of the abovementioned sources being located in and around cities. It has also been shown that indoor air is higher in mercury compared to outdoors because Hg is greatly diluted once it escapes outdoors (Cairns et al., 2011; Higuera et al., 2014). When mercury containing construction materials and consumer products are used indoors they produce vapours that can be inhaled (in the case of GEM) especially if those materials are disturbed (broken thermometer, thermostat, compact fluorescent light bulb) or absorbed through the skin (in the case of organic and inorganic mercury) by the application of skin-lightening creams, mascaras and eye-cleansing products (World Health Organization, 2011). This liberated mercury can eventually make its way back into the biogeochemical cycle by escaping to the atmosphere. For this reason, buildings are considered a point source of mercury in the context of urban environments.

1.3.3 Legacy sources / reemissions

Legacy emission sources refer to the reintroduction of previously liberated mercury to the biogeochemical cycle through natural or anthropogenic means. An example would be volatilization of Hg from contaminated soils by physical disturbance and/or solar radiation. Another example would be volatilization of Hg from bodies of water. There are large uncertainties in the estimates for Hg contribution by reemission because the parameters that determine the rate of Hg exchange between air-sea, air-soil and air-vegetation are poorly understood (Pirrone et al., 2013).

The most recent global emission estimates for total gaseous mercury (TGM) by a regulatory body were made in 2010 by the United Nations Environment Programme and reported in UNEP's Global Mercury Assessment document (2013). For 2010, an estimated total of 1960 (1010-4070) tonnes of mercury was released to the atmosphere as a direct result of anthropogenic activity. This accounts for 30% of the total mercury released to the atmosphere that year. Natural sources are estimated to contribute 10% and "legacy emissions" are thought to contribute 60% i.e., mercury that has been recirculated through the atmosphere by re-emission from terrestrial surfaces and aquatic bodies (UNEP, 2013).

Zhang *et.al* (2015) reports that two thirds of global Hg emissions to the atmosphere are due to reemissions based on the GEOS-Chem model, consistent with UNEP's estimate. The United Nations Environment Programme's 2013 report estimates natural and reemissions account for between 35-70% of mercury deposition in most regions. Deposition is generally greater in low and mid-latitude regions due to more intense solar radiation, a higher concentration of oxidants, and higher volume of precipitation (Pirrone et al., 2013; UNEP, 2013).

1.4 Mercury speciation in the atmosphere

Mercury in the atmosphere is operationally defined as gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM) and particulate-bound mercury (pHg). Total gaseous mercury (TGM) is the sum of the GEM and GOM species. In an urban environment, the distributions of these species are highly variable, especially near an emission source where local concentrations of any or all of the Hg species may be much higher than rural and remote background values.

GEM accounts for 95-98% of TGM in low- and mid-latitude rural areas while GOM and pHg make up the rest (Butler et al., 2007; Lin et al., 1999). GEM is relatively stable and quite a bit more volatile compared to its oxidized and particulate-bound counterparts. It also has a very slow deposition velocity, all factors which lead to its long residence time estimated between 6 months to 2 years (Lindberg et al., 2007; Schroeder et al., 1998). Elemental mercury also exchanges between air and surfaces due to its volatility. For the above reasons, GEM is capable of transport on a local, regional and global scale.

The background level of GEM in the northern hemisphere ranges from 1.5-1.7 ng/m³, and 1.1-1.3 ng/m³ in the southern hemisphere. The reason for the difference in values is twofold; more anthropogenic mercury is produced in the northern hemisphere, particularly from Asia, and secondly it takes a long time for GEM to cross hemispheres due to the behaviour of wind patterns at the equator (Kock et al., 2005; Pirrone et al., 2013; Temme et al., 2004).

The Hg⁰ to Hg¹⁺ and Hg²⁺ reactions in the troposphere (**Table 2**) are known to occur when GEM is in the presence of atmospheric oxidants and have been verified by reactor chamber experiments (Pirrone et al., 2009). The dominant oxidation species in the continental troposphere were thought to be ozone (O₃) and hydroxyl radical (·OH). A different trend is observed in the upper atmosphere and marine boundary layers where chlorine and bromine species (Cl, Cl₂, Br, Br₂, BrO) are the more dominant oxidants. Iodine and peroxide are also known to oxidize GEM (Lin et al., 2006). Due to the reactivity and high solubility of Hg²⁺ compounds, they tend to quickly dissolve into water droplets and return to the ground in precipitation (Lindberg et al., 1998).

Particulate-associated mercury is the third type of atmospheric mercury studied in the science of the atmosphere. As the name implies this species is one that is governed by its association with small particles and aerosols. The particles can arise from natural and anthropogenic sources (e.g., volcanoes, biomass burning, sea aerosol, mineral dust, coal fired power plants, etc.) and are distributed mainly by wind.

1.5 Transport

The troposphere is the lowest layer of the atmosphere spanning 18 km in the tropics to as low as 7 km in polar regions. It is the thinnest layer of the atmosphere but it is also the most interesting as this is where most weather phenomena occur (Elliot, 1996). It's also the most

relevant to pollutant distribution because almost all airborne pollutants travel solely through this layer; rarely, if ever, crossing the tropopause and into the stratosphere. The troposphere serves as the main distribution mechanism by which GEM can travel worldwide. Evidence of global transport can be seen in remote regions where there are no point source emissions but background levels of TGM/GEM are above estimated pre-industrial levels (Pirrone et al., 2009). There are a few mechanisms that assist in its transport and are discussed below.

Perhaps the most obvious mechanism in assisting pollutant transport is wind. The wind is responsible for the dispersion, mixing and dilution of pollutants through the atmosphere. Point and plume emissions are also influenced by wind patterns. Polluted air masses are able to be traced back to their sources using back-trajectory, dispersion models and meteorological data (Carslaw, 2006; Huang, 2012; Lindberg et al., 2007; Venter et al., 2015). This is particularly difficult in an urban environment however, due to turbulent wind patterns and irregularities in the topography, especially if the sampling sites are not high enough above the city canopy.

Particulate and GOM species are also transported through the atmosphere, albeit on a much shorter distance and timescale. GOM and pHg exists in the atmosphere on the order of hours to days and may travel tens to hundreds of kilometers (Schroeder et al., 1998). GOM is highly soluble and deposits to particles and surfaces or dissolves into water droplets. The captured mercury then deposits to surfaces and various environmental compartments, usually nearby the emission source. For this reason, GOM sources offer an immediate and acute risk to the surrounding environment compared to a GEM source whose effects threaten a long term chronic risk.

Aerosols play a role in the transport of mercury when particles are deposited to the ground or surface waters. Particle size is related to residence time in the atmosphere and therefore affects how far the particles can travel before settling. Ultrafine particles ($<0.01\ \mu\text{m}$) and coarse particles ($>20\ \mu\text{m}$) are removed within 24 hours by different mechanisms. The former are removed by phoretic diffusion to cloud particles and Brownian coagulation while the latter are removed by impaction and precipitation. Particles in the intermediate range ($0.01 - 10\ \mu\text{m}$) can remain in the lower troposphere for 1-2 weeks and much longer in the upper troposphere (Hobbs, 2000). Particulate mercury can be measured for a range of size fractions on the condition that it can be collected onto a filter (Pyta et al., 2016).

Global distillation is the phenomenon whereby substances volatilize in warmer equatorial regions, travel by air and condense in colder, polar regions. This is sometimes referred to as the 'grasshopper effect' (Wania et al., 1995). This applies not only to mercury but any volatile (VOC) and semi-volatile (SVOC) organic compounds. It is due to this process that we observe an accumulation of mercury and POP's in remote places like the arctic where there are no significant pollution sources.

1.6 Transformations and removal mechanisms

In the atmospheric environment mercury transformations fall into two main categories: gas-phase oxidation (**Table 2**) and aqueous phase oxidation which take place in cloud droplets.

The atmospheric oxidation of gaseous elemental mercury is important in the context of its biogeochemical cycle. Generally, GEM compared to other mercury species is not easily oxidized and is relatively volatile. Oxidation of GEM purely in the gas-phase by atmospheric oxidants is difficult to explain mechanistically and the kinetic and thermodynamic data for reactions between GEM with atmospheric oxidants do not agree. It was thought that the main gas-phase oxidants of Hg^0 are ozone and hydroxyl radicals however, in a re-evaluation of empirical data and mercury models, bromine has been shown to be the dominant atmospheric oxidant (Holmes et al., 2006). Overnight reactions of Hg^0 with nitrate (NO_3^-) in the atmosphere have also been quantified. Experiments mostly done in reaction chambers attempt to quantify rate laws pertaining to the reaction of Hg^0 and atmospheric oxidants, radicals, and halogens.

The product of the first 3 reactions in **Table 2** yields $\text{HgO}_{(s)}$ which precipitates as a small particle. The pHg exists in the fine particulate matter fraction ($<2.5 \mu\text{m}$) with a low deposition velocity of $<0.5 \text{ cm/s}$ and low concentration typically $<10 \text{ pg/m}^3$. The slow deposition velocity indicates that it is not a significant component of dry deposition but the $\text{HgO}_{(s)}$ particles are susceptible to scavenging by larger particles, aerosols, black carbon, and water vapour / cloud droplets. Because of this, the residence time of particulate-bound mercury is on the order of days to weeks and has been shown to negatively correlate with rain.

Table 2: Potential gas-phase mercury reactions

Reaction	K* at 25°C	Reference
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$\text{Hg}^0 + \text{O}_3 \rightarrow \text{HgO} + \text{O}_2$	7.5×10^{-19}	Pal et al. (2003)
$\text{Hg}^0 + \cdot\text{OH} \rightarrow \text{HgOH}$ $\text{HgOH} + \text{O}_2 \rightarrow \text{HgO} + \text{HO}_2\cdot$	8.75×10^{-14}	Sommar et al. (2001)
$\text{Hg}^0 + \text{NO}_3 \rightarrow \text{HgO} + \text{NO}_2$	4.0×10^{-15}	Sommar et al. (1997)
$\text{Hg}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Hg}(\text{HO})_2$	6.1×10^{-19}	Travnikov et al. (2002)
$\text{Hg}^0 + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{HgI}$	1.5×10^{-21}	Tokos et al. (1998)
$\text{Hg}^0 + \text{HCl} \rightarrow \text{HgCl}_2$	1×10^{-19}	Hall et al. (1993)
$\text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl}_2$	2.6×10^{-18}	Ariya et al. (2002)
$\text{Hg}^0 + \text{Br}_2 \rightarrow \text{HgBr}_2$	9.0×10^{-17}	Ariya et al. (2002)
$\text{Hg}^0 + \text{I}_2 \rightarrow \text{HgI}_2$	2.7×10^{-16}	Hall et al. (1995)
$\text{Hg}^0 + \text{Cl}^- \rightarrow \text{HgCl}$	1.0×10^{-11}	Ariya et al. (2002)
$\text{Hg}^0 + \text{Br}^- \rightarrow \text{HgBr}$	3.2×10^{-12}	Ariya et al. (2002)
$\text{Hg}^0 + \text{BrO} \rightarrow \text{HgO} + \text{Br}^-$	$\leq 1 \times 10^{-12}$	Calvert et al. (2003)

* k in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for 2nd order reactions which these all happen to be

In the arctic springtime for 3 months after polar sunrise, field measurements revealed episodic drop-offs in elemental mercury that were highly correlated with ozone depletion (Barrie et al., 1998). Ozone was later found to be depleted by reaction with high levels of Br and BrO during this time (Barrie et al., 1998). BrO was also found to oxidize Hg^0 and is the cause for the removal of Hg^0 from the atmosphere by forming $\text{HgO}_{(s)}$. The transformation of GEM to $\text{HgO}_{(s)}$ and the subsequent deposition is the mechanism that governs this removal process. It is not entirely certain where the Br is coming from, but leading hypotheses include sea-salt aerosols, sea-salt deposits on snow and new sea-ice surfaces. The settled mercury can volatilize back into the atmosphere driven by more intense sunlight and higher temperatures during warmer periods.

The last type of transformation is classified as biological, in that a living organism is required to metabolize, catalyze or otherwise facilitate the transformation. As mercury enters an aquatic ecosystem and moves through the water column or deposits to the sediment, sulphur- (*Desulfovibrio*) and iron-reducing (*Geobacter*) bacteria methylate Hg^{2+} through the methyl transferase metabolic pathway. The methylmercury $[\text{CH}_3\text{Hg}]^+$ produced by this pathway is much more harmful than its precursors and is prone to bioaccumulate in animal tissue to levels high enough to cause damage at the top of the food chain (Fitzgerald et al., 2007; Merritt et al., 2009).

1.7 Health effects

The common exposures routes for mercury compounds are different for each species. Elemental mercury has a high absorption of around 70-80% when inhaled as a vapour but negligible for ingestion (0.01%) as a liquid. It leaves the body through urine and feces. Inorganic

mercury salt absorption varies based on its form and host conditions. It is absorbed most aggressively through the stomach and intestines and leaves the body through urine and feces over the course of weeks to months. Organic mercury has a very high bioavailability and almost completely absorbs through the GI tract when ingested. Dermal absorption is the most severe for this class, especially concerning dimethylmercury where a few drops applied to bare skin can have lethal effects on the human body in less than 1 year. Mercury in this form readily accumulates in organs and crosses the blood-brain barrier. Mercury in this form is slowly excreted in feces over several months (Agency for Toxic Substances and Disease Registry, 1999).

Once elemental mercury vapour or inorganic mercury enters the bloodstream, it is rapidly oxidized by red blood cells via the hydrogen peroxide-catalase pathway to Hg^{2+} . Oxidation also occurs by this pathway in tissues such as the brain and liver. Organic mercury is also thought to be converted to Hg^{2+} by the hypothesized reaction between alkyl mercury and hydroxyl radicals produced by cytochrome P-450 reductase (Agency for Toxic Substances and Disease Registry, 1999).

It should be emphasized that people do not often find themselves at risk of dangerous levels of exposure to Hg^0 or Hg^{2+} . Methylmercury found in fish from contaminated water poses a much larger risk because consumption of contaminated fish leads to accumulation of MeHg in the body. There is virtually no way of knowing beforehand if fish is contaminated and the effects of MeHg build-up in the body won't manifest in symptoms until significant damage has been done. Lethal dose of organic mercury in humans is difficult to assess because they rely on case studies that are few and far between. The EPA estimates the lethal dose of MeHg is 10-60 mg/kg bodyweight. Victims affected by Minamata disease, aka mercury poisoning from contaminated fish, died from pneumonia, non-ischemic heart attack and non-inflammatory CNS disease (Agency for Toxic Substances and Disease Registry, 1999).

Divalent mercury acts on the body by binding to thiol (-SH) groups, such as the one on cysteine. Typically cysteine is associated with protein folding by means of a disulphide bridge. The interaction of Hg^{2+} with this amino acid may disrupt the folding of a protein and this can have a wide variety of unintended effects such as inactivation of enzymes, disrupted transport processes, changes in membrane permeability by the formation of thiolates (a salt with structure $\text{R-S}^-\text{M}^+$), increased oxidative stress, disruption of microtubule formation, increased permeability of blood-

brain barrier, disruption of protein synthesis, disruption of DNA replication and DNA polymerase, impairment of synaptic transmission, impairment of immune response, disruption in calcium homeostasis, and other detrimental health effects (Agency for Toxic Substances and Disease Registry, 1999). Mercury is allowed to cross the blood-brain barrier by mimicking methionine after binding cysteine through the thiol (-SH) group.

1.8 Global mercury emission and trends

There does not exist a single unified global monitoring network for mercury but rather numerous regional and national programs and long term monitoring sites. Since the early-to-mid 1990s large decreases in atmospheric mercury have been observed in both the Northern and Southern hemispheres from long-term monitoring stations in Cape Point, South Africa (Venter et al., 2015), Mace Head, Ireland (Ebinghaus et al., 2002), Neumayer, Antarctica (Temme et al., 2003), Mauna Loa, Hawaii (Krnavek et al., 2010) and from cruise ship campaigns over the Atlantic (Soerensen et al., 2012). At the same time, over this period, governments have been heavily regulating mercury emissions with an emphasis on power generation and industrial sources.

The mercury research community spends a great deal of effort to model mercury transportation, transformation and fate in the environment in an attempt to understand the variables and to what extent they affect the ecosystem, be it on a local, regional or global scale. In constructing these models all the steps need to be understood and quantified and herein lies the problem. Uptake rates by aquatic organisms, parameterization of rates of exchange between natural reservoirs, coordinated measurements of tropospheric distribution of GEM, and more accurate and extensive inventories are just some of the missing pieces needed to build better models (UNEP, 2013).

Even with the missing pieces, there are reasonable models that can estimate global emission trends using the current knowledge on mercury movement and transformation, national mercury budgets, natural, anthropogenic, and legacy emissions, and coordinated data from the various networks (section 1.7). Neglecting to account for the missing pieces means the models are over-simplified, especially if incorrect or inaccurate assumptions are made, or if the models are built using inaccurate or incomplete data. Zhang et al. (2015) compiled TGM data from various monitoring networks over 20 years and concluded that observed concentrations of Hg^0 have decreased $\sim 1\text{-}2\% \text{ y}^{-1}$ since 1990, but global emission inventories, whose data are used to construct

the models, project flat or increasing emissions over the same period. They resolve this inconsistency by identifying flaws with the current Hg inventories including (i) failure to account for release of Hg from commercial products, (ii) biased estimates of ASGM emissions, and (iii) failure to properly account for changes in Hg speciation in CFPPs after implementation of emission controls for SO₂ and NO_x. Their revised model was better able to predict the observed trends in the free troposphere in North America and Eastern Europe but had difficulty with high northern latitude regions, likely due to more complex interactions involving bromine radicals and AMDEs. Rerunning the model, Zhang et al. found a 20% decrease in total Hg emissions and a 30% decrease of anthropogenic emissions, with decreases in North America and Europe, offsetting Asian emissions.

1.9 Canada's role in mercury research and emission control

1.9.1 Monitoring networks

The Canadian Atmospheric Mercury Measurement Network (CAMNet) is one of a few large-scale mercury monitoring networks. Operated by Environment Canada, there are 11 rural and remote sites set up across Canada that have been running since 1994. The program seeks to advance the understanding of atmospheric transport, transformation and removal processes of Hg species, identify spatiotemporal trends in TGM, provide data to validate models and provide data for health-based studies and risk assessments (Puckett et al., 2010).

1.9.2 Latest Canadian emissions estimates

The Canadian government publishes air pollution data for 17 air pollutants including Hg, Pb, Cd, dioxins, NO_x, PM₁₀, PM_{2.5} and others in the Air Pollutant Emission Inventory Report (APEIR). In 2014, APEIR reports approximately 3.9 t of Hg were emitted in total to the air by sources within Canada. The largest contributors of Hg to air were from industrial sources, making up 38% (1.5 t). Industrial sectors such as iron & steel, concrete & cement, and non-ferrous smelting & refining industries contributed 1.2 t alone (30%); other industries make up the last 8%. The non-industrial sector makes up 24% (930 kg) and this mainly comes from electric power generation which alone accounts for 20% (760 kg). The third largest sector, making up 16% the Hg pollution are open sources which include waste management, agriculture, prescribed burnings,

mine tailings and construction operations (620 kg) (Environment and Climate Change Canada, 2014).

The Air Pollution Emission Inventory Report tracks 17 air pollutants from sources at the national and provincial level. This information is obtained by a reporting system with which companies producing these pollutants must comply. From 1990 to 2014, the APEI reported total Hg releases to air have decreased an average of 90% over all sectors. This breaks down to a 95% reduction from the industrial sector, 74% reduction from open sources, and a 62% reduction from the non-industrial sector. The largest emission reductions are attributed to changes in ore processing and shutting down of coal-fired power plants (Environment and Climate Change Canada, 2014).

1.9.3 Health Canada guidelines for mercury exposure

Health Canada has set guidelines on exposure to mercury by fish, air, soil, drinking water, and biological materials. In the gas phase alkyl, aryl and elemental/inorganic forms are each given different recommended threshold exposure values (**Table 3**).

Table 3: Health Canada guidelines for mercury exposure

Exposure	Source	Limit	
Oral Consumption	Drinking water max acceptable concentration	0.001 mg/L total mercury	
	Tolerable daily intake (TDI) (adults)	0.47 µg MeHg per kg of b.w.	
	TDI (children and women of childbearing age)	0.20 µg MeHg per kg of b.w.	
	Commercial fish	0.5 ppm total mercury	
Inhalation by Occupational Exposure	Alkyl mercury	0.01 mg/m ³	
	Aryl mercury	0.1 mg/m ³	
	Elemental & inorganic mercury	0.025 mg/m ³	
Biological Material	Mercury in blood and hair	Blood	Hair
	Normal acceptable level	< 20 ppb	< 6 ppm
	Increasing risk	20-100 ppb	6-30 ppm
	At risk	> 100 ppb	> 30 ppm

* Table constructed from Mercury: Your Health and the Environment. Government of Canada, 2004

The threat of mercury lies in the transport of mercury compounds from the atmosphere to bodies of water and wetlands and the transformation of these compounds from a relatively benign form into a bioaccumulative and highly poisonous organic form. Aquatic life exposed to

even low levels of mercury can experience accumulation up the food chain, affecting piscivorous predators, disrupting ecosystem dynamics and posing a threat to human populations that subsist on fish.

Table 4: Noteworthy mercury legislation in Ontario and Canada

Initiative Name & Starting Year	Coverage	Relevance to mercury
Canadian Environmental Protection Act (1999)	Canada-wide	Addresses Hg and compounds in releases, products, wastes, etc.
Canada-Wide Standards for Mercury Emissions from Coal-Fired Electric Power Generation Plants (2006) (Canadian Council of Ministers of the Environment, 2013)	Canada-wide	Commitment to reducing mercury waste from CFPP's
Ending Coal for Cleaner Air Act (2013) ("Legislative Assembly of Ontario Bills & Lawmaking Current Parliament Bill 138, Ending Coal for Cleaner Air Act, 2013," n.d.)	Ontario	Addresses Hg and compounds in power plant emission, wastes
Products Containing Mercury Regulations (2015)	Canada	Prohibits the manufacture and import of products that contain mercury and/or any mercury compounds.

1.9.3.1 Canadian Environmental Protection Act

The Canadian Environmental Protection Act (CEPA) came about as the result of an effort to develop a systematic approach for dealing with toxic substances. Prior to 1999, existing legislation was inadequate; a more comprehensive approach was needed to manage the full life-cycle of toxics (cradle-to-grave philosophy). CEPA provided a framework for the management and control of toxic substances at each stage of their cycle: development, manufacture, import, transport, distribution, use, storage, and disposal. CEPA granted federal authority to control ocean dumping through a permit system, regulate waste handling and disposal practices, and establish environmental guidelines & codes of practice (Environment and Climate Change Canada, 2009).

1.9.3.2 Mercury legislation in Ontario and Canada

Most people living in developed countries are not at risk of high levels of mercury exposure by air because the concentration required to cause harm is quite high, and practices and

regulations have been put in place that reduce and/or outright ban mercury in the indoor environment (**Table 4**).

The Canada-wide emissions for coal-fired electric power generation aims for a 60% reduction in emissions from CFPPs from 1998 to 2010 across Canada. Not all provinces shared the same burden of cutting their emissions based on their individual situation, however, Ontario committed to gradually phase out their 4 CFPPs. In 2014, they met their goal after closing the Nanticoke Generating Station. The Ending Coal for Cleaner Air act was then passed to ensure that no coal would ever be burned in the province starting in 2015.

1.9.3.3 Products Containing Mercury Regulations

This set of regulations applies to the prohibition of the manufacturing and import of products containing mercury or any of its compounds. Exceptions are made for products at the end of their useful life and intended for recycling or for products that have no technical or economically viable alternative. Examples of some exceptions include medical and research applications and dental amalgam.

1.10 Trends in Atmospheric Mercury from North American Cities

Atmospheric mercury monitoring studies have been intermittently conducted in Toronto, Canada. From June 2001 - February 2002, Denis et al. (2006) found GEM over sidewalk and tree canopy peaked in the fall and was lowest in the winter. Diurnal patterns were found to vary by season. Data from 2004 (Song et al., 2009) found GEM/GOM/pHg to be lowest in fall and highest during the summer months. Both studies also find GEM to be higher overnight compared to daytime hours.

Monitoring studies from other North American cities (**Table 5**) demonstrate similar patterns and trends in an urban environment. Two study locations in Michigan compared the GEM from urban Detroit with the nearby rural town of Dexter. Liu et. al. (2010) found that GEM was higher at the urban location compared to the rural location due to local and regional sources. GEM was also found to be higher overnight between the hours of 10 pm and 4 am, agreeing with studies from Toronto (Liu et al., 2010). TGM was measured in Houston, the most populated city in Texas, from August 2011 to October 2012. Lan et al. (2014) found the same diurnal variation and seasonal trends observed at other North American cities with a periodic night-time maximum and

daytime minimum. Maximum TGM measurements were observed in the summer while the lowest were recorded in the winter. It is expected that climate and population density play a role in the increased levels of TGM in an urban environment due to their proximity to industry and power generation facilities. It was shown that the increased ambient Hg in Houston during the warmer months correlated well (0.735, $p < 0.005$) to an increase in energy consumption.

A study by Wang et al. (2013) in Rochester, NY compared a 2-year data record of mercury species in ambient air with a period of time following the decommissioning of a CFPP 12 km to the northwest. Following the closing of the power plant, they observed a median decrease of 12% in GEM overall and a 25% reduction in median GEM from the direction of the power plant. They also found the largest decrease in median mercury species in winds associated with the northwest direction (Wang et al., 2013). A similar study in the Lake Wabamun area of Alberta, west of Edmonton, measured TGM, SO_2 , and NO_x from a site within 500 km of a chain of four CFPPs. Pollution data were analyzed for episodic events of high TGM. High levels of TGM correlated with both NO_x and SO_2 and were associated with wind from the direction of the power plants and from the city of Edmonton; northwest and east respectively (Mazur et al., 2009). Both studies made use of tracer gases SO_2 and NO_x to attribute high levels of TGM to wind in the direction of the CFPPs, and observed a significant decrease in TGM concentration after the closing of the power plant.

Table 5: Summary of GEM concentrations in urban air from cities in the northern hemisphere

Study Area	Sampling Campaign	[GEM] in ng/m^3	Reference
Toronto, ON	Oct 2015 – Oct 2016	1.62 ± 0.77	This study
	May 2008 – July 2009	1.89 ± 0.62	(Cairns et al., 2011)
	Dec 2003 – Nov 2004	4.5 ± 3.1	(Song et al., 2009)
	June 2001 – Feb 2002	2.39 ± 2.05	(St. Denis et al., 2006)
Detroit, USA	Jan – Dec 2004	2.5 ± 1.4	(Liu et al., 2010)
	2000 – 2002, in intervals	1.7 to 3.1	(Lynam et al., 2006)
Houston, USA	Aug 2011 – Oct 2012	1.54	(Lan et al., 2014)
Birmingham, USA	2005 – 2008	2.12	(Nair et al., 2012)
New York City, USA	June – Nov 2000, in intervals	$2.69\text{-}3.84 \pm 0.10$	(Carpi et al., 2002)
Rochester, USA	Dec 2007 – Nov 2009	1.6 ± 0.3	(Wang et al., 2013)
Reno, USA	Nov 2004 – Nov 2007	1.6 ± 0.5	(Peterson et al., 2009)
Elizabeth, USA	2.5 years starting in 2004	2.25 ± 0.04	(Aucott et al., 2009)
New Brunswick, USA		2.15 ± 0.02	
Seoul, Korea	Sept - Nov 2003	$5.35\text{-}7.86 \pm 2.74\text{-}3.52$	(Kim et al., 2006)
Chongqing, China	Aug 2006 – Sept 2007	$5.36\text{-}8.24 \pm 0.50\text{-}0.70$	(Yang et al., 2009)
Beijing, China	Oct 2003 – Sept 2004	17.1 ± 11.9	(Zhou et al., 2010)

Puertollano, Spain	2002	3.36 ± 2.38	(Higueras et al., 2014)
	2011	3.16 ± 2.16	
Seville, Spain	2011	2.62 ± 4.81	
Zingst, Germany	1998-2004	1.66	(Kock et al., 2005)

2.0 MATERIALS AND METHODS

2.1 Site and Experimental Setup

In this experiment, outdoor ambient air is sampled from two locations on the Ryerson University campus in Toronto, Canada (population 6.13 million) from October 2015 to October 2016 (Statistics Canada, 2015). Sampling stations are on the top floors of Kerr Hall North (43°39'33.68" N, 79°22'45.33" W) and Jorgensen Hall (43°39'32.53" N, 79°22'51.17" W) with air inlets situated 1.5 m above the roofs (**Figure 2**). The sites are located in the downtown core surrounded by moderate to heavy traffic, residential and commercial buildings and frequent construction projects. Monitoring was done using mercury vapour analyzers (model 2537A, Tekran Inc., Toronto, Canada) accompanied with portable weather stations (Onset HOBO Data Loggers) equipped with sensors to measure meteorological parameters (wind speed, direction, gust speed, precipitation, temperature, relative humidity, solar radiation, barometric pressure). Both the mercury analyzers and weather stations record a measurement every 5 minutes.

Figure 2: Map of sampling sites in downtown Toronto

Table 6: Site details

Site	Jorgenson Hall	Kerr Hall North	Aura Condominiums**
Height to tip	60 m*	29 m	275.2 m
Height to inlet	61.5 m*	30.5 m	N/A
Construction date	1972	1963	2010 – Summer 2014
Address	380 Victoria St.	31/43 Gerrard St. E	386 & 388 Yonge Street
GPS coordinates	43°39'32.61 79°22'51.19	43°39'33.64 79°22'45.34	43°39'33.80 79°22'58.04

* Heights are given as above ground. Ground is 96 m above sea level

** <http://www.skyscrapercenter.com/building/aura-at-college-park/919>

In addition to air sampling from the two sites, the experimental area also includes a large skyscraper located to the northwest of KHN (265-295°) and was constructed in the years 2010-2014 (**Table 6**).

2.2 Instrumentation

2.2.1 Mercury Vapour Analyzers

The Hg vapour analyzers (model 2537A, Tekran Inc., Toronto, Canada) used in this experiment employ a dual-channel design allowing for continuous monitoring of GEM. Ambient air is sampled at a rate of 1 L min^{-1} for 5 minutes while filtered for particulate matter and passed through a quartz tube containing gold-coated beads. The gold serves as a necessary pre-concentration step because the instrument would not be able to detect Hg if the measurements were taken in real time due to the real time concentration of GEM in air being lower than the detection limit of the analyzer. The gold cartridge is heated under argon atmosphere to $\approx 500^\circ\text{C}$ for a few seconds to desorb mercury. Argon serves as a carrier gas to move the analyte through the sample line to a quartz cuvette. A mercury vapour lamp produces collimated UV light at 253.7 nm which collides with mercury atoms in the cuvette and excites an electron in the outer shell ($5d^{10}(^1S)6s^2 \rightarrow 5d^{10}(^1S)6s6p$). As the excited electron relaxes back to its ground state, the atom emits energy as a photon of fluorescent light (Ball, 2006). Fluorescent radiation from the electron is detected by a photomultiplier tube. A series of dynodes amplify the intensity of the ejected photons until an anode measures the current produced by the cascade of electrons. The voltage produced is then proportional to the flux of photons from the photocathode and corresponds to a concentration (Ball, 2006).

2.2.2 Cleaning and storage of PTFE components

Before the monitoring, the PTFE components (e.g. unions, tees, tubing, filter housings, fasteners) were soaked in 1:3 HNO_3 overnight to dissolve any elemental mercury or other metal contaminants that may have been present. Nitric acid also dissolved oxidized mercury (Hg^{2+}).

The components were then rinsed 5 times with distilled water and 5 times with NANOpure water. Components were left to dry in a fume hood and placed in a plastic zip-lock bag and double bagged for storage. Subsequent handling of the cleaned components was done while wearing nitrile gloves.

2.2.3 Line setup & generation of zero air

Zero-air, that is, air free of mercury, moisture and interfering absorbing species is required for the operation of the analyzer. Zero air was made from the compressed air tap in the lab following the scheme in **Figure 3**.

Figure 3: Schematic diagram for producing zero air from the compressed air in the lab

Air from the tap was first run through a filter to remove the oil produced from the compressor. The air was then put through a column of soda lime (266434, Sigma Aldrich) to remove the CO_2 and other acidic gases, and a column of a silica gel desiccant (SiO_2) (85815, Sigma Aldrich) to remove moisture. The pressure was reduced to 20 psi before entering the first of two Hg scrubbers. A particulate filter was attached to the second Hg scrubber to catch any particles that may have leaked from upstream. The pressure was reduced one last time before entering the analyzer to 0.5 psi with an inline regulator. PTFE carrier lines were used throughout.

2.2.4 Ambient line setup

A $\frac{1}{4}$ " PTFE line was attached from the ambient air inlet on the back of the model 2537A and fed through the wall/roof to the roof of each respective building. The ambient line intake was fixed to a pole and set 1.5 m above the highest point of the roof. The intake end was equipped with an open-faced PTFE membrane filter (0.22 μm , 47 mm $\varnothing$, MKS Instruments) and pointed towards the ground. A small bucket served as a hood to protect the inlet from precipitation.

2.2.5 Calibration

Manual mercury vapour injections were made to the analyzers to calibrate the machines every ~14 days and to validate the calibration after it has been performed. Injections require a gas tight syringe with digital readout (1710N, 25 µL or 100 µL syringe, Hamilton Company), Tekran model 2505 mercury calibration unit and zero-air.

Air that is saturated with mercury vapour follows an empirical relationship governed by temperature. First discovered by Dumarey, the equation calculating the mass concentration of mercury as a vapour at a given temperature is given below (Dumarey et al., 2010). Although the formula was never formally published, it was alluded to in Dumarey et al. (1985). As long as the temperature can be carefully controlled and the container is air-tight, a saturated mercury vapour source can be used as a primary standard for calibrating this instrument. The equation below describes the mass concentration of mercury vapour in a sealed container

$$\gamma Hg = \frac{A}{T} 10^{-(B + \frac{C}{T})}$$

where: A = 3216523 K·ng/mL, B = -8.13446, C = 3240.872 K, and T = temperature in K

The calibration unit was set to at least 2°C below the room temperature and allowed to equilibrate overnight. Before making an injection, the syringe needle was left inserted into the calibration unit and the plunger fully extended for 24 hours. When the syringe was not in use, it was left inserted in the calibration unit.

2.2.6 Validation

Following a calibration operation on the 2573A analyzer, more injections were made to verify the accuracy. The model 2537A was set to sample zero air in order to clean the instrument and obtain a baseline reading of zero. Then a series of injections was made at around one third to one half of the calibration volume (e.g. if 30 µL was used to calibrate, 10-15 µL was used to verify). Three sets of injections were made according to the scheme below to avoid memory effect and contamination (i.e., avoid 6 back-to-back injections).

The model 2537A produced [Hg] = 0.000 ng/m³ (no peak) when no injection was made. If peaks were observed, zero air was continuously run until no peaks were observed. Small peaks

<0.100 ng/m³ following an injection were due to residual mercury either still adsorbed to the cartridge or the septa. When this happened, zero air was continuously drawn through the cartridge and the cartridge heated until no peaks were observed.

The calibration was deemed valid if the difference between the measured concentration and expected concentration was less than 5% and if the difference between cartridges was less than 5%. The analyzer was used for monitoring only after it had passed this test. If it failed, one or both of the cartridges were recalibrated.

2.2.7 Tekran model 2537A maintenance and operation

During the sampling period the machines and data are checked on for general maintenance and data quality. Weekly maintenance for the analyzers include checking for correct time and date, drifting or low baseline voltage, lamp performance indicated by a high baseline deviation (consistently <0.150V), peak status = OK, sample volume = 5.00 ± 0.01 L, argon tank > 300 PSI, and front panel LED indicators.

Biweekly maintenance included calibration and validation, injection port septa changed, outdoor sample inlet and machine inlet filters changed, syringe and needle inspected for damage.

Monthly maintenance included inspecting the nichrome heaters, measuring the UV lamp voltage, syringe maintenance included cleaning the syringe barrel, plunger and needle with nitric acid, DI water and methanol. Other components were maintained or replaced as required (UV lamp, Hg adsorbent canisters, 0.2 μ m front-end particulate filters, nichrome heaters), usually on an annual or semi-annual basis. The gold traps were conditioned if they were suspected to be underperforming by heating in ambient air and purged to remove impurities or washing with nitric acid, DI water and methanol. The cuvette was inspected and cleaned by the same procedure if there was reason to suspect a problem.

Each day's values were collected and tabulated for percent difference between cartridges. If they deviated by more than 5%, they were investigated for possible errors (heater malfunction, improper heating time, reduced cartridge efficiency, leaks in the sample line) and the values were either discarded or corrected to align the offending cartridge with the correct one. This was determined from the calibration data and by the standard operating procedure that assumed the

higher cartridge (following a valid calibration) is the correct one when compared with an underperforming cartridge.

2.3 Weather station setup

A weather station was setup at each sampling location to monitor meteorological parameters. The station consisted of a tripod and data logger with modular sensors. The tripod was affixed with sensors to measure solar radiation, precipitation (rain), wind direction, wind speed, gust speed, barometric pressure, temperature and relative humidity. Each of the sensors continuously monitored these parameters for the duration of the study. A solar panel recharged an onboard battery each day.

The weather station data logger was launched (initiated) by USB connection to a laptop containing HOBOWare software. The logger uploaded the sensor data to the manufacturer's server provided there is an active internet connection, otherwise data was manually downloaded from the onboard computer via USB connection. Data were downloaded once a week and inspected for sensor damage or malfunction.

2.4 Matching the analyzers

Part of the quality control process involved ensuring the performance of the two analyzers was within the tolerable variation range (5%) throughout the sampling campaign. In order to do this, both machines were placed side-by-side, calibrated and allowed to run while sampling outdoor air overnight from the same inlet. Their performance was verified by calculating the percent difference in observed values between the machines. Before the campaign started, the analyzers showed a disagreement of 4.03% (**Figure 4**). Following the campaign the difference was measured at 4.77% (**Figure 5**). The difference between analyzer measurements was quantified to eliminate the question of machine bias in measurements at either sampling site. It had to be reasonably certain that under identical sampling conditions, both analyzers produced the same data from which the same conclusions could be drawn. Otherwise one could not reliably compare measurements at two sites given that one or both machines are not working properly. The data selected for analyzer comparison were chosen for a period of relative stability in the baseline because these are representative of the majority of data collected. Machine performance also tended to deviate more greatly at higher concentrations ie. >5% difference at values >3 ng/m³.

Figure 4: Paired-machine sampling for an overnight period in 2015 before sampling campaign. Analyzer difference is 4.03% for n=176.

Figure 5: Paired-machine sampling for an overnight period in 2016 after sampling campaign. Analyzer difference is 4.77% for n=176.

2.5 Data handling

A systematic approach was implemented to process the large amount of data collected from both the weather station and mercury analyzer. **Figure 6** describes the general process of collecting, formatting and applying the quality control procedure.

Figure 6: Workflow for collecting, organizing, combining and analyzing GEM and weather data

2.5.1 Mercury data

The mercury vapour analyzers were required to be connected to a computer for the duration of the data collection period. The manufacturer supplied software automatically generated a text file every day the analyzer was active. Every couple of days the text files were copied to a USB, backed up onto another PC, and put through the data handling procedure. The text file from the analyzer contained the following parameters: date, time, status, active cartridge, user pre-set flag condition, sampling time, volume of air sampled, baseline voltage, baseline voltage deviation, max voltage, peak area, and concentration (ng/m^3) (see *Appendix A* for example).

The raw text files were backed up and manually transferred to a spreadsheet containing a single month's worth of data. Only the relevant data were copied to the spreadsheet while metadata, column headings and calibration summaries were omitted. If the mercury analyzer was stopped for any reason during the sample period, blank space was left in the spreadsheet for the

appropriate amount of time. A new spreadsheet was created for each month. At the end of each month the monthly sheet was copied into another spreadsheet containing all the data since the beginning of the study.

2.5.2 Weather station data

The files from the weather station were written to a .csv file and downloaded from HOBOLink.com or transferred from the data logger via USB. These data were then manually transferred into a spreadsheet containing a single month's worth of data. Metadata was omitted and blank space was left in the spreadsheet if any downtime was experienced during the month.

2.5.3 Combining Hg & weather data

The data from the weather station must be lined up and matched with the corresponding mercury data. A script in R was written and used to do this (*see Appendix B for script*). The monthly weather and mercury data are loaded into the R workspace, their columns renamed and then their data frames are fused together. Both the weather and Hg excel files have the same number of cells because they contain the same number of measurements in a given month at the same time resolution. Redundant and unnecessary columns are removed and the combined weather/Hg data frame was exported and saved as a .csv.

2.6 Post processing & quality control

Data quality control involved the identification, removal, correction or deletion of erroneous data. The combined Hg/weather files were submitted to an R script for data scrubbing and quality control (*see Appendix B for script*). Flagging criteria were coded to emulate a modified version of Environment and Climate Change Canada's research data management quality (RDMQ) for GEM. **Table 7** presents a modified version of the RDMQ found in Steffen et al. (2012). Data were removed if they violated a condition in the table and in the odd cases where Hg and wind direction are not both present simultaneously i.e. during analyzer maintenance.

Table 7: Modified Research Data Management Quality (RDMQ) for GEM

Description	Flagging Criteria	Conditions for Corrective Action
Baseline Voltage Shift	Baseline voltage change > of previous value	If GEM values change coincident with shift of baseline voltage, invalidate all data until next auto calibration
High Hg value	[Hg] > ng/m ³	Check site logs for potential activities that could explain high concentrations. Invalidate data if affected
Low Hg value	[Hg] < 0.20 ng/m ³	Examine instrument operation parameters and invalidate data if affected
Cartridge A/B difference	A/B cart. difference 10%-15%	Flag is applied to the lower reading cartridge. Examine standard addition values and invalidate if recovery <90% ** does not apply as std. additions were not performed
	A/B difference >15%	Invalidate data
High baseline deviation	baseline deviation voltage > 0.20V	Invalidate affected data
Low baseline deviation	baseline deviation voltage < 0.05V	Examine to see whether data is affected. Invalidate as necessary
Below detection limit	[Hg] < MDL	Invalidate affected data
Multiple Peaks Detected	Peak status > M1	Invalidate affected data
No Peak	No peak detected	Invalidate
Questionable sample volume	< or > 5% of expected volume	Examine data closely, invalidate affected data

2.7 Data treatment and analysis

2.7.1 OpenAir package for R

Observations for weather and Hg were made on a 5 minute interval and each variable was oriented as a column header. GEM values were retained only if the corresponding weather data was also present. GEM values with a missing case for wind direction, wind speed, solar radiation or pressure were excluded. Wind speeds below 0.5 m/s were set to zero to approximate calm conditions and wind direction is split into 36 sectors for polar plots and 16 sectors for the wind rose. GEM below the detection limit 0.1 ng/m³ were also removed from the data set. Flagging criteria for instrument error were coded to emulate those outlined in Environment and Climate Change Canada's research data management quality (RDMQ) for GEM. Data processing and quality control of the collected data were managed using a script written in R; an open-source programming language and statistical and graphics software environment. The data was analyzed and images produced using the OpenAir package, an add-in useful for analyzing air pollution data,

developed at King's College and University of Leeds. It is suited for handling meteorological parameters and pollution data. Images can then be produced from the input data and interpreted to give insight into temporal and spatial distributions, anomalous peak events and overall trends (Carslaw et al., 2012).

2.7.2 Data from CAMNet

The Canadian atmospheric mercury measurement network was started in 1994 and has expanded to include 15 sites over 22 years at rural and remote sites across Canada. Most of these sites are classified as rural, rural-affected (as in affected by nearby urban or industrial emissions), or remote. The objective of the network is to further the understanding of the transport, transformation and removal mechanisms of atmospheric mercury and to identify spatiotemporal trends, provide data to validate models and provide data to develop risk assessments (Puckett et al., 2010). Some of the CAMNet sites have since been shut down and only 8 are currently in operation.

Figure 7: Map of Canada depicting CAMNet (Canadian atmospheric mercury measurement network) and MDN (Mercury deposition network).

The CAMNet data is used here to make a comparison between 2004 data from sites in the network with that from KHN collected by Song *et. al* (2004) in the same year. The latest datasets from those same sites will also be used to compare to the 2015/2016 data collected in this study. Unfortunately 2010 is the latest available year for data from these sites. Environment Canada has been contacted in an attempt to acquire the 2014 or 2015 data but they are not willing to make the data public before performing their QA/QC.

2.8 Statistical Analysis

Normality was tested using Shapiro-Wilk test, qq plots and histograms. Data was determined not to be normally distributed. The data looks more like a log-normal distribution but does not fit into that distribution either. The non-parametric versions of a t-test are Kolmogorov-Smirnov test and Mann-Whitney U. Both were used to determine if mercury measurements between the two sites came from the same statistical population. The difference between the two is that in KS the test compares the cumulative distribution of two continuous variables and work out a p-value based on the largest discrepancy between the two distributions. MWU first ranks the data and works out a p-value based on the difference in mean ranks of the two groups. Both are used to confirm each other's' conclusion. Rank refers to sorting a numerical variable according to its magnitude, for example the number series [9, 3.14, 5, 0.77] has the ranking [4, 2, 3, 1].

A Kruskal-Wallis test is used when performing analysis of variance when assumptions for normality are violated. This test does not assume the data belong to any specific distribution. KW test is sometimes called 'one-way ANOVA on ranks'. Kruskal-Wallis tests the null hypothesis that all samples are drawn from identical populations (i.e. have the same distribution). It does not give pairwise comparisons between groups. This test was used on seasonal data at a site.

Spearman's rank correlation coefficient (ρ) is used to determine if there are any correlations between GEM received at the sampling sites and the meteorological parameters simultaneously measured. Spearman's rho (ρ) is the non-parametric version of Pearson's product-moment (r). Spearman's rho is used because data from both sites are non-normally distributed.

Spearman's correlation was run between the weather variables and Hg for each subset to see if any correlations existed between events of high Hg and any meteorological parameters.

After running the QC scripts over the data and combining it into spreadsheets, they were separated by [Hg] cut-offs based on percentiles of 90%, 99% and 99.9%. Correlations were done for both sites for each subset (90th, 99th and 99.9th percentiles). The whole dataset for each site was also treated this way (ie. with no cut-off values) in order to compare them to the peak events.

3.0 RESULTS AND DISCUSSION

The data collected from Kerr Hall and Jorgenson Hall for the 2015/2016 period are presented as an annual time series and various boxplots in section 3.1. Spatial distribution patterns are discussed in 3.2 with support from a map of regional source pollutants. A comparison of KHN values from 2015/2016 and 2004 are made in section 3.3. In section 3.4, peak GEM events are described and analyzed by Spearman's correlations and a discussion on local sources is presented. A historical comparison of 2015/2016, 2004, and CAMNet data are made in 3.5 with comments on policy change and its effect on the measured GEM in the atmosphere.

3.1 Temporal Trends

3.1.1 Annual Trends

It can be seen from

Figure 8: 1 hour average time series for (a) KHN and (b) JOR from Oct 2015 to Oct 2016

a and 8b that peak events that occur at one site often occur at the other at the same time. The set of observations also track to each other well and respond to GEM fluctuations in the atmosphere.

Figure 8: 1 hour average time series for (a) KHN and (b) JOR from Oct 2015 to Oct 2016

The KHN site showed larger variations in GEM. A reason for the discrepancy in variability between the sampling sites is its proximity to an Hg source. Suppose a ground level source was emitting GEM to the atmosphere, be it anthropogenic or reemissions from pre-existing sources, an air parcel containing GEM would be less evenly mixed at low elevation compared to one at high elevation because of a dilution effect that would no doubt take place on its way to the higher site. Support for the variability at KHN is given by the proximity of the inlet to rooftop exhaust vents from chemistry and biology labs. Building and room use have also been shown to influence indoor air concentrations of GEM for example in chemistry labs GEM is higher than other indoor environments (Cairns et al., 2011; Cizdziel et. al., 2011). The indoor-to-outdoor movement of air through ventilation or permeation through cracks and seals may explain the source and be the cause of the variability at the KHN site.

The similar general response to GEM in the atmosphere can be seen in **Figure 9 a-c** where the hourly, daily and weekly values track to each other but remain separated by ≈ 0.2 to 0.4

ng/m³. The arithmetic average for annual GEM measured at KHN and JOR are 1.78 ± 0.89 ng/m³ and 1.46 ± 0.54 ng/m³ respectively (**Table 8**).

Figure 9: Time variation of GEM over a 12 month period for Kerr Hall North and Jorgenson Hall. **(a)** is the variation per hour over the week; **(b)** mean hourly GEM; and **(c)** mean monthly GEM. The solid line through each plot represents the arithmetic mean value and the shaded region is the 95% confidence interval.

Table 8: Summary of statistics for GEM (in ng/m³) at the experiment sites. Seasons are defined as 3 month periods: (D,J,F), (M,A,M), (J,J,A), (S,O,N) for winter, spring, summer and fall respectively. Ar. mean is arithmetic mean and Geo.mean is geometric mean.

Site	Season	Ar.mean	SD	Median	Geo.mean	10%	90%
KHN	Winter	1.55	0.41	1.51	1.52	1.20	1.92
	Spring	1.68	0.67	1.56	1.62	1.26	2.16
	Summer	1.95	0.92	1.74	1.82	1.25	2.79
	Autumn	1.97	1.30	1.70	1.80	1.18	2.94
	Total	1.78	0.89	1.68	1.68	1.23	2.48
JOR	Winter	1.30	0.28	1.28	1.28	1.07	1.54
	Spring	1.45	0.55	1.40	1.42	1.14	1.77
	Summer	1.75	0.64	1.65	1.67	1.19	2.39
	Autumn	1.28	0.48	1.19	1.23	0.94	1.64
	Total	1.46	0.54	1.36	1.41	1.07	1.94
Both	Winter	1.43	0.38	1.38	1.40	1.12	1.98
	Spring	1.57	0.63	1.48	1.52	1.20	1.98
	Summer	1.85	0.81	1.70	1.75	1.23	2.59

	Autumn	1.69	1.11	1.44	1.55	1.04	2.57
	Total	1.63	0.77	1.48	1.55	1.14	2.25

3.1.2 Seasonal Trends

On the seasonal level, GEM was highest in the summer at both sites but lowest in winter at KHN (1.55 ng/m³) and lowest in autumn followed closely by winter (1.28 ng/m³, 1.30 ng/m³) at JOR (**Figure 10**). The seasonal mean and median values largely agree at both sites in that they follow a similar pattern (e.g., summer had the highest mean and median GEM, winter mean and medians are lower than spring and summer).

Spring has a lower median and a smaller range compared to summer for both sites. Winter has the smallest range of measurements for all seasons at both sites i.e. smallest standard deviation which agrees with previous studies in Toronto (Song et al., 2009). The values measured in autumn are not consistent between the sites (**Figure 10**). Autumn values were second highest at KHN but lowest at JOR. At the KHN site, there is no statistical difference between winter and spring and no statistical difference between summer and fall. All the seasonal measurements at JOR are statistically different from each other (*see Appendix C*). Ignoring autumn, the seasonal comparison between sites have nearly identical trends. The seasonal difference in autumn is due to the missing data from JOR at the beginning of the sampling campaign as can be seen when comparing the time series' in **Figure 8 a and b**. JOR consistently measured lower values than KHN for all time periods.

Figure 10: Boxplot of GEM by site and season for spring (MAM), summer (JJA), autumn (SON), and winter (DJF) where the three letters represent the names of three consecutive months which constitute a season.

3.1.3 Weekly Trend

As shown in **Figure 9 a) and c)** over the course of a week, GEM peaked on Thursday and decreased over the rest of the week with a sharper decrease over the weekend. The weekend minimums could be attributed to less activity from regional industrial polluters since some may operate at lower capacity or shut down all together over the weekend. Within the city there is a slowdown in construction due to noise bylaws that are in effect on the weekend; construction is permitted on Saturday from 9 am – 5 pm and not on Sunday (with exceptions). The decrease over the weekend is especially noticeable at the Jorgenson site where weekend values drop off to $\sim 1.39 \text{ ng/m}^3$ and remain until Monday. One might expect the mercury to quickly rise on Monday and stay relatively constant until dropping off during the weekend. Instead GEM picks up on Tuesday, peaks on Thursday and declines the rest of the week. The boxplot in **Figure 11** more clearly represents the smaller variability in measurements on the weekend compared to week days. The 100th percentiles, excluding outliers, also follow the same trend as the mean and medians with lower values observed over the weekend.

Figure 11: Boxplot of GEM by site and day of the week. Data collection began in October 2015 and finished in September 2016.

3.1.4 Diurnal Trend

The average GEM at both sites varied diurnally with an evening minimum (~6 pm) and morning maximum (~6 am) (**Figure 9 b**). This may be influenced by the atmospheric boundary layer; the layer of atmosphere between the ground and the inversion layer. As solar radiation heats the ground, air rises until its density matches that of the surrounding air and mixes. The daytime height is ~1 km and may drop to a few hundred meters at night due to the temperature difference between the ground and air. This is because air cools as it rises, however the rate of cooling changes based on moisture saturation, temperature, and expansion of air with elevation change. At night, the rate of change of air temperature, or lapse rate, is slower compared to the day causing less frequent and weaker turbulent fluctuations of air masses moving past each other. This leads to a deeper atmospheric boundary layer in the day and a shallower one at night (Colbert et al., 2008; Hemond et al., 2006; Schneider, 1996). The lower rate of cooling is directly related to higher mercury within the urban canopy because the cooler lapse rate at night slows the upward dispersion of air and, with it, pollutants. In this study, mercury climbs overnight and

peaks at both sites at or just before dawn. At this point the boundary layer is the lowest and has accumulated the most GEM. After dawn the boundary layer expands and dilutes the pollutants upward.

This pattern of higher night time values has been observed in other urban monitoring studies where a low nocturnal boundary layer allows mercury to accumulate overnight to reach a daily maximum before sunrise, followed by a rapid decline into the midday and afternoon. This scenario applies to an urban setting where local and regional anthropogenic sources dominate over background sources and reemissions (Lan et al., 2014; Song et al., 2009).

3.2 Spatial Distribution

Polar plots represent Hg data along with wind speed and wind direction. The data can also be subsetted to plot specific time periods (e.g., seasonally, weekly, daily, hourly, diurnally). Information is represented on 3 axes where the wind speed is indicated by dashed grey circular lines, wind direction is grouped into 10° increments and correspond to wind direction much like a wind rose, and the colour of a cell corresponds to the legend, indicating the value of that cell. The value contained in the cell can be calculated for mean, median, max, min and weighted mean. Cells are plotted with a minimum bin size of 1. A “bin” is defined as a region which corresponds to a particular wind direction and speed (Carslaw, 2015).

3.2.1 Annual - mean of GEM by site

During 2015/2016, JOR has the higher wind speed as indicated by the larger range in wind speed measurements (**Figure 12**). KHN rarely passed 5 m/s while JOR regularly does, and on average, higher mercury concentrations are measured under conditions of slow wind speeds (1-2 m/s) for both sites. This is observed on the plot at the inner-most rings where the warm colours (red, orange, yellow) are seen.

Higher wind speeds are expected at JOR because the building is higher and therefore subject to stronger winds. This might affect the motion of polluted air plumes passing over the sampling inlet. The higher elevation might also play into lower concentrations if Hg sources were at ground level due to a dilution effect. The higher values observed at low wind speed seems apparent because of a similar reasoning. Under strong wind conditions any pollutants would be dispersed more aggressively over a larger volume compared to under weaker wind speeds. In the

case that the GEM in the air is homogenously mixed, wind speed should not have any effect on concentration.

Figure 12: Polar plot of the mean GEM concentration by wind direction, speed and site for 2015/2016. Cells are separated into 1 m/s wind speed increments and 10° wind direction increments. Wind speed < 0.5 m/s are not shown. Arithmetic mean is represented by cell colour.

3.2.2 Annual – weighted mean of GEM by site

The **Figure 13** plot is coloured according to the percent contribution of Hg to the site. These plots do not give insight to the concentrations observed from any direction, rather it tells us where most of the mercury is coming from in terms of percentage by mass.

Figure 13: Annual weighted mean plot for both sites with wind speed components included as 1 m/s intervals. Speeds <0.5 m/s are rounded down to zero and are not plotted. Cell colours are assigned based on the percentage of Hg observed for any given wind speed and direction combination. Cell values are calculated according to this equation: $\frac{\text{bin mean} \times \text{bin freq.}}{\text{total freq.}}$

From **Figure 13**, the annual weighted mean polar plots for GEM at both sites indicate a strong contribution from the south west direction (4–8% of the total observed Hg if you add up all the cells in this direction) and a moderate contribution (3-6%) from the east (55°-95°). The KHN site also shows a very strong contribution from just north of east (25°-45°), recording between 6 and 8% of total Hg observations. Most of the mercury is recorded under conditions of low wind speed (1 - 2 m/s for KHN and 2 – 4 m/s for JOR) as indicated by the red shaded cells in the inner most rings of the polar plot.

3.2.3 Regional Source Attribution

If regional sources are expected, the polar plots should reveal relatively higher weighted averages from the same directions at both sites and pointing in the direction of the Hg source(s). This is the case for the south west direction where KHN and JOR both measured a high proportion of GEM. A weaker case is made for the north east direction as the two sites did not share a similar GEM profile in this direction; KHN measured a strong response while JOR is basically at a background level. The largest point sources of mercury pollution to air in Ontario are all located within 32 km of Ryerson University (**Figure 14**). The points on the map indicate mercury pollution sources by air according to the national pollution release inventory (NPRI). Only sites which produce more than 5 kg y⁻¹ of Hg are required to report. Values from 2016 are in white, values in 2004 are in yellow. Of the regional sources of Hg to air, it is notable that all the major Hg point sources are in the NE and SW directions, along the coast of Lake Ontario. These include two water treatment plants and metal recycling facility to the NE and a cement plant and a steel manufacturer to the SW.

Figure 14: Regional pollutants to the receptor sites in 2016 and 2004.

3.3 Comparison of average GEM values at KHN with 2004

In 2004 monitoring campaign was undertaken on the KHN building roof with the same equipment setup as 2015/16; both weather and mercury data were recorded. Comparing the two data sets for the same location gives information about past and present values. When comparing the weighted average of GEM to the KHN roof for a 1 year period, it is immediately evident from **Figure 15** that GEM pollution from the southwest direction was dominant in 2004 as well as for 2015/16, indicating local and regional sources from 12 years ago are also present today. The regional map of GEM polluters to air, **Figure 14**, in 2004 and 2015 supports this conclusion.

Figure 15: Annual weighted mean of GEM at KHN for 2004 and 2015/16. Radial axis is wind speed in 0.5 m/s increments, colours in the legend indicate percent contribution of Hg to the receptor site.

The wind frequency observed at the KHN sampling site also demonstrates a high frequency in the directions of the lakeshore, with a higher frequency of observations in the northeast and southwest directions as indicated by the wind rose (**Figure 16**). High mercury concentrations and a high frequency from the same directions give rise to heavily weighted values from those directions.

Figure 16: Wind rose plot showing the frequency of wind direction and speed at the KHN site over both of the sampling campaigns.

The pollutant release inventory for Canada does not account for illegal sources or multiple sources that may cumulatively contribute a significant amount of Hg to the atmosphere. For example crematoriums are estimated to contribute <1% of the global mercury burden via incineration of dental amalgam (UNEP, 2013) but no single crematorium produces enough Hg to be obligated to report their emissions. If there were many crematoria in a small area (there are ~12 or so within the boundary of the map in **Figure 14**) they might contribute a substantial amount of Hg to the surrounding environment.

3.4 Peak Event Analysis

The set of gaseous elemental mercury measurements for each site were analyzed for correlations to meteorological variables. The measurements obtained at both sites were found to be non-normally distributed (**Figure 17**) and tests for normality are presented in *Appendix C*. Spearman's rank correlations were used instead of Pearson's product-moment.

Figure 17: Probability distribution of GEM measurements made at KHN and JOR in 2015/2016 coplotted with Gaussian curves

A peak analysis was performed to determine if any relationship could be observed between meteorological variables and high GEM values (**Table 9 and Table 10**). Spearman's rho (ρ) describes the association between two variables. It should be interpreted just like Pearson's r . The correlation coefficient may take on a value between -1 and 1, with -1 indicating a perfectly negative correlation, +1 indicating a perfectly positive correlation, and 0 indicating no correlation at all. The correlation between two variables are deemed significant if $p < 0.01$. A 2-tailed significance is chosen because there is no a priori reason to expect a 1-tailed result.

At the KHN site, temperature is positively correlated with GEM for the whole set ($\rho=0.265$) but the trend disappears at higher GEM values e.g. 90th percentile ($\rho = 0.090$), 99th percentile ($\rho = -0.118$), and 99.9th percentile ($\rho = -0.078$). As a general trend, temperature and solar radiation have been observed to positively correlate with GEM in some urban and rural studies (Blanchard et al., 2002). Both of these variables accelerate the volatilization of GEM from the ground level at times of peak incident radiation (Poissant et al., 1998). Because of the lack of

correlation in this study, this suggests that surface reemissions are not a major contributor of GEM to the urban environment. For wind speed at both sites there is a weakly negative correlation indicating higher GEM readings are more prevalent at lower wind speeds. This is supported by the polar plot from **Figure 12** where the average GEM is higher for low wind speed. It would be expected that at high wind speeds GEM would be more vigorously dispersed compared to low wind speeds. Indeed this is what is observed when looking at the whole data set. However, when GEM is subsetting for 90 to 99.9 percentile values, wind speeds do not appear to have any association with the measurements.

The correlation coefficient for Spearman's rank, ρ , is weak and inconsistent for all of the subsetting percentile cut-offs for all variables at both sites, indicating that either the meteorological parameters measured have only a small or negligible influence or that other factors like anthropogenic pollution dominate the GEM in Toronto so much so that it buries the effect of meteorological influence. Other studies have also reported no clear correlation between meteorology and GEM but still find empirical trends between the two (Nair et al., 2012; Shon et al., 2008).

Table 9: Spearman's Rank Correlation for Kerr Hall

KHN full set n = 87858		Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1	-.083	-.004	-.180	-.334	-.290	.255	.265	.067	.299
	Sig. (2-tailed)		<.001	.190	<.001	<.001	<.001	<.001	<.001	<.001	<.001

90th percentile n = 8775		Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1.000	-.071**	-.035**	.033**	-.203**	-.200**	.029**	.090**	.040**	.102**
	Sig. (2-tailed)		<.001	.001	.002	<.001	<.001	.007	<.001	<.001	<.001

99th percentile n = 879		Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1.000	.238**	-.063	.144**	.246**	.192**	-.115**	-.118**	-.120**	-.145**
	Sig. (2-tailed)		<.001	.062	<.001	<.001	<.001	.001	<.001	<.001	<.001

99.9th percentile n = 88		Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1.000	.060	.	-.011	.152	.106	-.170	-.078	-.017	-.135
	Sig. (2-tailed)		.577	.	.920	.158	.327	.113	.473	.878	.210

* Correlation is significant at the 0.05 level (2-tailed)

Bold text indicates a correlation > 0.25

Table 10: Spearman's Rank Correlation for Jorgenson Hall

JOR full set	n = 84210	Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1.000	.093	.014	-.248	-.268	-.256	.084	-.229	-.150	.099
	Sig. (2-tailed)	.	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001

90th percentile	n = 8421	Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1.000	.007	-.024*	-.016	-.153**	-.173**	-.014	.030**	.056**	.038**
	Sig. (2-tailed)	.	.527	.029	.145	<.001	<.001	.189	.005	<.001	.001

99th percentile	n = 844	Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1.000	.024	-.028	.238**	-.043	-.084*	-.325**	-.151*	-.011	-.179*
	Sig. (2-tailed)	.	.487	.422	<.001	.213	.014	<.001	<.001	.758	<.001

99.9th percentile	n = 85	Hg	sol	rain	press	ws	gs	wd	temp	rh	dp
Hg	Spearman's Rho (ρ)	1.000	.134	.	-.132	.066	.129	.035	-.073	.050	.110
	Sig. (2-tailed)	.	.221	.	.229	.551	.240	.748	.506	.646	.315

* Correlation is significant at the 0.05 level (2-tailed)

Bold text indicates a correlation > 0.25

In addition to meteorological parameters, many studies used ‘tracer gases’ or ‘co-pollutants’ to gauge the relationship between criteria pollutants (PM, SO₂, NO_x, O₃, CO) and mercury. In Blanchard’s (2002) study found TGM at Egbert was strongly correlated to SO₂ ($R^2 = 0.85$ for logarithmic regression) in the winter, which led them to conclude TGM and SO₂ came from the same source; plumes of air from urban center where coal combustion was practiced for domestic heating. In Houston, highly concentrated plumes of THg were found to be related to combustion tracers (CO, CO₂, NO_x) and high spikes in CO, CO₂, NO_x, SO₂, CH₄ were usually found to be coincident with high TGM events. It was not determined if combustion tracers and atmospheric mercury are directly related or related by another or some combination of other mechanisms, for example planetary boundary layer height or vertical mixing rates (Lan et al., 2014). In Detroit from 2002-2004 mercury emissions, meteorological variables, and various pollutants were measured over 4 separate sampling campaigns. PCA revealed GEM was associated with a factor that has high loadings for CO and NO_x (Lynam et al., 2006). The authors suggest these are indicative of a combustion source and may be related to motor vehicles. The authors also point to Liang et al. (1996) who first measured mercury in gasoline and petroleum products and found diesel, heating oil and gasoline can contain up to 2.97, 0.59 and 3.20 ng/g respectively when extracted with BrCl. However US EPA National Emissions Inventory estimates <1 Mg of Hg is released by mobile sources per year which is less than 1% of the national annual output. Carpi and Chen (2002) presented data from Manhattan in 2000 and also pointed out that traffic may be a cause of elevated mercury in the city but could not associate spikes in TGM values with rush hour spikes motor vehicle traffic. Since Toronto has fewer people now than Manhattan did in 2000, and since motor vehicles have been evaluated to contribute so little Hg to the environment, it stands to reason that they are not a significant source of GEM in this study.

3.4.1 Identifying peak events using maxima polar plots

Another novel way to look at peak events is to plot the max values obtained for each combination of wind speed and direction. **Figure 18** depicts just that for both sampling sites in 2015/2016. The values above 20 ng/m³ were cut-off because there are so few values above 20 that the rest of the plot loses resolution. Similar trends to the mean and weighted mean plots are present here, for example the largest peaks are observed in the north east direction and south west direction for low wind speeds suggesting impact by local sources. Occasionally there are

some anomalously high readings picked up from other directions that cannot be so easily explained by regional sources. At KHN there are 3 large spikes from the south at about 18-20 ng/m³. At JOR there are some high values to the south and south east. It is possible that elevated values from directions that are not NE and SW may be due to local sources. It also may be that a plume originating from one of the aforementioned sources traveled in a non-direct path towards the city such that the plume first travelled one way according to wind direction, then as the wind direction changed, carried the plume to the receptor site. For example a pollutant originating from the NW may have travelled E, then the wind direction may have shifted to blow S where it was registered at the sampling site as coming from the north. The wind rose plot in **Figure 16** suggests that very little wind comes from the south. It seems more likely that local sources are the cause of peak mercury events from directions that are not related to large regional emissions.

Figure 18: Plot of GEM maxima for JOR and KHN from 2015/2016. The plot of maxima assigns cell colour according to the largest GEM value recorded at that site. Bin size = 1. N is equal to the number of wind speed and direction combination since only one Hg concentration is reported per cell.

3.4.2 Diurnal maxima and weighted average GEM by site and daylight

When sites are plotted for maxima separated diurnally in **Figure 19**, max values most often occur and are higher during the day. They also tend to not come from directions of regional sources. This narrows down the sources to daytime GEM pollutants within the city.

Figure 19: GEM maxima for KHN and JOR separated by day (6 am - 6 pm) and night (6 pm - 6 am).

Figure 20: GEM weighted mean separated by day (6 am - 6 pm) and night (6 pm - 6 am).

3.4.3 Weighted mean GEM by site and daylight

The day/night splitting of the weighted average site data in **Figure 20** show a markedly higher GEM contribution to the KHN site at night while the JOR site is relatively uniform regardless of time of day. In contrast to **Figure 19** which suggests local sources are

3.5 Comparison of GEM at urban vs. rural/remote sites and of current & historical data collected in Canada

Figure 21 compares TGM observed (given as arithmetic mean) at urban (KHN), rural (EGB) and remote (ALT) sites. The values are, in the order they appear, 1.62, 1.45, 1.58, 1.36, 4.40, 1.76 ng/m^3 and are for the periods of 2004 and 2010-2016. It is evident that TGM is higher in urban site than rural sites.

Figure 21: Boxplot of annual GEM collected from a remote (Alert, Nunavut) and rural (Egbert, Ontario) sites for 2004 and 2010 and an urban (KHN) site for 2004 and 2015/2016.

At each site, the average TGM decreased from 2004 to 2010 (or 2015/16). This is most noticeable at the KHN site where a 60.4% decrease is observed over 16 years. A 10.5% decrease is observed at Alert and a 13.9% decrease at Egbert over 8 years. The decreasing average GEM points to a reduction in overall mercury in Toronto's atmosphere in 2015/2016 compared to past years. Decreased variability also points to a reduction in frequent fluctuations in mercury concentration. The decrease in overall concentration and variability might be attributed to Ontario's ban on coal powered energy generation and the ban on importing mercury-containing products. Given there is an overall reduction in mercury pollution from nearby anthropogenic

sources, one would expect to measure a larger decrease closer to pollution sources compared to more distant sites.

In the 10 year period from 1995 to 2005 large declines of 16.6% and 13.1% were noticed at Point Petre and St. Anicet, the sites adjacent to Toronto and Montreal respectively. Egbert is also near Toronto, closer in fact than Point Petre, and only experienced a 2.2% decline while a further, more rural site Burnt Island experienced a 5.1% decline (Temme et al., 2007). The data do not necessarily overlap in the same time period. Another study from the CAMNet from 2000-2009 compared mercury at two Arctic sites, one of the being Alert, with 3 mid-latitude sites. The ten-year site trends listed in order of decreasing latitude are $-0.9\% \text{ yr}^{-1}$ at Alert, $-2.1\% \text{ yr}^{-1}$ at Kuujuarapik, $-1.9\% \text{ yr}^{-1}$ at St. Anicet, $-1.6\% \text{ yr}^{-1}$ at Kejimikujik, and $-2.2\% \text{ yr}^{-1}$ at Egbert (Cole et al., 2013). Trends were calculated using the seasonal Mann-Kendall test for monotonic trend and Sen's slope calculation.

The rural and remote CAMNet sites are located in regions free from direct influence of anthropogenic effects, thus approximate the background levels of mercury in ambient air as all the sites are located in regions free from direct influences of anthropogenic effects. Because of this, associations between meteorological variables and GEM become more apparent. In the above studies and Blanchard's 2002, all of which came from CAMNet data obtained by Environment Canada researchers, they come to similar conclusions on a variety of comparisons. For instance TGM reached maxima in the spring and winter, minima in the early fall (Blanchard et al., 2002; Temme et al., 2007). Sites in close proximity to urban centers or those receiving air masses from the direction of an urban center measured Hg to be higher than other rural sites with the exception of Alert due to different circumstances regarding arctic atmospheric and ocean chemistry. All the studies measured some statistically significant decreases in TGM over the sampling campaign for most, if not all sites. However the rate of decrease varied seasonally and mid-latitude sites showed faster decreases in median TGM compared to arctic sites (Cole et al., 2013).

3.6 Effect of Aura building

Between the sampling campaigns undertaken in Toronto in 2004 and 2015/2016 there was a large skyscraper built in 2010 and zoned for commercial and residential use in the 265-295° direction relative to KHN. The GEM and meteorological data collected in 2004 and 2015/2016 were compared for this subset of directions to see if the skyscraper has an effect on the

concentration and distribution of GEM. Looking back to **Figure 15** and comparing 265-295° directions (east and just north of east) for 2004 and 2015/2016, it is evident that the GEM profile to the site is largely the same over both sampling periods i.e. a high proportion of GEM is observed at low wind speeds. The plots even suggest that under 0.5 m/s winds from the east in 2004 are proportionally higher than from the same direction after the building was built. Suppose Aura building did contribute significant GEM to the sampling site, the polar plot in **Figure 15** would show higher proportions of GEM along the 265-295° directions for all wind speeds. This is not to say that the Aura building *might* not contributing Hg to the outdoor air, just that it was not determined to be a significant or measureable source in this experiment. It is also noteworthy to keep in mind that Hg in indoor air is directly related to Hg sources within the space, ventilation, and regulations pertaining to building materials.

Given that indoor air has been reported to have higher GEM than outdoor air, it was hypothesized that a higher proportion of GEM might come from the direction of the building or that GEM concentrations from that direction might be higher than others. Subsetting the data based on direction revealed very different GEM distributions between sampling campaigns as shown in **Figure 22 a) and b)** where the 2004 data span a larger concentration range compared to 2015/2016. Even without subsetting for direction, the shapes of the distributions for 2004 and 2015/2016 do not change much.

Figure 22: Histograms for GEM measured at KHN from the 265-295° direction from a) 2004 and b) 2015/2016; c) Boxplot of GEM measurements comparing KHN 2004 to 2015/2016 for wind direction 265-295°

Looking the box plot (**Figure 22 c)**) it is immediately clear that mercury pollution decreased between 2004 and 2016 as observed elsewhere. Because the 2004 background levels were so high and have since decreased, and because the Aura building was built during this period of mercury policy reform, it is very hard to tell from the data that was gathered if Aura even produced any mercury that could be measured at a site downwind. If the building does produce mercury, which we can expect to be true because generally indoor Hg levels are higher than outdoor, we were just not able to measure it because it got lost to the background GEM in the city. Huigeras et al. (2014) reported a similar phenomenon whereby high GEM measured in a herbarium tended to quickly disperse and dilute to much lower values. Since urban background levels are already very low and indoor air, while higher than outdoor air, is not orders of magnitude higher, it is reasonable to assume the indoor-to-outdoor exchange of mercury would be minimal and hard to measure at a site 300 m away in an urban atmosphere where there is much turbulence, pollutant dispersion and dilution as is the case with KHN and Aura.

4.0 CONCLUSION

Gaseous elemental mercury measured at 2 sites demonstrate similar behaviour in concentration in that GEM fluctuations, spikes and troughs coincide, and seasonal averages are largely consistent between the sites despite them being separated by a distance of 136 m and a height of 31 m. GEM concentration at Kerr Hall remained 0.2 to 0.4 ng/m³ higher than Jorgenson Hall for the majority of the study with the average annual concentration for the 2015/2016 year being 1.78 ± 0.89 ng/m³ and 1.46 ± 0.54 ng/m³ respectively.

Prolonged periods of elevated mercury levels are thought to be associated with regional sources and meteorological influence while short-lived spikes in GEM, especially when they appear simultaneously at both sites are thought to be associated with local sources. These sources, if they exist, are not registered to the NPRI and warrant further investigation.

Mercury measured at the sampling sites was highest from the northeast and southwest directions due to the strong presence of regional sources and a high frequency of wind from those directions. Comparing annual 2004 values from KHN to 2015/2016, the same heavily weighted pattern is observed in the southwest but a new source appears in the northeast for 2015/2016.

Spearman's correlations on the peak events from both sites in 2015/2016 did not reveal any strong associations between GEM and meteorological variables, suggesting local and regional sources are the primary actor in influencing GEM at the receptor sites. Large spikes (10 – 20 ng/m³) were also observed from directions not correlated with regional sources indicating that local emissions might be responsible for the occasional GEM spikes.

When GEM is compared across urban and rural sites from 2004 to 2010 or 2015/2016, decreases of 10.5% to 16.6% are observed in a rural setting while in Toronto, decreases of 60.4% have been measured. The dramatic decrease comes from provincial and national efforts to reduce and eliminate mercury waste to air.

Appendix A

Example of Tekran 2537A analyzer output

Date	Time	Typ	C	Stat	Flag	AdTim	Vol	BI	BIDev	MaxV	Area	ng/m3
16-01-11	15:03:40	CLN	A	NP	0	0	0	0.138	0.049	0	0	0
16-01-11	15:06:56	CLN	B	OK	0	195	3.34	0.135	0.109	0.13	23642	0
16-01-11	15:10:00	CONT	A	OK	0	300	4.99	0.137	0.031	0.14	15992	1.245
16-01-11	15:15:00	CONT	B	OK	0	300	5	0.139	0.043	0.142	18498	1.241
16-01-11	15:20:00	CONT	A	OK	0	300	5	0.139	0.051	0.142	17364	1.348
16-01-11	15:25:00	CONT	B	OK	0	300	5	0.139	0.041	0.143	19367	1.299
16-01-11	15:30:00	CONT	A	OK	0	300	5	0.139	0.051	0.143	17738	1.377
16-01-11	15:35:00	CONT	B	OK	0	300	5	0.139	0.053	0.143	19129	1.283
16-01-11	15:40:00	CONT	A	OK	0	300	5	0.14	0.047	0.143	17358	1.347
16-01-11	15:45:00	CONT	B	OK	0	300	5	0.139	0.052	0.143	18770	1.259
16-01-11	15:50:00	CONT	A	OK	0	300	5	0.14	0.056	0.143	17524	1.36
16-01-11	15:55:00	CONT	B	OK	0	300	5	0.139	0.052	0.142	18088	1.213
16-01-11	16:00:00	CONT	A	OK	0	300	5	0.139	0.045	0.143	18043	1.401
16-01-11	16:05:00	CONT	B	OK	0	300	5	0.139	0.07	0.143	19066	1.279
16-01-11	16:10:00	CONT	A	OK	0	300	5	0.14	0.043	0.142	16788	1.303
16-01-11	16:15:00	CONT	B	OK	0	300	5	0.139	0.044	0.143	18424	1.236

Appendix B

Data aggregation and quality control

```
#### Jorgenson Hall ####
# change month and output file name as necessary

library(XLConnectJars, pos=15)
library(XLConnect, pos=15)
library(stringr)
library(dplyr)

jor_weather <-
  readXL("C:/Users/Daniel/Documents/Weather Data/2016 Weather Data/Treated/JOR/JOR - JULY
2016.xlsx", rownames=FALSE, header=TRUE, na="", sheet="July", stringsAsFactors=TRUE)

names(jor_weather)[c(1,2,3,4,5,6,7,8,9,10,11,12,13)] <-
  c("#", "time", "sol", "rain", "press", "volt", "current", "ws", "gs",
    "wdir", "temp", "rh", "dp")

jor_weather <- within(jor_weather, {
  NA. <- NULL
  NA..1 <- NULL
  NA..2 <- NULL
  NA..3 <- NULL
  NA..4 <- NULL
  NA..5 <- NULL
  X <- NULL
  X. <- NULL
})      # sometimes extra empty columns are read in from excel and they are given these default names
names(jor_weather) <- make.names(names(jor_weather))

jor_hg <-
  readXL("C:/Users/Daniel/Documents/Mercury Analyzer Data/Formatted (pre QC)/0147/all daily JOR.xlsx",
  rownames=FALSE, header=TRUE, na="", sheet="Jul", stringsAsFactors=TRUE)

jor_hg$Time <- str_sub(jor_hg$Time, -8, -4)
nrow(jor_hg)
nrow(jor_weather)
comb_data <- data.frame(jor_hg, jor_weather)
comb_data$dp <- round(comb_data$dp, digits=1) ## if dp needs to be rounded

comb_data <- within(comb_data, {
  X <- NULL
  X. <- NULL
```

```

X.1 <- NULL
})

```

```

write.table(comb_data, "c:/Users/Daniel/Documents/Mercury Analyzer Data/Formatted Hg + Weather (pre
QC)/JOR 2016 JULY.txt", sep="\t")

```

```

# Turn this output into an excel file. At this point we want to rename the 'comb_data' and do the QC
# This is mostly simple subsetting commands but needs some column manipulation to compare
# consecutive rows ie. need to duplicate columns and shift down a row to compare Xn to Xn+1 when
# looking at shifts in baseline voltage

```

```

# duplicate BI column and bind to end of data frame
QC.df <- comb_data
QC.df <- cbind(QC.df, QC.df[,9])
names(QC.df) <- make.names(names(QC.df))

```

```

# rename for convenience
names(QC.df)[c(26)] <- c("BI.QC")

```

```

# function to shift column up by 1 row and pad with NA at the end
shift <- function(x, n){
  c(x[-(seq(n))], rep(NA, n))
}

```

```

# apply function to the test column
QC.df$BI.QC <- shift(QC.df$BI.QC, 1)

```

```

### QC parameters for Hg analyzer ###
QC.df$ng.m3[abs(QC.df$BI-QC.df$BI.QC) > 0.01] <- NA
QC.df$ng.m3[QC.df$BI.Dev > 0.1491] <- NA
QC.df$ng.m3[QC.df$BI < 0.01] <- NA
QC.df$ng.m3[QC.df$Vol > 5.05] <- NA
QC.df$ng.m3[QC.df$Vol < 4.95] <- NA
QC.df$ng.m3[QC.df$Stat != "OK"] <- NA
QC.df$ng.m3[QC.df$ng.m3 < 0.200] <- NA
QC.df$ng.m3[QC.df$Flag != 0] <- NA
QC.df$Flag[QC.df$Flag != 0] <- NA

```

```

# remove test column
QC.df <- within(QC.df, {
  BI.QC <- NULL
})

```

```

### Weather Parameters ###
# sensors output values of '-888.88' if they are not working properly

```

```
QC.df$ng.m3[QC.df$rain <0] <- NA
QC.df$ng.m3[QC.df$ws <0] <- NA
QC.df$ng.m3[QC.df$gs <0] <- NA
QC.df$ng.m3[QC.df$wdir <0] <- NA
QC.df$ng.m3[QC.df$sol <0] <- NA
QC.df$ng.m3[QC.df$press <0] <- NA
```

```
write.table(QC.df, "c:/Users/Daniel/Documents/Mercury Analyzer Data/QC treated Hg + Weather/JOR JUL
2016.txt", sep="\t")
```

Cartridge test for agreeability

```
ABcompare <-  
  read.table("C:/Users/Daniel/Documents/Mercury Analyzer Data/Raw/0147/TK160801.TXT",  
    header=FALSE, sep=";", na.strings="NA", dec=".", strip.white=TRUE)  
  
names(ABcompare)[c(1,2,3,4,5,6,7,8,9,10,11,12,13)] <- c("Date", "Time", "Typ",  
  "C", "Stat", "Flag", "AdTime", "Vol", "BI", "BIDev", "MaxV", "Area", "ng.m3")  
  
x1 <- na.omit(ABcompare)  
x2 <- subset(x1, subset=BIDev<0.150)  
x3 <- subset(x2, subset=Flag==0)  
x4 <- subset(x3, subset=Stat=="OK")  
x5 <- subset(x4, ng.m3 > quantile(x4$ng.m3, c(.05)) & ng.m3 < quantile(x4$ng.m3, c(.95)))  
  
# Do 5% test on x5  
x5$C <- as.character(x5$C)  
  
# Table for MEAN ng.m3:  
with(x5, tapply(ng.m3, list(C), mean, na.rm=TRUE))  
# Table for SD ng.m3:  
with(x5, tapply(ng.m3, list(C), sd, na.rm=TRUE))  
  
meanA <- mean(x5$ng.m3[x5$C=="A"])  
meanB <- mean(x5$ng.m3[x5$C=="B"])  
  
percent.diff <- abs((meanA-meanB)/((meanA+meanB)/2))*100  
percent.diff
```

Peak analysis and correlation tables

Peak Analysis with "COMBINED - removed NA's" excel sheet in

QC'd weather and Hg data folder

NB: I had to go into the excel file and remove the NA's manually from 1 column

```
all_data <-  
  readXL("C:/Users/Daniel/Documents/Mercury Analyzer Data/QC treated Hg + Weather/Combined.xlsx",  
    rownames=FALSE, header=TRUE, na="", sheet="linear corr", stringsAsFactors=TRUE)
```

```
all_data <- na.omit(all_data)
```

```
all_data <- within(all_data, {  
  AdTim <- NULL  
  volt <- NULL  
  Area <- NULL  
  BI <- NULL  
  BDev <- NULL  
  C <- NULL  
  current <- NULL  
  date1 <- NULL  
  Flag <- NULL  
  MaxV <- NULL  
  Stat <- NULL  
  time1 <- NULL  
  Typ <- NULL  
  volt <- NULL  
  X <- NULL  
})
```

Subset KHN and JOR

```
khn_pr <- subset(all_data, subset=site=="KHN")
```

```
jor_pr <- subset(all_data, subset=site=="JOR")
```

take the top 10% of observations for Hg at a site

```
khn_pr90 <- subset(khn_pr, ng.m3 > quantile(khn_pr$ng.m3, c(.90)))
```

```
khn_pr99 <- subset(khn_pr, ng.m3 > quantile(khn_pr$ng.m3, c(.99)))
```

```
khn_pr999 <- subset(khn_pr, ng.m3 > quantile(khn_pr$ng.m3, c(.999)))
```

```
jor_pr90 <- subset(jor_pr, ng.m3 > quantile(jor_pr$ng.m3, c(.90)))
```

```
jor_pr99 <- subset(jor_pr, ng.m3 > quantile(jor_pr$ng.m3, c(.99)))
```

```
jor_pr999 <- subset(jor_pr, ng.m3 > quantile(jor_pr$ng.m3, c(.999)))
```

Correlation Tables

with r and P values need to be obtained with library(Hmisc)

```
library(Hmisc)
```

```
# Remove variables that are not going to be used
```

```
khn_cor <- within(khn_pr, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
khn_cor90 <- within(khn_pr90, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
khn_cor99 <- within(khn_pr99, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
khn_cor999 <- within(khn_pr999, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
jor_cor <- within(jor_pr, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
jor_cor90 <- within(jor_pr90, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
jor_cor99 <- within(jor_pr99, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
jor_cor999 <- within(jor_pr999, {  
  site <- NULL  
  date <- NULL  
  Vol <- NULL  
})
```

```
rcK <- rcorr(as.matrix(khn_cor), type="spearman")
```

```
rcJ <- rcorr(as.matrix(jor_cor), type="spearman")
```



```
# Kerr Hall  
print(rcK$r, digits = 3)  
print(rcK$P, digits=3)
```

```
# Jorgenson  
print(rcJ$r, digits = 3)  
print(rcJ$P, digits=3)
```

Appendix C

i) Shapiro-Wilk

Shapiro-Wilk test for normality tests if a series of observations are normally distributed. The function in R only handles 1000 observations. Each site was randomly sampled from without replacement. The W value changes with each iteration because different values are sampled every time. The p-value does not change.

data: KHN QC'd Hg data $W = 0.78731$ $p\text{-value} < 2.2e-16$

data: JOR QC'd Hg data $W = 0.80219$ $p\text{-value} < 2.2e-16$

H_0 : data comes from a normally distributed population

$p < 0.05$ therefore reject the null hypothesis that data comes from normally distributed population

Proceed with the assumption that data is non-normally distributed

ii) Quantile-Quantile plots

iii) Kolmogorov-Smirnov test

The KS test is applied to two non-parametric samples to see if they came from the same distribution. It takes the 2nd data set and tests it against the 1st. No assumptions are made on the distribution except that it's non-normal and deals with a continuous variable.

iv) Kruskal-Wallis & Mann-Whitney U tests

Mann-Whitney U tests the null hypothesis that it is equally likely a randomly selected value from one sample will be less than or greater than a randomly selected value from a second sample .

Kruskal-Wallis rank sum test for ng.m3 by season for 250 observations per season

Ho : GEM measured at the sampling site are drawn from identical populations across 4 seasons

$$\chi^2 = 5095.4, \text{ df} = 3, \text{ p-value} = <2.2 \times 10^{-16}$$

$p < 0.05$ therefore reject Ho

Mann-Whitney U tests for comparisons between seasons at each site for n=250 for each season

Kerr Hall North	W	p-value	difference
summer-autumn	26342	0.9652	No
summer-winter	36153	1.306×10^{-6}	Yes
summer-spring	22769	1.734×10^{-5}	Yes
autumn-winter	31895	7.639×10^{-5}	Yes
autumn-spring	22026	.0008697	Yes
winter-spring	29814	0.7887	No

Jorgenson Hal	W	p-value	difference
summer-autumn	22604	$<2.2 \times 10^{-16}$	Yes
summer-winter	37751	$<2.2 \times 10^{-16}$	Yes
summer-spring	14678	1.454×10^{-9}	Yes
autumn-winter	12520	0.008651	Yes
autumn-spring	21226	4.65×10^{-14}	Yes
winter-spring	34031	2.993×10^{-14}	Yes

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