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Atmospheric Deposition Of Heavy Metals In Toronto

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ATMOSPHERIC DEPOSITION OF HEAVY METALS IN TORONTO

by

Muhammad Yousaf

Master of Science from University of the Punjab, Lahore, Pakistan, 1999

A Thesis

presented to Ryerson University

in partial fulfillment of the

requirements for the degree of

Master of Science

in the program of

Molecular Science

Toronto, Ontario, Canada, 2012

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ABSTRACT

ATMOSPHERIC DEPOSITION OF HEAVY METALS IN TORONTO

Muhammad Yousaf

Master of Science, Molecular Science, Ryerson University, 2012

Atmospheric deposition rates of heavy metals (As, Cd, Co, Cu, Hg, Mn, Ni, Pb, and Zn) were determined from July 2009–December 2010 in downtown Toronto. Atmospheric deposition samples were collected using samplers with plastic, glass and water surfaces from two rooftops (15 m and 59 m above ground) in the city core of Toronto. Mercury species were analyzed using Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) and the rest of metals were analyzed by acid digestion combined with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

The results showed that the deposition of heavy metals was higher on water surface as compared to both the plastic and glass surfaces and that Cu, Mn, Pb and Zn showed higher deposition rates as compared to As, Cd, Co and Ni. The deposition rates were higher on Kerr Hall North (KHN) site indicating contribution from local sources. For total mercury (THg) and methyl mercury (MeHg), the deposition rates were higher on Jorgenson (JOR) site as compared to KHN site.

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DEDICATION

I would like to dedicate this thesis to my parents for their endless support and blessings who educated and shaped me into the person I currently am.

TABLE OF CONTENTS

AUTHOR’S DECLARATION	ii
ABSTRACT	iii
ACKNOWLEDGEMENT	iv
DEDICATION	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xi
Part 1. ATMOSPHERIC DEPOSITION OF HEAVY METALS IN TORONTO	1
1. Introduction	1
1.1. Definition of heavy metals	1
1.2. Heavy metals in the atmosphere	1
1.3. Anthropogenic sources of heavy metals	2
1.4. Factors affecting the distribution of heavy metals in the atmosphere	4
1.5. Pathways of heavy metal access	6
1.6. Toxicity of the heavy metals	7
1.7. Atmospheric deposition of heavy metals	9
1.8. A literature review on the atmospheric deposition	9
1.9. Study objectives	13
2. Materials and Methods	14
2.1. Sampling Locations	14
2.2. Development of Samplers	14
2.3. Sample collection	16
2.4. Analysis of Heavy Metals	16
2.5. Calibration and standardization	17
2.6. Quality Control (QC)	20
2.7. Deposition rate’s calculation	23

2.8.	Calculating the enrichment factor.....	24
3.	Results and discussions	25
3.1.	Concentration of heavy metals at the KHN site	25
3.2.	Concentration of heavy metals at the JOR site.....	26
3.3	Deposition rates of heavy metals in Toronto.....	27
3.4.	Distribution of heavy metals on different surfaces.....	31
3.5.	Surface comparison	34
3.6.	Effect of height on the deposition of heavy metals (Sites Comparison)	35
3.7.	Comparison of deposition rates of heavy metals in Toronto with other studies	37
3.8.	Repetition of the atmospheric data	41
Part 2. ATMOSPHERIC DEPOSITION OF TOTAL MERCURY AND METHYL MERCURY		45
1.	Introduction.....	45
1.1.	Properties of Mercury	45
1.2.	Toxicity of Mercury.....	47
1.3.	Mercury in the atmosphere	48
1.4.	Atmospheric Deposition of Mercury	49
1.5.	Study Objectives.....	52
2.	Materials and Methods	53
2.1.	Sampling Locations	53
2.2.	Sampling and analytical procedures	53
2.3.	Determination of total mercury	53
2.4.	Determination of methyl mercury	56
2.5.	Calibration and standardization	58
2.6.	Quality Control (QC).....	60
3.	Results and Discussion.....	64
3.1.	Deposition of THg.....	64
3.2.	Distribution of THg among sites and surfaces	69
3.3.	Deposition of MeHg	70
3.4.	Distribution of MeHg among sites and surfaces	72

3.5. Surface and Site comparison by means of Enrichment Factor	74
3.6. THg vs MeHg	76
Conclusions	78
Future Work	79
Appendices	80
Appendix I	81
Appendix II	86
References	95

LIST OF TABLES

Table 1: Anthropogenic sources and uses of heavy metals, through which they can be introduced into the environment.....	3
Table 2: Ecotoxicological effects of heavy metals through which they can be harmful to the living organisms.	8
Table 3: Enrichment factors (EF) with glass surface as a reference.....	35
Table 4: Comparison of deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) for heavy metals in urban environments	39
Table 5 : Deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) of heavy metals from October–December 2011 in repetition samples.....	43
Table 6: The mass of THg (ng) deposited on each surface throughout the sampling period	65
Table 7: Comparison of total mercury deposition fluxes in urban environments.....	68
Table 8: The mass of MeHg (ng) deposited on each surface throughout the sampling period	71
Table 9: Enrichment factor (EF) for Hg species as a function of surface (to show surface comparison) when glass surface is taken as a reference.....	75
Table 10: Enrichment factor (EF) for Hg species as a function of sites (to show sites comparison) when KHN is taken as a reference.	76
Table 11: Comparison of THg and MeHg on plastic, glass and water surfaces at both sites.....	77

LIST OF FIGURES

Figure 1: Sampling locations in downtown Toronto	14
Figure 2: Samplers with plastic, glass and water surfaces.....	15
Figure 3: Calibration curves of the analyzed heavy metals with error bars shown as SD (n=3)..	19
Figure 4: Deposition rates of the individual metals deposited at KHN site.....	29
Figure 5: Deposition rates of the individual metals deposited at JOR site.	30
Figure 6: Box plots of the individual metals showing the distribution of data among sites.....	33
Figure 7: The deposition rates of the analyzed metals on plastic, glass and water surfaces.	36
Figure 8: Purge and trap assembly for the analysis of THg.....	54
Figure 9: Schematic diagram of the CVAFS system for the determination of THg.....	55
Figure 10: Purge and trap assembly for the analysis of MeHg.....	56
Figure 11: Schematic diagram of the CVAFS system for the determination of MeHg interfaced with isothermal GC and pyrolytic decomposition column.....	57
Figure 12: Comparison of THg's monthly deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) on different surfaces collected on the rooftops of JOR (a) and KHN (b) sites.	67
Figure 13: Box plots showing the distribution of THg among different sites and surfaces in downtown Toronto (January 2010 – December 2010).....	70
Figure 14: Comparison of MeHg deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) on different surfaces collected from the rooftops of JOR (a) and KHN (b) sites.	72
Figure 15: Box plots showing the distribution of MeHg among different sites and surfaces in downtown Toronto (January 2010 – December 2010).....	74

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
Ar	Argon
As	Arsenic
Cd	Cadmium
CF	Calibration factor
Co	Cobalt
Cr	Chromium
Cu	Copper
CVAFS	Cold vapor atomic fluorescence spectrophotometer
DPM	Diesel particulate matter
EF	Enrichment factor
GC	Gas chromatography
GEM	Gaseous elemental mercury
GI	Gastrointestinal
GOM	Gaseous oxidized mercury
GTA	Greater Toronto area
HDPE	High density polyethylene
Hg	Mercury
Hg ⁰	Elemental mercury
HM	Heavy metals

ICP-AES	Inductively coupled plasma atomic emission spectrophotometry
ICP-MS	Inductively coupled plasma mass spectrophotometry
IPR	Initial precision and recovery
JOR	Jorgenson
KHN	Kerr hall north
LFS	Laboratory fortified solution
LRB	Laboratory reagent blank
MDL	Method detection limit
MeHg	Methyl mercury
MMT	Methylcyclopentadienyl manganese tricarbonyl
Mn	Manganese
MS	Matrix spike
MSD	Matrix spike duplicate
N ₂	Nitrogen
Ni	Nickel
NIST	National institute of standards and technology
OPR	Ongoing precision and recovery
Pb	Lead
PBT	Persistent bioaccumulative toxin
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
QCS	Quality control sample

RPD	Relative percent deviation
RSD	Relative standard deviation
SD	Standard deviation
SRM	Standard reference material
TEL	Tetraethyl lead
THg	Total mercury
V	Vanadium
Zn	Zinc

Part 1

ATMOSPHERIC DEPOSITION OF HEAVY METALS IN TORONTO

1. Introduction

1.1. *Definition of heavy metals*

The term “heavy metals” has been defined in different ways over the years. It has been defined on the basis of density, specific gravity, atomic weight, atomic number, toxicity etc. (Duffus, 2002). It is often used as a group name for metals and metalloids that have been associated with contamination and potential toxicity or ecotoxicity (Duffus, 2002). It is a term generally used for metallic elements having higher atomic weight and associated with toxicity (Draghici *et al.* 2011). Trace elements, microelements, and trace metals are some other commonly used terms for heavy metals (Adriano, 2001).

1.2. *Heavy metals in the atmosphere*

Heavy metals exist naturally in the Earth’s crust at low concentration, generally less than 100 ppm. Minerals are important geological sources of heavy metals (Vladimir, 2002). They are transported out of soil through a number of processes like plant biomass removal and erosion/leaching (Schründer-Lenzen, 2007). They are also released into the environment by many human activities. The release of heavy metals to the environment starts at the beginning of the production chain (whenever ores are mined), continues during the use of products containing them, and also occurs at the end of the production chain (Bradl, 2005).

Heavy metals are carried in the atmosphere as gases, aerosols, and particulates (Bradl, 2005). Sources of heavy metals are mineral dusts, sea salt particles, extraterrestrial matter,

volcanic aerosols, forest fires, and industrial sources such as emissions from transportation, coal combustion, and fugitive particulate (particulate matter produced by activities such as construction projects, demolition, road repairs and) emission (Kouimtzis and Samara, 1995). The substances released into the air are spread and affect humans, animals, and plants. The pollutants are released at the point sources and are then transported by prevailing air currents. During transportation, they can become associated with precipitation or transformed into different forms by chemical reactions.. Heavy metals that are volatile or those attached to air-borne particles can be dispersed throughout the atmosphere, often thousands miles away from the site of initial release (Rashad and Shalaby, 2007).

1.3. Anthropogenic sources of heavy metals

Human activities have drastically altered the biogeochemical cycles and balance of heavy metals in the environment. Where natural sources are dominated by parent rocks and metallic minerals, the principal man-made sources of heavy metals are agricultural activities, as fertilizers, animal manures, and pesticides containing heavy metals are widely used, industrial point sources (e.g., mines, foundries and smelters), diffuse sources such as combustion by-product (Mohaupt *et al.*, 2001), vehicle emissions (Davis *et al.*, 2011), microelectronic products, and solid waste disposal. Public electricity and heating plus residential sectors have also been found as major contributors towards the emission of heavy metals (EMEP Status Report 2/2005). Table 1 shows some of the common uses of heavy metals by which they can be introduced into the environment.

Table 1: Anthropogenic sources and uses of heavy metals through which they can be introduced into the environment.

As	Additives to animal feed, wood preservative (copper chrome arsenate), special glasses, ceramics, pesticides, insecticides, herbicides, fungicides, rodenticides, algaecides sheep dip, electronic components (gallium arsenate semiconductors, integrated circuits, diodes, infra-red detectors, laser technology), non-ferrous smelters, metallurgy, coal-fired and geothermal electrical generation, textile and tanning, pigments and anti-fouling paints, light filters, fireworks, veterinary medicines.
Cd	Ni/Cd batteries, pigments, anti-corrosive metal coatings, plastic stabilizers, alloys, coal combustion, neutron absorbers in nuclear reactors. Electronics, plastics, air pollution, ceramic glazes/enamels, cigarette smoke, contaminated water, food (if grown in cadmium-contaminated soil), fungicides, mines, paints, power and smelting plants.
Co	Cobalt is not found as a native metal but is mainly obtained as a by-product of nickel and copper mining activities. It can be emitted from coal combustion and mining, processing of cobalt-containing ores and the production and use of cobalt chemicals. Power plants, metallurgy (in superalloys), ceramics, glasses, paints.
Cu	Good conductor of heat and electricity, and used in water pipes, roofing, kitchenware, chemicals and pharmaceutical equipment, pigments, alloys. Comes mainly from the erosion of overhead cables by railway traffic. In addition, as for the other heavy metals, ferrous and non-ferrous metal production processes, the treatment of waste, and combustion are all, to varying degrees, major sources of copper emissions.
Mn	Production of ferromanganese steels, electrolytic manganese dioxide for use in batteries, alloys, catalysts, fungicides, antiknock agents (e.g. methylcyclopentadienyl manganese tricarbonyl (MMT) $(CH_3C_5H_4)Mn(CO)_3$ supplement to the tetraethyl lead (TEL) to increase the fuel's octane rating), pigments, dryers, wood preservatives, coating welding rods.
Ni	As an alloy in the steel industry, electroplating, Ni/Cd batteries, arc-welding, rods, pigments for paints and ceramics, surgical and dental prostheses, molds for ceramic and glass containers, computer components, catalysts, cigarette smoke, tobacco. Nickel is released into the air by power plants and trash incinerators.
Pb	Antiknock agents (TEL), tetramethyl lead, lead-acid batteries, pigments, glassware, ceramics, plastic, in alloys, sheets, cable sheathings, solder, ordinance, pipes or tubing, smelting operations. Industrial, vehicular emission paints and burning of plastics, paper, many of the foods we eat, soil contamination. Lead pollution came primarily from cars in the past i.e. vehicle emission. Today, lead pollution primarily comes from lead smelters, metal processing plants and incinerators.
Zn	Zinc alloys (bronze, brass), anti-corrosion coating, batteries, cans, polyvinyl chloride (PVC) stabilizers, precipitating Au from cyanide solution, in medicines and chemicals, rubber industry, paints, printing plates, building materials, railroad car linings, automotive equipment, soldering and welding fluxes.

Modified from (Bradl, 2005, Siegel, 2002)

1.4 Factors affecting the distribution of heavy metals in the atmosphere

Different studies have determined different concentrations of the heavy metals in the atmosphere. The reason for this is the variety of factors that influence the levels of heavy metals. These factors can be the height of sampler above ground, distance from the source, distance from building, type of sampler, wind speed, wind direction, air stability, temperature, season, traffic volume, sampling period etc. (Fergusson, 1990; Ali *et al.*, 1986; Morselli *et al.*, 2003; Davis *et al.*, 2011; Hovmand *et al.*, 2008). Sampling media can be another factor. In recent years, studies have been conducted on moss plant (Aboal *et al.*, 2010), spinach (Sharma *et al.*, 2008), crops and vegetables (Pandey *et al.*, 2009; Azimi *et al.*, 2004). Some of the factors can be controlled by the experiment, e.g. the sampling equipment/position of sampler, but some are outside the control of the experiment, e.g. the weather. Some of the main factors are explained below.

1) Winds: Wind speed and wind direction are important factors in determining the atmospheric levels of heavy metals as wind promotes the dilution and dispersal of air pollutants. The low concentration because of the wind does not mean that the element is not being emitted from the source but rather it is more rapidly dispersed and diluted (Simmonds *et al.*, 1983).

2) Sampling factors: A number of sampling factors influence the observed levels of the heavy metals. Some of these factors are the length of the sampling time, direction of the wind with respect to the sampler, the distance from the source etc.

3) The climate in cities: The climate within cities can be different to surrounding rural areas, and is influenced by the terrain, i.e. buildings, high energy consumption and subsequent loss to the atmosphere, and reflecting surfaces. The reduced wind speed, loss of heat to the atmosphere at night from surfaces, which are good heat conductors, provide conditions that trap pollutants.

In addition cities become heat islands and air circulates within them which help to keep the material within the city (Fergusson, 1990).

4) Vehicle emission: The concentration of heavy metals in air is related to the traffic volume. Higher levels of heavy metals were observed along highways and roads of higher traffic density (Davis *et al.*, 2011; Sharma *et al.*, 2008). This could be because of the fact that the gasoline additives, used to increase the gasoline's octane rating, often are formulated with heavy metals. Those metal-containing additives mainly refer to antiknock agents such as tetraethyl lead (TEL), methylcyclopentadienyl manganese tricarbonyl (MMT), ferrocene etc. Diesel vehicles can produce black soot [diesel particulate matter (DPM)] from their exhaust, which consists of unburned carbon compounds together with those impurities of heavy metals bound to the particulate matters (Wang *et al.*, 2009). Also it has been shown that brake linings are a major source of metal emissions such as Cd, Cu, Pb and Zn in urban areas (Bergback *et al.*, 2001; Westerlund, 2001). Similar studies have reported that vehicle tires have been a great source of heavy metals such as Zn and Cd (Legret and Pagotto, 1999; Sorme and Lagerkvist, 2002).

5) Particle size and residence time: The size of particles plays an important role in the dispersion of pollutants from the source of their emission. The size of atmospheric particles ranges from 0.001 to 100 μm in diameter (Paulhamus, 1972; Brook *et al.*, 2007; wang *et al.*, 2006). Particles < 2 μm generally come from anthropogenic sources, whereas when they are above 2 μm , the main source is wind-blown and re-entrained dust. For a number of cities where anthropogenic sources dominate, the aerosol sizes mainly span 0.12-0.7 μm , of which 20-25% lies at the lower end of the range (Nriagu, 1978; Health Canada, 2007).

The lifetime of aerosols in the air, which contain heavy metals, is a function of the particle size. The smallest particles, 0.001-0.08 μm , have a lifetime of <1 hour, because of

coagulation into bigger particles, whereas in the accumulation range, 0.08-1.0 μm , the life time is 4-40 days and the large particles $>1.0 \mu\text{m}$ have a life time of minutes to days (Graedel, 1980; Power, 2003; Rasch *et al.*, 2008; Deschler, 2008). Because of the long residence times of small particles, transport of particulate material in the atmosphere can extend over long distances e.g. 100 to 1000 km (Fergusson, 1990; Kellos *et al.*, 2007; Turner, 2007).

1.5. Pathways of heavy metal access

In order to cause an effect in a living organism, heavy metals have to come into contact with this organism. This might happen through the following three principal ways.

Inhalation: Heavy metals can enter the organisms by respiration. Heavy metals, being volatile and particulate, are released into the atmosphere in large quantities (Pacyna and Keeler, 1995). Respiration of metal pollution through dust is one of the most serious threats to humans working in industrial workplaces. They may cause a variety of damage including cancer, liver and kidney diseases, neurological damage, cardiovascular toxicity and anemia (Siegel, 2002).

Ingestion: The second pathway of entering organisms is through ingestion (water + food). Water contaminated with heavy metals can be ingested directly by drinking or indirectly by using this water for cooking and irrigation. Heavy metals can be introduced into the body by ingestion of foods with high contents of heavy metals. This could be through plant uptake. If soil contains a high metal content, this will result in polluted food crops and animal forage (Bradl, 2005; Brown and Welton, 2008).

Absorption: Absorption through the skin could be another path for the heavy metals access to the living organism. Although heavy metals uptake through absorption is minimal when compared to

ingestion and inhalation, even then it contributes towards the heavy metals budget in the living organisms (Brown and Welton, 2008).

1.6. Toxicity of the heavy metals

Heavy metals being non-biodegradable, have long term impact on food safety which requires immediate remediation strategies (Lim *et al.*, 2005). As levels of heavy metals rise in the air, water, and topsoil, they also rise within our bodies, contributing to chronic diseases, learning disorders, cancer, dementia, and premature aging. For example heavy metals poison humans by disrupting cellular enzymes, which run on nutritional minerals such as magnesium, zinc, and selenium (Lindquist, 1995).

Some of the heavy metals are required by the human body in minute quantities e.g. Co and Zn to run different functions but when their concentrations exceed a certain limit in the body, they become toxic. Some other metals like Cd, Pb, Hg have no known functions in the human body. Once they enter the body, they cannot be degraded into a harmless product and they are accumulated to a level where they become toxic and sometimes fatal to living organisms. Studies have shown that metals like As, Cd, Ni and Hg are human genotoxic carcinogens and that there is no identifiable threshold below which these substances do not pose a risk to human health (Brown and Welton, 2008). Table 2 shows some of the harmful effects due to the excessive concentration of heavy metals.

Table 2: Ecotoxicological effects of heavy metals through which they can be harmful to the living organisms.

As	Well known for its suicidal and homicidal effects, neurological signs of toxicity, malfunctioning of liver, nasal cavity, lungs, skin, bladder, kidney, and prostate.
Cd	Toxic to plants and invertebrates. It causes plant root growth retardation, damage to internal and external root structure, reduction of chlorophyll content. In humans, it causes bone degeneration (osteoporosis), neurological disorder, irritation of the lungs and gastrointestinal tract, kidney damage, abnormalities of the skeletal system and cancer of lungs and prostate.
Co	Soil with high Co concentration usually also have high As and Ni concentrations and these elements are generally more toxic to plants and animals.
Cu	Chronic effects of copper exposure can damage the liver and kidneys. Its excessive concentration can cause vomiting, hematemesis, gastrointestinal distress, hemolytic anemia.
Mn	Manganese toxicity may result in multiple neurologic problems. Unlike ingested manganese, inhaled manganese is transported directly to the brain before it can be metabolized in the liver. It can be toxic to the respiratory and reproductive tract and damage the liver. It shows some psychiatric symptoms, such as irritability, aggressiveness and even hallucinations.
Ni	Ni components like $\text{Ni}(\text{CO})_4$, Ni_3S_2 , NiO and Ni_2O_3 leads to pneumonitis with adrenal cortical insufficiency, pulmonary oedema, and hepatic degeneration, cancer of the respiratory tract due to chronic inhalation of nickel oxide, pulmonary eosinophilia, asthma, nasal and sinus problems. It can also cause skin rash.
Pb	Pb poisoning includes general fatigue, tremors, headache, vomiting and seizures. Also it interferes with hemoglobin synthesis and damages kidney functions. It can damage internal organs, the brain and nervous system. Chronic exposure to Pb induces peripheral neuropathy accompanied by abdominal pain, constipation and microcytic anemia.
Zn	High Zn intake may affect cholesterol metabolism. Zinc chloride fumes have caused injury to mucous membranes and pale grey cyanosis, metal fume fever, anemia, pancreas damage and lower levels HDL. Inhalation causes throat dryness, cough, aching, chills, fever, nausea and vomiting.

Modified from (Bradl, 2005, Brown and Welton, 2008, Wang et al, 2009, Fergusson, 1990)

1.7. *Atmospheric deposition of heavy metals*

Atmospheric deposition is the transfer of pollutants from the atmosphere to the earth's surface and generally occurs through rain and snow, falling particles, and absorption of the gas form of the pollutants into water (USEPA, 2011). This serves as a pathway for transporting heavy metals in biogeochemical cycles due to the anthropogenic activities in major cities, thereby increasing their concentrations in soil and water and consequently in the food chain (Sharma *et al.*, 2008). In general, larger particles tend to settle to the ground by gravity within hours near the source of emission whereas the smaller particles stay in the atmosphere longer (weeks or months) and are spread to distant places, only to be removed by precipitation (Golubeva *et al.*, 2010).

1.8. *A literature review on the atmospheric deposition*

A number of studies have been conducted on the atmospheric deposition of heavy metals in the environment. Different studies have used different sampling techniques as well as the methods of analyzing the heavy metals. In a recent study done in Poland (Staszewski *et al.*, 2012), contamination of 23 Polish national parks with heavy metals was studied. The result showed that parks located in the southern part of the country (Babiogorski, Magurski, Ojcowski and Gorczanski) were the most polluted with the heavy metals. It was likely due to the higher industrial activity in this part of Poland and the transboundary transport of air pollutants from the neighbouring countries.

Another study was done on the atmospheric fall-out of heavy metals in the Cordoba province of Argentina (Bermudez *et al.*, 2012). They took the topsoil and atmospheric fall-out samples from ten areas of the province to detect the concentration of metals in wheat grains. The

samples were analyzed using atomic absorption spectrometry. The deposition rates of As, Cu, Pb and Zn were found to be higher, which reflects both natural and anthropogenic sources. Industries and the transport of airborne urban pollutants were the main anthropogenic sources of heavy metals.

A study that was done at two locations in the Castellon province Spain detected high concentrations of heavy metals in the settleable particulate matter. The most important source of atmospheric particulate present in both locations (Almazora and Vila-real) is associated with the presence of high industrial density (the manufacture of ceramic tiles and the activities derived from this, a petrochemical complex, power station and high traffic volume). Heavy metals in the soluble fraction of settleable air particles were analyzed by using ICP-MS. The soil samples were also analyzed by ICP-MS after microwave digestion. The results showed a high seasonal variability for heavy metal content and a strong dependence of the rainfall in the study area. The maximum concentrations of heavy metals were observed during the highest rainfall in spring (Soriano *et al.*, 2012).

A few studies were done to estimate the influence of local emissions to the sediment cores along the coastal line (Singhal *et al.*, 2012) or in lake (Li *et al.*, 2012) or river (Stoyanova *et al.*, 2012) waters. They found higher concentrations of heavy metals in areas near industrial and agriculture activities or where there was an accumulation of heavy metals over time.

A study was conducted on organic paddy fields to estimate the concentration of heavy metals present. The study was done in a low population density farming area where the deposition is only from natural sources. The results revealed a higher concentration of heavy metals which was due to the use of organic fertilizers and the detected heavy metals in the soil were matched with the constituents of the applied fertilizer (Su and Kao, 212).

A study on the spatial distribution of bulk atmospheric deposition of heavy metals was conducted in metropolitan Sydney, Australia, using high density polyethylene tanks (HDPE). The metals were analyzed using ICP-AES and the results showed that the deposition rates were temporally consistent, and they showed a strong correlation with road proximity and traffic volume, i.e. the deposition was found to be higher on the road sites with heavy traffic volume and vice versa (Davis *et al.*, 2011).

Another study (Aboal *et al.*, 2010) described the estimation of atmospheric deposition of heavy metals by analyzing terrestrial moss plants. They concluded that the analysis of moss does provide useful information in regards to the presence of contaminants in the atmosphere.

A study on the characterization of wet and dry atmospheric depositions have been carried out by Morselli *et al.*, (2003), in order to evaluate the impact of airborne heavy metals on the pollution load in Bologna, an Italian northern urban area. Wet precipitation samples were filtered and heavy metal contents in soluble and insoluble fractions were determined. The same procedure was applied to the water samples which were collected by dry deposition. The percentage of the heavy metal soluble fraction in dry deposition was generally lower than in wet deposition. Cd, V, Cu and Zn showed a higher average solubility than Cr, Ni and Pb both in wet and dry deposition.

Atmospheric heavy metal depositions have also been monitored in rural forest soils of southern Scandinavia. The results showed that the accumulated atmospheric inputs over 50 years played a dominant role in the buildup of heavy metals in the top soils of the forests providing between 50 and 90% of the estimated heavy metals increments (Hovmand *et al.*, 2008).

Rapid growth in urbanization and industrialization in developing countries can affect human health by contaminating vegetables with heavy metals through atmospheric deposition.

An assessment was made to investigate the spatial and seasonal variations in the deposition rates of heavy metals and its concentration to contamination of palak (*Beta Vulgaris*) in Varanasi, India. The results showed that the sampling locations near industrial or commercial areas with heavy traffic load showed significantly higher deposition rates of Cu, Zn and Cd as compared to those in the residential areas with low traffic load (Sharma *et al.*, 2008).

Other studies have also shown a relationship between atmospheric deposition and elevated elemental levels in crops and vegetables (Azimi *et al.*, 2004; Pandey *et al.*, 2009). Additional studies also describe that urban and peri-urban areas were the most contaminated with heavy metals (Polkowska *et al.*, 2001; Khillare *et al.*, 2004).

Atmospheric deposition of heavy metals in central Ontario was studied over 30 years ago (Jeffries and Snyder, 1981), where the magnitude of atmospheric inputs of materials into lakes was studied at four different locations in the Muskoka-Haliburton and Sudbury regions. The results of the study showed a large temporal variations in the monthly deposition of all metals. Concentration and deposition of all metals in Muskoka-Haliburton were generally low whereas, in Sudbury, the large local smelting industry contributed to elevated Cu, Ni, Zn and Fe deposition. Calculation of an enrichment factor (normalized against Mn) showed that the levels of Pb, Cu, Ni and Zn require an additional non-crustal source (either natural or anthropogenic) for explanation. Two years later a study (Taylor and Crowder, 1983) confirmed elevated concentration of Cu and Ni near the smelters.

1.9. Study objectives

Toronto is the biggest city in Canada and the downtown area is the site of more than 20 skyscrapers that are at least 150 m in height. Toronto is ranked the 5th among census subdivisions in the great Lakes basin for releasing toxic air pollutants (Pollution Watch Fact Sheet, 2008). Therefore, it is very important to study the atmospheric deposition of heavy metals in the city to understand the impact of local anthropogenic sources to the environment of the city. The first objective of the study was to identify and quantify heavy metals such as arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn) in atmospheric deposition samples.

The second objective of the study was to compare the deposition rates of heavy metals on different surface types which have never been studied together. The surfaces used for this study include both dry (plastic and glass) and wet (water). Also, two different sites varying in height were selected to see how deposition varies with elevation which could insight to the sources contributing towards the heavy metals' concentrations which eventually are deposited on the surface.

2. Materials and Methods

2.1. Sampling Locations

The sampling took place on two rooftops at Ryerson University located in the downtown core of Toronto (latitude, 43° 40' N and longitude, 79° 24' W): one (KHN) site having a height of ~15 m above ground and the other (JOR) having a height of ~59 m above ground (Figure 1). The city of Toronto has a population of 2.5 million and the four surrounding regional municipalities form the Greater Toronto Area (GTA) with over 5.6 million residents in a total area of 7,125 km² (Statistics Canada, Census 2006). The rooftop locations, compared to a ground surface location, provide wider exposure to the atmosphere and better security for the samplers.

Figure 1: Sampling locations in downtown Toronto.

2.2. Development of Samplers

In this study, atmospheric bulk deposition of heavy metals was studied on dry and wet surfaces. Plastic and glass surfaces were used to estimate the deposition on dry surface whereas water was used as a wet surface. A plastic container (39.5 cm × 59.5 cm) filled with nano-pure

water (~ 1.5 L) served as the wet sampler whereas for the dry deposition collectors, plastic [polypropylene – a thermoplastic polymer made from the monomer propylene having a molecular formula $(C_3H_6)_n$. Most commercial polypropylene is isotactic and has an intermediate level of crystallinity between that of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) and has a melting point that ranges from 160 to 166 °C] and glass [high-borosilicate glass also known as hard glass which mainly consists of silica and boron oxide. Borosilicate glass is known for being less dense than ordinary glass (soda-lime glass, often called "Soft Glass") and for having very low coefficients of thermal expansion, making it resistant to thermal shock, more so than any other common glass] sheets were housed in plastic containers of the same size as water container. The dry samplers had to be dry all the times in order to allow the heavy metals (particulate and gaseous) to deposit on the dry surface. For this purpose the glass sampler (placed in a container) was tilted on one side to allow any precipitation to slide into the box. The plastic surface was drilled with holes to allow any precipitation to drain through the holes leaving the surface dry. The sampler's set up is shown in Figure 2.

Figure 2: Samplers with plastic, glass and water surfaces.

2.3. *Sample collection*

To collect the samples, the volume of the contents of wet sampler (water + particulates) was measured and 500 mL of the sample was transferred into pre-cleaned polytetrafluoroethylene (PTFE) bottles. Deionized water was used to wash both the dry and glass surfaces to collect the deposited particulates and the washed water as well as any water present in the container was collected in PTFE bottles. The collected samples were acidified by the addition of 2 mL of concentrated HCl (PlasmaPure Plus) and stored in the refrigerator at 6–8°C until analysis. The samples were collected on a biweekly basis (once every two weeks) from both locations.

2.4 *Analysis of Heavy Metals*

Atmospheric samples were acid digested using Questron's QLAB Pro digestion microwave. For this purpose, 46 mL of deposition samples were transferred into separate digestion vessels and 4.00 mL of concentrated HNO₃ (PlasmaPure Plus, 67-70%) was added to each vessel. The vessels were capped and the contents were mixed thoroughly and placed in the microwave digestion chamber. The digestion was carried out by using EPA method 3015 which is a recommended method for microwave assisted acid digestion of aqueous samples and extracts. The microwave digestion system, used for the digestion purpose, was obtained from Questron Technologies Corp, Mississauga, Canada (Model: QLAB Pro, Serial: 11-1018). With the EPA method 3015, the samples are preheated to 100°C in 3 minutes and 30 seconds. Then they are heated to 160°C in 10 minutes and finally from 160°C to 170°C during the last 10 minutes. Once digestion was complete, the vessels were allowed to cool before the contents were transferred to clean I-CHEM 25 mL vials.

These digested samples were analyzed for the eight different heavy metals which include arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). The analysis was done by using ICP-AES (Spectro Analytical Instruments, Model Spectroflame, Type FCPEA83F) which make use of the atomic emission spectroscopic technique. Emission spectroscopy uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at certain wavelengths which are the characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element in the sample. As an output, the concentration ($\mu\text{g L}^{-1}$) of the selected metals is determined. These concentrations are then used to calculate the deposition rates of the analyzed metals. Operational parameters of ICP-AES that were used during analysis of the heavy metals in the atmospheric deposition samples are given in Appendix I, Table 1.

2.5 Calibration and standardization

After the samples were digested and ready for analysis, calibration was undertaken in order to convert the instrumental signals to the concentrations of heavy metals in the samples. The calibration contained five non-zero points, and three blanks. Ultrapure deionized water (18-M Ω) was used as a reagent water to prepare all the reagents and standards. The standard analytical solutions were obtained from Ultra Scientific with item numbers; ICP-033, IAA-048, IAA-027, ICP-129, IAA-025, IAA-028, IAA-082 and IAA-030 respectively for As, Cd, Co, Cu, Mn, Ni, Pb and Zn. The concentration of As standard was $1000 \mu\text{g mL}^{-1}$ whereas that of the other solutions was $10,000 \mu\text{g mL}^{-1}$.

To prepare a standard solution of $1 \mu\text{g mL}^{-1}$, 100 μL of As (having stock concentration $1000 \mu\text{g mL}^{-1}$) and 10 μL of each of Cd, Co, Cu, Mn, Ni, Pb & Zn (having stock concentration

10,000 $\mu\text{g mL}^{-1}$) were taken in a 100 mL flask. The flask was diluted to 100 mL with reagent water having a 5.6% HNO_3 solution. To prepare the rest of the standards, 25.0, 5.00, 0.50 & 0.05 mL of the above prepared ($1 \mu\text{g mL}^{-1}$) solution were taken in four separate 50 mL flasks and diluted to the mark with the 5.6% HNO_3 solution to get the solutions of 1000 , 500, 100, 10 and 1 $\mu\text{g L}^{-1}$ respectively. These standards were digested in the microwave and analyzed by ICP-AES using the same conditions as the atmospheric samples.

To construct the calibration curves, three sets of the standards were prepared and analyzed on different days. The average of the three analyses was used to construct the calibration curves shown in Figure 3 below.

Figure 3: Calibration curves of the analyzed heavy metals with error bars shown as SD (n=3).

As shown in figure 3, the coefficient of determination (R^2) was found to be in the range of 0.9937–1.0 (R^2 gives the proportion of the variance of one variable that is predictable from the other variables, i.e. it represents the percent of the data that is the closest to the line of best fit. For example $R^2 = 0.9950$ means that 99.50% of the total variation in y can be explained by the linear relationship between x and y).

2.6 Quality Control (QC)

2.6.1. Blanks

A set of blanks was analyzed by ICP–AES right after the calibration curves were constructed. Blanks were prepared and analyzed using lab-ware, reagents and analytical procedures identical to that used to prepare and analyze the standards and the samples. The purpose of running blanks was to check the reproducibility of the method. Blanks were also used to determine the method detection limits. The graphs of the blank data are shown in the Appendix I, Figure 1. The field blanks were also collected with each batch of samples and their concentrations were subtracted from the concentration of each sample in the batch in order to avoid any contamination during the process of sampling, transport, storage and analysis. To assess any contamination from the laboratory environment, laboratory reagent blanks (LRB) were analyzed at the rate of at least one LRB per 20 samples (the criteria was that the blanks should be below the method detection limit otherwise it indicates a source of contamination).

2.6.2. Method Detection Limit

Method detection limits (MDL) were established against the most sensitive wavelength for the individual element. The wavelengths used were 189.042 nm for As, 226.502 nm for Cd,

228.616 nm for Co, 654.792 nm for Cu, 257.610 nm for Mn, 231.604 nm for Ni, 168.215 nm for Pb and 213.856 nm for Zn. Blanks were used to calculate the MDL. The standard deviation of the blanks was used to calculate the MDL by using the following equation 1.1 (USEPA method “40 CFR Appendix B to Part 136”).

$$MDL = t \times S \text{ ----- (1.1)}$$

Where; t is the Students’ t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom and S is the standard deviation of the replicates. The student’s t-value (3.14) was taken at 99% confidence level against 6 degrees of freedom. The MDLs were found to be 1.78, 0.32, 0.45, 5.70, 0.33, 1.45, 0.22 and 5.81 µg L⁻¹ for As, Cd, Co, Cu, Mn, Ni, Pb and Zn respectively.

2.6.3. Method Validation

The quality control samples (QCS) were used to demonstrate the initial verification of the calibration standards in order to verify the instrument performance and to validate the method. The QCS were obtained from a source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. For this purpose a standard reference material (SRM) NIST 1643e (trace elements in water) was used. The mean concentrations from three analyses of the QCS were found to have percentage recoveries of 104.53% for As, 105.34% for Cd, 100.31% for Co, 96.88% for Cu, 101.73% for Mn, 104.56% for Ni, 105.66% for Pb and 95.27% for Zn. The exact values are given in Appendix I Table 2.

2.6.4. Assessing Laboratory Performance

To demonstrate that the analytical batch was within the performance criteria of the method and that acceptable precision and recovery was being maintained within each analytical

batch, the laboratory fortified solutions (also known as ongoing precision and recovery samples) having concentration $20 \mu\text{g L}^{-1}$ were analyzed prior to the analysis of each analytical batch. The % recovery of the elements in each batch was calculated by using the equation 1.2.

$$R = \frac{LFS - LRB}{C} \times 100 \text{ ----- (1.2)}$$

Where; R is % recovery, LFS is the laboratory fortified solution, LRB is the laboratory reagent blank and C is the concentration of analyte added to fortify the solution. The percent recovery which was obtained during the entire analysis was found to be in-between 90–110%.

2.6.5. Assessing matrix effects

To assess the performance of the method on the sample matrix, the samples were spiked with a known concentration to a minimum of 10% of the routine samples. For each case the spiked aliquot (spiked to a certain concentration) was a duplicate of the aliquot used for sample analysis. The concentrations of sample as well as the spiked sample were measured and the percent recovery in each of the spiked sample was calculated using the equation 1.3 which is given below.

$$R = \frac{(C_s - C_b)}{C} \times 100 \text{ ----- (1.3)}$$

Where; R is the percent recovery, C_s is the measured concentration of the analyte after spiking, C_b is the blank concentration (before spiking) and C is the spiked concentration. The % recoveries (R) ranged between 93–112% which were within the EPA range (70–130%) (USEPA Method 200.7).

2.7. Deposition rate's calculation

The atmospheric samples (Sept. 2009–Dec. 2010) were analyzed by using ICP–AES to get the concentrations of the different heavy metals. Since the sampling was done, most of the times, on a biweekly basis but sometimes randomly, the concentrations were averaged on monthly basis. The concentrations of the heavy metals were then used to calculate the deposition rates of these metals. The deposition rates were calculated as a mass deposited per unit area per unit time (Sharma *et al.*, 2008).

$$\text{Deposition rate (R)} = \frac{m}{t \times A} \text{----- (1.4)}$$

Where; m is the mass of the metal deposited (μg), A is the area (m^2) and t is the period of sample collection. To get the deposition rates per month ($\mu\text{g m}^{-2}\text{month}^{-1}$), monthly concentrations were used. The mass was calculated by multiplying the concentration ($\mu\text{g L}^{-1}$) by the total volume (L) of samples measured during sample collection. The deposition rates on each surface were then summed up to get the annual deposition rate ($\mu\text{g m}^{-2}\text{a}^{-1}$).

2.8. *Calculating the enrichment factor*

Enrichment factor (EF) can be calculated to do the comparison between sites/surfaces (Florence *et al.*, 2012; Fabian *et al.*, 2011; Jeffries and Snyder, 1981) by taking one of the sites/surfaces as a reference. According to Baut-Menard and Chesselet (1979), the enrichment factor (EF) can be defined by equation 1.5

$$EF = \frac{X_A}{X_B} \text{ ----- (1.5)}$$

Where; X_A is the deposition rate of a metal X on a surface A and X_B is the deposition rate of that metal in the reference surface B i.e. glass surface.

3. Results and discussions

3.1. Concentration of heavy metals at the KHN site

The monthly concentrations of the metals on KHN site showed that As ranged between 1.84–21.97 $\mu\text{g L}^{-1}$ (6.81 ± 6.32), 2.06–22.30 $\mu\text{g L}^{-1}$ (9.38 ± 7.37) and 2.67–37.82 $\mu\text{g L}^{-1}$ (15.59 ± 11.69) on plastic, glass and water surfaces respectively. For Cd, the values were 1.85–27.19 $\mu\text{g L}^{-1}$ (16.78 ± 9.94) on plastic, 0.61–33.70 $\mu\text{g L}^{-1}$ (15.76 ± 12.74) on glass and 0.54–57.40 $\mu\text{g L}^{-1}$ (22.74 ± 21.54) on water surface. The values for Co ranged between 0.65–15.15 $\mu\text{g L}^{-1}$ (4.97 ± 5.59) on plastic, 0.79–18.39 $\mu\text{g L}^{-1}$ (4.88 ± 5.88) on glass and 0.96–19.89 $\mu\text{g L}^{-1}$ (8.88 ± 7.51) on water surface. For Cu, they ranged between 5.75–86.10 $\mu\text{g L}^{-1}$ (32.43 ± 28.18) on plastic, 6.43–38.55 $\mu\text{g L}^{-1}$ (22.36 ± 11.00) on glass and 7.61–160.79 $\mu\text{g L}^{-1}$ (53.33 ± 43.29) on water surface. For Mn, their range was 1.43–71.71 $\mu\text{g L}^{-1}$ (33.56 ± 25.19) on plastic, 2.29–115.41 $\mu\text{g L}^{-1}$ (39.35 ± 39.81) on glass and 3.38–375.72 $\mu\text{g L}^{-1}$ (113.89 ± 106.48) on water surface. For Ni, their range was 1.49–114.06 $\mu\text{g L}^{-1}$ (19.17 ± 34.25) on plastic, 1.95–107.66 $\mu\text{g L}^{-1}$ (20.71 ± 33.88) on glass, and 2.72–134.46 $\mu\text{g L}^{-1}$ (42.20 ± 46.55) on water surface. For Pb, they ranged between 1.40–69.22 $\mu\text{g L}^{-1}$ (18.19 ± 20.84) on plastic, 1.18–294.99 $\mu\text{g L}^{-1}$ (32.38 ± 80.09) on glass and 1.38–350.07 $\mu\text{g L}^{-1}$ (51.42 ± 88.16) on water surface. For Zn they ranged between 8.51–364.21 $\mu\text{g L}^{-1}$ (90.11 ± 91.68) on plastic, 11.38–252.08 $\mu\text{g L}^{-1}$ (80.92 ± 80.78) on glass and 22.41–895.00 $\mu\text{g L}^{-1}$ (255.16 ± 236.49) on water surface. The graphs for the concentration of the individual metals are given in the Appendix I Figure 2.

3.2. Concentration of heavy metals at the JOR site

The concentration of heavy metals on JOR sites showed that the concentrations of As ranged between 2.50–23.18 $\mu\text{g L}^{-1}$ (11.23 ± 7.59), 2.02–21.13 $\mu\text{g L}^{-1}$ (8.21 ± 6.40) and 1.93–27.94 $\mu\text{g L}^{-1}$ (10.26 ± 9.75) respectively on plastic, glass and water surfaces. For Cd, on Aug. 09, 2009, huge values were found i.e. 2493.58 $\mu\text{g L}^{-1}$ on plastic, 2489.49 $\mu\text{g L}^{-1}$ on glass, and 2489.69 $\mu\text{g L}^{-1}$ on water surface. But these high values were not found on KHN site for the same date. So these values were taken out as an outlier assuming that it could be due to contamination in the JOR samples for that period. Instead of these high values, the average of the rest were taken for this date and the values were 0.35–26.19 $\mu\text{g L}^{-1}$ (11.75 ± 14.28) on plastic, 0.45–29.92 $\mu\text{g L}^{-1}$ (8.64 ± 10.39) on glass and 1.68–24.32 $\mu\text{g L}^{-1}$ (11.97 ± 7.80) on water surface. The values for Co ranged between 0.75–17.92 $\mu\text{g L}^{-1}$ (7.16 ± 6.96) on plastic, 0.58–11.24 $\mu\text{g L}^{-1}$ (4.15 ± 3.77) on glass and 0.48–16.43 $\mu\text{g L}^{-1}$ (4.18 ± 5.22) on water surface. For Cu, they ranged between 10.63–45.93 $\mu\text{g L}^{-1}$ (25.89 ± 13.72) on plastic, 6.26–113.11 $\mu\text{g L}^{-1}$ (35.03 ± 36.70) on glass and 10.41–133.00 $\mu\text{g L}^{-1}$ (47.15 ± 40.66) on water surface. For Mn, their range was 4.65–107.02 $\mu\text{g L}^{-1}$ (29.91 ± 31.71) on plastic, 2.04–117.95 $\mu\text{g L}^{-1}$ (24.67 ± 38.22) on glass and 2.93–197.14 $\mu\text{g L}^{-1}$ (59.87 ± 63.60) on water surface. For Ni, their range was 2.60–190.32 $\mu\text{g L}^{-1}$ (52.15 ± 67.31) on plastic, 1.86–158.62 $\mu\text{g L}^{-1}$ (43.03 ± 53.92) on glass, and 2.27–49.55 $\mu\text{g L}^{-1}$ (14.22 ± 14.33) on water surface. For Pb, they ranged between 1.54–179.1 $\mu\text{g L}^{-1}$ (33.66 ± 48.76) on plastic, 1.09–125.39 $\mu\text{g L}^{-1}$ (28.30 ± 39.08) on glass and 10.14–96.01 $\mu\text{g L}^{-1}$ (42.72 ± 26.13) on water surface. For Zn they ranged between 11.31–288.47 $\mu\text{g L}^{-1}$ (87.40 ± 86.03) on plastic, 18.15–246.58 $\mu\text{g L}^{-1}$ (85.97 ± 72.76) on glass and 18.21–378.59 $\mu\text{g L}^{-1}$ (150.09 ± 131.22) on water surface (Appendix I Figure 3).

3.3 Deposition rates of heavy metals in Toronto

Deposition rates were calculated using equation 1.4 and were plotted for individual metals. On KHN site (Figure 4), the average deposition rates on plastic were calculated as $45.90 \pm 73.65 \mu\text{g m}^{-2}\text{month}^{-1}$ for As, $52.28 \pm 99.68 \mu\text{g m}^{-2}\text{month}^{-1}$ for Cd, $34.74 \pm 63.98 \mu\text{g m}^{-2}\text{month}^{-1}$ for Co, $151.27 \pm 223.84 \mu\text{g m}^{-2}\text{month}^{-1}$ for Cu, $274.67 \pm 248.78 \mu\text{g m}^{-2}\text{month}^{-1}$ for Mn, $62.38 \pm 92.84 \mu\text{g m}^{-2}\text{month}^{-1}$ for Ni, $210.64 \pm 395.04 \mu\text{g m}^{-2}\text{month}^{-1}$ for Pb and $716.25 \pm 1212.13 \mu\text{g m}^{-2}\text{month}^{-1}$ for Zn. On glass surface, these values were As ($56.18 \pm 88.20 \mu\text{g m}^{-2}\text{month}^{-1}$), Cd ($86.53 \pm 153.89 \mu\text{g m}^{-2}\text{month}^{-1}$), Co ($43.16 \pm 71.94 \mu\text{g m}^{-2}\text{month}^{-1}$), Cu ($147.95 \pm 150.54 \mu\text{g m}^{-2}\text{month}^{-1}$), Mn ($324.68 \pm 430.45 \mu\text{g m}^{-2}\text{month}^{-1}$), Ni ($55.03 \pm 94.08 \mu\text{g m}^{-2}\text{month}^{-1}$), Pb ($471.28 \pm 1187.69 \mu\text{g m}^{-2}\text{month}^{-1}$), and Zn ($668.83 \pm 990.79 \mu\text{g m}^{-2}\text{month}^{-1}$) whereas on water surface these values were As ($93.25 \pm 108.39 \mu\text{g m}^{-2}\text{month}^{-1}$), Cd ($95.72 \pm 151.84 \mu\text{g m}^{-2}\text{month}^{-1}$), Co ($89.19 \pm 123.37 \mu\text{g m}^{-2}\text{month}^{-1}$), Cu ($538.69 \pm 553.45 \mu\text{g m}^{-2}\text{month}^{-1}$), Mn ($1212.41 \pm 1263.78 \mu\text{g m}^{-2}\text{month}^{-1}$), Ni ($331.83 \pm 783.05 \mu\text{g m}^{-2}\text{month}^{-1}$), Pb ($612.92 \pm 891.42 \mu\text{g m}^{-2}\text{month}^{-1}$), and Zn ($2383.93 \pm 2741.89 \mu\text{g m}^{-2}\text{month}^{-1}$).

Similarly the deposition rates were plotted on JOR site (Figure 5). On the plastic surface, the average deposition rates were calculated as As ($36.26 \pm 82.79 \mu\text{g m}^{-2}\text{month}^{-1}$), Cd ($67.88 \pm 141.50 \mu\text{g m}^{-2}\text{month}^{-1}$), Co ($31.30 \pm 62.74 \mu\text{g m}^{-2}\text{month}^{-1}$), Cu ($167.53 \pm 246.74 \mu\text{g m}^{-2}\text{month}^{-1}$), Mn ($278.57 \pm 379.55 \mu\text{g m}^{-2}\text{month}^{-1}$), Ni ($89.98 \pm 152.34 \mu\text{g m}^{-2}\text{month}^{-1}$), Pb ($160.62 \pm 213.64 \mu\text{g m}^{-2}\text{month}^{-1}$), and Zn ($654.63 \pm 981.54 \mu\text{g m}^{-2}\text{month}^{-1}$). On glass surface, these values were As ($47.31 \pm 82.49 \mu\text{g m}^{-2}\text{month}^{-1}$), Cd ($50.32 \pm 118.30 \mu\text{g m}^{-2}\text{month}^{-1}$), Co ($24.75 \pm 46.59 \mu\text{g m}^{-2}\text{month}^{-1}$), Cu ($253.90 \pm 404.75 \mu\text{g m}^{-2}\text{month}^{-1}$), Mn ($225.82 \pm 374.75 \mu\text{g m}^{-2}\text{month}^{-1}$), Ni ($64.49 \pm 104.95 \mu\text{g m}^{-2}\text{month}^{-1}$), Pb ($395.46 \pm 689.87 \mu\text{g m}^{-2}\text{month}^{-1}$), and Zn

($582.88 \pm 595.51 \mu\text{g m}^{-2}\text{month}^{-1}$) whereas on water surface these values were As ($79.21 \pm 114.94 \mu\text{g m}^{-2}\text{month}^{-1}$), Cd ($84.70 \pm 95.91 \mu\text{g m}^{-2}\text{month}^{-1}$), Co ($56.58 \pm 73.81 \mu\text{g m}^{-2}\text{month}^{-1}$), Cu ($696.26 \pm 905.17 \mu\text{g m}^{-2}\text{month}^{-1}$), Mn ($1060.55 \pm 1396.74 \mu\text{g m}^{-2}\text{month}^{-1}$), Ni ($122.87 \pm 159.29 \mu\text{g m}^{-2}\text{month}^{-1}$), Pb ($590.24 \pm 737.22 \mu\text{g m}^{-2}\text{month}^{-1}$), and Zn ($1935.91 \pm 2098.55 \mu\text{g m}^{-2}\text{month}^{-1}$).

The results showed that Zn had the higher deposition rates than other heavy metals. Other metals with the higher deposition rates were Mn, Cu and Pb. An evaluation of the relationships between the deposition rates of heavy metals revealed that some strong correlations exist among Cu, Mn, Pb and Zn as they increase and/or decrease. Local sources like vehicle emissions and domestic heating could be the possible sources of higher deposition rates of these metals in Toronto.

Figure 4: Deposition rates of the individual metals deposited at KHN site.

Figure 5: Deposition rates of the individual metals deposited at JOR site.

3.4. *Distribution of heavy metals on different surfaces*

A statistical test called analysis of variance (ANOVA) was conducted to conclude if the sets of data (deposition rates) on three surfaces were statistically significantly different from each other i.e. whether the surfaces behaved similarly or differently throughout the sampling period. For almost all the metals, on both sites, the $F_{\text{calculated}}$ was higher than F_{critical} ($F_{\text{calc}} > F_{\text{crit}}$). The F_{critical} value was found to be 2.01, on both the sites whereas the $F_{\text{calculated}}$ were found in the range of 3.52–7.87 (all different analyzed metals) for KHN site and 2.68–19.70 for JOR site which means that for all the analyzed metals, the deposition rates were statistically significantly different on different surfaces.

The variability of deposition rate showed that the minimum and maximum deposition rates, encountered during the studied period, were high and not proportionally distributed around the median (Figure 6) with the maximum values too high from the median in majority of the cases. The box plot show how the heavy metals were distributed on different surfaces. The medians of the heavy metals on plastic surface was found to be As (KHN=27.16 & JOR=13.80), Cd (KHN=13.74 & JOR=18.37), Co (KHN=7.88 & JOR=7.79), Cu (KHN=128.47 & JOR=108.26), Mn (KHN=262.95 & JOR=140.93), Ni (KHN=20.75 & JOR=49.27), Pb (KHN=93.18 & JOR=113.41) and Zn (KHN=426.39 & JOR=296.41), on glass surface, these values were As (KHN=16.63 & JOR=37.67), Cd (KHN=24.34 & JOR=27.00), Co (KHN=10.60 & JOR=9.98), Cu (KHN=238.45 & JOR=115.12), Mn (KHN=243.97 & JOR=54.40), Ni (KHN=20.16 & JOR=71.69), Pb (KHN=57.82 & JOR=106.62) and Zn (KHN=263.89 & JOR=558.38) and on water surface the medians were As (KHN=36.90 & JOR=30.86), Cd (KHN=42.04 & JOR=126.10), Co (KHN=22.34 & JOR=38.10), Cu (KHN=494.94 &

JOR=347.43), Mn (KHN=906.37 & JOR=500.43), Ni (KHN=96.12 & JOR=88.20), Pb (KHN=272.89 & JOR=368.75) and Zn (KHN=1394.38 & JOR=1006.85).

As the box plot (Figure 6) indicates, the general trend for most of the metals was that the medians were skewed more towards the lower side of the interquartile with a few exceptions, as Mn and Zn on plastic and wet surfaces of the KHN site were distributed equally on both side of the interquartile, Pb was thoroughly distributed equally except on the glass surface on JOR whereas Cu on glass surface of KHN site showed that the median was skewed more towards the upper side of interquartile. This indicated that, for majority of the metals, the maximum values of the deposition rates were too high than their median values.

Figure 6: Box plots of the individual metals showing the distribution of data among sites. The error bars show the maximum and minimum deposition rates for the individual elements. The intersection of the gray part and shaded part of the interquartile (box) shows the median of the entire data. The bottom line of the interquartile (25th percentile) shows the value of median of the first half of the data whereas the upper line (75th percentile) shows the median of the second half of the data.

3.5. *Surface comparison*

To study the deposition pattern on the three surfaces, deposition rates on these surfaces were compared by determining the elemental enrichment factor using equation 1.5. The mean values of the monthly deposition rates (Figure 3 & 4 for KHN and JOR sites respectively), on three surfaces, were used to calculate the EF. The results (Table 3) shows that the deposition rates were almost similar on both the plastic and glass surface (with exception of Cd and Pb) whereas they were different on water surface. The EF for water surface was more than twice the dry surfaces with the exception of As, Cd and Pb where they were almost 1.5 times higher. For Cu, Mn and Zn, they were more than three times higher than that of dry surfaces. So it was concluded that the tendency of water surface to absorb/retain heavy metals from the atmosphere was quite high when compared to dry surfaces. This could probably be due the reason that the particles could be easily trapped or absorbed in the water due to hydrogen bonding. Also the dry surfaces were more or less similar in their behavior. This could be due to the reason that the most of the deposited particles do not interact with the surface material instead they are attached to the surfaces because of the sticking properties. The particles could react with the surface material as the polypropylene (plastic) is liable to chain degradation from exposure to heat and UV radiation (such as that present in sunlight). Oxidation usually occurs at the tertiary carbon atom present in every repeat unit. A free radical is formed here, and then reacts further with oxygen, followed by chain scission to yield aldehydes and carboxylic acids but normally anti-oxidants are added to prevent polymer degradation. Also, borosilicate glass, having a very low thermal expansion coefficient, is so widely used (e.g. in laboratory equipment, telescope mirrors) due to its chemical and thermal resistance and good optical clarity, but the glass can be reacted with sodium hydride to produce sodium borohydride, a common laboratory reducing agent.

Table 3: Enrichment factors (EF) with glass surface as a reference.

Site	Surface	As (EF)	Cd (EF)	Co (EF)	Cu (EF)	Mn (EF)	Ni (EF)	Pb (EF)	Zn (EF)
KHN	Glass	1	1	1	1	1	1	1	1
	Plastic	0.8	0.6	0.8	1.0	0.9	1.1	0.5	1.1
	Water	1.7	1.1	2.1	3.6	3.7	6.0	1.3	3.6
JOR	Glass	1	1	1	1	1	1	1	1
	Plastic	0.8	1.4	1.3	0.7	1.2	1.4	0.4	1.1
	Water	1.7	1.7	2.3	2.7	4.7	1.9	1.5	3.3

3.6. *Effect of height on the deposition of heavy metals (Sites Comparison)*

The influence of height on the deposition rate of heavy metals was tested by comparing the deposition rates at two roofs of variable heights, viz. KHN (~15 m) and JOR (~ 59 m). The mean of the individual metals on three surfaces (Figure 7) showed that the deposition rates of heavy metals were higher at lower height (KHN) than at JOR (with the exception of Cu) indicating that most emissions from the ground level are deposited at lower heights. This suggested that local sources like vehicle emissions and residential heating emissions might have contributed to the heavy metals deposition (Davis *et al*, 2011; Popescu, 2011). Only Cu showed the opposite trend, i.e. it was found to be higher at JOR. It may be either due to the reason that local emission of Cu was comparatively less than regional one or the size of Cu particles was small so that they are less influenced by the gravity.

Figure 7: The deposition rates of the analyzed heavy metals on plastic, glass and water surfaces.

3.7. Comparison of deposition rates of heavy metals in Toronto with other studies

The deposition rates of heavy metals in Toronto were compared to those obtained in other cities (Table 4). It was difficult to verify whether the deposition rates of As and Co in Toronto were higher or lower due to lack of information about the deposition of these elements in other cities. For Ni, there was only one reference value found for Ni (Andersen *et al.*, 1978) which showed that the deposition rate of Ni ($317 \mu\text{g m}^{-2}\text{month}^{-1}$) in Denmark was comparable to that found in this study conducted in Toronto ($55\text{--}331 \mu\text{g m}^{-2}\text{month}^{-1}$). The deposition rate of Cd in Toronto ($50\text{--}96 \mu\text{g m}^{-2}\text{month}^{-1}$) was higher than Tokyo ($5 \mu\text{g m}^{-2}\text{month}^{-1}$), Amman ($12 \mu\text{g m}^{-2}\text{month}^{-1}$) and Bombay ($50 \mu\text{g m}^{-2}\text{month}^{-1}$), more comparable to Varanasi City ($20\text{--}253 \mu\text{g m}^{-2}\text{month}^{-1}$) but lower than Izmir ($720 \mu\text{g m}^{-2}\text{month}^{-1}$) and Lublin ($185 \mu\text{g m}^{-2}\text{month}^{-1}$). Copper's deposition rate in Toronto ($148\text{--}696 \mu\text{g m}^{-2}\text{month}^{-1}$) were more comparable to those obtained in Sydney ($542 \mu\text{g m}^{-2}\text{month}^{-1}$), Varanasi ($272\text{--}902 \mu\text{g m}^{-2}\text{month}^{-1}$), Tokyo ($630 \mu\text{g m}^{-2}\text{month}^{-1}$) and Amman ($463 \mu\text{g m}^{-2}\text{month}^{-1}$) but lower than that found in Michigan ($930 \mu\text{g m}^{-2}\text{month}^{-1}$), Bombay ($1416 \mu\text{g m}^{-2}\text{month}^{-1}$) and Izmir ($3720 \mu\text{g m}^{-2}\text{month}^{-1}$). Similarly, comparable deposition rate of Pb in Toronto was reported in other cities except in Izmir which is much higher (Table 4). The deposition rate of Mn was also comparable to the ones studied in Michigan and Tokyo. The deposition rate of Zn ($583\text{--}2384 \mu\text{g m}^{-2}\text{month}^{-1}$) was in agreement with Michigan and Lublin but less than all the other studies i.e., $2474 \mu\text{g m}^{-2}\text{month}^{-1}$, $8100 \mu\text{g m}^{-2}\text{month}^{-1}$, $873\text{--}7860 \mu\text{g m}^{-2}\text{month}^{-1}$, $3933 \mu\text{g m}^{-2}\text{month}^{-1}$, and $4500 \mu\text{g m}^{-2}\text{month}^{-1}$ as were reported in Amman, Bombay, Varanasi and Sydney and Tokyo respectively. This means that the deposition rate of Zn in Toronto was smaller than most of the other cities.

In general, annual atmospheric deposition of heavy metals in different studies showed large variations, suggesting that emissions of heavy metals vary significantly between cities due to variations in sampling media, viz., this study (plastic, glass and water surfaces), Sydney (HDPE tank), Varanasi (spinach leaves), Bombay (particulate matter) and Amman (Cypress tree bark), traffic volume and local industrial sources.

Table 4: Comparison of deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) for heavy metals in urban environments.

Analytes	This Study	Sydney, Australia ^a	SouthHaven ^b , Miomi	Al-Karak ^c Jordan	Komae, ^d Tokyo	Varanasi City, India ^e	Izmir ^f Turkey	Amman, Jordan ^g	Lublin Poland ^h	Bombay ⁱ , India
As	36–93	-	-	-	-	-	-	-	-	-
Cd	50–96	-	-	29	5	20–253	720	12	185	50
Co	25–89	-	-	-	-	-	-	-	-	-
Cu	148–696	542	930	415	630	272–902	3720	463	332	1416
Mn	226–1212	-	630	-	1020	-	4050	-	-	-
Ni	55–331	-	-	-	-	-	-	-	-	-
Pb	161–613	342	690	277	279	0–237	6600	350	450	958
Zn	583–2384	3933	1530	2964	4500	893–7860	57300	2474	1526	8100

^aDavis & Birch., 2011, ^bYi *et al.*, 2001, ^cJaradat *et al.*, 2004, ^dSakata & Marumoto, 2004, ^eSharma *et al.*, 2008, ^fOdabasi *et al.*, 2002,

^gMomani *et al.*, 2000, ^hKozak *et al.*, 1993, ⁱTripathi *et al.*, 1993.

The results generated from this study showed that the water surface observed the higher deposition rates compared to both plastic and glass surfaces in the urban environment of Toronto and that the deposition rate of heavy metals on plastic and glass surfaces were almost equal. It was also found that Zn had the highest deposition rates among other heavy metals. The other heavy metals with the higher deposition rates were Mn, Cu and Pb whereas the deposition rates of As, Cd, Co and Ni were considerably lower. It was also found that the deposition rates of heavy metals were also influenced by the height above the ground with higher deposition at lower rooftop of lower height (KHN) indicating contributions from local sources. Only Cu showed the higher deposition rates on JOR site instead of KHN whereas all the other analyzed heavy metals showed similar trend i.e. higher on KHN site.

3.8. *Repetition of the atmospheric data*

In order to study the atmospheric deposition pattern after almost one year, atmospheric samples were collected from October 2011–December 2011. A similar procedure was adopted from the collection till the analysis of the new samples. Same sites and surfaces were chosen with the only difference being the size of the surface of samplers exposed to the atmosphere. The sampling container's sizes were plastic (34 cm × 50 cm), glass (32 cm × 47 cm) and water (34 cm × 50 cm). The samples were analyzed using the same ICP–AES. The mass of the heavy metals deposited on each surface was calculated from the measured concentration ($\mu\text{g/L}$) and the volume of the sample collected.

The deposition rates were calculated by using equation 1.4. Table 5 shows the deposition rates for the period of three months. Among the analyzed heavy metals, Zn was found to have the highest deposition rate with a range of 1114–2192 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($1616 \pm 281 \mu\text{g m}^{-2}\text{month}^{-1}$). The metal with the second highest deposition rate was Mn, which was found in the range of 222–1072 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($672 \pm 219 \mu\text{g m}^{-2}\text{month}^{-1}$) followed by Pb with the range 417–922 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($661 \pm 160 \mu\text{g m}^{-2}\text{month}^{-1}$) and Cu 102–1068 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($545 \pm 211 \mu\text{g m}^{-2}\text{month}^{-1}$). The rest of the metals were found to be in the order of Ni > Cd > As > Co with the values 65–361 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($208 \pm 117 \mu\text{g m}^{-2}\text{month}^{-1}$), 40–373 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($194 \pm 128 \mu\text{g m}^{-2}\text{month}^{-1}$), 78–270 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($174 \pm 65 \mu\text{g m}^{-2}\text{month}^{-1}$) and 46–152 $\mu\text{g m}^{-2}\text{month}^{-1}$ ($99 \pm 33 \mu\text{g m}^{-2}\text{month}^{-1}$) respectively. When comparing surfaces, the water surface observed higher deposition rates compared to glass and plastic as the average deposition rates on water surface (908, 135, 240, 348, 779, 660, 222, and 1827 $\mu\text{g m}^{-2}\text{month}^{-1}$ for Mn, Co, Ni, Cd, Pb, Cu, As and Zn, respectively) was higher than plastic (554, 87, 209, 150, 597, 427, 133 and 1448 $\mu\text{g m}^{-2}\text{month}^{-1}$

for Mn, Co, Ni, Cd, Pb, Cu, As and Zn, respectively) as well as glass surface (476, 63, 150, 74, 519, 470, 142, and 1348 $\mu\text{g m}^{-2}\text{month}^{-1}$ respectively for Mn, Co, Ni, Cd, Pb, Cu, As and Zn). When compared for the two sites, the deposition rates were not found very different on KHN (749, 104, 220, 173, 696, 467, 178, and 1605 $\mu\text{g m}^{-2}\text{month}^{-1}$ respectively for Mn, Co, Ni, Cd, Pb, Cu, As and Zn) and JOR site (596, 94, 196, 217, 626, 623, 170 and 1626 $\mu\text{g m}^{-2}\text{month}^{-1}$ respectively for Mn, Co, Ni, Cd, Pb, Cu, As and Zn).

Table 5 : Deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) of heavy metals from October–December 2011 in repetition samples.

Sampling period	Location	Surface	Mn	Co	Ni	Cd	Pb	Cu	As	Zn
Oct-11	KHN	Glass	512	59	346	64	837	639	247	1635
		Plastic	706	121	361	211	772	604	200	1125
		Water	1020	145	356	371	922	794	238	1739
	JOR	Glass	411	46	323	40	417	499	85	1652
		Plastic	222	72	314	243	483	482	227	1188
		Water	907	152	335	373	902	1068	270	1486
Nov-11	KHN	Glass	763	67	93	50	443	459	132	1762
		Plastic	565	112	343	72	471	259	78	1447
		Water	1072	128	126	325	547	370	260	1712
	JOR	Glass	542	78	107	239	620	515	158	1575
		Plastic	468	58	65	138	553	551	86	1564
		Water	882	131	247	373	673	581	244	1780
Dec-11	KHN	Glass	571	88	95	47	672	604	188	1113
		Plastic	704	89	77	91	701	102	86	1722
		Water	830	127	183	322	895	372	170	2191
	JOR	Glass	537	105	88	80	646	573	185	1698
		Plastic	657	71	97	143	605	565	123	1642
		Water	734	129	190	325	732	776	149	2051

The first two conclusions were almost in accordance with the previous results i.e. Zn, Mn, Pb and Cu had the higher deposition rates (with Zn having the highest) as compared to As, Cd, Co & Ni and that the water surface had the higher deposition rate compared to plastic and glass. The third conclusion i.e. both the KHN and JOR sites had almost comparable deposition rates, was different from the previous results which indicate that KHN showed higher deposition than JOR. Overall, the results of the repetition samples showed the similar trend. So this could be taken as the validation of the data and also indirectly the validation of the method.

Part 2

ATMOSPHERIC DEPOSITION OF TOTAL MERCURY AND METHYL MERCURY

1. Introduction

1.1. *Properties of Mercury*

Mercury (Hg) is a naturally occurring element generally referred to as a heavy metal. Elemental mercury (Hg^0) is a liquid at room temperature with melting point of $-38.9\text{ }^\circ\text{C}$ and boiling point of $357.3\text{ }^\circ\text{C}$. It is one of the most volatile metals known and once it gets evaporated, it becomes a colourless, odourless gas. In the atmosphere, it can be transformed into its various forms through abiotic and biogeochemical processes (Environment Canada, 2004; Gochfeld, 2003).

Mercury has different common species which can have their own unique impact on the environment. In the atmosphere, mercury can be present in a gaseous phase, incorporated with atmospheric precipitation or associated with air borne particulate matter (Hg_p). Hg in the gaseous phase has been operationally divided into gaseous elemental mercury (GEM) and gaseous oxidized mercury (GOM). Hg in aqueous media can be in the form of inorganic and organic mercury derivatives. Landfills and the oceans have been found to be the known sources of organic mercury compounds to the atmosphere (Pongratz and Heumann, 1999; St. Louis *et al.*, 2005). Mercury can exist as two different kinds of cations: Hg^{2+} and Hg_2^{2+} . The cation, Hg^{2+} , is generally more stable and can form inorganic compounds with sulfur, oxygen, and hydroxyl ions (Environment Canada, 2004; Tan *et al.*, 2000). Some other common mercury compounds are: mercuric chloride (HgCl_2), mercurous chloride (Hg_2Cl_2), methyl mercury (CH_3Hg) and dimethyl mercury ($(\text{CH}_3)_2\text{Hg}$) (CLS, 2000; Gochfeld, 2003). Mercury also combines readily with other

elements such as tin, copper, gold and silver to form mercury alloys known as amalgams (Environment Canada, 2004).

Under normal conditions, about 98% of atmospheric mercury is in the form of Hg^0 , with a residence time of 1-1.5 years (Environment Canada, 2004). This can allow mercury to be transported in the atmosphere on a regional or global scale (Gochfeld, 2003; Lindqvist, 1994). This tends to create Hg^0 air pollution, which is less localized and more pervasive than other mercury species. High levels of Hg^0 have been observed in remote regions far from anthropogenic sources (Fitzgerald *et al.*, 1998). The Hg^0 can be deposited into aquatic systems via deposition to water surfaces directly, or to land with eventual runoff which may eventually be converted into methyl mercury (MeHg) via bacterial interactions (Gochfeld, 2003).

GOM is less volatile and more water-soluble than Hg^0 and is more likely to be removed by rain, absorbed by terrestrial surfaces and adhered to atmospheric particulate matter. GOM and Hg_p are the primary atmospheric forms responsible for the dry deposition of Hg (Lyman *et al.*, 2007). Hg^{2+} has a residence time of less than two weeks in the atmosphere, and may be rapidly taken up in rain, water, snow, or adsorbed onto small particles through wet or dry deposition (Environment Canada, 2004). It is also possible for Hg^{2+} to gain a methyl group, normally through biological processes, producing MeHg, which can be emitted to the atmosphere (Environment Canada, 2004). Any dimethyl mercury (Me_2Hg) that is released into the atmosphere tends to be short-lived, and undergoes rapid oxidation (Schroeder and Munthe, 1998). The release of Me_2Hg from upwelling areas in the ocean can lead to a reaction with hydroxide (OH) and chlorine (Cl) radicals to form MeHgCl or MeHgOH (Niki *et al.*, 1983; Schroeder and Munthe, 1998). This can lead to small concentrations of MeHg in both the air and precipitation which can then be deposited away from its source through both wet and dry

deposition (Schroeder and Munthe, 1998). The hydride species, MeHgH is known to be unstable in water and is known to decompose rapidly to Hg⁰ and MeHg (Filippelli *et al.*, 1992).

1.2. Toxicity of Mercury

Mercury is a highly toxic metal that can pose health risks to humans and wildlife (Clarkson, 1993; Facemire *et al.*, 1995; Meyer *et al.*, 1995). Classified as a persistent bioaccumulative toxin (PBT), mercury does not break down over time but undergoes transformation from one form to the other in the natural environment. Toxicological concerns of mercury contamination focus primarily on MeHg, a highly toxic compound that readily accumulates in organisms and biomagnifies in food webs to concentrations that vastly exceed those in surface water (Scheuhammer *et al.*, 2007; Chasar *et al.*, 2009; Rolfhus *et al.*, 2011). For example, due to the processes of bioaccumulation, even small quantities of MeHg in water can result in levels 1-10 million times higher in fish and fish-eating animals such as loons (Driscoll *et al.*, 2007).

The level of toxicity can be connected with the different chemical characteristics of the mercury species like a compound's lipid solubility, giving these compounds the ability to bioaccumulate and biomagnify (Clarkson, 1994; MassDEP, 1996; CLS, 2000; Goldman *et al.*, 2001). A mercury species level of toxicity can also be linked to its method of absorption (Environment Canada, 2004; Gochfeld, 2003). Hg⁰, for instance, is well absorbed by the lungs, but not the skin or gastrointestinal (GI) tract (Gochfeld, 2003). On the other hand, MeHg, has been found to be easily absorbed through the lungs, blood-brain barrier, GI tract, liver and the skin (Clarkson, 1994; MassDEP, 1996; Schroeder and Munthe, 1998; CLS, 2000; Gochfeld, 2003; Environment Canada, 2004). This means that MeHg can affect an individual via

inhalation, ingestion, and direct dermal contact (Clarkson, 1994; Schroeder and Munthe, 1998; Goldman *et al.*, 2001; Gochfeld, 2003). However, regardless of the organ, MeHg can be absorbed into the body about six times more easily than inorganic mercury compounds (Environment Canada, 2004). MeHg can also cross the placental barrier, affecting the fetal brain (Clarkson, 1994; Schuurs, 1999; Rice *et al.*, 2000; Environment Canada, 2004). MeHg may even inhibit gap junctional intercellular communication of cells, which is a trait shared by some carcinogens (Zefferino *et al.*, 2005). After it is transported to cells, MeHg can be broken down into Hg^{2+} (Clarkson, 1994; CLS, 2000). Once broken down, inorganic mercury is mainly excreted via urine and feces (MassDEP, 1996; CLS, 2000). MeHg, on the other, can take anywhere between 70 days to 4 months to be eliminated from the body, with the possibility of bioaccumulation of the compound during this period (MassDEP, 1996; CLS, 2000).

1.3. *Mercury in the atmosphere*

The atmosphere receives most of the emitted Hg, thus, it is the major pathway of transporting Hg from its sources. Mercury can be released into the environment by either natural processes such as emissions from the earth's crust, water bodies, vegetation surfaces, wild fires, volcanoes (Schroeder and Munthe, 1998) or anthropogenic processes such as coal combustion, waste incineration, commercial product manufacture and disposal, metals refining, cement production and artisanal gold mining (Pacyna *et al.*, 2006; Lindberg *et al.*, 2007, Munthe *et al.*, 2003; Pirrone and Mason, 2009). Although mercury can be found naturally in the environment, the anthropogenic activities have drastically increased the rates of mercury emissions to the atmosphere (Mason *et al.*, 2005; UNEP Chemicals Branch, 2008). For instance, polar background levels of atmospheric Hg^0 have been found, on average, to range between 1.0 and 1.6 ng m^{-3} ,

compared to mid-1850 estimates of 0.8 ng m^{-3} (Environment Canada, 2004; Cobbett *et al.*, 2007; Ferrari *et al.*, 2008; Kellerhals *et al.*, 2003; Brooks *et al.*, 2008). In 2000, the National Pollutant Release Inventory (NPRI) reported that nearly 47% of the released mercury was the result of industrial sources and 24% was from the primary base metal sector (NPRI, 2000). In the residential areas, mercury can also be released by a number of sources viz; Phenylmercuric acetate or phenylmercuric nitrate has been found in latex paints, contact lens solution, nasal spray and some other medications due to its inhibition of fungal, bacterial, and microbial growth (Swensson and Ulfvarson, 1963; Agocs *et al.*, 1990; Carpi and Chen, 2001). Hg^0 has also been used in equipment like thermometers, fluorescent light bulbs, thermostat switches, float controls in sump pumps, barometers, and gas flow meters (Spedding and Hamilton, 1982; Carpi and Chen, 2001).

1.4. Atmospheric Deposition of Mercury

Atmospheric deposition has been identified as an important source of mercury to earth's surfaces like aquatic and terrestrial environments (Buehler and Hites, 2002; Landis and Keeler, 2002; Rolfhus *et al.*, 2003). Atmospheric bulk deposition constitutes the mercury deposited through wet and dry processes. Wet deposition of Hg is defined as the air-to-surface flux in precipitation (occurring as rain, snow, or fog), whereas dry deposition is the Hg deposition in the absence of precipitation (Sakata and Marumoto, 2005; Lindberg *et al.*, 2007). Although both dry and wet deposition processes contribute to the total atmospheric mercury budget, it has been estimated by a number of researchers that more than 50% of mercury entering the surface waters is a result of direct wet deposition (Sorensen *et al.*, 1990; Lamborg *et al.*, 1995; Scherbatskoy *et al.*, 1997; Mason *et al.*, 1997; Landis and Keeler *et al.*, 2002). GOM is less volatile and more

water-soluble than Hg^0 and is more likely to be removed by rain, absorbed by terrestrial surfaces and adhered to atmospheric particulate matter. A study has shown that Hg^0 dry deposition rates may be more significant than previously understood (Lindberg *et al.*, 2004). However, GOM and Hg_p are the primary atmospheric forms responsible for the dry deposition of Hg (Lyman *et al.*, 2007).

Quantifying Hg bulk deposition is necessary in order to reduce the large gaps that exist in the global Hg mass balance estimates (Mason and Sheu, 2002) and also to attribute the sources of Hg for the development of policies regarding the control of Hg emissions (Lindberg *et al.*, 2007). The atmospheric mercury depositions to watersheds result in an increase in concentrations of MeHg in aquatic biota including fish (Harris *et al.*, 2007; Munthe *et al.*, 2007). This is because following deposition, Hg(II) can be converted to MeHg in anaerobic environments such as lake sediments (Gilmour *et al.*, 1992), hypolimnetic waters (Eckley and Hintelmann, 2006), and wetlands (St. Louis *et al.*, 1994).

Understanding the mercury emissions-to-deposition cycle is required for the assessment of the environmental risks posed by methyl mercury (Schroeder and Munthe, 1998; Sakata and Asakura, 2007). It has been recognized for many years that accurate measurement of relevant atmospheric mercury species is necessary to help elucidate the processes of emission, transportation, transformation, and deposition of atmospheric mercury. Since atmospheric deposition accounts for the Hg input to the surface environment, monitoring Hg species is the most direct way of assessing inputs from the atmosphere (Fitzgerald *et al.*, 1998; Rice *et al.*, 2009; Conaway *et al.*, 2010; Leopold *et al.*, 2010).

Some of the previous studies have shown higher Hg in the urban atmosphere, which varied with the urban structure and height (Witt *et al.*, 2010, Song *et al.*, 2009; St. Denis *et al.*,

2006; Carpi and Chen, 2002; Liu *et al.*, 2002). One of the studies (Cheng *et al.*, 2009) showed that local sources which have never been identified nor reported might have contributed to the high Hg levels in the atmosphere. Also a recent study showed that buildings could be a major source of Hg to urban atmosphere (Cairns *et al.*, 2011).

This study will mainly focus on the analysis of atmospheric total mercury (THg) and MeHg. The majority of airborne mercury is Hg^0 which makes ~ 90–99% of the THg. Hg^0 is important because of its abundance in the atmosphere, as well as its extended residence time, allowing deposition to a wide range of locations (Lindqvist, 1994; Gochfeld, 2003; Environment Canada, 2004). MeHg is important because of its conversion from a wide range of mercury species, including Hg^{2+} , Me_2Hg , and Hg^0 , as well as its biomagnification potential and its ability to migrate through living cell membranes (Schroeder and Munthe, 1998; Gochfeld, 2003; Environment Canada, 2004).

1.5. Study Objectives

1. To determine mercury (Hg) species i.e. methyl mercury (MeHg) and total mercury (THg) in atmospheric deposition samples.
2. To compare the deposition rates of Hg species on plastic, glass and water surfaces in order to understand which surface has the higher deposition.
3. To compare the deposition rates on two sites i.e. rooftops of KHN and JOR, varying in heights in order to study the effect of elevation on the deposition of mercury.

2. Materials and Methods

2.1. *Sampling Locations*

The sampling locations and the samplers used for sample collections were same as explained in Part 1. Please refer to sections 2.1 and 2.2 of Part 1 (page 14) for this information.

2.2. *Sampling and analytical procedures*

The information regarding sampling of atmospheric samples is given in 2.3 of Part 1 (page 15). The methods for the determination of THg and MeHg are were different than the rest of metals which are explained below.

2.3. *Determination of total mercury*

To determine the total mercury (THg) concentration, USEPA Method 1631, Revision E (USEPA, 2002) was followed. For the analysis, 0.5 mL aliquot of bromine monochloride (BrCl) solution (see next page) was added to 100 mL of atmospheric sample in a bubbler and the mixture was left to react for 12 hours until all of the mercury was oxidized to Hg(II). After 12 hours, if the yellow colour disappears, it means that all of BrCl has been consumed. If so, more BrCl (~ 0.5 mL) was added and again left to react for 12 h). After that, the excess BrCl was removed by the addition of 0.25 mL of hydroxylamine hydrochloride (NH₂OH·HCl) and left it to react for 5 minutes. To reduce Hg(II) to Hg(0), 0.5 mL of stannous chloride (SnCl₂) solution (see page 55) was added and left to react for 20 minutes. The resultant elemental Hg was then removed from the sample solution by purging with nitrogen (N₂) at a flow rate of 250 mL min⁻¹ and was collected in a gold trap. Figure 8 shows the experimental set up for the purge and trap assembly.

Figure 8: Purge and trap assembly for the analysis of THg.

The collected Hg was then thermally released by heating to 500°C and carried under argon atmosphere to the cell of CVAFS for quantification. Software Hg Guru 2.2 was used to integrate the peak area (or identify the peak height, if desired) of the detected signals. For the detection of THg, the “Total Hg” was chosen under the “Mode” menu and the run time was adjusted to 3 minutes. The experimental setup for the determination of THg is shown in Figure 9.

Preparation of reagents: Among the reagents used during the experiment, BrCl was prepared by dissolving 2.7g of reagent grade KBr in 250mL of Ultra-Purity HCl inside a fume hood. The solution was kept well mixed by using a magnetic stirring bar and was stirred for approximately 1 hour. Then 3.8g of reagent grade potassium bromate (KBrO_3) was slowly added to the acid

Figure 9: Schematic diagram of the CVAFS system for the determination of THg.

solution while stirring. When all of the KBrO₃ was added, the solution color changed from yellow to red to orange. After all KBrO₃ has been added, it was capped and was stirred for one hour. The BrCl prepared in concentrated HCl (strong acid) is also used to break all organic matrices (Hg-C) surrounding Hg. The reducing agent SnCl₂ was prepared adding 10g of SnCl₂·2H₂O to 5 mL of Ultra-Purity HCl in a 250 mL glass beaker. The beaker was swirled to mix until all SnCl₂·2H₂O was dissolved. The solution was then transferred to a 50mL volumetric flask and filled to mark using nano pure water. The reagent NH₂OH·HCl was prepared by dissolving 3g of NH₂OH·HCl in reagent water and making the volume to 100 mL. To remove any traces of mercury present in the solution, 1.0 mL of SnCl₂ solution was added and then purged overnight at 200 mL min⁻¹ with mercury free N₂ (USEPA method 1631-E).

2.4. Determination of methyl mercury

For the determination of methyl mercury (MeHg), USEPA Method 1630 was followed: 45 mL of the preserved precipitation sample were pipetted into a fluoropolymer distillation vessel and the distillation was carried out at 25°C under Hg-free N₂ flow until approximately 35 mL distillate was collected in the receiving vessel. The collected sample was adjusted to pH 4.9 with the addition of 2 mol L⁻¹ acetate buffer and another 10 mL of reagent water were added to the vial to make the volume of the sample close to 50 mL. The sample was then transferred into a bubbler, and 0.04 mL of freshly thawed 1% sodium tetraethyl borate (NaBEt₄) was added. The contents of the bubbler were allowed to react for 17 min so that all MeHg in the sample was converted to ethyl derivatives. After reaction, a Tenax trap (Carbotrap) was attached to the bubbler and the sample was purged with N₂ (at 250 mL min⁻¹) to transport the methylated mercury into the Tenax trap.

Figure 10: Purge and trap assembly for the analysis of MeHg.

Tenax-TA traps are also made of quartz tubing (10-cm long x 6.5-mm diameter). The tube is filled with ~3.4 cm of 20/35 mesh Tenax-TA graphitic carbon adsorbent. The ends are plugged with quartz wool. Tenax-TA is a porous polymer that is based on 2,6-diphenyl-*p*-

phenylene oxide and can be used as both a column packing and as a trapping adsorbent for organic volatile and semi-volatile compounds. Figure 10 shows the purge and trap assembly for purging MeHg.

Mercury was then thermally desorbed from the trap by heating the trap at 450°C for a period of 45 seconds. The desorbed Hg species were carried by an Ar gas stream, separated in a custom fabricated GC column, and converted to elemental mercury (in a pyrolytic column that was maintained at 700°C) before being transported into the cell of CVAFS for detection and quantification. For the detection of MeHg, “Speciate Hg” Mode was used and the run time was adjusted at 6 min. The experimental setup for the determination of MeHg is shown in Figure 11.

Figure 11: Schematic diagram of the CVAFS system for the determination of MeHg interfaced with isothermal GC and pyrolytic decomposition column.

Preparation of reagents: To prepare the 1% NaBEt₄, the reagent is purchased in 1.0 g air-sealed bottles as 1% Sodium tetraethyl borate (NaBEt₄). First, 100 ml of 2% KOH in reagent water was prepared in a fluoropolymer bottle and cooled to 0°C. The bottle of NaBEt₄ was then rapidly opened and 5 mL of the KOH solution was poured in it. The reagent bottle was capped and shaken vigorously to dissolve the NaBEt₄. This was poured into the 100 mL bottle of KOH solution, and shaken to mix. The solution of 1% NaBEt₄ in 2% KOH was then poured into small fluoropolymer bottles (7ml) and was placed in the freezer. Before and after using NaBEt₄, the small vials were kept frozen at all times. Citrate buffer was prepared using 5.40 g citric acid and 7.34 g sodium citrate to make up 50 mL buffer solution. To purify the buffer solution of any traces of CH₃Hg, 0.5 mL of 1% NaBEt₄ was added and purged overnight with Hg-free N₂ or Ar.

2.5. Calibration and standardization

After the laboratory had established conditions necessary to purge and trap Hg species from the bubbler and to desorb them from the traps so that they can be analyzed by the CVAFS, calibration was done in order to calculate the Hg concentrations in the samples. The calibration contained five non-zero points and the results of analysis of three bubbler blanks (EPA methods 1631 & 1630). Ultrapure deionized water (18-MΩ) was used as a reagent water to prepare all the reagents and standards for both THg and MeHg.

2.5.1 Calibration for THg

National Institute of Standards and Technology (NIST) certified 10,000 µg mL⁻¹ aqueous Hg solution (NIST-3133) was used as a stock mercury standard. To prepare secondary Hg standard solution, 0.5 L of reagent water and 5 mL of BrCl solution was added to a 1.00 L

volumetric flask followed by the addition of 0.100 mL of the stock mercury standard. The flask was filled to 1.00 L with reagent water to obtain solution containing $1.00 \mu\text{g mL}^{-1}$ of mercury. To prepare Hg working standard, 1.00 mL of the above prepared secondary Hg standard was diluted to 100 mL with reagent water containing 0.5% BrCl solution. The resulting solution contained $10.0 \mu\text{g L}^{-1}$. Aliquots of 0.025, 0.05, 0.10, 0.25, 0.50 and 1.0 mL of this working solution were respectively diluted to 100 mL with reagent water containing 0.5% BrCl to get standards of 2.5, 5.0, 10.0, 25.0, 50.0 and 100.0 ng L^{-1} . These standards were taken into bubblers, and excess BrCl was reduced by the addition of 0.25 mL of NH_2OH solution, and finally the reduced sample was reacted with 0.5 mL of SnCl_2 solution which converted the Hg into volatile Hg which was purged out and trapped in the gold traps and finally analyzed by CVAFS which gave the peak area as an output. For each calibration point, the mean peak area of the three blanks was subtracted from the peak area of each standard.

The calibration factor (CF_X) for Hg in each of the five standards was calculated using the following equation.

$$\text{CF}_X = \frac{(A_X) - (A_B)}{(C_X)} \quad \text{-----} \quad (2.1)$$

Where; A_X is peak area for Hg in standard, A_B is the mean peak area of the blank and C_X is the concentration (ng L^{-1}) of Hg in that standard. Then, mean of all the calibration factors (CF_m) was calculated along with the standard deviation (SD, $n-1$) and the relative standard deviation (RSD), where $\text{RSD} = 100 \times \text{SD}/\text{CF}_m$. The RSD was found to be $\leq 15\%$ and the % recovery for the standards was in the EPA recommended range (75–125%) (see Appendix II, Tables 1, 2 & 3). The concentration of mercury in the samples was found by dividing the peak area of the samples by the CF_m .

2.5.2 Calibration for methyl mercury

Stock methyl mercury standard was used to prepare MeHg working standard. Stock methylmercury standard was obtained from Brooks Rand Ltd. This stock solution contained methyl mercury as MeHgCl source and had a concentration of $1 \mu\text{g mL}^{-1}$ of MeHg. To prepare MeHg working standard, 0.10 mL of the stock solution was diluted to 100.0 mL with nanopure water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl in a fluoropolymer bottle. The concentration of MeHg in the resulting solution was 1.00 ng mL^{-1} . Aliquots of 0.005, 0.02, 0.05, 0.1 and 0.2 mL of the working solution were diluted to 50.0 mL with reagent water to get standards of 0.1, 0.4, 1, 2 and 4 ng L^{-1} . These standards were taken into bubblers, the MeHg was converted to volatile MeHg by reacting it with 1% NaBEt₄ (prepared in 2% KOH solution) which was then purged out with N₂ gas and trapped in the Tenax traps and finally analyzed by CVAFS.

Calibration was done using different standards and calibration factors were calculated for each standard using equation 2.1. The mean value of the calibration factors and standard deviations (SD) were used to calculate RSD which was found to be below the EPA recommended limit i.e. < 15 (see Appendix II, Tables 4, 5, 6 & 7).

2.6. Quality Control (QC)

2.6.1. Blanks

Blanks are important quality control tools. During the entire study, field (method) blanks were collected with each batch of samples in order to determine any contamination introduced during sampling period as well as during sampling, transport, storage and analysis activities. Field blanks were analyzed along with each batch of samples and their concentrations were

subtracted from the concentration of each sample in the batch. This practice was carried out through the entire study period.

2.6.2. Method Detection Limit (MDL)

Method detection limits (MDL) were calculated by using EPA method “40 CFR Appendix B to Part 136”. For total mercury, seven replicates with a known concentration of 2.5 ng/L were analyzed using the laboratory equipment and the above mentioned method. Similarly, seven replicates were prepared for methyl mercury with a known concentration of 0.4 ng L⁻¹ and analyzed under laboratory conditions. The standard deviation of the peak areas was used to calculate the MDL by using equation 1.1 (page 21). The student’s t-value (3.14) was taken at 99% confidence level against 6 degrees of freedom. For THg, the MDL was found to be 1.11 ng L⁻¹ whereas, for MeHg, this value was 0.11 ng L⁻¹ (see Appendix II, Tables 8 & 9).

2.6.3. Initial Precision and Recovery (IPR)

To establish the ability to generate acceptable precision and recovery, four replicates of the IPR solution (10 ng L⁻¹ for THg and 0.4 ng L⁻¹ for MeHg) were analyzed and their mean, SD and RSD were calculated. For total mercury, the IPR solutions with four replicates of 10 ng L⁻¹ were found to have an average percent recovery of 109 % (101–118%) which was within the “EPA 1631-E” recommended range i.e. 75-121. The RSD was found to be 11 which was below the recommended value (21) in the EPA 1631-E. For MeHg, according to the EPA method 1630, the IPR should be in the range of 79-121%. Our average IPR (for four replicates of 0.4 ng L⁻¹) was 93.99 % (86–104%) which is within the recommended limit (see Appendix II, Tables 10 & 11).

2.6.4. Ongoing Precision and Recovery (OPR)

To demonstrate that the analytical batch was within the performance criteria of the method and that acceptable precision and recovery was being maintained with in each analytical batch, OPR solutions (25 ng L⁻¹ for THg, prepared from SRM NIST-3133 and 0.5 ng L⁻¹ for MeHg, prepared from MeHgCl standard solution obtained from Brooks Rand Ltd) were analyzed prior to the analysis of each analytical batch as well as after every 10 samples during the analysis. The percent recovery was found to be within the EPA recommended range (77–123%).

2.6.5. Method validation

The quality control samples (QCS) were obtained from a source different than the Hg used to produce the standards routinely in this method; QCS were analyzed as an independent check of system performance. For THg, NIST 1641d and for MeHg, MeHgOH from Brooks Rand were used to prepare the QCS. The average % recoveries of 107.2% and 90.7% were obtained for THg and MeHg respectively (see Appendix II, Table 12).

2.6.6. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

To assess the performance of the method on the sample matrix, the samples were spiked in duplicate, at a minimum of 10% interval (1 sample in 10). For this, the concentration of sample was measured. The sample was then spiked to get MS and MSD. The percent recovery in each of the MS and MSD were calculated using the equation.

$$\% R = 100(A-B)/C$$

Where; A is the measured concentration of the analyte after spiking, B is the concentration before spiking and C is the spiked concentration. The % recoveries (R) ranged between

97–110% and 91–102%, respectively for the THg and MeHg which were within the EPA range (71–125%). Also the relative percent difference (RPD) between the MS and MSD were calculated by using the equation

$$RPD = 200 \times \frac{(D1 - D2)}{(D1 + D2)} \text{ ----- (2.2)}$$

Where D1 is concentration in the MS sample and D2 is the concentration in MSD sample. The RPD values were always found below the recommended limit (24%).

3. Results and Discussion

3.1. Deposition of THg

The samples were analyzed by using CVAFS to get the concentrations of the THg in the samples. Since the sampling was done by using the manual samplers, the volume was different in sampler. The mass of total mercury (ng) deposited on each surface was calculated by multiplying the concentration (ng L^{-1}) by the volume (L) of each sample. Table 6 show the amount of total mercury (ng) deposited on each surface throughout the sampling period.

The deposition rates for THg were calculated as a mass deposited per unit area per unit time using equation 1.4 (Part 1). Generally the samples were collected biweekly and then were averaged for a month to get the deposition rate per month. The deposition rates on each surface were summed up to get the annual deposition rates ($\mu\text{g m}^{-2}\text{a}^{-1}$).

Table 6: The mass of THg (ng) deposited on each surface throughout the sampling period.

Date of Sampling	KHN			JOR		
	Plastic	Glass	Water	Plastic	Glass	Water
Jan. 12	29.02	21.82	27.01	-	-	-
Jan. 20	17.94	16.31	26.70	-	-	-
Jan. 28	86.44	72.12	75.30	-	-	-
Feb. 11	40.92	38.72	61.86	62.47	-	132.52
Feb. 26	95.30	64.06	70.13	62.15	66.85	74.34
Mar. 11	-	-	-	40.40	-	25.50
Mar. 25	18.73	40.25	43.03	42.76	39.63	45.06
Apr. 15	42.51	56.95	-	51.00	52.42	54.84
May. 19	83.36	76.46	61.24	68.33	71.04	-
Jun. 03	72.98	45.44	88.17	45.30	51.76	47.84
Jun. 23	119.72	111.58	227.03	161.55	137.31	349.20
Jul. 06	63.75	77.09	40.29	152.93	83.62	84.74
Jul. 23	76.37	42.49	126.84	85.39	62.39	148.36
Aug. 09	43.75	25.90	50.65	15.27	7.50	49.85
Aug. 26	37.46	60.99	47.49	74.99	111.32	120.27
Sept. 13	73.30	22.59	36.21	40.06	20.47	25.44
Sept. 30	53.53	87.25	78.73	56.25	50.17	78.81
Oct. 19	136.76	76.16	117.66	157.69	118.13	199.55
Nov. 11	43.50	33.05	81.00	21.86	36.99	28.13
Dec. 17	222.24	194.94	353.05	241.32	189.78	339.19

The data was used to calculate the monthly deposition rates. This was done by dividing the deposition rate values by the number of days for each sampling periods and then putting the number of days in a particular month. For example, to calculate the deposition rate for the month of February, the sampling was done on Feb. 11 and Feb. 28. Prior to Feb. 11, the sampling was done on Jan. 28. So the sampling period was 14 days. The 3/14 parts of deposition rate were put

in January and 11/14 were counted towards February. From Feb. 11 to Feb. 28, all the days were in February. So the month of February contains 28 days (11 + 17). Similarly, the deposition rates were calculated for each month. The monthly deposition rates for all the three surfaces on both sites are plotted in Figure 13.

At the JOR site, the values for water surface lay between $0.47\text{--}2.38 \mu\text{g m}^{-2} \text{month}^{-1}$ (with an average of $1.12 \pm 0.57 \mu\text{g m}^{-2} \text{month}^{-1}$), for plastic surface between $0.40\text{--}1.49 \mu\text{g m}^{-2} \text{month}^{-1}$ (with an average of $0.78 \pm 0.33 \mu\text{g m}^{-2} \text{month}^{-1}$) and for glass surface between $0.47\text{--}1.29 \mu\text{g m}^{-2} \text{month}^{-1}$ (with an average of $0.77 \pm 0.28 \mu\text{g m}^{-2} \text{month}^{-1}$). These values at KHN site ranged between $0.51\text{--}1.79 \mu\text{g m}^{-2} \text{month}^{-1}$ ($0.96 \pm .43 \mu\text{g m}^{-2} \text{month}^{-1}$), $0.24\text{--}1.26 \mu\text{g m}^{-2} \text{month}^{-1}$ ($0.72 \pm 0.27 \mu\text{g m}^{-2} \text{month}^{-1}$) and $0.51\text{--}1.12 \mu\text{g m}^{-2} \text{month}^{-1}$ ($0.71 \pm 0.20 \mu\text{g m}^{-2} \text{month}^{-1}$) for water, plastic and glass surfaces respectively. Figure 12 shows clear variation in the deposition rates of the three surfaces with the highest deposition found in June and December 2010. The higher deposition in the month of June was probably due to the large amount of precipitation during the month and also because of the fact that dry deposition is higher during the summer period (Zhang *et al.*, 2012).

(a)

(b)

Figure 12: Comparison of THg's monthly deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) on different surfaces collected on the rooftops of JOR (a) and KHN (b) sites.

The previous studies have shown that there is no significant difference between the bulk deposition and wet deposition fluxes (Guentzel *et al.*, 1995; Iverfeldt and Munthe, 1993 and Guentzel, 2001). The comparison shown in Table 7 is done mostly with the wet deposition but some of the studies analyzed bulk deposition (due to the lack of data on bulk deposition). The

estimated total annual Hg deposition found in this study (JOR site = $13.49 \mu\text{g m}^{-2}\text{a}^{-1}$ on water surface, $9.36 \mu\text{g m}^{-2}\text{a}^{-1}$, on plastic and $9.20 \mu\text{g m}^{-2}\text{a}^{-1}$ on glass surface and KHN = $11.52 \mu\text{g m}^{-2}\text{a}^{-1}$ on water, $8.62 \mu\text{g m}^{-2}\text{a}^{-1}$ on plastic and $8.55 \mu\text{g m}^{-2}\text{a}^{-1}$ on glass surface) was comparable to the annual average of $13.50 \mu\text{g m}^{-2}\text{a}^{-1}$ obtained in Steubenville (Keeler *et al.*, 2006) and lower than the annual average of $16.70 \mu\text{g m}^{-2}\text{a}^{-1}$, $18.60 \mu\text{g m}^{-2}\text{a}^{-1}$, $39.00 \mu\text{g m}^{-2}\text{a}^{-1}$, $30.1 \mu\text{g m}^{-2}\text{a}^{-1}$ and $34.7 \mu\text{g m}^{-2} \text{a}^{-1}$ reported by Sakata and Marumoto, 2005; Zhang *et al.*, 2012; Feng *et al.*, 2002; Dvonch *et al.*, 2005; and Guo *et al.*, 2008, respectively (Table 7). The total mercury deposition found in this study is higher than $6\text{--}8 \mu\text{g m}^{-2}$ reported in the Great Lakes Region (Gay, 2009). This is because this study was carried out in an urban environment whereas the reported values for the Great Lakes Region were mostly from rural locations.

Table 7: Comparison of total mercury deposition fluxes in urban environments.

Experimental Location	Study Period	Annual deposition rate ($\mu\text{g m}^{-2}\text{a}^{-1}$)	Reference
Toronto, Canada	Jan 2010–Dec 2010	8.55–13.50	This study
Davie, USA	1995–1996	30.1	Dvonch <i>et al.</i> , 2005
Steubenville, USA	Jan 2003–Dec 2003	13.5	Keeler <i>et al.</i> , 2006
Toronto, Canada	Jun 2005–Mar 2008	18.60	Zhang <i>et al.</i> , 2012
Guiyang, China	1996	39.0	Feng <i>et al.</i> , 2002
Wujiang, China	Jan 2006–Dec 2006	34.7	Guo <i>et al.</i> , 2008
Komae, Japan	Dec 2002–Nov 2003	16.7	Sakata & Marumoto, 2005

3.2. *Distribution of THg among sites and surfaces*

The box plot shows how the THg is distributed on different sites in Toronto (Figure 13). The median of plastic surface on JOR site ($0.69 \mu\text{g m}^{-2}\text{month}^{-1}$) in the boxplot is slightly skewed towards the lower side of the interquartile indicating that majority of the values are less than $0.70 \mu\text{g m}^{-2}\text{month}^{-1}$ (with the maximum at $1.49 \mu\text{g m}^{-2}\text{month}^{-1}$ and minimum at $0.40 \mu\text{g m}^{-2}\text{month}^{-1}$) whereas on KHN site, the median ($0.77 \mu\text{g m}^{-2}\text{month}^{-1}$), is skewed more towards the upper side of the interquartile (with maximum at $1.13 \mu\text{g m}^{-2}\text{month}^{-1}$ and minimum at $0.24 \mu\text{g m}^{-2}\text{month}^{-1}$) indicating that the most of the samples have deposition rates of higher than $0.70 \mu\text{g m}^{-2}\text{month}^{-1}$. On the glass surface, the median at JOR site ($0.79 \mu\text{g m}^{-2}\text{month}^{-1}$) is more towards the upper side of the interquartile showing that majority of the samples have a deposition rate higher than $0.75 \mu\text{g m}^{-2}\text{month}^{-1}$ (with maximum value at 1.29 and minimum at $0.43 \mu\text{g m}^{-2}\text{month}^{-1}$). On the other hand, the glass surface at KHN site have most of the values below $0.75 \mu\text{g m}^{-2}\text{month}^{-1}$ (with maximum being at 1.12 and minimum at 0.51) and are skewed more towards the lower half of the interquartile. For the water surface at JOR site (0.47–2.38), the median ($1.11 \mu\text{g m}^{-2}\text{month}^{-1}$) is more skewed towards the upper side of the interquartile (with the maximum value way far from the interquartile) indicating that majority of the samples have the deposition rates higher than $1.00 \mu\text{g m}^{-2}\text{month}^{-1}$ whereas on KHN site, the majority of values were found to be below $0.90 \mu\text{g m}^{-2}\text{month}^{-1}$ (0.51–1.79 with median at 0.83).

Figure 13: Box plots showing the distribution of THg among different sites and surfaces in downtown Toronto (January 2010 – December 2010).

3.3. Deposition of MeHg

The amount of MeHg (ng) deposited on each surface was calculated by multiplying the concentration (ng L^{-1}) to the volume (L) of the sample. Table 8 show the mass of MeHg deposited on each surface throughout the sampling period. The deposition rates were calculated by using equation 1.4. The data was used to calculate the monthly deposition rates in a similar way as described in case of THg.

Monthly deposition rates of MeHg are presented in Figure 14. The values for wet, plastic and glass surfaces on JOR site lay between $0.020\text{--}0.067 \mu\text{g m}^{-2}\text{month}^{-1}$ (with average $0.042 \pm 0.017 \mu\text{g m}^{-2}\text{month}^{-1}$), $0.005\text{--}0.036 \mu\text{g m}^{-2}\text{month}^{-1}$ (with average $0.012 \pm 0.009 \mu\text{g m}^{-2}\text{month}^{-1}$) and $0.04\text{--}0.034 \mu\text{g m}^{-2}\text{month}^{-1}$ (with average $0.014 \pm 0.008 \mu\text{g m}^{-2}\text{month}^{-1}$) respectively whereas on KHN site, these values were $0.009\text{--}0.064 \mu\text{g m}^{-2}\text{month}^{-1}$ (with average $0.032 \pm 0.016 \mu\text{g m}^{-2}\text{month}^{-1}$), $0.003\text{--}0.035 \mu\text{g m}^{-2}\text{month}^{-1}$ (with average $0.011 \pm 0.008 \mu\text{g m}^{-2}\text{month}^{-1}$) and

0.05–0.032 $\mu\text{g m}^{-2}\text{month}^{-1}$ (with average $0.009 \pm 0.008 \mu\text{g m}^{-2}\text{month}^{-1}$). On plastic and glass surfaces, the highest deposition was observed during the month of December whereas, on wet surface there was reasonably high deposition during June which indicates that on wet surface, MeHg deposited either through dry deposition or wet deposition contributes to the total yearly MeHg budget whereas on dry surfaces, the MeHg deposition was only higher during winter.

Table 8: The mass of MeHg (ng) deposited on each surface throughout the sampling period.

Sampling	KHN			JOR		
Dates	Plastic	Glass	Water	Plastic	Glass	Water
Feb. 11	1.14	0.60	2.73	0.60	-	3.64
Feb. 26	0.62	0.15	1.00	0.86	0.54	1.13
Mar. 11	-	-	-	0.68	-	1.43
Mar. 25	0.42	0.46	1.75	0.78	0.48	1.93
Apr. 15	0.89	0.54	-	1.49	0.67	1.85
May. 19	2.53	1.46	2.99	1.59	0.22	-
Jun. 03	0.77	0.81	1.43	0.38	0.58	4.32
Jun. 23	0.73	0.69	6.86	1.48	0.97	7.60
Jul. 06	0.39	0.54	1.28	1.18	1.13	3.96
Jul. 23	0.89	0.61	1.79	0.42	0.47	2.52
Aug. 09	0.60	0.32	2.60	0.26	0.06	1.78
Aug. 26	0.33	0.21	3.36	1.02	1.05	1.59
Sept. 13	0.32	0.56	0.59	1.03	0.53	1.46
Sept. 30	0.22	0.26	1.84	-	-	2.02
Oct. 19	1.91	0.57	6.19	1.43	0.88	7.53
Nov. 11	0.48	0.72	1.64	0.34	1.13	0.57
Dec. 17	5.57	5.19	12.56	6.21	5.25	13.25

(a)

(b)

Figure 14: Comparison of MeHg deposition rates ($\mu\text{g m}^{-2}\text{month}^{-1}$) on different surfaces collected from the rooftops of JOR (a) and KHN (b) sites.

3.4. Distribution of MeHg among sites and surfaces

The box plot (Figure 15) shows how the MeHg is distributed among the sites and surfaces during the study period. The median of plastic surface on JOR site ($0.009 \mu\text{g m}^{-2}\text{month}^{-1}$) in the boxplot is skewed towards the bottom of the interquartile indicating that

majority of the values are less than $0.010 \mu\text{g m}^{-2}\text{month}^{-1}$ (please see Figure 10 for maximum and minimum values) whereas on KHN site, the median ($0.010 \mu\text{g m}^{-2}\text{month}^{-1}$), is skewed more towards the upper side of the interquartile indicating that the most of the samples have deposition rates of higher than $0.010 \mu\text{g m}^{-2}\text{month}^{-1}$. On glass surface, the median at JOR site ($0.007 \mu\text{g m}^{-2}\text{month}^{-1}$) is more towards the lower side of the interquartile showing that majority of the samples have a deposition rate of lower than $0.01 \mu\text{g m}^{-2}\text{month}^{-1}$. On the other hand, glass surface on KHN site have the median (0.006) at the center of the interquartile showing that the MeHg is proportionally distributed with the maximum far above the interquartile during the month of December. For water surface on JOR site, the median ($0.028 \mu\text{g m}^{-2}\text{month}^{-1}$) is more skewed towards the lower side of the interquartile (with the maximum value during December) indicating that majority of the samples have the deposition rates below $0.030 \mu\text{g m}^{-2}\text{month}^{-1}$. Similarly on KHN site, the majority of values were found to be below $0.030 \mu\text{g m}^{-2}\text{month}^{-1}$ (with median at 0.026). The maximum deposition was found to be during the month of December for almost all of the sites and surfaces.

Figure 15: Box plots showing the distribution of MeHg among different sites and surfaces in downtown Toronto (January 2010 – December 2010).

3.5. Surface and Site comparison by means of Enrichment Factor

The monthly deposition rates of Hg species (THg & MeHg) in the atmospheric samples collected on both the sites (presented in Figures 12 and 14 respectively) showed that the deposition rates were almost similar on both of the dry surfaces (plastic & glass) whereas they differed on the water surface. To identify the best surface for heavy metals deposition, the surfaces were compared by determining the enrichment factor (Florence *et al.*, 2012; Fabian *et al* 2011). Table 9 shows enrichment factor (EF) calculated by using equation 1.5, for all the three surfaces considering glass surface as a reference.

The enrichment factors of THg on KHN site were found to be 1.0 for plastic surface and 1.4 for water surface whereas on JOR site they were 1.0 for plastic and 1.5 for water surface. In case of MeHg, the EF were found to be 1.2 for plastic and 3.6 for water surface on KHN and 0.9 and 3.1 respectively on JOR. These results show that the plastic and glass surfaces behaved quite

similarly towards the deposition of THg as well as MeHg whereas the water surface had higher deposition. So in general, it could be concluded that the water surface had the higher deposition than plastic and glass which were more or less similar in their behavior.

Table 9: Enrichment factor (EF) for Hg species as a function of surface (to show surface comparison) when glass surface is taken as a reference.

Hg Species	Surface	KHN		JOR	
		Mean ($\mu\text{g m}^{-2}\text{month}^{-1}$)	EF	Mean ($\mu\text{g m}^{-2}\text{month}^{-1}$)	EF
THg	Plastic	0.719	1.0	0.782	1.0
	Glass	0.712	1	0.767	1
	Water	0.960	1.4	1.124	1.5
MeHg	Plastic	0.011	1.2	0.012	0.9
	Glass	0.009	1	0.014	1
	Water	0.032	3.6	0.044	3.1

Table 10 shows the EF for both sites, using KHN as a reference site. The EF for THg was found to be 1.1, 1.1 and 1.2 for plastic, glass and water surface respectively. For MeHg, the EF was 1.1, 1.6 and 1.3 for plastic, glass and water surfaces, respectively. The results show that for THg, although the JOR site had more deposition, they were not significantly different but for MeHg the deposition was significantly higher on JOR site especially for glass and water surface.

Table 10: Enrichment factor (EF) for Hg species as a function of sites (to show sites comparison) when KHN is taken as a reference.

Hg Species	Site	Plastic surface		Glass surface		Water surface	
		Mean ($\mu\text{g m}^{-2}\text{mon}^{-1}$)	EF	Mean ($\mu\text{g m}^{-2}\text{mon}^{-1}$)	EF	Mean ($\mu\text{g m}^{-2}\text{mon}^{-1}$)	EF
THg	KHN	0.719	1	0.712	1	0.96	1
	JOR	0.782	1.1	0.767	1.1	1.124	1.2
MeHg	KHN	0.011	1	0.009	1	0.032	1
	JOR	0.012	1.1	0.014	1.6	0.042	1.3

3.6. THg vs MeHg

The MeHg contribution to the THg (Table 11) was found to be highest on wet surface as the percentage of MeHg with reference to THg (averaged on two sites) was 3.18% for wet, 1.50% for plastic and 1.34% for glass surface. This illustrates that the MeHg concentrations were always a fraction of the THg concentration thereby confirming the conclusions in other studies (Lee *et al.*, 2000; St Louis *et al.*, 2001; Zhang *et al.*, 2012). However, overall, MeHg tends to be a small percentage (< 5 %) of total mercury in larger systems, including soil, sediment, water, snow, and air (Bloom and Fitzgerald, 1988; Horvat *et al.*, 2003; Munthe *et al.*, 2003; Macleod *et al.*, 2005; Rolfhus *et al.*, 2003; St. Louis *et al.*, 2005; Hammerschmidt *et al.*, 2006).

Table 11: Comparison of THg and MeHg on plastic, glass and water surfaces at both sites.

Location	Hg species	Surface		
		Plastic	Glass	Water
KHN	THg	$8.62 \mu\text{g m}^{-2}\text{a}^{-1}$	$8.55 \mu\text{g m}^{-2}\text{a}^{-1}$	$11.52 \mu\text{g m}^{-2}\text{a}^{-1}$
	MeHg	$0.13 \mu\text{g m}^{-2}\text{a}^{-1}$	$0.11 \mu\text{g m}^{-2}\text{a}^{-1}$	$0.38 \mu\text{g m}^{-2}\text{a}^{-1}$
	% MeHg	1.50 %	1.33 %	3.30 %
JOR	THg	$9.36 \mu\text{g m}^{-2}\text{a}^{-1}$	$9.20 \mu\text{g m}^{-2}\text{a}^{-1}$	$13.49 \mu\text{g m}^{-2}\text{a}^{-1}$
	MeHg	$0.14 \mu\text{g m}^{-2}\text{a}^{-1}$	$0.12 \mu\text{g m}^{-2}\text{a}^{-1}$	$0.42 \mu\text{g m}^{-2}\text{a}^{-1}$
	% MeHg	1.51 %	1.34 %	3.08 %

The results generated from this study indicate that the deposition was highest on the wet surface, whereas the plastic and glass surfaces had almost equal deposition. When the two sites were compared, JOR with more height (~59 m) showed a higher deposition than KHN (height ~15 m) which indicated that the mercury deposition is influenced by global affects more than local ones. Seasonally, the deposition rates were higher in summer as well as in winter showing that in summer, the dry deposition might have contributed significantly whereas in winter the wet deposition might have contributed more towards higher deposition.

Conclusions

The monitoring of heavy metals in Toronto showed that Zn had the highest deposition rates among the analyzed heavy metals. The other metals with the higher deposition rates were Mn, Cu, and Pb whereas the deposition rates of As, Cd, Co and Ni were considerably lower. The deposition rates for most of the heavy metals were found to be comparable to the deposition rates found in other studies across the globe. Mercury was found to be low among all the referral studies.

When surfaces were compared, the deposition was found to be higher on wet surface (water surface) as compared to dry surfaces (plastic and glass) whereas the dry surfaces were found to have almost equal deposition rates. Among the mercury species, MeHg contribution to the THg was 1.50% on plastic surface, 1.34% on glass surface and 3.18% on wet surface.

It was also found that the deposition rates of heavy metals were influenced by the height above the ground with higher deposition on KHN site (lower elevation from ground level) as opposed to the JOR site (higher elevation from ground level). This gives indication that local sources might have contributed more to the surfaces at lower height as the heavier particles tends to settle faster under the influence of gravity. This trend was found to be opposite in case of mercury, i.e. the deposition rates were higher on JOR site as compared to KHN site which means that the global and the regional impact of mercury was higher than the local impact.

Future Work

It would be ideal to work concurrently at several other sampling locations. This could include other locations in the city of Toronto and across the Greater Toronto Area (GTA). At least one sampling location should be close to the point emission sources which would give a more accurate idea of the contribution of the local sources to the total atmospheric budget. Also it would be an interesting idea to determine the heavy metal identity and concentrations in other environmental samples like plants, soil and sediments.

As the sampling involved the development of manual samplers, future studies may wish to focus on the plausibility and reliability of other sampling techniques. The automatic samplers could be used for the further studies which could reduce the chances of contamination.

Also there are a lot of high rise buildings in the downtown area which are built of either glass or plastic materials and they are vertical. Further avenues to explore would be conducting deposition studies on the surfaces placed vertical. Based on the results of this study, the studies may also be carried out in order to identify the potential sources of heavy metals as well as to assess their impact on human health.

Appendices

Appendix I

Table 1: Operational parameters of ICP-AES for the determination of heavy metals in the atmospheric deposition samples.

Parameter	Value
RF power	1200 W
Auxiliary gas Flow-rate	20 mL min ⁻¹
Coolant gas Flow-rate	40 mL min ⁻¹
Nebulizer gas Flow-rate	30 mL min ⁻¹
Integration time	10 s
Analyte lines	As 189.04 nm, Cd 226,50 nm, Co 228.62 nm, Cu 654.79 nm, Mn 257.61 nm, Ni 231.61 nm, Pb 168.22 nm, Zn 213.86 nm

Table 2: Calculation of the percent recoveries in the quality control samples (SRM-NIST 1643e).

# of Trials	Concentration ($\mu\text{g L}^{-1}$)	As	Cd	Co	Cu	Mn	Ni	Pb	Zn
Trial 1	Original	53.38	5.80	23.89	20.09	34.41	55.11	17.33	69.24
	Detected	55.66	5.85	24.36	19.37	34.96	57.71	17.61	64.84
	% Recovery	104.27	100.87	101.95	96.40	101.60	104.72	101.60	93.65
Trial 2	Original	53.27	5.79	23.85	20.05	34.34	55.00	17.30	69.10
	Detected	54.12	6.54	23.66	20.63	34.28	56.53	18.37	67.62
	% Recovery	101.59	112.99	99.22	102.88	99.82	102.78	106.20	97.86
Trial 3	Original	52.44	5.70	23.47	19.74	33.81	54.14	17.03	68.02
	Detected	56.49	5.82	23.42	18.03	35.08	57.48	18.59	64.15
	% Recovery	107.72	102.15	99.77	91.34	103.77	106.17	109.18	94.31
Average	Original	53.03	5.76	23.74	19.96	34.19	54.75	17.22	68.79
	Detected	55.42	6.07	23.81	19.34	34.77	57.24	18.19	65.54
	% Recovery	104.53	105.34	100.31	96.88	101.73	104.56	105.66	95.27

Figure 1: Graphs showing the analysis in a set of blanks.

Figure 2: The concentration of the metals deposited on all the three surfaces at KHN site.

Figure 3: The concentration of the metals deposited on all the three surfaces at JOR site.

Appendix II

Table 1: Calibration of CVAFS for the determination of total mercury with Trap # 4 by means of calculating the calibration factors and percent recoveries.

Concentration (ng L ⁻¹)	Peak Area	Blank (Average)	Net Peak Area	Calibration Factor	Detected Concentration	% recovery
2.50	11397546	8718571	2678975	1071590	2.59	103.59
5.00	13245963	8718571	4527392	905478	4.38	87.54
10.00	19257767	8718571	10539196	1053920	10.19	101.89
25.00	36876263	8718571	28157692	1126308	27.22	108.88
50.00	57817363	8718571	49098792	981976	47.47	94.93
100.00	1.15E+08	8718571	1.07E+08	1067239	103.17	103.17
Mean				1034418		
St. Dev				78305		
RSD				8		

Table 2: Calibration of CVAFS for the determination of total mercury with Trap # 5.

Concentration (ng L ⁻¹)	Peak area	Blank (Average)	Net peak area	Calibration Factor (CFm)	Detected Concentration	% recovery
2.50	9547271	6452137	3095134	1238054	2.61	104.30
5.00	12364210	6452137	5912073	1182415	4.98	99.62
10.00	18131862	6452137	11679725	1167973	9.84	98.40
25.00	32734963	6452137	26282826	1051313	22.14	88.57
50.00	67569739	6452137	61117602	1222352	51.49	102.98
100.00	132418792	6452137	125966655	1259667	106.13	106.13
Mean				1186962		
St. Dev				74740		
RSD				6.3		

Table 3: Calibration of CVAFS for the determination of total mercury with Trap # 8.

Concentration (ng L ⁻¹)	Peak Area	Blank (Average)	Net Peak Area	Calibration Factor (CF)	Detected concentration	% Recovery
2.50	13617028	10282485	3334543	1333817	2.95	117.82
5.00	15390634	10282485	5108149	1021630	4.51	90.25
10.00	22276007	10282485	11993522	1199352	10.59	105.95
25.00	36491176	10282485	26208691	1048348	23.15	92.61
50.00	66799039	10282485	56516554	1130331	49.92	99.85
100.00	1.16E+08	10282485	1.06E+08	1058777	93.53	93.53
Mean				1132042		
St. Dev.				118161		
RSD				10		

Table 4: Calibration of CVAFS for the determination of MeHg with Trap # 1.

Concentration (ng L ⁻¹)	Peak area	Blank (Average)	Net peak area	Calibration Factor	Detected Concentration	% recovery
0.40	1430062	1211150	218912	547280	0.35	87.90
1.00	1867203	1211150	656053	656053	1.05	105.37
2.00	2441709	1211150	1230559	615280	1.98	98.82
4.00	3898918	1211150	2687768	671942	4.32	107.92
Mean				622639		
St. Dev.				55619		
RSD				8.93		

Table 5: Calibration of CVAFS for the determination of MeHg with Trap # 3.

Concentration (ng L ⁻¹)	Peak area	Blank (Average)	Net peak area	Calibration Factor	Detected Concentration	% recovery
0.40	962899	720898	242001	605003	0.39	98.19
1.00	1352468	720898	631570	631570	1.02	102.50
2.00	1866793	720898	1145895	572948	1.86	92.99
4.00	3341513	720898	2620615	655154	4.25	106.33
Mean				616168		
Std. Dev				35354		
RSD				5.74		

Table 6: Calibration of CVAFS for the determination of MeHg with Trap # 7.

Concentration (ng L ⁻¹)	Peak area	Blank (Average)	Net peak area	Calibration factor	Detected Concentration	% recovery
0.40	604445	355689	248756	621890	0.42	105.86
1.00	947915	355689	592226	592226	1.01	100.81
2.00	1453736	355689	1098047	549024	1.87	93.46
4.00	2702193	355689	2346504	586626	3.99	99.86
Mean				587441		
St. Dev.				29923		
RSD				5.09		

Table 7: Calibration of CVAFS for the determination of MeHg with Trap # 10.

Concentration (ng L ⁻¹)	Peak area	Blank (Average)	Net peak area	Calibration factor	Detected Concentration	% recovery
0.40	803127	530850	272277	680693	0.39	98.02
1.00	1274479	530850	743629	743629	1.07	107.09
2.00	1878403	530850	1347553	673777	1.94	97.03
4.00	3249142	530850	2718292	679573	3.91	97.86
Mean				694418		
St. Dev.				32947		
RSD				4.74		

Table 8: Method Detection Limit calculation for total mercury with seven replicates of 2.5 ng L⁻¹ using EPA method 40 CFR Appendix B to Part 136.

Initial Concentration (ng L ⁻¹)	Net Peak area	Mean calibration factor (CFm)	Detected concentration (ng L ⁻¹)
2.50	2309499	1034418	2.23
2.50	2755632	1034418	2.66
2.50	2455950	1034418	2.37
2.50	3078373	1034418	2.98
2.50	3186121	1034418	3.08
2.50	2710967	1034418	2.62
2.50	3253646	1034418	3.15
Mean			2.73
St. Dev.			0.35
MDL			1.11

Table 9: Method Detection Limit calculation for methyl mercury with seven replicates of 2.5 ng L⁻¹ using EPA method 40 CFR Appendix B to Part 136.

Initial Concentration (ng L ⁻¹)	Net Peak area	Mean calibration factor (CFm)	Detected concentration (ng L ⁻¹)
0.40	260014	622639	0.42
0.40	237843	622639	0.38
0.40	214823	622639	0.35
0.40	229352	622639	0.37
0.40	277644	622639	0.45
0.40	244826	622639	0.39
0.40	221799	622639	0.36
Mean			0.39
Std. Dev			0.04
MDL			0.11

Table 10: Calculation of % recovery and relative standard deviation (RSD) of the initial precision and recovery (IPR) replicates for the determination of total mercury using trap # 4.

Concentration	Net Peak Area	Recovery	% Recovery
10.00 ng L ⁻¹	13312833	11.78	117.81
10.00 ng L ⁻¹	11030928	10.59	105.90
10.00 ng L ⁻¹	10748952	10.32	103.19
10.00 ng L ⁻¹	10494473	10.08	100.75
Mean			109.41
St. Dev			12.44
RSD			11.37

Table 11: Calculation of average % recovery of the initial precision and recovery (IPR) replicates for the determination of methyl mercury using trap # 1.

Concentration	Net Peak area	Recovery	% Recovery
0.40 ng L ⁻¹	260014	0.42	103.77
0.40 ng L ⁻¹	237843	0.38	94.92
0.40 ng L ⁻¹	214823	0.34	85.73
0.40 ng L ⁻¹	229352	0.36	91.53
Average	235508	0.38	93.99

Table 12: Analysis of Quality Control Samples to determine total mercury using standard reference material NIST 1641d.

Concentration (ng L ⁻¹)	Net peak area (Trial 1)	Net peak area (Trial 2)	Net peak area (Trial 3)	Average peak area	Detected Concentration	% Recovery
12.54	12126751	13910764	12004516	12680677	12.26 ± 1.03	97.78
25.08	27345079	29065112	25891490	27433894	26.52 ± 1.54	105.75
50.16	59112307	53892571	59387568	57464149	55.55 ± 2.99	110.75
75.24	87686306	84046352	85354108	85695589	82.84 ± 1.78	110.12
100.32	117937140	111610389	114352214	1.15E+08	110.82±3.07	110.47
125.40	143133723	137755406	140880547	1.41E+08	135.91±2.61	108.38

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