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A comparison of methyl and gaseous elemental mercury in the urban atmosphere

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A COMPARISON OF METHYL AND GASEOUS ELEMENTAL MERCURY IN THE URBAN ATMOSPHERE

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Abstract

A COMPARISON OF METHYL AND GASEOUS ELEMENTAL MERCURY IN THE URBAN ATMOSPHERE

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This study was carried out to compare the levels of mercury species, i.e., elemental mercury (Hg^0) and methyl mercury (MeHg), in indoor and outdoor air in urban areas in Canada. Offices, laboratories for undergraduate studies, and laboratories for research, in a public building located in the downtown core of the city of Toronto, were selected. Hg^0 was measured using an automated mercury vapour analyzer. MeHg in the air was collected using a carbotrap, and the trapped MeHg was thermally desorbed and analyzed using a CVAFS. The results showed that both indoor MeHg and Hg^0 levels were related to location function and air circulation. Outdoor MeHg levels were significantly elevated, ranging between 21 and 41% of total mercury (THg) levels, compared to those reported from previous studies. Outdoor Hg^0 fluctuations were not found to be significantly related to temperature or sunlight exposure, and outdoor MeHg levels were connected to soil and vegetation abundance. Average indoor Hg^0 levels were found to be between 1.4 and 15 times higher than outdoor levels, whereas MeHg indoor levels were not consistently higher than outdoor levels. Although the mercury concentrations in the indoor environment are still lower than the safety standard for Hg^0 and organic mercury, they are comparable to those observed near point sources. Thus, indoor air can be a source of mercury to the atmosphere.

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1. Introduction

1.1 Properties of Mercury

Mercury is a naturally occurring element, and is generally referred to as a heavy metal (Environment Canada, 2004a). Elemental mercury (Hg^0) has a melting point of -38.9^0C and a boiling point of 357.3^0C (Environment Canada, 2004a). It is liquid at room temperature, and is one of the most volatile metals known (Environment Canada, 2004a; Gochfeld, 2003). Once it vapourizes, mercury becomes a colourless, odourless gas (Environment Canada, 2004a). It can be transformed into its various forms through abiotic and biogeochemical processes during transportation in the atmosphere (Environment Canada, 2004a).

There are several different common mercury species, each of which can impact the environment in its own unique way. In the environment, mercury is normally found as an atmospheric gas, both in organic and inorganic forms (Environment Canada, 2004a). Elemental mercury is one of the most common forms of mercury in the atmosphere (Environment Canada, 2004a). Mercury can also exist as two different kinds of cations: Hg^{2+} and Hg_2^{2+} (Environment Canada, 2004a). Hg^{2+} is generally more stable and can form inorganic compounds with sulfur (like in the mineral cinnabar), oxygen, and hydroxyl ions (Environment Canada, 2004a; Tan et al, 2000). Some other common mercury compounds include: mercuric chloride ($HgCl_2$), mercurous chloride (Hg_2Cl_2), methyl mercury (CH_3Hg) and dimethyl mercury ($(CH_3)_2Hg$) (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, 2004a).

The reactions taking place during atmospheric mercury cycling depend on the type of mercury species. About 98% of atmospheric mercury is in the form of Hg^0, with a residence time of 1-1.5 years (Environment Canada, 2004b). This can allow mercury to be transported in the atmosphere on a regional or global scale (Gochfeld, 2003; Lindqvist, 1994). Exactly where mercury is deposited, relative to the pollution source, depends on such conditions as meteorology, temperature, humidity, solar radiation, speciation, source type, height of emission, and atmospheric circulation processes (Environment Canada, 2004b). This tends to create Hg^0 air pollution, which is less localized and more pervasive than other mercury species.

This Hg^0 can then be deposited into aquatic systems via deposition to water surfaces directly, or to land with eventual runoff (Gochfeld, 2003). This inorganic mercury may then settle onto the sediment surface or onto algal mats, where it may then be converted into methyl mercury (MeHg) via bacterial interactions (Gochfeld, 2003). Hg^0 may then be transported via the aquatic system, through rivers, lakes, reservoirs, and oceans (Environment Canada, 2004b). In fact, almost 1/3 of total mercury emissions cycle between the ocean and the atmosphere (Environment Canada, 2004b).

Hg^{2+}, on the other hand, 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, 2004c). 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, 2004c). Micro-organisms, like methanogenic and sulfate-dependent bacteria, are thought to facilitate the conversion of Hg^{2+} to MeHg under anaerobic conditions, such as that found in wetlands,

some sediments, and soils (Environment Canada, 2004c). 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).

Any dimethyl mercury (Me$_2$Hg) that is released into the atmosphere tends to be short-lived, and undergoes rapid oxidation (Schroeder and Munthe, 1998). The release of Me$_2$Hg from upwelling areas in the ocean can lead to a reaction with hydroxide (OH) and chlorine (Cl) radicals to form MeHg (Niki et al, 1983; Schroeder and Munthe, 1998).

$$(CH_3)_2Hg + Cl \rightarrow CH_3HgCl + CH_3$$

$$(CH_3)_2Hg + OH \rightarrow CH_3HgOH + CH_3$$
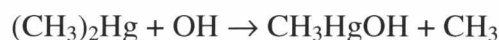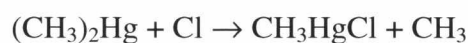
This can lead to small concentrations of MeHg in both the air and precipitation (Schroeder and Munthe, 1998). MeHg can then be deposited away from this pollution source through both wet and dry deposition (Schroeder and Munthe, 1998).

Methyl mercury is a major concern because it has the ability to migrate through living cell membranes and bioaccumulate there (Environment Canada, 2004a; Environment Canada, 2004d). The rate and extent of bioaccumulation can depend on a number of factors, including organism of concern, pollutant emission rate, temperature, and water chemistry (Environment Canada, 2004d). In the case of MeHg, this bioaccumulation can lead to biomagnification (Environment Canada, 2004d). This leads to high concentrations in animals that are commonly caught and eaten by humans, such as fish (Environment Canada, 2004d). In fact, it is estimated, in aquatic systems, that

MeHg could be magnified more than a million fold (Gochfeld, 2003; Schroeder and Munthe, 1998).

This paper will explore atmospheric Hg^0 and MeHg. Atmospheric mercury is of importance to the overall mercury cycle, as it is the conduit that allows the deposition of mercury to terrestrial and aquatic locations (Lindqvist, 1994; Schroeder and Munthe, 1998; Gochfeld, 2003; Environment Canada, 2004c; Environment Canada, 2004c). 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, 2004b). 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 (Schroeder and Munthe, 1998; Gochfeld, 2003; Environment Canada, 2004a; Environment Canada, 2004b; Environment Canada, 2004c). Table 1.1 outlines some important physical properties of these two species.

Table 1.1

Common Physical Characteristics of Methyl and Elemental Mercury

Species	Hg^0	MeHg
Vapour Pressure at 20^0C	0.16 Pa	1.13 Pa [a]
Specific Gravity at 20^0C	13.456	4.06
Saturated Atmospheric Concentration at 20^0C	15 mg/m^3	90 mg/m^3 [b]
Solubility at 21^0C	5.6×10^{-5} g/L	0.100 g/L

(Swensson and Ulfvarsson, 1968; WHO, 1976; WHO, 1990; CLS, 2000; NRC, 2000; PTCL, 2003)

[a]MeHgCl

[b]MeHgOH

1.2 Mercury in the Environment

Natural releases of mercury to the atmosphere occur on a regular basis (Environment Canada, 2004e). Some of these sources include volcanic eruptions, weathering of soils and rocks, and vapourization from oceans (Environment Canada,

2004d). Mercury also tends to be found in sulfide compounds, especially in the form of cinnabar or red sulfide (Friberg and Vostal, 1972; Feng et al, 2004a). MeHg and Me_2Hg have also been found to be produced by polar marine bacteria (Pongratz and Heumann, 1999). However, MeHg may be a breakdown product of Me_2Hg, as opposed to being independently produced (Pongratz and Heumann, 1999). The methylation of Hg^{2+} may also be taking place in sediments and soil, due to bacterial processes (Horvat et al, 2003; Rolfhus et al, 2003; Macleod et al, 2005; St. Louis et al, 2005; Hammerschmidt et al, 2006).

Since toxic mercury compounds can only be biodegraded as far as elemental mercury itself, mercury is an especially persistent environmental pollutant (Environment Canada, 2004a). Although mercury can be found naturally in the environment, the rate of anthropogenic emissions of mercury species have increased in recent years (Environment Canada, 2004e). 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, 2004e; Cobbett et al, 2007; Ferrari et al, 2008; Kellerhals et al, 2003; Brooks et al, 2008). As can be seen, the anthropogenic impact to rising mercury concentrations in the atmosphere has been significant.

Looking at the composition of anthropogenic mercury emissions, Rutter et al (2008) found that coal fired power plants, industrial inorganic chemical manufacturers, and chlor-alkali plants emitted 54, 17, and 8% of anthropogenic mercury sources surrounding Devils Lake and Milwaukee, WI. Streets et al (2005), on the other hand, looked at mercury emissions in China for the year 1999. It was estimated that 45% of the Hg came from non-ferrous metals smelting, 38% from coal combustion, and 17% from

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miscellaneous activities, including battery and fluorescent lamp production and cement production (Streets et al, 2005). In 2000, of the mercury releases to air reported to the National Pollutant Release Inventory (NPRI), nearly 47% were the result of industrial sources, 24% of which was a result of the primary base metal sector (NPRI, 2000). Over 30% of mercury emissions were found to be the result of non-industrial fuel combustion (NPRI, 2000).

Of the common industrial sources, those that have been confirmed to release MeHg include coal burning plants, sewage sludge application to land, mining and refining, fungicide, industrial waste, landfill gas, thermal power plants, and waste incinerators (Carpi et al, 1997; Kotnik et al, 2000; Tan et al, 2000; Goldman et al, 2001; Lindberg et al, 2001; Munthe et al, 2003; Feng et al, 2004a; Lindberg et al, 2005).

There are also a number of mercury sources that can be found in residential areas. Phenylmercuric acetate or phenylmercuric nitrate has been found in latex paints before the late 80s, contact lens solution, nasal spray, and 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 on the other hand has been used in thermometers, fluorescent light bulbs, thermostat switches, float controls in sump pumps, barometers, and gas flow meters (Spedding and Hamilton, 1982; Carpi and Chen, 2001).

1.3 Impacts of Mercury on Humans

Hg^0 and MeHg are naturally occurring in the environment and vary in their relative toxic effects on humans, with the compound MeHg being one of the most dangerous, next to Me_2Hg (Gochfeld, 2003). This difference can be related to the different chemical characteristics of the mercury species (Refer to Table 1.1). For

instance, the organic compounds, which include MeHg, have the highest toxicities of all the common mercury species (Environment Canada, 2004a; Gochfeld, 2003). This level of toxicity can be connected with the compounds' lipid solubility, giving these compounds the ability to bioaccumulate and biomagnify (Clarkson, 1994; MassDEP, 1996; CLS, 2000; Goldman et al, 2001). The vapour pressure and saturated atmospheric concentration of a mercury compound, on the other hand, indicates whether it could be found at poisonous levels in the ambient atmosphere (Swensson and Ulfvarsson, 1968; WHO, 1976; WHO, 1990). A mercury species' level of toxicity can also be linked to its method of absorption (Environment Canada, 2004a; Gochfeld, 2003).

Hg^0, for instance, is well absorbed by the lungs, but not the skin or gastrointestinal (GI) tract (Gochfeld, 2003). On the other hand, organic mercury compounds, such as MeHg, have 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, 2004f). 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). MeHg can also cross the placental barrier, affecting the fetal brain (Clarkson, 1994; Schuurs, 1999; Rice et al, 2000; Environment Canada, 2004f). MeHg may even inhibit gap junctional intercellular communication of cells, which is a trait shared by some carcinogens (Zefferino et al, 2005).

MeHg may be absorbed in different concentrations depending on the organ involved. For instance, between 1 and 100% of ingested MeHg can be absorbed, depending on whether the bloodstream or the GI tract is the area of concern (Clarkson,

1994; MassDEP, 1996; CLS, 2000; Goldman et al, 2001). On the other hand, only 3-5%

of MeHg applied to the skin is absorbed (CLS, 2000). The rate of absorption via

inhalation could also be high (MassDEP, 1996), although to this researcher's knowledge

it has not been assessed in-depth. However, regardless of the organ, MeHg can be

absorbed into the body about six times more easily than inorganic mercury compounds

(Environment Canada, 2004f).

After transport 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). However, mercury is also secreted during lactation, 16%

of which is secreted in the form MeHg, which can be harmful to nursing babies (CLS,

2000). It is currently estimated that it takes anywhere between 70 days and four months

for MeHg to be eliminated from the body, with bioaccumulation of the compound as a

possibility during that time (MassDEP, 1996; CLS, 2000).

The traditional ways to sample for exposure to MeHg would be through hair,

blood, and placental cord samples (Magos, 1998; CLS, 2000). For instance, levels of 0.2

mg/L or higher in blood samples have been associated with poisoning (Health Canada,

1986). Unfortunately, a residential air guideline has not yet been established for MeHg

(ANL, 2001). However, guidelines (See Table 1.2) have been set up for Hg^{0} in drinking

water, residential air, and industrial environments, as well as for organic mercury in

seafood and industrial environments.

Table 1.2

Mercury Maximum Allowable Limits as per Health Standard Guidelines

Agency	Compound	Standard				
		Drinking Water (mg/L)	Residential Air (ng/m^3)	8h TWA (ng/m^3)[a]	STEL (ng/m^3)[b]	Seafood (mg/L)
USEPA	Hg	0.002				
ATSDR	Hg		5×10^4	5×10^4		
Health Canada	Hg	0.001				
NOHSC	Alkyl Mercury			1×10^4	3×10^4	
OSHA	Organic Mercury			1×10^4	3×10^4	
FDA	MeHg					1

(OSHA, 1993; ATSDR, 1999; Environment Australia, 2001; Goldman et al, 2001; Health Canada, 2007)

[a] eight-hour time weighted average

[b] short term exposure limit

The main sources of exposure to MeHg are through the consumption of fish, marine mammals, crustaceans, and animals and poultry that have been fed fish meal (CLS, 2000; Environment Canada, 2004g). Another pathway of exposure to MeHg is the consumption of crops that have been contaminated by a mercury-containing pesticide (Environment Canada, 2004g).

The symptoms of MeHg poisoning are commonly referred to as Minamata disease, and generally affect the central nervous system (Fthenakis et al, 1995; MassDEP, 1996; Magos, 1998; Rice et al, 2000; Goldman et al, 2001; GOJ, 2002; Gochfeld, 2003; Environment Canada, 2004g; Trasande et al, 2005). One issue with identifying MeHg poisoning is the latency period that is involved (CLS, 2000). In some cases it can take anywhere from a couple of weeks to over a year for any warning signs to show (Magos, 1998; CLS, 2000). The signs of MeHg poisoning can also be quite variable, making it hard to make a diagnosis if an unknown MeHg exposure has occurred (Fthenakis et al,

1995; MassDEP, 1996; Magos, 1998; Rice et al, 2000; Goldman et al, 2001; GOJ, 2002; Gochfeld, 2003; Environment Canada, 2004g; Trasande et al, 2005). A summary of the kinds of symptoms that have been displayed in documented cases is provided in Table 1.3. Generally, mild symptoms such as parathesia and ataxia will be presented, and then over a period of time, dependent on whether the exposure is chronic or acute, more severe symptoms such as generalized weakness, tremors, muscle spasticity, blindness, coma, or even death can occur (OSHA, 1993; Fthenakis et al, 1995; MassDEP, 1996; Magos, 1998; Rice et al, 2000; Goldman et al, 2001; GOJ, 2002; Gochfeld, 2003; Environment Canada, 2004g; Trasande et al, 2005).

Cases affecting large numbers of individuals in a population tend to stem from chronic MeHg poisoning over a number of years. For instance, starting in 1956, spanning 39 years, in Minamata Japan, an outbreak of MeHg poisoning in over 2000 individuals, with 1000 fatalities, occurred (Environment Canada, 2004g). And in Iraq, in 1971 and 1972, over 2000 individuals were diagnosed with MeHg poisioning, resulting in 500 deaths (Environment Canada, 2004g). Takaoka et al (2008) studied over 600 individuals from Minamata that had been admitted into Minamata Kyoritsu Hospital between 2004 and 2005. It was found that somatosensory symptoms, such as problems with tactile, vibration, and position sense, occurred in individuals that were exposed to MeHg (Takaoka et al, 2008).

Hg^0 poisoning can also occur, especially in industrial-related situations. Some studies have looked at gold mining areas, smelting workers, and factory workers. It has been found that in such situations, individuals being exposed to Hg^0 in this fashion have significantly higher concentrations of it in their urine, blood, and hair samples, even

higher than recommended exposure levels (Bose-O'Reilly et al, 2008; Li et al, 2008). Generalized symptoms include excessive salivation, metallic taste in mouth, ataxia, dysdiadochokinesia, discoloration of gums, gingivitis, finger and eyelid tremors, decreased visual sensitivity, and abnormal reflexes (Barboni et al, 2008; Bose-O'Reilly et al, 2008; Costa et al, 2008; Li et al, 2008).

Table 1.3
Common Documented Symptoms of Methyl Mercury Poisoning

Adult Exposure	Pre-natal Exposure
Tunnel vision	Delayed developmental milestones
Blindness	Poor hearing
Loss of hearing	Poor verbal development
Altered muscle tone	Reduced growth
Deep tendon reflexes	Reduced coordination
Ataxia	Lower intelligence
Generalized weakness	Cerebral palsy
Tremors	Behavioural problems
Muscle spasticity	Coma
Loss of weight	Death
Parathesia	
Skin rashes	
Possible human carcinogen	
Cardiovascular effects	
Immune system effects	
Drowsiness	
Cerebral palsy	
Intellectual impairment	
Difficulty speaking	
Abnormal behaviour	
Coma	
Death	

(Environment Canada, 2004g; Fthenakis et al, 1995; Gochfeld, 2003; Goldman et al, 2003; GOJ, 2002; Magos, 1998; MassDEP, 1996; Rice et al, 2000; Trasande et al, 2005)

2. Literature Review

As previously outlined, the remaining paper will be looking at atmospheric Hg^0 and MeHg. Atmospheric mercury is such an important topic, as it is the main pathway of transporting

mercury between source and sink. Hg^0 and MeHg are important mercury species, due to their prevalence, transportation distance, and effects on human health.

2.1 Sampling Methods

Gaseous elemental mercury sampling has become fairly routine in past years. There are two main types of sampling involved, the pre-concentration of mercury onto an adsorbent trap, and the direct sampling of air. Sampling of air directly involves the use of an automatic analyzer and atomic absorption spectrometer (AAS) (Orloff et al, 1997; Garcia-Sanchez et al, 2006; Garetano et al, 2006). This can have a detection limit between $2.0x10^3$ and $8.9x10^8$ pg, with a sampling rate of 20 L/min (Orloff et al, 1997; Garcia-Sanchez et al, 2006; Garetano et al, 2006).

Adsorbent traps used for pre-concentration can include hopcolite, carbotrap, Anasorb C300, and gold (Bloom and Fitzgerald, 1988; Temmerman et al, 1990; Beusterien et al, 1991; Carpi and Chen, 2001; Gioda et al, 2007). These traps can then be analyzed using an AAS or cold vapour atomic fluorescence spectrometer (CVAFS) (Bloom and Fitzgerald, 1988; Temmerman et al, 1990; Beusterien et al, 1991; Gioda et al, 2007). One method is to acid digest the adsorbent trap, in order to release any captured Hg^0, and then analyze the solution using an AAS (Gioda et al, 2007). This can have a detection limit (DL) of $\sim1.0x10^4$ pg (Gioda et al, 2007). The second method involves thermally desorbing the trap, with the resulting gaseous Hg^0 flowing through a CVAFS or AAS, with the help of a carrier gas of argon or helium, where the resulting spectrum would then be analyzed (Bloom and Fitzgerald, 1988; Temmerman et al, 1990; Beusterien et al, 1991; Carpi and Chen, 2001). DL for this method can range between 0.2 and $3.0x10^3$ pg, with sampling rates around 1 L/min (Bloom and Fitzgerald, 1988; Temmerman et al, 1990; Beusterien et al, 1991; Carpi and Chen, 2001).

The rest of this section will be addressing MeHg sampling methods, which are not as formalized. One obstacle to overcome in this type of research is the fact that the concentration of MeHg in the atmosphere is much lower than that of Hg^0, between 0 and 5% of total mercury (THg), which poses some difficulties when it comes to sampling (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Brosset and Lord, 1995; Carpi et al, 1997; Pongratz and Heumann, 1999; Kotnik et al, 2000; Lee et al, 2003; Munthe et al, 2003; Feng et al, 2004a; Huang and Klemm, 2004; Lindberg et al, 2005). Previous studies have focused on the effect that mercury pollution has had on surrounding communities. However, to this researcher's knowledge, there has yet to be a study investigating MeHg concentrations of indoor air.

Several different methods have been used in the past to sample MeHg in air. These include: adsorbent trap sampling (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a), a bubbler system (Brosset and Lord, 1995; Carpi et al, 1997; Pongratz and Heumann, 1999; Huang and Klemm, 2004; Lindberg et al, 2005), and a mist chamber (Lee et al, 2003). The adsorbent trap method involves drawing air through a tube filled with an adsorbent material (gold, silver, carbon, soda lime), which would then capture atmospheric mercury (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a). This material would be heated to release any captured mercury, passed through a gas chromatograph (GC) column to separate mercury species, then through a pyrolyzer which would convert all mercury species to Hg^0, which would then be swept into a CVAFS, where it could be quantified as MeHg by peak area and retention time (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a).

The type of adsorbent in previous studies has ranged from gold to silver to carbon to soda lime (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a).

Sampling flow rates have varied between 0.1 and 10 L/min (Slemr et al, 1979; Bloom and Fitzgerald, 1988; Larsson and Frech, 2003; Lindberg et al, 2005). Desorption temperature for traps have varied between 45^0C to 900^0C (Slemr et al, 1979; Bloom and Fitzgerald, 1988; Lindberg et al, 2001; USEPA, 2001). Finally, sampling time has ranged from several days to several hours (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a).

A bubbler system entails bubbling sample air through deionized water, where gaseous mercury would then be captured (Brosset and Lord, 1995; Carpi et al, 1997; Pongratz and Heumann, 1999; Huang and Klemm, 2004; Lindberg et al, 2005). This solution would then be converted to methylethyl mercury (MeEthHg), and then purged onto an adsorbent trap and thermally desorbed and analyzed using CVAFS, following EPA method 1630 (USEPA, 2001).

The mist chamber is a slight improvement to the bubbler technique, involving the pulling of sampled air through a mist of dilute HCl or ammonium salt of pyrrolidine-1-dithiocarboxylic acid (APDC), which would then capture gaseous mercury (Lee et al, 2003). Volatile forms of MeHg (such as MeHgCl) could then form a complex with APDC, hopefully causing an increase in MeHg captured per air volume (Lee et al, 2003). This solution would then similarly be converted to MeEthHg, and then purged onto an adsorbent trap and thermally desorbed and analyzed using CVAFS, following EPA method 1630 (USEPA, 2001).

These three main methods of MeHg sampling vary in their mobility, sampling time, DL, and sample variation, which are outlined in Table 2.1. For the current study, it was known that several different sampling locations were required. Given this, it was decided that a mobile sampling system would be desired. The adsorbent trap method was chosen for this reason,

although reproducibility was not as good as other methods. It is also the method that has the most

field-testing behind it.

Table 2.1
A Comparison of Several Different Factors Between Three Different MeHg Sampling Methods

Sampling Method	Mobility	Sampling Time	DL (pg/m^3)	Reproducibility[a]		Sample Size	Previous Work	References
				%SD[b]	SD (ng/m^3)			
Adsorbent Trap	Most Mobile	1h-several days	2-50	50-113.3	0.01-49	4-6	Outdoor	Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a
Bubbler System	Less Mobile	20 min.-1 week	0.5-1.5	3.3-185.7	5.90×10^{-5}-8	2-9	Outdoor	Brosset and Lord, 1995; Carpi et al, 1997; Pongratz and Heumann, 1999; Huang and Klemm, 2004; Lindberg et al, 2005
Mist Chamber	Least Mobile	3-6h	2	17.7-63.1	0.005-0.006	4-5	Outdoor	Lee et al, 2004

[a]parallel samples: taken at the same time in the same location

[b]% of sampling average

2.2 Mercury in the Atmosphere

Atmospheric Hg^0 and MeHg have been studied in a wide variety of locations, as outlined

in Table 2.2. Indoor Hg^0 levels have been shown to be significantly elevated over outdoor

levels, in some cases higher than suggested safety standards (ATSDR, 1999). In urban areas,

point source pollution sampling has been shown to be elevated over non-point source sampling

schemes. However, there is not always a consistent pattern when it comes to rural areas. In some

cases, mercury levels can actually be higher at rural locations. In the case of MeHg, this could be

linked to mercury methylation in surrounding wetland soils and sediments, as well as the

interaction of Me_2Hg with hydroxide and chlorine radicals (Downs et al, 1998; Schroeder and

Munthe, 1998a; Schwesig and Matzner, 2000). Hg^0 levels, on the other hand, could be elevated

in rural areas because of inorganic and MeHg conversions by plants to Hg^0 or the emission of Hg^0 from soil (Heaton et al, 1998; Gustin et al, 2003; Gustin et al, 2006; Xin and Gustin, 2007; Batke et al, 2008). Two areas that have yet to be looked at in-depth, for MeHg atmospheric levels, are polar background and indoor air levels. In any case, MeHg levels appear to be much more variable than Hg^0 levels. It has been estimated that MeHg may be between 0 and 5% of THg concentrations in the atmosphere (Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Munthe et al, 2003).

Table 2.2

A Comparison of Average (ng/m^3) Atmospheric Mercury Levels Recorded for Various Locations

Species	Polar Background	Rural	Outdoor: Point Source[a]	Outdoor: Ambient[b]	Indoor
				Urban	
Hg^0	1-1.6	1.6-20	5-81	2.6-10	$0.9-3.3x10^6$
MeHg		$1.06x10^{-3}-8$	$1.5x10^{-4}-60$	$1.5x10^{-3}-38$	
References	Cottrell et al, 2007; Ferrari et al, 2008; Kellerhals et al, 2003; Brooks et al, Rutter et al, 2008	Talmi et al, 1981; Bloom and Fitzgerald, 1988; Brosset and Lord, 1995; Huang and Klemm, 2004; Rutter et al, 2008	Talmi et al, 1981; Carpi et al, 1997; Kotnik et al, 2000; Lindberg et al, 2001; Feng et al, 2004; Lindberg et al, 2005; Gustin et al, 2008	Talmi et al, 1981; Pecheyran et al, 2000; Huang and Klemm, 2004; St Denis et al, 2006; Rutter et al, 2008	Baeyens et al, 1991; Orloff et al, 1997; Pecheyran et al, 2000; Carpi and Chen, 2001; Garcia et al, 2006; Gustin et al, 2007

[a] Samples taken in the vicinity of a localised pollution source such as a chlor-alkali plants, sewage sludge application, thermal power plants, and landfill

[b] Samples taken without knowledge of localised pollution source

2.3 Indoor Mercury Sources

Homes have been built more airtight over the years (Hamlin, 1992). It is thought that an individual may spend up to 90% of their time indoors (Baker, 1998). This causes the indoor environment to play a large role in the health of most individuals. Indoor air is normally viewed as innocuous, providing a safe habitat from outside. However, this may not always be the case. Sources of indoor THg and Hg^0 can include homes where mercury is used for cultural purposes (Garetano et al, 2006), residential buildings contaminated by previous industrial use (Orloff et al, 1997), latex paint applications (Agocs et al, 1990; Beusterien et al, 1991), proximity to chemical labs (Carpi and Chen, 2001), communities surrounding old mercury mines (Maramba et al, 2006; Garcia-Sanchez et al, 2006) and contamination due to dental practices (Temmerman et al, 1990; Gioda et al, 2007). Some other minor sources of Hg^0 may include thermometers, fluorescent light bulbs, thermostat switches, float controls in sump pumps, barometers, and gas flow meters (Spedding and Hamilton, 1982; Carpi and Chen, 2001).

2.4 The Relationship Between Mercury and Sunlight

A problem with the sampling of mercury in air over a 24h period is the idea that sunlight may be affecting both MeHg and Hg^0 concentrations. Previous studies have investigated the rate of mercury flux between water and air (Boudala et al, 2000; Feng et al, 2004b), the snowpack and air (Cobbett et al, 2007), and soil and air (Carpi and Lindberg, 1997; Gustin et al, 2003; Xin and Gustin, 2007), and other substrates (Gustin et al, 2006). Some studies have also worked to identify sunlight interactions that are occurring in water as well (Suda et al, 1993).

Mercury fluxes from water to air have been found to be affected by sunlight (Boudala et al, 2000; Feng et al, 2004b). It was found that mercury fluxes ($ng/m^2/h$) were higher during

daytime hours compared to night (Boudala et al, 2000; Feng et al, 2004b). When investigating

snowpack interactions, there has been found to be mercury deposition to the snowpack during

polar night and mercury emission to the atmosphere during polar day (Cobbett et al, 2007).

Similarly, soils, mine wastes, and other mercury-containing substrates, have been found to emit

Hg^0 to the air during light conditions and absorb Hg^0 during dark conditions (Gustin et al, 2003;

Gustin et al, 2006; Xin and Gustin, 2007). These patterns may be explained by sunlight reactions

with Hg^{2+} to form Hg^0 species, which can then be emitted (Carpi and Lindberg, 1997; Gustin et

al, 2003; Feng et al, 2004b). Temperature may also be a factor, as mercury levels in air have

been found to be positively correlated with temperature changes (Feng et al, 2004b; St. Denis et

al, 2006; Rutter and Schauer, 2007).

This relationship is similar to that which happens with MeHg and ethyl mercury (EthHg)

species as well. For instance, Suda et al (1993) found that when seawater was exposed to

sunlight, UVA light, or UVB light, MeHg and EthHg concentrations decreased (Suda et al,

1993). This leads to the assumption of photodegradation of either of the species, leading to Hg^0

emissions to the air (Suda et al, 1993). This means that MeHg sunlight patterns should be

opposite that of Hg^0 patterns.

2.5 Factors Affecting Indoor Air Quality

Factors that may affect the results of indoor air samples can include building ventilation

systems (Collett and Sterling, 1988), temperature, and humidity levels (Godish and Rouch, 1986;

Feng et al, 2004b; St. Denis et al, 2006; Rutter and Schauer, 2007). It has been found that

inadequate fresh air supplies and insufficient air circulation can be related to "sick building

syndrome" (Collett and Sterling, 1988). This supports the possibility that ventilation systems

may be contributing to indoor air contaminant levels.

Temperature and humidity may also affect pollutant levels in indoor air, which are normally assumed to have a stable temperature range. For instance, Godish and Rouch (1986) investigated the effects of indoor climate on formaldehyde contamination in a mobile home. It was found that temperature and humidity levels may have an effect on this contamination, with temperature and humidity being positively correlated with temperature changes (Godish and Rouch, 1986). It also has been found that average outdoor Hg^0 levels tend to be higher in the summertime, compared to fall (Feng et al, 2004b; St. Denis et al, 2006). There is also a positive correlation between temperature and the partitioning of reactive mercury in the air (Rutter and Schauer, 2007). Temperature may in fact be an important contributor to mercury levels, both inside and out.

3. Study Objectives

1. To select a method of sampling and analysis of atmospheric MeHg.

2. To measure Hg^0 and MeHg concentrations in indoor and outdoor air simultaneously.

3. To measure Hg^0 and MeHg concentrations in indoor and inner ceiling air simultaneously.

4. To study the factors that affects the concentration of Hg^0 and MeHg in indoor and outdoor air in the city of Toronto.

4. Materials and Methods

4.1 Experimental Location and Sampling Sites

Sampling took place in Kerr Hall, at Ryerson University, at the corner of Gerrard St. and Church St. The university is located in the downtown of Toronto, Ontario. Five different locations in Kerr Hall were sampled, the details of which can be seen in Table 4.1. The relative position of each location can be seen in Fig. 4.1. At each location, for at least a two-day period, sampling of indoor and outdoor air took place. Another sampling period then took place in the chemistry labs, sampling indoor and inner ceiling air in the same fashion. Indoor temperature readings were also collected during sampling times, using a wireless weather station (La Crosse, Canadian Tire). Temperature readings were recorded at 3h intervals. Outdoor temperature readings were estimated using readings from the Toronto Lester B Pearson International Airport weather station (Environment Canada, 2008). Temperature readings were recorded at 1h intervals.

Table 4.1

Details of Sampling Locations of Current Study

Location	Room Type	Sampling Environment	Sampled Species	Exterior Environment	Additional Information		
					Mercury Compound On Site	Recent Renovations	Room Air Flow
KHE213a (1)	Research Lab	Outdoor, Indoor, Inner Ceiling	Hg^0 / MeHg	Major Street	Yes	Renovated 2001	Window closed for sampling. Daily room traffic during sampling
KHE120 (2)	Office	Outdoor, Indoor	Hg^0 / MeHg	Courtyard	No	Painted 2007	Window open during sampling. Little daily room traffic during
KHN303b (3)	Research Lab	Outdoor, Indoor, Inner Ceiling	Hg^0 / MeHg	Courtyard	Yes	Renovated 2005	Window open during sampling. Little daily room traffic during. Hole from interior to roof, which has exhaust outlets
KHN308a (4)	Office	Outdoor, Indoor	Hg^0	Courtyard	No		Window open during sampling. Little daily room traffic during
KHN209 (5)	Student Lab	Outdoor, Indoor	Hg^0	Major Street	Yes		Window open during sampling. Little daily room traffic during

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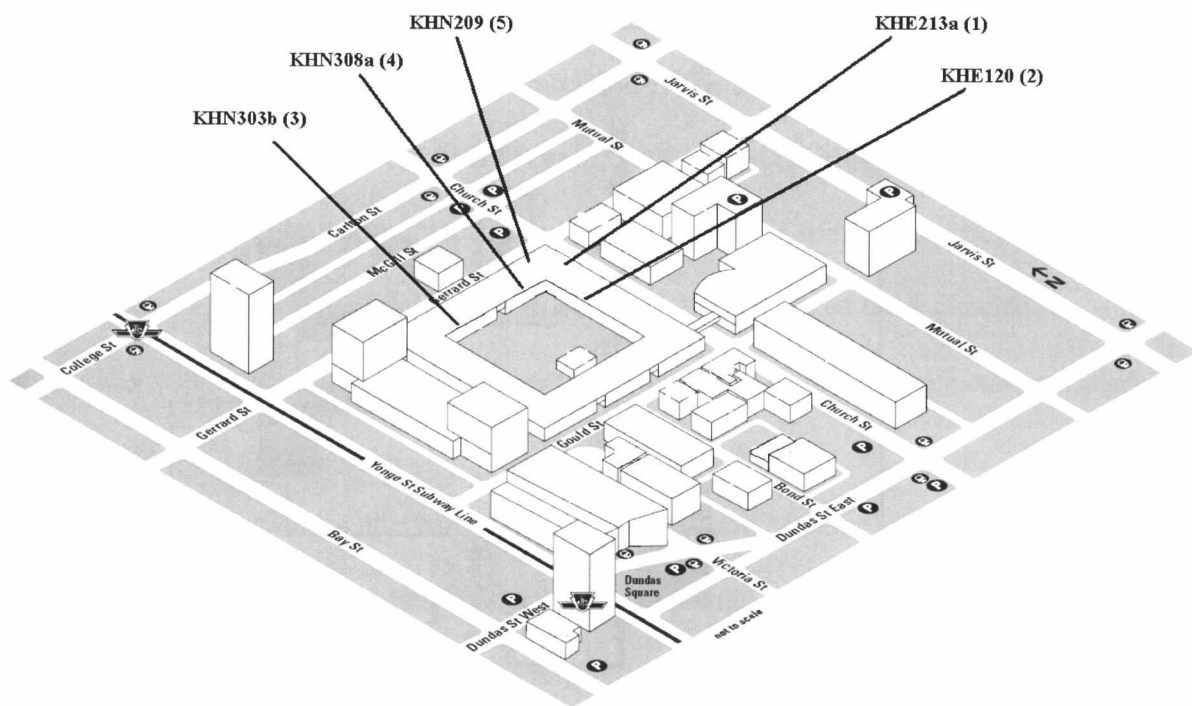
Fig. 4.1. Relative Position of Sampling Locations in Toronto, ON (Ryerson, 2008)

4.2 Elemental Mercury Sampling and Analysis

The Tekran 2537a Mercury Vapour Analyzer was used in the collection and analysis of Hg^0. The analyzer was connected to the carrier gas argon 5.0, UHP, and a Tekran Model 1100 Zero Air Generator (See Fig. 4.2). A Koby Mercury Adsorber (MF-2JKCB) was connected to the zero air line. The analyzer was also connected to a Tekran two-way valve unit combined with the Tekran series 1100 controller, allowing sampling from two locations to occur alternatively. Each sampling line was connected to a 0.45 µm pore filter, with a 47 mm diameter, to remove particulates. Data was collected and analyzed using the ComCap RS232 Data Capture Program v1.0.5.
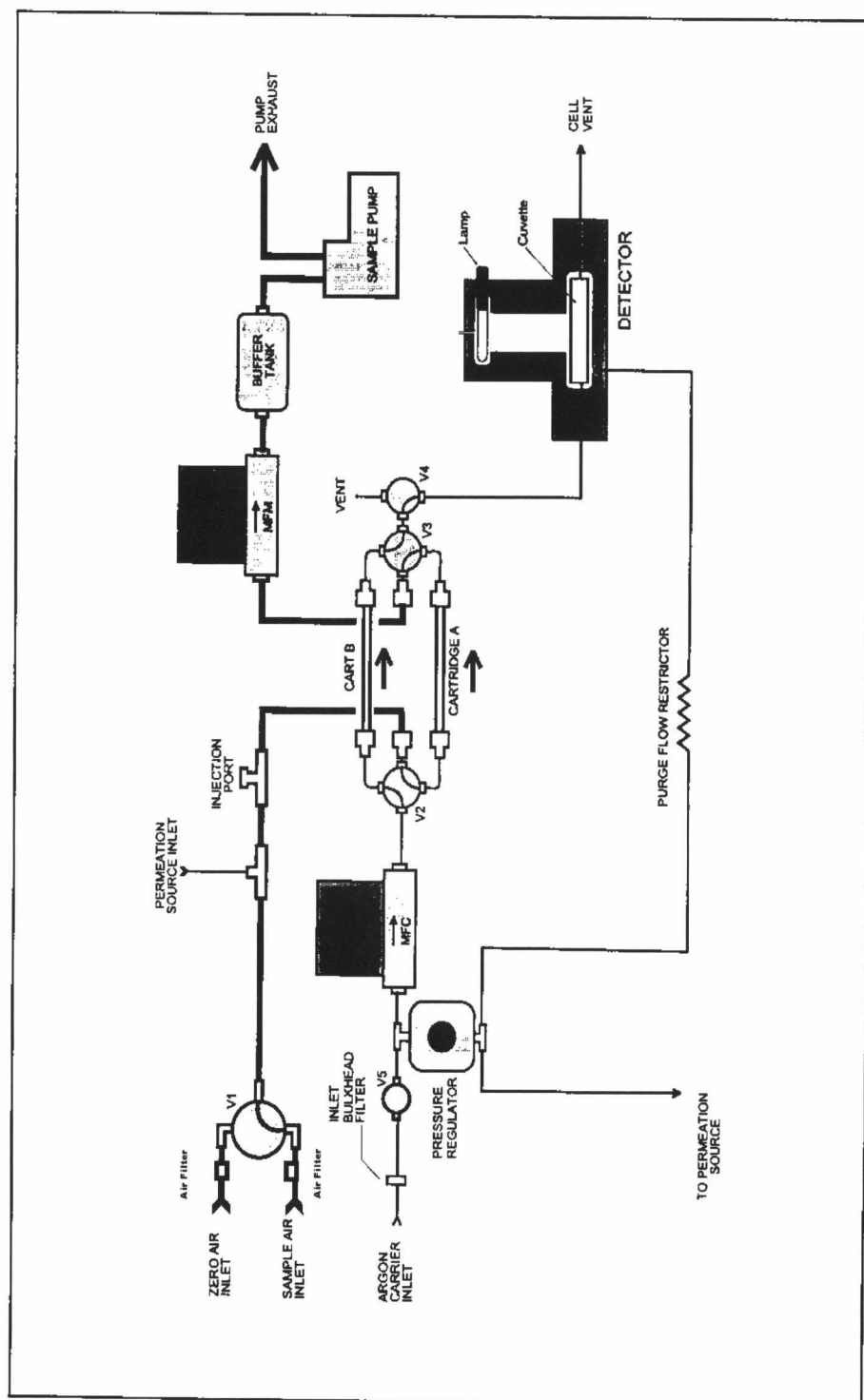
Fig. 4.2. Flow Diagram for the Tekran 2437a Mercury Vapour Analyzer (Tekran, 1999)

The analyzer works by sampling air and trapping mercury vapour onto a cartridge containing ultra pure gold adsorbent (Tekran, 1999). The adsorbent is then thermally desorbed and detected using a CVAFS (Tekran, 1999). Dual cartridges allow continuous sampling, with collection taking place at five-minute intervals for each cartridge, at a sampling rate of 1L/min. (Tekran, 1999). The gold traps may need to be cleaned periodically with nitric acid, deionized water, and methanol if they become contaminated (Tekran, 1999).

Hg^0 was sampled by alternating between indoor and outdoor air (or indoor and inner ceiling air) every 10 minutes, which is two sampling intervals. The average of two five-minute intervals was used in the data analysis, which were considered to be parallel samples. The analyzer was automatically calibrated on a daily basis and manually calibrated every two months. Automatic calibration involved the determination of blank values by supplying zero air through the analyzer and the determination of mercury peak areas for a particular concentration by supplying mercury vapour from an internal mercury permeation source (Tekran, 1999). Manual calibration involved the injection of selected volumes of air, saturated with mercury vapour, at a preset temperature from an external source (Model 2505 Mercury Vapor Calibration Unit, Tekran), to calibrate the internal permeation source and validate the readings (Tekran, 1999).

4.3 Methyl Mercury Sampling and Analysis

4.3.1 Methods Development

As previously mentioned, the adsorbent trap sampling and analysis method was chosen for the current study. The adsorbent trap method involves drawing air through a

tube filled with an adsorbent material, in the case of the current study, carbotrap, which is a carbon based non-specific adsorbent resin, which would then capture gaseous mercury species (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a). This material would be heated to release any captured mercury, passed through a gas chromatograph (GC) column to separate mercury species, then through a pyrolyzer which would convert all mercury species to Hg^0, which would then be swept into a CVAFS, where it could be quantified as MeHg by peak area and retention time (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Feng et al, 2004a).

There were several factors that had to be tested, during the methods development for MeHg sampling and analysis. These factors were sampling parameters, analysis parameters, and MeHg standards. The sampling parameter tested was sampling flowrate. Total MeHg in air was sampled during these tests; therefore, no filter was used during sampling.

Several different flowrates were tested, in determining the optimum flowrate for MeHg air sampling, with a GAST (115v, 5.5a) vacuum pump, capable of pumping air at 108 L/min. These flowrates varied between 0.04 to 0.8 L/min. Sampling took place overnight, with sampling time varying between 15 and 20h. Only same-day results were compared, in which sampling time and flowrate were equivalent.

Analysis parameters tested included carbotrap-heating method and argon flowrate. During sample analysis, four different trap-heating methods were evaluated. Method one involved heating a carbotrap for one minute once, then taking that peak area as the total MeHg reading for that trap. Method two involved heating the trap for two minutes once,

then taking that peak area as total MeHg reading for the trap. Method three involved heating the trap for two minutes at a time, repeatedly, until the peak area reading equalled 2000 or less. Peak areas would then be added up to contribute to the total MeHg reading for that trap. Finally, method four involved heating the trap for one minute at a time, until the elemental mercury reading was found to have a peak area of less than 50 000, which has a shorter retention time to that of MeHg. The trap would then be heated for two minutes once, taking that peak area as the total MeHg reading for the trap.

Finally, the comparison of argon flowrates during trap analysis was evaluated, comparing the rates of 58 and 73 mL/min. Flowrates were compared by injecting a MeHgCl vapour standard directly into the CVAFS system.

In determining the type of standard to use, two different standards were compared: a liquid MeHgCl solution which was purged onto carbotraps, based on EPA Method 1630 (USEPA, 2001), and a solid MeHgCl standard, from which vapour was withdrawn from the headspace. The average detection limit (DL) was defined as three times the standard deviation of blank results (Dumarey et al, 1979; Lee et al, 2003; Huang and Klemm, 2004).

4.3.2 Sampling System

The results of the previous tests can be found in the results sections, but for simplicity the finalized sampling and analysis protocol will be described. For the current study, total MeHg in air (i.e. total gaseous MeHg + total particulate MeHg) was collected. The sampling system consisted of six carbotraps connected to two GAST vacuum pumps (115v, 5.5a), which then drew air through each of the traps (Dumarey et al, 1979; USEPA, 2001; Larsson and Frech, 2003; Lindberg et al, 2005) (See Fig. 4.3). Sampling

took place at a flowrate between 0.1 and 0.3 ± 0.05 L/min, with no attached filter. The constricted end of each trap was placed downstream. MKS flowmeters were connected to 2 MKS type 247 4-channel readouts, for flowrate accuracy (Dumarey et al, 1979; Slemr et al, 1979; Lindberg et al, 2005). Teflon tubing connected the system together.
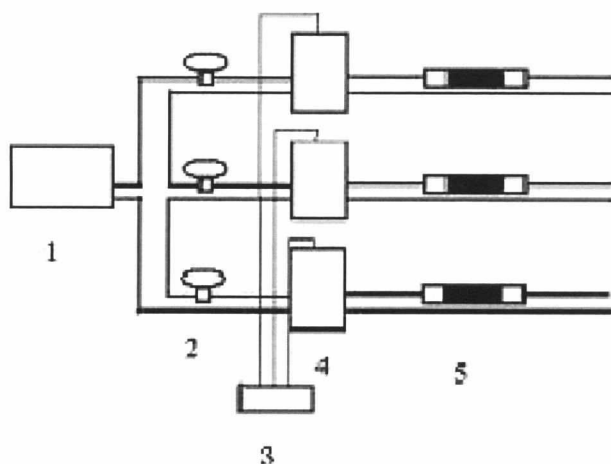
Fig. 4.3. Diagram of MeHg Air Sampling System, Including: 1-Vacuum Pump, 2-Needle Valve, 3-Power Supply and Channel Readout, 4-Flowmeter, 5-Carbotrap

Air inlet placement was the same as elemental mercury sampling. For each condition (indoor, outdoor, inner ceiling), two traps were used for simultaneous sampling and one sample was used for a simultaneous blank. The blank consisted of placing a carbotrap in the sampling system, for the same amount of time as the air samples, without air being passed through the trap. Traps were then analyzed the same day sampling was completed.

Traps were made of a quartz tube constricted at one end, purchased from Brooks Rand (Dumarey et al, 1979; Bloom and Fitzgerald, 1988; Lindberg et al, 2001; Larsson and Frech, 2003; Lindberg et al, 2005). The tubes were approximately 100mm long, with an outer diameter of 7 mm; with the length to the constriction at one end being 27 mm (Rick Manson, Personal Communication, May 4, 2007). The tubes were each filled with

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carbotrap from two Supelco Orbotrap 101 Adsorbent Tubes, totalling 350 mg (Dumarey et al, 1979; Bloom and Fitzgerald, 1988; Lindberg et al, 2001; Larsson and Frech, 2003; Lindberg et al, 2005). The carbotrap within each tube was ~19.5 mm long. Quartz wool was used at either end of the tube to keep the carbotrap in place (Dumarey et al, 1979; Bloom and Fitzgerald, 1988; Lindberg et al, 2001; Larsson and Frech, 2003; Lindberg et al, 2005).

4.3.3 Sample Analysis

The analysis of MeHg samples involved the thermal desorption of each carbotrap, leading to the analysis of released MeHg vapour, using a Brooks Rand Model III CVAFS (See Fig. 4.4). The carrier gas used for the system was argon 5.0 UHP, flowing at 73 mL/min. A nichrome wire heater was used to heat up individual carbotraps (Dumarey et al, 1979; Fitzgerald and Gill, 1979; Slemr et al, 1979; Bloom and Fitzgerald, 1988; USEPA, 2001; USEPA, 2002). Each carbotrap was placed inside the nichrome wire, with the constricted end downstream. Then, the trap was heated for one minute, repeatedly if necessary, to rid the trap of excess Hg^0. Then, it was heated for two minutes, to ~71^0C, for a MeHg reading. The GC column was heated to 105^0C at a constant rate and the pyrolyzer was heated to 409^0C at a constant rate (USEPA, 2002). The CVAFS and heater were connected to a computer, which ran the Mercury Guru 2.1 analysis program. The entire system was connected with Teflon tubing. Retention time and peak area for each sample were recorded.
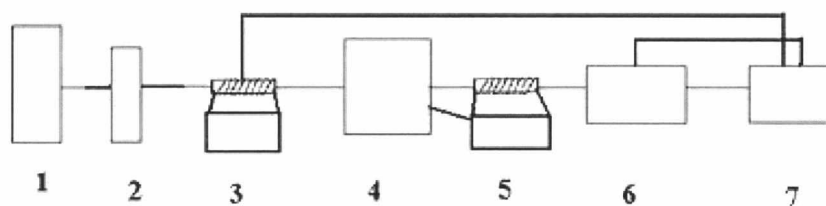
Fig. 4.4. Diagram of Analysis System for MeHg Air Samples, Including 1-Argon 5.0 UHP Tank, 2-Bubble Flowmeter, 3-Nichrome Wire Heater, 4-GC Column, 5-Pyrolyzer and Controller, 6-Brooks Rand Model III CVAFS, and 7-Computer

4.3.4 Standard

A MeHg standard was developed using 100 mg of a methyl mercury chloride (MeHgCl) standard, which was 99.2% pure. The standard was kept in a small, amber glass container. When working with the standard, the container was placed in a 80 mL glass beaker filled with 55 mL of water, that was heated to 20.5^0C using a hotplate (Dumarey et al, 1979; Dumarey et al, 1985). This was measured using a VWR dual channel thermometer. This was then allowed to stand for at least 24 hours to allow the standard to equilibrate. A Hamilton 50 mL gas tight syringe was used to withdraw MeHg vapour from the headspace above the standard (Dumarey et al, 1979; Dumarey et al, 1985; Bloom and Fitzgerald, 1988). The syringe was kept in the vial of MeHg in between injections, and when an injection was being performed the syringe was pumped up and down 3 times before withdrawing the desired amount of vapour (USEPA, 2002). A set volume of vapour was withdrawn and then injected into the system via a T connection.

In order to develop a standard curve, several different volumes of MeHg vapour needed to be injected (Dumarey et al, 1979; Fitzgerald and Gill, 1979; Bzezinska et al, 1983; Dumarey et al, 1985; Lindberg et al, 2005). These volumes were: 2 µL, 10 µL, and 20 µL, with a calculated partial pressure of 1.115×10^{-5} atm and molecular mass of 251.1

g/mol, for MeHgCl (WHO, 1990; ATSDR, 1999). The mass of MeHg contained in each injection was calculated using the ideal gas law.

Mercury vapour was injected in front of the carbotrap of interest, which was then allowed to sit in the argon flow path for five minutes (Slemr et al, 1979; Bloom and Fitzgerald, 1988; USEPA, 2002). The nichrome wire was heated for 1 minute initially to get rid of any large Hg^0 build up. It was then heated for 2 minutes to 71^0C to thermally desorb any MeHg contained in the trap. The retention time and peak area were then recorded. The carbotrap was then heated for five minutes, 1-4 times, depending on the amount of MeHg that was adsorbed by the trap, before its next use (Dumarey et al, 1979). This injection was repeated 3-5 times for each designated volume. A standard curve of ng MeHg vs Average Peak Area was then developed (Fitzgerald and Gill, 1979; Bzezinska et al, 1983; Lindberg et al, 2005). This process was repeated for each carbotrap being used.

4.4 Statistical Analysis

Data was analyzed using ranked ANOVAs and the program SPSS (Conover and Iman, 1981; Seaman et al, 1994; Helsel and Hirsh, 2002). A p value of 0.05 or less was taken as a significant result, and a p value between 0.05 and 0.10 was taken as marginally significant. The mean, standard deviation, and sample size were also reported. Several comparisons took place, using the previously mentioned statistical program. First, indoor air was compared to outdoor air, for both MeHg and Hg^0 in all locations where both species were analyzed. Second, indoor air was compared to inner ceiling air, for both MeHg and Hg^0 in the chemistry labs. Third, indoor air mercury fluctuations connected to the university climate control system, which circulates the indoor air, was compared for

Hg^0 in all locations. Finally, outdoor air levels between sunrise and sunset, daylight, were compared to those between sunset and sunrise, night, for Hg^0 in all locations. Indoor and outdoor temperature readings were also compared when analyzing Hg^0 fluctuations.

5. Results and Discussion

5.1 Methods Development

5.1.1 Methyl Mercury Sampling Parameter Results

Although similar MeHg sampling studies have been performed previously, there is not much consistency when it comes to standard use, sampling flowrate, carrier gas flowrate, and trap desorption temperature. This is why it was necessary to perform preliminary tests, in order to maximize sampling concentration and analysis accuracy.

Overall results for sampling flowrates can be seen in Table 5.1. Using ranked ANOVAs where appropriate, it was found that on April 17, a flowrate of 285 ± 5 standard cubic centimetres per minute (sccm) produced significantly higher results than a flowrate of 780 ± 1 sccm (p=0.030). However, on April 19 there was no significant difference between these two flowrate (p=0.476). It was also found that on April 20, a flowrate of 175 ± 2 sccm gave marginally higher results than a flowrate of 305 ± 3 sccm (p=0.106). However, on April 30 and May 1, there was no significant difference between flowrates that were compared (p>0.500).

One reason for no significant difference between varying flowrates may be the high variability of sample results. Reasons for this may include interference from other substances in the air and the process by which MeHg was identified during analysis. These will be discussed in a later section.

In both instances where flowrates were found to be significantly different it was found that the lower flowrate collected more MeHg than the higher flowrate. As it is expected that an increase in flowrate should increase collection this needs an explanation. Increasing airflow beyond the optimal flowrate may decrease contact with the adsorbent,

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decreasing the adsorption efficiency (Pitiyont et al, 1999; Qing et al, 2003; Zhang et al, 2006).

From results, it appeared that sampling flowrates of 175-285 sccm should produce better results than those of 305-780 sccm. Due to the restraints of the sampling device, sampling flow rates during the project were found to vary between 0.1 and 0.3 L/min. This is within the range of sampling volumes used in past studies, although it is at the lower end of the range (Slemr et al, 1979; Bloom and Fitzgerald, 1988; Larsson and Frech, 2003; Lindberg et al, 2005).

Table 5.1

A Comparison of Average MeHg (ng) Results at Varying Sampling Flowrates (sccm), Inside KHE213a in 2008, ±SD (n)

Date	40 ± 3	80 ± 6	175 ± 2	285 ± 5	305 ± 5	780 ± 1	Statistical Difference (p)
Apr. 17				2.2±3.1 (4)		0.2 ±0.1 (4) 0.2±0.2×10^{-1} (6)	0.03
Apr. 19				1.8±2.5 (4)	0.6 (1) 0.4±0.4×10^{-1} (2)		0.478
Apr. 20			0.7±0.5×10^{-3} (2)				0.106
Apr. 30	15.5±0.6 (3)	23.6±19.0 (2)					>0.500
May. 1				7.3±9.3 (2)	1.4±0.8 (2)		>0.500

5.1.2 Methyl Mercury Analysis Parameter Results

Trap-heating protocols were tested using sampling protocols previously described, in order to take into account any interference that may occur during sampling. Overall results can be seen in Table 5.2. Using ranked ANOVAs where appropriate, it was found that method four and method three would always desorb more MeHg per sampling time than method one. In fact, heating traps at one minute proved to have negligible results, less than 1% of peaks attained using other heating methods during four out of five sampling days. This pattern held for both indoor and outdoor air samples. Since MeHg desorption was shown to be negligible in most cases, while using method one, and results were not significantly different for methods two and three (p>0.300), it was decided that method four would be ideal for getting rid of excess Hg^0 before MeHg analysis, in case of interference. All future carbotrap analyses were carried out using method four. This is different from previous studies, which had only one cycle of heating before peak analysis (Takizawa et al, 1981; Bloom and Fitzgerald, 1988).

However, there are some inconsistencies, which need to be addressed. Once again, there was large variation between samples, in some cases standard deviation (SD) was greater than 100% of sample averages. Reasons for this may include interference from other substances in the air and the process by which MeHg was identified during analysis. The way in which MeHg was identified during analysis will be addressed in another section. When analyzing gaseous Hg^0 through sorbent digestion it has been found that, during sampling, particulate mercury and gaseous organo-mercury compounds can cause positive interference (OSHA, 1991; ISO, 2004). However, this involves total mercury analysis performed without and GC column and pyrolyzer, so

these interferences may not apply. When analyzing MeEthHg it has been found that

$MeHg^+$ may be formed in the GC column from Hg^{2+}, which may be elevating $MeHg^+$

estimates (Tseng et al, 1999). Further testing would need to be performed to determine if

a similar case is happening here. On the other hand, adsorbed water vapour may cause a

decrease in desorption efficiency when working with charcoal, especially with polar

compounds (Bloom and Fitzgerald, 1988; Woolfenden, 2008).

Table 5.2

A Comparison of Average MeHg Concentration (ng/m^3) Results Using Four Different
Heating Protocols, Inside and Outside KHE213a in 2008, ±SD (n)

Environment	Date	Method One	Method Two	Method Three	Method Four	Statistical Difference (p)
Inside	Apr. 17	0.2±0.3 (2)	0.3 (1)	0.8 (1)	3.9±4.0 (2)	0.106[a]
	Apr. 19		2.1±2.9 (3)	3.0±3.5 (3)		0.438
	Apr. 23		4.8±5.6 (2)	6.0±4.8 (2)		>0.500
	Apr. 24		0.6±0.6 (3)	1.0±1.0 (3)		>0.500
	Apr. 25		0.6±0.5 (3)	2.4±2.0 (3)		0.331
	May. 6	<IDL[b] (3)			3.5±2.2 (3)	0.035
	May. 19	<IDL (3)			5.5±4.7 (3)	0.195
Outside	May. 6	<IDL (3)			5.7±7.9 (3)	0.035
	May. 7	<IDL (3)			2.0±2.0 (3)	0.035

[a]Statistical comparison could only be performed between methods 1 and 4
[b]IDL: Instrument Detection Limit

Another problem is the fact that MeHg has a higher vapour pressure than Hg^0,

which would suggest that it should be released earlier than Hg^0 as an adsorbent trap is

heated up, but the opposite pattern was observed. It has been found that surface

roughness may increase required thermal desorption temperatures, which may be

affecting $MeHg^+$ compounds (Heras, 1993). In addition, decreased desorption efficiency

of polar compounds due to water vapour interference may also be affecting the desorption

of $MeHg^+$ compounds (Bloom and Fitzgerald, 1988; Woolfenden, 2008).

Overall results of argon flowrate can be seen in Table 5.3. Using ranked ANOVAs where appropriate, it was found, overall, that a flowrate of 58 mL/min produced negligible results, when MeHgCl standard was injected into the system. However, when a flowrate of 73 mL/min was used, a peak of 3.09×10^5 resulted, with a %SD of 19 (p=0.012). It has been found that increasing flowrate may increase thermal desorption efficiencies, which may be contributing to the significant differences found (Emamipour et al, 2007; Tan and Lee, 2008; Vilar et al, 2008). Given these results, an argon flowrate of 73mL/min was adopted for the remainder of the experiment.

Table 5.3

A Comparison of Average Peak Area (PA) Results Using Two Different Argon Flowrates, with a 5uL Injection of MeHgCl Vapour Standard, Directly Into the CVAFS System, ± SD (n)

Argon Flowrate	PA	Statistical Difference (p)
58 mL/min	<IDL[a] (3)	0.012
73 mL/min	$3.09 \times 10^5 \pm 5.8 \times 10^4$ (4)	

5.1.3 Methyl Mercury Standard Results

Overall results for liquid and vapour MeHg standards can be seen in Tables 5.4 and 5.5. The repeatability of liquid and vapour MeHg standards was found to be similar. Peak values for the vapour standard appeared to be lower, per ng MeHg added, than the liquid standard. This may be connected to the properties of the different MeHg compounds being used in each standard. Methylethyl mercury has a lower molecular weight than MeHgCl, 244.7 compared to 251.1, which would cause a higher peak at lower injected mass. This would make it appear like it has a higher peak per injected mass.

It was determined that the vapour standard should be used, as it would more closely approximate MeHg in air. A standard curve was developed, using analysis parameters set out above, correlating the mass of vapour injected, with the peak area that the CVAFS system provided, for each carbotrap that was used.

Overall PA results for vapour standard injections, by carbotrap, can be seen in Table 5.6. When considering an injection amount of 2.3 ng, the %SD was found to average 17%. At an injection amount of 1.2 ng, the %SD was found to average 18% of average peak area. When considering an injection amount of 0.2 ng, the %SD was found to average 18% of average peak area. This range of variation was about twice as high as a previous study (Bloom and Fitzgerald, 1988), but with an injection amount one quarter of the size. However, this is an expected result, as %SD tends to decrease with increasing injection amounts. Due to variation between traps, results were calculated using an individual calibration curve for each trap (See Fig. 5.1).

Table 5.4
MeEthHg Standard Results After Ethylation of MeHgCl Solution

Mass (ng)	Retention Time (s)	PA	Average PA ±SD	%SD
0.20	2.25	2.87×10^5	$3.23 \times 10^5 \pm 5.6 \times 10^4$	17
0.20	2.26	2.64×10^5		
0.20	2.27	3.74×10^5		
0.20	2.28	3.69×10^5		
0.10	2.27	1.56×10^5	$1.65 \times 10^5 \pm 3.7 \times 10^4$	22
0.10	2.27	1.71×10^5		
0.10	2.37	1.22×10^5		
0.10	2.28	2.11×10^5		
0.05	2.20	6.22×10^4	$7.55 \times 10^4 \pm 1.1 \times 10^4$	14
0.05	2.23	8.16×10^4		
0.05	2.31	8.68×10^4		
0.05	2.29	7.16×10^4		

Table 5.5

MeHgCl Standard Results during Vapour Injection of MeHgCl Directly into CVAFS System

Mass (ng)	PA	Average PA±SD	%SD
0.6	3.02×10^5	$3.09 \times 10^5 \pm 5.8 \times 10^4$	19
0.6	3.74×10^5		
0.6	3.26×10^5		
0.6	2.34×10^5		
1.2	8.30×10^5	$1.02 \times 10^6 \pm 1.4 \times 10^5$	13
1.2	1.19×10^6		
1.2	9.55×10^5		
1.2	1.13×10^6		
1.2	1.07×10^6		
1.2	9.20×10^5		

Table 5.6

Average Peak Area Results of MeHgCl Vapour Injected Standard, ±SD (n)

Trap	2.3 ng	1.2 ng	0.2 ng	0.0 ng
1	$1.74 \times 10^6 \pm 2.1 \times 10^5$ (3)	$4.79 \times 10^5 \pm 6.3 \times 10^4$ (3)	$1.52 \times 10^5 \pm 2.8 \times 10^4$ (3)	$6.28 \times 10^3 \pm 2.9 \times 10^2$ (2)
2	$1.48 \times 10^6 \pm 2.3 \times 10^5$ (3)	$6.87 \times 10^5 \pm 2.3 \times 10^4$ (3)	$1.05 \times 10^5 \pm 2.3 \times 10^4$ (3)	$8.67 \times 10^3 \pm 1.7 \times 10^3$ (3)
3	$1.92 \times 10^6 \pm 4.1 \times 10^5$ (3)	$6.34 \times 10^5 \pm 5.9 \times 10^4$ (3)	$9.20 \times 10^4 \pm 1.5 \times 10^4$ (3)	$2.82 \times 10^3 \pm 7.5 \times 10^2$ (2)
4	$1.05 \times 10^6 \pm 1.7 \times 10^4$ (3)	$7.45 \times 10^5 \pm 2.0 \times 10^5$ (3)	$6.16 \times 10^4 \pm 5.5 \times 10^3$ (3)	<IDL (2)
5	$2.04 \times 10^6 \pm 2.3 \times 10^5$ (3)	$7.36 \times 10^5 \pm 1.6 \times 10^5$ (3)	$6.05 \times 10^4 \pm 8.4 \times 10^3$ (3)	<IDL (2)
6	$1.65 \times 10^6 \pm 3.4 \times 10^5$ (3)	$6.65 \times 10^5 \pm 2.1 \times 10^5$ (3)	$3.90 \times 10^4 \pm 1.1 \times 10^4$ (3)	$4.78 \times 10^3 \pm 1.0 \times 10^3$ (2)

The average DL for vapour MeHg standard was found to be 2.7 pg, which is slightly higher than the lowest detection limit found for this type of sampling and analysis, which is 2.0 pg (Takizawa et al, 1981; Bloom and Fitzgerald, 1988). It appears that the variation of blanks was larger than in previous studies, which could indicate a problem in the method of the cleaning of traps in between samples. Overall, it appeared that the highest injection amount was less variable than lower injection amounts, which was expected from previous results. The injection amount of 1.2 ng, the middle injection

amount, was found to be the most similar among all the carbotraps, with the other

injection amounts being more variable.

Retention times for the MeHgCl standard were found to vary between 2.02 and

2.54 min, when argon flowrates were the same as that used for the MeEthHg standard,

58mL/min. A retention time of 2.02-2.54 min is similar to the MeEthHg standard, which

had retention times that varied between 2.20 and 2.37 min. Previous work has found

MeEthHg can have a retention time of ~2.5 min at 58mL/min, similar to that of the

current study (USEPA, 2001). Similar to previous results, it appears that, in general,
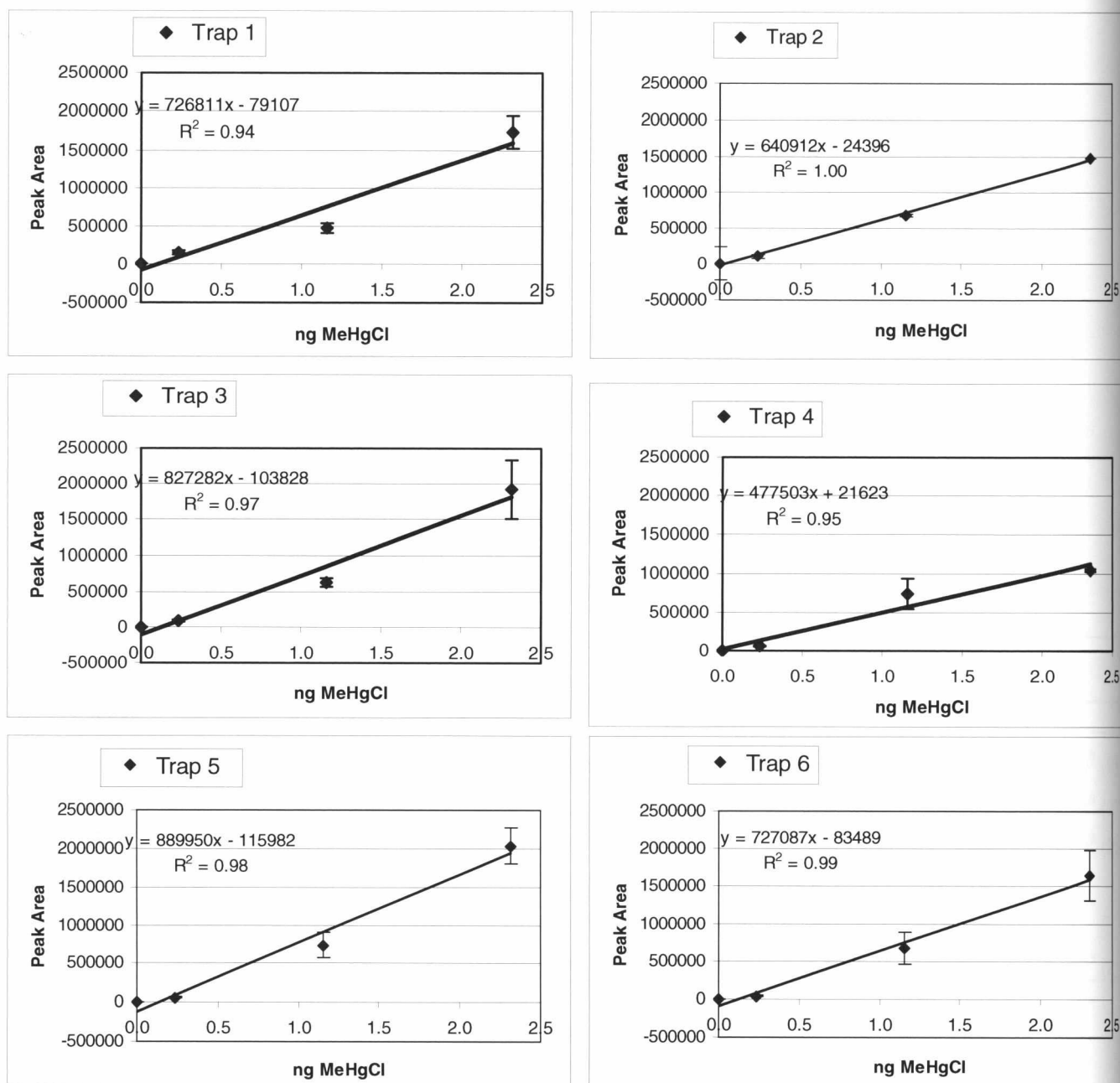
Fig. 5.1. Comparison of MeHg Standard Calibration Curves for Individual Carbotraps, with Error Bars Shown as SD (n=3)

MeHg compounds have retention times, which are similar to each other, and cannot be differentiated using this method (WHO, 1990).

The way in which MeHg was identified during analysis may cause increased error and variability. More specifically, MeHg identification depends on peak area and

retention time. It is possible that other mercury compounds may have similar retention times as that of $MeHg^+$, which could cause positive interference. Further research into other common mercury compounds, such as $HgCl_2$ and $Hg(OH)_2$, and their retention times is needed.

As stated in the materials and methods section, it was decided that for the current study, total MeHg in air (i.e. total gaseous MeHg + total particulate MeHg) would be collected. Two GAST vacuum pumps (115v, 5.5a), would be used for sampling, with a flowrate between 0.1 and 0.3 ± 0.05 L/min, with no attached filter. The carrier gas used for the system was argon 5.0 UHP, flowing at 73 mL/min. Each carbotrap was heated for one minute, repeatedly if necessary, to rid the trap of excess Hg^0. Then, it was heated for two minutes, to $\sim71^0C$, for a MeHg reading. A vapour MeHgCl standard was used, with calibration curves for each trap as stated previously.

5.2 Comparing Indoor and Outdoor Air

5.2.1 Methyl Mercury Air Levels

5.2.1.1 Methyl Mercury Air Fraction

Overall results for MeHg air fractions can be seen in Table 5.7. Median values were compared due to the variability of individual samples. While comparing the amount of MeHg in air found when sampling with a filter (gaseous MeHg) compared to that without a filter (total MeHg), using ranked ANOVAs where appropriate, it was found that median values of MeHg when sampling without a filter were marginally to significantly higher than sampling with a filter (p=0.190-0.049). In fact, it was found that median peak levels of gaseous MeHg were less than the instrument detection level, compared to median levels of total MeHg of 9.16×10^2 to 5.42×10^3. This is indicating a negligible

amount of MeHg can be found in gaseous form, with the majority of MeHg in air being

found associated with particulates. To this researcher's knowledge, this is the first study

to look at the makeup of MeHg in air fractions.

Table 5.7

A Comparison of Median MeHg Peak Area Results, Between Two MeHg Fractions in Air,
Inside KHE213a in 2008, ±SD

Date	Gaseous MeHg	Med. Gaseous MeHg	Total MeHg	Med. Total MeHg	Statistical Difference (p)
Jan. 11	<IDL[a]	<IDL	4.12×10^3	$5.42 \times 10^3 \pm 5.8 \times 10^4$	0.049
	<IDL		5.42×10^3		
			1.05×10^5		
Jan. 15	<IDL	<IDL	<IDL	$9.16 \times 10^2 \pm 2.6 \times 10^3$	0.190
	<IDL		<IDL		
			5.41×10^3		
			1.83×10^3		

[a]Instrument Detection Limit

5.2.1.2 Methyl Mercury Air Levels, Daytime and Overnight

The majority of sampling took place overnight, to ensure that analysis could occur

very soon after air sampling. However, a small number of daytime sampling took place

during preliminary tests, the results of which can be seen in Table 5.8. Using ranked

ANOVAs where appropriate, MeHg concentrations outside KHE213a were found, on

average, to be 2.7 times higher than indoor concentrations ($p < 0.001$). However, sampling

for indoor and outdoor air did not take place on the same sampling day, so these numbers

should be considered with caution.

Some daytime values appear to be extremely high, up to 24 ng/m^3. There is also

quite a large variation within daily samples, with %SD being greater than 100% in some

cases. This may be due to previously mentioned positive interference sources, including

the conversion of Hg^{2+} to $MeHg^+$ within the GC column, and other mercury compounds which may have similar retention times as $MeHg^+$ (Tseng et al, 1999).

Table 5.8
Average MeHg Concentrations (ng/m^3) at KHE213a During Daytime Sampling in 2008, ±SD (n)

Environment	Date	Sampling Time	Daily Results	Overall Results	Statistical Difference (p)
Inside	Feb. 20	11:00-14:00	19.9±17.5 (4)	5.3±7.2 (41)	<0.001
	Feb. 21	11:00-14:00	0.2±0.6 (9)		
	Feb. 23	11:00-14:00	1.7±2.5 (8)		
	Feb. 26	11:00-14:00	0.9±2.1 (8)		
	Apr. 7	11:30-13:00	0.8±1.4 (3)		
	Apr. 11	11:00-14:00	0.5±10.0 (5)		
	Apr. 30	11:30-15:30	9.3±11.8 (4)		
Outside	Jan. 24	11:00-14:30	16.8±11.3 (4)	14.3±8.2 (18)	
	Feb. 5	11:00-14:30	5.4±3.3 (5)		
	Feb. 7	11:00-14:30	24.4±16.6 (4)		
	Feb. 14	11:00-14:30	10.5±1.2 (5)		

MeHg concentrations measured at locations 1-3 overnight are listed in Table 5.9. All sampling took place in 2008. Ranked ANOVAs, where appropriate, were used during analysis. During overnight sampling, inside KHE213a, % difference between parallel samples was found to range between 48 and 95% for indoor air samples, and between 13 and 67% for outdoor air samples. In both cases the highest variability within daily samples were found for the same sampling day. MeHg concentrations inside were found to be between 1.6 and 8.8 times higher than outside concentrations. This difference was found to be marginally significant in two of the three sampling days (p=0.106). The sampling day which was not found to have a significant difference between indoor and outdoor air was the same day which had the highest relative variability, which can explain the result.

Table 5.9
Average MeHg Concentrations (ng/m^3) at Three Different Locations at University, During Overnight Sampling in 2008, ± difference (daily n=2), with significant differences highlighted

Location	Date	Sampling Time	Indoor	Outdoor	Statistical Difference (p)
1. KHE213a	**May. 20**	**16:39-09:40**	**4.8 ± 3.0**	**0.5 ± 0.1**	0.106
	May. 21	17:05-09:43	2.7 ± 2.6	1.7 ± 1.1	>0.500
	May. 22	**17:37-09:17**	**2.3 ± 1.1**	**0.8 ± 0.3**	0.106
2. KHE120	**Jun. 17**	**13:30-09:36**	**0.4 ± 0.1**	**0.8 ± 0.4x10^{-1}**	0.156
	Jun. 18	**15:53-09:12**	**0.4 ± 0.2**	**0.8 ± 0.3x10^{-1}**	0.156
	Jun. 19	**16:26-09:14**	**0.5 ± 0.2**	**0.9 ± 0.1**	0.106
	Jun. 20	**16:44-08:06**	**0.6 ± 0.2x10^{-1}**	**0.9 ± 0.7**	0.156
	Jun. 21	16:04-08:20	0.6 ± 0.1	0.7 ± 0.2	>0.500
3. KHN303b	**Jun. 23**	**15:48-09:14**	**0.5±0.2**	**1.7 ± 0.2**	0.106
	Jun. 24	17:13-09:24	1.1±0.9	1.4 ± 1.5	>0.500
	Jun. 25	**17:07-09:42**	**2.7±1.9**	**5.8 ± 1.6**	0.106
	Jun. 26	17:10-09:38	3.1±0.2	6.3 ± 11.2	>0.500
	Jun. 27	**16:38-10:02**	**1.1±0.9**	**0.2 ± 0.1**	0.106

Inside KHE120, % difference was found to range between 4 and 51%, and between 3 and 82% for outdoor air samples. MeHg concentrations outside were found to range between 1.2 and 2.0 times higher than indoor concentrations. This difference was found to be marginally significant in four of five sampling days (p=0.106-0.156).

Inside KHN303b, % difference was found to range between 7 and 85%, and between 13 and 176% for outdoor air samples. During the first four days of sampling, MeHg concentrations outside were found to range between 1.3 and 3.6 times higher than indoor concentrations. These differences were marginally significant for two of those four days (p=0.106). For those two days in which there was no significant difference between outdoor and indoor air samples, the daily outdoor air relative variance was the highest of all five sampling days, which can explain the results. However, on the fifth

day, MeHg concentrations inside were 4.6 times higher than outdoor concentrations (p=0.106). It appears that outdoor MeHg air levels dramatically decreased on this day, rather than a spike in indoor air levels. This may be due to varying wind patterns and resulting pollutant levels in the outdoor environment, which are beyond the scope of this study.

Previous studies have found parallel sample variation between 50 and 113.3 %SD (Bloom and Fitzgerald, 1988; Kotnik et al, 2000). Although the variation in samples in the current study were very similar to previous studies, for the most part there was a marginal improvement. Previously mentioned interference sources, including the conversion of Hg^{2+} to $MeHg^+$ within the GC column, other mercury compounds which may have similar retention times as $MeHg^+$, and water vapour, may be contributing to this variation (Bloom and Fitzgerald, 1988; Tseng et al, 1999; Woolfenden, 2008).

Overall, average MeHg concentrations inside locations 1-3, during overnight sampling, were found to range between 0.5 and 4.8 ng/m^3. MeHg concentrations outside locations 1-3 were found to range between 0.2 and 6.3 ng/m^3. In comparison to urban ambient air sampling, this is the second highest concentration of outdoor gaseous MeHg found to date, second only to Takizawa et al's (1981) sampling in Japan (Refer to Table 2.2) (Brosset and Lord, 1995; Bloom and Fitzgerald, 1988; Lee et al, 2003). Outdoor levels may be high enough to indicate a weak point source contamination (Kotnik et al, 2000; Lindberg et al, 2001; Feng et al, 2004a; Lindberg et al, 2005). However, since past studies have occurred under different sampling conditions they should only be considered a guideline. Possible point source MeHg pollutants include coal burning plants, industrial waste, landfill gas, thermal power plants, and waste incinerators (Kotnik et al, 2000; Tan

et al, 2000; Goldman et al, 2001; Lindberg et al, 2001; Munthe et al, 2003; Feng et al, 2004a; Lindberg et al, 2005). At least one of each of these sources is located in the Toronto area and may be affecting the Ryerson campus.

The overall pattern of overnight MeHg concentrations at KHE213a indicated that inside concentrations were significantly higher than outdoor concentrations (See Fig. 5.2). In past studies, it was found that indoor Hg^0 air levels were significantly elevated over outdoor levels (Pecheyran et al, 2000; Garetano et al, 2006). A similar pattern appears to be occurring with MeHg air levels. During daytime sampling, the opposite pattern was shown to emerge. However, in this case, indoor and outdoor sampling did not take place on the same day, so the ability to make a direct comparison is poor. It appears that average indoor MeHg levels during daytime and overnight sampling are similar, but outdoor levels are higher during daytime sampling. However, since MeHg levels should decrease during daylight hours, this may not be related to sunlight (Suda et al, 1993). It could however, be related to temperature, since there tends to be higher temperature levels during daytime hours, and temperature can be positively correlated with mercury levels (Godish and Rouch, 1986; Feng et al, 2004b; St. Denis et al, 2006; Rutter and Schauer, 2007). This will be discussed further in later sections.

The overall pattern of overnight MeHg concentrations at KHE120 and KHN303b indicated that outdoor concentrations were elevated over indoor concentrations. This is a significantly different pattern from previous Hg^0 studies, and may be connected to other environmental factors (Pecheyran et al, 2000; Garetano et al, 2006). One possibility is the fact that both locations face a courtyard, which contains several trees and a grass-covered lawn. Several studies have shown the ability of plants to bioaccumulate both inorganic

and methyl mercury species, such as water spinach, coriander, and *Elodea densa* from

water (Mortimer and Czuza, 1982; Karunasager, 2005; Goethberg and Greger, 2006).

MeHg species can also be produced by microorganisms, especially in anaerobic

conditions such as soil, via Hg^{2+} conversion (Gochfeld, 2003; Environment Canada,

2004c).
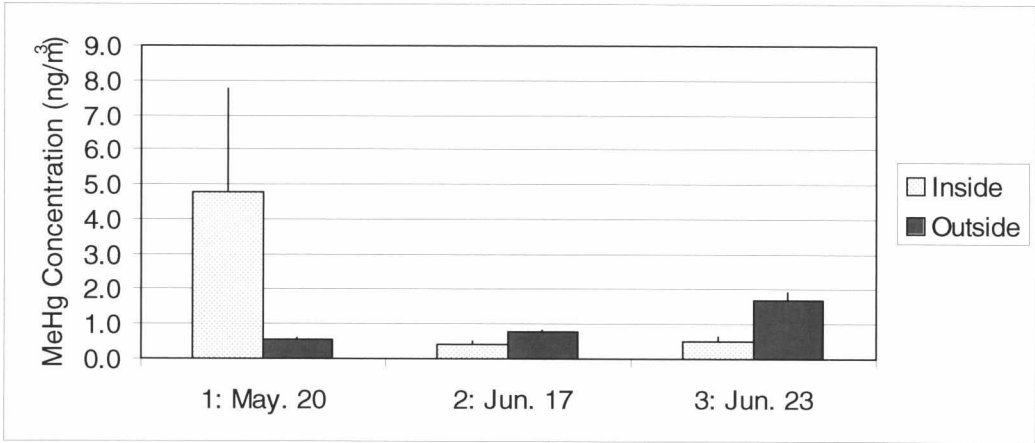
Fig. 5.2. Overall Pattern of Atmospheric MeHg Concentrations at Three Different
Locations at University from May-June 2008, with Error Bars Shown Representing
Difference Between Samples

While comparing indoor and outdoor air concentrations, it was found that MeHg

concentrations were significantly higher inside KHE213a, followed by KHN303b, and

then KHE120 (p<0.001). It was thought that KHE213a and KHN303b should have higher

levels of MeHg as they have been exposed to mercury containing compounds on a daily

basis, although the predominant compound used in KHE213a is MeHg. It is not unusual

for KHE120 to have the lowest MeHg levels, as it has not been exposed to mercury

standards. This location was painted in 2007, but this does not appear to have affected

MeHg levels.

5.2.2 Elemental Mercury Air Levels

5.2.2.1 Measured Concentrations

Overall results for Hg^0 levels at locations 1-5 can be seen in Table 5.10. All sampling took place in 2008. Analysis involved paired t-tests and ANOVAs where appropriate. Inside KHE213a %SD was found to range between <1 and 33%, and between <1 and 51% for outdoor air samples. Hg^0 concentrations inside KHE213a were found to be between 12 and 15 times higher than outside concentrations. These differences were significant for all sampling days ($p<0.001$).

Inside KHE120 %SD was found to range between <1 and 17%, and between 3 and 103% for outdoor air samples. Hg^0 concentrations inside KHE120 were found to be between 4 and 5 times higher than outside concentrations. These differences were significant for all sampling days ($p<0.001$).

Inside KHN303b %SD was found to range between <1 and 29%, and between 1 and 71% for outdoor air samples. Hg^0 concentrations inside KHN303b were found to be between 4 and 9 times higher than outside concentrations. These differences were significant for all sampling days ($p<0.001$).

Inside KHN308a %SD was found to range between <1 and 16%, and between 1 and 29% for outdoor air samples. Hg^0 concentrations inside location 4 were found to be ~1.4 times higher than outside concentrations. These differences were significant for all sampling days ($p<0.001$).

Inside KHN209 %SD was found to range between <1 and 29%, and between <1 and 36% for outdoor air samples. Hg^0 concentrations inside KHN209 were found to be

~2 times higher than outside concentrations. These differences were significant for all

sampling days (p<0.001).

Table 5.10

A Comparison of Average Indoor and Outdoor Hg^0 Concentrations (ng/m^3) at Five Different Locations at University in 2008, ±SD (n), p<0.001

Location	Date	Indoor	Outdoor
1. KHE213a	May. 20	33.1 ± 8.5 (72)	2.3 ± 0.5 (72)
	May. 21	25.2 ± 6.2 (70)	2.1 ± 0.3 (70)
	May. 22	23.4 ± 8.3 (71)	1.9 ± 0.3 (71)
2. KHE120	Jun. 19	13.4 ± 8.5 (67)	2.7 ± 1.3 (67)
	Jun. 20	15.7 ± 7.9 (68)	3.9 ± 1.4 (68)
	Jun. 21	16.2 ± 6.4 (71)	2.9 ± 0.6 (71)
3. KHN303b	Jun. 25	34.0 ± 9.2 (71)	3.7 ± 2.2 (71)
	Jun. 26	29.0 ± 10.8 (71)	4.8 ± 2.3 (71)
	Jun. 27	22.6 ± 4.9 (71)	4.6 ± 2.2 (71)
4. KHN308a	Aug. 26	16.3 ± 6.4 (65)	11.6 ± 4.3 (65)
	Aug. 27	24.2 ± 3.9 (68)	16.2 ± 2.0 (68)
5. KHN209	Aug. 28	29.9 ± 24.0 (65)	13.1 ± 8.2 (65)
	Aug. 29	29.4 ± 13.0 (70)	13.5 ± 5.8 (70)
	Aug. 30	17.1 ± 8.7 (70)	8.8 ± 4.1 (70)
	Aug. 31	18.8 ± 8.9 (70)	9.4 ± 4.1 (70)
	Sept. 1	22.9 ± 8.2 (67)	11.6 ± 4.2 (67)

There have been several studies looking at the levels of Hg^0 contamination of

outdoor and indoor air, both in urban settings and areas with point source pollutants

(Refer to Table 2.2). Overall, average Hg^0 concentrations inside locations 1-5 were found

to range between 15.0 and 28.5 ng/m^3. Indoor Hg^0 levels at the university are somewhere

in the middle, being higher, for the most part, than buildings in New York, and Bordeaux,

France, and where cultural mercury use is ongoing, but lower than dentistry labs, mercury

contaminated residences, and homes after latex paint applications (Temmerman et al,

1990; Beusterien et al, 1991; Orloff et al, 1997; Pecheyran et al, 2000; Carpi and Chen,

2001; Garetano et al, 2006; Gioda et al, 2007). Once again, these comparisons should

only be treated as guidelines.

Hg^0 concentrations outside locations 1-5 were found to range between 2.1 and 14.0 ng/m3. In comparison to urban outdoor areas, Hg^0 levels outside the university are somewhere in the middle, lower than Sakata City, Japan and Gent, Belgium, but in some instances higher than Long Island Sound, Bordeaux, France, and Wisconsin (Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Temmerman et al, 1990; Pecheyran et al, 2000; Rutter et al, 2008).

The overall pattern of Hg^0 concentrations at all five locations indicates that indoor air concentrations are significantly higher than outdoor concentrations (See Fig. 5.3). This is similar to patterns found previously in direct and indirect comparisons (Dumarey et al, 1979; Takizawa et al, 1981; Bloom and Fitzgerald, 1988; Agocs et al, 1990; Temmerman et al, 1990; Orloff et al, 1997; Pecheyran et al, 2000; Beusterien et al, 2001; Garcia-Sanchez et al, 2006; Garetano et al, 2006; Gioda et al, 2007; Rutter et al, 2008).
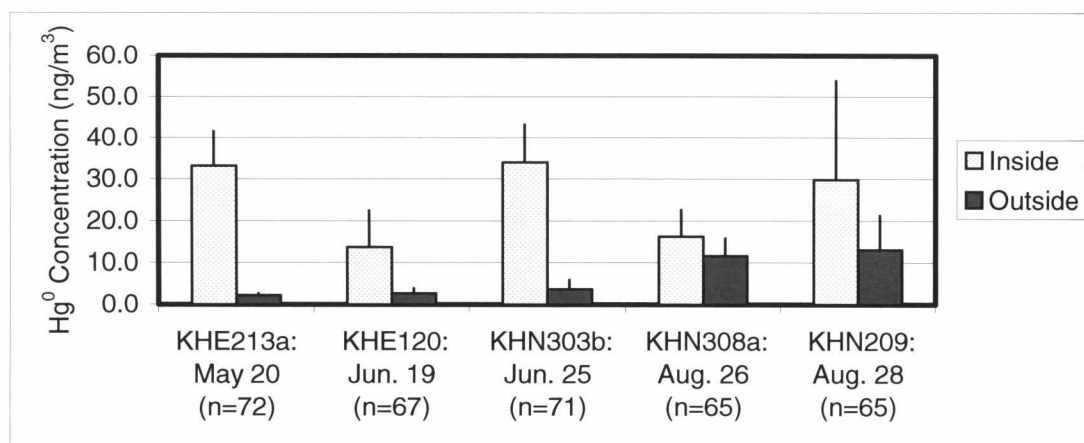
Fig. 5.3. Overall Pattern of Atmospheric Hg^0 Levels at Five Locations at University from May-August 2008, with Error Bars Shown Representing SD

It was found that Hg^0 concentrations inside KHE213a and KHN303b were not significantly different from each other (p=0.990). Hg^0 concentrations inside KHE213a and KHN303b were found to be significantly higher than those found in KHE120, KHN308a, and KHN209 (p<0.001). Concentrations inside KHN209 were found to be

higher than KHN308a (p=0.049), followed by KHE120 (p<0.001). It was expected that KHE213a and KHN303b should have higher Hg^0 levels, as both locations had been exposed to mercury standards on a regular basis. KHN209 has storage space for mercury containing compounds, but they are not being used on a regular basis. KHE120 and KHN308a are both offices, and have not been exposed to any mercury standards, which explains the lower indoor Hg^0 levels.

It was found that Hg^0 concentrations outside KHN308a were significantly higher than those outside KHN209, followed by KHE213a, KHE120, and KHN303b (p<0.001). This difference may be connected to outdoor temperatures or wind patterns, which will be discussed in a later section.

5.2.2.2 Impacts on Indoor Mercury Air Levels

The overall fluctuations in Hg^0 concentration and temperature, for both indoor and outdoor air, can be seen in Fig. 5.4. This section will be focusing on the factors affecting indoor air mercury levels. It has been found that the interior ventilation system of a building can affect many factors, including temperature, humidity, and air circulation (Godish and Rouch, 1986; Collett and Sterling, 1988; Feng et al, 2004b; Mysen et al, 2005; St. Denis et al, 2006; Rutter and Schauer, 2007). These factors in return have been found to affect the rate of vapourization to air (Godish and Rouch, 1986; Feng et al, 2004b; St. Denis et al, 2006; Rutter and Schauer, 2007). Indoor air quality is such a concern because of the amount of time an individual may spend inside during their life, which may well lead to some sort of illness (Collett and Sterling, 1988; Baker, 1998).

The climate control system at the university is a factor, which may be affecting indoor Hg^0 levels. As can be seen from Fig. 5.4, there appears to be a pattern of overnight

Hg^0 concentration decrease, which appears to be related to the climate control system's on-off cycle. It also appeared that there were different daytime fluctuation patterns,
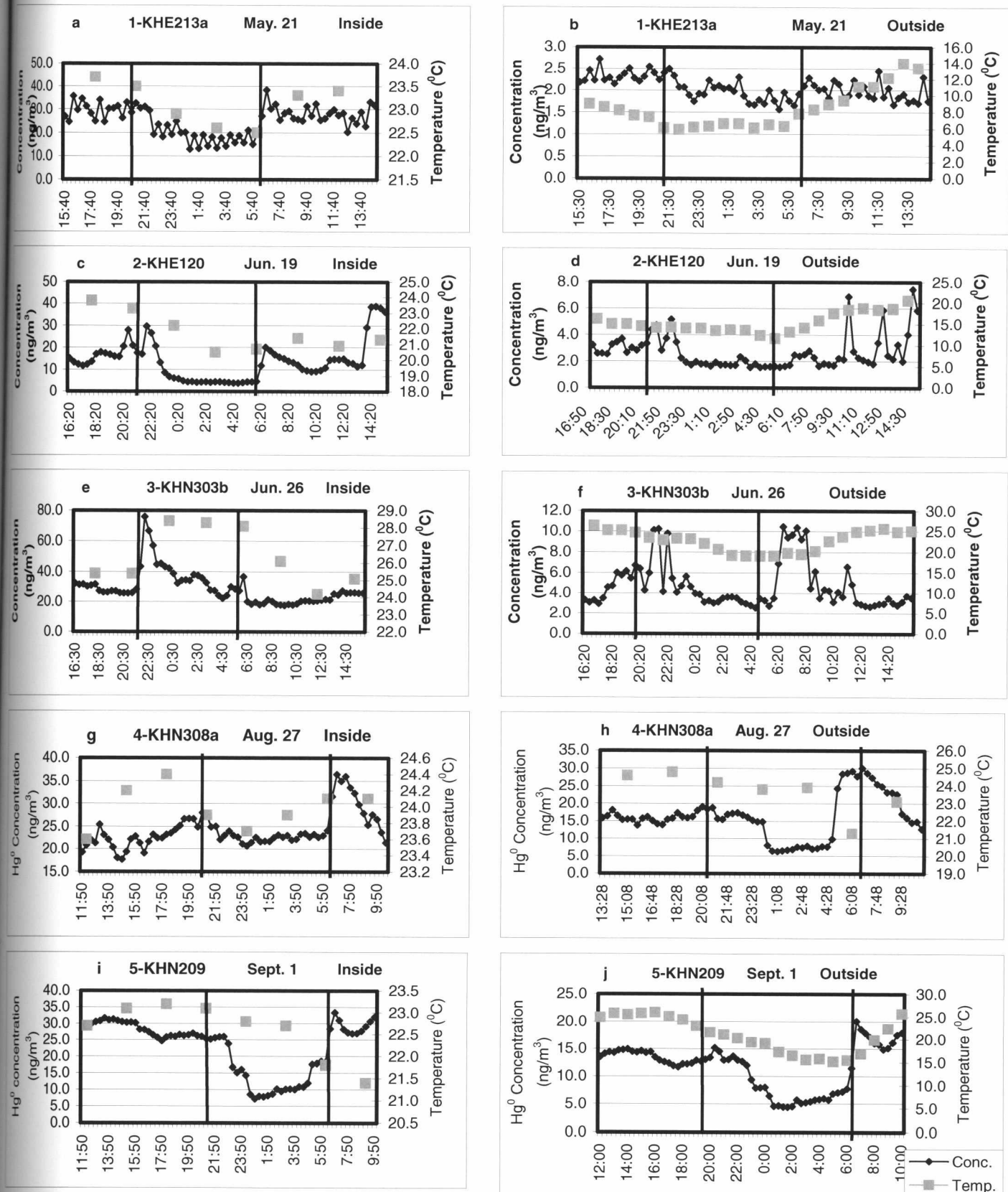
Fig. 5.4. Comparison of Atmospheric Hg⁰ Patterns at Five Locations. Samples Inside Vertical Lines were Taken During the Climate Control Off Cycle (Inside) or Overnight (Outside) in 2008

depending on whether the samples were taken before or after the climate control system was turned off for the night. Due to this, three different times of day were examined and compared. During the week, the off cycle was 21:00-06:00, and on-one and on-two cycles were before 21:00 and after 06:00. On the weekend, the off cycle was 18:00-08:00, and on-one and on-two cycles were before 18:00 and after 08:00. An ANOVA and Games-Howell post hoc test were used to compare the concentration and temperature difference at three different times of day. The correlation between temperature and Hg^0 concentrations were determined using the Pearson Correlation coefficient. Overall results from locations 1-5 can be seen in Table 5.11.

Inside KHE213a it can be seen that on two of the three sampling days average off concentrations were significantly lower than any of the on averages (p<0.001). On these days it was found that average off temperature readings were either significantly lower than either of the daytime averages (p<0.050) or significantly lower than the second-on average (p=0.017). On both days temperature was found to be positively correlated with Hg^0 concentration (R^2=0.65, p<0.001; R^2=0.31, p<0.001). On the first day of sampling, however, it was found that the average second-on concentration was significantly lower than the other two times of day (p<0.020). It was also found that the average second-on temperature reading was significantly higher than the off temperature (p=0.051). In this case temperature was found to be negatively correlated with Hg^0 concentration (R^2=0.07, p=0.037).

Inside KHE120 it can be seen that on two of three sampling days average off concentrations were significantly lower than either of the on averages (p<0.001). On these days it was found that average off temperature readings were either significantly

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Table 5.11

Average Hg^0 Air Concentration (ng/m^3) and Location Temperature (^{0}C) During Climate Control On-Off Cycle at University in 2008. ±SD (n)

Location	Date	Concentration			Temperature		
		On One[a]	Off	On Two[b]	On One	Off	On Two
1. KHE213a	May. 20	35.6 ± 10.0 (21)	35.5 ± 8.3 (27)	28.3 ± 4.5 (24)	23.2 ± 0.3 (3)	22.6 ± 0.3 (3)	23.5 ± 0.1 (2)
	May. 21	29.8 ± 3.5 (17)	19.5 ± 5.0 (27)	28.2 ± 3.7 (26)	23.6 ± 0.1 (2)	22.7 ± 0.2 (3)	23.4 ± 0.1 (2)
2. KHE120	May. 22	26.8 ± 4.7 (15)	15.2 ± 5.7 (27)	29.2 ± 4.9 (29)	22.8 ± 0.4 (2)	22.6 ± 0.1 (3)	23.3 ± 0.2 (3)
	Jun. 19	17.0 ± 4.4 (13)	8.4 ± 7.4 (27)	16.7 ± 8.9 (27)	23.6 ± 0.4 (2)	21.1 ± 0.9 (3)	21.2 ± 0.3 (3)
	Jun. 20	28.6 ± 6.3 (14)	12.2 ± 4.5 (33)	12.5 ± 2.0 (21)	23.3 (1)	21.6 ± 1.1 (4)	21.6 ± 0.3 (2)
	Jun. 21	20.6 ± 1.2 (5)	13.0 ± 3.0 (42)	21.0 ± 7.7 (24)	21.4 (1)	21.5 ± 0.7 (4)	22.6 ± 0.3 (3)
3. KHN303b	Jun. 25	22.7 ± 5.0 (16)	42.3 ± 7.7 (27)	32.5 ± 1.8 (28)	25.0 ± 0.1 (2)	27.3 ± 0.2 (3)	24.5 ± 0.9 (3)
	Jun. 26	28.6 ± 2.6 (14)	37.2 ± 12.8 (27)	21.9 ± 4.1 (30)	25.4 (1)	27.4 ± 1.7 (3)	25.9 ± 1.7 (4)
	Jun. 27	19.0 ± 2.2 (13)	26.7 ± 4.5 (27)	20.4 ± 3.2 (31)	26.9 ± 0.5 (2)	30.5 ± 0.6 (3)	26.1 ± 1.7 (3)
4. KHN308a	Aug. 26	16.3 ± 1.5 (23)	12.8 ± 6.7 (27)	22.6 ± 5.9 (15)	24.7 ± 0.1 (2)	24.0 ± 0.2 (3)	22.2 ± 1.3 (2)
	Aug. 27	22.7 ± 2.7 (28)	22.9 ± 1.4 (27)	30.0 ± 4.5 (13)	24.1 ± 0.4 (3)	23.8 ± 0.1 (3)	24.1 ± 0.0 (2)
5. KHN209	Aug. 28	17.5 ± 1.5 (23)	42.9 ± 33.1 (27)	25.5 ± 2.9 (15)	23.0 ± 0.3 (3)	22.0 ± 0.6 (3)	21.4 ± 0.2 (2)
	Aug. 29	40.2 ± 4.0 (28)	20.0 ± 12.3 (33)	30.4 ± 5.0 (9)	22.7 ± 0.5 (3)	22.6 ± 0.4 (4)	21.1 (1)
	Aug. 30	24.3 ± 1.6 (19)	12.1 ± 8.0 (42)	24.8 ± 2.5 (9)	22.5 ± 0.1 (2)	22.5 ± 0.4 (5)	21.3 (1)
	Aug. 31	26.7 ± 1.2 (19)	14.3 ± 8.8 (42)	22.9 ± 1.9 (9)	22.6 ± 0.3 (2)	22.8 ± 0.4 (5)	22.1 (1)
	Sept. 1	29.4 ± 2.0 (29)	17.7 ± 7.6 (36)	28.4 ± 3.8 (12)	22.9 ± 0.3 (3)	23.0 ± 0.2 (4)	21.6 ± 0.3 (2)

[a] Sampling before climate control system is turned off overnight

[b] Sampling after climate control system is turned on during the day

Numbers highlighted in bold depict a significant difference from two other categories. $p < 0.090$

Numbers underlined depict a significant difference from one other category. $p < 0.090$

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lower than the first-on temperatures (p=0.002) or marginally lower than the second-on temperatures (p=0.055). On both days temperature was found to be weakly positively correlated with Hg^0 concentration (R^2=0.09, p<0.017; R2=0.03, p<0.132). However, on the second day of sampling it was found that the average first on concentration was significantly higher than the other two times of the day (p<0.001). Unfortunately, a statistical test could not be performed to compare the average first-on temperature reading to the other two times of day as there was only one reading, although it appears to be higher than the other two times of day. In this case it was found that temperature was positively correlated with Hg^0 concentration (R^2=0.71, p<0.001).

Inside KHN303b it can be seen that on all three sampling days average off concentrations were significantly higher than either of the on averages (p<0.001). It was also found that on the first day of sampling the average first-on concentration was significantly lower than the second daytime concentration (p=0.049), whereas the reverse pattern was seen on the second day of sampling (p<0.001). It was found that on the first and last day of sampling the average off temperature readings were significantly higher than the other two times of day (p<0.090). However, on the second day of sampling there was no significant temperature change between times of day (p=0.409). On all three sampling days temperature was found to be positively correlated with Hg^0 concentration (R^2=0.71, p<0.001; R^2=0.67, p<0.001; R^2=0.66, p<0.001).

Inside KHN308a it can be seen that on both sampling days average second on concentrations were significantly higher than the other two times of the day (p<0.003). On the first day of sampling it was also found that the average off concentration was significantly lower than the first-on concentration (p=0.039). On the first day of sampling

it was found that the average second-on temperature reading was significantly higher than the other two times of day (p<0.100). On the second day of sampling it was found that average off temperature reading was significantly lower than the second-on reading (p=0.068). On both sampling days temperature was found to be negatively correlated with Hg^0 concentration, with this relationship being marginally significant for one of those sampling days (R^2=0.04, p=0.134; R^2<0.01, p>0.500).

Inside KHN209 it can be seen that on four of five sampling days average off concentrations were significantly lower than either average daytime concentrations (p<0.002). However, on the first day of sampling average off concentrations were significantly higher than either average on concentrations (p<0.030). It was also found that on the second and fourth day of sampling the average first-on concentration was significantly higher than the second daytime concentration (p<0.002), with the reverse being true on the first day of sampling (p<0.001). It was found that on the first day of sampling the average first-on temperature reading was significantly higher than the second-on temperature reading (p=0.048). On the second, third, and fifth day of sampling the average second on temperature readings were significantly lower than the other two times of day (p<0.090). On the first and fourth day of sampling temperature was found to be negatively correlated with Hg^0 concentration, with only one of these days having a significant relationship (R^2=0.21, p<0.001; R^2<0.01, p>0.500). On the second, third, and fifth day of sampling temperature was found to be positively correlated with Hg^0 concentration, with the relationship on the fifth day being marginally significant (R^2=0.01, p<0.500; R^2<0.01, p>0.500; R^2<0.03, p=0.152).

The overall pattern of Hg^0 concentration in KHE213a, KHE120, KHN308a, and KHN209 appeared to indicate that Hg^0 decreased during the climate control off cycle (See Fig. 5.5). On sampling days in which this was not the case Hg^0 fluctuations appeared to be negatively correlated with temperature fluctuations, with R^2 values averaging 0.14, indicating that these fluctuations were not closely related to temperature. This may indicate a spike due to standard use or spill. However, in KHN303b the opposite pattern emerged, with Hg^0 levels increasing during the climate control off cycle. It was found that Hg^0 and temperature fluctuations were positively correlated in KHE213a, KHE120, and KHN303b, with R^2 values averaging 0.48. This is not a very strong relationship overall.
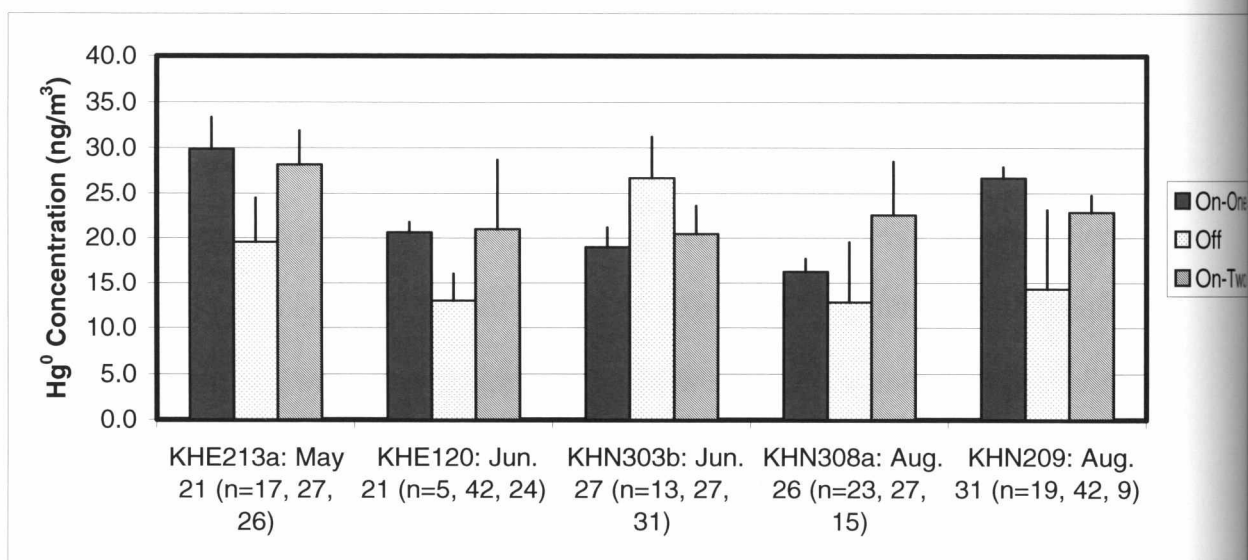
Fig. 5.5. Overall Pattern Of Indoor Hg^0 Levels at Five Different Locations During Climate Control Cycle at University from May-August 2008, with Error Bars Shown Representing SD

It appears that the indoor climate control cycle is a better indicator of Hg^0 fluctuations than temperature readings. It is known that increasing the flowrate of air tends to increase the vapourization of a substance to air, which explains the relationship

between the climate control system and Hg^0 concentration in four of five of the rooms. When the climate control system is turned off, the circulation of air within the building is stopped, decreasing the rate of vapourization.

However, in the case of KHN303b the emission of Hg^0 to indoor air actually increased. This discrepancy could be related to the previously mentioned hole leading to the roof, with possible exhaust outlet contamination. With the climate control system off, the lack of air circulation can cause an increase the mercury level inside the room. Some preliminary sampling that took place in December 2007 showed a significant correlation between indoor air samples and samples taken on the roof in close proximity to the exhaust outlet ($R^2=0.96$, $p<0.001$).

5.2.2.3 Impacts on Outdoor Mercury Air Levels

This section will be focusing on the factors affecting outdoor air mercury levels. Mercury concentrations in air could be affected by factors other than strictly pollutant sources. Increases in Hg^0 levels have been shown to be correlated with solar radiation, due to the reduction of Hg^{2+} (Carpi and Lindberg, 1997; Feng et al, 2004b). This is supported, as it has been found that mercury fluxes from soil to air tend to be higher during the day compared to overnight (Boudala et al, 2000; Gustin et al, 2006; Xin and Gustin, 2007). Mercury fluxes from mine waste contaminated soil, as well as sludge-amended soil, to the air has also been shown to increase during daylight hours (Gustin et al, 2003). More Hg^0 is released from snowpacks to the atmosphere during polar day (Cobbett et al, 2007).

Temperature can also have the ability to affect pollutant levels (Godish and Rouch, 1986; Feng et al, 2004b; St. Denis et al, 2006; Rutter and Schauer, 2007). It has

been found that indoor air levels of formaldehyde and mercury are significantly higher when indoor air temperatures are higher (Godish and Rouch, 1986; Feng et al, 2004b; St. Denis et al, 2006; Rutter and Schauer, 2007).

The sunlight levels, more specifically, the day-night cycle, is a factor, which may be affecting indoor Hg^0 levels. As can be seen from Fig. 5.4, there appears to be a pattern of overnight Hg^0 concentration decrease, which appears to be related to sunlight levels. It also appeared that there were different daytime fluctuation patterns, depending on whether the samples were taken before or after nightfall. Due to this, three different times of day were examined and compared. The night cycle was identified as that between sunset and sunrise, and daytime-one and daytime-two cycles were before sunset and after sunrise (CNRC, 2003). An ANOVA and Games-Howell post hoc test were used to compare the concentration and temperature difference at three different times of day. The correlation between temperature and Hg^0 concentrations were determined using the Pearson Correlation coefficient. Overall results from locations 1-5 can be seen in Table 5.12.

Inside KHE213a it can be seen that on all three sampling days the average first daylight concentrations were significantly higher than the other two times of day ($p < 0.065$). On these days it was found that average night temperature readings were significantly lower than the first daylight averages ($p < 0.006$). On the first and last day of sampling temperature fluctuations were found to be positively correlated with Hg^0 fluctuations ($R^2 = 0.16$, $p = 0.001$; $R^2 = 0.10$, $p = 0.005$). However, on the second day of sampling temperature levels were found to be negatively correlated with Hg^0 fluctuations ($R^2 = 0.04$, $p = 0.092$).

Table 5.12

Average Hg[0] Air Concentration (ng/m³) and Outdoor Temperature Readings (°C) During Daylight and Night Hours at University in 2008. ±SD (n)

Location	Date	Concentration			Temperature		
		Daylight One[a]	Night	Daylight Two[b]	Daylight One	Night	Daylight Two
1. KHE213a	May. 20	**2.7 ± 0.7 (20)**	**2.2 ± 0.2 (27)**	**2.0 ± 0.2 (25)**	**14.9 ± 0.9 (6)**	6.3 ± 2.3 (9)	7.7 ± 1.4 (8)
	May. 21	**2.3 ± 0.2 (16)**	2.0 ± 0.2 (27)	2.0 ± 0.2 (27)	**8.0 ± 0.6 (5)**	**6.3 ± 0.2 (9)**	**10.9 ± 2.1 (9)**
	May. 22	**2.1 ± 0.5 (15)**	1.8 ± 0.2 (26)	1.8 ± 0.2 (30)	13.5 ± 1.3 (5)	**8.1 ± 1.2 (9)**	13.1 ± 2.5 (10)
2. KHE120	Jun. 19	3.1 ± 0.5 (13)	2.2 ± 1.0 (25)	2.9 ± 1.6 (29)	**15.3 ± 0.7 (4)**	**13.5 ± 0.9 (9)**	**17.3 ± 2.4 (9)**
	Jun. 20	4.5 ± 1.9 (14)	4.3 ± 1.3 (25)	**3.3 ± 0.8 (29)**	21.5 ± 1.7 (5)	**15.3 ± 1.9 (8)**	19.3 ± 1.8 (10)
	Jun. 21	**3.6 ± 0.8 (15)**	**2.9 ± 0.4 (25)**	**2.6 ± 0.3 (31)**	19.1 ± 0.4 (5)	**15.7 ± 1.3 (8)**	19.2 ± 2.6 (10)
3. KHN303b	Jun. 25	**2.4 ± 0.3 (16)**	**3.1 ± 0.4 (26)**	**5.0 ± 3.0 (29)**	24.4 ± 22 (6)	**20.2 ± 0.8 (8)**	24.9 ± 2.9 (10)
	Jun. 26	4.8 ± 1.3 (15)	4.5 ± 2.2 (25)	4.9 ± 2.7 (32)	**25.0 ± 1.1 (5)**	21.2 ± 1.9 (8)	22.8 ± 2.6 (11)
	Jun. 27	**3.1 ± 1.0 (13)**	4.8 ± 2.4 (26)	5.1 ± 2.2 (32)	**24.6 ± 0.6 (5)**	20.5 ± 1.5 (8)	21.2 ± 1.1 (11)
4. KHN308a	Aug. 26	11.2 ± 0.8 (21)	10.4 ± 4.7 (31)	**15.3 ± 4.8 (13)**	20.0 ± 1.5 (7)	**14.0 ± 2.4 (10)**	18.1 ± 2.7 (4)
	Aug. 27	**15.1 ± 1.6 (25)**	**16.2 ± 0.7 (31)**	**18.9 ± 2.8 (12)**	21.0 ± 1.2 (9)	19.2 ± 0.4 (10)	20.2 ± 1.3 (4)
5. KHN209	Aug. 28	**8.3 ± 0.8 (20)**	15.6 ± 10.8 (32)	14.1 ± 1.1 (13)	16.8 ± 0.3 (7)	16.9 ± 0.3 (11)	**19.7 ± 1.6 (5)**
	Aug. 29	**18.6 ± 2.6 (24)**	8.8 ± 4.2 (33)	**16.1 ± 3.9 (13)**	**24.0 ± 0.6 (8)**	19.0 ± 2.2 (11)	20.3 ± 2.6 (5)
	Aug. 30	11.8 ± 0.8 (24)	5.3 ± 2.9 (33)	11.8 ± 3.8 (13)	**25.3 ± 1.5 (8)**	**18.1 ± 2.5 (12)**	**21.7 ± 2.4 (5)**
	Aug. 31	**12.6 ± 0.7 (24)**	6.2 ± 3.9 (33)	**11.7 ± 1.3 (13)**	24.3 ± 0.8 (8)	**18.2 ± 2.4 (11)**	21.8 ± 3.3 (5)
	Sept. 1	**13.5 ± 1.1 (24)**	8.7 ± 4.0 (33)	**16.7 ± 1.3 (10)**	25.1 ± 1.0 (8)	18.0 ± 2.4 (11)	21.2 ± 3.7 (4)

[a] Sampling before nightfall
[b] Sampling after nightfall
Numbers highlighted in bold depict a significant difference from two other categories, p<0.160
Numbers underlined depict a significant difference from one other category, p<0.160

Inside KHE120 it can be seen that on the first and last day of sampling the average first-daylight concentrations were significantly higher than night concentrations (p<0.030). On the second day of sampling it was found that the average first-daylight and night concentrations were significantly higher than the second daylight concentrations (p<0.100). On all three days of sampling it was found that average night temperature readings were significantly lower than either of the daytime cycles (p<0.020). On the first day of sampling temperature was found to be positively correlated with Hg^0 concentrations (R^2=0.09, p=0.017). However, on the second and third day of sampling it was found that temperature was negatively correlated with Hg^0 concentrations, although this relationship was not significant (R^2=0.02, p=0.211; R^2<0.01, p>0.500).

Inside KHN303b it can be seen that on the first and third day of sampling the average first-daylight concentrations were significantly lower than the other two times of day (p<0.010). However, on the second day of sampling there was no significant difference in average concentration between any of the three time cycles (p>0.500). On all three sampling days it was found that the average first-daylight temperature readings were significantly higher than at night (p<0.015). On all three sampling days temperature was found to be negatively correlated with Hg^0 concentration, although on only one day was this relationship significant (R^2<0.01, p>0.500; R^2=0.04, p>0.500; R^2=0.24, p<0.001).

Inside KHN308a it can be seen that on both sampling days the average second daytime concentrations were significantly higher than the other two times of the day (p<0.025). On both days of sampling it was found that the average night temperature

readings were significantly lower than the first-daylight cycle (p<0.004). On the first

sampling day temperature was found to be positively correlated with Hg^0 fluctuations,

although this relationship was not significant (R^2=0.01, p=0.403), whereas on the second

day temperature was found to be negatively correlated with Hg^0 fluctuations (R^2=0.06,

p=0.047).

Inside KHN209 it can be seen that on four of five sampling days average night

concentrations were significantly lower than either average daytime concentrations

(p<0.001). However, on the first day of sampling the average night and second-daylight

concentrations were significantly higher than the average first-daytime concentration

(p<0.003). It was found that on all five sampling days the average night temperature

readings were significantly lower than the one or both of the daytime temperature

readings (p=<0.160). On all five sampling days temperature was found to be positively

correlated with Hg^0 concentration, with four of five of these days having a significant

relationship (R^2=0.01, p=0.332; R^2=0.53, p<0.001; R^2=0.59, p<0.001; R^2<0.39, p<0.001;

R^2<0.48, p=<0.001).

The overall pattern of Hg^0 concentration at all locations appeared to indicate that

Hg^0 decreased during the night, and increased during one or both daylight cycles (See

Fig. 5.6). The relationship between temperature and Hg^0 fluctuations was found to be

unpredictable, with both positive and negative relationships being found at the same

location. The average R^2 values for positive relationships was found to be 0.33, and 0.11

for negative relationships, indicating that these fluctuations were not closely related to

temperature. However, with such a weak relationship between Hg^0 concentrations and

sunlight conditions, it does not seem like a very compelling explanation for the variation

in outdoor Hg^0 concentrations. Another explanation may be wind direction and flow patterns, which are beyond the scope of this study.
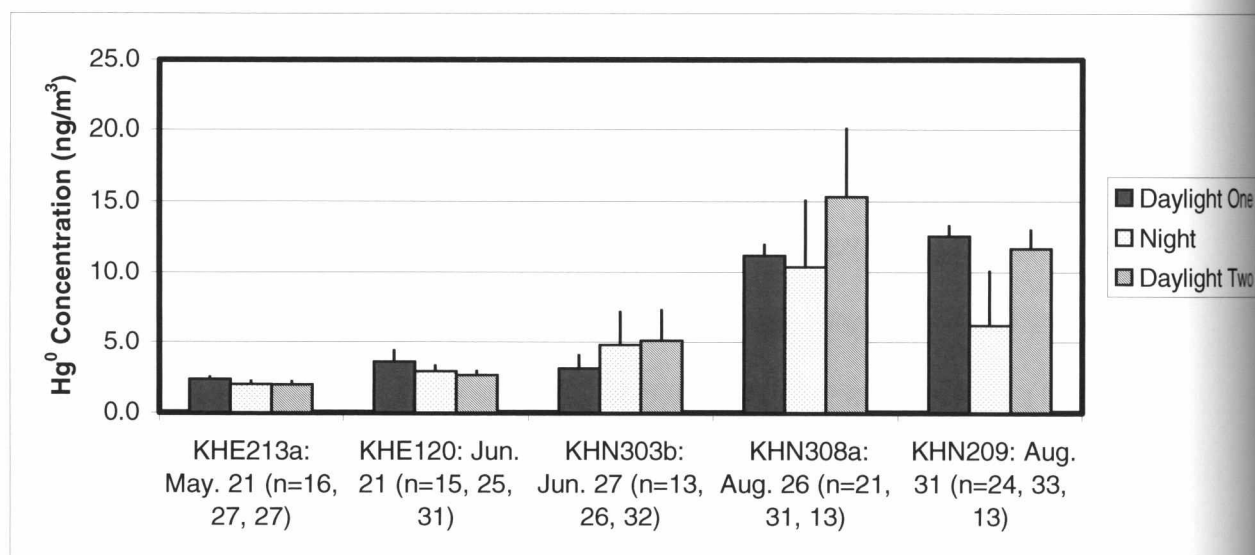

Fig. 5.6. Overall Pattern Of Outdoor Hg^0 Levels at Five Different Locations at University from May-August 2008, with Error Bars Representing SD

5.2.3 Comparing Outdoor and Indoor MeHg and Hg^0 Air Levels

When comparing indoor and outdoor air concentrations, from previously mentioned samples, average indoor Hg^0 concentrations were found to be significantly higher than MeHg concentrations in all sampling situations ($p<0.020$). When considering THg as Hg^0+MeHg, average inside MeHg concentrations were found to be between 3.6 and 10.4% of THg (See Figure 5.7). It was found that average outside Hg^0 concentrations were also significantly higher than MeHg concentrations ($p<0.020$). Average outside MeHg concentrations were found to be between 21.0 and 41.0% of THg.

This was a higher relative concentration of MeHg in outdoor air than was expected (Bloom and Fitzgerald, 1988; Kotnik et al, 2000; Munthe et al, 2003). It has been estimated that MeHg species in outdoor air can be between 0 and 5 % of THg

(Bloom and Fitzgerald, 1988; Munthe et al, 2003). This also points to a MeHg contamination source that is contributing to these higher than normal levels, as previously mentioned.
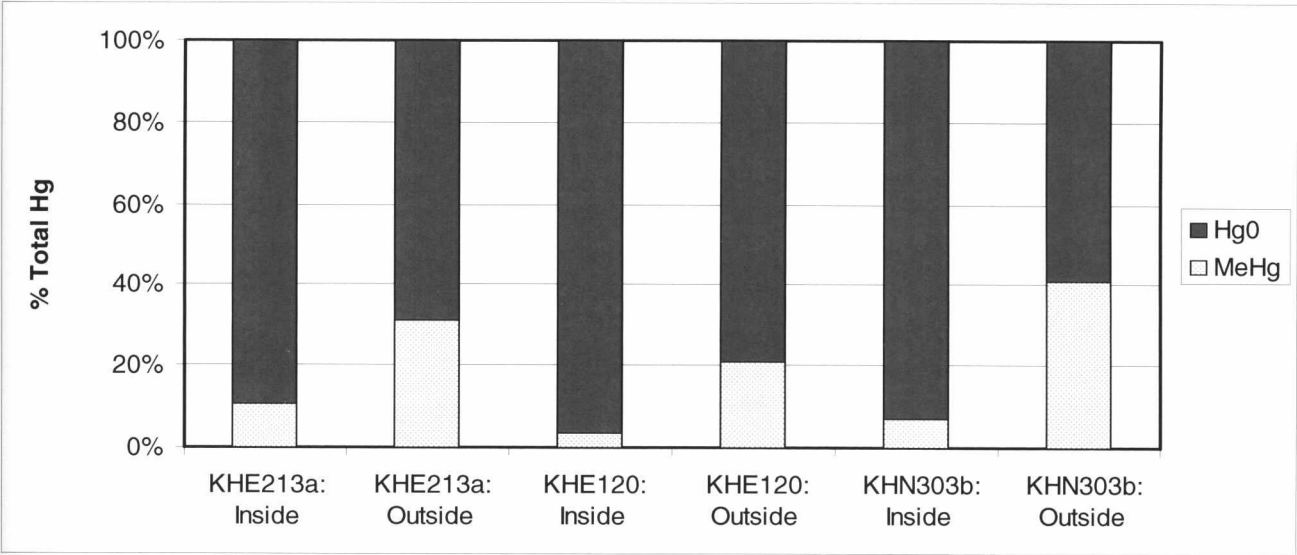
Fig. 5.7. A Comparison of Average MeHg and Hg^0 in Air at Three Locations at University from May to June 2008

5.3 Comparing Indoor and Inner Ceiling Air

5.3.1 Methyl Mercury Air Levels

The concentrations of MeHg measured in indoor and inner ceiling air are compared in Table 5.13. All sampling took place in 2008. Ranked ANOVAs, where appropriate, were used during analysis. Inside KHE213a, on June 6, 9, 11, and 12, % difference was found to range between 56 and 200% for indoor air samples, and between 1 and 160% for inner ceiling air samples. In both cases the lowest variability within daily samples were found for the same sampling day, June 6. MeHg concentrations in the inner ceiling were found to be between 1.1 and 17.3 times higher than inside concentrations.

There was only one sampling day in which this difference was marginally significant, June 8 (p=0.106).

Inside KHN303b, from June 28-30, % difference was found to range between 13 and 29% for indoor air samples, and between 9 and 20% for inner ceiling air samples. On June 28 and 29, MeHg concentrations in the inner ceiling were found to be between 1.4 and 1.9 times higher than inside concentrations. However, on June 30, inside MeHg concentrations were found to be 1.3 times higher than that of inner ceiling levels. However, these differences were not significant (p>0.500).

Table 5.13
Average MeHg Concentrations (ng/m^3) at Three Different Locations at University in 2008, ± difference (daily n=2)

Location	Date	Sampling Time	Indoor	Inner Ceiling	Statistical Difference (p)
1. KHE213a	Jun. 6	15:59-10:09	4.6 ± 2.6	5.0 ± 0.1	>0.500
	Jun. 9	16:11-09:34	**0.3 ± 0.6**	**5.1 ± 0.7**	0.106
	Jun. 11	17:18-09:44	0.3 ± 0.6	2.0 ± 2.7	>0.500
	Jun. 12	18:24-09:26	0.3 ± 0.6	2.8 ± 4.4	>0.500
3. KHN303b	Jun. 28	17:18-09:00	3.2 ± 0.4	2.3 ± 0.5	>0.500
	Jun. 29	17:08-08:29	1.8 ± 0.5	2.4 ± 0.2	>0.500
	Jun. 30	17:00-09:26	2.7 ± 0.6	1.4 ± 0.3	>0.500

Previous studies have found parallel sample variation between 50 and 113.3 %SD (Bloom and Fitzgerald, 1988; Kotnik et al, 2000). The variation in KHE213a samples appeared to be elevated over these levels, suggesting that inner ceiling air may be affecting the results or sampling error may have occurred. Previously mentioned interference sources, including the conversion of Hg^{2+} to $MeHg^+$ within the GC column, other mercury compounds which may have similar retention times as $MeHg^+$, and water vapour, may be contributing to this variation (Bloom and Fitzgerald, 1988; Tseng et al, 1999; Woolfenden, 2008).

The overall pattern of MeHg concentrations was unclear, with no significant

pattern emerging, due to the large variability in daily sampling (See Fig. 5.8). It was

found that inside MeHg concentrations were not significantly different when location was

considered (p>0.500), although inner ceiling concentrations were marginally different

(p=0.148). This may indicate a change in MeHg levels in inner ceiling air from location

to location, but more locations would need to be sampled to confirm this.
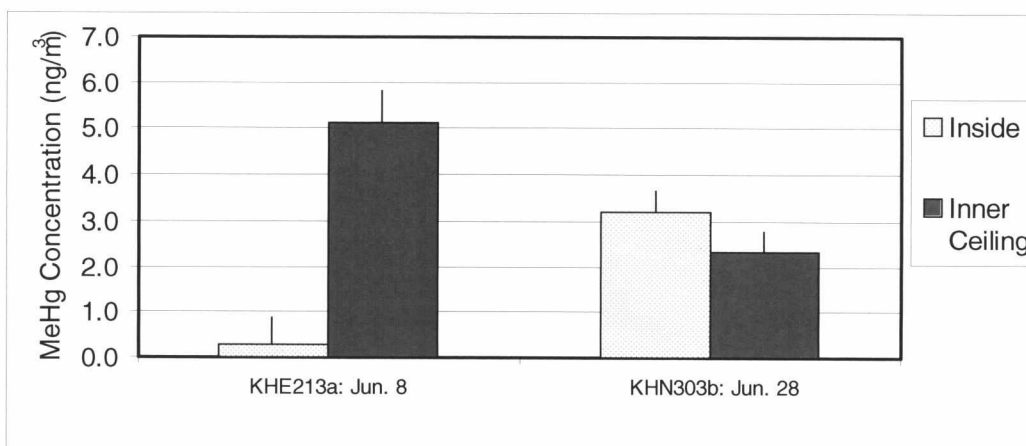
Fig. 5.8. Overall Pattern of Average Atmospheric MeHg Levels at Two Locations at University in June 2008, with Error Bars Shown Representing Difference Between Samples

5.3.2 Elemental Mercury Air Levels

5.3.2.1 Measured Concentrations

Overall results of Hg^0 levels at KHE213a and KHN303b can be found in Table

5.14. All sampling took place in 2008. Analysis involved paired t-tests and ANOVAs

where appropriate. Inside KHE213a, during the sampling period of June 6 and June 9-12,

%SD of parallel samples was found to range between 2 and 20% for indoor air samples,

and between <1 and 21% for inner ceiling air samples. Average Hg^0 concentrations in the

inner ceiling were found to be between 1.2 and 1.9 times higher than indoor

concentrations. These differences were found to be significant for all sampling days (p<0.001).

Inside KHN303b, during the sampling period of June 28-30, %SD was found to range between <1 and 49% for indoor air samples, and between <1 and 66% for inner ceiling air samples. Hg^0 concentrations in the inner ceiling were found to be between 1.1 and 1.5 times higher than indoor concentrations. These differences were found to be significant for all sampling days (p<0.001).

Table 5.14
Average Hg^0 Concentrations (ng/m^3) in Two Different
Locations at University in 2008, ±SD (n), p<0.001

Location	Date	Indoor	Inner Ceiling
1. KHE213a	Jun. 6	182.6 ± 66.5 (54)	223.6 ± 66.6 (54)
	Jun. 9	85.3 ± 50.6 (71)	150.8 ± 92.3 (71)
	Jun. 10	56.7 ± 24.2 (82)	105.9 ± 44.3 (82)
	Jun. 11	37.1 ± 6.5 (50)	55.2 ± 11.7 (50)
	Jun. 12	39.6 ± 13.8 (72)	65.0 ± 22.9 (72)
3. KHN303b	Jun. 28	60.1 ± 62.0 (69)	80.6 ± 91.5 (69)
	Jun. 29	49.7 ± 59.9 (69)	73.2 ± 108.3 (69)
	Jun. 30	57.8 ± 61.1 (49)	59.4 ± 74.4 (49)

Overall, average Hg^0 concentrations inside both locations were found to range between 37.1 and 182.6 ng/m^3. Hg0 concentrations in the inner ceiling of both locations were found to range between 55.2 and 223.6 ng/m^3. Inner ceiling Hg^0 levels at the university are once again somewhere in the middle, being higher, for the most part, than buildings in New York and Bordeaux, France, locations where cultural mercury use is ongoing, and close to levels of homes after latex paint applications, but still significantly lower than dentistry labs and mercury contaminated residences (Temmerman et al, 1990; Beusterien et al, 1991; Orloff et al, 1997; Pecheyran et al, 2000; Carpi and Chen, 2001; Garetano et al, 2006; Gioda et al, 2007).

The overall pattern at both locations indicates that inner ceiling Hg^0 concentrations were found to be significantly higher than inside concentrations (See Fig. 5.9). Previous studies have found emissions of air Hg^0 levels during daytime hours, compared to night (Carpi and Lindberg, 1997; Boudala et al, 2000; Feng et al, 2004b; Cobbett et al, 2007; Gustin et al, 2003; Xin and Gustin, 2007). Considering the dark environment of the inner ceiling, it would be expected that inner ceiling levels were lower than inside levels. It appears other factors may play a role in this difference in concentration, such as temperature differences or lack of circulation. This will be discussed further in the following section. While comparing indoor and inner ceiling air concentrations, it was found that Hg^0 concentrations, both inside and in the inner ceiling of, KHE213a were significantly higher than KHN303b ($p<0.001$). This may once again be linked to the relative use of Hg^0 standards at both locations.
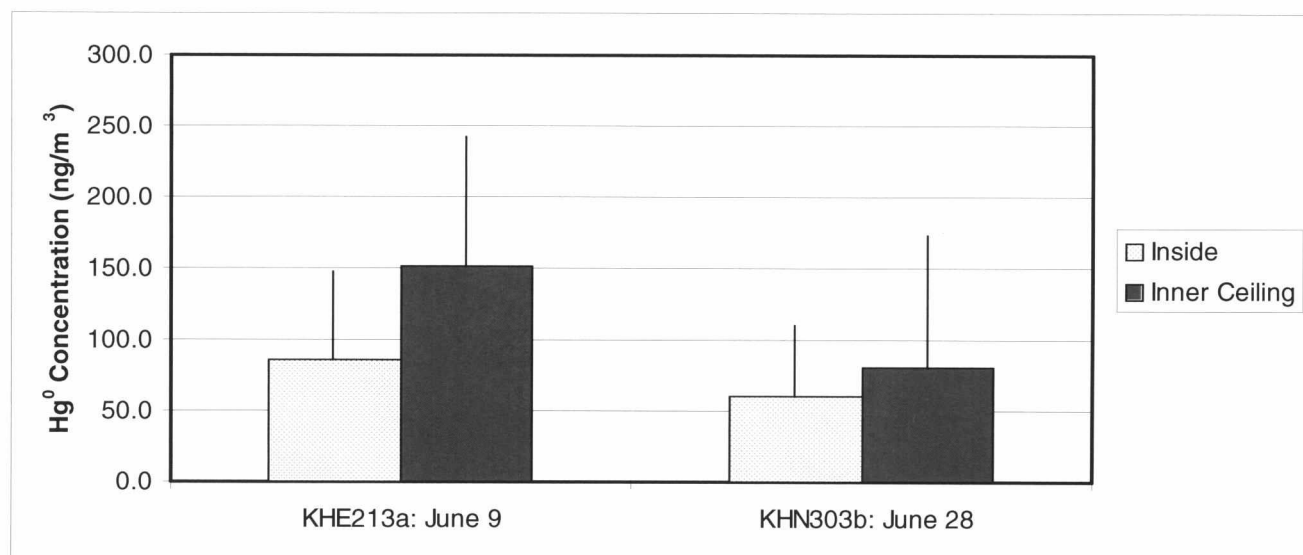

Fig. 5.9. Overall Pattern of Average Hg^0 Levels at Two Locations at University in June 2008, with Error Bars Representing SD

5.3.2.2 Impacts on Indoor and Inner Ceiling Elemental Mercury Air Levels

It has been found that the interior ventilation system of a building can affect many factors, including temperature, humidity, and air circulation (Godish and Rouch, 1986; Collett and Sterling, 1988; Feng et al, 2004b; Mysen et al, 2005; St. Denis et al, 2006; Rutter and Schauer, 2007). These factors in return have been found to affect the rate of vapourization to air (Godish and Rouch, 1986; Feng et al, 2004b; St. Denis et al, 2006; Rutter and Schauer, 2007). Indoor air quality is such a concern because of the amount of time an individual may spend inside during their life, which may well lead to illness (Collett and Sterling, 1988; Baker, 1998).

The climate control system at the university is a factor, which may be affecting indoor and inner ceiling Hg^0 levels. As can be seen from Fig. 5.4, there appears to be a pattern of overnight Hg^0 concentration decrease, which appears to be related to the climate control system's on-off cycle. It also appeared that there were different daytime fluctuation patterns, depending on whether the samples were taken before or after the climate control system was turned off for the night. Due to this, three different times of day were examined and compared, for both indoor and inner ceiling air. During the week, the off cycle was 21:00-06:00, and on-one and on-two cycles were before 21:00 and after 06:00. On the weekend, the off cycle was 18:00-08:00, and on-one and on-two cycles were before 18:00 and after 08:00. An ANOVA and Games-Howell post hoc test were used to compare the concentration and temperature difference at three different times of day. The correlation between temperature and Hg^0 concentrations were determined using the Pearson Correlation coefficient. Overall results for KHE213a and KHN303b can be seen in Table 5.15.

Inside KHE213a, it can be seen that on all sampling days average off concentrations were significantly higher than the other two times of day (p<0.060). The same pattern held for inner ceiling concentrations (p<0.120). There was only one sampling day in which there was a significant difference between average temperature readings, with average off temperature readings being significantly higher (p=0.007). It was found that on all sampling days temperature was positively correlated with Hg^0 fluctuations (R^2=0.31, p<0.001; R^2=0.45, p<0.001; R^2=0.34, p<0.001; R^2=0.52, p<0.001). Data from June 11-12 sampling were excluded from this part of the analysis, as ~6h of data were missing due to an equipment malfunction.

Inside KHN303b, it can be seen that on all sampling days average off concentrations were significantly higher than the other two times of day (p<0.001). The same pattern held for inner ceiling concentrations (p<0.001). On two of the three sampling days average off temperature readings were found to be significantly higher than the other two times of day (p<0.090). It was found that on all sampling days temperature was positively correlated with Hg^0 fluctuations (R^2=0.71, p<0.001; R^2=0.67, p<0.001; R^2=0.66, p<0.001).

The overall pattern of Hg^0 concentration indicated, for both locations that Hg^0 increased during the climate control system off cycle. This is the opposite pattern for KHE213a than was found when indoor and outdoor air were sampled. This reinforced the notion that the inner ceiling air was affecting the indoor air sampling. If you look at the daily fluctuations of both rooms, in Fig. 5.10, the indoor and inner ceiling air have almost identical patterns. It was found that indoor and inner ceiling fluctuations were significantly correlated, with and average R^2 value of 0.89 for KHE213a, and 0.71 for

KHN303b (p<0.001). Temperature was found to be correlated with these patterns, with an average R^2 value of 0.52. This is a stronger relationship than was seen when comparing indoor and outdoor air samples. Similar to MeHg, these results indicate that the inner ceiling environment is having an effect on a room's air quality, which may be related to air circulation issues or limitations of sampling apparatus.

Table 5.15

Average Hg⁰ Air Concentration (ng/m³) and Location Temperature (°C) During Climate Control On-Off Cycle at University in 2008, ±SD (n)

Location	Date	Concentration			Temperature		
		On One[a]	Off	On Two[b]	On One	Off	On Two
1. KHE213a, Inside	Jun. 6	118.9 ± 4.7 (15)	222.9 ± 54.7 (33)	120.0 ± 7.2 (6)	26.8 ± 0.4 (2)	**29.9 ± 0.5 (3)**	26.6 (1)
	Jun. 9	**56.0 ± 6.5 (22)**	119.6 ± 68.1 (27)	**72.6 ± 13.4 (22)**	23.8±0.7 (2)	24.1 ± 1.2 (3)	23.9 ± 1.2 (3)
	Jun. 10	**55.8 ± 10.5 (34)**	72.3 ± 33.8 (27)	**38.3 ± 4.2 (21)**	22.9 ± 0.3 (3)	23.2 ± 0.7 (3)	22.8 ± 1.2 (3)
	Jun. 12	**29.0 ± 4.0 (24)**	51.6 ± 15.1 (27)	**36.2 ± 4.1 (21)**	22.9 ± 0.1 (2)	23.4 ± 0.8 (3)	23.3 ± 0.8 (3)
1. KHE213a, Inner Ceiling	Jun. 6	**169.9 ± 13.6 (15)**	261.2 ± 58.8 (33)	**261.2 ± 58.8 (33)**	N/A	N/A	
	Jun. 9	105.7 ± 12.1 (22)	216.9 ± 122.1 (27)	114.7 ± 25.7 (22)	N/A	N/A	
	Jun. 10	**107.6 ± 13.5 (34)**	133.0 ± 62.6 (27)	**68.1 ± 5.4 (21)**	N/A	N/A	
	Jun. 12	**47.1 ± 4.5 (24)**	83.5 ± 26.6 (27)	**61.6 ± 8.0 (21)**	N/A	N/A	
3. KHN303b, Inside	Jun. 28	**20.3 ± 1.0 (2)**	91.4 ± 61.7 (42)	**10.6 ± 0.8 (25)**	26.5 (1)	**29.7 ± 1.7 (4)**	26.1 ± 1.7 (3)
	Jun. 29	9.8 ± 0.2 (2)	86.1 ± 63.9 (36)	10.0 ± 7.0 (31)	N/A	28.2 ± 1.9 (4)	26.8 ± 2.4 (4)
	Jun. 30	6.9 ± 0.3 (12)	100.4 ± 51.8 (27)	4.0 ± 5.3 (10)	26.6±0.3 (2)	**29.7 ± 0.5 (3)**	26.9 (1)
3. KHN303b, Inner Ceiling	Jun. 28	**18.8 ± 1.0 (2)**	125.3 ± 93.1 (42)	**10.4 ± 0.9 (25)**	N/A	N/A	N/A
	Jun. 29	9.7 ± 0.1 (2)	132.0 ± 123.0 (36)	9.1 ± 3.4 (31)	N/A	N/A	N/A
	Jun. 30	7.1 ± 0.5 (12)	102.4 ± 76.8 (27)	8.1 ± 10.4 (10)	N/A	N/A	N/A

[a] Sampling before climate control system is turned off overnight
[b] Sampling after climate control system is turned on during the day
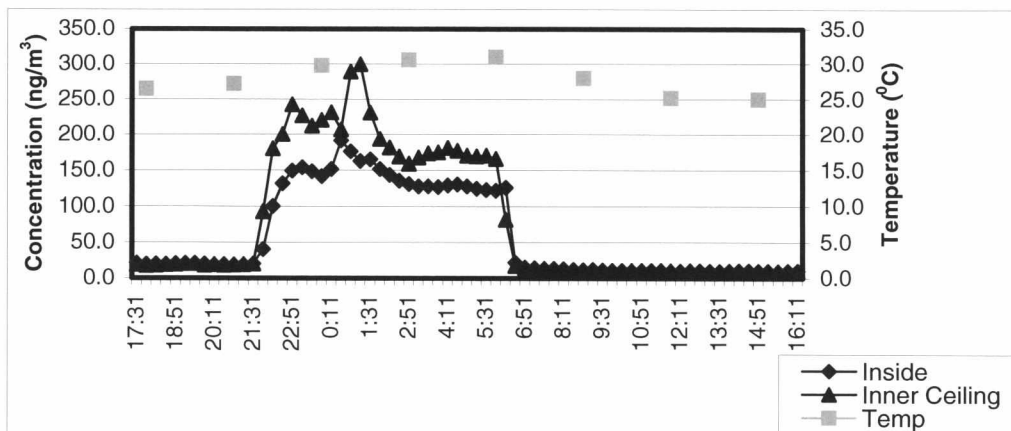Numbers highlighted in bold depict a significant difference from two other categories, p<0.120

Fig. 5.10. Hg^0 Fluctuations in KHN303b at University on June 28, 2008

5.3.3 Comparing Inner Ceiling and Indoor MeHg and Hg^0 Air Levels

When comparing indoor and inner ceiling air, average indoor Hg^0 concentrations were found to be significantly higher than MeHg levels in all sampling situations (p<0.001). Average inside MeHg concentrations were found to be between 1.1 and 4.3% of THg levels (See Figure 5.11). Average inner ceiling Hg^0 concentrations were also found to be significantly higher than MeHg concentrations (p<0.001). Inner ceiling MeHg concentrations were found to be between 2.7 and 3.3% of THg levels. As previously stated, it has been estimated that MeHg species in outdoor air can be between 0 and 5 % of THg (Bloom and Fitzgerald, 1988; Munthe et al, 2003). This is once again indicating that it is the outdoor air around Ryerson University that has elevated levels of MeHg.
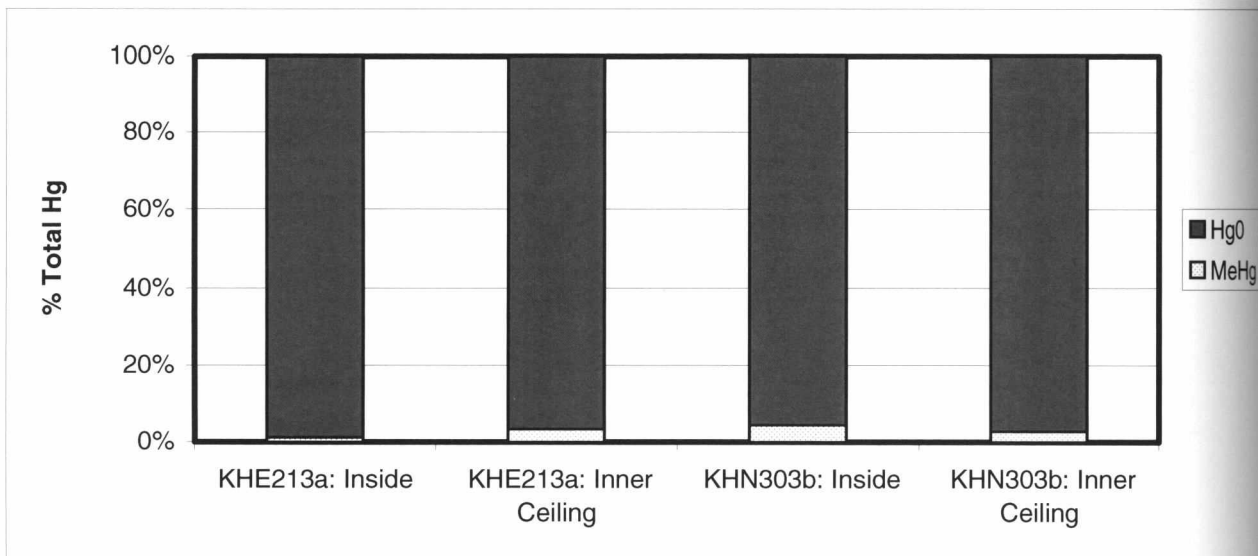
Fig. 5.11. A Comparison of Average MeHg and Hg^0 in Air in Two Locations at University in June 2008

6. Conclusions

6.1 Summary

A new desorption protocol for the adsorbent trap technique was established for MeHg analysis, utilizing a two-part heating process; the first part to rid traps of excess Hg^0, and the second at ~71^0C for MeHg release. An average detection limit of 2.7 pg was found for standard results, which is at the lower end of detection limits found in previous studies.

The fraction of MeHg in air was studied, which has not been done before. It was determined that the majority of MeHg in air can be found associated with particulates, as opposed to gaseous MeHg.

This was the first known study to record MeHg levels in Toronto and indoor air MeHg levels period. Outdoor MeHg levels were found to be the second highest recorded to date. It was found that outdoor MeHg levels were well above the normal 0-5% of total mercury levels outside one location, which may be linked to microorganism interactions. It was found that indoor MeHg levels were related to location function, whereas outdoor levels were related to soil and vegetation abundance. Inner ceiling MeHg levels were not significantly different from indoor levels.

It was found that Hg^0 inside and outside the university were comparable to reported literature values, not extraordinarily high or low. Indoor Hg^0 levels were consistently higher than outdoor levels. Once again, indoor Hg^0 levels were related to location function. Inner ceiling Hg^0 levels were found to be consistently higher than indoor levels. These higher levels may be linked to a lack of air circulation.

Indoor Hg^0 fluctuations were found to be related to the university's climate control system. In most cases, it was found that the climate control system may actually increase Hg^0 levels when in use. This was the first known study to look at indoor mercury fluctuations in relation to a climate control system.

6.2 Recommendations for Future Work

Although MeHg sampling results were adequate, the reproducibility between replicates were not significantly different from previous studies. Although the adsorbent trap method may be convenient in regards to its mobility and ease of transport and analysis, its variable results are cause for concern. Future studies may wish to focus on the plausibility and reliability of other sampling techniques, such as passive sampling, especially for indoor MeHg sampling.

Outdoor MeHg levels indicated an effect of vegetation and soil, possibly due to microorganism interactions. Further investigation into this area would be instructive, especially comparing daytime and overnight levels, in rural and urban areas.

Further work should be done on the climate control system and its exact effect on indoor Hg^0 levels. Further avenues to explore would be monitoring air circulation overnight, monitoring temperature levels and air circulation in the inner ceiling overnight, and investigating any Hg^0 fluctuations when temperature is held at a constant.

Finally, it would be interesting to work with several more sampling locations. This could include other buildings at the university, or even other locations around the city, developing a mercury map for the Toronto area, for both indoor and outdoor locations.

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