Chemical Processes Influencing Mercury Transformations And Atmospheric Fluxes In The Atmospheric Boundary Layer In Coastal Regions

Susan Warau Gichuki

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The atmosphere has been recognized as the major contributor of mercury inputs to terrestrial and aquatic environments. While considerable research on atmospheric concentrations and fluxes of Hg has been carried out in the Northern Hemisphere, this is not the case for the Southern hemisphere, remote islands and parts of the open ocean. In this work, atmospheric Hg concentrations and fluxes were determined for locations in South Africa and Bermuda. The concentrations of Hg and other trace metals (Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) in precipitation are presented for Pretoria, an urban center and Cape Point, a Global Atmospheric Watch (G.A.W.) site in a nature reserve in South Africa. For Bermuda, Hg concentrations in air, precipitation and particles and deposition fluxes were determined.

While these places have distinct differences, these results demonstrate that these locations share similarities in terms of the factors and atmospheric processes that influence deposition. Further, at both locations atmospheric Hg inputs pose a threat to coastal ecosystems, and chemical reactions in the atmosphere enhance the production of reactive gaseous Hg (RGHg) species, which is readily deposited. Additionally, ancillary data and atmospheric back-trajectories help to determine potential sources. Associations between Hg and other trace metals and concentrations of radon (222Rn) and carbon monoxide (CO) help to determine the relative strength of anthropogenic influences at the South African sites. The role of particles and
chemical processes that enhance inputs to the coastal ecosystem in Bermuda are discussed. Finally, the importance of sampling and analytical methods & procedures in Hg research and indeed all trace metal research is demonstrated through participation in an international inter-comparison exercise under the GEOTRACES program.
Chemical Processes Influencing Mercury Transformations And Atmospheric Fluxes In The Atmospheric Boundary Layer In Coastal Regions

By

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Chemical Processes Influencing Mercury Transformations and Atmospheric Fluxes in the Atmospheric Boundary Layer

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University of Connecticut
2013
DEDICATION

To my parents Allan Gichuki & Anne Wairimu Gichuki who made it all possible

To my brothers Muchiri & Ngugi for their unwavering support and encouragement
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1. LITERATURE REVIEW AND HYPOTHESIS

1.1 Sources of mercury to the atmosphere and atmospheric mercury speciation

Mercury (Hg) is a group 12 transition metal and exists as a silver white liquid at 25 °C. It has an atomic number of 80 and a closed shell electronic configuration (5d$^{10}$ 6s$^2$) (Lin & Pehkonen, 1999). Mercury (Hg) is emitted to the atmosphere from a variety of anthropogenic and natural sources. Natural sources include volcanoes and related geological activities as well as land emissions from areas naturally enriched in mercury. There are global mercuriferous belts where areas of the earth along plate tectonic boundaries are geologically enriched in mercury, including western North America, central Europe and southern China. Mercury is present as cinnabar ore (HgS) that has a characteristic red color (Selin, 2009). It is emitted as both elemental mercury (Hg$^0$) and ionic mercury (Hg$^{II}$). Anthropogenic sources include waste incineration, cement production, coal burning whereas the natural emissions come from volcanoes, crustal degassing and the oceans (Sprovieri et al, 2010). There are three forms of Hg identified in the atmosphere based on their physical and chemical properties: gaseous Hg$^0$, gaseous ionic divalent Hg (Hg$^{II}$), which is also referred to as reactive gaseous Hg (RGHg) and particulate Hg (HgP). While most trace metal pollutants tend to exist in the particulate phase in the atmosphere (Pacyna & Pacyna, 2001), Hg mainly exists in the gaseous phase due to its unique physicochemical properties. Elemental Hg has a relatively high vapor pressure of 0.246 Pa at 25 °C and a low Henry’s law constant, which makes it less soluble in water. As a result removal by rainwater is less efficient compared to the more water-soluble RGHg and the scavenging of HgP (Mason & Sheu, 2002). The main sink of Hg$^0$ in the atmosphere is oxidation to Hg (II), which is driven by reactions with a variety of atmospheric oxidants such as ozone.
(O₃), hydroxyl radicals (OH•), halide radicals such as bromine (Br•) and chlorine (Cl•) (Mason and Sheu, 2002; Selin, 2009).

1.2 Air sea exchange and the global mercury cycle

A large percentage of Hg in the atmosphere is Hg⁰, which has a residence time of 9 months to 1 year and can travel over long distances (Lin and Pehkonen, 1999). Atmospheric oxidants such as bromine, chlorine and to a lesser extent, hydroxyl radicals readily convert Hg⁰ to Hg (II). These reactions are photochemically driven and occur in the atmosphere and at the air-sea interface as illustrated in the schematic diagram in Figure 1.1:

![Schematic diagram of conversion reactions involving Hg⁰ and Hg (II) and exchange at the air-sea interface](image)

**Figure 1-1:** Schematic diagram of conversion reactions involving Hg⁰ and Hg (II) and exchange at the air-sea interface

According to experimental evidence hydrogen peroxide (H₂O₂), nitrate (NO₃) radical, ozone (O₃), hydroxyl (OH) radical and halogen atoms and molecules (Br, Cl, Br₂, Cl₂) can oxidize Hg⁰ (Lin & Pehkonen, 1999). Although there are a number of atmospheric oxidants reactions, of Hg⁰
and halogen species are dominant because they have larger rate constants and as a result oxidation by these species proceeds much faster in certain locations. Halogen mediated reactions are especially important in the polar-regions as well as the marine boundary layer (MBL) in certain mid-latitude regions. The production of these halogen species involves reactions with O\textsubscript{3} and were first recorded in the Arctic and referred to as “ozone depletion” episodes. Ozone mixing ratios dropped from 30 to 40 ppb to almost zero in a span of a few hours to a day. There was a strong anti-correlation between daily mean concentrations of O\textsubscript{3} and Br (Barrie et al., 1988), which recorded a noticeable increase (Spicer et al., 2002). The hyper-saline brine surfaces on young sea ice and saline snow packs are the source of the halogen atom precursors (Stephens et al., 2012). In the MBL halogen species are released from sea-salt aerosol (Mason and Sheu, 2004). A heterogeneous reaction of bromide and ozone on seawater ice initiates the formation of gas phase bromine compounds.

\[
\begin{align*}
\text{O}_3 (g) + \text{Br}^-(g) & \rightarrow \text{BrO}^-(g) + \text{O}_2(g) \quad (1) \\
\text{BrO}^- (g) + \text{H}^+(aq) & \leftrightarrow \text{HOBr} (aq) \quad (2) \\
\text{HOBr}(aq) + \text{Br}^-(aq) + \text{H}^-(aq) & \rightarrow \text{Br}_2(g) + \text{H}_2\text{O}(aq) \quad (3)
\end{align*}
\]

HOBr is known to react with Br\textsuperscript{−} as shown in reaction (3) to produce Br\textsubscript{2} in solution and also when the bromide is present in salts or ice. However, since sea salt is the source of bromide ions this means chloride ions are also present. HOBr also reacts with chloride ions:

\[
\text{HOBr}(aq) + \text{Cl}^-(aq) + \text{H}^-(aq) \rightarrow \text{BrCl}(aq) + \text{H}_2\text{O}(aq) \quad (4)
\]

Since there is a large Cl:Br ratio (650:1) in seawater, the reaction with Cl\textsuperscript{−} may be expected to dominate. However, BrCl is more soluble in water compared to Br\textsubscript{2}, this means the former is more likely to undergo secondary reactions in the surface film. This is further supported by measurements by Spicer and co-workers (2002) who report an enhancement of Br\textsubscript{2} in snow pack
interstitial air compared to the air above it. Additionally, Cl is largely released as HCl that is stable chemically and photolytically, whereas Br\textsubscript{2} and BrCl are rapidly photolyzed to their photochemical constituents (Ariya and Peterson, 2005). The production of Hg\textsuperscript{II} from oxidation by halogen atoms involves a 2-step mechanism:

\[ \text{Hg(g)} + \text{Br(g)} \rightarrow \text{HgBr (g)} \quad (5) \]
\[ \text{HgBr} + \text{X} \rightarrow \text{HgBrX} \quad (6) \text{ where X = Br, Cl, I, OH} \]

It is worth noting that in the clean MBL the contribution of OH (g) is likely to be less important compared to Br (g) due to low O\textsubscript{3} concentrations found and low concentrations of O\textsubscript{3} precursors such as nitrogen oxide (NOx) species. However, in regions where the MBL is influenced by continental air-masses that contain urban or industrial emissions it is possible that OH (g) production may lead to it playing a more important role (Ariya and Peterson, 2005).

Once produced, Hg (II) may exist in the gas phase or it may adhere to particles, and both forms can be dry deposited onto terrestrial or aquatic ecosystems, or scavenged by wet deposition. Hg (II) can also be reduced back to Hg\textsuperscript{0} or alternatively, it may undergo biotic or abiotic transformations that lead to methylation (Fitzgerald et al., 2007). In the aquatic environment there are three chemical forms of mercury: elemental Hg (Hg\textsuperscript{0}), divalent ionic Hg (Hg(II)) and methylated forms of mercury, namely monomethylmercury (CH\textsubscript{3}Hg\textsuperscript{+}) and dimethylmercury ((CH\textsubscript{3})\textsubscript{2}Hg). When surface waters become super saturated, evasion of Hg\textsuperscript{0} also occurs (Ci et al., 2011). The cycling at the air-sea interface is a significant part of the global mercury cycle. The operational term reactive gaseous mercury (RGHg) is used to refer to the species formed from the oxidation of Hg\textsuperscript{0} (HgBr, HgBrO, HgBr\textsubscript{2}, HgCl\textsubscript{2} etc). In field observations, RGHg concentrations typically peak at mid-day with a decline in the afternoon falling to detection limit at night. This diurnal cycle is driven by in-situ production of RGHg via
the reactions described above in the MBL or during polar spring (Holmes et al., 2009). Unlike Hg⁰ that is long lived in the atmosphere (~1 year) (Bullock, 2005) RGHg is readily deposited. Hence, the atmosphere is the most important source of mercury to terrestrial and aquatic environments because it is the main pathway by which Hg is dispersed and transported globally (Laurier and Mason, 2007; Strode et al., 2007). Humans have altered the biogeochemical cycling of mercury through anthropogenic activities such as coal burning, mining and industry removing it from long term sedimentary storage into the atmosphere. Figure 1.2 illustrates the current global mercury cycle incorporating the influence of anthropogenic activities. According to model estimates, since the pre-industrial age there has been a three to five fold enrichment in the global atmospheric mercury pool (Mason & Sheu, 2002; Selin, 2009).

![Figure 1-2: The current global mercury cycle. All fluxes are in Mmol per year (Mason and Sheu, 2002).](image)

With increased industrialization and economic growth especially in emerging nations such as China and India, this is expected to continue. Global mercury emissions have been
estimated at between 2190-4000 tonnes per year (Selin, 2009; Li et al., 2009). About two-thirds of these emissions come from fossil fuel combustion. Asian countries contributed about 54% of the total emissions of Hg globally in the year 2000. For the same year, it has been estimated that China emitted 536 tonnes of Hg in 1999. The major contributing activities are non-ferrous metal smelting, coal combustion and other activities such as battery production, fluorescent lamp production and cement production. The country produces the largest amount of zinc (Zn) in the world estimated at 1.95 million tons in 2000. It is also the largest producer and consumer of coal in the world estimated at 1.25 billion and 1 billion tons respectively in 2000 (Zhang & Wong, 2007). India, Japan, Kazakhstan and the Democratic Republic of Korea are also major Hg emitters (Li et al., 2009). The organic form of Hg, methyl mercury (CH$_3$Hg) is known to bio-magnify up the food chain and human exposure is primarily through consumption of higher trophic level fish and marine mammals. Methyl mercury crosses the placenta and readily passes through the blood brain barrier. Low levels of childhood prenatal exposure may cause early childhood neurocognitive effects (Karagas et al., 2012). Measuring deposition is one way of estimating the extent of emissions as well as quantifying fluxes. It is also a necessity in order to better refine atmospheric mercury models which are often used to estimate emissions and fluxes in areas where there is a paucity of data such as certain parts of the open ocean and the Southern Hemisphere. Still, measuring Hg concentrations in environmental samples remains a challenge since ambient concentrations are low especially in the atmosphere and natural waters. Therefore analytical instrumentation used should be able to achieve low detection limits, and process a large number of samples from various matrices. A review of the current state of the field, including a historical perspective showing the development of the field to date follows in the next section.
1.3  A Historical Perspective Of Trace Metal And Mercury Analysis

It is not possible to recount the progress of Hg research over the years without considering the advances made in the broader field of trace element research in the ocean. The term “trace” comes from an even broader definition that refers to the minor elements in seawater i.e. those existing at concentrations less than 1 mg/kg but excluding nutrients, dissolved gases and the radioactive elements. The term “trace elements” encompasses a wide array of elements including the transition metals, the metalloids, lanthanides (rare earths) and actinides. These elements find their way into the ocean through two major external sources: atmospheric or riverine inputs and introduction of material when seawater interacts with newly formed oceanic crustal basalt (Bruland, 1983). It is now widely recognized that trace elements and their isotopes can function as nutrients (e.g. Fe), contaminants (e.g. Hg, As), and tracers or proxies of various oceanographic processes (Cutter and Bruland, 2012). Much of this recognition is credited to work done by early pioneers such as Clair Patterson and programs such as the Geochemical Ocean Sections Study (GEOSECS) in the 1970’s (Cutter & Bruland, 2012). GEOSECS was a global survey of the distribution of chemical, isotopic and radiochemical tracers in the ocean. Unfortunately only a few trace elements could be determined in these early programs due to various shortcomings of the available protocols in use at the time. While most environmental analyses can be performed in any “ordinary” environmental or geochemical lab, trace element analysis is more challenging due to low levels in the environment and the high risk of sample contamination.

The rest of this discussion will focus on the gains made through technological advancement and researchers’ efforts to overcome these challenges. Further, the spotlight will be on work involving transition metals, including metalloids, loosely classified as “trace metal(loid)s”. Some elements such as Fe are abundant in the earth’s crust and function as micronutrients in the ocean. However, Fe concentrations in the ocean are low (<0.2 Nm)(Moore & Braucher, 2007), which
affects primary productivity and other biogeochemical processes, and this has been a topic of major study. Since pre-industrial times, the concentrations of metals such as Pb have been increasing in the environment, raising concern due to associated deleterious effects. In the 20th century coal combustion, industrial emissions and the use of tetra-ethyl lead as a gasoline additive were all important contributors to the contamination of atmospheric, aquatic and terrestrial systems. Efforts to carry out environmental studies followed, often with considerable difficulty. A prime example is the problem encountered in the measurement of lead with accuracy at sub-nanomolar levels in natural water.

This was first highlighted by Patterson & Settle (1976) in their ground-breaking paper, “The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collection and analyses”. They noted that lead concentrations in water could not be reliably determined at the 1 ng/g level due to an inability to determine the extent of lead artifacts introduced to the sample during sampling, collection and analysis. Without accounting for these artifacts, the values reported by most researchers were much higher than the actual level in the environment. To appreciate the effects of this consider this example: Bradford and co-workers (1968) measured lead in 170 lakes in High Sierra California, reporting an average of 0.3 ng/g Pb. In contrast, Hirao et al. (1974) reported 0.015 ng/g Pb, having analyzed fresh stream waters from the same region (Patterson & Settle & references therein). In the former, contamination from gasoline in the helicopter used for sampling caused the high sampling artifact. Benoit (1994) provides similar evidence by acknowledging that reliability of most data collected prior to 1975 for trace metals in natural waters is questionable. Indeed, measurements he made in 1993 of Pb and Cd in the Quinnipiac river, CT were in the parts-per-
trillion (ppt) range, while values from the USGS between 1981-1991 for the same locations are in the parts-per-billion range (ppb) (Benoit, 1994). While it may seem that metal concentration declined, the real reason is the improvement in analytical techniques. These examples underscore the challenges faced by all trace metal researchers in the early days. Clair Patterson instituted methods to prevent contamination of samples by introducing steps such as: acid cleaning of laboratory glassware and plastics, sampling devices and storage containers; use of gloves and using specific materials such as Teflon which are less likely to propagate contaminants. These measures are adequate for sampling surface waters or shallow depths. However, seawater sampling especially at deeper depths still posed a challenge. The samplers in use then were made of neoprene, polyvinylchloride & polystyrene and also contained lots of metal parts. In addition, the “aura of contamination” around marine vessels was not considered, sampling ahead of the vessel remedied this. Further, new deep-water samplers were constructed which are triggered at depth to prevent contamination (Patterson & Settle, 1976). The current models in use are discussed in greater detail in the next section. The development of appropriate devices and rigorous protocols was the precursor of the so-called “clean techniques” still in use today.

**CURRENT STATE OF FIELD**

At present Hg analysis is performed with good precision in various matrices: air, water, sediments and biological materials such as blood, hair and urine. However, this discussion will be restricted to Hg analysis in natural water samples and atmospheric particles collected on membrane filters. Generally, Hg speciation involves the following steps: extraction of Hg from sample matrix and/or pre-concentration, separation of Hg species of interest and detection
(Leermakers et al., 2005). These are described in brief in the following sections for both water and atmospheric particulate samples.

1.4 Handling of water samples

1.4.1 Sample collection, preservation and storage

When collecting samples for THg analysis appropriate containers to use are Teflon or glass bottles with a Teflon-lined lid. Containers should always be tightly capped. If trace metal analysis is also likely to be done, borosilicate is preferred. Commercial options that are “certified clean for trace metals sampling” such as I-CHEM® Level 300 are also good (Parker and Bloom, 2005). For field campaigns, surface waters can be sampled with peristaltic, pneumatic or diaphragm pumps, through Teflon tubing and into the collection vessel. General Oceanics (GO) Go-Flo bottles (www.generaloceanics.com) or Varn-Dorn bottles can used for deeper depths especially during oceanographic cruises (Stoichev et al., 2006). Single Teflon coated Go-Flo samplers on nonmetallic Kevlar hydroline are effective at eliminating trace metal contamination. They also have minimal metal parts. Go-Flos are designed to enter the air-sea interface closed, and triggered to open at ~10 m by a pressure-release mechanism allowing water to continuously flow through as they descend until they reach the desired depth. At this point they close when tripped by a hydroline messenger (Hunter et al, 1996). However the procedures involved are labor intensive and time consuming if multiple daily profiles of the water column are required. To overcome this issue, trace metal (TM) rosettes were designed. An early model developed by the TM/Plankton group at the Moss Landing Marine Labs was composed of eight standard 30 litre General Oceanics (GO) Go-Flo bottles mounted on a Nylon II coated stainless steel frame (Sanderson et al., 1995). The Nylon coating is applied as a powder and heated to melting
temperature (310°C) thus sealing the steel completely from exposure to seawater, and withstands shipboard use well. In terms of “clean” sampling of water for trace metal analysis, the rosette system compared well with the conventional single Go-Flo mechanism as illustrated in Figure 1.3 by results from the U.S. JGOFS cruise in the Equatorial Pacific in the Spring & Fall 1992. Shipboard contamination can be minimized by wearing gloves for all handling procedures, placing Rosette systems on a polypropylene pad while on deck, drawing samples in a positive pressure filtered-air trace metal clean vans and covering the rosette between deployments (Hunter et al., 1996).

**Comparison of T.M. concentrations from samples collected using Go-Flo bottles vs T.M. Rosette**

![Bar chart](chart.png)

**Figure 1-3:** Plot of results from the U.S. JGOFS cruise in the Equatorial Pacific in Spring & Fall 1992. Comparison of trace metal (TM) concentrations obtained from water sampled using Go-Flo bottles vs. a trace metal clean rosette. NB: Rosette values plotted represent an average of 8 bottles. All metals are similar except for Zn where contamination was suspected (Hunter et al., 1996) possibly due to a zinc “sacrificial electrode” on the rosette.
For effective preservation, a strong oxidizer such as acidic bromine monochloride (BrCl) should be added. BrCl is a good choice owing to lower Hg blanks and lower degree of toxicity for waste disposal compared to alternatives such as chromic acid. It is important to note that the use of BrCl destroys speciation information, but it also degrades organic matter preventing wall losses & releasing strongly bound mercury. If speciation information is desired e.g. methyl mercury (MMHg), less aggressive preservation methods should be used. Samples should be spiked with 0.5% (v/v) hydrochloric acid (HCl) and stored in the dark at 1-4 °C. For seawater, sulfuric acid (H₂SO₄) is best to prevent the volatilization of HCl and which may co-distill in the distillation step normally part of MMHg sample analysis. This is likely to cause analytical interferences in the ethylation step of MMHg analysis. If well-preserved, THg samples can maintain their stability for over a year, for MMHg stability is limited to 6-12 months (Parker and Bloom, 2005).

1.4.2 Extraction of sample matrix, pre-concentration and analysis.

Unlike other matrices, water samples do not have to undergo additional processing before analysis. For both fresh water and sea-water, if preservation was carried out by other means, 0.5% (v/v) bromine monochloride (BrCl) (v/v) is added in an oxidation/digestion step that proceeds overnight. Afterwards the sample is pre-reduced with hydroxylamine hydrochloride (NH₂OH•HCl) to destroy the excess bromine, prior to ionic Hg(II) being reduced to Hg⁰ with stannous chloride (SnCl) and purged from solution and trapped on a gold-coated sample trap. Purging should progress until a volume of gas at least 15 times the volume of liquid has been purged, and at a volumetric flow rate of no more than 1 L/min (US EPA method 1631- www.epa.gov; Lamborg et al., 2012). The gold-coated sample trap acts as a pre-concentration
step, with a heating coil volatilizing the Hg\(^0\) onto an analytical trap that then feeds the analyte into the detector. This approach allows the achievement of lower detection limits (Stoichev et al., 2006). A Tekran\(^\text{TM}\) Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) is used for sample analysis.

### 1.5 Handling of atmospheric particulate samples

#### 1.5.1 Sample collection, preservation and storage

Concentrations of Hg (and other trace metals) vary temporally and spatially depending on the environment. While HgP concentrations in ambient air can be low (pg/m\(^3\)), values similar to Hg\(^0\) (ng/m\(^3\)) have been measured in urban and industrial areas (Lu & Schroeder, 1999). There are 2 main systems currently used to measure HgP: conventional “pump” based systems and denuder-based systems. For the latter, a brief description follows: a classic diffusion denuder is a cylindrical tube chemically coated to remove selected gas-phase species that diffuse to the walls when a stream of air is flowing through. Fine particles (< 2.5 \(\mu\)m) pass through unaffected in the laminar air stream because they have insufficient diffusion coefficients to be deposited to the walls. Silver (Ag)-coated denuders are used to capture Hg\(^0\), while a potassium chloride (KCl) coat is used for RGHg. The Tekran automatic mercury speciation unit uses these kind of denuders. In the automated Tekran Hg speciation unit, coarse particles (> 2.5 \(\mu\)m) are removed by aerodynamic impaction onto a glass impactor plate. There is a glass elutriator/acceleration jet with a short residence time and which is made of cross-linked Teflon to minimize loss of RGHg (Landis et al., 2002). It is therefore important for the blank contribution of the filter material used in sampling for the analyte(s) of interest to be low in contamination or easily cleaned when the expected particle loading will be low.
Conventional “pump” based systems consist of an air-pump, a flow measuring/regulating device and a particulate trap. Figure 1.3 shows a schematic diagram of an air filtration setup.

![Figure 1-4: Schematic diagram showing the setup of a conventional pump based filtration system. (1) Particulate trap which can be a filter pack or cascade impactor, (2) Flow regulation/measuring system & (3) Air Pump. (Diagram adapted from Lu & Schroeder, 1999)](image)

The particulate trap may be a single filter pack or cascade impactor. Single filter packs trap particles irrespective of size on a filter substrate. On the other hand cascade impactors have a variable number of stages, each with a filter substrate for particle collection. Particles are accelerated through progressively smaller orifices, hence segregating them according to size. Commonly used substrates are Glass/Quartz Fiber, Cellulose and Teflon. Cellulose and Teflon filters have low levels of trace metals and can be used for HgP collection. Teflon however, is expensive compared to cellulose filters. Glass/Quartz fiber filters are not “trace metal clean” and should only be used as backup filters to prevent backflow from the pump (Lu & Schroeder, 1999). Filter substrates should only be loaded into the filter packs or cascade impactor in a clean room or in a laminar flow hood if a clean room is unavailable.

1.5.2 Extraction of sample matrix, pre-concentration and analysis.

Upon retrieval from the field, filter substrates should be retrieved and placed in individual trace metal clean Petri-dishes. The samples should be stored in a freezer and then digested in
trace metal clean centrifuge tubes. Prior to use, the centrifuge tubes are soaked overnight in 10% (v/v) nitric acid. To prevent contamination and reduce the risk of artifacts acid cleaned plastic forceps should be used to handle each individual filter. 5 ml of a 2N nitric acid (HNO₃) acid solution is added to each tube, followed by overnight digestion in a drying oven at 70 °C. After cooling, 5 mL D.I. water is added to each tube, followed by 0.2 mL bromine monochloride (BrCl), and samples are allowed to react for a minimum of one hour. Before analysis, 0.1 mL hydroxylamine hydrochloride (NH₂OH.HCl) is added as a pre-reduction step. Sample Hg is reduced to Hg⁰ with stannous chloride (0.1 mL) and quantified with dual Au-amalgamation CVAFS.

1.6 Handling error

In performing chemical analyses it is not possible to completely eliminate error. However, it is possible to minimize errors and estimate their magnitude in measurements made. Chemical analyses are affected by at least two types of error: Random or indeterminate error and systematic or determinate error. In general, random error is affected by precision, which describes the reproducibility of measurements i.e. the closeness of results that have been obtained in exactly the same way. Systematic errors have an assignable cause and a definite value and are of the same magnitude for replicate measurements made in the same way. In mercury analyses systematic errors may originate from the instrument or method used or human error. This section details how each of these errors were estimated and handled for the analysis of precipitation collected in this study. In order to describe the precision of these measurements, the detection limit, range, mean, standard deviation (SD) and relative standard deviation (RSD) are presented in the table below. The RSD is expressed as a percentage and is calculated by
multiplying the standard deviation by 100 and dividing by the mean of the set of data i.e. 100* S.D/mean. This is sometimes referred to as the coefficient of variation which can also be expressed in parts per thousand (ppt) (Skoog, West & Holler, 1996).

Table 1.1: Descriptive statistics for analysis of precipitation for studies done in South Africa, Bermuda and Avery Point in Groton, CT

<table>
<thead>
<tr>
<th>Location</th>
<th>N</th>
<th>Detection Limit (DL)</th>
<th>Range</th>
<th>Arithmetic mean</th>
<th>Standard deviation</th>
<th>Relative Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Africa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cape Point</td>
<td>47</td>
<td>1.5</td>
<td>1.2-52.5</td>
<td>14.3</td>
<td>12.3</td>
<td>86.3</td>
</tr>
<tr>
<td>Pretoria</td>
<td>47</td>
<td>1.2</td>
<td>3.8-60.7</td>
<td>20.6</td>
<td>13.8</td>
<td>66.6</td>
</tr>
<tr>
<td>Bermuda</td>
<td>24</td>
<td>0.7</td>
<td>&lt;0.7 -16.2</td>
<td>5.8</td>
<td>4.9</td>
<td>85.5</td>
</tr>
<tr>
<td>Avery Point</td>
<td>28</td>
<td>0.6</td>
<td>2.3 - 20.8</td>
<td>8.1</td>
<td>5.7</td>
<td>70.4</td>
</tr>
</tbody>
</table>

Relative standard deviation and coefficient of variation are measures of central tendency. In this case the coefficient of variation is used to compare the relative amounts of variation in these data sets. It is also a good choice given that there is an appreciable difference in the means i.e. Bermuda vs. South Africa. From an analytical chemistry perspective, larger values may suggest errors or large variability in analytical methods. However, it is important to note that these studies were designed to monitor changes or fluctuations in the natural environment and how they affect mercury cycling in the environment.

The simplest way of indicating the probable uncertainty associated with an experimental measurement is to round the result so that it contains only significant figures. The significant figures in a number are all of the certain digits and the first uncertain digit (Skoog, West & Holler, 1996). The following example shows how the THg concentration in a rain sample from
Pretoria collected from 2-9 Feb 2009 was calculated. The sample volume analyzed for mercury was determined by weight:

**Volume of sample analyzed for THg: 11129.82 – 1107.84 = 21.98 grams**

The peak area is the area as reported by the integration software after the sample is analyzed. Here the peak area associated with the deionized water used to prepare the reagents is shown, followed by the peak area associated with the sample.

**Blank Peak area recorded: 0.005**

**Sample Peak area recorded: 0.228**

Subtracting the blank peak area and multiplying the result by the slope of the calibration curve corrects for the blank. A calibration curve should be generated for each day of analysis and the R² has to be at least 0.99 or greater before analysis can proceed. Please note that in this calculation all the figures generated are carried forward until the calculation is complete.

\[(0.228-0.005) \times 0.3716 = 0.0828668\]

**Mass of Hg in nanograms in sample: 0.0828668/21.98 = 0.0037701**

**Conversion to ng/L: 0.0037701\times1000 = 3.7701**

Rounding off is done after the calculation is complete. The final answer is rounded off to two decimal places since the weight of the sample to be analyzed was reported to 2 decimal places. THg concentration is reported as **3.77 ng/L**.

Further, it is important to note that when observations contain measurements are used to calculate other values, the errors are transmitted to a greater or lesser extent into the calculated values (Berthouex & Brown, 1994). In reporting the measurement, the standard deviation associated with the computed results has to be estimated. To illustrate this consider duplicate
analysis done for a rain sample collected in Pretoria from 3-9 April 2008. The formula below is used:

\[
THg \text{ in rain} = (\text{Peak area } \pm SD - \text{Blank } \pm SD) \times \text{Slope from calibration curve } \pm \text{error}
\]

Peak areas associated with both analysis:

\[
A - 21.675 \quad \text{and} \quad B - 14.769 \rightarrow \text{Standard deviation (SD)} = 4.88
\]

Average blank area: \(0.28 \pm 0.15\)

\[
\text{Slope of the calibration curve} = 0.0321 \pm 0.002
\]

To calculate the uncertainty associated with sample concentration associated with peak area A:

\[
THg \text{ in rain} = (21.675 \pm 4.88 - 0.28 \pm 0.151) \times 0.0321 \pm 0.002
\]

\[THg \text{ in rain sample A: } (21.675-0.28) \times 0.0321 = 0.687 \text{ ng}\]

Because the calculation involves subtraction and multiplication, this S.D. will be computed in 2 steps. To calculate error propagation for operations involving addition and subtraction the formula below is used:

\[
\text{S.D.} = \sqrt{s_a^2 + s_b^2 + s_c^2 + ...}
\]

\[
\text{S.D.} = \sqrt{4.88^2 + 0.151^2} = 4.88
\]

For calculations involving multiplication or division

\[
\text{S.D.} = \sqrt{(s_a/a)^2 + (s_b/b)^2 + ...}
\]

where \(a\) and \(b\) are experimental variables whose standard deviations are \(s_a\) and \(s_b\) respectively.

\[
\text{S.D.} = \sqrt{(4.88/21.395)^2 + (0.002/0.0321)^2}
\]

\[
\text{S.D.} = \sqrt{0.0559}
\]

Standard Deviation = 0.236 \(\approx\) 0.24
For sample A THg in rain: (0.686 ng/12.29 ml) ± 0.236 = 0.05581 ± 0.24 ng/mL
Converting to ng/L: 0.05581 ng/mL * 1000 mL/1 L = 55.81 ± 0.24 ng/L

1.7 INTER-COMPARISON OF METHODS

The methods described above are widely used but slight variations in procedure exist between institutions and laboratories. This has necessitated the carrying out of laboratory inter-comparison of protocols in order to identify the optimal procedures for both at-sea and on shore analysis of Hg in natural waters and aerosol samples collected on filter substrates. For Hg, the most recent of these activities was done as part of the GEOTRACES program, and the resulting published papers where this writer is a co-author are as follows: Lamborg et al. (2012) and Morton et al. (2013). GEOTRACES (www.geotraces.org) is a multi-national, multi-investigator exercise that seeks to dramatically increase the available data concerning trace elements and isotopes in the ocean (Lamborg et al., 2012). Expeditions are carried out in various parts of the world as part of this endeavor.

The first inter-comparison activity was carried out on a cruise sponsored by the National Science Foundation (NSF). It occupied the Bermuda Atlantic Time Series (BATS)(31°40’N 64°10’W) from 8-27 Jun 2008. The focus of this cruise was to compare methods for THg analysis, and the inter-comparability of sampling and filtering methods. Filtered seawater was analyzed for THg and compared to results from analysis by colleagues from the Woods Hole Oceanographic Institute (WHOI). The seawater analyzed was collected from one of two systems, the GEOTRACES Clean Rosette (similar to the rosette described in the earlier section) and the CLIVAR clean rosette. Water for Hg vertical profiles was collected at BATS. Generally there was good agreement of results between both laboratories i.e. WHOI and Uconn (See Figure 1: Lamborg et al., 2012 in appendix) irrespective of rosette and filters used for filtration, with the
exception of the sample at 800 m. Therefore, this means that various sampling equipment currently available could be used for THg sampling provided proper cleaning procedures are followed.

For aerosols, the purpose of the exercise was to test and intercalibrate high volume and size-fractionated aerosol sampling equipment in a field experiment. All the aerosols samples were collected at the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS), Miami, FL. Particulate samples were collected on Whatman quartz microfiber filters, which had been heated in an oven to drive off volatile species to reduce the risk of contamination. Whatman filters are manufactured from 100% pure borosilicate glass of special purity to enable detailed analysis of trace pollutants with minimum interference and background (www.whatman.com). There were two trials carried out with samples being sent to the University of Connecticut, Avery Point and another set to researchers at WHOI. Both labs used similar extraction and digestion procedures. The WHOI lab extracted THg from the filters by adding 10% (v/v) nitric acid (HNO₃) and BrCl directly to the filter. This lab reported higher Hg concentrations. On the other hand, at the University of Connecticut THg extraction was extracted from the filters by adding 25% HNO₃ followed by overnight oven digestion and BrCl was added to the extract a minimum of one hour to analysis. This lab reported concentrations lower than those of WHOI. These differences between the results obtained by the two labs were thought to be due to differences in the extraction procedures. However, results from a follow up trial where each lab used their own and the other’s procedure produced comparable results. The final conclusion was that the analytical protocols used are both effective and reproducible. The differences observed in the first trial were attributed to random factors. For more details on this work, please see Morton et al. (2013).
1.8 INSTRUMENTATION

Given the low concentrations of mercury in the environment, the analytical method chosen has to be sensitive, reliable and cost-effective. In the early days of trace metal analysis atomic absorption (AA) spectrometers equipped with source furnaces were used for low-level determination with high accuracy and sensitivity (Patterson & Settle, 1976). This kind of detector is still used today along with atomic fluorescence spectrometers (AFS) and inductively coupled mass spectrometers (ICP-MS) (Stoichev et al., 2006). For the determination of mercury, the use of a flame to atomize the sample is unnecessary because of elemental mercury’s volatility. As mentioned earlier for natural water samples, stannous chloride is used to reduce ionic Hg (II) in solution to Hg⁰, which is swept onto the detector by an inert gas such as argon. This is referred to as cold vapor (CV) generation. Currently, CVAFS and CVAAS are commonly used methods for THg determination.

Still, the measurement of THg alone is not sufficient to understand its fate in the environment. For comprehensive understanding of the fate and transport of Hg in the environment, speciation is required. Speciation allows the measurement of the other chemical forms of the element such as methyl-mercury and di-methylmercury. Speciation analysis involved the coupling of a separation technique such as chromatography and an element specific detector like some of the aforementioned ones. Commonly used separation techniques are high performance liquid chromatography (HPLC) and gas chromatography (GC) (Stoichev et al., 2006). It is important to note that although ICP-MS incurs high instrumental and operational costs, it offers the advantage of analyzing for many other trace metals with relative ease and in a short period of time. The benefits of this added capability for environmental studies is illustrated in Chapter 2.
1.9 OBJECTIVES AND HYPOTHESIS

It has been established that atmospheric Hg is the main source of Hg to terrestrial and aquatic ecosystems. Although numerous measurements have been carried out around the world, especially in the Northern hemisphere, this is not the case for the Southern hemisphere, in both remote locations as well as the open ocean. While emissions estimates and modeling efforts have attempted to estimate mercury inputs in these areas, these efforts are hampered by limited data sets. This work was done in two main countries: South Africa and Bermuda. In South Africa, two sites were chosen; Cape Point, which is part of a nature reserve and Pretoria, an urban centre. Among other things, this research sought to bridge the gap by providing credible data while fulfilling the following objectives with regards to Hg contamination in these locations:

a) To quantify mercury concentrations in the atmosphere i.e. air, precipitation and particles,
b) To estimate deposition fluxes, the resulting inputs to the environment, and
c) To identify possible sources of mercury contamination at these sites.

In the past, measurements of Hg in the atmosphere in South African have been confined to Hg\(^0\) only at the Cape Point Global Atmospheric Watch (G.A.W.) site. Additionally, depletion events (DE) similar to those observed in the Arctic have been observed which is unusual for a location in this part of the world (Brunke et al., 2010). Additionally for Bermuda, studies have shown elevated concentrations of Hg in fish (Dewailly et al., 2008) even though the island is isolated with minimal industrial activity. Past measurements of Hg\(^0\) at these coastal sites (Cape Point & Bermuda) mirror the expected low concentrations often found in unpolluted (Brunke et al., 2010) or remote ocean air (Mason & Sheu, 2001). Still, the aforementioned studies show there is considerable Hg deposition to these sites. I hypothesize that the scavenging via wet deposition...
of RGHg that is locally produced in the MBL provides significant Hg inputs to remote coastal or marine locations.
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2. MERCURY AND METALS IN SOUTH AFRICAN PRECIPITATION

2.1 INTRODUCTION

Even though mercury (Hg) is a global pollutant there are few studies of its concentration in the Southern Hemisphere, either in the atmosphere (Slemr et al., 2011) or in atmospheric deposition, or from emissions in developing countries, especially in Africa. The same is true for other pollutant metals. As South Africa is the largest producer of primary metals in the world, ranking first in the production of gold (Au), lead (Pb) and copper (Cu) (Masekoameng et al., 2010), there is substantial potential for its emissions from human activity to contribute to local and regional contamination. Overall, 40% of the world’s gold reserves are in South Africa and the country is responsible for 12% of global production of this precious metal. The country also relies on coal combustion for the production of electricity, and this could contribute substantially to emissions of Hg. In addition, the country is the 3rd largest coal producer in the world. Coal accounts for 64% of the country’s energy supply (Dabrowski et al., 2008). Mercury, which is emitted as both elemental mercury (Hg0) and ionic mercury (HgII) (Sprovieri et al., 2010), and other metal emissions from these activities could be substantial. There are two fractions of atmospheric HgII operationally defined according to their physicochemical properties; the gaseous ionic HgII fraction termed reactive gaseous mercury (RGHg) and particulate mercury (HgP) (Landis et al., 2002). The speciation of RGHg mercury is thought to consist of compounds resulting from reactions with halides and other oxidants (Holmes et al., 2009; Mason and Sheu, 2002).

There has been growing concern over the increasing emission levels of mercury in the world. For example, a global anthropogenic Hg emissions inventory for the year 2000 (Pacyna et al., 2006)
ranked China as the number one Hg emitter in the world and South Africa as second. The elevated Hg emission for South Africa was attributed to gold mining and stationary coal combustion. However, a recent re-evaluation (Dabrowski et al., 2008; Leaner et al., 2009) suggests that previous estimates were high by more than an order of magnitude, and that emissions from coal fired power plants in South Africa are 9.8 tonnes per annum, and approximately 50% of the total emissions. More recent estimates (Pirrone et al., 2010; Streets et al., 2011) are also lower than the initial Pacyna et al. (2006) value, but suggest emissions from Africa are increasing. While coal contains natural trace amounts of Hg that is released during combustion (Dabrowski et al., 2008), gold mining operations in South Africa mainly use the MacArthur Forrest process that uses cyanide instead of mercury amalgamation for extraction (Naicker et al., 2003). However, there are traces of Hg in the ore that could be released during processing but the overall emission is small (Leaner et al., 2009). While many developed countries have established monitoring programs to track trends in emissions and deposition, little has been done in developing countries especially in Africa. Measuring deposition is one way of evaluating the impact of Hg emissions and while both wet and dry deposition of mercury is important, it has been shown that quantifying the amount of mercury in precipitation is an effective way of estimating the relative fluxes, and comparing across global locations. This is especially important for areas where there is a paucity of data, such as in South Africa. In addition, properly chosen monitoring stations can provide more accurate estimates of wet deposition at regional scales that can help constrain mercury fate and transport models (Zhang et al., 2009).
Recent modeling of emissions and deposition suggest that net Hg deposition is not substantially higher around South Africa than over other continents at comparable latitudes, or in much of the Northern Hemisphere remote from major anthropogenic inputs (Corbitt et al., 2012). The data presented here provides the first glimpse of the deposition over the interior (Pretoria) and a coastal region (Cape Point) of South Africa for Hg. Measurements of total gaseous Hg at Cape Point suggest that concentrations in the atmosphere at Cape Point are somewhat lower than the Northern Hemisphere, varying between 0.8 and 1.0 ng m$^{-3}$ (Slemr et al., 2011). There is also an indication of decreasing concentrations since the early 1990’s. This suggests, contrary to the models (e.g. Soerensen et al., 2010), that Hg deposition may be lower at Cape Point that at locations in the Northern Hemisphere. We investigate these ideas below and through comparison with concentrations and relative ratios of other metals in precipitation, we also discuss the potential sources of Hg to the sampling sites.

MATERIALS AND METHODS

2.2 Study area, sampling, and analysis protocol

Rain samples were collected from two sites: Cape Point and Pretoria (Fig. 2.1). The Cape Point site is located at the southern tip of the Cape Peninsula within the Cape of Good Hope nature reserve atop a peak 230 m above sea level and about 60 km south of Cape Town (34° 21' S, 18° 29' E). It also functions as a Global Atmospheric Watch (GAW) site and is operated by the World Meteorological Organization (WMO) (Slemr et al., 2008). The site receives clean air masses most of the time and was chosen because it could provide a Southern Hemisphere background signal. The site in Pretoria (25° 44' S, 28° 16' E) was located on a building rooftop at the Council for Scientific and Industrial Research (CSIR) campus. Pretoria is an urban area
located 50 km north of Johannesburg, the commercial and industrial hub of the country. Much of the gold mining and other precious metal mining occurs in the regional vicinity of Johannesburg. Pretoria is also in relative close proximity to industrial activity in the northern reaches of the country where many of the coal-fired power plants are located in proximity to the major coal mining areas. Additionally, steel and other metal refining is also concentrated northwest of Pretoria (Masekoameng et al., 2010).

![Maps showing sampling sites in South Africa shown by the blue markers. In the left Panel: Pretoria and Cape Point, in the right panel: the site at Cape Point shown in relation to Cape Town. (Generated by Google Maps)](image)

Precipitation samples were collected from June 2007 to December 2009. The sampling setup comprised a homemade glass funnel connected to a PTFE (Teflon) bottle. Sampling was done weekly and the equipment was transferred between the two sites because the rain falls in alternate seasons i.e. in the Cape region, the rain falls mostly in the winter (Mediterranean climate), whereas the winters in Pretoria are dry. Conversely, in the summer, rain falls in Pretoria, whereas the Cape region is dry. Each sample was preserved after collection by spiking
with 0.5% (v/v) trace metal grade hydrochloric acid (HCl) prior to refrigeration and shipping to
the University of Connecticut, Avery Point campus for analysis. On arrival at Avery Point, the
bottles were weighed so that the rain weight (volume) could be determined by subtracting the
bottle weight.
To prepare samples for analysis, 0.5% (v/v) bromine monochloride (BrCl) was added in an
oxidation/digestion step that proceeded overnight. Afterwards the sample was pre-reduced with
hydroxylamine hydrochloride (NH₂OH•HCl) to destroy the excess bromine, prior to ionic Hg(II)
being reduced to Hg⁰ with stannous chloride (SnCl) (US EPA method 1631- www.epa.gov;
Lamborg et al., 2012) and purged from solution and trapped on a gold-coated sample trap. A
Tekran™ Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) was used for sample
analysis. The detection limit (D.L.) for rain was calculated as three times the standard deviation
of the blank values. The D.L. for Cape Point was 1.5 ng/L, whereas that of Pretoria samples was
1.2 ng/L. The overall detection limit for all samples was 1.4 ng/L. The average relative percent
difference (RPD) for duplicate runs of samples was 2.8% for Cape Point, and 7.7% for Pretoria.
In addition to THg analysis, trace metal analysis was done whenever sufficient sample volumes
were available. Calibration standard solutions were prepared from a multi element metals
solution purchased from SPEX Certiprep. Metal analysis of acidified samples was done on a
Perkin Elmer Elan DRC II Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) coupled to
an autosampler. The rain samples were introduced to the plasma by means of a peristaltic pump,
via a nebulizer and spray chamber. The instrument was optimized daily according to
manufacturer’s instructions to ensure proper functioning at optimal conditions. Optimization
involved plasma alignment, mass calibration and auto-tuning using a multi-element tuning
solution (Ba, Be, Ce, Co, In, Pb, Mg, Tl, Th, all at 1 ug/ L in 5% (v/v) nitric acid). The
acceptable performance criteria of the ICP-MS are: CeO/Ce < 3%, Ba²⁺/Ba <3%; sensitivity of the 1 µg/L Indium solution > 40,000 counts per second (cps); and the instrument background level of m/z 220 < 2 cps. The detection limits for each metal analyzed are as follows: (Al: 0.70; Co: 0.31; Cu: 0.69; Mn: 1.83; Zn: 2.58; Ni: 0.31; Fe: 4.55; Cd: 0.02; Pb: 0.10; all values in ng/L). The operational criteria used for the ICP-MS analysis were as described in the operational manual, with some minor modifications depending on the method being used for analysis as shown in Table 2.1.

<table>
<thead>
<tr>
<th>Instrument settings</th>
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<tbody>
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<td>Curve type</td>
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</table>

*Table 2.1: Operational settings for the Elan DRC-II ICP-MS*

RESULTS

2.3 Total Hg (THg) in precipitation and deposition fluxes

Figure 2.2(a & b) and Table 2.2 summarize the concentrations of Hg in rain and fluxes at the two sites in South Africa and show that the average concentration in Pretoria is approximately 150% of that at Cape Point while the difference is larger for the flux, illustrating the importance of rainfall amount in determining Hg deposition flux. This is further illustrated in the plots comparing the results at both locations in Figures 2.2a (concentrations) and 2.2b (fluxes).
Table 2.2: Volume weighted mean concentrations, fluxes and standard deviation for Cape Point and Pretoria. Values on the upper row are reported in nanograms per litre (ng/L), while those in brackets represent picomolar (pM) concentrations. Totals represent values tallied for each year (2007-2009) at each site.

<table>
<thead>
<tr>
<th></th>
<th>2007 (n=7)</th>
<th>2008 (n = 22)</th>
<th>2009 (n= 18)</th>
<th>Total (n=47)</th>
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<tbody>
<tr>
<td>Cape Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V.W.M. Conc.(ng/L) (pM)</td>
<td>6.0 ± 3.0 [30]</td>
<td>20.1 ± 13.0 [100]</td>
<td>6.80 ± 5.1 [34]</td>
<td>10.6 ± 12.3 [53]</td>
</tr>
<tr>
<td>Flux (ng m(^{-2}) wk(^{-1}))</td>
<td>186.9 ± 169.2</td>
<td>242.3 ± 179.1</td>
<td>65.4 ± 41.4</td>
<td>166.3 ± 160.6</td>
</tr>
<tr>
<td>Pretoria</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V.W.M. Conc. (ng/L) (pM)</td>
<td>15.5 ± 12.0 [77]</td>
<td>16.9 ± 15.7 [84]</td>
<td>15.0 ± 11.0 [75]</td>
<td>15.8± 13.8 [79]</td>
</tr>
<tr>
<td>Flux (ng m(^{-2}) wk(^{-1}))</td>
<td>281.5 ± 286.7</td>
<td>371.6 ± 295.1</td>
<td>476.5 ± 326.5</td>
<td>385.6 ± 307.3</td>
</tr>
</tbody>
</table>
Figure 2-2: Comparison of a) the volume weighted concentrations (V.W.M) concentrations of Hg in rain at Cape Point and Pretoria from 2007-2009 and b) the weekly fluxes in ng m\(^{-2}\) wk\(^{-1}\). The error bars are based on standard error of the mean.
It should be noted that these concentrations and fluxes represent total or ‘bulk’ deposition since the rain funnel was open to the atmosphere at all times. This means that particulates and RGHg from the atmosphere could have dry deposited on the funnel surface in between rainfall, contributing dry deposition that would then be washed into the collection bottle by rain. According to estimates by Lamborg et al. (1999), the particulate dry depositional flux is 0.4-1.0% of the overall flux from the atmosphere so it is unlikely that any particulate deposition would substantially alter the flux except in locations adjacent to urban environments where particulate material is associated with coarser material that is rapidly deposited (Mason et al., 2002). However, some estimates for coastal environments predict that dry deposition of RGHg could be equivalent to that of wet deposition (e.g. Holmes et al., 2009; Laurier and Mason, 2007), and if so this could substantially alter the flux. It is not clear what fraction of any RGHg deposited could be reduced and reemitted but this is likely a small fraction. Therefore, actual wet deposition may be lower than the total deposition fluxes calculated here. However, the Soerensen et al. (2010) GEOS-Chem model predicts the wet deposition of Hg at Cape Point as 24 nmol m\(^{-2}\) yr\(^{-1}\), which is equivalent to 0.92 nmol m\(^{-2}\) wk\(^{-1}\) (185 ng m\(^{-2}\) wk\(^{-1}\)), assuming rainfall for a total of 6 months on average. This is similar to the estimate in Table 2.2 suggesting that dry deposition does not contribute substantially to the flux measured using the open collector. Also, the model estimates for dry particulate and RGHg deposition are about 25% of the wet flux (Soerensen, pers. comm.) again suggesting that dry deposition would not contribute substantially to the fluxes obtained with the open collector. Guentzel et al. (1995) found similar results in Florida where open collectors were co-deployed with automatic collectors. They found no statistical difference in the bulk versus wet collector Hg fluxes and others have found similar results (Iverfeldt and Munthe, 1993). Given these previous results and the comparison between the
measurements and models, we conclude that the measurements using the open collectors primarily reflect the wet deposition Hg flux at this location.

While there have been other measurements of Hg made in the aquatic environment and in air in South Africa (Walters et al., 2011; Slemr et al., 2008; Papu-Zamxaka et al., 2009; Kading et al., 2009), these are the first measurements of Hg in rain in South Africa. The concentrations at Pretoria are higher than those at Cape Point as expected given Pretoria’s close proximity to many Hg sources, although there is substantial variability at each location. Figure 2.3 shows the weekly volume-weighted concentrations and deposition fluxes at Pretoria, while Figure 2.4 shows comparable data for Cape Point. There are no obvious trends over time in terms of changes in concentration and this reflects findings by other investigators.
Figure 2-3: (A) Weekly volume-weighted concentrations of total mercury (THg) over 3 years 2007-2009 and (B) Weekly total deposition flux for Pretoria.
**Figure 2-4:** (A) Weekly volume-weighted concentrations of total mercury (THg) in rain (B) Weekly total deposition for Cape Point
If “wash-out” of particulate or RGHg is the major contributor to the Hg in rain at these locations, then there could be a “scavenging effect” where low rainfall events have higher concentrations due to the removal of the particulate and RGHg in the initial rainfall. This has been shown in other studies (Guo et al., 2008; Hall et al., 2005). It has also been shown that during rainfall RGHg concentrations are very low (e.g. Laurier and Mason, 2007) suggesting that this fraction is readily scavenged. Under such scenarios, during large rain events, the THg wet deposition flux increases although continuous rain dilutes the THg concentration (Seo et al., 2012). The relationship between rainfall amount and concentration for both sites are shown in Fig. 2.5. It should be reiterated that as the rain collections are weekly, there is the potential for more than one rain event per week, and this may therefore obscure any trends that exist. However, even so, higher amounts of rainfall are associated with lower THg concentrations overall.

**Figure 2-5:** Rainfall depth versus THg concentration for Pretoria and Cape Point respectively
If there are continual sources of Hg to the air mass during a rain event, or if the scavenging does not completely occur, then there should be a relationship between the Hg flux and the amount of rainfall. Figure 2.6 shows the relationship between rainfall depth and deposition flux at both locations. Linear regression analysis of this data yielded an R-value of 0.597 (p < 0.05) for Pretoria and 0.428 (p < 0.05) for Cape Point, demonstrating significant positive relationships between rainfall amounts and total deposition fluxes at both locations. However, there are clearly other factors that influence the overall flux of Hg, such as the impact of anthropogenic and other sources.

**Figure 2-6**: Rainfall depth vs. deposition flux at Cape Point and Pretoria respectively.
2.4 Trace metals in precipitation

Trace metal concentrations in the atmosphere can be good indicators of pollution from anthropogenic activities as they are often associated primarily with a particular source category/activity (e.g. Se emissions are primarily from coal). However, although man made activities, such as fossil fuel combustion, release metals such as Cu, Zn and Cd into the atmosphere, other metals, such as Al, Fe and Mn, do not have a dominant anthropogenic source, and most of the particulate in the atmosphere comes from natural sources (soil and bedrock particulate) where they are naturally abundant (Vuai & Tokuyama, 2011). By looking for relationships or correlations between these metals and with Hg, and by examining ratios to so-called “crustal” elements (Al, Fe), we can identify the importance of contamination sources in contributing to the metals collected in rainfall over time. Table 2.3 summarizes the concentration data for the metals while the individual data are contained in Tables S1 and S2 for Pretoria and Cape Point respectively. To put the values in context, the relative concentrations of the metals to Al are compiled in Table 2.4, and these values compared with those of some potential natural sources (crustal particulate and sea salt) as well as data collected by others for atmospheric particulates in locations in South Africa (Sekonya, 2009). These locations are Khayelitsha, a rapidly expanding urban environment with both formal houses and so-called “informal” dwellings built from a variety of materials on the outskirts of Cape Town, about 25 miles northwest of Cape Point, and Ferrobank, a location within the industrial heart of the northwest region of South Africa, about 65 miles west of Pretoria, where iron and other industrial activities using coal are concentrated.
Table 2.3: Mean trace metal concentrations at Cape Point and Pretoria (µg/L) as volume weighted mean (VWM) values and as an average and standard deviation, and the relative differences in the averages and their significance.

<table>
<thead>
<tr>
<th>Metal</th>
<th>V.W.M Pretoria</th>
<th>Avg. Pretoria</th>
<th>StDev Pretoria</th>
<th>V.W.M Cape Point</th>
<th>Avg. Cape Point</th>
<th>StDev Cape Point</th>
<th>Rel % Diff.*</th>
<th>Signif.** 95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>58.3</td>
<td>78.0</td>
<td>66.0</td>
<td>9.0</td>
<td>9.9</td>
<td>7.6</td>
<td>550</td>
<td>Yes</td>
</tr>
<tr>
<td>Fe</td>
<td>45.0</td>
<td>62.3</td>
<td>63.3</td>
<td>44.9</td>
<td>31.8</td>
<td>77.5</td>
<td>&lt;1</td>
<td>No</td>
</tr>
<tr>
<td>Mn</td>
<td>9.9</td>
<td>13.7</td>
<td>14.5</td>
<td>2.0</td>
<td>1.8</td>
<td>2.7</td>
<td>410</td>
<td>No</td>
</tr>
<tr>
<td>Co</td>
<td>0.22</td>
<td>0.30</td>
<td>0.27</td>
<td>0.19</td>
<td>0.17</td>
<td>0.36</td>
<td>16</td>
<td>No</td>
</tr>
<tr>
<td>Ni</td>
<td>0.58</td>
<td>0.82</td>
<td>0.94</td>
<td>8.9</td>
<td>8.3</td>
<td>19.2</td>
<td>-94</td>
<td>No</td>
</tr>
<tr>
<td>Cu</td>
<td>1.9</td>
<td>2.5</td>
<td>2.4</td>
<td>0.81</td>
<td>0.81</td>
<td>0.55</td>
<td>130</td>
<td>Yes</td>
</tr>
<tr>
<td>Zn</td>
<td>10.3</td>
<td>11.1</td>
<td>13.0</td>
<td>56.6</td>
<td>68.5</td>
<td>86.3</td>
<td>-80</td>
<td>No</td>
</tr>
<tr>
<td>Cd</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>50</td>
<td>No</td>
</tr>
<tr>
<td>Pb</td>
<td>1.2</td>
<td>1.5</td>
<td>1.52</td>
<td>1.0</td>
<td>1.2</td>
<td>2.2</td>
<td>16</td>
<td>No</td>
</tr>
<tr>
<td>Hg</td>
<td>0.016</td>
<td>0.019</td>
<td>0.009</td>
<td>0.011</td>
<td>0.011</td>
<td>0.014</td>
<td>50</td>
<td>No</td>
</tr>
</tbody>
</table>

Notes: * Rel. % Diff. = 100(C_Pretoria – C_CapePoint)/C_CapePoint

** Signif. = Tukey’s test of significant difference (two sided test with a 95% confidence interval)

The relative difference in the concentrations of the metals provides some initial indication of potential sources and the validity of the results. For most of the metals the concentrations are within a factor of 2 between sites (rel. diff. ± 100%) suggesting similar sources, either crustal or anthropogenic. However, statistically significant differences in concentration between the two locations were only found for Al and Cu. For some metals such as Zn and Ni, the mean concentrations are substantially different but the standard deviations are also large. The lack of difference is further confirmed by the comparisons in Table 2.4, which shows the ratio of each metal (E) in each sample relative to that of Al (E/Al). These indicate how well the relative rain concentrations correspond to those of regional aerosols, which should be the primary source of the metal in deposition. For Al, the concentration is much higher in Pretoria and this likely
reflects a higher dust component in this more arid location. Similarly, Mn is also elevated in Pretoria but this is not the case for Fe. Contrary to the other metals, the concentrations of Zn and Ni are higher at Cape Point. An examination of the individual data (Table S2) shows that there are high concentrations of both elements on occasion. It is possible that these elevated concentrations represent local contamination. This could be the GAW sampling equipment as the air-sampling tower is galvanized or from nearby buildings and human activity, or the local area, which is a tourist attraction although access to the sampling site is limited (e.g. diesel-derived Ni). If these higher values are not considered (> 20 µg/L Zn; > 5 µg/L Ni), then there is little difference between the two locations in the concentration of these metals.

A comparison of the metals ratios to Al (Table 2.4) in precipitation in Pretoria to the aerosols from Ferrobank shows comparable values in most cases, except for Fe. This is not the case for Cape Point as the ratios are much higher for Khayelitsha aerosols, which are also much higher than those at Ferrobank. The Khayelitsha aerosols were low in Al. This indicates that the local contamination sources (wood and coal heating/cooking, vehicle emissions) at this location overwhelm the regional aerosol signal. The ratios for most metals at Cape Point are more similar to those at Ferrobank, likely indicating the importance of regional aerosols in contributing to precipitation even at Cape Point, even though it is considered to be remote from pollution sources.
Table 2.4: Average values (plus standard deviation) for all the data for each location calculated from the ratios of each element measured to that of aluminum in each weekly sample. Also shown is the range in values for these metal in crustal rock and in sea salt, compiled from the literature (Chester, 2003 and references therein). Also shown are the ratios found for atmospheric aerosols collected at Khayelitsha and at Ferrobank, two locations proximate to the rain sampling sites, taken from Sekonya (2009).

<table>
<thead>
<tr>
<th>Element (E)</th>
<th>(Av E/Al) Deposition</th>
<th>St Dev (E/Al) Deposition</th>
<th>(E/Al) Sea Salt</th>
<th>(E/Al) Khayelitsha</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cape Pt.</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.019</td>
<td>0.033</td>
<td>0.5 – 4</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>0.15</td>
<td>0.22</td>
<td>0.01 - 0.1</td>
<td>121</td>
</tr>
<tr>
<td>Mn</td>
<td>0.20</td>
<td>0.25</td>
<td>0.1 - 0.4</td>
<td>34.1</td>
</tr>
<tr>
<td>Zn</td>
<td>24.9</td>
<td>60.3</td>
<td>0.1 – 5</td>
<td>91.8</td>
</tr>
<tr>
<td>Ni</td>
<td>0.87</td>
<td>1.70</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>3.80</td>
<td>9.79</td>
<td>1 - 3.4</td>
<td>628</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0041</td>
<td>0.0067</td>
<td>6 - 8 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.21</td>
<td>0.39</td>
<td>0.01-1</td>
<td>36.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element (E)</th>
<th>(Av E/Al) Precipitation</th>
<th>St Dev (E/Al) Precipitation</th>
<th>(E/Al) Crustal Abundance</th>
<th>(E/Al) Ferrobank</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pretoria</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>3.8 x 10⁻³</td>
<td>1.3 x 10⁻³</td>
<td>2.46 x 10⁻⁴</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>0.037</td>
<td>0.022</td>
<td>6.77 x 10⁻⁴</td>
<td>0.033</td>
</tr>
<tr>
<td>Mn</td>
<td>0.16</td>
<td>0.055</td>
<td>0.012</td>
<td>0.28</td>
</tr>
<tr>
<td>Zn</td>
<td>0.18</td>
<td>0.21</td>
<td>8.61 x 10⁻⁴</td>
<td>0.22</td>
</tr>
<tr>
<td>Ni</td>
<td>0.010</td>
<td>3.5 x 10⁻⁴</td>
<td>9.84 x 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.76</td>
<td>0.28</td>
<td>0.62</td>
<td>2.9</td>
</tr>
<tr>
<td>Cd</td>
<td>8.2 x 10⁻⁴</td>
<td>1.1 x 10⁻⁴</td>
<td>1.35 x 10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.022</td>
<td>9.7 x 10⁻⁵</td>
<td>1.6 x 10⁻⁴</td>
<td>0.11</td>
</tr>
</tbody>
</table>

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DISCUSSION

2.5 Comparison of precipitation results with other locations around the world

To put the South African data in context, comparison is made to other locations around the world in Table 2.5. Measurements have been made in some other sites in the Southern Hemisphere, most notably in Australia (Dutt et al., 2009) and Brazil (Lacerda et al., 2002). Lacerda et al. (2002) attribute the low values at the Brazil sites to the lack of point sources and the strong influence of marine air masses along the Rio de Janeiro State coastline. The site at Mace Head, another WMO site located to sample primarily marine air, is most similar to Cape Point but in the Northern Hemisphere, as it is located on the west coast of Ireland, 88 km away from Galway city. It has a clean sector zone from 180 to 300° with open access to the North Atlantic Ocean, which represents marine background conditions for atmospheric mercury and other background trace gases. The range of concentration at this site is similar to that at Cape Point (1.2-52.5 ng/L) even though only a few samples were analyzed as part of a larger international field inter-comparison effort (Ebingerhaus et al., 1999). When compared to data from the Mercury Deposition Network (MDN), concentrations are comparable to those on the U.S. east coast for Cape Point and those in Florida for Pretoria (Mercury Deposition Network (MDN)-NADP- http://nadp.sws.uiuc.edu/mdn/). The same applies to deposition fluxes. The MDN samples are collected on a weekly basis, hence making a direct comparison easier. Further, rainfall amounts are known to influence deposition fluxes. For instance, in the Australian study (Dutt et al., 2009), the average annual rainfall depths were 94 mm for Sydney (urban) and 60 mm at Hunter Valley (near a coal fired power station). At Pretoria, the average annual rainfall, calculated from weather data (www.tutiempo.net), is typically between 40 and 100 cm. Rainfall at Cape Point was 29 cm in 2009. Cape Town rainfall varies from 40 to 70 cm/yr but Cape Point
receives less rain than Cape Town and the rest of the peninsula. Rainfall differences are one reason why sites with similar THg concentrations in rain could have different deposition fluxes. The flux measured at Cape Point is similar to that of remote sites in eastern North America (Table 2.5) and comparable to those of other coastal locations. Concentrations and fluxes are higher in Florida, USA than the other east coast sites and Cape Point. The data from the Brazilian study appear to be anomalously low compared to the other data in Table 2.5. The small differences in the precipitation concentrations for the coastal WMO sites (Cape Point and Mace Head) contrasts the differences in atmospheric total gaseous Hg (1.4-1.6 ng m⁻³ at Mace Head and 0.8-1.0 ng m⁻³ at Cape Point for 2007-2009) (Slemr et al., 2011). This suggests that atmospheric chemistry is more important than absolute concentration in driving the concentrations of Hg in precipitation at these remote coastal sites. However, an alternative explanation is that the Cape Point site is more impacted by local particulate sources, such as the city of Cape Town. The flux for Pretoria is elevated compared to Cape Point but is within the range of the other sites in urban and/or impacted locations (Toronto and the Australian and Asian sites). It is however lower than the two impacted locations in China listed in Table 2.5.

The differences in Hg flux between the remote Cape Point site and the more impacted Pretoria site, a factor of 2-3, and is of similar magnitude to that found in a regional study in Maryland, USA where concentrations and fluxes in Baltimore were twice that found at Solomons, MD, a coastal site about 60 miles south of Baltimore and a similar distance from Washington, DC (Mason et al., 2002). For the other metals, that study found that Pb was nearly three times higher at the urban site while the other metals had relatively similar concentrations at both sites. This contrasts the South African data (Table 2.3) where concentrations of Ni and Zn were 5-10 times
higher at Cape Point than in Pretoria, while Cu and some of the crustal elements were higher in Pretoria.

The crustal trace metals (Al and Fe) and Zn had the highest concentrations for both Pretoria and Cape Point suggesting a mixed influence of crust soil and anthropogenic emissions (Song and Gao, 2009) at both locations, although local sources are the likely explanation for the Zn data at Cape Point. The South African results are similar to findings in areas in or close to urban environments such as Newark, NJ (Song & Gao, 2009) and Okinawa Island, Japan (Vuai & Tokuyama, 2011). The sampling site in Pretoria is located in an area with more anthropogenic activity than Cape Point. In addition, Pretoria is not subject to marine air masses that can be less polluted, compared to continental air masses. The concentrations of the rest of the metals are not markedly different from measurements in other parts of the world.
Table 2.5: A comparison of the concentrations of mercury (volume weighted mean (VWM)) for Pretoria and Cape Point with other studies. For deposition flux, data from the literature are converted to similar units (ng/m²/wk). In some instances the mean (average) and standard deviation are given as these were the values published. The referenced literature is indicated below the table.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling type and Period</th>
<th>THg (ng/L) range: VWM or mean ± s.d.</th>
<th>Range or mean flux (ng/m²/wk)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Urban</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NSW, Australia</td>
<td>Daily, 6/06-12/07</td>
<td>1-19</td>
<td>21-1700</td>
<td>1</td>
</tr>
<tr>
<td>Toronto, Canada</td>
<td>Event 2006-2008</td>
<td>4.0-122</td>
<td>80-2140</td>
<td>2</td>
</tr>
<tr>
<td>Chongqing, China</td>
<td>Event, 7/2010-6/2011</td>
<td>5.8-158; 30.7</td>
<td>640</td>
<td>3</td>
</tr>
<tr>
<td>Guizhou, China</td>
<td>Monthly, 2006</td>
<td>7.5-149; 36</td>
<td>710</td>
<td>4</td>
</tr>
<tr>
<td>Remote sites, China</td>
<td>Various, 2005-2009</td>
<td>1 - 31</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td><strong>Coastal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mace Head, Ireland</td>
<td>Event, 11-15/9/95</td>
<td>4-12.2</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Brazil</td>
<td>Event, 10/98-12/99</td>
<td>&lt; 0.02-2.95</td>
<td>8-63</td>
<td>7</td>
</tr>
<tr>
<td>Japan, various</td>
<td>Biweekly, 2003-2005</td>
<td>2-18; 5.8</td>
<td>250</td>
<td>9</td>
</tr>
<tr>
<td>California, USA</td>
<td>Event, 2007-2008</td>
<td>4.7</td>
<td>140</td>
<td>13</td>
</tr>
<tr>
<td>Bermuda</td>
<td>Weekly, 2008-2009</td>
<td>7.8-10.5</td>
<td>190</td>
<td>14</td>
</tr>
<tr>
<td><strong>North America</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Underhill, VT</td>
<td>Event, 1/93-12/03</td>
<td>14.4 ± 11.3</td>
<td>510 ± 690</td>
<td>10</td>
</tr>
<tr>
<td>MDN, site FL11</td>
<td>Weekly, 2007-2010</td>
<td>8.3 ± 5.0</td>
<td>190 ± 200</td>
<td>11</td>
</tr>
<tr>
<td>MDN, site SC05</td>
<td>Weekly, 2007-2010</td>
<td>13.0 ± 10.7</td>
<td>220 ± 210</td>
<td>11</td>
</tr>
<tr>
<td>MDN, site MD99</td>
<td>Weekly, 2007-2010</td>
<td>8.7 ± 8.4</td>
<td>190 ± 210</td>
<td>11</td>
</tr>
<tr>
<td>MDN, site NJ30</td>
<td>Weekly, 2007-2010</td>
<td>3.8-9.4*</td>
<td>70-200*</td>
<td>12</td>
</tr>
<tr>
<td>MDN, 13 sites in New England</td>
<td>Weekly, 1996-2002</td>
<td>1.4 - 65</td>
<td>210</td>
<td>8</td>
</tr>
<tr>
<td>New Hampshire, USA</td>
<td>Weekly, 7/2006-8/2009</td>
<td>3.8-60.7; 15.8</td>
<td>390</td>
<td>14</td>
</tr>
</tbody>
</table>

| This study                |                          |                                      |                             |      |
| Pretoria, South Africa    | Weekly, 2007-2009        | 1.2-52.5; 10.6                       | 170                         | 14   |
| Cape Point, South Africa  | Weekly, 2007-2009        | 210                                  |                             |      |

References: 1: Dutt et al. (2009); 2: Zhang et al., 2012; 3: Wang et al.(2012); 4. Guo et al. (2008); 5. Taken from ref. 3; 6: Ebinghaus et al.(1999); Lacerda et al., (2002); 8: Lombard et al.(2011); 9: Sakata et al. (2006); 10: Keeler et al. (2005) 11: MDN website; 12: Vanarsdale et al. (2005); 13: Conaway et al.(2010); 14: This study and our unpublished data. Notes:* range in VWM and weekly deposition for each site across years; averages for entire sampling period.
Table 2.6: Trace metal concentrations at Pretoria and Cape Point compared to other locations around the world. Concentrations are volume-weighted averages and the units are in ppb.

<table>
<thead>
<tr>
<th>Location</th>
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<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>Cd</th>
<th>Pb</th>
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<td>44.9</td>
<td>0.02</td>
<td>1.0</td>
<td>6</td>
</tr>
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References: 1: Vuai & Tokuyama, (2011); 2: Song & Gao, 2009; 3: Al-Momani et al., 2008; 4: Halstead et al., 2000; 5: Mason et al., 2002 (3 sites; Chesapeake Bay) 6: This study & unpublished data

2.6 Relationships between trace metals and links to potential contamination sources

To examine further the relationships between metals, which may further indicate potential sources, the interactions of these metals were investigated using Pearson correlation coefficients as shown in Tables 2.7 and 2.8. At Cape Point, Hg did not correlate with any other metal except for Pb. This is not surprising given that the particulate flux, and the scavenging of particulate by precipitation, is not the dominant source of Hg in rain as it is for metals in general. The Hg in precipitation at this location may be associated with terrestrial or ocean air masses. Other studies have similarly found no correlation between Hg and other metals in precipitation (e.g. Mason et al., 2002). At Cape Point, Al and Fe have moderately strong correlations with Cu, Ni and Co. Al and Fe are both crustal elements, and the moderate strong relationship with Cu, Co, and Mn
indicates that these metals, while having an anthropogenic source, are also derived from crustal sources. Similarly, in the study around the Chesapeake Bay (Mason et al., 2002) most of the metals (Al, Fe, Mn, Cu, Cd, Zn and Pb) were reasonably well correlated at the more remote site in Solomons, MD. The stronger relationship between some metals (Co, Cu, Mn and Ni), indicates a commonality in sources most likely anthropogenic. High temperature processes such as non-ferrous metal smelting and fossil fuel combustion are known to liberate metals such as Cu, Ni and Pb (Herrera et al., 2009). Some metals (e.g. Cu and Zn) are also associated with wearing of vehicle parts such as brakes and tyres (Thorpe & Harrison, 2009), and metals can also be released from oil refining, which occurs within the greater Cape Town region, or in association with vehicle tailpipe emissions. Mixed sources are likely. For example, Mn in atmospheric waters is derived from windblown dust, anthropogenic activities such as waste incineration, iron and steel manufacture, mining and fossil fuel combustion (Willey et al., 2009).

Table 2.7: Pearson correlation coefficients for trace metals in precipitation collected at Cape Point. Bold values indicate correlations that are significant for the number of observations.

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>Al</th>
<th>Co</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>Cd</th>
<th>Pb</th>
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<tr>
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<tr>
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<tr>
<td>Cu</td>
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<td></td>
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<tr>
<td>Mn</td>
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<td>0.376</td>
<td>0.971</td>
<td>0.857</td>
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<tr>
<td>Zn</td>
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<td>0.056</td>
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<td>Ni</td>
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<td>0.994</td>
<td>0.803</td>
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<td>0.023</td>
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<td>0.381</td>
<td>0.530</td>
<td>-0.212</td>
<td>0.587</td>
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<tr>
<td>Cd</td>
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<td>0.110</td>
<td>0.201</td>
<td>0.116</td>
<td>0.170</td>
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<tr>
<td>Pb</td>
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<td>0.130</td>
<td>-0.069</td>
<td>0.260</td>
<td>-0.093</td>
<td>0.195</td>
<td>-0.094</td>
<td>-0.166</td>
<td>0.004</td>
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</table>
Table 2.8: Pearson correlation coefficients for trace metals in precipitation collected in Pretoria. Bold values indicate correlations that are significant for the number of observations.

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>Al</th>
<th>Co</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>Cd</th>
<th>Pb</th>
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<tbody>
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<td>Hg</td>
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<tr>
<td>Al</td>
<td>0.613</td>
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<tr>
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<td>0.923</td>
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<tr>
<td>Cu</td>
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<tr>
<td>Mn</td>
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<td>0.857</td>
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<td>Ni</td>
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<td>0.951</td>
<td>0.930</td>
<td>0.992</td>
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<td>1.000</td>
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<tr>
<td>Fe</td>
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<td>0.911</td>
<td>0.875</td>
<td>0.834</td>
<td>0.760</td>
<td>0.232</td>
<td>0.728</td>
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<tr>
<td>Cd</td>
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<td>0.465</td>
<td>0.369</td>
<td>0.419</td>
<td>0.261</td>
<td>0.448</td>
<td>0.242</td>
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<tr>
<td>Pb</td>
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<td>0.963</td>
<td>0.969</td>
<td>0.342</td>
<td>0.958</td>
<td>0.861</td>
<td>0.429</td>
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</table>

At Pretoria, there are a significant number of strong relationships between metals of crustal origin and anthropogenic derived metals. Most notably, Hg exhibits very strong relationships with Al, Co, Cu, Mn, Ni, Fe, Cd and Pb, which is not the case for Cape Point. This is further evidence that in Pretoria, Hg emissions come from a variety of anthropogenic processes, and potentially that Hg in precipitation is more strongly related to particulate scavenging at this inland location. It is also worth noting that at this location, Pb has strong relationships with Al, Co, Cu, Mn, Ni, and Fe. Lead is associated with many industrial processes especially as a result of the introduction of tetraethyl Pb in gasoline in the 1920’s (Cho et al., 2011). However, with the discovery of the harmful effects of lead, its use has gradually been phased-out worldwide but the complete phase-out of leaded gasoline in South Africa was only achieved in 2006. Therefore, there is a likelihood that Pb is still present in the surface soils, which could be contributing to Pb in precipitation. Also, Pb was replaced with methylcyclopentadienyl manganese tricarbonyl (MMT) in gasoline in 2000 as Pb was phased out. MMT also functions as an octane booster (“anti-knock” additive) and could result in elevated levels of Mn in areas where it is used (Batterman et al., 2011). It is worth noting that the volume weighted average concentration of
Mn is approximately 5 times higher at Pretoria than at Cape Point (Table 2.6). Overall, this confirms the stronger anthropogenic influences in Pretoria but suggests that there are anthropogenic sources impacting Cape Point as well. The situation is more complex at Cape Point. Firstly, the variance in the ratio data is much higher for the Cape Point samples (%RSD >100% for all metals) compared to that of Pretoria (RSD 30-60% for all metals except Zn and Cd) suggesting that there is less consistency in the sources of the metals to rain, and that the ratios vary widely between weekly collections. This is evident from an examination of the individual data. In terms of sources, comparison of the ratios to Al for the rain compared to the range of values measured in sea salt (Table 2.4) suggest that for many of the metals that the sources are similar to that of sea salt, mostly from regional marine air but with the potential for some anthropogenic impact. However, in many cases the values are at the high end of the range of sea salt values, which suggests that these aerosols are impacted by anthropogenic sources. This idea is reinforced by comparison of the ratios to that measured at Khayelitsha, which has a much higher ratio for the metals measured compared to both the Cape Point rain and the sea salt ratios. This suggests that the Cape Point site is not “pristine” but the concentration data suggest that it is not as highly impacted as the Pretoria site, although there are few differences that are statistically significant. The ratios of the average values(E/Al Cape Point/E/Al Pretoria) for each metal are similar (range 1-10) except for Zn and Ni. This analysis confirms the notion expressed above that there are local sources of Zn and Ni that are contributing to these metals in the rain at Cape Point.
2.7 Linking rainfall concentrations and air mass sources

The GAW site at Cape Point was set up in 1977 with the primary role of monitoring long-term trends of trace gases in air representing background conditions, not affected by local or regional pollution. However, although the dominant wind direction is from the southeastern sector, which is representative of clean maritime air from the Southern Ocean, Cape Point is also occasionally subjected to air from the north to northeastern sector mainly during the austral winter. This suggests that the site may receive polluted continental air masses, or relatively local sources given its proximity to Cape Town. In addition to the rain collections done for this project, $\text{Hg}^0$ is monitored at the site and both pollution events (high Rn, CO and $\text{Hg}^0$ concentrations) and $\text{Hg}^0$ depletion events (i.e. enhanced local atmospheric chemistry) have been reported (Brunke et al., 2004; 2010; Slemr et al., 2008). Pollution events involve the influx of continental air masses whereas depletion events constitute rapid atmospheric oxidation processes that lead to the production of RGHg, which has a high potential for deposition. This may explain some of the more elevated concentrations recorded at Cape Point. In addition, it explains why no correlation was found between Hg and other trace metals of anthropogenic origin in Table 2.7. If a large fraction of the Hg is from in-situ atmospheric production within the local marine boundary layer or in the regional troposphere, atmospheric back trajectories may help in identifying time periods when there was continental air mass inflows. However, given that rain collections at Cape Point were done weekly, this presents a challenge in figuring out which time periods experienced an influx of polluted air masses. The overall information can be pieced together using hourly rain data and ancillary data from the site (for example, CO and Rn) which shed light on the origin of some of the air masses traveling to the site during the sampling period as they are, respectively, indicative of polluted and terrestrially-derived air masses. CO has proved to be an effective
indicator of how large scale distribution of atmospheric pollutants by the long-range transport of polluted air masses resulting from anthropogenic combustive processes (Duflot et al., 2010) and correlations between CO and Hg\(^0\) for polluted air masses have been documented (Jaffe et al., 2005). Many processes (oxidation of methane and other biogenic hydrocarbons, fossil fuel combustion, biofuel use and biomass burning) produce CO and its lifetime of weeks to months makes it an interesting tracer for studying atmospheric transport. Biomass burning is a leading pollution source in the tropics and more biomass burning occurs in Africa than any other continent (Hao and Liu, 1994). Therefore CO can also represent either a terrestrial or a pollution signal at Cape Point. In contrast, 99% of the \(^{222}\text{Rn}\) in the atmosphere comes from rocks and minerals in the earth’s crust where it is dispersed by diffusion and advection after its production by decay of radium. Atmospheric \(^{222}\text{Rn}\) that has a half-life of 5.53 days (and decays to \(^{210}\text{Pb}\)) is not removed by either physical or chemical means and is dispersed sufficiently throughout the atmosphere to be a regional tracer (Baskaran, 2011). The mean lifetime of \(^{222}\text{Rn}\) is generally comparable to the time it takes air masses to move across continents and/or oceans but is short compared to the mixing time scale of the atmosphere. As a result \(^{222}\text{Rn}\) has been used across the globe as a signature for land-derived air masses. The \(^{222}\text{Rn}\) detector at Cape Point was installed in 1999 and the efficacy of using those measurements in conjunction with wind direction and CO to classify air masses, either as maritime, continental or mixed has previously been demonstrated (Brunke et al., 2004). For Cape Point, \(^{222}\text{Rn}\) levels below 100 mBq/m\(^3\) are considered to be typical of maritime air while levels between 100-250 mBq/m\(^3\) have some terrestrial influences (Brunke et al., 2004). For CO, levels about 100 ppb or strong peaks in the signal are indicative of pollution inputs.
Ancillary data was used to try and deduce the origin of air masses to examine the potential for terrestrial air masses to impact the sampling site during a rain event. Two examples are shown which indicate the difficulty in making such assignments given the nature of the Hg data – weekly total values. They also indicate that the airflow around the sampling site is complex and changes direction and source relatively rapidly. Firstly, consider the week of 26 May to 3 June 2008, where the volume weighted rainfall concentration was 23.2 ng/L and the flux 495 ng m⁻² wk⁻¹; i.e. a relatively high concentration and flux. Hourly rain data showed it rained on the 28, 29 and 30th of May, followed by a few dry days and more rainfall on the 2nd and 3rd of June 2008. It rained between 9.00 pm and 1.00 am from 2nd June 2008 into the early hours of 3 June 2008 and there was more rain at 11.00 am and again at 7.00 pm on 3 Jun 2008. During that period ²²²Rn values ranged from 54-5239 mBq/m³, with a median of 705 mBq/m³. Values < 200 mBq/m³ were only recorded from around 12 noon to midnight on 3 June 2008 (Fig. 2.7). This suggests that air masses were of non-marine origin most of the time during the rainfall. Brunke et al (2004) showed that ²²²Rn and CO strongly correlate when air masses pass over terrestrial regions with strong CO sources. However, in some instances these species strongly diverge, for example instances of high ²²²Rn/low CO levels may occur when air masses pass over sparsely populated regions with few CO sources such as the granite/gneiss region in the north Western Cape. Conversely, low ²²²Rn/high CO concentrations are encountered when maritime air moves across the greater Cape Town area that has many anthropogenic sources such that by the time it reaches Cape Point, the terrestrial contribution is negligible (Brunke et al., 2004).

Back trajectories support the CO/Rn data (Fig. 2.8). The 72-hour back trajectory ending at 1400 UTC(1600 local time) on 3 June 2008 showed that over a period of 3 days air masses traveled from a height of 1500- 2000 m from areas to the east of Cape Point. After the passage of the rain
event, winds switched to more westerly flow as indicated by the 72 hr back trajectories arriving at Cape Point on Jun 6. Wet weather in this region during winter normally arrives with the storms from the south and the wind directions and change during the passage of the rain event on June 2 and 3 suggest this. Prior to the storm event, the more easterly winds were likely more impacted by anthropogenic sources, as suggested by the CO and Rn data and became more oceanic during the rain event. Our evaluation suggests that rain collected during the week of 26 May-3 June 2008 was subject to anthropogenic influences, and this is reflected in the relatively high concentration and flux for this week. These mixed with other air masses traveling at a height of about 500 m bringing in maritime air. It is therefore clear that rain collected during the week of 26 May-3 June 2008 was subject to anthropogenic influences, and this is both reflected in the relatively high concentration and flux for this week.

It is worth noting that Brunke et al. (2012) used the trace gas signals at Cape Point from identified pollution events to reconstruct the emissions inventory for South Africa, further confirming the importance of pollution inputs as source for Hg and metals at Cape Point. They identified polluted air masses arriving from the east, which likely reflects local inputs from the industrial sector in the Western Cape region which is concentrated east of the city centre, and from the informal housing, such as Khayelitsha, where heating in winter relies on coal and biomass burning.

We also generated trajectories for the week of 30 June to 7 July 2008, where the THg concentration was 10.7 ng/L but where the flux (450 ng m^{-2} wk^{-1}) was relatively comparable to the previous example. During this time period the rain occurred from 3-7 July 2008. A 72-hour back trajectory ending on 3 July 2008 shows some influence from the continent and the northwesterly flow characteristics of a storm and again the winds switch to more marine sources
over time. Overall, $^{222}\text{Rn}$ values were elevated from 1-3 July 2008 peaking at 6059 mBq/m$^3$ on the night of 1$^{st}$ July 2008; with a minimum of 1107 mBq/m$^3$ on 3 July 2008 and a median value of 2395 mBq/m$^3$ over the whole period, suggesting that the longer-term origin of the air was not totally marine. This indicates terrestrial influences especially as values were over 5000 mBq/m$^3$ (Brunke et al., 2004). Even given that there is a seasonal cycle with elevated $^{222}\text{Rn}$ values (> 1000 mBq/m$^3$) during the winter months of April to August at Cape Point, these values are elevated. During this time CO values ranged from 58 to 227 ppb whereas background levels are ~ 45 ppb (Brunke et al., 2010) showing elevated peaks over the period.
Figure 2-7: a) Plot of carbon monoxide and radon levels for June 1-5, 2008: $^{222}\text{Rn}$ values are $>1000$ mBq/m³ which is evidence of terrestrial influences. CO peaks $>100$ ppb are indicative of pollution inputs. b) 72 hr back trajectory showing air masses from areas to the east of Cape Point arriving on 3 June 2008. These air masses were likely more impacted by anthropogenic sources as suggested by CO and Rn data. After the rain event, winds change to a westerly flow as shown by the back-trajectory ending on 6 Jun 2008.
Figure 2-8: a) A selection of CO and $^{222}$Rn measurements measured at Cape Point from 30 June to 7 July 2008. $^{222}$Rn values were consistently over 1000 mBq/m$^3$ until which is indicative of terrestrial influences. This is also shown by the peaks in CO values) 72 hr back trajectory showing the north-westerly flow of air masses arriving at Cape Point on 3 July 2008. They were subject to influences from the continent according to CO and Rn data. However, direction changes, they flow from a marine origin as shown by the trajectory ending on 7 July 2008.
Overall, these two examples of sources of air masses during deposition, and other similar situations which are documented in the Rn and CO data demonstrate that Cape Point is subject to both marine and continental air masses and is not a background location especially during the majority of the wet season. Sectored sampling of air removes such biases but this was not possible with the wet deposition samples collected here. However, while these results may not provide a clear signal of the regional background deposition at this site, they do indicate the ranges in concentrations and fluxes to the region, and the potential importance of anthropogenic inputs to deposition at Cape Point. Clearly, more data is needed to elucidate the chemical and atmospheric processes driving deposition at Cape Point, and associated events such as Hg depletion events.
**SUPPORTING INFORMATION**

*Table S1: Trace metal concentrations at Pretoria in ppb*

<table>
<thead>
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<th>Elements (ppb)</th>
<th>Al</th>
<th>Co</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>Cd</th>
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<td>Detection limits</td>
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<td>0.03</td>
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<td>0.19</td>
<td>15.6</td>
<td>0.02</td>
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*Table S2: Trace metal concentrations at Cape Point in ppb*

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<th>Al</th>
<th>Co</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>Cd</th>
<th>Pb</th>
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<td>5.2</td>
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<td>2-9 Jul 2007</td>
<td>18.2</td>
<td>0.04</td>
<td>0.82</td>
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<td>9.3</td>
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<td>22-29 Sep 2008</td>
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<td>0.20</td>
<td>0.23</td>
<td>&lt;3.3</td>
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<td>6.03</td>
<td>0.01</td>
<td>0.18</td>
</tr>
<tr>
<td>12-20 Nov 2008</td>
<td>7.0</td>
<td>0.01</td>
<td>0.09</td>
<td>0.14</td>
<td>&lt;3.3</td>
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<td>0.51</td>
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</table>
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3. MERCURY IN BERMUDA

3.1 INTRODUCTION

Remote islands offer a unique opportunity for the study of inputs of elements and compounds to the ocean depending on their remoteness and location. Bermuda is situated in the middle of the North Atlantic Ocean at 32 degrees latitude, about 586 miles from Cape Hatteras, North Carolina and roughly 770 miles from New York, and given typical wind patterns receives both open ocean air masses and contaminated outflow from North America at different times of the year. It is therefore a useful location to study both inputs to the open-ocean and examination of regional contamination. Bermuda includes several islands that grouped together cover 21 square miles with a population of about 62,000. Being an island nation, fish is widely consumed for it’s nutritional value and also because it forms an integral part of the people’s cultural identity. The ubiquity of mercury as a pollutant in the world’s oceans has resulted in mercury’s bioaccumulation in fish even in remote locations, and consequently in people who consume the seafood. Hence, there are human health concerns related to fish consumption. In 2003, the University of Laval’s Atlantis Mobile Lab carried out a study in Bermuda aimed at providing baseline data for pre-natal exposure to Hg and other environmental contaminants. Mean Hg concentrations of umbilical cord blood from healthy newborns were higher than expected with a mean value of 8.3 µg/L, with values ranging from undetected to 32.1 µg/L (Dewailly et al., 2012). The U.S. Environmental Protection Agency (EPA) reference dose is 5.8 µg/L in whole blood, and levels above this are associated with adverse health effects (EPA- http://www.epa.gov/mercury/exposure.htm). Based on an analysis of 2 out of 42 samples Dewailly and coworkers (2012) estimate that 85% of the mercury measured in cord blood
was in the form of methyl mercury (MeHg) one of the more toxic forms of this pollutant, suggesting that contaminated seafood was the main source of exposure. In addition, there was a significant association between mercury in cord blood and the consumption of two local fish species, wahoo and snapper, both predatory fish, in the Laval study (Dewailly et al., 2012). It is quite clear therefore that mercury contamination is a public health concern in Bermuda. The atmosphere is the most important source of mercury to most terrestrial and aquatic environments because it is the main pathway by which Hg is dispersed and transported globally (Laurier and Mason, 2007) as discussed in Chapter 1. This is especially true for the open-ocean and remote islands where riverine inputs are small. As such, investigating atmospheric inputs in and around Bermuda can help quantify the fluxes to the environment while providing clues as to the origin of the sources of Hg to this region.

MATERIALS AND METHODS

3.2 Study area, sampling and analysis protocol

Sampling was done at Tudor Hill, Southampton on the south west coast of Bermuda. Since March 2003, the Bermuda Institute of Ocean Sciences (BIOS) has operated the Tudor Hill observatory with funding from the National Science Foundation (NSF) Chemical Oceanography section. E.L. Marks, a Harvard Biologist founded the institution as the Bermuda Biological Station for Research (BBSR) in 1903 as an outpost of U.S. Science (Michaels and Knap, 1996), The Tudor Hill station is located on a cliff overlooking the ocean and is surrounded by grass and short shrubbery with a golf course close by.
Figure 3-1: In the left panel: map showing the Tudor Hill sampling site in Bermuda shown by the blue markers (Generated by Google Maps). The Bermuda Institute of Ocean Science (BIOS) is located on the opposite side of the island. In the right panel: photo capturing the atmospheric observations tower at Tudor Hill and nestled at it’s foot, the buildings housing the Tekran™ 2537A.

An N-CON MDN automatic precipitation collector was erected atop a 23m high walkup tower that is also used for various other atmospheric observations. The rain collector has an optical sensor that detects the onset of precipitation, opening the sample container within the first five drops of rain. When precipitation stops the sample container closes within two minutes to minimize exposure to dry deposition (www.n-con.com). Weekly precipitation samples were collected between July 2008 and December 2009. Each sample was preserved after collection by spiking with 0.5% (v/v) by volume trace metal grade hydrochloric acid (HCl) prior to refrigeration and shipping to the University of Connecticut, Avery Point campus for analysis. On arrival, the bottles were weighed so that the rain weight (volume) could be determined by subtracting the bottle weight. To prepare liquid samples for analysis for total Hg, 0.5 % (v/v) bromine monochloride (BrCl) was added in an oxidation/digestion step that proceeded overnight. Afterwards the
sample was pre-reduced with hydroxylamine hydrochloride (NH₂OH·HCl) to destroy the excess bromine, prior to ionic Hg (II) being reduced to Hg⁰ with stannous chloride (SnCl₂)(U.S. EPA method 1631-www.epa.gov; Lamborg et al., 2012) and purged from solution by argon gas and trapped on a gold-coated sample trap. A Tekran™ Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) was used for analysis. The detection limit (D.L.) for the samples was calculated as three times the standard deviation of the blank values. The D.L. for Bermuda rain samples was 0.7 ng/L.

In addition to rain, weekly particulate samples were collected by pumping air through a Teflon filter holder for mercury analysis. A mass flow meter was connected to the setup for the purpose of recording start and stop readings to enable the calculation of air volumes pumped through the setup. It should be noted that this sampling setup was sectored to prevent local contamination from the site or nearby human activity. This sampling system was set to switch on the pump when wind direction was in the sector 210-315 degrees and if the wind speed was > 1m/sec. However, the system was dismantled in August 2009 to prevent damage from Hurricane Bill. On reinstallation on Sep 1 2009, the system was faulty and consequently the sampling was determined by wind direction only (Andrew Peters, personal communication). Particulate sampling was done from March to October 2009. The filter holders were packed with filters at the Avery Point campus and shipped to BIOS. Typically, each filter holder would contain 2 Teflon filters, one as the sample filter with the other acting as a blank. A third glass fiber filter (GFF) acted as a backup in case of pump back flow and contamination from the exhaust line. After sample collection, the filter holders were refrigerated prior to shipment back to the University of Connecticut.
On arrival, filter holders were disassembled in a Class 100 clean room where each filter was stored in trace metal clean Petri dishes and frozen until analysis. Subsequently, the filter holders were rinsed with deionized water and then acid cleaned before reuse. Particulate filters underwent acid digestion prior to analysis: 5 ml of a 2N HNO₃ acid solution was added to each filter in a vial, followed by overnight digestion in a drying oven at 60 °C. After cooling, 5 mL D.I. water was added to each vial, followed by BrCl (2ml per 100ml). The samples were allowed to react for a minimum of one hour. Before analysis, 0.1 mL hydroxylamine hydrochloride (NH₂OH.HCl) was added as a pre-reduction step. Sample Hg was reduced to Hg⁰ with stannous chloride (0.1 mL) and quantified with dual Au-amalgamation CVAFS. On each analytical day, a calibration curve and bubbler blanks were established for both precipitation and particulate samples. Reagent blanks were prepared in the same manner as the samples.

This procedure is similar to the extraction and digestion procedure employed for the GEOTRACES inter-comparison study (Morton et al., 2013). However, the filters used for particle collection in that study were Whatman quartz microfiber filters, while Teflon filters were used in Bermuda. Both are suitable for collection of trace pollutants with the Whatman filters being well suited to high volume sampling that requires good mechanical strength. Teflon filters on the other hand are expensive.

Further, elemental mercury (Hg⁰) was measured at Tudor Hill (June-Aug 2009) and during cruises to the waters surrounding the island in the summer of 2009, and 2010. A Tekran™ 2537A Mercury analyzer (www.tekran.com) was used at the station, and it was also mounted at the front of the ship away from any exhaust outlets of the vessel during the cruises. A continuous flow of trace metal clean argon gas was provided throughout
the entire operational period for the automated analyzer. Calibration and maintenance was carried out as described in the operational manual. The crew on the R/V Atlantic Explorer provided technical and logistical support to ensure smooth installation and running of the instrument.

### 3.3 RESULTS

Table 3.1 summarizes the concentrations of Hg in rain and fluxes in Bermuda with comparison to measurements made at Avery Point (Gichuki S.W., unpublished data), a regional campus of the University of Connecticut located on the shores of Long Island Sound in a suburban residential area. Both are coastal sites that are removed from major industrial activity.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Volume weighted mean concentration (ng/L)</th>
<th>Std. dev.</th>
<th>Flux (ng/m²/wk)</th>
<th>Std. dev.</th>
</tr>
</thead>
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<td>4.9</td>
<td>138.1*</td>
<td>147.0</td>
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<tr>
<td>Avery Point</td>
<td>28</td>
<td>6.1</td>
<td>5.7</td>
<td>108.8</td>
<td>138.5</td>
</tr>
</tbody>
</table>

**Table 3.1**: Volume weighted concentrations of mercury and deposition fluxes in rain at Bermuda and Avery Point. For Bermuda, the asterisk (*) signifies that fluxes were only calculated for samples from 2009 (N= 17) due to uncertainty in accuracy of sample volumes in 2008 due to loss as a result of sampling setup problems.

Figure 3.3 (a) and (b) respectively show the weekly volume-weighted concentration and deposition fluxes in Bermuda. It should be noted that while THg concentrations are reported for the entire sampling period, fluxes are only shown for 2009. This is because during the 2008 sampling period, there were problems in the sampling setup that caused some loss of rainfall volumes. For rainfall sampling in 2008 the funnel was connected to the bottle via a piece of “trace metal clean” tubing. Although this had worked in other
setups such as at Avery Point, in Bermuda this connection between the bottle and funnel would sometimes slip off resulting in loss of samples. This problem was remedied by having a custom connector made out of Teflon by staff at the Avery Point machine shop. The connector is a hollow Teflon cylinder with “threading” that allows one end to screw into a 1 Litre Teflon bottle, while the other screws into a glass funnel. Whereas fluxes calculated for 2008 could be inaccurate due to losses of rainfall, this is not the case for subsequent sampling because these problems were eliminated. Figures 4 (a) and (b) were plotted to determine whether relationships exist between rainfall amount and concentration or rainfall amount and deposition flux. The Pearson’s correlation coefficient for the Rainfall depth vs. THg concentration is -0.24 that signifies that no significant relationship exists between the two for this data set. This is unlike the results from the South African study in Chapter 2. On the other hand, the Pearson’s correlation coefficient for rainfall depth and wet deposition flux is 0.64. This was calculated only for samples from 2009 (N=17), which signifies the existence of a positive relationship between these two variables for this data set. An increase in wet deposition flux with increasing rainfall has been shown in other studies, although this also leads to dilution of the THg in solution (Seo et al., 2012).
Figure 3-2: (A) Volume weighted mean concentrations of total mercury (THg) in rain in Bermuda. (B) Total deposition flux by week for Bermuda. NB: Fluxes were only calculated for dates in 2009. Due to sampling setup problems, there could have been some inaccuracies for sample volumes in 2008.
Figure 3-3: (A) Rainfall depth (mm) vs. V.W.M THg concentration and (B) Rainfall depth (mm) vs. Wet deposition flux in Bermuda. NB: For B, a plot was only generated for values from 2009 (n=17), due to sampling setup problems, there could have been some inaccuracies for sample volumes in 2008.
For particulate mercury, the results are as follows:

**Table 3.2:** Average concentrations of particle bound Hg in Bermuda from March to October 2009. *The average concentration was calculated without a large value (47.2 pg/m$^3$), which is an outlier.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Average (pg/m$^3$)</th>
<th>Stdev</th>
<th>Range (pg/m$^3$)</th>
</tr>
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<tr>
<td>Bermuda</td>
<td>10</td>
<td>9.5*</td>
<td>12.9</td>
<td>2.2 – 23.2</td>
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</tbody>
</table>

Figure 5 shows a plot of all the values for each week of the entire sampling period. All the values range from about 2-25 pg/m$^3$ with the exception of that from the week of 20 July – 3 Aug 2009 which is an outlier, and there is no discernible trend. As earlier mentioned, this sampling was sectored and therefore only sampled air masses blowing to the island from the ocean.

**Figure 3-4:** Particulate Hg by week from March to October 2009 in Bermuda.
Figure 3-5: Plot of elemental mercury ($Hg^0$) measured at Tudor Hill, Bermuda from 24 June 2009 to 20 Aug 2009 using the Tekran™ 2537A. These are daily averages for a period of 24 hours with the exception of the value for 20 August 2009, which only covers 12 hours. Overall the average is $1.34 \pm 0.12$ ng/m$^3$ with a range of 1.07–1.63 ng/m$^3$. Error bars are standard error of the mean.

$Hg^0$ was monitored at the Tudor Hill atmospheric station and the results from 24 June 2009 to 20 Aug 2009 are presented in Figure 5. The sampling resolution was 5 minutes. The average $Hg^0$ concentration in air is 1.34 ng/m$^3$ with a range of 1.07 to 1.63 ng/m$^3$. These results are daily averages covering a period of 24 hours with the exception of values recorded on 20 August 2009, which cover 12 hours only.
DISCUSSION

3.4 Comparison of THg concentrations in rain, particulate Hg and Hg^0 concentrations with other locations around the world.

Although Bermuda and the BATS (Bermuda Atlantic Time Series) station have been the site of numerous atmospheric and oceanic observations, there are few studies in the literature (DeWailly et al., 2012; 2008; Laurier and Mason, 2007; Luckhurst et al., 2006) of Hg concentrations in the marine environment as well as in aquatic organisms. Bermuda has unique attributes: it is the 2\textsuperscript{nd} most remote island community in the world (DeWailly et al., 2012), on a small land-mass with little industrial activity. As such Hg concentrations may be expected to mirror those measured in the open ocean as opposed to measurements on the continents. Here, comparison is made to other locations around the world to put these results in context.

3.4.1 Gaseous elemental mercury (Hg^0)

Values measured at Bermuda are comparable to Hg^0 measurements at other remote locations and the open ocean. A cruise between Bahamas and Bermuda in the sub tropical North-Atlantic ocean recorded an average value of 1.63 ±0.08 ng/m\textsuperscript{3} for Hg^0. Figure 3.8 shows a compilation of these results where Hg^0 shows little variability for the entire study period. In contrast, the changes in UV and RGHg occur in a similar fashion indicating that the processes that lead to a buildup in RGHg are photo-chemically linked (Laurier and Mason, 2007). Still, the values for Hg^0 are within the range expected for the open ocean as has been reported in literature (Slemr et al., 2011 & 2003).
Figure 3-6: (Top) Elemental mercury and UV concentrations and (bottom) ozone and reactive gaseous mercury concentrations for the 11-day cruise from Bahamas to Bermuda. The dips in ozone and Hg\(^0\) concentrations tend to coincide with peaks in RGHg concentrations which is indicative of photochemically mediated oxidation of Hg\(^0\) to RGHg (Laurier and Mason, 2007).

Similar measurements made on a cruise from Montevideo, Uruguay to Bridgetown, Barbados as part of the I.O.C. Trace Metal Baseline Program reported values of 1.61 ng/m\(^3\) with a range of 1.17-1.99 ng/m\(^3\) (Lamborg et al., 1999). At Mace Head a Global Atmospheric Watch (G.A.W.) site on the Irish west coast, Hg\(^0\) has been monitored since September 1995. It is one of the longest running time series of atmospheric mercury observations in a temperate marine environment, and the long-term average up to 2001 is 1.7 ng/m\(^3\) (Ebinghaus et al., 2002). However, a recent reevaluation of data at Mace Head shows an observed decrease to 1.4 ng/m\(^3\) (Ebinghaus et al., 2011). Cape Point, South Africa is another G.A.W. site where continuous measurements are made and where Hg\(^0\) annual median values of Hg\(^0\) decreased from 1.29 ng/m\(^3\) in 1996 to 1.19 ng/m\(^3\) in 2004.
In contrast Hg\textsuperscript{0} values in urban or highly industrialized areas in other parts of the world tend to be well over 2.5 ng/m\textsuperscript{3}, going as high as 20 ng/m\textsuperscript{3} in heavily polluted parts of Asia. It is also worth noting that the majority of emissions of mercury are in the Northern Hemisphere as opposed to the Southern Hemisphere (Sprovieri et al., 2010).

### 3.4.2 Mercury in precipitation (THg)

Table 3.3 compares the THg concentrations in rain at Bermuda to measurements from other locations around the world. The volume-weighted mean concentration of Hg in rain and the wet deposition fluxes at Bermuda are comparable to values measured in North America such as the site in Potsdam, NY and on the west coast in Monterey, CA. Results from THg measurements in rain at Avery Point are also included in Table 3.1. This is also a coastal site in a suburban area on the shores of Long Island Sound and the values are similar to Bermuda. Further comparison is made to data collected through the Mercury Deposition Network (MDN) that is run by the National Atmospheric Deposition Program (NADP) (www.nadp.sws.uiuc.edu). Results from the North Atlantic Coastal Lab, MA and Pettigrew State Park, NC are comparable to those of Bermuda. Both sites are coastal: the North Atlantic Coastal Lab in Barnstable county, MA is on the Cape Cod National Seashore, while the Pettigrew State Park is located about 50 miles from the Cape Hatteras National Seashore in Manteo, NC. Cape Hatteras is directly west of Bermuda. Further comparison is made to an inland site at Candor in Montgomery County, NC that is now inactive where the V.W.M THg concentration is 68% higher than at Bermuda. The amount of rainfall recorded at the site in 2007 is also higher by the same
margin than that from Bermuda for the study period. However, the wet deposition flux in both places is identical.
Table 3.3: Comparison of volume-weighted mean (V.W.M) THg concentrations in Bermuda with other locations around the world. For deposition flux data from literature, published values are converted to similar units (µg/m²/wk) for ease of comparison with Bermuda data. For the South and Equatorial Atlantic Ocean (Lamborg et al., 1999), the rainfall amount was reported in Liters but converted to cm for ease of comparison. The flux reported for Potsdam, NY is the total for the entire study period of September 2003-April 2005. Data from the Mercury Deposition Network (MDN)-NADP was obtained from the website (www.nadp.sws.uiuc.edu) and was calculated for the years given in the table. The numbers in brackets refer to the code for each site. The site in Candor, NC is no longer active, 2007 was the last year for which data is available.

<table>
<thead>
<tr>
<th>Location</th>
<th>Site Description</th>
<th>Sampling Period</th>
<th>Sample Type</th>
<th>THg (ng/L)</th>
<th>Wet Flux (µg/m²/wk)</th>
<th>Average Rainfall depth (cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potsdam, NY</td>
<td>Rural</td>
<td>Sept 2003- Apr 2005</td>
<td>Event based</td>
<td>5.5</td>
<td>7.6 (total)</td>
<td>140</td>
<td>1</td>
</tr>
<tr>
<td>Monterey Bay, CA</td>
<td>Coastal</td>
<td>2007-2008</td>
<td>Event based</td>
<td>5.8</td>
<td>0.08</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>South and Equatorial Atlantic Ocean</td>
<td>Open ocean</td>
<td>1996</td>
<td>Event based</td>
<td>3.6</td>
<td>0.07-0.13</td>
<td>150</td>
<td>3</td>
</tr>
<tr>
<td>Equatorial Pacific Ocean</td>
<td>Open ocean</td>
<td>1990</td>
<td>Event based</td>
<td>2.9</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Taiwan (2 sites) Anbu Taipei</td>
<td>Mountain &amp; urban</td>
<td>Jan-Mar 2009</td>
<td>Event</td>
<td>11.6 19.2</td>
<td>11.6</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>North Atlantic Coastal Lab, MA(MA01)</td>
<td>Coastal</td>
<td>2009</td>
<td>Weekly</td>
<td>4.6</td>
<td>0.12</td>
<td>128</td>
<td>6</td>
</tr>
<tr>
<td>Pettigrew State Park, NC (NC42)</td>
<td>Coastal</td>
<td>2009</td>
<td>Weekly</td>
<td>5.6</td>
<td>0.17</td>
<td>140.8</td>
<td>6</td>
</tr>
<tr>
<td>Candor, NC (NC26)</td>
<td>Inland</td>
<td>2007</td>
<td>Weekly</td>
<td>7.9</td>
<td>0.14</td>
<td>87.5</td>
<td>6</td>
</tr>
<tr>
<td>Bermuda</td>
<td>Coastal</td>
<td>2008-2009</td>
<td>Weekly</td>
<td>4.7</td>
<td>0.14</td>
<td>51.8</td>
<td>7</td>
</tr>
</tbody>
</table>

References: 1: Lai S.-O et al. (2007); 2: Conaway et al., (2010); 3: Lamborg et al. (1999); 4: Mason et al. (1992); 5: Sheu G.-R. et al.(2011); 6: MDN-NADP website 7: This study
3.4.3 Particulate Mercury (HgP)

In Table 3.3, further comparisons of results from Bermuda to particulate collections in other locations. The particulate mercury values in Bermuda are similar to values measured in other coastal areas, most notably Connecticut. Comparison is also made to studies done in the Chesapeake Bay area. Unlike Bermuda, areas near the Chesapeake Bay have greater anthropogenic inputs particularly urban centers such as the Maryland Science Center in downtown Baltimore. It’s also worth noting that Hg⁰ concentrations in some of these areas are also much higher than those at Bermuda. The average Hg⁰ concentration at each of these locations is as follows: Maryland Science Center, 4.4 ng/m³; Stillpond, 1.7 ng/m³ and shipboard measurements, 2.2 ng/m³. This reflects the much higher emissions present. The particulate samples collected at Bermuda were sectored, which means the air masses were of oceanic origin as opposed to the island itself. Therefore it is quite interesting that the values are similar to those from continental land-masses.
Table 3.4: Values of average particulate mercury data from Bermuda and other locations around the world. The values for the South and Equatorial Pacific ocean is the time-weighted average and numbers in brackets refer to the range of values for Total particulate Hg in this study (Lamborg et al., 1999). The Chesapeake Bay study by Sheu and co-workers includes weekly samples for SC and STP, and ship-board (*) samples were collected daily. Sampling was done at the Maryland Science Center, Stillpond on the eastern shore of Maryland and on board a ship. Measurements at the Bermuda Atlantic Time Series (BATS) site were done in September and Dec of 1999 and March and May of 2000 (Sheu et al., 2001). The value for Miami, FL is the mean of data from the GEOTRACES aerosol intercalibration data (Morton et al., 2013).

<table>
<thead>
<tr>
<th>Location</th>
<th>Site description</th>
<th>Sampling period</th>
<th>Sample type</th>
<th>Average (pg/m$^3$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>South and Equatorial Atlantic Ocean</td>
<td>Open ocean</td>
<td>1996</td>
<td>Event based</td>
<td>1.9 (1.5-4.8)</td>
<td>1</td>
</tr>
<tr>
<td>Bermuda &amp; BATS*</td>
<td>Coastal Open ocean</td>
<td>Dec 1999-Nov 2000</td>
<td>Weekly</td>
<td>1.0 4.0</td>
<td>2</td>
</tr>
<tr>
<td>Gdynia, Poland</td>
<td>Urban</td>
<td>Dec 2007-Dec 2008</td>
<td>Daily</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Chesapeake Bay Science center Stillpond Ship*</td>
<td>Urban Coastal Offshore</td>
<td>1997-1998</td>
<td>*Daily &amp; Weekly</td>
<td>74 42 24</td>
<td>4</td>
</tr>
<tr>
<td>Connecticut, USA</td>
<td>Inland &amp; coastal</td>
<td>1997-1999</td>
<td>Weekly</td>
<td>10.5</td>
<td>5</td>
</tr>
<tr>
<td>Chesapeake Bay (2 seasons) Summer Winter</td>
<td>Coastal</td>
<td>Jun-Jul 1995; Nov-Apr 1996</td>
<td>-</td>
<td>18 (avg) 19 21</td>
<td>6</td>
</tr>
<tr>
<td>Miami, FL</td>
<td>Coastal</td>
<td>September 2008</td>
<td>Event based</td>
<td>5.5</td>
<td>7</td>
</tr>
<tr>
<td>Bermuda</td>
<td>Coastal</td>
<td>Jul-Aug 2009</td>
<td>Weekly</td>
<td>9.5</td>
<td>8</td>
</tr>
</tbody>
</table>

Given that HgP is formed when RGHg binds to particles (Feddersen et al., 2012), in-situ production of RGHg in the marine boundary layer may be reason for this. Numerous studies (Gratz et al., 2013, Mao & Talbot, 2012, Sprovieri et al., 2010) have documented the diurnal cycle of RGHg, which is produced when Hg$^0$ is oxidized by various atmospheric oxidants such as the hydroxyl (OH•), chlorine (Cl•) or bromine (Br•) radicals. In the marine environment especially, bromine atoms are the primary oxidant (Obrist et al., 2011; Soerensen et al., 2010). The reactions are photo-chemically driven, characterized by an increase in RGHg levels after sunrise, with a peak at midday followed by a decline in the afternoon and a low in the night-time (Laurier et al., 2003; Laurier & Mason, 2007; Obrist et al., 2011). Modeling studies by Holmes et al. (2009), have further highlighted the importance of this phenomenon in the marine environment. A box model of the MBL suggests that dry deposition alone would be too slow to account for the rapid decrease in RGHg values observed in the afternoon and evening hours. Uptake by sea-salt aerosols is suggested instead. The Holmes et al model predicts that > 80% of MBL Hg$^{II}$ formed is taken up and precipitated as sea-salt aerosol rather than directly as RGHg, which represents gas phase Hg$^{II}$ (Holmes et al., 2009). In one of the few studies to measure HgP in different particle size fractions, HgP levels were higher in coarse sea salt aerosols. 50-60% of HgP was found mainly in coarse fractions of 1.1 to 5.8 µm composed of sea salt particles at both a coastal site (Thompson Farm) and a marine site (Appledore Island). Sea salt aerosols are formed from waves breaking and bubbles bursting during white-cap formation in the open-ocean. This has been found to affect areas up to 25 km from the coastline (Athanasiopolou et al., 2008, De Leeuw et al., 2000). Table 3.4 shows the size distribution of HgP at these sites. The HgP concentration
reported is the total amount collected over the entire study period: 2 weeks in the summer of 2010. The distribution of HgP between fine and coarse size fractions is similar at both sites. However, Appledore Island has about 40% more total HgP than Thompson Farm especially in the sea-salt region of the size distribution. This is attributed to the halogen chemistry in the MBL that leads to RGHg production that then leads to more HgP. It is worth noting that in this study, total HgP recorded for one week in summer 2009 was double (4.10 pg/m³) what it had been the previous week (2.05 pg/m³) when it was stormy (Feddersen et al, 2012).

**Table 3.5:** Size distribution of HgP at Appledore Island a marine site and Thompson farm a coastal site during summer 2010. There are similar distributions of HgP at both sites but Appledore Island exhibits twice as much total HgP. These results reflect the total amount of HgP collected over the entire study period (2 weeks) (Feddersen et al., 2012)

<table>
<thead>
<tr>
<th></th>
<th>Appledore Island (marine site)</th>
<th>Thompson Farm (coastal site)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine (&lt;2.5 µm)</td>
<td>30%</td>
<td>28%</td>
</tr>
<tr>
<td>Coarse (&gt;2.5 µm)</td>
<td>50%</td>
<td>47%</td>
</tr>
<tr>
<td>Total HgP concentration (ng/m³)</td>
<td>126.6</td>
<td>50.4</td>
</tr>
</tbody>
</table>

Therefore such processes could explain the HgP values recorded in Bermuda. In addition, given the high solubility of RGHg and HgP, in the event of rain they would be scavenged from the atmosphere contributing to the wet deposition flux.

Finally, the impact of long-range transport cannot be discounted. While RGHg and HgP have short atmospheric residence times, Hg⁰ is a more long-lived species and inert species that can be in the atmosphere for up to a year (Lin and Pehkonen, 1999). Studies have demonstrated transport across continents and oceans during so called “pollution...
episodes” (Brunke et al., 2010; Weiss-Penzias et al., 2007). In studies where they have been observed, these pollution events are further characterized using ancillary data such as radon (\(^{222}\text{Rn}\)) and carbon monoxide (CO) measurements. Other species like nitrogen oxides (NOx) and sulfur oxides (SOx) have been shown to reach Bermuda depending on the direction of air-flow with higher levels recorded when air masses arrived from the North Eastern U.S. (Wolff et al., 1988), so it is not implausible that emissions from North America could impact the island. However, in this study there was minimal variation in Hg\(^{0}\) levels and therefore there is no discernible evidence for this having taken place during the study period. A longer-term study is required in order to ascertain whether similar phenomena occur in Bermuda as well as to check for any seasonal trend.

Still, as an example, 3-day back-trajectories of air masses flowing to Bermuda were run for some of the more elevated HgP concentrations. As earlier mentioned, HgP sampling was sectored, the particles on the filter were collected when the wind was blowing from the ocean. The back trajectories were run using the NOAA HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php) at 500m, 1000m and 1500m, which covers the marine boundary layer (MBL). The diagrams generated (Figure 3.7 (a) and (b)) show transport paths mainly from the South East U.S. region. This would suggest that long-range transport of anthropogenic mercury might impact the island. Given that particulate samples were collected over one week it is not possible to further constrain these trajectories.
**Figure 3-7** (A-left panel): Back-trajectory showing air masses from the SE U.S. flowing to Bermuda. Week of 2-9 Jun 2009, HgP conc.: 8.2 pg/m$^3$ (B-right panel) Back-trajectory showing air masses from the SE and mid-west U.S. flowing to Bermuda. Week of 17-26 Jun 2009, HgP conc.: 23.2 pg/m$^3$
3.5 Conclusion

While Hg$^0$ concentrations in Bermuda are not very elevated and are quite similar to open ocean values and those from remote locations, THg concentrations in precipitation and HgP in air values compare well with some North American locations. Since the latter two species are more readily deposited, it presents a risk to the surrounding aquatic ecosystems. Future studies may examine aspects not covered in this study such as: mercury concentrations in different particle size fractions or event-based sampling of precipitation. It is also important to continue programs providing education to consumers especially at-risk groups to ensure they make smart seafood choices. A recent study has shown the impact such interventions can have by demonstrating a 5-fold reduction in Hg in cord-blood from pregnant women in Bermuda following the introduction of fish consumption guidelines (DeWailly et al., 2012)
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4. CONCLUSIONS AND FUTURE WORK

4.1 Importance of mercury deposition in the global mercury cycle

The central goal in this work was to quantify mercury inputs to the two locations studied while identifying the likely sources. The atmosphere is the main contributor of Hg to terrestrial and aquatic environments. Therefore measurements of Hg in the atmosphere provide a reliable estimate of the deposition fluxes in a given area.

While atmospheric deposition is well constrained in the Northern hemisphere after years of measurements, this is not the case for large portions of the Southern hemisphere and remote locations such as Bermuda. The measurements from South Africa add to a small pool of data available for this part of the world. Pacyna and coworkers (2006) placed South Africa second to China in a global mercury emissions inventory by for the year 2000. In this study, estimates were based on collated emissions data from country or international bodies that collected such data and estimates of emissions factors & statistical data on the production of industrial goods and/or consumption of raw materials.

Coal combustion and gold mining were thought to be the major contributors to South African Hg emissions estimated at 256.7 tons (Pacyna, 2006). However, large-scale gold mining operations in South Africa mainly use the MacArthur Forrest process, which uses cyanide instead of mercury amalgamation for extraction (Naicker et al, 2003). There is small-scale artisanal gold mining in some parts of the country. A subsequent desktop study intended to reevaluate Hg emissions in South Africa focused on those from coal combustion. The country is the 3rd largest coal producer in the world and coal accounts for 64% of the energy supply. Coal contains trace amounts of Hg and the amount emitted is a function of: the Hg content of the coal (0.2 ppm), the type and efficiency of control
devices used to reduce gaseous and particulate emissions, and the total amount of coal combusted. From this study, Hg emissions from coal combustion range between 2.6 to 17.6 tonnes per year, with an estimated average emission of 9.8 tonnes per year (Dabrowski et al., 2008). Coal combustion is a major contributor to atmospheric Hg emissions in South Africa (Leaner et al., 2009). Still, in the absence of data large uncertainties are inherent in these estimates. As such, the measurements of THg in precipitation at Cape Point and Pretoria are important because they provide a reasonable projection of the extent of mercury deposition in South Africa. The THg concentrations in rain and bulk deposition fluxes at Cape Point are 10.6 ng/L and 166.3 ng/m²/wk and 15.8 ng/L and 385.6 ng/m²/wk at Pretoria. The associations between trace metals and Hg at both Pretoria and Cape Point are also important. In Pretoria, they point to a strong anthropogenic influence. But at Cape Point, different atmospheric processes are at play. These values are similar in range to measurements made in other locations with similar characteristics around the world. It is likely that mercury deposited finds it’s way into aquatic systems posing a risk to biota, wildlife and human health in fishing areas. Mercury measurements in South Africa’s rivers show the presence of contamination in the water column, sediments and biota. For instance, the THg concentrations in rivers across the country range from detection limit (0.02 ng/L) to 26.65 ng/L (Walters et al., 2011).

The nature of atmospheric Hg transport and fate in the environment means that its presence is detected in areas far removed from anthropogenic activities. As a remote island, Bermuda is a unique living laboratory when it comes to studying environmental contamination. Elevated Hg concentrations in fish and in the cord blood of post-partum
mothers are proof of the contamination of the surrounding ecosystem. Hg⁰ measurements on the island range between 1.06 to 1.63 ng/m³, the average concentration of HgP measurements is 12.4 pg/m³ and the volume weighted average THg concentration in rain is 4.7 ng/L. The wet deposition flux in Bermuda is 138.07 ng/m²/wk. While the Hg⁰ concentrations are similar to the open-ocean, the HgP and precipitation concentrations are similar to levels in areas with greater anthropogenic impacts.

Overall the results from these locations provide reliable estimates for mercury inputs in areas where there was a paucity of data. Further, they demonstrate the presence of atmospheric processes that may enhance the deposition of RGHg and HgP that are yet to be elucidated.

4.2 Sources of mercury to deposition and the human impact.

Anthropogenic emissions of Hg to the environment have increased 3 fold since pre-industrial times. This is due to the escalation of human activities intended to propel economic growth such as fossil fuel burning for electricity production & transportation, industry and more recently artisanal gold mining. Still, these characterizations are broad and it is often difficult to pinpoint the sources in a particular region. However, looking for associations between Hg and other trace elements in the atmosphere has proven to be a useful tool. For example, generating Pearson’s product moment correlation matrices for Hg and trace metals may reveal a commonality in sources. Some metals such as Al are known to have a crustal source and high temperature processes such as non-ferrous smelting and fossil fuel combustion are known to liberate metals such as Cu, Ni and Pb (Herrera et al., 2009). Additionally, Hg⁰ concentrations in air correlate with other trace
gases. For example, observations of depletion events (DE) in the arctic have shown a rapid fall in concentrations of both Hg\(^0\) and O\(_3\) that ultimately results in the production of RGHg.

Statistical tools help identify relationships that point to specific industries that have a major impact on the environment as well as chemical reactions that produce readily deposited forms of Hg. Atmospheric models such as the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) (www.arl.noaa.gov/HYSPLIT.php) model are also useful in tracing the origin of air masses. In the South African study for example, this model was used to generate back-trajectories over a number of hours in an effort to show the travel pattern of air masses that found their way to Cape Point just before a rain event.

4.3 Overall conclusion

Although reliable estimates of Hg deposition at these locations have been determined, some aspects of the atmospheric processes that drive the oxidation of Hg\(^0\) are still not well understood. Although atmospheric oxidants such as bromine, chlorine or hydroxyl radicals oxidize Hg0 to produce RGHg, the chemical reactions in the South Africa and Bermuda are yet to be elucidated. Although Hg\(^0\) depletion events have been observed at Cape Point, unlike the arctic there is no correlation between Hg\(^0\) and other trace gases such as O\(_3\). Further, these depletion events are embedded in different kinds of air masses, from background marine air to polluted continental air (Brunke et al., 2010).

In Bermuda, the concentrations of Hg\(^0\) are similar to those in the open ocean, but the concentrations of HgP and THg in rain are an indication of the presence of RGHg in
the atmosphere. This is a short-lived atmospheric species that is likely produced in the Marine Boundary Layer (MBL) and mediated by photochemical reactions with a high potential for deposition. Field observations have already documented the diurnal cycle of RGHg, which concentrations exhibit a peak at midday followed by a decline in the afternoon and evening hours. Modelling by Holmes and coworkers (2009) suggests that dry deposition alone cannot account for this decline and that a substantial amount of Hg(II) in the MBL is take up by sea-salt aerosols. It is therefore important to investigate these processes further because understanding will enhance knowledge of the global mercury cycle at a fundamental level.

4.4 Scientific gaps and future work.

The results from this work highlighted some knowledge gaps that can be filled through further work in this area. Continuous monitoring of Hg (i.e. in air, waterways and sediments) in all the locations is necessary in order to mitigate the risks posed by Hg contamination identified in the environment. It is important to introduce or continue with public health education programs aimed at ensuring people make safe seafood choices. Such public health interventions have already made gains in Bermuda. Additionally, continuous monitoring could also include other trace metals especially if high throughput analytical tools such as ICP-MS are available.

Event based sampling should be explored. Although weekly sampling provides useful information, identifying sources is more challenging when samples are collected over a long time period. Tools such as back-trajectories generated using the HYSPLIT model
are likely to be more accurate when the period under consideration spans a few hours as opposed to a number of days.

The role of particles could be further investigated through measurements of Hg in different particle size fractions. Such studies also have the potential to be included in other programs concerned with the effects of atmospheric particulate matter on human health. Atmospheric processes governing certain phenomenon such as depletion events in non-polar zones could also be investigated through lab studies.

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