Gaseous Oxidised Mercury Compounds Captured by Membrane Technologies at Two Australian Sites

Dan Sawyer

Supervised by Grant Edwards

A thesis submitted to Macquarie University

for the degree of Masters of Research

Department of Environmental Science

October 10th 2016

Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

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Dan Sawyer

Acknowledgements

Firstly to my family who have supported me throughout this project. I am very thankful for them and their encouragement to me throughout long and tiring days of thesis work.

Thanks to Mae Gustin and her lab at UNR for analysis of CEM and Nylon filters for GOM and speciation data, and also for partially funding this research. Thanks to Matthieu Miller at UNR for assistance with UNR active system commissioning.

Thanks to Macquarie University Engineering and Technical Services for fabrication of various brackets for supporting my experimental setup. Thanks to Dr. Kaushal Tewari for helping every fortnight with filter changes. Thanks to Katrina Macsween and David Safari for helping when Kaushal wasn't available.

Thanks also to Etienne Cheynet, for designing the Matlab wind rose plot template used in this experiment.

Thanks to Grant Edwards for being a tremendous supervisor and being patient with my sometimes slow progress, and for always being willing to talk through experimental issues.

And most of all, thanks to God for sustaining me through the entire process, and for creating all things, including mercury.

Abstract

Mercury (Hg) is a significant environmental pollutant, due its detrimental effects on both humans and ecosystems. The atmosphere is the largest natural pathway for global mercury distribution, and so understanding atmospheric mercury transport is of primary importance. Both the physical and chemical properties of gaseous oxidised mercury (GOM) in the atmosphere are poorly understood.

Nylon and cation-exchange membranes have recently been pioneered as measurement tools for GOM. This study measured GOM using nylon and cation-exchange membranes at 2 sites in South Eastern Australia. One site, the Macquarie University campus, is located within an urban and industrial zone. The other, Cape Grim, is a rural site located far from urban or industrial environments. The ambient concentrations of GOM were analysed at both sites, and speciation data was analysed at Cape Grim. Values from both sites were examined for correlations with a variety of meteorological conditions.

Higher average concentrations were observed at the Macquarie University site (20.2pg m^{-3}, σ=5.4) than at Cape Grim (15.7pg m^{-3}, σ=4.7) (P = 00348). A possible negative correlation was observed at both sites with relative humidity, in line with previous observations. Initial GOM speciation at Cape Grim using nylon membranes indicated the presence of $Hg(NO_3)_2$ and $Hg(SO)_4$, with little evidence of $HgCl_2$, $HgBr_2$ or HgO.

Contents

1. Introduction

Mercury is a heavy metal, with an atomic number of 80. It is the only metal that remains a liquid in standard conditions (0℃ and 100 kPa). Mercury also has a comparatively high vapour pressure (0.17 Pa at 20℃) and a relatively high density (13.55 g/ml at 20℃) (CRC 2007). Mercury is a significant environmental pollutant, due its detrimental effects on both humans and the environment (Mergler et al 2007). Mercury is present throughout a variety of the environmental regions of the planet, particularly in the oceans and soils. Although the atmosphere contains relatively low concentrations of mercury compared to these larger reservoirs, it remains a significant medium for rapid global mercury transportation, and is the largest natural pathway for mercury distribution (Gustin et al 2015).

Mercury may damage the central nervous system in humans if exposure occurs. Mercury is particularly potent when it undergoes methylation to form methylmercury. This persistent bioaccumulative toxic chemical passes up the food chain when it enters an aquatic environment. Aquatic organisms that have absorbed substantial quantities of methylmercury may then be consumed by humans. This is the primary pathway of human exposure to mercury (Huang et al. 2014). Methylmercury causes a variety of developmental and reproductive disorders in high doses (Clarkson and Megos, 2006), and has also been linked to cardiovascular issues in adults (Mozaffarian et al. 2011).

Of particular concern is how the atmosphere may transport mercury far from emission sources, where it may eventually deposit to form methylmercury. The effect of meteorological conditions in transporting and depositing mercury is thus a significant area for research. It is the effects of meteorological parameters on both elemental and oxidised gaseous mercury transport which is examined in this report.

2. Literature Review

2.1. Atmospheric Mercury Fundamentals

Atmospheric mercury is typically split into three forms: gaseous elemental mercury (GEM), and two divalent Hg(II) forms: gaseous oxidised mercury (GOM) and particulate bound mercury (PHg). GEM is the elemental form of mercury, and is the most prevalent species in the atmosphere, with estimates suggesting that around 98% of atmospheric mercury consists of GEM (McClure et al. 2014). This figure has been challenged, however, by new research providing a figure closer to 75%, and suggesting the previous inaccuracies have been due to poor measurement techniques (Gustin et al. 2015). PHg consists of mercury bound to particles usually smaller than 2.5µm diameter. Similarly to GOM, PHg is very difficult to measure due to its complex physical and chemical properties. GOM and PHg concentrations are often combined under the term reactive mercury (RM), where RM = GOM + PHg (Rutter and Schauer 2007). The term reactive gaseous mercury (RGM) may also be used elsewhere to describe GOM individually. Due to possible confusion from differences in terms, GOM in this report refers to gaseous oxidised mercury compounds of the form HgX_2. Total gaseous mercury (TGM) is defined as GEM + GOM + PHg. Atmospheric concentrations of speciated mercury are often in the order of ng m^{-3} and pg m^{-3}, providing a serious challenge for researchers designing methods for sampling these compounds.

Unlike most other metals, which exist in the atmosphere in the solid phase bound to aerosols, atmospheric mercury exists primarily in the vapour phase (Schroeder and Munthe 1998). Atmospheric mercury also has a high residence time in the atmosphere, approximately 1 year in the form of GEM. This is due to its relative inertness to other atmospheric chemicals, and its low solubility in atmospheric water vapour (Schroeder and Munthe 1998). These factors allow mercury to potentially be transported throughout the globe from an emission source.

A number of previous studies have strengthened this theory. These studies have provided scientific evidence linking anthropogenic emissions of mercury from industrial sources with

heightened concentrations in remote locations around the globe (Lindberg et al. 2007). Using cores sampled primarily from lake sediments, a threefold increase in mercury deposition rates from the atmosphere is believed to have occurred since pre-industrial times (Lamborg et al. 2002). This has been supported by more recent data from tree rings (Wright et al. 2014a).

2.2. Emission

Mercury is emitted to the atmosphere both from natural and anthropogenic sources, and the atmosphere is the central pathway for its global distribution (Edwards & Howard 2013). Natural sources include volcanic eruptions, bushfires, water bodies, soils and vegetation. Anthropogenic sources consist of mine-waste, sewerage, coal-fired power plants, artisanal gold mining, cement production and landfill (Gustin, 2003, UNEP 2013).

Recent estimates have suggested that approximately 10% of global emissions annually are from natural sources, 30% from anthropogenic emissions, and 60% from reemission of previously released and deposited mercury (Amos et al. 2013). This re-emission process of deposited mercury provides a complicating factor in identifying the original point of emission of the majority of airborne mercury (Schroeder and Munthe 1998).

Mercury may be emitted as GEM, GOM, PHg, or organic forms (such as methylmercury) (Nelson et al. 2012). GEM is emitted from both natural and anthropogenic sources. The majority of all natural emissions are in the form of GEM (Mason et al. 2008). GOM compounds are emitted primarily from anthropogenic sources (Pirrone et al. 2013). PHg makes up a small fraction of natural inputs to atmospheric mercury, due to its emission from volcanic eruption or natural particulate matter entering the atmosphere (Mason et al. 2008). The remaining fraction of PHg is emitted from anthropogenic sources (Pirrone et al. 2013).

2.3. Atmospheric Transport

The global background concentration of TGM has previously been estimated in the range of 1-4 ng m^{-3} (Lin and Pehkonen 1999). Later estimates for the Northern Hemisphere narrowed this range to around 1.7 ng m^{-3} (Kim et al. 2005). Compared to the Northern Hemisphere, our knowledge of atmospheric mercury distribution in the Southern Hemisphere is significantly smaller (Slemr et al. 2011). A recent comparison of Southern Hemisphere measurement sites for background TGM concentration has estimated a range of 0.85 – 1.05 ng m^{-3} (Slemr et al.

2015). Mason 2008 concluded an average concentration in the remote atmosphere of 1-2.5 ng m^{-3}, with higher concentrations in emissions-impacted areas.

Based on previous interpretations of emission and concentration records in the Northern Hemisphere, TGM concentrations appear to have increased between 1977, when the first measurements were conducted, until the late 1980s, when a maximum occurred. Concentrations then decreased until 1996, before stabilising at a constant level (Lindberg et al. 2007). Those authors, however, noted strong uncertainties and assumptions in these estimates, and concluded a null hypothesis (TGM levels have remained relatively stable) was equally likely. More recent measurements have shown a decreasing trend across both hemispheres since the mid 1990s (Slemr et al. 2011). This data suggests that the global burden of atmospheric mercury has decreased since 1995 by 30%.

GEM is the form of atmospheric mercury that is most readily transported great distances from its point of emission (Pirrone et al. 2013) and has been shown to be transported up tens of thousands of kilometres in the atmosphere (Nguyen et al. 2010). Measured atmospheric concentrations of GEM vary considerably depending on proximity to emission sources and atmospheric transport, however the process of measuring GEM concentrations has shown to be reliable (Huang and Gustin, 2015a). Previous estimates of background GEM concentrations for the Southern Hemisphere are around 1.3 ng m^{-3}, and for the Northern Hemisphere around 1.7 ng m^{-3} (Temme et al. 2003). Higher concentrations of TGM and GEM in the Northern Hemisphere have been attributed to the higher rates of anthropogenic emissions (Pacyna et al. 2006, Slemr et al. 2011).

The atmospheric lifespan of GOM is much shorter than GEM due to its higher reactivity. GOM compounds can be removed fairly readily from the atmosphere within only a few hundred kilometres of the source (Nguyen et al. 2010). While in the atmosphere, GEM may undergo various physical and chemical transformations, and through these processes may be oxidised to form GOM (Gustin, 2003). This relationship was previously observed during mercury depletion events occurring in the Arctic spring at sunrise. TGM concentrations were observed to rapidly plummet as solar radiation caused GEM to be transformed to GOM before subsequently being deposited (Schroeder et al. 1998, Steffen et al. 2014). Thus atmospheric GOM values may be higher than those resulting from emissions alone.

Observations of seasonal variations in GEM and diurnal cycling of GOM have shown that photochemical reactions are responsible for the oxidation of GEM (Laurier and Mason, 2007, Selin et al. 2007). These photochemical reactions have been observed to occur under high solar intensity, and in the presence of a variety of oxidising compounds (Engle et al. 2008). Observations have shown increasing GOM concentrations with altitude (Selin et al. 2007), and aircraft measurements have shown high levels of oxidised mercury in the lower stratosphere (Murphy et al. 2006).

GOM levels in the marine boundary layer have been shown to follow a diurnal pattern, with peaks around midday and deposition during the night (Laurier and Mason, 2007). The hydroxyl molecule was believed to play a role in this process, but the process has now been shown to result from photochemical reactions with bromine (Holmes et al. 2009). These reactions result in the elevated midday concentrations, and scavenging of GOM at night into aerosols of sea salt such as $HgCl_4^{2-}$ and $HgCl_3^{-}$ leads to the rapid afternoon decline. Both relative humidity and solar radiation have been shown control the diurnal cycle of GOM concentrations (Soerensen et al. 2010). Solar radiation levels exceeding 200W m^{-2} have been correlated with an increase in GOM levels (Peleg et al. 2015). GOM oxidation is believed to occur in the upper troposphere and lower stratosphere, as both depletion of GEM and an enrichment in both GOM and PHg have been observed (Murphy et al. 2006, Slemr et al. 2009).

An issue which remains a significant area of research in atmospheric speciated mercury is the chemical identification of GOM compounds. It was first hypothesized in 1974 that the chemical forms of GOM may consist mercury halides and HgO (Johnson and Braman, 1974). This suggestion remains a common hypothesis (Jones et al. 2016). Bromine, as well as other halogen species, has previously been identified as a potential oxidant of GEM, due to its presence in arctic ozone depletion events (Steffen et al. 2008). Bromine and other halogens have also been linked to GEM oxidation in the free troposphere (Holmes et al. 2006) and the marine boundary layer (Laurier et al. 2003). Field studies and modelling have also put forward ozone (O_3), nitrogen dioxide (NO_2) and the hydroxyl (OH) radical as potential GEM oxidants (Angot et al. 2014). GOM and PHg exist in a temperature dependent equilibrium (Rutter and Schaurer, 2007). Increasing temperature leads to increased PHg partitioning to GOM. This relationship is also seen during increased levels of particulate matter.

It is known that the chemical composition of GOM compounds varies with both location and season (Gustin et al. 2012, Huang et al. 2013). The physical and chemical properties of GOM

are dependant both on the individual compounds present, and the relative abundance of these compounds in a particular location (Rutter and Schauer, 2007). GOM concentrations have also been shown to be affected by water vapour and ozone, leading to measurements with a low bias (Huang et al. 2015). The challenge of measuring GOM compounds is further increased by the inherent "stickiness" of GOM, and its ability to attach to a wide variety of surfaces, including the inner surfaces of instruments designed to measure it (Gustin et al 2015).

Despite the fact that our understanding of the speciation and oxidisation pathways of mercury in the atmosphere remains limited, some chemical species of GOM compounds have recently been confirmed (Huang and Gustin, 2015a). Thermal desorption profiles of mercury have recently been used, utilising high-purity permeation tubes and nylon membranes (Gustin et al. 2015, Huang et al. 2015), to enable the potential identification of GOM species. A series of gaseous neutral GOM complexes have been identified: $HgBr_2$, $HgSO_4$, $Hg(NO_3)_2$, $HgCl_2$ and HgO (Huang and Gustin, 2015a). GOM emissions from coal combustion are thought to be primarily in the form of $HgCL_2$ (Galbreath and Zygarlicke 2000), due to chlorination with emitted $HCl_{(g)}$.

A more recent investigation using a similar method, utilising a cryofocuser, gas chromatograph, and a mass spectrometer to separate mercury halides, has provided another set of compounds (Jones et al. 2016). This experiment identified $HgBr_2$, $HgCl_2$, however it was not able to unequivocally observe mass spectra from HgO or $Hg(NO_3)_2$.

2.4. Deposition

Atmospheric mercury is deposited from the atmosphere by both wet and dry deposition processes. Under wet deposition processes, mercury is primarily removed as GOM rather than GEM, due to GOM having both a lower vapour pressure and higher solubility (Lin and Pehkonen 1999, Huang and Gustin 2015a). This allows GOM to be more readily precipitated from the atmosphere in wet deposition. The primary pathway for removal of GEM from the atmosphere is its oxidation to GOM and subsequent removal (Mason et al. 2008).

Mercury levels in precipitation have been estimated within the range of 5-100 ng l^{-1} (Lin and Pehkonen 1999). Mercury in the form of PHg is believed to be mostly insoluble, and thus is unlikely to settle by wet deposition (Pirrone et al. 2013). The size of the particles determines the atmospheric lifespan of PHg, and its atmospheric residence time is typically fewer than 10 days (Schroeder and Munthe, 1998).

Dry deposition rates of mercury are governed by three primary factors: atmospheric turbulent diffusive transport, diffusive transport through the near-laminar ground surface atmospheric sub-layer, and the rate of uptake by the surface (Poissant et al. 2004). Each of the three main forms of atmospheric mercury has its own rate of dry deposition. Dry deposition velocity (V_d) is a value often used to relate the concentration with the mass flux density of the chemical species to the surface, and represents the rate of aerosol particles depositing onto a surface (Zhang et al. 2009). GEM was previously considered unlikely to deposit in dry conditions due to its relative inertness (Poissant et al. 2004), however it has been shown to deposit at high rates in some conditions (Lindberg et al. 2007). Active uptake by vegetation has been found to be an important means of GEM deposition, and over vegetated surfaces, the V_d of GEM has been observed in the range of 0.1-0.4 cm s^{-1} (Zhang et al. 2009)

Measured dry deposition rates of GOM currently have large uncertainties (Zhang et al. 2009), however all measurements show a relatively high rate of deposition. Current estimates are from 0.19±0.42 cm s^{-1} (Zhang et al. 2005) to around 5 cm s^{-1} (Lindberg and Stratton, 1998, Skov et al. 2006). GOM has also been shown to deposit at higher rates over snow and forest canopies than over grassland (Skov et al. 2006). Diurnal variations observed in GOM deposition have been attributed to variations in surface turbulence (Poissant et al. 2004). Dry deposition of PHg has been observed to be slower than GOM, but at a higher rate than GEM (Poissant et al. 2004). Measured PHg deposition rates have large variation, with observed V_d values ranging from 0.02 (Zhang et al. 2005) to 2.1 cm s^{-1} (Poissant et al. 2004).

2.5. Atmospheric Mercury Measurement Techniques

The standard practice for measurement of atmospheric speciated mercury is either atomic absorption spectroscopy (AAS) or atomic fluorescence spectroscopy (AFS). These processes utilize the strong absorption line of mercury at 253.65nm in order to determine atmospheric concentrations. This process cannot be done directly in real time, however, due to the ambient concentrations of mercury being too small for detection. Rather, mercury is deposited over a sampling period onto an absorption plate, usually made of gold, until concentrations reach adequate levels for spectroscopy. It has been determined, however, that under some conditions, gold absorption plates may become passivated and ineffective in collecting mercury (Huang et al. 2014). Thermal desorption is then used to remove the sampled mercury from the absorption plate, and the desorption process has the effect of

converting both GOM and PHg into GEM due to the high temperatures. Concentrations observed using this process, therefore, will be the total gaseous mercury (TGM), or in the case of PHg being present, the total atmospheric mercury (TAM).

Measurement techniques for atmospheric speciated mercury can be divided into passive and active sampling methods. Passive samplers naturally absorb mercury due to their physical and chemical properties, and include both natural and artificial systems. Active sampling methods use automated systems to selectively sample mercury in the atmosphere.

2.6. History of Atmospheric Mercury Measurement

Work on identifying and understanding mercury species in the atmosphere began to increase in the early 1970s, with a small wave of research attempting to fractionally determine the quantities of a variety of mercury species, as well as beginning to investigate mercury fluxes. Braman and Johnson in 1974 used sequential, selective absorption tubes to separate mercury species, and a spectral emission detector tuned to the 253.65nm mercury emission line to determine concentrations. Takizawa et al. in 1981 pioneered an early method for determining mercury species in the atmosphere using a variety of simple methods available at the time (Takizawa et al. 1981).

Brosset 1982 observed high levels of mercury deposition in Scandinavia. The concentration decreased with increasing latitude, and appeared to result from mercury having been transported from Central Europe. He suggested that the presence of divalent mercury species could explain this trend. Brosset went on to observe that these divalent compounds appeared to be of anthropogenic origin, and are readily removed from the atmosphere in precipitation (Brosset & Iverfeldt 1989).

Since then, researchers have been working to determine the identities, concentrations and physical and chemical processes of the mercury species present in the atmosphere. The arrival of cold vapour atomic fluorescence spectroscopy (CVAFS) was rapidly utilized as a potential method for measuring mercury species in the atmosphere. Bloom and Fitzgerald utilized this technique to determine concentrations of gaseous mercury at the pg m^{-3} level (Bloom & Fitzgerald 1988). CVAFS also gave rise to the Tekran 2537 Mercury Vapour Analyser system in 1993. The Tekran provided a fast, automated method for measuring atmospheric mercury. The Tekran system samples air and collects GEM onto gold cartridges. The GEM is then desorbed and analysed using CVAFS. The Tekran 2537 is one of the

instruments utilised in this project, and its operation will be examined later in this report. The use of CVAFS revealed that mercury emitted from coal-fired power plants and public waste contained a far greater fraction of GOM than previously estimated (Prestbo & Bloom 1995).

This knowledge led to a push for an effective method for measuring concentrations of atmospheric GOM. The results of this push were three research groups, each of which produced a potential method for measuring atmospheric GOM (Landis et al. 2002). Refluxing mist chambers were the first methodology (Lindberg & Stratton 1998). These chambers had previously been utilized to scrub soluble gases from the air. This process operates by aspiring sample air into the mist chamber, and allowing the water-soluble GOM to be absorbed by the nebulised mist. These droplets coalesce onto a hydrophobic membrane, before draining into the chamber (Lindberg and Stratton 1998). This method has proven relatively successful and continues to be utilized at present (Gustin et al. 2015).

The second methodology was the use of potassium chloride (KCl)-coated tubular denuders (Xiao et al. 1997). Prior laboratory tests had shown that KCl denuders have a high average efficiency of absorbing GOM (~98%) and that GEM is able to pass through freely. The technique involves creating a glass tube (denuder) with a high collection efficiency for internal gas flow. The denuder is then soaked in a KCl solution, producing a coating of KCl crystals on its surface. As the sample air passes through the denuder, the volatile GOM compounds are absorbed onto the KCl surface, while the GEM passes through and is absorbed on a subsequent gold trap (Xiao et al. 1997).

This denuder technique has evolved to become a widely used technique, particularly due to its commercialisation in the Tekran 1130/1135 system. This system absorbs GOM on KCl denuders in a similar way to that previously mentioned. The collected GOM is then thermally desorbed and measured as GEM using a Tekran 2537 (Gustin et al. 2013). This instrument is unable to determine the individual species of GOM compounds present, as the desorption process to GEM results in the chemical identity of GOM being lost (Deeds et al. 2015). Recent research (Gustin et al. 2013, Huang et al. 2013) has suggested that denuders are unable to effectively absorb GOM, and so underestimate concentrations. It has been suggested that since GOM is composed of a variety of chemical compounds, denuders may not have the correct chemistry to effectively collect all compounds (Huang et al. 2013). Further it has been

suggested that GOM may decompose during the sampling process and be wrongly analysed as GEM (Lyman et al. 2010b). This is an area of ongoing research.

The third technique suggested for measuring atmospheric GOM was to use ion-exchange membranes placed behind quartz particulate filters (Ebinghaus et al. 1999). Ion exchange membranes have for over a century been utilized for their effectiveness in atmospheric gas measurement (Dasgupta et al. 1986). Researchers pumped sample air through ion-exchange membranes at a high flow rate ($\sim$9-10L min^{-1}), which was shown to be effective in collecting GOM. The quartz filters were used to collect particulate mercury and other particulates. The membranes were then refluxed with an oxidizing acid solution, and reduced with stannous chloride solution, before being analysed using CVAFS (Ebinghaus et al. 1999).

Ion-exchange membranes remain in use, and have been recently shown to be more effective in collecting atmospheric GOM compounds than the KCl denuders (Gustin et al. 2013). This technique has been recently redesigned by the University of Nevada Reno (UNR), into the UNR Active System for Measuring GOM. This system utilizes ion-exchange membranes, as well as nylon membranes, which have more recently been hypothesized to be effective in collecting GOM (Gustin et al. 2015).   An adaptation of the UNR system is utilised for this project, and a description of its operation can be found later in this report.

2.7. Mercury in Australia

The Australian continent is the second driest following Antarctica, with the majority of the landmass covered by arid to semi-arid climates. Despite this, Australia has a wide range of climate zones, ranging from equatorial and tropical to grassland, temperate and small alpine areas. Australia's climatic conditions are affected by the El Niño Southern Oscillation, which can result in large variations in temperature and precipitation from year to year.

Data on Mercury emission in Australia remains limited, with a recent report collating data to form an inventory of Australia's natural sources (Nelson et al. 2009). Researchers have estimated the total natural mercury emissions in Australia to be anywhere from 117 to 567 tonnes each year (Nelson et al. 2004). The majority of Australia's emissions are from natural sources, with only 15 tonnes attributed to anthropogenic sources in 2006, which represents approximately 7% of the total (Nelson et al. 2012). Australia's background TGM concentration is similar to the global average, around 1.1-1.3 ng m^{-3} (Nelson et al. 2009).

Australia's anthropogenic emissions increased two-fold between 1990 and 1995, and remained relatively stable between 1995 and 2000 (Pacyna et al. 2006). According to the Australian National Pollutant Inventory (NPI), Australia's total anthropogenic mercury emissions have been steadily increasing from 2010/2011 to 2014/2015, rising from 9800 to 11000 kg year $^{-1}$. Anthropogenic mercury emissions in Australia have previously been reported to be largely due to three key sectors: gold production (49.7%), coal fired power plants (14.8%) and production of aluminium from bauxite (12.2%) (Nelson et al. 2009). Little data is available on mercury content in petroleum, with no reported measurements performed on Australian emissions (Nelson et al. 2012). Estimates of total GOM emissions in Australia are 5.5 tonnes (Nelson et al. 2012). The majority of these emissions are split between industrial sources (2.4t) and fires (3t).

2.8. Recent GOM observations

GOM concentrations have been shown to be highly influenced by the diurnal cycle, with elevated concentrations (up to 97 pg m^{-3}) observed around midday (Engle et al. 2008). High solar intensity and subsequent high ozone concentrations are strongly correlated with peaks in GOM, as these factors result in the oxidation of GEM (Engle et al. 2008). Other chemical compounds linked to GOM formation are atmospheric oxidants, particularly OH$^{\cdot}$, and halogen radicals including Br$^{\cdot}$ (Calvert and Lindberg. 2003). The same authors of those observations subsequently noted that the presence of iodine-containing compounds may enhance the rate of oxidization and subsequent deposition of gaseous mercury (Calvert and Lindberg 2004). Peaks in GOM have also been strongly correlated with peaks in atmospheric SO_2, during periods of high O_3 concentrations and high solar intensity (Engle et al. 2008).

Global and regional models are used to estimate GOM concentrations. Models are generally accurate in predicting GEM concentrations within 30% of observations, but modeled and experimental GOM concentrations often vary by a factor of 2-10 (Zhang et al. 2012). Models predict high GOM concentrations around point sources in both air and precipitation, however concentrations in remote areas are observed to be similar to those in close proximity to point sources (Kos et al. 2013). These discrepancies are believed to be due to uncertainties in mercury species present, in measurement techniques and in rates of emission (Kos et al. 2013).

Several oceanographic voyages have previously measured GOM concentrations (Laurier et al 2003; Laurier and Mason, 2007) including one in the Southern Hemisphere (Temme et al 2003). A 2003 experiment measuring GEM and GOM using a Tekran 2537A/1130 system at the Cheeka Peak Observatory on the north-western tip of the USA (Weiss-Penzias et al. 2003). The experiment compared mercury concentrations in air masses from continental origin with those in air from the marine boundary layer. Polluted air of continental origin was observed on average to contain 5.3% lower GEM than marine air, likely due to GEM oxidisation. This process is likely to occur as continental air masses passed over the volatile organic compound (VOC)-producing eastern Washington forests, which may contribute to GOM and O_3 formation (Gustin et al. 2015). GOM concentrations were observed to be strongly dependent on wind direction, with significantly higher values observed during easterly winds. This relationship supports the hypothesis that GEM from westerly-moving continental air was oxidised to form GOM, and thus higher GOM concentrations from that direction were observed.

A ten year record of GOM concentrations, as well as GEM and PHg, has been measured from 2002 to 2012 in Alert, Canada (Steffen et al. 2014). Mercury concentrations were determined using the Tekran 2537A/1130/1135 system. During spring, GOM concentrations were observed to rise significantly, with a mean concentration of 55.14pg m^{-3}. This is compared with an annual median concentration of 3.16pg m^{-3}. Such high concentrations in spring are due to atmospheric mercury depletion events (AMDEs), which occur in conditions below 0°C. GEM is rapidly oxidised to RGM and depleted from the atmosphere. As these values were taken using the Tekran 1130 system, known to underestimate GOM concentrations, the actual values may be significantly higher.

A two-year record of atmospheric GOM concentrations for the Southern Hemisphere has recently been produced for the first time from a measurement station on Amsterdam Island, a small island in the southern Indian Ocean (Angot et al 2014). Measurements were taken using a Tekran 2537B/1130/1135 system. Measured GOM values from this experiment were at the low end of those recorded from ship voyages, with a mean concentration of 0.34 pg m-3. Slightly higher concentrations were
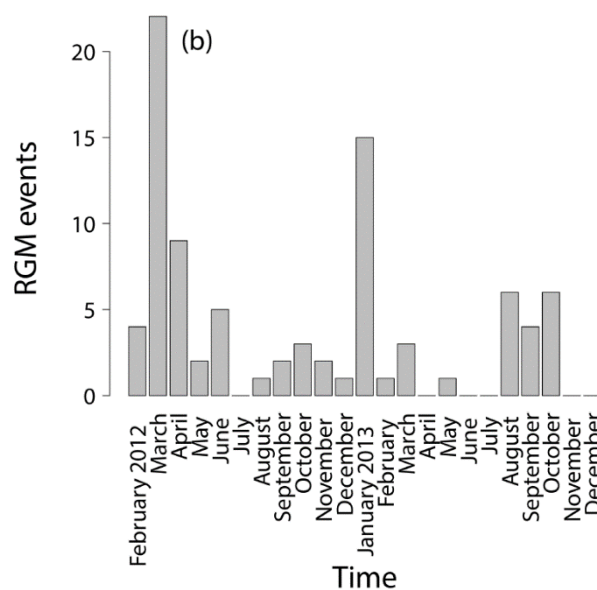
Figure 1 – An annual time series of GOM (RGM) events recorded using a Tekran 1130 at Amsterdam Island. From *Angot et al.* 2014

observed in summer compared to winter, which the authors attributed to enhanced photochemical reactions occurring in the summer months. The number of GOM events (events being defined as values 3.3 times above the instrumental detection limit) were observed to be low in June-July for both years, with annual peaks around January to March. A smaller peak period for both years was observed between August and October. GOM values during late spring in November and December were consistently at a minimum. This is compared to peak spring GOM in regions experiencing AMDEs, and shows the strong influence these depletion events have on GOM concentrations. Values observed in that experiment are seen in Figure 1.

The Amsterdam Island experiment also observed no correlation between GOM concentrations and any meteorological parameters. This is possibly attributed to the fact that few GOM measurement (3%) were above the quantification limit (Angot et al. 2014). The low values recorded at the site may have resulted from the frequent precipitation in the local climate, which potentially scavenges GOM from the atmosphere before it can be measured (Angot et al. 2014). Significantly, no anticorrelation been GEM and GOM concentrations was observed in this experiment. Such a relationship would be evidence towards the atmospheric oxidation of GEM to GOM. More recent experiments have possibly observed this relationship (Weiss-Penzias et al. 2015).

The Reno atmospheric mercury intercomparison experiment (RAMIX) was run from August 22 to September 16, 2012, and demonstrated the underestimation of GOM concentrations by the Tekran 1130 system. This experiment tested several developing techniques for measuring GOM, including the University of Washington Detector for Oxidized Hg Species (DOHGS). This instrument, designed for airborne measurements, concurrently measures TAM and GEM, and calculates TAM - GEM for an approximation of GOM+PHg.

UNR Method

The UNR system is a recently developed setup designed to both measure GOM concentrations in ambient air and identify individual GOM compounds (Gustin et al. 2015). The system collects GOM using both nylon and cation-exchange membranes. Nylon membranes have historically been used for measuring nitric acid (HNO_3) (Appel et al. 1981). As HNO_3 can be used as a surrogate for GOM (Marsik et al. 2007), it was hypothesized and subsequently proven that they may be effective in collecting GOM (Gustin et al. 2015). The system is

currently limited to a temporal resolution of two weeks due to the potential for GOM to be lost. As a surrogate surface, cation-exchange membranes are known to only collect GOM (Lyman et al. 2009). It has been speculated that these membranes may collect PHg as well as GOM, however recent research suggests this is not the case (Matthieu Miller, Personal Communication).

In the UNR system, cation-exchange membranes are used to determine the concentration of GOM, and nylon membranes are desorbed to identify individual compounds. Cation-exchange membranes are not able to determine GOM speciation in this way, as they can only be analysed by wet digestion (Huang et al. 2013). Binding to the surface of nylon membranes is caused by electrostatic interaction, due to the dominance of hydrogen bonds. It has been suggested based on the polarizability of mercury, that this electrostatic force strongly contributes to the ability of nylon to collect GOM (Huang et al. 2013). Experimental tests using $HgBr_2$, HgO and $HgCl_2$ showed nylon membranes were able to capture all three compounds with similar efficiency (Huang et al. 2013). A further experiment testing GOM discharge by desorption showed release beginning at 75°C, with peaks at 105°C for HgO and at 115°C for both $HgBr_2$ and $HgCl_2$. Desorption profiles for each compound were then observed to extend to around 190°C. Based on these results, it is thought that GOM compounds emitted from nylon membranes will be desorbed at temperatures ranging from 50°C to 200°C.

A recently published experiment measured GOM concentrations in Florida, USA, over a 12 month period using cation-exchange and nylon membranes as per the UNR method, as well as a Tekran 2537/ 1130/1135 system (Huang et al. 2015). The annual mean GOM concentration
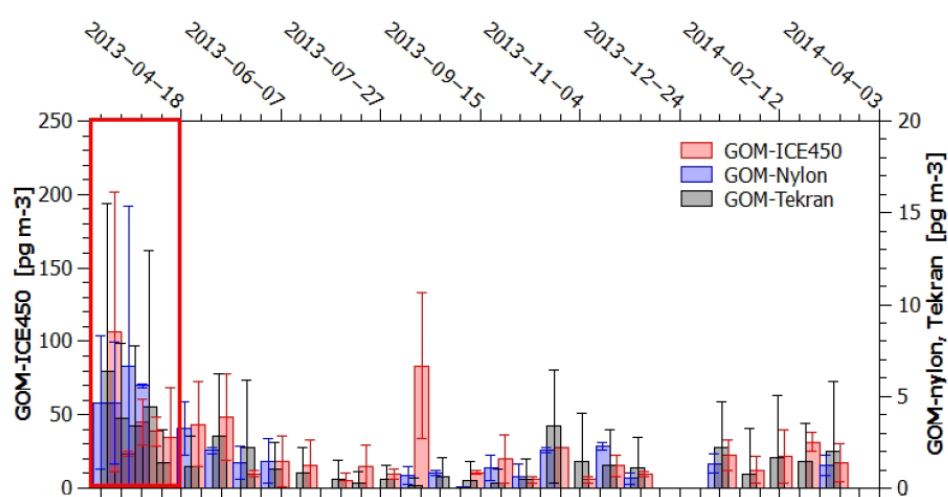
Figure 2 – GOM measurements from cation-exchange (ICE450), Nylon membranes and the Tekran 1130 system. From *Huang et al.* 2015

observed in ambient air was 2-7pg m^{-3}. GOM measured in that experiment is seen in Figure 2. The highest GOM concentrations were observed during the spring, which correlated to peak mean ozone concentrations. GOM values were relatively low in summer and autumn. It is

unlikely that AMDEs affect this subtropical region, but the high relative humidity likely results in reduced GOM concentrations, particularly in summer. Concurrently, high relative humidity has also been shown to facilitate GOM collection by cation-exchange membranes, and reduce GOM collection on nylon membranes. Although previous experiments have also suggested that the marine boundary layer is not a significant source of GOM (Engle et al. 2008), evidence from this experiment suggested this layer may be a source of gaseous mercury. The sources of GOM measured at the Florida site were determined to likely be from oxidation of local GEM, and emissions from fossil fuel combustion.

A significant area of present research is the lack of calibration for most GOM measurement techniques (Gustin et al. 2015). Calibration processes are difficult to implement, due to the characteristics of GOM to stick to a range of surfaces, and also its tendency to decompose to GEM (Jaffe et al. 2014). A lack of calibration techniques leaves GOM measurements invalidated, and restricts attempts to quantify uncertainties or place strong confidence in results.

2.9. Research Aims

This experiment aims to provide some of the first GOM measurements in the relatively unmeasured Australian continent, using this newly developed membrane technique. As well as providing valuable GOM data, the experiment also aims to compare GOM concentrations between the rural Cape Grim and urban Macquarie University sites, and examine correlations with meteorological conditions, air pollutants, and GEM.

It is hypothesized that GOM concentrations will be higher at Macquarie University, due to the greater number of sources of both GOM, and GEM for oxidation, in this urban setting. Similarly to the results of Angot et al. 2014, it is not expected that correlations with meteorological conditions will be seen, other than the previously observed correlation with relative humidity. An inverse relationship with GEM is expected to be observed if GEM oxidation is the primary source of GOM at either site.

3. Research Methods

3.1. Field Site Descriptions

The Macquarie University site (33°46' S, 151°7' E) in Sydney, Australia, is located adjacent to the University campus on the grounds of a large sports field complex. The site has been run as an automatic weather station (AWS) since 1998, and measures temperature, pressure, relative humidity, wind speed and direction, solar radiation and soil temperature. The site is located within the urbanized and commercial suburb of Macquarie Park, and is bordered by bushland to the northeast. The Sydney basin has a temperate climate, with comparatively low seasonal variation, due to moderation by the adjacent ocean. The basin is influenced by sea breezes, and boundary layer trapping of pollutants in winter may occur for extended durations of time. A previous experiment measuring TGM occurred at Macquarie University in December 2007 using a Tekran 2537a (Nelson et al. 2009). Concentrations observed during that period varied between 1.1 - 1.3 ng m^{-3}.


Figure 3 - TGM concentrations measured at Macquarie University in 2007 - from Nelson et al. 2009

The observations of that experiment are seen in Figure 3.

The Cape Grim Baseline Air Pollution Station (40°41' S, 144°41' E) has been running since 1976, as part of the Global Atmospheric Watch (GAW) baseline monitoring program run by the World Meteorological Organization (WMO). The station is located on the north-western tip of Tasmania, Australia. The measuring site sits on a cliff 94m above the beach, and is bordered by ocean to the west. The site is surrounded immediately on the remaining borders by productive farmland. The station measures meteorological parameters including temperature, wind speed and direction, air pressure, precipitation, humidity, solar radiation and aerosol concentrations. The site also conducts measurements of atmospheric gases such as CO_2, CH_4, O_3, N_2O, chlorofluorocarbons (CFCs), nitrogen oxides and radon. As well as these gases, GEM is sampled in 15 minute averages using a Tekran 2537A Mercury Vapor Analyser.

Tasmania is classified as having a temperate and marine climate (ACE CRC 2010) and sits near the northern limit of the belt of westerly winds dominating the mid-latitudes of the Southern Hemisphere (Grose et al. 2013). The island is thus dominated by prevailing westerly winds blowing from the Southern Ocean.
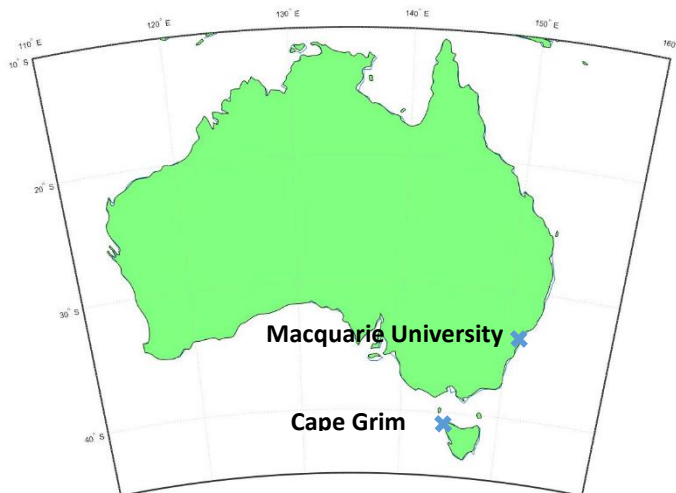
Figure 4 – Experimental Site Locations

Although eastern Tasmania experiences a relatively stable climate throughout the year, the west coast is highly variable (ACE CRC 2010). Mean annual rainfall for Cape Grim is in the 1000-1200mm bracket (Grose et al. 2013). The climate of Tasmania is strongly influenced by the Southern Annular Mode (SAM) (ACE CRC 2010). From November 2015 to April 2016, the SAM index was positive, which is often correlated with stable, dry conditions as the mid-latitude westerly belt contracts poleward.

The site experiences baseline conditions for 30-40% of the year (Cainey et al. 2007). The baseline conditions at this site are defined as those with a wind direction at an altitude of 50m between 190 and 280°, and that meet a cloud condensation nuclei (CCN) concentration number that varies according to season. This baseline air flows from the Southern Ocean and has little to no interaction with land masses before reaching the site.

Potential Sources of Mercury at Each Site

The nearest coal fired power generation plants to the Macquarie University site are the Vales Point Station located 78km to the NNE, and the Erraring Station located 86km to the NNE. The Vales Point station has been noted as a significant source of atmospheric mercury, a significant source being one emitting over 100kg per year (Nelson. et al. 2012). Due to the distance from the Macquarie University site, it is unlikely GOM from either of these plants reaches the site before being deposited. Other significant sources identified within 100km of the Macquarie University site are the Illawarra and Corrimal Coke plants, located to the SSE 55km and 69km respectively. Both plants subsequently closed in 2013, so emissions at present are likely to be substantially lower from the remaining coal dust at these sites.

Of note are two crematoriums located 3.7 and 4.6km SE of the site. Crematoriums are likely emission sources due to the cremation of bodies containing mercury amalgam dental fillings. Previous studies have shown approximately 31% of mercury emissions from crematoriums are in the form of oxidised mercury, with that value dependent on the gas composition (Takaoka et al. 2010). Emissions from soil and vegetation in Australia have been shown not to contain GOM, so any mercury emitted from the nearby bushland is likely to be GEM (Nelson et al. 2012).

According to the definition by Nelson 2012, there are no significant sources of atmospheric mercury located in Tasmania. The latest NPI database lists only one source emitting over 1kg year^{-1} within 100km of the Cape Grim site, an open cut magnetite mine located 61km to the ESE. The NPI reports total mercury emissions rates for this site are 6.8kg year^{-1}. With such a low emission of TAM at a large distance from the site, if any emission of GOM occurs is may be considered unlikely to reach Cape Grim. The possibility of GOM reaching Cape Grim from this site is further reduced due to the strong westerly winds that dominate the region. The absence of point sources of any mercury species around the site makes it an ideal location to study both atmospheric transport and oxidization of GEM, as it is unlikely that any significant direct emissions of GOM reach the site.

3.2. Sampling Methods

GOM was measured on the Macquarie University site using triplicate polysulfone cation-exchange membranes (ICE450, Pall Corp., MI, USA) and nylon membranes (0.45μm Sartorius Stedim), set up in similar design to the UNR Method. This setup is referred to as the

Macquarie University Active Reactive Mercury System. Observations begun on March 21 2016, and continue until August 8.

The membranes were housed within a 6 port sampling system, each port with duplicate in-line membranes to determine GOM breakthrough. In addition a single blank for each type of membrane was deployed, each stored in an acid clean jar for the duration of the sampling period. Thus 14 membranes in total were used for each active sampling period. Ports 1-3 contained cation-exchange membranes, and ports 4-6 contained nylon membranes.

Air was sampled at a height of 3.25 meters, with an in-line Wizit Dongdo dry gas meter on each port to measure the total volume. Flow measurements were also taken from the input line using a TSI 4100 Mass Flowmeter. Each set of membranes was sampled for a two week period. After collection, the membranes were stored in sterile tubes within a Ziploc® bag, at a temperature of -22°C. The samples were then shipped to the University of Nevada Reno (UNR) laboratory in the USA for analysis, in a thermally isolated cooler. Cation-exchange membranes were digested and analyzed according to EPA Method 1631E at UNR labs. Nylon membranes underwent thermal desorption before being analyzed using EPA method 1631E.

Nylon membranes are known to underestimate ambient GOM concentrations (Huang and Gustin, 2015a), and Huang et al. 2013 showed cation-exchange membranes measure concentrations 1.1-3.7 times higher than those from nylon membranes. Research is ongoing to quantify and understand the mass balance between CEM and nylon membranes through collaboration between UNR and Macquarie University (Grant Edwards, personal communication). As nylon membranes may not capture all the GOM, and their purpose is to identify compounds of GOM present, more research is needed to evaluate the effectiveness of nylon membranes.

The Cape Grim GOM measurements were conducted in the same manner, using comparable equipment, and equivalent sampling and examination procedures. Although Cape Grim data is used for this project, the bi-weekly experimental procedure was not carried out as part of this project, but by other personnel working at the site. The Cape Grim experiment began monitoring on November 3 2015, and data for this experiment continues until the sampling period ending on June 29. Nylon membranes were analysed to produce speciation data for three bi-weekly sampling periods beginning on March 23 and finishing on May 3. Due to the lack of GOM calibration, the membrane systems at both sites were not calibrated.

GOM concentrations observed in the blank for each period were subtracted from concentrations observed in each membrane. The mercury amounts on the two in-line filters for each port were added to obtain a total concentration for the port, and then the mean of the three CEM ports for each sampling period was taken to find an average GOM concentration for that period.

Mercury Speciation

Mercury speciation was determined using the nylon membranes shipped to the UNR laboratory. Nylon membranes are known to have a higher collection efficiency for a variety of GOM compounds compared with cation-exchange membranes (Gustin et al. 2015). The membranes were thermally desorbed, with the temperature gradually increasing from 50 to 200°C at 5°C increments, in line with previous experiments (Huang et al. 2013, Huang et al. 2015). The amount of mercury released at each increment was determined using a Tekran 2537a Mercury Vapor Analyser. The desorption curves generated were then compared with those seen by Huang et al. 2013, and are used to discern the species of GOM present at the site.

Tekran 2537 System

For the majority of the Cape Grim experimental duration, and for a portion of the Macquarie University experiment, a Tekran 2537 was set up alongside the GOM experiment. It is unknown whether the 2537 standalone unit measures GEM or TGM (Gustin et al. 2015). The unit at Macquarie University ran with a Teflon filter at the inlet, and 5 m of Teflon sampling line to the filter at the Tekran sample line intake. The Cape Grim unit was operated with a PTFE (Teflon) at the inlet and 30 m of heated Teflon sample line into the filter at the back of the Tekran 2537. It has been suggested that sampling trains of this design essentially remove most GOM and that the 2537 is essentially measuring GEM. While this was not tested it is assumed for this reason that the Tekran 2537 units at both sites were measuring GEM. Slemr et al., 2015 suggested that the difference measured between TGM and GEM at sites such as Cape Grim will be less than 1%.

The 2537 inputs air samples and collects GEM onto dual gold cartridges. Mercury readily amalgamates with gold, which provides an effective method of pre-concentration before analysis (Schroeder and Munthe 1998). After a five minute sampling period for each cartridge, the gold traps are thermally desorbed, and the GEM is quantified using Cold Vapour

Atomic Fluorescence Spectroscopy, and measured in ng m^{-3}. As one cartridge undergoes desorption and analysis, the second cartridge collects GEM, allowing for continual analysis. Once setup, the Tekran is able to operate continually, although regular maintenance and checks are required. The 2537A has a detection limit of 0.5 ng m^{-3} in ambient air (Gustin et al. 2015).

3.3. Other Site Details

Criteria meteorological and air pollutant data were concurrently measured for each site, although for Macquarie University this data was not collected directly onsite. Due to technical difficulties with the Macquarie University AWS, continuous meteorological data for the Macquarie University site was obtained from the Australian Bureau of Meteorology (BOM) Weather Observation Station in Terrey Hills. Daily values of each meteorological parameter at 9am and 3pm were averaged for a daily mean, and sets of daily means were averaged for each bi-weekly sampling period. Global shortwave radiation values, however, were taken where available from the on-site AWS, due to the lack of data from nearby locations. This radiation data was sampled by a Kipp and Zonen CNR1 Net Radiometer and collected using a Campbell Scientific CR23x Datalogger.

Air pollutant data for the Macquarie University site was taken from the NSW Office of the Environment and Heritage (OEH) monitoring station in Lindfield (33°45'58" S, 151°09'00") located 3.2km to the South East, at an elevation of 60m. This site continuously monitors O_3, NO_x, PM_{10} and SO_2. Data for CO was taken from the (OEH) station in Rozelle, located 12km SSE at an elevation of 22m, due to CO not being measured at Lindfield.

Meteorological data for Cape Grim was taken from the onsite monitoring station, providing an ideal data series to analyse correlations.

4. Results and Discussion

4.1. Initial comments on Observations and Main Graphs

Due to delays at the UNR labs, not all nylon membranes were processed before the deadline for this experiment. Thus GOM speciation from nylon membranes is only available for three bi-weekly sampling periods at Cape Grim. GOM desorption peaks observed from these sampling periods correlated strongly to standard peaks associated with $HgSO_4$ and $Hg(NO_3)_2$, indicating the likely presence of these compounds in GOM at Cape Grim.

Cation-exchange membrane blanks at Macquarie University recorded a median concentration of 0.02 pg m^{-3}, with a slightly higher value of 0.05 pg m^{-3} at Cape Grim. Observed breakthrough for cation-exchange membranes varied between 0-73% at the Macquarie University site, with a median breakthrough of 20.8% and mean of 26.7% (σ=19.6). Cation-exchange membrane breakthrough for Cape Grim was slightly lower, varying from 0-46% with median 21.5% and mean 23.8% (σ=15.4). As would be expected, increased GOM concentration over the sampling period will result in greater breakthrough. R^2 values of this relationship were 0.39 for Macquarie University, and 0.21 for Cape Grim. Increased breakthrough may be caused by individual high GOM events during the sampling period. Events of this kind have previously been observed (Angot et al. 2014). It is also possible, however, that increased ambient concentration results in higher breakthrough. Breakthrough can also occur due to a filter tear or filter holder sealing issues.
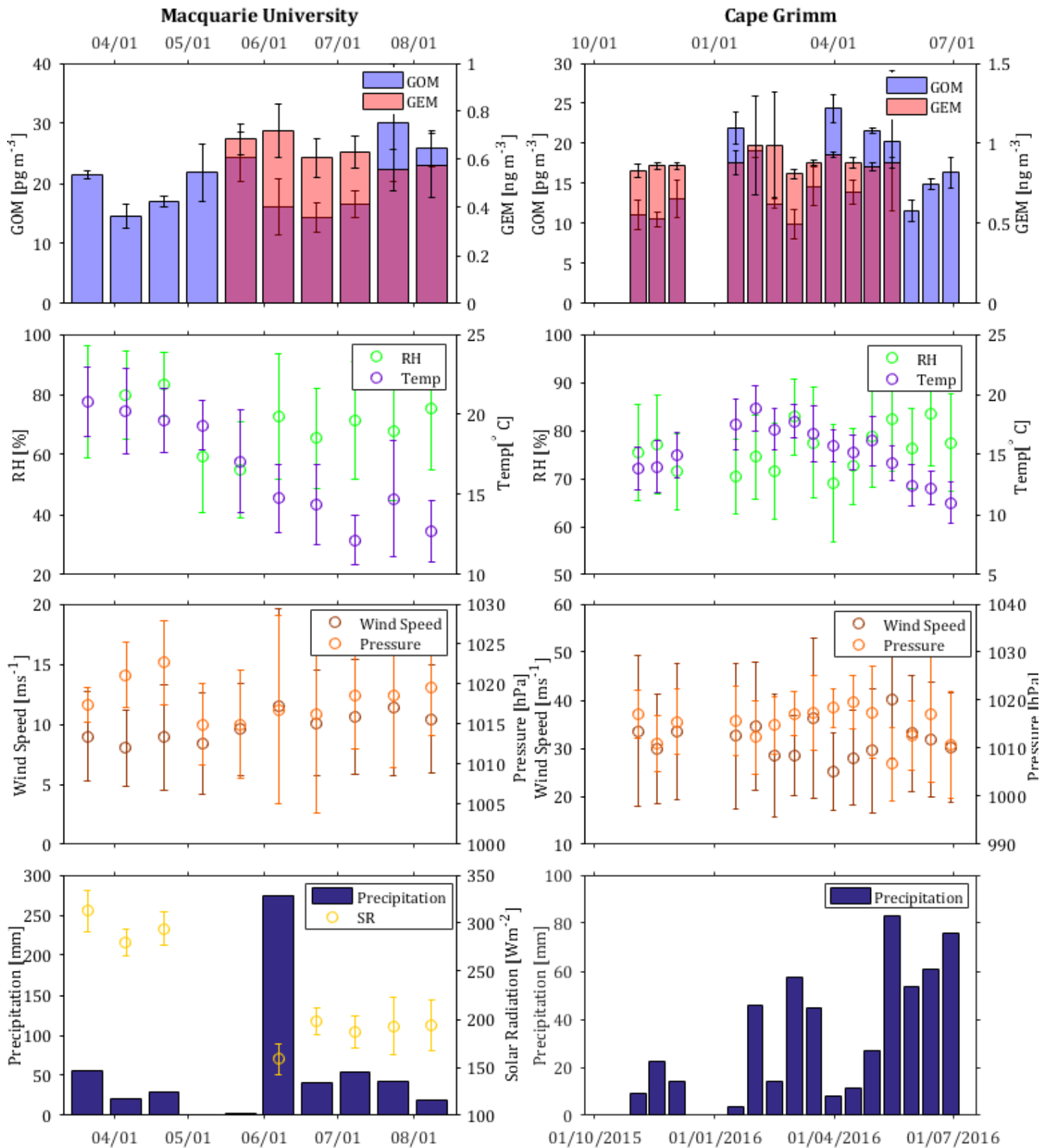
Figure 5 – Temporal variation of mercury species and meteorological conditions throughout the experimental periods for both Macquarie University and Cape Grim. Data points are an average for each by-weekly sampling period. The left column shows data from Macquarie University, and the right column from Cape Grim

GOM concentrations observed from the cation-exchange membranes and nylon membranes available for each site are shown in Figure 5. Each figure also shows a concurrent mean of relative humidity, temperature, wind speed, pressure and precipitation for each site. Solar radiation data available only at Macquarie University is also shown.

An annual data series was not able to be collected at either site due to time constraints. Due to the observations from previous experiments, it should be expected that GOM values are lower in winter months, during periods of lower solar radiation and lower ozone concentration. Previous Southern Hemisphere measurements follow this trend of peak GOM concentrations in the summer.

GOM concentrations at the Macquarie University site varied from 14-30pg m^{-3} over the period of April to August, with relatively high inter-sample variation (σ=5.4pg m^{-3}). Similar high variation using cation-exchange membranes has previously been observed (Huang et al. 2015). An increase in mean GOM over time was observed throughout the experimental duration (m [slope of regression] = 0.05, r^2=0.16). This trend is influenced by two strong peaks during the sampling periods ending May 30 and July 25, hence the low r^2 value. A downward trend was likely to be expected moving from warmer to cooler months, due to lower solar radiation and thus lower oxidation. Since this relationship between radiation and GOM is known (Lin and Perkonen, 1999), other factors must be explored to understand this observation.

Cape Grim mean concentrations varied between 10-24 pg m^{-3} over the period of November to June. The site also showed relatively high inter-sample variation (σ=5.0pg m^{-3}). Although strongly fluctuating, a slight upward trend in concentrations was observed between November and March (m=0.05, r^2=0.22). This trend is similar to that observed by Angot et al. in 2012, with peak annual RGM events observed in March. From April to June the concentration was observed to follow a slight although negligible downward trend (m=-0.03, r^2=0.05). Due to events at the site, GOM data was not collected from Cape Grim between December 29 2015 and January 12 2016.

Although Cape Grim measurements are during the likely elevated period of GOM values in spring to autumn, the range of concentrations observed were lower than those seen in autumn to winter at Macquarie University, when conditions are likely to be lowest for the year (P=0.0348). Although an annual data series is required to draw conclusions, it is likely

that the mean annual GOM concentration at Macquarie University is higher than at Cape Grim. This may be due to a greater number of local sources of both GEM and GOM at the Macquarie University site, and higher pollutant concentrations in the Sydney area, providing oxidants for GEM. Macquarie University also experiences higher incoming solar radiation due to its lower latitude, another catalyst to increase the photochemical reactions which produce GOM.

4.2. Meteorological Influences on GOM

Meteorological Parameter	Macquarie University Correlation (r^2 value)	Cape Grim Correlation (r^2 value)
Relative Humidity	0.12	0.46
Temperature	0.02	0.05
Wind Speed	0.08	0.00
Pressure	0.03	0.00
Precipitation	0.09	0.00

Table 1 – Correlations observed between GOM and meteorological conditions at both Macquarie University and Cape Grim

Due to the temperature dependent equilibrium of GOM and PHg, it is possible that reduced ambient temperatures may result in lower GOM concentrations as a greater percentage of reactive mercury is partitioned into GEM (Rutter and Schauer, 2007). Such a correlation would be difficult to discern, due to the known relationship between temperature and solar radiation, and the subsequent relationship between solar radiation and GOM. No correlations were observed at either site between ambient GOM concentrations and temperature. Similarly no relationship was observed with pressure, or wind speed. This is similar to previous observations (Angot et al. 2014). R^2 values for each variable are reported in Table 1. Other experiments have also shown an absence of correlation between GOM and wind speed (Peleg et al. 2015). No correlation was observed with solar radiation, however data was unavailable during the GOM peak recorded in May. This lack of correlations with meteorological parameters is similar to that observed by Angot et al. 2014, and is possibly due to the relatively slow rate of accumulation of GOM on surfaces. It is possible that this relatively long accumulation time results in meteorological phenomena being unable to affect GOM deposition, due to the relatively quick changing of weather conditionsresults

Wind Direction and GOM

A significant aim for the project was to compare GOM concentrations measured at each site with the prevailing wind for each sampling period. This would provide valuable information on the possible origin of GOM being measured, and help to reveal any possible natural or anthropogenic sources of GOM at each site.

Winds at the Macquarie University site were generally from the westerly direction. The sampling periods ending May 30 and July 27, when two significant GOM peaks were observed, both experienced prevailing winds around 293°. The period ending June 30, however, with prevailing winds at 303°, experienced the lowest mean GOM concentrations of 14.3 ng m^{-3}. According to the NPI database, there are no sources of gaseous mercury emitting over 0.2kg per year within 100km from this direction. A single source from this directional origin located 94km away in Lithgow emits 0.12kg/year, however due to both distance and rate of emission, it is unlikely that this source has any influence on concentrations at Macquarie University. A single sampling period experienced prevailing winds from an easterly direction, the period ending April 18, with winds at 100°. GOM concentrations during this period were 14.4 ng m^{-3}, which is close to the lowest value observed. It is possible that greater quantities of marine air were experienced during this period, due to the coastal boundary to the east of the site. No sampling period experienced prevailing winds from the SSE, which may have identified potential emissions from the nearby crematoriums.

Previous observations on other locations have shown heightened GOM with prevailing winds blowing from the direction of coal fired power plants (Laurier et al. 2007). Notably this relationship was only seen during wind speeds <2m s^{-1}. No sampling periods at Macquarie University had a mean wind direction originating from the NNE, the direction of the closest coal power plants. Due to the lack of correlation between GOM and winds with directions of continental origin, it cannot be shown that any significant point sources of GOM affect Sydney concentrations.

Prevailing winds at Cape Grim varied more significantly, with winds falling within those defined as baseline conditions for 6 out of 9 sampling periods. The criteria for CCN, however, were met for only a small portion of each sampling period. Prevailing winds during several sampling periods were from the south, and one period experienced prevailing winds from the SSE. It is likely therefore that continental-contaminated air was sampled for the majority of the experimental duration. Examination of wind direction with GOM species, determined from nylon membranes observed at Cape Grim, are discussed later in this report.

The majority of prevailing winds at Cape Grim originated from around 250-260°, consistent with the regional climate. No significant relationship was observed between GOM and wind directions, with concentrations varying between 10.5 and 24.3 pg m^{-3} being observed during 250-260° prevailing winds.

Anomalous GOM Values

Peaks in ambient GOM at the Macquarie University site were observed during the 16-30 May and 11-25 July sampling periods. The first peak is investigated later in the report, and correlates with both a pollution event and anomalously low relative humidity. The second peak from 11-25 July does not correlate with any measured pollutant concentrations, and was not particularly correlated with any meteorological conditions. Average relative humidity for the period was low compared to that recorded by the sampling periods, but not as low as that recorded earlier in the year. This spike is discussed later in regard to possible GEM oxidization.

A pair of spikes was also observed in the Cape Grim GOM data. The first spike, at 22 pg m^{-3}, occurred during the January 12-26 sampling period. This spike was associated with a local pollution event, and will be discussed in detail further in the report. The second peak, recorded during the March 22 to April 5 period, was the highest recorded GOM concentration, at 24 pg m^{-3}. This spike in concentration is similar to that observed by Angot et al. in March-April 2012, which was attributed to heightened phytoplankton activity which led to production of elevated levels of GOM oxidants.

Case Study: Relative Humidity Influences

Nylon membranes have been shown to be influenced by relative humidity (RH) (Huang et al. 2013). GOM recovery from nylon membranes has been shown to decrease with high RH, however increased RH has been shown to enhance collection of GOM on cation-exchange membranes (Huang and Gustin, 2015a). Observations from this experiment, however, appear to show a partial negative correlation between RH and GOM concentrations measured on cation-exchange membranes. This relationship was observed for a period of the Macquarie University data (r^2 = 0.12), and also seen for a period of the Cape Grim data (r^2 = 0.46).

This correlation was highlighted during May 2016 at the Macquarie University site, particularly during the May 15-29 sampling period. Sydney experienced its fifth-driest May

on record, with both precipitation and RH below average. This period coincided with a peak in GOM concentrations, particularly in the second half of May, when conditions became drier. It must also be noted, as will be discussed later, that this peak in GOM concentrations also coincided with a significant fire event.

The relationship at Cape Grim was highlighted by several events, but particularly the sampling period from February 23 to March 8. This period recorded the lowest mean GOM value, at 9.9 pg m^{-3}, and was also associated with a spike in mean RH to 83%. A similar spike of RH (82%) occurring on the sample period ending May 17, however, did not coincide with a concurrent drop in GOM concentrations. It is thus likely that factors other than relative humidity affected GOM concentrations in that case.

A relationship between GOM and RH is to be expected, so this relationship observed at both sites may not be due to an effect of cation-exchange membranes, but the chemical characteristics of GOM. Due to the relatively high solubility and low vapor pressure of GOM, it is likely that periods of high RH lead to increased rates of GOM absorption into water vapor. An increase in RH may also lead to increased wet deposition of GOM from dew or rain, lowering measured concentrations. Observations using a Tekran 1130 system have previously shown a significant decrease in GOM concentrations during dew events (Malcolm and Keeler, 2002). GOM measurements in high humidity environments have shown a seasonal minimum in summer, due to both absorption into water vapour and subsequent wet deposition.

Due to lack of knowledge regarding the identity of GOM compounds in the experimental vicinity and the physiochemical properties of these compounds, particularly the Henry's Law constant, it is difficult to estimate the effects of relative humidity on GOM species. At present the lack of this data prevents a correction for the influence of relative humidity on GOM measurements from being developed. The influence of other meteorological parameters on GOM may also depend on the physiochemical chemicals of the various possible GOM compounds. Thus the likelihood of different GOM compounds being present in each sampling period, similar to observations of Huang et al. 2015, may be responsible for concealing possible correlations between GOM and meteorological parameters.

4.3. Meteorological Influences on GEM

Averaged GEM data from the Tekran 2537 system installed at each site is shown in comparison with meteorological conditions in Figure 5.

GEM data was gathered between November 2015 and May 2016 at Cape Grim, with some data missing due to various issues. A slight although negligible upward trend in GEM concentrations over the sample period was observed (r^2=0.08). GEM observations at Cape Grim in 2012 showed a similar pattern, although with high variability (Slemr et al. 2015). These observations are shown in Figure 6, along with observations at other Southern Hemisphere sites. High inter-month variability was also observed in this study. Of all the Southern Hemisphere locations measured by Slemr et al., Cape Grim was shown to have the largest seasonal variation, around 0.25 ng m^{-3}. A small GEM spike in February observed in that study is similar to observations made here, however exceptional local influences are likely responsible for this value, as discussed later.
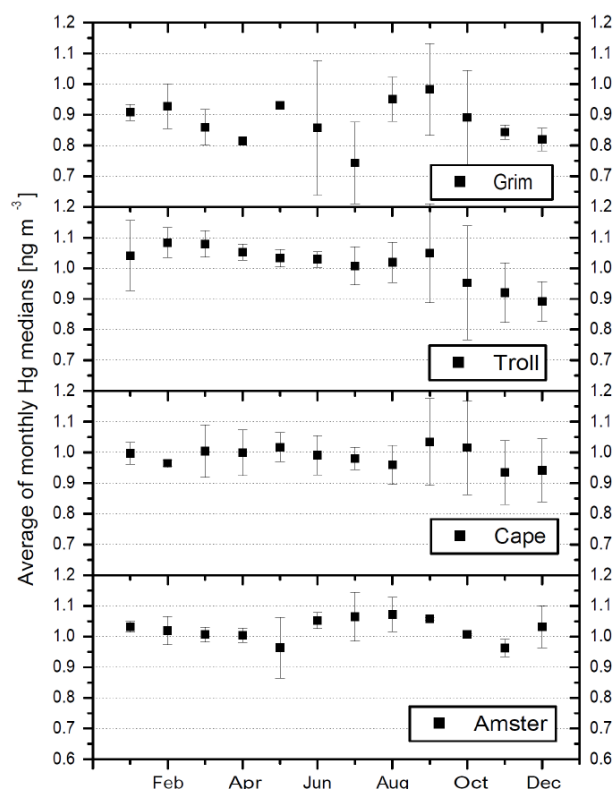
Figure 6 – Observed monthly GEM concentrations for 2012 at several Southern Hemisphere locations. From *Slemr et al.* 2015

GEM values from Macquarie University were available from May to August 2016, again with missing data throughout due to technical difficulties. A downward trend in GEM concentrations over the experimental period was observed (r^2=0.17). This trend possibly reflects a drop in GEM concentrations in Sydney over winter. If the primary source of GEM in Sydney is coal fired power plants, as these plants are the only known significant anthropogenic point sources of mercury in the area, then on this basis GEM values may be expected to rise in winter, due to increased demand for electricity. A lowering suggests either a drop in natural emissions, or the effects of meteorological influences. An examination of possible meteorological factors is discussed below.

Observations at both Macquarie University and Cape Grim showed a diurnal trend in GEM. Concentrations were observed to be higher during the night for both sites. This diurnal cycling was of a greater magnitude at Macquarie University compared to Cape Grim. Average

concentrations for night and day at Cape Grim were 0.88 and 0.84 ng m^{-3} respectively. Night and day values at Macquarie University were 0.69 and 0.58 ng m^{-3} respectively. This nightly peak in GEM is significant, as lower GEM concentrations during the day are possibly indicative of oxidation process occurring, producing GOM. The lack of temporal resolution of cation-exchange and nylon membrane system means this relationship cannot be supported by examining diurnal shifts in GOM concentrations. Also if this relationship is the case, other factors must also be responsible, as if the entire diurnal difference in GEM was due to oxidation, this would results in GOM being produced at far greater concentrations than have been observed. The diurnal cycle has been shown to depend on season (Weiss Penzias et al. 2003). Peak GEM concentrations in summer have been observed around 4am, and peaks in winter around 6pm. This cycle, however, is seen to be highly variable dependent on location (Cole et al. 2014). Changing atmospheric conditions due to the cycling of the diurnal boundary layer depth may also be responsible for this diurnal variation.

Average GEM concentrations for the entire sampling period were 0.64 ng m^{-3} for Macquarie University and 0.86 ng m^{-3} for Cape Grim. Higher average GEM concentrations at the rural Cape Grim is significant, although these values are slightly lower than those observed around the same period at Cape Grim in 2012 with an average concentration around 1 ng m^{-3} (Slemr et al. 2015). Of significance rather is the low average GEM concentrations observed in the urban Macquarie University site. These values are far lower than previous TGM measured at Macquarie University in 2007, when concentrations around 1.1-1.3 ng m^{-3} were observed (Nelson et al. 2009). These reading may be due to the Macquarie University Tekran 2537a not functioning optimally during the experimental period, as a high baseline deviation was observed. This data is still useful, however, for analyzing trends and possible correlations with other parameters.

Peaks in GEM during the sample periods ending February 9 and 23 are likely associated with the pollution events recorded and are discussed below.

Meteorological Parameter	Macquarie University Correlation (r^2 value)	Cape Grim Correlation (r^2 value)
Relative Humidity	0.11	0.24
Temperature	0.00	0.23

Wind Speed	0.06	0.01
Pressure	0.04	0.03
Precipitation	0.39	0.01

Table 2 – Correlations observed between GEM and meteorological conditions at both Macquarie University and Cape Grim

R^2 values for both sites comparing GEM and meteorological parameters are shown in Table 2. GEM concentrations measured at Cape Grim showed no correlation with pressure, wind speed or precipitation. Possible correlations were observed between relative humidity and temperature, although still with low r^2 values. The Macquarie University site showed absent relationships for temperature, and pressure. A slight positive correlation with relative humidity (r^2=0.11) was observed. The relatively high correlation with precipitation is possibly due to a low number of data points.
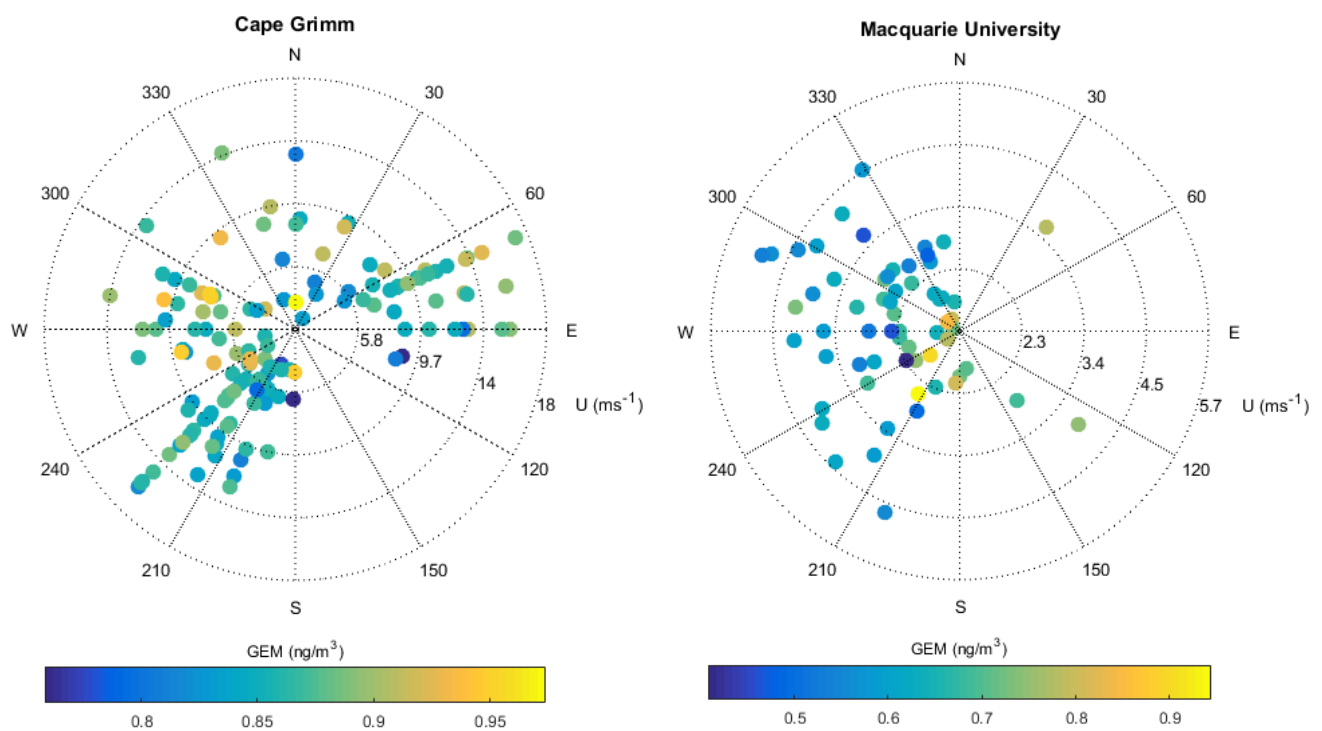
Figure 7 – GEM concentrations plotted against wind speed and direction for Cape Grim and Macquarie University

No strong correlation was observed with wind direction at Cape Grim or Macquarie University, as seen in Figure 7. Although no daily winds were recorded originating from 120-170° at Cape Grim, the lowest GEM concentrations were recorded during winds blowing at the limits of this range. This suggests a possible lower concentration during ESE-SSE winds. Such a correlation is notable as these winds likely originate from mainland Tasmania. It is thus

possible that mainland mercury emissions do not have a large influence on GEM, or are lower than those from other sources. With higher GEM values being recorded during offshore winds from all other directions, the GEM recorded at Cape Grim is potentially due to long range transport from distant emission sources, or local oceanic sources. Thus oceanic air is not expected to reduce GEM concentrations compared with air of Tasmanian origin, which is expected to contain GEM from any local sources.

4.4. Pollutant Influences on GEM and GOM

Temporal profiles of pollutants measured in Sydney throughout the duration of the Macquarie University experiment are seen in Figure 10. Due to unforeseen issues, averages of pollution data from Cape Grim for each sampling period were not available. R^2 values for each pollutant's correlations with GOM are shown in Table 3. The few GEM data points available at Macquarie University prevented any meaningful correlations being revealed.

Pollutant	Macquarie University GOM Correlation (r^2)
PM_{10}	0.00
Ozone	0.01
CO	0.01
NO_2	0.07
SO_2	0.11

**Table 3** - Correlations observed between GOM and pollutants at both Macquarie University

Mean PM_{10} concentrations showed a possible seasonal decrease across the sampling periods at Macquarie University (m=-0.078, r=0.58). Oxidation of GEM may result in increased PHg over GOM in heightened concentrations of particulate matter (Amos et al. 2014). No correlation between GOM and PM10, however, was observed.

Mean ozone concentrations appear to follow a seasonal trend. Ozone concentrations are expected to be lower during the winter months due to decreased incoming solar radiation and thus reduced photochemical production. Throughout the experimental duration, a slight downward trend in ozone was observed entering into winter (m=-0.02, r^2=0.22). As mentioned, elevated ozone levels have been observed to result in increased GOM concentrations. Despite this, ozone concentrations have also been shown to reduce the capturing efficiency of GOM on nylon membranes, due to the possible passivation of the membranes under high ozone (Huang and Gustin, 2015a). It is suspected that ozone does not

play as large a role in GEM oxidization as previously thought, with other experiments observing no apparent relationship between O_3 and GOM (Peleg et al. 2015). No correlation between the two was observed at Macquarie University ($r_2 < 0.01$).

No seasonal variation was observed for SO_2 concentrations and CO concentrations, and neither of these pollutants showed any relationship with GOM. NO_2 showed a slight upward trend moving towards winter (m=0.017, r^2=0.2), and a slight although negligible correlation between NO_2 and GOM was observed (r^2=0.06).

4.5. GOM Desorption Profiles from Nylon Membranes
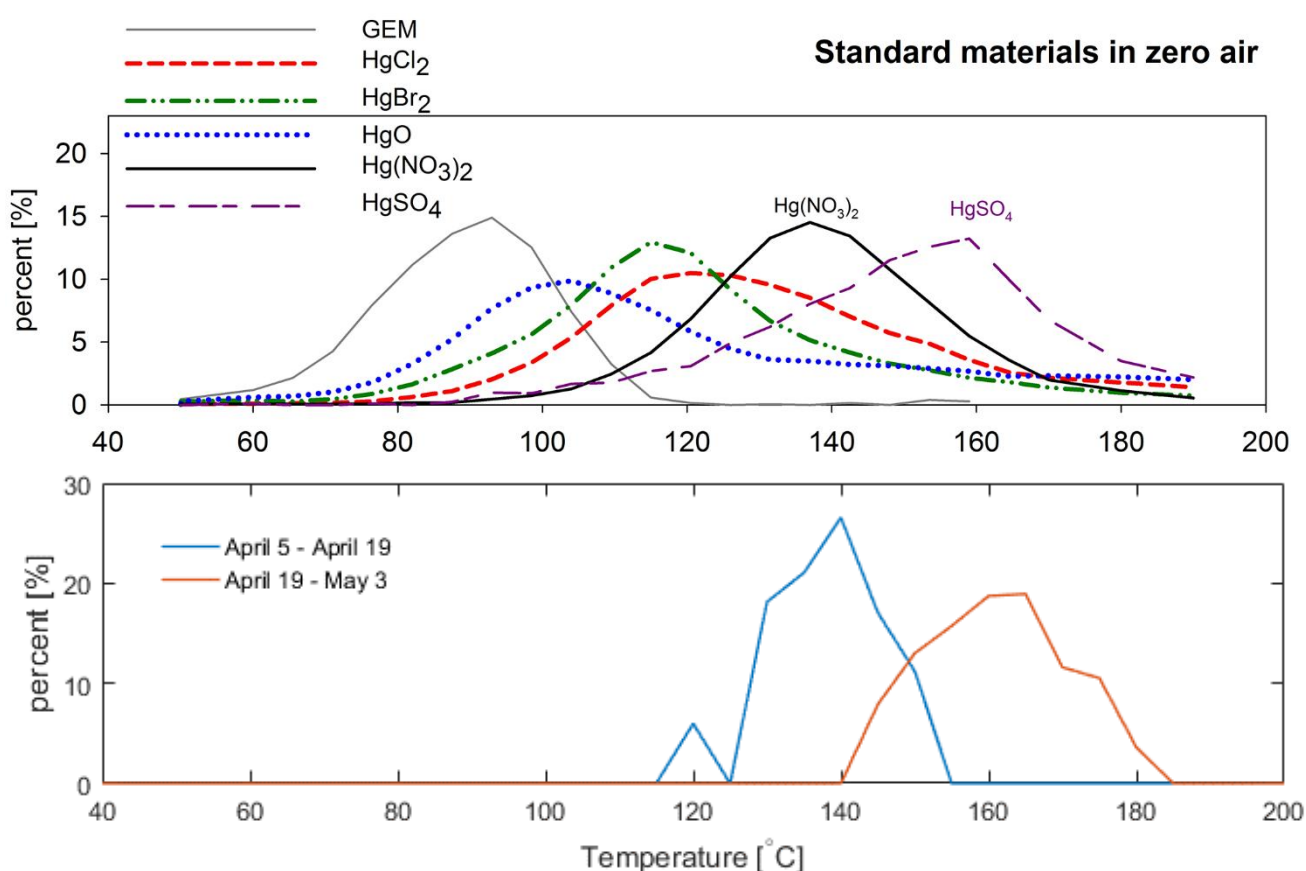
Figure 8 – Standard desorption curves from *Huang et al.* 2013. Plotted underneath are curves obtained from desorption of Cape Grim nylon membranes for two sampling periods

Thermal desorption profiles for both sites can be seen in Figure 8. Plotted above are the standard desorption profiles for a range of oxidised mercury species in the laboratory, obtained by Huang et al. 2013. Profiles were generated for the bi-weekly sampling periods at Cape Grim ending on April 5, April 19 and May 3.

Mercury release was observed from the A-side nylon membranes only. This may be due to nylon membranes greater effectiveness in capturing GOM than cation-exchange membranes, such that little to no GOM is collected on the backup in-line membrane. If this is the case, it is likely that values from the B-side were below the detection limit. One exceptional case occurred when all mercury was observed in the B-side membrane in port 4 of the April 5 sample. Due to physical implausibility of such an occurrence, the likely cause was a labeling error of the primary and backup membranes.

The April 5 samples showed no correlation between the three ports, and so have not been extensively analysed. It is possible that an error occurred in collecting or processing the GOM from these membranes, however no definite cause for these results has been found. Both the April 19 and May 3 samples showed agreement between the membranes of each port, and these are analysed in further detail. Average GOM concentrations measured during these periods by cation-exchange membranes for April 19 and May 3 were 13.9 (σ=1.48) and 21.6 pg m^{-3} (σ=0.32) respectively.

The April 19 sampling period showed a peak at 145°C from all three ports, peaks at 135 °C, 140 °C and 150 °C from two ports, and peaks at 120°C and 155°C for one port. A significantly different desorption profile was observed from the May 3 samples. Triple correlated peaks were observed at 155 °C, 160 °C and 165 °C, with double correlated peaks at 145 °C, 150 °C, 170 °C, 175 °C and 180 °C. A peak at 140°C was observed from one port. The strong variability between adjacent sampling periods is similar to previous observations (Huang et al. 2015).

Comparing each of these curves with the standard desorption curves, several possible species may be identified. The April 19 samples have a strong peak at 140°C, the peak desorption temperature for $Hg(NO_3)_2$. This peak was not observed in any of the samples analysed by Huang et al. 2015. 5% of mercury was released at 120°C, indicating the possible presence of $HgCl_2$ or $HgBr_2$.

The May 5 sampling period values peaked at 160-165°C, with 38% of mercury released between these two temperatures. 160°C is the peak release temperature of $HgSO_4$, and this peak indicates its possible presence. The expected downward trend above 160°C is interrupted by a slight increase in the negative gradient at 175°C, indicating a possible unknown species desorbing at this temperature. A similar result was observed by Huang et al. 2015, observing both a strong residual tail above 160°C, and peaks around 170°C. The

slight residual tail of the desorption profiles of all compounds to around 190℃ seen by Huang et al. 2013 was not observed in the April 19 profile, however this may have contributed to the tail seen in the May 5 profile. Laboratory profiles show the amount of GOM released in each tail is only a minor percentage of the total GOM for each compound. Thus these values may have been beyond the sensitivity of the instrument used in this experiment

$HgBr_2$ and $HgCl_2$ are likely to be found in marine air masses, whereas continental air masses may be expected to contain HgO, $HgSO_4$, $Hg(NO_3)_2$ and other like compounds (Gustin et al. 2015). The connection of these compounds with continental air is due to their association with agriculture (especially $Hg(NO_3)_2$ and $HgSO_4$), industry and point sources (Gustin et al. 2015). Cape Grim is a low NO_x and VOC environment (Cainey et al. 2007). The lack of $HgBr_2$ and $HgCl_2$ is indicative of a lack of marine air masses being observed during the sampling periods. This is confirmed when baseline conditions are taken into consideration. The April 19 samples experienced baseline conditions for 34% of the sampling period, and the May 3 samples experienced these conditions for 20% of the time. With neither sample experiencing even a majority of marine air, it is likely that the majority of sampled air from both analysed periods is continental in origin, or at least impacted to some degree by continental mercury sources. Nylon filters do not capture all GOM compounds equally, but are shown to have a higher efficiency for capturing $HgBr_2$ and $HgCl_2$ than for HgO, $HgSO_4$ and $Hg(NO_3)_2$ (Huang et al. 2013). The lack of strong peaks correlating to either of these compounds thus further adds to the unlikelihood of marine air having been measured.

Due to this potential continental origin, the observed peak in $HgNO_3$ in the April 19 sample may have therefore originated from NO_x emissions associated with agricultural fertilizer in the surrounding region. It may be considered more likely, however, that oceanic air was responsible for this peak, despite the low incidence of baseline conditions. This is due to previous observations that the ocean is the dominant source of NO at Cape Grim, which in turn is the primary source of NO_x at the site (Cainey et al. 2007). Baseline conditions were also experienced for a 1.5 times longer duration than during the April 19 sampling period, in which $HgSO_4$ was the dominant species. This being a key conditional difference between the two periods, it is possible that increased baseline air during the April 19 sample is the cause of this peak, providing NO_x which reacts in the atmosphere to form $HgNO_3$.

The $HgSO_4$ peak dominating the May 3 sample may be considered more likely to be continental in origin, due to the lower duration of baseline conditions. $HgSO_4$ is associated

with pollutant emissions of SO_2. According to the NPI, the closest point sources of SO_2 are located in Smithton, 40km ESE of Cape Grim, and emit a total of 18t of SO_2 annually. The most significant source within 100km is the Port Latta Pelletising Plant located 61km ESE, which emits 3600t per year. These anthropogenic sources in relatively close proximity to Cape Grim may indicate that SO_2 emissions from these sites provide the oxidants required for $HgSO_4$ formation. Prevailing winds during this sampling period, however, were from the NW, not from the ESE as would be expected for this relationship. Both SO_2 and mercury are products of combustion, so relatively high concentrations of $HgSO_4$ may also suggest an unknown combustion source.

It is notable that mean GOM breakthrough vs. concentration measured by cation-exchange membranes was higher at Cape Grim in the sample period ending April 19 (23.9%) compared with the period ending May 3 (14.7%), whilst GOM concentrations from cation-exchange membranes were considerably higher during the May 3 sampling period. This is despite the observed positive correlation between breakthrough and concentration at both sites. Based on this observation, and the species present in each of the samples, it is possible that cation-exchange membranes may not be as effective at collecting $Hg(NO_3)_2$ as at collecting other GOM compounds. Previous GOM retention tests for cation-exchange membranes did not examine either $HgSO_4$ of $Hg(NO_3)_2$ (Huang et al. 2013).

4.6. GEM and GOM correlation

GEM and GOM at Cape Grim show a slight positive correlation ($r^2 = 0.13$), however a stronger correlation is seen if data is removed for the two periods known to be influenced by pollution ($r^2 = 0.52$). If peaks in GOM concentrations correlate with decreased GEM, this may indicate oxidation as the source. The small number of data points, due to the low temporal resolution of the GOM system, does not provide enough data points to highlight any correlations with reasonable confidence. Previous GEM data from Cape Grim in 2012 recorded a relatively stable annual concentration, with a slight increase in September to October, followed by a dip in November to December, as well as a slightly lower concentration during mid-February (Slemr et al. 2015).

A slight negative correlation between GEM and GOM was observed at Macquarie University ($r^2=0.26$), however this is determined from only 6 data points. A negative correlation

between GEM and GOM is expected to be observed if GEM oxidization is the primary means of GOM production at the site. The spike in GOM concentration measured in sample periods ending July 25 and August 8 is notable, due to the correlation with low ambient GEM concentration. It is therefore possible that elevated GOM in this period is due to GEM oxidization. There was not, however, any correlated increase in solar radiation which is a likely driver of the photochemical oxidization process, with a relatively low mean daytime value of 193 Wm^{-2}. This is below the 200Wm^{-2} point where oxidization has been observed to begin occurring (Peleg et al. 2015). However since 193Wm^{-2} is the daytime average, peak solar radiation values on most days during the sampling period did exceed the threshold for oxidization to occur. If this peak in GOM was due to photochemical oxidization, it is unknown why similar oxidization did not occur during other sampling periods, in particular those with higher mean daytime solar radiation levels. No significant peaks in ozone or any other measured potential oxidizing pollutants were observed during this period.

4.7. Case Study – Influence of Fire Events at Cape Grim and Macquarie University
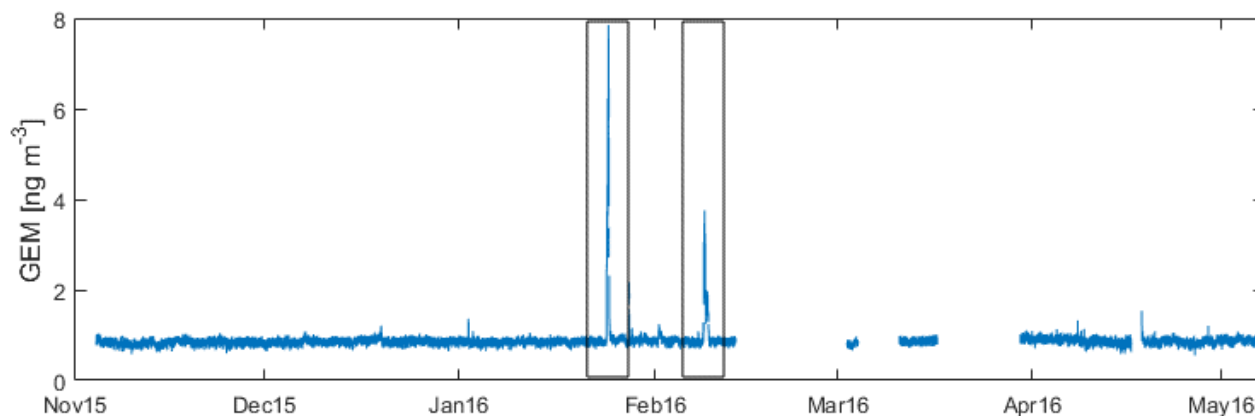
Figure 9 – GEM profile for Cape Grim. Elevated concentrations from smoke plumes are highlighted

In January and February 2016, Tasmania experienced a widespread fire event, with up to 70 fires burning. These fires produced smoke plumes which led to pollution events recorded at Cape Grim on the 25-26th of January, and the 12 of February. Spikes in concentration of CO, CO_2, CH_4 and O_3 were observed during these events. GEM and GOM data for Cape Grim during this period in seen in Figure 5.

GEM spikes correlating with both fire events can be seen in Figure 9. The Jan 25-26 event resulted in sustained GEM 5 min averages above 2ng m^{-3}, with a peak concentration of 7.9ng

m^{-3} recorded at 4:25am on the 26th. GEM concentrations during the February 12 event peaked at 3.7 ng m^{-3}. The January 26-February 9 sampling period recorded an average GEM concentration of 0.99m^{-3}, which was the same value as that recorded during the February 9-23 samples, as seen in Figure 5. These two readings were the highest ambient GEM levels recorded at Cape Grim during the experimental duration. It is thus likely that the fires caused GEM emissions from mercury stored in either plants or soils to be released.

Both the January 12-25 and the January 25 – February 9 sampling periods showed elevated GOM concentrations from cation-exchange membrane values, which may have resulted from the January 25-26 fires. The February 9-23 sampling period, however, did not show any significant increase in GOM concentrations from cation-exchange membranes, despite the February 12 burn within this period.

The site experienced similar meteorological conditions during both periods, with comparable mean relative humidity, temperature and pressure. Mean wind speed was around 20% lower in the period ending February 23, compared with those ending on both February 9 and January 25. Stronger winds may have assisted in the transport of pollutants and any GEM or GOM during the fire period, but are unlikely to have had any effect to increase GOM levels at the site.

A previous spike in GOM was observed in the month of January 2013 at the Amsterdam Island station, the highest of any month observed for 2013 (Angot et al. 2014). A possible explanation given for this value is the increased oceanic biological activity in summer, which may lead to production of halogenated species (Gschwend 1985). It is thus possible that the spike in GOM is due to a similar biological mechanism. It is also possible, due to the increase in GEM during this period, that higher GEM concentrations provided greater potential for GEM oxidation and thus higher GOM levels. Although solar radiation data was not available during this period, it is likely that radiation would be relatively high due to the time of year, which also provides greater potential for GEM oxidisation.

Due to the heightened concentrations of particulate matter, it is possible that GEM oxidization during pollution events such as this may favor formation of PHg over GOM (Amos et al. 2012). A previous analysis of wildfires concluded the great majority of mercury emissions were GEM (Friedli et al. 2003), however GOM was not directly measured in that experiment, but only inferred from GEM and PHg measurements.
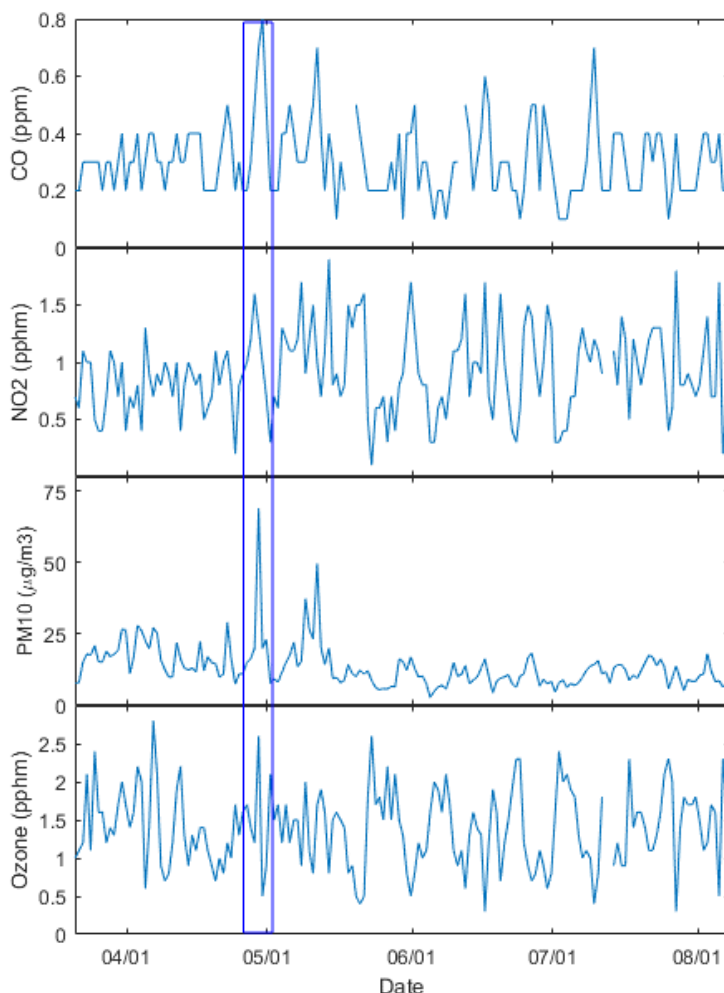
Case Study – May Fires in Sydney

Of note at the Macquarie University site was a similar pollution event which occurred in Sydney throughout May 2016. This event was caused by widespread hazard reduction burns across the Sydney basin. Several dozen burns were carried out during the month. The closest burn occurred on May 18 in the Lane Cove National Park, located 2.2km from the Macquarie University site.

These burns coincided with the elevated mean GOM concentration measured in May, observed during the sampling periods ending on both May 16 and May 30. The fires resulted in observed elevated concentrations of PM_{10}, NO_2, PM10 and CO as seen in the highlighted region of Figure 10. Average PM_{10},

Figure 10 – Daily pollutant series for Macquarie University. Concurrent peaks associated with one fire event are highlighted

NO_2 and SO_2 in this sampling period were the highest of any recorded throughout the Macquarie University experiment. Mean ozone concentrations were not elevated during this period, making ozone unlikely as an oxidation mechanism. Solar radiation data at the site was not available during this period due to technical difficulties. GEM measurements from the Tekran 2537 at Macquarie University were also not running during this period.

The origin of elevated GOM concentrations as a result of these wildfires has several potential sources. It is possible that GOM was released directly from the combustion process. Emissions of GOM have previously been observed from soils during fires, with greater release of GOM than GEM in some cases (Melenzed-Perez et al. 2014). Mercury emissions from fires

in Australia are believed to consist of 7% GOM (Nelson et al. 2012). It is also possible that elevated GOM concentrations were resultant from heightened photochemical oxidization due to increased levels of oxidizing pollutants. Despite the absence of Tekran 2537 data from this period, it is likely that GEM concentrations were elevated during the fire event, due to GEM peaks observed at Cape Grim during fire events, and estimates that 80% of mercury emissions from fires in Australia are in the form of GEM (Nelson et al. 2012).

It is clear from both this event and those recorded at Cape Grim that fires have the potential to cause significant increases in GOM concentrations, whether through direct emissions or by emitting GEM which is subsequently oxidised.

5. Key Findings and Conclusion

Both oxidised and elemental mercury were sampled using membranes and Tekran systems, as well as meteorological conditions and air pollutants, to understand GOM chemistry and transport at Macquarie University and Cape Grim, Australia. Based on observations, it is unlikely that the GOM present at either site originates from direct emissions, but is formed locally through GEM oxidation. The possible exception is during pollution events associated with local bushfires. Despite this, no clear anticorrelation between GEM and GOM was observed. Negative correlations between GOM and relative humidity at both sites agree with previous research on the impacts of water vapor on GOM concentrations. Understanding this effect is vital to improving our ability to measure ambient GOM. The influence of bushfires on both GEM and GOM levels has also been observed, and is clear that pollution events associated with fires have the capacity to significantly increase ambient mercury levels, particularly GEM.

Higher ambient GEM at Cape Grim compared to Macquarie University highlight the possibility of either long range atmospheric transport of GEM to Cape Grim, or high rates of oxidation occurring at Macquarie University. It is also possible as noted that technical errors were responsible for this observation. Future high-temporal-resolution measurements of GEM and GOM at both sites will help to resolve this question.

GOM speciation at Cape Grim indicates both $Hg(NO_3)_2$ and $Hg(SO)_4$ as contributing significantly to the composition of GOM in the area, although further measurements and a greater seasonal resolution of data are required to verify these findings. The physiochemical properties of GOM compounds must also be better understood in order to understand how

different GOM species are affected by meteorological and other conditions. In particular, the Henry's Law constant is required to understand how relative humidity affects each individual GOM compound.

Further experiments should be carried out at both sites with a greater temporal duration to examine GOM fluctuations in all seasons. Nylon membranes from Macquarie University should be desorbed to determine GOM species present, and a comparison of species between sites should be carried out. It is also recommended to run a Tekran 1130 Unit alongside the membrane system, in order to understand the diurnal variation of GOM at both sites. Investigations should also be conducted into the ability of cation-exchange membranes to capture GOM species, particularly $Hg(NO_3)_2$ and $Hg(SO)_4$. The effectiveness of nylon membranes in capturing GOM should also continue to be investigated.

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