Using observations and modelling to quantify mercury biogeochemical cycling in the Australian context

Neil Christopher Page

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Using observations and modelling to quantify mercury biogeochemical cycling in the Australian context

Neil Christopher Page

Supervisors:
Dr. Jenny Fisher and Assoc. Prof. Stephen Wilson

This thesis is presented as part of the requirement for the conferral of the degree:
Master of Research

This research has been conducted with the support of the Australian Government Research Training Program Scholarship

The University of Wollongong
School of Earth and Environmental Sciences

October 2017
Abstract

The GEOS-Chem biogeochemical Hg model (like every other major Hg model) has historically been developed and evaluated using observations from the northern hemisphere, which are significantly more abundant than observations in the southern hemisphere. A recent evaluation of GEOS-Chem against a global database of Hg observations found significant biases in the simulation of Hg in the southern hemisphere (Song et al., 2015; Horowitz et al., 2017); however, only three southern hemisphere sites were included and none were in Australia.

The Australian climate, its flora, fauna and soil types are unique from those in other regions of the world. There are a lack of reliable estimates for the Australian region regarding the cycling of mercury emissions (both natural and anthropogenic) between the atmosphere and terrestrial surface (Edwards & Howard, 2013). To date, limited research has been undertaken on modelling and quantifying the sources and quantities of atmospheric Hg in Australia.

Gaseous elemental mercury (Hg\(^0\)) observations from five southern hemispheric sites were used to evaluate the performance of GEOS-Chem in the Australasian region. It was found that GEOS-Chem simulates an atmospheric Hg budget for the Australian region of approximately 110 to 144 Mg yr\(^{-1}\). Hg exchange from the ocean accounts for approximately 22.5 to 35.3 % of this total. Once oceanic sources were removed, the budget was estimated at 93.2 Mg yr\(^{-1}\), slightly lower than previous estimates. The key findings are that: (i) GEOS-Chem is generally able to reproduce the observed seasonal cycle of Hg\(^0\) at southern hemisphere sites, but not the daily variability; (ii) the simulations tend to overestimate Hg\(^0\) concentrations; (iii) Australian and southern hemispheric sites are heavily influenced by oceanic emissions; and (iv) the Australian terrestrial surface may provide a net sink for atmospheric Hg.

Australian and southern hemispheric Hg simulations in GEOS-Chem may benefit from: (i) using daily averages for bromine (rather than monthly averages) for driving the atmospheric chemistry; (ii) coupling vegetation with soil emissions/deposition, which are currently treated independently but would be more accurately represented by bi-directional exchange; (iii) additional observation sites and measurements of gaseous oxidised mercury (Hg\(^{\text{II}}\)) and particulate bound mercury (Hg\(^{\text{P}}\)) to provide an improved understanding of Hg speciation, chemical redox reactions and Hg fluxes (both evasion and deposition) in the region; (iv) customization of the emission factors relating to soil, biomass burning and vegetation processes.

In summary, this work provides the first evaluation of the GEOS-Chem Hg model over Australia, paving the way for model development that will improve Hg simulation in this part of the world. Future work will specifically target inclusion of moisture limitation for emissions from tropical soils, investigation of chlorine chemistry in the marine boundary layer, focusing on scavenging in the tropical regions, and customization of emissions factors for Australian soils and vegetation.
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Thanks to the faculty of Science, Medicine and Health (SMAH) for providing me with a faculty stipend scholarship.

This Research has been conducted with the support of the Australian Government Research Training Program Scholarship.
Certification

I, Neil Christopher Page, declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree Master of Research, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

______________________________
Neil Christopher Page
13th October 2017
List of abbreviations

AMDE     Atmospheric Mercury Depletion Event
APMMN    Asia Pacific Mercury Monitoring Network (Asia/Pacific)
ASGM     Artisanal and Small-scale Gold Mining
CAMNet   Canadian Atmospheric Mercury Network (Canada)
CARIBIC   Civil Aircraft for Regular Investigation of the Atmosphere Based on an
          Instrumented Container
CH: Hg+  Methylmercury
(CH3):Hg+  Dimethylmercury
CTM      Chemical Transport Model
DFC      Dynamic Flux Chamber
EMEP     European Monitoring and Evaluation Programme (EU)
ENSO     El Nino Southern Oscillation
EPA      Environmental Protection Agency (USA)
GEM      Gaseous Elemental Mercury
GEOS     Goddard Earth Observation System (NASA)
GMAO     Global Modelling and Assimilation Office (NASA)
GMOS     Global Mercury Observation System
Hg       Mercury
Hgo      Elemental Mercury
Hgl      Monovalent Mercury
HgII     Oxidised Mercury
Hp       Particulate Bound Mercury
ITCZ     InterTropical Convergence Zone
KCl      Potassium Chloride
MC       Mean Contribution
MD       Mean Difference
MDN      Mercury Deposition Network (USA)
MM       MicroMeterological
MNB      Mean Normalised Bias
MNE      Mean Normalised Error
NADP     National Atmospheric Deposition Programme (USA)
NAMDE    Nocturnal Atmospheric Mercury Depletion Event
NCI      National Computational Infrastructure (Australia)
NPI      National Pollutant Inventory (Australia)
PBL      Planetary Boundary Layer
PBM      Particulate Bound Mercury
ppm      Parts Per Million
SOM      Soil Organic Matter
TGM      Total Gaseous Mercury (Hgo + HgII)
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<tr>
<td>TM</td>
<td>Total Mercury (Hg$^0$ + Hg$^{II}$ + Hg$^{III}$)</td>
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<tr>
<td>µg</td>
<td>Microgram</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environmental Programme</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-Violet</td>
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Chapter 1

1. Introduction

Mercury (Hg) is a trace metal that is widespread and persistent in the environment. It occurs naturally in its elemental form (Hg^0), which is liquid at ambient temperatures with a reasonably high vapour pressure, presenting a hazard through its emission into the atmosphere (Levy et al., 2011). Primary emissions of Hg to the atmosphere occur via both anthropogenic (human) and natural processes, with approximately 29-33% of total Hg emissions stemming from anthropogenic sources (including: mining, coal and fuel combustion and manufacturing) and 5-13% of total Hg emissions stemming from natural geogenic sources (such as: volcanism and soil/rock erosion) (Agnan et al., 2015). As anthropogenic emissions exceed natural geogenic emissions this results in the overall increase of Hg in the atmosphere. Secondary emissions of Hg to the atmosphere (Hg which has previously been deposited from the atmosphere) are estimated to account for about 56-65% of total Hg emissions to the atmosphere and are therefore an important flux in the biogeochemical cycling of Hg (Agnan et al., 2015).

The atmosphere provides the dominant pathway for the distribution of Hg emissions, while interactions with land and ocean processes influence its biogeochemical cycling between atmospheric, aquatic and terrestrial reservoirs. Some forms of Hg (such as Hg^0) have an atmospheric residence time of 6-12 months, allowing for its global distribution from emission sources to remote locations (e.g. the Artic and Antarctica) (Driscoll et al., 2013). Hg is eventually removed from the atmosphere via deposition processes to sinks on the Earth’s surface, including the hydrosphere, pedosphere, cryosphere, and both aquatic and terrestrial ecosystems (Gustin, 2011).

Once in these ecosystems, methanogenic bacteria can ingest Hg^0, converting it to its methylated form (CH_3Hg^+), which allows it to bind to the proteins within living organisms. CH_3Hg^+ is considered a pollutant of global concern due to its toxicity, ability to bioaccumulate in and biomagnify up the food web, resulting in adverse effects on both human health and the environment (Levy et al., 2011). Human exposure most commonly occurs through the consumption of contaminated fish, although rice cultivated in mercury-contaminated areas also presents a risk (Zhu et al., 2016).

In 2009, the United Nations Environment Programme (UNEP) agreed that a global treaty on Hg was necessary and this resulted in the Minimata Convention, a multilateral agreement designed to protect human health and the environment from anthropogenic emissions of Hg and Hg compounds (UNEP, 2013a). On 10 October 2013 Australia became one of more than 100 countries to have signed the Minimata Convention and the Australian Government is now considering ratifying the convention. This would make Australia a full party, which would then legally bind Australia to the convention’s obligations (Department of the Environment, 2014). This would require Australia to monitor and control Hg releases from anthropogenic sources to the atmosphere, pedosphere, biosphere and hydrosphere.
Over the last three decades there have been extensive efforts to measure, model and estimate the quantities of atmospheric Hg exchange in Europe, North America and Asia (Zhu et al., 2016). However, the Australian climate, its flora, fauna and soil types are different from those in other regions of the world and there is a lack of reliable estimates for the Australian region regarding the cycling of both natural and anthropogenic emissions between the atmosphere and terrestrial surface (Edwards & Howard, 2013). To date, limited research has been undertaken on modelling and quantifying the sources and quantities of atmospheric Hg in Australia. This thesis aims to start filling in these gaps by providing a first evaluation of Hg models in Australia.
Chapter 2

2. Literature review

2.1. Risk to humans and the environment

Once in the environment gaseous oxidised Hg (Hg$^{II}$) tends to accumulate in methylation zones (such as water bodies, wetlands, riparian zones and bottom sediments), where it is then converted primarily by biotic processes and/or abiotic processes into its organic (methylated) forms: methylmercury (CH$_3$Hg$^+$) and dimethylmercury ($(CH_3)_2$Hg$^{2+}$) (AMAP/UNEP, 2015). Biotic process are largely orchestrated by sulfate (SO$_4^{2-}$) and iron (Fe) reducing bacteria (Driscoll et al., 2013), but can also include other microbial species that carry the methylating genes (hgcA/hgcB), including methanogens, and syntrophic, acetogenic, and fermentative Firmicutes (Chakraborty et al., 2016; Gilmour et al., 2013). These organic forms are highly toxic and CH$_3$Hg$^+$ presents a risk because it can bind to proteins, allowing it to be readily absorbed and retained by organisms where it can then bioaccumulate. This then presents a pathway for CH$_3$Hg$^+$ to biomagnify up aquatic food webs (Levy et al., 2011). In contrast to CH$_3$Hg$^+$, there are no current data that (CH$_3)_2$Hg$^{2+}$ bioaccumulates and thus it is not believed to biomagnify up food webs (Lehnherr, 2014). As such CH$_3$Hg$^+$ tends to be the dominant form in higher order organisms, where concentrations can reach a factor of 106 above water concentrations (Camargo, 2002; Meng et al., 2011). Australian studies have found elevated CH$_3$Hg$^+$ concentrations in a number of high trophic order marine organisms including: dolphins (Monk et al., 2014) and sharks (Pethybridge et al., 2010), while it is a worldwide problem in piscivorous fish (e.g. tuna and swordfish) (Zhu et al., 2016).

Human exposure most commonly occurs through the consumption of contaminated fish where CH$_3$Hg$^+$ concentrations are particularly elevated, as observed in some piscivorous fish, such as tuna and swordfish (Zhu et al., 2016). Many populations are dependent upon fish as a food source. Fish provides over 1.5 billion people with their main source of protein and its contribution to global diets is increasing (Driscoll et al., 2013). Exposure can also occur through the consumption of rice cultivated in mercury-contaminated areas (Driscoll et al., 2013; Wang et al., 2016). In the soil, the roots first absorb CH$_3$Hg$^+$, before it is transported to the edible portions of rice plants, where Hg concentrations have been found to exceed 100 µg/kg (Meng et al., 2011). As a grain, rice is particularly prone to the uptake of CH$_3$Hg$^+$; this is because it is cultivated under standing water, which provides a productive zone for Hg methylation from anaerobic organisms (Rothenberg et al., 2016).

CH$_3$Hg$^+$ poisoning in adults has been linked to: (i) decreased fertility; (ii) neurological disorders; (iii) nerve and brain cell damage; and (iv) heart disease (Department of the Environment, 2014). It also has the ability to pass through the placenta and affect the neurological development of foetuses in pregnant women (Pacyna et al., 2016). The highest profile incident occurred at
Minamata, Japan where the release of CH$_3$Hg$^+$ contaminated wastewater from local industry between the 1930s and 1960s resulted in what was termed Minimata Disease (Ariya et al., 2015). In 1958 CH$_3$Hg$^+$ poisoning was identified as the cause of Minimata Disease in over 2000 people. It resulted from the local populace consuming contaminated fish with extremely high CH$_3$Hg$^+$ concentrations (>10 µg g$^{-1}$) (Lehnherr, 2014). The result was that affected people suffered from neurological disorders (such as visual, auditory and sensory disturbances, numbness and difficulty walking), while their children suffered from serious neurological birth defects (including: mental retardation cerebral palsy, deafness, blindness) (Driscoll et al., 2013; Selin, 2009).

Even exposure to low doses of CH$_3$Hg$^+$, occurring from normal environmental exposure, has been linked with effects on cardiovascular function, including: increased arterial blood pressure, myocardial infarction, coronary dysfunction, and atherosclerosis (Department of the Environment, 2014). Mercury is believed to cause toxic effects on the cardiovascular system through an increase in oxidative stress (Azevedo et al., 2012). As a result, the US Environmental Protection Agency (EPA) has set a reference dose for CH$_3$Hg$^+$ of 0.1 µg/kg body weight/day to minimize the risks of CH$_3$Hg$^+$ poisoning (Selin, 2009).

Hg contamination also presents a hazard to ecosystem health, where its impact is related to: (i) levels of global and regional fluxes; (ii) the potential for ecosystems to convert Hg$^{II}$ into CH$_3$Hg$^+$; (iii) the concentration that inhibits organism functioning; (iv) its ability to biomagnify in food webs; and (v) the impact of disturbances to alter these rates (Driscoll et al., 2013). The adverse effects of CH$_3$Hg$^+$ exposure on wildlife health have been shown to include behavioral, neurochemical, hormonal, and reproductive impacts (Selin, 2009). Studies have found that elevated Hg concentrations in fish affect reproduction, embryonic development, biochemical processes and result in cell and tissue damage (Meng et al., 2011; Pacyna et al., 2016; Selin, 2009). This may impair the health of fisheries and so poses a risk to global food security (Department of the Environment, 2014).

2.1.1. The role of the atmosphere
The atmosphere is of great importance for the biogeochemical cycling of Hg because it provides the dominant pathway for the distribution of Hg emissions. As a reservoir the atmosphere is estimated to contain between 4600-5600 Mg of Hg (Amos et al., 2013). More recently Horowitz et al. (2017) estimated that the tropospheric reservoir contains about 3900 Mg of total gaseous mercury (TGM), with 3500 Mg as Hg$^0$ and 400 Mg as Hg$^{II}$; this is smaller than the 4500 Mg RM reservoir estimated by (Holmes et al., 2010). Estimates for the ocean and pedosphere are approximately 3.57 x 10$^5$ and 1.2 x 10$^6$ Mg of Hg respectively (Zhu et al. 2016), see Figure 2.

2.1.2. The Minamata Convention on mercury
The environmental and socio-economic consequences of CH$_3$Hg$^+$ exposure have prompted regulations and policies to limit Hg releases from human activities since the 1970’s. These early efforts saw international policies focus on Hg contamination in regional water bodies, such as the
In 2002, the United Nations Environment Programme (UNEP) released a scientific report entitled the “Global Mercury Assessment”. The main conclusion of this report was that there is “sufficient evidence of global adverse impacts to warrant international action to reduce the risks to human health and/or the environment arising from the release of mercury into the environment” (UNEP, 2002).

By 2009, UNEP concluded that a global treaty on Hg was necessary due to the scientific consensus that anthropogenic activities had dramatically altered the global biogeochemical cycle of Hg from its preindustrial baseline (Selin, 2013). This resulted in the Minimata Convention, a multilateral agreement designed to protect human health and the environment from anthropogenic emissions of Hg and Hg compounds (UNEP, 2013a). Once the Australian Government has ratified the convention, then under article 21 it would be required to monitor, control and report on Hg releases from anthropogenic sources to the environment, including the atmosphere (UNEP, 2013b). It is expected that reductions in anthropogenic Hg emissions under the Minimata Convention will have an effective impact on levels of environmental Hg contamination (Lehnerr, 2014).

On the 18 May 2017, the number of countries that have ratified the Minamata Convention reached 50, the milestone required for it to enter into force and become legally binding for all full parties (UNEP, 2017). Full parties are required document national emissions inventories for defined anthropogenic sources (AMAP/ UNEP, 2013).

### 2.2. Forms of atmospheric mercury

In the atmosphere, Hg is measured in three operationally defined forms: (i) gaseous elemental Hg (Hg$^0$); (ii) gaseous oxidised Hg (Hg$^\text{II}$); and (iii) particulate bound Hg (Hg$^\text{P}$) (Wright & Zhang, 2015). The form of Hg is extremely important for atmospheric transport as it determines the atmospheric residence time and hence transportation distance before deposition (De Simone et al., 2017). Hg is converted from one form to another via processes such as: (i) oxidation/reduction reactions; (ii) the formation of chemical complexes (e.g. organo-metallic complexes); (iii) phase transitions; (iv) biodegradation; and (v) surface and heterogeneous interactions with aerosols, clouds, snow, water droplets (Subir et al., 2011). More information on these processes will be provided in Section 2.3.

Hg$^0$ is the dominate form and accounts for roughly 95-99% of Hg in the atmosphere (Gustin, 2011), with concentrations (ocean and terrestrial) averaging from 1.0 to 1.7 ng m$^{-3}$ in the northern hemisphere and from 0.5 to 1.2 ng m$^{-3}$ in the southern hemisphere (Agnan et al., 2015). Terrestrial background concentrations are approximately 1.5 to 1.7 ng m$^{-3}$ and 1.0 to 1.3 ng m$^{-3}$ in the northern and southern hemispheres respectively (Sprovieri et al., 2016). Measurements of Hg$^0$ concentrations are normally reported in ng m$^{-3}$ at a standard temperature of 273.15 K and standard pressure of 1013 hPa (Slemr et al., 2015). Hg$^0$ is relatively unreactive and is sparingly soluble in water, resulting in an estimated atmospheric lifetime of several months to a year before it is
oxidised into Hg\textsuperscript{II} (Camargo, 2002; Corbitt et al., 2011). This allows Hg\textsuperscript{0} to be transported around the world and deposited in remote regions far from sources, such as the Arctic and Antarctic (AMAP/UNEP, 2015). Although Hg\textsuperscript{0} is known to be transported and deposited efficiently within its hemisphere of origin, cross hemisphere transport is less efficient and this is an underlying reason for the lower concentrations (typically 30\%) observed in the southern hemisphere (Driscoll et al., 2013; Howard et al., 2017; Horowitz et al., 2017; Song et al., 2016).

Hg\textsuperscript{II} and Hg\textsuperscript{0} account for the remaining 1-5\% of Hg in the atmosphere, with lower concentrations at typically 0-50 pg m\textsuperscript{-3} (Gustin, 2011). In contrast to Hg\textsuperscript{0}, Hg\textsuperscript{II} is water soluble and reactive with inorganic and organic matter, and anions (including: Cl\textsuperscript{-}, OH\textsuperscript{-}) and molecules (such as CO\textsubscript{2} and SO\textsubscript{2}) (Camargo, 2002). As such, Hg\textsuperscript{II} is easily removed by scavenging and surface uptake (AMAP/UNEP, 2015) and so has a far shorter atmospheric lifetime (hours to days) and tends to be deposited locally or regionally (Driscoll et al., 2013).

Hg\textsuperscript{P} has a similarly short atmospheric lifetime to Hg\textsuperscript{II} (hours to days). It is relatively insoluble, but is easily scavenged (as it provides a surface on which cloud water droplets can form), resulting in mostly local and regional deposition (De Simone et al., 2017; Driscoll et al., 2013; Nelson et al., 2009).

As a result, national and international policies that focus on the reduction of Hg\textsuperscript{II} and Hg\textsuperscript{P} will have local and regional benefits, while a focus on Hg\textsuperscript{0} will have global benefits (Selin, 2009).

2.2.1. Vertical distribution of mercury species

Although Hg\textsuperscript{0} dominates total atmospheric Hg concentrations in the planetary boundary layer (PBL), aircraft-based observations have indicated that the oxidation of Hg\textsuperscript{0} increases with altitude in the free troposphere and towards the tropopause. In the stratosphere Hg\textsuperscript{II} has been found to dominate total mercury concentrations (Bieser et al., 2017). These observations suggest that there is an inverse relationship between Hg\textsuperscript{0} and Hg\textsuperscript{II} at high altitudes, above approximately 2500m in the troposphere and also in the stratosphere (UNEP, 2013a). Holmes et al., (2010) simulated the vertical Hg\textsuperscript{0} and Hg\textsuperscript{II} mixing ratios and found that the inverse relationship is driven by changes in the atmospheric chemistry, due to differences in oxidant concentrations with altitude.

2.3. Chemical mechanisms for atmospheric redox chemistry

2.3.1. Oxidation of Hg\textsuperscript{0} to Hg\textsuperscript{II}

Oxidation of Hg\textsuperscript{0} to Hg\textsuperscript{II} occurs predominantly in the gas phase via (i) direct processes and (ii) two-stage processes with competing reactions. Oxidation also occurs sparingly in the aqueous phase (Horowitz et al., 2017; Wang et al., 2014).

The rate of Hg\textsuperscript{0} oxidation by a given reactant is dependent upon: (i) the reactivity of Hg\textsuperscript{0} with the reactant under the environmental conditions (e.g. temperature, pressure, humidity, etc.); (ii) the atmospheric concentration of the oxidant; and (iii) the presence of additional reactants that can lead to side and competing reactions (Ariya et al., 2015).
2.3.1.1 Gas phase direct oxidation process

Table 1 shows the software representations (used by CTMs, e.g. GEOS-Chem) of the chemical reactions proposed in the literature. The suggested pathway for the direct oxidation process is detailed below:

Direct process: \( \text{Hg}^0 + \text{AB} + \text{M} \rightarrow \text{Hg}^{II} \text{A} + \text{B} + \text{M} \)

Where:
- \( \text{AB} \) is the direct \( \text{Hg}^0 \) oxidant;
- \( \text{A} \) and \( \text{B} \) are the products of the reaction; and
- \( \text{M} \) is a molecule from the air, most likely \( \text{N}_2 \) or \( \text{O}_2 \).

For example: \( \text{Hg}^0 + \text{BrO} + \text{M} \rightarrow \text{Hg}^{II} \text{O} + \text{Br} + \text{M} \). Where: (\( \text{AB} \)) is the oxidant \( \text{BrO} \), (\( \text{A} \)) represents \( \text{O} \) in the product \( \text{Hg}^{II} \text{O} \), (\( \text{B} \)) represents the product \( \text{Br} \), and (\( \text{M} \)) is a molecule from the air, most likely \( \text{N}_2 \) or \( \text{O}_2 \) (Wang et al., 2014).

The most common direct-process oxidants (\( \text{AB} \)) of \( \text{Hg}^0 \) include \( \text{O}_3 \), \( \text{OH} \), \( \text{Br}_2 \), \( \text{BrO} \) and \( \text{ClO} \). Other suggestions for direct-process oxidants include \( \text{I} \), \( \text{I}_2 \), \( \text{NO}_3 \), \( \text{HO}_2 \) and \( \text{HCl} \) (Hynes et al., 2009; Wang et al., 2014).

Although direct oxidation has been inferred from kinetic studies, the reactions are too slow to make anything other than a minor contribution to the oxidation of \( \text{Hg}^0 \). It is argued that the bulk of \( \text{Hg}^0 \) oxidation takes place via the two-stage oxidation process (Horowitz et al., 2017; Jiao & Dibble, 2017; Shah & Jaegle, 2017).

2.3.1.2 Gas phase two-stage oxidation process

Table 1 shows the software representations (used by CTMs, e.g. GEOS-Chem) of the chemical reactions proposed in the literature. The mechanism for the two-stage oxidation process is detailed below:

Stage 1: \( \text{Hg}^0 + \text{X} + \text{M} \rightarrow \text{Hg}^{I} \text{X} + \text{M} \)

Competing reactions: \( \text{Hg}^{I} \text{X} + \text{Y} \rightarrow \text{Hg}^0 + \text{XY} \)
\( \text{Hg}^{I} \text{X} + \text{Y} + \text{M} \rightarrow \text{Hg}^0 \text{XY} + \text{M} \)

Stage 2: \( \text{Hg}^{I} \text{X} + \text{Y} + \text{M} \rightarrow \text{Hg}^{II} \text{XY} + \text{M} \)

Where:
- \( \text{X} \) is the first-stage \( \text{Hg}^0 \) oxidant;
- \( \text{Hg}^{I} \) is the reaction intermediate/monovalent mercury (lifetime < 1 second);
- \( \text{Y} \) is the second-stage \( \text{Hg}^{I} \) oxidant; and
- \( \text{M} \) is a molecule from the air, most likely \( \text{N}_2 \) or \( \text{O}_2 \).
Stage 1

The most effective first-stage Hg\(^0\) oxidants (X) are Br\(^*\) and Cl\(^*\), resulting in HgBr and HgCl (Horowitz et al., 2017). Br and Cl initiated oxidation is prominent in the marine boundary layer where they are released from sea salt particles (Parrella et al., 2012). The oceans are generally regarded as the primary source of halogens in marine regions, although halogens also occur from volcanoes, industrial activity and oil burning wells (Ariya et al., 2015) OH and O\(_3\) have also been proposed as major oxidants of Hg\(^0\), but these mechanisms are subject to debate as theoretical calculations suggest that Hg\(^O\), the product of oxidation by O\(_3\) and OH, is too weakly-bound to be of atmospheric importance as it rapidly dissociates (Jiao & Dibble, 2017; Shah & Jaegle, 2017). Oxidation by OH and O\(_3\) may be mediated by some form of surface or intermediate species (Timonen et al., 2011); while laboratory kinetic studies suggest that they are viable mechanisms in the presence of tropospheric aerosols (Rutter et al., 2012).

Other proposals for first-stage Hg\(^0\) oxidants include I, I\(_2\), Br\(_2\), Cl\(_2\), BrO, ClO, HCl, HO\(_2\) and NO\(_2\). However, these are thought to be less important as oxidants (Holmes et al., 2010; Horowitz et al., 2017), while the oxidation reactions may be implausible when considering thermodynamic properties and kinetic studies (Zhang et al., 2017).

Competing reactions

After stage 1 there is the possibility for competing reactions to reduce Hg\(^I\) back into Hg\(^0\) instead of proceeding to stage 2. The likelihood of this happening is dependent upon the relevant reaction rate (Jiao & Dibble, 2017).

Stage 2

The most effective second-stage Hg\(^I\) oxidants (Y) are Br and NO\(_2\), but may also include OH and HO\(_2\) (Horowitz et al., 2017; Jiao & Dibble, 2017; Wang et al., 2012). However, as the exact chemical mechanism is uncertain Y could potentially be other oxidants.

2.3.1.3 Bromine as an atmospheric oxidant

Evidence from theoretical and field studies suggests that Br atoms (as BrO) may provide the dominant atmospheric oxidant for Hg\(^0\) in a number of environments, including: (i) the polar regions; (ii) the marine boundary layer; and (iii) the upper troposphere/lower stratosphere (Gratz et al., 2015; McClure et al., 2014; Pacyna et al., 2016). It is thought that Br radical chemistry may be important for the free troposphere, with aircraft observations reporting concentrations of several pmol/mol (Parrella et al., 2012).

The evidence increasingly suggests that daytime BrO mixing ratio (hereafter referred to as “concentration” following conventions in the atmospheric chemistry community) in the troposphere are on the order of 1 parts per trillion by volume (pptv), while satellite observations have indicated that tropospheric background concentrations of BrO vary between 0.5 and 2.0 pptv (Driscoll et al., 2013; Lindberg et al., 2007). This would imply that BrO concentrations are sufficiently high to provide the main atmospheric oxidant for Hg\(^0\) and thus provide a major
driving force for Hg deposition (Schmidt et al., 2016).

Sources for Br atoms within the troposphere include (i) the photolysis and oxidation of bromoform (CHBr$_3$), dimethylbromide (CH$_2$Br$_2$), and methyl bromide (CH$_3$Br); (ii) the debromination of sea salt aerosol; and (iii) the transport of inorganic bromine (Br$_2$) from the stratosphere, where Br$_2$ is a product of the photochemical decomposition of organobromines and halons (Parrella et al., 2012; Schmidt et al., 2016).

The oxidation process of Hg$^0$ via BrO is a two-stage exothermic reaction: (i) in the first stage Hg$^0$ oxidation is initiated by Br atoms of marine origin; (ii) while in the second-stage HgBr oxidation is induced by NO$_2$ and HO$_2$ atmospheric radicals (Table 1) (Horowitz et al., 2017). HgBr is notoriously unstable; therefore the oxidation of Hg$^0$ to Hg$^{II}$ is dependent upon both temperature and Br concentrations (Goodsite et al., 2012). In general, the oxidation rate of Hg$^0$ tends to be faster in the southern hemisphere than in the northern hemisphere and this has been attributed to the greater oceanic source of bromocarbons (Driscoll et al., 2013; Holmes et al., 2010). However, the region around Antarctica and over Southern Ocean has lower Br concentrations and thus Hg$^0$ oxidation and the subsequent deposition of Hg$^{II}$ and Hg$^P$ in the region are lower (Schmidt et al., 2016).

2.3.1.4 Aqueous phase oxidation of Hg$^0$ to Hg$^{II}$

Although Hg$^0$ is sparingly soluble in water, limited aqueous-phase oxidation of Hg$^0$ to Hg$^{II}$ may take place within cloud water droplets and in the marine boundary layer (Ariya et al., 2015; Horowitz et al., 2017; Soerensen et al., 2010; Zhang et al., 2017). Table 1 shows the software representations (used by CTMs, e.g. GEOS-Chem) of the chemical reactions proposed in the literature, these are shown as. Other aqueous phase oxidants that have been proposed include HOBr$_{aq}$, OBr$_{aq}$, and Br$_2(aq)$, however these are mostly thought to be too slow to be of relevance (Horowitz et al., 2017).

Table 1: Software representations of the mechanisms and estimated reaction rate coefficients for the oxidation of Hg$^0$ to Hg$^{II}$. References: (1) Wang et al., (2014); (2) Horowitz et al., (2017); and (3) Hynes et al., (2009). Note that these references are summaries and not the primary source.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Reaction</th>
<th>Rate coefficient$^{ab}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X = O$_3$)</td>
<td>Hg$^0$ + O$_3$ → HgO + O$_2$</td>
<td>$3 \times 10^{-20}$</td>
<td>(1)</td>
</tr>
<tr>
<td>(X = OH)</td>
<td>Hg$^0$ + OH → HgOH</td>
<td>$3.55 \times 10^{-14}$ e$^{-2440/T}$</td>
<td>(1)</td>
</tr>
<tr>
<td>(X = Br$_2$)</td>
<td>Hg$^0$ + Br$_2$ → HgBr$_2$</td>
<td>$3.2 \times 10^{-13}$</td>
<td>(3)</td>
</tr>
<tr>
<td>(X = BrO)</td>
<td>Hg$^0$ + BrO → HgO + Br</td>
<td>$9 \times 10^{-17}$</td>
<td>(1)</td>
</tr>
<tr>
<td>(X = ClO)</td>
<td>Hg$^0$ + ClO → HgO + Cl</td>
<td>$1 \times 10^{-15}$</td>
<td>(1)</td>
</tr>
</tbody>
</table>
### Gas phase two-stage oxidation process

#### Stage 1

| (X = Br\(^d\)) | \(Hg^0 + Br + M \to HgBr + M\) | \(1.46 \times 10^{-32} (T/298)^{-1.86}\) (2) |
| (X = Cl\(^d\)) | \(Hg^0 + Cl + M \to HgCl + M\) | \(2.2 \times 10^{-32} e^{(680/(1/T-1/298))}\) (2) |

**Competing reactions**

| (X = Br\(^d\)) | \(HgBr + M \to Hg^0 + Br + M\) | \(1.6 \times 10^{-9} (T/298)^{-1.86} e^{-7801/T}\) (2) |
| (Y = Br\(^d\)) | \(HgBr + Br \to Hg^0 + Br_2\) | \(3.9 \times 10^{-11}\) (2) |
| (Y = NO\(_2\)^d) | \(HgBr + NO_2 \to Hg^0 + BrNO_2\) | \(3.4 \times 10^{-12} e^{391/T}\) (2) |

| (X = Cl\(^d\)) | (Y = Cl\(^d\)) | \(HgCl + Cl \to Hg^0 + Cl_2\) | \(1.20 \times 10^{-11} e^{-5942/T}\) (2) |

#### Stage 2

| (X = Br): (Y = Br\(^d\)) | \(HgBr + Br \to HgBr_2\) | \(3.0 \times 10^{-11}\) (2) |
| (Y = NO\(_2\)^d) | \(HgBr + NO_2 \to HgBrNO_2\) | \(k_{NO_2}([M], T)\) (2) |
| (Y = OH) | \(HgBr + OH \to HgBrOH\) | \(6.33 \times 10^{-11}\) (1) |
| (Y = HO\(_2\)) | \(HgBr + HO_2 \to HgBrO_2\) | \(8.2 \times 10^{-11}\) (1) |
| (Y = Other oxidant\(^d,e\)) | \(HgBr + Y \to HgBrY\) | \(k_{HO_2}([M], T)\) (2) |

| (X = Cl): (Y = Br\(^d\)) | \(HgCl + Br \to HgBrCl\) | \(3.0 \times 10^{-11}\) (2) |
| (Y = NO\(_2\)^d) | \(HgCl + NO_2 \to HgClNO_2\) | \(k_{NO_2}([M], T)\) (2) |
| (Y = Other oxidant\(^d,e\)) | \(HgCl + Y \to HgClY\) | \(k_{HO_2}([M], T)\) (2) |

### Aqueous phase oxidation process

\[
Hg^{0\,(aq)} + O_3^{\ast\,(aq)} \to Hg^{II\,(aq)} + \text{products} \\
4.7 \times 10^7 \quad (2)
\]

\[
Hg^{0\,(aq)} + HOCl^{\ast\,(aq)} \to Hg^{II\,(aq)} + OH^{\ast\,(aq)} + Cl^{\ast\,(aq)} \\
2 \times 10^6 \quad (2)
\]

\[
Hg^{0\,(aq)} + OH^{\ast\,(aq)} \to Hg^{II\,(aq)} + \text{products} \\
2.0 \times 10^9 \quad (2)
\]

**Footnote:**

\(^a\)Rate coefficient for gas-phase processes are for 1 atm and have units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). [M] is the number density of air, and \(T\) is the temperature in Kelvin. Rate coefficients for aqueous-phase processes have units of mol L\(^{-1}\) s\(^{-1}\).

\(^b\)The reaction rate coefficients are subject to uncertainties due to assumptions in their determination (Subir et al., 2011).
Where “Other oxidant” is an unknown second-stage Hg^0 oxidant.

2.3.1.5 Atmospheric mercury depletion events

Atmospheric mercury depletion events (AMDEs) are periods of low atmospheric Hg^0 levels (far below standard concentrations) that occur over a short time period (24 hours or less) and are generally accompanied by low O_3 levels (Steffen et al., 2008). They largely occur in the Arctic and Antarctic regions and are linked to the rapid oxidation of Hg^0 initiated by high concentrations of halogens (most notably Br and BrO) following the catalytic cycle in their photochemical release from sea salt during the spring time (Fisher et al., 2012; Lindberg et al., 2007). This causes atmospheric Hg^0 concentrations to drop well below their usual background concentrations and Hg^0 and Hg^II concentrations to initially increase before their subsequent deposition to surface reservoirs (Obrist et al., 2011; Steffen et al., 2008). At the Alert research station in northern Canada, atmospheric Hg^0 concentrations decreased from approximately 1.7 ng/m^3 to less than 0.1 ng/m^3 in under 24 hours (Steffen et al., 2008).

AMDEs are generally limited to the boundary layer (<1 km altitude) and the strength and frequency of events tends to correlate with local meteorological conditions (Steffen et al., 2008). AMDEs are not limited to the polar regions and have also been observed in the midlatitudes within the marine boundary layer, over salt lakes and in the free and upper troposphere (Sun et al., 2016a). AMDEs have been observed in the summertime over the Dead Sea where they were found to be concurrent with high BrO concentrations and temperatures reaching up to 45°C (Ariya et al., 2015; Mao et al., 2016). Currently the extent to which reactive halogens may initiate AMDEs in the low latitudes and at temperatures well above freezing remains unclear (Obrist et al., 2011).

There is growing recognition in the literature of the occurrence of nocturnal atmospheric mercury depletion events (NAMDEs), whereby atmospheric Hg^0 concentrations are found to dip overnight, before rebounding to pre-depletion levels following sunrise (Mao et al., 2008; Howard et al., 2017). Observations suggest that NAMDEs are most pronounced when accompanied by O_3 depletion and dew formation under calm boundary layer conditions. One hypothesis, based on observations in mid-latitude Australia, is that Hg^0 depletion is due to oxidation by O_3, the subsequent uptake by dew (Howard & Edwards, 2017). However, Mao et al. (2008) estimated that this only explains about 30% of their observed NAMDEs in North America and attributed the remaining 70% to dry deposition.
2.3.2. Reduction of Hg\textsuperscript{II} to Hg\textsuperscript{0}

Mechanisms for the atmospheric reduction of Hg\textsuperscript{II} to Hg\textsuperscript{0} are poorly understood, these processes are assumed to occur in the aqueous phase (e.g. in cloud water droplets, precipitation and aerosols) where Hg can exist as free ions or complexes and undergo photo-reduction (Horowitz et al., 2017; Subir et al., 2011). Table 2 shows the software representations (used by CTMs) of the reduction reactions proposed in the literature.

The predominant Hg\textsuperscript{II} species in the gas phase is thought to be HgCl\textsubscript{2}, while in the aqueous phase it is thought to be HgCl complexes; however these are resistant to photoreduction (Holmes et al., 2009; Selin et al., 2007). Hg\textsuperscript{II} binds to the organic ligands, found in natural water and organic aerosols and this allows HgCl complexes to subsequently undergo photoreduction (Horowitz et al., 2017). Therefore, the rate of atmospheric photoreduction is dependent upon UV levels and organic aerosol concentrations (Tong et al., 2013; Zheng & Hintelmann, 2009).

Solar radiation can influence Hg\textsuperscript{II} reduction either directly, via a ligand that absorbs light energy and releases electrons that subsequently reduce Hg\textsuperscript{II}; or indirectly, through the production of precursors (reactive intermediates) that then react with Hg\textsuperscript{II} (Ariya et al., 2015; Subir et al., 2012). The mechanism for aqueous-phase photoreduction of Hg\textsuperscript{II} is proposed as follows (de Foy et al., 2016; Horowitz et al., 2017):

\[ Hg^{II}_{(aq)} + hv \rightarrow Hg^0_{(aq)} + \text{products} \]

Rate coefficient (M s\textsuperscript{-1}): \( k_g = SR_{norm}/\tau_{Solar} \)

Where:
- \( hv \) = a photon of solar radiation;
- \( SR_{norm} \) = is the shortwave downward solar radiation flux (s\textsuperscript{-1}); and
- \( \tau_{Solar} \) = is the lifetime against reduction of Hg\textsuperscript{II} due to solar radiation (s\textsuperscript{-1}).

Hg\textsuperscript{II} has a strong attraction to both organic and inorganic ligands, especially those containing sulfur (S) (Steffen et al., 2008). It has been proposed that HgSO\textsubscript{3} may undergo reduction to Hg\textsuperscript{0} as follows:

\[ HgSO_3_{(aq)} \rightarrow Hg^0_{(aq)} + \text{products} \]

However, it is thought that HgSO\textsubscript{3} concentrations are too low under standard atmospheric SO\textsubscript{2} levels and therefore the reaction rate would be too low for this to be a viable reduction pathway (Horowitz et al., 2017; Subir et al., 2011).

Hg\textsuperscript{II} may undergo aqueous-phase reduction to Hg\textsuperscript{I} and then Hg\textsuperscript{0} via an endothermic reaction in the presence of HO\textsubscript{2} and/or O\textsubscript{2} (Horowitz et al., 2017):

\[ Hg^{II} \xrightarrow{HO_2/O_2} Hg^{I} \xrightarrow{HO_2/O_2} Hg^{0} \]

Mercury reduction mechanisms are subject to uncertainty due to: (i) only a limited number of reduction pathways having been identified; (ii) the assumption that reduction is only taking place
in the aqueous-phase; (iii) the assumption that Hg\textsuperscript{II} is chemically inert and therefore has no influence; and (iv) the fact that Hg\textsuperscript{II} is typically operationally defined and most measurement techniques cannot distinguish between the different Hg\textsuperscript{II} compounds (Subir et al., 2011; Subir et al., 2012).

Table 2: Software representations of the mechanisms and estimated reaction rate coefficients for the reduction of Hg\textsuperscript{II} to Hg\textsuperscript{0}. References: (1) Horowitz et al., (2017); (2) de Foy et al., (2016); (3) Subir et al., (2011); and (4) Xiao et al. 1994. Note that these references are summaries and not the primary source.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficients\textsuperscript{ab}</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg\textsuperscript{II} ( (aq) ) + hν ( \rightarrow ) Hg\textsuperscript{0} ( (aq) )</td>
<td>( k_g = SR_{norm}/\tau_{Solar}s^{-1} )</td>
<td>(1, 2)\textsuperscript{d}</td>
</tr>
<tr>
<td>Hg\textsuperscript{II} ( \rightarrow ) Hg\textsuperscript{I} + Hg\textsuperscript{0} ( (aq) )</td>
<td>( 1.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1} )</td>
<td>(3)</td>
</tr>
<tr>
<td>Hg\textsuperscript{II} ( (aq) ) + HO\textsubscript{2}(aq) ( \rightarrow ) Hg\textsuperscript{I} ( (aq) ) + O\textsubscript{2} + H\textsuperscript{+} ( (aq) )</td>
<td>( 1.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1} )</td>
<td>(3)</td>
</tr>
<tr>
<td>Hg\textsuperscript{II} ( (aq) ) + O\textsubscript{2}(aq) ( \rightarrow ) Hg\textsuperscript{I} ( (aq) ) + O\textsubscript{2}(aq)</td>
<td>( 0.0106 \text{ s}^{-1} ) to 0.6 s\textsuperscript{-1}</td>
<td>(3)</td>
</tr>
<tr>
<td>HgSO\textsubscript{3}(aq) ( \rightarrow ) Hg\textsuperscript{0} ( (aq) ) + S(VI)</td>
<td>( &lt; 10^4 \text{ s}^{-1} )</td>
<td>(1,3)\textsuperscript{d}</td>
</tr>
<tr>
<td>Hg(SO\textsubscript{2})\textsubscript{2}(aq) ( \rightarrow ) Hg\textsuperscript{0} ( (aq) ) + S(VI)</td>
<td>( 3.7 \times 10^{-7} \text{ s}^{-1} )</td>
<td>(3,4)</td>
</tr>
<tr>
<td>Hg(OH)\textsubscript{2}(aq) + hν(( \lambda &lt; 290\text{nm} )) ( \rightarrow ) Hg\textsuperscript{0} ( (aq) ) + Products</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Footnote:
\textsuperscript{a}The reaction rate coefficients are subject to uncertainties due to assumptions in their determination (Subir et al., 2011).
\textsuperscript{b}Units for rate coefficients are shown in the table. (aq) denotes the concentration in mol L\textsuperscript{-1}. hν = a photon of solar radiation, SR\textsubscript{norm} = is the shortwave downward solar radiation flux; and \( \tau_{Solar} \) is the lifetime against reduction of Hg\textsuperscript{0} due to solar radiation (de Foy et al. 2016).
\textsuperscript{d}Thought to be the most atmospherically relevant.

2.3.3. Mercury surface/heterogeneous chemistry

The chemical interactions that Hg undergoes in the atmosphere extend beyond gas and aqueous phase chemistry to include mercury surface/heterogeneous chemistry. Atmospheric surfaces that serve as sites for gaseous Hg interactions/reactions include (i) suspended solids and liquid particles, such as aerosols (e.g. salts, organic compounds, microorganisms and mineral dust); (ii) cloud water droplets; and (iii) ice crystals (Subir et al., 2012). These allow atoms and molecules to adsorb, deposit or collide and subsequently undergo heterogeneous and surface interface processes (Ariya et al., 2015).

Gaseous Hg species can be adsorbed onto atmospheric surfaces and from here they may: (i) be desorbed back to the atmosphere; (ii) undergo chemical/photochemical reactions and equilibrium processes; or (iii) diffuse into the aqueous compartment and undergo heterogeneous reactions.
(e.g. complex formation, solid precipitation and oxidation/reduction) (Subir et al., 2012). The quantity that is absorbed depends on the concentrations of gaseous Hg species and the composition of the atmospheric surface, adsorption tends to be higher for particulate matter that is rich in carbon (Nelson et al., 2004).

Studies have shown that Hg$_0$ oxidants such as O$_3$ and OH have a preference for reactions via surface adsorption (Ariya et al., 2015). The different Hg species are thought to have different rates for surface adsorption and desorption; however this area is currently uncertain. The interactions between the different Hg species and an aerosol particle are shown in Figure 1.

![Figure 1: Representation of the chemical interactions between the different Hg species and an aerosol particle. Areas of uncertainty are represented by question marks. Figure reproduced from (Subir et al., 2012, p.2).](image)

2.3.4. Partitioning between Hg$^{II}$ in gas-phase and Hg$^{P}$ in particulate phase

Atmospheric gas-aerosol partitioning between Hg$^{II}$ in gas-phase ($Hg^{II}_{g}$) and Hg$^{P}$ in particulate phase ($Hg^{P}_{p}$) has direct implications for deposition because gases and particles undergo different depositional processes and at different rates. Hg$^{II}$ undergoes efficient dry and wet deposition, but Hg$^{P}$ does not undergo efficient dry deposition (Amos et al., 2012).

Amos et al. (2012) used long-term observations of $Hg^{II}_{g}$, $Hg^{P}_{p}$ and fine particulate matter (PM$_{2.5}$) to derive the empirical gas-particle partitioning relationship. This shows that the partitioning between $Hg^{II}_{g}$ and $Hg^{P}_{p}$ is based on temperature and aerosol surface area.

$$\log_{10}(K^{-1}) = a + \frac{b}{T}$$

Where:

- $K =$ the partitioning coefficient;
\( a \) and \( b = \) coefficients; and

- \( T = \) the local temperature (in K).

- \( K \) is calculated from the following equation:

\[
K = \left( \frac{r_{Hg^p}}{PM_{2.5}} \right) / r_{Hg^{II}}
\]

Where:

- \( r_{Hg^p} \) and \( r_{Hg^{II}} = \) the atmospheric mixing ratios (ppq); and

- \( PM_{2.5} = \) the dry mass concentration of particulate matter with an aerodynamic diameter of <2.5 micron (\( \mu g \) m\(^{-3} \)).

However, there are some suggestions that this method for gas-particle partitioning may be oversimplified and should also consider surface adsorption onto aerosol particles, ligand chemistry while in aqueous solution and the size dependent microphysics of fine-mode and coarse-mode aerosols (Ariya et al., 2015; Zhang et al., 2017). Although the majority of \( Hg^p \) is distributed into \( PM_{2.5} \) rather than coarser particles (with aerodynamic diameter > 2.5 \( \mu m \)), these coarser \( Hg^p \) are known to have a faster deposition velocity (Wright et al., 2016).

### 2.4. Mercury sources

Bottom-up estimates of total global \( Hg \) emissions to the atmosphere are in the range of 6500-8200 Mg yr\(^{-1} \) (Driscoll et al., 2013). More recently Song et al., (2015) estimated 5800 Mg yr\(^{-1} \) based on inverse modeling. Roughly 4600-5300 Mg yr\(^{-1} \) (or 70% of total emissions) of which occurs from natural geogenic processes and secondary reemissions (known as legacy emissions, this is \( Hg \) that has been deposited to surface from the atmosphere and is then subsequently reemitted). The remainder is primary anthropogenic emissions (Driscoll et al., 2013; EU GMOS, 2017). Overall about 45-47% of total \( Hg \) emissions occur from the terrestrial surface (anthropogenic and natural), while 53-55% occurs from surface waters (Pacyna et al., 2016; Song et al., 2015). It is important to note that estimates of \( Hg \) emissions and deposition are subject to uncertainty due to challenges in quantifying flux levels and modelling the mechanisms involved (Zhu et al., 2016). Figure 2 provides a representation of \( Hg^0 \) exchange fluxes between the atmosphere and Earth surfaces.
2.4.1. Primary mercury emissions

The primary emission of Hg into the atmosphere from lithospheric reservoirs occurs via both anthropogenic and natural processes (Driscoll et al., 2013).

Natural geogenic sources (including volcanic activity, crustal degassing, weathering and biological particles) account for approximately 80–600 Mg yr$^{-1}$ (5-13% of total emissions) (Agnan et al., 2016; Amos et al., 2013; Driscoll et al., 2013; Edwards et al., 2005). Nriagu and Becker (2003) estimate that the average fluxes of Hg from volcanic eruptions and degassing plumes are 57 Mg yr$^{-1}$ and 37.6 Mg yr$^{-1}$ respectively, based on known ratios Hg/SO$_2$. However, their estimates don’t include the Hg fluxes from some geothermal sources as measurements of SO$_2$ where not available.

Anthropogenic sources (including: mining, fossil fuel combustion, metal smelting, waste treatment, artisanal and small-scale gold mining (ASGM), agriculture and biomass burning) are responsible for approximately 1875–2900 Mg yr$^{-1}$ (29-33% of total emissions) (Agnan et al., 2016; AMAP/UNEP, 2015; Camargo, 2002; Driscoll et al., 2013; EU GMOS, 2017). While the uncertainty range is estimated at 1010–4070 Mg yr$^{-1}$ (Selin, 2013). ASGM is the largest sector, followed by the burning of coal; they account for about 35% and 24% of total anthropogenic emissions respectively (UNEP, 2013a).

The current largest anthropogenic source region is Asia, which accounts for about 65% of global anthropogenic Hg emissions (Amos et al., 2013; Fu et al., 2015), while Australia is estimated to contribute roughly 22 Mg yr$^{-1}$ (2%) of global anthropogenic emissions (AMAP/UNEP, 2015). The spatial distribution of global anthropogenic Hg emissions in 2010 is presented in Figure 3.
In developing countries coal combustion is the single largest source of Hg to the atmosphere (Corbitt et al., 2011), while biomass burning is another important source and a contributor to the interannual variations in Hg concentration observed in the troposphere (De Simone et al., 2017; Fu et al., 2015). In Australia, the three largest sources are: (i) gold smelting (~49.7%); (ii) coal combustion in power plants (~14.8%); and (iii) alumina production from bauxite (~12.2%) (Nelson et al., 2012).

Anthropogenic emissions from Europe and North America have progressively decreased since 1990, largely due to the introduction of pollution control technology, whereas emissions from developing regions (Asia) have continued to grow due to an increase in the burning of fossil fuels (Lehnherr, 2014). One study estimated that global anthropogenic emissions decreased from 2890 Mg yr$^{-1}$ in 1990 to 2160 Mg yr$^{-1}$ in 2000 and have since increased slightly to 2280 Mg yr$^{-1}$ in 2010 (Zhang et al., 2016).

Pollution control technologies can help to reduce Hg emissions. For example, flue gas desulfurization technologies aimed at SO$_2$ control were also found to reduce Hg$^{II}$ concentrations (Strezov et al., 2010). However, pollution control technologies also have an effect on the speciation of Hg within emissions. For example, selective catalytic reduction aimed at NO$_x$ control was found to oxidize Hg$^0$ to Hg$^{II}$ (Zhang et al., 2016), while other technologies may reduce Hg$^{II}$/Hg$^0$ to Hg$^0$; this will then have implications for atmospheric transport (Shah et al., 2010; Giang et al., 2016).

At the global scale, anthropogenic emissions exceed natural geogenic emissions and this results in the overall increase of Hg$^0$ in the atmospheric reservoir that is then available for long-range transport and deposition to surface reservoirs (Driscoll et al., 2013). However, emissions studies in Australia have found that regional emissions are dominated by natural/legacy emissions accounting for 93%, with the remaining 7% due to anthropogenic sources (Nelson et al., 2009).

An inventory by Streets et al. (2011) estimated that total anthropogenic Hg emissions to the atmosphere since 1850 are 215 Gg. This inventory was more recently updated to include previously unquantified commercial sources and showed that an additional 540 Gg of Hg has
been released to environmental reservoirs (air: 20%; water: 30% and terrestrial: 50%) (Horowitz et al., 2014).

2.4.2. Secondary (legacy) mercury emissions

Secondary (or Legacy) emissions of Hg⁰, refers to Hg which have previously been deposited into the surface reservoir and are then subsequently reemitted to the atmosphere. Legacy emissions are estimated to account for about 56-65% of total atmospheric Hg emissions and are therefore an important flux in the biogeochemical cycling of Hg (Agnan et al., 2016). They include the reemission of Hg that has previously been deposited from local (domestic) emissions and Hg that has been transported in from other regions and is then deposited (AMAP/UNEP, 2015).

Legacy emissions use the atmosphere to exchange and redistribute Hg among and within surface reservoirs, such as water bodies and ecosystems (Driscoll et al., 2013). It is thought that legacy mercury is more likely to accumulate within terrestrial ecosystems than in the ocean (Song et al., 2015).

2.4.3. Isotopic fractionation of Hg

Hg (mostly as Hg⁰ and HgⅡ, but also a limited fraction as CH₃Hg⁺ and (CH₃)₂Hg²⁺ exists as a mixture of seven stable isotopes (¹⁹⁶Hg, ¹⁹₈Hg, ²⁰₀Hg, and ²⁰₄Hg) (Sun et al., 2016a). There is a mass difference of approximately 4% between the different Hg isotopes, resulting in a distinctive chemical signature for each Hg isotope (Demers et al., 2013; Sun et al., 2016b). The isotopic signatures of Hg can therefore be used as a tracer for identifying the chemical mechanisms involved during atmospheric redox processes (Blum et al., 2014) and for identifying different sources of Hg to the atmosphere (Zhang et al., 2017). Experiments by Sun et al. (2016a) found that the oxidation of Hg⁰ by Cl results in the faster removal of lighter isotopes in the reactant, whereas oxidation by Br is slower and depletes the heavier isotopes. This leaves a signature hinting at the particular oxidant involved.

Isotopic signatures can also be useful for constraining and differentiating between emissions sources of Hg to the atmosphere and the subsequent deposition to surface reservoirs (Zhang et al., 2017). Anthropogenic sources are typically associated with high temperatures (e.g. from combustion, smelting and heating processes) and this tends to result in high Hg isotope mass dependent fractionation signatures, but none from mass independent fractionation. Natural sources are typically associated with photochemical activity that induces Hg isotope mass independent fractionation signatures (Sun et al., 2016b). Hg isotopes can therefore be used to identify the trace sources that have accumulated in surface reservoirs, e.g. soils and vegetation (Demers et al., 2013). It has been demonstrated using isotopic signatures that the majority of Hg deposition to soils occurs from vegetation, accounting for approximately 57-94% of Hg deposition to soils in central North America (Obrist et al., 2017).

Currently, measurements of the isotopic composition of atmospheric Hg are sparse and limited to a small scale as a sufficient mass of Hg is required for analysis (Zhang et al., 2017). It is thought
that passive air samplers may provide a suitable measurement method when utilized with an extended sampling period (Blum & Johnson, 2017; McLagan et al., 2016). No isotopic measurements currently exist for Australia, which means that Hg models are required to get at this information instead.

2.5. **Mercury enriched sites**

Hg occurs naturally in the Earth’s crust with an abundance of about 0.08 parts per million by mass (ppmm), although rarely as a free element and is primarily found as cinnabar ore (HgS), as well as livingstonite (HgSb₄S₈) and corderoite (Hg₃S₂Cl₂) (Ariya et al., 2015; Camargo, 2002; Rytuba, 2003). There are 26 mercury mineral belts distributed globally, with one extending down the east coast of Australia and into Tasmania. These belts are associated with tectonic activity and volcanic processes (both current and previously active) that enriched the Hg concentration within the substrate (Gustin et al., 2006; Rytuba, 2003; Selin, 2009). These mineral deposits have been found to contain up to 1200 ppm of Hg (Edwards & Howard, 2013), with estimates suggesting that globally they contribute 500–1500 Mg/year to the atmosphere (Gustin, 2011).

Soils are considered to be Hg enriched when their concentration exceeds 0.1 µg of Hg per g of soil (Gustin et al., 2006). Edwards and Howard (2013) compared Hg enriched sites to background sites in Australia and found a strong correlation between substrate Hg concentration and flux levels. The Hg enriched sites showed a greater net emission to the atmosphere with average fluxes ranging from 14 ± 1 ng m⁻² h⁻¹ to 113 ± 6 ng m⁻² h⁻¹.

2.6. **The atmospheric reservoir**

2.6.1. **Inter-hemispheric transport**

The northern and southern hemispheres can be thought of as quasi-independent atmospheric Hg reservoirs because the atmospheric transport of Hg across the equator is limited by the intertropical convergence zone (ITCZ) and the role of Hadley circulation which reduces the tropospheric exchange of air masses (Hamilton et al., 2008; Holmes & Prather, 2017, in press). The ITCZ is formed where trade winds from the northern and southern hemispheres meet and create a low-pressure region that circulates the globe. This provides a meteorological barrier to the inter-hemispheric transport of Hg, due to the associated heavy rainfall and rapid vertical motion of air masses (Hamilton et al., 2008). The effect of Hadley circulation can both reduce inter-hemispheric transport, by pushing air masses upward and poleward, or contribute to it through its seasonal oscillation (Holmes & Prather, 2017, in press). The ITCZ shifts north and south between seasons in response solar heating. This can result in the interhemispheric mixing of air as it is switched between northern and southern Hadley cells (Bowman & Cohen, 1997). On occasions the top of northern Australia is located north of the ITCZ/chemical equator and so sits within the atmospheric northern hemisphere (Howard et al., 2017).
2.6.2. Atmospheric mercury observation systems

There are a number of atmospheric mercury observation systems in place: the European Monitoring and Evaluation Programme (EMEP), the National Atmospheric Deposition Programme’s (NADP) Mercury Deposition Network (MDN) in the United States, the Canadian Atmospheric Mercury Network (CAMNet), the Asia Pacific Mercury Monitoring Network (APMMN) and more recently the European Union (EU) Global Mercury Observation System (GMOS).

The GMOS network (Figure 4) consists of 43 ground-based Hg monitoring stations distributed around the globe. One of its goals is to “broaden Hg observation capability, particularly in the southern hemisphere” (EU GMOS, 2017) and hence the network contains a number of southern hemisphere sites: (i) Amsterdam Island, Indian Ocean; (ii) Cape Point, South Africa; (iii) Cape Grim, Australia; (iv) Bariloche, Argentina; (v) Dome Concordia, Antarctica; (vi) Dumont d’Urville, Antarctica; and (vii) Gunn Point (EU GMOS, 2017).

![Ground-based monitoring sites](image)

Figure 4: Ground-based monitoring sites included in the GMOS global network. Figure reproduced from (EU GMOS, 2017). Note that Gunn Point, NT is a secondary site, but not shown in the Figure.

2.7. Mercury exchange flux

2.7.1. Evasion and deposition

The exchange flux of Hg between the atmosphere and Earth’s surfaces is bidirectional and occurs via three processes: (i) evasion/emission; (ii) wet deposition; and (iii) dry deposition. All atmospheric forms of Hg (Hg$_0$, Hg$^II$ and Hg$^I$) can be deposited onto terrestrial surfaces, however the pathway depends upon the form of Hg, the surface type and environmental conditions (Gustin,
The flux strength is strongly correlated with temperature, radiation and substrate parameters (Edwards & Howard, 2013).

$\text{Hg}^0$ can be removed by dry deposition, or oxidized to $\text{Hg}^{II}$ and removed via wet deposition. As $\text{Hg}^{II}$ is highly soluble its atmospheric residence time is far shorter (hours to days) and so it tends to be deposited locally or regionally (Driscoll et al., 2013). More recently it has been suggested that the long-range atmospheric transport of Hg may not occur via continuous transport, but instead undergo a process of prompt recycling (or hopping) whereby the Hg undergoes surface deposition at night and subsequent remission at sunrise (Hintelmann et al., 2002; Howard et al., 2017; Selin, 2009).

Dry deposition involves the transfer of both $\text{Hg}^0$ and $\text{Hg}^{II}$ from the atmosphere to sinks on the Earth’s surface (e.g. soil, water and vegetation) (Driscoll et al., 2013). $\text{Hg}^0$ may undergo dry deposition via the gravitational settling of particles (Nelson et al. 2009). Wet deposition involves the transfer of Hg from the atmosphere to the Earth’s surface via precipitation scavenging. As $\text{Hg}^0$ is largely insoluble its removal via this process is negligible, however $\text{Hg}^{II}$ is highly soluble, while $\text{Hg}^0$ provides a surface on which cloud water droplets can form (Driscoll et al., 2013; Lindberg et al., 2007). Dry deposition rates for Australia were estimated to be between 20 to 70 $\mu$g m$^{-2}$ yr$^{-1}$, however this is based on modelling efforts where the empiricisms are derived from the northern hemisphere (Nelson et al., 2009). Recent observations of Australian fluxes at a site in Snowy Mountains in southern Australia have seen this estimate revised to between 14 to 62 $\mu$g m$^{-2}$ yr$^{-1}$, (Howard & Edwards, 2017).

The majority of atmospheric $\text{Hg}^0$ losses occur via its oxidation into $\text{Hg}^{II}$, which is more soluble and subsequently prone to wet deposition. The redox cycling of $\text{Hg}^0$ to $\text{Hg}^{II}$ (see Section 2.3) is largely controlled by photochemistry as the main oxidants of $\text{Hg}^0$ ($\text{BrO}$ and $\text{OH}$) are photochemically produced. This also explains why $\text{Hg}^{II}$ production has a diurnal cycle with the maximum occurring around midday and the minimum at night (Selin, 2009). This pathway represents the most common route for the removal of atmospheric Hg to terrestrial reservoirs (Amos et al., 2012).

Once deposited, $\text{Hg}^{II}$ can then be reduced (photochemically and/or biochemically) to $\text{Hg}^0$ and re-emitted to the atmosphere, or it can bind with organic carbon and be sequestered into soil pools (Corbitt et al., 2011). If the overall flux is positive, then it indicates that Hg evasion is greater than its deposition (Song et al., 2016). $\text{Hg}^0$ exchange fluxes are important for understanding Hg emissions from anthropogenic and natural processes. A diagrammatic representation is provided in Figure 2.

Sedimentary records suggest that anthropogenic Hg emissions between preindustrial times and the present have enriched the atmospheric reservoir by a factor of 3 (Agnan et al., 2016; Krabbenhoft & Sunderland, 2013; Smith-Downey et al., 2010). This corresponds with the factors reported in archives (such as lake sediment and peat bogs) that show an increase in Hg in atmospheric deposition from approximately 3 to 10–20 $\mu$g m$^{-2}$ yr$^{-1}$ (Enrico et al., 2017; Gustin, 2011). Figure 5 shows a reconstruction of atmospheric $\text{Hg}^0$ levels from 8000 BCE until present.
using core samples from two peat bogs (Pinet and Estibere). The reconstructed values from 1970 onwards show a good agreement with atmospheric Hg\(^0\) observations from monitoring stations (Enrico et al., 2017).

![Reconstructed atmospheric Hg\(^0\) levels](image)

**Figure 5: Reconstructed atmospheric Hg\(^0\) levels.** Figure reproduced from (Enrico et al., 2017. P.5899).

Hg deposited to the terrestrial surface from the atmosphere ultimately accumulates in recalcitrant soil pools, peat bogs, lake sediments and ice cores over a period of centuries (Driscoll et al., 2013). These archives provide an understanding of whether the terrestrial surface is a source or sink of Hg. These archives all indicate that globally there has been a three-fold enrichment in the levels of atmospheric Hg deposition since pre-industrial times (approximately 1850), suggesting that atmospheric Hg concentrations have increased in recent times. However, greater levels of enrichment (over five-fold in some cases) have been noted in areas that are prone to elevated deposition levels due to regional sources (Amos et al., 2013; Corbitt et al., 2011; Driscoll et al., 2013; Horowitz et al., 2014). Overall it is estimated that between 1850 and 2010, 112 Gg (gigagrams) of anthropogenic Hg were directly emitted from byproduct sectors (e.g. fossil fuel combustion). However, during this period an additional 720 Gg of Hg was mined for commercial use and of this about 310 Gg is actively cycling and contributing to present-day enrichment (Horowitz et al., 2014).

Greater levels of enrichment tend to be a characteristic of the major industrial regions of the world (both past and present), reflecting the growth of Hg emissions in Europe and North America during the twentieth century and the growth of Asia in recent decades (Amos et al. 2013; AMAP/UNEP, 2015). Overall about 60% of Hg deposition from the atmosphere occurs from legacy anthropogenic Hg emissions, 23% from primary anthropogenic emissions and 13% natural emission sources (Amos et al., 2013).

Hg deposited to the terrestrial ecosystems eventually accumulates in the pedosphere where it has an approximate lifetime of 80 years before it is re-emitted to the atmosphere through soil respiration. In contrast, Hg deposited to the surface ocean layer has a lifetime of approximately 6 months before it is re-emitted to the atmosphere or transferred to the subsurface ocean layer.
Studies suggest that soils store over 90% of Hg in the terrestrial surface, with the top 40 cm of soil in the U.S. containing an estimated 15,230 Mg of Hg, when this is extrapolated globally it accounts for over 300,000 Mg (Obrist et al., 2014).

Hg is emitted from the terrestrial surface to the atmosphere through: (i) photoreduction; (ii) the respiration of organic carbon; (iii) biomass burning; and (iv) river runoff into the surface ocean (Amos et al., 2013; Kocman et al., 2017). However, enriched isotope spike experiments have shown that freshly wet-deposited Hg may have a higher availability for reemission than the older Hg already present, as this is more likely to be bound to vegetation and soil (Hintelmann et al., 2002; Lehnherr, 2014; Selin et al., 2008). It has also been found that freshly wet-deposited Hg is more readily transformed to CH$_3$Hg$^+$ and so poses a greater risk for bioaccumulation (Meng et al., 2011).

It was estimated in 2004 that Australian Hg emissions were in the range of 117 to 567 Mg yr$^{-1}$ (Nelson et al., 2004); however these estimates are based on data from the National Pollutant Inventory (NPI) and subject to bias due to reliance on overseas information, the use of emissions factors and assumptions (Nelson, 2007). A more recent estimate suggests that TGM being emitted/remitted from natural sources throughout Australia are around 95-285 Mg yr$^{-1}$, with approximately 4-12 Mg yr$^{-1}$ from vegetation, 70-120 Mg yr$^{-1}$ from soils and 21-63 Mg yr$^{-1}$ from fires; anthropogenic sources are estimated to contribute around 10-20 Mg yr$^{-1}$ (Nelson et al., 2012).

### 2.7.2. Quantifying mercury flux and atmospheric concentrations

Understanding the global biogeochemical cycling of Hg requires quantification of the air-surface fluxes of Hg$^0$. Over the last three decades there have been extensive efforts to measure, model and estimate these fluxes between the atmosphere and various surfaces (e.g. ocean, freshwater, soil, vegetation, etc.) in Europe, North America and Asia. However, uncertainties remain due to a lack of high-quality data on Hg$^0$ directional exchange, limitations of techniques for quantifying fluxes and challenges involved in modelling (Zhu et al., 2016).

There are a number of methods for quantifying Hg flux and atmospheric concentrations, including: (i) dynamic flux chambers (DFC’s); (ii) micrometeorological techniques (MM); and (iii) bulk methods. All methods typically show that Hg$^0$ evasion dominates during the day, while Hg$^0$ deposition dominates at night (Zhu et al., 2016). As the exact chemical mechanisms for redox reactions and transformations between different Hg species are uncertain, the best plan for monitoring atmospheric concentrations and fluxes is to measure all three species (Selin, 2013).

#### 2.7.2.1 Measuring TGM and Hg$^0$

Measurements of TGM concentrations in the air are typically made through use of cold vapour atomic fluorescence spectrophotometry (Osterwalder et al., 2016). The most commonly utilised analyser is the Tekran 2537™ Mercury Vapor Analyzer, which operates by passing air over two gold cartridges (traps) working in tandem to capture and determine the concentration of TGM in the air. One-trap captures TGM, while the other is heated to thermally desorb the Hg into an inert
carrier gas (usually argon) that carries it for analysis by cold vapor atomic fluorescence spectrometry. Their functions are then reversed at 5-minute intervals to allow for the near continuous measurement of TGM (Fu et al., 2015; Sprovieri et al., 2016; Steffen et al., 2008; Steffen et al., 2012). The Tekran 2537™ analyzer can be adapted to include a Teflon filter at the front end to remove HgII and HgP. If a Teflon filter is used then the sample collected is Hg⁰ (Steffen et al., 2012).

2.7.2.2 Measuring HgII and Hg⁰

Measurements of HgII are typically made through use of the Tekran Mercury Speciation units (models 1130/1135™) with a potassium chloride (KCl) coated annular denuder to absorb HgII from the air, typically over a 1-hour sampling period (Sprovieri et al., 2016; Steffen et al., 2012). After collection the denuder is heated to 500°C and the HgII is thermally desorbed into a stream of Hg-free air. This is then passed over a quartz chip pyrolysis chamber with a temperature of 525-800°C where the HgII is thermally reduced to Hg⁰, before analysis via spectrometry (Steffen et al., 2008). Measurements of HgII concentrations tend to be operationally defined, partly due to the unreliability of calibration techniques for monitoring equipment, while several studies have suggested that HgII is inefficiently collected with a KCl-coated denuder and so HgII may be underestimated by a factor of 1.6 to 3.7 times (Angot et al., 2016; Morrison et al., 2015).

Hg⁰ typically accounts for only a few percent of total atmospheric Hg concentrations; although it is more abundant over polluted areas due to emissions from industry and coal burning (Nelson et al., 2004). It originates from the adsorption of HgII onto airborne particles (such as dust, soot, and sea-salt aerosols), with adsorption driven by particle concentrations and air temperature (Amos et al., 2012). It is collected and measured by passing air through a filter, made from Teflon, cellulose, quartz or glass fiber, that traps airborne particles. The Hg⁰ is then released from the filter by wet digestion or pyrolysis and analyzed via spectrometry (Steffen et al. 2008). However, measurements cannot quantitatively distinguish between Hg⁰ and HgII. HgII tends to stick to inlets, tubes and filters before later revolatilizing and contaminating the collection and measurement of Hg⁰ (Slemr et al., 2016a; Zhang et al., 2017). Measurements of Hg⁰ are subject to sampling errors due to sampling duration and difficulties in differentiating between HgII and Hg⁰ with current sampling methods (Amos et al., 2012).

HgII and Hg⁰ measurements are not currently available from any Australian sites. However, cation exchange membranes are currently being explored and tested as a new measurement in Australia (Fisher, 2017, personal communication, 2 October).

2.8. Factors that influence mercury flux

2.8.1. Ocean mercury flux

The ocean-atmosphere exchange of Hg is extremely important to the biogeochemical cycle of Hg, with wet and dry deposition accounting for 70% of Hg inputs to the ocean and gas exchange accounting for 90% of outputs from the ocean (Mason et al., 2017). The ocean-atmosphere
exchange also helps to mediate the rate at which Hg increases within the upper ocean and so it helps to limit increases in CH$_3$Hg$^+$ concentrations. This is important as the upper oceans are home to the majority of the fish and seafood that humans consume (Mason et al., 2017).

Overall Hg evasion is believed to dominate ocean mercury fluxes and therefore the global oceans are thought to be a net source of Hg$^0$ to the atmosphere, although the magnitude is uncertain (Mason et al., 2017; Song et al., 2016).

Hg$^0$ evasion from the surface ocean is the single largest source of atmospheric Hg. It plays a central role in driving the biogeochemical cycling of Hg around the world (Amos et al., 2013). In the southern hemisphere the oceans cover a larger proportion of the Earth’s surface and here they are estimated to contribute over half of the atmospheric Hg$^0$ concentrations (Angot et al., 2014; Sprovieri et al., 2017). Hg evasion varies between oceans and across ocean basins (Mason et al., 2017), with evasion fluxes largely driven by sea-surface temperature (De Simone et al., 2017), although other factors including wind speed, primary productivity, solar radiation levels and air temperature in the surface boundary layer also have an impact (Kwon et al., 2016; Soerensen at al., 2010). The upwelling of colder and nutrient-rich waters (particularly in the tropics) is associated with increased Hg evasion due to: (i) increased phytoplankton concentrations in these regions and their ability to reduce Hg$^{II}$ within seawater to Hg$^0$; and (ii) the photochemical reduction of Hg$^{II}$ (Semeniuk & Dastoor, 2017; Wang et al., 2012).

Oceanic Hg can exist as one of several forms: (i) a dissolved elemental and cationic Hg; (ii) dissolved CH$_3$Hg$^+$; and (iii) oxidised ligand-bound Hg$^{II}$. Fractionation between these forms is influenced by both microbial and photochemical reactions that drive oxidation, reduction and methylation processes (Blum et al., 2014). Hg seawater concentrations vary between oceans/regions and are influenced by their proximity to anthropogenic sources, coastal regions and precipitation levels, which in turn affect wet deposition fluxes (Soerensen et al., 2010). In coastal and estuarine regions, Hg tends to be scavenged by particulate matter that is suspended in the water column and is subsequently deposited to bottom sediments (Chakraborty et al., 2016). Studies have shown that recent decreases in Hg emissions in Europe and North America (due to emissions control), have been reflected by decreasing Hg seawater concentrations in the surrounding regions (Mason et al., 2012).

Deposition of Hg$^{II}$ to the surface ocean is composed predominantly of legacy emissions, with primary anthropogenic emissions accounting for approximately a third and the remainder resulting from natural sources (Corbitt et al., 2011). Overall atmospheric deposition to the surface ocean is estimated at ~18.5 Mmol y$^{-1}$ (Soerensen at al., 2010). Once in the ocean, Hg$^{II}$ can be reduced into Hg$^0$ by a combination of photochemical and biological processes. Photolytic processes drive the majority of Hg$^{II}$ reduction in the surface ocean, with biological processes becoming more significant with depth (Soerensen at al., 2010). Overall about 89% of Hg$^{II}$ reduction is thought to result from biological processes (mostly due to aquatic microorganisms) and abiotic processes, while the remaining 11% is due to photochemical processes (Nerentorp Mastromonaco et al., 2016).
Hg concentrations in the surface layer are affected by upwelling, Ekman pumping and seasonal entrainment (Nerentorp Mastromonaco et al., 2016). However, oceanic Hg can also undergo horizontal and vertical transport through ocean circulation. The extent of vertical transport is affected by upwelling and deep-water formation across ocean basins (Soerensen et al., 2010). Anthropogenic Hg enrichment in the deep ocean layer (> 1500m depth) is less than in the surface and subsurface layers (Mason et al., 2012). Hg transport to and accumulation in the deep ocean reservoir occurs over a period of centuries, before Hg is eventually being deposited in sediments and undergoing burial into the deep mineral reservoir over millennia. Estimates suggest that this burial removes approximately ~180–260 Mg yr⁻¹ (Amos et al., 2013). Hydrothermal vents in the deep ocean also act as a natural source of Hg to the surrounding water (Ariya et al., 2015).

Hg⁰ in the water column can also undergo aqueous phase oxidation through reactions with photochemically produced hydroxyl radicals (OH) (see Section 2.3.1.4) allowing for its reemission to the atmosphere (Soerensen et al., 2010). It is thought that oceanic oxidation rates are influenced by reactions between OH⁻ and halides (halogen anions such as Cl⁻ and Br⁻), which produce aqueous halogen radicals. This in turn increases overall oxidation levels, resulting in higher Hg⁰ evasion fluxes. Overall about 80% of Hg deposited into the surface ocean is reemitted to the atmosphere (mostly as Hg⁰) (Driscoll et al., 2013; Soerensen et al., 2010). Hg reemissions from the oceans are thus a major factor in driving atmospheric Hg⁰ concentrations, particularly in the southern hemisphere (Angot et al., 2014).

Observations in the western Pacific Ocean have found that Hg concentrations have been increasing in the surface and subsurface waters since the year 2000. This is believed to reflect anthropogenic inputs from increasing emissions in Asia (Driscoll et al., 2013). There are suggestions that Hg levels in the ocean have yet to reach a steady state with regard to deposition levels and therefore Hg concentrations in the ocean are expected to continue increasing (Selin, 2009). However, recent observations have suggested that atmospheric Hg⁰ and TGM concentrations over the oceans are decreasing (Fu et al., 2015), possibly due to changes in anthropogenic emissions, decreases in legacy Hg emissions and enhanced oxidation rates (Zhang et al., 2017).

2.8.2. Terrestrial mercury flux

A number of studies have been undertaken over the past three decades to measure, model and estimate Hg fluxes between the atmosphere and various surfaces. Gustin (2011) explains that global model scenarios, which balance out projected emissions with the known atmospheric burden and projections of deposition rates, indicate that the terrestrial surface provides a net sink for atmospheric Hg. An analysis of Hg concentrations within surface soils and sediment cores support this conclusion. It is likely that the terrestrial surface displays seasonal variability and is generally a net sink of Hg during the spring and summer (Song et al., 2016).

The different terrestrial reservoirs principally exchange Hg with the atmosphere-ocean system, with only minor levels of Hg exchange directly between themselves (Amos et al. 2013). The
The majority of Hg is stored in soils and the biosphere as Hg\textsubscript{II}, but if this is converted back to Hg\textsubscript{0} then it can be emitted to the atmosphere (Driscoll et al., 2013). The terrestrial Hg exchange with the atmosphere is sensitive to a number of factors, as described below.

### 2.8.2.1 Solar radiation

Agnan et al. (2016), Edwards and Howard (2013) and Zhu et al. (2016) report that there is positive correlation between solar radiation and Hg\textsubscript{0} flux. UV-B radiation is attributed with photochemically enhancing the reduction of soil Hg\textsubscript{II} into volatile Hg\textsubscript{0} and therefore facilitating Hg\textsubscript{0} evasion. These authors suggest that UV-A, visible light, biotic and abiotic processes also facilitate the reduction of Hg\textsubscript{II} into Hg\textsubscript{0}, although these have a smaller contribution than UV-B. In general, Hg\textsubscript{0} fluxes exhibit diurnal variations with emissions tending to occur during the day, as solar radiation and temperature levels are at their highest, while deposition occurs overnight (Wright & Zhang, 2015).

### 2.8.2.2 Temperature

Soil and air temperatures are regarded as an important factor in the promotion of Hg\textsubscript{0} evasion and generally have a positive correlation that is collinear to radiation. This relationship typically follows the Arrhenius equation:

\[
k = A e^{-E_a/(RT)}
\]

Where:

- \( k \) = rate constant;
- \( T \) = absolute temperature (in kelvin);
- \( A \) = pre-exponential factor (frequency factor);
- \( E_a \) = activation energy; and
- \( R \) = universal gas constant.

The Arrhenius equation can be used to summarise how temperature affects \( k \) and therefore the rate of a chemical reaction. It suggests that temperature is linked to either the activation energy of Hg\textsubscript{0}, or that it stimulates microbial activity within the soil, which then promotes Hg\textsubscript{0} evasion (Agnan et al., 2016). However, Zhu et al. (2016) explain that some studies have observed spikes in Hg\textsubscript{0} flux at sub-zero temperatures and this suggests that other mechanisms must also be involved.

### 2.8.2.3 Seasonality

Hg\textsubscript{0} fluxes vary between seasons due to changes in air temperature and levels of solar radiation. Emissions are generally higher during the summer, when solar radiation and temperature levels are higher (Wright & Zhang, 2015). Studies in North America have found that Hg\textsubscript{0} deposition tends to occur in spring with the growth of new foliage as this helps to facilitate the accumulation of Hg\textsubscript{0} within vegetation, emissions then increase during the transition into summer as the foliage reaches senescence which limits the ability for Hg\textsubscript{0} to be further accumulated (Wright & Zhang,
Seasonal variations have also been observed in the southern hemisphere (South America and Australia), with the maximum deposition occurring during the summer and the minimum during winter (AMAP/UNEP, 2015).

2.8.2.4 Precipitation
Wet deposition (via precipitation) provides the major route for removing Hg\textsuperscript{II} from the atmosphere. The magnitude of Hg\textsuperscript{II} wet deposition is a product of atmospheric Hg concentration and precipitation volume; therefore greater deposition fluxes tend to occur over the wettest periods (Holmes et al., 2016). It has been shown that differences in Hg wet deposition fluxes vary geographically, seasonally and annually due in part to differences in precipitation rates, but are also affected by climatic conditions, atmospheric chemistry and anthropogenic influences (Lindberg et al., 2007; Sprovieri et al., 2017). This is particularly true in the tropics, where high precipitation rates during the wet season have been shown to significantly increase the level of Hg\textsuperscript{II} wet deposition. Higher levels of relative humidity may increase the conversion rates of Hg\textsuperscript{0} to Hg\textsuperscript{II} via aqueous phase oxidation and subsequently increase wet deposition fluxes (Holmes et al., 2016; Howard et al., 2017).

Hg wet deposition is also influenced by the type of rainfall event. Holmes et al. (2016) found that for the same precipitation depth, Hg wet deposition increased by 50% for thunderstorms compared to convective or stratiform events. This is because thunderstorms can reach and scavenge Hg\textsuperscript{II} from the upper troposphere where Hg\textsuperscript{II} is found in higher concentrations and represents a greater percentage of total Hg (Holmes et al., 2016; Nair et al., 2013).

2.8.2.5 Atmospheric conditions
Atmospheric turbulence and Hg\textsuperscript{0} concentrations are influenced by seasonal variables, including: (i) wind speed; (ii) atmospheric composition; (iii) stability of the boundary layer; and (iv) spatial variability (Wright & Zhang, 2015). In general, higher levels of atmospheric turbulence (e.g. wind and surface friction speeds) promote Hg\textsuperscript{0} evasion as this enhances the mass transfer of Hg\textsuperscript{0} within soil and promotes its evasion from the soil surface (Zhu et al., 2016). Atmospheric Hg\textsuperscript{0} concentrations can both positively and negatively influence the level of Hg\textsuperscript{0} fluxes (Agnan et al., 2016). This is because atmospheric Hg\textsuperscript{0} concentrations influence the air-surface Hg\textsuperscript{0} exchange (Wright & Zhang, 2015). Evasion tends to occur with lower atmospheric Hg\textsuperscript{0} concentrations, while deposition occurs with higher atmospheric Hg\textsuperscript{0} concentrations. The abundance of Hg within foliage is also influenced by the atmospheric Hg\textsuperscript{0} concentration and this in turn has an impact on the air-vegetation flux of Hg\textsuperscript{0} (Zhu et al., 2016).

2.8.2.6 Soil characteristics
Hg\textsuperscript{0} flux is influenced by the characteristics of the soil substrate; these include the soil type, soil porosity, soil moisture, Hg content and soil chemistry. Higher soil porosity helps to promote Hg\textsuperscript{0} evasion as this facilitates the reduction of Hg\textsuperscript{II} and the transfer of Hg\textsuperscript{0} to the atmosphere. It has been found that soils with a higher surface area (those that have a smaller grain size and contain clay and silt particles) tend to have both a higher Hg content and levels of Hg\textsuperscript{0} flux (Zhu et al.,
Hg$^0$ flux may also be influenced by soil chemistry and therefore the constituents that comprise a soil (e.g. clay minerals, organic or carbon matter, iron oxides, and sulfur (S) compounds) are important (Gustin et al., 2011). It is thought that sulfur and also selenium (Se) influence Hg dynamics in soils and this in turn reduces the rate of CH$_3$Hg$^+$ uptake by plants. This is attributed to a reduction in the photoavailability of CH$_3$Hg$^+$ in the presence of sulfur and Se (Wang et al., 2016). There are also suggestions that soil organic matter (SOM) influences the level of Hg$^0$ flux from soils, with lower levels of Hg flux thought to correlate with higher concentrations of SOM. However, a study by Edwards and Howard (2013) did not find sufficient data to fully support this correlation. Hg stored in soils can roughly be divided into three classes: (i) Hg bound to the soil mineral fraction; (ii) Hg bound to soil organic carbon content; and (iii) Hg adsorbed to the negatively charge surface of soil particles (Smith-Downey et al., 2010).

Measurements taken with dynamic flux chambers indicate that there is a diurnal cycling of Hg$^0$ flux from soils, although soils with a high mineral content show a consistent uptake of Hg$^0$ (Edwards & Howard, 2013). Once Hg is deposited into mineral soils it is unlikely to be reemitted, unless subject to disturbance (e.g. from runoff or erosion) and therefore provides a role in the long-term sequestration of Hg (Obrist et al., 2014). The process of weathering controls the release of Hg from mineral soils back into the atmosphere over long time scales (Smith-Downey et al., 2010).

The majority of studies show a positive correlation between soil moisture and Hg$^0$ evasion. It is proposed that soil moisture promotes the reduction of Hg and desorption of Hg$^0$ from soil particles into the soil pore space. In general Hg fluxes increase with an increase in soil moisture as this helps to mobilise the Hg$^0$ towards the soil surface and so facilitate its evasion into the atmosphere. However, there is an optimum range and Hg flux decreases once soil moisture increases over this range. When soils become water saturated, Hg$^0$ evasion decreases as water blocks the soil pore space preventing the transfer of Hg$^0$ (Agnan et al., 2016; Gustin et al., 2006). Therefore, irrigation and precipitation levels are likely a factor in determining levels of Hg$^0$ flux from soil (Zhu et al., 2016).

The Hg concentration within soils affects Hg$^0$ flux between the soil and atmosphere. Soils that contain higher concentrations of Hg were also found to have higher levels of Hg$^0$ evasion. The concentrations of other reactants (e.g. carbon and O$_3$) impact upon Hg flux between the soil and atmosphere (Wright & Zhang, 2015).

Most studies suggest that the soil-air interface provides a net source of Hg emissions, with Hg$^0$ emission dominant during the daytime and deposition limited to night periods. For example, observations by Zhu et al. (2016) suggest that the combined Hg$^0$ flux from uncontaminated soil and water bodies accounts for approximately 64% of total atmospheric Hg emissions. Of this it is estimated that globally bare soil releases ~550 Mg yr$^{-1}$. Hg deposited into soils is suggested to accumulate within SOM (Driscoll et al., 2013). This is because Hg$^{II}$ is the dominant Hg form within soil and it strongly binds to organic matter through complexation by one or two thiol groups (Obrist et al., 2014).
Obrist et al. (2014) found that Hg\(^0\) emissions are dominant from the soil surface, but that they are decoupled from Hg\(^0\) diffusion within the underlying soil and that overall mineral soils immobilise Hg\(^0\) suggesting that they may provide a net sink. The transfer of Hg\(^0\) within mineral soil occurs via diffusion within the soil pore space, whereby Hg\(^0\) is immobilised via sorption, oxidation, or dissolution processes. They found that Hg\(^0\) concentrations within soil air are lower than Hg\(^0\) concentrations found in the atmosphere and as these aren’t in equilibrium it suggests that Hg\(^0\) immobilisation within mineral soils provides a net sink. They produced a soil diffusion model based on Fick’s First Law:

\[ J = -D \left( \frac{\Delta C}{\Delta z} \right) \]

Where:

- \( J \) = the diffusion flux;
- \( D \) = the Hg\(^0\) diffusion coefficient in the soil;
- \( \Delta C \) = the change in Hg concentration; and
- \( \Delta z \) = the change in depth between the soil and atmosphere.

Their model estimates that diffusion produces a downward flux of 0.2 and 0.7 ng of Hg m\(^{-2}\) day\(^{-1}\) at two forests in the Sierra Nevada mountains, California, USA. This is equivalent to a rate of 79 and 258 ng of Hg m\(^{-2}\) y\(^{-1}\).

2.8.2.7 Vegetation characteristics

Vegetation cover alters Hg\(^0\) flux from soils by: (i) reducing the level of incident solar radiation; (ii) decreasing the adjacent soil and air temperature; (iii) providing a barrier against atmospheric turbulence; (iv) promoting litter cover of the soil surface; and (v) providing a surface for the deposition of Hg\(^0\) (Zhu et al., 2016).

The production of leaf litter biomass represents a major pathway for the input of Hg from vegetation to the soil layer and its subsequent transformation and sequestration (Wang et al., 2016; Wright et al., 2016). The fraction of Hg that is effectively sequestered from litterfall into soils is linked to the levels of sulfur and nitrogen present in the soil during carbohydrate mineralisation of the leaf litter (Wang et al., 2016).

Vegetation type has also been shown to have an influence on Hg\(^0\) flux, with factors such as foliage type, moisture content, plant species and combustion properties having an influence (De Simone et al., 2017). Gustin (2011) explains that for similar atmospheric Hg\(^0\) concentrations, deposition and emission levels are typically lower in grassland plant species compared to evergreen trees, which are in turn lower than deciduous trees. A study by Wright and Zhang (2015) suggests that Hg\(^0\) deposition is the dominant process over grassland species.

Measurements of flux suggest that the air–vegetation exchange of Hg\(^0\) is bidirectional and depends on the lifecycle of vegetation. Modelling estimates that growing plants remove 1024.2 Mg yr\(^{-1}\) Hg globally through leaf assimilation, while emissions from foliage contribute 237.6 Mg
yr\(^{-1}\). This suggests that growing plants act as a net sink (Zhu et al., 2016). Similarly, Song et al. (2016) found that during the summer in the eastern United States there are relatively low levels of soil Hg\(^0\) evasion and there are high levels of Hg uptake by foliage. Therefore, it is likely that the terrestrial surface provides a net sink during the summer. It has been found that Hg emission fluxes from vegetation exhibit a strong diurnal variation, with higher emissions during the day (Nelson et al., 2009).

It is estimated that vegetation in forest ecosystems deposits 1232 Mg yr\(^{-1}\) of atmospheric Hg through global litterfall, while 1338 Mg yr\(^{-1}\) of atmospheric Hg is deposited directly onto the soil surface as throughfall. Of this 381 Mg yr\(^{-1}\) of Hg is reemitted back into the atmosphere from the forest floor (Zhu et al., 2016). Most of the Hg deposited by litterfall and throughfall is immobilized by SOM and through binding with sulfur functional groups (Driscoll et al., 2013; Wright et al., 2016).

It has been shown that Hg\(^0\) flux varies with vegetation type. Studies suggest that grassland and forest ecosystems may provide a large sink for atmospheric Hg; however these studies quantify Hg flux with the use of bulk methods and although these provide an indication they aren’t sophisticated enough to provide a sufficient answer (Zhu et al., 2016). Current Hg flux data does not provide reliable estimates for the role of foliage in air-vegetation exchanges due to the large uncertainties in quantifying Hg budgets when using bulk methods (e.g. correlation analyses (slopes) between atmospheric Hg\(^0\) and other trace gases (e.g. CO, CO\(_2\) and CH\(_4\)). DFC’s provide a more reliable measurement (but are limited by their footprint size) and so Hg flux in other land covers are better defined, with grasslands showing a net deposition of 89 Mg yr\(^{-1}\) and bare soils showing a net emission of 17 Mg yr\(^{-1}\) (Agnan et al., 2016).

Growing plants are particularly effective at removing atmospheric Hg, with foliage uptake a factor of: (i) Hg air concentrations; (ii) position within the canopy (concentrations are higher in those closer to the ground); (iii) leaf age (older leaves have higher Hg concentrations, but are slower with uptake compared to young leaves); and (iv) environmental conditions, e.g. solar radiation level, temperature and CO\(_2\) concentration (Gustin, 2011).

### 2.8.2.8 Anthropogenic activities

Anthropogenic activities have a direct influence on Hg\(^0\) flux. Deforestation and biomass harvesting reduce vegetation cover increasing the exposure of the soil surface to solar radiation and higher temperatures. Agricultural activities (such as tilling) increase soil disturbance and this helps to mobilise Hg within the soil and increase Hg\(^0\) emissions (Zhu et al., 2016).

Land use and cover types have a significant impact on Hg fluxes. Emission rates tend to be higher for agricultural and pasture land in comparison to forests and natural grasslands due to greater rates of soil organic matter turnover and higher levels of incident solar radiation on topsoil (Driscoll et al., 2013). However, it can be difficult to quantify Hg\(^0\) fluxes from agroecosystems (e.g. cropland and plantations) as they undergo large leaf area index and canopy cover changes in a very short period of time (days to months) during harvesting (Pattey et al., 2005). Land
management practices also influence the exchange of Hg between different surface reservoirs (terrestrial, freshwater and ocean) through changes to erosion and hydrological pathways; this in turn influences Hg fluxes to the atmosphere from these reservoirs (Kocman et al., 2016).

Anthropogenic impacts on land cover and land use are controlling factors for Hg flux on the terrestrial surface (Driscoll et al., 2013). For example, agricultural and pastoral lands experience higher levels of disturbance through tilling and grazing resulting in higher levels of incident solar radiation and turnover rates of SOM that increase the rates of Hg\textsuperscript{0} evasion compared to natural surfaces. However, it is unclear as to whether this results in a net source of Hg emissions to the atmosphere.

Surfaces that have been influenced by anthropogenic activities (such as urban areas, agricultural fields and mining/industrial sites) tend to be a net source of Hg to the atmosphere. It was found that the median level of Hg evasion from these areas is 5-10 times higher than the background values for uncontaminated soils. It is estimated that biomass burning and non-point sources contribute 300–600 Mg yr\textsuperscript{-1} of Hg emissions to the atmosphere (Driscoll et al., 2013). While natural surface areas (soil and vegetation) near to point sources of anthropogenic Hg emissions were found to have higher Hg concentrations, possibly due to enhanced rates of atmospheric Hg\textsuperscript{0} and Hg\textsuperscript{g} deposition (Zhu et al., 2016).

Contaminated surfaces are sites comprised of Hg mining, non-ferrous metal production, precious metal processing and polluted industrial sites. These are known to contribute to Hg evasion and thus provide a net source of Hg to the atmosphere (Zhu et al., 2016). Esbri et al. (2016) found that average atmospheric Hg\textsuperscript{0} concentrations at Almadén (a contaminated site in Spain) were 27.4 ng m\textsuperscript{-3}, well above the background level for Europe of 1.6 ng m\textsuperscript{-3}. Modelling with the use of known Hg fluxes from over 3000 Hg contaminated sites suggests that global Hg emissions from contaminated sites contribute 82 Mg yr\textsuperscript{-1}. However, as contaminated sites have a limited surface area they have a limited contribution to total emissions from the terrestrial surface and pose more of a risk to the surrounding environment (Zhu et al., 2016).

### 2.8.3. Impact of climate change

Climate change is likely to have an impact on the global biogeochemical cycling of Hg. In the atmosphere, rising air temperatures, weaker circulation and changes to precipitation patterns and intensity will have an impact on chemical transformations and Hg deposition at local, regional and global scales (Krabbenhoft & Sunderland, 2013). Hg emissions from ocean and soil reservoirs may increase as a result of increased volatilization from rising air temperatures (Giang et al., 2015), while changes to wildfire frequency, intensity and scale have the potential to mobilize Hg stored in soils and vegetation (Ariya et al., 2015). Warmer temperatures have the potential to increase rates of ecosystem primary productivity, thus stimulating sequestration in plants and the activity rates in bacteria, potentially increasing the conversion of Hg to CH\textsubscript{3}Hg\textsuperscript{+} (Krabbenhoft & Sunderland, 2013). Climate change may also release significant amounts of long-stored Hg into the atmosphere and freshwater reservoirs through the thawing of permafrost at
high latitudes (UNEP, 2013a).

2.9. Atmospheric mercury in Australia

The Australian climate, its flora, fauna and soil types are different from those in other regions of the world and there is a lack of representative data for the Australian region regarding the cycling of both natural and anthropogenic emissions between the atmosphere and terrestrial surface (Edwards & Howard, 2013). Australia is mostly an arid and dry continent, but it is host to a range of climates zones that include equatorial, tropical, subtropical, desert, grassland and temperate regions. As Hg fluxes are influenced by precipitation rates, temperature and vegetation type it is expected that Hg fluxes will differ between these different climate zones.

A 2009 emissions inventory found that about 93% of Australia’s total Hg emissions are from natural and legacy sources (with emissions from soil and vegetation contributing 66% and 4% of total Hg emissions respectively). However, these estimates are uncertain due to a lack of Australia-specific data and uncertainties inherent in estimating emissions factors. The remaining 7% of Hg emissions are from anthropogenic sources, with the biggest contribution (49.7%) coming from a single gold smelting operation in Kalgoorlie, Western Australia (Nelson et al., 2009; Nelson et al., 2012). The next biggest contributions are coal combustion in power plants (14.8%) and alumina production from bauxite (12.2%) (Nelson et al., 2009; Nelson et al., 2012). However, it should be noted that there have been recent changes to Australia’s emissions from the gold smelting due to the introduction of ultrafine grinding technology and the closure of the Gidji roaster at Kalgoorlie in 2015 (KCGM, 2017). These are estimated to have reduced emissions from the gold smelting operation at Kalgoorlie by ~90% (Nelson, 2017, personal communication, 18 August). Estimates of Hg emissions from coal combustion (2-8 Mg yr⁻¹) are subject to uncertainties regarding the mercury content of the coals burnt and the capture efficiency in particulate control devices used at power plants (Nelson, 2007). Sampling of Hg speciation in flue gas emissions from Australian coal-fired power stations found that total mercury concentrations are in the range of 1.9 to 5.6 µg m⁻³. Hg₀ and Hg¹ᴵ account for the largest proportion (96.3-99.7%), with Hg²⁰ accounting for a small proportion (0.3-3.7%) as it was readily captured by existing pollution control technologies (Shah et al., 2010).

The majority of efforts on modelling and quantifying Hg flux from the terrestrial surface have taken place at northern hemisphere sites in North America, Europe and Asia; therefore the emission factors and empiricism that underlie existing Hg models rely on data from these regions (Edwards & Howard, 2013). As a result, the models have a high degree of uncertainty for estimating southern hemisphere and Australian cycling (Pirrone et al., 2010; Horowitz et al., 2017). Attempts at modelling the southern hemisphere by Holmes at al. (2010) and Horowitz et al. (2017) have proven unsuccessful and indicated that existing Hg models suffer from bias (due to uncertainties).

Existing measurements for atmospheric Hg in Australia are limited to a few published studies by: (i) Edwards and Howard (2013) at Pulganbar, NSW; (ii) Slemr et al. (2015) at Cape Grim, TAS;
(iii) Morrison et al. (2015) at Glenville, NSW; (iv) Howard et al. (2017) at Gunn Point, NT; and (v) Howard and Edwards (2017) in the Snowy Mountains, southern Australia. These show that Australian Hg\textsuperscript{0} concentrations vary from an average of 0.86 ng m\textsuperscript{-3} at Cape Grim, TAS (southern Australia) to 0.95 ng m\textsuperscript{-3} at Gunn Point, NT (northern Australia).

Edwards and Howard (2013) found that the key factors that influence Hg emissions from soils at a site in Pulganbar, NSW are solar radiation and temperature, with the atmospheric temperature having a greater influence than soil temperature over bare soils. They also found that the average temperature over Australian sites was 1.2°C warmer than for comparable North American data and this resulted in a 30% increase in Hg emissions to the atmosphere. There are a number of other unique characteristics in Australia that mean that northern hemisphere results may not be relevant to the Australian context.

The majority of atmospheric Hg losses occur via the oxidation of Hg\textsuperscript{0} into Hg\textsuperscript{II}, which is subsequently removed via wet deposition. Therefore, deposition rates in Australia are expected to show seasonal and regional variability related to precipitation levels; with higher deposition rates in northern Australia during the wet season and lower deposition rates in drier areas (e.g. inland deserts) and during the winter months. The atmospheric transport of Hg was also found to be affected by the Australian monsoon during the wet season in northern Australia (Howard et al., 2017).

Hg flux varies with vegetation type (De Simone et al., 2017) and so it is expected that evasion and deposition rates will vary with different regions. Higher deposition rates are hypothesised for rainforests as they experience faster foliage growth (Gustin et al., 2011), with potentially higher emission rates from grassland and eucalypts forests as they are more susceptible to bushfires (Howard et al., 2017; Howard & Edwards., 2017).

The Australian climate also experiences variability due to the influence of El Niño-Southern Oscillation (ENSO), with El Niño being the warm phase and so bringing higher temperatures and reduced rainfall to Australia and La Niña being the cool phase accompanied by cooler temperatures and heavy rainfall. In turn this climate variability has an impact on Australian Hg fluxes that are thought to differ from other regions of the world (Pirrone et al., 2010). Slemr et al. (2016b) found that ENSO affects the tropospheric concentrations of Hg by driving interannual variations in biomass burning emissions. ENSO will also have an impact on Australian temperatures (which are significantly higher than in the northern midlatitudes), which may have an effect on emissions and atmospheric chemistry.

Overall atmospheric Hg cycling (including the emission amounts, flux rates, sources and sinks) remains highly uncertain over Australia.
Chapter 3

3. Aims and objectives of this project

3.1. Aim 1

To date, limited research has been undertaken on measuring, modelling and quantifying the sources and quantities of atmospheric Hg in Australia. We have reasonable estimates of the mercury budget for northern hemisphere regions (such as the US, Europe and Asia) and global mercury budgets. Few studies have explicitly quantified Hg in southern hemisphere environments, and only one has attempted to provide a budget for Australian Hg (Nelson et al., 2012). Thus, the first aim of this project is to:

1. Develop an improved estimate of the mercury budget for the Australasian region, including the influence of the ocean.

3.2. Aim 2

Australia presents a unique environment, with its climate, vegetation and soil types differing from other regions of the world. To date, there has only been limited research undertaken on measuring and modelling mercury fluxes in Australia. No global-scale Hg models have been evaluated against any Australian observations, and it is known that these models do not generally perform well at southern hemisphere sites (Horowitz et al., 2017; Song et al., 2016), it is less clear what needs to be done to improve the simulation. The first step of determining that is to figure out the sensitivities in the simulation of Australian Hg to better direct future research efforts. Thus, the second aim of the project is to:

2. To provide the first evaluation of a global biogeochemical Hg model (GEOS-Chem) over Australia and use GEOS-Chem to determine which sources most influence the simulations over Australia.

3.3. Aim 3

The results from achieving Aims 1 and 2 provide a first assessment of GEOS-Chem’s modelling capabilities and sensitivities over Australia. Thus, the third aim of the project is to:

3. Formulate informed recommendations about future targeted research for Hg observations and model development that would facilitate improved accuracy of Hg models in this region.
Chapter 4

4. Methods

The majority of published knowledge regarding mercury concentrations and distributions in the southern hemisphere is based on measurements from ship cruises and from a limited number of remote-monitoring stations at Cape Point, South Africa and Antarctica (Slemr et al., 2015). Hg⁰ concentrations have been measured at a number of additional southern hemisphere sites since 2013, including for the first-time sites in Australia. These observations were compared against modelling simulations from the GEOS-Chem biogeochemical Hg model (described below in Section 4.3.1) to assess model performance in regards to Australia and the southern hemisphere mid-latitudes background.

4.1. Methods of analysis

This involved the following tasks:

1. The existing available Hg data in Australia and the southern hemisphere was collated and used to identify relationships between atmospheric Hg and physical parameters.

2. Modelling was undertaken using GEOS-Chem to evaluate the existing simulation of Hg⁰ against the existing data.

3. Sensitivity studies were used to estimate the contributions of different sources to total Australian Hg concentrations.

4. Model output was used to estimate the budget of atmospheric Hg over the Australasian region.

5. Python was used to write scripts (programming code) for manipulating the observational and GEOS-Chem data; this included removing outliers, statistical analysis and the generation of figures, maps and tables. An example of the Python code used is included in Appendix 2.

4.2. Ground-based observation Sites

The project makes use of newly available observations provided by collaborators from Macquarie University from three ground-based GEM monitoring sites in Australia. The sites are located at (see Figure 6):

- Cape Grim, Tasmania (40.6832°S, 144.6899°E);
- Gunn Point, Northern Territory (12.2491°S, 131.0447°E); and
- Glenville, Hunter Valley, NSW (32.4777°S, 151.1018°E).

Additional observations are also provided by collaborators at the Laboratoire de Glaciologie et Géophysique de l'Environnement, and the Max Planck Institute for Chemistry from two ground-
based GEM monitoring sites in southern hemisphere. The sites are located at (see Figure 6):

- Amsterdam Island, TAAF, Indian Ocean (37.4748°S, 77.3423°E); and
- Cape Point, South Africa (34.3535°S, 18.4897°E).

All observations were taken with a Tekran 2537™ Hg vapour analyser using the techniques described in Section 2.7.2. The sites used in this study only take measurements of Hg\textsubscript{0} at present, as this is the only Hg species subject to long distance transport. Although I was not responsible for collecting any of the Hg observation used in this study, I assisted in measuring Hg with a Tekran 2537™ at a site in Oakdale, NSW as part of a research campaign being undertaken by collaborators at Macquarie University. Table 3 provides an overview of the ground-based monitoring sites used in this study.

![Figure 6: Locations of the ground-based Hg\textsubscript{0} monitoring sites.](image-url)
**Table 3: Overview of the ground-based observation sites.**

<table>
<thead>
<tr>
<th>Monitoring Site:</th>
<th>Local Area Map:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Site:</strong> Cape Grim, Tasmania</td>
<td>![Map of Cape Grim, Tasmania]</td>
</tr>
<tr>
<td><strong>Latitude/Longitude:</strong> 40.6832°S, 144.6899°E</td>
<td></td>
</tr>
<tr>
<td><strong>Altitude:</strong> 104 m a.s.l.¹</td>
<td></td>
</tr>
<tr>
<td><strong>Climate Zone:</strong> temperate</td>
<td></td>
</tr>
<tr>
<td><strong>Data Availability:</strong> 2013 - present</td>
<td></td>
</tr>
<tr>
<td><strong>Description:</strong> the site has a baseline oceanic fetch, with winds coming off the Southern Ocean (direction is 190° – 280°). This baseline fetch was accounted for 33% of the time in 2013.⁶,⁷ The site also receives air masses from the Australian mainland and Tasmania, these represent anthropogenic and biomass burning events.⁷</td>
<td></td>
</tr>
<tr>
<td><strong>Credit:</strong> (Slemr et al., 2015).</td>
<td></td>
</tr>
</tbody>
</table>

| Site: Gunn Point, Northern Territory | ![Map of Gunn Point, Northern Territory] |
| **Latitude/Longitude:** 12.2491°S, 131.0447°E |  |
| **Altitude:** 25 m a.s.l.¹ |  |
| **Climate Zone:** tropical |  |
| **Data Availability:** 2014 - present |  |
| **Description:** observations are collected from the Australian Tropical Atmospheric Research Station (ATARS) located in the Northern Territory of Australia, northeast of Darwin. The site is surrounded by savannah vegetation and is located 10 km south of the northern coast, 2 km east of the western coast.³ |  |
| **Credit:** (Howard et al., 2017). |  |

<p>| Site: Glenville, Hunter Valley, NSW | ![Map of Glenville, Hunter Valley, NSW] |
| <strong>Latitude/Longitude:</strong> 32.4777°S, 151.1018°E |  |
| <strong>Altitude:</strong> 78 m a.s.l.¹ |  |
| <strong>Climate Zone:</strong> temperate |  |
| <strong>Data Availability:</strong> 2013 - present |  |
| <strong>Description:</strong> the site is located in the Hunter Valley 10 km south-east of two coal fired power stations (Bayswater and Liddel) and is within 3 km of operating coal mines. The site is considered to be seasonally influenced by anthropogenic emissions, mostly in the winter when the winds blow from the NW.⁵ |  |
| <strong>Credit:</strong> (Morrison et al., 2015). |  |</p>
<table>
<thead>
<tr>
<th>Site: Amsterdam Island, TAAF, Indian Ocean</th>
<th>Site: Cape Point, South Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Latitude/Longitude:</strong> 37.4748°S, 77.3423°E</td>
<td><strong>Latitude/Longitude:</strong> 34.3535°S, 18.4897°E</td>
</tr>
<tr>
<td><strong>Altitude:</strong> 55 m a.s.l.¹</td>
<td><strong>Altitude:</strong> 230 m a.s.l.¹</td>
</tr>
<tr>
<td><strong>Climate Zone:</strong> mild oceanic, frequent cloud cover</td>
<td><strong>Climate Zone:</strong> temperate</td>
</tr>
<tr>
<td><strong>Data Availability:</strong> 2013 - present</td>
<td><strong>Data Availability:</strong> September 1995 – December 2004 (manual) and March 2007 to present (automated).</td>
</tr>
<tr>
<td><strong>Description:</strong> small island (55 km²) located in the Indian Ocean, nearest land is Madagascar 3400 km to the east. Observations are collected from Base Martin de Vivies. The site is considered to represent ocean conditions due to its isolated location and oceanic fetch from the Indian and Southern Oceans.²,⁷</td>
<td><strong>Description:</strong> receives clean marine air masses most of the time with an oceanic fetch from the Southern Ocean. Occasionally experiences continental air masses and biomass burning events.⁴,⁷</td>
</tr>
</tbody>
</table>

Footnotes:

¹ metres above sea level (a.s.l).
² Angot et al., 2014.
³ Desservettaz et al., 2017.
⁴ Martin et al., 2017.
⁵ Morrison et al., 2015
⁶ Slemr et al., 2015.
⁷ Zahorowski et al., 2013.

### 4.3. Chemical transport modelling

Chemical transport modelling (CTM) provides a useful tool for assessing the biogeochemical cycle of Hg in the atmosphere and for determining fluxes to and from surface reservoirs (both terrestrial and ocean). CTMs need to accurately represent four primary processes with regards to Hg: (i) emissions; (ii) transport; (iii) atmospheric redox chemistry; and (iv) deposition (Driscoll et al., 2013). However, this is complicated by the considerable uncertainty regarding Hg speciation, the atmospheric redox chemistry of Hg and the surface exchange processes (e.g.
emissions and deposition) (Amos et al., 2012).

4.3.1. GEOS-Chem

GEOS-Chem is the biogeochemical Hg model used in this study. It is described as “a global 3D chemical transport model (CTM) for atmospheric composition driven by meteorological input from the Goddard Earth Observing System (GEOS) of the NASA Global Modelling and Assimilation Office” (GEOS-Chem, 2016).

GEOS-Chem is an Eulerian model. It operates by dividing the atmosphere into a number (104-108) of 3D grid boxes (based on latitude/longitude/altitude) and then simulating the atmospheric composition within each grid box. This is done by solving the coupled continuity equation for the number of chemical species (m), each with the number density vector \( \mathbf{n}(U) = (n_1, ..., n_m)^T \) for individual grid boxes defined within the Eulerian model (Long et al. 2015; Philips et al. 2016).

\[
\frac{\partial n_i}{\partial t} = -\nabla(n_i U) + P_i(n) - L_i(n) \quad i \in [1, m]
\]

Where:

- \( \frac{\partial n_i}{\partial t} \) = the local transport evolution of \( n \);
- \( -\nabla(n_i U) \) = the transport flux divergence term. This acts as an operator that separately and successively updates the concentration of each chemical species over each time;
- \( U \) = the wind velocity vector;
- \( i \) = the chemical species;
- \( P \) = the local production of chemical species; and
- \( L \) = the local loss of chemical species.

In brief, GEOS-Chem computes the number density of species \( i \) in a given box by calculating transport to and from neighboring boxes based on wind velocity and the production and loss of chemical species depending on the concentrations of other chemical species and also rates of emissions and deposition.

4.3.1.1 GEOS-Chem’s ability to accurately simulate observations

GEOS-Chem is one of the main/top biogeochemical Hg models available. It is applied by research groups around the world covering the academic, private and government sectors to help solve a range of problems related to atmospheric composition, chemical transport and international assessment. Figure 7 shows the number of citations that GEOS-Chem has had per year since it was first introduced in 1997. Since then it has had regular revisions (multiple times per year) that have vastly improved modeling performance.
As a model, GEOS-Chem is considered to represent the current state of knowledge regarding atmospheric Hg transport and fluxes. It has been widely used in the northern hemisphere in North America, Europe and Asia. In these regions it has been widely assessed and found to accurately match observations from cruises, flights and ground-based monitoring stations. Figure 8 and 9 show the ability of GEOS-Chem to match observations of the mean seasonal variation and existing global observations of TGM in surface air. It can be seen that GEOS-Chem’s performance is far more accurate in the northern hemisphere.

**Figure 7:** Number of citations making reference to GEOS-Chem per year. Figure reproduced from (GEOS-Chem, 2017).

**Figure 8:** Ability of GEOS-Chem to match observations of the mean seasonal variation. Figure reproduced from (Horowitz et al., 2017, p.30).
4.3.1.2 Model description

In this work version 11-01 of the GEOS-Chem Hg coupled atmosphere-ocean-land model was used. The model includes a 3D atmosphere coupled to a 2D ocean slab and terrestrial reservoir. The simulation was conducted with the GEOS-FP assimilated meteorology from the NASA Global Modelling and Assimilation Office (GMAO) Goddard Earth Observation System (GEOS). The original GEOS-FP data has a horizontal resolution of 0.3125° longitude, by 0.25° latitude, with 72 vertical levels up to 0.01 hPa (Lucchesi, 2013). This is regridded here to a coarser resolution of 2° x 2.5° with 47 vertical levels for input to GEOS-Chem as: (i) most inputs aren’t available at high resolution; (ii) the reduced computational time and resources allows for longer simulations and more sensitivity tests; (iii) global simulations are necessary for representing intercontinental transport and can only be conducted at coarser resolution; and (iv) simulations over Australia can, at the time of writing, only be conducted at coarser resolution. It should be noted that this is the usual process for Hg modelling and has been used in a number of other studies (Bieser et al., 2017; Gencarelli et al., 2017; Holmes et al., 2010; Horowitz et al., 2017; Long et al., 2015).

The period January 2013 to December 2016 was simulated, preceded by a 5-year spin-up to achieve steady state for the size of the Hg reservoir within GEOS-Chem. The spin-up repeated simulations for the year 2013 repeatedly, and the end results for each spin-up year were compared to make sure that there were no changes related to initial conditions. The results presented here are 4-year averages from 2013-2016, unless noted otherwise. All the simulations were run on the National Computational Infrastructure (NCI) Australia’s high-performance research computer Raijin. The simulations required scripts that contained specifications for the simulation to be
submitted to Raijin. It was found that a 1-month simulation required around 1 hour 6 minutes of CPU time and 8 CPUs for running.

The model allows for the emission (natural, anthropogenic and reemission), transport (advection, convective transport and turbulent mixing) and deposition (both wet and dry) of Hg$^0$, Hg$^{II}$ and Hg$^P$ from the atmosphere (Shah & Jaegle, 2017). The emissions inventories for: (i) global anthropogenic Hg emissions are taken from the United Nations Environmental Programme (UNEP) for 2010 (AMAP/UNEP, 2013); and (ii) biomass burning Hg emissions are taken from the Global Fire Emissions Database (GFED) and Fire Inventory from NCAR (FINN) (GEOS-Chem, 2016).

The atmospheric redox chemistry in GEOS-Chem uses a two-step oxidation mechanism with Br, BrO, O$_3$ and OH available for the oxidation Hg$^0$ to Hg$^{II}$ (see Section 4.2.1.3). The reduction of Hg$^{II}$ to Hg$^0$ occurs as photoreduction in the aqueous-phase and is scaled to NO$_2$ photolysis frequency, which is used as a proxy for the UV actinic flux (Song et al., 2016).

GEOS-Chem uses a monthly mean value for Br concentrations (taken from the separate bromine simulation) that varies between each grid box (2° x 2.5°) in the model. This is designed to capture the spatial variability. However, as Br concentrations are represented by a monthly average value GEOS-Chem is unable to simulate daily variability in Br levels and the impact of this on Hg concentrations. Temporal variations are therefore poorly represented (Ariya et al., 2015). The impacts of this are discussed in Section 5.

4.3.1.3 Atmosphere-surface exchange in GEOS-Chem

In GEOS-Chem Hg$^0$ emissions are attributed to both natural and anthropogenic sources, while the direct emission of Hg$^{II}$ is assumed to be entirely anthropogenic (Amos et al., 2012). The wet deposition of mercury is only applied to Hg$^{II}$ and Hg$^P$, due to the low Henry’s Law constant (0.11 mol$^{-1}$ L$^{-1}$ atm$^{-1}$ at 298K) of Hg$^0$ and hence low solubility (Selin et al., 2007). Wet deposition includes both rainout losses in precipitation and washout losses in convective updrafts (Chen et al., 2014).

Atmosphere-ocean exchange of Hg$^0$

The atmosphere–ocean exchange of Hg$^0$ is estimated in GEOS-Chem through a standard two-layer diffusion model (Liss & Slater, 1974):

$$ F = K \left( \frac{Hg_{aq}^0 - Hg_{air}^0}{H} \right) $$

Where:

- $F$ = the net emission flux between oceanic and atmospheric reservoirs (ng m$^{-2}$ h$^{-1}$);
- $K$ = the mass transfer coefficient estimated by wind speed and temperature-corrected Schmidt numbers for CO$_2$ and Hg$^0$ (m h$^{-1}$); and
- $H$ = a temperature dependent Henry’s law constant for $Hg_{aq}^0$ and $Hg_{air}^0$.  

43
The 2D ocean slab is a collection of grid boxes that represent the ocean surface layer within GEOS-Chem. These boxes allow for Hg exchange with the atmosphere, particulate settling (sedimentation) with the subsurface ocean and redox chemistry induced by biological and photochemical processes (Soerensen et al., 2013). At the surface level there is one ocean box for every atmospheric box, but subsurface there are only large basins and hence the slab-ocean lacks spatial resolution at the subsurface levels. The ocean boxes also neglect vertical and horizontal oceanic transport via diffusion and circulation (Semeniuk & Dastoor., 2017; Travnikov et al., 2017), but as horizontal oceanic transport is much slower than atmospheric transport this simplification is considered reasonable for the short time scales used in this study. Hg cycling in the ocean-slab is represented in a simplified manner via rate coefficients that control: (i) the net reduction of Hg\textsuperscript{II} deposited from the atmosphere; (ii) the partitioning of Hg\textsuperscript{II} to Hg\textsuperscript{P}; (iii) the particulate settling of Hg\textsuperscript{P}; and (iv) the oxidation of Hg\textsuperscript{0} back to Hg\textsuperscript{II} (Soerensen et al., 2010).

Two full simulations were used in this study (Default and InvOcean), these have different rate coefficients for the previous processes and are described in more detail in Section 4.3.1.4.

**Atmosphere-terrestrial surface exchange**

Hg\textsuperscript{0} evasion from the terrestrial reservoir includes emissions from vegetation, soil, biomass burning, geogenic sources, anthropogenic sources and re-emissions. Emissions from soil allows for volatility (related to solar radiation and soil Hg content) and the rapid recycling of freshly deposited Hg (Holmes et al., 2010; Travnikov et al., 2017).

In GEOS-Chem dry deposition is calculated using the equation (Gustin, 2011):

\[
F = V_d C
\]

Where:

- \( F \) = flux;
- \( C \) = the concentration of the species of interest; and
- \( V_d \) = the dry deposition velocity.

The dry deposition velocity can be estimated using the resistance in series method (Wesely, 1989):

\[
V_d = \frac{1}{(R_a + R_b + R_c)}
\]

Where:

- \( R_a \) = the is the aerodynamic resistance;
- \( R_b \) = the near-surface boundary-layer resistance (or quasi-laminar subsurface resistance); and
- \( R_c \) = the surface resistance term that is applied for leaf and soil surfaces.

It should be noted that: (i) the dry deposition velocity is not calculated over the ocean, because the ocean-atmosphere exchange is treated separately as a bi-directional process; and (ii) the
calculation is completely decoupled from emissions, so there are no bi-directional effects over land.

4.3.1.4 Chemical mechanisms in GEOS-Chem

The following differential equations are used for oxidation and reduction:

\[
\begin{align*}
\frac{\partial Hg^0}{\partial t} &= -(k_{on}^0 + k_{dep}^0) + k_{red}^0 \\
\frac{\partial Hg^0}{\partial t} &= -(k_{on}^0 + k_{dep}^0) + k_{red}^0 \\
\frac{\partial Hg^{II}}{\partial t} &= k_{on}^{II} - (k_{red}^{II} + k_{dep}^{II}) \\
\frac{\partial Hg^{II}}{\partial t} &= -(k_{red}^{II} + k_{dep}^{II})
\end{align*}
\]

Where:

- \( k_{on}^0 \) = the rate coefficients for Hg^0 oxidation (see Table 4);
- \( k_{dep}^0 \) = the rate coefficients for Hg^0 deposition (see Table 4);
- \( k_{red}^{II} \) = the rate coefficients for Hg^{II} reduction (see Table 4);
- \( k_{on}^{II} \) = the rate coefficients for Hg^{II} oxidation (see Table 4);
- \( k_{dep}^{II} \) = the rate coefficients for Hg^{II} deposition (see Table 4); and
- \( k_{dep}^0 \) = the rate coefficients for Hg^0 deposition (see Table 4).

Gas-phase Hg reactions in GEOS-Chem

Table 4 shows the software representations (used by CTMs) of the gas-phase Hg reactions simulated in GEOS-Chem:
Table 4: Gas-phase Hg reactions simulated in GEOS-Chem References: (1) Goodsite et al., 2012; (2) Holmes et al., 2010; (3) Hall, 1995; and (4) Sommar et al. 2001.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M}$</td>
<td>$5 \times 10^{-32} \times \left(\frac{T}{298}\right)^{-1.76} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{HgBr}^M \rightarrow \text{Hg}^0 + \text{Br}$</td>
<td>$3.9 \times 10^9 \times \exp\left(-\frac{8357}{T}\right) \left(\frac{T}{298}\right)^{0.51} \text{s}^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$\text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2$</td>
<td>$2.5 \times 10^{-10} \times \left(\frac{T}{298}\right)^{-0.57} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$\text{HgBr} + \text{OH}^M \rightarrow \text{HgBrOH}$</td>
<td>$2.5 \times 10^{-10} \times \left(\frac{T}{298}\right)^{-0.57} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$\text{HgBr} + \text{Br} \rightarrow \text{Hg}^0 + \text{Br}_2$</td>
<td>$3.9 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{II}$</td>
<td>$3.0 \times 10^{-20} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</td>
<td>(3)</td>
</tr>
<tr>
<td>$\text{Hg}^0 + \text{OH} \rightarrow \text{Hg}^{II}$</td>
<td>$8.7 \times 10^{-14} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$</td>
<td>(4)</td>
</tr>
</tbody>
</table>

**Footnote:**

Where: $[\text{M}]$ is the number density of air (molecules cm$^{-3}$) and $T$ is the temperature in kelvin (K).

**Partitioning between Hg$^{II}$ and Hg$^p$**

Partitioning between Hg$^{II}$ and Hg$^p$ in GEOS-Chem is based on temperature and aerosol surface area, as derived by the empirical gas-particle partitioning relationship in Amos et al., (2012). The partition coefficient ($K$) is defined as:

$$K = \frac{r_{\text{Hg}^p}/PM_{2.5}}{r_{\text{Hg}^{II}}}$$

Where:

- $r_{\text{Hg}^{II}}$ and $r_{\text{Hg}^p}$ = the atmospheric mixing ratios (ppq); and
- $PM_{2.5}$ = the dry mass concentration (µg m$^{-3}$) of non-Hg aerosols with an aerodynamic diameter <2.5 micron.

$$\log_{10}(K^{-1}) = a + \frac{b}{T}$$

Where:

- $K$ = the partition coefficient;
- $a$ and $b$ = coefficients ($a = 10\pm1$ and $b = 2500\pm300$); and
- $T$ = the local temperature (in K).

For sea-salt aerosols GEOS-Chem simulates the partitioning between Hg$^{II}$ and Hg$^p$ as a kinetic
process, while it is simulated as an equilibrium process for other aerosols (Shah & Jaegle, 2017).

4.3.2. Model simulations performed

Multiple GEOS-Chem simulations were performed with a focus over Australia and the surrounding region of the southern hemisphere to reveal uncertainties, constraints and controlling factors that govern the speciation, transport, emission and deposition of Hg in the study area. These model simulations are outlined below:

4.3.2.1 Full simulations

1) Default: uses the standard GEOS-Chem configuration for Hg simulations as described in previous sections;

2) InvOcean: this uses the optimized configuration described in Song et al. (2015). The configuration is optimized through the use of Bayesian inversion methods that combine GEOS-Chem simulations with Hg\(^0\) observations from a number of reference sites. It should be noted that none of the reference sites are in Australia and only two sites (Amsterdam Island and Cape Point, both used in this study) are located in the southern hemisphere mid-latitudes. The inversion assumes that there is a linear relationship as follows:

\[
y_{obs} = y_{ref} + Hx + E
\]

Where:

- \(y_{obs}\) = is the observation vector;
- \(y_{ref}\) = is the monthly Hg\(^0\) concentrations from GEOS-Chem using emissions and parameters from the reference sites;
- \(H\) = the sensitivity matrix. It describes how the observations of monthly Hg\(^0\) concentrations at the reference sites respond to \(x\);
- \(x\) = the state vector; and
- \(E\) = the model and observational errors.

The sensitivity matrix (H) is denoted by:

\[
h_{ij} = \frac{y_i - y^\text{ref}}{x_j - x^\text{ref}} \approx \frac{\partial y_i}{\partial x_j}
\]

Where:

- \(i\) = the observational vector; and
- \(j\) = the state vector.

The end result is that the simulation implies changes to ocean evasion are necessary for both the northern and southern hemispheres (Song et al., 2015). Table 5 details the differences between the parameters used in the Default and InvOcean simulation. Song et al. (2015) identified two
ocean parameters in GEOS-Chem that required improvement: (i) \( k_{\text{ox\_dark}} \) (the rate coefficient of dark oxidation of \( \text{Hg}^{0}_{\text{aq}} \)); and (ii) \( K_{\text{d\_part}} \) (the partition coefficient between \( \text{Hg}^{0}_{\text{aq}} \) and \( \text{Hg}^{2+}_{\text{aq}} \)).

They suggested that the \(-\log\) of 7.0 for \( k_{\text{ox\_dark}} \) (used in the Default simulation) was too low and that a more appropriate range of \(-\log\), based on laboratory studies was 4.0-6.0. For the InvOcean simulation they started with an ‘A priori’ value of 5.0 and used a number of iterations to finally constrain an ‘A posteriori’ value of 5.2 for \( k_{\text{ox\_dark}} \). Similarly, for \( K_{\text{d\_part}} \) they used a number of iterations to constrain an ‘A posteriori’ \(-\log\) value of 4.2.

**Table 5: Differences between the InvOcean and Default simulations (GEOS-Chem, 2016).**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default</th>
<th>InvOcean</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{ox_dark}} )</td>
<td>1.0e-7 (6 x 10^{-6} \text{ s}^{-1})</td>
<td>1.0e-5.2 (6 x 10^{-6} \text{ s}^{-1})</td>
</tr>
<tr>
<td>( K_{\text{d_part}} )</td>
<td>10^{4.5} (3.2 x 10^{4} \text{ L kg}^{-1})</td>
<td>10^{4.2} (1.6 x 10^{4} \text{ L kg}^{-1})</td>
</tr>
</tbody>
</table>

**Footnote:** Uncertainties for \( k_{\text{ox\_dark}} \) and \( K_{\text{d\_part}} \) in the InvOcean simulation are 0.1 and 0.2 respectively (Song et al., 2015).

### 4.3.2.2 Sensitivity simulations

All of the sensitivity simulations below (except NewChem/SlabOcean and NewChem/NewOcean) started from the InvOcean simulation and had one component changed. They were all run for the same Four-year period (2013-2016) and included the same 5-year spin up.

3) **Anthro**: no emissions are included from anthropogenic sources at the global scale;

4) **Soil**: no emissions are included from soil sources at the global scale;

5) **Biomass**: no biomass burning emissions are included at the global scale;

6) **Geogenic**: GEOS-Chem includes emissions from geogenic sources, but not for Australia. Rytuba (2003) detailed an Hg-enriched mineral belt running down the east coast of Australia and into Tasmania. Based on this, Hg emissions from geogenic sources were added to the grid-boxes in GEOS-Chem that overly these regions;

7) **NewChem/SlabOcean**: this simulation was made available by Dr Hannah Horowitz and was run in GEOS-Chem v9-02 for the period January 2009 to December 2011 (following a with a three-year spin up). It uses the updates to GEOS-Chem described by Horowitz et al. (2017), which includes new chemical mechanisms for atmospheric Hg\(^0\)/Hg\(^2+\) redox chemistry in GEOS-Chem. It uses the standard slab-ocean included in GEOS-Chem. Differences between the Default simulation and this simulation relate purely to changes made to the redox chemistry; and

8) **NewChem/NewOcean**: this simulation was made available by Dr Hannah Horowitz and was run in GEOS-Chem v9-02 for the period January 2009 to December 2011 (following a with a three-year spin up). It uses the updates to GEOS-Chem described...
by Horowitz et al., (2017), which includes new chemical mechanisms for atmospheric \( \text{Hg}^0/\text{Hg}^{II} \) redox chemistry in GEOS-Chem. It also couples GEOS-Chem to an ocean general circulation model (MITgcm) for simulating Hg transport within the ocean and fluxes to/from the atmosphere. Differences between the Default simulation and this simulation are due to changes made to the redox chemistry and the enhanced oceanic Hg modeling. While differences between NewChem/SlabOcean and NewChem/NewOcean are related to ocean coupling only.

9) A 9th sensitivity simulation Bromine\textsubscript{x3} was run in GEOS-Chem. This sensitivity simulation intended to use the proxy described by Shah et al., (2016) as a shortcut to new chemical mechanisms described by Horowitz et al. (2017). However, there were inconsistencies in the output that implied that this sensitivity simulation failed to replicate the proxy described by Shah et al., (2016) and so hadn’t run as intended. It was therefore omitted from this study. Additionally, the simulation outputs provided by Dr Hannah Horowitz show that the new chemical mechanism doesn’t improve the simulation for Australia (discussed in Section 5.2) and so this simulation was not revisited.

4.3.3. Observational and modelling uncertainties

There are number of uncertainties related to observational methods and the CTM of atmospheric Hg. These uncertainties relate to: (i) chemical mechanisms for atmospheric redox processes; (ii) land-atmosphere and ocean-atmosphere exchange; (iii) techniques and methods used for gathering observations; and (iv) oceanic processes (Selin, 2009). Figure 10 highlights some of the most important uncertainties in atmospheric Hg modeling.
A detailed list of the observational and modeling uncertainties relating to atmospheric Hg are detailed below:

4.3.3.1 **Observational uncertainties**

1) Inconsistencies in Hg flux measurements due to a lack of standardisation in methodologies and time of measurement. Therefore, it can be difficult to compare data between separate studies and cross-evaluate the controlling factors (Agnan et al., 2016);

2) Measurements of Hg\textsuperscript{II} concentrations and fluxes are subject to interferences from the background concentrations of ozone, water vapor and other atmospheric compounds. This can make it hard to compare measurements between sites and different measurement methods (Jaffe et al., 2014);

3) Estimates of emissions for the tropics and southern hemisphere are uncertain due to the low number of observational sites and lack of long-term records that can be used to identify trends (Sprovieri et al., 2016);

4) Observational data suffers from a lack of detailed Hg chemical speciation due to analytical challenges and environmental influences. This is particularly true for Hg\textsuperscript{II} and Hg\textsuperscript{P} measurements which are typically operationally determined and subject to errors arising from sampling duration and difficulties in distinguishing between the two forms (Angot et al., 2014; Kwon et al., 2016);
4.3.3.2 Modelling uncertainties

1) Emissions estimates are subject to large uncertainties regarding both the total amounts of Hg emitted and the speciation between Hg$_0$, Hg$^{II}$ and Hg$^I$ (Nelson et al., 2012);

2) There is a lack of direct and accurate methods for measuring Hg dry deposition. Therefore, models have to estimate dry deposition rates using measured atmospheric concentrations of Hg and meteorological parameters (Sprovieri et al., 2016);

3) The emissions factors for natural sources and other parameters driving GEOS-Chem are based on data derived from northern hemisphere sites. This limits the ability to directly depict fluxes in the southern hemisphere (Pirrone et al., 2010);

4) GEOS-Chem simulations depend on large grid squares with different values for land and ocean, and grid squares that are a mixture of land and ocean may not accurately represent the real data results (Fisher et al., 2013). This means that if a grid square is half ocean and half land, but the observation sites is on land and mostly experiences fetch from upwind land site, then GEOS-Chem will artificially mix in more ocean air than is actually observed at the site;

5) The fate and recycling rates of Hg within different ecosystems following deposition is extremely uncertain, especially as parameterized in GEOS-Chem (Corbitt et al., 2011);

6) In GEOS-Chem the ocean is simulated by a 2D ocean slab and as a result it: (i) lacks the horizontal and vertical ocean transport processes via circulation and diffusion and (ii) suffers from a low spatial resolution (Semeniuk & Dastoor, 2017). The NewChem/NewOcean simulation includes a fully coupled ocean, allowing an exploration of this uncertainty;

7) The atmospheric redox chemistry of Hg is uncertain and so CTMs are limited by assumptions regarding the oxidation and reduction processes and reaction rates. As measurements of Hg$^{II}$ are unreliable, the actual products of the chemistry are unknown, which has limited definitive understanding of the chemistry and kinetics (Gustin, 2011; McClure et al., 2014). The reduction rate of Hg$^{II}$ following emission is particularly uncertain (Horowitz et al., 2017).

8) GEOS-Chem (and all existing CTMs) are imperfect due to forcing errors. These are errors in the meteorological data that drive the CTMs (Song et al., 2015). However, this is very small relative to the other errors discussed;

9) Observations in the USA have shown that increased freshwater runoff into oceans following periods of heavy rainfall also increases Hg concentrations and fluxes in the ocean (Song et al., 2016). The same principle may apply for Australia following periods of heavy rainfall from storms and cyclones. There is also a possibility that high soil moisture after heavy rainfall limits/prevents the re-emission of Hg from soil (Howard, 2017, personal communication). However, neither of these processes are
included in GEOS-Chem;

10) CTMs such as GEOS-Chem involve considerable computational expense. As a result, there is a tradeoff between fine temporal and spatial resolutions, which offer accuracy when calculating the concentrations of chemical species against the expense of computational time needed to run the model. The relative simulation error increases by a greater order of magnitude when using a coarser spatial resolution (e.g., degrading from 2° × 2.5° to 4° × 5°), than when using a coarser temporal resolution (e.g. degrading from 5-min to 60-min operator duration) (Philips et al., 2016). The spatial resolution of CTMs is limited by processing power and run times. This means that a number of atmospheric processes have to be parameterized which introduces uncertainties relating to meteorological properties and airborne chemical components;

11) Although Br is thought to be the dominant atmospheric oxidant of Hg⁰, there are large uncertainties regarding atmospheric Br concentrations and large discrepancies in its theoretical and experimentally determined rate coefficients that are used in GEOS-Chem. The techniques used for determining rate coefficients require assumptions and are carried out in controlled conditions that may not directly reflect atmospheric processes (Subir et al., 2011); and

12) The influence of legacy Hg provides one of the largest uncertainties to the biogeochemical cycling of Hg. This especially true for source-receptor analysis as it is very difficult to distinguish legacy emissions to those from natural sources and means that fractions have to be estimated in models (Kwon et al., 2016; Selin, 2013).

These uncertainties are revisited in Section 6 and used to guide recommendations for improving our ability to model Hg in Australia and the southern hemisphere mid-latitudes.

4.4. Model evaluation and analysis

The model evaluation used daily model results for the four-year period running from January 2013 to December 2016. Results from both the full and sensitivity simulations were compared with observational data from 5 monitoring sites to assess model performance and analyze the relative contributions and influence of different emissions sources on the atmospheric concentration of Hg⁰. Simulated Hg values were obtained by sampling GEOS-Chem in the grid boxes corresponding to coordinates of the ground-based observation sites and averaging the time series data to obtain daily average values. As stated in Section 4.3.1.2, each grid box has a resolution of 2° x 2.5°. This means that the grid-boxes not only contain the observational sites, but much of the surrounding area. The grid boxes can therefore include oceanic surfaces and different terrain types, which presents a degree of bias when comparisons are made with the observational data. To determine the capability of GEOS-Chem to reproduce the observed Hg⁰ concentrations statistical analysis was undertaken to determine the mean normalized bias, mean normalized error, correlation coefficient and coefficient of determination as detailed in the equations below:
Mean normalized bias (MNB) = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{M_i - O_i}{O_i} \right)

Mean normalized error (MNE) = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{|M_i - O_i|}{O_i} \right)

Mean (\overline{O}) = \frac{1}{N} \sum_{i=1}^{N} O_i; \quad (\overline{M}) = \frac{1}{N} \sum_{i=1}^{N} M_i

Standard deviation (σ_\overline{O}) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (O_i - (\overline{O}))^2}

Pearson correlation coefficient (r) = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{O_i - (\overline{O})(M_i - (\overline{M}))}{\sigma_\overline{O} \sigma_M} \right)

Coefficient of determination (r^2) = \text{(Pearson correlation coefficient)}^2

Where:

- \( M \) = the predicted value from the model simulation;
- \( O \) = the observed values from measurement; and
- \( N \) = the sample size.

For the statistical analysis, the observed Hg\(_0\) concentrations were filtered to remove any outliers, as this would skew the dataset. Outliers were removed under the following conditions: (i) \( x > \overline{O} + 2\sigma_\overline{O} \); and (ii) when \( x < \overline{O} - 2\sigma_\overline{O} \). The modeled Hg\(_0\) dataset was filtered to remove days when there was a modeled value but no observational value, as this would skew the statistical relationship between the two datasets. The MNB and MNE were chosen as they provide more weight to the individual data points instead of the overall mean value (Bieser et al., 2017).

The sensitivity simulations were compared against the InvOcean simulation by calculating the mean contribution and mean difference as detailed in the below equations:

\[
\text{Mean difference (MD)} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{S_i - F_i}{F_i} \times 100\% \right)
\]

\[
\text{Mean contribution (MC)} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{S_i}{F_i} \times 100\% \right)
\]

Where:

- \( S \) = the predicted value from the model sensitivity simulation; and
- \( F \) = the predicted value from the full (InvOcean) simulation.

The MD tells us the percentage difference between the sensitivity simulations and the full (InvOcean) simulation. This allows us to see how excluding certain emissions sources, or including new emissions sources, affects the modeled atmospheric concentration of Hg\(_0\) at the observation sites. The MC tells us what percentage the sensitivity simulations contribute to the full (InvOcean) simulation; the Geogenic simulation adds an additional emissions source on top of the InvOcean simulation, therefore the MC is not relevant for this simulation. The MD and MC are useful to understand which emission sources are having the greatest influence on the Hg\(_0\) concentrations at each of the sites within GEOS-Chem.
The model simulations were assessed for errors using three metrics: (i) the MNB, which represents systematic errors within GEOS-Chem; (ii) the variance, represented by the daily variability between the full simulations and mean value, and between the sensitivity simulations and the InvOcean simulation; and (iii) covariance, the correlation between modeled and observed values, represented by $r$ and $r^2$ (Bieser et al., 2017).

The programming language ‘Python’ was used to write scripts (programming code) for analysing and manipulating the observational and GEOS-Chem data. Scripts were written to remove outliers, undertake both trend and statistical analysis (according to the equations above) and for the generation of the figures, maps and tables included in Section 5. An example of one of the Python code used is included in Appendix 2.
5. Results and discussion

All three species of Hg were simulated in each of the simulations, but comparisons to observations only show Hg$^0$ as none of sites have observations for Hg$^{II}$ and Hg$^P$.

5.1. Atmospheric mercury concentrations

5.1.1. Global and regional distributions

Figure 11 shows the global distribution of Hg$^0$ concentrations at the surface layer (the lowest model layer) as simulated by the InvOcean simulation in GEOS-Chem. It shows that Hg$^0$ concentrations are higher in the northern hemisphere mid-latitudes (particularly over East-Asia), compared to the tropical low-latitudes and southern hemisphere. This is because the majority of Hg emissions and re-emissions are from the northern hemisphere and is supported by measurements from mercury observation networks (Sprovieri et al., 2016).

Figure 11: Global distribution of Hg$^0$ concentrations in the surface boundary layer. Note: (i) the location markers display the mean observed Hg$^0$ concentrations; (ii) values represented in the graph are multi-year mean values for the period 2013-2016.

Figure 12 shows the regional (study area) distribution of Hg$^0$ and Hg$^{II}$ concentrations at the surface layer. The top map shows that on average Hg$^0$ concentrations are higher over the ocean (~1.05 ng m$^{-3}$) compared to the terrestrial surface (~0.9 ng m$^{-3}$), while the bottom graph shows...
that Hg\textsuperscript{0} concentrations are lower over the ocean (~10\textsuperscript{-3} ng m\textsuperscript{-3}) compared to the terrestrial surface (~10\textsuperscript{-2} ng m\textsuperscript{-3}). This suggests that (i) the concentrations of Hg\textsuperscript{0} and Hg\textsuperscript{II} are probably being influenced by atmospheric redox chemistry; (ii) the terrestrial surface may be a net sink for atmospheric Hg\textsuperscript{0}; and (iii) that the ocean is probably a net source of Hg\textsuperscript{0}. The simulated Hg\textsuperscript{0} concentrations are in good agreement with the expected range for the southern hemisphere, falling within the range of Hg\textsuperscript{0} concentrations, 0.84 to 1.09 ng m\textsuperscript{-3}, observed at southern hemisphere sites (including Cape Point and Amsterdam Island) by Sprovieri et al. (2016) and slightly lower than the suggested southern hemisphere background of 1.1 ng m\textsuperscript{-3} (Angot et al., 2014; Slemr et al., 2015). The location markers (top graph) display the mean observed Hg\textsuperscript{0} concentrations at each of the ground-based monitoring sites. This shows that GEOS-Chem overestimates the simulated Hg\textsuperscript{0} concentrations at all of the sites, with the exception of Amsterdam Island. However, this is not surprising as Amsterdam Island was one of the reference (calibration) sites that Song et al. (2015) used for the optimized calibration in the InvOcean simulation. Note that for all the maps in this section, the modeled Hg concentrations were averaged over all days and times, not just when the observational data was available. However, for the statistical analysis (shown later) the modeled values were matched to the availability of observations.

*Figure 12:* Regional distribution of Hg\textsuperscript{0} and Hg\textsuperscript{II} concentrations in the surface boundary layer. Note: (i) the scales for the different Hg species are not the same; and (ii) the location markers on the top graph
display the mean observed \( \text{Hg}^0 \) concentrations.

Figure 13 shows the Australian distribution of \( \text{Hg}^0 \) concentrations in the surface boundary layer. The higher \( \text{Hg}^0 \) concentrations over Kalgoorlie, WA are probably overestimated as the suspected emissions source, the Gidji roaster, closed in 2015, but GEOS-Chem Version 11-01 does not reflect this. The simulation period thus includes 2-3 years before closure and 1-2 years post closure.

![Australian distribution of Hg\(^0\) concentrations in the surface boundary layer](image)

**Figure 13:** Australian distribution of \( \text{Hg}^0 \) concentrations in the surface boundary layer.

### 5.1.2. Concentrations at monitoring sites

Table 6 shows the mean, standard deviation, r- and r\(^2\)- values for the modelled \( \text{Hg}^0 \) concentrations at each of the monitoring sites. Both the Default and InvOcean simulations overestimate the annual averages relative to the observations at Cape Grim and Gunn Point and underestimate the annual average at Glenville. At Cape Point and Amsterdam Island the InvOcean simulation produces an almost exact match to the magnitude of the observations, while the Default simulation underestimates the annual average. The biggest discrepancies between the simulated and observed multi-year averages are at Cape Grim, where the Default simulation averages \( 0.99 \pm 0.14 \text{ ng m}^{-3} \), the InvOcean simulation averages \( 1.02 \pm 0.08 \text{ ng m}^{-3} \), compared to the observed average of \( 0.90 \pm 0.10 \text{ ng m}^{-3} \). It should be noted that these values are within experimental uncertainty. GEOS-Chem is thought to overestimate \( \text{Hg}^0 \) concentrations at the Australian sites as it has historically
been developed and evaluated using observations from the northern hemisphere. A recent evaluation of GEOS-Chem against Hg observations from a global database found significant biases in the simulation of Hg at southern hemispheric sites (Song et al., 2015; Horowitz et al., 2017).

Figure 14-18 show the ‘daily mean’, ‘monthly mean’ and ‘bias corrected daily mean’ concentrations for the monitoring sites (the figures for each site use different scales for y-axis to show the full range of the data). The bias corrected daily mean shows the (simulation-MNB) to better evaluate the daily variability. Note that the top two panels show the Default and InvOcean simulations and all of the sensitivity simulations, the third panel only shows the Default and InvOcean simulations for clarity. The daily variability (variation between days) of the sensitivity simulations are discussed in the next section.

Each of the sensitivity simulations started with the InvOcean simulation and then turned off one source. The larger the difference between the sensitivity simulation and the InvOcean simulation, the more that source contributes to the overall simulation. The sensitivity simulations show that soil and anthropogenic emissions have the greatest contribution to Hg\(^0\) concentrations at all of the sites. There are smaller contributions resulting from biomass burning emissions and limited influence from geogenic emissions.

At Gunn Point, both the Default and InvOcean simulations significantly underestimate the seasonal decrease from peak concentrations in September/October to minimum concentrations in April/May. This is clearly visible in 2014-2015 and also in late 2016. This indicates that there may be an issue with the scavenging of atmospheric Hg within GEOS-Chem in the southern hemisphere tropics.

The observational data shows that the annual averages at Cape Point (1.03 ± 0.12 ng m\(^{-3}\)) and Amsterdam Island (1.03 ± 0.07 ng m\(^{-3}\)) differ by only 0.002 ng m\(^{-3}\) for the period January 2013 to December 2016. The InvOcean simulation also produces similarly close annual averages that differ by 0.003 ng m\(^{-3}\), but the difference is greater in the Default simulation (0.02 ng m\(^{-3}\)), suggesting that this may be due to differences in the way the ocean is simulated. These values are close the median value of 1.0 ng m\(^{-3}\) for southern hemisphere sites reported by Sprovieri et al., (2016). The multi-year averages from observations at all three Australian sites, Cape Grim (0.90 ± 0.10 ng m\(^{-3}\)), Gunn Point (0.97 ± 0.12 ng m\(^{-3}\)) and Glenville (0.83 ± 0.23 ng m\(^{-3}\)), are largely consistent with the southern hemispheric background reported in the literature. The values are lower than those at Cape Point and Amsterdam Island differing by 0.13 and 0.13 ng m\(^{-3}\) (Cape Grim), 0.07 and 0.07 ng m\(^{-3}\) (Gunn Point) and 0.20 and 0.21 ng m\(^{-3}\) (Glenville) respectively. This suggests that the Australian landmass differs slightly from the southern hemisphere background, perhaps due to the continent’s unique climate, vegetation and soil types.

Hg\(^0\) observational data at Cape Point for the period June 2015 to April 2016 suffers from bias due to the monitoring station being struck by lightning in June 2015. During this period the Tekran instrument was still making measurements, but a later maintenance inspection found that a part inside the instrument was damaged giving it lower readings than expected. The observational data
for this period has been adjusted with an algorithm (provided by the instrument team) (Martin, 2017, personal communication, 14 August).

Although the monitoring station at Glenville is located close to two coal-fired power stations and open cut mines, the multi-year annual average (0.83 ± 0.23 ng m$^{-3}$) is the lowest of the three Australian sites. It is unknown if these low values are an artifact of sampling procedures, or due to Glenville being located further inland and therefore prone to greater dry deposition and surface uptake. The observational data does show that Glenville occasionally experiences ambient concentrations that are significantly higher than the southern hemisphere background, as was the case in December 2013, April 2014 and December 2016. However, based on simultaneous measurements of SO$_2$ (the only significant point sources of SO$_2$ are the two power stations), that don’t show a corresponding spike, this is not thought to be associated with plume incursion from the power station emissions. Overall it is thought that anthropogenic emissions from the power stations make only a small contribution, 0.07 to 0.15 ng m$^{-3}$, to ambient Hg$^0$ concentrations at Glenville (Morrison et al., 2015).
Figure 14: ‘Daily’, ‘monthly’ and ‘simulation/observation – MNB’ Hg\(^0\) concentrations at Cape Grim, TAS.
Figure 15: ‘Daily’, ‘monthly’ and ‘simulation/observation – MNB’ Hg\(^0\) concentrations at Gunn Point, NT.
Figure 16: ‘Daily’, ‘monthly’ and ‘simulation/observation – MNB’ Hg$^0$ concentrations at Glenville, NSW.
Figure 17: ‘Daily’, ‘monthly’ and ‘simulation/observation – MNB’ Hg0 concentrations at Amsterdam Island, TAAF.
Figure 18: 'Daily', 'monthly' and 'simulation/observation – MNB' Hg\textsuperscript{0} concentrations at Cape Point, South Africa.
Table 6: Mean, standard deviation, r and r² values for the observed and simulated Hg⁰ concentrations at each site for the period 2013-2016.

<table>
<thead>
<tr>
<th>Site</th>
<th>N</th>
<th>Observations</th>
<th>Simulation</th>
<th>Sensitivity Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Default</td>
<td>InvOcean</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>M / σ</td>
<td>r / r²</td>
</tr>
<tr>
<td>Cape Grim</td>
<td>1172</td>
<td>0.90 ± 0.10</td>
<td>0.99 ± 0.14</td>
<td>0.45 / 0.21</td>
</tr>
<tr>
<td>Gunn Point</td>
<td>640</td>
<td>0.97 ± 0.12</td>
<td>0.98 ± 0.09</td>
<td>0.62 / 0.39</td>
</tr>
<tr>
<td>Glenville</td>
<td>664</td>
<td>0.83 ± 0.23</td>
<td>0.95 ± 0.12</td>
<td>-0.07 / 0.01</td>
</tr>
<tr>
<td>Amsterdam Island</td>
<td>922</td>
<td>1.03 ± 0.07</td>
<td>1.00 ± 0.14</td>
<td>0.40 / 0.16</td>
</tr>
<tr>
<td>Cape Point</td>
<td>1822</td>
<td>1.03 ± 0.12</td>
<td>0.98 ± 0.13</td>
<td>-0.01 / 0.00</td>
</tr>
</tbody>
</table>

Footnote:
Where: (N) is the number of observations/modelled values; (œ) is the observational mean concentration; (M) is the modeled mean concentration; (r) is the coefficient of correlation; and (r²) is the coefficient of determination.
5.1.3. **Daily variability of Hg$^0$ concentrations**

Figure 19-23 show the daily variability of the full simulations, observational data and sensitivity simulations at each of the monitoring sites (the figures for each site use different scales for the y-axis to show the full range of the data). The daily variability was calculated for: (i) the Default and InvOcean simulations by subtracting the annual mean value for Hg$^0$ from the daily value for Hg$^0$; (ii) the Anthro, Biomass and Soil sensitivity simulations by subtracting the sensitivity simulation from the InvOcean simulation; and (iii) the Geogenic sensitivity simulation by subtracting the InvOcean simulation from the Geogenic Simulation.

At all sites, the daily variability shows that emissions from biomass burning contributes to specific events, spikes in simulated Hg$^0$ concentrations. This is particularly evident at Cape Grim where biomass burning can be seen to contribute to events between February and March in 2014, 2015 and 2016. Similar events also occur at Glenville in October 2013; and Cape Point in July 2013, August to September 2014 and September to October 2015.

The daily variability also shows that both Gunn Point and Cape Point experience events relating to emissions from anthropogenic sources. This appears to be an annual phenomenon at Gunn Point, occurring every year during the summer months (December to February), while a strong event is evident at Cape Point in June 2016.

The spikes in the simulated Hg$^0$ concentrations at Gunn Point appear to be due to anthropogenic influence, as their influence is decreased in the Anthro simulation when anthropogenic emissions are turned off. However, as these spikes occur during the dry season, they have been suggested to be a result of biomass burning events that occur throughout northern Australia at this time of year (Howard et al., 2017). The daily variability shows that biomass burning contributed to spikes at Gunn Point in February 2014, August to September 2015 and June to October 2016. It also suggests that biomass burning drives most of the seasonal cycle in the simulation. A study by Mallet et al., (2016) observed emissions from nine localized biomass burning events at Gunn Point between the 29th May 2014 and 30th June 2014. During this period Hg$^0$ concentrations averaged 0.99 ± 0.08 ng m$^{-3}$, slightly higher than the annual average of 0.97 ± 0.12 ng m$^{-3}$ for Gunn Point and similar to the average for the same period (0.96 ng m$^{-3}$) observed at five other southern hemisphere sites (Sprovieri et al., 2016). This suggests that localized biomass burning events have only a rather minor influence on Hg$^0$ concentrations at Gunn Point. Howard et al. (2017) noted on a couple of occasions that Hg$^0$ concentrations at Gunn Point increased in unison with radon tracer values, indicating that the ITCZ was at its southernmost position and passing over Gunn Point and allowing the site to sample both northern and southern hemispheric air masses. Gunn Point was shown to experience 13 of these events during the wet season (December to February). These northern hemispheric air masses were found to mostly pass over Indonesia (prior to Gunn Point), indicating that they are likely influenced by anthropogenic, biomass burning and ASGM that represent significant emission sources in Indonesia (Arifin et al., 2015; Hamilton et al., 2008; Sprovieri et al., 2016). When the ITCZ then moves over Gunn Point during the wet season it causes a spike in ambient Hg$^0$ concentrations. A similar finding was reported by
Muller et al. (2012) for a tropical site in Suriname, where TGM concentrations were found to be 10% higher for northern hemisphere air masses (1.45 ng m$^{-3}$) than for southern hemisphere air masses (1.32 ng m$^{-3}$). However, as these events coincide with tropical rain events it could increase wet deposition rates, resulting in a decrease of atmospheric Hg concentrations (Sprovieri et al., 2016; Wang et al., 2014). Lower atmospheric Hg concentrations, may also result from inhibited re-emission in saturated soils, following heavy precipitation events (Howard et al., 2016).

The daily variability suggests that emissions from other sources largely contribute to background concentrations and influence the seasonal cycle. The variability from these sources is likely due to variability in atmospheric transport to the site, rather than variability in emissions from the sources.

Table 7 shows the mean difference (MD) and mean contribution (MC) between each of the sensitivity simulations and the InvOcean simulation at the sites. This shows that for Cape Grim and Gunn Point the simulated Hg$^0$ concentrations overestimate the observed concentrations by 13.3% and 10.2% respectively. Concentrations at Glenville where overestimated by 19.8%, but observations at this site are influenced by localized conditions and not thought to represent the typical Australian background.

Anthropogenic sources had the greatest contribution to the InvOcean simulation across all of the sites, with an average MD of 20.8% and an average MC of 79.2%. Anthropogenic sources contributed the most at Gunn Point (MD = 23.0% and MC = 77.0%) and the least at Amsterdam Island (MD = 19.3% and MC = 80.7%). This makes sense as Gunn Point is known to occasionally be influenced by northern hemisphere air masses (Howard et al., 2017), while Amsterdam Island is the most isolated site, located in the Indian Ocean (Angot et al., 2014). Soil sources have the second greatest contribution to the InvOcean simulation, with an average MD of 12.6% and an average MC of 87.4%. Soil sources were found to have the greatest contribution at Glenville with an MD of 15.1% and MC of 84.9%. Both biomass burning and geogenic sources were found to have only a minor difference from the InvOcean simulation, with MDs of 3.7% and 1.6% respectively. This suggests that these sources (at least within GEOS-Chem) are only having a limited effect on Hg$^0$ concentrations at each of the sites.
Figure 19: Daily variability of Hg\textsuperscript{0} concentrations at Cape Grim, TAS.
Figure 20: Daily variability of Hg\(0\) concentrations at Gunn Point, NT.
Figure 21: Daily variability of $\text{Hg}^0$ concentrations at Glenville, NSW.
Figure 22: Daily variability of $\text{Hg}^0$ concentrations at Amsterdam Island, TAAF.
Figure 23: Daily variability of Hg$^0$ concentrations at Cape Point, South Africa.
Table 7: The mean difference (MD) and mean contribution (MC) for the sensitivity simulations at each site.

<table>
<thead>
<tr>
<th>Site</th>
<th>N</th>
<th>Anthro MD (%)</th>
<th>Anthro MC (%)</th>
<th>Biomass MD (%)</th>
<th>Biomass MC (%)</th>
<th>Geogenic MD (%)</th>
<th>Geogenic MC (%)</th>
<th>Soil MD (%)</th>
<th>Soil MC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cape Grim</td>
<td>1461</td>
<td>19.4</td>
<td>80.6</td>
<td>3.2</td>
<td>96.8</td>
<td>2.1</td>
<td>n/a</td>
<td>11.5</td>
<td>88.5</td>
</tr>
<tr>
<td>Gunn Point</td>
<td>1461</td>
<td>23.0</td>
<td>77.0</td>
<td>5.4</td>
<td>94.6</td>
<td>0.3</td>
<td>n/a</td>
<td>13.7</td>
<td>86.3</td>
</tr>
<tr>
<td>Glenville</td>
<td>1461</td>
<td>21.7</td>
<td>78.3</td>
<td>3.8</td>
<td>96.2</td>
<td>5.1</td>
<td>n/a</td>
<td>15.1</td>
<td>84.9</td>
</tr>
<tr>
<td>Amsterdam Island</td>
<td>1461</td>
<td>19.3</td>
<td>80.7</td>
<td>3.0</td>
<td>97.0</td>
<td>0.3</td>
<td>n/a</td>
<td>11.0</td>
<td>89.0</td>
</tr>
<tr>
<td>Cape Point</td>
<td>1461</td>
<td>20.7</td>
<td>79.3</td>
<td>3.2</td>
<td>96.8</td>
<td>0.3</td>
<td>n/a</td>
<td>11.5</td>
<td>88.5</td>
</tr>
<tr>
<td>Average</td>
<td>1461</td>
<td>20.8</td>
<td>79.2</td>
<td>3.7</td>
<td>96.3</td>
<td>1.6</td>
<td>n/a</td>
<td>12.6</td>
<td>87.4</td>
</tr>
</tbody>
</table>

Footnote: Where: (N) is the number of observations; (MD) is the mean difference; and (MC) is the mean contribution. The MD and MC are calculated in comparison to the InvOcean simulation (InvOcean – Sensitivity Simulation); the Geogenic simulation adds an additional emissions source on top of the InvOcean simulation to represent how much extra Hg would be present if this source was included, therefore the MC is not relevant for this simulation.

5.1.4. Relationship between simulated and observed values of Hg⁰

Figure 24-28 shows the relationship between the ‘simulation–MNB’ and ‘observed’ values of Hg⁰ at each of the monitoring sites; note that the slope shown on the graph are for the ‘simulated’ values, not the ‘simulated-MNB’. The simulated values of Hg⁰ are known to suffer from bias as most of the chemistry and sources in GEOS-Chem have been developed based on northern hemisphere data. Horowitz et al. (2017) shows the lingering biases in southern hemisphere. As this bias exists at all of the sites, it is expected to be a large-scale issue and not-caused by individual source influences at any of the sites. To better explore observed vs simulated variability, the MNB was subtracted from the simulated values before showing the relationship against observed values. The graphs highlight that although the filter removes the majority of outliers (those outside of the upper and lower limits, see Section 4.4), there are probably some outliers that aren’t being caught and these have the potential to skew the dataset. The outliers shown on the graph are removed before calculating the slopes and correlation coefficients.

The graphs show that at Cape Grim, Gunn Point and Amsterdam Island there is a weak positive correlation between the observed and simulated values of Hg⁰, while at Glenville and Cape Point
there is a slight negative correlation. The Default and InvOcean simulations produce similar r-values for Cape Grim 0.45 (slope: 0.22, intercept: 0.01) and 0.45 (slope: 0.40, intercept: 0.02) respectively; and for Amsterdam Island, 0.40 (slope: 0.15, intercept: 0.01) and 0.47 (slope: 0.34, intercept: 0.02) respectively. The InvOcean simulation is essentially the same as the Default simulation, except it involved the inversion of data (including Amsterdam Island and hence the better correlation there) to update the coefficients driving the parameters relating to ocean evasion in GEOS-Chem (see Section 4.3.2.1). At Gunn Point, the Default simulation produces an r-value of 0.62 (slope: 0.77, intercept: 0.04) compared to 0.49 (slope: 0.78, intercept: 0.05) for the InvOcean simulation. This suggests that the Default simulation can more accurately reproduce the observed values at Gunn Point and that the “improved” southern hemisphere ocean parameters of Song et al. (2015) are not applicable to tropical waters and that there are other factors at play in the tropics.

Both the Default and InvOcean simulations produce very low r-values at Glenville, -0.07 (slope: -0.09, intercept: 0.05) and -0.05 (slope: -0.11, intercept: 0.08) respectively; and at Cape Point, -0.01 (slope: -0.01, intercept: 0.02) and -0.01 (slope: -0.02, intercept: 0.03). These numbers suggest that the simulation has no predictive power at these sites. However, the observations at Glenville are known to be influenced by localized atmospheric conditions that restrict air movement and cause spikes in Hg⁰ concentrations at the monitoring site (Morrison et al., 2015), reducing the comparability to simulated values. The Cape Point observations are known to contain inaccuracies relating to when the station was hit by lightning in 2015 (Martin, 2017, personal communication, 14 August). However, this can’t be the only reason for the low r-values at Cape Point. If it was solely to blame then there should be a stronger correlation for points prior to the lightning strike and a subset of wild (outlier) points afterwards. This suggests that GEOS-Chem is inaccurately representing processes at the site, perhaps due to an unknown mechanism or parameterization within the model, but the exact reason remains unknown.

The figures show that GEOS-Chem has a poor ability to simulate daily variability. Even in the best case (the Default simulation at Gunn Point), the model can only reproduce <40% of the observed variability. This likely due to a combination of: (i) the lack of daily variability in Br concentrations (monthly averages) driving the atmospheric chemistry in GEOS-Chem; (ii) the large area of the grid boxes in the model that contain the sites; (iii) the grid boxes straddle both ocean and terrestrial surfaces for coastal sites; and (iv) GEOS-Chem uses a very simplified representation of soil and vegetation emissions that is likely not appropriate for Australian landscapes.
Figure 24: Relationship between (simulation – MNB) and observed values of Hg⁰ at Cape Grim, TAS.
Figure 25: Relationship between (simulation – MNB) and observed values of Hg$^0$ at Gunn Point, NT.
Figure 26: Relationship between (simulation – MNB) and observed values of Hg$_0$ at Glenville, NSW.
Figure 27: Relationship between (simulation – MNB) and observed values of Hg⁰ at Amsterdam Island, TAAF.
Figure 28: Relationship between (simulation – MNB) and observed values of $\text{Hg}^0$ at Cape Point, South Africa.
5.2. Mean seasonal variation

The MNB, MNE, MD and MC are given in Table 8 and defined in Section 4.4. This shows that the Default and InvOcean simulations both exhibit on average a positive MNB and overestimate Hg\(^0\) concentrations by 7.0% and 11.6% respectively. An average MNE of 15.2% is obtained for the InvOcean simulation, slightly smaller than that of 15.8% for Default simulation. This indicates that on average the InvOcean simulation can better reproduce the observations at the ground-based monitoring sites. The values highlighted in orange include outliers; these show that the inclusion of outliers during statistical calculations increases the MNE by approximately 2% and the MNB by approximately 1% for both the Default and InvOcean simulations.

In comparison, the NewChem/NewOcean and NewChem/SlabOcean simulations (both of which include new chemical mechanisms for atmospheric Hg\(^0\)/Hg\(^2\) redox chemistry in GEOS-Chem. The NewChem/NewOcean simulation is also coupled to an ocean model to improve ocean Hg cycling) exhibit on average a negative MNB of -18.8% and -16.0% respectively; and an average MNE of 19.9% and 19.4%. This suggests that the updates to GEOS-Chem by Horowitz et al. (2017) may have a limited impact on the overall performance of simulations in the southern hemisphere mid-latitudes. However, they do reverse the bias, turning a model overestimate into an underestimate. The small difference between these two simulations suggests that most of this change comes from the updated redox chemistry rather than coupling to an ocean model. It should be noted that the simulations by Horowitz et al. (2017) did a much better job at representing the northern hemisphere mid-latitudes. This indicates that there are clear hemispheric differences and that they are still not understood.

Table 9 shows the month of maximum average Hg\(^0\) concentrations, the month of minimum average Hg\(^0\) concentrations and the amplitudes for each site. The monthly averages are the mean value observed/simulated at each site for the period 2013-2016. The amplitude was calculated by subtracting the month with the minimum average from the month with the maximum average and then dividing by two. This shows that overall the Default and InvOcean simulations do a better job of predicting the months with the maximum and minimum average Hg\(^0\) concentrations. It also suggests that the NewChem/NewOcean and NewChem/SlabOcean simulations have some issues with matching the observed seasonal cycles at southern hemisphere sites. This is certainly the case with Cape Grim, which shows an inverted seasonal cycle.

A more comprehensive version of this table (which includes the average Hg\(^0\) concentration for each month of the year) is included in Appendix 2.
Table 8: The mean normalised bias (MNB) and mean normalised error (MNE) for the simulated Hg⁰ concentrations at each site.

<table>
<thead>
<tr>
<th>Site</th>
<th>N</th>
<th>Default</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>InvOcean</th>
<th></th>
<th></th>
<th></th>
<th>NewChem/ NewOcean</th>
<th></th>
<th>NewChem/ SlabOcean</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MNB (%)</td>
<td>MNE (%)</td>
<td>MNB (%)</td>
<td>MNE (%)</td>
<td></td>
<td>MNB (%)</td>
<td>MNE (%)</td>
<td></td>
<td></td>
<td>MNB (%)</td>
<td>MNE (%)</td>
<td>MNE (%)</td>
<td>MNE (%)</td>
</tr>
<tr>
<td>Cape Grim</td>
<td>1172</td>
<td>12.6</td>
<td>15.0</td>
<td>15.7</td>
<td>16.0</td>
<td>12</td>
<td>-15.5</td>
<td>15.6</td>
<td>-10.7</td>
<td>16.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1236</td>
<td>11.3</td>
<td>15.7</td>
<td>14.5</td>
<td>16.2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gunn Point</td>
<td>640</td>
<td>2.3</td>
<td>7.5</td>
<td>10.8</td>
<td>12.0</td>
<td>12</td>
<td>-18.0</td>
<td>18.0</td>
<td>-18.0</td>
<td>18.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>674</td>
<td>2.5</td>
<td>8.2</td>
<td>11.1</td>
<td>12.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glenville</td>
<td>664</td>
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<td>30.5</td>
<td>33.6</td>
<td>12</td>
<td>-6.2</td>
<td>11.3</td>
<td>-2.9</td>
<td>14.4</td>
<td></td>
<td></td>
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<td></td>
<td>697</td>
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<td>34.4</td>
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</tr>
<tr>
<td>Amsterdam Island</td>
<td>922</td>
<td>-2.8</td>
<td>11.1</td>
<td>0.5</td>
<td>5.3</td>
<td>12</td>
<td>-24.7</td>
<td>24.7</td>
<td>-21.1</td>
<td>21.1</td>
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<tr>
<td></td>
<td>979</td>
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<td>1.0</td>
<td>5.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cape Point</td>
<td>1282</td>
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<td>12</td>
<td>-29.7</td>
<td>29.7</td>
<td>-27.3</td>
<td>27.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>1321</td>
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<td>19.7</td>
<td>7.5</td>
<td>16.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
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<td>11.6</td>
<td>15.2</td>
<td>12</td>
<td>-18.8</td>
<td>19.8</td>
<td>-16.0</td>
<td>19.4</td>
<td></td>
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<tr>
<td></td>
<td>981</td>
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<td>17.9</td>
<td>12.7</td>
<td>17.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Footnote:

Where: (N) is the number of observations; (MNB) is the mean normalised bias and (MNE) is the mean normalised error. The values highlighted in orange include outliers to show how this influences N, MNB and MNE.

For the NewChem/NewOcean and NewChem/SlabOcean simulations (provided by Dr Hannah Horowitz) only monthly average data was available.
Table 9: The month of max Hg\textsuperscript{0}, the month of min Hg\textsuperscript{0} and the amplitudes for observational and simulated Hg\textsuperscript{0} concentrations at each site.

<table>
<thead>
<tr>
<th>Site</th>
<th>Parameter</th>
<th>Observation</th>
<th>Default</th>
<th>InvOcean</th>
<th>NewChem / NewOcean</th>
<th>NewChem / SlabOcean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cape Grim</td>
<td>Month of max</td>
<td>April</td>
<td>April</td>
<td>April</td>
<td>September</td>
<td>September</td>
</tr>
<tr>
<td></td>
<td>Max value</td>
<td>0.95</td>
<td>1.22</td>
<td>1.13</td>
<td>0.91</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Month of min</td>
<td>September</td>
<td>September</td>
<td>September</td>
<td>February</td>
<td>February</td>
</tr>
<tr>
<td></td>
<td>Min value</td>
<td>0.68</td>
<td>0.67</td>
<td>0.74</td>
<td>0.63</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Amplitude</td>
<td>0.13</td>
<td>0.28</td>
<td>0.20</td>
<td>0.14</td>
<td>0.22</td>
</tr>
<tr>
<td>Gunn Point</td>
<td>Month of max</td>
<td>February</td>
<td>February</td>
<td>February</td>
<td>October</td>
<td>October</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>0.95</td>
<td>1.22</td>
<td>1.13</td>
<td>0.90</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>Month of min</td>
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<td>July</td>
<td>July</td>
<td>May</td>
<td>April</td>
</tr>
<tr>
<td></td>
<td>Min</td>
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<td>0.63</td>
<td>0.69</td>
<td>0.70</td>
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<tr>
<td></td>
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<td>0.59</td>
<td>0.44</td>
<td>0.20</td>
<td>0.24</td>
</tr>
<tr>
<td>Glenville</td>
<td>Month of max</td>
<td>December</td>
<td>December</td>
<td>December</td>
<td>September</td>
<td>September</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>0.96</td>
<td>1.22</td>
<td>1.13</td>
<td>0.91</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>Month of min</td>
<td>May</td>
<td>May</td>
<td>May</td>
<td>March</td>
<td>February</td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>0.58</td>
<td>0.58</td>
<td>0.62</td>
<td>0.64</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>Amplitude</td>
<td>0.19</td>
<td>0.32</td>
<td>0.25</td>
<td>0.14</td>
<td>0.18</td>
</tr>
<tr>
<td>Amsterdam Island</td>
<td>Month of max</td>
<td>October</td>
<td>October</td>
<td>October</td>
<td>September</td>
<td>September</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>0.95</td>
<td>1.22</td>
<td>1.13</td>
<td>0.93</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>Month of min</td>
<td>July</td>
<td>March</td>
<td>March</td>
<td>February</td>
<td>February</td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>0.59</td>
<td>0.49</td>
<td>0.56</td>
<td>0.65</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Amplitude</td>
<td>0.18</td>
<td>0.37</td>
<td>0.28</td>
<td>0.14</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Table 1: Comparison of Observed and Simulated Seasonal Cycles of Hg at the Monitoring Sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Parameter</th>
<th>Observation</th>
<th>Default</th>
<th>InvOcean</th>
<th>NewChem / NewOcean</th>
<th>NewChem / SlabOcean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Month of max</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cape Point</td>
<td>August</td>
<td>August</td>
<td>August</td>
<td>August/Sept</td>
<td>September</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>0.96</td>
<td>1.22</td>
<td>1.13</td>
<td>0.84</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>Month of min</td>
<td>May</td>
<td>January</td>
<td>May</td>
<td>January</td>
<td>February</td>
</tr>
<tr>
<td></td>
<td>Min</td>
<td>0.52</td>
<td>0.59</td>
<td>0.63</td>
<td>0.62</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>Amplitude</td>
<td>0.22</td>
<td>0.31</td>
<td>0.25</td>
<td>0.11</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Figure 29-33 compare the simulated and observed seasonal cycles of Hg at each of the monitoring sites (top graphs); also shown are the results of the sensitivity simulations with emission sources excluded and included in the case of the Geogenic simulation (bottom graph). Note that the NewChem/NewOcean and NewChem/SlabOcean simulations are for the period Jan 2009 to Dec 2012. MNB* and MNE* include outliers to highlight how this skews the dataset.

At all of the sites, both the Default and InvOcean simulations predict a greater seasonal amplitude than is shown in the observations. The amplitude is lower at all of the sites for the InvOcean simulation than for the default simulation. This suggests that the changes from the inversion reduce the amplitude of the seasonal cycle through changes to oceans processes. This then affects atmospheric concentrations of Hg through ocean evasion.

The NewChem/NewOcean simulation predicts smaller seasonal amplitude at all sites except Cape Grim, while the NewChem/SlabOcean simulation predicts greater seasonal amplitude at Cape Grim and Amsterdam Island, but smaller seasonal amplitude at Gunn Point, Glenville and Cape Point. The reason for the differences in seasonal amplitude is likely due to the NewChem/NewOcean simulation being coupled to an ocean model. Horowitz et al. (2017) found that coupling GEOS-Chem with the ocean model reduced ocean evasion and improved seasonal amplitude over the North Atlantic by removing the simplified subsurface ocean boundary in the slab ocean. Both of these simulations were found to lower oceanic evasion and always get the timing of the seasonal maximum and minimum wrong.

Of the three Australian sites, the seasonal cycle is most apparent at Cape Grim. Both the Default and InvOcean simulations estimate greater the seasonal amplitudes (0.28 and 0.19 ng m⁻³) than is shown in the observations (0.13 ng m⁻³), with peak Hg concentrations occurring in August and the minimum occurring in December to January. These are similar to the findings of Slemr et al., (2015), which found that for the period 2011 to 2013 Cape Grim showed a seasonal amplitude of 0.13 ng m⁻³, larger than Amsterdam Island and Cape Point that share a seasonal amplitude of 0.005 ng m⁻³. Cape Grim was also found to have an annual average concentration of ~0.85 ng m⁻³, about 15% below the annual average observed at other southern hemisphere sites. However, the observational data for Cape Grim, used by Slemr et al. (2015), were biased because of the issue of passivation with the instrument (Edwards, 2017, personal communication, 23 July). The
data used in this study has been corrected for this issue and shows a slightly higher multi-year annual mean of 0.99 ng m\(^{-3}\).

The seasonal cycles at Gunn Point and Glenville are less pronounced than at Cape Grim, but show that Hg\(^0\) concentrations are typically higher during the winter/dry season. It may be that simulated Hg\(^0\) concentrations are lower during the summer/wet-season due to higher atmospheric temperatures, UV-levels and precipitation rates that would enhance the Hg\(^0\) oxidation and washout rates. The observations indicate that Cape Grim and Gunn Point both experience seasonal variations in Hg\(^0\), with Gunn Point observing higher values during the tropical dry season and Cape Grim observing higher values during the winter (June – September). This matches with the findings of Howard et al., (2017), which showed that Hg\(^0\) concentrations at Gunn Point are typically lower during the wet season than during the dry season, resulting from differences in atmospheric humidity, convective mixing, oceanic/terrestrial wind fetch and wet deposition rates. It also agrees with the findings of Morrison et al. (2015) who found that TGM concentrations are higher at Glenville during the winter. It was suggested that Hg concentrations at Glenville are seasonally dependent upon wind direction, which flows predominantly from the southeast during the summer and from the NW, past the power stations, during the winter.

Very small seasonal variations were reported at Amsterdam Island by Angot et al. (2014), with a maximum during the winter (1.06 ng m\(^{-3}\)) and a minimum during the summer (1.04 ng m\(^{-3}\)). This is concurrent with the observational data used in this study and in agreement with the InvOcean simulation, however the Default, NewChem/NewOcean and NewChem/SlabOcean simulations fail to replicate this trend and suggest a somewhat larger seasonal variation. Wind sector analysis, radon tracers and the simultaneous maximum of CO have indicated that high Hg\(^0\) concentrations at Amsterdam Island are influenced by biomass burning from the African continent between July and September (Angot et al., 2014). However, this is not really shown in the sensitivity simulation without biomass burning emissions (see Figure 22). Low Hg\(^0\) concentrations are associated with marine air masses from Southern Oceans and southern Indian Ocean (Angot et al., 2014; Mao et al., 2016).

Brunke et al. (2010) and Martin et al. (2017) showed that Cape Point has a seasonal cycle with maximum in summer, a minimum in winter and an average seasonal amplitude of ~0.13 ng m\(^{-3}\). The simulations all show a larger seasonal variation for Cape Point, suggesting that the model incorporates large biases for simulations at Cape Point. Hg\(^0\) concentrations at Cape Point are mainly influenced by marine air masses from the Southern Ocean, although terrestrial air masses from the African continent influence the site during the winter months and bring with them anthropogenic emissions from coal combustion and metal refining (Brunke et al., 2004; Brunke et al., 2010). This is clearly visible in the Anthro sensitivity simulation, with bigger spikes from anthropogenic influence in the austral winter (see Figure 23). Additional influence results from biomass burning in southern Africa and South America (Martin et al., 2017).

GEOS-Chem can reasonably accurately simulate the observed seasonal cycle at all the sites, but that Hg\(^0\) concentrations for all sites in the southern hemisphere are overestimated by 11.6%. This
suggests that GEOS-Chem is missing some of the chemical mechanisms and processes relevant to the southern hemisphere. The inversion used for the InvOcean simulation was based in part on data from Amsterdam Island. The InvOcean simulation can thus be seen to have a positive impact at the mid-latitude, marine influenced sites (Amsterdam Island and Cape Grim), but this dampening leads to larger overestimates of Hg⁰ concentrations at Gunn Point during the wet season. Further work is needed to ascertain if the tropical ocean functions differently to the mid-latitude ocean, or if the default representation of the ocean masked other issues in the simulation of tropical processes.

The NewChem/NewOcean and NewChem/SlabOcean simulations do a reasonable job with the January to April drawdown (similar to the Default simulation) at Gunn Point, but there is a big offset in the timing of the April to September (dry season) increase, and a 1-month delay in the peak. The Default simulation does a better job at replicating the dry season increase, although it peaks 1-month too early. It appears that these differences are not sensitive to the ocean updates and therefore must be related to the chemistry updates provided by Horowitz et al. (2017). However, these simulations don’t improve modeling of the seasonal cycle at Cape Grim, Glenville, Amsterdam Island and Cape Point. They show that the chemical and ocean updates have a big impact, but not necessarily a positive one, at the southern hemisphere mid-latitudes. This again raises the question of if the chemistry is therefore significantly different in the southern hemisphere, or if the original chemistry in GEOS-Chem was masking other problems.
Figure 29: Mean seasonal variation and temporal standard deviation of Hg$^0$ at Cape Grim, Tas.
Figure 30: Mean seasonal variation and temporal standard deviation of $\text{Hg}^0$ at Gunn Point, NT.
Figure 31: Mean seasonal variation and temporal standard deviation of Hg$^0$ at Glenville, NSW.
Figure 32: Mean seasonal variation and temporal standard deviation of Hg⁰ at Amsterdam Island, TAAF.
Figure 33: Mean seasonal variation and temporal standard deviation of Hg$^0$ at Cape Point, South Africa.
5.3. **Annual mercury emissions**

*Figure 34* shows the regional distribution of Hg\(^0\) emissions to the atmosphere from different surface sources. It is known that southern hemispheric sites are heavily influenced by Hg emissions from the ocean. The use of radon-222 as a tracer has shown that the Southern Ocean is an important fetch area for Cape Grim, Cape Point and Amsterdam Island, with Southern Ocean air masses representing 27% of baseline conditions at Cape Grim in spring and summer and 23% in the autumn and winter (Zahorowski et al., 2013). It is important to note that simulated emissions from the ocean are net levels (“i.e., the difference between evasion from the ocean and deposition to the ocean”).

Studies of biomass burning events at Gunn Point have shown that the site is affected by emissions from biomass burning during the dry season (Desservettaz et al., 2017; Mallet et al., 2016). Emissions factors for Hg\(^0\) over savannah grasslands were calculated to be 0.0035 and 0.032 g of Hg per kg dry fuel, about 2 orders of magnitude higher than previous estimates (Desservettaz et al., 2017). This suggests that the emission factors used in GEOS-Chem (calculated by assuming a Hg/CO emission ratio of 100 nmol/mol based on aircraft data over the U.S. (Holmes et al., 2010)) may not be representative of the Australian situation and thus the values for Hg\(^0\) emissions from biomass burning may be inaccurate.

Glenville is known to be influenced by anthropogenic emissions due to its close proximity to two coal-fired power stations, potentially enhanced by the fact that Australian power stations aren’t equipped with wet scrubbing technology (Shah et al., 2010).

At Cape Point it is thought that the seasonal differences in Hg\(^0\) concentrations are affected by anthropogenic sources during the winter months, when the site experiences terrestrial air masses. Emissions from biomass burning also display seasonal variation, with a maximum in August to September for African sources (Martin et al., 2017). Atmospheric observations taken during flights with CARIBIC (Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrumented Container) encountered seasonal plumes with elevated Hg concentrations at Cape Point. The Hg/CO\(_2\) emissions ratio at Cape Point was 109 ± 27 pg m\(^{-3}\) ppm\(^{-1}\), suggesting that the plumes originate from biomass burning and that this is having a regional influence on Hg concentrations (Slemr et al., 2014).
5.4. Hg$^{\text{II}}$ deposition fluxes

Figure 35 show the simulated regional pattern of Hg$^{\text{II}}$ dry, wet and total deposition fluxes from the Geogenic simulation. It shows that Hg$^{\text{II}}$ deposition fluxes are generally higher over the terrestrial surface than over the ocean, perhaps due to atmospheric redox reactions and a closer proximity to anthropogenic, biomass burning and soil emission sources. Observations from the GMOS network suggest that magnitude of Hg$^{\text{II}}$ wet deposition is affected by: (i) atmospheric Hg concentrations and speciation; (ii) predominant wind directions in relation to emission sources; (iii) precipitation amount and length of precipitation events; (iv) cloud type and the degree of convection involved as this influences the altitude at which Hg$^{\text{II}}$ is scavenged; and (v) the oxidizing capacity of the atmosphere (Sprovieri et al., 2017). Hg$^{\text{II}}$ deposition is higher during heavy rainfall and high humidity, leading to a distinct regional pattern and seasonal cycle in atmospheric Hg$^{\text{II}}$ concentrations (Mao et al., 2016).

The bulk of annual average Hg$^{\text{II}}$ deposition over Australia is simulated to occur via wet deposition and is in the region of $10^7$ to $10^2$ µg m$^{-2}$ yr$^{-1}$ (see top panel). Annual Hg$^{\text{II}}$ dry deposition is simulated to make a smaller contribution, in the region of $10^{-7}$ to $10^{-6}$ µg m$^{-2}$ yr$^{-1}$ (see middle panel). Observations of wet and dry deposition fluxes in Australia are sparse, however at Glenville, annual average TM wet deposition fluxes were found to be 29.13 µg m$^{-2}$ yr$^{-1}$, with a range of $5.77 \times 10^4$ to $3.62 \times 10^3$ µg m$^{-2}$ yr$^{-1}$ (Dutt et al., 2009). The simulated values (in Hg$^{\text{II}}$) are not directly comparable to the observations (in TM = Hg$^0$ + Hg$^{\text{II}}$ + Hg$^+$). However, the simulated and observed values share the same order of magnitude and it is known that the vast
The majority of Hg that undergoes wet deposition is in the form of \( \text{Hg}^{\text{II}} \). Dutt et al. (2009) found that \( \text{Hg}^{\text{II}} \) total deposition fluxes at Glenville were generally higher during the drier winter months, due to a combination of prevailing wind direction, lower mixing heights and inversions that reduce dilution and allow atmospheric concentrations of \( \text{Hg}^{\text{II}} \) to build up.

In tropical regions, wet deposition is known to be a significant pathway for the removal of atmospheric Hg, predominantly as \( \text{Hg}^{\text{II}} \), but also \( \text{Hg}^{0} \) in small quantities. Furthermore, high levels of humidity can increase the atmospheric oxidation of \( \text{Hg}^{0} \) to \( \text{Hg}^{\text{II}} \) and subsequently increase \( \text{Hg}^{\text{II}} \) wet deposition fluxes (Brunke et al., 2016; Howard et al., 2017). As a result, wet deposition fluxes should be greatest in tropical northern Australia during the wet season due to the high level of humidity and frequent thunderstorms, with dry deposition fluxes being more significant during the dry season and in the drier regions of the country. Figure 35 doesn’t show much of distinction between northern Australia and the rest of country, suggesting that one possible avenue for model improvement would be to focus on scavenging in the tropics.
Figure 35: Regional pattern of Hg\textsuperscript{II} deposition fluxes from the atmosphere to the surface. Note that the scales for wet, dry and total deposition are not the same.
5.5. Australian budget of atmospheric mercury

Figure 36-39 show TM (Hg\(^0\) + Hg\(^{II}\) + Hg\(^P\)) surface fluxes at the global, southern hemispheric and Australian scale. These figures are produced from the Geogenic simulation. The black line represents the net emissions flux, values above zero represent a net source to the atmosphere, while values below zero represent a net sink from the atmosphere. Note that ‘dry deposition’ fluxes are over the terrestrial surface only. Over the ocean, GEOS-Chem simulates the 2-way exchange of Hg and the output is provided as ‘ocean net’ flux. It can be seen that the anthropogenic sources have a smaller contribution, while oceanic sources have a greater contribution to total Hg surface fluxes at the southern hemispheric scale in comparison to the global scale.

The Australian region was assumed to have a minimum latitudinal and longitudinal boundary of 11° to 39° south and 114° to 153° east. This was designed to exclude as much ocean influence as possible, however it also excludes Tasmania and a small part of the Australian mainland. The maximum latitudinal and longitudinal boundaries are 10° to 45° south and 110° to 155° east. This was designed to cover the wider Australian region.

The minimum and maximum boundaries for Australia (see Figure 40 and 41) show that the Australian terrestrial surface provides a net sink for atmospheric Hg during the summer months (November to March) and a net source during the winter months (June to October). It should also be noted that the minimum boundary for Australia contains less ocean area than the maximum boundary and so the contribution of oceanic Hg fluxes are smaller.

Table 10 details the modelled values for Hg surface fluxes.

![Global Hg surface fluxes](image)

**Figure 36**: Global Hg surface fluxes. *dry deposition fluxes are over the terrestrial surface only.*
Figure 37: Southern hemisphere Hg surface fluxes. *dry deposition fluxes are over the terrestrial surface only.

Figure 38: Australian Hg surface fluxes. (Maximum Boundary). *dry deposition fluxes are over the terrestrial surface only. Note the maximum boundary corresponds to a box around Australia for the latitudes 10° to 45° south and longitudes 110° to 155° east.
Figure 39: Australian Hg surface fluxes. (Minimum Boundary). *dry deposition fluxes are over the terrestrial surface only. Note the minimum boundary corresponds to a box around Australia for the latitudes 11° to 39° south and longitudes 114° to 153° east.

Figure 40: The box representing the minimum latitudinal and longitudinal boundaries for Australia.
Figure 41: The box representing the maximum latitudinal and longitudinal boundaries for Australia.
Table 10: A comparison of modelled Hg surface fluxes (µg/m²/month) at global, southern hemisphere Australia (max) and Australia (min) scales.

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<td>2.90</td>
<td>3.04</td>
<td>3.18</td>
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<td>3.52</td>
<td>3.60</td>
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<tr>
<td></td>
<td>Geogenic</td>
<td>0.43</td>
<td>0.39</td>
<td>0.43</td>
<td>0.42</td>
<td>0.43</td>
<td>0.42</td>
<td>0.43</td>
<td>0.43</td>
<td>0.42</td>
<td>0.42</td>
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<td>5.07</td>
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<td>0.46</td>
<td>0.39</td>
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<td>0.45</td>
<td>0.64</td>
<td>0.60</td>
<td>0.50</td>
<td>0.39</td>
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<td></td>
<td>Ocean (net)</td>
<td>2.22</td>
<td>1.53</td>
<td>1.58</td>
<td>1.64</td>
<td>1.87</td>
<td>1.90</td>
<td>1.83</td>
<td>1.63</td>
<td>1.56</td>
<td>1.89</td>
<td>1.60</td>
<td>1.78</td>
<td>1.75</td>
<td>21.02</td>
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<td>Total Sources</td>
<td>8.55</td>
<td>7.25</td>
<td>7.16</td>
<td>6.98</td>
<td>7.37</td>
<td>7.36</td>
<td>7.41</td>
<td>7.95</td>
<td>8.26</td>
<td>9.96</td>
<td>8.57</td>
<td>7.97</td>
<td>7.90</td>
<td>94.80</td>
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<td>Deposition Dry</td>
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<td>3.91</td>
<td>3.84</td>
<td>4.08</td>
<td>4.05</td>
<td>4.30</td>
<td>4.40</td>
<td>4.09</td>
<td>3.80</td>
<td>3.43</td>
<td>4.30</td>
<td>3.70</td>
<td>46.79</td>
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<td></td>
<td>Deposition Wet</td>
<td>6.01</td>
<td>4.41</td>
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<td>3.35</td>
<td>3.48</td>
<td>2.75</td>
<td>3.11</td>
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<td>3.74</td>
<td>4.59</td>
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<td>6.88</td>
<td>4.36</td>
<td>52.35</td>
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<td>Total Sinks</td>
<td>9.74</td>
<td>7.96</td>
<td>8.72</td>
<td>7.19</td>
<td>7.56</td>
<td>6.80</td>
<td>7.41</td>
<td>7.28</td>
<td>7.83</td>
<td>8.97</td>
<td>9.77</td>
<td>10.51</td>
<td>8.26</td>
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<td>Net Emissions Flux</td>
<td>-1.19</td>
<td>-0.71</td>
<td>-1.56</td>
<td>-0.21</td>
<td>-0.19</td>
<td>0.57</td>
<td>-0.002</td>
<td>0.67</td>
<td>0.44</td>
<td>1.58</td>
<td>-1.20</td>
<td>-2.54</td>
<td>-0.36</td>
<td>-4.34</td>
</tr>
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</table>
Table 11 shows the global, southern hemispheric, Australia (max) and Australia (min) budgets of Hg from the InvOcean simulation. Global emissions are estimated at 5870 Mg yr\(^{-1}\), slightly lower than the range of 6500 to 8200 Mg yr\(^{-1}\) reported by Driscoll et al. (2013). It is also lower than previous GEOS-Chem based evaluations, that estimated global emissions budgets of 8300 Mg yr\(^{-1}\) (Holmes et al., 2010) and 8540 Mg yr\(^{-1}\) (Horowitz et al., 2017). Globally, anthropogenic emissions are estimated to contribute 1790 Mg yr\(^{-1}\), while natural/legacy emissions contribute 4080 Mg yr\(^{-1}\); again these are slightly below the ranges reported in the literature and discussed in Section 2.4.

Total Hg emissions from the southern hemisphere are estimated to be 2220 Mg yr\(^{-1}\), approximately 37.9\% of global total Hg emissions. Anthropogenic sources in the southern hemisphere account for 364 Mg yr\(^{-1}\), approximately 20.3\% of global anthropogenic emissions. This shows that anthropogenic emissions are far lower in the southern hemisphere, while land-based emissions sources are compensated by oceanic sources.

The Geogenic simulation produces an atmospheric Hg budget for the Australian region of approximately 110 to 144 Mg yr\(^{-1}\). Previous estimates of the Hg budget for Australia didn’t include emissions from oceanic sources. To compare with these estimates the oceanic emissions were removed from the Australian maximum budget (Australia Max – Ocean (net)). This produces an estimated Australian budget of 93.2 Mg yr\(^{-1}\). This is slightly lower than previous estimates of 117 to 567 Mg yr\(^{-1}\) (Nelson et al., 2004) and 105 to 305 Mg yr\(^{-1}\) (Nelson et al., 2012). The difference seems to mostly come from lower biomass burning, soil and legacy emissions within GEOS-Chem.

Australian anthropogenic emissions are estimated to be 18.3 to 20.1 Mg yr\(^{-1}\), approximately 13.9-16.7\% of total emissions, while natural and legacy emissions are estimated to be 91.6 to 124.1 Mg yr\(^{-1}\), approximately 83.3-86.1\% of total emissions. These budgets fall within the ranges estimated by Nelson et al. (2012) of 10-20 Mg yr\(^{-1}\) for anthropogenic emissions and 70-210 Mg yr\(^{-1}\) for natural/legacy emissions. The ocean is also shown to have a large influence on Australian Hg\(^{0}\) concentrations, as it accounts for 24.7 to 50.9 Mg yr\(^{-1}\), approximately 22.5 to 35.3\% of the Australian Hg budget.
Table 11: Budget of Hg (rates are in Mg yr\(^{-1}\)) in GEOS-Chem for the globe, southern hemisphere, Australia (max) and Australia (min).

<table>
<thead>
<tr>
<th>Flux Type</th>
<th>Global</th>
<th>Southern Hemisphere</th>
<th>Southern Hemisphere Percentage of Global Total (%)</th>
<th>Australia (Min(^a) – Max(^b))</th>
<th>Australia Percentage of Global Total (%)</th>
<th>Australia (Nelson et al. 2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic</td>
<td>1790</td>
<td>360</td>
<td>20.4</td>
<td>18.3 - 20.1</td>
<td>1.02 - 1.12</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Biomass</td>
<td>240</td>
<td>120</td>
<td>47.8</td>
<td>10.3 - 10.6</td>
<td>4.28 - 4.43</td>
<td>21 - 63</td>
</tr>
<tr>
<td>Soil</td>
<td>840</td>
<td>260</td>
<td>31.3</td>
<td>45.6 - 46.5</td>
<td>5.45 - 5.56</td>
<td>70 – 210(^c)</td>
</tr>
<tr>
<td>Geogenic</td>
<td>2600</td>
<td>40</td>
<td>15.1</td>
<td>5.5 - 10.3</td>
<td>2.10 - 3.95</td>
<td>n/a</td>
</tr>
<tr>
<td>Land Legacy</td>
<td>90</td>
<td>28</td>
<td>30.8</td>
<td>5.4 - 5.7</td>
<td>5.94 - 6.24</td>
<td>n/a(^c)</td>
</tr>
<tr>
<td>Snow</td>
<td>67</td>
<td>43</td>
<td>64.2</td>
<td>4.76E-8 - 5.07E-8</td>
<td>7.05E-8 – 7.51E-8</td>
<td>n/a</td>
</tr>
<tr>
<td>Ocean (net)</td>
<td>2580</td>
<td>1370</td>
<td>53.2</td>
<td>24.7 - 50.9</td>
<td>0.96 - 1.97</td>
<td>n/a</td>
</tr>
<tr>
<td>Total Sources</td>
<td>5870</td>
<td>2220</td>
<td>37.9</td>
<td>109.9 - 144.2</td>
<td>1.87 - 2.46</td>
<td>105 – 305(^d)</td>
</tr>
<tr>
<td>Deposition Dry</td>
<td>1300</td>
<td>390</td>
<td>30.2</td>
<td>54.5 - 56.9</td>
<td>4.19 - 4.37</td>
<td>n/a</td>
</tr>
<tr>
<td>Deposition Wet</td>
<td>2570</td>
<td>1290</td>
<td>50.2</td>
<td>60.5 - 84.4</td>
<td>2.35 - 3.28</td>
<td>n/a</td>
</tr>
<tr>
<td>Total Sinks</td>
<td>3870</td>
<td>1690</td>
<td>43.5</td>
<td>115.1 - 141.3</td>
<td>2.97 - 3.65</td>
<td>n/a</td>
</tr>
<tr>
<td>Net Emissions</td>
<td>1990</td>
<td>538</td>
<td>27.0</td>
<td>-5.1 - 2.9</td>
<td>-0.26 - 0.15</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Footnote:
\(^a\)The minimum boundary corresponds to a box around Australia for the latitudes 11° to 39° south and longitudes 114° to 153° east; and
\(^b\)The maximum boundary corresponds to a box around Australia for the latitudes 10° to 45° south and longitudes 110° to 155° east.
\(^c\)Nelson et al., (2012) includes land legacy emissions within the soil emissions estimate.
\(^d\)The total emissions estimate of Nelson et al., (2012) excludes emissions from oceanic sources.

5.6. Hg\(^0\)-air humidity relationship

It has been suggested in the literature that there is a positive linear relationship between Hg\(^0\) concentrations and relative humidity. The suggestion is that higher levels of relative humidity promote the aqueous-phase reduction of Hg\(^0\) into Hg\(^\text{II}\) (Timonen et al., 2013) with evidence provided by multiple linear regression analysis that relative humidity may be a controlling factor for Hg\(^0\) levels during the winter (Esbri et al., 2016).

Figure 42-46 show the relationship between Hg\(^0\) concentrations and relative humidity at each of
the sites. The strongest relationship was detected at Glenville, which produced an r-value of 0.42 (slope: 0.0035, intercept: 0.0003) and 0.50 (slope: 0.0025, intercept: 0.0002) for the Default and InvOcean simulations, suggesting a weak positive relationship. Note that this analysis is for the model only as observational measurements of the relative humidity was not available for any of the sites.

The r-values for the other sites generally suggested that there wasn’t a relationship between Hg$_0$ and relative humidity, with values close to zero. However, the Default simulation produced an r-value of -0.31 (slope: -0.0025, intercept: 0.0003) for Gunn Point suggesting a weak negative relationship. This could indicate that relative humidity is highest when precipitation is also highest, and so the Hg$^{II}$ is undergoing wet deposition faster than it can be converted to Hg$_0$. **Figure 43** appears to show that at Gunn Point, the distribution does not fit particularly well with a linear correlation. The InvOcean simulation shows that the highest Hg$_0$ concentrations also occur when the relative humidity is highest, potentially occurring at the times when Gunn Point experiences northern hemispheric air masses. These air masses are known to have higher Hg$_0$ concentrations and as they have travelled across the tropical equatorial regions they would also be expected to have higher levels of relative humidity.

Overall, GEOS-Chem is generally unable to discern a linear relationship between Hg$_0$ and relative humidity at southern hemisphere sites.
Figure 42: Relationship between Hg\(^0\) concentrations and relative humidity (%) at Cape Grim, Tas.
Figure 43: Relationship between \( \text{Hg}^0 \) concentrations and relative humidity (%) at Gunn Point, NT.
Figure 44: Relationship between $\text{Hg}^0$ concentrations and relative humidity (%) at Glenville, NSW.
Figure 45: Relationship between Hg$^0$ concentrations and relative humidity (%) at Amsterdam Island, TAAF.
**Figure 46:** Relationship between $\text{Hg}^0$ concentrations and relative humidity (%) at Cape Point, South Africa.
5.7. **Latitudinal gradient in Hg concentrations**

*Figure 47 and 48* show the latitudinal variation in Hg concentrations at the global and study area scales; note that the Hg concentrations are multi-year means for the period January 2013 to December 2016. The top graphs show how simulated Hg\(^0\) concentrations vary at the longitudes corresponding to each of the sites, while the bottom graph shows the simulated latitudinal variations (averaged for all longitudes) between the different Hg species. Measurements from ship cruises and the GMOS network have observed that Hg\(^0\) decreases from the high latitudes of the northern hemisphere towards the equator and then on towards the south pole (Mao et al., 2016; Sprovieri et al., 2016). This trend is clearly represented in the GEOS-Chem simulation and is largely due to greater Hg emissions in the northern hemisphere.

At the global scale, Hg\(^0\) concentrations are known to be highest in the northern hemisphere and reduce as you move towards the southern pole. Therefore, there should be a slight latitudinal gradient of Hg\(^0\) across Australia, with concentrations decreasing from the northern tropics to the southern mid-latitudes. Howard et al. (2017) reported a mean Hg\(^0\) concentration at Gunn Point of 0.95 ng m\(^{-3}\) for June 2014 to June 2016; compared to 0.86 ng m\(^{-3}\) for 2014 to 2015 at Glenville (Morrison et al., 2015) and 0.86 ng m\(^{-3}\) for 2012 to 2013 at Cape Grim (Slemr et al., 2015). The upper graph in *Figure 48* shows that there is an observed Australian gradient (north to south) of -0.0022 ng m\(^{-3}\) degree\(^{-1}\), greater than the simulated Australian gradient of -0.0015 ng m\(^{-3}\) degree\(^{-1}\). The differences in the two simulated transects suggests that some of the observed gradient could be due to longitudinal differences and spatial variability in emissions sources between the two sites.

Both the Cape Grim and Gunn Point transects show a slight decrease in Hg\(^0\) concentrations at the latitudes corresponding to the majority of the Australian landmass (~20° to -35° S), suggesting that there could be net deposition over the terrestrial surface. In comparison, the Amsterdam Island transect, which is representative of oceanic conditions, doesn’t decrease at the same latitudes, suggesting that the ocean provides a greater source of Hg\(^0\) to the atmosphere than the Australian terrestrial surface. The Hg speciation plot shows that there is a large spike in Hg\(^{II}\) and a smaller spike in Hg\(^0\), which correspond with the dips in Hg\(^0\) concentrations for the Cape Grim and Gunn Point transects; this suggests that the simulated dips over the Australian landmass could be driven by Hg\(^0\) oxidation to Hg\(^{II}\) in the model.

Note that: (1) Cape Point was not included in *Figure 48* as it has different dynamics to the other sites and this affects axis range; and (2) the observed Australian gradient is shown between Gunn Point and Cape Grim, because Glenville does not appear to be representative of typical Australian conditions.
Figure 47: Latitudinal variation of Hg concentrations in the surface boundary layer at the global scale. Note that: (i) in the top panel each model line represents a transect at the longitude of the observation site; and (ii) in the bottom panel model lines are averaged for all longitudes.

Figure 48: Latitudinal variation of Hg concentrations in the surface boundary layer at the study area scale. Note that: (i) in the top panel each model line represents a transect at the longitude of the observation site; and (ii) in the bottom panel model lines are averaged for all longitudes.
Chapter 6

6. Conclusion

Gaseous elemental mercury (Hg\(^0\)) observations from five southern hemisphere sites were used to evaluate the performance of the GEOS-Chem biogeochemical Hg model. The key findings are that: (i) GEOS-Chem is generally able to reproduce the observed seasonal cycle of Hg\(^0\) at southern hemisphere sites, but not the daily variability; (ii) the simulations tend to overestimate Hg\(^0\) concentrations; (iii) Australian and southern hemispheric sites are heavily influenced by oceanic emissions; and (iv) the Australian terrestrial surface may provide a net sink for atmospheric Hg.

Analysis of the daily variability using sensitivity simulations that isolate the influence of individual sources suggests that Australian sites are most sensitive to contributions from anthropogenic and soil sources, with smaller contributions resulting from biomass burning. Gunn Point experiences spikes in Hg\(^0\) concentrations relating to anthropogenic emissions. This occurs during the wet season (December to February), when the Intertropical Convergence Zone (ITCZ) is at its southernmost point and allows the site to sample northern hemispheric air masses. These events typically coincide with heavy rainfalls, resulting in Hg washout, followed by periods of low atmospheric Hg concentrations. It is thought that Hg re-emission may be inhibited from saturated soils following heavy precipitation events (Howard et al., 2016), a process that is not currently included in the model. GEOS-Chem simulations (particularly in the tropical regions) may benefit from reduced Hg emissions in moisture-laden soils.

The relationship between simulated and observed Hg\(^0\) concentrations shows that GEOS-Chem generally has a poor ability to simulate the daily variability. Simulations could be improved by: (i) using daily averages for Br (rather than monthly averages) for driving the atmospheric chemistry; (ii) improving the representation of soil and vegetation emissions, which are probably not accurate for Australia; (iii) coupling vegetation with soil emissions/deposition, which are currently treated independently but would be more accurately represented by bi-directional exchange; and (iv) using a finer resolution for simulations (e.g. smaller grid-boxes), although this would increase computational time and resources.

The InvOcean simulation uses Bayesian inversion methods to update the ocean parameters used in GEOS-Chem (Song et al., 2015). When compared against the Default simulation, this improves representation of the mean seasonal variation at all the southern hemisphere sites, except Gunn Point. As the InvOcean simulation performs worse at Gunn Point these updates may not apply in the tropics and further work is needed to understand oceanic influence in this region.

The NewChem/NewOcean and NewChem/SlabOcean simulations update the chemical mechanisms in GEOS-Chem; the NewChem/NewOcean simulation is also coupled to an ocean Hg model to improve oceanic Hg cycling (Horowitz et al., 2017). Both of these simulations exhibit a negative Mean Normalized Bias (MNB), while the Default and InvOcean simulations (don’t include the chemistry updates) exhibit a positive bias. This suggests that the chemistry updates by Horowitz et
al. (2017) have a big impact (but not a positive one) on the overall performance of simulations in the southern hemisphere and indicates that there are clear hemispheric differences that are still not very well understood. Further work is needed to ascertain if the chemistry is therefore significantly different in the southern hemisphere. Another possibility is that the original chemistry in GEOS-Chem was masking other problems within the model.

The simulations in this study suggest that some of the bias relates to the chemical mechanisms included in GEOS-Chem. Neglecting oxidation by Cl₂ and aqueous-phase HOCl/OCl⁻ in the marine boundary layer is one limitation of GEOS-Chem. The inclusion of this process may improve simulations at southern hemispheric sites as oceanic processes heavily influence them.

The Default simulation suggests that there is a weak negative relationship (correlation coefficient of \( r = -0.3134 \)) between Hg\(^0\)-air humidity at Gunn Point. This may be because relative humidity and precipitation tend to be positively correlated, and so Hg\(^{II}\) is undergoing wet deposition faster than it can be converted to Hg\(^0\). The InvOcean simulation shows that high Hg\(^0\) concentrations are concurrent with high relative humidity and may be due to northern hemispheric air masses that have travelled across the tropical equatorial regions. More work is needed to understand the relationship between Hg\(^0\) and relative humidity at southern hemispheric sites, as primary analysis in GEOS-Chem indicates that this relationship is distinctly non-linear.

The wet deposition of Hg\(^{II}\) is known to be a significant pathway for the removal of atmospheric Hg in the tropics. However, analysis of Hg\(^{II}\) depositional fluxes in GEOS-Chem does not indicate much of a distinction between tropical northern Australia and the rest of country. The mean seasonal variation shows that the Default and InvOcean simulations significantly underestimate the seasonal drawdown at Gunn Point from maximum to minimum concentrations. Together these indicate that the model may underestimate scavenging of atmospheric Hg in the southern hemisphere tropics. Therefore, one avenue for model improvement would be to focus on scavenging in the tropical regions.

It is suspected that GEOS-Chem overestimates Hg\(^0\) concentrations in Western Australia, due to the inclusion of the Gidji roaster, which closed in 2015. This source was estimated to contribute 49.7\% of Australian anthropogenic emissions (Nelson et al., 2009), so its inclusion is most likely affecting simulations over the Australasian region. At present there are no observations in the vicinity of the site, or indeed within Western Australia that would enable quantification of this change or its impacts.

Observations from Australia indicate the presence of a latitudinal gradient in Hg\(^0\), both between the northern and southern hemispheres and potentially across Australia. GEOS-Chem simulates a gradient of -0.0015 ng m\(^{-3}\) degree\(^{-1}\) between Cape Grim and Gunn Point, slightly smaller than the observed gradient of -0.0022 ng m\(^{-3}\) degree\(^{-1}\). These latitudinal gradients are relatively small and close to the uncertainty of the measurements. The simulated latitudinal transects at Cape Grim and Gunn Point indicate that there could be net deposition over the Australian landmass, while the Hg speciation transects suggest that this may be driven by the oxidation of Hg\(^0\) to Hg\(^{II}\). Australia requires additional observation sites and measurements of Hg\(^{II}\) and Hg\(^0\) to provide an improved
understanding of Hg speciation, chemical redox reactions and Hg fluxes (both evasion and deposition) in the region.

It was found that GEOS-Chem simulates an atmospheric Hg budget for the Australian region of approximately 110 to 144 Mg yr\(^{-1}\). Hg exchange from the ocean accounts for approximately 22.5 to 35.3\% of this total. Once oceanic sources were removed, the budget was estimated at 93.2 Mg yr\(^{-1}\), slightly lower than previous estimates. GEOS-Chem indicates the difference is due to lower emissions from biomass burning, soil and legacy sources. However, emission factors in GEOS-Chem are based exclusively on data from the northern hemisphere mid-latitudes and model simulations may benefit from customization of the emission factors relating to soil, biomass burning and vegetation processes.

Currently, Hg measurements from isotopic fractionation are unavailable for Australia. These would be useful for constraining the influence of different Hg sources, which currently can only be estimated through bottom-up emissions inventories and sensitivity simulations, like the ones conducted here.

In summary, this work provides the first evaluation of the GEOS-Chem Hg model over Australia, paving the way for model development that will improve Hg simulation in this part of the world. Future work will specifically target inclusion of moisture limitation for emissions from tropical soils, investigation of chlorine chemistry in the marine boundary layer, focusing on scavenging in the tropical regions, and customization of emissions factors for Australian soils and vegetation.
7. List of References


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Appendices

Appendix 1: Example of Python code

The Python code below was used to produce “Figure 37: Southern hemisphere Hg surface fluxes. Similar code was used to undertake statistical analysis and to produce the figures and maps (except where noted otherwise).

```python
#!/usr/bin/env python2
# -*- coding: utf-8 -*-
""
Created on Tue May 2 10:50:22 2017
@author: ncp532
""

# File system packages
from netCDF4 import Dataset # function used to open single netCDF file
from netCDF4 import MFDataset # function used to open multiple netCDF files
import netCDF4
from pylab import *

# Drawing packages
import matplotlib.pyplot as plt             # import package as shorter nickname
import matplotlib.dates as mdates
import matplotlib.ticker as ticker

# Data handing packages
import numpy as np                          # import pack - Numpy as great at handling multidimensional data arrays.
import pandas as pd
from scipy import signal, stats

# Date and Time handling package
from datetime import datetime,timedelta     # functions to handle date and time

# Define the dataset
dataset1 = MFDataset('/Users/ncp532/Desktop/Some_scripts_/nc_Geogenic_Files/trac_avg.201*.nc') # InvOcean

# Get the variables needed for calculations
airdena = dataset1.variables['BXHGHT_S__AIRNUMDE'][;] # dry air number density in (molecules air/m3)
area = dataset1.variables['DXYP__DXYP'][;0:45,;]         # Grid box surface area (m2)
timea = dataset1.variables['time'][;]                   # in minutes
leva = dataset1.variables['lev'][;]                    # atmospheric level (0 to 46)
lata = dataset1.variables['lat'][;]                    # latitude

# Get the source data
wet0 = (dataset1.variables['IJ_AVG_S__Hg0'][;]*(1e-3)*200.59/(6.0221*1e23)*airdena*1e6
anthro1 = (dataset1.variables['HG_SRCE__Hg0_an'][;0:45,;]) # Hg0 anthro emissions (kg/month)
anthro2 = (dataset1.variables['HG_SRCE__Hg2_an'][;0:45,;]) # Hg2 anthro emissions (kg/month)
```
anthro3 = (dataset1.variables['HG_SRCE__HgP_an'][::,0:45,:])  # HgP anthro emissions (kg/month)
anthro = (anthro1 + anthro2 + anthro3)  # anthro emissions (kg/month)
biomass = (dataset1.variables['HG_SRCE__Hg_bb'][::,0:45,:])  # biomass emissions (kg/month)
soil = (dataset1.variables['HG_SRCE__Hg_so'][::,0:45,:])  # soil emissions (kg/month)
geogenic = (dataset1.variables['HG_SRCE__Hg0_na'][::,0:45,:])  # land natural emissions (kg/month)
land_leg = (dataset1.variables['HG_SRCE__Hg0_ln'][::,0:45,:])  # land legacy/re-emissions (kg/month)
ocean = (dataset1.variables['HG_SRCE__Hg0_oc'][::,0:45,:])  # ocean net emissions (kg/month)

hg0_dd=(dataset1.variables['DRYD_FLX__Hg0df'][::,0:45,:])     # Hg0 dry deposition flux (molec/cm²/s)
hgII_1=(dataset1.variables['WETDLS_S__Hg2'][::,0:45,:])       # Loss of Hg2 in precipitation (kg/s)
hgII_2=(dataset1.variables['WETDCV_S__Hg2'][::,0:45,:])       # Rainout loss of tracer in convective updrafts (kg/s)
hgII_wd = (hgII_1 + hgII_2)                                       # HgII wet deposition flux (kg/s)

# Convert the dataset from pptm to ng/m³ = pptm*(10^-12)*(molecular mass Hg/molar volume Hg)
# * (molar volume Hg/Avogadro's number)*(10^9)*(air density in molecules/m³)
#---------------------------------------------------------------------------------------------
days=np.array([31,28,31,30,31,30,31,31,30,31,30,31,
               31,28,31,30,31,30,31,31,30,31,30,31,
               31,28,31,30,31,30,31,31,30,31,30,31,
               31,29,31,30,31,30,31,31,30,31,30,31])
#---------------------------------------------------------------------------------------------

# Convert the source data from units (kg/month) into units (kg/m²/month)
anthro = anthro/area
biomass = biomass/area
soil = soil/area
geogenic = geogenic/area
land_leg = land_leg/area
ocean = ocean/area

# Convert the source data from units (molec/cm²/s) into units (kg/m²/month)
# kg/m²/month = (molecules/cm²/s) * (1e4 cm² / m²) / (6.0221e23 molecules/mol) 
# * (200.59 g/mol) * (1e-3 kg/g) * (86400 s/d) * (days_in_month d/month)
HgTimeD, HglatD, HglonD = np.shape(hg0_dd)
HG0_DD = np.copy(hg0_dd)
for i in range(HgTimeD):
    HG0_DD[i,:,:] = hg0_dd[i,:,:]*days[i] # Overall
HG0_DD = HG0_DD/area*86400

# Convert the source data from units (kg/s) into units (kg/m²/month)
# Convert the source data from units (molec/cm²/s) into units (kg/m²/month)
# kg/m²/month = (molecules/cm²/s) * (1e4 cm² / m²) / (6.0221e23 molecules/mol)
# kg/s = (200.59 g/mol) * (1e-3 kg/g) * (86400 s/d) * (days_in_month d/month)
HgTimeD, HglatD, HglonD = np.shape(hgII_wd)
HGII_WD = np.copy(hgII_wd)
for i in range(HgTimeD):
    HGII_WD[i,:,:] = hgII_wd[i,:,:]*days[i] # Overall
HGII_WD = HGII_WD/area*86400

# Convert the source data from units (kg/m²/month) into units (kg/m²/month)
# kg/m²/month = (molecules/cm²/s) * (1e4 cm² / m²) / (6.0221e23 molecules/mol)
# * (200.59 g/mol) * (1e-3 kg/g) * (86400 s/d) * (days_in_month d/month)
hgII_wd = np.sum(hgII_wd, axis=1)
HgTime, Hglat, Hglon = np.shape(hgII_wd)
HGII_WD = np.copy(hgII_wd)
for i in range(HgTime):
    HGII_WD[i,:,:] = hgII_wd[i,:,:]*days[i] # Overall
HGII_WD = HGII_WD/area*86400

# Convert the dataset from pptm to ng/m³ = pptm*(10^-12)*(molecular mass Hg/molar volume Hg)
# * (molar volume Hg/Avogadro's number)*(10^9)*(air density in molecules/m³)
#---------------------------------------------------------------------------------------------

# DATETIME
# InvOcean

131
# Convert GEOS-Chem time into standard time (GEOS-Chem time is hours since 1985/01/01/0000)
d0=datetime(1985,1,1,0)
datea = []
for t in timea:
    hrs=timedelta(hours=int(t))
datea.append(d0+hrs)
# Calculate the seasonal variation

# Anthro
monthavg1=np.zeros([12]) # Set the size
monthvals1= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
dataind=monthvals1 == monthind+1
monthavg1[monthind] = np.mean(anthro[:,:,;:][dataind]) # find the mean of months with same month value

# Biomass
monthavg2=np.zeros([12]) # Set the size
monthvals2= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
dataind=monthvals2 == monthind+1
monthavg2[monthind] = np.mean(biomass[:,:,;:][dataind]) # find the mean of months with same month value

# Soil
monthavg3=np.zeros([12]) # Set the size
monthvals3= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
dataind=monthvals3 == monthind+1
monthavg3[monthind] = np.mean(soil[:,:,;:][dataind]) # find the mean of months with same month value

# Geogenic
monthavg4=np.zeros([12]) # Set the size
monthvals4= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
dataind=monthvals4 == monthind+1
monthavg4[monthind] = np.mean(geogenic[:,:,;:][dataind]) # find the mean of months with same month value

# Land Legacy
monthavg5=np.zeros([12]) # Set the size
monthvals5= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
dataind=monthvals5 == monthind+1
monthavg5[monthind] = np.mean(land_leg[:,:,;:][dataind]) # find the mean of months with same month value

# Ocean
monthavg6=np.zeros([12]) # Set the size
monthvals6= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
dataind=monthvals6 == monthind+1
monthavg6[monthind] = np.mean(ocean[:,:,;:][dataind]) # find the mean of months with same month value
# Hg0 Dry Deposition
monthavg7=np.zeros([12]) # Set the size
monthvals7= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
    dataind=monthvals7 == monthind+1
    monthavg7[monthind] = np.mean(HG0_DD[:,:,::][dataind]) # find the mean of months with same month value

# HgII Wet Deposition
monthavg8=np.zeros([12]) # Set the size
monthvals8= [ dt.month for dt in datea ] # Extract the month values from the date
for monthind in np.arange(12):
    dataind=monthvals8 == monthind+1
    monthavg8[monthind] = np.mean(HGII_WD[:,:,::][dataind]) # find the mean of months with same month value

# Calculate the Net Emissions Flux
NEF = (monthavg1+monthavg2+monthavg3+monthavg4+monthavg5+monthavg6)-(monthavg7+monthavg8)

#Multiply by 1e8 easier for plotting
monthavg1=monthavg1*1e10
monthavg2=monthavg2*1e10
monthavg3=monthavg3*1e10
monthavg4=monthavg4*1e10
monthavg5=monthavg5*1e10
monthavg6=monthavg6*1e10
monthavg7=monthavg7*1e10
monthavg8=monthavg8*1e10
NEF=NEF*1e10

# Plot the axis for each graph
fig = plt.figure()
plt.subplots_adjust(hspace=0.5)

# SIMULATIONS
# Plot the monthly mean for the location
lines1 = ax.bar(datea[0:12], monthavg1, width=22, color='red', label="Anthropogenic")
lines2 = ax.bar(datea[0:12], monthavg2, width=22, color='blue', bottom=monthavg1, label="Biomass")
lines3 = ax.bar(datea[0:12], monthavg3, width=22, bottom=monthavg1+monthavg2, color='yellow', label="Soil")
lines4 = ax.bar(datea[0:12], monthavg4, width=22, color='green', bottom=monthavg1+monthavg2+monthavg3, label="Geogenic")
lines5 = ax.bar(datea[0:12], monthavg5, width=22, color='cyan', bottom=monthavg1+monthavg2+monthavg3+monthavg4, label="Land Legacy")
lines6 = ax.bar(datea[0:12], monthavg6, width=22, color='magenta', bottom=monthavg1+monthavg2+monthavg3+monthavg4+monthavg5, label="Ocean (net)")
lines7 = ax.bar(datea[0:12], monthavg7*(-1), width=22, color='orange', label="Deposition Dry$^*$")
lines8 = ax.bar(datea[0:12], monthavg8*(-1), width=22, bottom=monthavg7*(-1), color='darkslategray', label="Deposition Wet")
lines9 = plt.plot(datea[0:12],NEF, "o--",color='black', linewidth=1, label="Net Emissions Flux")
# plt.xlim(datetime(2013,01,1),datetime(2013,12,31)) # set the date limits
date_formatter = mdates.DateFormatter('%b') # format how the date is displayed
ax.xaxis.set_major_formatter(date_formatter)
ax.xaxis.set_major_locator(mdates.MonthLocator(interval=1)) # set the interval between displayed dates
plt.axhline(0, color='black')
ax.yaxis.set_ticks_position('both')
ax.set_ylim(-7.0, 8)
#ax.set_ylim(-0.5e-9, 1.0e-9)
#ax.yaxis.set_major_locator(ticker.MultipleLocator(5))
ax.yaxis.set_minor_locator(ticker.MultipleLocator(1))

# Plot the axis labels, legend and title
plt.ylabel('Hg surface fluxes (1e-9 Kg/m2/month)', fontsize=10)
plt.ylabel('Hg surface fluxes ($\mu$g/m2/month)', fontsize=10)
plt.xlabel('Month', fontsize=10)
plt.title("Southern Hemisphere Hg surface fluxes", fontsize=15)
plt.legend(bbox_to_anchor=(1.05, 1), loc=2, borderaxespad=0.)
Appendix 2: Monthly average, maximum, minimum and amplitudes for observational and simulated Hg\(^0\) concentrations at each site.

<table>
<thead>
<tr>
<th>Site</th>
<th>Month</th>
<th>Observ</th>
<th>Defa</th>
<th>InvO</th>
<th>Anth</th>
<th>Biom</th>
<th>Geogenic</th>
<th>Soil</th>
<th>NewChem / NewOcean</th>
<th>NewChem / SlabOcean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cape Grim</td>
<td>Jan</td>
<td>0.891</td>
<td>1.030</td>
<td>1.053</td>
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<td>1.022</td>
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<td>0.924</td>
<td>0.677</td>
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<td>0.935</td>
<td>1.122</td>
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<td>1.059</td>
<td>1.107</td>
<td>0.959</td>
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<td>0.935</td>
<td>1.192</td>
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<td>1.095</td>
<td>1.140</td>
<td>0.988</td>
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<td>1.222</td>
<td>1.133</td>
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<td>1.102</td>
<td>1.151</td>
<td>1.000</td>
<td>0.685</td>
<td>0.703</td>
</tr>
<tr>
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<td>1.122</td>
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<td>0.901</td>
<td>0.953</td>
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<td>0.601</td>
<td>0.717</td>
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<td>0.659</td>
<td>0.911</td>
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<td>Maximum</td>
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<td>0.905</td>
<td>1.102</td>
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<td>1.000</td>
<td>0.911</td>
<td>1.020</td>
</tr>
<tr>
<td>Minimum</td>
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<td>0.744</td>
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<td>0.631</td>
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<td>Defa</td>
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<td>Anthr</td>
<td>Biom</td>
<td>Geogenic</td>
<td>Soil</td>
<td>NewChem / NewOcean</td>
<td>NewChem / SlabOcean</td>
</tr>
<tr>
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