IDENTIFYING THE POTENTIAL INFLUENCE OF CLIMATE CHANGE ON MERCURY AIR-SURFACE EXCHANGE



Katrina Macsween, BENV Department of Environmental Sciences, Faculty of Science and Engineering

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Declaration

I hereby declare that this thesis has not been previously submitted to any other institution or university for a higher degree. Except where otherwise acknowledged, this thesis is comprised entirely of my own work.

meet

Katrina Macsween,

9th October, 2015

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Abstract

Human activities over the last few centuries have altered the earth's climate system and added to the global mercury budget. In order to understand how future climate predictions may influence future mercury emissions it is important to first understand how current climate parameters influence mercury exchange from different surfaces. This research aimed to investigate the relationship between climate controls and mercury air-surface exchange and determine the potential implications of these findings with future climate change. Mercury flux data was obtained for a number of sites using micrometeorological methods and comprised of both background and enriched sites. The Arrhenius equation was applied to gain a better understanding of which parameters control mercury flux. Environmental parameters were found to have a significant relationship with Hg air-surface exchange at the study sites. Interactions between the parameters and the Hg fluxes varied depending on sites and classification. Flux adjustments indicated that with temperature increase it is likely there will be an increase in Hg emissions from natural substrates. Flux increases calculated here range between a 30 and 40% increase for a 1 to 2°C rise in temperature by 2050 and a 30 to 52% increase for temperature rise between 1 and 3.7°C by 2100.

Chapter 1: Introduction

Mercury (Hg) is a highly mobile environmental pollutant that is toxic to humans, wildlife and ecosystems (Carpi, 1997). The atmosphere is an important pathway for the global distribution and transport of Hg. This global distribution pathways forms the dominate source of Hg in terrestrial and aquatic ecosystems (Laurier and Mason, 2007), causing the contamination of pristine environments (Schroeder and Munthe, 1998;Jackson, 1997;Boening, 2000). Currently there is a lack of understanding as to how anthropogenic modification of the environment, Hg budget and earth's climate system may have affected or will affect Hg air-surface exchange. These modifications and the interactions between them may affect natural Hg pools and associated air-surface exchange processes, thereby posing significant long-term risks to humans and the environment as a result of anthropogenic activities.

Mercury is released into the atmosphere naturally, anthropogenically or through re-emission from both of these sources. Natural emissions include outgassing from the earth's crust, evasion from surface soils, water bodies, vegetation surfaces, wild fires, volcanoes, and geothermal sources. Anthropogenic sources include, coal combustion, waste incineration, commercial product manufacture and disposal, metals refining, cement production, and artisanal gold mining (Gustin et al., 2008). Re-emission is caused mostly by the atmospheric cycling of anthropogenic Hg emissions, often referred to as legacy emissions (Amos et al., 2015). Globally 7527 Mg y⁻¹ of mercury is emitted into the atmosphere from both anthropogenic and natural sources. Anthropogenic sources contribute 2320 Mg y⁻¹, the majority of these emissions originate from the combustion of fossil fuels, accounting for 18% of anthropogenic emissions. Natural sources, including both emission and re-emission contribute 5207 Mg y⁻¹, with terrestrial surfaces emitting 2429 Mg y⁻¹ (Pirrone et al., 2010). Globally, these emissions have been increasing with time, increasing the amount of Hg present within the global Hg cycle. Increases to the Hg budget means there is a greater rate of re-emission and an increased lag time between emissions reductions and lower Hg levels in environmental exposure pathways (UNEP, 2013).

Once Hg enters the atmosphere, from a combination of natural and anthropogenic sources, it can remain in the atmosphere for up to 2 years, where it is subjected to a number of physical and chemical processes before it is deposited onto terrestrial, aquatic and ocean surfaces (Dastoor and Larocque, 2004;Choi and Holsen, 2009;Pirrone and Mason, 2009;Carpi and Lindberg, 1998;Boening, 2000;Moore and Carpi, 2005). Within the atmosphere Hg exists in three dominant forms: gaseous elemental mercury (GEM), gaseous oxidised mercury (GOM),

and particulate bound mercury (PBM). The chemical and physical states of Hg determine the fate and distribution of the element in the environment (Clarkson, 1992;Blackwell et al., 2014;Choi and Holsen, 2009;Gabriel et al., 2006). GEM accounts for approximately 90% of Hg found in the atmosphere. The high vapour pressure and low solubility and reactivity allow it to exist in the atmosphere for between 2 and 18 months, where it can travel across hemispheric and global scales (Gustin et al., 2015a). The fundamental physio-chemical properties of GOM and PBM makes it difficult to operationally define the species in the atmosphere. Therefore, they are collectively referred to as reactive mercury (RM) (Gustin et al., 2015a, b;Huang et al., 2015;Weiss-Penzias et al., 2015). RM has a much shorter atmospheric lifetime, usually being deposited onto surfaces within a few days of formation. RM can vary considerably both spatially and temporally, making the relationship between RM and GEM poorly understood (Huang et al., 2015). These processes together form the global Hg cycle and are key for understanding the transport of Hg on global, regional and local scales (Holmes et al., 2009).

The accumulation of Hg to terrestrial surfaces usually takes place through either wet or dry deposition. Dry deposition is controlled by atmospheric processes, earth surfaces and Hg speciation and determines whether it is deposited on vegetation, soil, water or snow. Dry deposition occurs slowly and continuously and at all times on all surfaces. However, the rate is dependent on Hg species. Wet deposition occurs at a faster rate but episodically (Risch et al., 2012). Hg introduced into ecosystems through deposition is either stored in the substrate or reemitted. A small percentage may be transported to aquatic systems where it can undergo methylation and bioaccumulates through food chains (Risch et al., 2012;Laurier and Mason, 2007;Gabriel and Williamson, 2004).

Natural sinks of atmospheric Hg are soils, plant foliage and regions where the atmospheric chemistry initiates the formation of GOM such as polar regions and the marine boundary layer (Gustin et al., 2008). Large leaf surface areas and rough surfaces commonly found in forest ecosystems facilitate a larger uptake of Hg than is seen in other ecosystems. Dry deposition in forests can occur 2-5 times faster than seen on non-vegetated surfaces or other vegetated ecosystems (Risch et al., 2012). These sinks are often found to be areas where the re-emission of Hg back into the atmosphere occurs. Re-emission involves gaseous emission of previously deposited Hg from a surface (Zhang et al., 2012). The subsequent re-emission of Hg deposited to these surfaces has been shown to be a major contributor to the global Hg cycle (Moore and Carpi, 2005;Lindberg et al., 1995). The re-emission of Hg from land surfaces is thought to contribute between 14% and 24% to the global Hg budget (Baya and Van Heyst, 2010). However, the continual re-emission of Hg from soils and lack of global inventories means that

there are considerable uncertainties associated with estimations of re-emission to the atmosphere (Wang et al., 2006).

Human's industrial advancement since mid-1700s has led to considerable alterations to the planet caused by both the chemical contamination of the environment and atmosphere, and through global anthropogenic climate change (Blackwell et al., 2014). Sedimentary and icecore records indicate that present atmospheric Hg deposition is two to five times higher compared to pre-industrial levels (Amos et al., 2013). Global anthropogenic emissions appear to have been stable from 1990 to 2010 as a result of decreasing emissions in North America and Europe being offset by rising emissions in Asia. These emissions are largely driven by increased coal combustion and heat generation for industrial activities and power generation (Sundseth et al., 2015). In order to mitigate against the potential risks to humans and the environment resulting from Hg pollution the Minamata convention was introduced in 2013. The treaty aims to introduce a number of comprehensive regulatory control strategies at a global scale, encompassing the entire life cycle of Hg. Once the convention has been ratified by 50 countries, becoming globally legally binding, it is hoped that global anthropogenic emissions will be significantly reduced, leading to reduced Hg pollution risk (Selin, 2014).

Predicting future atmospheric Hg trends has become an important focus among the current literature. The uncertainties of future climate conditions and the introduction of the Minamata convention has seen an increased focus on the development of predictive models in the hope of understanding how the global Hg budget may change in the future. While considerable research has been undertaken into global Hg pollution and climate change separately, there is still considerable uncertainty surrounding both and very little work has focused on understanding how chemical contamination may affect climate change or how climate change may affect environmental chemical contamination (Wang et al., 2010). The unique vaporisation properties of Hg means it susceptible to changes in climate induced by greenhouse gas pollutants. This relationship results in a potential close relationship between climate change trends and Hg geochemistry (Jacob and Winner, 2009;Bahlmann et al., 2006). Terrestrial surfaces are among the largest natural contributors of atmospheric Hg. Understanding the controls of emissions from these natural substrates is vital for balancing the global Hg biogeochemical cycle and determining local, regional and global environmental impacts (Gustin et al., 2002).

The generation of a sufficient regional or global air-surface Hg exchange model requires a detailed understanding of the physical, chemical and biochemical processes that occur within the soil, as well as an understanding of the role of meteorology and soil properties on Hg emissions and deposition (Scholtz et al., 2003). The introduction of the international Minamata

convention and its impending future global enforcement, has seen and will continue to see a global reduction in Hg emissions from anthropogenic sources. A dramatic shift in the Hg global budget will make understanding how natural source emissions may change in the future all the more important. Terrestrial surfaces are extremely important natural stores of Hg within the global Hg budget. Long storage terms and global transport of Hg suggest this is unlikely to change in the short-term. Many previous studies have found that Hg emissions exhibits a strong positive relationship with solar radiation and temperature (Choi and Holsen, 2009;Gustin et al., 2002;Moore and Carpi, 2005;Park et al., 2014). These relationships are commonly attributed to the interaction between the physiochemical properties between elemental mercury (Hg⁰) and abiotic processes occurring within the substrate. Hg emissions have been shown to be particularly sensitive to temperature rises, commonly expressed as the activation energy (E_a), through the application of the Arrhenius equation (Bahlmann et al., 2006).

1.1 Research Scope

The strong correlation between soil Hg emissions and meteorological parameters will likely mean that as these controlling parameters change in the future with projected climate change so will Hg air-surface exchange. Potential links between climate change and natural Hg emissions have not been adequately explored within current literature. In order to understand how future climate predictions may influence future Hg emissions it is important to first understand how current climate parameters influence Hg exchange from different surfaces. Increasing industrial activity has led to an increase in the amount Hg cycling through the atmosphere and terrestrial systems. This, in conjunction with growing climate concerns, suggests that more research is needed to identify links between climate change and air-surface Hg exchange. This research will investigate if there is a significant relationship between climate controls and Hg air-surface exchange and determine the potential implications of these findings with future climate change. The aims of this research are as follows:

- To compare relationships between background and enriched mercury substrate sites and environmental controls, and identify any common trends between the six sites investigated.
- To further understand how meteorological parameters influence the rate of mercury emissions from a substrate through the application of the Arrhenius equation
- To determine if climate change predictions can be used to indicate future mercury flux patterns.

The following chapters will attempt to address the aims identified here in order to demonstrate the importance of understanding mercury air-surface exchange in the context of environmental change. Chapter 2 will highlight the current state of knowledge regarding the influence of meteorological parameters on Hg air-surface exchange and the knowledge gaps that still exist. It will also describe current predictions of climate change and consequent changes to mercury biogeochemical cycling is predicted to be altered. Chapter 3 will describe the field and data methods employed to gather the air-surface exchange information used to address the aims of this research. Chapter 4 will describe and interpret the exchange patterns at the chosen field sites and the role of environmental parameters. This chapter will also identify how these controls differ between site classifications and why this occurs. Chapter 5 will investigate the role of soil kinetics in air-surface exchange through the application of the Arrhenius equation. In an attempt to further understand how temperature and solar radiation influences the emission of Hg from a substrate. Chapter 6 will combine the findings from chapters 4 and 5 to establish possible prediction of how these controlling parameters may change air-surface exchange patters as they adapt under future climate change scenarios. Chapter 7 will interpret these findings with in a context if predicted alterations to the global mercury cycle and the implications of this with future climate change. Chapter 8 provides a summary of the key findings of this research and the concluding implications.

Chapter 2: Literature review

2.1 Atmosphere terrestrial surface exchange

Exchange of mercury between terrestrial surfaces is an important component of the global atmospheric cycle. Natural sources of Hg are thought to contribute between 800-3000Mg y⁻¹ to the global cycle (Gustin et al., 2008;Nriagu, 1989;Mason and Sheu, 2002;Lindqvist et al., 1991;Seigneur et al., 2001). These sources comprise a combination of geogenic sources and wet and dry atmospheric deposition. Emission of Hg from substrates predominantly occur in the form of elemental mercury (Hg⁰). Once Hg⁰ has been emitted into the atmosphere it can undergo oxidisation where it is transformed most commonly to divalent mercury (Hg⁺²) and quickly deposited on to the surface. Hg⁺² can form organic complexes of Hg such as monomethylmercury and dimethyl-mercury which are the most environmentally toxic Hg species (Ullrich et al., 2001) or it can be re-emitted to the atmosphere after it has been reduced back to Hg⁰ in the substrate. The only long-term sink for removal of Hg from the biosphere is thought to be deep-sea sediments (Holmes et al., 2009).

Naturally enriched soils occur due to mineralization initiated by ancient geological processes. Soils are classified as enriched if concentrations are greater than 100 ppb (Gustin et al., 2008). These geological driven sources mean that enriched areas occur in global belts close to tectonic boundaries. Soils with lower levels of Hg contamination are dominantly the result of emitted Hg deposited on the surface through either wet or dry deposition. These soils are referred to as background soils and contain less than 100 ppb of Hg (Gustin et al., 2008). Hg in the soil column is bound to carbon and organic matter. Highest concentration are found in the surface layer, decreasing with depth (Hararuk et al., 2013). The emission of Hg from these soils has been shown to be influenced by a number of chemical and physical processes such as Hg concentrations in the soil, organic matter content, soil temperature and soil moisture content (Bash et al., 2004;Moore and Carpi, 2005;Wang et al., 2006;Liang et al., 2014). Hg emissions from soils are also positively correlated with soil temperature, air temperature, solar radiation and soil moisture content and negatively correlated with relative humidity (Moore and Carpi, 2005).

In terrestrial ecosystems, bare soils exhibit bidirectional Hg fluxes between the surface and the atmosphere (Converse et al., 2010). The flux is defined as the net exchange between Hg entering and exciting a surface. When net flux is positive the surface is emitting Hg, if flux is negative Hg is being deposited on the surface (Carpi and Lindberg, 1998). These fluxes are believed to be controlled by the soil properties, biological processes, meteorological conditions and

atmospheric chemistry and physics (Baya and Van Heyst, 2010). Unlike measurement of Hg release from point sources, characterization of emissions from nonpoint sources is difficult because of spatial and temporal variability. Natural terrestrial non-point sources of atmospheric Hg include geologically enriched substrates and active geothermal areas, biomass burning, soils/substrate, lakes, and wetlands (Eckley et al., 2010). There have been a number of studies which have attempted to measure, in situ, the rate at which Hg vapour is emitted from or deposited on soil with different environmental parameters, such as air/soil temperature, solar radiation, and precipitation (Gillis and Miller, 2000;Gabriel et al., 2006;Baya and Van Heyst, 2010;Bahlmann et al., 2006;Gustin et al., 1997;Scholtz et al., 2003;Zhu et al., 2013)

2.1.1 Temperature and Solar radiation

The role of temperature as a Hg flux-controlling parameter has long been identified. Ambient air temperature, soil surface temperature and solar radiation are all positively correlated with Hg⁰ emissions resulting in diurnal and seasonal flux patterns (Choi and Holsen, 2009). Hg fluxes have been shown to sharply increase from early morning until noon where it reaches peak emissions. Emissions then start to decrease at a slowed rate from noon to early evening. These patterns of flux follow closely the diurnal soil and air temperature trends (Gabriel et al., 2006). Seasonal cycling indicates that maximum Hg flux occurs during the summer months occurring around noon when temperature and solar radiation are at their highest (Wang et al., 2006). Minimum Hg flux occurs during the winter months and during night when temperature and solar radiation are at their lowest (Corbett-Hains et al., 2012). However, other factors are known to influence long term seasonal trends, increased canopy cover and decreased soil moisture can cause lower Hg emissions during summer (Hartman et al., 2009;Kuiken et al., 2008). Uncertainties still surround the relative role of temperature and solar radiation in controlling Hg flux (Bahlmann et al., 2006). These observed diel and seasonal trends suggest that long-term climate trends may have a significant influence on flux trends despite the existing uncertainties with the roles of temperature and solar radiation.

Ambient air temperature and surface temperature play a significant role in the flux of Hg from soils, with increases in Hg flux positively correlated with increasing soil temperatures. Choi and Holsen (2009) in a laboratory experiment indicated that Hg flux from soils originating from deciduous forest ecosystems rose from 10ng m⁻² at 25°C to 120ng m⁻² when temperatures were increased to 35°C. Wang et al (2006) used the Arrhenius equation to determine the temperature at which Hg began to be released from soils. Their results recorded an activation energy (E_a) of 31.1kcal mol⁻¹. This was observed to be significantly higher than Hg vaporisation heat of 14kcal mol⁻¹, indicating that Hg emissions from soils are not solely caused by the vaporisation of Hg.

Activation energies are used to determine processes controlling Hg evasion from soils. Background soils have been found to have an activation energy twice that of enriched soils (Wang et al., 2006). Temperature disparity between Northern and Southern Hemisphere Hg flux showed that emissions from naturally enriched soils in Australia were 30% higher than those observed in the Northern Hemisphere under similar climate and soil conditions. The Australian study's temperatures were 1.2 °C warmer than those recorded in the Northern Hemisphere studies (Edwards and Howard, 2013).

The Arrhenius equation is often applied to Hg fluxes to determine the relationship between Hg emissions and temperature. The equation determines the minimum energy required for a thermal reaction to occur, termed the activation energy (E_a) . By comparing the E_a with the point of volatilisation for Hg, which is 14.5 kcal mol⁻¹, it is possible to identify those factors believed to be influencing Hg emissions (Wang et al., 2006). In a comparison of activation energies under light and dark conditions the Ea varied depending on Hg speciation. The Ea calculated for pure and natural cinnabar (HgS) substrates with varying light intensities was significantly higher than the volatilisation energy, indicating the consumption of excess energy during release of Hg⁰ and that photo-reduction was occurring simultaneously (Gustin et al., 2002). Opinion varies on whether soil temperature or solar radiation is the dominant control of Hg airexchange even with the application of the Arrhenius equation. Carpi and Lindberg (1997) found that despite strong E_a correlation with soil temperatures, across seasonal cycles the data correlated more strongly with solar radiation. The sensitivity to temperature of the mechanisms responsible for Hg emissions result in diel trends, with the effects of temperature reducing with depth. This results in higher apparent activation energies if the volitation of Hg occurs at shallower depth than the point of temperature measurement (Carpi and Lindberg, 1997).

The influence of solar radiation on Hg flux is still not fully understood although two dominant hypothesises have emerged throughout the literature. The first hypothesis is that high levels of solar radiation may cause a reduction in the activation energy required to induce the emission of Hg from soils (Lin et al., 2010). The second hypothesis suggests that solar radiation may be a catalyst for the transformation of divalent Hg in the soil to Hg⁰, which can then be emitted to the atmosphere (Carpi and Lindberg, 1997;Gustin et al., 2002;Moore and Carpi, 2005). Moore and Carpi (2005) provide evidence in support of the second hypothesis. In their experiment, initial samples showed low levels of Hg⁰ present in the soil. Once the samples were exposed to ultraviolet (UV) light at a wavelength of 315 nm the emission of Hg increased significantly. This indicated that the light affected the reduction of Hg⁺² to Hg⁰, which then allowed temperature to control the volatilisation of the Hg in the soil. Wang et al (2006) showed that

Hg flux closely followed solar radiation trends. From this they concluded that Hg emissions increased due to the transfer of photo energy to the Hg atoms and increased soil temperature through the conversion of solar energy to thermal energy, indirectly increasing Hg flux.

Types of incoming radiation have been shown to effect Hg flux differently with varying wavelengths. In laboratory experiments exposing soil samples to different types of UV radiation, UV-A was shown to have little effect on the emission of Hg from the soils. Exposure to UV-B radiation increased Hg emissions dramatically by approximately 20 ng m⁻² h⁻¹. This increase was believed to be caused by increased reduction of Hg⁺² to Hg⁰ initiated by the exposure to UV-B. Exposure to UV-C resulted in the deposition of Hg on the soil rather than the emission (Choi and Holsen, 2009). Edwards and Howard (2013) found that diurnal flux from background and enriched soils correlated higher with total incoming solar radiation than with UV-B radiation. Both soils showed secondary peaks in flux that corresponded with peaks that only occurred in the total solar radiation. UV-B does not exhibit this secondary peak as the angle of the sun increases the absorption of UV-B in the ozone layer.

In laboratory experiments isolating the effects of temperature and solar radiation, samples exposed to 320 Wm⁻² flux increased by a factor of between 3 and 7. Soil surface temperature, measured at a depth of 0.5 cm, increased by 4°C over the course of the experiment. It was concluded that the observed changes in soil temperature only accounted for a small percentage of the changes in Hg flux. The researchers also found that Hg flux increased independently of soil surface temperatures between -10°C and 20°C, providing evidence to support that lightinduced release of Hg from soils is not related to soil temperature (Bahlmann et al., 2006). Moore and Carpi (2005) found that when samples were exposed to full spectrum radiation Hg⁰ fluxes increased on average 221% above those recorded for dark flux samples. This increase in flux appeared to occur independently of temperature increase caused by the presence of solar radiation. These findings are somewhat contradicted by Edwards and Howard (2013) field experiments, which found that UV-B weakly influence background fluxes but had a stronger influence over enriched soils. Additionally, they found the strongest correlation between total solar radiation and GEM fluxes in enriched soils, suggesting that GEM fluxes are more temperature driven. It is possible that the relationship between radiation and temperature at higher temperatures could result in a kinetic enhancement of Hg⁺² photo-reduction in soils, which produces more Hg^0 vapour and enhances flux (Lin et al., 2010).

2.1.2 Precipitation

Precipitation and soil moisture play a significant role in the emissions of Hg from soils. The positive correlation between soil moisture and Hg emissions is dominantly hypothesised to be

caused by the displacement of air within the soil pours containing Hg^0 by the infiltrating rain water, enhancing the mobility of Hg^{+2} due to an increase in the soil pore water content and enabling redox reactions associated with the incoming water and soil exchange effects (Song and Van Heyst, 2005). This hypothesis was supported by Lin et al (2010) who found that Hg emissions increased from 6 to 390 ng m⁻² h⁻¹ after the initial wetting of background soils. However, a second wetting did not produce the same response with Hg emissions only recording an increase to 42ng m⁻² h⁻¹. Wetting of dry soils has been shown to induce a greater flux than additional moisture added to already wet soils. The wetting of dry soils resulted in a 2-17 fold increase depending on precipitation type, amount, intensity and timing (Eckley et al., 2011). Gillis and Miller (2000) also provided evidence to support this hypothesis, showing through the use of flux chamber measurements that increasing soil pore water content resulted in an increase in Hg emissions due to the displacement of interstitial air by the infiltrating water.

The addition of water results in an immediate release of Hg from soils. The magnitude of flux is correlated with Hg concentrations found in the soil substrates. Repeated water additions have been shown to decrease the amount of Hg released from soils, indicating that the effects of precipitation events are dependent on the amount of Hg in the soils available for emission (Song and Van Heyst, 2005). Controlled studies have also shown that the duration of exacerbated flux after watering is a function of the amount of water added and the rate at which soil dries (Gustin et al., 2006). Eckley et al (2011), in simulated rain experiments on mine waste, showed that when these soils were rewetted to 20% soil water content shortly after they had dried a smaller increase in Hg emissions was observed compared to initial wetting emissions. This suggests that for the initial wetting a component of the Hg released is part of a changing fraction of the substrate Hg pool that is depleted and not quickly replenished. These fluxes are thought to be caused by the water movement in the soil, facilitating transport of Hg within the soil column from the deep layer to the soil surface, where it is made available for subsequent release. Capillary action causes water and pollutants to move towards the soil surface as the soil dries and water evaporates. Surface processes then facilitate and enhance their release to the air (Liang et al., 2014).

Studies have shown that Hg emissions from soils are highly dependent on soil moisture content. At a soil moisture content of 13%, mean diel Hg flux are higher than those observed for dry soils over a 24 hour emission period. Night-time fluxes at 13% soil moisture in the same experiment were greater than those measured from dry soil over the same period. When the soil moisture was increased to 23%, flux became similar to those from dry soil with no diel pattern. Once soil moisture was increased above 30% Hg flux was suppressed (Gustin et al., 2006).

Briggs and Gustin (2013) recorded an increase 1 to 2 times higher following the wetting of dry soils. These increases were attributed to: the displacement of Hg^0 present in the soil gas, aqueous facilitation of reduction of Hg^{+2} compounds, the movement of Hg compounds toward the surface associated with soil moisture evaporation, desorption of loosely bound Hg^0 as the more polar water molecules outcompetes it for binding sites

The combined effects of air temperature and soil moisture enhances water evaporation at higher temperature, subsequently promoting additional Hg evasion from soil surfaces (Lin et al., 2010). Liang et al (2014) over the course of two wetting periods found that the first wetting period had higher Hg emissions because it took place during summer when air temperature and solar radiation were higher. Gustin et al (2006) suggests that the Hg emissions recorded from the soil samples with 13% soil moisture would have been higher if light intensity was higher than the 150 W m⁻² the samples were exposed to under laboratory conditions.

Increases to average temperatures and precipitation are likely to cause alterations to transpiration rates within forest ecosystems (Hayhoe et al., 2008;Plummer et al., 2006;Pourmokhtarian et al., 2012). Changes to water characteristics within the forests could cause changes to total Hg deposition, deposition pathways, transport fate and bioaccumulation (Blackwell et al., 2014). As soil Hg is dominantly bound to organic matter (Ravichandran, 2004), temperature increases will result in an increase in soil respiration and a subsequent increase in Hg emissions (Raich and Schlesinger, 1992). As terrestrial ecosystems are the greatest source of Hg, increased volatilisation as a result of climate change will lead to increased cycling between surfaces and the atmosphere.

2.2 Future predictions

2.2.1 Climate change

Changes to Earth's climate system as a result of human activities have already become evident over recent decades. Human influences over the climate system are no longer contested in the literature. Since 1880, combined global air surface and ocean temperatures have risen 0.85° C. The atmosphere has warmed at a rate of 0.05° C per decade since 1998 and the ocean warming at a rate of 0.11° C per decade since 1970. Since 1770, Earth's total radiative forcing has shifted to positive forcing resulting in an uptake of energy in the climate system. The large quantities of CO₂ released into the atmosphere now means that a significant proportion of climate change is irreversible unless there is a continued reduction in anthropogenic CO₂ emissions (IPCC, 2013b).

Global mean surface air temperatures by 2035 are very likely to exceed 1.5°C above 1850-1900 averages. Surface air temperatures between 2081-2100 are likely to increase by 0.3°-0.7°C under RCP2.6 scenario, 1.1°C-2.6°C (RCP4.5), 1.4°-3.1°C (RCP6.0), 2.6°-4.8°C (RCP8.5) relative to 1986-2005 temperatures. The rate of warming over land surfaces is expected to exceed that of the ocean by a factor of 1.4-1.7, with the Artic predicted to exceed this still further. The North Atlantic and Southern Oceans are projected to experience the smallest temperature changes across the planet under all scenarios. Warming is predicted to be highest in the northern high latitudes and the upper troposphere, while the stratosphere will experience cooling. Across all continents these temperature increases are likely to cause more hot extremes and a reduction in cold temperature extremes on both daily and seasonal time scales. This will also result in an increase to the frequency, duration and magnitudes of heat waves. Increases in hot extremes are also likely to extend fire seasons and fire intensity due to increased fuel load (IPCC, 2013).

Changes to radiative forcing by 2030 are relatively small with the biggest disparity felt by 2100 and dominantly controlled by CO₂ emissions. Since 2007, methane emissions have increased by 2% leading to an extra 0.48 W m⁻² of energy within the climate system. N₂O emissions have risen by 6% over this time, promoting it to the third largest contributor to radiative forcing and contributing an extra 0.17 W m⁻². CFC's were once the third largest contributor to radiative forcing. However the Montreal protocol and subsequent phasing out of these pollutants have led to a significant decline in their presence in the atmosphere (IPCC, 2013).

Changes to precipitation in the future are highly likely to exhibit significant spatial variations. Globally, precipitation is expected to increase by 1 to 3% per degree in temperature rise and could see a further rise to 4% per °C by the end of the 21st century. The contrast between current wet and dry regions across the planet is expected to increase further throughout the 21st century. High latitude regions are likely to experience greater quantities of rainfall due to increased humidity and increase water transportation from the tropics. Mid-latitudes and subtropical arid regions are likely to experience a decrease in precipitation while mid-latitude wet regions are likely to experience and could be the tropics.

While meteorological variables have been found to greatly influence Hg air-surface exchange, to date the impact of climate change on Hg cycling processes has received little consideration in the literature (Jacob and Winner, 2009). Changes to temperature are expected to increase transpiration rates and water stress and alter physiological processes within forest ecosystems (Pourmokhtarian et al., 2012). Changes in watershed processes are likely to alter not only total Hg deposition but also the pathways of Hg deposition in forests and subsequent transport, fate

and bioaccumulation (Blackwell et al., 2014). Changes to temperatures may change partitioning between the different media, enhancing re-volatilization from historically deposited compounds, leading to greater atmospheric transport (Hansen et al., 2015).

2.2.2 Mercury emissions

As has been shown here, meteorological parameters are known to influence global Hg cycling. However, very little research exists into the influence future climate change may play in this global cycling (Jacob and Winner, 2009). Future global Hg emissions also need to be taken into account in order to understand the quantities of Hg within the global biogeochemical cycle. Current anthropogenic emissions are thought to contribute 2000t of Hg to the atmosphere per year (Krabbenhoft and Sunderland, 2013). Streets et al. (2009) used IPCC emission scenarios to predict future emissions out to 2050. Under these scenarios emissions are predicted to rise to between 2630 Mg and 4856 Mg. However, Rafaj et al. (2013) found that current air pollution controls could result in a reduction of up to 25% of Hg emission by 2050. Technological advancements in Europe and the US have led to a stabilisation of Hg emissions which will decline towards the mid-century. Despite rapid economic and coal combustion growth in China and India Rafaj et al (2013) concluded that global greenhouse gas emission reductions and mitigation in both China and India would result in a 70% and 80% reduction in Hg emission by 2050 respectively. Hg emission scenarios vary greatly across the literature from a reduction to 800 t per year under best case or an increase to 3400 t per year under worse case scenarios (Krabbenhoft and Sunderland, 2013).

The models that have been developed to predict future changes to Hg biogeochemical cycles were mainly developed to understand atmospheric transport and deposition characteristics on a global scale (Holmes et al., 2010). Large uncertainties still exist within these models, such as understanding the atmospheric chemistry of Hg, natural sources and the relationship between kinetic processes and Hg soil emissions. Understanding into the role of natural sources is limited, particularly in regards to re-emissions (Dastoor and Larocque, 2004). Naturally enriched soils are given the most attention throughout the literature in relation to natural sources, while background sites still are not well understood in terms of their contribution to the global cycle (Xin and Gustin, 2007). The development of global Hg air-surface exchange models requires sufficient understanding of the physical, chemical and biochemical processes that occur within a substrate. Extensive field and laboratory studies have been undertaken to understand the kinetic processes that control the transformation of Hg⁺² to Hg⁰ and the subsequent flux. However, the process is still not well understood (Scholtz et al., 2003).

The effects of climate change will vary regionally. As a result, so will the impacts on Hg cycling, depending on predicted changes to rainfall and temperature. However, predictive climate models still have a degree of uncertainty particularly with respect to precipitation. As such, predicting regional changes to Hg cycling is difficult (IPCC, 2013). Megaritis et al. (2014) developed a model based on future climate changes to predict future regional Hg deposition. They found that overall deposition increased due to increasing temperatures effecting the oxidation conversion of Hg⁰ to Hg⁺². Linear regression analysis showed predicted concentration change of Hg⁺² is well correlated with changes in temperature and precipitation across the United States Hg⁺² increased throughout summer predominantly in the southeast, with highest increases predicted for Florida. Predictions across winter were highly variable, further indicating the influence of meteorological variables on Hg deposition. Highest wintertime deposition was predicted to occur throughout the southern parts of the United States.

The parameters often employed by those models that consider natural emissions from soils often vary between models. Soil temperature is often used as a controlling parameter as this is thought to also adequately incorporate the role of solar radiation in the production and emission of Hg^0 from the substrate (Wright and Zhang, 2015), while other models use substrate concentrations (Amos et al., 2013;Holmes et al., 2010). Selin et al. (2008) used a combination of solar radiation and surface air temperature as part of a regression model to determine the rate of volitation from soil surfaces. These models appeared to over simplify the role of air-surface exchange in the global Hg cycle, creating a bias in the estimations for emission and deposition from natural sources (Xu et al., 1999). Understanding the role of natural source emissions is important for the development of accurate predictions of Hg behaviour within the atmosphere (Gbor et al., 2006).

Projected changes to these climate controls would suggest a future further increase to the global Hg budget. Further increases to air surface temperatures and alterations to Earth's radiation budget could see an increase in the amount of Hg exiting the soil (Streets et al., 2009). Determining how rainfall will influence future Hg emissions is harder to determine as there are still large uncertainties surrounding future rainfall prediction and the role rainfall plays in Hg flux, although it is evident that increased soil moisture can cause increases to Hg emissions (Briggs and Gustin, 2013). Increased volatilization of Hg from ocean and land reservoirs as a result of climate change would transfer Hg between ecosystems via atmospheric transport, redepositing it in a more mobile and presumably more toxic form. Increased volatilization of soil Hg could potentially be of considerable importance, as the amount of Hg stocked in soil (1.2106 Mg) dwarfs that in the atmosphere (6103 Mg) and in the ocean (4104 Mg) (Selin et al., 2008).

2.3 Summary

Investigations into the impacts of climate change on global Hg cycling are starting to emerge. However, published research primarily focuses on Hg deposition's response to changing climate with little consideration for the emissions of Hg from surfaces. Current research into the role of temperature and solar radiation in air-surface Hg exchange suggests that solar radiation may be the dominant control, although there are still considerable uncertainties as to the causation. Changes to earth's radiation budget caused by anthropogenic greenhouse gas emission are likely to result in temperature changes, precipitation changes and circulation changes that will greatly influence Hg biogeochemical cycling. While the current understanding of the influence of meteorological parameters on Hg flux allows us to hypothesise how it may change in the future, the large uncertainties and lack of research make it impossible to establish accurate predictions. More research is required into understanding these parameters, particularly solar radiation versus temperature and precipitation to allow us to develop an accurate understanding of how this may change in the future.

Current research has moved away from the individual effects of temperature to both the combined and individual influence of solar radiation (Choi and Holsen, 2009;Briggs and Gustin, 2013;Bahlmann et al., 2006). As temperature is highly dependent on solar radiation it is thought that the correlation between temperature and Hg flux may just be the reflection of the relationship between solar radiation and Hg flux (Wang et al., 2005). Two main hypotheses have emerged in order to explain the role of solar radiation. The first hypothesis is that high levels of solar radiation may cause a reduction in the activation energy required to induce the emission of Hg from soils (Lin et al., 2010). The second hypothesis suggests that solar radiation may be a catalyst for the transformation of Hg⁺² in the soil to Hg⁰, which can then be emitted to the atmosphere (Carpi and Lindberg, 1997;Gustin et al., 2002;Moore and Carpi, 2005). However, while there is evidence to support both hypotheses, large uncertainties remain.

Chapter 3: Methods

Field data collected from a number of naturally enriched and background sites across North America and Australia form the basis for this study. Air-surface exchange measurements were conducted at these sites along with simultaneous environmental correlates measurements. This extensive data set provides sufficient information for the analysis of Hg evasion in the context of climate change. This chapter describes the characteristics of the sites used for this research and the methods used to gather the air-surface exchange and environmental measurements.

3.1 Site descriptions

Site choice for this study was based on the suitability of the physical site characteristics to conform to micrometeorological aerodynamic flux gradient method requirements. In order for sites to provide accurate flux measurements they require continuous uniform, flat surfaces to ensure that the horizontal concentration gradients are negligibly small. A total of six sites were chosen to represent different types of natural Hg bearing substrates in contrasting geological settings. These sites were mainly located within Canada, with one site located in Nevada, United States and another in South Eastern Australia. The sites analysed here consisted of three enriched sites and three background sites. Sites were deemed a background site if average substrate concentration was less than 100 ppb. Pinchi Lake (British Columbia), Thunder Bay Ontario (referred to as Klages) and steamboat springs (Reno, Nevada) were all characterised as enriched sites, while Macmillan Pass (Yukon), Rouyn-Noranda (Quebec) and Nimmo (New South Wales, Australia) were background sites. The inclusion of both enriched and background sites fluxes, as well as a more detailed understanding of how background sites are influenced by these variables (the least studied of the two).

3.1.1 Rouyn

Rouyn-Noranda presented as a background site. This site consisted of unconsolidated glacial sediment located within a sand and gravel pit with sparse vegetation cover. Fetch was slightly constrained by a small sandy ridge to the west. However, it was still sufficient to allow the application of the micrometeorological methodology, with a footprint of approximately 100 m by 300 m. Measurements took place during summer from July 24th to August 3rd, 2000. The region experiences cool summers with high humidity and regular rainfall.

3.1.2 Klages

The Thunder Bay, Ontario site (henceforth referred to as Klages) was located in a quarry on Klages Road. The site was chosen as it had elevated Hg levels with little variability in substrate

concentrations across the entire site. Sampling took place during the Canadian summer in 1997, from 25th July to 9th August. The site presented with sufficient uniform flat fetch suitable for the application of the micrometeorological methodology. The geology of the quarry was fissile black shale located within a Proterozoic rove formation. The black shale forms an unweathered parent material that is coated by a 5 to 10 cm weathered surface layer. Klages experienced cool summers and moderate rainfall during this period.

3.1.3 Reno

Steamboat springs, Reno, Nevada was located in a geothermal, semi-arid desert environment. Site was sparsely vegetated with desert vegetation. Sampling took place over three days from 31st August to 3rd September, 1997 as part of the Nevada STORMS project. The Reno site is a naturally Hg enriched location caused by geothermal activity. The site is composed of Mesozoic metavolcanic and metasedimentary rocks, with unconsolidated alluvial deposits and tertiary andesite and basalt was found at the site. The site was found to have highly heterogeneous Hg substrate concentrations that ranged from 0.1 to 15 ppm. Steamboat springs is located on eastern side of the Sierra mountain range and as a result receives little rainfall throughout the year. During summer Reno commonly experiences warm temperatures and low relative humidity.

3.1.4 Pinchi

The Pinchi Lake site was located on a large cinnabar deposit (mercuric sulphide, HgS). The very high naturally enriched site was once a former mercury mine. However, measurements took place on an undisturbed hill top with a weathered substrate overlooking the former mine. The experiment took place over a three week period from July 5th to 18th, 1998. The hill top plateau provided a sufficient fetch for the micrometeorological method intakes. Pinchi Lake is located within the semi boreal climate zone, experiencing moderately warm summers and severe winters. During the summer rainfall occurs semi-regularly, occurring on average 13 days out of the month.

3.1.5 Yukon

Macmillan pass is located in the central east of Yukon, near Canada's continental divide and is one of two alpine sites presented here. The site was characterised by the presence of weathered and eroded Devonian carbonaceous black shale. Macmillan pass is located within a regional scale mercury anomaly covering an area of about 25,000 km² in southeast Yukon Territory. However, low substrate concentrations at the field site led to its classification as a background site. Flux measurements were taken over a three week period from 5th July to 31st, 2001. Summers in the region are moderate with average temperatures in the low 20°C, moderate rain fall and low humidity.

3.1.6 Nimmo

Nimmo Plains is located within Snowy Mountain region in South Eastern Australia. The site was characterised by its flat vegetated surface which dominantly consisted of grass species. The site was used predominantly for cattle grazing and as a result vegetation had been mostly compacted to a height of 2cm. Soil was characterised as a sandy clay, with Hg substrate concentrations dominantly homogeneous across the entire site. The Flux study took place during the Austral summer from 26th January to 18th February, 2013. Nimmo Plains is located within Australia's alpine climate zone. During summer the region often experiences mild summer temperatures and rainfall is often low, occurring primarily in the form of thunderstorms.

3.2 Micrometeorological method

Micrometeorological aerodynamic flux gradient methods were applied across all six sites used for this study, following the procedure detailed in Edwards et al. (2005). The flux gradient method is based on the Monin-Obukhov similarity theory, where the turbulent bi-directional flux of an emitting surface scalar is proportional to the vertical concentration gradient and eddy diffusivity of sensible heat (Zhu et al., 2015). The eddy diffusivity is a function of friction velocity and the Monio-Obukhov similarity theory, which is a dimensionless stability parameter used to characterise atmospheric stratification (Fritsche et al., 2008). As this theory is based on idealised atmospheric conditions correction are made to the flux calculations to adjust for atmospheric stability (Edwards et al., 2005). The relationship between the flux (F) and the concentration difference is expressed as:

$$F = -K\frac{\partial c}{\partial z} \tag{3.1}$$

Where K is the eddy diffusivity (m^2s^{-1}), and $\partial c/\partial z$ is the vertical concentration gradient of the gas (kg m⁻⁴). The vertical concentration gradient is determined by alternating the measurement of a gas concentrations at two heights above the intended surface, in this case total gaseous mercury (TGM). The magnitude of the TGM concentration gradient depends on both the strength of the source or sink and atmospheric turbulence. The micrometeorological approach

spatially averages the flux over an area termed the "footprint". The footprint depends on turbulence which is characterized by wind speed, atmospheric stability, and surface roughness (Businger, 1986).

Equation 3.1 is based on assumptions made under neutral atmospheric conditions, when atmospheric motion is reduced. However, as atmospheric conditions are not often neutral, tending towards stable or unstable, a stability correction must be applied to the equation:

$$F = -K\frac{\Delta C}{\Delta z} = \frac{u_* k(C_2 - C_1)}{\ln(z_2 - d/z_1 - d) - \Psi_{h2} + \Psi_{h1}}$$
(3.2)

Where u* is the friction velocity, k is Von Karmans constant (0.4), z_1 and z_2 are the lower and upper sample intake heights, respectively, C₁ and C₂ are the concentrations at z_1 and z_2 , Ψ_1 and Ψ_2 are the integrated similarity function for heat at z_1 and z_2 . The integrated similarity functions for heat are required in order to correct for the heat density effects on fluxes caused by the sensible heat transfer from the surface. This function is stability dependent and therefore varies depending on atmospheric conditions:

$$\Psi_H = -4.7 \frac{z-d}{L}$$
 for stable conditions (3.3)

$$\Psi_H = 0$$
 for neutral conditions (3.4)

$$\Psi_H = 2 \ln \left(\frac{1+x^2}{2}\right)$$
 for unstable conditions (3.5)

Where

$$x = \left[1 - 15\frac{z-d}{L}\right]^{0.25} \tag{3.6}$$

L(m) is the Monin-Obukhov length given by:

$$L = \frac{-u_*^3 T_\rho C_p}{kgH} \tag{3.7}$$

Where:

g= acceleration due to gravity (9.81 m s⁻²)

H= sensible heat flux (W m⁻²)

 ρ = air density (kg m⁻³)

T= temperature (K)

 C_p = specific heat at constant temperature (J kg⁻¹ K⁻¹).

The apparatus set up consists of two Teflon intakes positioned above a surface, Teflon tubing, particulate filter, pump and a Tekran 2537A Mercury Vapour Analyser (Figure 3.1). Sonic anemometer was used to derive u* as describe in equation 3.2 and for determining the stability corrections required for equations 3.3, 3.4, 3.5 and 3.7. As this method was developed to measure small footprints the two sampling intakes are placed as low to the ground as possible at sampling heights of 0.59 and 0.87 m. Alternation between the two heights is controlled by a Teflon solenoid. In order to prevent the creation of an artificial flux in the upper and lower inlets caused by the pumping of air through the inlets, they were split into four inlets at each height (see inset in figure 3.1). Two heights were used as opposed to multiple heights as it allows for a better resolution of the gradient due to the increased number of samples collected per integration period. Teflon tubing was chosen as it reduces the influence of sorption effects as the mercury passes through the system. As this method is based on idealised atmospheric conditions fluxes tend to be overestimated during periods of weakly developed turbulence or when sensible heat is too low. This tends to occur during stable nocturnal periods.



Figure 3. 1 Schematic of micrometeorological gradient sampling technique, adapted from Edwards et al., (2005)

The Tekran 2537A Mercury vapour Analyser was employed to determine the average concentration gradient at the two measurement heights. The Analyser consists of a dual cartridge systems (A and B) that switches every 5 minutes, providing a continuous analyse of TGM. Each cartridge consists of a gold trap which causes the Hg to amalgamate onto its surface through thermal desorption. A sample average was taken at each height every 10 minutes and

an average gradient was constructed every 90 minutes. Average gradient consisted of 5, 10 minute samples at one height and 4, 10 minute samples at the other height. Once the first 90 minute average gradient was constructed the flux gradient was updated every half hour after. The sampling period of the mean gradient was required to be long enough to reduce variability in the gradient, while short enough so the micrometeorological assumptions of stationarity and homogeneity of turbulent properties remained valid. Concentration resolution for this method across all sites was found to be 0.01 ng m⁻³, with an average K of 0.01 m² s⁻¹ and a typical ∂z of 0.30m. Application of this method at these presented sites were found to have a flux resolution of 1.5 ng m⁻³ h⁻¹.

Standard quality assurance methods were applied to the micrometeorological data. This included editing for low wind speeds (< 1.0 m/s for cup anemometers or 0.5 m/s for the sonic anemometer) and wind direction, to allow for sufficient fetch. Additionally, since the flux is determined from $1\frac{1}{2}$ hours of concentration data, data were also edited for stability transition periods when stationarity assumptions of the method might be violated. Highly stable and unstable conditions (stability parameter, z/L, less than -5 or greater than 5), were also removed since micrometeorological methods are most suitable for slightly stable to slightly unstable conditions.

Micrometeorological methods are able to provide non-intrusive, continuous data over a large surface area. The use of this method is often preferred over flux chamber when conditions permit as they provide data over large areas and do not interfere with natural environmental Hg exchange processes (Edwards et al., 2005;Lindberg et al., 1995). Flux chamber measurements consist of small chambers placed over bare surfaces. Flux is calculated based on Hg concentrations within the chamber and the flow rate through the chamber. This technique provided a more direct measurement of Hg flux. However, the chamber seals off surfaces from the influence of the atmosphere, essentially creating its own microclimate and limiting its ability to adequately understand the role of meteorology on Hg flux rates (Kim et al., 1995;Lindberg et al., 1995;Gustin et al., 1999). As a result, micrometeorological methods were chosen over the more widely used flux chamber method.

3.3 Environmental Variables

A number of environmental parameters were measured concurrently with the micrometeorological method to allow for the investigation into the controls on air-surface exchange rates of Hg from substrates. Sonic anemometers (5 cm TR-9OAH DA-600. Kaijo

Denki Co. Ltd.. Tokyo) were employed to simultaneously provide high frequency wind speed and direction and air temperature measurements. However, as the sonic anemometers do not function correctly during rainfall cup anemometers (Model F460. Climatronics Corporation) were also used to provide continuous wind speed measurements during these times. A minimum of four cups at various vertical heights were employed at each site to establish the vertical wind speed profiles. Sensible heat flux was determined by measuring the fluctuations in temperature and vertical velocity recorded from sonic anemometer. Sensible heat flux was also used to calculate Monin-Obukhov length required for stability corrections in the aerodynamic wind profile method.

Substrate temperature profiles was measured using T-type copper constantan thermocouples. Soil temperature was measured just below the surface and at depths of 5, 10 and 15 cm, in order to estimate the heat storage capacity of the substrate. A net radiometer (Radiation Energy Balance Systems, Seattle) was used to measure the net all-wave radiation at a height of 1 m above the surface. Data from all devices was collected using a Campbell Scientific data logger (Model 21X) at a frequency of O. 1 Hz and averaged every half-hour.

3.4 Substrate Analyses

Substrate samples at all measurement sites were collected for total mercury determination on a consistent size fraction (<63 µm). Substrate samples were collected within the footprint of the micrometeorology tower at a depth of 0-2cm below the surface. Samples of soil and unconsolidated surface material (<2 mm), were collected using plastic equipment to minimize sample contamination and were submitted to Chemex (ACS) Laboratories Ltd., Vancouver, Canada for drying, sieving and Hg determination using *aqua regia* digestion and cold vapour atomic absorption spectrometry. Other elements were determined using *aqua regia* digestion and ICP-MS determination. Accuracy and reproducibility were determined to be acceptable (within 10%) using blind replicates of CCMRP Till-1 Standard Reference Material inserted after every 10 samples to determine accuracy and reproducibility. Rock samples were pulverized and analyzed for Hg by Activation Laboratories, Ontario using cold vapour atomic absorption spectrometry. Whole rock analysis (SiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, and LOI) was conducted by Activation Laboratories using lithium metaborate/tetraborate fusion ICP.

3.5 Arrhenius

The Arrhenius equation was applied to each flux data set to determine the physical and physiological processes involved in the biogeochemical cycling of Hg. Through the measurement of Hg emissions from a substrate and either the ambient air temperature and or substrate temperature it is possible to calculate the energy required for the release of Hg from a substrate (Siegel and Siegel, 1998). The Arrhenius equation was applied to determine the processes involved in the volatilisation or release of Hg from a substrate. The application of the equation is used to determine the general dependence of Hg emissions on temperature, through the calculation of an activation energy:

$$\ln(Hg flux) = \ln A + \frac{-E_a}{RT}$$
(3.8)

Where A is a rate limiting constant that determines the number of times the atoms are close enough to collide, R is the gas constant (1.9872 cals K⁻¹ mol⁻¹), T is temperature (K) and E_a is the apparent activation energy (kcals mol⁻¹). The E_a is defined as the minimum energy required for a chemical reaction to take place. The volatilisation of Hg from liquid to gas phase has a theoretical E_a of 14.0 kcal mol⁻¹ at 20°C (Poissant and Casimir, 1998). As temperature increase so does the vapour pressure of a substance, causing the volatilisation to also increase. Sorption of a chemical within the soil matrix will result in an increase to the activation energy required for volatilisation to occur (Gustin et al., 1997). The comparison of different E_a to the volatilisation of Hg allows for the identification of other factors that may be influencing Hg flux emission rates.

The equation was applied to the data because Hg emissions from substrates have been found to be particularly sensitive to temperature rise, and therefore can be expressed in terms of activation energy. The Arrhenius equation was developed to determine the point when a reaction would begin. It was noted that while the concentrations of a reactant remained constant the active fraction of the reactant increased exponentially with temperature (Davidson and Janssens, 2006), a trend observed in Hg emission-temperature trends. E_a values have often been derived to estimate the partitioning of Hg evasion from substrates between physical vaporization (due to its volatility) and other soil processes with more biological/chemical nature, such as photochemical reduction (Kim et al., 2012).

Chapter 4: Determining environmental controls across multiple field sites

4.1 environmental controls across all sites

4.1.1 Overall site characteristics

Substrate Hg concentrations varied between sites as they were a combination of both background (Yukon, Rouyn, Nimmo) and enriched sites (Pinchi, Klages and Reno) (Table 4.1). Substrate concentrations were generally uniform at all sites, within the Micrometeorological method's footprints. Reno's substrate concentrations varied within the measurement footprint and was therefore split into three section, Reno all (7.15 ppm), Reno High (7.8 ppm) and Reno Low (3.1 ppm). Pinchi presented with the highest substrate concentration of 179.5 ppm as the site was located on a cinnabar enriched fault zone, while Rouyn was found to have the lowest Substrate concentrations (0.01 ppm). Ambient Hg concentrations were highest at the enriched sites, with Reno producing the highest ambient concentration (11.90 ng m⁻³). Ambient concentrations varied throughout the day with typical peak concentrations occurring around midnight and minimum concentrations occurring between early morning and midday. The unstable atmospheric conditions typically experienced during this time of year creates a higher boundary layer and greater turbulent mixing causing the emitted Hg to be quickly transported away. During nocturnal periods atmospheric conditions are stable with reduced turbulent mixing, allowing Hg to pool near the surface and resulting in higher ambient Hg concentrations (Baya and Van Heyst, 2010).

Highest average fluxes were found to coincide with highest substrate concentrations, while background sites all presented with the lowest average fluxes. Table 4.2 presents average fluxes at each site, along with average day and night fluxes. Average Meteorological parameters are also given. All sites exhibited bidirectional fluxes, with emissions generally occurring during the day and deposition occurring mostly at night. All sites, with the exception of Nimmo, were found to be a net source of atmospheric Hg, meaning that fluxes were generally in the form of emission. Emissions are considered dependent on surface properties, while deposition is largely considered to be controlled by atmospheric mixing (Xu et al., 1999). The background sites were the only sites to experience regular deposition, mainly occurring at night. Nimmo was the only site to present as a net sink for atmospheric Hg, as significant deposition occurred throughout both the day and night. As was expected based on previous flux studies, day fluxes were significantly higher than average night fluxes.

Site	Substrate characteristics	Hg substrate concentration	Ambient Hg Concentration
Site		(ppm)	(ing in)
Pinchi	Cinnabar enriched fault zone	179.5	7.4
	Fissile black shale in Proterozoic rove		
Klages	formation	0.845	5.9
	Silicious substrate in active geothermal		
Reno	region	7.15	11.9
Reno high		7.18	14.1
Reno low		3.1	9.8
Yukon	Devonian carbonaceous black shale	0.358	1.6
Rouyn	Sand and gravel pit	0.01	1.3
Nimmo	Sandy clay substrate	0.048	0.6

Table 4. 1 Substrate characteristics for all field sites. Average substrate concentration and average study ambient Hg concentrations are provided.

The sampling periods for all six sites took place during the summer months of their respective hemispheres. Air temperatures averaged between 13.75 and 20.09 °C. Both Nimmo and Yukon were located in alpine regions and experienced the lowest average temperatures. Day and night fluxes were determined from the net radiation. Positive net radiation was used to approximate day fluxes, while negative net radiation was used to approximate night fluxes. As all field studies occurred during the summer, the overall study conditions were dominated by clear sunny weather conditions with very few rain periods occurring. Yukon was the only site to experience any significant period of rainfall. The manner in which these climate variables interacted with the Hg fluxes will be discussed further in the following sections.

Table 4. 2 Site Characteristics. Overall average Hg fluxes, air and soil temperature and sensible heat for each field site along with day and night averages are presented. RN represents net radiation, where maximum and minimums are provided for each site

		Hg flux	Air temp	Soil temp	RN max	Sensible heat
		(ng m ² h ⁻¹)	(°C)	(°C)	(W m ⁻ 2)	(W m ⁻²)
Pinchi	day	873.49	19.45	22.04	226.48	N/A
	night	273.15	13.57	15.44	-57.48	N/A
	all	666.71	16.57	18.83		N/A
Reno	day	363.28	20.08	30.06	236.49	100.27
	night	97.86	13.70	22.20	-52.64	-15.65
	all	239.19	16.43	25.06		48.50
Klages	day	63.63	23.87	39.90	350.72	2.41
	night	2.14	16.65	20.78	-63.00	129.27
	all	34.31	20.10	29.77		62.08
Rouyn	day	10.72	20.90	22.43	206.72	74.42
	night	1.94	16.22	21.59	-49.29	-17.75
	all	6.05	18.23	21.84		27.32
Yukon	day	11.10	12.58	18.32	211.09	45.22
	night	4.07	11.61	12.41	-42.79	-8.86
	all	8.03	11.88	15.21		19.16
Nimmo	day	1.36	17.2	16.07	898.61	159.87
	night	-1.35	9.74	14.65	-80.59	-4.95
	all	0.16	13.75	15.42		91.12

4.1.2 All sites

Investigation into the role of environmental parameters on Hg fluxes has been undertaken numerous times throughout the literature (Gustin et al., 2002;Scholtz et al., 2003;Baya and Van Heyst, 2010). Soil and air temperature and solar radiation are often attributed to having the largest influence on Hg fluxes, as all three exhibit strong diel trends (Choi and Holsen, 2009;Gustin et al., 2006). In order to investigate further how these environmental parameters interacted with Hg fluxes a number of correlation trends were established. Air temperature, soil temperature and net radiation were the three principle parameters focused on as they are believed to have the most influence on flux rates during dry conditions. Soil moisture is also an
important controlling parameter for Hg emissions. However, data was not available for these studies. Regression coefficients (R^2) for each site are presented in Table 4.3.

	Air temperature	Soil temperature	Net radiation	
Site	(R ²)	(R ²)	(R ²)	
Pinchi	0.81	0.75	0.57	
Klages	0.46	0.48	0.65	
Reno	0.11	0.19	0.24	
Yukon	0.23	0.36	0.43	
Rouyn	0.47	0.034	0.62	
Nimmo	0.34	0.29	0.17	

Table 4. 3 regression coefficients for environmental trends compared to Hg fluxes at each site.

At Pinchi and Nimmo, air temperature had the strongest correlation with Hg flux, while net radiation had the weakest. At both sites, soil temperature had a weaker correlation than air temperature, although stronger than net radiation. This suggests that different processes are controlling the flux at these sites compared to the other four sites. Overall, Nimmo's correlations were weaker than those witnessed at Pinchi. Of all the sites, Pinchi presented with the strongest correlation between these environmental parameters and Hg fluxes. The two sites do not have any obvious common traits that would constitute these similarities; Nimmo is an alpine background site, while Pinchi is characterised as an enriched cinnabar deposit. Air temperature is important for the evasion of Hg through the laminar sub-layer immediately above the surface and temperature influences the turbulent diffusion in the boundary layer, determining the height of the laminar sub-layer. Higher air temperatures allow for increased diffusion, promoting greater turbulence within the laminar layer (Edwards and Howard, 2013). As micrometeorological methods are conducted in the atmosphere rather than at the direct surface (as with chamber methods) it is not surprising that a stronger correlation was seen with air temperature. However, as this was only found to occur at two out of the total six sites presented here, it is difficult to determine if air temperature is a significant control on Hg flux.

The other four sites all demonstrated a stronger correlation with net radiation than any other parameter. This was followed by soil temperature with the second strongest correlation. The stronger correlation with soil temperature than air temperature may be caused by solar radiation increasing soil temperature through the conversion of solar energy to thermal energy (Zhang et al., 2001). As soil temperature is a product of the substrates interaction with solar radiation in

nature, these correlations may simply be a reflection of the correlation between solar radiation and Hg flux (Wang et al., 2005). Solar radiation enhances Hg fluxes on short time scales through the transfer of photo-energy (Zhang et al., 2001). This light-enhanced volatilisation cause a photochemical reaction that reduces Hg^{+2} to the more volatile Hg^0 (Gustin et al., 1999). In controlled laboratory experiments light induced Hg emissions initially increased and then gradually decreased over time. This was thought to be caused by a decrease in available Hg for reduction (Park et al., 2014). As these site are all naturally enriched substrates, depleted Hg stores are all replenished over night by atmospheric deposition as solar radiation is no longer available to influence emissions. Further analysis of this is undertaken in Chapter 5.

In order to further investigate these relationships, multivariate regression analyse in the form of Principle Component Analysis (PCA) was undertaken on all sites to determine which parameter had the greatest influence of Hg fluxes. PCA is a multivariate technique commonly applied to identify patterns within data sets with multiple variables. PCA was initially conducted for the diel data across all sites (Figure 4.1) in order to identify which variables were closely related to the flux and each other. Variables were chosen to represent those that have been previously shown to influence Hg flux rate. They included: air and soil temperature, net radiation, sensible heat, ambient Hg concentrations and soil concentrations. The natural log of the flux was used to represent the flux across all sites as it was found to be more normally distributed (a requirement for PCA).



Figure 4. 1 principle component analysis for all measured parameters across all sites. Soil Hg represent the substrate concentration, Ln flux is the natural logarithm of the flux, H is sensible heat, RN is net radiation and T is temperature.

The PCA indicated that across all sites the natural log of the flux and the environmental parameters are all closely related (Figure 4.1). This is determined from the proximity of the independent variables to each other in the graph. The first two principal components (PC) were significant, accounting for 75% of the variance in the data. The first PC accounted for 46% of the variance (the full PCA table can be viewed in Appendix 1). PCs were consider significant if the eigenvalue was greater than 1. An eigenvalue of 1 represents the amount of variance in the data explained by an original variable, while anything greater than 1 explains a greater variance than any of the original variables (Jolliffe, 2002). As can be expected, sensible heat and net radiation were very closely related. This is not surprising as sensible heat is derived from the shortwave radiation. Likewise, both soil and air temperature have been shown to be closely related.

Soil Hg concentrations and ambient Hg concentrations appear to be closely related to each other. However their distance from the environmental parameters indicates that they have little influence over each other. Ln flux and soil Hg and ambient Hg are still within reasonable proximity to each other, implying that while the environmental parameters may not have much influence on Hg concentrations there is still a possible relationship between fluxes and soil Hg concentrations and ambient Hg concentrations. This relationship has been observed previously; Gillis and Miller (2000) proposed that deposition occurred when ambient Hg concentrations were higher than soil air pore concentrations. When the opposite occurred and ambient Hg concentrations where lower than soil pore concentrations, emissions would occur. This was found to result in a negative correlation with Hg flux (Gillis and Miller, 2000).

4.2 Background sites

Background sites are thought to have different interactions with environmental parameters than enriched substrate site. It is assumed that these areas contribute to the atmospheric cycle predominately through re-emission of atmospherically deposited Hg. As a result, these sites occupy vast areas and can occur in any environment (Gustin et al., 2008). Despite this, background sites are still an under-explored area and the factors influencing Hg exchange are little understood (Schlüter, 2000). The fact that these sites can occur in any environment makes them an important part of the global Hg cycle. In order to understand how the measured environmental parameters interacted with the background sites present here, diel composite trends were constructed using half hour flux measurements for each site to demonstrate how fluxes change over a twenty-four hour period. Diel air and soil temperature, and net radiation and sensible heat were also included to demonstrate how they changed in relation to the fluxes throughout the day (Figure 4.2). Fluxes at all sites experienced highest emissions during the day, with maximums occurring in the afternoon. Night-time to early morning fluxes tended to be smaller and often experienced deposition. Low wind velocities and reduced convective mixing associated with nocturnal conditions means that Hg fluxes are controlled by slow molecular diffusion, rather than the turbulent mixing seen during the day (Gustin et al., 1999).

Rouyn's peak flux was the only background site to coincide with the peak in solar radiation (Figure 4.2d). Yukon's diel trends exhibited two distinctive dips during the day for both temperature and solar radiation (Figure 4.2a, b). Less dramatic, but still prevalent, dips in flux also occurred but lagged slightly behind these metrological parameters. This lag was seen to a greater extent at Nimmo across the entire diel composite. While net solar radiation at Nimmo reaches its highest at midday, peak flux does not occur until approximately 2pm. The overall flux pattern appears to follow one similar to net radiation but with this 2 hour lag. It is possible that this lag response is influenced by the rate at which Hg^0 can be diffused from the soil layer. The high volatility of Hg^0 should mean that emission rates respond quickly to any changes in temperature. However, the diffusion of Hg from the lower substrate to the surface occurs at a much slower rate, influenced by substrate characteristics and Hg concentrations. As these sites are classified as background sites, we see this lag between the meteorological parameters and Hg flux rates (Lindberg et al., 1995).



Figure 4. 2 Diel composite trends for three background sites, Yukon (a-b), Rouyn (c-d), Nimmo (e-f). Graphs on the left side compare half hour fluxes of a 24-hour period to soil and air temperature. Right side compares the same fluxes to net radiation (RN) and sensible heat.

A PCA was run for the background sites only to further explore the interactions between Hg flux and environmental parameters (Figure 4.3). As with Figure 4.1, the natural log of the flux was used, as well as the same parameters. The analysis was found to have two PCs with an eigenvalue greater than 1, accounting for 79% of the variance within the data. The first PC accounted for 47% of the variance. Figure 4.3 shows that soil temperature, net radiation and flux are closely related. Air temperature and sensible heat appear to have less of an influence on the flux, although they are still close enough that their influences cannot be ruled out. As with the all site PCA's, soil and ambient Hg concentrations appear to be less closely related to environmental parameters, but are reasonably closely related to Hg flux.



Figure 4. 3 PCA for three background sites, Yukon, Rouyn and Nimmo. Soil Hg represent the substrate concentration, Ln flux is the natural logarithm of the flux, H is sensible heat, RN is net radiation and T is temperature

Background site analysis suggests that Hg flux is closely related to net radiation and soil temperature. As substrate concentrations are low it is reasonable to suspect that simple vaporisation cannot account for the emissions of Hg from the substrate alone (Ericksen et al., 2006). Incoming solar radiation promotes the reduction of Hg^{+2} to Hg^{0} and soil temperatures cause the evasion of Hg from the soils (Choi and Holsen, 2009). This is supported by the lag between peak net radiation and peak Hg flux. During light periods solar radiation is initiating the reduction of Hg^{+2} to Hg^{0} , causing the background sites to become a source of Hg. When

there is no longer any solar radiation to initiate Hg reduction background soils become a net sink (Xin and Gustin, 2007).

Over longer periods of time solar radiation is able to influence Hg flux by increasing the soil temperature through the conversion of solar energy to thermal energy (Zhang et al., 2001). High soil temperatures drive abiotic and biotic processes within the substrate. Heating increases the air volume within the soil pores, allowing the diffusion of Hg⁰ to the atmosphere (Liu et al., 2014). At the same time vapour pressure is increased and bacteria activity responsible for the reduction of Hg is enhanced (Schlüter, 2000). As soil temperature is mainly controlled by solar radiation, the positive relationship between soil temperature and Hg flux is most likely a reflection of the interaction of solar radiation with the substrate (Liu et al., 2014) It has been suggested that some of these processes are not dependent on light and therefore occur without the presence of solar radiation (Choi and Holsen, 2009). It is possible that these light-independent processes drive the Hg emissions that have been observed during nocturnal periods.

4.3 Enriched sites

Diel composite flux trends at the three enriched sites followed a closer trend with the diel meteorological trends than seen with the background sites (Figure 4.4), particularly with respect to temperature. Sensible heat was not measured during Pinchi's field study period and is therefore not presented. Similarly soil temperature at Reno was only measured for half the study period, resulting in the data being too limited to produce a composite diel trend. Pinchi's diel flux patterns followed very closely both soil temperature and air temperature diel patterns (Figure 4.4a). However, net radiation experienced a significant drop prior to and shortly after midday that was not echoed in the flux data (Figure 4.4b). Reno was the only site where rainfall occurred during the diel composite trend (Figure 4.4f, e). The rainfall event is made obvious by the sharp increase in flux and the decrease in both air temperature and net radiation, suggesting that the short rainfall event resulted in increased Hg flux.

The faster response between Hg flux and the environmental variables is most likely a product of the higher substrate concentrations. As the Hg at these sites a dominantly from geogenic sources Hg^0 is already available within the substrate. The reduction of Hg^{+2} does not need to take place within the substrate before emissions can take place and the Hg^0 has the ability to respond quickly to changes (Kim et al., 1995). Engle and Gustin (2002) determined using stepwise multivariate regression that Hg substrate concentrations alone accounted for approximately 40% of the variability in the data, when combined with the environmental

parameters 60 to 80% of the variance was accounted for. The environmental parameters therefore have a greater influence over the diel trends, while substrate concentrations govern the long term flux patterns.



Figure 4. 4 Diel composite trends for three enriched sites, Pinch (a-b), Reno (c-d), and Klages (e-f). Graphs on the left side compare half hour fluxes of a 24-hour period to soil and air temperature. Right side compares the same fluxes to net radiation (RN) and sensible heat. Rainfall period represented in shaded green.

Diel Hg fluxes were significantly reduced between night fall and early morning. This is thought to be caused by stable atmospheric conditions causing Hg flux to be controlled by molecular diffusion rather than turbulent diffusion (Lindberg et al., 1995). Stability becomes the dominate control as kinetic processes are significantly reduced during this period. However, some emissions still occurs, particularly at the enriched sites, likely a product of soil heat stored within the substrate. As these measurements were collected during the summer it is likely that this is a reflection of increased solar intensity and duration, allowing greater storage of heat within the substrate (Baya and Van Heyst, 2010). Diel trends for most sites show that deposition mostly occurred at night and emissions were reduced until early evening. Enriched sites dominantly only experienced reduced emissions during this time likely because photo reduction of Hg was not required for emissions to occur.



Figure 4. 5 PCA for enriched substrate sites. Soil Hg represent the substrate concentration, Ln flux is the natural logarithm of the flux, H is sensible heat, RN is net radiation and T is temperature.

The PCA established for enriched sites infers that the environmental parameters have a closer relationship with each other than observed across all sites (Figure 4.5). Only the first two PC's were considered significant with an eigenvalue greater than one and account for 77% variance in the data. The first principle component accounts for 59% of the variance. As with the PCA conducted for all sites, ambient and soil Hg concentrations appear to have a weak relationship with the environmental parameters. The four environmental parameters used for the PCA are all situated closely to each other, indicating a strong relationship. Flux appears to be situated an

equal distance from substrate concentration and the environmental parameters, suggesting that the two groups influence flux separately. Substrate concentrations are considered to be the dominant control of Hg fluxes at enriched sites, while environmental parameters are thought to have a secondary influence (Liu et al., 2014;Gustin et al., 1997;Gustin et al., 2008).

The metrological parameters are all closely related, indicating that they have a similar level of influence on the Hg fluxes. Lin et al. (2010) found that the simultaneous influence of two parameters caused a greater correlation with Hg flux than a single parameter. Air temperature and soil moisture were found to have the greatest correlation, followed by air temperature and solar radiation. As soil moisture was not available, it cannot be compared here. However, air temperature and solar radiation are closely related in the PCA. This indicates that they have a similar influence on Hg flux at these sites. These environmental parameters are all known to have a strong correlation with solar radiation. It is therefore likely that the grouping of these parameters are a reflection of Hg fluxes correlation with solar radiation (Feng et al., 2005).

4.4 precipitation

Precipitation data were limited for all studies with only the timing of rainfall events recorded. Neither rainfall quantities nor rates, or soil moisture content were recorded at the time, limiting the ability to adequately interpret the influence of precipitation on Hg fluxes. Table 4.3.1 shows the average fluxes recorded at each site during rainfall and no rainfall, as well as the ratio of rain to no rain fluxes. The three enriched sites (Pinchi, Klages and Reno) all demonstrated higher average fluxes during rainfall than periods of no rainfall and were found to have the highest rain to non-rain ratio. The increase in Hg emissions from these sites is most likely caused by the displacement of interstitial air by the infiltrating water (Gillis and Miller, 2000). The background sites all displayed a decrease in flux during rainfall. As the magnitude of flux is related to substrate concentrations, the same increase in fluxes was not observed as the substrate does not contain enough Hg to cause the same interstitial release of air (Gustin et al., 2006), as is evident by the low rain to no rain ratios seen at these sites.

In order to investigate this further, diel trends were established for those sites that experienced rain events during the day (Figure 4.6). Days were only considered if there were sufficient data across a 24 hour period and rainfall started and ended during the daytime. Night time rain events were not considered, as the role of controlling parameters such as atmospheric stability on fluxes are not as well understood. Klages experienced a clear spike in flux, starting shortly after rainfall occurred (Figure 4.6a). Increase in flux coincided with a decrease in air temperature and net radiation. Fluxes steadily decreased again once the rain event ceased. The correlation

between the temperatures, net radiation and Hg^0 emissions were no longer as strong. Pinchi experienced a similar trend to Klages except the spike in emissions occurred sooner into the rain event (Figure 4.6b). It is possible that the disparity between the spikes in emissions at these two sites is a reflection of rain intensity. Klages fluxes took longer to respond to the rain event than Pinchi, suggesting that rain intensity was lower, due the water taking longer to infiltrate the substrate or low soil permeability (Liang et al., 2014).

				No.			
		No.	No rain	ements		No.	Ratio
	Avg flux	measure	flux		Rain flux	measur	Rain: no
Sites	$(ng m^2 h^{-1})$	ments	$(ng m^2 h^{-1})$		$(ng m^2 h^{-1})$	ements	rain
	666.71		645.66		835.09		
Pinchi	(653.5)	459	(610)	408	(922.3)	51	1.29
	34.31		28.62		156.57		
Klages	(64.97)	450	(48.7)	441	(184.3)	18	5.47
	239.19		223.24		632.52		
Reno	(320.99)	77	(305.3)	74	(521.8)	3	2.83
			10.02				
Yukon	8.03 (12.7)	379	(13.4)	262	3.56 (9.3)	118	0.36
Rouyn	6.05 (6.08)	121	6.41 (7.1)	106	4.38 (2.3)	13	0.68
	0.16		0.28		-6.31		
Nimmo	(13.27)	719	(13.24)	706	(16.43)	13	-22.25

Table 4. 4 overall average fluxes for all sites compared to average rain and no rain fluxes. Standard deviation given in brackets.

These sudden spikes in Hg with rainfall appear to be caused by the displacement of interstitial air from the infiltrating water. As the rain falls, the water is soaked into the soil pours, causing an initial pulse of Hg to be released from the surface. This initial pulse is dependent on the amount of Hg available to be depleted (Briggs and Gustin, 2013). Fluxes then quickly decrease shortly after the rain event, with the rate of decrease declining until it returns to a flux similar to that before the rain occurred (Song and Van Heyst, 2005). Song and Van Heyst (2005) suggest that fluxes after a single rain event will remain slightly higher as a result of increased soil moisture. However, without the recorded soil moisture content at these sites it is not possible to determine whether this was the case for these sites.

Nimmo is the only background site presented (Figure 4.6c). Flux patterns here were vastly different to the other two sites. Fluxes decreased during the rainfall, ultimately resulting in net depositions. Fluxes then increased again after the rain event. This was also reflected in the rain to no rain ratio (-22.25). The negative ratio would suggest that deposition would commonly

occur at this site during periods of rainfall. No other site presented with a negative ratio, although both Yukon and Rouyn had small ratios, 0.36 and 0.68 respectively, indicating suppressed fluxes during rainfall. This would imply that the amount of Hg available for interstitial release was too limited during the rainfall period (Gabriel et al., 2011).

While not measured here, soil moisture is an important parameter that is considered to significantly influence Hg flux patterns. Soil moisture content has the ability to both increase Hg emissions and suppress them. Initially increasing soil water pore content has generally been shown to increase Hg fluxes (Gillis and Miller, 2000). However, sequential wettings have been found to diminish these enhancements, likely caused by a depletion of available Hg soil pool (Eckley et al., 2011). Bahlmann et al. (2004) suggested that maximum flux occurred when soil moisture was increased to approximately 30%. Increasing soil moisture content above this level results in decreasing fluxes until eventually flux is suppressed. The combined influence of air temperature and soil moisture may promote increased Hg emissions from substrates as a result of enhanced water evaporation experienced at higher temperatures (Lin et al., 2010). This makes understanding the influence of soil moisture on Hg fluxes an important consideration when determining the potential impacts of climate change on Hg air-surface exchange.

4.5 Summary

Overall, environmental parameters were shown to have a vital influence in governing Hg flux patterns. Background sites were dominantly controlled by solar radiation and soil temperature. Solar radiation is thought to cause a reduction in atmospherically deposited Hg^{+2} to Hg^{0} that can be emitted to the atmosphere, while increasing soil temperature opens up the soil pore space allowing the photo-reduced Hg^{0} to be emitted into the atmosphere (Zhang et al., 2001). Enriched sites displayed a more combined influence of meteorological parameters. Fluxes appeared to be more influenced by evaporation and volatilisation of Hg from the substrate than by photo-reduction of Hg^{+2} . Substrate concentrations were found to be an important parameter controlling Hg flux across all sites. Substrate concentrations most likely reflect the long-term trends in flux, while the meteorological parameters reflect day-to-day and seasonal variations (Johnson et al., 2003). This is an important consideration when determining the influence of climate change on Hg air-surface exchange.



Figure 4. 6 Diel trends for selected sites when rainfall occurred at Klages (a), Pinchi (b) and Nimmo (c). Rainfall duration is represented in green. Net radiation and air temperature is also compared. X-axis is the Julian day that these events occurred on.

Chapter 5: Determining of Hg flux using Arrhenius

5.1 Activation energies across all site

Temperature and Hg flux rates have been found to exhibit an exponential relationship. This relationship was found to exist for both soil and air temperature across the majority of sites. An example of this is given in Figure 5.1 The curve of the temperature-flux relationship is closely related to that of the vapour pressure curve of Hg (Lindberg et al., 1995), suggesting that this temperature relationship is strongly influenced by the vapour pressure of Hg⁰ (Gustin et al., 1997). As the temperature increases so does the vapour pressure, increasing the volatilization of the Hg⁰. This is thought to be caused by the interaction between the physicochemical properties of Hg⁰ and biotic/abiotic processes occurring within the soil matrix (Kim et al., 2012). This relationship follows closely that of the Arrhenius relationship, suggesting that Hg flux is temperature influenced. The activation energy is derived from the Arrhenius equation (equation 3.8) described in Chapter 3.



Figure 5. 1 TGM flux as a function of air temperature (a) and soil temperature (b) at Pinchi

The Arrhenius equation was applied to different flux conditions in each site's data set in order to determine how different environmental parameters may influence the recorded fluxes. Apparent activation energies (E_a) were calculated for day and night fluxes and rain and no rain fluxes as well as for the entire data set (Table 5.1). E_as calculated for all fluxes at each site using soil temperatures were below the vaporisation of Hg⁰, with the exception of Nimmo, which had an E_a much higher (31.61 kCal mol⁻¹ K⁻¹). The vaporisation of liquid Hg occurs at 14.5 kcal mol⁻¹ K⁻¹ at a temperature of 20°C. When the same E_a was calculated using air temperature they were found to be closer to the vaporisation of Hg⁰. Nimmo still had an activation energy higher than the vaporisation, although it was to a much lesser a degree. Rouyn also had an E_a higher than the vaporisation of Hg⁰.

Activation energies are commonly calculated using soil temperatures because Arrhenius is used to determine the temperature at which a chemical reaction is likely to occur. This takes place in the soil and it therefore seems logical to use the soil temperature. As Arrhenius is often applied to describe the temperature dependence of kinetic constraints on Hg emissions, this would suggest that using air temperature is also acceptable, particularly as micrometeorology measurements are taken within the atmosphere and not within the substrate.

							Hg soil
		All	Rain	no rain	Day	Night	concen.
		kcal mol ⁻¹	(ppm)				
Pinchi	E _a soil	14.11	34.89	13.78	7.60	9.51	179.50
	E _a air	13.05	23.00	6.66	6.49	5.55	
Klages	E _a soil	7.87	4.23	8.50	2.94	7.92	0.85
	E _a air	14.74	25.04	15.06	4.62	12.34	
Reno	E _a soil	8.05	-22.58	10.31	6.33	-0.05	7.15
	E _a air	14.17	-63.09	14.79	22.93	5.64	
Nimmo	E _a soil	31.61	259.12	31.53	21.45	19.61	0.05
	E _a air	16.44	34.89	16.39	-13.35	9.08	
Rouyn	E _a soil	6.60	-64.86	4.80	6.45	-0.20	0.01
	E _a air	19.99	-143.99	20.65	13.38	-0.06	
Yukon	E _a soil	13.48	22.68	11.47	10.73	14.30	0.36
	E _a air	14.42	26.39	13.08	13.00	11.62	

Table 5. 1 Activation energies constructed for each site using both soil and air temperature. Only positve fluexes were used to calculate activation energies for different environmental conditions.

The majority of sites presented here were found to have an E_a close to or below the vaporisation of Hg⁰, with the exception of Nimmo. The low E_a 's suggest that emission of Hg from the substrate is controlled by desorption and volatilisation. As the E_a is below the vaporisation of Hg, less energy is required for volatilisation of Hg⁰ as a phase change is not required to initiate release. Instead, Hg⁰ that has accumulated within the soil pores is released (Gustin et al., 1997). The higher E_a found at Nimmo suggests the process of emission is more complicated and that more energy is being consumed to facilitate the release of Hg⁰ from the soil matrix, likely as a result of photo-reduction (Gustin et al., 2002). The low E_a 's indicate vaporisation of Hg as the dominant control on emissions, which is a function of temperature. Soil temperature is thought to accelerate the photo-reduction of Hg^{+2} while simultaneously expanding soil pore volume, allowing for elevated Hg^0 emissions and low E_a 's (Wang et al., 2005). Nevertheless, temperature, particularly soil temperature, remains heavily influenced by solar radiation and therefore its influence cannot be ruled out.

Arrhenius is often applied to demonstrate the dominant role of solar radiation using the apparent activation energies. Two main hypothesis permeate the literature. The first is that the absorption of solar energy by gaseous Hg^0 atoms causes the excitation of the atoms, reducing the E_a for emission and desorption of Hg (Zhang et al., 2001). The second suggests that solar radiation increases the E_a through photo-reduction of Hg^{+2} , as more energy is consumed to sustain the reaction (Gustin et al., 2003). The low activation energies found in this study suggest that the majority of sites conform to the first hypothesis. Nimmo conforms more to the second hypothesis as the activation energy at this site was well above that required for volatilisation. Given that Nimmo is a background site, substrate concentrations are low and therefore reduction of Hg^{+2} needs to occur to account for the emissions from the soils and energy is required to initiate this reaction (Wang et al., 2006). This energy consumption is reflected in the E_a .

These low E_a indicate that light-enhanced desorption of Hg^0 from the substrate is the most likely mechanism controlling emissions. Gustin et al. (2002) suggested that initial photo-reduction occurred at sunrise, producing sufficient Hg^0 for subsequent release throughout the day, reducing the E_a for emission to occur through the day. However, it is unlikely that the initial solar radiation could produce enough Hg^0 at the background sites to sustain this low activation energy, as the substrate concentrations are too low.

 E_a 's calculated using air temperature appear to decrease as substrate Hg concentrations increase (Figure 5.2). E_a 's calculated with soil temperature also show a decreasing trend. However, this appears to be driven by a single value as evident by the R² value. A similar trend was also noticed by Bahlmann et al. (2006), wherein E_a 's decreased logarithmically as substrate concentrations increased. Substrates with elevated concentrations are generally thought to require less energy to release Hg⁰ from the substrate, likely as a result of increased abiotic and biotic processes available for the reduction to Hg⁰ within the soil (Schlüter, 2000). Background sites are typically thought to require a higher E_a as the reduction of Hg⁺² is required to initiate the release of Hg from the substrate (Wang et al., 2006). Despite the high substrate concentrations found at Cinnabar sites, these site are generally considered to have higher activation energy as the Hg is in an insoluble form and is therefore more commonly associated 42

with photo-reduction (Gustin et al., 2002). However, Pinchi (a cinnabar deposit) was found to have an E_a lower than the vaporisation energy of Hg⁰, falling more in line with the geothermally enriched site.



Figure 5.2 Site E_a 's compared to substrate concentrations at all sites. E_a 's calculated using both air temperature ($R^2 = 0.75$, P = 0.025) and soil temperature ($R^2 = 0.03$, P = 0.74) are used for comparison.

The low E_a 's observed here are not often reflected in the literature and have not been reported for background sites. The low E_a 's suggest that reduction of Hg^{+2} does not need to occur for Hg^0 to be emitted from the substrate. This is an reasonable assumption for the enriched sites as they have sufficient substrate concentration to suggest that emissions can be sustained without the need for further reduction to occur (Schlüter, 2000). However, the substrate concentration at the background sites are not sufficient enough to constitute the emission fluxes observed. Therefore excess energy must be consumed to reduce the deposited Hg^{+2} to allow emission of Hg^0 to occur (Moore and Carpi, 2005). This energy required for this reaction to occur is not reflected in the apparent activation energy. If photolytic reduction is controlling Hg emissions than the application of Arrhenius at these sites may not be applicable as it is used to determine thermally controlled reactions (Bahlmann et al., 2006).

Another possible explanation for the low E_a 's observed at the background sites is the substrate properties. Factors such as organic matter, soil type and microbial activities are known to influence E_a and as such temperature may not be the only explanation. High organic carbon levels and high rates of enzyme activity are known to reduce activation energies (Davidson and Janssens, 2006;Qi et al., 2002;Lloyd and Taylor, 1994). Hg concentrations are also highest where organic matter is highest (Meili, 1991), suggesting that the low E_a 's observed, may be a reflection of carbon levels and enzymes activity within the substrate (Davidson and Janssens, 2006). However, as the measurements required to quantify these influences were not recorded during these field campaigns it cannot be satisfactorily determined if this is the case at these site. In addition to substrate composition and temperature, temporal and spatial differences in substrate availability may also contribute to the large variability in E_a observed in nature and need to be taken into account (Qi et al., 2002).

5.2 Activation energies during rain events

Generally activation energies were found to be higher during periods of rain (Table 5.1). This was observed regardless of whether it was a background or enriched site, with the exception of Klages, which saw the soil activation energy almost halve following rain. Nimmo experienced the most significant increase in activation energy during rainfall, with an E_a of 259.12 kcal mol⁻¹. It is possible that the larger E_a is a result of the presence of water within the soil matrix causing an alteration to the diffusion characteristics or the processes that cause the reduction of Hg⁺² to Hg⁰ within the substrate (Lindberg et al., 1995). The presence of water in the substrate may initiate a phase change to gaseous Hg⁰ before it is emitted from the substrate, requiring increased energy consumption (Song and Van Heyst, 2005). At the same time that water that has infiltrated the soil pores is undergoing a similar phase change for liquid water to vapour, where it can be evaporated along with Hg⁰ (Wilson et al., 1994). The excess energy consumed during these phase changes is likely what generates the higher E_a 's observed during rainfall.

Reno and Rouyn both experienced negative activation energies during periods of rain, a previously unobserved phenomenon for soil. Relatively little is understood about what causes negative activation energy and virtually none of the literature considers it in the context of soil chemistry. Positive activation energy restricts the ability for a reaction to occur until there is sufficient energy within the system (Laidler, 1984), while negative activation energy implies that there is already enough energy within the system. The reaction has thermodynamic

momentum that can only be restricted by the molecules ability to collide (Shimomura et al., 1967). When this occurs, the reaction rate falls as temperature increases. This was observed in Rouyn's rainfall Arrhenius plot (Figure 5.3). The fact that these negative activation energies only occurs during rain periods suggests that the sudden spike in the amount of water within the soil matrix causes a sudden shift in the controls of the reaction, resulting in an increase in Hg emissions and negative activation energy. However, this cannot be confirmed without knowledge of the change in soil water content during the rainfall event, which was not recorded at the time of the experiment.

The spikes observed in Hg fluxes as a result of rainfall indicated that physical mechanisms caused the interstitial displacement of Hg^0 vapour from the substrate and not a thermal or photolytic reaction. Corbett-Hains et al. (2012) observed that during the freeze-thaw stage of the sub-zero temperature cycle, spikes in Hg fluxes would occur as a result of soil column cracking increasing interstitial pore space and releasing Hg^0 vapour. This reduced the strength of Hg flux correlation with soil temperatures and produced small negative activation energies. A similar mechanism is thought to cause the almost instantaneous spikes observed in Hg flux associated with rainfall. As water makes its way into the dry soil column, it forces Hg^0 vapour out of the soil pore space (Briggs and Gustin, 2013). As this is a physically forced enhancement and not a kinetically enhanced Hg emission, it is possible that this is the reason for the negative activation energies observed at Reno and Rouyn during rainfall.



Figure 5. 3 Natural log of the flux as a function of the inverse temperature (in Kelvin) at Rouyn for nonrain fluxes (a) and rain fluxes (b).

5.3 Summary

The low activation energies found here indicates that minimal energy is required to initiate Hg emissions for open field substrates, as there is enough energy in the system to initiate the release of Hg from the substrate. If this energy input was to change in the future such as by increases to temperatures or increased radiation intensity these reaction are likely to occur at a faster rate. Not only will the photo-reduction of Hg^{+2} within the substrate be enhanced, increasing the pool of Hg^{0} within the substrate but the ease of which Hg can be emitted from the substrate will also be enhance. Understanding how these rates change is important for determining whether or not Hg as the ability to sequester deep enough into the substrate for it to become a store. The majority of those processes that drive air-surface exchange occur in the top 0.5 cm, and therefore are the most vulnerable to alterations to meteorology (Carpi and Lindberg, 1997).

Chapter 6: Future Mercury flux prediction as a result of Climate Change

6.1 Adjusted fluxes

The relationships identified throughout the previous chapters indicate that changes to environmental parameters cause alterations to Hg fluxes. Human activities have caused substantial disruptions to those meteorological parameters that influence Hg emissions. Understanding how future climate change will impact natural sources of Hg is important not only for determining the impacts of climate change but also for the development of more accurate global Hg biogeochemical models. To understand how Hg fluxes from background and enriched substrates may be influenced by future climate change, analyses were undertaken to determine if the environmental controls identified previously could be utilised to predict Hg flux patterns with projected temperature increases.

The exponential relationships between temperature and fluxes, at those sites that were found to have a correlation, were all found to have similar slopes (Figure 6.1). The only exception to this was Yukon, which had a slope of 0.15, which was more than double the average slope of the other sites. This is possibly a reflection of the frequency of rain events observed during the field campaign. Soil moisture is known to influence the rate of Hg emissions from a substrate. Similar trends were found to exist for both soil and air temperature, although air temperature did show slightly greater variability. This relationship was found in other studies throughout the literature with slopes for relationships between log-flux and temperature ranging between 0.3 and 0.7 (Carpi and Lindberg, 1998;Lindberg et al., 1995;Xu et al., 1999;Scholtz et al., 2003). The reasonably consistent slopes for five out of the six sites indicate that the rate of change in flux with temperature is reasonably constant despite different substrate relationships. Figure 6.2 further corroborates this. When the y-intercepts taken from the trend lines found in figure 6.1 were plotted against the substrate Hg concentrations, a logarithmic relationship is observed, suggesting the Hg concentrations are not always the major control of Hg flux rates. Moore and Carpi (2005) noted that as soil temperature changed, the flux increased proportionately. This was found to be true regardless of whether solar radiation was present at the time. Based on this finding, it is thought that fluxes can adjust to changes in temperature.



Figure 6. 1 log flux as a function of air temperature across all sites



Figure 6. 2 Y-intercepts plotted against substrate concentrations for sites found to have a correlation with air temperature. Y-intercepts were determined for trend line equations of air temperature vs flux measurements for each of these sites.

Figures 6.1 and 6.2 together, suggest that it is possible to adjust the fluxes based on changes in temperature using the following:

$$adj flux = EXP\left(Lnflux \frac{m * T_{adj} + b}{m * T + b}\right)$$
(6.1)

Where ln flux is the natural log of the measured flux, m is the slope of the best fit line for ln flux verses temperature and b is the y-intercept from the same best fit trend. T_{adj} is the temperature the flux is being adjusted to and T is the measured temperature. Measured air temperature was used here, consistent with the majority of climate change prediction models. Fluxes were first adjusted using the linear trend line equation for natural log- temperature-flux relationship at each site before they were adjusted to potential temperature changes. The initial adjustment was applied to account for the diel trends within the data, as emissions peaked at midday and decreased during the evening (Coolbaugh et al., 2002).

The equation was developed from a combination of those developed by Carpi and Lindberg (1998) and Zehner and Gustin (2002). Zehner and Gustin (2002) found that the average daily Hg emissions could be calculated using the log-flux-log-substrate, while Carpi and Lindberg (1998) suggested that the log of the flux was related to the linear relationship with soil temperature. As has been suggested by the data presented in Figure 6.2, when examining the relationship between flux and temperature, substrate concentration is not always the dominant parameter. When scaling up Hg emissions, accounting for substrate concentrations alone does not provide an adequate prediction as these relationships are not as strong at background sites and meteorological parameters are known to have significant influence (Gustin et al., 2008).

Air temperature was chosen as the parameter for adjusting Hg fluxes, as it is the preferred predictor for IPCC reports. Air temperature predictions have less uncertainty than predictions developed for solar radiation, whose effects would be reflected in the use of soil temperature. Alternations to solar radiation are highly dependent on alternations to cloud physics and are therefore inherently difficult to predict (IPCC, 2013a). Despite soil temperature having a stronger correlation with flux than air temperature, the regression coefficients for air temperature-flux relationships and soil temperature-flux relationships were not significantly different, suggesting that their level of influence may be similar. This is further corroborated by the results of the PCA, which showed that soil and air temperature were closely related. Air temperature and soil temperature were also both strongly influenced by solar radiation. Therefore, the influence of solar radiation can to some extent be accounted for despite the difficulties in predicting how it may be altered in the future. Overall, the choice to use air

temperature for the adjusted flux does not undermine examination of the processes that are considered to control Hg flux rates.

Fluxes were initially adjusted to a temperature of 20°C and 10°C (Figure 6.3). Average temperature across all sites was 16.6°C. Yukon was not included in the adjustments as the site did not have a slope similar to the other sites and therefore the assumptions made for the other sites could not be applied. The adjustments clearly show that when temperature is increased so too is the flux and vice versa for decreases in temperature, irrespective of substrate concentration. This is a log-log relationship and therefore a temperature increase will result in an exponential Hg flux increase. The flux adjustments indicate that substrate concentrations are still an important indicator for high Hg fluxes at individual sites. However, the percentage increase with temperature will remain the same regardless of substrate concentrations.



Figure 6. 3 Adjusted fluxes plotted against substrate concentrations for all sites. Fluxes were adjusted to 20°C (red), 10°C (Green) average adjusted fluxes are in blue.

The alteration to the fluxes as are result of increasing temperature occur regardless of substrate concentrations. Substrate concentrations appear to determine the baseline flux, while meteorological parameters such as air temperature increases the variability. However, a sustained increase in average temperatures will cause a sustained increase in the overall flux. The removal of vegetation has been found to have a similar influence on the enhancement of Hg emissions from substrates. This is predominantly assumed to be caused in increased ability of solar radiation to reach the terrestrial surface (Carpi et al., 2014). As there is no longer any leaves to filter out sunlight before it reaches the surface there is increased photo-reduction and soil temperatures, inducing an increase to Hg emissions. This was found to occur despite there being no increased to substrate Hg concentrations (Magarelli and Fostier, 2005). This demonstrates that Hg fluxes are heavily influenced by the interaction of meteorological parameters with a substrate, causing alterations to the magnitude of diel trends and their contribution to global atmospheric cycles.

6.2 Fluxes adjusted to future climate predictions.

Fluxes have been adjusted to demonstrate how they may change under the IPCC emission scenarios. The scenarios were developed using climate models developed as part of the Coordinated Model Intercomparison Project 5 (CMIP5) and are based on current global policy scenarios. Each scenario is derived from approximate total radiative forcing, relative to 1750, caused solely by anthropogenic influences out to 2100 (i.e. potential volcanic eruptions are not taken into consideration). Scenarios are referred to as Representative Concentration Pathways (RCP) and are as follows, with total radiative forcing given in parentheses: RCP2.6 (2.6 W m⁻ ²), RCP4.5 (4.5 W m⁻²), RCP6.0 (6.0 W m⁻²) and RCP8.5 (8.5 Wm⁻²). Scenarios were chosen to represent a future with low levels of forcing (RCP2.6), where radiative forcing peaks and declines prior to 2100, two stabilisation scenarios (RCP4.5 and RCP6.0) and one scenario where greenhouse gas emissions are extremely high (RCP8.5). Radiative forcing under both RCP6.0 and RCP8.5 does not peak until after 2100, while forcing for RCP4.5 stabilises by 2100 (IPCC, 2013). Table 6.1 shows the predicted temperature increases under each of these climate scenarios. Temperature increases were split into two time periods, near future (2050) and long term (2100) and the mean predicted temperature increase for each scenario was used to predict how fluxes may change in response.

	2050			2100			
			Flux			Flux	
	Mean	Likely range	increase	Mean	Likely range	increase	
Scenario	(°C)	(°C)	(%)	(°C)	(°C)	(%)	
RCP2.6	1.0	0.4 – 1.6	30.7	1.0	0.3 -1.7	30.7	
RCP4.5	1.4	0.9 – 2.0	34.4	1.8	1.1 – 2.6	35.8	
RCP6.0	1.3	0.8 - 1.8	33.5	2.2	1.4 - 3.1	41.2	
RCP8.5	2.0	1.4 – 2.6	39.6	3.7	2.6 - 4.8	52.2	

Table 6. 1 global average temperature rise under IPCC emission scenarios and predictedincrease in Hg fluxes

Fluxes for each site were adjusted for each of the proposed scenarios. The predicted temperature increase for each scenario was added to the average temperature for each site to give an approximate estimate of how temperature may change at each site. Adjusted fluxes were then calculated using Equation 6.1. Fluxes at each site showed an increased emission rate out to 2050 (Figure 6.4). As there is little variability between the scenarios, the percentage change in flux for each predicted temperature increase has little variation (Table 6.1). Flux increase was calculated from the difference in y-intercepts between each scenario. A 1°C increase in temperature predicted under RCP2.6 predicts a 30.7% increase in flux. Flux increase for RCP4.5 and RCP6.0 is 34.4% and 33.5% respectively. As can be expected RCP8.5 had the largest increase in flux with 39.6%. This is in reasonable agreement with Edwards and Howard (2013), who suggest that a change of 1.2°C results in a 30% increase in Hg flux.

Fluxes adjusted to 2100 predicted temperature increases with greater variability between emission scenarios (Figure 6.5). This is caused by the disparity between temperature increases caused by emission scenarios reaching different levels of stability. Under RCP2.6, temperature rise is stable at 1°C and therefore flux does not increase. Temperature rise under RCP4.5 has stabilised by 2100 and as a result flux only increases from 34.5% to 35.8% between 2050 and 2100. Both RCP6.0 and RCP8.5 have large temperature increases and will continue to increase after 2100. Flux increase for this time is predicted to be 41.2% and 52.2% respectively. These values are not definative as they only take into account one of the meterological paramteters believed influece Hg flux. However, they do provide an indication that changes to climate will significantly influece Hg emissions from natural surfaces.



Figure 6. 4 Average flux adjusted to IPCC predicted temperature rise under each emission scenario for 2050 plotted against substrate concentrations at each site. Initial adjusted fluxes are in blue.



Figure 6. 5 Average flux adjusted to IPCC predicted temperature rise under each emission scenario for 2100 plotted against substrate concentrations at each site. Initial adjusted fluxes are in blue.

6.3 Implications of adjustments with climate change

Very few models exist that solely predict emissions from natural substrates. The majority of models focus on deposition and how it is influenced by natural emissions rates. This is mainly to do with the large uncertainties that surround Hg air-surface exchange. Lin et al. (2010) found, using factorial experiments, that air temperature increases resulted in the greatest increase to Hg emissions, with fluxes increasing by 140 % when temperature was raised from 15°C to 30°C. It was noted however, that the increase might have been larger if the experiment allowed for more realistic sunlight conditions. Lin and Tao (2003) found, using a one month modelled simulation, that 9120 kg of Hg was emitted from natural surfaces across eastern North America. This model is one of few that attempts to take into account air-surface exchange. Under the predictions developed here, it is possible that this could increase by between 2736 and 4760 kg by 2100. As it was found that 94% of the Hg emitted became part of the global Hg cycle, this could lead to an increase in Hg available for deposition (Lin and Tao, 2003).

The majority of Hg emitted from natural sources is from the deposition of anthropogenically sourced Hg. This re-emission is thought to cause background flux and accounts for 60% of the Hg emitted from natural sources (Amos et al., 2013). A top-down global Hg model that incorporated biogeochemical cycling indicated that terrestrial emissions contributed 340 Mg yr⁻¹. Subsequently, once biomass burning and geogenic emissions were discounted, the net exchange was zero (Song et al., 2015). The model uses solar radiation and substrate concentration as the controlling parameters for Hg exchange, however it does not take into account how changes to meteorological parameters in the future may influence Hg emissions. The increases shown in figures 6.4 and 6.5 may see terrestrial surfaces shift into a net source of Hg. It has been suggested that increased atmospheric temperatures will increase the amount of oxidants in the atmosphere available to reduce Hg⁰ to Hg⁺² before deposition, causing little change to Hg⁰ concentrations, particularly during summer (Megaritis et al., 2014). However, with the kinetic enhancement of Hg flux and the photo reduction of Hg⁺² in the substrate it is possible that there will simply be a reduction in the time between deposition and re-emission from terrestrial surfaces.

6.4 Summary

The proposed model takes a very simplistic form and therefore only provides a rudimental prediction of what may happen in the future. The Hg biogeochemical cycle is immensely complex with a large number of uncertainties that still exist, particularly in regards to the controls on Hg flux. In order to accurately scale up air-surface exchange measurements form

the local field sites presented here to the global scale, detailed understanding of the physical, chemical and biological processes that drive the flux are required (Zhang and Lindberg, 1999). As measurements were only undertaken during the summer months, extrapolating the fluxes out to annual and future trends using temperature alone may not accurately represent how the fluxes will change (Scholtz et al., 2003). The underlying principles for the relationships between environmental parameters and Hg flux are not fully understood and are found to vary both between seasons and annually (Scholtz et al., 2003). The influence of environmental parameters vary spatially and seasonally. While the sites used here represent a wide spatial variability they are not representative of the entire globe and only cover the summer months and therefore may not provide an accurate basis for estimating Hg trends. The varying types of substrate and the large surface they are able to cover make understanding even the smallest Hg fluxes important when scaling trends (Gustin et al., 2006).

Chapter 7: Future implications of altered global Mercury cycles

7.1 Implications of climate change on global mercury cycles

As has been demonstrated throughout the previous chapters, meteorological parameters have a significant influence on Hg flux, particularly temperature and solar radiations. The kinetic enhancement of Hg flux, although mechanistically not fully understood, has been shown to cause exponential enhancement of Hg emissions. These parameters are the most likely to be influenced by future climate change and are therefore likely to further influence Hg exchange. Weaker global circulation and increased air temperatures are likely to cause changes to deposition patterns and atmospheric oxidisation of Hg. Changes to precipitation regimes are likely to result in increased Hg inputs to aquatic systems through direct deposition, runoff, and erosion, as well as increasing Hg sequestration in terrestrial soils (Krabbenhoft and Sunderland, 2013). Very few models take into consideration how these changes will impact future Hg emissions from natural surfaces. Streets et al. (2009) incorporated IPCC climate scenarios into their development of future Hg emissions. However, the projections used only take into account alteration to energy usage and do not consider how alternation to climate may influence future Hg emissions.

Current global Hg biogeochemical models still contain a large number of uncertainties when it comes to air-surface exchange. Some models employ a simplistic approach to air-surface exchange, using an average substrate concentration and therefore treating emission and deposition as two separate processes (Amos et al., 2013;Holmes et al., 2010;Corbitt et al., 2011). The lack of understanding of air-surface exchange has led to large variability in the estimates for natural emissions, ranging between 1500 and 5207 Mg yr⁻¹ globally (Wang et al., 2014). This can cause an over- or underestimation of fluxes. Those models that attempt to incorporate air-surface exchange often employ varying equations depending on controlling environmental parameters. Some use air temperature (Wright and Zhang, 2015;Poissant and Casimir, 1998), or a combination of solar radiation and substrate concentrations (Zhang et al., 2001;Selin et al., 2008;Song et al., 2015;Bash, 2010;Scholtz et al., 2003). These approaches tend to over simplify the interaction of these environmental parameters with Hg in the substrate. The complex interactions between the different parameters makes determining their relative importance complicated (Wang et al., 2014). Furthermore, alteration to future climates also adds another layer of complexity that is important to consider but often neglected.

The most up-to-date global atmospheric Hg models suggest that there is less evasion of Hg⁰ from natural substrates than previously thought, leading to a future increase in Hg stored in substrate (Amos et al., 2015). Hg⁰ is considered to be immobile within mineral soils, suggesting that once it is deposited and sequestered into the substrate it is no longer available for reemission. It was proposed that the diel trends observed in the Hg flux only occurs in the surface layer (Obrist et al., 2014). The immobilisation of Hg within the substrate should not influence air-surface exchange as those metrological parameters shown to have the strongest influence on emissions rates mostly only interact with the surface layer. Solar radiation only penetrates the top 0.5 cm of a substrate and the influence of temperature decreases with depth. Therefore, this is where photo-reduction predominantly occurs (Carpi and Lindberg, 1997). Increases in air temperature and solar radiation intensity may increase the rate at which deposited Hg is reemitted before it can be transported below the penetration of solar radiation.

The projections developed here suggest an increase in Hg emissions from natural terrestrial sources under projected climate change scenarios. The most current Hg cycle models suggest that Hg emissions from anthropogenic emissions will be significantly reduced with implementation of the Minamata convention (Amos et al., 2015). Re-emissions from natural sources therefore have the potential to become an increasingly significant source of atmospheric Hg, particularly with respect to legacy Hg from historical Hg emissions (Hararuk et al., 2013). Only one-third of present day anthropogenic Hg emissions are believed to be from direct anthropogenic emissions, the remainder is comprised of historical emissions that are continually recirculated through the atmosphere. The long-time scales associated with Hg biogeochemical cycling suggest that while anthropogenic emissions may be reduced, the long lasting impacts of Hg cycling could be present decades to centuries into the future (Selin, 2014).

Background sites are primarily contributed to by atmospheric deposition, which is sequestered into the substrates before re-emission. A proportion of background Hg concentrations are also thought to originate from geogenic sources. However, it is unclear how much of this contributes to the overall air-surface exchange at these sites (Gustin et al., 2006). The diel cycling observed at the background sites suggests that atmospheric deposition experienced after nightfall replenishes the Hg substrate pool that is depleted during the day when volatilisation is taking place (Bahlmann et al., 2006). If the amount of atmospheric Hg available for deposition is reduced and emissions from terrestrial surfaces are increased by climate change, it is possible that the contribution of background sites to the global Hg cycle will be reduced. Laboratory studies have found that if the Hg substrate pool is not replenished, the influence of solar radiation is reduced over time, leading to a reduction in the overall Hg flux (Park et al., 2014).

Increased kinetic enhancement and increased water evaporation at higher temperatures will create a synergistic effect that will increase the photo-reduction of Hg and evasion from substrates, inciting a positive feedback until eventually the influence of background sites as natural sources is reduced (Lin et al., 2010). It is unclear as to what time scales this will occur over, particularly as it is uncertain what percentage of background sites are formed from geogenic sources or legacy anthropogenic sources.

As enriched substrates are formed from geogenic sources it is likely that they will increase flux magnitudes with increasing temperatures. These sites do not rely on atmospheric deposition to replenish the Hg pool reductions in atmospheric cycles and therefore, reduced deposition unlikely to significantly influence enriched sites contributions to the global cycle. Increased temperatures and solar radiation will increase photo-reduction of Hg⁺² and emission of Hg⁰ without the store being depleted leading to an overall increase in the contributions to the global cycle. This could cause a shift in the global Hg budget as emissions from background sites decrease and enriched sites increase.

The majority of models assume that the rate of deposition increasing as a result of anthropogenic emissions, leading to natural surfaces becoming an increased sink of Hg. As Hg is continually cycled between the surface and the atmosphere increasing sinks of Hg would lead to a greater availability of Hg to be emitted back into the atmosphere. This coupled with increased temperatures and solar radiation (the parameters used within the models) will result in an increase in the rate of Hg emitted into the atmosphere, creating a positive feedback. Understanding the roles of natural sources is important for determining the loads available for long term atmospheric transport and the assessment of large scale environmental impacts (Gustin et al., 2002).

7.2 Rainfall Implications with climate change

Two possible scenarios are proposed for changes to Hg flux in relation to precipitation. These scenarios are based on the limited data presented here, understanding of the role of soil moisture in Hg flux and current IPCC predictions. Global precipitation is predicted to increase between 1 and 3% $^{\circ}C^{-1}$ (IPCC, 2013a). This would lead to an overall increase in soil moisture content. This thermodynamic precipitation increase is found to be particularly prominent in the mid to high latitudes, where climate models predict increased water vapour in the lower troposphere and assumed fixed atmospheric flow patterns. An increase in both soil moisture and air temperature would mean an increase in the amount of Hg emitted from soils through increased evaporation. The rising temperatures increases the vapour pressure and the thermal motion of

the Hg compounds within the substrate, as well as enhancing water evaporation (Liang et al., 2014;Lin et al., 2010). However, if soil moisture is too high, Hg emissions will be suppressed as soil gas is inhibited by low diffusivity through the water (Briggs and Gustin, 2013). This is thought to occur when soil water content reaches 15%, Although this does vary depending on substrate type (Song and Van Heyst, 2005). This is when the evaporation of Hg transitions from being controlled by meteorological parameters to being limited by soil properties controlling the movement of water through the soil column (Briggs and Gustin, 2013).

Single rain events have been shown to have a significant influence on Hg fluxes. The time between rain events and rainfall intensities are predicted to increase in the future. Storm tracks are predicted to move poleward, further into the mid to high latitudes, and increase in intensity. On a seasonal timescale, minimums and maximums in rainfall are expected to increase, with the largest increases in the maximums. This is particularly prevalent during North American winters (IPCC, 2013a). With warmer temperatures and more evaporation, especially during summer when rainfall is lowest, substrates will become drier, allowing for greater storage of Hg⁰ within the soil pores (Gabriel et al., 2011). If there is more Hg available in the substrate for interstitial release, the initial peak in Hg flux as a result of increased intense rainfall is likely to be higher. However, as these spikes only last the duration of the rain event it is unlikely to have any significant influence on global Hg atmospheric cycles. The prolonged high emissions after the rain, due to increased soil moisture content, are more likely to have the greatest influence (Song and Van Heyst, 2005).

Chapter 8: Key findings and conclusion

Environmental parameters investigated here were found to have a significant relationship with Hg air-surface exchange at the study sites. Interactions between the parameters and the Hg fluxes varied depending on sites and classification. All sites displayed strong diel trends that mimicked closely those of soil and air temperature, net radiation and sensible heat. Background sites exhibited the strongest relationships with solar radiation and soil temperature. This is most likely a reflection of the photo-reduction that needs to occur at these sites to account for the observed fluxes. This was further substantiated by the deposition observed during night-time, indicating that Hg soil pools are depleted during the day when emissions are occurring and replenished during the night by atmospheric deposition. This implies that there is significant importance in understanding the role of whole ecosystem-air exchange in the global Hg cycle.

Enriched sites demonstrated a close relationship with all environmental parameters, suggesting that photo-reduction is a less dominant control on fluxes at these sites. The combination of diel trends and activation energies suggest that volatilisation was an important control, evidenced by the emission of Hg that still occurred at night. The amount of Hg available in the substrate at these enriched sites was sufficient enough to allow emissions to continue at night through volatilisation as the substrate released the heat stored during the day. Overall, the role of environmental parameters appears to be reasonably consistent across all sites, signifying that substrate concentrations influence long term trends while meteorological parameters influence diel and seasonal variability.

The application of Arrhenius to determine activation energies and the influence of temperature and solar radiation indicated that volatilisation was the dominant control on Hg flux. This is a reasonable assumption for enriched sites due to the high Hg concentrations found within the substrates. The activation energies calculated for the background sites were similarly low, suggesting that similar kinetic enhancement occurs across all sites. This, however, could not be corroborated in the literature, where it is commonly proposed that higher activations are required at sites with low Hg concentrations to promote the photo-reduction of Hg⁺² to Hg⁰ before it can be emitted from the substrate. This suggests that the processes of photo reduction may not be represented within the Arrhenius equation.

The role of precipitation at these sites seemed to be dominantly controlled by the interstitial release of Hg^0 . Lack of rainfall and soil moisture made it difficult to determine to a great extent the influence of rainfall had on Hg fluxes. The role of soil moisture most likely has some influence over the air surface exchange, particularly at other times of the year, when rainfall is

higher and as such needs to be taken into consideration. It is unlikely that these spikes in Hg emissions will have a great influence on Hg cycles. However, increases to soil moisture content due to increased rainfall are more likely to have a greater influence. However, as soil moisture content was not available for this research, no definitive conclusions can be drawn.

Flux adjustments indicated that with temperature increase it is likely there will be an increase in Hg emissions from natural substrates. Flux increases calculated here range between a 30 and 40% increase for a 1 to 2°C rise in temperature by 2050 and a 30 to 52% increase for temperature rise between 1 and 3.7°C. This is likely to significantly influence the role of natural sources in the global Hg budget. However, as has been demonstrated here, predicting changes to Hg emissions is inherently difficult, with multiple meteorological parameters influencing Hg exchange on varying timescales. Anthropogenic emissions are also expected to change in the future, likely resulting in an overall decrease in the amount of Hg available for deposition. This will result in dramatic alteration to the global Hg cycle, making understanding air-surface exchange important for determining the impacts this may have.

Enriched sites are liable to become a more significant source of Hg as atmospheric deposition does not appear to have a significant influence on the exchange rate. Increases in temperature and solar radiation will likely increase the rate at which Hg can be emitted from the substrate. Increases to soil moisture may also further enhance the role of enriched sites. Understanding how background sites may be altered is more complex. Background sites have been proposed to rely on atmospheric deposition to replenish Hg substrate stores. If this source were to be significantly reduced, as is predicted, it is possible that the contribution of background sites to the global Hg cycle will be reduced. Further research is required in order to understand what proportion of background sites comprises geogenic sources and what portion is legacy anthropogenic sources that have been deposited and re-emitted into the atmosphere.

The research presented here only explored air-surface exchange processes that occurred during summer. Therefore, it does not necessarily represent the influence of environmental parameters across the entire year. Seasonality has been found to be highly influential on Hg flux trends and therefore needs to be taken into consideration when predicting long-term trends. Lack of rainfall data also made it difficult to determine to the full extent how precipitation may influence air-surface exchange. Not all of the influencing environmental parameters were able to be explored here, such as soil pH, CO₂ flux and soil content and soil moisture, as well as turbulent diffusion, atmospheric stability and relative humidity. All of which have been found to exhibit influence on Hg flux trends. The model used to predict future Hg fluxes only focused on one meteorological parameter considered to influence air-surface exchange. Air temperature was

used to make these predictions as it was considered to have the most reliable future climate predictions. As has been shown here and in other studies, more than one parameter influences Hg emissions and therefore needs to be taken into consideration. Solar radiation has the largest influence and therefore should be taken into greater consideration.

A number of uncertainties still exist into the role of air-surface exchange in the global Hg cycle. As such further research is required if these complex processes are to be adequately incorporated into global Hg atmospheric models. A particular focus needs to be given to how climate change may alter current prediction of how biogeochemical cycles will change in the future. An important aspect of this will be understanding how solar radiation will be altered in the future and the impact it is likely to have on Hg air-surface exchange. Further consideration also needs to be given to how and why precipitation influences Hg exchange and the impacts this will have on regional and global scales.

Background sites appear to be a great unknown and as such further research is needed to understand the sources that create background sites and the implication of this if anthropogenic emission were to be significantly reduced over the next few decades. Consideration also needs to be given to different terrestrial surfaces. Vegetated surfaces are vastly underrepresented throughout the literature but important for understanding net ecosystem exchange. Furthermore, there is extensive disparity between the numbers of studies undertaken in the Northern Hemisphere compared to the Southern Hemisphere. Comparison of Northern and Southern Hemisphere sources is important for understanding global atmospheric transport and accurate balancing of the global Hg budget.
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Appendix 1

Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Air T	0.491	-0.085	0.013	0.374	0.213	-0.664	0.355
soil T	0.459	-0.145	0.257	0.53	-0.448	0.35	-0.314
Rn	0.47	0.267	0.045	-0.253	0.117	0.526	0.593
Н	0.464	0.27	-0.038	-0.275	0.457	-0.049	-0.651
Hg amb	0.036	-0.586	-0.575	0.209	0.411	0.334	-0.009
ln flux	0.333	-0.41	-0.264	-0.582	-0.517	-0.21	-0.019
soil Hg	-0.027	-0.561	0.728	-0.239	0.308	0.041	0.02
Eigenvalue	3.2086	2.0188	0.564	0.4383	0.3904	0.2711	0.1088
Proportion	0.458	0.288	0.081	0.063	0.056	0.039	0.016
Cumulative	0.458	0.747	0.827	0.89	0.946	0.984	1

Table 4.2.1 Principle component correlation matrix for all sites using all measured environmental parameters

Table 4.2.2 Principle component correlation matrix for enriched sites using all measured environmental parameters

Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Air T	0.466	0.069	-0.045	0.263	0.487	-0.548	-0.41
soil T	0.455	-0.056	-0.178	0.423	0.304	0.518	0.468
Rn	0.475	-0.001	0.056	0.014	-0.49	0.418	-0.597
Н	0.47	0.041	0.106	-0.034	-0.543	-0.474	0.496
Hg amb	-0.11	-0.587	0.69	0.407	-0.02	-0.033	-0.019
ln flux	0.313	-0.549	0.02	-0.721	0.274	0.056	0.049
Soil Hg	-0.139	-0.586	-0.69	0.256	-0.245	-0.168	-0.083
Eigenvalue	4.1511	1.203	0.9788	0.416	0.1971	0.0355	0.0184
Proportion	0.593	0.172	0.14	0.059	0.028	0.005	0.003
Cumulative	0.593	0.765	0.905	0.964	0.992	0.997	1

Table 4.2.3 Principle component correlation matrix for background sites using all measured environmental parame	eters
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Variable	PC1	PC2	PC3	PC4	PC5	PC6	PC7
AirT	0.525	-0.006	-0.13	-0.246	-0.366	0.711	-0.084
soilT	0.294	-0.43	-0.202	-0.646	-0.06	-0.495	0.147
Rn	0.408	-0.327	0.485	0.066	0.68	0.156	-0.008
Н	0.47	0.005	0.404	0.439	-0.522	-0.383	0.054
Hg Amb	-0.299	-0.549	0.188	-0.003	-0.237	0.042	-0.718
ln Flux	0.195	-0.398	-0.684	0.565	0.126	-0.012	-0.001
Soil conc	-0.35	-0.498	0.201	0.074	-0.235	0.275	0.673
Eigenvalue	3.3063	2.2193	0.6814	0.6316	0.1009	0.0515	0.0089
Proportion	0.472	0.317	0.097	0.09	0.014	0.007	0.001
Cumulative	0.472	0.789	0.887	0.977	0.991	0.999	1