



Statistical assessment of atmospheric mercury passive samplers

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“Therefore, I tell you, whatever you ask for in prayer, believe that you have received it, and it will be yours.” Mark 11:24 NIV

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“Difficult roads often lead to beautiful destinations.” Zig Ziglar

ABSTRACT

South Africa has been ranked among the top ten mercury (Hg) emitters globally, with emissions from coal-fired power plants being the most significant contributor. The expansion of atmospheric Hg measurement networks in southern Africa is vital within the global context but is constrained by high costs and logistics. Passive air samplers were developed to address these issues and expand atmospheric monitoring networks. A commercially available passive sampler widely used for atmospheric Hg monitoring is the Mercury Passive Air Sampler (*MerPAS*[®]). Therefore, this study aimed to statistically evaluate the performance of these samplers in the unique South African environment by comparing Hg concentrations determined with *MerPAS*[®] with active *in situ* atmospheric Hg sampling conducted in this region. Measurements were conducted at the Welgegund atmospheric monitoring station, considered one of Africa's most comprehensively equipped atmospheric measurement sites. Hg concentrations measured with *MerPAS*[®] were derived for different sampling rates (SR), i.e., the original SR (OSR) provided by the supplier, an adjusted original SR (AOSR), a recalibrated SR (RSR) derived from active *in situ* measurements, and an adjusted recalibrated SR (ARSR). Hg levels calculated utilising the OSR and AOSR were generally higher than the active *in situ* measurements, while Hg concentrations determined with the RSR and ARSR were lower and closer to the atmospheric Hg levels determined with the active *in situ* samplers. ANOVA, *t*-test, linear regression and Bland-Altman analysis revealed, in general, good agreement between active *in situ* measurements and Hg levels derived from *MerPAS*[®] utilising the different SRs. Overall, Hg concentrations derived from the recalibrated SRs indicated better comparisons between active *in situ* measurements and *MerPAS*[®]. However, considering that these samplers were developed as a low-cost alternative to be deployed at sites that are logistically difficult to access, it is recommended that the AOSR be used at sites in southern Africa where *MerPAS*[®] is deployed. Similar seasonal trends were observed for atmospheric Hg concentrations determined with *MerPAS*[®] utilising the AOSR and active *in situ* measurements, with the highest concentrations determined in winter. Finally, a brief assessment of a manual active sampler also revealed good agreement with active *in situ* measurements.

Keywords: gaseous elemental mercury, passive sampling, *MerPAS*, statistical analysis, temporal assessment

ABBREVIATIONS

AMNet	Atmospheric Monitoring Network
ANOVA	Analysis of variance
AOSR	Adjusted original sampling rate
ARSR	Adjusted recalibrated sampling rate
CI	Confidence interval
ECCC-AMM	Environment and Climate Change Canada Atmospheric Mercury Monitoring Network
GEM	Gaseous elemental mercury
GMOS	Global Mercury Observation System
GOM	Gaseous oxidised mercury
Hg	Mercury
a.s.l	above sea level
MDL	Method detection limit
<i>MerPAS</i> ®	Mercury Air Passive Sampler
MND	Mean normalised difference
OSR	Original sampling rate
PAS	Passive air sampler
PBM	Particle-bound mercury
PQL	Practical quantification limit
RSD	Relative standard deviation
RSR	Recalibrated sampling rate
SAMNet	South African Mercury Network
SR	Sampling rate

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CHAPTER 1 INTRODUCTION

This chapter provides a brief discussion of the importance of monitoring atmospheric mercury (Hg) in South Africa. An overview of the measurement methods used to estimate atmospheric Hg concentrations is presented. Finally, the general aim and specific objectives, as well as a dissertation outline, are provided.

1.1 Background and motivation

In the last 20 years, South Africa has been ranked among the top ten mercury (Hg) emitters globally (Pacyna *et al.*, 2006), with emissions from coal-fired power plants being the most significant contributor (Masekoameng *et al.*, 2010). According to Zhao *et al.* (2019), the Hg contents in coal from South Africa (0.2 mg/kg) were higher than the world average Hg content (0.1 mg/kg). South Africa became a signatory of the Minamata Convention on Mercury in 2013, which is a global treaty aimed at reducing mercury emissions worldwide (Scott & Mdluli, 2012). Since then, Hg has been identified as a pollutant of national future concern in South Africa (South Africa, 2018).

Given that the atmosphere represents the primary pathway for the global distribution of Hg (Driscoll *et al.*, 2013; Schroeder & Munthe, 1998; Selin, 2009), the monitoring of atmospheric Hg is essential in achieving the above-mentioned objectives. Existing atmospheric Hg monitoring networks, such as the Global Mercury Observation System (GMOS), the Atmospheric Monitoring Network (AMNet), and the Environment and Climate Change Canada Atmospheric Mercury Monitoring Network (ECCC-AMM), have greatly improved the understanding of atmospheric Hg (Li & Lee, 2014), while it also contributed to the development of global atmospheric dispersion models (Lin *et al.*, 2006) such as GEOS-Chem, GLEMOS, GEM-MACH-Hg and ECHMERITRADM (Travnikov *et al.*, 2017). However, the spatial coverage of these networks is limited, especially for the southern hemisphere and Africa (Li & Lee, 2014), which lead to large gaps in understanding atmospheric Hg cycling. Therefore, it is globally acknowledged that further network expansion is pivotal (Pirrone *et al.*, 2013; Sprovieri *et al.*, 2017).

The expansion of atmospheric Hg measurement networks in Africa, in particular, is constrained by high costs, logistics (e.g. availability of electricity and specialised materials), as well as underdeveloped capacity and expertise (e.g. technical training) (Huang *et al.*, 2014; Jaars *et al.*, 2014; McLagan, Mazur, *et al.*, 2016; Pirrone *et al.*, 2013).

Addressing this deficiency in atmospheric Hg network coverage in Africa is crucial to our global understanding of atmospheric Hg distribution and the assessment of its impacts. In order to overcome these limitations in spatial coverage of atmospheric Hg monitoring, an alternative approach has been followed through the development of passive air samplers (PASs), which have the potential to significantly improve the spatial resolution of atmospheric Hg measurements (Huang *et al.*, 2014; McLagan, Mazur, *et al.*, 2016; Pirrone *et al.*, 2013). These passive samplers offer a range of benefits, which include lower costs and no electricity requirements, and can be deployed in large numbers, especially in the afore-mentioned regions. However, PAS does have certain limitations. One deficiency is the relatively longer time required for the collection of sufficient analyte, which limits the temporal resolution of the data obtained. Additionally, the measurement of other states than gaseous elemental mercury (GEM), such as gaseous oxidised mercury (GOM) and particulate-bound mercury (PBM) with PAS, remains challenging.

In passive sampling, the gaseous analyte diffuses through a barrier into a chamber at a known rate into the specially designed sampler. The analyte is trapped inside the chamber on a sorbent material, which is analysed after the deployment period. One commercially available PAS widely used in Hg monitoring is the Mercury Passive Air Sampler (*MerPAS*®) developed by Tekran® (McLagan, Mitchell, *et al.*, 2016). This sampler has a unique design that utilises sulphur-impregnated activated carbon as the sorbent material and incorporates a diffusive barrier to control the sampling rate. It also features a protective shield, allowing deployment in outdoor environments for extended periods. The *MerPAS*® method has been evaluated in North America, Asia, Australia and Europe at atmospheric monitoring sites located in different types of regions with variable atmospheric Hg concentrations (e.g. Jeon *et al.*, 2020; McLagan, Mitchell, *et al.*, 2018). However, the performance of these samplers was not evaluated in Africa in any of these studies. Therefore, the aim of this study was to statistically evaluate the accuracy, precision and reliability of *MerPAS*® (McLagan, Mitchell, *et al.*, 2016), specifically in the unique South African environment, through a comparison of Hg concentrations determined with these samplers with well-established active *in situ* atmospheric Hg sampling conducted in this region. *MerPAS*® was deployed at a comprehensively equipped regional atmospheric monitoring station in the South African interior. This station provides a reliable benchmark for comparison. Measurements were conducted through the recently established South African Mercury Network (SAMNet), which aims to expand the spatial resolution of atmospheric Hg measurements conducted in this

region. The use of *MerPAS*[®] is crucial to the successful rollout and establishment of this expanded atmospheric Hg monitoring network. In addition to the detailed statistical comparison between *MerPAS*[®] and active *in situ* measurements, atmospheric Hg concentrations determined with a newly developed manual active atmospheric Hg sampler are also briefly explored.

1.2 Aim and objectives

The aim of this study was to statistically evaluate the performance of *MerPAS*[®] through comparison with atmospheric Hg concentrations measured with active *in situ* samplers. The specific objectives are as follows:

- i. To deploy *MerPAS*[®] samplers, active *in situ* samplers, and manual active samplers concurrently at the Welgegund measurement site, which is a regional atmospheric monitoring station, in order to monitor atmospheric Hg concentrations.
- ii. To determine atmospheric Hg concentrations using *MerPAS*[®] at Welgegund.
- iii. To statistically assess the precision and accuracy of *MerPAS*[®] atmospheric Hg concentration measurements alongside active *in situ* atmospheric Hg concentration measurements.
- iv. To identify a temporal pattern of atmospheric Hg concentrations.

1.3 Dissertation outline

This dissertation comprises five chapters. Following this introduction, Chapter 2 looks at important concepts associated with Hg, which include its history, speciation, biogeochemical cycle, and health effects. This section is also concerned with the measurement technique of passive sampling. Chapter 3 provides a description of the measurement station, as well as the main experimental and statistical methods employed in this study. Chapter 4 presents the results of the atmospheric Hg concentrations estimated from the three Hg measurement methods. These datasets are statistically evaluated to observe the performance of *MerPAS*[®] when compared to active *in situ* sampler. Chapter 5 provides the main conclusions obtained from the results based on the aim and objectives of this study. It further gives suggestions for future research.

CHAPTER 2 LITERATURE REVIEW

This chapter provides a general introduction to the history and speciation of mercury. The biogeochemical cycle of mercury is discussed in terms of sources, transport, chemistry, and deposition. Thereafter, the health effects of Hg are presented. Lastly, the theory of passive sampling together with the global networks of passive sampling are presented.

2.1 Introduction to mercury

2.1.1 History of Hg

Elemental mercury (Hg) is naturally occurring in the Earth's crust. Hg exists in abundance as cinnabar (HgS) and has less abundant minerals such as Livingstonite, Tiemannite, and calomel (Bank, 2012; Jaishankar *et al.*, 2014). Mercury is an odourless liquid at 25 °C, and when heated, converts into colourless and odourless gas (Ariya *et al.*, 2015; Jaishankar *et al.*, 2014). It is liquid at room temperature because of the relativistic contraction of the 6s orbitals that do not participate in metal-metal bonds, which results in weak Hg-Hg bonds (Norrby, 1991; Parsons & Percival, 2005). Hg is a d-block element, relatively inert and has chalcophile (sulphur loving) affinities (Ariya *et al.*, 2015; Fitzgerald & Lamborg, 2007; Parsons & Percival, 2005; Schroeder & Munthe, 1998). It has seven stable isotopes and 35 unstable radioactive isotopes and isomers. Hg has a melting point of -39°C, boiling point of 357°C, high surface tension, low electrical resistance, and is a conventional superconductor (Bank, 2012; Parsons & Percival, 2005; Schroeder & Munthe, 1998). Mercury is a versatile metal that has numerous unique applications in the world.

The discovery and uses of mercury and cinnabar date to prior the 15th century. Mercury and cinnabar are commonly found in Almaden, Spain and the Sizma district, Turkey (Bank, 2012). Cinnabar is a bright red mineral made of mercury and sulphur. It is the primary ore mineral of mercury that was used as a pigment (vermillion) to decorate Egyptian tombs and synthesise cosmetic products. During the Neolithic Age, cinnabar was used to preserve human bones in Italy and Spain (Parsons & Percival, 2005). In the 1st century, cinnabar was employed to yield mercury through the process of distillation, while mercury was used to extract alluvial gold from sediments as an amalgam (Bank, 2012; Parsons & Percival, 2005). Europeans used mercury to gild religious figures and

cathedral interiors, as well as for mirror backing in the 18th century (Bank, 2012). Over the past centuries, the application of mercury in science, industry, medicine and agriculture has increased. These applications include the production of barometers, thermometers, dental amalgams, and chlor-alkali products (Parsons & Percival, 2005; Zhao *et al.*, 2022).

2.1.2 Hg speciation

Mercury is present in the environment in various chemical species of metallic, inorganic and organic compounds (Bhagi & Chatwal, 2009). Hg can exist in three oxidation states, which are: 0 (elemental mercury, Hg^0), +1 (mercurous, Hg_2^{2+}) and +2 (mercuric, Hg^{2+}). Hg^0 and Hg^{2+} are the most important species in the environment, whereas there is a possibility that Hg_2^{2+} does not exist (Schroeder & Munthe, 1998; Segade *et al.*, 2011). Metallic Hg^0 is highly volatile, susceptible to oxidation, relatively stable in the environment, and has low solubility in water (Carpi, 1997; O'Connor *et al.*, 2019).

In the environment, Hg^0 reacts with halogens such as chlorine and bromine and other elements to form inorganic mercury compounds (Risher & De Rosa, 2007). The inorganic species of mercury are the mercurous ions and mercuric ions, such as HgS (mercury sulphide), HgO (mercury oxide), HgCl_2 (mercuric chloride), HgSO_4 (mercuric sulphate), and $\text{Hg}(\text{NO}_3)_2$ (mercuric nitrate) (Park & Zheng, 2012; Vostal & Clarkson, 1973). The mercuric ion is reactive and soluble in water, it can bind to several ligands in water bodies or particles in the atmosphere. On the other hand, mercurous ions partake in a disproportionation reaction where it is simultaneously oxidised and reduced into elemental mercury and mercuric ions due to having a short half-life (O'Driscoll *et al.*, 2005). HgCl_2 is an example of a soluble inorganic compound that is extremely toxic, while HgS and HgO are the less toxic compounds because they are insoluble in water (Bank, 2012; Park & Zheng, 2012).

Connell (2005) has provided a definition of organic mercury compounds as: “compounds having metal-carbon bonds, where the carbon atom is part of an organic group”; for example, methyl mercury (MeHg , CH_3Hg), dimethyl mercury (Me_2Hg , $\text{C}_2\text{H}_6\text{Hg}$), ethyl mercury ($\text{C}_2\text{H}_5\text{Hg}^+$), and phenyl mercury ($\text{C}_6\text{H}_5\text{Hg}$) (O'Driscoll *et al.*, 2005). These organic compounds can bioaccumulate in the environment, resulting in high levels of Hg in aquatic animals (Carpi, 1997; O'Driscoll *et al.*, 2005). The biological, chemical, and

physical conditions existent in nature determine the type of Hg species to be formed in the environment (O'Driscoll *et al.*, 2005).

2.2 Hg biogeochemical cycle

It is important to understand the sources, transport, transformations, and removal processes of Hg in the atmosphere (Huang *et al.*, 2014; Schroeder & Munthe, 1998). In the surface atmospheric boundary layer, Hg occurs predominantly as gaseous elemental mercury (GEM, Hg^0) with less than 1% being gaseous oxidised mercury (GOM, Hg^{2+}), and particle-bound mercury (PBM, Hg_p) (Gustin *et al.*, 2011). Hg^0 and Hg^{2+} are collectively referred to as total gaseous mercury (TGM) (Gao *et al.*, 2017; Luo *et al.*, 2021).

After entering the environment, Hg partakes in a complicated biogeochemical cycle that can be defined as a model that describes the movement of a chemical element in different compartments of the environment (Bhagi & Chatwal, 2009; Liu *et al.*, 2012). In Figure 2-1, the biogeochemical transformations of mercury in the environment are shown. Hg^0 is emitted from natural and anthropogenic sources, and it can traverse long distances in the atmosphere because it has a lifetime of approximately one year (Gonzalez-Raymat *et al.*, 2017; Pandis & Seinfeld, 2016). Subsequently, Hg^0 is oxidised and removed from the atmosphere by particle and gas phase dry deposition and wet scavenging (Driscoll *et al.*, 2013). In the aquatic and soil environments, Hg is primarily present in an oxidised (Hg^{2+}) form, which can be converted into inorganic and organic Hg compounds (see section 2.1.2) (Liu *et al.*, 2012).

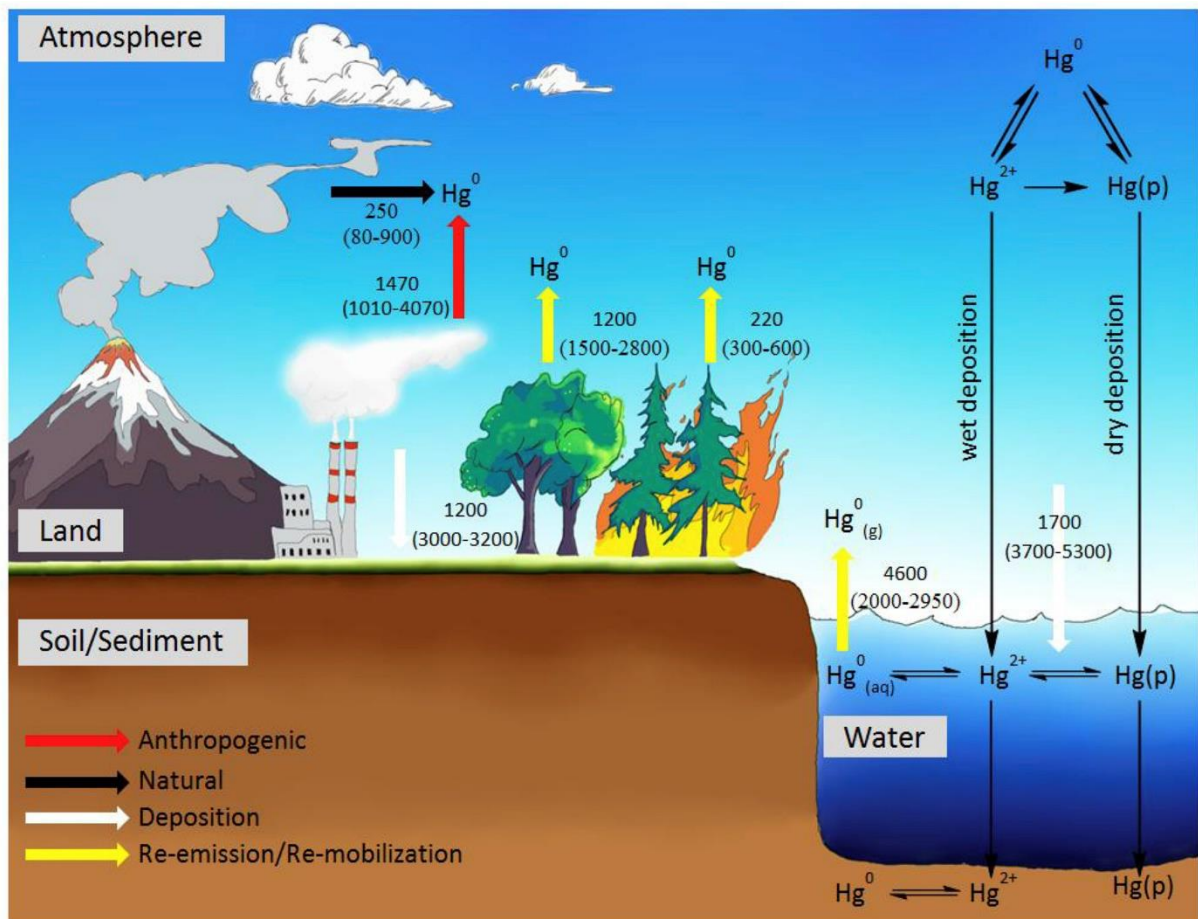


Figure 2-1: Conceptual diagram of mercury cycling in the atmosphere and atmospheric interfaces. The recent global gaseous elemental mercury fluxes and global mercury budget estimates are indicated in brackets. The red arrow represents anthropogenic sources, the black arrow represents natural sources, the white arrow represents deposition, and the yellow arrow represents the re-emission or re-mobilisation of Hg (Gonzalez-Raymat *et al.*, 2017).

2.2.1 Sources and emissions

Atmospheric mercury is emitted from two categories, i.e., primary and secondary sources (Nipen *et al.*, 2022; Szponar *et al.*, 2020). The former consists of natural and anthropogenic sources, while the latter includes the re-emission and re-mobilisation of legacy Hg in the ecosystem (Bank, 2012; Driscoll *et al.*, 2013; UNEP, 2013a). Driscoll *et al.* (2013) determined that a range of 6500 to 8200 Mg/yr of total global Hg is emitted into the atmosphere. Evidence suggests that Africa is a major contributor of global Hg emissions, with an estimated annual increase of 1.3% in mercury released during the 2010-2015 period (Streets *et al.*, 2019).

2.2.1.1 Natural sources

Emissions of atmospheric mercury originate from natural sources. The term natural emission sources refer to the natural biotic and abiotic factors that influence the release or transformation of geologically-bound Hg in the atmosphere (Ebinghaus, Tripathi, *et al.*, 1999; Lindberg *et al.*, 2007). Hg is released into the atmosphere from primary natural sources mainly as gaseous elemental mercury (GEM) (Gworek *et al.*, 2020; Lindberg *et al.*, 2007; Liu *et al.*, 2012; Schroeder & Munthe, 1998).

Various natural sources, such as volcanic activity, wildfires, evasion from soils and vegetation, and oceanic emissions contribute to the natural emission of mercury into the atmosphere (Gonzalez-Raymat *et al.*, 2017; Lindqvist, 1985; Qin *et al.*, 2019). Natural sources account for about 4600 to 5300 Mg/yr of total global Hg emissions (Driscoll *et al.*, 2013). Pirrone *et al.* (2010) highlight that volcanoes and geothermal activities release approximately 90 Mg of mercury annually. The process of tectonic movements and magmatic activity during volcanic eruptions result in the emission of Hg in both the gas phase (Hg^0 and Hg^{2+}) and the particle phase (Hg_p) (Gonzalez-Raymat *et al.*, 2017; Gworek *et al.*, 2020). It is postulated that oceanic emissions are a major component of all natural emissions (Bank, 2012; Selin *et al.*, 2007). Moreover, global Hg emissions from the oceans, biomass burning, and evasion after Hg depletion events are estimated to be 2682, 675, and 200 Mg/yr, respectively (Pirrone *et al.*, 2010).

2.2.1.2 Anthropogenic sources

Mercury is naturally present in the environment; however, anthropogenic sources have substantially increased atmospheric mercury emissions by a factor of three (Bank, 2012; Selin, 2009). Anthropogenic sources is defined by Ebinghaus, Tripathi, *et al.* (1999) as “the mobilisation or release of geologically bound mercury by man’s activities, with mass transfer of mercury to the atmosphere.” Coal combustion, mining, industrial activities, waste incineration, and cement production are the most important sources of anthropogenic emissions (Ebinghaus, Tripathi, *et al.*, 1999; Qin *et al.*, 2019; UNEP, 2013a). A further definition of anthropogenic sources is given by Lindberg *et al.* (2007), who state that “the direct emissions of Hg from current human activities.”

In 2005, it was reported that approximately 1930 tonnes of global atmospheric Hg were released from human activities (Pacyna *et al.*, 2010). Over the past two decades, Hg

emissions in North America and Europe have decreased because of the implementation of strict regulations and the control of emissions of Hg. In contrast, emissions of Hg in Asia and Africa are increasing due to the usage of coal and economic growth (Bank, 2012; Kim & Zoh, 2012; Steffen *et al.*, 2008). Pacyna *et al.* (2010) reported that global Hg emissions were from coal combustion (45%), artisanal and small-scale gold mining (18%), and industrial gold production (5-6%). Masekoameng *et al.* (2010) reported that South Africa accounted for more than 75% of Hg emissions from anthropogenic sources from 2000 to 2006. Figure 2-2 illustrates the global trends for the period 2010 to 2015 for the four sectors driving anthropogenic Hg emissions. An overall growth was observed in the fossil fuel combustion, industrial metals extraction, and ASGM sectors at 2.0%, 3.0%, and 1.3% per year, respectively (Streets *et al.*, 2019). However, mercury production and use are continuing to decline rapidly at 4.1% per year. This results from phasing out the use of Hg in electrical devices and industrial processes (Streets *et al.*, 2019).

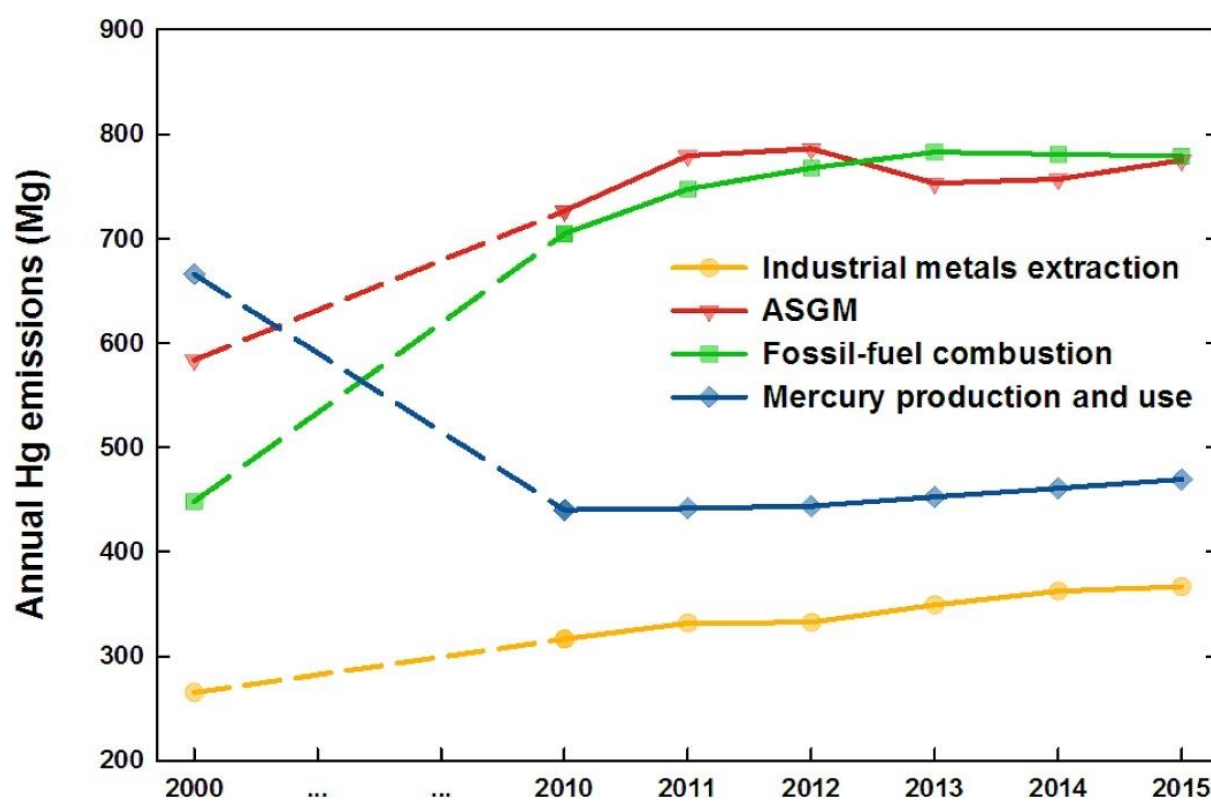


Figure 2-2: Global mercury (Mg/yr) emissions from industrial metals extraction (yellow circle), ASGM (red triangle), fossil-fuel combustion (green square), and mercury production and use (blue diamond) sources for the period 2010-2015 (Streets *et al.*, 2019).

2.2.1.3 Re-emissions

Re-emission of previously deposited mercury from natural or anthropogenic sources represents about 60% of atmospheric Hg emissions (UNEP, 2013a; Zhang *et al.*, 2017). The re-emission process is influenced by factors such as sunlight and temperature (Liu *et al.*, 2012). This process involves the conversion of inorganic and organic species of Hg to elemental mercury (UNEP, 2013a). For instance, biomass burning is considered to volatilise Hg stored in terrestrial ecosystems to the air (Budnik & Casteleyn, 2019; Ebinghaus, Tripathi, *et al.*, 1999; Lindberg *et al.*, 2007). The processes of biomass burning and rain re-mobilise Hg that was previously deposited on the soils and sediments to enter or re-enter the biogeochemical cycle of Hg (UNEP, 2013a). Similarly, re-emissions from the oceans contribute a significant amount of 2400 Mg/yr and land with 1500 Mg/yr (Selin *et al.*, 2007). It is challenging to quantify the total amount of present emissions that are natural against anthropogenic (Bank, 2012). Therefore, modelling approaches are applied to estimate re-emission levels of Hg (UNEP, 2013a).

2.2.2 Transport

Once emitted into the air, Hg can traverse over long distances on local, regional, and global scales (Kim & Zoh, 2012). The atmospheric transport of Hg occurs in the planetary boundary layer close to the Earth's surface and in the free troposphere. The nature of Hg atmospheric transport is influenced by the chemical speciation and the long residence time of Hg in the atmosphere (Liu *et al.*, 2012). Hg^{2+} and Hg_p are highly reactive and soluble in water. Consequently, they are readily removed by wet and dry deposition from the atmosphere owing to their short residence times (Belelie *et al.*, 2019; Carpi, 1997).

On the other hand, Hg^0 can travel aurally in the atmosphere for approximately one year due to its low reactivity and solubility (section 2.1.2) (Schroeder & Munthe, 1998). Hence, Hg^0 can be transported in air masses over long distances between the hemispheres and remote regions. The differences in the residence time of Hg species can be attributed to the different concentrations of the main Hg oxidants such as ozone, hydroxyl radical, and reactive halogen species that affect the transformation of Hg in the biogeochemical cycle (Beckers & Rinklebe, 2017).

2.2.3 Chemistry

Numerous studies have investigated the chemistry of atmospheric mercury by employing models such as GEOS-Chem (for example, Horowitz *et al.*, 2017; Shah *et al.*, 2021). The chemistry of mercury in the atmosphere and environment is complex and is influenced by oxidation and reduction processes, as shown in Figure 2-3 (Driscoll *et al.*, 2013; Sonke *et al.*, 2023). Gao *et al.* (2022) and Shah *et al.* (2021) demonstrated that Hg^0 (elemental mercury) transforms to Hg^{II} (divalent mercury) through redox pathways, which are driven by sunlight and atmospheric oxidants such as ozone (O_3) and hydroxyl (OH) radicals in the atmosphere.

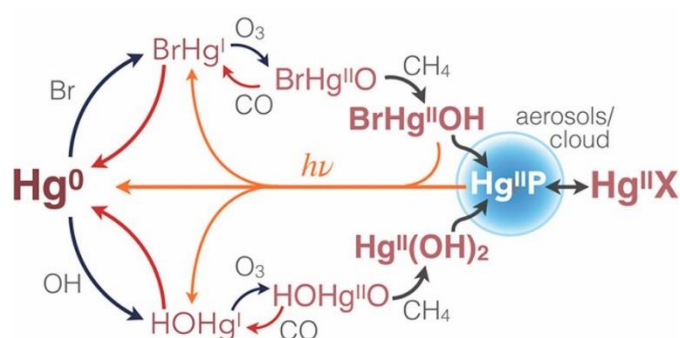


Figure 2-3: Major atmospheric mercury redox pathways. Hg^0 denotes elemental mercury, Hg^{II} denotes divalent mercury, $\text{Hg}^{\text{II}}\text{P}$ represents particulate Hg^{II} , and $\text{Hg}^{\text{II}}\text{X}$ represents the gas-phase Hg^{II} species that volatilise from $\text{Hg}^{\text{II}}\text{P}$ (Shah *et al.*, 2021).

2.2.3.1 Oxidation of Hg^0

Elemental mercury participates in gas-phase and aqueous-phase oxidation reactions with ozone (Lindberg *et al.*, 2007). However, Hg^0 cannot partake in any direct photochemical oxidation, because it lacks solar radiation of 290 nm wavelength that can reach the troposphere. The gas-phase reaction encompasses oxidising species that can aid the oxidation of Hg^0 . These include reactive halogens, O_3 , NO_3 , H_2O_2 , and OH (Gonzalez-Raymat *et al.*, 2017). OH radicals are formed from four sources, which are: the reaction of oxygen atoms produced from the photolysis of O_3 with water molecules, the reaction of hydroperoxyl radicals with nitric oxide, the photolysis of nitrous acid, and the photolysis of hydrogen peroxide. The above-mentioned photolysis reactions take place in the presence of solar radiation. Nitrogen trioxide (NO_3) is produced through the oxidation of O_3 by NO_2 during the night (Connell, 2005). O_3 is formed in the troposphere from photochemical reactions with hydrocarbons and NO_2 . Hydrogen peroxide (H_2O_2) is

produced from formaldehyde's photooxidation and the hydroperoxyl radical's self-reaction (Gonzalez-Raymat *et al.*, 2017). Furthermore, sea salt aerosols autocatalytically produce other gaseous reactive halogen species such as Cl, ClO, Br, and BrO (Liu *et al.*, 2012).

In previous studies on the oxidation of Hg^0 to Hg^{II} in the air, it was postulated that O_3 and OH radicals were the principal oxidants of mercury (Bank, 2012). Other writers have argued that Br may be the primary oxidant of mercury (Bank, 2012; Driscoll *et al.*, 2013). For instance, Brooks *et al.* (2006) observed a direct relationship between the reactive gaseous mercury (RGM) and BrO, whereas O_3 decreased with increased Br during an atmospheric mercury depletion event. The gas-phase oxidation reaction of Hg^0 to Hg^{II} involves a two-stage process, according to Eq. (2-1, 2-4), with competing reactions Eq. (2-2, 2-3) (Horowitz *et al.*, 2017; Shah *et al.*, 2021):



Where M is a molecule of air, Br is the first stage Hg^0 oxidant, and OH is the second stage Hg^{I} oxidant. In the troposphere, the Hg^{I} intermediate has a lifetime of about 60 s (Horowitz *et al.*, 2017). It is believed that Br and OH oxidise Hg^0 to Hg^{I} at similar rates, with ozone acting as a principal oxidant of Hg^{I} to Hg^{II} (Figure 2-3) (Shah *et al.*, 2021). The reaction between Hg^0 and Br is barrierless and exothermic. Similarly, the second oxidation pathway initiated by OH of Hg^0 to Hg^{II} is exothermic and fast and follows a two-stage process (see Figure 2-3). $\text{BrHg}^{\text{II}}\text{OH}$ and $\text{Hg}^{\text{II}}(\text{OH})_2$ are the primary product of the oxidation of elemental Hg to divalent Hg (Shah *et al.*, 2021).

Mercury can exist in liquid states such as clouds, fog, and raindrops. The end-product of the dissolved Hg is found in the ionic form of Hg^{2+} (Gworek *et al.*, 2017). The main oxidising species of aqueous-phase oxidation reactions are OH, O_3 , and aqueous halogen species such as Br_2 , HOBr, and HOCl (Gonzalez-Raymat *et al.*, 2017). The aqueous-phase oxidation process is affected by Henry's law, which states that "at a given pressure and temperature, a liquid, which is water in the present case, contains a certain amount of dissolved gases" (Gworek *et al.*, 2017). The solubility of atmospheric Hg is

directly proportional to pressure and inversely proportional to temperature. Aqueous OH and O₃ are likely to be scavenged from gaseous OH (Henry's constant = 25 M/atm at 298 K) and O₃ (Henry's constant = 0.013 M/atm at 298 K), respectively (Liu *et al.*, 2012). Halogen species such as aqueous Br₂ and HOBr have slow oxidation rates, hindering their participation in the aqueous-phase oxidation with Hg⁰. In contrast, at night, a few aqueous chlorine species, such as HOCl, can oxidise Hg⁰ to Hg^{II} (Gonzalez-Raymat *et al.*, 2017).

2.2.3.2 Reduction of Hg^{II}

Hg^{II} compounds are highly water-soluble because of their lower Henry's constant, and some species, such as HO₂, have extremely low gas-phase concentrations. Therefore, the reduction of Hg^{II} to Hg⁰ primarily occurs in the clouds, and the gas-phase process is negligible (Gonzalez-Raymat *et al.*, 2017). Reduction of Hg^{II} to Hg⁰ is associated with ligands, which include sulphite (SO₃²⁻). SO₃²⁻ and dissolved Hg^{II} create strong complexes since sulphite is a soft ligand (Liu *et al.*, 2012). Consequently, the reduction of Hg^{II} to Hg⁰ by SO₃²⁻ can be observed in Eq. (2-5) (Gworek *et al.*, 2017):



There are photochemical reactions that participate in the reduction of Hg^{II} complexes. A two-step reduction mechanism of aqueous Hg^{II} by HO₂ is shown in Eq. (2-6, 2-7). Hg^{II} can be reduced to Hg⁰ through the ligand-to-metal charge transfer mechanism, where [Hg(OH)]* in the presence of solar radiation becomes unstable and loses an electron to Hg(OH)_{aq}, causing the reduction to elemental Hg (Gonzalez-Raymat *et al.*, 2017; Liu *et al.*, 2012). Dicarboxylic acids and hydroperoxyl radicals also take part in the reduction of Hg^{II} in a two-step reaction.



2.2.4 Deposition

In Figure 2-1, Hg enters the ecosystems by dry and wet deposition, after undergoing numerous physical and chemical transformations in the atmosphere (Lin & Pehkonen, 1999; Sonke *et al.*, 2023). Wet and dry deposition removes Hg⁰ slowly because Hg⁰ has

a low dry deposition of about 0.01 cm^{-1} over land and has low solubility in water. In comparison, Hg^{II} species are rapidly removed from the air because they are water-soluble (Pandis & Seinfeld, 2016). Dry deposition is defined as the direct deposition of gaseous and particulate mercury onto surfaces without precipitation (Wu *et al.*, 2024). Dry deposition can occur through the subsidence of gaseous particles containing Hg and direct gas-phase deposition onto surfaces.

Moreover, the dry deposition process is known to be enhanced by vegetation (Lindberg *et al.*, 2007). Dry deposition of Hg^0 is regarded as a sink of Hg, because the diurnal cycle of Hg^0 and RGM indicates that these species are quickly removed from the atmosphere onto the land (Driscoll *et al.*, 2013). Wet deposition refers to the removal of atmospheric Hg through precipitation, such as snow or rain to aquatic and terrestrial environments (Wu *et al.*, 2024). The primary mechanisms that drive wet deposition are the gas-phase oxidation of Hg^0 by OH and O_3 , and the in-cloud oxidation of Hg^{II} by OH and O_3 (Lindberg *et al.*, 2007; Tripathy *et al.*, 2019). Wet deposition functions as a sink for divalent Hg (Driscoll *et al.*, 2013). Shah *et al.* (2021) determined that 71% of Hg^{II} deposition is in the global oceans, which are the major source of Hg in the marine environment. Horowitz *et al.* (2017) found that 80% of total Hg^{II} deposition was over the oceans and it was influenced by the low concentrations of organic aerosols for Hg^{II} reduction. Total (wet + dry) Hg^{II} deposition is estimated as 5.5 Gg per annum. The total Hg^{II} wet deposition flux and the global dry deposition of Hg^0 were found to be 2.6 and 1.2 Gg per annum, respectively.

In the marine ecosystem, the deposited atmospheric Hg can be methylated into methylmercury (MeHg) and bioaccumulate along the food chain causing detrimental effects on the environment and human health (Li *et al.*, 2019; Liu *et al.*, 2012). The process of converting inorganic Hg into MeHg is driven by certain anaerobic bacteria existing in sediments and water (Wu *et al.*, 2024).

In summary, it has been shown from this review that the biogeochemical cycle of Hg involves complex interactions among the lithosphere, atmosphere, and hydrosphere. This cycle is influenced by environmental conditions and natural and anthropogenic processes. It is crucial to comprehend these chemical and physical processes to assess environmental risks, develop effective mitigation strategies, and protect the health of humans and the ecosystem.

2.3 Health effects of Hg

The chemical composition, duration of exposure, and concentration of different Hg species negatively impact humans and the environment (Leiva González *et al.*, 2022). Humans are exposed to Hg and its compounds from various pathways in acute and chronic manners (Beckers & Rinklebe, 2017; Park & Zheng, 2012). The sources of human exposure to Hg are inhalation of elemental Hg vapours, ingestion of MeHg in fish and rice, and dermal applications of inorganic Hg (Beckers & Rinklebe, 2017; Park & Zheng, 2012; Risher & De Rosa, 2007).

Acute inhalation exposure to GEM causes shortness of breath, fever, and headache. Whereas inhalation of high GEM levels causes acute corrosive bronchitis, interstitial pneumonitis, as well as damage to the kidneys and central nervous system (Park & Zheng, 2012; Wu *et al.*, 2024). GEM can easily diffuse within the body because it has a high affinity with membrane lipids. Therefore, it can amass in the central nervous system before being oxidised (Ciani *et al.*, 2021; Park & Zheng, 2012). Mercury can damage the tertiary and quaternary protein structure and change the cellular function, which hinders the cellular structure (Jaishankar *et al.*, 2014).

Ingestion of inorganic Hg or mercuric salts results in vomiting, renal tubular necrosis, and abdominal pain (Wu *et al.*, 2024). The primary route of MeHg exposure is ingesting fish and rice (Beckers & Rinklebe, 2017). In 1953, a pollution event of MeHg poisoning occurred in Minamata Bay, Japan, due to ingesting contaminated fish and seafood (Bhagi & Chatwal, 2009; Eto, 2000; Ninomiya *et al.*, 1995). Human exposure to MeHg poisoning results in distal sensory disturbances, cerebellar ataxia, and cardiovascular diseases (Li *et al.*, 2010). Skin-lightening products containing inorganic Hg, such as creams and ointments, cause dermatitis, corrosive burns, and discoloration of the nails (Beckers & Rinklebe, 2017; Park & Zheng, 2012).

2.4 Passive air sampling

Numerous sampling systems, such as manual and active methods, are employed to measure atmospheric mercury (Huang *et al.*, 2012). Gustin and Jaffe (2010) described the basic operation principle of the active method as the collection of gaseous Hg from the atmosphere onto a gold cartridge; then, Hg is subjected to thermal desorption followed by the quantification of GEM using cold vapour atomic fluorescence spectrometry

(CVAFS). A considerable amount of literature has been published on active methods. These studies identify that active methods provide high-quality continuous measurements of GEM at low detection levels and fine temporal resolution (Gurjar *et al.*, 2010; Lyman *et al.*, 2010; McLagan, Mazur, *et al.*, 2016; Pirrone *et al.*, 2013; Tekran, 2022; UNEP, 2022). Similarly, manual methods employ air pumps to draw ambient air at low flow rates and capture gaseous Hg onto a precious metal collection surface. Subsequently, the collected gaseous Hg sample is analysed in the laboratory using CVAFS (Ebinghaus, Jennings, *et al.*, 1999; Gustin & Jaffe, 2010; Gustin *et al.*, 2015; UNEP, 2022). However, certain drawbacks are associated with using the active sampling technique. They are expensive, labour intensive, and require electricity, calibrated pumps, a carrier gas, an air-conditioned setting and trained personnel (Gurjar *et al.*, 2010; Gustin *et al.*, 2011; Jeon & Cizdziel, 2019; Jeon *et al.*, 2019; Lyman *et al.*, 2010; McLagan, Mazur, *et al.*, 2016; Pirrone *et al.*, 2013; Skov *et al.*, 2007). These limitations hinder the spatial expansion of monitoring atmospheric Hg in the world (Campos *et al.*, 2010; McLagan, Mitchell, *et al.*, 2018).

To overcome these limitations, passive air samplers (PASs) have been developed to monitor atmospheric Hg (Avossa *et al.*, 2020; Skov *et al.*, 2007). PASs rely on the molecular diffusion of gaseous pollutants to draw ambient air to the sorbent without using a pump, and concentrations of atmospheric pollutants from the exposed samplers are determined, and quantified in the laboratory (Campos *et al.*, 2010; Jeon & Cizdziel, 2019; McLagan, Mazur, *et al.*, 2016; Pienaar *et al.*, 2015; Snow *et al.*, 2021; UNEP, 2022; Vallero, 2014). There are several advantages of employing passive sampling methods. They are economical, portable, easy to deploy and do not require a power supply or pumps (Pienaar *et al.*, 2015; Salim & Górecki, 2019; Skov *et al.*, 2007). The above-mentioned benefits allow multiple PASs to be deployed, thereby providing the possibility of monitoring atmospheric Hg at high spatial resolution (Campos *et al.*, 2010; Jeon & Cizdziel, 2019; Naccarato *et al.*, 2021). Furthermore, PASs collect the time-weighted average of atmospheric Hg concentrations. Conversely, the disadvantages of this method are the meteorological factors (wind, temperature, and relative humidity) that influence the sampling rate (SR) of the sampler and the coarse temporal resolution measurements owing to the extended deployment duration of days to weeks (Avossa *et al.*, 2020; Guo *et al.*, 2014; Mills *et al.*, 2007; Salim & Górecki, 2019).

2.4.1 The theory of passive sampling

The theory and functioning of passive sampling were briefly highlighted in the previous section, which is defined by Górecki and Namieśnik (2002) as “Any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potentials of the analyte between the two media.” Passive sampling uses the principles of mass transport across a diffusive layer (Greenwood *et al.*, 2007). In Figure 2-4, the diffusion principle utilised in the design of a passive sampler is shown. The pollutant gas diffuses through a well-defined inlet of a PAS. Furthermore, toward the end of the tube, a collection medium removes the pollutant gas for subsequent analysis and maintains a concentration gradient between the inlet of the tube and the collection medium (Vallero, 2014). Additionally, the sampling rate of a PAS is controlled and governed by the diffusion principle and the geometry of the passive sampler, respectively (Campos *et al.*, 2010; Pienaar *et al.*, 2015).

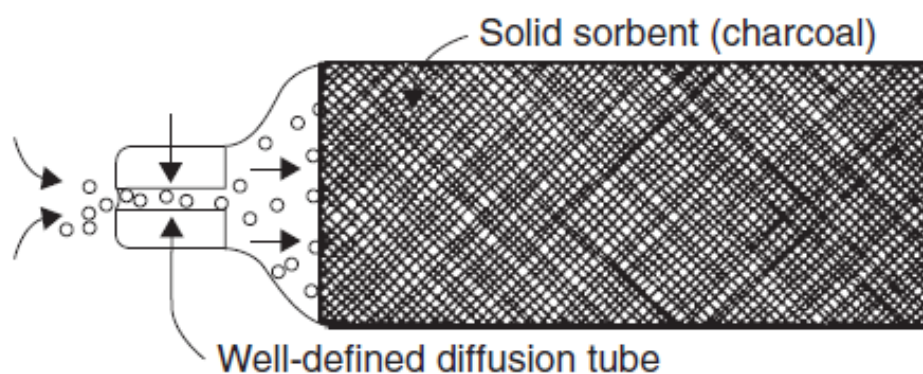


Figure 2-4: Illustration of a passive sampler based on the principle of diffusion (Vallero, 2014).

In this study, the PAS used (Figure 2-5) has been described in detail by McLagan, Mitchell, *et al.* (2016) (see section 3.2.1). Mercury Passive Air Sampler (*MerPAS*®) incorporates a sulphur-impregnated activated carbon sorbent (HGR-AC; Calgon Carbon Corporation) and is housed in a stainless-steel mesh cylinder (height of 60 mm, diameter of 5.8 mm, mesh size of 165,47% open area, open at the top, closed at the bottom with a 0.1 mm stainless steel plate). The mesh cylinder is placed inside a high-density polyethylene white Radiello diffusive barrier (Sigma Aldrich; porous section height of 47 mm, porous barrier thickness of 1.7 mm, diameter of 16 mm), which constrains the sampling rate. The diffusive barrier is attached to the interior of a protective shield

(polyethylene terephthalate, height of 75 mm, diameter of 72 mm) to minimise and control the effects of precipitation and wind on the rate of Hg uptake from the atmosphere (Jeon & Cizdziel, 2019; McLagan, Mitchell, *et al.*, 2016). The protective shield also serves as a storage and shipping container. During deployment, gaseous Hg is captured into the HGR-AC sorbent by undergoing radial molecular diffusion through the diffusive barrier.

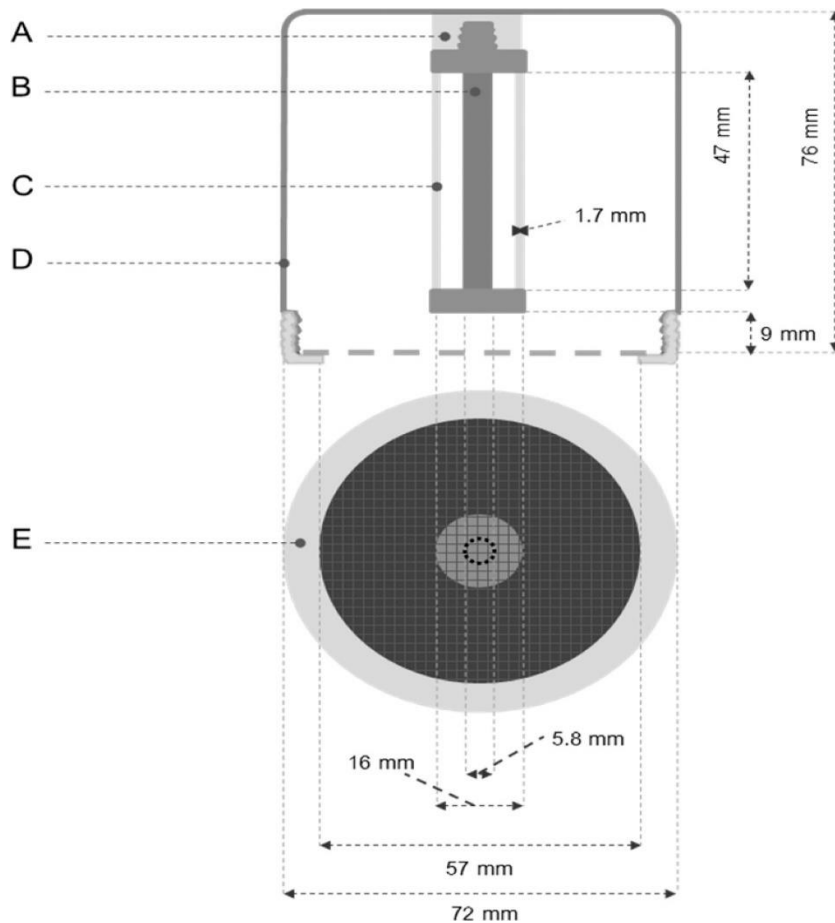


Figure 2-5: Schematic representation of the gaseous Hg passive sampler: (A) polytetrafluoroethylene screw cap, (B) sulphur-impregnated activated carbon sorbent housed in a stainless-steel mesh cylinder, (C) high-density porous polyethylene diffusive barrier, (D) polyethylene terephthalate protective shield, and (E) mesh screened polypropylene lid, replaced with a closed lid for storage and transport (McLagan, Mitchell, *et al.*, 2016).

The mass transfer of the pollutant gas through the diffusive barrier in passive samplers can be described by Fick's first law of diffusion, which states that diffusional flux is proportional to the diffusivity of the pollutant gas and a concentration gradient over a distance (Górecki & Namieśnik, 2002; Jeon *et al.*, 2019). This can be expressed as:

$$J = -D \frac{\partial C}{\partial x} \quad (2-8)$$

Where J is the diffusion flux of the pollutant gas (ng/cm²/s), D is the diffusivity of the pollutant gas (cm²/s) and $\partial C/\partial x$ is the concentration gradient consisting of C , the concentration (ng/cm³) difference over the distance x (cm).

For diffusive PASSs, the sampling rate (SR) can be determined by applying the mass transfer coefficient (k) according to Eq. (2-9):

$$k = \frac{D}{L}; SR = k \times A \quad (2-9)$$

From the above equation, the SR is directly proportional to the diffusivity of the pollutant gas in the atmosphere and the cross-sectional area (A , cm²). Moreover, it is inversely proportional to the length of the diffusion layer (L , cm) (Brown, 1993; Huang *et al.*, 2014; Pienaar *et al.*, 2015).

The diffusion coefficient of a chemical C and gases ($D_{C,g}$, cm²/s) can be theoretically calculated and predicted according to the Lennard-Jones equation (Eq. (2-10)) and the Fuller equation (Eq. (2-11)) as follows (Greenwood *et al.*, 2007; Huang *et al.*, 2014):

$$D_{C,g} = \frac{0.001858 T^{3/2}}{P \sigma_{C,g}^2 \Omega_D} \left(\frac{1}{M_c} + \frac{1}{M_g} \right)^{1/2} \quad (2-10)$$

$$D_{C,g} = \frac{10^{-3} T^{3/2}}{P (V_{C,d}^{1/3} + V_{g,d}^{1/3})^2} \left(\frac{1}{M_c} + \frac{1}{M_g} \right)^{1/2} \quad (2-11)$$

Where T (K) is the temperature, P (atm) is the total pressure, $\sigma_{C,g}$ (Å) is a Lennard-Jones parameter, Ω_D is a dimensionless number, $V_{C,d}$ and $V_{g,d}$ are atomic diffusion volumes for C and gas and M_c and M_g are the molar masses for C and gas (Huang *et al.*, 2014). Table 2-1 presents the diffusion coefficients of different GOM species estimated from the Fuller equation, while the diffusivity of GEM is reported to be 0.112 cm²/s at 273 K, 1 atm.

Table 2-1: Molar mass, diffusivity, partitioning coefficients between octanol and water (K_{ow}) of Hg-related compounds. Adapted from Huang *et al.* (2014)

Gas	Molar mass (g/mol)	Diffusivity (cm ² /s)	K_{ow} (Hg)
HgCl ₂	271.5	0.095	0.5
HgBr ₂	360.4	0.089	-
HgO	216.6	0.122	-
Hg(NO ₃) ₂	324.6	0.078	-
HgSO ₄	296.7	0.082	-
Hg	200.9	0.112	4.2

When D is known, a theoretical sampling rate (SR) can be determined and the gaseous Hg concentration C can be calculated according to Eq. (2-12):

$$C = \frac{m}{S R t} \quad (2-12)$$

Where m (ng) is the amount of the analyte collected by the PAS and t (days) is the deployment duration (McLagan, Mitchell, *et al.*, 2016).

2.5 Global networks

Around the mid-1970s and the mid-1990s, much more information became available on ambient Hg concentration measurements for the Northern and Southern Hemispheres, respectively (Sprovieri *et al.*, 2010). However, these early efforts to monitor atmospheric Hg concentrations were often region-specific and lacked standardisation.

Given our limited understanding of the impact of Hg pollution on a global scale, global initiatives such as the Global Mercury Observation System (GMOS), the Atmospheric Monitoring Network (AMNet), and the Environment and Climate Change Canada Atmospheric Mercury Monitoring Network (ECCC-AMM) have greatly improved the understanding of atmospheric Hg (Li & Lee, 2014). Over time, the need for a coordinated global monitoring network became apparent (Pirrone *et al.*, 2013). Recently, the Minamata Convention on Mercury was adopted in 2013 to protect human health and the environment from man-made emissions and releases of Hg (Sprovieri *et al.*, 2016; UNEP,

2013b). One of the objectives of the Convention (Article 19) was to develop and improve current techniques to monitor Hg levels in the environment, by expanding existing monitoring networks and research programmes (Sheu *et al.*, 2019; UNEP, 2013b).

Pirrone *et al.* (2013) mention passive sampling techniques as a valuable and efficient tool to expand global mercury monitoring networks. PASs such as *MerPAS*® offer numerous advantages as mentioned above (Section 2.4). They are useful in the mapping of atmospheric Hg concentrations (Kot-Wasik *et al.*, 2007; McLagan, Hussain, *et al.*, 2018; Pienaar *et al.*, 2015). PASs offer an opportunity for global harmonisation and standardisation of monitoring protocols. A network of networks using *MerPAS*® was established by Canada to expand the global coverage of Hg monitoring. In 2019, the network was composed of more than 69 sites operating in 27 countries. It reported a global mean atmospheric Hg concentration of 1.44 ng/m³ for the period between 2019 and 2022 (Macswen *et al.*, 2022). Similarly, on 1 April 2020, the South African Mercury Network (SAMNet) was established to improve spatial coverage of atmospheric Hg measurements conducted throughout the country.

CHAPTER 3 EXPERIMENTAL

The purpose of this chapter is to discuss the measurement station utilised for the deployment of passive, active, and manual active mercury (Hg) samplers. To explain the procedures followed during the sampling of atmospheric Hg concentration, the laboratory techniques used to analyse the Hg content collected on the sorbent materials of the passive and manual active samplers are discussed, respectively. Finally, the data quality and calculations, and the statistical methods in this study, are explained.

3.1 Site description

Measurements were conducted at the Welgegund atmospheric monitoring station (26.57°S, 26.94°E, 1480 m above sea level), which can be considered one of the most comprehensively equipped atmospheric measurement sites in Africa. Detailed descriptions of the site in terms of geographical location, meteorology and vegetation type are presented in numerous papers (e.g. Jaars *et al.*, 2014; 2016; Kok *et al.*, 2021; Laban *et al.*, 2018; Räsänen *et al.*, 2020). The site is located on a commercial farm approximately 100 km southwest of Johannesburg, as indicated by Figure 3-1. Although there are no large point sources within proximity of Welgegund, the site is impacted by major source regions in the north-eastern South African interior, also indicated in Figure 3-1. In addition, air masses passing over a relatively clean western sector also impact Welgegund (Figure 3-1). Previous research has demonstrated the influence of these regional sources on the atmospheric composition at Welgegund (e.g. Booyens *et al.*, 2015; Venter *et al.*, 2017; 2020). During the sampling period in this study, meteorological conditions were characterised by an average temperature of $15.5 \pm 6.5^\circ\text{C}$ (ranging between -6.9 and 37.7°C) and an average relative humidity of $51.4 \pm 24.5\%$ (ranging between 4.7 and 100%). The total rainfall during June 2021 to September 2022 was 1 172 mm. The prevailing wind direction was from the north-northwest, with an average speed of 3.6 ± 2.9 m/s (ranging between 0 and 6.9 m/s). The location of two additional sites, i.e., the Cape Point Global Atmosphere Watch station (32.21°S, 18.29°E, 230 m above sea level) and the South African Weather Service station in De Aar (30.67°S, 24.01°E, 1286 m above sea level), where manual active atmospheric Hg samplers were deployed, are also presented in Figure 3-1. A photograph of the Welgegund atmospheric monitoring station is shown in Figure 3-2.

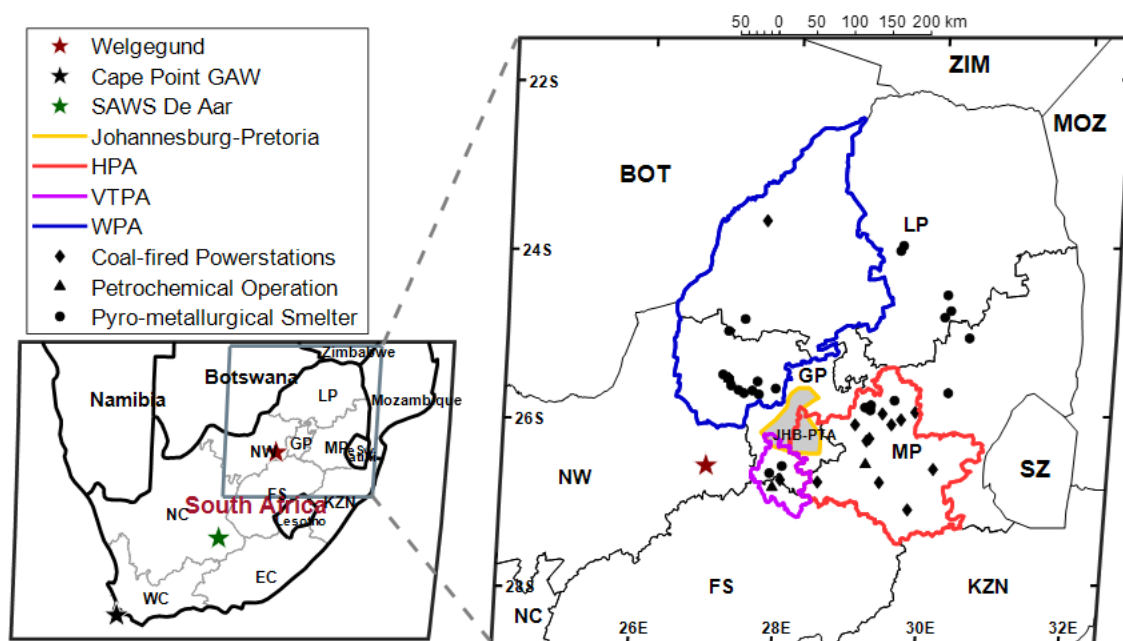


Figure 3-1: Map of Southern Africa with the zoomed-in area presenting the Welgegund atmospheric monitoring station (red star) in relation to major large point sources impacting air masses measured at Welgegund. Also indicated are the Jhb-Pta megacity and the three air quality priority areas as identified by the South African government. Two additional SAMNet sites are also shown (green and black stars).



Figure 3-2: Welgegund measurement station during the summer season.

3.2 Measurement methods

3.2.1 Passive sampling (*MerPAS*®)

The theory and functioning of *MerPAS*® have been described in detail in the literature (McLagan *et al.*, 2017; McLagan, Mitchell, *et al.*, 2016; McLagan, Mitchell, *et al.*, 2018; Stupple *et al.*, 2019). This sampler incorporates a cylindrical stainless-steel mesh, containing sulphur-impregnated activated carbon (HGR-AC; Calgon Carbon Corporation) as the sorbent material. The mesh is placed within a microporous diffusive barrier (white Radiello®, Sigma Aldrich), which regulates the sampling rate. GEM diffuses through the barrier and is retained by the sorbent. The diffusive barrier is securely attached to a protective shield designed for outdoor deployment, featuring an opening at the bottom to facilitate air circulation and prevent precipitation from entering. The rate at which *MerPAS*® absorbs GEM is minimally influenced by meteorological factors, e.g. wind speed and temperature (McLagan *et al.*, 2017; McLagan, Mitchell, *et al.*, 2018). Recently, Naccarato *et al.* (2021) showed that *MerPAS*® is currently the best available passive sampler for GEM concentration monitoring, while McLagan, Mitchell, *et al.* (2018) indicated that the uncertainty and precision of these samplers range between 2 and 4% through the analysis of several *MerPAS*® deployed globally.

The *MerPAS*® utilised in this study was assembled at the University of Toronto Scarborough. The samplers were sealed tightly with Teflon™ tape, individually placed into zip-lock plastic bags (Figure 3-3a), and shipped and stored in sturdy foam-lined aluminium or hard plastic cases. At Welgegund, three *MerPAS*® were removed from the plastic bags. The solid lids of two samplers were removed and replaced with black mesh screens, with their top facing into the samplers (Figure 3-3b). The third *MerPAS*® was used as a blank to monitor possible contamination during assembly, handling, transport, and storage of these samplers. Duplicate *MerPAS*s® were deployed monthly from June 2021 to September 2022. The samplers were attached to a mounting bracket 4 m above ground level, with the open side of the samplers facing downward (Figure 3-4). After exposure, the *MerPAS*® was removed from the mounting brackets, capped, sealed with polytetrafluoroethylene tape, again placed in plastic bags, and shipped in the aforementioned plastic cases to the University of Toronto Scarborough for analysis.



Figure 3-3: Photos of the *MerPAS*® (a) samplers placed into zip-lock plastic bags, and (b) assembled samplers with black mesh screens.



Figure 3-4: Photos showing the deployment of the *MerPAS*®.

The *MerPAS*® were analysed with a Direct Mercury Analyzer (DMA-80; Milestone Inc., Shelton, CT, USA) (Figure 3-5), which determines the total Hg mass absorbed by the passive sampler. The analysis followed the modified US EPA method 7473, which is commonly used to determine Hg in complex matrices such as fish, sediment, and coal (Chen *et al.*, 2015; Cizdziel *et al.*, 2002; Lopez-Anton *et al.*, 2010). Prior to analysis, the stainless-steel cartridges of the *MerPAS*® containing the sorbent were removed. Approximately half of the contents were transferred to a preheated quartz sample boat and weighed, after which ~0.2 g of Na₂CO₃ was added directly to the sorbent to reduce the amount of SO₂ (McLagan *et al.*, 2017) formed during the combustion of the sulphur-impregnated carbon sorbent in order to minimise analytical artifacts. In addition, 5 g of Na₂CO₃ powder was also placed in the catalyst tube. This process was repeated for the other half of the sorbent. The two quartz boats containing the *MerPAS*® sorbent were loaded onto an auto-sampler, which sequentially introduced the boats into the furnace. The samples were thermally decomposed at 750 °C, releasing oxygenated Hg species to the catalyst, which are reduced to GEM and trapped by amalgamation with gold. The instrument was configured to collect Hg from the two quartz boats on the amalgamator.

The trap was then heated to 900 °C to release Hg, which was subsequently quantified in an absorption cell at 253.7 nm.



Figure 3-5: Direct Mercury Analyzer (DMA-80) system setup in a laboratory.

3.2.2 Active sampling

Continuous *in situ* atmospheric GEM measurements were conducted with a Tekran® 2537X ambient Hg cold vapour atomic fluorescence spectrometer (CVAFS) at Welgegund during June 2021 to September 2022, the same sampling period that MerPAS® was deployed (Figure 3-6). The instrument has a 5-min sampling frequency, with GEM concentrations being determined by alternating collection and analysis on one of the two gold traps within the analyser. The analysis phase is initiated by heating a gold trap to ~500 °C, releasing the sorbed Hg into pure argon gas (> 99.999 % purity, Afrox), which carries the Hg to the detector. The analyser was automatically calibrated every 24 hours using an internal permeation source. Site visits were conducted weekly to ensure the instrument was fully operational according to a predetermined checklist.



Figure 3-6: Deployment setup of the Tekran 2537X active sampler at Welgegund.

3.2.3 Manual active sampling

The manual active sampler is a newly developed analyser (Ambient Air Sampling Kit Model SK-1000A, Nippon Instruments Corporation) that uses the essential workings of the *in situ* active sampler while being more mobile and low-cost (Figure 3-7) (NIC, 2023). In this study, Hg concentrations determined with this analyser was only briefly explored due to very limited data collected and in-depth discussion on the development and functioning of this instrument are therefore not presented. A Hg collector tube was connected to an air pump pulling ambient air into a collector tube for 30 to 80 min at a flow rate of 0.5 L/min (Figure 3-8). 24-hour samples were collected once a week from 11 May to 7 September 2022 at Welgegund. The Hg collected in the tube was analysed using double amalgamation CVAAS with a WA-4 mercury analysis system. The Hg samples contained in porous gold-filled tubes were heated in a furnace at approximately 500 °C. The generated Hg vapour was transported to the Hg trapping chamber containing a porous gold collector, then heated to approximately 500 °C. The liberated Hg vapour was introduced into a quartz cell, and its absorption at 253.7 nm was measured.



Figure 3-7: Deployment setup of the manual active sampler at Welgegund showing the simultaneous duplicate sampling of (a) gold cartridges and (b) air pumps.

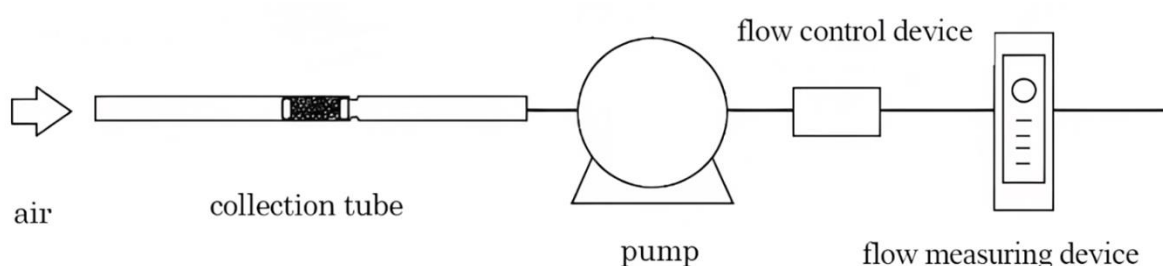


Figure 3-8: A schematic diagram of a manual active sampler for monitoring atmospheric mercury.

3.3 Data quality and calculations

Field blanks are crucial for reliable sampling with *MerPAS*[®] since they directly impact the method detection limit (MDL) and practical quantification limit (PQL). In total, nine field blanks were used during the entire *MerPAS*[®] sampling period at Welgegund. Hg content in these field blanks ranged between 0.381 and 2.417 ng Hg per gram of carbon (ng/g_{HGR-AC}), with an average of 1.107 ± 0.817 ng/g_{HGR-AC}. In order to provide context, Figure 3-9 compares the mean blank levels determined for Hg in this study with mean values reported in other studies utilising *MerPAS*[®]. Blank levels below or in the order of 0.5 ng/g_{HGR-AC} are only achievable when minimal transportation is involved and storage time after sampling is limited (Hoang *et al.*, 2023; McLagan, Mazur, *et al.*, 2016; McLagan *et al.*, 2017; McLagan, Hussain, *et al.*, 2018; Naccarato *et al.*, 2021). Studies involving inter- and intra-regional transport, extended sampler storage and conducted at Hg-

contaminated sites indicated slightly higher blank levels ranging between 0.5 ng/g_{HGR-AC} and 2 ng/g_{HGR-AC} (McLagan *et al.*, 2019; Quant *et al.*, 2021). However, Snow *et al.* (2021) and Naccarato *et al.* (2021) reported that it is feasible to maintain low blank levels for long-range transport (transatlantic) of these samplers. Field blank levels exceeding 3 ng/g_{HGR-AC} have been observed during a study involving 20 global sampling sites (McLagan, Mitchell, *et al.*, 2018), as well as during measurements conducted at a gold mine in Ghana (Snow *et al.*, 2021) and a site in New Zealand (Si *et al.*, 2020). In addition, blank levels higher than 3 ng/g_{HGR-AC} were also reported during studies conducted at the most extreme, remote and challenging global environments, i.e., at the Antarctic plateau, Amsterdam (AMS) Island and La Réunion (Hoang *et al.*, 2023). Therefore, considering the transport and storage of MerPAS[®] deployed at Welgegund, the average field blank concentration determined could be regarded as relatively low and in the same order than blank levels determined in other studies. Hg concentrations determined for the field blanks were used to calculate the MDL (three times the standard deviation) and PQL (ten times the standard deviation), which were determined to be 0.17±0.14 ng and 0.58±0.45 ng, respectively. None of the exposed passive samplers in this study exceeded the MDL and the PQL.

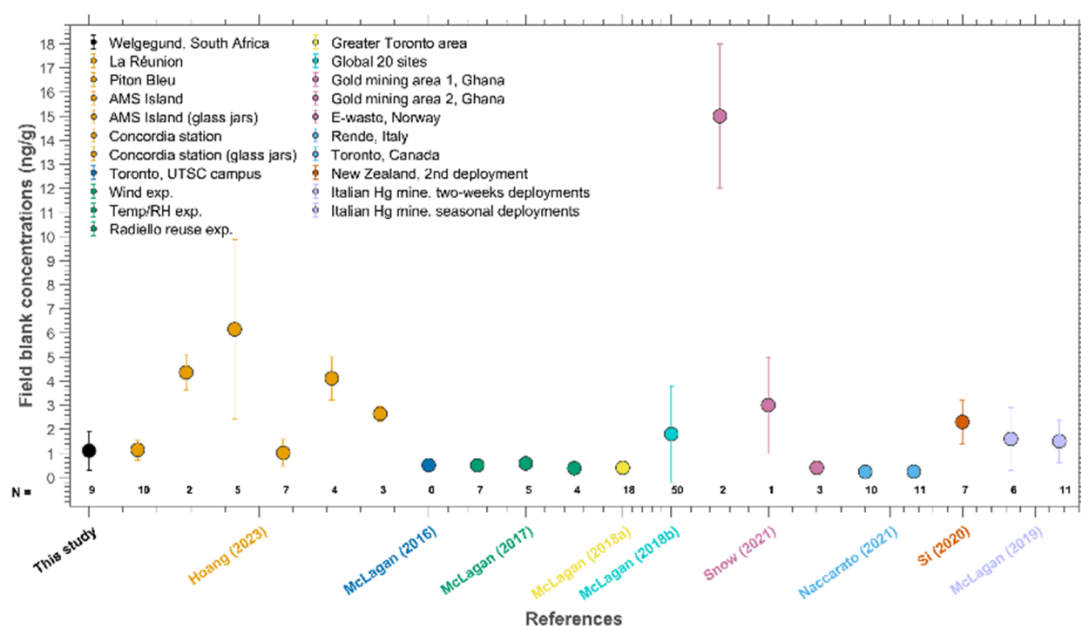


Figure 3-9: Error bar plot (mean±SD) comparing field blank concentrations determined in different studies utilising MerPAS[®]. The number (N) of blanks deployed during each study is indicated at the bottom.

Monthly average concentrations were calculated for GEM levels determined with the continuous *in situ* sampler. Hg concentrations measured with *MerPAS*[®] were calculated from the blank-corrected Hg mass according to Eq. (3-1):

$$C = \frac{m}{(SR \times t)}, \quad (3-1)$$

where C (ng/m³) is the Hg concentration, m (ng) is the blank-corrected Hg mass, t deployment time (days), and SR (m³/day) is the sampling rate of the *MerPAS*[®]. Similar to McLagan, Mitchell, *et al.* (2018), atmospheric Hg concentrations were calculated for four different SRs: (1) the original SR (OSR) provided by Tekran for the *MerPAS*[®] (0.111±0.017 m³/day); (2) the adjusted original SR (AOSR) where the sampling rate provided by Tekran was adjusted according to mean temperature (T_{exp}) and wind speed (WS_{exp}) as follows:

$$SR_{adj} = SR + (T_{exp} - 9.89^{\circ}\text{C}) \times 0.0009 \frac{\text{m}^3}{\text{day } ^{\circ}\text{C}} + (WS_{exp} - 3.41 \frac{\text{m}}{\text{s}}) \times 0.003 \frac{\text{m}^2 \text{s}}{\text{day}}; \quad (3-2)$$

(3) the recalibrated SRs (RSR) determined from the slope of a plot (Figure A1) of the Hg m determined with the *MerPAS*[®] against the monthly average GEM concentration measured with an active sampler multiplied with the deployment time (McLagan, Mitchell, *et al.*, 2016; Restrepo *et al.*, 2015); (4) the adjusted recalibrated SR (ARSR) where the recalibrated SR was adjusted according to Equation 3-2. In Table A1, all these parameters utilised in the calculations of Hg concentrations with *MerPAS*[®] are summarised.

Another good indicator of data quality is the percentage by which the Hg amount determined with the exposed samplers is reduced during the blank correction, which is also listed in Table A1. On average, blank contamination in the *MerPAS*[®] deployed at Welgegund was 10% (ranging between 7% and 14%) of the amount quantified in an exposed sampler, which is in the same range as determined in other studies (e.g. Hoang *et al.*, 2023; Naccarato *et al.*, 2021).

3.4 Statistical methods

Statistical analyses were performed with fit-for-purpose scripts in MATLAB R2020b and RStudio (version 4.2.2). Prior to the statistical correlation analyses, exploratory, descriptive statistic calculations (mean, median, minimum, maximum and standard deviation) were performed for the active Hg dataset (monthly averages), as well as the

blank corrected Hg concentration datasets determined for the four different SRs with MerPAS®, in order to gain a general overview of variations in monthly average Hg concentrations. In addition, the normality and homoscedasticity of these datasets were also exploratively evaluated with the Lilliefors and Bartlett tests, respectively. Both these tests revealed a normal distribution for each of these datasets suitable for parametric correlation analysis. Variances in the monthly average Hg concentrations can mainly be attributed to temporal variations, as indicated and discussed in the subsequent *Results* section. Bayes factor (BF) analysis was also done, which represents the likelihood ratios of the data under a normal distribution to the probability of it being non-parametric. Statistical analyses were performed with the R package ggstatsplot (Patil, 2021).

Statistical correlation analysis between active *in situ* measurements and Hg concentrations derived from MerPAS® with the four SRs was performed with four methods, which include one-way analysis of variance (ANOVA), the dependent sample *t*-test, linear regression and Bland-Altman analysis. ANOVA compares the means of two or more methods, while the dependent sample *t*-test compares the means of two dependent methods to determine whether there is statistical evidence that the associated population or sample means are significantly different (Ross & Willson, 2018). *Post hoc* analysis of ANOVA was performed using a pairwise *t*-test with Bonferroni adjustment, while the effect size was calculated using a partial Omega squared (ω_p^2). For the *t*-test, the effect size was calculated using Cohen's *d* with values of 0.2, 0.5, and 0.8, which were considered to be small, medium, and large, respectively.

Bland-Altman analysis is a statistical method used to assess the agreement between two datasets. It involves plotting the difference between the measurements obtained from two sampling techniques against the average of the measurements. The Bland-Altman plot can be used to identify any systematic biases or trends between the two datasets, as well as determine the magnitude and direction of the differences between the methods. Bland-Altman analysis conducted in this study aimed to assess the agreement between Hg concentrations measured with the active *in situ* sampler and Hg levels determined with MerPAS® utilising the above-mentioned four SRs. This statistical analysis provides valuable insights with regard to the accuracy, precision, and agreement of different measurement methods. Like Silveira et al. (2021), a three-step approach was applied to verify strict equivalence between the two measurement techniques. The first step involves evaluating the equivalence of structural means, which tests the similarity of accuracy

between the two methods. This step determines whether the two measurement methods produce similar average measurements for the same samples. The second step evaluates the equivalence of structural variances, which tests the correspondence of precision between the two methods and determines whether the two measurement methods have similar variances when measuring the same samples. The third step involves testing the agreement with the structural bisector line, which tests for equivalent measurements obtained from the same subject. This step determines whether a systematic difference exists between the two measurement methods for the same subject. Complete similarity can be established when all three tests showed non-rejection of equivalence at a 5% significance level.

The mean normalised difference (MND) and relative standard deviation (RSD) were also calculated for the datasets obtained from MerPAS® with the four SRs in relation to the active *in situ* measurements. MND and RSD also reflect the accuracy and variability in datasets. The MND is calculated as follows:

$$MND\% = \left(\frac{1}{n} \sum_{i=1,n} \frac{|C_{ACT,i} - C_{PAS,i}|}{C_{ACT,i}} \right) \times 100, \quad (3-3)$$

where n is the number of comparisons, C_{PAS} (ng/m³) the MerPAS® derived Hg concentrations and C_{ACT} (ng/m³) monthly average Hg levels determined with the active *in situ* sampler. RSD is calculated by dividing the standard deviation of a dataset by its mean and then multiplying it by 100. Lower MND values are indicative of good agreement between datasets, whereas lower RSD implies all datapoints are relatively close to the mean of the dataset.

CHAPTER 4 RESULTS AND DISCUSSION

This chapter presents the results of gaseous Hg concentrations measured at the Welgegund atmospheric monitoring station. The performance of *MerPAS*® is statistically assessed through comparison with the active *in situ* sampler. An exploration of the temporal pattern of the gaseous Hg concentrations is presented. Comparison of Hg measurements determined with the manual active sampler is briefly discussed.

4.1 Hg concentrations and descriptive statistics

In Table 4-1, the monthly average gaseous Hg concentrations determined with the active *in situ* analyser and *MerPAS*® with the different SRs are listed, while Table 4-2 summarises the descriptive statistics. The sampling campaign mean of the Hg concentrations determined with the AOSR (1.87 ng/m³) and OSR (1.97 ng/m³) were higher than the average Hg levels determined with the active *in situ* sampler (1.70 ng/m³) with the average of the AOSR-derived Hg concentration being closer to the mean of Hg concentrations determined with the active *in situ* sampler. In addition, the averaged Hg concentrations calculated with RSR (1.69 ng/m³) were very close to the means of the Hg levels determined with the active *in situ* sampler, while the average calculated with the ARSR was slightly lower (1.62 ng/m³). These results are further explored through in-depth statistical analyses in subsequent sections.

Table 4-1: Monthly average gaseous Hg concentrations (ng/m³) determined with the active *in situ* sampler and derived from MerPAS[®] utilising different SRs

Month	Active <i>in situ</i>	MerPAS [®] OSR	MerPAS [®] AOSR	MerPAS [®] RSR	MerPAS [®] ARSR
06/2021	1.819	1.813	1.828	1.560	1.571
07/2021	2.398	3.119	3.188	2.683	2.735
08/2021	1.650	2.323	2.225	1.999	1.926
09/2021	1.319	1.925	1.739	1.657	1.517
10/2021	1.410	1.925	1.738	1.656	1.516
11/2021	1.591	2.163	1.894	1.861	1.658
12/2021	1.333	1.481	1.245	1.275	1.096
01/2022	1.746	1.777	1.633	1.529	1.421
02/2022	1.527	1.656	1.518	1.425	1.322
03/2022	1.916	2.179	2.057	1.875	1.784
04/2022	1.637	1.730	1.672	1.489	1.445
05/2022	2.022	2.063	2.022	1.775	1.744
06/2022	1.768	1.866	1.859	1.605	1.600
07/2022	1.774	1.710	1.674	1.472	1.445
08/2022	1.517	1.816	1.721	1.562	1.491

Table 4-2: Descriptive statistics of datasets obtained from the active *in situ* sampler and derived from MerPAS® utilising different SRs

	Active <i>in situ</i>	MerPAS® OSR	MerPAS® AOSR	MerPAS® RSR	MerPAS® ARSR
Mean	1.695	1.969	1.868	1.695	1.618
Median	1.650	1.866	1.739	1.605	1.517
SD	0.281	0.387	0.433	0.333	0.367
Minimum	1.319	1.481	1.245	1.275	1.096
Maximum	2.398	3.119	3.188	2.683	2.735
95% CI of Mean	1.539; 1.851	1.755; 2.184	1.628; 2.107	1.510; 1.879	1.415; 1.821

4.2 Statistical analysis

4.2.1 Analysis of variance (ANOVA)

In Figure 4-1, the ANOVA results are presented, which include descriptive statistics, inferential statistics, an estimate of effect size and its uncertainty, pairwise comparisons, Bayesian hypothesis testing, as well as a Bayesian posterior assessment and its uncertainty. All these parameters, determined with ANOVA, indicate statistically meaningful differences between the average Hg concentrations determined with *in situ* measurements and the means of the Hg levels derived from MerPAS® with the four different SRs for the entire sampling period. Although statistically significant differences were determined between Hg concentrations determined with the active sampler and MerPAS® samplers, the Hg levels are in good agreement. The results demonstrate a statistically significant main effect ($F(1.36, 19.08) = 21.57$ $p = 5.73 \times 10^{-5}$), indicating that some differences between certain means are statistically meaningful. Furthermore, the 95% confidence interval (CI) for the mean difference was [0.00, 1.00], indicating that the actual mean difference between the methods will likely be positive and relatively small. The omega-squared effect size ($\omega_p^2 = 0.11$) was moderate. The BF also indicated

meaningful differences between the averages of the Hg concentrations determined with the different methods, which are, however, acceptable and reliable.

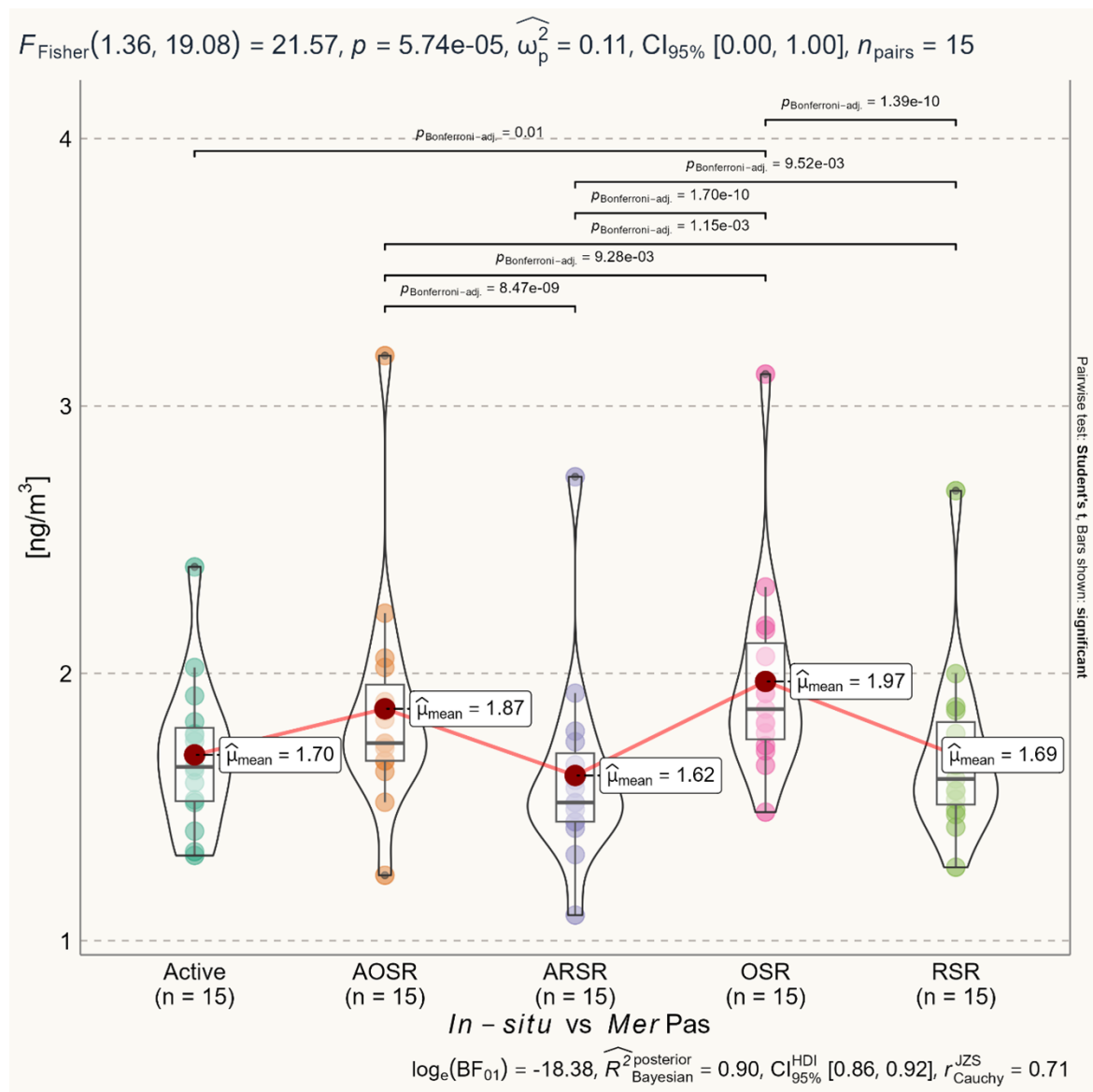
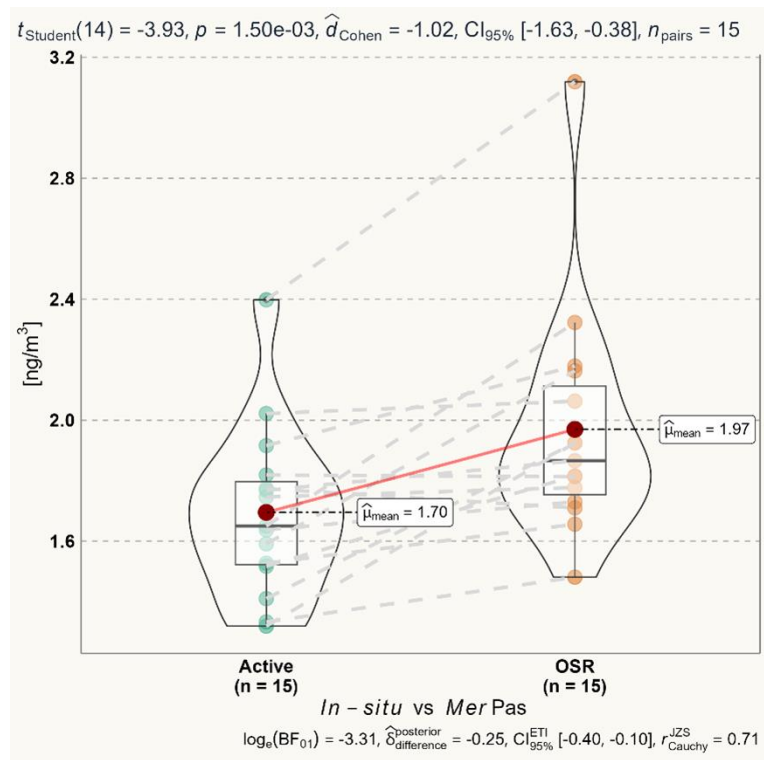


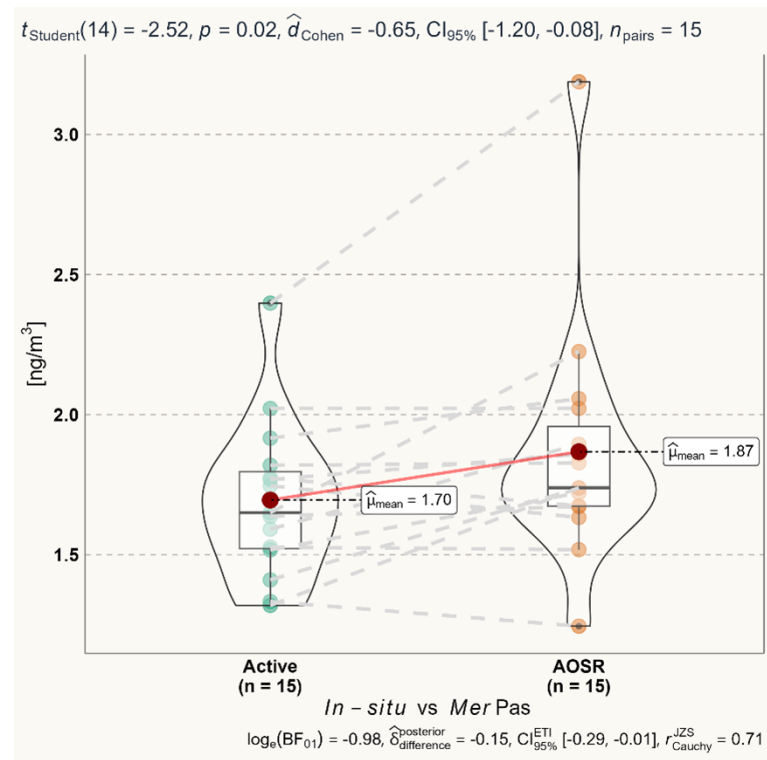
Figure 4-1: A combination of a violin, box and jittered plot of the monthly average Hg concentrations determined with the active *in situ* sampler and Hg levels determined with MerPAS® for different SRs. Descriptive statistics, inferential statistics, an estimate of effect size and its uncertainty, pairwise comparisons, Bayesian hypothesis testing, as well as a Bayesian posterior assessment and its uncertainty, are also shown.

4.2.2 T-test

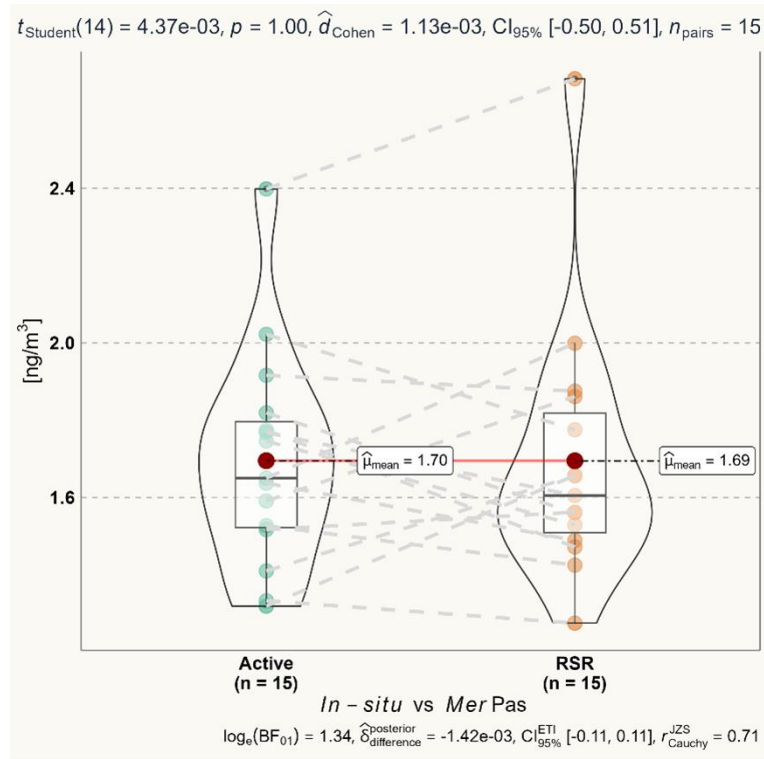
The results of the t-tests in which active *in situ* measurements are compared to the Hg concentrations derived with each of the four different SRs for MerPAS® are presented in Figure 4-2. A statistically meaningful difference is evident when comparing Hg levels measured with the active sampler to the Hg concentrations determined with MerPAS® using the OSR (Figure 4-2a) with the negative t-value and Cohen's d value associated with higher Hg concentrations determined with MerPAS®. The statistically significant difference is also supported by the BF and the relatively large effect size ($d_{\text{cohen}} = -1.02$). The 95%CI [-1.63, -0.38], which does not include zero, proves that the difference is not the result of chance or random variation, and gives 95% confidence that the true values fall within this range. Similar statistically significant differences are observed for the t-test conducted to compare *in situ* measurements with the MerPAS® derived concentrations with the AOSR (Figure 4-2b). Smaller differences are, however, calculated due to the Hg levels calculated with AOSR being closer to active *in situ* measurements. Comparison between active *in situ* data with the Hg concentrations derived from MerPAS® with the RSR with the t-test indicated no statistically significant differences ($t(14) = 4.37 \times 10^{-3}$, $p = 1$). This is supported by the 95%CI for the mean difference of [-0.50, 0.51] that is a large range that includes zero, the small effect size ($d_{\text{cohen}} = 1.13 \times 10^{-3}$) and the BF. Furthermore, no statistically meaningful differences were also observed through the t-test performed between the active *in situ* measurements and Hg levels determined with MerPAS® using the ARSR ($t(14) = 1.34$, $p = .2$), which is also supported by the large 95%CI for the mean difference [-0.18, 0.86], the moderate effect size ($d_{\text{cohen}} = 0.35$) and the BF. Also presented in Figure 4-2 are grey lines that indicate the pairing of the data points. If these grey lines consistently have positive or negative slopes, it can be deduced that the MerPAS® constantly has higher or lower values, respectively. It is evident that the grey lines for the OSR (Figure 4-2a) and AOSR (Figure 4-2b) mostly had positive slopes, indicating that the MerPAS® might overpredict concentrations, whereas the RSR (Figure 4-2c) and ARSR (Figure 4-2d) consistently had negative slopes, indicating that the MerPAS® might underpredict concentrations.



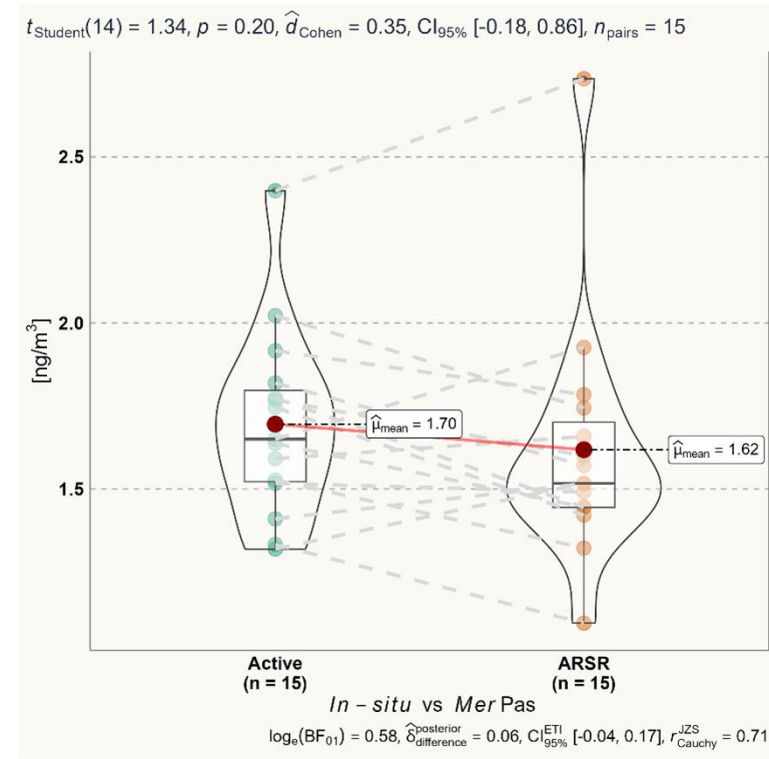
(a)



(b)



(c)

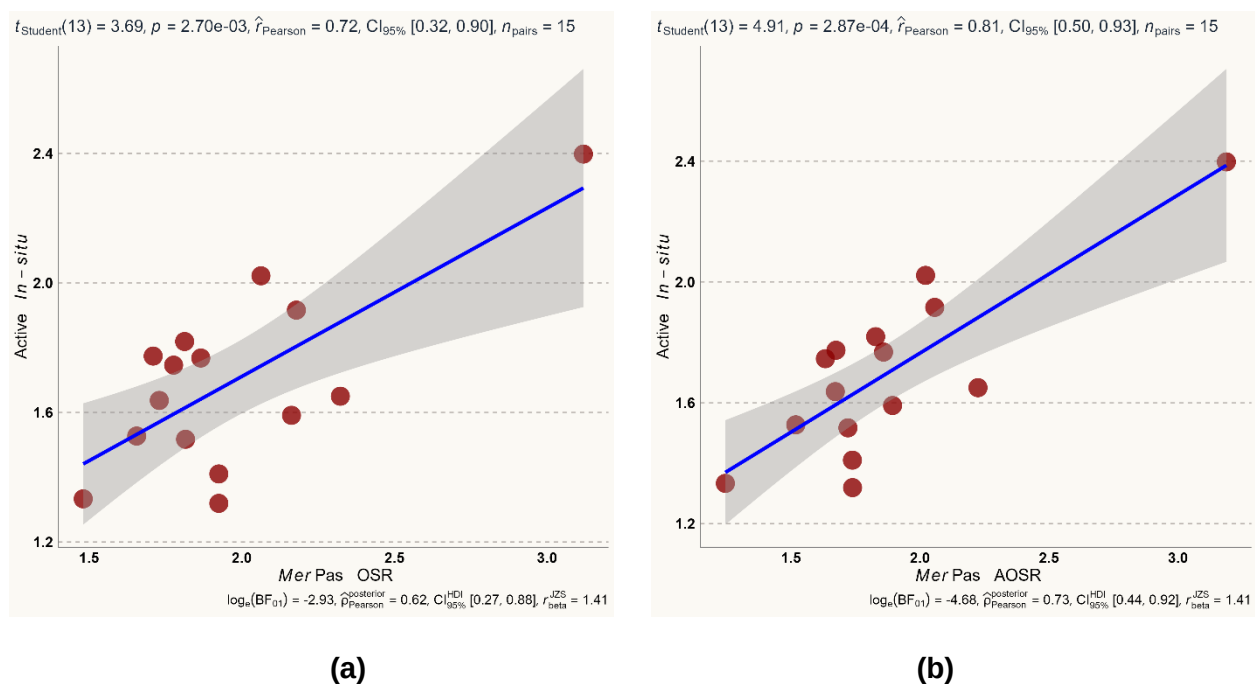


(d)

Figure 4-2: A combination of a violin, box and jittered plot of the monthly average Hg concentrations determined with the active *in situ* sampler and monthly Hg levels determined with MerPAS® derived from (a) OSR, (b) AOSR, (c) RSR and (d) ARSR. Descriptive statistics, inferential statistics, an estimate of effect size and its uncertainty, pairwise comparisons, Bayesian hypothesis testing, as well as a Bayesian posterior assessment and its uncertainty are also shown. The grey dashed lines indicate the pairing of the jittered points.

4.2.3 Linear regression

In Figure 4-3, the Hg levels measured with the active *in situ* samplers are plotted against the Hg concentrations derived from *MerPAS*® with each of the different SRs. The Pearson correlations (r) range between 0.72 and 0.81, which could be considered strong/significant correlations (Jaars *et al.*, 2014; Kleynhans *et al.*, 2017; Sheskin, 2003). These strong correlations are also supported by statistically significant t-values and low p-values, which is also indicative of the correlations not being due to chance. The 95%CI for the mean differences was relatively narrow and did not include zeros, implying that the true mean difference between active *in situ* measurements and *MerPAS*® (calculated with different SRs) will most likely fall within the reported ranges. BF also confirmed a good correlation between the active *in situ* measurements and Hg concentrations derived from *MerPAS*® with the different SRs.



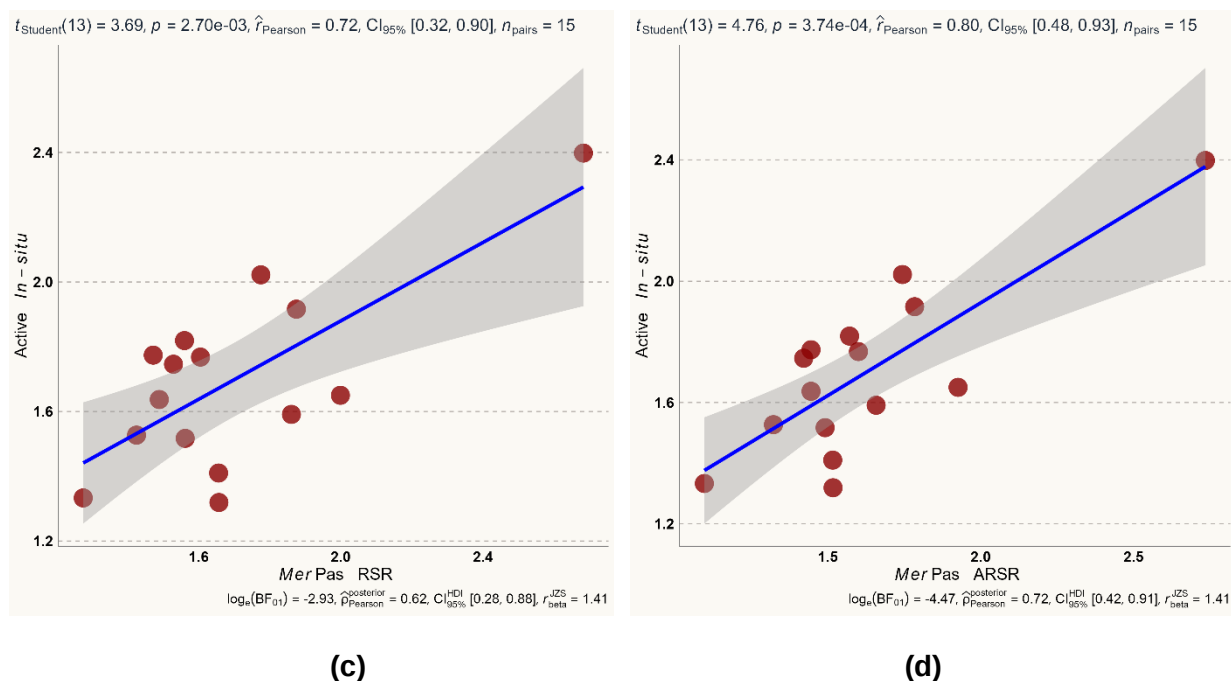


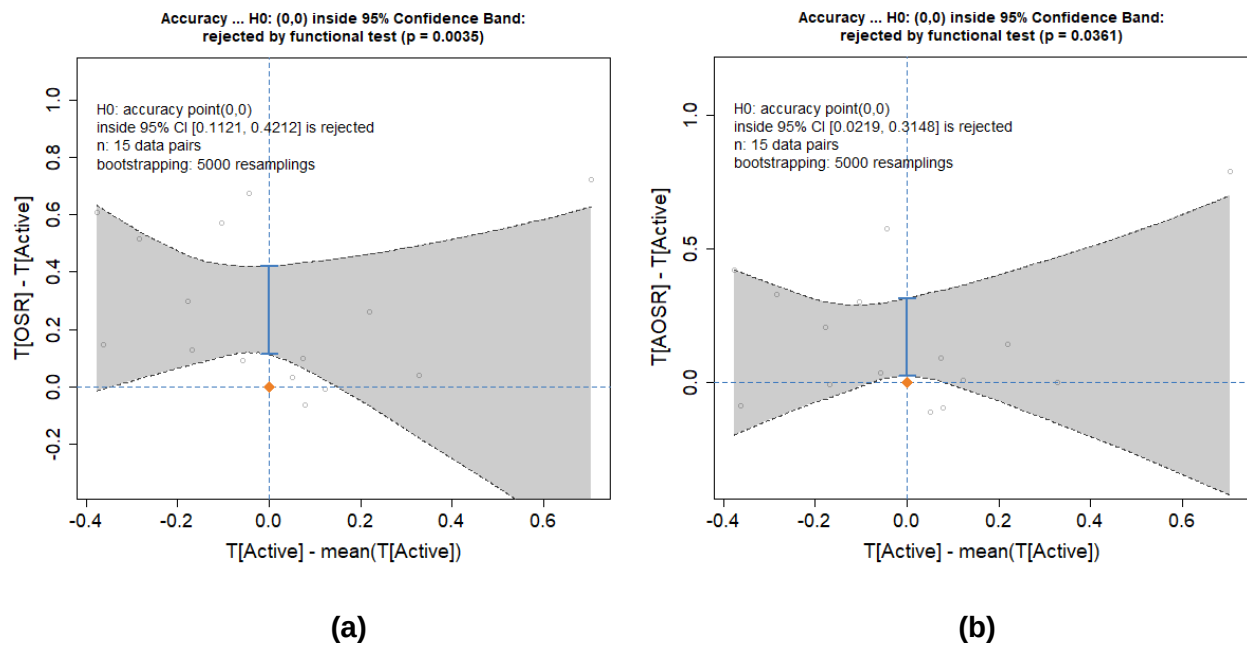
Figure 4-3: Linear regression of active *in situ* measurement against MerPAS[®] derived Hg concentrations from (a) OSR, (b) AOSR, (c) RSR and (d) ARSR. The grey area shows the 95% *CI*. Inferential statistics, an estimate of effect size and its uncertainty, pairwise comparisons, Bayesian hypothesis testing, as well as a Bayesian posterior assessment and its uncertainty, are also shown.

4.2.4 Bland-Altman analysis

4.2.4.1 Test for structural accuracy

Here, it is aimed to statistically test whether the data retrieved from active *in situ* Hg measurements compared to the data obtained from MerPAS[®] with the different SRs have similar structural means (accuracy), i.e., whether Hg concentrations are measured similarly by the sampling techniques. The results are presented in Figure 4-4, with the shadowed areas representing the structural regression bands obtained by bootstrapping. This statistical analyses of the active *in situ* datasets and the data retrieved from MerPAS[®] utilising the OSR and the AOSR reveal that there are statistical differences related to the accuracy of these datasets (p -value = 0.0035 and 0.0361 for OSR and AOSR, respectively). In addition, bootstrapping, which verifies the accuracy point (0,0), rejects the H_0 (null hypothesis indicative of the relationship between two datasets) of the accuracy point being inside the 95% *CI* (grey area) and reflects different levels of accuracy. In contrast, statistical evaluation of the active *in situ* measurements with the Hg levels determined with the RSR and the ARSR indicate good correspondence between

the accuracy of data derived from these measurement techniques (p -value = 0.9969 and 0.2477 for RSR and ARSR, respectively). Bootstrapping also validates similar levels of accuracy between these datasets, with the H_0 of the accuracy point being inside the 95% *CI*. Although this statistical analysis reveals differences in the accuracy of active *in situ* Hg measurements compared to the datasets retrieved from MerPAS® utilising the OSR and the AOSR, this statistical evaluation does not consider the influence of underlying mechanisms on Hg levels derived from MerPAS®. For example, external factors, such as variations in meteorological conditions, are not considered in the statistical analyses. Furthermore, this statistical analysis was conducted with a relatively small dataset. The accuracy of Hg concentrations determined with MerPAS® utilising OSR and AOSR could be improved for a larger dataset. However, it can be assumed that the results presented here is a representative sample of a statistical population.



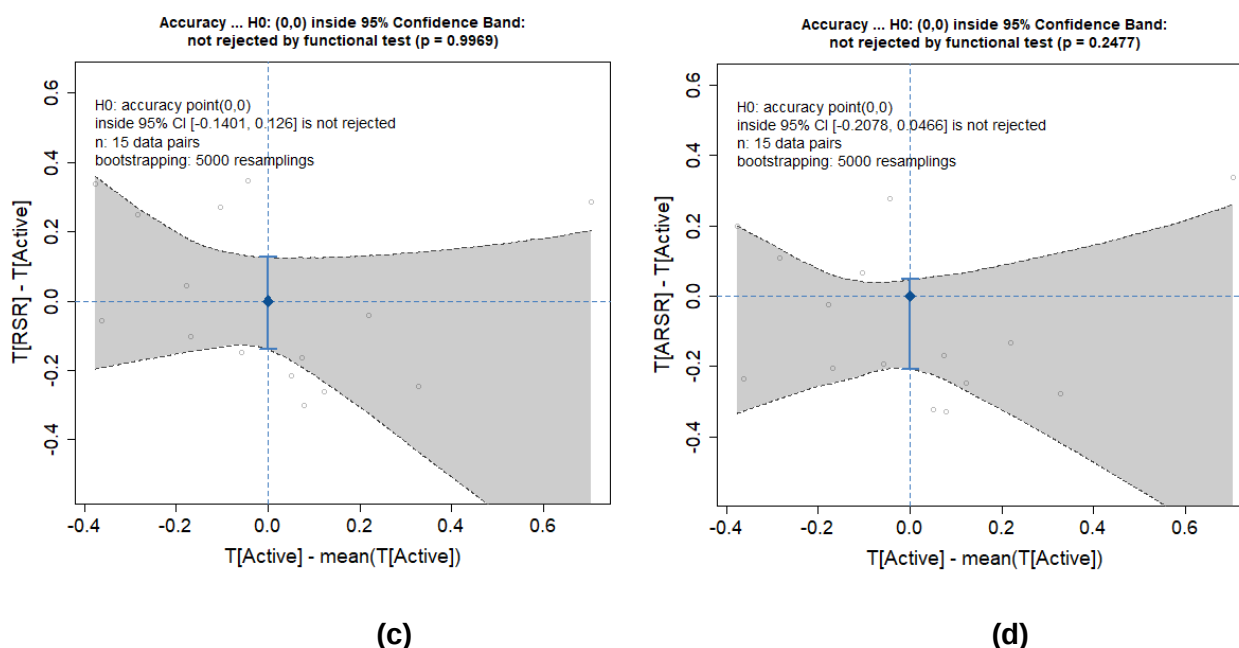


Figure 4-4: Bland-Altman analysis for structural accuracy of Hg concentrations determined with the active *in situ* sampler and MerPAS[®] derived from (a) OSR, (b) AOSR, (c) RSR and (d) ARSR. The shadowed area is the structural regression bands obtained by bootstrapping. The diamond symbol (orange when outside and blue when within the 95% confidence band) represents H_0 at the coordinates (0, 0).

4.2.4.2 Test for structural precision

In this statistical evaluation, the precision of datasets obtained with active *in situ* measurements and MerPAS[®] (calculated with different SRs) is compared, which are presented in Figure 4-5. The results indicate similar levels of precision between datasets retrieved from active *in situ* measurements and Hg concentrations derived from MerPAS[®] for all SRs utilised (p-value = 0.0537, 0.0274, 0.3451 and 0.1830 for OSR, AOSR, RSR and ARSR, respectively). The lower p-value of AOSR does, however, indicate a weaker comparison to the precision of the active *in situ* sampler. Bootstrapping analysis (resampling the data to generate multiple estimates of the precision line and calculating the confidence interval around the estimate) also indicated that the H_0 of the precision lines of OSR, AOSR, RSR and ARSR were inside the 95% CI, which further confirms similar levels of precision within the datasets. As mentioned in the previous subsection, it is also important to note that this statistical assessment could be improved by better understanding other factors influencing Hg concentrations measured with MerPAS[®] and increasing the sample size.

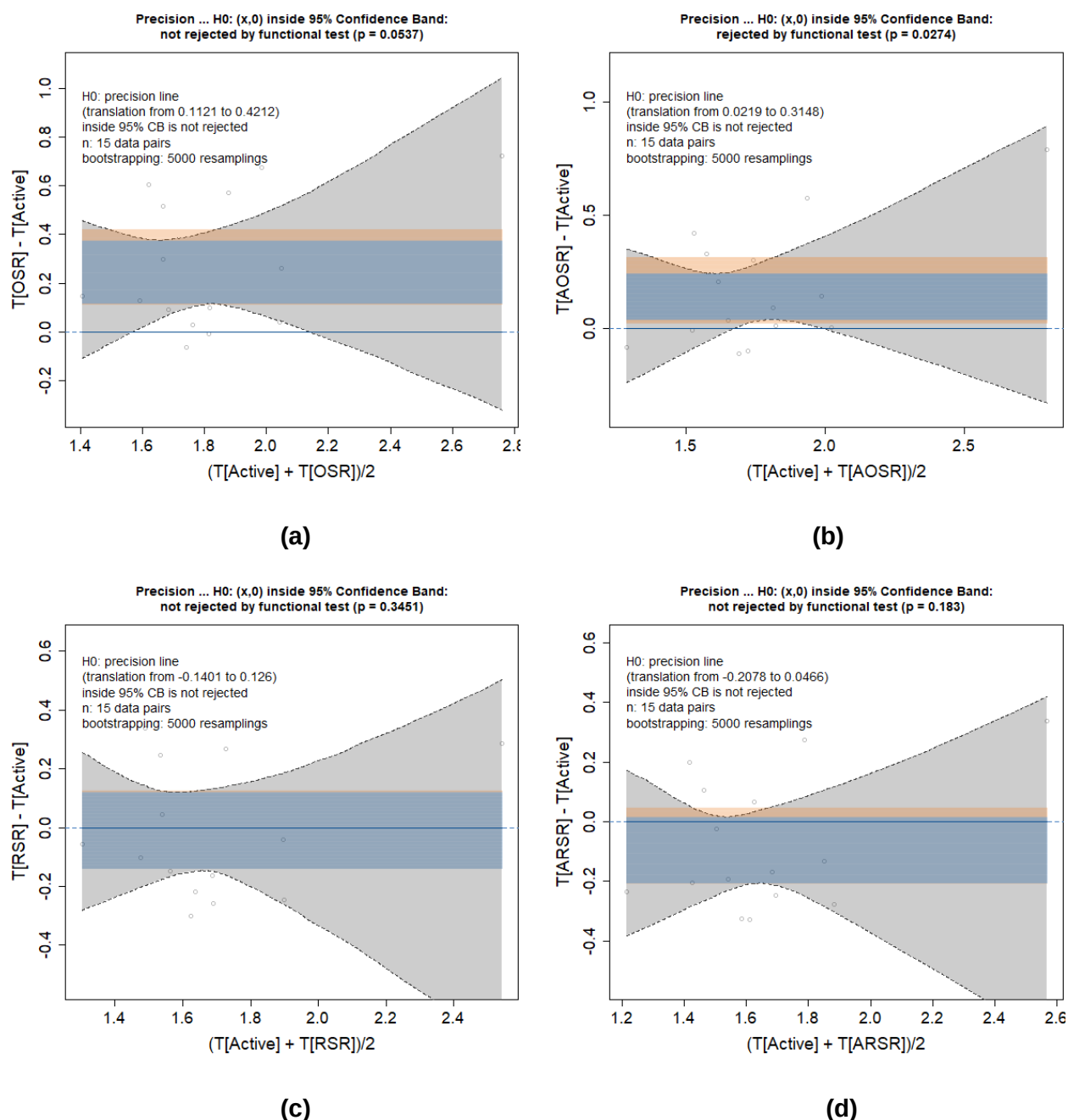
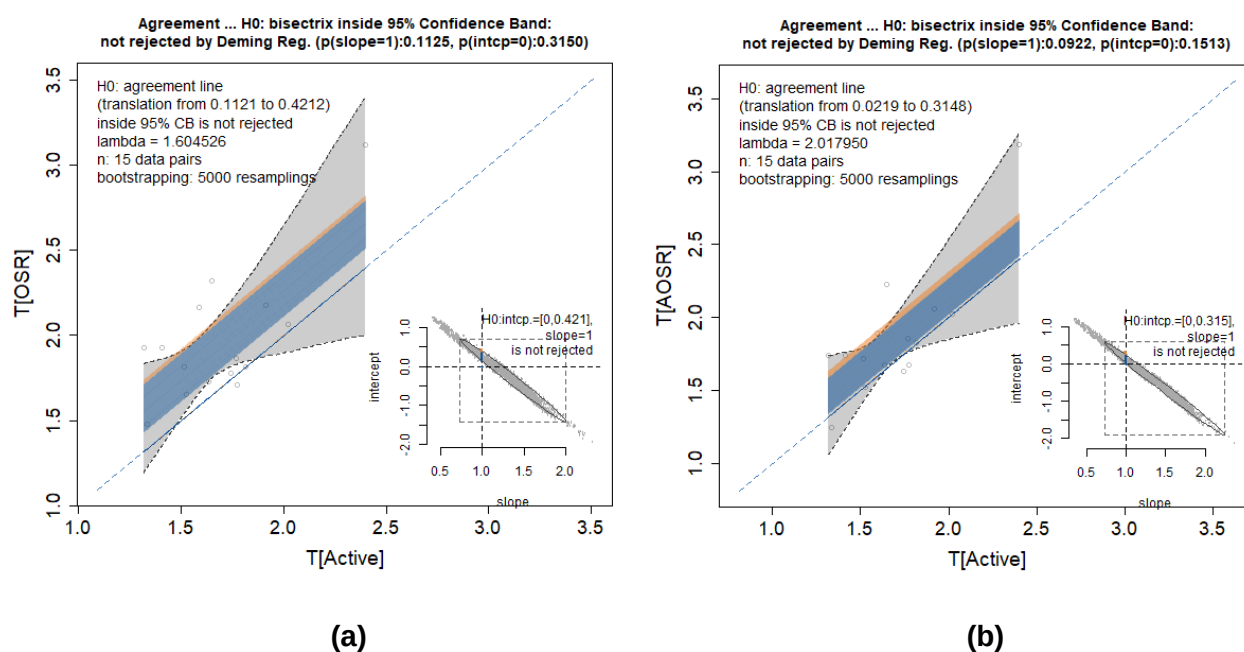


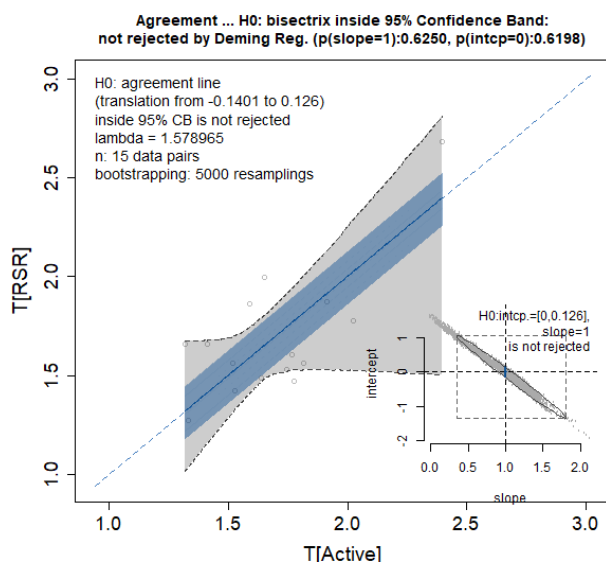
Figure 4-5: Bland-Altman analysis for structural precision of Hg concentrations determined with the active *in situ* sampler and MerPAS® derived from (a) OSR, (b) AOSR, (c) RSR and (d) ARSR. The shadowed area is the 95% confidence band defined by the structural regression, and the horizontal blue line represents H_0 .

4.2.4.3 Test for structural agreement

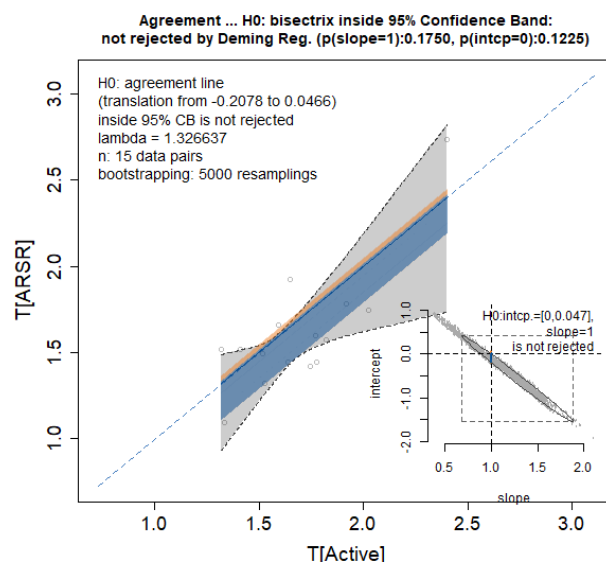
Deming regression was used to assess similarity in the Hg concentrations determined with the active *in situ* sampler and Hg levels derived from MerPAS® with the different SRs, while the structural bisector line was used to test for equivalent measurements obtained from the same sampled air. These methods provide a robust statistical framework to

compare the two measurement methods. The results are presented in Figure 4-6 and, in general, good agreement was observed between active *in situ* measurements and Hg concentrations calculated with the different SRs for MerPAS[®] with the correspondence to the bisector line within the 95% CI and low p-values determined for the slopes and intercepts. The bootstrapping analysis also indicated that the H_0 of the agreement lines of OSR, AOSR, RSR and ASRS was inside the 95% CI, confirming the agreement between the datasets. Also included in each plot in Figure 4-6 are the 95% prediction ellipses (in the bottom right of each graph), which is an alternative plot to test the slope and intercept jointly. These plots also supported good agreement between the datasets. The λ values determined in each of these statistical evaluations indicated some degree of heteroscedasticity in the dataset.





(c)



(d)

Figure 4-6: Bland-Altman analysis for structural agreement of Hg concentrations determined with the active *in situ* sampler and MerPAS® derived from (a) OSR, (b) AOSR, (c) RSR and (d) ARSR. The shadowed area is the 95% confidence band defined by Deming regression for bisector concordance (λ), and the horizontal blue dashed line represents H_0 . Additionally, the right panel shows the 95% prediction ellipse, an alternative way to test slope and intercept jointly.

4.2.5 Mean normalised difference (MND) and relative standard deviation (RSD)

The MND and RSD calculated for each of the datasets derived from MerPAS® with the four SRs in relation to the active *in situ* dataset are listed in Table 4-3. The average MND of the OSR, AOSR, RSR and ARSR were $17.42 \pm 16.06\%$, 12.65 ± 12.53 , $12.23 \pm 6.73\%$ and $12.20 \pm 5.22\%$, respectively, which are slightly higher compared to MND values reported by McLagan, Mitchell, *et al.* (2018) for Hg concentrations measured with MerPAS® in the global evaluation calibration. The RSD of OSR and RSR was 19.65 %, while the RSDs of AOSR and ARSR were 23.20% and 22.68%, respectively, which are also higher than the precisions reported by McLagan, Mitchell, *et al.* (2016) for the original outdoor calibration experiment ($2 \pm 1\%$) in Canada and the global evaluation calibration ($3.6 \pm 3.0\%$; McLagan, Mitchell, *et al.*, 2018) of MerPAS®.

Table 4-3: MND and RSD for each of the datasets derived from *MerPAS*[®] with the four SRs in relation to the active *in situ* measurement

Month	<i>MerPAS</i> [®] OSR	<i>MerPAS</i> [®] AOSR	<i>MerPAS</i> [®] RSR	<i>MerPAS</i> [®] ARSR
	RSD (%)			
	19.65%	23.20%	19.65%	22.68%
	Uncertainty MND (%)			
06/2021	0.34	0.50	14.25	13.62
07/2021	30.05	32.95	11.90	14.04
08/2021	40.78	34.84	21.14	16.72
09/2021	45.97	31.81	25.60	14.97
10/2021	36.53	23.26	17.48	7.52
11/2021	35.95	19.03	16.98	4.23
12/2021	11.12	6.57	4.38	17.78
01/2022	1.78	6.46	12.42	18.60
02/2022	8.43	0.57	6.70	13.44
03/2022	13.73	7.37	2.14	6.88
04/2022	5.70	2.12	9.05	11.71
05/2022	2.04	0.01	12.20	13.72
06/2022	5.53	5.13	9.19	9.49
07/2022	3.60	5.62	17.05	18.55
08/2022	19.68	13.43	2.98	1.68

4.3 Temporal pattern

Although the statistical analysis conducted in this study revealed a better comparison between active *in situ* Hg measurements and Hg levels derived from *MerPAS*[®] with recalibrated sampling rates obtained from the active *in situ* sampler, in practice, the *MerPAS*[®] will be deployed at sites where no active *in situ* Hg sampling will be conducted within proximity of the area. Furthermore, as previously mentioned, the aim of *MerPAS*[®], or passive sampling in general, is to conduct atmospheric measurements in regions that are logistically difficult to access, while also being a low-cost alternative to active *in situ* sampling. In addition, the aim of SAMNet is to improve the spatial coverage of atmospheric Hg measurements conducted in South Africa. Therefore, the AOSR is recommended to be used at the sites where *MerPAS*[®] will be deployed in this region.

In Figure 4-7, the monthly average Hg concentrations derived with the *MerPAS*[®] with the AOSR are presented together with the monthly average Hg levels determined with the active *in situ* sampler for the entire sampling period. Also indicated are the monthly average Hg concentrations determined with the manual active samplers during the last four month of the sampling period with *MerPAS*[®] (with the exception of July 2022 due to the Hg collector tube not been available for sampling). Similar temporal patterns are observed for atmospheric Hg concentrations determined with *MerPAS*[®] and active *in situ* measurements. The seasonal average Hg levels determined with *MerPAS*[®] during winter 2021, spring 2021, summer 2021/2022, autumn 2022 and winter 2022 were 2.52, 1.88, 1.54, 1.99 and 1.84 ng/m³, respectively. The seasonal mean Hg levels determined with the active *in situ* sampler during winter 2021, spring 2021, summer 2021/2022, autumn 2022 and winter 2022 were 1.96, 1.44, 1.54, 1.86 and 1.69 ng/m³, respectively. No significant seasonal variation in Hg levels is evident during the 15-month sampling period, with the exception of higher Hg concentrations determined during winter in 2021. The highest monthly average Hg levels were determined in July 2021 with *MerPAS*[®] and the active *in situ* sampler. Increases in concentrations of atmospheric pollutants typically occur in South Africa due to more pronounced low-level inversion layers trapping pollutants near the surface and changes in pollutant source contributions such as increased household combustion for space heating (e.g. Laban *et al.*, 2018; Lourens *et al.*, 2011). However, increased atmospheric Hg concentrations are not observed during winter in 2022, with Hg levels being similar compared to other seasons. This difference between Hg concentrations determined during the winter seasons in 2021 and 2022 could

be attributed to changes in air mass movement passing over source regions impacting Welgegund, which could be assessed through in-depth air mass back trajectory analysis. However, this type of analysis was beyond the scope of this study and will be conducted in future research where longer-term (at least two full years) active *in situ* atmospheric Hg measurements conducted at Welgegund will be explored. The lowest seasonal average Hg concentrations were determined in summer with MerPAS® and in spring with the active *in situ* sampler. It is also of interest to note that the largest difference between monthly average Hg concentrations determined with MerPAS® and the active *in situ* sampler occurred during winter and spring in 2021 with, especially, significant differences observed in July and August 2021. However, these differences were not observed in the winter and spring months in 2022.

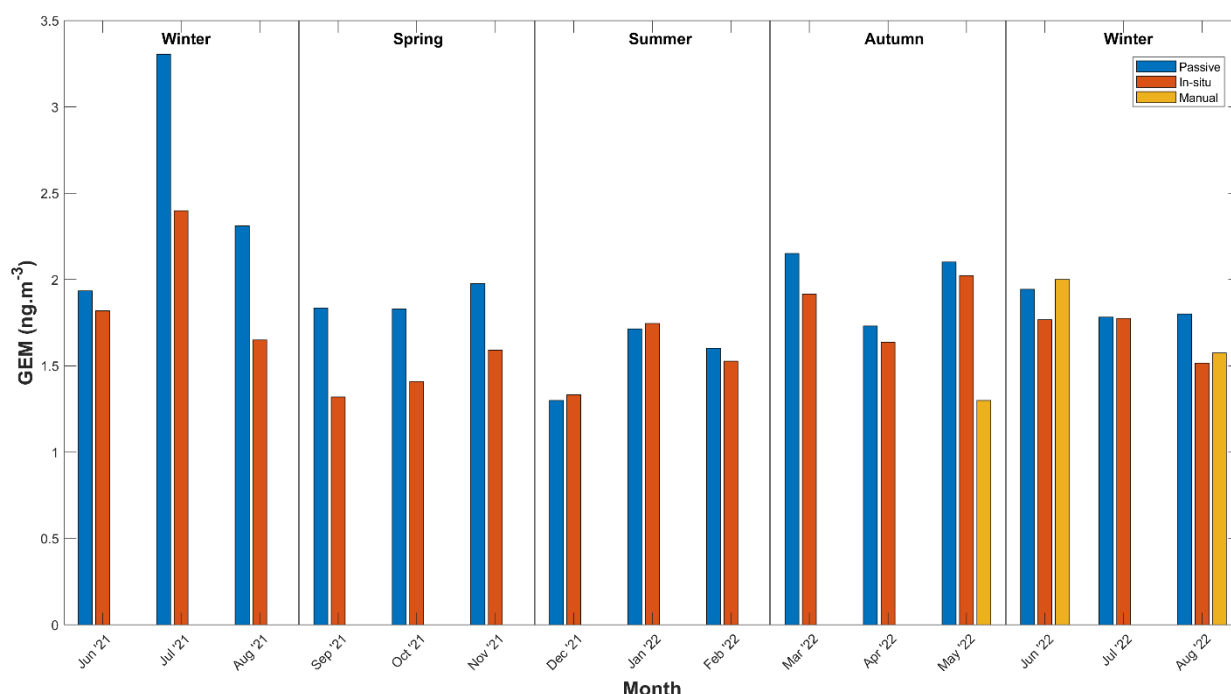


Figure 4-7: Comparison of the monthly average GEM concentrations determined with MerPAS®, active *in situ*, and manual active samplers during the sampling period.

As mentioned above, this study also briefly assessed the performance of a newly developed manual active atmospheric Hg sampler. The monthly average Hg concentrations determined with these samplers, presented in Figure 4-7, compared with MerPAS® and active *in situ* measurements. The monthly average Hg concentrations determined by the manual active sampler were 1.30 ng/m³ in May 2022, 2.00 ng/m³ in June 2022, and 1.58 ng/m³ in August 2022. In Figure 4-8, the 24-hour Hg concentrations determined with the manual active are compared to the 24-hour average active *in situ*

measurements during the manual active sampling period. Hg levels determined with the manual active samplers compared well with the Hg concentrations measured with the active *in situ* sampler, and, similar to *MerPAS*® measurements, in most instances, were moderately higher than active *in situ* measurements. On 31 August and 7 September, manual active sampling was conducted in duplicate, which, during both instances, measured the exact same Hg concentrations.

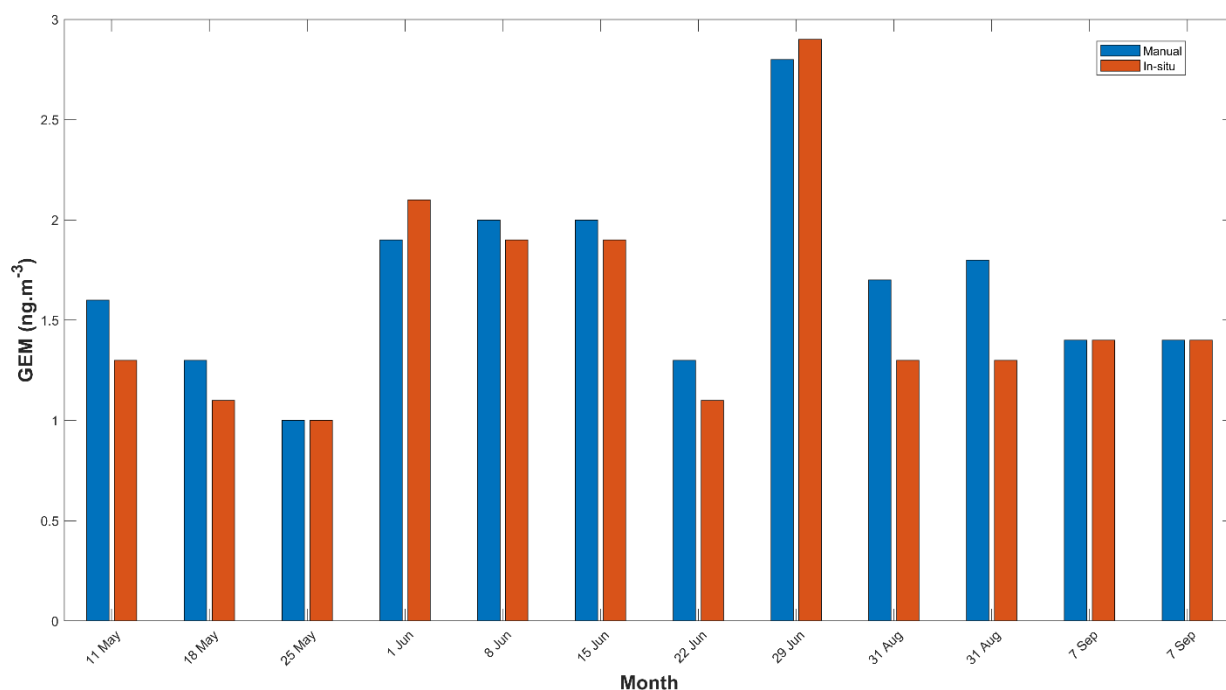


Figure 4-8: Comparison of 24-hour manual active measurements with 24-hour average atmospheric Hg concentrations determined with active *in situ* sampler.

CHAPTER 5 CONCLUSIONS AND PROJECT EVALUATION

This chapter presents the main conclusions based on research findings from atmospheric Hg data collected with passive and active samplers. The study is evaluated in terms of the successes and shortcomings in relation to the objectives listed in Chapter 1, while recommendations for future work is also presented.

5.1 Conclusions

In this study, atmospheric Hg concentrations determined with a passive sampler, i.e., *MerPAS*[®], were statistically evaluated through comparison with atmospheric Hg levels determined with an active *in situ* sampler at a regional background site in the South African interior. Hg concentrations measured with *MerPAS*[®] from June 2021 to September 2022 were derived utilising four different sampling rates, i.e., the original SR (OSR) provided by Tekran for the *MerPAS*[®], an adjusted original SR (AOSR) where the sampling rate (SR) provided by Tekran was adjusted according to temperature and wind speed, a recalibrated SR (RSR) derived from active *in situ* measurements, and an adjusted recalibrated SR (ARSR) where the RSR was adjusted according to temperature and wind speed. Hg levels calculated utilising the OSR and AOSR were generally higher compared to the active *in situ* measurements, while Hg concentrations determined with the RSR and ARSR were lower and closer to atmospheric Hg levels determined with the active *in situ* samplers.

ANOVA, t-test, linear regression and Bland-Altman statistical analyses were performed. ANOVA and t-tests revealed statistically meaningful differences between Hg concentrations determined with active *in situ* measurements and Hg levels derived from *MerPAS*[®] utilising the OSR and AOSR, while no statistically significant differences were evident compared to Hg concentrations derived from *MerPAS*[®] utilising the RSR and ARSR. However, all Hg levels were in good agreement. Linear regression analysis indicated a strong correlation between Hg concentrations determined with the active *in situ* sampler and Hg levels derived from *MerPAS*[®] with all four SRs. Bland-Altman analysis evaluated the structural accuracy, -precision and -agreement of the datasets obtained from *MerPAS*[®] utilising the different sampling rates in relation to active *in situ* measurements. Good correlations were determined for all four *MerPAS*[®] datasets in terms of accuracy, precision and agreement, with the exception of the accuracy of the

datasets derived with OSR and AOSR from *MerPAS*[®]. In general, statistical analysis revealed better comparison between active *in situ* Hg measurements and Hg levels derived from *MerPAS*[®] utilising recalibrated sampling rates. However, passive samplers were developed as low-cost alternatives to active *in situ* sampling and to measure atmospheric Hg in regions that are logistically difficult to access, which means that recalibrated sampling rates will not be available in the practical application of *MerPAS*[®]. Therefore, according to the statistical assessments conducted in this study, it is recommended that the AOSR is used at sites in southern Africa where *MerPAS*[®] is deployed. Furthermore, the statistical analysis performed in this study did not consider the influence of underlying mechanisms on Hg levels derived from *MerPAS*[®]. In addition, although the results presented here can be considered a representative sample of a statistical population and correlations were observed between active and passive measurements, larger datasets could be used for more in-depth statistical assessments in future studies.

Similar seasonal trends were observed for atmospheric Hg concentrations determined with *MerPAS*[®] utilising the AOSR and active *in situ* measurements, with the highest concentrations determined in winter. Finally, a brief assessment of a manual active sampler also revealed good agreement between active *in situ* measurements and a similar temporal pattern. Notwithstanding the relatively limited dataset, this work offers valuable insight into the possibility of producing a diurnal pattern of ambient Hg from shorter temporal resolution of the manual active sampler.

5.2 Project evaluation

In order to evaluate the successes and/or shortcomings of the project, the outcomes of this study, related to the objectives presented in Chapter 1 (section 1.2), were considered.

Objective i: “To deploy *MerPAS*[®] samplers, active *in situ* sampler, and manual active sampler concurrently at Welgegund measurement site, which is a regional atmospheric monitoring station, in order to monitor atmospheric Hg concentrations.”

MerPAS[®] samplers were successfully deployed at the Welgegund atmospheric measurement station for a period of 15 months (June 2021 to September 2022). During this sampling period, with the passive samplers, active *in situ* measurements of atmospheric gaseous elemental mercury (GEM) were also conducted with a Tekran[®]

2537X analyser with a collection efficiency of 91%, which could be considered very good. In addition, a brief assessment of a manual active sampler was also conducted. Welgegend can be considered the most comprehensively equipped atmospheric monitoring station in southern Africa, which provides a good platform and logistics to conduct this type of study. Furthermore, Welgegend is also impacted by the most important source regions of atmospheric pollutants in the north-eastern interior of South Africa, while also being impacted by a relatively clean sector to the west of the station. Therefore, it is representative of different potential atmospheric concentrations of Hg. As previously mentioned, passive samplers, such as *MerPAS*[®], are inexpensive, do not require electricity and allow expansion of atmospheric monitoring networks in regions that are logistically difficult to access.

Objective ii: “To determine atmospheric Hg concentrations using *MerPAS*[®] at Welgegend.”

Hg concentrations measured with *MerPAS*[®] were successfully derived utilising four different sampling rates, i.e., the OSR provided by Tekran for the *MerPAS*[®], an AOSR where the SR provided by Tekran was adjusted according to ambient temperature and wind speed, an RSR derived from active *in situ* measurements, as well as an ARSR where the RSR was adjusted according to ambient temperature and wind speed. Hg levels calculated utilising the OSR and AOSR were generally higher compared to the active *in situ* measurements, while Hg concentrations determined with the RSR and ARSR were lower and closer to atmospheric Hg levels determined with the active *in situ* samplers. A limitation of *MerPAS*[®], which is the case in general for passive samplers, is that it provides an averaged concentration of atmospheric Hg over a specific period (one month in this study) and therefore short-term variability (e.g. diurnal patterns) cannot be established (McLagan *et al.*, 2021). In addition, pollution events are not captured with passive samplers, while relating air mass history to ambient Hg concentrations is also challenging.

Objective iii: “To statistically assess the precision and accuracy of *MerPAS*[®] atmospheric Hg concentration measurements alongside active *in situ* atmospheric Hg concentration measurements.”

The performance of *MerPAS*[®] in relation to active *in situ* measurements was statistically assessed by utilising different statistical methods, which included ANOVA, t-test, linear regression, and Bland-Altman statistical analysis. In general, these statistical methods successfully revealed good correlations between Hg concentrations derived from

MerPAS[®] using the four SRs and the active GEM measurements. These assessments covered structural accuracy, -precision, and -agreement. Although Hg levels derived from *MerPAS*[®] utilising recalibrated SRs compared slightly better to active *in situ* measurements, passive samplers are low-cost alternatives with the aim to measure concentrations of atmospheric species in regions that are logistically difficult to access. Therefore, recalibrated sampling rates will not be available in the practical application of *MerPAS*[®]. However, deriving atmospheric Hg levels from *MerPAS*[®] using the OSR or, preferably the AOSR (considering wind speed and temperature) is acceptable and could provide valuable measurements for data scarce regions. This study successfully demonstrated that *MerPAS*[®] has the potential to enhance the spatial resolution of atmospheric Hg monitoring in South Africa. Another limitation highlighted by this study is the availability of meteorological data and/or active *in situ* measurements within proximity of the region where *MerPAS*[®] is deployed.

Objective iv: “To identify a temporal pattern of atmospheric Hg concentrations.”

Since the AOSR is recommended to be used at the sites where *MerPAS*[®] will be deployed in South Africa, seasonal patterns derived from *MerPAS*[®] utilising the AOSR were compared to seasonal trends determined with the active GEM sampler. Similar seasonal trends were observed for atmospheric Hg concentrations determined with these two sampling techniques. The highest atmospheric Hg levels were determined during winter. A brief assessment of a manual active sampler also revealed good agreement between seasonal patterns determined with active *in situ* measurements.

5.3 Recommendations and future perspectives

The statistical analysis conducted in this study showed that *MerPAS*[®] can be successfully rolled out in South Africa to expand the spatial resolution within this region, which is therefore recommended to be used in the South African Mercury Network (SAMnet).

The following aspects should be addressed in future investigations:

- It is recommended that future work should also consider the influence of underlying mechanisms on Hg levels derived from *MerPAS*[®]. The chemistry of Hg in the atmosphere and environment is complicated (Driscoll *et al.*, 2013; Sonke *et al.*, 2023), as discussed in Chapter 2. Additional measurements of species interacting

with atmospheric Hg, e.g. ozone or halogens, could be included in the statistical analysis.

- The statistical assessment of larger datasets, i.e., deploying *MerPAS*® for longer periods in conjunction with active atmospheric Hg measurements, could also be performed to further improve the statistical significance.

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ANNEXURES

Table A1: Auxiliary data used in calculation of Hg concentrations with MerPAS®

Month	Deployment period (days)	T (°C)	WS (m/s)	mc (g)	mc-avg (g)	mHg (ng)	mHg-avg (ng)	ng/g	Blank	Blank corrected (ng)	Uptake rate (ng/day)	Calculated SR (m ³ /day)	Active conc. X days	Temp./wind speed adjusted SR (m ³ /day)
Jun-21	29.04	11.21	2.70	0.60 0.62	0.61	5.36 7.68	6.52	10.72	13% 10%	5.78	0.199	0.109	52.824	0.127
Jul-21	28.10	9.49	2.72	0.63 0.60	0.62	11.48 9.34	10.41	16.83	7% 8%	9.67	0.344	0.143	67.394	0.125
Aug-21	34.93	13.37	4.00	0.62 0.60	0.61	10.52 8.84	9.68	15.89	7% 8%	8.94	0.256	0.155	57.627	0.133
Sep-21	27.90	18.02	4.95	0.62 0.58	0.60	8.33 4.93	6.63	11.05	9% 14%	5.90	0.212	0.160	36.805	0.140
Oct-21	30.06	17.88	5.00	0.59 0.62	0.61	5.54 8.65	7.09	11.70	13% 9%	6.36	0.212	0.150	42.383	0.140
Nov-21	32.90	21.49	5.19	0.61 0.62	0.61	6.72 10.43	8.58	13.99	11% 7%	7.84	0.238	0.150	52.337	0.144
Dec-21	35.24	29.49	4.54	0.51 0.54	0.52	5.71 7.04	6.37	12.17	11% 9%	5.74	0.163	0.122	46.973	0.149
Jan-22	27.83	20.66	3.44	0.56 0.53	0.54	5.96 6.23	6.09	11.18	11% 10%	5.43	0.195	0.112	48.586	0.138
Feb-22	28.94	21.73	3.21	0.58 0.56	0.57	6.12 5.78	5.95	10.49	11% 12%	5.26	0.182	0.119	44.194	0.138
Mar-22	27.02	18.95	2.88	0.57 0.57	0.57	7.13 7.20	7.17	12.60	10% 10%	6.48	0.240	0.125	51.776	0.134
Apr-22	35.09	15.36	3.07	0.49 0.53	0.51	6.98 7.64	7.31	14.29	8% 8%	6.69	0.191	0.116	57.450	0.132

May-22	27.98	14.43	2.81	0.55 0.50	0.53	7.24 6.73	6.99	13.31	9% 9%	6.35	0.227	0.112	56.568	0.130
Jun-22	34.99	11.23	3.15	0.59 0.60	0.59	8.20 7.62	7.91	13.29	9% 10%	7.19	0.205	0.116	61.870	0.128
Jul-22	28.03	12.49	3.42	0.61 0.61	0.61	5.57 6.43	6.00	9.83	13% 11%	5.26	0.188	0.106	49.730	0.130
Aug-22	34.95	15.02	3.91	0.60 0.59	0.60	7.72 7.68	7.70	12.93	9% 9%	6.98	0.200	0.132	53.015	0.134

