

Emissions of mercury from the power sector in South Africa

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“The health effects of air pollution imperil human lives. This fact is well-documented”

- Eddie Bernice Johnson

DEDICATION

I dedicate this dissertation to my mother, Kathleen Belelie, and aunt, Elize October whose support and words of encouragement from the outset and throughout, kept me afloat. You've provided me with unconditional love, wisdom, and unceasing motivation, without which I would not be the person I am today.

PREFACE

This research is original work by the author, not previously submitted for the purposes of a degree at any university. I was engaged in the research presented in this document from January 2016 to November 2017, and involved in the formulation, conducting, and writing thereof.

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ABSTRACT

Mercury (Hg) is an extremely important element as it is ubiquitous, toxic, and considered a global pollutant. The atmospherically significant forms of Hg include inorganic gaseous elemental (Hg^0), inorganic gaseous reactive (Hg^{2+}), and inorganic particle-bound Hg (HgP). The former species, due to its stability and low reactivity has a long atmospheric lifetime. Due to these characteristics, it may be transported from where it was emitted to distant locations as far as the poles, hence why Hg is considered as a global pollutant. Mercury has one other form which is known as methylmercury. This species is formed after the deposition of Hg^{2+} and is considered as the most toxic form of environmental Hg. Due to their high reactivity and solubility, Hg^{2+} and HgP have short residence times (hours to days) and tend to be deposited near their emission source. The recurrent oxidation and reduction conversions between Hg^0 and Hg^{2+} is important in determining the atmospheric lifetime of Hg.

Mercury may be emitted by both natural and anthropogenic sources. Natural sources essentially reemit Hg that was previously deposited onto and into the Earth. The input that anthropogenic sources add increases this amount and essentially intensifies the global burden of this pollutant, as it cannot be removed from the environment. The leading anthropogenic source of Hg has been identified as coal-fired power plants, both annually and globally. In South Africa, most of these plants are located in the Highveld region – an area that is well-known for its anthropogenic activities. The state of Hg emitted by the power sector on the South African Highveld is, however, unclear. It is thus important to generate knowledge on Hg emissions in this region as it represents one of the most concentrated source regions of Hg in the world.

The state of Hg over the Highveld region was investigated by firstly characterising ambient Hg concentrations. This was done by analysing spatial, seasonal, and diurnal variation of total gaseous mercury (TGM) at Balfour (BF), Middelburg (MB), and Standerton (ST). Additionally, relationships between TGM and criteria pollutant concentrations were established. Concentrations ranged 0.40–28.72, 0.12–9.91, and 0.21–32.10 ng/m^3 at BF, MB, and ST, respectively, with mean concentrations of $1.99 \pm 0.94 \text{ ng/m}^3$ ($n = 6378$), $1.04 \pm 0.62 \text{ ng/m}^3$ ($n = 5473$), and $1.25 \pm 1.38 \text{ ng/m}^3$ ($n = 3568$). Seasonally, concentrations at the sites varied as follows: summer>spring>winter>autumn; summer>winter>autumn>spring; and winter>spring>summer, respectively. Unfortunately, no data was captured during autumn at ST. The only pronounced diurnal pattern was observed at ST where local domestic combustion appears to have been the dominant source. The likelihood of the aforementioned is corroborated by the observed relationship between TGM and CO concentrations at this site.

The penultimate part of the investigation involved estimating emissions from power plants using the bottom-up-approach. This entailed the estimation of emissions from 13 power plants during 2014 – 12 of which are located on the Highveld. This also involved an investigation on the influence of emission control devices and Hg-coal content on estimates. Emission control devices are installed in power plants to regulate emissions of particulate matter, SO₂, and NO_x, and indirectly Hg. The control devices used in South African power plants are fabric filters (FFs) and electrostatic precipitators (ESPs). Their Hg removal efficiencies vary from 89% (FFs), 36% (ESPs), and 62.5% where they are used collectively. Some power plants also install a flue-gas conditioning (FGC) system to enhance the performance of an ESP. It was found that if all power plants were to use FFs, the amount of emitted Hg would be substantially lower. This is an important finding as some power plants currently still use ESPs. Previous Hg emission studies in South Africa adopted Hg-coal content from literature. This study utilised Hg-coal content measured at each respective power plant. By comparing estimations using adopted and actual Hg-coal content values, it was found that estimates for 2014 were much lower when using actual values. This, therefore, highlights that actual Hg-coal content values should allow for more refined estimates.

In the final part of the investigation, the spatial distribution of the atmospherically significant forms of Hg was modelled with CALPUFF. Additionally, concurrent wet and dry deposition were simulated to investigate their effect on the spatial distribution of these species. As Hg⁰ is the only species that pose a threat to human health via the inhalation pathway, a health risk assessment was conducted. It was found the highest concentrations of the species were found in the centre of the domain where there is a cluster of power plants. Based on the results, the emissions from the power plants seem to be accumulating in an area of already high concentrations. Wet deposition of Hg²⁺ and HgP was observed to occur near the power plants with the highest removal occurring in the immediate vicinity of the modelled sources (<1 km). The species most affected by wet deposition was found to be Hg²⁺. The wet deposition of Hg⁰ was not modelled due to its low solubility and reactivity. The dry deposition of the species was highest in the centre of the domain with Hg⁰ the species most affected. The health risk assessment revealed that the exposed population in the Highveld region may be at risk to adverse health effects. The work done in this research may pave the way for prospective Hg studies over the South African Highveld. It also provides unique contributions to the broader area of knowledge regarding Hg in South Africa, as well as globally, and may subsequently enhance the understanding thereof.

Keywords: *Mercury, coal-fired power plant, South African Highveld, bottom-up-approach, CALPUFF*

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GLOSSARY

BF	Balfour
°C	Degrees Celsius
C ₂ H ₆ Hg	Dimethyl Mercury
C	Mercury Coal Content
CC	Coal Consumption
CH ₃ Hg ⁺	Organic Methyl Mercury
Cl	Chlorine
cm ² /s	Square Centimetre per Second
DEA	Department of Environmental Affairs
ESP	Electrostatic Precipitator
FF	Fabric Filter
FGC	Flue Gas Conditioning
FGD	Flue Gas Desulphurization
g/s	Grams per Second
g/t	Grams per Tonne
Hg	Mercury
Hg ⁰	Elemental Mercury
Hg ²⁺	Divalent Inorganic Mercury
HgP	Particle-bound Mercury
HNO ₃	Nitric Acid
INC	Intergovernmental Negotiating Committee
g/ha yr ⁻¹	Kilogrammes per Hectare per Year
K	Kelvin
km	Kilometre
l/m	Litres per Minute
LCC	Lambert Conic Conformal
m	Metre

m/s	Metres per second
MB	Middelburg
ME	Mercury Emission
MeHg	Methylmercury
mg/kg	Milligrams per Kilogram
mg/m ³	Milligrams per Cubic Metre
mg/t	Milligrams per Tonne
Mg/yr	Mega grams per Year
mm/hr	Millimetres per Hour
MM5	Fifth-Generation Penn State/NCAR Mesoscale Model
Mt/yr	Megatonnes per Year
MW	Megawatt
n	Count
ng/m ³	Nanogrammes per Cubic Metre
OH	Hydroxyl Radical
PM	Particulate Matter
ppb	Parts Per Billion
ppm	Parts Per Million
s ⁻¹	Per Second
SAHA	South African Highveld Area
SAMA	South African Mercury Assessment
SANAS	South African National Accreditation System
SO ₂	Sulphur Dioxide
SO ₃	Sulphur Trioxide
ST	Standerton
t/yr	Tonnes per Year
TGM	Total Gaseous Mercury
UNEP	United Nations Environment Programme

U.S. EPA	U.S. Environmental Protection Agency
UTM	Universal Transverse Mercator
WHO	World Health Organisation
μm	Micron
$\mu\text{g}/\text{m}^3$	Micrograms per Cubic Metre

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CHAPTER 1

INTRODUCTION

This chapter provides a brief overview on environmental mercury focussing specifically on its atmospherically significant forms. The importance of this study, its aim and objectives, and the study design and dissertation outline are also provided.

1.1 Background

Mercury (Hg) is a highly noxious and ubiquitous volatile metal, which is environmentally persistent and prone to long-range atmospheric transport (Angot *et al.* 2014). It subsequently leads to adverse health effects in distant regions compared to where it was emitted (Pacyna & Pacyna 2002). Mercury is therefore regarded as a global pollutant threatening both the health of humans and ecosystems (Lindqvist & Rodhe 1985; Boudala *et al.* 2000; Pacyna & Pacyna 2002; Angot *et al.* 2014). The ecological behaviour of the Hg emitted depends on the different environmental forms it can assume, as these chemical forms have different chemical properties (Lindqvist & Rodhe 1985; Boudala *et al.* 2000). Environmental Hg may exist as elemental, inorganic, and organic Hg (WHO 2003). It is important to differentiate between these forms as each one has a different fate and effect in and on the environment (Dabrowski, Ashton, Murray, Leaner, & Mason, 2008).

Unlike other heavy metals in the environment, atmospheric Hg generally occurs in its gaseous phase (Ebinghaus *et al.* 1999). It may be emitted into the atmosphere as inorganic gaseous elemental (Hg^0), inorganic reactive gaseous (Hg^{2+}), and inorganic particle-bound Hg (HgP) (Poissant *et al.* 2005; Prestbo & Gay 2009). Atmospheric emissions of Hg are dominated by Hg^0 (53%), followed by Hg^{2+} (37%) and HgP (10%) (Carpi 1997). Although Hg^0 is the predominant form in the gaseous phase (Carpi 1997; Lin & Pehkonen 1999), Hg^{2+} significantly influences the total deposition of atmospheric Hg (Ebinghaus *et al.* 2001). Under certain conditions, Hg^0 may be removed by dry deposition processes (Lindberg *et al.* 1992).

Dry deposition occurs when Hg^{2+} , and occasionally Hg^0 , adheres to soot and/or other particulate matter (PM) to form HgP in clouds (Seigneur *et al.* 1998). Deposition, together with the continuous chemical transformation between Hg^0 and Hg^{2+} , are important factors in the determination of the atmospheric lifetime of Hg (Lindberg *et al.* 2007). Due to their high solubility in water and reactivity, Hg^{2+} and HgP have short residence times (Schroeder & Munthe 1998) and are prone to be deposited near their emission sources (Carpi 1997; Driscoll *et al.* 2007). In contrast, Hg^0 may persist in the atmosphere (~1 year) (Lindqvist & Rodhe 1985; Schroeder & Munthe 1998; Bergan & Rodhe 2001; Lindberg *et al.* 2007) due to its stability, low solubility and low reactivity in the atmosphere (Poissant *et al.* 2005; Liu *et al.* 2007). The deposition of Hg, under favourable conditions, can lead to the formation of methylmercury. This neurotoxin has adverse impacts relating to human health, after bioaccumulation and biomagnification in the food chain (Celo *et al.* 2006). The severity of the effects depends upon the degree of exposure and Hg species exposed to (WHO 2008).

Mercury can be emitted into the atmosphere through natural (volcanoes, windblown dust, soils and vegetation, ocean and other water bodies) and anthropogenic (mining and smelting, fossil fuel combustion, agriculture, waste incineration, cement production) activities (Lindqvist & Rodhe 1985; Ebinghaus *et al.* 1999). Anthropogenic emissions are considered to be the leading source of atmospheric Hg with 2880 t/yr (Mason 2009; Pirrone *et al.* 2010a). It is sequentially followed by emissions from marine (2680 t/yr) and terrestrial (1850 t/yr) systems. Although the contribution of Hg from natural activities is substantial, anthropogenic activities result in the larger part of annual atmospheric emissions (Prestbo & Gay 2009).

Of all possible anthropogenic sources of Hg, combustion in coal-fired power plants dominates the contribution to its environmental burden (Pacyna *et al.* 2001). Approximately 56% of the global Hg pool originates from coal-fired power plants (Pirrone & Mason 2009). Coal combustion contributed to about 72.7% of the country's primary energy supply in 2003, 68.2% in 2004, 71.8% in 2005, and 65.9 % in 2006 (South Africa Department of Energy 2009). The amount of Hg emitted from coal depend on the coal's Hg content, the installed emission control device and its efficiency, and the quantity of combusted coal (Pavlish *et al.* 2003; Wagner & Hlatshwayo 2005). Approximately 458.6 Mg/yr of Hg were emitted from coal-fired power plants worldwide during 1996-2006, even though coal solid wastes contain relatively small amounts thereof (Streets *et al.* 2009). Moreover, inventories of numerous countries have identified coal combustion as an

imperative source of Hg emissions (Pacyna *et al.* 2006; Dabrowski *et al.* 2008). Recent inventories also show an increase in total Hg emission estimations for South Africa, where Leaner *et al.* (2009) reported 40 tonnes for 2004 and Masekoameng *et al.* (2010) 50 tonnes for 2006. If better control measures are not applied, an upsurge in emissions of Hg seems unavoidable.

A past study listed South Africa as the second highest source of global atmospheric Hg emissions (about 16% of total global Hg emissions) (Pacyna *et al.* 2006). In this study, gold production was assumed as one of the main sources of Hg. However, South African mines utilize cyanidation and not amalgamation for gold extraction (Leaner *et al.* 2009). Nevertheless, this led to the establishment of the South African Mercury Assessment (SAMA) programme (Leaner *et al.* 2009) and also triggered subsequent Hg emission estimate studies (Dabrowski *et al.* 2008; Leaner *et al.* 2009; Masekoameng *et al.* 2010).

The South African Highveld Area (SAHA) was identified as an area associated with poor air quality due to high emissions of criteria pollutants, and additionally a potential area of high concentration of atmospheric Hg species (Masekoameng *et al.* 2010). This region is well-known for its various anthropogenic emission sources that consist of coal-fired power plants, coal landfills, metallurgy and mines, agriculture, and transportation (Freiman & Piketh 2003; Dabrowski *et al.* 2008). Not long ago, coal-fired power plants were estimated as the leading possible anthropogenic source of ambient Hg emissions in South Africa (72-78 %) (Masekoameng *et al.* 2010). It is sequentially followed by cement manufacturing, gasification of coal to produce synthetic fuel, the production of ferrous and non-ferrous metals, residential heating, minerals and crude oil refining, and fluorescent tubes.

The Minamata treaty, an international agreement that protects human and ecosystem health from anthropogenic emissions of Hg, was signed by South Africa in 2013 together with 98 other countries (Venter *et al.* 2015), but there is no legislation regulating emissions of Hg in South Africa. Emissions thereof are mostly governed in the USA, Canada, Germany, and the Netherlands; and partially in Australia, China, Korea, and the Philippines (Sloss 2012). The National Environmental Management: Air Quality Act (Act no. 39 of 2004) of South Africa, however, regulates emissions of criteria pollutants SO₂, NO_x, and PM. It consequently and indirectly reduces emissions of Hg depending on the emission control device installed at each respective power-generating plant, albeit not the case for other possible Hg sources. The Hg

content in the raw materials, and the installed emission control devices in other South African industries have been identified as major gaps in our knowledge of Hg emissions (Leaner *et al.* 2009). Adequate data and knowledge about environmental Hg pollution can further the understanding of its behaviour and fate, while consequently advancing the scientific basis and prevention thereof (Fang *et al.* 2004).

One tool used by the scientific community, which helps us better understand the environmental behaviour and fate of Hg, is an atmospheric dispersion model. Primarily, they are quantitatively used for the correlation between concentration and emission levels observed in an area (Oshan *et al.* 2006). Understanding the difficulties related to source-specific air pollution control and air quality management, however, can be quite challenging because a wide range of contaminants is emitted from various sources over different spatial and temporal scales. Specialists involved in controlling and managing air pollution, therefore, rely on these models to aid them in decision-making processes for different pollution control settings. Rather than comparing an air pollution source's compliance to results obtained from air pollution sampling, they are being based on emission estimates from atmospheric dispersion models (DEA 2013). These models use different tools and strategies, such as Lagrangian, Eulerian, Computational Fluid Dynamics, and Gaussian models (Leelőssy *et al.* 2014). The Lagrangian CALPUFF model was selected as the most suitable model for this study as it is able to simulate long-range atmospheric transport, handle complex three-dimensional wind fields, and as it is endorsed by the U.S. EPA for exactly the aforementioned purposes (U.S. EPA 2000). The former reason is of cardinal importance as Hg⁰, as previously mentioned, is prone to long-range atmospheric transport (Poissant *et al.* 2005; Liu *et al.* 2007).

There is uncertainty regarding the current state and impact of Hg over the South African Highveld. The state of Hg emitted by the power sector on the SAHA is unclear. It is plausible to assume that the geographical distribution of the power plants should cause this region to be the highest area of Hg concentrations in South Africa. This study may help in determining whether Hg is a potential problem over this region. It may also pave the way for prospective studies regarding knowledge of Hg on the South African Highveld.

1.2 Motivation for this research

Southern Hemisphere ambient monitoring research on Hg has been identified as a requirement (Baker *et al.* 2002). Research on ambient Hg has frequently been conducted at the Global Atmospheric Watch station located at Cape Point (Leaner *et al.* 2009) where biomass burning was studied as a likely and significant Hg source in the Southern hemisphere (Brunke *et al.* 2001; Baker *et al.* 2002; Brunke *et al.* 2009; Brunke *et al.* 2012; Venter *et al.* 2015). This is the most comprehensive longstanding South African station (Beukes *et al.* 2013). A recent study was also done on Amsterdam Island (Angot *et al.* 2014) where the influence of rapidly transported air from Southern Africa during the biomass burning period is investigated. To the best of our knowledge, there is presently no peer-reviewed publications relating to ambient Hg concentrations on the SAHA. There are, however, currently ongoing studies which consider atmospheric Hg concentrations for the SAHA (Meyer 2017) and a background site (Bredenkamp 2017), respectively.

Developing a country-specific Hg emission inventory can further the understanding of its behaviour and fate, while subsequently advancing the scientific basis thereof (Fang *et al.* 2004). The majority of developing countries, especially those in Africa, require Hg emission inventories (Masekoameng *et al.* 2010). Studies estimating the emission of Hg from various anthropogenic activities in South Africa have been conducted (Dabrowski *et al.* 2008; Masekoameng *et al.* 2010). Separate studies by (Roos (2011), and more recently by (Garnham & Langerman (2016) estimated emissions of Hg from ESKOM (the primary provider of electricity in South Africa) coal-fired plants in the Highveld region for the periods of 2010 and 2010 - 2015 respectively. In addition, this study will model the atmospheric dispersion of Hg from 12 of these power plants for the period of 2011 - 2013 over the SAHA.

The atmospheric dispersion of Hg has been simulated at Cape Point using GEOS-Chem (Selin *et al.* 2007; Travnikov *et al.* 2017), GLEMOS, and ECHMERIT (Travnikov *et al.* 2017); and the CAM-Chem (Lei *et al.* 2013) models. To date, no literature has been found that describes air pollution dispersion modelling of Hg on the SAHA, or with CALPUFF for South Africa. The purpose of this research is to fill this knowledge gap. Collectively, the results obtained in this study may pave the way for subsequent Hg studies over the South African Highveld region.

1.3 Aim and Objectives

The overall aim of this research was to improve the understanding of ambient Hg concentrations in South Africa, paying special attention to the SAHA. The following are the objectives of this study:

Objective 1: Characterise ambient Hg concentrations over the South African Highveld

Objective 2: Estimate Hg emissions from ESKOM coal-fired power plants

Objective 3: Model the atmospheric dispersion of Hg resulting from coal-fired power plant emissions

1.4 Study Design and Dissertation Outline

In order to characterise ambient Hg concentrations on the SAHA, available Hg data for 2009 for three monitoring sites, namely, Balfour, Middelburg, and Standerton, is statistically analysed. The locations of these sites are important as they are surrounded by a fleet of ESKOM coal-fired power plants. The analysed data is compared to obtain spatial and temporal variation. This dataset, however, consists of noticeable gaps in data leading to the selection of only one year and three monitoring sites for analysis. Chapter 3 discusses this in more concise detail. Importantly, this dataset comprises of monitored data of ambient total gaseous mercury (TGM), which of course excludes HgP.

Emissions of Hg are estimated from 12 coal-fired power plants for 2014: Arnot, Camden, Duvha, Grootvlei, Hendrina, Kendal, Kriel, Lethabo, Majuba, Matimba, Matla, Tutuka. These plants, excluding Matimba, surround Balfour, Middelburg, and Standerton. The bottom-up-approach is utilized to estimate Hg emissions from these plants. This calculation requires the fuel consumption, Hg-coal content used, and removal efficiencies of the emission control device/s installed. In addition, the effect of different emission control devices and Hg-coal contents on the resulting estimation is investigated.

The atmospheric dispersion of Hg emitted by the aforementioned plants is modelled on a 250 km x 250 km domain with Matimba not being considered, as it is outside the modelling domain. The three atmospherically significant forms of Hg (Hg^0 , Hg^{2+} , and HgP) were modelled by using the

CALPUFF model and its components with the concurrent simulation of wet and dry deposition at the specified receptors on the domain. Collectively, the objectives provide both spatial and temporal variability of Hg over the South African Highveld priority area. The data and knowledge generated through this study may assist air quality authorities to determine the most appropriate techniques and/or legislation for Hg emission control.

This dissertation is presented in the traditional format. It is formatted according to the Post-graduate Manual of the North-West University and consists of 7 chapters. Chapter 2 provides a review of relevant literature regarding the most important environmental emission, transformation and transportation, and deposition concepts associated with Hg. The significant role of coal-fired power plants on environmental Hg cycling is also discussed and outlined in this chapter. Chapter 3 provides a detailed discussion of the data and methods used to meet each of the three objectives. This section also presents data and information that is not included in the methodology discussions of each article. Chapter 4 presents quantified results of the ambient concentrations of Hg based on data for 2009. This dataset comprises of data obtained from three sites which are considered to be representative of the SAHA, for the purpose of this study. These results have been submitted as an article entitled 'Characterisation of ambient Total Gaseous Mercury concentrations on the South African Highveld', to a peer-reviewed journal - currently under review. Chapter 5 presents Hg emission estimate findings for 13 coal-fired power plants located on the SAHA, established through utilisation of the bottom-up-approach. It also provides findings based on the hypothetical use of different emission-control devices and Hg-coal contents. The results in this section have been presented as a paper at the peer-reviewed annual National Association for Clean Air (NACA) conference (Nelspruit, 5–7 October 2017). This paper, entitled "Mercury emissions from the power sector in South Africa", was awarded the best scientific student paper. Chapter 6 presents findings on the atmospheric dispersion of three Hg species resulting from emissions from 12 ESKOM power stations, modelled between 2011 and 2013. For context, the modelled concentration of one of the species is evaluated through use of a health risk assessment. This section also reports concurrent simulations of wet and dry deposition. The final chapter provides the conclusions of the obtained results for each respective objective. It also discusses the limitations and research needs of each study and highlights unique contributions made to the broader field of knowledge.

CHAPTER 2

LITERATURE REVIEW

This chapter provides insight into the most important environmental emission, transformation and transportation, and deposition concepts associated with Hg. The emissions section in this chapter draws special attention to Hg emissions resulting from coal-fired power plants. It is essential to understand how Hg is interchanged between and within the atmosphere, lithosphere, and hydrosphere; and how this relates to anthropogenic emissions from, especially coal-fired power plants. A power-generating plant in itself is a chamber where Hg is converted between its three significant forms through the interaction with other products resulting from coal combustion. This chapter also conceptualizes the health effects related to Hg and provides a brief overview of the most commonly used techniques to model its atmospheric dispersion.

2.1 Sources of emission

Mercury may be emitted into the atmosphere by both natural and anthropogenic sources (Table 2-1) (Ci *et al.* 2011). Primary and secondary sources exist and understanding the difference between the two is extremely important. Both natural and anthropogenic primary sources transfer inorganic elemental Hg (Hg^0) from lithospheric pools to the atmosphere. Once in the atmosphere, it is oxidised to inorganic reactive divalent Hg (Hg^{2+}) and deposited back onto and into the surface of the Earth and oceans. This species may then be reduced back to (Hg^0) and reemitted to the atmosphere. The reemitted Hg represents secondary sources which exchange Hg amongst between pools and the atmosphere. Primary sources intensify the global burden of Hg in surface pools, whereas secondary sources redistribute it between and inside ecologies (Driscoll *et al.* 2013).

2.1.1 Natural emissions

Natural sources contribute about 69.2% of the total global Hg amount emitted into the atmosphere (Table 2-1). Oceans dominate this contribution (35.6%), followed by biomass burning (9%), desert, non-vegetated, & metalliferous areas (7.3%), vegetation (6%), forests (4.5%), Hg evasion (2.7%), agriculture (1.7%), lakes (1.3%), and geothermal activities and volcanoes (1.2%). Oceans (Fitzgerald *et al.* 1984) and vegetation (Lindberg *et al.* 1998) are not only able to emit Hg into the atmosphere but can also act as a sink for the uptake thereof (Ericksen *et al.* 2003; Gustin *et al.* 2006). Vegetation, although able to emit Hg, is not necessarily a source thereof (Sexauer *et al.* 2008). Mercury can, however, be emitted when the vegetation is exposed to wildfires (Friedli 2003). The amount of Hg emitted when exposed to wildfires depend on Hg uptake from the atmosphere and roots, and deposition on the vegetation (Rea *et al.* 2002). Mercury emitted through biomass burning eventually gets deposited and later gets transformed to toxic organic methyl Hg (MeHg) (Friedli *et al.* 2009). Mercury emitted from volcanic activity and biomass previously deposited Hg. The amount of Hg input from volcanoes varies depending on whether they're degassing or erupting (Pirrone *et al.* 2010a). Changes in land use, meteorology, and mechanisms controlling the exchange of environmental Hg are factors that influence the reemission of Hg from biomass burning (European Commission 2001; Mason 2009).

2.1.2 Anthropogenic emissions

Anthropogenic sources of Hg are classified into two major groups: primary and secondary (Pacyna *et al.* 2010). Primary anthropogenic sources of Hg are geologic in origin. After mobilisation, these sources emit Hg into the environment through either mining and/or fossil fuel combustion, where Hg is present in trace amounts and unintentionally released as a by-product. Secondary anthropogenic sources are those ascribed to where Hg is intentionally used and emitted. This includes the use of Hg in industrial processes and small-scale artisanal gold mining.

Table 2-1: Estimated global Hg emissions by natural and anthropogenic (primary + reemitted) Hg sources (European Commission 2001; USGS 2004; Pacyna *et al.* 2006; Telmer & Veiga 2009; Pirrone *et al.* 2010a).

	Source	Hg Emitted (Mg/yr)	Contribution (%)
Natural	Oceans	2682	35.6
	Biomass Burning	675	9.0
	Desert, Non-vegetated, & metalliferous areas	546	7.3
	Vegetation (savannah, grassland, tundra, prairie, chaparral)	448	6.0
	Forests	342	4.5
	Hg Evasion	200	2.7
	Agriculture	128	1.7
	Lakes	96	1.3
	Geothermal Activity & Volcanoes	90	1.2
	Total	5207	69.2
Anthropogenic	Fossil fuel combustion	810	10.8
	Artisanal gold mining production	400	5.3
	Non-ferrous metal production	310	4.1
	Cement production	236	3.1
	Waste incineration	187	2.5
	Caustic Soda production	163	2.2
	Other	65	0.9
	Hg production	50	0.7
	Pig iron & steel production	43	0.6
	Coalbed fires	32	0.4
	Vinyl Chloride Monomer production	24	0.3
	Total	2320	30.8

Possible anthropogenic sources of Hg, from a South African perspective, includes artisanal gold mining, ferrous and non-ferrous metals production, and coal combustion (Masekoameng *et al.* 2010). Masekoameng *et al.* (2010) reported estimated anthropogenic source contributions during 2000-2006 (Figure 2-1). Emissions relating to artisanal gold mining, a prohibited activity in South Africa (Leaner *et al.* 2009), is not conveyed. The leading contributor during this period, and evidently in the figure, was coal-fired power plants. Leaner *et al.* (2009) estimated that in 2004 in South Africa alone, this source emitted about 32.6 tonnes of Hg. Similarly, Masekoameng *et al.* (2010) estimated about 30 tonnes of Hg for the same year.

Masekoameng *et al.* (2010) estimated emissions from 10 out of the 13 currently operating coal-fired power plants (Figure 2-2), as Komati, Camden, and Grootvlei were only re-commissioned at a later stage due to an increased demand for electricity (Figure 2-3). Medupi came online in 2015 and Kusile is still under construction. Of these plants, Kriel, Kendal, Tutuka, and Matla dominated atmospheric Hg emissions (Figure 2-4). These plants are situated in Mpumalanga province on the larger part of the Highveld region, hence why the area is regarded as a potential area of high concentration of atmospheric Hg species (Masekoameng *et al.* 2010).

About two-thirds of atmospheric Hg is derived from either direct or reemitted anthropogenic sources (Driscoll *et al.* 2007). Overall, emissions of Hg to the atmosphere are estimated to be between 6600 and 7000 Mg/yr, and between 36 and 57% are primary direct emissions from anthropogenic sources (Lindberg *et al.* 2007). In 2000, as estimated by a global study (Pacyna *et al.* 2006), more or less 2189.9 tonnes of Hg was emitted through anthropogenic activities (Table 2-2). This was dominated by stationary combustion processes on each and every continent. Other reported anthropogenic Hg sources are Hg manufacturing, production of gold, the manufacturing of cement, the production of caustic soda, the manufacturing of non-ferrous metals, the production of steel and pig iron, the disposal of waste, and other minor Hg sources. In most countries, the predominant anthropogenic sources of Hg include artisanal gold mining and metal processing, cement production, waste incineration, and several industrial processes (Schroeder & Munthe 1998; Pacyna *et al.* 2006). In South Africa, however, artisanal gold mining is not a leading source.

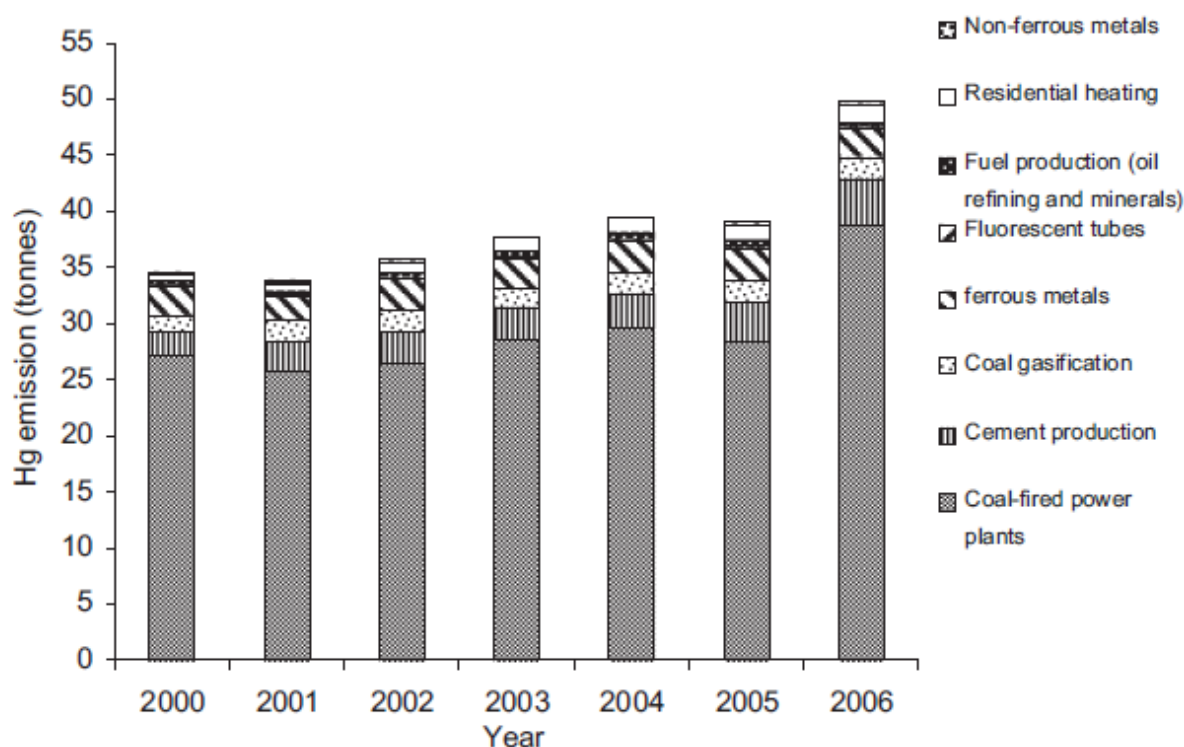


Figure 2-1: Estimated Hg emission by various anthropogenic sources in South Africa during 2000-2006 (Masekoameng *et al.* 2010).

Emissions of Hg from mining and metal processing sources result from both fossil fuel combustion and the presence of Hg as an impurity in the ores, whereas Hg released from cement production occurs primarily as coal and waste fuels combust (Pacyna *et al.* 2010). The aforementioned activities are regarded as critical as almost all of these activities occur in developing countries (Pirrone *et al.* 2010a). The most critical of these sources in South Africa is coal combustion in power plants (Leaner *et al.* 2009).

Table 2-2: Estimated global anthropogenic Hg emissions inventory for 2000 (tonnes)
(Pacyna *et al.* 2006).

Continent	Stationary Combustion	Cement Production	Non-ferrous metal production	Pig Iron & Steel production	Caustic soda production	Hg Production	Gold production	Waste Disposal	Other	Total
Africa	205.3	5.3	7.9	0.4	0.3	0.1	177.8	-	1.4	398.4
Asia (Excluding Russia)	878.7	89.9	87.6	11.6	30.7	0.1	47.2	32.6	0.9	1179.3
Australasia	112.6	0.8	4.4	0.3	0.7	-	7.7	0.1	-	126.6
Europe (Excl. Russia)	88.8	26.5	10.0	10.6	12.4	-	-	11.5	15.3	175.1
Russia	26.5	3.7	6.9	2.7	8.0	-	3.1	3.5	18.2	72.6
South America	31.0	6.5	25.4	1.4	5.0	22.8	-	-	-	92.1
North America	79.6	7.7	6.4	4.3	8.0	0.1	12.2	18.7	8.8	145.8
Total	1422.4	140.4	148.6	31.3	65.1	23.1	248.0	66.4	44.6	2189.9

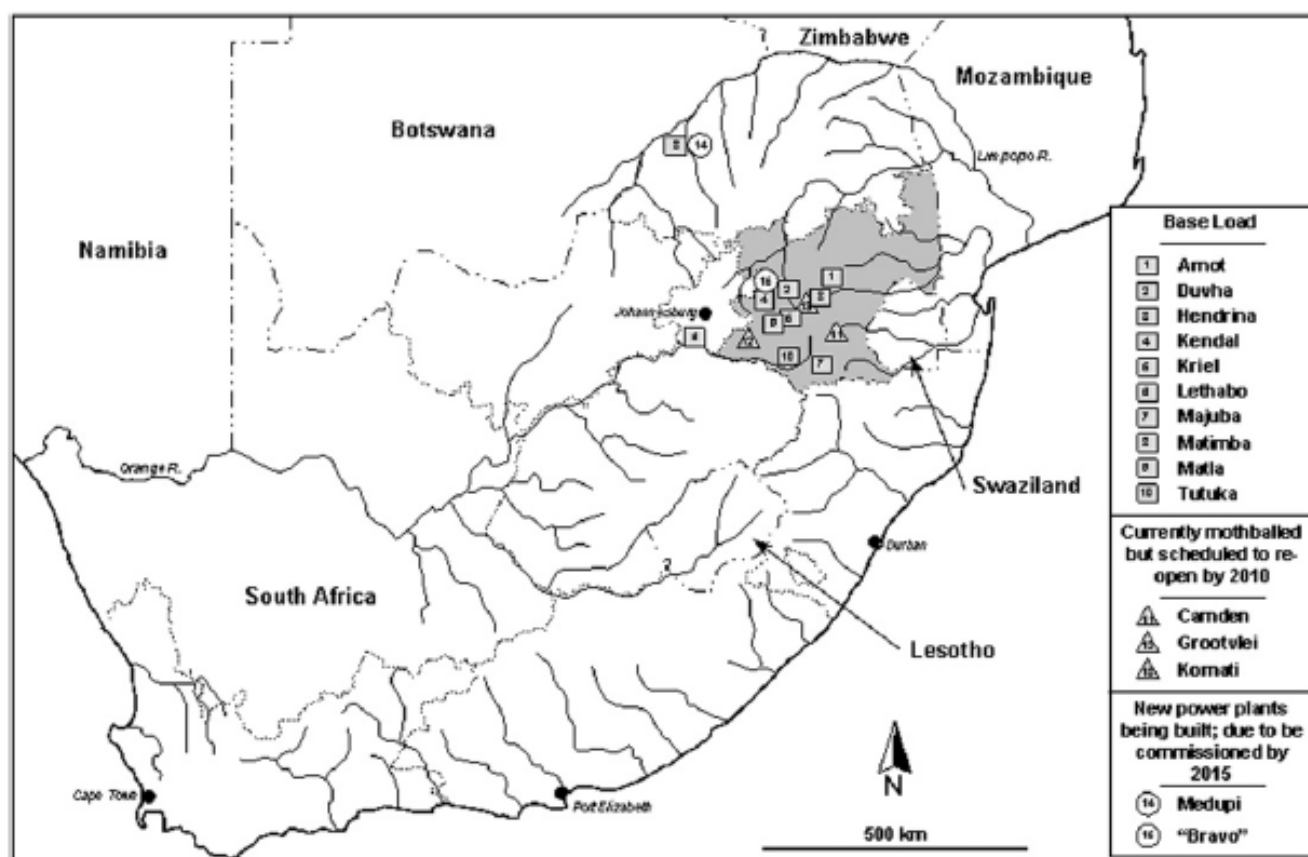


Figure 2-2: Location of the coal-fired power plants considered by Masekoameng *et al.* 2010 (Dabrowski *et al.* 2008).

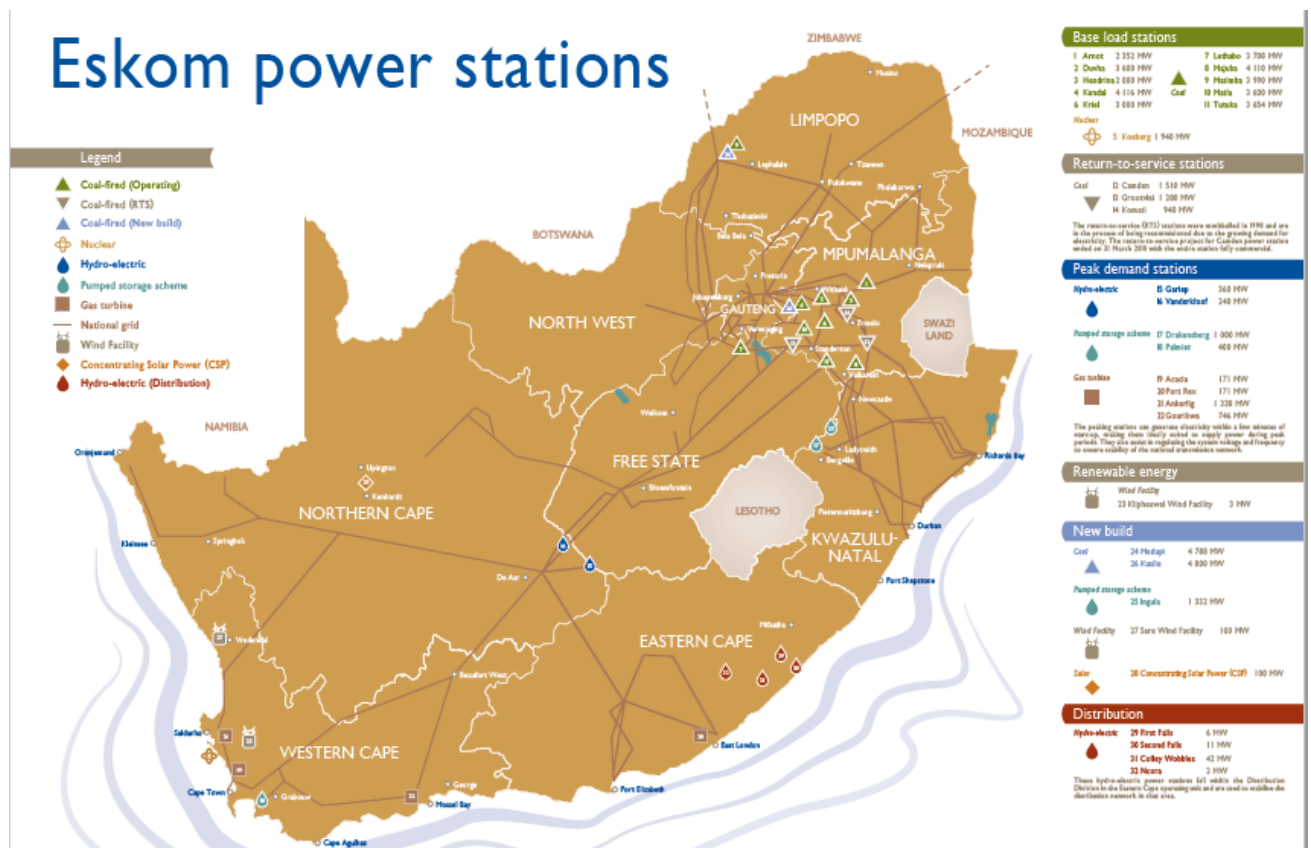


Figure 2-3: All currently active ESKOM coal-fired power plants including re-commissioned stations (Komati, Camden, and Grootvlei) (Eskom 2013).

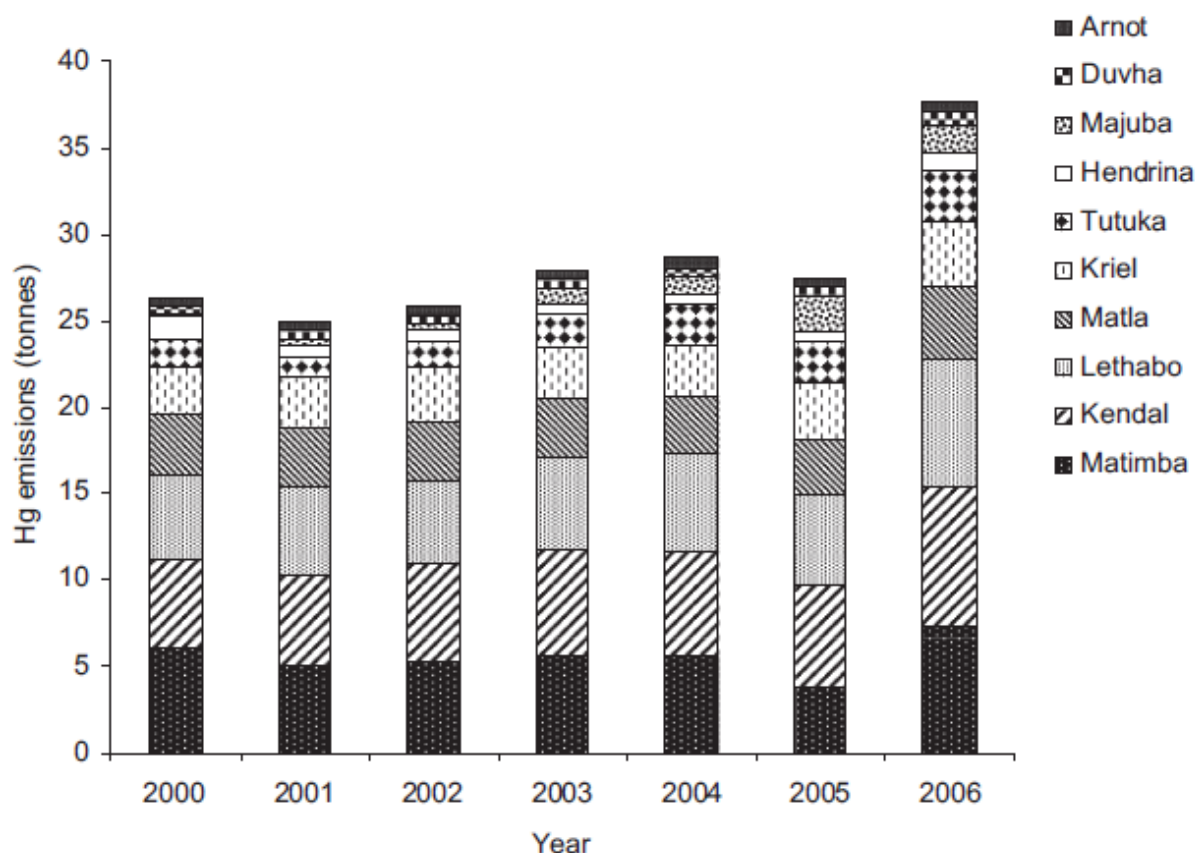


Figure 2-4: Estimated atmospheric Hg emissions from major South African coal-fired power plants during 2000–2006 (Masekoameng *et al.* 2010).

2.1.2.1 Coal combustion in South African coal-fired power plants

The increase in emissions of Hg to the atmosphere provoked immediate research on the quantification of Hg emissions from several anthropogenic sources (Dabrowski *et al.* 2008). Of all possible anthropogenic sources of Hg, coal-fired power plants dominate the contribution to the environmental burden thereof (Pacyna *et al.* 2001). Approximately 56% of the global Hg pool originates from this source (Pirrone & Mason 2009). This huge amount is attributable to the amount of coal burnt and not necessarily the Hg-coal content (Pacyna *et al.* 2010). In a South African context, it was estimated that between 72 and 78% of atmospheric Hg concentrations during 2000 - 2006, resulted from power plants (Masekoameng *et al.* 2010). South Africa,

regarded as the 6th largest coal producer globally, depended on coal to contribute about 72.7% of its primary energy supply in 2003, 68.2% in 2004, 71.8% in 2005, and 65.9% in 2006 (DOE 2009).

Approximately 75% of the African continent's coal reserves are within South Africa (Figure 2-5) (Wagner & Hlatshwayo 2005). The Witbank, Highveld, and Ermelo coalfields provide the majority of coal used by coal-fired power plants located on the SAHA. As a collective, they account for about 48% of the country's power generating capacity (Hobbs *et al.* 2008). The Highveld and Witbank coalfields were, however, reported to near their point of exhaustion (Jeffrey 2005). This means that by now, these same coalfields should be even closer to exhaustion.

The most important varieties of coal are sub-bituminous, bituminous, and anthracite coal. South African ESKOM power plants were primarily designed to burn low-grade bituminous coal, as higher grade coal types are exported (Roos 2011). Due to heat, pressure, and buried remnants of vegetation, peat (not coal) is converted to lignite (brown coal), then to sub-bituminous and bituminous coal (soft coal), and finally anthracite (hard coal) (Miller 2007). Coal comprises of mostly ash and carbon and small amounts of nitrogen and sulphur (Küçük *et al.* 2003; Tan *et al.* 2006). In a study conducted on bituminous coal mined at Kleinkopje from the Witbank coalfield, the composition thereof was dominated by carbon (60.4%) and ash (15.2%) (Cloke *et al.* 2002). Coal may also consist of trace amounts of Hg, typically bound to a sulphur particle and released when coal combusts (Miller 2007). However, inadequate data exists on the Hg content of these coals (Dabrowski *et al.* 2008). The Hg coal-content is essentially subject to the coal type or rank, and the investigated average of this in South African Highveld coals is about 0.15 ppm (ranging between 0.04 and 0.27 ppm) (Wagner & Hlatshwayo 2005). A later study (Pacyna *et al.* 2006) reported a higher average value of about 0.51 ppm (ranging between 0.01 and 1.0 ppm). The study by Pacyna *et al.* (2006), however, reported Hg coal-content for South African, and not for South African Highveld coal where most ESKOM coal-fired power plants receive their coal from. The Hg coal-content in South African coal is generally, but not significantly lower when compared to concentrations in those of other countries (Table 2-3).

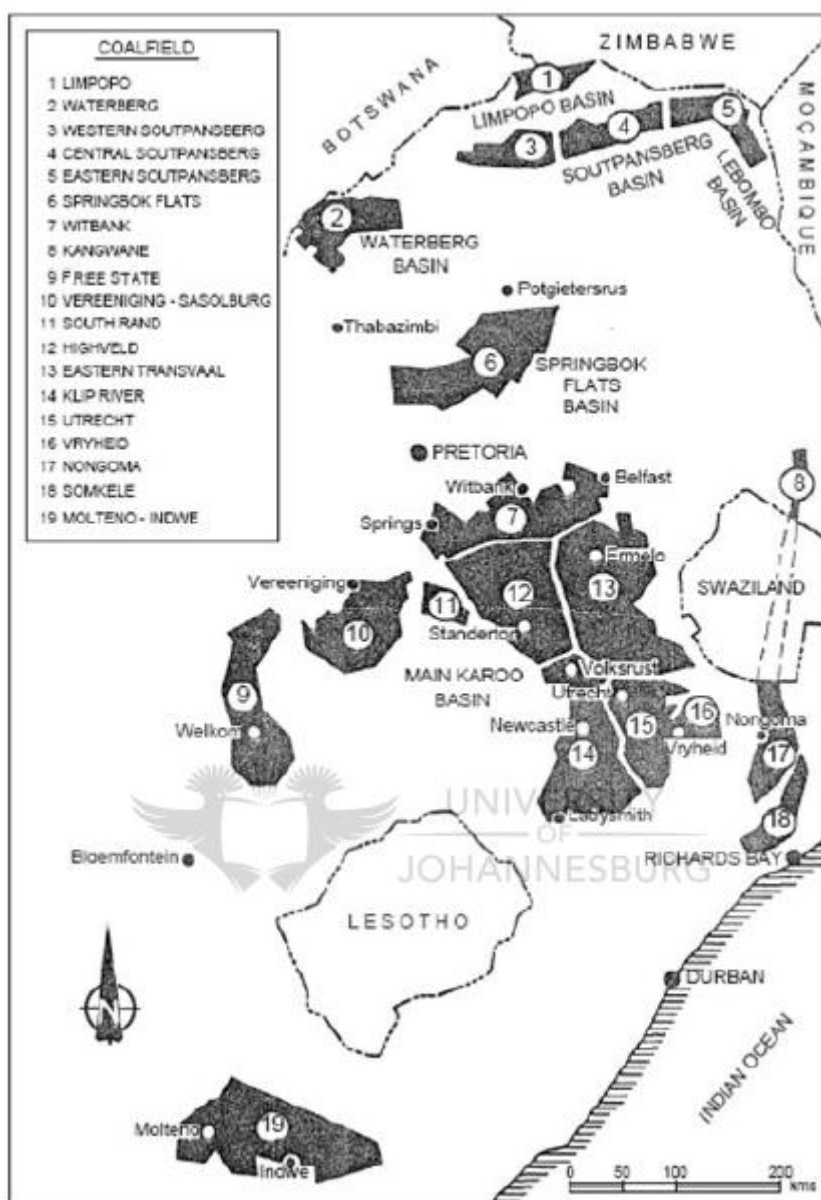


Figure 2-5: Coalfield distribution in South Africa (Wagner & Hlatshwayo 2005).

Table 2-3: **Mercury concentrations in various fossil fuel types** (Pacyna *et al.* 2006).

Country	Fossil Fuel Type	Hg Concentration (ppm)
South Africa	Hard coal (g/t)	0.01–1.0
Europe	Hard coal (g/t)	0.01–1.5
USA	Hard coal (g/t)	0.01–1.5
Australia	Hard coal (g/t)	0.03–0.4
Russia	Hard coal (g/t)	0.02–0.9
Europe	Brown coal (g/t)	0.02–1.5
USA	Brown coal (g/t)	0.02–1.0
N/A	Crude Oil (g/t)	0.01–0.5
N/A	Natural Gas (g/t)	0.0–0.5

2.1.2.2 Emission Control Devices and Techniques

As coal combustion results in various gaseous products, including Hg to be emitted into the atmosphere, devices that control these emissions are installed in coal-fired power plants to curtail their concentrations. Power plants owned by ESKOM mainly use fabric filters (FF), flue gas conditioning systems (FGC), and electrostatic precipitators (ESP) to control Hg emissions (Dabrowski *et al.* 2008). Emissions of PM are reduced by ESPs and FFs, while gaseous SO₂ emissions are reduced by an FGC (Pavlish *et al.* 2003). An FGC involves the spraying of an additive (SO₃, NH₃, and salts of Na) into the flue gas; essentially changing fly-ash characteristics and in turn, increasing removal efficiency (Reese & Greco 1968; Alvarez *et al.* 2000; Shanthakumar *et al.* 2008). ESKOM power plants utilize primary PM reducing control devices (Table 2-4), while most also use SO₃ flue gas conditioning systems to improve the overall performance of an ESP (Roos 2011). The type and efficiency of the control device utilized at each respective power plant will directly affect the amount of emitted Hg into the atmosphere (Pacyna *et al.* 2006). This reduction can be anything between 0 and 90% (Pavlish *et al.* 2010) depending on the type of coal combusted, and emission control device installed.

Table 2-4: Current emission control devices installed in ESKOM coal-fired power plants (Roos 2011).

Power Plant	Coal Washing	Primary Emission Control	Secondary Emission Control
Arnot	Partial	FF	None
Duvha	Partial	FF & ESP (cold-side)	SO ₃ FGC*
Hendrina	Partial	FF	None
Kendal	None	ESP (cold-side)	SO ₃ FGC
Kriel	None	ESP (cold-side)	SO ₃ FGC
Lethabo	Partial	ESP (cold-side)	SO ₃ FGC
Majuba	None	FF	None
Matimba	Yes	ESP (cold-side)	SO ₃ FGC
Matla	None	ESP (cold-side)	SO ₃ FGC
Tutuka	None	ESP (cold-side)	None
Camden	None	FF	None
Grootvlei	None	FF & ESP (cold-side)	None
Komati	None	ESP (cold-side)	SO ₃ FGC

*SO₃ FGCs: Sulphur trioxide flue gas conditioning system

Emission control devices typically have better removal efficiencies when used as a collective, as opposed to operating individually. This is especially derivable for the co-benefit use of an FF and wet Flue Gas Desulphurisation (FGD) system (Table 2-5) and expected regardless of the coal type combusted. Some unconventional emission control techniques are being discovered and used to enhance the performance of FFs, ESPs, and FGCs. This includes coal washing/coal pre-treatment, coal blending, sorbent and scrubbing technologies, coal and sorbent additives (induces oxidation and enhances capture of Hg), and boiler treatment additives. Not all techniques can be utilized at every coal-fired power plant located around the world though. This is mainly due to the differences in how these plants are configured, and the types of coal they combust (Pavlish *et al.* 2010).

Table 2-5: Anticipated removal efficiencies of emission control devices installed in U.S. coal-fired power plants (Pavlish *et al.* 2010).

Emission Control Device	Removal Efficiency based on aggregate data (%)			
	Bituminous	Sub-bituminous	Lignite	All coal types
Cold-side ESP	30–40	0–20	0–10	0–40
Cold-side ESP + wet FGD*	60–80	15–35	0–40	0–80
Cold-side ESP + dry FGD	35–50	10–35	0–10	0–50
Fabric Filter	40–90	20–75	0–10	0–90
Fabric Filter + wet FGD	75–95	30–75	10–40	10–95
Fabric Filter + dry FGD	65–95	20–40	0–20	0–95
Coal washing	20–40	-	-	0–40

*FGD = Flue Gas Desulphurisation

2.2 Environmental forms, transport, and transformation of Hg

2.2.1 Forms

The environmental behaviour of emitted Hg is determined by the various chemical forms it can assume, as these forms have different chemical properties (Lindqvist & Rodhe 1985; Boudala *et al.* 2000). The speciation of these forms is important as they have different fates and effects in and on the environment (Dabrowski *et al.* 2008). Environmental Hg may exist as inorganic elemental (Hg^0), inorganic mercurous (Hg^+) and mercuric (Hg^{2+}), and organic methyl and dimethyl Hg (WHO 2003).

Atmospherically, inorganic gaseous elemental (Hg^0), inorganic reactive gaseous (Hg^{2+}) and inorganic particle-bound (HgP) Hg are the currently differentiated forms (Poissant *et al.* 2005; Prestbo & Gay 2009). Mercury is dissimilar from other heavy metals in that it primarily occurs in the gaseous phase (Ebinghaus *et al.* 1999). Its forms are converted when continuously cycled between the atmosphere, oceans, soil, biota, and lakes (Figure 2-6) (Boudala *et al.* 2000). Gaseous elemental Hg is the predominant atmospheric operational species in the atmosphere (WANG *et al.* 2007), especially in remote or rural areas (Ebinghaus *et al.* 1999). It dominates the contribution to atmospheric emissions by 53%, followed by Hg^{2+} (37%) and HgP (10%) (Carpi 1997). Reactive gaseous Hg and HgP have short residence times (hours-days) as they are

reactive and highly soluble in water (Schroeder & Munthe 1998) and tend to be deposited near sources of emission (Carpi 1997; Driscoll *et al.* 2007). Gaseous elemental Hg, however, has long residence times (approximately 1 year) (Lindqvist & Rodhe 1985; Schroeder & Munthe 1998; Bergan & Rodhe 2001; Lindberg *et al.* 2007) due to its stability, low solubility and reactivity in the atmosphere (Poissant *et al.* 2005; Liu *et al.* 2007). As a result, emissions of Hg^0 tend to persist and get transported over large distances in the atmosphere (Angot *et al.* 2014). The repeated chemical transformation between Hg^0 and Hg^{2+} is regarded as important in the atmospheric lifetime of Hg (Lindberg *et al.* 2007).

It is generally assumed that Hg emitted by natural activities predominantly exists as Hg^0 (Schroeder & Munthe 1998; Dastoor & Larocque 2004; Shetty *et al.* 2008), although the emission of dimethyl Hg ($\text{C}_2\text{H}_6\text{Hg}$) from ocean bodies has been reported (Kirk *et al.* 2008) and gaseous oxidized Hg from soils (Engle *et al.* 2005). Mercury emitted by anthropogenic activities, depending on the sector involved, is believed to mainly occur as Hg^{2+} and HgP (Carpi 1997; Pacyna *et al.* 2001; Pacyna & Pacyna 2002; Dastoor & Larocque 2004).

Once deposited, bacteria are able to convert inorganic Hg^{2+} to any of its organic forms (Bisogni & Lawrence 1975). Organic methylmercury (MeHg) is well documented as the most toxic environmental form of Hg. This neurotoxin is mainly produced by anaerobic bacteria in aquatic ecosystems (Jensen & Jernelöv 1969; Compeau & Bartha 1985) but it can also form under aerobic conditions (Bisogni & Lawrence 1975). The leading sources of MeHg formation are believed to be atmospheric deposition (Munthe *et al.* 1995) and surface runoff (Driscoll *et al.* 1998).

2.2.2 Transport

Mercury partakes in a number of complex and intertwined environmental cycles, converting between its chemical forms. The atmospheric and aquatic-biological cycles are two of the most important of these cycles. The most important feature of the aquatic-biological is the formation of MeHg when Hg^{2+} (strong affinity for various inorganic and organic ligands) binds with a carbon, and the demethylation thereof (Lindqvist & Rodhe 1985). This species gets transported in the biological food chain by bioaccumulation, while at the same time undergoing bio-magnification (Celo *et al.* 2006).

The global cycling of Hg results from it naturally entering the atmosphere, hydrosphere, lithosphere, and eventually also the biosphere. The primary sources this natural emission are geologic of origin. This consists of volcanic activity and associated geological activities, and emissions from soil enriched in Hg (Selin 2009). An addition of substantial amounts of Hg to the atmosphere can be initiated by a volcanic eruption, hence why the natural occurring Hg cycle should not be thought of as constant throughout time. Eventually, these amounts emitted by volcanoes into the atmosphere are transported to the hydrosphere and lithosphere by deposition processes. After deposition, it can be reemitted back into the atmosphere, with time frames as short as hours to as long as decades (Pirrone *et al.* 2010a). The transportation of Hg is significantly faster in the atmosphere than in the hydrosphere, hence why the atmosphere is considered to be the major pathway for global Hg distribution (Zhang *et al.* 2012; Pirrone *et al.* 2010b).

Mercury naturally occurs in the biogeochemical cycle, but due to anthropogenic activities such as the combustion of fossil fuel and mining, its atmospheric, oceanic, and terrestrial amounts have increased (Mason & Sheu 2002). Within this cycle, natural flux estimates to the atmosphere during the pre-industrial age, appear to be much lower as opposed to those from anthropogenic activities (Figure 2-6) (Selin 2009).

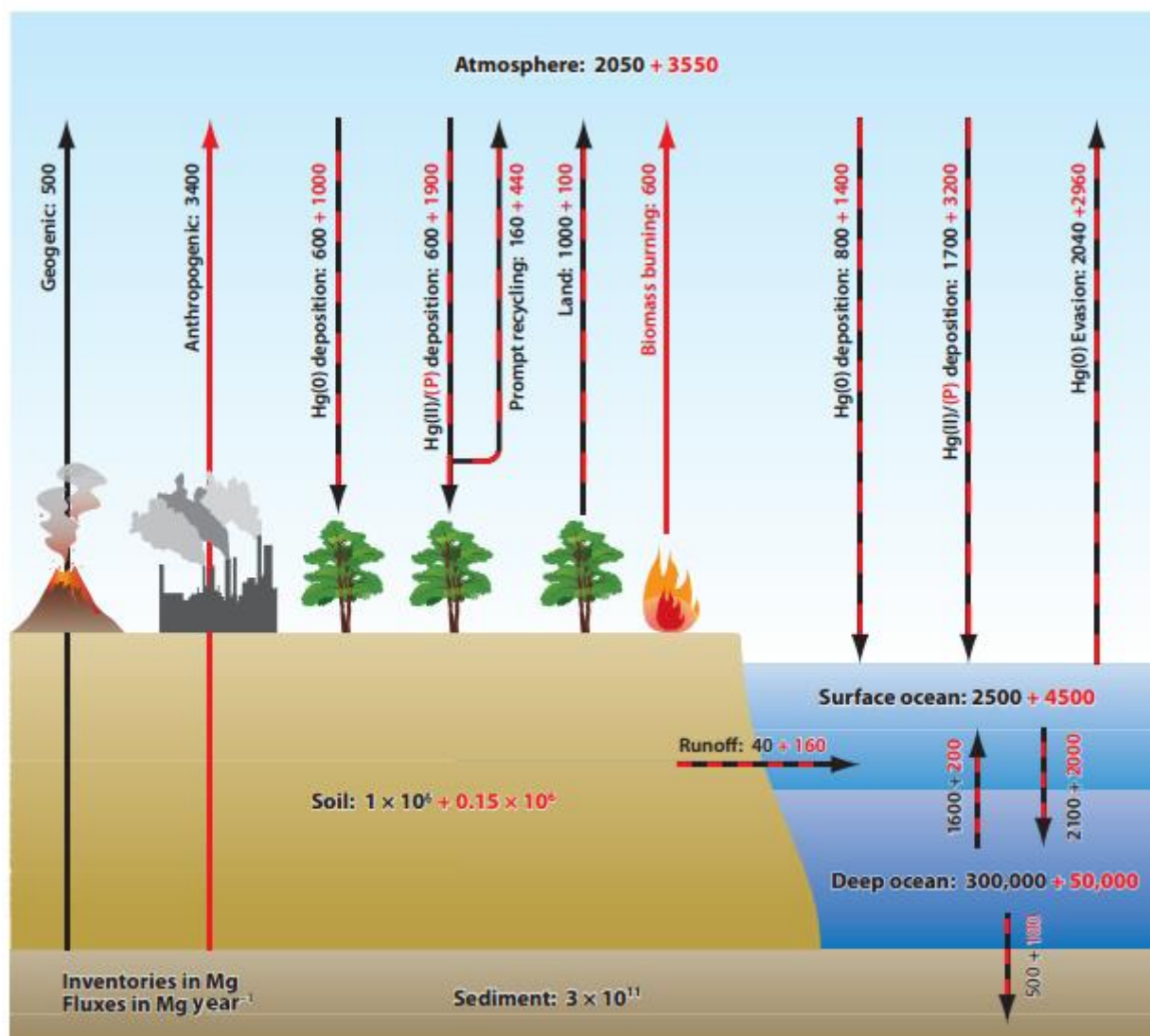


Figure 2-6: The Global biogeochemical cycle for Hg. Black represents pre-industrial (natural) fluxes, while red indicates the contributions from anthropogenic activities (Selin 2009).

2.2.3 Transformation

The chemical and physical transformation processes involved with atmospheric Hg^0 are fairly poorly understood (Schroeder & Munthe 1998). The compounds that are involved in the oxidation of Hg^0 to Hg^{2+} , for instance, are not known definitely. Reactions with the OH radical (Bergan & Rodhe 2001; Pal & Ariya 2004), soot and PM (Seigneur *et al.* 1998; Berg *et al.* 2003), halogens (Lu *et al.* 2001; Ebinghaus *et al.* 2002; Ariya *et al.* 2004; Holmes *et al.* 2006; Dastoor *et al.* 2008; Auzmendi-Murua *et al.* 2014), ozone (Bergan & Rodhe 2001; Ebinghaus *et al.* 2002; Steffen *et al.* 2002; Berg *et al.* 2003; Skov *et al.* 2004; Engle *et al.* 2005; Lyman *et al.* 2010), and fly ash (Laudal *et al.* 2000; Dunham *et al.* 2003) have been investigated and/or proposed in empirical and modeling studies.

The proposed transformation of Hg in a coal-fired power plant plume is indicated in Figure 2-8 (Seniora *et al.* 2000). The oxidation of Hg in the combustion chamber of a coal-fired power plant, is thought to occur through both heterogeneous and homogeneous pathways (Krishnakumar & Helble 2007), and this is usually facilitated by Cl. The atomic cycling of Cl has been investigated and reported as the dominant enforcer of Hg^0 oxidation (Niksa *et al.* 2001). Almost all the Hg in coal is emitted as Hg^0 into the coal combustion flue gas (Zhang *et al.* 2016). As the temperature of the flue gas decreases, some of the Hg^0 is oxidised to Hg^{2+} by active atomic chlorine (Cl) produced by HCl, Cl_2 or HOCl (Seniora *et al.* 2000). The temperature of the flue gas directly affects the amount of Hg that can be captured. The ability of Hg to be oxidised increases as the temperature decreases and this subsequently allows for more Hg to be adsorbed onto unburnt carbon and fly ash (Sloss, 2002; Sloss, 2008). Temperatures below 600 °C allow for the best potential of Hg oxidation reactions with atomic Cl (Naruse *et al.* 2010). Where temperatures are below 700 °C, HgCl_2 is the predominant form, whereas Hg^0 is in abundance above 700 °C (Sloss 2002).

Some evidence suggests that Hg^{2+} may be reduced to Hg^0 in power plant plumes (Edgerton *et al.* 2006). SO_2 is assumed to be the reducing agent (Lohman *et al.* 2006), as Hg in coal tends to combine with sulphur compounds (Wagner & Hlatshwayo 2005). This reduction may decrease Hg^{2+} deposition by as much as 10% at areas located downwind of power plants (Selin 2009). Soft bituminous coal, combusted at South African power plants, and brown coal, have higher overall sulphur and carbon contents than anthracite (Miller 2007), making the latter a more

desirable source of fuel. As opposed to other trace metals in coal, where the emphasis is put on vaporisation, all the processes leading to the condensed phase of Hg is focussed upon.

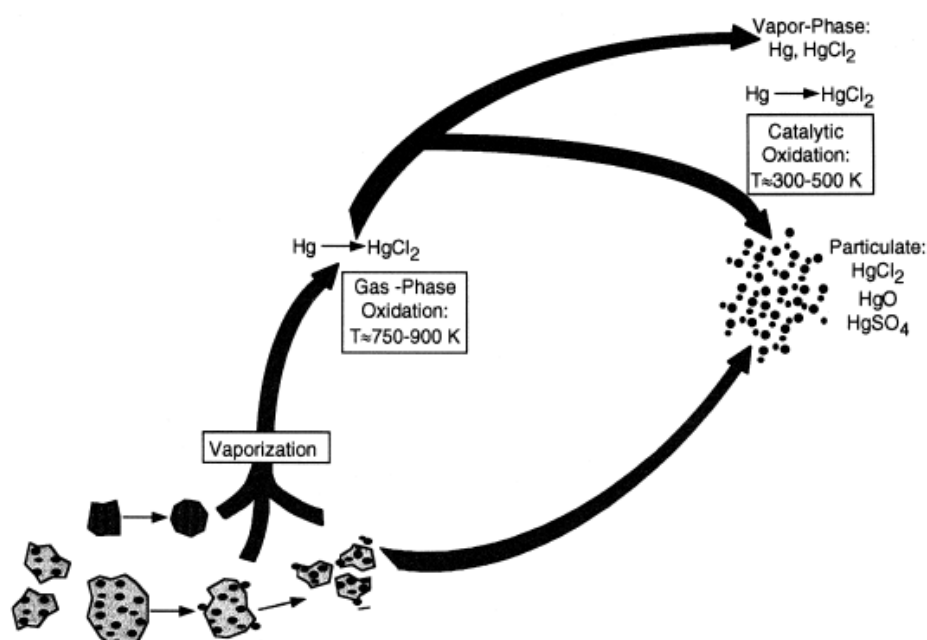


Figure 2-7: Mercury transformation in a power plant plume (Seniora *et al.* 2000)

2.3 Deposition of Hg

The main pathway of Hg to aquatic and terrestrial bodies is deposition (Gustin *et al.* 2015). This is critical in understanding the biogeochemical cycle of Hg (Lindberg *et al.* 2007). It either occurs as wet (precipitation) or dry (direct uptake at the surface) deposition (Figure 2-8) (Lindqvist & Rodhe 1985). Both processes are important for the removal of Hg from the atmosphere to water and land surfaces (Prestbo & Gay 2009). It is believed that Hg^{2+} is the main species affected by atmospheric deposition processes (Bergan *et al.* 1999), but an earlier study suggests that dry deposition may remove Hg^0 from the atmosphere, provided that the surface air Hg^0 concentration is high enough (Lindberg *et al.* 1992).

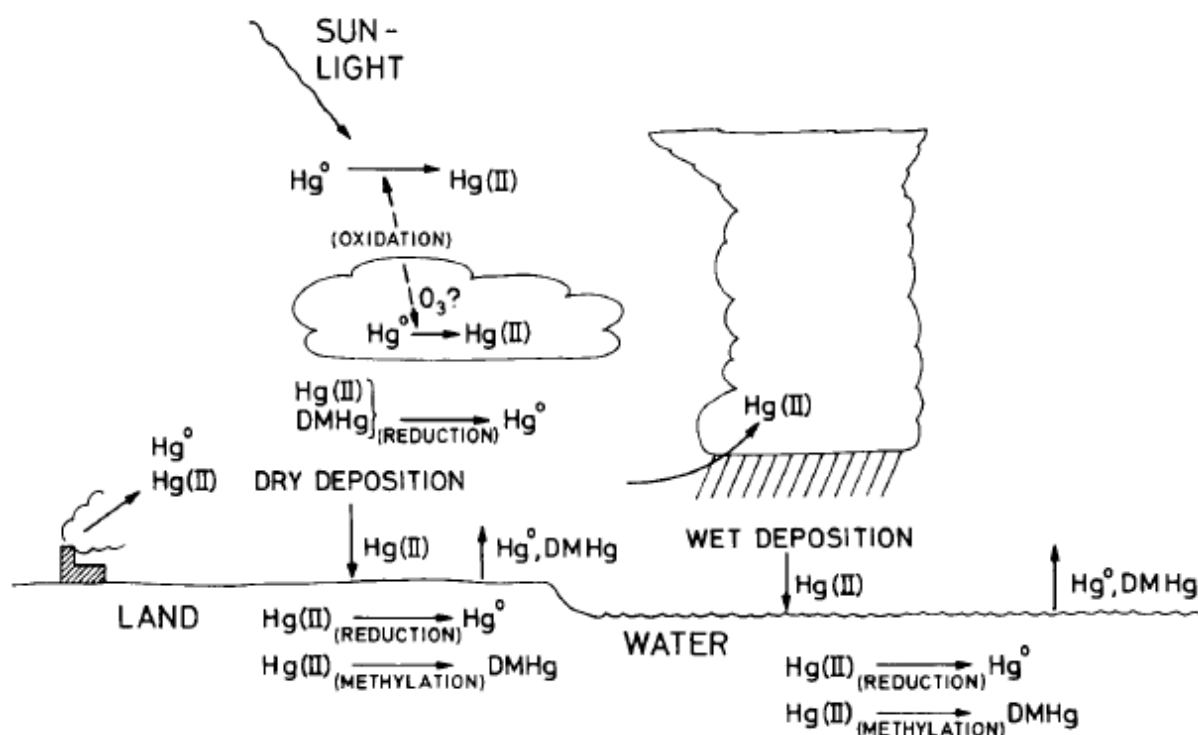


Figure 2-8: Atmospheric Forms, Transportation, Transformation and Deposition of Hg (Lindqvist & Rodhe, 1985).

Prior to deposition, constituents such as aerosols, water, and ozone must be present (Schroeder & Munthe 1998). Both gaseous- and aqueous-phase processes are therefore important for the atmospheric cycling of Hg. Although Hg^0 is only faintly soluble, aqueous oxidation pathways exist by which it may be converted to a more soluble form after dissolution in cloud water (Lin & Pehkonen 1999). Due to Hg^{2+} being less volatile and more soluble than Hg^0 , they are more likely to be removed from the atmosphere by either wet deposition or adhering to HgP (Prestbo & Gay 2009). The latter occurs when Hg^{2+} , and occasionally Hg^0 , gets adsorbed by soot and/or PM in gas and aqueous phases of clouds (Seigneur *et al.* 1998).

Deposition is increased when Hg^0 undergoes oxidation to Hg^{2+} and decreased when Hg^{2+} is reduced. The gas-to-particle conversion that takes place between gases and particles also affects the deposition of Hg, depending on the size of the particles the Hg is bound to (Lindberg *et al.* 2007). The common deposition of Hg^{2+} and HgP near their sources may be enhanced due to

them often being emitted at higher concentrations from anthropogenic activities, such as coal-fired power plants (Landis *et al.* 2002; Lohman *et al.* 2006). Anthropogenic activities have led to the removal of more Hg from the atmosphere through deposition, and in turn, doubled the estimated amounts re-emitted by land and ocean bodies (Pirrone *et al.* 2010b).

2.4 Health effects

The most common targets for Hg compounds are the kidneys and cardiovascular and nervous systems. The extent to which Hg may affect each system is discussed in detail elsewhere (Rice *et al.* 2014), and the degree to which exposure can cause adverse effects ultimately depends on the level of exposure (WHO 2008). Inhalation is the major exposure pathway to Hg⁰ as Hg vapour (Park & Zheng 2012) and may cause neurological and behavioural conditions in humans (WHO 2008). It can easily be absorbed by the lungs and quickly spread into the blood and the organs. Prior to absorption and being rapidly oxidised to Hg²⁺, Hg vapour is able to pass through the blood-brain barrier where it may accumulate in the brain (Park & Zheng 2012). Aside from the brain, the other main endpoint of Hg⁰ is the kidneys. Inorganic Hg compounds can be absorbed after ingestion in the gastrointestinal tract (Park & Zheng 2012) and there is even a suggested pathway through the skin (Chan 2011). This form reaches its highest concentration within the kidneys, which is usually the focal point. The health effects of Hg⁰ vary from acute to chronic (Park & Zheng 2012), of which most acute conditions are reversible.

The most toxic environmental form of Hg is formed after deposition of atmospheric Hg compounds to aquatic and terrestrial surfaces. This form is known as methylmercury (Hong *et al.* 2012; Celo *et al.* 2006) and it has detrimental renal, cardiovascular, reproductive, and immune system effects (Li *et al.* 2010). The respiratory, hematologic, and gastrointestinal systems may also be affected (WHO 2008). The first discovery of its fatal effects on the development of the brain and fetus was during the 1950s in Minamata, Japan (Hong *et al.* 2012). The critical target of methylmercury is the central nervous system as neurotoxicity is the most sensitive. Once absorbed into the body, methylmercury has the ability to effortlessly pass through the placental and blood-brain barriers (WHO 2008).

2.5 Mercury Legislation

In 2003, governments around the world agreed upon the need for an intervention on Hg, as it is a global pollutant. In 2009, these governmental bodies negotiated a legally binding document on this pollutant which led to the subsequent establishment of the Intergovernmental Negotiating Committee (INC) (Gololo 2015). The INC held five negotiating meetings, with the last of them being held on 19 January 2013 in Geneva where an agreement was met. This agreement is known as the Minamata Convention and was officially signed in Japan, on 11 October 2013 by South Africa and 98 other countries (Venter *et al.* 2015). This convention is a treaty to protect both human and environmental health from the adverse effects of Hg.

The USA and Canada have legally binding legislation regulating Hg emissions from coal-fired power plants within their respective countries. Germany and the Netherlands control Hg emissions by applying the best possible and available techniques. Partial control of Hg is being monitored and maintained in Australia and Asia, although this seems to be done without the outright urgency required by both national and regional legally binding laws. Chinese legislation is target based, while Japan allows legislation at the discretion of individual companies. Other Asian countries applying Hg emission legislation are the Philippines and Korea (Sloss 2012). Currently, there exist no environmental laws governing and regulating emissions of anthropogenic Hg in South Africa. Emissions of criteria pollutants (SO_2 , NO_x , and PM) are, however, regulated by the National Environmental Management: Air Quality Act (Act no. 39 of 2004), and this indirectly controls Hg emissions

2.6 Modelling atmospheric Hg

The Department of Environmental Affairs (DEA 2014) recommends SCREEN3, AERSCREEN, AERMOD, CALPUFF, and SCIPUFF as South African atmospheric dispersion models, with all being U.S. EPA regulatory approved models. South Africa lacks extensive research relating to these models for the modelling of Hg. The atmospheric dispersion, chemical transformation, and removal of Hg has, however, been modelled at Cape Point using GEOS-Chem (Selin *et al.* 2007; Travníkov *et al.* 2017), GLEMOS (Travníkov *et al.* 2017), GEM-MACH-Hg (Pacyna *et al.* 2016), ECHMERIT (Travníkov *et al.* 2017), and CAM-Chem (Lei *et al.* 2013), although these models entailed the simulation of global Hg concentrations with no particular interest in Cape Point. These

studies modelled Hg for 2000-2005 (Selin *et al.* 2007) 1999-2001 (Lei *et al.* 2013), and 2013 (Travnikov *et al.* 2017) for all atmospheric Hg species (Hg^0 , Hg^{2+} , and HgP).

If a study aims to assess a pollutant prone to long-range atmospheric transport (between 50 and 300 km), CALPUFF is typically the recommended model. This model is a non-steady state puff model that is able to simulate the dispersion of multiple species at different spatial and temporal scales, and what effects this has on the transport, transformation, and removal of a pollutant (DEA 2014). Locally, the model has been used for the modelling of SO_2 from an oil refinery in Cape Town (Mtiya 2013), and for SO_2 , NO_x , and primary and secondary PM_{10} over the SAHA (Pretorius *et al.* 2017). Internationally, the model has been used to approximate population exposure from power plant emissions to $\text{PM}_{2.5}$, SO_2 , SO_4 , NO_x , NO_3 , and HNO_3 in Beijing, China (Zhou *et al.* 2003); an exposure assessment to Zn, Pb, and Cd from a Zinc smelter in Spelter, West Virginia (MacIntosh *et al.* 2010); and for a health risk assessment to Hg emissions from a solid waste gasification plant located South-East of Milan, Italy (Lonati & Zanoni 2013).

CHAPTER 3

DATA AND METHODS

The purpose of this chapter is to provide a detailed discussion of the data and methods used in this research. Techniques used and procedures followed to analyse the data are concisely defined. Accompanying formulas and calculations are also provided and elucidated. The atmospheric model utilized to study the dispersion of Hg over the South African Highveld, is described as comprehensive as possible. This modelling study is the first of its kind over the South African Highveld region.

3.1 Characterisation of ambient Hg concentrations over the South African Highveld

3.1.1 Sampling site

The South African Highveld (Figure 3-1) - a region adversely affected by emissions from power stations, mining activities, informal settlements, motor vehicles, and light and heavy industries - is by far the most industrialised area in the country; Eskom currently has extensive air quality monitoring campaigns located throughout the area, which dates as far back as the early 1980's (Mkhatshwa, 2008). Concentrations of total gaseous mercury (TGM) were monitored at three sites located in this region, with the first being the Balfour monitoring site (BF) (S26°39'47"; E28°35'08") situated at I.M Manchu High School in Balfour town. The second monitoring station is located to the north-east in Middelburg (MB) (S25°46'22"; E29°26'18"), at a church to the west of the town. The third and final monitoring station, is located to the south in Standerton (ST) (S26°57'53"; E29°13'22"), at Igugulabasha Primary School. Although only three sites, they are located in industrially different regions on the South African Highveld (Figure 3-2) and are considered to be representative of TGM concentrations over the region. A number of potential anthropogenic sources may contribute to the overall TGM concentrations with coal-fired power plants expected as the predominant source, as found in past and recent local and international studies. In a past international estimation study, gold mining was estimated to be one of the major

sources of Hg in South Africa (Pacyna *et al.* 2006) based on a debatable assumption. This study assumed that South African mines utilize amalgamation for the extraction of gold, where in contrast to other countries they utilise cyanidation. Other major sources surrounding and located sparsely around the sites could be ferrous and non-ferrous metals production, domestic fuel use, and cement manufacturing plants and illegal artisanal gold mining. Knowledge regarding the contribution of the latter is essentially unknown but has been reported to mainly occur in the Mpumalanga and Limpopo Provinces (Leaner *et al.* 2009).

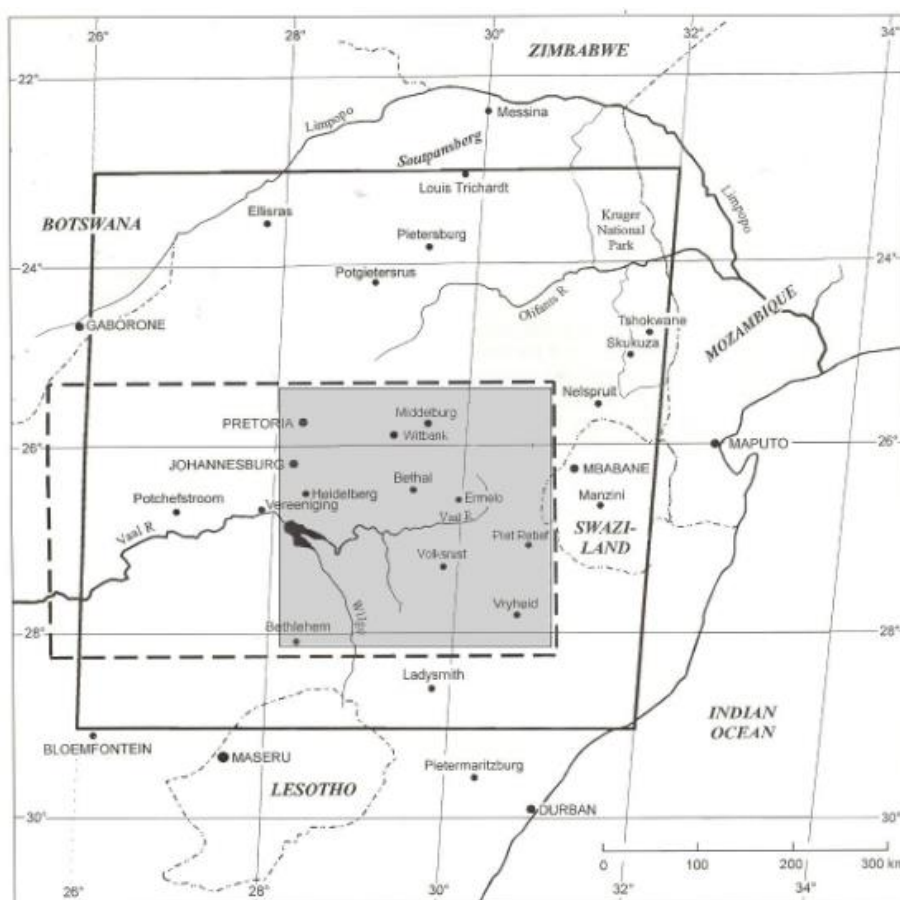


Figure 3-1: The industrialised South African Highveld region (grey area) (Mkhatshwa 2008).

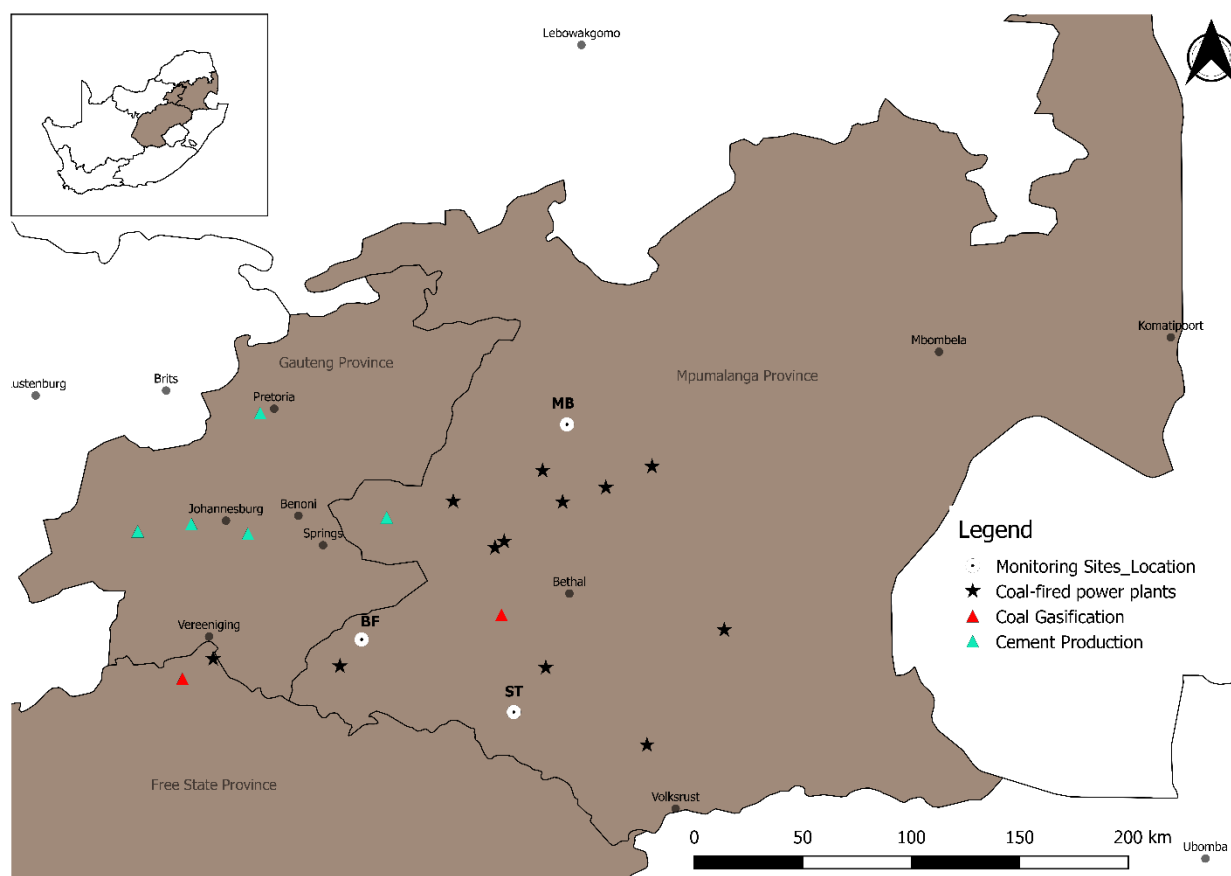


Figure 3-2: Locations of the monitoring sites relative to those of potential anthropogenic Hg sources.

3.1.2 Measurements of TGM and meteorological parameters

The dataset used in this study was obtained from the Mpumalanga Air Quality Network, which is owned by the Mpumalanga Department of Agriculture, Rural Development, and Land and Environmental Affairs. Concentrations of TGM contained within this dataset was sampled between 01 January 2009 and 17 December 2015. However, only the concentrations sampled in 2009 is considered in this study due to the rest, not meeting evaluation requirements. This is addressed in a detailed discussion in the following section.

Ambient TGM monitoring was performed during the selected period, by utilising an in-situ automated Tekran Hg vapour analyser (model 2537A) (Tekran 1999). The analyser measured

concentrations at 5-min intervals and was automatically calibrated every 24 hours using its internal Hg permeation source. Information regarding the sampling rate the instrument operated at during this period is assumed to be the factory default of 1.5 l/m (Tekran 1999). The TGM limit of detection while operating in this mode is 0.1 ng/m³. Measurements taken concurrently with ambient TGM concentrations are those of criteria pollutants (including O₃), temperature, relative humidity, pressure, rainfall, wind direction, and wind speed.

3.1.3 Quality control

Generally, a dataset comprising of at least 80% data capture is required for quality assurance and to qualify for data manipulation and summary (SANAS 2000). As portrayed in Table 3-1 none of the sites or years met this requirement. For the purpose of this study, seeing as Hg characterisation studies are desperately needed, this was lowered to an annual data threshold of at least 70%. The three monitoring sites discussed in the previous section were, therefore, selected as they meet this requirement during 2009 (year for which results are presented) where sufficient data were available. The dataset for these three sites also, to an acceptable extent, adhere to SANAS requirements for data analysis. Two additional monitoring sites were available but lacked adequate data for analysis for this year. Gaps in data for 2009 mainly resulted from power failures, load shedding, instrument fails, where the instrument was removed for repair, and communication errors between the instrument and PC.

Table 3-1: Data completeness (%) of 5-min TGM concentrations monitored at available sites.

Monitoring site	Year (%)						
	2009	2010	2011	2012	2013	2014	2015
Balfour	81.93	-	17.74	37.01	-	-	-
Standerton	79.46	23.84	9.34	17.92	0.27	-	-
Middelburg	75.52	-	0.01	-	0.55	-	-
Greendale High	-	13.80	12.91	12.03	29.53	-	-
Witbank	-	15.79	-	-	-	-	-

Data quality control considerably lessened the amount of data available for analysis of MB. For the sake of comparison, some months were selected to be representative of spring and summer, while available data for September and October are representative of spring, and good data capture during December of summer. Comparisons of its summer and spring data with those of the other two sites should, therefore, be viewed with caution. Appropriate data capture was observed for winter, where data is available for the entire season. Data for the autumn sampling period was absent.

Table 3-2: Seasonal correlation of TGM concentrations and meteorological parameters at Balfour (BF), Middelburg (MB), and Standerton (ST).

		P	R	RH	T	WD	WS
BF	Summer	-0.29	-0.04	0.15	-0.05	-0.06	-0.35
	Autumn	-0.04	-0.02	0.07	-0.14	-0.11	-0.16
	Winter	0.23	0.01	0.02	-0.08	-0.05	-0.23
	Spring	0.02	-0.04	0.03	-0.16	-0.02	-0.24
MB	Summer	0.04	0.01	0.21	-0.33	-0.06	-0.22
	Autumn	-0.14	0.01	-0.11	-0.11	-0.002	-0.25
	Winter	0.03	-0.03	0.04	-0.11	-0.07	-0.21
	Spring	0.20	0	-0.31	0.24	0.10	-0.10
ST	Summer	-0.17	0.03	-0.08	0,21	0,74	0,85
	Autumn	-	-	-	-	-	-
	Winter	0.10	-0.01	-0.07	-0.08	0.04	-0.25
	Spring	-0.08	-0.03	-0.09	0.02	0.04	-0.27

3.1.4 Statistical analysis

The 5-min measurements were averaged as hourly values, and where there was not 70% or more measurements available for an hour, the average was rejected. All statistical analyses were performed using R (Carslaw, 2015) for windows. The relationships between concentrations of TGM and those of other pollutants were evaluated by applying Pearson product moment

correlation coefficient. The results of the statistical analyses were considered to be significant where a single factor ANOVA test resulted in $p < 0.05$.

3.2 Estimation of Hg emissions from ESKOM coal-fired power plants in 2014

Mercury emission data for this objective was obtained from ESKOM Holdings SOC Limited. This dataset presents Hg emission data for 13 coal-fired power plants for 2014, and consists of (i) the amount of coal burnt in 2014 (tonnes); (ii) the Hg coal content (ppm); and (iii) the removal efficiencies of the pollution control devices installed at each plant (Roos 2011). The majority of South African ESKOM owned power plants are situated in the Highveld Priority Area in Mpumalanga province, with the exception of Lethabo (Vaal Triangle Airshed Priority area) and Matimba (Waterberg Priority Area) (Figure 3-3).

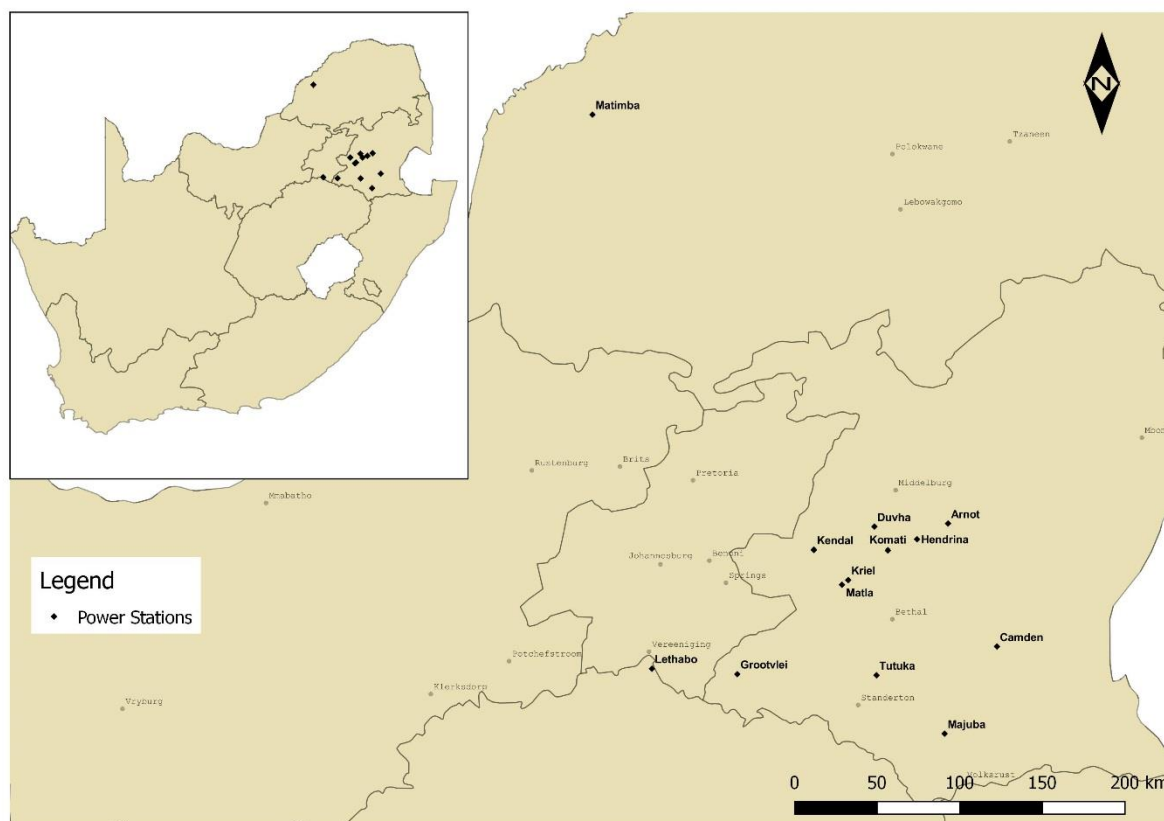


Figure 3-3: Locations of the 13 coal-fired power plants considered and used to estimate emissions of Hg in this study.

3.2.1 Data analysis

This study utilized the bottom-up approach (Zysk *et al.* 2011) to estimate Hg emissions from each power plant:

$$ME = CC \times C \times (1 - n) \quad (1)$$

where: ME, Hg emission in (kg); CC, coal consumption (Mt/y); C, Hg concentration in coal (mg/t); n, Hg removal efficiency (%/100). The amounts of combusted coal, Hg-coal content, and removal efficiencies are discussed in the following sections.

3.2.1.1 The amount of coal burnt

The amounts of coal combusted at each ESKOM power plant in 2014 are presented in Table 3-3. These amounts are calculated by measuring the amount of coal consumed at the power plant and comparing them to the dimensions of the coal stockyards (Roos 2011). The uncertainty of these calculated amounts is within 1% of a tonne. The quantity of coal is established and weighed as it arrives at each plant.

Table 3-3: Coal consumption (t/yr) at each plant during 2014.

Power-generating Plant	Output Capacity (MW)	Coal Consumption (t/yr)
Arnot	1680	6 066 013
Camden	1650	5 297 913
Duvha	1590	9 741 615
Grootvlei	1600	4 613 355
Hendrina	1610	5 323 902
Kendal	1550	16 190 242
Komati	1650	2 979 546
Kriel	1550	8 147 633
Lethabo	1440	16 317 957
Majuba	1700	13 087 805
Matimba	1100	13 911 050
Matla	1610	10 076 382
Tutuka	1600	10 663 894

3.2.1.2 Mercury coal content

To investigate the influence of measured and published Hg coal content on emission estimates, Hg coal content measured by ESKOM for 2014 (Table 3-4) were compared to those reported in the literature. Wagner and Hlatshwayo (2005) found an average Hg-coal content of 0.15 mg/kg, while Gericke *et al.* (2007) reported an average of 0.31 mg/kg. These averages are different as the first study investigated the Hg content of coal on the Highveld, while the latter reported averages in South African coal. Although all South African power plants use bituminous coal, they do not have the exact same Hg content.

Table 3-4: Average Hg in coal content (mg/kg) of composite samples of coal used at ESKOM's power plants in 2014.

Power-generating Plant	Average Hg in coal content (mg/kg)
Arnot	0.174
Camden	0.299
Duvha	0.232
Grootvlei	0.299
Hendrina	0.206
Kendal	0.312
Komati	0.299
Kriel	0.333
Lethabo	0.364
Majuba	0.288
Matimba	0.452
Matla	0.298
Tutuka	0.292

3.2.1.3 Mercury removal efficiency

Emission reduction factors are used to assume the amount of Hg removed by the emission control device installed at each respective power plant. As coal combustion results in various gaseous products (including Hg) to be emitted into the atmosphere, devices that control their emissions are installed in power plants to curtail emissions of controlled pollutants. South African power plants use fabric filters (FF), electrostatic precipitators (ESP), and installation varies from one power plant to the next (Table 3-5). Some power plants also have flue-gas conditioning systems (FGC) installed to enhance the performance of the ESP.

Table 3-5: Emission control devices installed at South African power plants (Dabrowski *et al.* 2008; Leaner *et al.* 2009; Masekoameng *et al.* 2010; Pretorius *et al.* 2017), and the removal efficiencies of these emission control devices (EPA, 2013).

Power-generating Plant	Emission Control Device	Removal efficiency (%)
Arnot	FF	89
Camden	FF	89
Duvha	ESP+FF	62.5
Grootvlei	ESP+FF	62.5
Hendrina	FF	89
Kendal	ESP	36
Komati	ESP	36
Kriel	ESP	36
Lethabo	ESP	36
Majuba	FF	89
Matimba	ESP	36
Matla	ESP	36
Tutuka	ESP	36

Emissions of PM are reduced by ESP and FF, while gaseous SO₂ emissions are reduced by FGC (Pavlish *et al.* 2003). All these devices have been shown to also remove a significant amount of total atmospheric Hg emissions (Dabrowski *et al.* 2008). The efficiency and type of the installed emission control device will directly affect the amount of emitted Hg into the atmosphere (Pacyna *et al.* 2006). Removal efficiencies for these devices were adopted from (EPA, 2013) (89% for FF, 36% for ESP, and 62.5% where they are used collectively) (Table 3-1). The default values reported by the UNEP Toolkit (50% for FF, 25% for ESP, and 37.5% for simultaneous use) give the impression of being too traditional and not fully symbolic of the removal competency of these emission control devices (Roos *et al.* 2011). The factors reported by the UNEP Toolkit provide a

general guideline for Hg emission estimates, but one should also take into consideration the type of coal combusted in each respective country (bituminous in South Africa).

3.3 Modelling the atmospheric dispersion of Hg resulting from power-generating plant emissions

3.3.1 Modelling structure and domain

Mercury has been shown to be transported over long distances in the atmosphere, in some cases even reaching the poles (Pacyna and Pacyna, 2002). Due to the concentration of major sources over the Highveld, it is expected that Hg is transported and deposited over large portions of South Africa (Freiman & Piketh 2003). It was decided that the California Puff (CALPUFF) modelling system is the most suitable for the purpose of this study, due the fact that it is able to handle complex three-dimensional wind fields on large domains between 50 km–300 km (DEA 2014). CALPUFF, one of the recommended atmospheric dispersion models by the South African Department of Environmental Affairs (DEA 2014), is a Lagrangian, multi-layer source-receptor model (MacIntosh *et al.* 2010). It is also endorsed by the U.S. EPA for complex topographies and for modelling the atmospheric dispersion of pollutants prone to long-range transport (U.S. EPA, 2000). The model has been used to approximate population exposure from power-generating plant emissions to PM_{2.5}, SO₂, SO₄, NO_x, NO₃, and HNO₃ in Beijing, China (Zhou *et al.* 2003); an exposure assessment to Zn, Pb, and Cd from a Zinc smelter in Spelter, West Virginia (MacIntosh *et al.* 2010); and for a health risk assessment to Hg emissions from a solid waste gasification plant located South-East of Milan, Italy (Lonati & Zanoni 2013).

A 250 km by 250 km modelling domain was selected for this study spanning over the South African Highveld Area (Figure 3-4). The modelling domain hosts various anthropogenic sources of Hg, including the 12 power plants illustrated in Figure 3-4. Other possible sources are combustion in gasification plants, ferrous and non-ferrous metal production, domestic burning, crude oil refining, cement production, waste deposition and incineration, and illegal artisanal gold mining. The Lambert Conic Conformal projection was used to keep map distortion to a minimum over this domain size. The components of the CALPUFF modelling system sequentially consist of CALMET, CALPUFF, and CALPOST. In the most recent version of the model, a new feature

known as CALSUM was introduced which allows the user to combine multiple outputs from CALPUFF into a single file to considerably lessen the runtime.

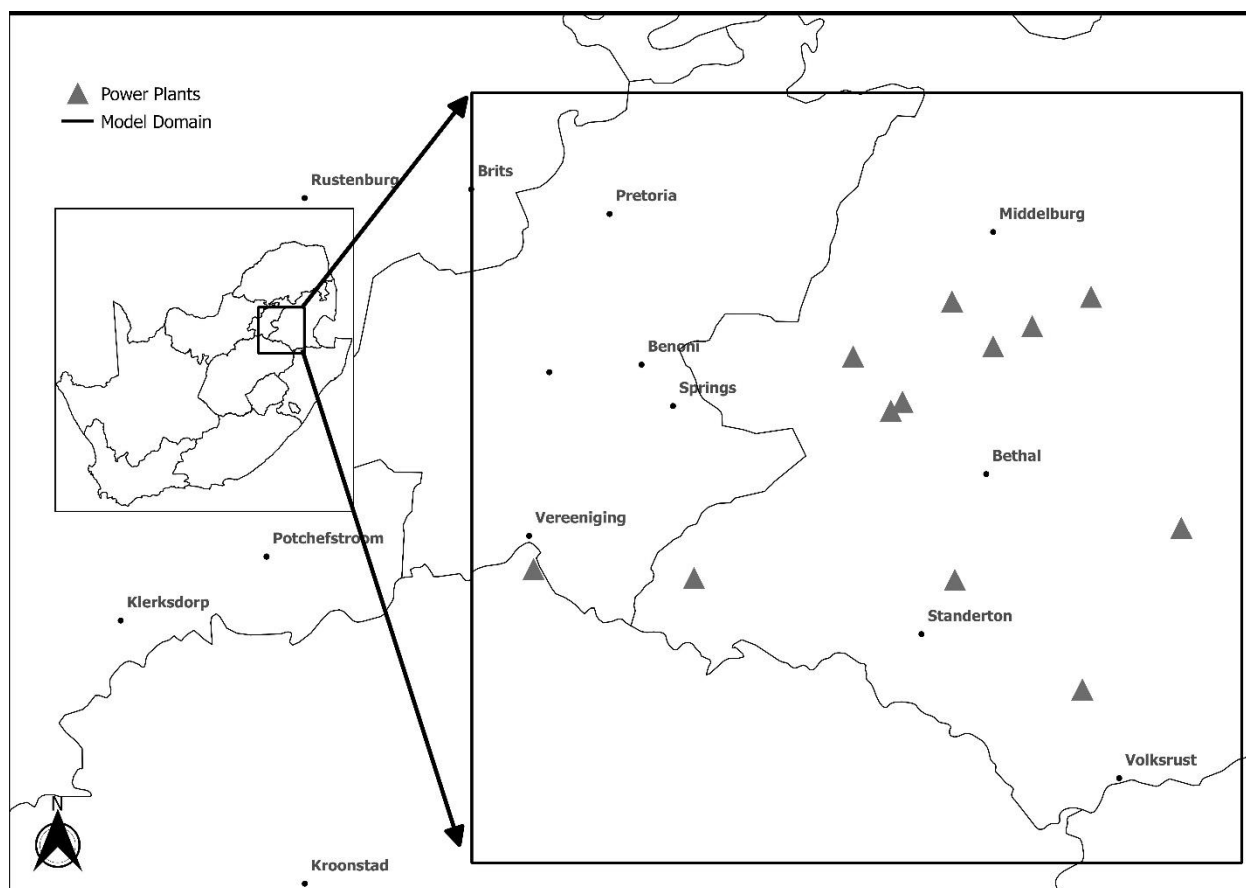


Figure 3-4: Locations of the 12 coal-fired power-generating plants used to model the atmospheric dispersion of Hg^0 , Hg^{2+} , and HgP in this study. The black box represents the modelling domain.

3.3.2 CALMET

CALMET meteorological model generates hourly temperature and wind files for the selected domain on a three-dimensional grid (Zhou *et al.* 2003). In addition, two-dimensional surface and dispersion characteristics and properties, and atmospheric mixing heights files are created (Scire *et al.* 2000). For this study, CALMET was run in a hybrid mode from January 2011 to December

2013 (period for which Hg dispersion and wet and dry deposition was simulated) at a resolution of 1 km by 1 km on a 12 km by 12 km grid. The input data fields were obtained from Mesoscale Model (MM5) prognostic meteorological data. The MM5 dataset comprises of precipitation, wind speeds and vectors, boundary layer heights, and temperatures. A recent study by Pretorius *et al.* (2017) used the same domain and meteorological fields from CALMET for an evaluation of health risk exposure to PM, SO₄, and NO₃. This study evaluated the performance of CALMET for the Highveld region and found the created fields to adequately simulate the actual fields (Pretorius *et al.* 2017). The default CALMET options were mainly used, but some were altered to suit the needs of this study. These alterations and the motivations associated with them are summarised in Table 3-6 and were based on a peer-reviewed report (Exponent Inc 2014). South Africa does not have the MM5 dataset commercially available yet and it was, therefore, bought from Lakes Environmental Software, Canada. At a resolution of 12 km along with 18 vertical heights, it was the best accessible dataset with its centre at 26.47 S; 29.03 E.

Table 3-6: CALMET options which were altered from the default settings (Exponent Inc 2014).

Description	Default setting	Used setting	Motivation
Map projection	UTM	LCC	To keep map distortion to a minimum
No observation mode	Observations only	No surface, overwater, or upper air observation. Use of MM5 data for these observations	Limited observational data
Extrapolation of surface wind	Ignore upper air station data	No extrapolation	Exclusion of observations
Gridded prognostic wind field	No	Yes	Exclusion of observations
3D Relative humidity	Use observations	Use prognostic data	Exclusion of observations
3D Temperature	Use observations	Use prognostic data	Exclusion of observations

3.3.3 CALPUFF

The model was used to simulate the hourly dispersion concentrations of the three important atmospheric species of Hg (Hg^0 , Hg^{2+} , and HgP), along with concurrent wet and dry deposition at selected receptor locations. The emission rates of Hg utilized in this study were calculated using estimated emission rates for each power-generating plant (Belelie *et al.* 2016) (Table 3-7). The Hg speciation was assumed to be consistent with values reported by Carpi (1997), namely, of Hg^0 (53%), Hg^{2+} (37%) and HgP (10%). Source-specific characteristics of the 12 power-generating plants are summarised in Table 3-8. Chemical and deposition parameters required for the simulation of wet and dry deposition during the period were obtained from a past study (McGuire *et al.* 2009) and are summarised in Table 3-8.

The atmospheric lifetime of Hg^0 is approximately 1 year (Lindqvist & Rodhe 1985; Schroeder & Munthe 1998; Bergan & Rodhe 2001; Lindberg *et al.* 2007) due to its stability, and low solubility and reactivity in the atmosphere (Poissant *et al.* 2005; Liu *et al.* 2007). The wet scavenging of Hg^0 has been described as trivial (Zysk *et al.* 2015). It's thought to be primarily removed after being oxidized to Hg^{2+} and consequent deposition. It may, however, occasionally be adsorbed by soot and/or PM in gas and aqueous phases of clouds (Seigneur *et al.* 1998). When this occurs, it may be removed from the atmosphere by dry deposition, provided that the surface air Hg^0 concentration is high enough (Lindberg *et al.* 1992). (Rutter *et al.* 2011). Dry deposition parameters for Hg^0 were assumed to be the same as those adopted for Hg^{2+} , to provide a conservative basis for highest potential dry deposition (McGuire *et al.* 2017) (this bias model input should provide for a high uncertainty factor of the dry deposition of Hg^0 in this study). The dry deposition of Hg^0 is a potentially important removal pathway of the species (Schroeder & Munthe, 1998), hence this assumption and since the dry deposition of Hg^0 is often omitted (Ryaboshapko *et al.*, 2007). A study published after the model was ran for this study (Garcia *et al.*, 2017) adopted similar parameters for Hg^0 from the CALPUFF model (diffusivity = 0.1509 cm^2 ; $\alpha^* = 1$; reactivity = 8; Henry's law coefficient = 0.04 – comparable to the assumed parameters presented in Table 3-8). Presumably, the study used a newer version of the model, as these values were unavailable in the version utilized in this study.

The Hg^{2+} and HgP species are believed to be dispersed locally and their deposition patterns to be dependent on sources located locally (Zysk *et al.* 2015). The deposition parameters for Hg^{2+}

are assumed to be similar to those of nitric acid (HNO_3) provided in the model (Scire *et al.* 2000). These parameters were also adopted by McGuire *et al.* (2009) as they provide for a conservative basis of deposition for this species. This is usually assumed in many settings (Zhang *et al.* 2009), as both these species are highly soluble and reactive (Yarwood *et al.* 2003; Zhang *et al.* 2009). From the limited measurements made regarding the deposition of Hg^{2+} , it may be derived that its deposition velocity magnitude is analogous to HNO_3 (Zhang *et al.* 2009). The parameters for HgP were adopted from those given for NO_3 in the model (Scire *et al.* 2000). McGuire *et al.* (2009) made this assumption to provide for a conservative basis of deposition of this species, and it was decided to make this same conservative assumption. In theory, this assumption seems plausible in that HgP mainly consists of particles smaller than $2.5 \mu\text{g}/\text{m}^3$ (Dastoor & Larocque 2004). According to Aneja *et al.* (2006) and Tsai *et al.* (2005), to further justify this assumption, NO_3 is one of the dominant constituents of the fine PM fraction. Deposition velocities of particulate species are mostly dependent on the distribution of their size (Zhang *et al.* 2009). Therefore, a mass mean diameter of 0.48 was selected as particulates resulting from combustion sources are generally less than one micron (McGuire *et al.* 2009), providing an additional conservative basis for this study. An earlier study used very similar deposition parameters for this species, assuming the same geometric mass mean diameter (Sang-sup & Keener 2005). To make deposition modelling of HgP more reliable, Zhang *et al.* (2009) suggest that prospective studies regarding the size of these particles should be improved. The deposition parameters for Hg^{2+} and HgP were selected because it implies that the highest possible amount of these deposition-prone species can be removed from the atmosphere, which will have a subsequent and indefinite impact on the modelled Hg concentration. This supposition is not made for Hg^0 as Lindqvist and Rodhe (1985) describes both deposition process to be inefficient in the removal thereof.

Table 3-7: Per annum emission rate of Hg⁰, Hg²⁺, and HgP, in grams per second (g/s) investigated in this study, and the emission control device/s installed at each power-generating plant.

Power Plant	Emission Control Device	Emission rate per annum (g/s)		
		Hg ⁰	Hg ²⁺	HgP
ARNOT	FF	0.00212	0.00148	0.0004
CAMDEN	FF	0.00318	0.00222	0.0006
DUVHA	ESP+FF	0.01431	0.00999	0.0027
GROOTVLEI	ESP+FF	0.00848	0.00592	0.0016
HENDRINA	FF	0.00212	0.00148	0.0004
KENDAL	ESP	0.05406	0.03774	0.0102
KOMATI	ESP	0.00954	0.00666	0.0018
KRIEL	ESP	0.02915	0.02035	0.0055
LETHABO	ESP	0.0636	0.0444	0.0102
MAJUBA	FF	0.00689	0.00481	0.0013
MATLA	ESP	0.03233	0.02257	0.0061
TUTUKA	ESP	0.03339	0.02331	0.0063

Table 3-8: Source-specific parameters of each power-generating plant investigated in this study.

Power Plant	Coordinates		Output Capacity (MW)	Stack Height (m)	Effective Stack Diameter (m)	Exit Velocity (m/s)	Exit Temperature (K)
	x (m)	y (m)					
ARNOT	-25.944	29.792	1680	195	16	25	418
CAMDEN	-26.62	30.091	1650	155	17	14	423
DUVHA	-25.961	29.339	1590	300	18	27	413
GROOTVLEI	-26.77	28.5	1600	152	13	22	418
HENDRINA	-26.031	29.601	1610	155	16	22	418
KENDAL	-26.088	28.969	1550	275	19	24	413
KOMATI	-26.091	29.422	1650	220	17	10	418
KRIEL	-26.254	29.18	1550	213	20	19	413
LETHABO	-26.740	27.975	1440	275	17	28	433
MAJUBA	-27.28	29.771	1700	250	17	35	398
MATLA	-26.28	29.142	1610	275	19	26	408
TUTUKA	-26.776	29.352	1600	275	17	19	413

Table 3-9: Deposition and Chemical Parameters of the three species modelled in this study.

Dry Deposition (Gases)					
Species	Diffusivity (cm ² /s)	Alpha Star	Reactivity	Meso. Resistance	Henry's Law Coefficient.
Hg ⁰	0.1628	1	18	0	1.00E-07
Hg ²⁺	0.1628	1	18	0	1.00E-07
Dry Deposition (Particles)					
Species	Geometric Mass mean diameter (microns)		Geometric Standard Deviation (microns)		
HgP	0.48		2		
Wet Deposition					
Species	Scavenging Coefficient (liquid) s ⁻¹		Scavenging Coefficient (Frozen) s ⁻¹		
Hg ²⁺	6.00E-05		0		
HgP	0.0001		3.00E-05		

After the completion of each individual run, the 36 output files (12(concentration + wet deposition + dry deposition)) were combined by using CALSUM. This was possible because the modelling period during each run was all alike, and the species were identical and in the exact same order for each run. To calculate the accumulative concentration and wet and dry deposition averages during the period, use was made of CALPOST.

3.4 Assessment of potential health risk

As described previously, exposure to Hg could cause adverse human impacts on human health. To put the model results into perspective, the potential impact of the simulated emissions from the power plants on health is assessed. A previous study in this region assessed human health exposure to PM, SO₂, and NO_x emissions from power plants based on intake and intake fraction (Pretorius *et al.* 2017). The methodology used in this assessment is discussed in detail in previous

publications (Barnes & Dourson 1988; Louvar & Louvar 1998; U.S. EPA 2005). It was recently utilized in a health risk study (Mokhtar *et al.* 2014) where Hg was one of the pollutants under investigation. It essentially entails the execution of four steps which are discussed in the following sections.

3.4.1 Hazard Identification

Hazard identification is an exercise to determine whether the exposure to the pollutant under investigation can cause an intensification in the occurrence of a specific severe health effect in humans. Mercury, a non-carcinogenic pollutant (IRIS 1995), may cause neurological and behavioural conditions in humans (WHO 2008). These conditions can be acute, chronic and even fatal (U.S. Department of health and human services 1999), and their severity depends on the level of exposure (WHO 2008). The main exposure pathway is through the inhalation of inorganic Hg^0 (U.S. Department of health and human services 1999). Reactive and particulate Hg are commonly removed near their sources due to their high solubility and reactivity in the atmosphere (Landis *et al.* 2002; Lohman *et al.* 2006). They pose a risk to human health after deposition, when methylmercury, the most toxic form of Hg, may be formed (Hong *et al.* 2012; Celo *et al.* 2006). This study, however, only considers the inhalation exposure pathway to Hg^0 .

3.4.2 Dose-response

Fundamentally, this step of the risk assessment process establishes an exposure-response relationship. The toxicological factors that are used to establish this relationship are Reference Concentration (RFC) and Reference Dose (RFD). The RFC is utilized to evaluate risks to inhalation, while the RFD assesses the risks associated with oral exposure. Both reference doses are benchmarks of daily human exposure. Barnes and Dourson *et al.* (1988) and IRIS (1995) defines them as average daily exposure levels that are not likely to pose a threat to human health throughout a lifetime. Normally, this step requires the implementation of an equation to calculate an RFD value, which can be adjusted to calculate RFC. This practice is not recommended, however, for use in studies investigating inorganic compounds (U.S. EPA 2005). Since an RFC value was readily available, this study deviates from the standard procedure. The RFC value used in this risk assessment, and which is associated with Hg^0 inhalation, is adopted from IRIS (1995)

(0.3 $\mu\text{g}/\text{m}^3$). This value is used to characterise the risk exposure to Hg^0 in the fourth step of this process. It is also assumed to be identical for acute and chronic exposure periods.

3.4.3 Assessment of exposure

The exposure of the human population to Hg^0 was predicted using CALPUFF as described in section 3.3.3. The simulation returned average modelled hourly, 8-hourly, and periodic (annual average) Hg^0 concentrations. These values were used to assess potential acute and chronic impacts on human health.

3.4.4 Characterisation of risk

The U.S. EPA (2005) recommends Risk Exposure Levels (REL) (OEHHA 2014) as the preferred choice to assess acute inhalation values. Similar to an RCF, a REL is the air concentration at or beneath which no severe health impacts are expected in the overall population, over a given exposure period. This includes susceptible subgroups such as children and the elderly (U.S. EPA 2005). The average hourly, 8-hourly, and annual Hg^0 concentrations are compared to acute (1 hourly and 8-hourly) and chronic REL values to assess potential health impact. Additional information, including associated uncertainty factors, are provided in Table 3-8.

Table 3-10: Uncertainty associated with REL values (OEHHA 2014) used for comparison.

RFC comparison	Species	Study population	Exposure continuity	Exposure duration	Composite uncertainty factor
Acute (1 hour)	Rats	12	-	1 hour per day	3000
Acute (8 hours)	Humans	236	8 hours per day, 5 days a week	13.7–15.6 years	3000
Chronic	Humans	236	8 hours per day, 5 days a week	13.7–15.6 years	300

To characterise health risk for a non-carcinogenic pollutant by way of inhalation, the hazard must be quantified through the use of the Hazard Quotient (HQ) (U.S. EPA 2005) given by:

$$HQ = EC/RFC \quad (2)$$

where EC represents the exposure concentration in the air ($\mu\text{g}/\text{m}^3$); and RFC the reference concentration ($\mu\text{g}/\text{m}^3$). If HQ is smaller than 1, it's an indication that the concentration of the pollutant is less than the RFC benchmark value. If this is the case, it means no subsequent action is necessary, because the likely risk is within the admissible threshold. This, in other words, means that $HQ < 1$ is considered safe. This does not mean that $HQ > 1$ should be construed as causing potential severe health impacts. It should rather be deduced as an indication of potential severe health impacts (U.S. EPA 2013).

CHAPTER 4

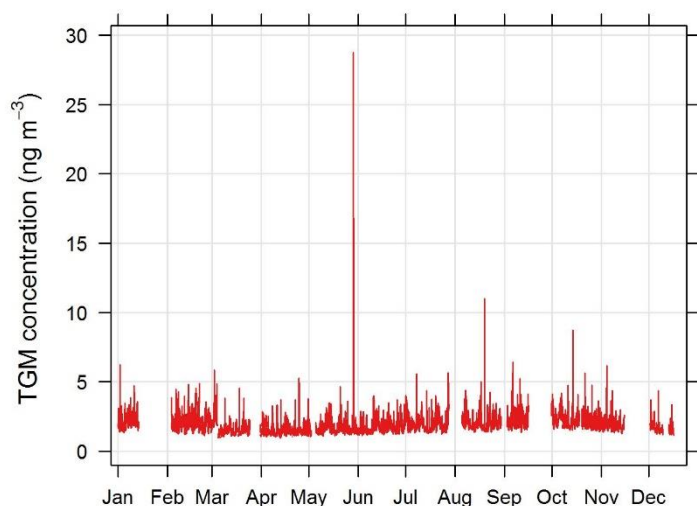
CHARACTERISATION OF AMBIENT TOTAL GASEOUS MERCURY CONCENTRATIONS

This chapter presents the results of the characterisation of ambient total gaseous mercury (TGM) concentrations over the South African Highveld region. Research on ambient TGM concentrations over this region is important, and required, because of the high prevalence of anthropogenic emission sources in the area. The obtained results were submitted as an article to a peer-reviewed journal as a pilot study characterising ambient TGM concentrations at three monitoring sites, to obtain both spatial and temporal variability. Thus, section one presents the findings on spatial variation; section two describes the seasonal variation, and also provides a brief correlation between meteorological variables and TGM concentrations per season; section three compares the different diurnal variation patterns at the sites; section four discusses the relationships between TGM and criteria pollutants; and the final section provides a brief conclusive summary of this chapter.

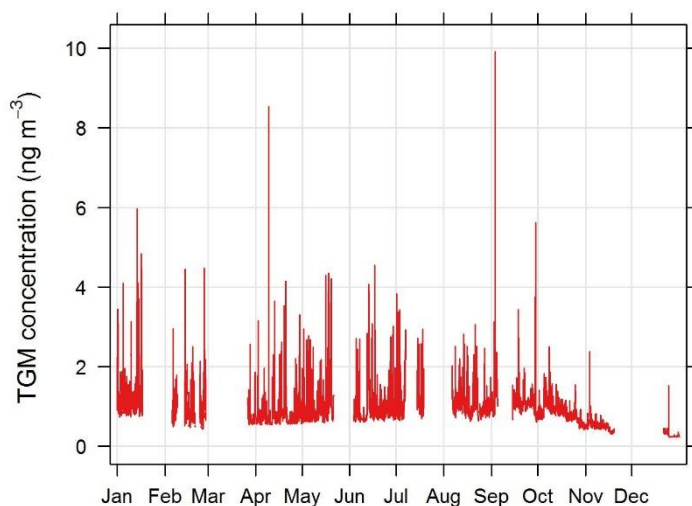
4.1 Spatial variation of TGM concentrations

Average hourly TGM concentrations during the monitoring period ranged from 0.40 to 28.72 ng/m³, 0.12 to 9.91 ng/m³, and 0.21 to 32.10 ng/m³ at BF, MB, and ST, respectively, with mean concentrations of 1.99 ± 0.94 ng/m³ (n = 6378), 1.04 ± 0.62 ng/m³ (n = 5473), and 1.25 ± 1.38 ng/m³ (n = 3568) (time series of TGM concentrations at the sites are illustrated in Figure 4-1). These concentrations are compared to measurements made at different locations globally (Table 4-1). Compared with background TGM concentrations measured at Cape Point, South

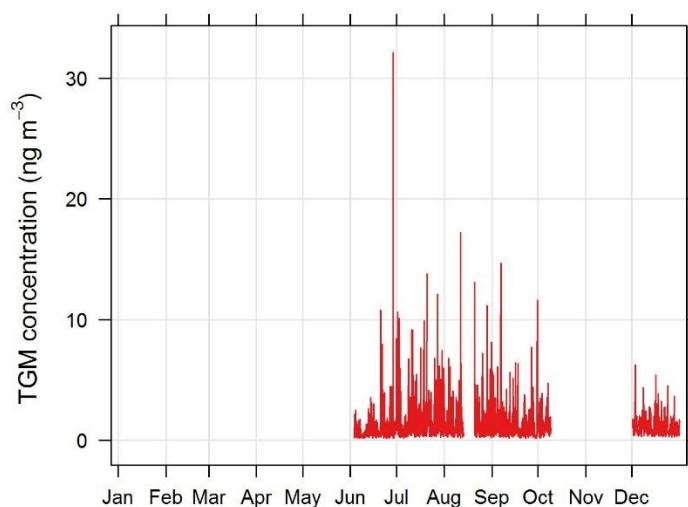
Africa (Baker *et al.* 2002; Slemr *et al.* 2008), and the accepted background TGM concentration in the northern hemisphere ($1.5 - 1.7 \text{ ng/m}^3$) (Kim *et al.* 2005), these values



(a)



(b)



(c)

Figure 4-1: Time series of TGM concentrations using hourly averages at (a) Balfour; (b)Middelburg; and (c)Standerton (ST).

are obviously significantly higher. The concentrations measured at especially BF and MB are also higher than those observed in Canada (Mazur *et al.* 2009) and Taiwan (Sheu *et al.* 2010; Jen *et al.* 2014), and substantially higher than levels measured in France (Maruszczak *et al.* 2016), India (Karthik *et al.* 2017), Scotland (Kentisbeer *et al.* 2011), Ireland (Ebinghaus *et al.* 1999), and the USA (Obrist *et al.* 2008). A profoundly influential factor in the difference in concentrations may be that the sites considered in this study are situated in a more industrialised and domestic fuel use afflicted region than those in the aforementioned studies.

There are parts of the world where TGM concentrations are higher than those measured at the SAHA sites. Compared to a Mexican study (de la Rosa *et al.* 2004), for example, where one of the considered sites is an urban place, measured concentrations in this study are much lower. The main activity surrounding this site is silver and gold mining where amalgamation is used for extraction. This is also true for a Venezuelan study (Garcia-sanchez *et al.* 2007) where concentrations are also much higher than those observed in this study. The data reported in both these studies, however, represent very short periods of about three days and one month, respectively. The TGM concentrations reported in the present study are higher than levels measured at urban Chinese locations (Fang *et al.* 2004; Chen *et al.* 2013). Concentrations measured in Korea also far surpasses those in this study (Seo *et al.* 2016) by more than 2.5 times.

Table 4-1: Comparison of TGM concentrations (ng/m³) observed in this study with those at different locations around the world.

Location	Site Type	TGM	Monitoring Period	Reference
Cape Point, South Africa	Coastal	1.2–1.4	1995–1999	Baker <i>et al.</i> 2002
		1.203 ± 0.038	1996–2004	Slemr <i>et al.</i> 2008
La Seyne-sur-Mer, France	Coastal	2.20 ± 0.54	2009	Maruszczak <i>et al.</i> 2016
Kodaikanal, Tamil Nadu, India	Rural	1.53 ± 0.25	Nov 2012–Sep 2013	Karthik <i>et al.</i> 2017
Genesee, Alberta, Canada	Rural	1.57 ± 0.29	2004–2007	Mazur <i>et al.</i> 2009
Auchencorth Moss, Scotland	Rural	1.44	2005–2008	Kentisbeer <i>et al.</i> 2011
Mace Head, Ireland	Coastal	1.75	1995–2002	Ebinghaus <i>et al.</i> 1999
Zacatecas, Mexico	Urban	20–100	17–20 Sep 2002	de la Rosa <i>et al.</i> 2004
El Callao, Venezuela	Rural	0.28–100	Feb–Mar 2004	Garcia-sanchez <i>et al.</i> 2007
Mt. Dinghu, China	Rural	5.07 ± 2.89	Oct 2009–April 2010	Chen <i>et al.</i> 2013
Changchun, China	Urban	18.4	Jul 1999–Jul 2000	Fang <i>et al.</i> 2004
Guangzhou, China	Urban	4.60 ± 1.36	Nov 2010–Oct 2011	Chen <i>et al.</i> 2013
Mt. Front Lulin, Taiwan	Rural	1.73	Apr 2006–Dec 2007	Sheu <i>et al.</i> 2010
Penghu Islands, Taiwan	Coastal	3.17 ± 1.06	Mar 2011–Jan 2012	Jen <i>et al.</i> 2014
Pohang, Korea	Urban	5.0 ± 4.7	2012–2013	Seo <i>et al.</i> 2016
Colorado, USA	Rural	1.51 ± 0.12	Oct 2006–May 2007	Obrist <i>et al.</i> 2008
Balfour, South Africa	Rural	1.99 ± 0.94 (n = 6378)	2009	This study
Middelburg, South Africa	Rural	1.04 ± 0.62 (n = 5473)	2009	This study
Standerton, South Africa	Rural	1.25 ± 1.38 (n = 3568)	2009	This study

Polar plots of mean TGM concentrations during the monitoring period at the sites are illustrated in Figure 4-2, and prevailing wind direction in Figure 4-3. Spring, summer, autumn, and winter consist of September, October, November; December, January, February; March, April, May; and June, July, August, respectively. North-easterly and north-westerly were the prevailing wind directions during the monitoring period with a slightly smaller frequency from the south-west. As a result, BF is located downwind from most potential point-sources of TGM emission (power-generating and cement production plants), and upwind from a power-generating plant situated to its south-west. The predominant source of TGM surrounding the site appears to be transported by strong winds from the northwestern region (>10 m/s), but also from within the immediate vicinity surrounding the monitoring site and the north-east. Potential sources located to the north-west include cement production and other industrial emissions in Gauteng province. Domestic coal combustion in the township located in the northeastern part of the BF site may be the source of TGM from that direction. Coal is used in South African townships for cooking and heating purposes and has been estimated to emit about 0.75 tonnes of TGM (Leaner *et al.* 2009).

The closest potential sources of TGM are located within MB to the north-east (alloys production) and the south-east (ferrous and non-ferrous metal production and steel production). The prevailing wind observed at the station, however, came from the west and north-west and to some extent from the south-west. It's in arguably the most industrialised region with potential leading sources of TGM within the town and power-generating plants to its south-west, south, and south-east. Interestingly though the lowest TGM concentrations were observed at this site. Given the direction of the third most prevailing wind, however, one expects a stronger contribution from the power-generating plant to the south-west, and this seems to be the case. A strong influence is observed from a local source to the south west of the town, but more importantly from the western and northwestern directions. The closest potential major source of TGM located to the west of this monitoring site is assumed to be cement production. One of the major transport pathways of air masses into the industrialised region is recirculation (Freiman & Piketh 2003), which may last between 2 and 9 days. Theoretically, given the location of MB, together with the high wind speeds and elemental mercury's ability to be transported over large atmospheric distances, this is not impossible.

The predominant wind directions observed at ST were northeasterly and northwesterly. This does not seem to have had a noticeable influence on the distribution of TGM concentrations, however.

A rather interesting phenomenon is observed for this site. The dominant source of TGM during the sampling period appears to be local in origin. The chances of this source possibly being domestic coal combustion is more than likely given that the monitoring site is located within a township. This is a potential cause for concern as approximately 90% of Hg emitted from domestic coal combustion is Hg^0 and Hg^{2+} (Pacyna *et al.* 2003). Given an estimated 0.75 tonnes of Hg from this source, the residents may be exposed to about 0.66 tonnes of gaseous Hg during combustion (Leaner *et al.* 2009). Possible sources of TGM to the north of the site could be the coal gasification plants and township located in that region.

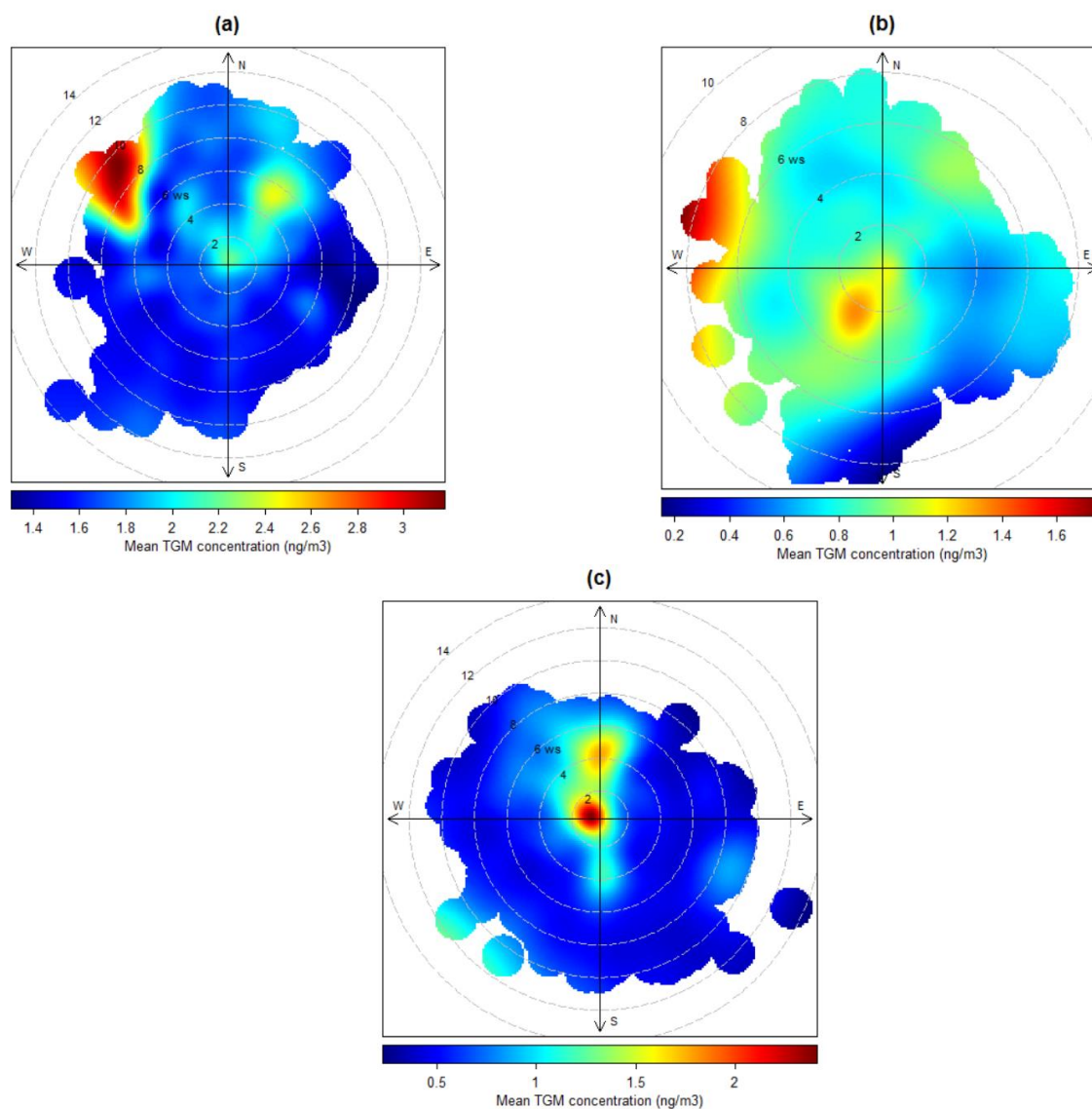


Figure 4-2: Polar plots illustrating mean TGM concentrations (ng/m^3) over the sampling period relative to predominant wind speed and direction at (a) Balfour (BF); (b) Middelburg (MB); and (c) Standerton (ST).

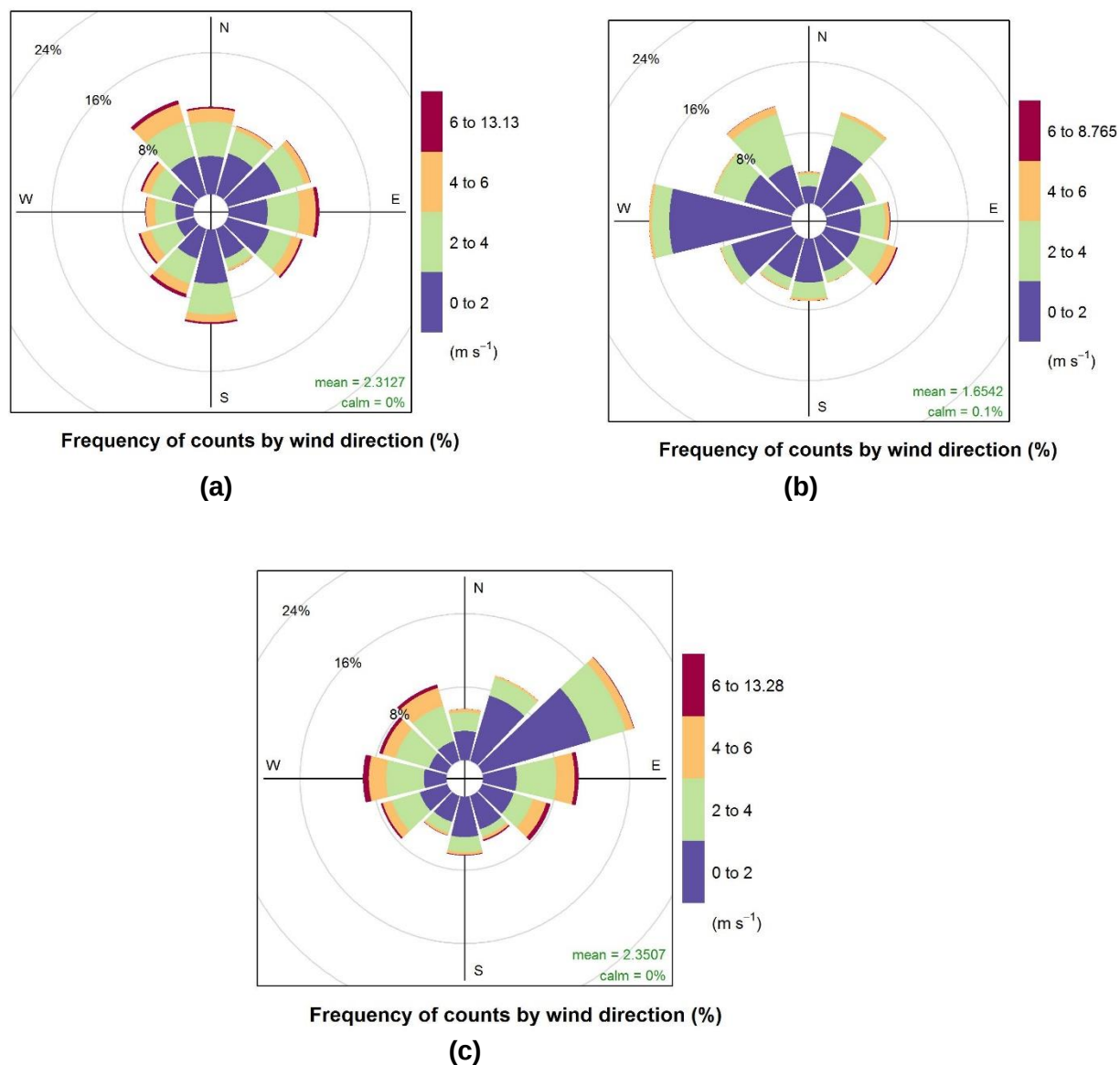


Figure 4-3: Prevailing wind direction during the sampling period at (a) Balfour; (b) Middelburg; and (c) Standerton.

4.2 Seasonal variation of TGM concentrations

Seasonal average hourly TGM statistics during the monitoring period at the sites are presented in Table 4-2. The seasonal variation of TGM concentrations at BF, MB, and ST are illustrated in Figures 4-4, 4-5, and 4-6, respectively. The highest hourly concentration of TGM at BF was observed for summer (2.38 ng/m³), followed in descending order by spring (2.16 ng/m³), winter (1.96 ng/m³), and autumn (1.67 ng/m³). The highest concentration occurred in May (28.72 ng/m³), whereas the lowest was measured in December (0.40 ng/m³). In contrast to BF, the highest hourly TGM concentration at MB occurred during summer (1.44 ng/m³), followed by winter (1.06 ng/m³), autumn (0.96 ng/m³), and spring (0.86 ng/m³), with the highest and lowest concentrations being observed in September (9.91 ng/m³) and March (0.12 ng/m³), respectively. It is important to mention that data capture for summer at MB is much lower compared to the other seasons.

Concentrations of TGM at ST declines from winter (1.36 ng/m³) to spring (1.14 ng/m³) and summer (1.09 ng/m³) with the highest concentration occurring in July (32.10 ng/m³) and the lowest in October (0.19 ng/m³). Importantly, the average concentration reported for summer represents about a third of the season. The highest mean seasonal TGM concentration at this site was observed in winter and this may be explained by more consistently present and persistent inversion layers during this season. As illustrated in Figure 4-1, the predominant source of TGM in and surrounding the site is local. This is presumed to be domestic fossil fuel combustion as colder temperatures lead to more coal combustion for heating purposes, and due to many residents in the Highveld region relying on coal for cooking purposes. This should inevitably lead to higher TGM concentrations and is evident in the results. Furthermore and unlike in power-generating plants, emissions of Hg from domestic coal combustion is not controlled by emission control technologies.

The seasonal variation of TGM at all sites was relatively small. At BF it was highest in autumn (SD = 1.11 ng/m³) and smallest in spring (SD = 0.63 ng/m³). Similarly, at the MB site, the variation was highest in summer (SD = 0.91 ng/m³) and lowest in spring (0.45 ng/m³). In contrast, at the ST site the variation was highest in winter (1.63 ng/m³) and lowest in summer (0.74 ng/m³). Transport of air masses into this region is primarily controlled by easterly or westerly direct transport, or recirculation (Freiman & Piketh 2003). In summer, on the SAHA, the atmospheric circulation is consistently subject to easterly disturbances, whereas during winter anticyclones are

prevalent (Laakso *et al.* 2012). Under low-pressure circumstances, where easterly air mass transport is predominant, meteorological conditions are typically unstable. This subsequently leads to an increase in vertical movement and dispersion of TGM concentrations (Tyson *et al.* 1996). In winter, stable anticyclonic conditions can trap a pollutant for numerous days before being transported to the south Indian ocean (Piketh *et al.* 2000; Freiman & Piketh 2003). Winters are also characterised by persistent inversion layers which can trap emissions of TGM. The atmospheric boundary layer may, of course, also have an influence on seasonal variation as it directly influences the manner in which a pollutant is transported and diluted. In a study conducted at a background site on the western part of the Highveld region, the annual cycle of the stable, mixed, and residual layers were determined to be highest in winter and lowest in summer (Gierens 2015).

Table 4-2: Summary of statistics of TGM concentrations (ng/m³) at Balfour (BF), Middelburg (MB), and Standerton (ST).

		N (hourly)	Mean	Max	Min	SD	Median
BF	Summer	1225	2,385	7,43	0,40	1,10	2.383
	Autumn	1912	1,67	28,72	0,50	1,11	1,46
	Winter	1947	1,96	11,01	1,13	0,66	1,77
	Spring	1294	2,16	6,41	1,27	0,63	2,00
MB	Summer	959	1,44	6,65	0,16	0,91	1,51
	Autumn	1331	0,96	8,53	0,12	0,58	0,77
	Winter	1517	1,06	4,55	0,60	0,47	0,93
	Spring	1666	0,86	9,91	0,16	0,45	0,82
ST	Summer	682	1,09	6,27	0,21	0,74	0,85
	Autumn	-	-	-	-	-	-
	Winter	1970	1,36	32,10	0,20	1,63	0,89
	Spring	916	1,14	14,66	0,19	1,12	0,84

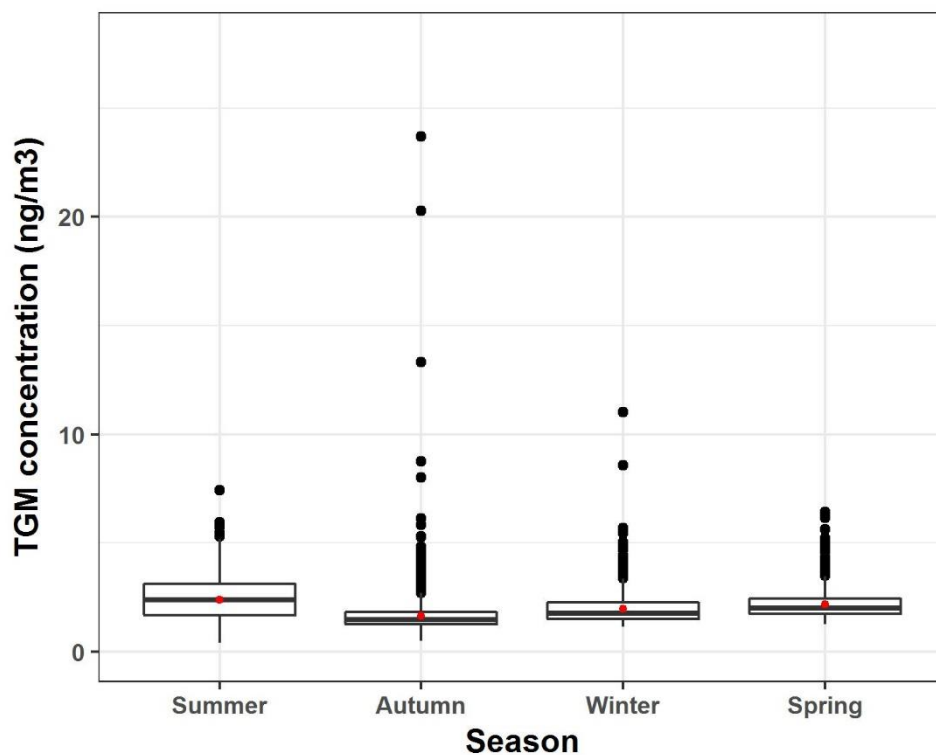


Figure 4-4: Seasonal variation of TGM concentrations (ng/m³) at Balfour (BF). The horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles. The red dots within the boxes represent the mean TGM concentration. The top and bottom whiskers extend to the most extreme data point which is within 1.5 times the interquartile range.

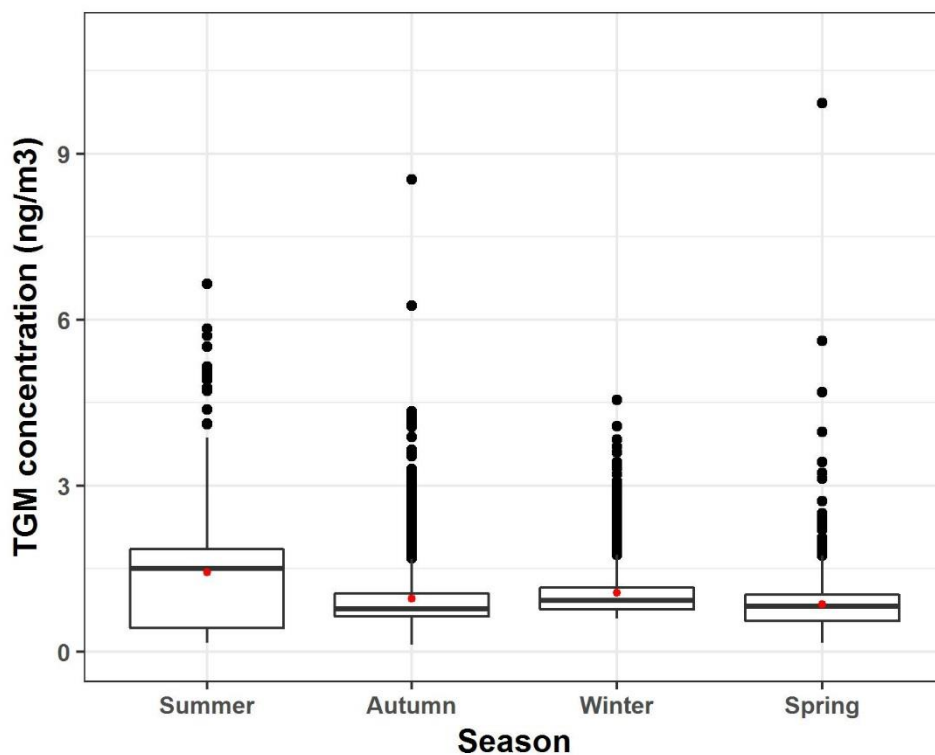


Figure 4-5: Seasonal variation of TGM concentrations (ng/m³) at Middelburg (MB). The horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles. The red dots within the boxes represent the mean TGM concentration. The top and bottom whiskers extend to the most extreme data point which is within 1.5 times the interquartile range.

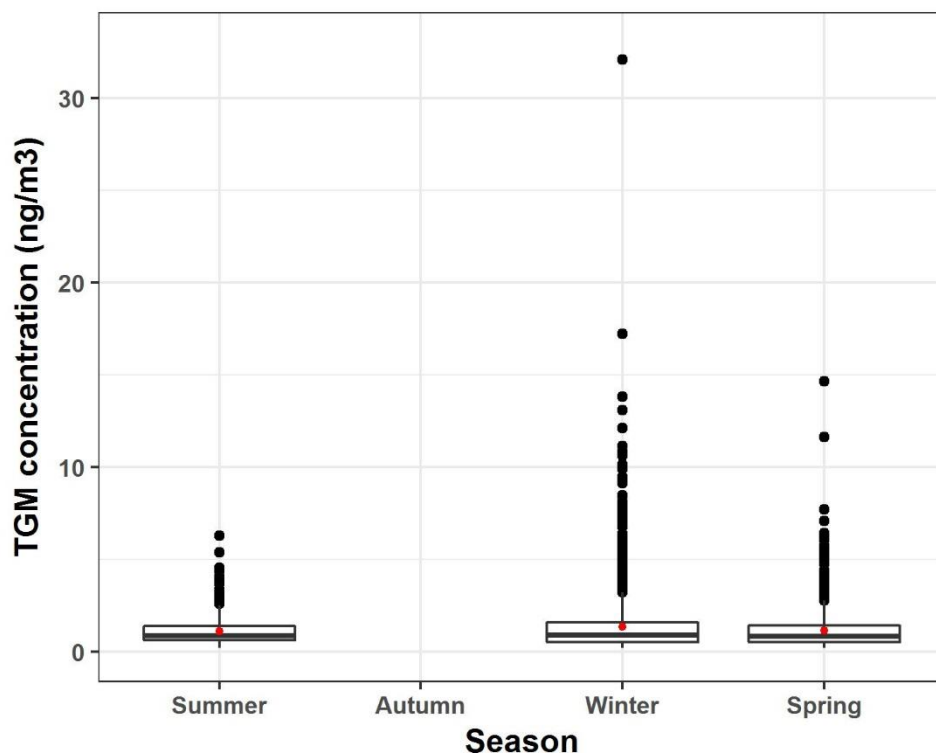


Figure 4-6: Seasonal variation of TGM concentrations (ng/m³) at Standerton (ST). The horizontal lines in the boxes represent the 25th, 50th, and 75th percentiles. The red dots within the boxes represent the mean TGM concentration. The top and bottom whiskers extend to the most extreme data point which is within 1.5 times the interquartile range.

A seasonal correlation of TGM concentrations at the sites with various meteorological parameters is presented in Table 4-4. Very small correlations were found at each site, in each season, for most correlation analyses of TGM with the meteorological parameters. A significant positive correlation against wind speed ($r = 0.85$) is observed at ST during summer, where insufficient Hg concentrations capture data was available.

Table 4-3: Seasonal correlation of TGM concentrations (ng/m³) and meteorological parameters at Balfour (BF), Middelburg (MB), and Standerton (ST).

		P	R	RH	T	WD	WS
BF	Summer	-0.29	-0.04	0.15	-0.05	-0.06	-0.35
	Autumn	-0.04	-0.02	0.07	-0.14	-0.11	-0.16
	Winter	0.23	0.01	0.02	-0.08	-0.05	-0.23
	Spring	0.02	-0.04	0.03	-0.16	-0.02	-0.24
MB	Summer	0.04	0.01	0.21	-0.33	-0.06	-0.22
	Autumn	-0.14	0.01	-0.11	-0.11	-0.002	-0.25
	Winter	0.03	-0.03	0.04	-0.11	-0.07	-0.21
	Spring	0.20	0	-0.31	0.24	0.10	-0.10
ST	Summer	-0.17	0.03	-0.08	0.21	0.74	0.85
	Autumn	-	-	-	-	-	-
	Winter	0.10	-0.01	-0.07	-0.08	0.04	-0.25
	Spring	-0.08	-0.03	-0.09	0.02	0.04	-0.27

P = Pearson product moment correlation coefficient; R = Rainfall; RH = Relative humidity; T = Temperature; WD = Wind direction; WS = Wind speed.

4.3 Hourly mean variation of TGM concentrations

The diurnal variation at the three sites averaged hourly over the entire period, is depicted in Figure 4-7. The BF and MB sites did not exhibit a prominent diurnal pattern, whereas a distinct one is apparent at ST. Concentrations of TGM at BF during night (18:00–06:00) and day (06:00–18:00) were 2.05 ng/m³ and 1.93 ng/m³, respectively. The concentrations reached maxima at 00:00 and minima at 15:00. A similar daily maxima and minima pattern of TGM was observed at La Seyne-sur-Mer (Maruszczak *et al.* 2016). Night-time and day-time TGM concentrations at MB were 1.06 ng/m³ and 1.03 ng/m³, respectively. Concentrations of TGM at MB reached maxima at 10:00 and

minima at 03:00. This daily maxima and minima pattern is in general agreement with one observed at Mt. Dinghu, China (Chen *et al.* 2013). The contribution of TGM from anthropogenic activities and photochemical production at these sites appear to be minimal. However, the small peaks around 07:00 at BF and 10:00 at MB can be attributed to sparse combustion sources located locally or regionally. The extent to which Hg concentrations varies at any given site is, importantly, largely dependent on the presence or absence of significant point and/or area sources within its vicinity (Schroeder & Munthe 1998), and although BF and BF are located relatively close to large point sources, this seems to have had no noticeable effect on TGM daily variation.

This seems to be exactly the opposite at ST where local combustion sources appear to have a significant effect on the daily pattern. This pattern was observed during winter and spring. At this site, night-time and day-time TGM concentrations were 1.38 ng/m³ and 1.24 ng/m³, respectively. Concentrations of TGM at reached maxima at 18:00 and minima at 13:00. Concentrations at this site gradually increased from ~00:00 to around 07:00, after which it decreased to 15:00, increased for a second time to its maximum at 18:00, and finally decreased again to ~00:00. At sunrise, when the sun starts to warm the earth's surface, an unstable convective boundary layer forms (Garratt 1994). This increases the height of the mixing layer (Xu *et al.* 2011) and thus promotes circulation of air masses which may explain why the TGM concentration starts to decline at around 07:00. After sunrise, O₃ decreases until approximately 09:00 (Schanz *et al.* 2014). Subsequently, concentrations of Hg⁰ (the dominant TGM constituent) should decrease, as an increase in O₃ depletes Hg⁰ concentrations (Engle *et al.* 2005). The decrease at night may be due to the formation of a stable nocturnal layer. Stable conditions are generally more favourable for O₃ accumulation (Balashov *et al.* 2014) as O₃ cannot be transported from where it has formed. Night-time is characterised by the cooling of the earth's surface and this usually favours the formation of a stable nocturnal boundary layer, and tropospheric layers near the surface to be stratified (Stull 1997).

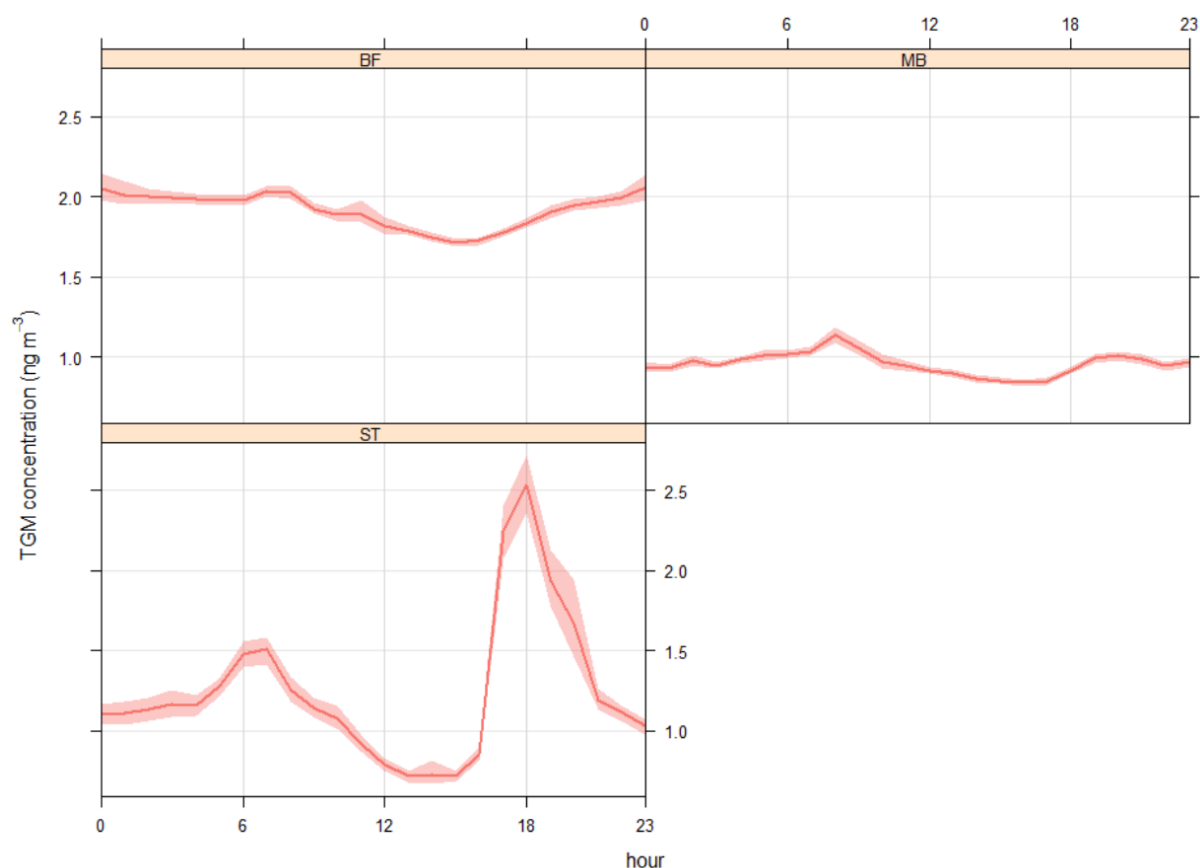


Figure 4-7: Average hourly variation of TGM concentrations (ng/m³) at Balfour (BF), Middelburg (MB), and Standerton (ST) during the entirety of the observational period.

4.4 Relationship between TGM and criteria pollutant concentrations

The relationship between hourly average concentrations of TGM and criteria pollutants measured at BF, MB, and ST are depicted in Table 4-5. Coal combustion has been identified as the dominant source of Hg in South Africa (Leaner *et al.* 2009) and an important source of ambient NO₂, SO₂, and Hg (Chen *et al.* 2013). Attributing this to a specific source, however, is particularly difficult due to the emission of Hg from various source types (Streets *et al.* 2005). A significant positive correlation was found between TGM and NO₂ at the BF site ($r = 0.36$, $p < 0.001$). Although the significance between TGM and the CO and SO₂ levels at this site were smaller ($r = 0.25$, $p < 0.001$;

$r = 0.21$), the chances of the attributable source being coal combustion is more than likely. Daily concentrations of TGM and NO_2 and CO were significantly positively correlated at the MB site ($r = 0.44$, $p < 0.001$; $r = 0.42$, $p < 0.001$) with a somewhat smaller significant correlation with NO ($r = 0.28$, $p < 0.001$). In order to establish the diurnal relationship between TGM and criteria pollutants, the observations at ST are used, as a distinct pattern was observed at this site (Figure 4-8).

A significant positive correlation was found between the daily TGM concentration and CO at the site ($r = 0.67$, $p < 0.001$). Concentrations of CO followed a very similar diurnal trend as TGM, and this compatibility may suggest that their variation is affected by a similar source such as domestic fossil fuel combustion. The fact that a very similar trend is observed for NO_2 , albeit no significant correlation was found ($r = 0.12$, $p < 0.001$), further suggests that coal combustion source is the potential source of TGM constituents. Coal gasification processes in the plant located to the north of the site may also be a potential source of TGM. This may serve as an explanation of the significant positive correlation between these two pollutants, as incomplete combustion emits high concentrations of CO. In contrast to the diurnal pattern of TGM, CO and NO_2 , O_3 concentrations portrayed an increasing trend from morning (~09:00) to its maximum in the afternoon (~15:00). An earlier study demonstrated the importance of O_3 in the oxidation of Hg^0 and the atmospheric cycling thereof (Shon *et al.* 2008).

Table 4-4: Correlation between hourly concentrations of TGM and criteria pollutants measured at Balfour, Middelburg, and Standerton.

Site		O_3 (ppb)	SO_2 (ppb)	NO (ppb)	NO_2 (ppb)	CO (ppm)
BF	n	7131	5930	4565	6174	7159
	r	-0.07	0.21	0.07	0.36	0.25
MB	n	5471	6549	6614	6610	6730
	r	-0.10	-0.11	0.28	0.44	0.42
ST	n	5092	5979	4558	4438	6485
	r	-0.21	0.15	-0.03	0.12	0.67

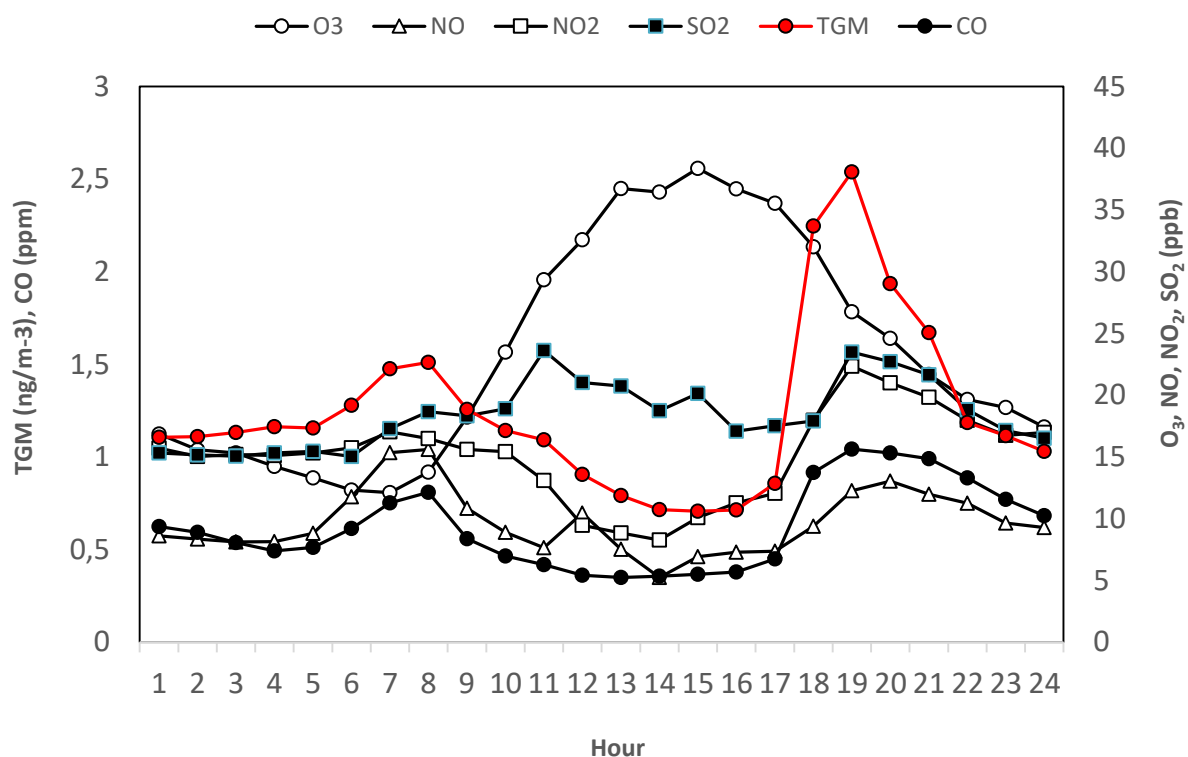


Figure 4-8: Mean diurnal variation of TGM (ppm), O₃ (ppb), NO (ppb), NO₂ (ppb), SO₂ (ppb), and CO (ppm) concentrations monitored at ST.

CHAPTER CONCLUSIONS

The objective of the results portrayed and discussed in this chapter is to characterise ambient TGM concentrations on the South African Highveld.

The following main inferences can be made:

Ambient TGM concentrations vary between the sites, with MB, the site located in arguably the most industrialised region not portraying the highest concentrations. This, of course, signals, a profound influence from meteorology. ST, the site with the least amount of potential large point-sources in its vicinity, returned the highest TGM concentrations. The observed different seasonal variation at the sites, suggests a probable influence by easterly air mass transport in summer, and anticyclonic conditions during winter. It may also, of course, have been influenced by the boundary layer due to its seasonal variability. The distinct diurnal pattern at ST appears to have been significantly influenced by local combustion sources, while the patterns at BF and MB resembles patterns possibly attributable to sparse local and regional sources. The relationship between TGM and CO at ST and their very similar diurnal patterns may suggest coal combustion as the predominant source of TGM at this site. Source-apportionment may be helpful in ascribing the emissions to a specific source. This would be particularly helpful in determining the contribution from coal-fired power plants. This is important as combustion in coal-fired power plants is considered as the dominant source of Hg in South Africa. The majority of these plants are situated on the South African Highveld. This deems it plausible to assume that this is an area of interest regarding potentially high Hg emissions, and subsequent concentrations. As an alternative to source-apportionment, emission estimation techniques may be utilized.

CHAPTER 5

ESTIMATION OF MERCURY EMISSIONS FROM ESKOM POWER PLANTS

This chapter provides Hg emissions estimates from ESKOM power plants during 2014. These estimates were obtained through the utilisation of the bottom-up approach. Previous South African Hg emission estimated studies, adopted Hg-coal content from literature. The emission estimates in this chapter, however, utilized Hg-coal content measured in coal samples at each of the 13 power plants considered in this study. This is done to investigate and establish the impact of assuming Hg-coal content values from literature, versus actual measured values, on Hg emission estimates. This chapter also reports the resultant effect of emission control devices on estimates. This is achieved by comparing estimates using currently installed devices, to those obtained through the theoretical assumption that all power plants are retrofitted with Fabric filters. Lastly, this chapter reports the estimated Hg contribution from each considered ESKOM power plant to the atmosphere in 2014.

5.1 Influence of Hg-coal content on Hg emission estimates

Previous South African Hg estimation studies adopted Hg-coal content from literature to estimate emissions, as described in chapters 2 and 3. To investigate the influence of the aforementioned on estimates, estimations using Hg-coal content measured at each of the respective 13 power plants is compared to those made by assuming Hg-coal content values from literature. Figure 5-1 illustrates the estimated Hg emissions through a comparison of the Hg content of coal measured at each respective power plant (ESKOM), and the average Hg-coal contents reported by Gericke *et al.* 2007 and Wagner and Hlatshwayo 2005. Higher estimations

are observed for Kendal, Lethabo, and Matimba (highest coal consumption and fitted with an ESP), while lower values were estimated for especially Arnott, Camden, and Hednrina (retrofitted with an FF). Majuba, although fitted with an FF, has a slightly higher estimated emission due to its coal consumption being more than double that of the aforementioned plants. A close relation is clearly observed between emission estimates of this study and that of Gericke *et al.* 2007. However, relatively lower emissions were estimated for the majority of power plants by means of the average Hg content reported by Wagner and Hlatshwayo 2005, especially those of Kendal, Lethabo and Matimba.

The total Hg emissions in 2014 for all Eskom power stations were 19.47 Mg/yr (Table 5-1). When compared to the total Hg emissions estimated by using the average Hg content in coal of Gericke *et al.* 2007 and Wagner and Hlatshwayo 2005, the former is closest with 18.23 Mg/yr while the latter is significantly lower with an estimated 8.81 Mg/yr. It should be noted, however, that Gericke *et al.* 2007 reported the average Hg content of South African Highveld coal, while Wagner and Hlatshwayo 2005 solely reported the average content of one coal seam on the Highveld. A possible explanation for the rationale behind the aforementioned may be due to the majority of power plants receiving their coal from Highveld coalfields (Dabrowski *et al.* 2008), and especially the coal seam investigated by Wagner and Hlatshwayo 2005. The slight difference in estimations by this study and that of Gericke *et al.* 2007 can be ascribed to the latter measuring Hg content in coal of only 10 out of the 13 power plants. Komati, Camden, and Grootvlei were only recommissioned at a later stage due to an increased demand for electricity. Therefore, the importance of Hg content in coal when estimating emissions from power plants is clearly apparent. It may be debatable that this study's estimates are more refined as they are based on power plant specific Hg contents in coal.

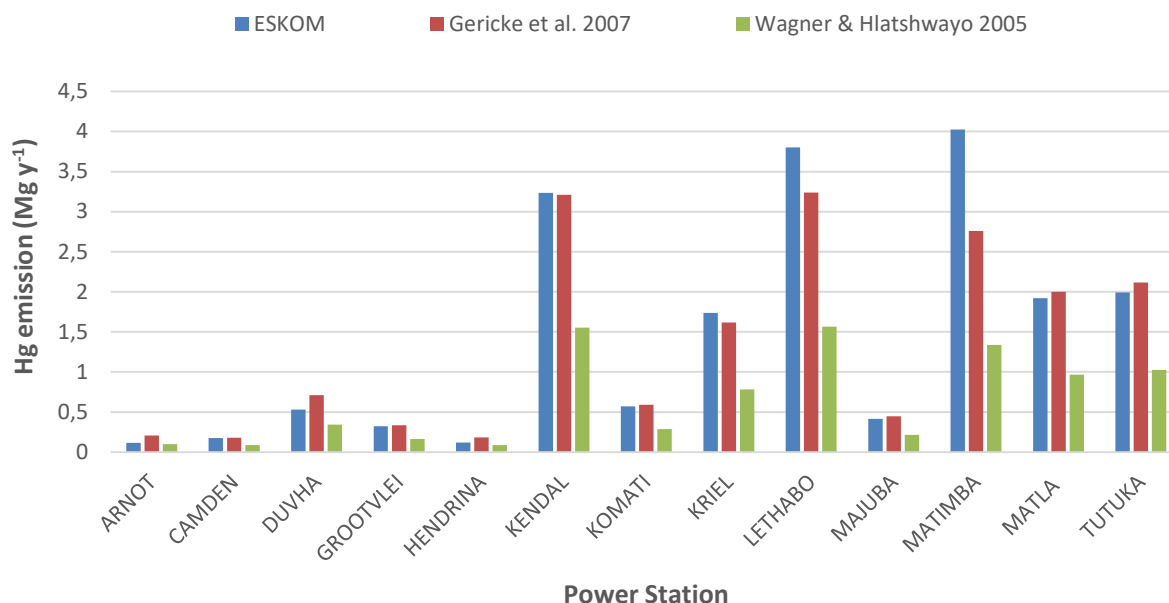


Figure 5-1: Mercury emission estimates (Mg/yr) using power plant specific Hg contents of coal (ESKOM), compared to average Hg coal contents reported by Gericke *et al.* 2007 and Wagner and Hlatshwayo 2005.

5.2 Influence of emission control devices on emission estimates

As discussed in chapters 2 and 3, emission control devices have different removal efficiencies of pollutants. Fabric filters (FF) have the highest removal efficiency of Hg emissions (89%), followed by where it is used simultaneously with electrostatic precipitators (ESP) (62.5%), and where an ESP is used as the sole emission control device (36%). Only 6 of the 13 power plants, however, uses this device. This poses the question: By how much would Hg removal be increased if all power plants were retrofitted with an FF? To answer this question, Hg emission estimates using currently installed control devices, are compared to those obtained through the theoretical usage of only FFs. This is collectively compared in Table 5-2, using the different Hg-coal content discussed in the previous section.

The power plants with the largest possible future reduction in Hg emissions are Kendal, Lethabo, and Matimba (Figure 5-2). These power plants, interestingly enough, had the largest coal

consumption in 2014, have the lowest output capacities, and are all fitted with an ESP emission control device. The power stations with an installed FF were observed to have significantly lower Hg emission estimates (Arnot, Camden, Hendrina, and Majuba). A mix of control devices installed at both Duvha and Grootvlei, together with a very low coal consumption at Komati may explain the relatively low estimates observed at these stations.

Table 5-1: Estimated Hg emissions (Mg/yr) for 2014 using current and proposed (all FF) control technologies.

	2014 Current	All FF
Measured Hg content for each power station	19.47	4.20
Gericke <i>et al.</i> 2007	18.23	4.17
Wagner and Hlatshwayo 2005	8.81	2.02

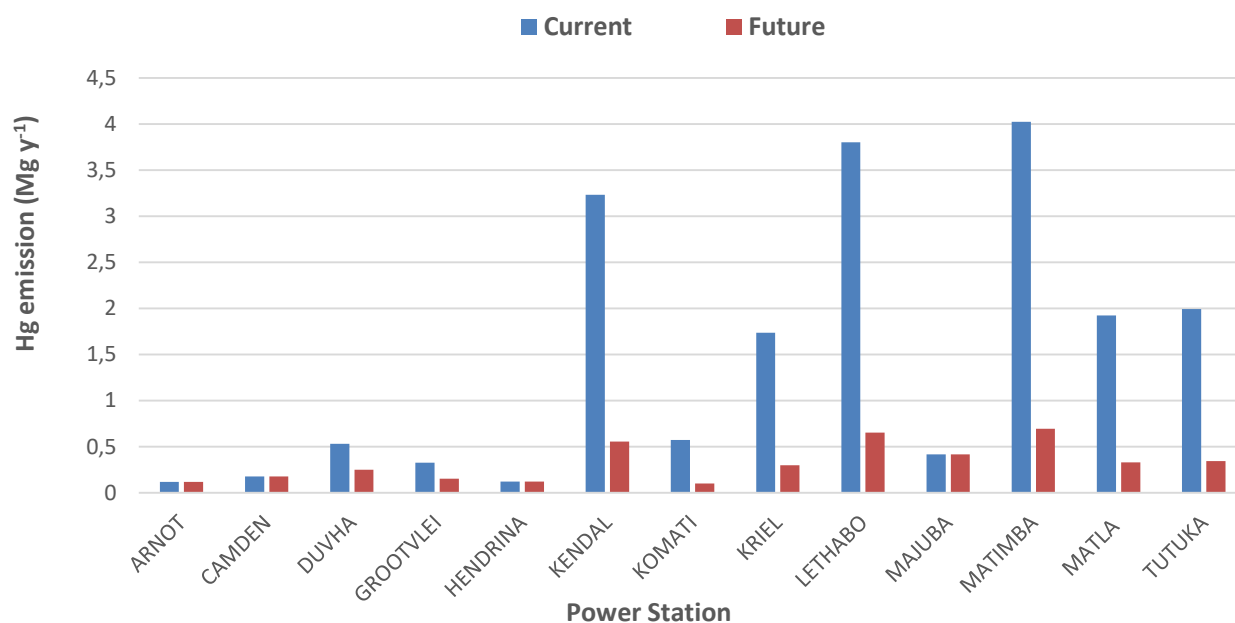


Figure 5-2: Current vs possible future Hg emissions (Mg/yr) from power plants.

5.3 Estimated Hg emission from the power plants

The approximated Hg emissions from the power plants to the atmosphere in 2014 (Figure 5-3) was dominated by Matimba (20.67.85%) followed by Lethabo (19.52%), Kendal (16.60%), Tutuka (10.24%), Matla (9.87%), Kriel (8.92%), Komati (2.93%), Duvha (4.35%), Majuba (2.13%), Grootvlei (2.66%), Camden (0.89%), Hendrina (0.62%), and Arnot (0.60%). The amount of Hg emitted by a power plant, of course, depends on the amount of coal combusted, the retrofitted emission control device, and the Hg-coal content. The dominant contributions Matimba, Lethabo, and Kendal, may be explained by their dominance in the annual amount of coal combusted in 2014, while the low contributions from the three latter plants, as discussed before, may most probably be due to the retrofitted fabric filters. Studies by Dabrowski et al. (2008) and Masekoameng et al. (2010) yielded similar results; Matimba, Lethabo, and Kendal were estimated to have had the highest atmospheric emissions of Hg during 2004, and 2000-2006, respectively. This signals an important influence from the amount of coal combusted, as the aforementioned plants had more than double the amount of coal combusted by the other plants that were active during 2000-2006. Importantly, each plant receives its coal from a different coal mine, meaning that the Hg-coal content may vary from plant-to-plant.

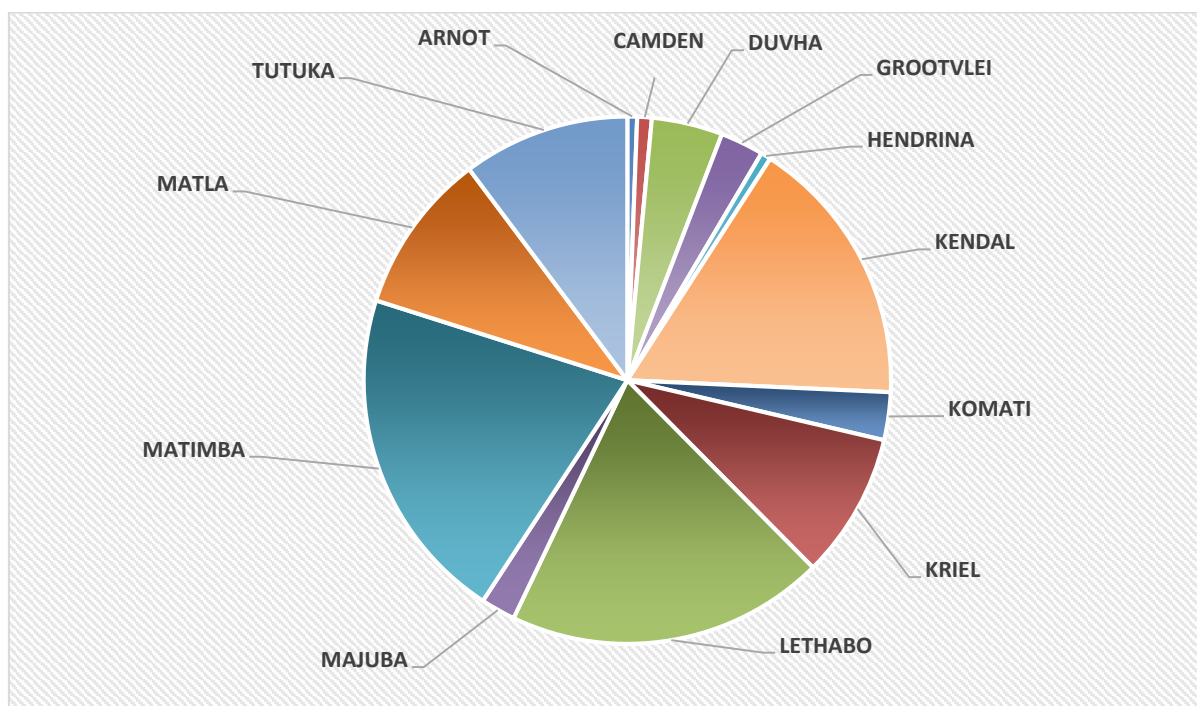


Figure 5-3: Contribution to atmospheric Hg emissions (%) by ESKOM power plants in 2014.

CHAPTER CONCLUSIONS

The objective of the results depicted and discussed in this chapter is to estimate Hg emissions from 13 ESKOM owned power plants during 2014.

The main conclusions are as follows:

It is quite evident that the Hg content used to estimate emissions from power plants has a noteworthy influence on the results obtained. Using power plant specific coal Hg contents should allow more refined Hg emission estimates, rather than assuming average contents from published literature. The effect of emission control devices on total Hg emitted to the environment cannot be denied. Fabric filters are far more efficient in regulating emissions, and should henceforth be installed at all power plants to reduce emissions. A clear relation was observed between amounts of Hg emitted by power plants in 2014, the control device installed, and the total amount of coal combusted. Reducing the amount of consumed coal simply won't be enough, hence why plants fitted with and ESP should adopt the use of an FF. Even though current plans to convert all power plants to FFs are aimed at reducing PM, this will also lead to a significant reduction in Hg emissions. However, the substantial cost involved in this conversion should be weighed against the expected benefit. The full impact of Hg emissions on ecosystems and human health in South Africa should, therefore, be quantified. An atmospheric dispersion study, coupled with a health risk assessment may partially address this need.

CHAPTER 6

DISPERSION MODELLING OF MERCURY OVER THE SOUTH AFRICAN HIGHVELD

The results presented in this chapter provide the first ever modelling study regarding Hg concentrations and wet and dry deposition thereof on the South African Highveld region. The atmospherically significant forms of Hg (Hg^0 , Hg^{2+} , and HgP) were modelled from 12 coal-fired power plants during 2011-2014. The assumptions made prior to modelling should cause for a certain extent of uncertainty, as arguably every modelling study does. As Hg^0 has been identified as the only Hg species to pose a threat via the inhalation pathway, a brief health risk assessment is conducted to put the results in perspective. The quality and reliability of the output of a dispersion model is, of course, dependent on the input parameters.

6.1 Atmospheric Dispersion of Hg species

The spatial distribution of Hg^0 , Hg^{2+} , and HgP concentrations modelled with CALPUFF are illustrated in Figures 6-1, 6-2, and 6-3, respectively. The highest ambient concentrations of all three Hg species were calculated over the central parts of the modelled domain. As expected, this is the same spatial distribution as the other major pollutants from power plants modelled for the Highveld region (Pretorius *et al.* 2017). Moreover, the highest modelled concentrations were, as expected, observed for Hg^0 and the lowest for HgP given the conservative basis of this study. The modelled concentrations of Hg^0 , Hg^{2+} , and HgP ranged 0.0028–0.0631, 0.0028–0.0497, and 0.0008–0.0137 ng/m^3 , respectively.

Kriel and Matla may collectively be acting as one stack in the centre of the domain, as they are located in extremely close proximity to each other. Polluted air from the other power plants is thus accumulating in an already polluted area of high concentrations. These two plants have fairly low

emission profiles and shorter stacks leading to lower emission heights, and subsequently dispersion potential. For the purpose of comparison, the measured concentrations in this study are compared to those obtained by other selected studies. As can be observed in Table 6-1, there is a significant difference in the number of sources modelled in the current study, and those in the international studies. One would subsequently expect the concentrations in the current study to be much higher. Notwithstanding, the domain size considered in the current study is much bigger, and this should have consequent implications on modelled concentrations.

Table 6-1: Comparison of modelled species concentrations in this study, to those modelled internationally.

Study	Study location	Model/s used	Modelling domain size	Modelled source	Modelled species	Annual average concentration (ng/m ³)
Garcia <i>et al.</i> 2017	Pacific coast, Mexico	CALPUFF	65 km x 60 km	Coal-fired power plant	Hg ⁰	2.8
Heckel & LeMasters 2011	Cincinnati, Ohio, USA	AERMOD	10 km x 10 km	Coal-fired power plant	Hg ⁰	0.1 ^a 0.2 ^b
Sang-sup & Keener 2005 ^c	Coshocton and Manchester, Ohio, USA	AERMOD and ISCST3	5 km x 5 km	2 Coal-fired power plants	Hg	0.036 and 0.085 ^d and 0.014 and 0.041 ^e
Lonati and Zanoni 2013 ^f	South-east of Milan, Italy	CALPUFF	10 km x 10 km	Gasification plant	Hg ⁰ Hg ²⁺ HgP	0.00047–0.0063 0.0023–0.031 0.00022–0.0031
Current study ^g	Highveld region, South Africa	CALPUFF	250 km x 250 km	12 Coal-fired power plants	Hg ⁰ Hg ²⁺ HgP	0.0028–0.0631 0.0028–0.0497 0.0008–0.0137

a Modelled for a flat terrain.

b Modelled for a mountainous terrain.

c Modelled species of Hg is not specified.

d Modelled for Coshocton using AERMOD and ISCST3, respectively.

e Modelled for Manchester using AERMOD and ISCST3, respectively.

f Annual average concentration not provided.

g Presented as ranges for comparison with Lonati and Zanoni 2013.

Theoretically, if the size of the domain is bigger, it should pave the way for more of a species to be removed by deposition processes - in this case especially Hg^0 , given its solubility and reactivity, and consequent atmospheric lifetime. In addition, the different considered emission rates coupled with meteorology, and the difference in deposition parameters, should provide for different modelled concentrations. Furthermore, this does not entail the modelling of Hg species through the utilization of an identical model. This is important, due to atmospheric dispersion models using different schemes and strategies in their respective computations. Modelled Hg^0 concentrations are somewhat lower than the results obtained by Garcia *et al.* (2017) and Heckel and LeMasters (2011). The concentrations modelled are, however, fairly higher compared to those modelled by Lonati *et al.* (2013).

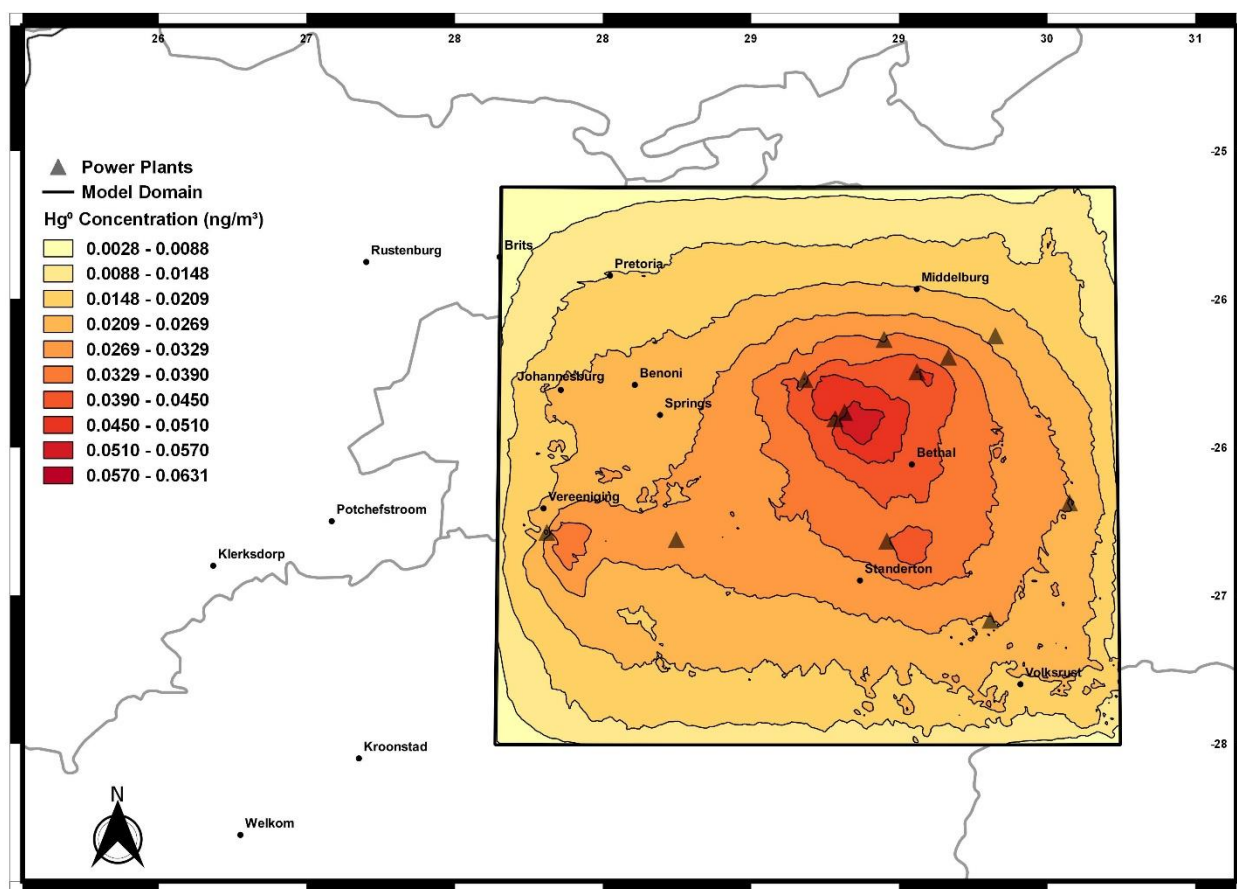


Figure 6-1: The spatial distribution of three year (2011-2013) modelled average Hg^0 concentrations (ng/m³) originating from power-generating plants on the South African Highveld.

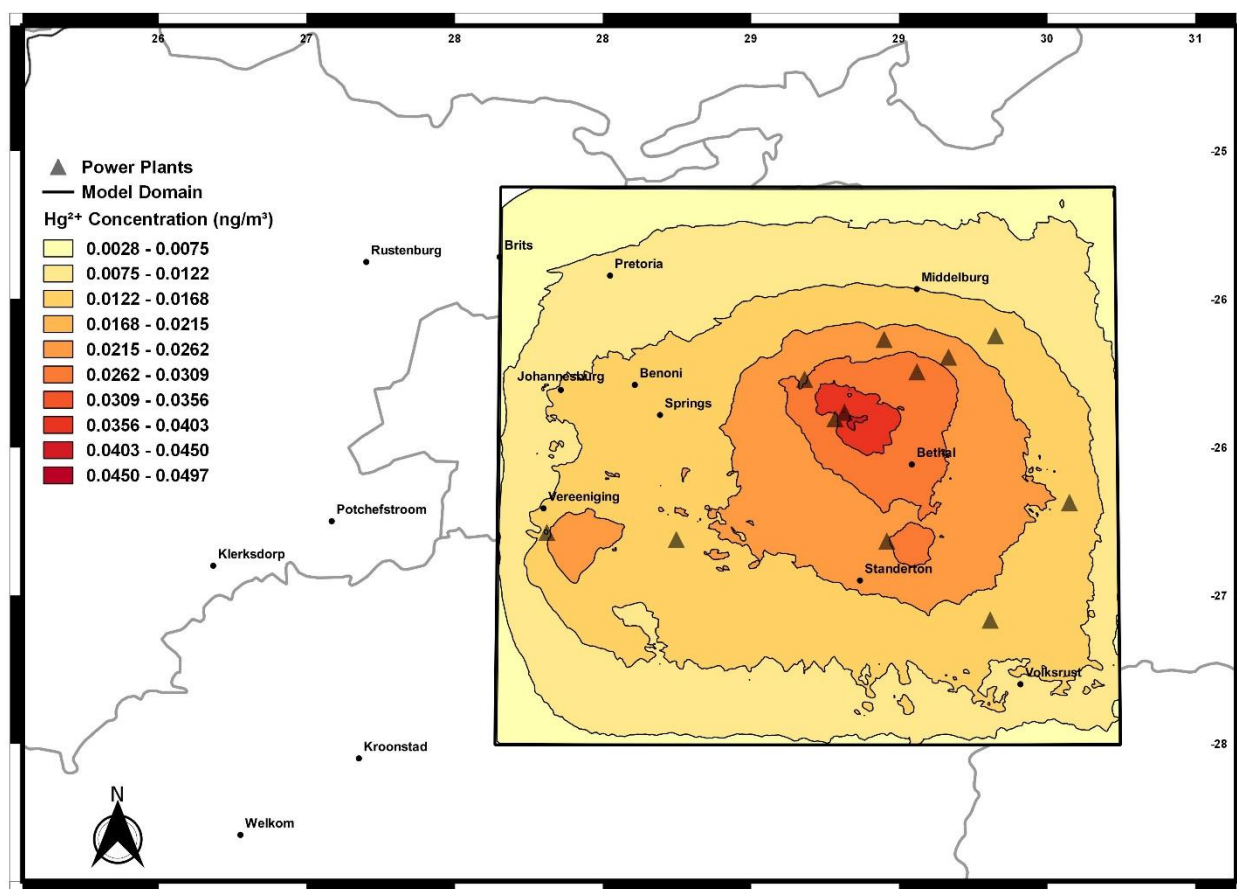


Figure 6-2: The spatial distribution of three year (2011-2013) modelled average Hg²⁺ concentrations (ng/m³) originating from power-generating plants on the South African Highveld.

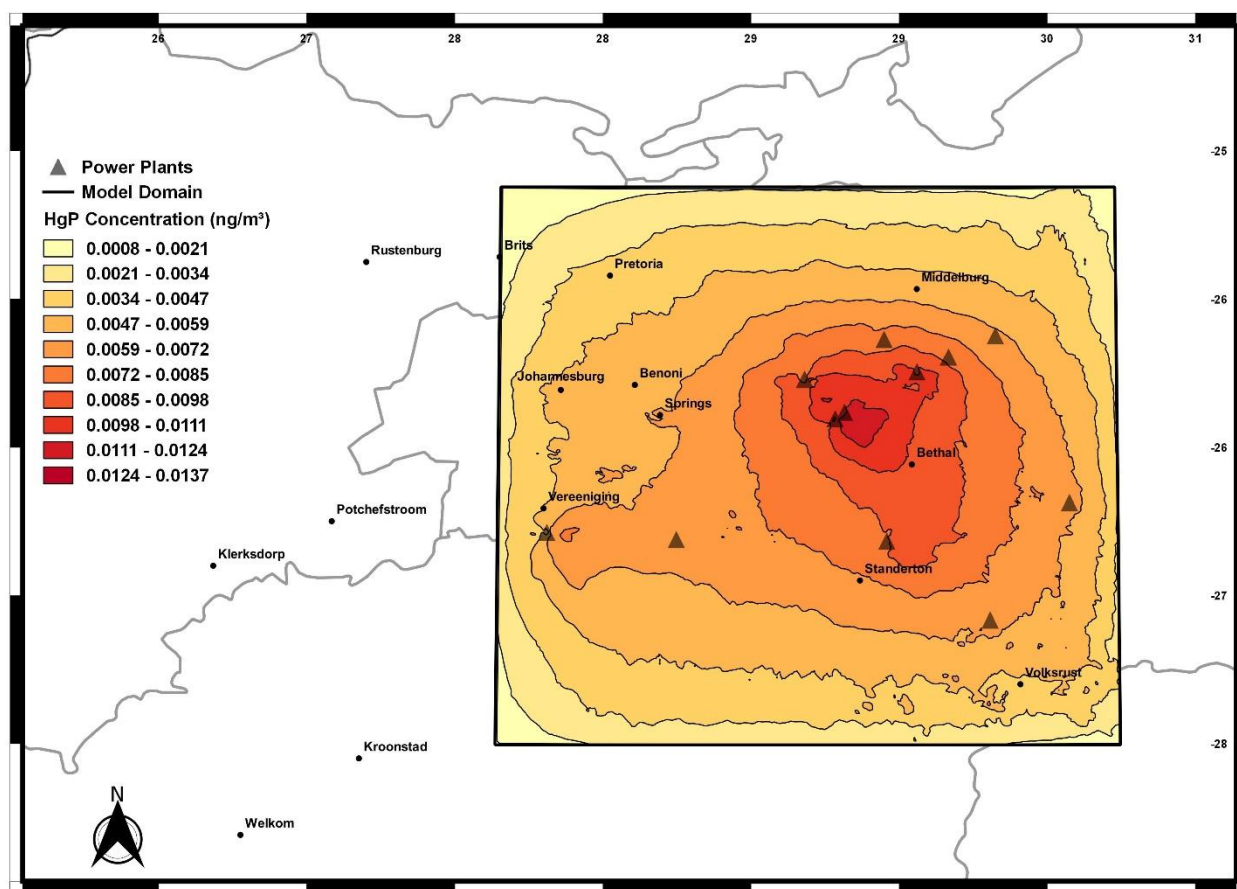


Figure 6-3: The spatial distribution of three year (2011-2013) modelled average HgP concentrations (ng/m³) originating from power-generating plants on the South African Highveld.

6.2 Wet and dry deposition

The modelled average wet deposition of Hg²⁺ and HgP during the modelling period are illustrated in Figures 6-4, 6-5 and 6-6. These figures represent the highest amounts of the species that could possibly be removed from the atmosphere during the period. The wet deposition of Hg⁰, due to reasons discussed in Chapter 3, section 3.3.3, is ignored.

The results reveal that relatively low amounts of each species were removed from most of the modelled region. Over four locations on the domain, however, higher amounts were removed. This is in the immediate vicinity (<1km) of the locations and is not identifiable on the figures. This

was simulated in the atmosphere above Kriel and Matla, Lethabo, Kendal, and Tutuka. This observation may be explained by the fact that species of Hg tend to be deposited near their emission source (Carpi 1997; Driscoll *et al.* 2007). The simulated wet deposition of Hg^{2+} and HgP at the specified receptors during the modelling period ranged 0.07–7.46 and 0.03–3.33 (g/ha)/yr, respectively.

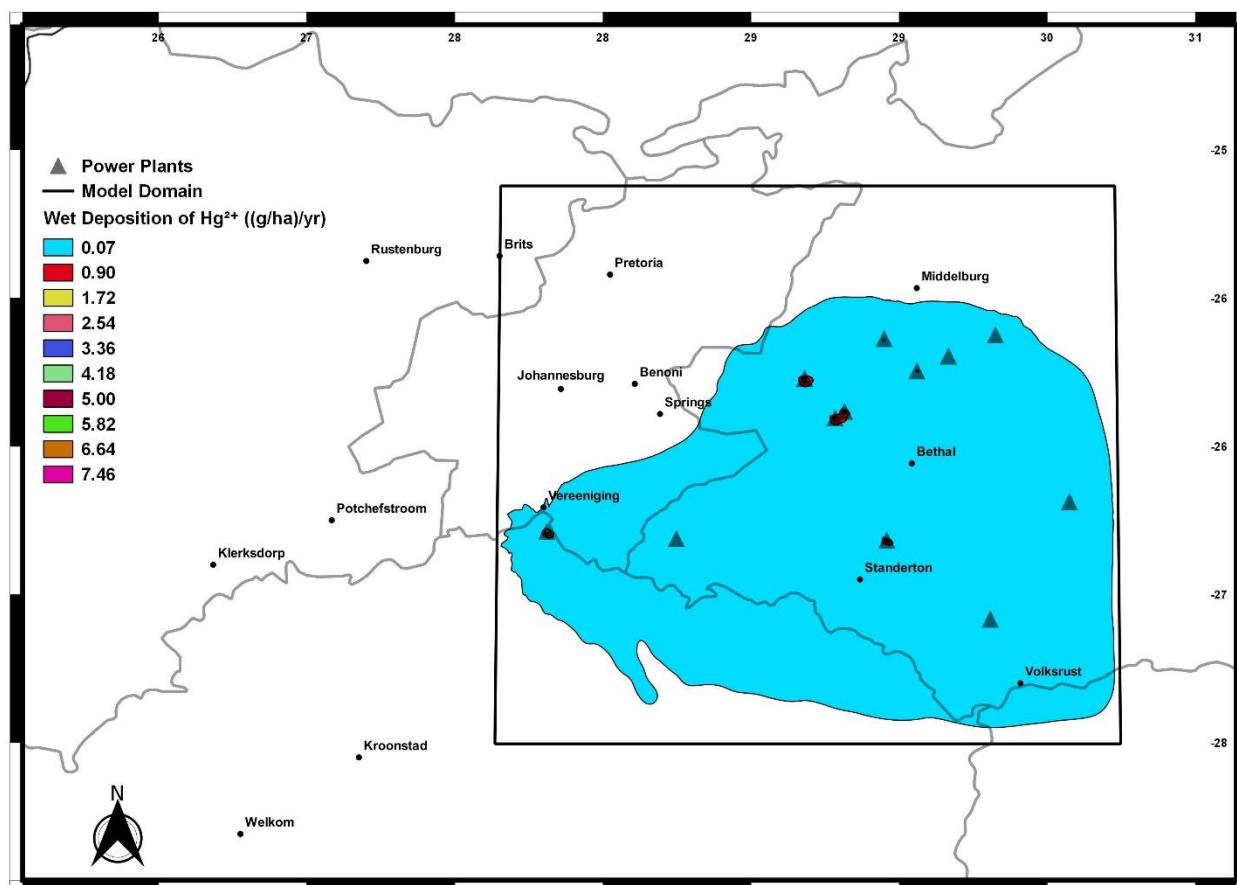


Figure 6-4: The spatial distribution of averaged three year (2011-2013) modelled wet deposition ((g/ha)/yr) of Hg^{2+} on the South African Highveld.

Critical for wet deposition to occur, of course, is precipitation. The average deposition rate during the modelling period over the domain was 1.0125×10^{-2} mm/hr. The average wet deposition over Kriel and Matla was simulated to be 5.18091×10^{-1} mm/hr. Compared to the amount of wet deposition measured for total Hg at rural and urban sites in China (0.02–0.07 and 0.12 (g/ha)/yr,

respectively) (Fu *et al.* 2016), the values in the current study are somewhat higher. Given the conservative basis of the current study, the modelled deposition of HgP is much higher than Hg²⁺. Fu *et al.* (2016) utilized direct measurements of precipitation which should provide for more refined estimates of deposition. Zysk *et al.* (2015) modelled very similar total wet deposition values (0.08–0.8 kg/ha/annum) to those measured by Fu *et al.* (2016) for Hg.

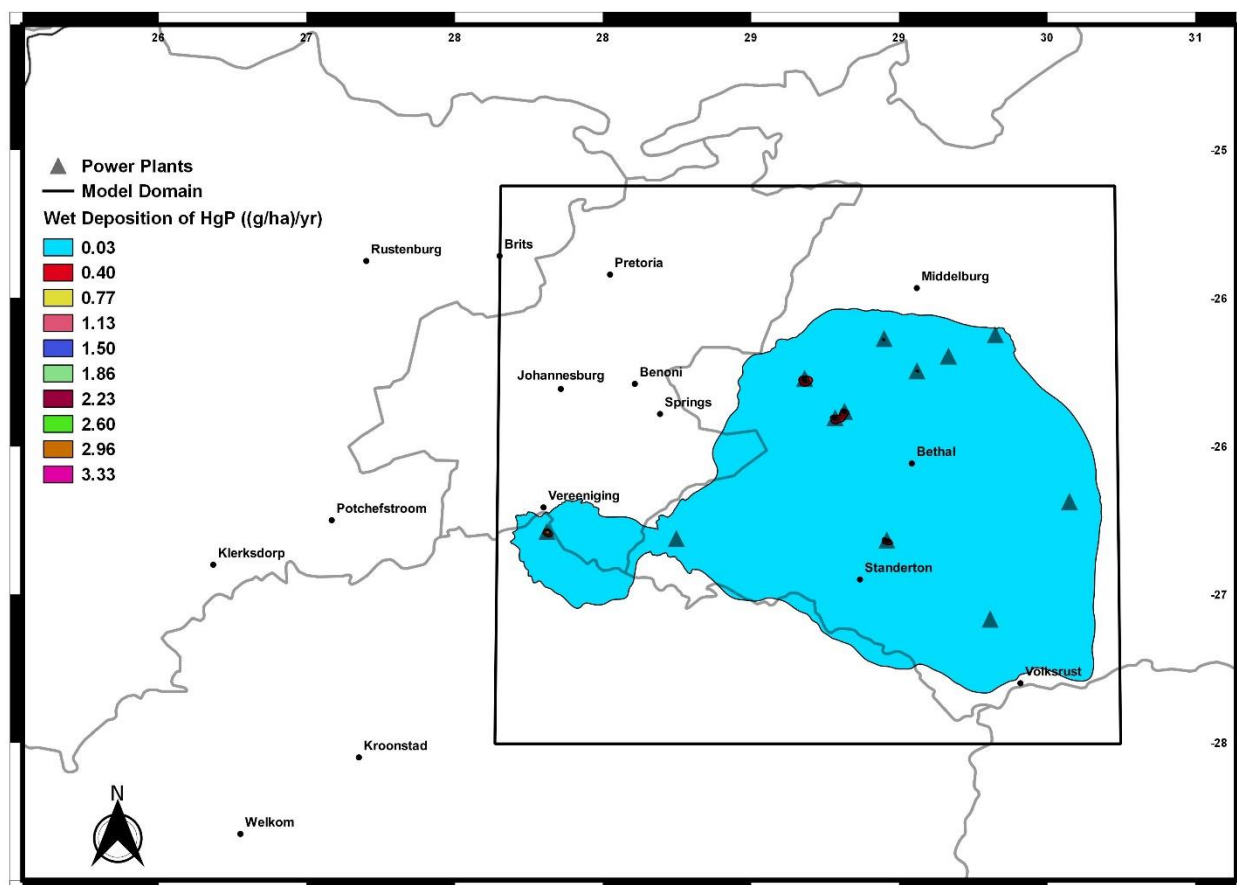


Figure 6-5: The spatial distribution of averaged three year (2011-2013) modelled wet deposition ((g/ha)/yr) of HgP on the South African Highveld.

The modelled averaged dry deposition of Hg⁰, Hg²⁺, and HgP during the modelling period are illustrated in Figures 6-8, 6-9, and 6-10. Importantly, the dry deposition of Hg⁰ should be viewed with caution, as its dry deposition parameters were assumed to be identical to those adopted for Hg²⁺ which provides conservative estimates of highest potential dry deposition of this species.

Dry deposition is another mechanism by which species of Hg may be transferred from the atmosphere to aquatic and terrestrial surfaces. This mechanism, of course, occurs in the absence of precipitation. The modelled dry deposition of the species closely resembles one another with the central parts of the domain being the region most affected, followed by the southwestern part. Dry deposition rates decrease from the centre of the domain to the outskirts.

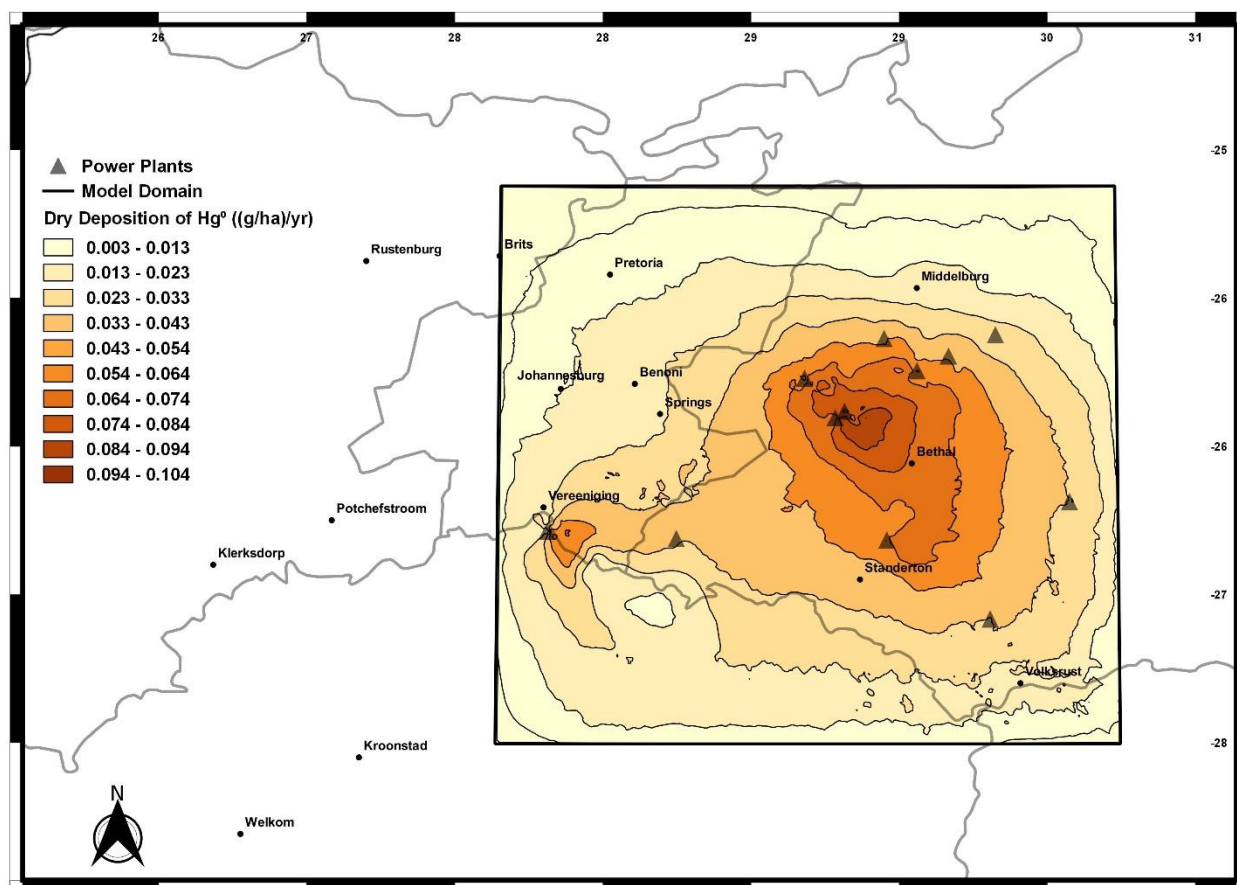


Figure 6-6: The spatial distribution of **three year (2011-2013)** modelled dry deposition ((g/ha)/yr) of Hg^0 on the South African Highveld.

The results reveal that extremely low amounts of each species were removed from most of the modelled region. The dry deposition of Hg^0 , Hg^{2+} , and HgP ranged 0.003–0.104, 0.002–0.081, and 0.00002–0.00052 (g/ha)/yr, respectively. The average modelled deposition of Hg^0 (1.4 (g/ha)/yr) is smaller than what was observed by Garcia *et al.* (2017) (4.4 (g/ha)/yr) (for a coal-fired

power plant in Mexico) and larger compared to the average reported by Zysk *et al.* (2015) (0.25 (g/ha)/yr) (modelled for the Polish power sector). The aforementioned study accounts for natural emissions and chemical transformation, which indicates that dry deposition of Hg^0 in this study is considerably overestimated. This may subsequently be derived for Hg^{2+} and HgP as well.

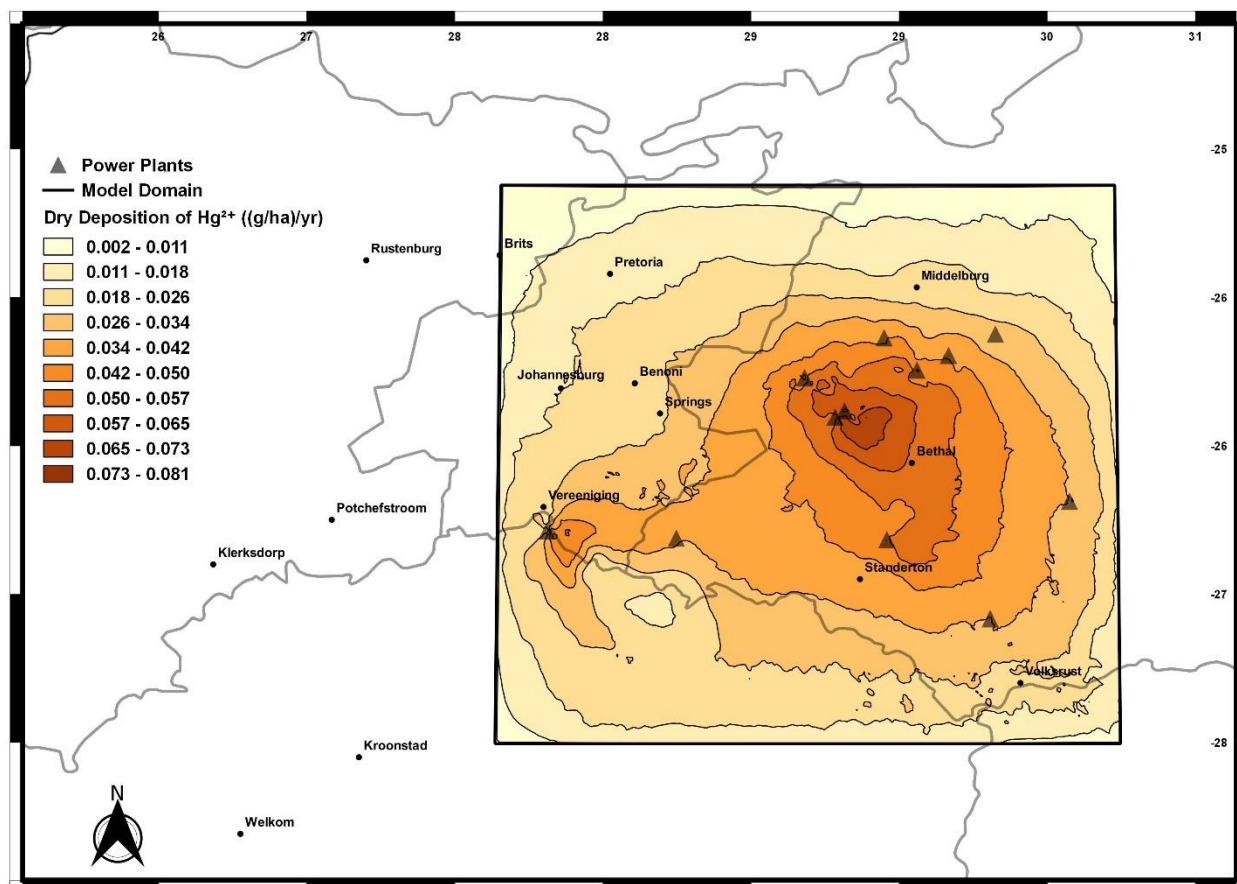


Figure 6-7: The averaged three year (2011-2013) modelled dry deposition ((g/ha)/yr) of Hg^{2+} on the South African Highveld.

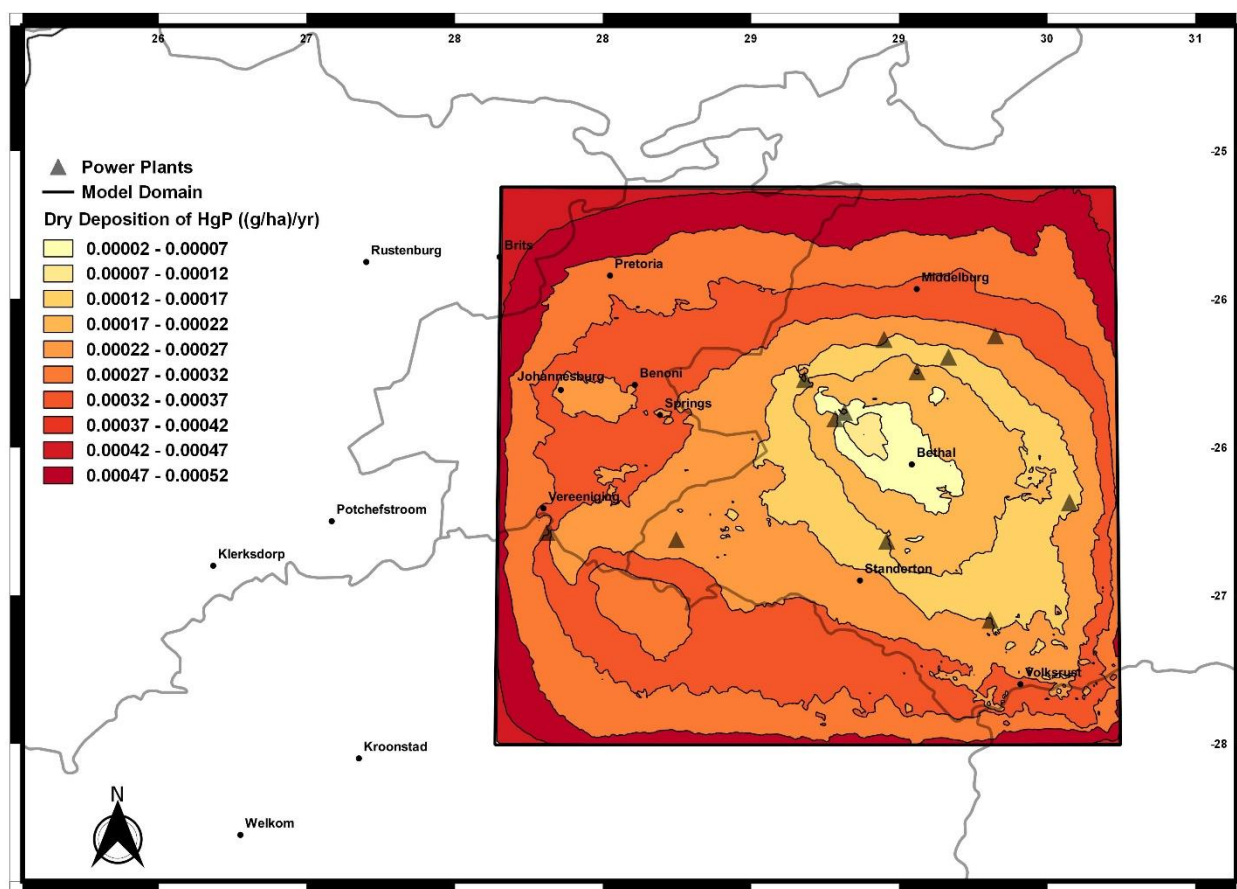


Figure 6-8: The averaged three year (2011-2013) modelled dry deposition ((g/ha)/yr) of HgP on the South African Highveld.

6.3 Assessment of potential health risk

The Hazard Quotient (HQ) has been calculated for the Highveld as an annual spatial average (baseline scenario) as well as maximum annual values (worst case scenario) within the study area. These values represent an HQ range which at its highest level gives a conservative estimate of the health risk to the population on the Highveld. The quantified acute and chronic HQ values for the baseline scenario shows a tolerable exposure level to concentrations of Hg^0 ($\text{HQ} < 1$ in all cases). The average exposure concentrations for this scenario are also lower than the recommended REL values.

In terms of the worst case scenario, however, acute (1 hour and 8 hours) quotients exceed one ($HQ > 1$). This suggests a potentially severe health effect. The maximum predicted exposure levels are also above the REL values for the corresponding exposure periods. The HQ value for the chronic exposure period is below one ($HQ < 1$) suggesting that the likely risk is negligible. Considering the uncertainty in the modelled concentrations of Hg^0 , these values may either be higher or lower. There is currently no South African national ambient standard for comparison.

Table 6-2: Assessment of potential health risk to emissions of Hg^0 from modelled power plants.

Exposure period	Average predicted exposure ($\mu g/m^3$)	Maximum predicted exposure ($\mu g/m^3$)	REL ($\mu g/m^3$)	RFC ($\mu g/m^3$) used for HQ quantification	Baseline HQ	Worst case HQ
Acute (1 hour)	0.002	2.001	0.6	0.3	0.007	6.67
Acute (8 hours)	0.001	0.791	0.06	0.3	0.003	2.637
Chronic	0.00003	0.02625	0.03	0.3	0.0001	0.0875

CHAPTER CONCLUSIONS

This chapter provides the first ever dispersion modelling study of Hg over the South African Highveld. The obtained results may serve as a baseline for prospective studies in broadening the knowledge regarding Hg over and in this region.

The following main conclusions can be made:

As expected, the concentrations of the Hg species are highest over the cluster of power plants that are situated in the centre of the domain. Moreover, the results convey that concentrations of the species are accumulating in an area of already high concentrations over Kriel and Matla. This part of the domain also yielded maximum wet and dry deposition. It is thus clear that the proximity of the power plants lead to higher deposition. The formation of methylmercury is, therefore likely to occur due to the possibility of these high modelled concentrations to be removed by deposition. The high wet deposition results for Hg^{2+} covers the same spatial area as the modelled concentration, which thus corroborates the aforementioned statement. This could expose the population dependent on fishing to supplement their nutritional needs. Although, conservative estimates, the results identify a potential need to assess the possible impact of toxic methylmercury on the South African Highveld. The health risk assessment suggests that the population working and living in proximity to power plants may be at risk to acute adverse health impacts due to inhalation. The prospective modelling of Hg over this region should be evaluated against ambient monitored concentrations to account for uncertainty and fractional bias. This may be further enhanced by concurrent direct measurements of precipitation to provide more refined deposition modelling.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Mercury is a highly toxic and ubiquitous volatile metal, which is environmentally persistent. Inorganic ambient Hg may be inhaled, while organic methylmercury may bio-accumulate and biomagnify in the food chain. The dominant source of Hg in South Africa is coal combustion in power plants. The majority of these power plants are situated on the South African Highveld, a region well-known for its anthropogenic activities. This represents one of the most concentrated source regions of Hg in the world, given the geographical distribution of the plants. The study of Hg over this region is important, as the species have implications ranging from local to global. Despite the importance of environmental Hg, it appears to be a rather inadequately studied pollutant in South Africa. This study, therefore, investigated Hg emission from the power plants, of which most are located on the South African Highveld. The first part of this investigation entailed the characterisation of ambient total gaseous mercury (TGM) concentrations over the Highveld. This was sequentially followed by Hg emission estimates resulting from power plants, and atmospheric dispersion modelling of the three atmospherically significant forms.

7.1 Ambient Hg concentrations over the South African Highveld

Characterisation took place on the basis of spatial, and diurnal and seasonal variation of TGM concentrations observed at Balfour (BF), Middelburg (MB), and Standerton (ST). Additional characterisation took place by establishing the relationships between TGM and criteria pollutant concentrations. The conclusions drawn from this study are as follow:

1. The annual average TGM concentration over the SAHA (1.4 ng/m^3) is lower than the accepted background range ($1.5\text{--}1.7 \text{ ng/m}^3$).
2. Unexpectedly, the highest TGM concentrations were observed at ST - arguably the least industrialised site. Despite the absence of data in autumn, and the lack thereof during summer, the pattern at ST appears to have been significantly influenced by local combustion sources; most probably domestic combustion. This is a potential cause for

concern as approximately 90% of Hg emitted from domestic coal combustion is Hg^0 and Hg^{2+} .

3. Seasonal variation in TGM concentrations at BF, MB, and ST were dissimilar with descending orders of:
 - a) Summer, spring, winter, autumn;
 - b) Summer, winter, autumn, spring; and
 - c) Winter, spring, summer at ST, respectively.
4. Diurnally, no profound patterns were observed at BF and MB where sparse local and regional sources appear to have been the predominant sources.
5. The relationship between TGM and CO at ST and their very similar diurnal patterns suggest coal combustion as the predominant source of TGM at this site.
6. Coal-fired power plants seem to have had no observable impact on the variation in TGM concentrations. This does not mean that it should be disregarded as the leading source of Hg. It should, in fact, highlight meteorology as a significant factor in controlling the spatial distribution of TGM concentrations.

7.2 Emission estimation of Hg resulting from power plants

This study estimated emissions of Hg from 13 power plants located on the South African Highveld during 2014 by using the bottom-up approach. The following inferences can be derived from the obtained results:

7. It is quite evident that the Hg content used to estimate emissions from power plants has a noteworthy influence on the results obtained.
8. Using power plant specific coal Hg contents should allow more refined Hg emission estimates, rather than assuming average contents from published literature.

9. This study shows that the effect of emission control devices on total Hg emitted to the environment cannot be denied.
10. Fabric filters are far more efficient in regulating emissions, and should henceforth be installed at all power plants to reduce emissions.
11. A clear relation was observed between amounts of Hg emitted by power plants in 2014, the control device installed, and the total amount of coal combusted.
12. Reducing the amount of consumed coal simply won't be enough, hence why plants fitted with and ESP should adopt the use of an FF.
13. Even though current plans to convert all power plants to FFs are aimed at reducing PM, this will also lead to a significant reduction in Hg emissions. However, the substantial cost involved in this conversion should be weighed against the expected benefit.

7.3 Modelling the spatial distribution of Hg on the South African Highveld

The dispersion of Hg^0 , Hg^{2+} , and HgP was modelled with the CALPUFF modelling system together with concurrent wet and dry deposition simulations. Dispersion modelling is important as it provides the link between the environment and emissions to the atmosphere. The wet deposition of Hg^{2+} may lead to the formation of toxic methylmercury. This form may bio-accumulate and biomagnify in the food chain and have adverse health impacts on humans. This study also involved a health risk assessment of Hg^0 as people may expose to it via the inhalation pathway.

14. As expected, the concentrations of the Hg species are highest where a cluster of power plants are situated in the centre of the domain.
15. More specifically, the concentrations of the species are accumulating in an area of already high concentrations over Kriel and Matla.
16. This part of the domain also yielded maximum wet and dry deposition.
17. It is thus clear that the proximity of power plants lead to higher deposition.

18. The formation of methylmercury is likely to occur at high concentrations in this region. The wet deposition results for Hg^{2+} corroborates this statement.
19. The population that may be dependent on fishing to supplement their nutritional needs may be exposed to this toxic form.
20. The health risk assessment suggests that the population working and living in proximity to power plants may be at risk to acute adverse health impacts due to inhalation.

7.4 Research constraints

Study 1 involved the analysis of TGM concentrations at 3 monitoring sites, due to the lack of data at others. Only one year's worth of data was available. It is somewhat difficult to ascribe the monitored emissions to a specific source. Study objective 2 did not consider the other power station owned by ESKOM: Medupi coal-fired power station situated near Lephalale in Limpopo province. This power station was commissioned in 2015, has a generating capacity of 4 764 MW, and is retrofitted with a fabric filter. This study also disregarded Kusile power station, located in close proximity to Kendal, as it's currently still under construction. Furthermore, this study focused on estimating emissions for the South African Highveld and Limpopo regions, and not South Africa as a whole. Based on the conservative assumptions, one would expect over- and/or underestimation for the modelling study. This is true for both the modelled concentrations and wet and dry deposition.

7.5 Research needs

Additional studies at locations in immediate proximity to those of large point sources (especially coal-fired power plants) are needed to shed light on the observed influence of domestic coal combustion. The atmospheric transport, transformation, and deposition of TGM in this region should be studied in detail, as they directly affect the atmospheric lifetime of ambient Hg. Source-apportionment may be used to establish source contribution from especially coal combustion in power plants. Source contribution from illegal artisanal gold mining should be quantified, as Hg is used for extraction. Inadequate to no data and knowledge exists for Hg contribution from this source. The full impact of Hg emissions on ecosystems and human health in southern Africa should, therefore, be quantified. Although based on conservative estimates, the modelling results

identify a potential need to assess the possible impact of toxic methylmercury on the South African Highveld. The prospective modelling of Hg over this region should be evaluated against ambient monitored concentrations to account for uncertainty and fractional bias. This may be further enhanced by concurrent direct measurements of precipitation to provide more refined deposition modelling

7.6 Unique contributions to the broader area of knowledge

In study objective 1, TGM concentrations over the South African Highveld region were characterised for the first time. This study builds on previous emission estimates by uniquely emphasising the importance of adopting Hg coal-content values from the literature versus actually obtaining measured content from the source. Study objective 3 provides a first time ever atmospheric dispersion modelling study of Hg over the South African Highveld by use of CALPUFF.

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