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Occurance and levels of total mercury in selected landfill sites inn Gauteng and Limpopo Provinces, South Africa.

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OCCURRENCE AND LEVELS OF TOTAL MERCURY IN SELECTED LANDFILL SITES IN GAUTENG AND LIMPOPO PROVINCES, SOUTH AFRICA

by

VHODAHO NEVONDO

Submitted in partial fulfilment of the requirements for the degree

MAGISTER TECHNOLOGIAE: ENVIRONMENTAL MANAGEMENT

in the

Department of Environmental, Water and Earth Sciences

FACULTY OF SCIENCE

TSHWANE UNIVERSITY OF TECHNOLOGY

Supervisor: Prof OJ Okonkwo

Co-supervisor: Dr AP Daso

September 2018

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V Nevondo

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DEDICATION

This study is dedicated to God who through His grace made it possible for me to complete my project despite all the hardships and obstacles that were encountered. To God, who gave me the grace to persevere and for financial providence throughout my studies. To my mom, Nevondo Ntshumeleni Lucy, for her love and prayers, and for accompanying me to the study area. To Dr Kyei, for being a father figure to me, for his prayers and emotional support, and for believing in me and for always seeing the best in me.

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ABSTRACT

Mercury has been used for many centuries in the production of consumer products such as thermometers, electrical switches, fluorescent light bulbs, batteries, biocides and pesticides, cosmetics, and dental amalgam fillings, among others. After use, these mercury-containing consumer products form part of municipal solid waste (MSW). As a result of un-separated solid waste collection system, mercury-containing wastes tend to end up in landfills where mercury and other pollutants can leach out of products into landfill leachates. Therefore, the aim of the present study was to determine the total mercury (THg) concentrations in leachate and sediment samples collected from four selected landfill sites (three in Gauteng Province - Soshanguve, Hatherley, Onderstepoort, and one in Limpopo Province - Thohoyandou). Groundwater samples were collected from the monitoring boreholes at the four selected landfill sites during summer and winter periods.

The acid digestion method was employed for sample preparation and this was followed by analysis using cold vapour atomic absorption spectrophotometry (CVAAS). The concentration of total mercury in Thohoyandou leachate, sediment and groundwater samples ranged from 0.12±0.002 - 2.07±0.28 µg/L, 0.03±0.001 - 0.48±0.002 µg/g and 0.09±0.001 - 2.12±0.28 µg/L, respectively, and in Soshanguve the concentration ranged from 0.10±0.01 - 1.20±0.27 µg/L, 0.04 ±0.01 to 0.62±0.61 µg/g and ND to 1.66±1.18 µg/L, in Hatherley from 0.42±0.01 - 1.31±0.51 µg/L and 0.06±0.02 - 0.78±0.53 µg/g for leachate and sediment, respectively (groundwater samples were not accessible at Hatherley site), and in Onderstepoort from 0.12±0.01 - 2.41±0.35 µg/L, 0.03±0.001 - 0.50±0.18 µg/g, and 0.05±0.001 to 2.44±0.47, respectively. The mean concentration ranges of total mercury in

leachate, sediment and groundwater samples in winter were 1.20±0.27 to 2.41±0.35 µg/L, 0.48±0.002 - 0.78±0.53 µg/g and 1.66±0.18 - 2.44±0.47 µg/L, respectively, and in summer the concentration ranges were 0.10± 0.01 - 0.42±0.001 µg/L, 0.03±0.001 - 0.06±0.02 µg/g and ND to 0.09±0.001 µg/L, respectively.

The determination of cations and anions was conducted along with the determination of total mercury. Moderate positive and strong positive correlations were observed between mercury and selected cations in leachate, sediment and groundwater samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites during summer and winter. From the established relationship between mercury and cations, it was suggested that cations are likely to influence the behaviour of mercury and its mobilisation from leachate and sediment into groundwater. Furthermore, anions were also found to form strong complexes with mercury in leachate and sediment and thereby facilitating its mobility into groundwater.

The findings of this study suggest that there is a strong likelihood of groundwater contamination by mercury from landfill leachate seepage, particularly for landfills that are not lined with geomembrane material.

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GLOSSARY

AAS	atomic absorption spectrometry
FAAS	flame atomic absorption spectrometry
CVAAS	cold vapour atomic absorption spectroscopy
MUV	mercury vapour unit
IC	ion chromatograph
MCL	maximum contaminant level
CH_3Hg	methyl mercury
CH_3Hg^+	methyl mercury
HgS	mercuric sulphide
LOD	limit of detection
Hg^0	elemental mercury
USEPA	United States Environmental Protection Agency
EPA	Environmental Protection Agency
WHO	World Health Organization
UNEP	United Nations Environment Programme

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND ON MERCURY

Mercury is a silvery-white metallic element and when compared with other metals, it is a poor conductor of heat but a fair conductor of electricity (Senese, 2007). Mercury can also dissolve many other metals including gold and silver to form amalgams (Soratur, 2002). Because of its unique characteristics, mercury has been used for many centuries in the production of consumer products such as thermometers, electrical switches, fluorescent light bulbs, batteries, biocides and pesticides, paints, pharmaceuticals, cosmetics, dental amalgam fillings, and others (Pacyna *et al.,* 2003).

There are mainly three different forms of mercury, namely, elemental mercury (Hg^0), organic mercury and inorganic mercury (Drasch *et al.,* 2004). Elemental mercury is liquid at room temperature which makes it less toxic than inorganic or organic bound mercury. If it is heated, elemental mercury may evaporate and become highly toxic. Inorganic mercury occurs in the form of salts such as mercury(II) chloride (Langford & Ferner, 1999). The inorganic ions of mercury differ according to their solubility in water (Drasch *et al.,* 2004). Organic mercury is the most toxic form of mercury and it includes methyl mercury, ethyl mercury, and phenyl mercury. Mercury is emitted into the environment from both natural and anthropogenic sources. Volcanic eruptions, soil erosion and the release of mercury from rock weathering are the natural sources of mercury (Pirrone *et al.,* 2010). The major anthropogenic

sources of mercury include coal combustion (Feng *et al.*, 2002), waste incineration (Mukherjee *et al.*, 2004) metal mining (gold and silver), refining and manufacturing of mercury containing consumer products (Feng *et al.*, 2004; Streets *et al.*, 2005; Wu *et al.*, 2006) and chlorine production (Southworth *et al.*, 2004). Mercury is rare in the Earth's crust, and it has an average crustal abundance by mass of only 0.08 mg/L (Ehrlich & Newman, 2008). However, because mercury does not blend geochemically with those elements that form the majority of the crustal mass, its ores can be extraordinarily concentrated depending on the element's abundance in ordinary rock (Ehrlich & Newman, 2008).

Mercury is a neurotoxin in all its forms. The first health effects of mercury on humans were documented in the early 1950s and 1960s following a well-known incident of mercury poisoning which took place in Minamata, Japan where mercury-contaminated fish were consumed by the local population (Harada, 1995). Following this incident, the Minamata Convection on Mercury was authorised by the United Nations through the United Nations Environment Programme (UNEP). Routes of exposure to mercury for the general population are through inhalation of mercury vapours, ingestion of drinking water and food stuffs contaminated with mercury and through dental amalgams and medicinal treatments (NIOSH, 1973). Acute exposure to elemental mercury (Hg^0) vapours causes respiratory distress whereas chronic exposure affects the central nervous system (CNS) resulting in tremors, delusions, memory loss and neurocognitive disorder (Clarkson & Magos, 2006). Exposure to inorganic mercury causes corrosive effects in the intestine and causes kidney failure (Pollard & Hultman, 1997). Furthermore, methyl mercury, an organometallic cation (CH_3Hg^+), is the most toxic form of mercury and exposure to it causes neurological problems such as blurred vision, hearing impairment, and clumsiness of the hands, somatosensory and psychiatric

disorders. In the foetus, exposure to methyl mercury damages mental development and motor development (Ekino *et al.,* 2007; Eto, 2000).

The disposal of municipal solid waste (MSW) contributes to an important and emerging environmental pollution problem because landfills are globally considered to be the most cost-effective method for solid waste disposal (Williams, 2005). Over two-thirds of municipal solid waste is made up of household waste and internationally about 70% of municipal solid waste is disposed of in landfills (OECD, 2001; Zacarias-Farah & Geyer-Alley, 2003). Unscientific methods of collection, transportation and disposal of municipal solid waste are mostly used in developing countries (Gupta *et al.,* 1998). As a result of the non-separated MSW collection system, mercury-bearing solid wastes such as fluorescent lights, batteries, and thermometers are collected and disposed of in landfills. Landfill leachate is generated when rainwater percolates through waste layers (Kjeldsen *et al.,* 2002) and mercury is also leached from the waste layers and forms part of the leachate which is characterised by dissolved organic matter, inorganic macro-components, metals and xenobiotic organic compounds (Christensen *et al.,* 1994 & Christensen *et al.,* 2001). Under anaerobic conditions in the landfill sites, a significant fraction of Hg is transformed into other toxic species such as methyl mercury, ethyl mercury and phenyl mercury through the activity of sulphate- and iron-reducing bacteria (Acha *et al.,* 2012). Landfills are identified as one of the major threats to groundwater quality throughout the world (Fatta *et al.,* 1999). The leachate that contains organic and inorganic compounds normally accumulates at the bottom of the landfill and percolates through the soil down to the groundwater (Mor *et al.,* 2006), particularly for landfill sites that are not lined with geomembrane materials. Advection and diffusion are transport processes responsible for contaminant mixing and movement of leachate into groundwater (De Soto *et al.,* 2012; Regadio *et al.,* 2012). Bakare *et al.,* (2000)

reported that a small amount of leachate has the ability to pollute a large volume of groundwater. This may result in environmental risks as well as health risks to people using groundwater. In terms of the South African (SA), Netherlands (NL), European Union (EU), World Health Organization (WHO) United Kingdom (UK) and the United States Environmental Protection Agency (USEPA) national drinking water standards, the guideline values for mercury are 1.00 µg/L, 1.00 µg/L, 1.00 µg/L, 1 µg/L, and 2.00 µg/L, respectively (Christensen *et al.,* 2001).

Therefore, the presence of mercury in the environment is not desirable because of its adverse health effects.

1.2 PROBLEM STATEMENT

The majority of studies and reviews done on mercury in the environment have been focusing on atmospheric inputs and the fate of mercury, as well as its transport in soils, sediments and surface water (Engstrom *et al.,* 2007; Bradley *et al.,* 2011). Many of these studies have placed emphasis on the production, mobility and bioaccumulation of methyl mercury. However, fewer studies have so far been undertaken and published on mercury in landfill leachates and sediment, and groundwater, particularly in South Africa. The present study, therefore, focuses on the determination of the occurrence and levels of mercury in landfill leachate, sediment and groundwater samples from two South African provinces, Gauteng and Limpopo.

Mercury (Hg) is an element which is considered to be a global toxic pollutant because it persists and bio-accumulates in the environment (USEPA, 1997; Pacyna *et al*., 2006). Mercury levels in different environmental media in South Africa have been studied by other researchers (Malehase *et al*., 2016; Williams *et al*., 2011; Oosthuizen *et al*., 2010). However, there is limited information on contamination of groundwater with mercury from landfill leachate in South Africa. Furthermore, South Africa is a water-scarce country (Blignaut & Van Heerden, 2009), and as a result many people rely on borehole water for their livelihood. For those boreholes which may be located near municipal landfills, there is a high possibility of groundwater contamination, particularly where the landfill site is not lined with geomembrane material.

1.3 HYPOTHESIS

- ➢ Landfill leachates and sediments in Gauteng and Limpopo are most likely to be contaminated with mercury as a result of the disposal of waste that may contain mercury.
- ➢ Groundwater (boreholes) close to landfill sites are likely to be contaminated with mercury where the landfill site is not lined with geomembrane material.

1.4 OBJECTIVES OF THE STUDY

1.4.1 General objectives

The general objective of the present study is to determine the occurrence and levels of mercury in selected landfill sites, sediments and groundwater in Gauteng Province (highly

industrialised) and Limpopo Province (low level of industrialisation) in order to assess the exposure of people living close to landfill sites and the surrounding areas.

1.4.2 Specific objectives

- ➢ To determine the occurrence and levels of mercury in selected landfill leachate, and in sediments and in groundwater samples;
- ➢ To compare the levels of mercury in selected landfill site leachates, sediments and groundwater in Gauteng Province and Limpopo Province, South Africa;
- ➢ Observe seasonal trends of mercury levels.

CHAPTER 2

LITERATURE REVIEW

2.1 PREAMBLE

This chapter provides the literature review on mercury with the aim of providing the background for a detailed discussion under the following sub-headings: physical properties of mercury, forms of mercury, sources of mercury, routes of exposure and health effects, landfill, groundwater contamination, concentrations of total mercury (THg) in landfill media, chemical parameters that may influence the behaviour of mercury, analytical methods and techniques used for the determination of mercury, and the national drinking water regulations or standards for mercury.

2.2 PHYSICAL PROPERTIES OF MERCURY

Mercury is a metal element with chemical symbol Hg, atomic number 80 and atomic weight of 200.59. It has a melting point of -38.87 °C, a boiling point of 356.58 °C and a density of 13.546 g/mL at 20 °C (ATSDR, 1999). When mercury is compared with other metals, it is a poor conductor of heat and a fair conductor of electricity (Senese, 2007). Mercury is also known as quicksilver and it can dissolve many other metals including gold and silver to form amalgams (Soratur, 2002). Mercury has been used for many centuries in the production of consumer products such as thermometers, electrical switches, fluorescent light bulbs, batteries, biocides and pesticides, paints, pharmaceuticals, cosmetics, dental amalgam filling and others (Pacyna *et al.*, 2003). Mercury pollution has become a worldwide problem given

the effects of its toxicity on humans, persistence and ability to bio-accumulate in the environment (Pacyna *et al.,* 2006; Feng & Qiu, 2008; Zhang *et al.,* 2008). This study, therefore, is undertaken because of the concern over the health effects of mercury exposure, with particular emphasis on mercury wastes in landfills.

2.3 DIFFERENT FORMS OF MERCURY

According to Drasch *et al.* (2004) and Bjørklund *et al.* (2017), there are mainly three different forms of mercury, namely elemental (metallic) mercury, organic mercury and inorganic mercury.

2.3.1 Elemental mercury

Elemental (metallic) mercury is a silver-white shiny metal, liquid at room temperature and pressure with zero oxidation state (Hg^0). Many consumer products including thermostats, thermometers and dental amalgams have been produced using elemental mercury (Patrick, 2002). Elemental mercury plays an important role in the global cycling of mercury and in comparison with other forms of mercury, it is less toxic than inorganic and organic mercury compounds. If elemental mercury is heated, it evaporates and becomes highly toxic (WHO, 2003). Elemental mercury is the most volatile form of mercury with a vapour pressure of 0.3 Pa at 25 °C and it evaporates to form colourless and odourless vapours (WHO, 2003). At higher temperatures, more mercury vapours are released into the atmosphere (UNEP, 2002).

2.3.2 Inorganic mercury

When elemental mercury combines with elements such as chlorine, sulphur and oxygen, it forms inorganic mercury. Inorganic mercury compounds exist in two oxidative states (mercurous, Hg^{+} and mercuric, Hg^{++}) and occur in the form of salts such as mercuric chloride, mercurous chloride and mercuric sulphide (Langford & Ferner, 1999). Inorganic mercury normally occurs in the environment in diverse colours such as white oxides, and brown and black oxides of the sulphide compounds (Langford & Ferner, 1999). This form of mercury is mainly found in contaminated soils as either monovalent (Hg^{+}) or divalent (Hg^{2+}) mercury salts (Park & Zheng, 2012). Inorganic mercury salts are mostly used in industries; they have been used for antibacterial and antiseptic purposes and in the production of consumer products including teething powders, skin-lightening creams, laxatives and diuretics (Tchounwou *et al.,* 2003; Ozuah, 2000). Once inorganic mercury is in water it can be transformed by microorganisms to form organic mercury (methyl mercury).

2.3. 3 Organic mercury

Organic mercury is the most toxic and most frequently found form of mercury in the environment. The main forms of organic mercury include methyl mercury, phenyl mercury and ethyl mercury (Crowe *et al.,* 2017). Once naturally occurring mercury is deposited in the environmental media (water, soil, sediment and biota) through natural and human activities, some bacterial species are capable of transforming and converting elemental mercury into the organic form (Tan & Perkin, 2000; Goldman & Shannon, 2001). The organic forms of mercury have been primarily used as biocides and pesticides and they are also found in household antiseptics, Mercurochrome and Merthiolate (Mathieson *et al.,* 1992; Elferink,

1999). Organic mercury can bio-accumulate and bio-magnify in food chains, more especially in aquatic environments in fish species.

2.4 SOURCES OF MERCURY

Mercury occurs naturally in the environment and can cycle across the atmosphere, terrestrial and aquatic ecosystem. It is ubiquitous in the biophysical environment (Donovan *et al.,* 2016; Hui *et al.,* 2016; Wang *et al.,* 2016). Mercury in the atmosphere comes from both anthropogenic and natural sources (Pirrone *et al.,* 2010; Streets *et al.,* 2011). Processes such as erosion and volcanic eruptions and human activities are responsible for mercury contamination of the environment due to mercury emissions which end up in the atmosphere and in water. According to the USEPA (1997), there are mainly three major sources of environmental mercury emissions, which are natural, anthropogenic and re-emitted sources.

2.4.1 Natural sources of mercury

Mercury occurs naturally in the environment as a mineral called cinnabar (HgS) with concentrations of approximately 80 µg/kg in the Earth's crust and 0.3 ng/L in seawater (Ferguson, 1990; Jonasson, 1970; Gworek *et al.,* 2016). Mercury is also present in minerals such as livingstonite and carderoite. It is considered to be one of the elements with low concentrations in crustal rocks ranging from 0.01-2 mg/kg (Fleischer, 1970). Elemental mercury vapour is the main form in which mercury from natural sources is released into the atmosphere (Schroeder & Munthe, 1998). A number of natural processes are responsible for the release of mercury into the environment, including volcanic and geothermal activities

(Ferrara *et al.,* 2000; Loppi, 2001; Nriagu *et al.,* 2003), emission from surface soils (Gustin, 2003; Gustin *et al.,* 2003; Feng *et al.,* 2005), water bodies (Lindberg & Zhang, 2000; Monson *et al*., 2001; Zhang & Lindberg, 2001) and wild fires (Brunke *et al.,* 2001; Friedli *et al.,* 2003; Sigler *et al.,* 2003). Mason *et al.* (1994) reported that the amount of mercury emitted into the atmosphere from natural sources globally was 2 000 t annually.

2.4.2 Anthropogenic sources of mercury

Human activities are responsible for much of the mercury that is released into the environment. The major anthropogenic sources of mercury in the industrialised world include coal combustion (Carpi, 1997; Wang *et al.,* 2000; Feng *et al.,* 2002; Hassett *et al.,* 2004), waste incineration (Alvim-Ferraz & Afonso, 2003; Mukherjee *et al.,* 2004) metal mining, refining and manufacturing of consumer products (Feng *et al.,* 2004; Streets *et al.,* 2005; Wu *et al.,* 2006) and chlorine production (Qi *et al.,* 2000; Landis *et al.,* 2004; Southworth *et al.,* 2004). The metal smelting industry (mainly zinc, lead and copper) emits mercury vapour into the environment when metal is smelted from sulphide ore. Globally, China produces the largest amount of zinc with an estimate of 1.95 million tons in 2000 which makes zinc smelting the most important anthropogenic source of mercury emission in China (Liu & Ou, 2003). Mercury is also released into the environment from coal combustion. According to Jensen *et al.* (2004) coal-burning power plants release a large amount of mercury into the air and are responsible for about one-third of anthropogenic emissions of mercury. China is the largest producer of coal in the world producing about 1.25 billion tons of coal (NBSC, 2002).

Mercury-bearing consumer products such as batteries, lamps, and electric switches are mostly dumped of in landfills as part of the general waste disposal practice which makes landfills an

important source of mercury emission. About 95% of South Africa wastes are disposed of in landfills (DWAF, 1998) and spent consumer products such as fluorescent light bulbs and compact fluorescent lamps are not separated from general waste that is disposed of in a landfill. In 2004, the Department of Trade and Industry (DTI, 2004) reported that a total of 1 829 066 fluorescent light tubes were imported into South Africa with an estimation of 0.46 kg of mercury being released from this source. However, the production of batteries in China is the highest in the world which results in a high portion of used batteries forming part of waste which is the source of mercury occurrence in landfills.

Furthermore, South Africa has been estimated to be second to China in terms of mercury emission to the environment (Pacyna *et al.,* 2006). About 90% of South Africa's electricity is generated from coal-fired power plants which are the biggest source of mercury in the country because these power plants consume 112 Mt of coal annually and release 9.8 t of mercury (Oosthuizen *et al.,* 2009). Other sources of mercury include dental fillings that contain 50% of mercury, fish that are contaminated with mercury and breakage of mercury-containing devices such thermometers and fluorescent lights (ATSDR, 2006). The use of mercury in some industrial processes also contributes to mercury pollution of the environment. According to Pacyna *et al.* (2003) the chlor-alkali process, vinyl-chloride-monomer and acetaldehyde emit mercury into the environment.

2.5 MERCURY CYCLE IN THE ENVIRONMENT

Mercury contamination in different environmental media (i.e. in soil, water, air and wildlife) makes an important contribution to the environmental pollution problem given its persistence

in the environment, toxicity, high volatility, bioaccumulation, bio magnification and long-range transport on a global scale (Walters *et al.*, 2016; Zhang *et al.*, 2015). All chemical forms of mercury circulate between air, water, soil and biota through its release from both human activities such as mining and fossil fuel burning and natural activities such as volcanic eruptions (Mason & Sheu, 2002; Pacyna *et al.*, 2006; Fitzgerald & Lamborg, 2005) (Figure 2.1.). The atmosphere is the main transport pathway for mercury emissions; meanwhile land and ocean processes help in the redistribution of mercury in terrestrial and aquatic systems (Driscoll *et al.*, 2013). Mercury is emitted into the atmosphere mainly in its elemental form (Hg^0) where it interacts with different small particles such as dust, soot and sea salt aerosol through sorption and desorption. According to Lin & Pehkonen (1999), mercury has a global mean concentration of about 1.6 ng/m^3 in the surface air. Mercury travels long distances through water and air masses in the environment where some chemical reactions are capable of converting it into methyl mercury which bio-accumulates and bio-magnifies through the food chains to levels that are harmful to human health (Sundseth *et al.*, 2017).

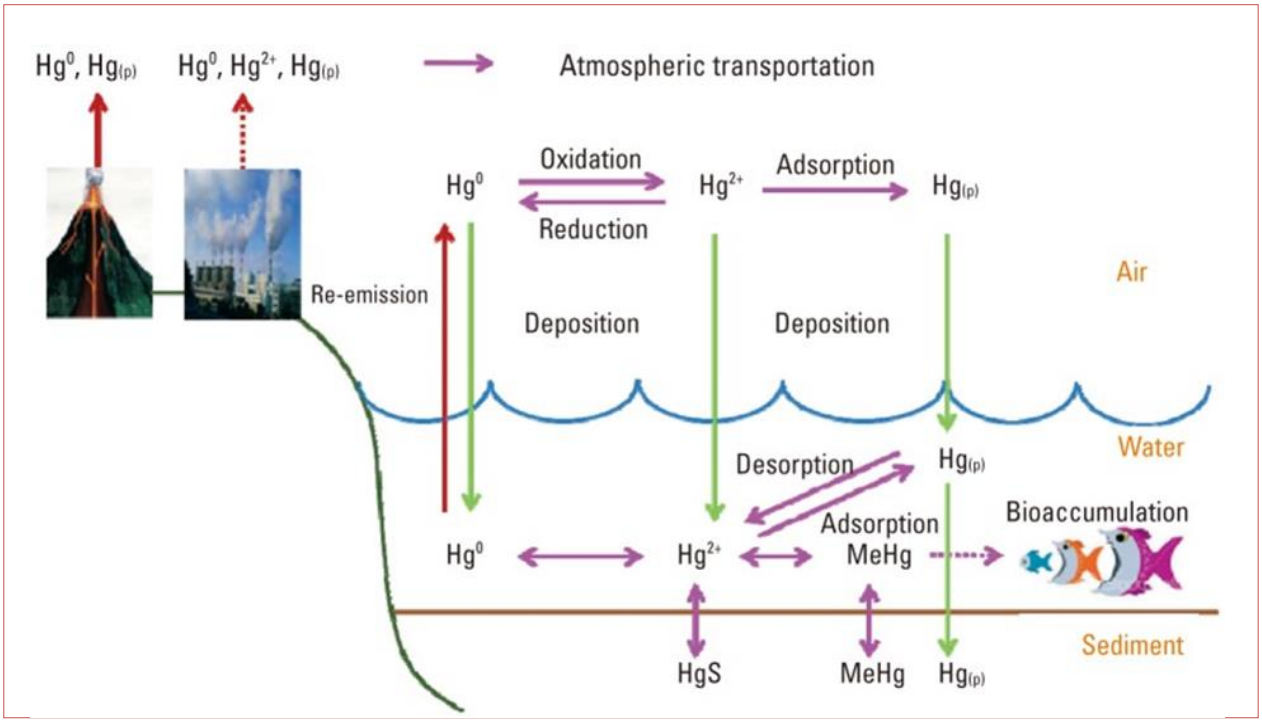

Figure 2.1: The biogeochemical cycle of mercury

Mercury can also be thoroughly mixed and transported over long distances (i.e. locally, regionally and globally) in the troposphere (Schroeder & Munthe 1998; Schuster *et al.*, 2002). Seigneur *et al.* (2004) reported that an estimated 21% of total mercury from wet deposition in the United States originated from China and previous studies have reported high concentrations of methyl mercury in fish in non-industrialised areas including the Arctic (Wagemann *et al.*, 1996; Evers *et al.*, 1998).

Mercury occurs in three valence states in the environment, namely elemental (Hg^0), monovalent (Hg^+) and divalent (Hg^{2+}). Divalent mercury is more stable than monovalent mercury in the environment (Cheng *et al.*, 2011). The oxidised elemental mercury can remain in the atmosphere for a long period of time (0.5 – 2 years) before it undergoes wet or dry

deposition and, in general, it accounts for 95% of atmospheric mercury (Nriagu, 1989; Luo, 2004). Mercury enters the aquatic environment through different processes such as wet and dry deposition were it can be sorbed or desorbed into suspended particulate matter (SPM) or it can interact with dissolved organic matter (DOM).

2.6 EXPOSURE PATHWAYS AND HEALTH EFFECTS OF MERCURY

Mercury is a neurotoxin in all its forms (Figure 2.2). In 2013, 128 countries signed the Minamata Convention on mercury in order to protect human health and the environment (Evers *et al.,* 2016; Mao *et al.,* 2015). There are notable differences in the toxicity of elemental mercury, inorganic mercury and organic mercury. Therefore, the toxicity of mercury species and its exposure pathways are discussed below.

2.6.1 Elemental mercury

Elemental mercury (Hg^0) vapour is harmful to human health. Exposure to mercury vapour occurs in homes, workplaces and in laboratories through broken thermometers and the use of elemental mercury in chlor-alkali processes, dental amalgam and others (Syversen & Kaur, 2012). Elemental mercury plays an important role in occupational health problems. Humans are exposed to elemental mercury vapours mainly through inhalation of the contaminated air were mercury vapour is taken up through the lungs and is distributed throughout the body and passes through the cell membranes such as the blood-brain barrier and the placenta and can be retained in the brain for years (Clarkson & Magos, 2006). According to Akyildiz *et al.* (2012) acute exposure to elemental mercury vapours may cause headaches, abdominal pain,

chest tightness, and fever. Dermal effects may include excessive perspiration, and a desquamating rash of the hands and the feet. Chronic exposure to elemental mercury induces changes in the central nervous system such as insomnia, irritability, memory loss, emotional liability, withdrawal, shyness and tremor.

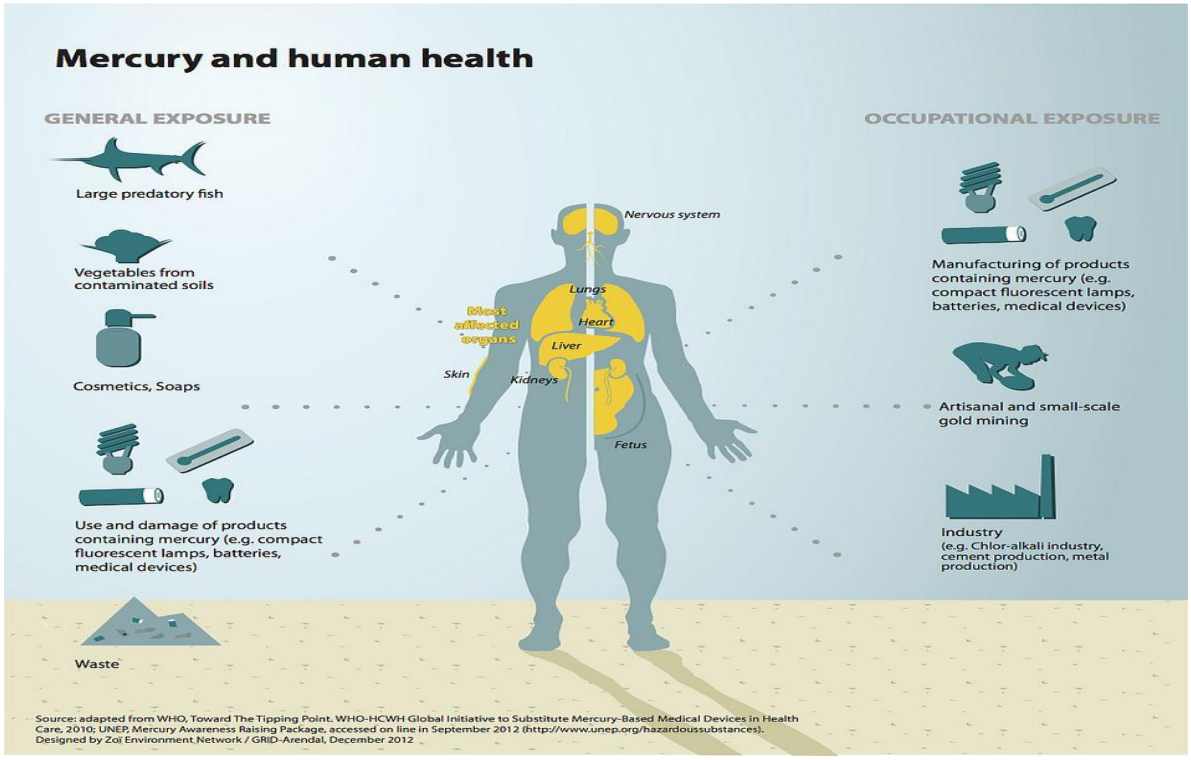

Figure 2.2: Health effects of exposure to mercury from different sources (UNEP, 2016)

2.6.2 Inorganic mercury

The toxicity of inorganic mercury salts varies with their solubility. Mercury (I) compounds are of low solubility and less toxic compared to mercury(II) compounds (Langford & Ferner, 1999). Once inorganic mercury salts are ingested, they accumulate in the kidneys and the liver (Rahola *et al*., 1973). The symptoms of inorganic mercury poisoning are burning pain in

the chest, rapid discolouration of the mucous membranes and gastrointestinal pain (Langford & Ferner, 1999). These symptoms may grow further to vomiting, diarrhoea which can lead to hypovolemic shock and death. Furthermore, after acute exposure to mercuric mercury, the target organs are the intestine and the kidneys resulting in corrosive effects in the intestine and renal failure. Chronic exposure to inorganic mercuric mercury salts causes tubular necrosis in the kidney, glomerulonephritis and autoimmune disease (Pollard & Hultman, 1997).

2.6.3 Organic mercury

Among other forms of organic mercury which are mostly detected as methyl mercury (MeHg) and ethyl mercury (EtHg), organic mercury is the most toxic form with the largest range of adverse effects on human health and in the environment (Crowe *et al.*, 2017). People are mainly exposed to methyl mercury through ingestion of foodstuff like fish (Mergler *et al.*, 2007), through aerosol and through direct skin absorption. Exposure to organic mercury can also be through vaccines containing the preservative thimerosal that is metabolised to ethyl mercury. The first methyl mercury poisoning took place in Minamata, Japan, during the early 1950s to 1960s where methyl mercury was released from a factory as a by-product of acetaldehyde production into the Minamata Bay (Ekino, 2007; Eto, 2000). Approximately 200 000 people were exposed to methyl mercury through the consumption of contaminated fish and other seafood (Ekino, 2007; Eto, 2000). The health effects that were observed in adults included neurological problems such as blurred vision, hearing impairment, ataxic gait, clumsiness of hands, and psychiatric disorders. Mental and motor development disturbances were observed in unborn babies (Ekino, 2007; Eto, 2000). In the 1970s another methyl mercury poisoning incident occurred in Iraq where people were exposed to methyl mercury

by eating bread that was baked with grain treated with mercury-containing fungicide. The same health effects observed in the Minamata incident victims were also observed in the victims of the Iraq incident (Harada, 1995).

2.7 LANDFILL

A landfill can be described as a site or a physical space used for the disposal of solid waste in the surface of the soil by burial which is the oldest form of waste treatment. In this present age, landfill (Figure 2.2) refers to an engineered space which is designed for the disposal of municipal solid waste and it is operated to minimise human health effects and environmental impacts (Renou *et al.,* 2007). Landfills have served for many years as disposal sites for waste from different sources, including residential, industrial, commercial, institutional, construction and demolition and from manufacturing processes in both developed and developing countries (Abu-Rukah & Al-Kofahi, 2001; Nagendran *et al.,* 2006). Solid waste is mainly disposed to landfills considering that landfills are the cheapest and most cost-effective method of disposing of waste (Barrett & Lawler, 1995). There are two primary types of landfills which include engineered and non-engineered landfills.

2.7.1 Engineered landfills

Engineered landfills (Figure 2.3) are modern and are constructed with a base liner, leachate collection system, monitoring boreholes, gas extraction and a cap system (UNEP 2002). There are different types of landfill liners that are used to contain the waste, such as compacted clay barriers (CCB), geosynthetic clay liners (GCLs), geomembrane liners,

amended soil or the combination of all (Divya *et al.,* 2012). The geomembrane is commonly used in modern landfills for lining (Rowe & Sangam, 2002; Take *et al*., 2007; Brachman & Gudina, 2008; Bouazza *et al.,* 2008). Though landfill liners prevent leachate contamination of the groundwater, the risk of groundwater contamination is still there (Slack *et al.,* 2005). Failure of landfill bottom liners may lead to the release of the leachate (Schwarzbauer *et al*., 2002). It has been reported that liners deteriorate with time which allows the leachate to leak, leading to groundwater contamination (Jagloo, 2002). The loss of leachate from landfills and contamination of groundwater form part of environmental pollution (Jagloo, 2002).

2.7.2 Non-engineered landfills

Old landfills are non-engineered, without geomembrane liners and leachate drainage systems. This allows the leachate from the landfill to seep slowly out of the landfill into the soil, surface water and groundwater which contributes to the problem of environmental pollution (Fatta *et al.,* 1999). According to Fatta *et al.* (1999), groundwater near unlined landfills is not suitable for irrigation since its physical and chemical parameters are characterised by colour, conductivity, TDS, hardness, Cl^-, NH_3^-, N, COD, K^+, Na^+, Ca^{2+}, Fe, Ni and Pb which exceeded the water quality standards given by EE, EPA and the Greek Ministry of Agriculture.

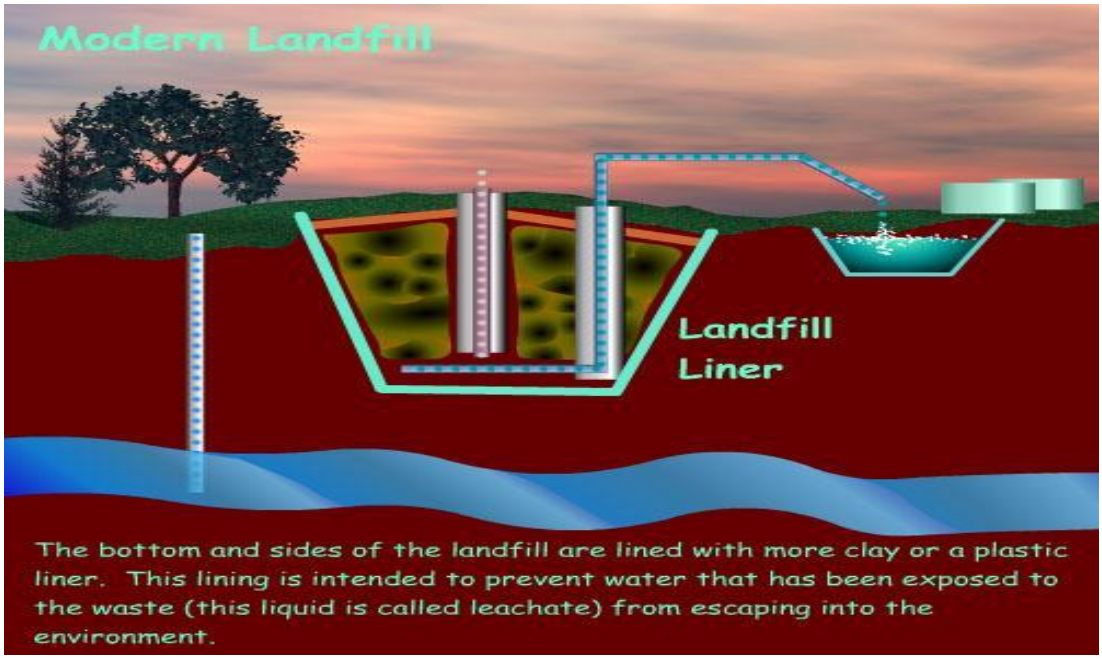

Figure 2.3: A picture of an engineered landfill (Sanitary landfill, waste management system environmentally orientation, 2011)

2.7.3 Municipal solid waste

The rapid increase in the level of economic activity and population growth, as well as industrial development coupled with urbanisation has resulted in a constant increase in the generation of municipal solid waste (MSW) in most countries (Naveen *et al.*, 2016; Renou *et al.*, 2007). Municipal solid waste mainly comprises general and hazardous wastes in the form of bio-degradable waste, paper, plastic, glass, metal, textile and leather. Globally, about 10 billion tonnes of municipal solid waste is produced every year (Ke, 2002). Waste is generated universally as a result of human activities and can be classified into solid, liquid and gaseous wastes (Taylor & Allen, 2006). Furthermore, although in the European Union there are policies of reduction, reuse and diversion from landfills that are strongly promoted, roughly 75% of the waste generated in the United States of America is still disposed of in landfills.

Wastes that are produced from a domestic source are categorised as household waste and they represent two-thirds of the municipal solid waste (OECD, 2001). According to OECD (2001) and Zacarias-Farah and Geyer Alley (2003), approximately 70% of municipal solid waste is disposed of in landfills. Household hazardous waste is disposed of to the landfill along with the general household waste (Schrab *et al.,* 1993; Kjeldsen *et al.,* 2002). Hazardous substances occur in municipal solid waste in the form of paints, vehicle maintenance products, mercury-containing waste, and pharmaceuticals (Slack *et al*., 2004).

2.7.4 Landfill leachate

Landfill leachate has been defined as an aqueous effluent that is generated as a result of rainwater percolating through waste layers, biochemical processes in waste cells and the inherent water content generated by the waste (Renou *et al.,* 2007; Chofqi *et al.,* 2004; Mukherjee *et al.,* 2014). Christensen *et al.* (1994) and Christensen *et al*. (2001) also defined landfill leachate as a dark liquid with a foul smell and complex composition which is characterised by dissolved organic matter which is expressed as chemical oxygen demand (COD) or total organic carbon (TOC) including methane (CH_4) and volatile fatty acids, inorganic macro-components such as Ca, Mg, Na, K, NH_4^+ Fe, Mn, Cl, and others, as well as metals such as Cd, Hg, Cr, Cu, Pb, Ni and Zn, and xenobiotic organic compounds. Under anaerobic conditions in the landfill site, a significant fraction of elemental mercury in the landfill leachate is transformed into other toxic forms such as methyl mercury, ethyl mercury and phenyl mercury through the activity of sulphate- and iron-reducing bacteria (Acha *et al*., 2012; Aderemi *et al*., 2012; Christensen *et al*., 2001; Liu *et al*., 2015; Moravia *et al*., 2013; Qin *et al*., 2016). According to Kulikowska & Klimiuk (2008), landfill leachate is highly variable and heterogeneous. The chemical and microbial composition of landfill leachate

differs from landfill to landfill depending on factors such as the type of waste contained in a landfill (i.e. biodegradable or non-degradable, soluble or insoluble, organic or inorganic, liquid or solid and toxic or non-toxic waste materials), age of the landfill, environmental conditions, landfill operational practices, climatic conditions of the area, the hydrology of the landfill site and the mechanism of organic matter degradation in the landfill (Kjeldsen *et al*., 2002; Moravia *et al*., 2013; Chofqi *et al*., 2004).

Different phases of decomposition of solid waste normally occur in a landfill site (Aucott, 2008). Anaerobic digestion is the main process and occurs in four stages, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis. During hydrolysis the complex organic molecules in the biomass are broken down into fractions that can be utilised by the bacteria. The process of acidogenesis results in further breakdown of components by acidogenic bacteria and carbon dioxide (CO_2) is produced as well as organic acids, resulting in a decrease in the pH of the leachate. Acetogenesis is the third stage during which acetogens digest the simple molecules created during acidogenesis and acetic acid as well as CO_2 and hydrogen are produced. The terminal stage of anaerobic digestion in the landfill is the methanogenic phase during which methanogens use the intermediate products of the preceding stages to produce methane; this stage is characterised by a decrease in acetic acid and an increase in pH (Castello *et al*., 2008; Christensen *et al*., 2001; Porowska, 2015; Wimmer *et al*., 2013). The leachate of newly constructed landfills is normally characterised by the presence of volatile acids as a result of anaerobic acidification while the leachate of mature landfills is mainly characterised by organics in the form of humic and fulvic acid fractions. According to Chang (1989) and Chen (1996), the concentration of organics is related to chemical oxygen demand (COD); in leachate from newly constructed landfills the COD is 10 000 mg/L while in landfills that are more than 10 years old, the COD of the

leachate is below 3 000 mg/L. This sharp drop in COD is influenced by the recirculation of leachate in the landfill which improves its quality in terms of chemical oxygen demand (Chan *et al*., 2002).

2.7.5 Groundwater contamination

Groundwater is the fresh water that collects and soaks into the soil and is stored in the tiny spaces (pores) between the rocks and particles of the soil. Groundwater can be stored underground for hundreds and thousands of years where it has the potential to come up to the surface to help fill the rivers, streams, lakes, ponds and wetlands. Groundwater can also come up to the surface in the form of a spring and can also be pumped from boreholes. According to the US Environmental Protection Agency (EPA), about 50% of municipal, domestic, and agricultural water supply is derived from groundwater (UNEP, 1989). However, groundwater can be polluted by metals including mercury (Hg) contained in the landfill leachates, especially when aquifers are in the vicinity of landfill sites.

Landfills have been identified as a major threat to the quality of groundwater resources, especially for landfills that are not lined with geomembrane material (Figure 2.3) (Fatta *et al*., 1999; Mor *et al*., 2006). Although modern sanitary landfills are known to be well engineered with geomembrane barriers, threats of groundwater contamination from sanitary landfills have been widely reported (Mikac *et al*., 1998; Abu-Rukah & Al-Kofahi, 2001; Ahmed & Sulaiman, 2001; Srivastava & Ramanathan, 2008; Han *et al*., 2013). It is evident from these studies that landfill leachate may lead to groundwater contamination problems. According to Abu- Rukah & Al-Kofahi, (2001), the contamination of groundwater by landfill leachate may reach distances of up to 6 km from the landfill sites.

Water contamination and a shortage of clean water resources contribute to the environmental pollution problems of this present age while water demand levels in homes and industries are on the increase (Zawala *et al*., 2007). Water quality assessment is of importance in order to apply the appropriate water pollution control strategies (Sánchez *et al*., 2007). Many studies have indicated that landfills are a potential source of mercury into the environment (Lindberg & Price, 1999; Lindberg *et al*., 2001; Li *et al*., 2001). These studies have focused mainly on the various forms of mercury in landfill gas while groundwater contamination by landfill leachate containing mercury has been rarely studied.

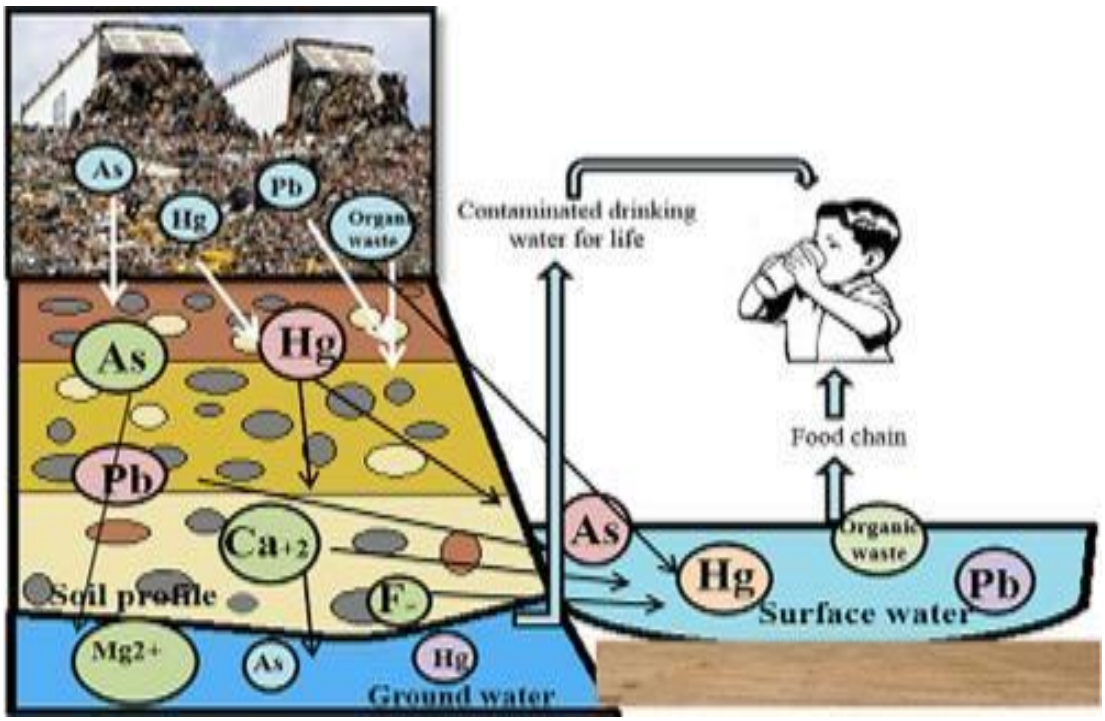

Figure 2.4: Schematic representation of groundwater contamination with metals from landfill leachate (Samadder *et al*., 2017)

2.8 CONCENTRATIONS OF TOTAL MERCURY (THg) IN LANDFILL MEDIA

Mercury and its compounds have been used for many centuries in industries and for domestic purposes (Lee & Lee, 2012; Lin *et al.,* 2016) and in the production of consumer products such as batteries, electronics, thermometers, electrical switches, fluorescent light bulbs, batteries, biocides and pesticides, paints, pharmaceuticals, cosmetics and dental amalgam fillings (Pacyna *et al*., 2003). At the end of their life cycle, these mercury-containing products form part of municipal solid waste which then enters the landfill via waste stream (Lindberg *et al*., 2005; Zhu *et al.,* 2013). According to Lin *et al*. (2016) sources of mercury-containing solid waste in landfills are more complicated in developing countries and the fate of mercury-containing solid waste is mostly determined by management policies for solid waste disposal governing the landfill. Batteries and fluorescent lamps are counted to be the main contributors of mercury-containing solid waste in landfills. More than 100 tons of mercury-containing waste disposed of in landfills was reported in China where batteries and fluorescent lamps accounted for 54% and 20%, respectively (Zhu *et al*., 2013).

As a result of the un-separated solid waste collection system, mercury-bearing waste such as fluorescent lights, batteries and thermometers is collected and disposed of in landfills (Chai *et al*., 2015). During precipitation, rainwater provides a medium in which waste undergoes decomposition through biochemical reactions such as dissolution, hydrolysis, oxidation and reduction under the influence of bacteria (Taylor & Allen, 2006). Mercury is also leached from the waste layers and forms part of the leachate that is produced in the landfill. Mercury can be released from landfills into the environment through different pathways. This includes

the release of mercury from landfill via upward emission and downward leaching to groundwater (Walvoord *et al*., 2008).

Mercury levels in different environmental media in South Africa have been studied by other researchers (Malehase *et al*., 2016; Williams *et al*., 2011; Oosthuizen *et al*., 2010). However, there is limited information on contamination of groundwater with mercury from landfill leachate in South Africa. Furthermore, South Africa is a water-scarce country (Blignaut & Van Heerden, 2009); as a result, many people tend to use borehole water. For those boreholes which may be located near municipal landfills, there is a high possibility of groundwater contamination, particularly where the landfill site is not lined with geomembrane material.

2.8.1 Concentrations of total mercury in landfill leachate

Concentrations of total mercury in landfill leachate have also been determined by other researchers in various countries (Table 2.1).

TABLE 2.1: Concentrations of total mercury in landfill leachate

Country	**Environmental matrix**	**THg concentrations (µg/L)**	**References**
China	Leachate	0.079	Li *et al*., 2005
China	Leachate	0.1-1.016	Tang *et al*., 2003
USA	Leachate	7.15	Aucott, 2006
India	Leachate	1.7-8.3	Esakku *et al*., 2003
Western Norway	Leachate	0.013-0.027	Øygard *et al*., 2004
South Africa (Durban)	Leachate	02-0.3	Schoeman *et al*., 2003
South Africa (Pretoria)	Leachate	15	Tshibalo, 2017
Poland	Leachate	0.017	Kulikowska and Klimiuk, 2008.
Ireland	Leachate	0.28-0.32	Brennan *et al*., 2016
South Africa (Durban)	Leachate	<0.05-2.2	Robinson, 2007
South Africa (Durban)	Leachate	<50	Robinson, 2007
South Africa	Leachate	12.75	Ntsele *et al*., 2000
Sweden	Leachate	0.1-1	Morling, 2007
Ghana	Leachate	342	Sulemana *et al*., 2015
New South Wales	Leachate	0.1-1	Percy and Truong 2003
India	Leachate	12.75	Keenan *et al*., 1984
Denmark	Leachate	5.2	Kjeldsen and Christophersen, 2001

In most of these studies, metals were discussed in general terms; the toxic effects of mercury from landfill media on the environment and human health were barely discussed. In a study conducted in the USA, Aucott (2006) stated that the concentrations of total mercury that were determined in the landfill leachate samples were low enough to be of little concern from a state-wide emission perspective. Esakku *et al*. (2003) determined the concentrations of total mercury in landfill leachate that ranged from 1.7 – 8.3 µg/L. These concentrations exceeded the limits of Indian standards for compost. In another study conducted in four landfill sites by Øygard *et al*. (2004), the concentration range of total mercury in landfill leachate was 0.013 – 0.027 µg/L. In that study, Øygard and co-workers suggested that the results obtained are in agreement with the theory that metals in landfill leachate exist either as colloids and solid matter or as complex metal ions rather than dissolved ions.

Kulikowska and Klimiuk (2008) reported that the concentrations of total mercury in landfill leachate were fairly low (0.017 µg/L). It has been stated that slightly higher concentrations of metals will only occur in younger landfills during the acidification stage because of the high degree of metal solubilisation. In a study conducted by Robinson (2007) in Mariannhill and Bisasar Road landfill sites, the total mercury concentration ranges in leachate samples were <0.05 – 2.2 µg/L and <50 µg/L, respectively. Mariannhill landfill is counted amongst the three large landfills in the City of Durban which receives 700 tons of solid waste each day and Bisasar Road landfill is considered the largest and the busiest landfill in Africa, receiving different categories of waste including domestic, commercial, industrial and hazardous waste. Morling (2007) reported that the concentrations of total mercury obtained from La Mercy landfill leachate do not pose a threat to the environment. Higher concentrations of total mercury in leachate samples were recorded in a study conducted by Sulemana *et al*. (2015). The occurrence of mercury in the landfill leachate was due to mercury-containing waste such

as cathodes for the production of chlorine and caustic soda, mercury vapour lamps, mirror coatings and boilers that were disposed of at landfills.

2.8.2 Concentrations of total mercury in sediment

Only a few studies have been conducted on the concentrations of total mercury in landfill leachate sediment (Table 2.2). Machado *et al*. (2002) conducted a study in the mangrove sediments surrounding a large landfill in southeast Brazil. The concentrations of total mercury in sediment samples ranged from 0.29 – 0.76 µg/g. These concentrations were found to be higher compared to concentrations obtained from those sites that are located far from higher contamination sources in the bay. It was stated that elevated concentrations of total mercury that were detected in the landfill cover soil were due to the release and emissions from mercury-containing waste products buried in the landfills. Raman and Narayanan (2008) reported concentrations of total mercury that ranged from 0.029 – 0.20 µg/g; the authors stated that the increase in the global population and the growing demand for food and other essentials had resulted in a rise in the amount of waste being generated daily by each household.

TABLE 2.2: Concentrations of total mercury in sediment and soil samples

Country	**Environment**	**THg concentrations (µg/g)**	**References**
Brazil	Sediment	0.29-0.76	Machado *et al*., 2002
South Africa	Sediment	314	Tshibalo, 2017
China	Landfill cover soil	0.64	Cheng and Hu, 2011
China	Landfill cover soil	6.53	Cheng and Hu, 2011
China	Landfill cover soil	3.12-6.53	Cheng and Hu, 2011
China	Landfill cover soil	0.188	Cheng and Hu, 2011
China	Landfill cover soil	0.037-0.099	Cheng and Hu, 2011
India	Soil	0.029-0.20	Raman and Narayanan, 2008

2.8.3 Concentrations of total mercury in groundwater samples

TABLE 2.3: Concentrations of total mercury in groundwater samples

Country	Environmental media	THg concentration (µg/L)	References
India	Groundwater	1-32	Samadder *et al*., 2017
South Africa (Pretoria)	Groundwater	2.0-5.0	Tshibalo, 2017
Ghana	Groundwater	2.0-27.0	Sulemana *et al*., 2015
Zambia	Groundwater	0.4-13	De Waele *et al*., 2004

Table 2.3 shows the concentration of total mercury in groundwater samples. Only a limited number of studies have been conducted on groundwater pollution with mercury from landfill sites. Studies that have been undertaken listed other metals (lead, chromium, manganese, cadmium, copper, iron, etc.) as part of pollutants that occur in the landfill leachate (Abu-Rukah & Al-Kofahi, 2001; Christensen *et al*., 1998; Flyhammar, 1995; Looser *et al*., 1999; Rapti-Caputo & Vaccaro, 2006; Saarela, 2003), but mercury was rarely listed as part of the metals that pollute groundwater. Samadder *et al*. (2017) reported concentrations of total mercury in groundwater samples that ranged from 1 – 32 µg/L. It was stated in this study that the metals that are determined in landfill groundwater samples rarely cause groundwater pollution problems since landfill leachates usually contain relatively low concentrations of metals which are subjected to strong attenuation by both sorption and precipitation (Vogl & Angino, 1985; Bourg *et al*., 1992; Regadio *et al*., 2015). The concentrations of total mercury in groundwater samples reported by Sulemana *et al*. (2015) were found to be within the World Health Organization (WHO) guideline value of 0.006 mg/L. the It was mentioned in

this study that mercury may occur naturally in groundwater, mostly in lower concentrations (about 2 µg/L), due to the presence of mercury in geological deposits. De Waele *et al*. (2004) reported concentrations of total mercury in groundwater samples that ranged from 0.4 – 13 µg/L. These concentrations exceeded the guideline value of 1 µg/L for mercury in drinking water proposed by the World Health Organization (WHO, 1993).

2.9 CHEMICAL PARAMETERS THAT MAY INFLUENCE THE BEHAVIOUR OF MERCURY

The behaviour of mercury in landfill leachate, sediments and groundwater may be influenced by certain chemical parameters. These parameters include the occurrence of trace metals and anions in the landfill leachate, the occurrence of dissolved organic matter (DOM) and sorptive capacity, pH level of the leachate and the occurrence of colloids and particles (Aucott, 2006).

2.9.1 The potential influence of trace metals

Trace metals such as lead (Pb), chromium (Cr), copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), cadmium (Cd) and others occur together with mercury (Hg) in the landfill sites (Zhou *et al*., 2015; Wuana & Okieimen, 2011). The occurrence of these metals in landfill leachate is caused by the disposal of electronic devices such as cell phones and computer systems in the landfill sites (Al Raisi *et al*., 2014). These metals are likely to influence the behaviour of mercury in the landfill leachate and sediment which may enhance the bioavailability and mobilisation of mercury from landfill leachate into groundwater.

According to Lide (2012), metals in the landfill leachate may occur in the form of sulphides such as mercury sulphide (HgS) and oxides including cadmium oxide (CdO), lead oxide (Pb_3O_4, Pb_4O_3 and Pb_2O) which are insoluble in water Nevertheless, some oxygen-containing metals including mercury oxide (HgO), cadmium hydroxide ($Cd(OH)_2$), lead oxide (PbO) and lead sulphate ($PbSO_4$) are soluble in water. It is known that cations including trace metals bind strongly to organic matter because of the capacity of the organic matter to adsorb cations (Aucott, 2006). Iron is known to be capable of influencing the mobility of mercury in soil through sorption reactions. The geochemistry of iron and mercury are considered to be closely related. In some anaerobic column experiments conducted by Bower *et al*. (2008), it was reported that mercury oxide can sorb onto iron oxides, while Barringer and Szabo (2006) stated that the sorption of mercury onto iron hydroxide is its method of attenuation in soil but in the presence of sulphide, iron will be reduced resulting in the increase of dissolved mercury concentrations. However, it has been discovered that under oxygen-depleted conditions, reductive dissolution of iron hydroxide may occur, thereby releasing the sorbed mercury oxide (Charlet *et al*., 2002).

2.9.2 The potential influence of anions, dissolved organic matter (DOM) and pH

Anions such as fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^-) and others may form complexes with mercury in landfill leachate, and in sediment which may promote the mobilisation of Hg from the sediment into groundwater. According to Schuster (1991) mercury tends to form strong complexes with Cl^-, OH^-, and S^{2-} because of their high abundance and stability resulting in the formation of mercury chloride ($HgCl_2$), mercury(II) hydroxide and mercury sulphide (HgS). In the presence of dissolved organic matter (DOM) in soils, surface water and wastewater, mercury tends to bind strongly to sulphur-containing

groups such as thiols (Gabriel & Williamson, 2004; Ravichandran, 2004). Gabriel and Williamson (2004) reported that in oxygen-depleted areas mercury will bind with sulphur to form mercury sulphide (HgS). Furthermore, where dissolved organic matter is low or absent, mercury will occur as hydroxide or chloride complexes in fresh waters (Stumm & Morgan, 1996).

Lower pH values or acidic conditions in landfill leachate are known to favour the solubility of metals. The pH of landfill leachate can decrease from greater than 7 to pH 5 as a result of the production of organic acids that are formed as by-products of fermentation that takes place in the landfill (Aucott, 2006; Mahapatra *et al*., 2011). In a study conducted by Naveen *et al*. (2017), the pH values detected in leachate from three landfills were 7.4, 7.6 and 7.5. The Naveen *et al*. (2017) study reported that a pH above 7 can carry a greater load of dissolved substances; the alkaline nature of the leachate also indicates the mature stage of a landfill (Jorstad *et al*., 2004).

2.10 ANALYTICAL METHODS AND TECHNIQUES USED FOR THE DETERMINATION OF MERCURY

A number of analytical methods and techniques can be employed to determine mercury in different environmental media or matrices (i.e., in the soil, sediment, wastewater, leachate and water). In order to obtain data that are reliable during sample analysis, appropriate sampling procedures and sample preparation processes must be followed (López-Antón *et al*., 2012). The following section, therefore, will give a brief discussion on the different methods and techniques that are used for the determination of mercury in leachate, sediment and groundwater.

2.10.1 Methods used for the determination of mercury

Methods and reagents that are employed for the analysis of mercury are normally selected based on the analytical technique to be used and the type of the matrix to be digested (Issaro *et al*., 2009; López-Antón *et al*., 2012). Extra care must be taken during sampling, sample preparation and analytical procedures since contamination and loss of mercury may occur. Different methods and procedures that are available for the determination of mercury in liquid and solid samples have been reviewed in many studies. A process of digestion, oxidation and reduction before instrumental analysis is generally required for the determination of organic and inorganic mercury compounds in liquid and solid samples since these mercury forms are not volatile. The majority of instrumental techniques that are used for the analysis of mercury require this compound to be in solution. To achieve this goal, acid digestion is, therefore, an appropriate method to liberate mercury from compounds and sample matrixes. Acids such as hydrofluoric acid (HF), nitric acid ($HN0_3$), sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) are added to digest the sample. The liberated mercury is then oxidised using a variety of oxidants which are also selected based on the analytical technique to be used and the type of matrix to be digested. A hot solution of potassium permanganate ($KMnO_4$) has been found a suitable oxidising agent for natural water, sediments and soil, while potassium persulphate ($K_2S_2O_2$) and UV light have been proven to effectively oxidise mercury (Leopold *et al*., 2010). However, $K_2S_2O_2$ has been found to be unsuitable for natural water samples (Sánchez-Rodas *et al*., 2010). Hydrogen peroxide (H_2O_2) is also an effective oxidant of mercury.

According to Bansal *et al*. (2013), mercury analysis normally requires chemical vapour generation (CVG) and detection by an instrument. The advantages of using chemical vapour

generation include its ability to separate the analyte from the complex matrix, high selectivity and easy automation (Bansal *et al*., 2013). Methods such as chemical vapour generation (CVG) by reduction, chemical vapour generation by photoreduction, electrochemical vapour generation and ultrasound-promoted cold vapour generation can be employed for the generation of mercury vapour. In chemical vapour generation by reductant method, mercury vapour can be generated from digested or aqueous samples using stannous chloride ($SnCl_2$), sodium borohydride ($NaBH_4$) and sodium hydroxide (NaOH). Stannous chloride was first used as a reducing agent by Poluektovet *et al*. (Welz, 1986), but sodium borohydride has been used as a reducing agent in the place of stannous chloride due to its stronger reducing properties compared to stannous chloride. It has been stated that despite the stronger reducing property, sodium hydroxide is still known to have some drawbacks but despite that, chemical vapour generation is still recommended by many researchers (Chan & Sadana, 1993; Gomes Neto *et al*., 2000; Araujo *et al*., 1996; Serafimovski *et al*., 2008).

Another method that can be used to generate mercury vapour is the photoreduction method. This method involves mixing samples with low-molecular-weight organic compounds such as acetic acid, formic acid and oxalic acid followed by the exposure of the sample to ultraviolet (UV) radiation (Han *et al*., 2007). The addition of a photocatalyst such as titanium dioxide (TiO_2) improves the sensitivity of the method as it is capable of enhancing the photoreduction with the potential to reduce mercury strongly (Gil *et al*., 2010). Furthermore, electrochemical (EC) vapour generation method can also be used to generate mercury vapour. This method uses electrons as a reductant of mercury contained in the samples which is based on the electrode reduction of mercury(II) at the cathode (graphite and glassy carbon). Two processes are involved in this method: the first step involves reduction on the cathode which results in deposition of mercury as Hg from the soluble aqueous phase; and the second step

involves the generation of mercury cold vapour after removal from the cathode. Ultrasound-promoted cold vapour generation is also suggested as a method for generating mercury vapour. In this method, mercury vapours are generated by mixing the samples with an organic acid such as formic acid and irradiating the mixture with ultrasonic radiation. This method is known to produce less waste (Gil *et al*., 2006). The generated mercury vapour can then be analysed using different techniques.

2.10.2 Analytical techniques for mercury determination

A number of techniques for the determination of mercury in various samples have been employed by other researchers. Amongst others, atomic absorption spectrometry (AAS) is the most commonly used technique for the determination of mercury in various samples. Atomic absorption spectrometry is a procedure for measuring the absorbed radiation by mercury element contained in the environmental samples (García & Báez, 2012). The absorbance of the samples is measured by the amount of emitted light of a 253.7 λ absorbed in a sample compared to the originally emitted light. This is done by reading the spectra produced when mercury is absorbed on the optical path (Shrander & Hobbins, 1983). The concept of atomic absorption spectrometry was first introduced by Walsh in Australia and in the Netherlands by Alkemade and Milatz (Vandecasteele & Block, 1993). The following AAS techniques are available: Flame atomic absorption spectrometry (FAAS), solid sampling-graphite furnace atomic absorption spectrometry (SS-GFAAS), and cold vapour atomic absorption spectroscopy (CVAAS).

As shown in (Figure 2.4), flame atomic absorption spectrometry (FAAS) has been used as a method of sample atomisation since the early stages of the development of the AAS

technique. Flame atomic absorption spectrometry has a detection limit of 0.2 mg/L and shows 1% characteristic absorption at a concentration of 5 mg/L (Bansal *et al*., 2013). In FAAS, the sample solution is sucked into a nebuliser and mixed with the gaseous fuel (acetylene) and oxidant (air), and then carried into the flame where atomisation occurs. The beam from the hallow cathode lamp (HCL) and the beam from the deuterium lamp (for background corrections), are split in the beam splitter, one half passing through the flame (sample beam) and the other one around it (reference beam). The two beams are then recombined by a chopper mirror and pass into the monochromator for the scanning of the spectrum; the ratio between reference and sample signal is then amplified, then passes to the detector, following signal processing and finally to the display for the readout. This instrument (atomic absorption spectrometer, Shimadzu AA-7000) model with air-acetylene adjustable burner assembly was used for measurements of trace metals (cations). It incorporates newly developed 3D double-beam optics, designed to produce maximum performance for each measurement method through optimal adjustment of the light beam and light beam digital filter.

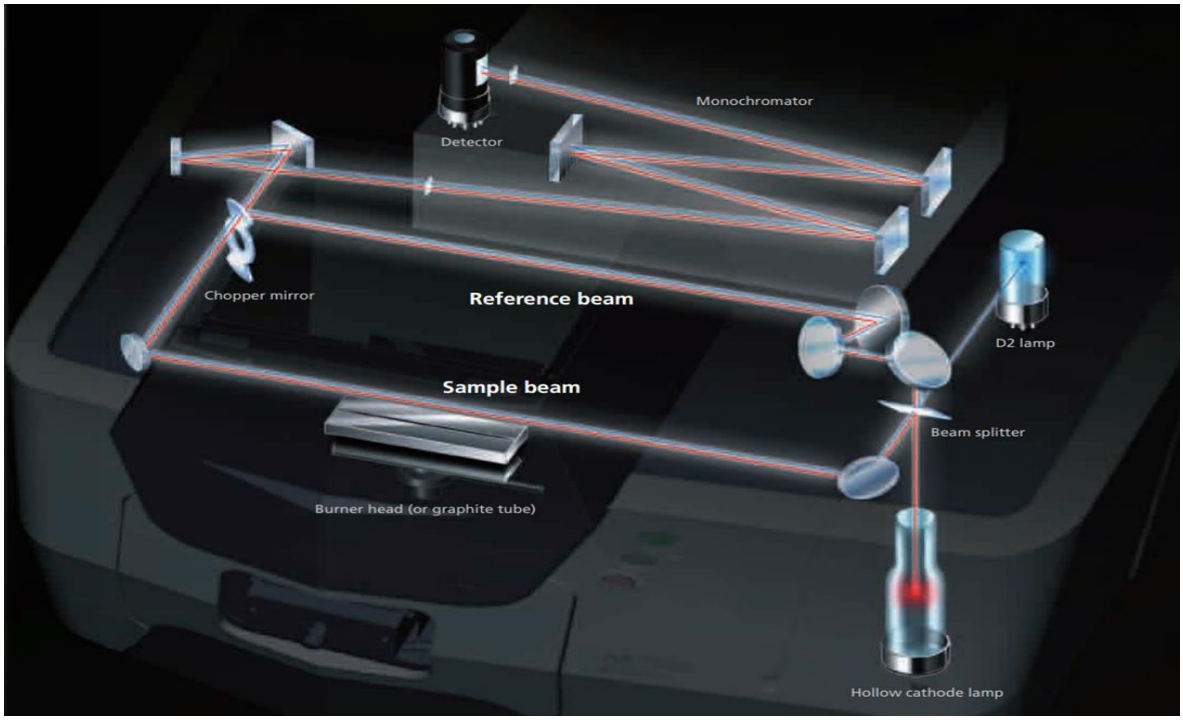

FIGURE 2.5: Optical configuration of F-ASS (AA-7000) configuration (Shimadzu Corporation, 2004)

However, solid sampling-graphite furnace atomic absorption spectrometry (SS-GFAAS) technique determines mercury in solid samples directly. Resano *et al*. (2009) developed a method for the determination of mercury in polymers which covered mercury concentrations that ranged from 20 to 1 100 µg/g with a detection limit of 2.2 µg/g. Furthermore, cold vapour atomic absorption spectroscopy (CVAAS) (Figure 2.5) is the commonly and successfully used technique for mercury determination. The distinctive properties of mercury allow it to be analysed without using any atomiser. Stannous chloride is used to reduce mercury in the sample solution into vapour during cold vapour analysis. After volatilisation, the mercury vapour is released from the solution and carried by an inert gas to the absorption cell with the absorption line of 253.7 nm. The amount of mercury contained in the sample is reflected by the magnitude of the signal on the instrument.

Figure 2.6: Mercury vapour unit for reduction vaporisation of mercury

Apart from AAS, other techniques that can be used to determine mercury include atomic emission spectrometry (AES), atomic fluorescent spectrometry (AFS), inductively coupled plasma-mass spectrometry (ICP-MS), neutron activation analysis, X-ray fluorescence analysis, electroanalytical methods and mercury sensors (Bansal *et al*., 2013). Atomic emission spectrometry can be used for both qualitative and quantitative analysis. According to Wu *et al*. (2011), Zhu *et al*. (2008) and de Wuilloud *et al*. (2002), ICP-AES is the most popular plasma source for the determination of mercury. Zhu and Alexandratos (2007) suggested a method for mercury determination which involved the addition of mercury to complexing agents such as gold(III) chloride, to reduce the memory effect, whereas Han *et al*. (2006) suggested a method for the determination of mercury in soil samples by optimising the conditions of ICP-AES with s detection limit of 20 µg/L. Atomic fluorescence spectrometry (AFS) measures the degree of fluorescence emission through determination of the degree of atom excitation by absorption of the radiation of the desired frequency. The

AFS technique is considered to be highly sensitive for the measurement of metals like mercury due to its low background signal and it was first used by Winefordner and Staab in 1964 to determine mercury (Winefordner & Staab, 1964.)

On the other hand, inductively coupled plasma-mass spectrometry (ICP-MS) involves the use of high-temperature argon plasma as the ionisation source and a mass spectrometer (MS). This technique involves the introduction of samples in the form of aerosol into the plasma. The ICP-MS technique has also become popular for the determination of mercury due to its high sensitivity and wide linear range. Nevertheless, neutron activation analysis is known to be highly sensitive and selective based on its ability to convert samples into radioactive isotope which emits gamma radiation whereas the X-ray fluorescence (XRF) analysis technique is considered a non-destructive analytical method which involves bombarding the sample with X-rays, and the elements in the samples are excited and emit characteristic X-rays whose wavelength is used to identify the particular element and whose intensity is related to the amount present in the sample. In the electroanalytical technique, voltammetric stripping analysis of mercury is used for the measurement of mercury in dilute aqueous solution with a detection limit of as low as 10^{-14} M (Meyer *et al*., 1996). Researchers are also working on developing mercury sensors for fast mercury determination. Sensors may include nanosensors, optical, chemical sensors, biosensors or piezoelectric sensors.

2.11 ION CHROMATOGRAPHY (IC)

In IC, ion exchange resins are used to separate anions based on their interaction with the resin; a column that contains anion exchange resins was used. Once the sample is injected, it

enters into the column by the help of the pump and the separation occurs inside the column based on their polarity towards the stationary phase. Inside the column, the anions form a weak bond with the stationary phase resin (R^+) and the separation is achieved with the help of a pumping system and metal column. The more weakly held anion elutes first and the more strongly held elutes last. The eluent ion (E^-) helps to displace an anion of the analyte (X^-) bonded to the resin. After the separation, the anions are detected and quantified by conductivity detectors.

2.12 MERCURY DRINKING WATER STANDARDS

Different organisations including World Health Organization (WHO), United States Environmental Protection Agency (USEPA), European Union (EU), Netherlands (NL) and South Africa (SA) have set standards or guidelines values for metals in drinking water, including mercury. According to *The Water Wheel* (2008), drinking water standards should be set based on the national, regional and local situations. Drinking water standards differ across the world. It is stated that in many countries, the monitoring of regulations is done by the water suppliers while the data is audited by the public health authorities responsible for environmental health (*The Water Wheel*, 2008). Drinking water standards often provide the basis for the safety of drinking water with respect to the contaminants of concern and the guidelines usually cover contaminants and features that are considered important in the supply of acceptable and safe drinking water.

The United States Environmental Protection Agency (USEPA) and the California Department of Public Health (CDPH) have set the maximum contaminant level (MCL) of mercury at 2

µg/L (USEP, 2006; USGS, 2008). According to the World Health Organization, European Union, The Netherlands and South Africa, the maximum limit for mercury in drinking water is 1 µg/L (*The Water Wheel*, 2008). A water supply is always expected to be continuously assessed in terms of emerging pollutants and appropriate actions should be taken to reduce the concentrations to safe levels.

CHAPTER 3

MATERIALS AND METHODS

3.1 PREAMBLE

In this chapter, different methods of sample preparation and analysis of total mercury in leachate, sediment and groundwater samples are described. The details of sampling, standard reagents, chemicals and instrumentation are also discussed.

3.2 MATRIALS, STANDARDS AND REAGENTS

3.2.1 Cleaning of glassware and apparatus

All glassware used were thoroughly washed with liquid detergent and were subsequently soaked overnight in 10% nitric acid, then rinsed three times with deionised water and dried in an oven at ±95 ^{o}C. Teflon plastic-containers for leachate, sediment and groundwater samples were thoroughly washed using 10% nitric acid and then rinsed with deionised water.

3.2.2 Standards and reagents

Standard solutions for AAS supplied by Fluka® Analytical (St. Gallen, Switzerland) and Merck (Darmstadt, Germany) of mercury (Hg), chromium (Cr), copper (Cu), cobalt (Co), iron (Fe), zinc (Zn), manganese (Mn) and lead (Pb) were used for instrument calibration, and certified multi-element standard solution (Fluka, Switzerland) containing fluoride (F^-),

chloride (Cl^-), nitrate (NO_3^-), and sulphate (SO_4^-), was used for instrument calibration and spiking experiments. For the determination of cations, sample preparation was undertaken using chemicals such as 70% nitric acid (HNO_3), 37% hydrochloric acid (HCL) purchased from Sigma-Aldrich (Germany) and 30% hydrogen peroxide (H_2O_2) from SSM Instrument (Pty). The following reagents were used throughout the experimental procedure: Potassium permanganate (≥99%, low in Hg), potassium persulphate (≥99%), sodium chloride (≥99%) and hydroxylamine sulphate (99%) (Sigma-Aldrich Germany). To reduce and vaporise elemental mercury in the samples for instrumental analysis, aqueous tin chloride ($SnCl_2$) dihydrate prepared from tin(II) chloride dihydrate was used. Ultrapure water was prepared in our laboratory using SG Series Compact purchased from Evoqua Water Technologies (United Kingdom) was used for all experimental procedures.

3.3 METHOD

3.3.1 Study area

Gauteng Province is the most urbanised, industrialised and highly populated province in South Africa with the cities of Pretoria and Johannesburg being the two major cities located within the province. The city of Pretoria is located approximately 50 km north of Johannesburg. The city has a humid sub-tropical climate with long mild to moderately warm days and lies within a valley, surrounded by the hills of the Magaliesberg mountain range, 1 370 m above sea level. Pretoria's summer runs from October to March while winter occurs between June and August. The average rainfall and temperature values for summer and winter are: 3 mm of rainfall in July and 154 mm of rainfall in January; and temperatures of 3

°C – 19 °C in July and 16 °C – 27 °C in January. The map of the study area is shown in Figure 3.1.

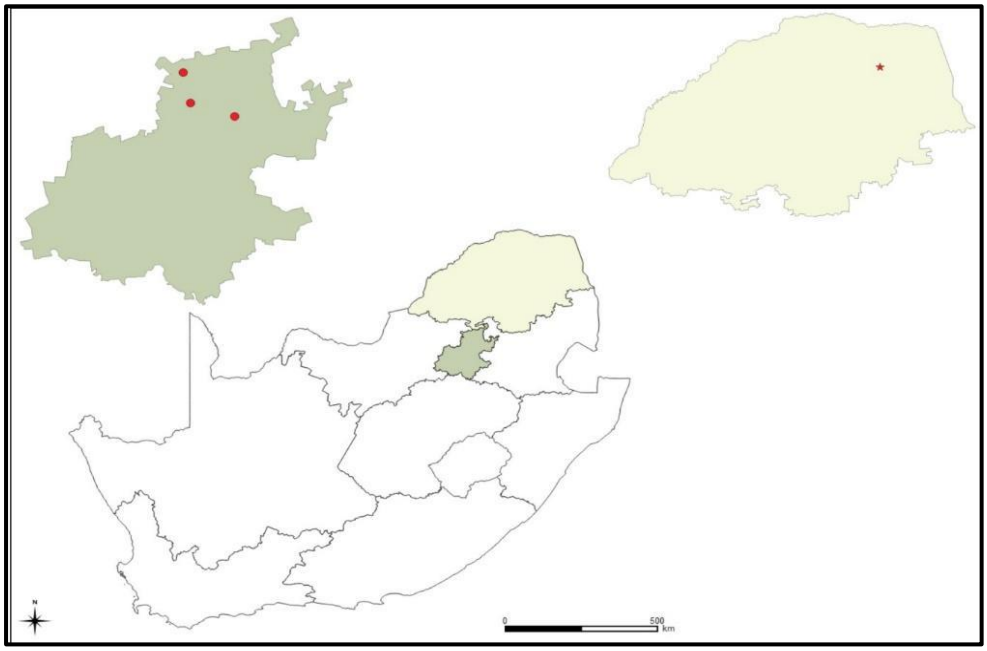

FIGURE 3.1: Maps of South Africa (bottom left) Gauteng Province (top left) and Limpopo Province (top right) showing selected landfill sites

Limpopo Province is considered as a developing area and it is located in the most northerly part of South Africa with Polokwane as the administrative capital of the province. Thohoyandou, however, is one of the small towns located within the province, in the far northern part of Venda and it is surrounded mainly by rural communities. It falls within the tropical belt of South Africa. Thohoyandou receives roughly 752 mm of rainfall per year and the peak of precipitation usually occurs during the mid-summer (January) period. The average rainfall and temperature values for Thohoyandou in summer and winter are 4 mm and 22 °C and 154 mm and 30.3 °C, respectively.

3.3.2 Sample collection

3.3.2.1 Collection of leachate, sediment and groundwater samples

Leachate, sediment, and groundwater samples were collected from the four selected landfill sites, three in Gauteng Province (Soshanguve, Hatherley and Onderstepoort, Table 3.1) and one in Limpopo Province (Thohoyandou, Table 1), South Africa. About 2 L of raw leachate and 1 000 g of sediment samples were collected into pre-washed Teflon plastic containers for winter and summer, respectively. Two litres of groundwater was collected from monitoring boreholes (25 m depth) within the selected landfill sites for winter and summer. The grab sampling method was used to collect leachate samples from the leachate ponds and sediment samples were collected by scooping sediment below the surface of the leachate pool (sampling depth of 0 – 5 cm) at the same point where the leachate samples were collected. The collected samples were labelled and covered immediately after sampling, kept in cooler bags and transported to the laboratory where they were kept at -4 °C in a refrigerator until further analysis. The pH of leachate and groundwater samples was measured immediately on arrival at the laboratory using the Hach HQ40d dual input multi-parameter portable meter.

TABLE 3.1: Detailed description and general information on selected landfill sites

Site Name	**Landfill age (years)**	**Type of geomembrane liner**	**Size (km^2)**
Soshanguve	18	No liner	0.392*
Hatherley	15	No liner	0.960*
Onderstepoort	16	No liner	0.518*
Thohoyandou	15	No liner	

*Source: Sibiya *et al*., 2017. Adapted from general waste minimisation plan for Gauteng

3.3.3 Sample preparation

For determination of total mercury in sediment, leachate and groundwater samples using cold vapour atomic absorption spectroscopy (CVAAS), the acid digestion method procedures as outlined in USEPA method 245.1 for the preparation of water samples, and the USEPA method 7471B for the preparation of solid and semi-solid samples were employed, respectively. Sediment samples were air dried and homogenised prior to extraction. One gram of homogenised sediment sample was weighed out and carefully transferred to a 250 mL sample bottle with a screw cap. Working under a fume hood and treating each sample individually, 10 mL of ultrapure water was added followed by the addition of aqua regia (3:1). The sample bottles were then closed tightly to avoid loss of mercury vapour and heated in a water-bath for 2 min at 95 ± 5 °C. The sample mixture was allowed to cool down, and then 50 mL of ultrapure water was added followed by the addition of freshly prepared potassium permanganate solution to oxidise mercury. In order to allow complete oxidation of the samples, the sample was allowed to stand for 15 min, and it was further heated for 30 min. After cooling, 6 mL of sodium-chloride hydroxylamine hydrochloride was added to remove excess potassium permanganate and the samples were filled to the mark (250 mL) and analysed. For leachate and groundwater samples, 100 mL of the sample was used and the procedure as outlined above was carried out with the addition of 8 mL of potassium persulphate and the samples were heated for 3 h. For analysis of mercury in leachate, sediment and groundwater samples, 6 mL of aqueous tin chloride dihydrate was added to the samples to reduce mercury to elemental mercury vapour.

To determine cations using flame atomic absorption spectroscopy (FAAS), the acid digestion procedure for preparing sediment for analysis as outlined in USEPA method 3050B was

employed. About 1.5 g of sediment was weighed out and then transferred to 250 mL conical flask, followed by addition of 10 mL deionised water and nitric acid and heated at ±95 °C using a hot plate without boiling for 15 min. The sample was then allowed to cool down and, thereafter, 5 mL nitric acid was added and the mixture was heated for 30 min. In order to achieve total decomposition, the sample was further heated for 2 h without boiling. After allowing the sample to cool down to room temperature, 2 mL of deionised water and 3 mL of hydrochloric acid was added. To minimise the effervescence, 1 mL (×3) of hydrogen peroxide was added sequentially and then heated for 2 h without boiling and thereafter allowed to cool. Thereafter, the sample was filtered through a Whatman filter paper into a 100 mL graduated volumetric flask and filled with deionised water to the graduation mark while rinsing the filter paper. For analysis of leachate and groundwater samples, 100 mL of the sample was used. All experiments were carried out under a fume hood.

Determination of anions was undertaken using ion chromatography (IC) and the USEPA method 300.0 was employed. The procedure was carried out by first weighing out 1 g of sediment sample which was then transferred into a 250 mL conical flask and then 100 mL of deionised water was added and stirred with a magnetic stirrer for 15 min. The sample was then filtered through a Whatman filter paper and finally through a 0.45 µm syringe filter. A similar filtration procedure was employed for leachate and groundwater samples.

3.4 QUALITY ASSURRANCE

Method validation was conducted using certified reference material (CRM) for mercury NCS DC 73312, purchased from Industrial Analytical (Pty), Kyalami, South Africa, and an

average recovery of 94% was obtained. Adequate care was taken to avoid loss of mercury during sample digestion. To avoid carryover during analysis, ultrapure water and reagent blanks were analysed in between samples. For the selected anions and cations, due to the absence of certified reference materials, quality checks were conducted by spiking leached soil samples in ultrapure water with certified standards of known concentrations. One gram of leached soil and 100 mL of ultrapure water were spiked with anion standard (5 mg/L) and cation standard (1 mg/L). Percentage recoveries were calculated and the mean average percentage of recoveries of mercury on spiked leached soil sample and ultrapure water was 98% ±6.6 and 102% ±4.7, respectively.

3.9 DETERMINATION OF INSTRUMENT DETECTION LIMIT AND CALIBRATION

The instrument detection limit (IDL) (lowest and highest) was evaluated and the standard deviation was calculated. The IDL was determined by running a series of reagent blank samples, spiked and un-spiked samples. The mean blank value and the standard deviation (SD) were calculated, in order to obtain the precision of the instrument. The lowest and the highest detection limits were determined by measuring the lowest and highest (increasingly lowering or increasing concentration of analytes) concentration that can be measured by the instrument under optimised conditions. Calibration curves for the determination of total mercury in sediment, leachate and groundwater samples are shown in Figures 3.2 and 3.3, respectively.

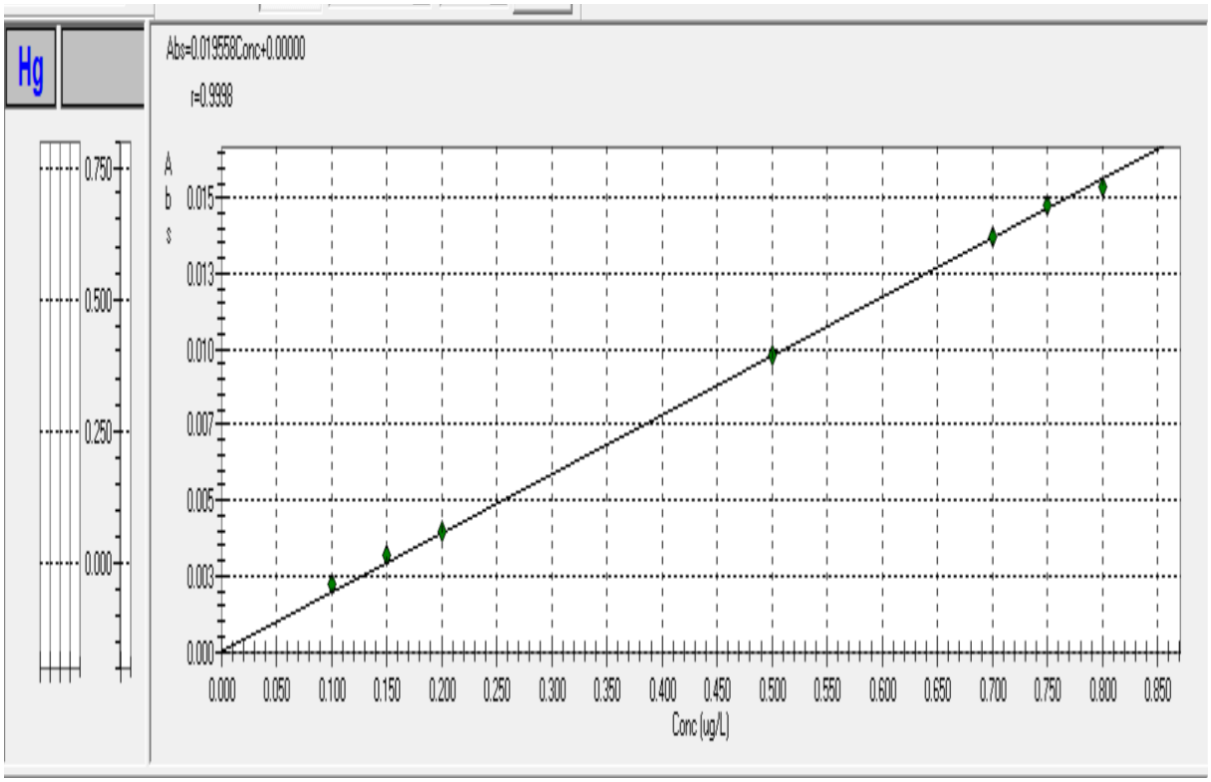

FIGURE 3.2: Calibration curve for the determination of total mercury in sediment samples

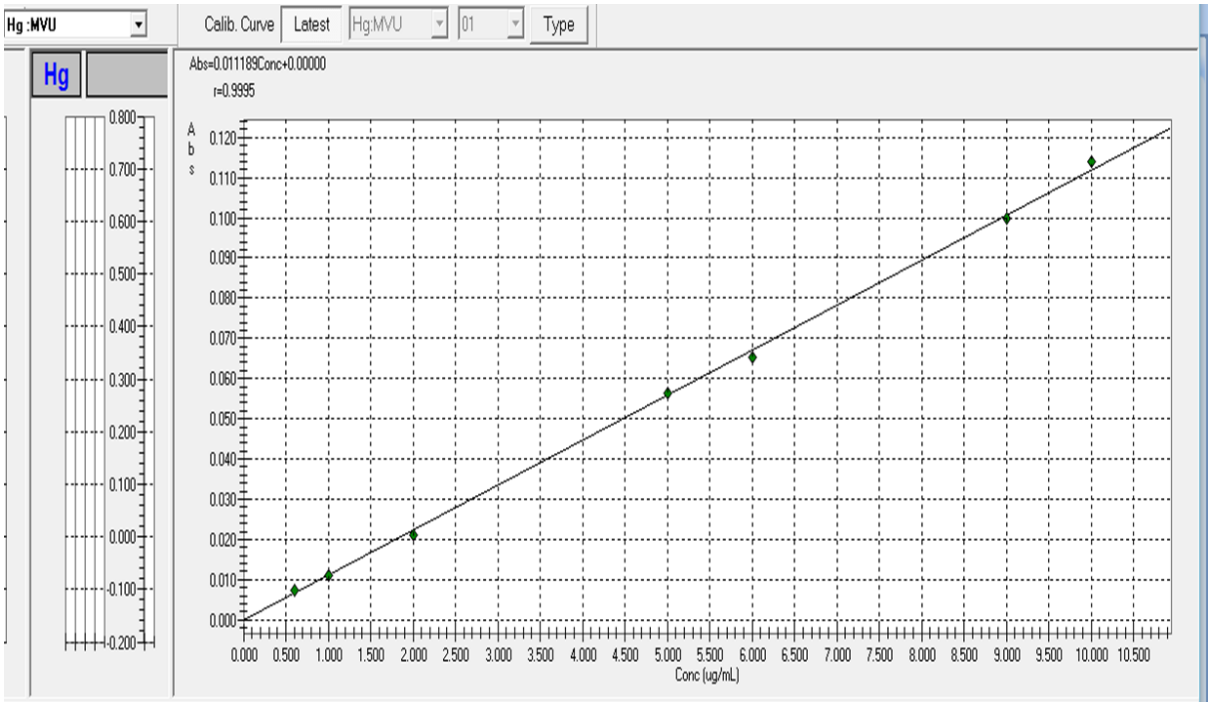

FIGURE 3.3: Calibration curve for the determination of total mercury in leachate and groundwater samples

3.10 STATISTICAL ANALYSIS

All the samples were prepared in triplicate and from the triplicate measurements the mean and standard deviations were calculated. Statistical analysis was done using Windows Microsoft Excel and Pearson's correlation coefficient (*r*) was used to test for relationship and significance.

3.11 INSTRUMENTATION

3.11. 1 Flame atomic absorption spectrometry (FAAS)

Flame atomic absorption spectrometry (FAAS) was used to determine the concentrations of selected cations such as Mn, Cr, Cu, Co, Pb, Zn and Fe in leachate, sediment and groundwater samples. The concentrations of cations were correlated with the concentrations of mercury in order to determine their influence on the behaviour of mercury in landfill leachate, sediment and groundwater. The analysis of cations was conducted using an atomic absorption spectrometer from Shimadzu AA-7000 (Japan). Calibration standards were prepared from certified standards (1 000 mg/L) supplied by Fluka Analytical (Switzerland) and Merck (Germany). A correlation coefficient of 0.999 was obtained for all cation calibration curves used. A minimum of six concentration points were used for external standard calibration. Table 3.1 shows the optimal conditions for flame atomic absorption spectrophotometry (FAAS) required for the analysis of cations and mercury.

TABLE 3.2: Optimal conditions for FAAS for determination of cations and total mercury

Instrument information Flame atomic absorption spectrometry: Shimadzu, Model AA-7000									
	Optical parameters				Atomiser/gas flow rate				Calibration curve regression (r^2)
Metal	**Lamp current low (mA)**	**Wavelength (nm)**	**Slit width (mn)**	**Lamp mode**	**Fuel gas flow rate (L/min)**	**Support gas flow rate (L/min)**	**Flame type**	**Burner height**	
Zn	8	213.9	0.7	BGC-D2	1.1	15	Air-C_2H_2		0.9988
Ag	10	328.1	0.7	BGC-D2	2.4	15		5	0.9995
Au	10	242.8	0.7		1.8	15		7	0.9993
Co	12	240.7	0.2		1.6	15		7	0.9963
Cr	11	357.9	0.7		2.8	15		7	0.9993
Cu	8	324.8	0.7		1.4	15		5	0.9993
Fe	12	248.3	0.2		2.2	15		9	0.9904
Mn	10	279.5	0.2		2.2	15		5	0.9967
Ni	10	232.0	0.2		1.9	15		5	0.9915
Pb	10	283.3	0.7		2.1	15		5	0.9986
Instrument information Atomic absorption spectrometry - mercury vapour unit: (Shimadzu, Model AA-7000, Shimadzu MVU-A1)									
Hg	4	253.7	0.7		2.7	15	None	17.5	

3.11.2 Cold vapour atomic absorption spectrometry (CVAAS)

The mercury vapour unit (MVU-A1) system was mounted on the atomic absorption spectrometer, Shimadzu AA-7000 model, for determining total mercury in leachate, sediment and groundwater samples. Mercury was measured by carefully transferring 250 mL sample to the mercury vapour unit reaction vessel. About 6 mL of stannous chloride was used to reduce mercury into elemental mercury vapour and the mercury was vaporised in approximately 30 seconds. Mercury vapour generated is then transported to the gas cell assembled on the burner head of AAS by a pump, where the amount of mercury can be determined by measuring the absorption at the resonance wavelength of 253.7 nm. After waiting for about 1.5 min for the mercury absorption signal to build up to a steady noise-free plateau, the amount of total mercury in the sample was then measured.

3.11.3 Ion chromatography (IC)

The analysis of selected anions in leachate, sediment and groundwater samples (F^-, Cl^-, SO_4^- and NO_3^-) was undertaken using ion chromatography (IC). Anions are known to play a role in the complexation of mercury in leachate, sediment and soil. The concentrations of anions obtained were correlated with the concentration of mercury in order to determine their influence in the behaviour of mercury in leachate, sediment and groundwater samples. The analysis of anions was conducted on a Metrohm 883 basic IC plus from Switzerland. Four external level calibrations were used for quantification. A stock solution of certified mixed standards (1 000 mg/L) supplied by Merck Chemicals (Pretoria, South Africa) was used for preparing calibration standards.

CHAPTER 4

LEACHATE SEEPAGE FROM SELECTED LANDFILL SITES AS A SOURCE OF MERCURY CONTAMINATION OF GROUNDWATER IN SOUTH AFRICA

4.1 PREAMBLE

This chapter contains a discussion of the results of the research work submitted for consideration for publication in the journal *Water SA*, by Vhodaho *et al*. (2018). The concentrations of total mercury in leachate, sediment and groundwater samples were determined. A paper entitled "Leachate seepage from selected landfill sites as a source of mercury contamination of groundwater in South Africa" was also presented at the *3rd Annual Symposium and Workshop on Environmental Research and Pollution Monitoring of Environmental Persistent Pollutants*, 2 – 7 October, 2017, Pretoria, South Africa.

4.2 INTRODUCTION

The rapid increase in economic activities and population growth, as well as industrial development coupled with urbanisation, has resulted in a continuous increase in the generation of municipal solid waste (MSW) in most countries, including South Africa (Gwebu, 2003; Ayuba *et al*., 2003). Mercury is known to cause health problems such as tremors, delusions, memory loss and neurocognitive disorders (Clarkson & Magos, 2006). Given its unique characteristics, mercury has been used for many centuries in the production of consumer products such as thermometers, electrical switches, fluorescent light bulbs, batteries, biocides and pesticides, cosmetics, dental amalgam filling and others (Pacyna *et al*.,

2003). At the end of their life span, mercury-containing products form part of municipal solid waste (MSW) that are collected and disposed of into landfills where mercury and other pollutants could be leached into landfill leachates. Consequently, mercury may become an important constituent of the resulting leachate which is often characterised by high loads of dissolved organic matter, inorganic macro-components, metals and other xenobiotic organic compounds (Christensen *et al*., 1994; Christensen *et al*., 2001). The leachate may percolate through the soil to contaminate the groundwater, particularly in an unlined landfill (Mor *et al*., 2006)

South Africa is a water-scarce country and as a result, many people tend to rely on borehole water as a source of drinking water (Blignaut & Van Heerden, 2009). This may result in their exposure to the toxic effects of mercury, particularly for those who are living within the vicinity of landfills. Therefore, the aim of this chapter is to determine the concentrations of total mercury in leachate from landfill sites as well as in the sediment samples and groundwater samples collected from monitoring wells within the investigated landfill sites.

4.3 EXPERIMENTAL PROCEDURE

4.3.1 Materials and methods

Details of the materials and method procedures employed in this research work are described in Chapter 3. The sample collection and preparation procedures for analysis are outlined in Section 3.3.2. Leachate, sediment and groundwater samples were collected from the four selected landfill sites (Thohoyandou, Soshanguve, Onderstepoort and Hatherley) in Limpopo and Gauteng Provinces during summer and winter.

4.4 RESULTS AND DISCUSSION

4.4.1 Total mercury concentrations in leachate, sediment and groundwater samples

Table 4.1 shows the mean concentrations of total mercury (THg) in leachate, sediment and groundwater samples from the four selected landfill sites (Thohoyandou, Soshanguve, Hatherley and Onderstepoort) during winter and summer. The mean concentrations and standard deviations presented are the results of triplicate extraction and analysis of each sample. The mean concentrations of total mercury obtained in leachate, sediment and groundwater samples were higher in winter than in summer. Several factors, including the age of the landfill (Kjeldsen *et al*., 2002), the composition of the waste materials disposed of into the landfill, and the prevailing climatic conditions of a particular area are known to influence the composition and the chemistry of landfill leachate. In this study, the measured concentrations of the total mercury in leachate, sediment and groundwater samples in winter and summer are likely to have been affected by any of the aforementioned factors. For instance, the intensity of precipitation is known to have a strong influence on leachate composition because rainwater infiltration into the landfill leachate can dilute chemical components contained in the landfill leachate (Vadillo *et al*., 1999).

TABLE 4.1: Mean concentrations of total mercury in leachate, sediment and groundwater ± SD (standard deviation)

Landfill ID	**Leachate (µg/L)**		**Sediment (µg/g)**		**Groundwater (µg/L)**	
	Winter	Summer	Winter	Summer	Winter	Summer
Thohoyandou	2.07 ± 0.28	0.12 ± 0.002	0.48 ± 0.002	0.03 ± 0.001	2.12 ± 0.28	0.09 ± 0.001
Soshanguve	1.20 ± 0.27	0.10 ± 0.01	0.62 ± 0.61	0.04 ± 0.01	1.66 ± 1.18	ND
Hatherley	1.31 ± 0.51	0.42 ± 0.001	0.78 ± 0.53	0.06 ± 0.02	NA	NA
Onderstepoort	2.41 ± 0.35	0.12 ± 0.01	0.50 ± 0.18	0.03 ± 0.001	2.44 ± 0.47	0.05 ± 0.001

ND: not detected; NA - not analysed (groundwater samples were not accessible at the Hatherley landfill site)

Winter and summer seasons in Gauteng and Limpopo Provinces are characterised by low and high precipitation, respectively. The seasonal precipitation trend in both provinces may explain the higher and lower concentrations of total mercury obtained during winter and summer in leachate, sediment and groundwater samples. Furthermore, waste-pickers were observed at all the landfill sampling sites where they often undertake on-site waste sorting for recycling purposes. It is, therefore, possible that the low concentrations of total mercury determined in leachate, sediment and groundwater samples from these sites may have been influenced by these practices. The Onderstepoort landfill site exhibited the highest mean concentration of total mercury (2.41 ± 0.35 µg/L) in leachate samples during winter. This suggests that more mercury-bearing waste may have been disposed of at this site compared to Thohoyandou, Soshanguve and Hatherley landfill sites.

Although the Thohoyandou landfill site is situated in Limpopo Province, a developing area, and it is surrounded mainly by rural communities, much higher concentrations of total mercury in leachate (2.07 ± 0.28 µg/L) and groundwater (2.12 ± 0.28 µg/L) samples were detected in samples collected during winter compared to those collected during winter from Soshanguve and Hatherley landfill sites, which are situated in a more developed, highly populated and industrialised part of the country (Gauteng Province). The concentration profiles observed in the investigated matrices may be a reflection of the consumption or usage patterns of mercury-containing products in these areas. Additionally, the observed pattern may be an indication of the ratio of waste items containing mercury to the overall waste materials disposed of into a particular landfill. It is, therefore, expected that landfills situated in areas with low population densities may contain high levels of mercury and other contaminants because of the relatively lower quantities of the overall waste materials being received. Furthermore, Limpopo Province is richly endowed with geothermal springs which

are natural sources of mercury. In a study conducted by Olivier *et al*. (2010), the concentrations of total mercury determined from Siloam and Tshipise geothermal springs were 0.53 and 0.33 µg/L, respectively. The natural occurrence of mercury in groundwater is another important factor that needs to be considered, which may have contributed to the relatively higher concentrations of total mercury detected in the groundwater samples from Thohoyandou landfill site. The mean concentrations of total mercury in groundwater samples in Thohoyandou, Soshanguve and Onderstepoort landfill sites during winter exceeded the maximum contaminant level (MCL) for mercury in drinking water of 1.00 µg/L and 2.00 µg/L set by WHO, NL, USEPA and SA, respectively (Table 4.2). Mercury in all its forms is toxic to human health. Exposure to mercury may lead to health problems such as tremors, delusions, memory loss and neurocognitive disorders (Clarkson & Magos, 2006). People living in the areas surrounding Thohoyandou, Soshanguve and Onderstepoort landfill sites may be susceptible to the toxic effect of mercury through the consumption of contaminated water.

TABLE 4.2: Maximum contaminant level (MCL) of mercury in drinking water compared to concentrations obtained in the present study

Organisation	**Maximum contaminant level**	**Unit**	**Present study (µg/L)**	
			Winter	**Summer**
WHO	1*	µg/L	2.12 ± 0.28	0.09 ± 0.001
USEPA	2	µg/L	1.66 ± 1.18	ND
SA	1*	µg/L	2.44 ± 0.47	0.05 ± 0.001

*Source: Adapted from Mamba *et al*.(2008). Data from World Health Organization, European Union, The Netherlands, United States Environmental Protection Agency (USEPA) and South Africa.

4.4.2 Comparison with other studies

The concentrations of total mercury in leachate, sediment and groundwater samples obtained in the present study were compared to concentrations obtained in other studies (Table 4.3). The concentrations of total mercury in leachate samples obtained in the present study were in the same range as those reported by Schoeman *et al*. (2003), which ranged from 0.2 – 0.3 µg/L. It is possible that factors similar to those reported in the present study may have influenced the measured mercury levels in Schoeman *et al*. (2003) study. In another study conducted by Tshibalo (2017), the concentration of total mercury in leachate samples from Onderstepoort landfill was found to be 15.0 µg/L, which is significantly higher than those observed in the present study. This can be attributed to the different sampling points for leachate samples for both studies.

Other studies conducted in China by Li *et al*. (2005) and Tang *et al*. (2003) gave concentrations of total mercury in leachate samples of up to 0.08 µg/L and 0.1 – 1.016 µg/L, respectively; both these concentrations of total mercury in leachate were within the same range as the concentrations determined in the present study. This finding may imply that the waste composition and the quantity of mercury-containing consumer products contained in the studied Chinese landfill sites may be similar to those contained in South African landfills. In the USA, Aucott (2006) reported the concentration of total mercury in leachate to be 7.15 µg/L. This is higher compared to the concentrations determined in the current study.

TABLE 4.3: Mean concentrations of total mercury in other studies compared to those determined during the present study

Matrixes	THg concentrations	References
Leachate	0.2-0.3 µg/L	Schoeman *et al*., 2003
Leachate	15.0 µg/L	Tshibalo, 2017
Leachate	0.079 µg/L	Li *et al*., 2005
Leachate	0.1-1.016 µg/L	Li *et al*., 2005
Leachate	7.15 µg/L	Aucott, 2006
Leachate	1.7-8.3 µg/L	Esakku *et al*., 2003
Leachate	0.013-0.027 µg/L	Øygard *et al*., 2004
Leachate	**1.20-2.41 µg/L**	**Present study Winter**
Leachate	**0.10-0.42 µg/L**	**Present study Summer**
Sediment	0.29-0.76 µg/g	Machado *et al*., 2002
Sediment	0.188-6.53 µg/g	Cheng and Hu, 2011
Sediment	314 µg/g	Tshibalo, 2017
Sediment	**0.48-0.78 µg/g**	**Present study Winter**
Sediment	**0.0-0.06 µg/g**	**Present study Summer**
Groundwater	1-32 µg/L	Samadder *et al*., 2017
Groundwater	2-5 µg/L	Tshibalo, 2017
Groundwater	**1.06-2.44 µg/L**	**Present study Winter**
Groundwater	**nd-0.09 µg/L**	**Present study Summer**

According to the US Environmental Protection Agency (EPA), about 54% of the municipal solid waste in the USA is disposed of in a landfill (Tolaymat *et al.,* 2010). Considering that the USA is a highly developed country, landfills are likely to be constructed with geomembrane liners and with good leachate drainage systems which may yield leachate with high mercury concentrations. This may explain the higher concentration of total mercury determined in the USA study compared to that observed in the current study. Furthermore, the occurrence of mercury-containing products may be higher in USA landfill sites compared to South African landfill sites. According to Esakku *et al*. (2003), the concentrations of total mercury in seven leachate samples from selected landfill sites in India ranged from 1.70 to 8.3 µg/L. Only two of the samples from the Esakku *et al*. (2003) study were found to have higher concentrations of total mercury than those observed in the present study. The solid waste management practices in India are mostly based on open dumping with poorly constructed drainage systems, if any. These factors may partly be responsible for the low concentrations determined in the present study. In Western Norway, Øygard *et al*. (2004) determined the concentrations of total mercury from four landfill sites leachate samples, and these ranged from 0.013 to 0.027 µg/L. The occurrence of mercury-containing products in Western Norway landfills may be lower and thus the reported low concentrations. The concentrations of total mercury in landfill sediment samples have been determined by other researchers. Studies conducted on a landfill site in Brazil gave concentrations of total mercury in sediment samples of 0.76 µg/g, 0.29 µg/g and 0.36 µg/g (Machado *et al*., 2002). In another study conducted in China, Cheng and Hu (2011) reported mercury concentrations of 0.188-6.53 µg/g in landfill sediment samples, and in South Africa, Tshibalo (2017) reported a total mercury concentration of 314 µg/g in sediment samples from the Onderstepoort landfill site. The concentrations obtained by these three researchers were higher compared to the concentrations obtained in the current study. In a study conducted by

Samadder *et al*. (2017), the levels of total mercury from 15 landfill borehole water samples were reported and the measured concentrations ranged from 1 to 32 µg/L; these mercury concentrations are more than an order of magnitude higher than those reported in the present study. The high concentrations of total mercury obtained in the Samadder *et al*. (2017) study can be attributed to the high population and possibly due to other socio-cultural practices in India which may have resulted in higher generation of mercury-containing wastes. Tshibalo (2017) reported total mercury concentrations of 2 to 5 µg/L in two borehole water samples from the Onderstepoort landfill site.

4.5 CONCLUSIONS

The present study has shown the occurrence and concentrations of total mercury in landfill leachate, sediment and groundwater samples from selected landfill sites in winter and summer seasons. The concentrations of total mercury were notably markedly higher in winter compared to summer in all analysed samples, possibly due to the dilution effects caused by the high precipitation in summer. It can be concluded that the possibility of landfill leachate contaminating groundwater exists, especially were the landfills are not lined with geomembrane material. Although the Thohoyandou landfill site is located in Limpopo Province, a typical developing area, the concentrations of total mercury measured at this site were relatively higher compared to the concentrations determined at landfills situated within the Gauteng Province. Considering the fact that the concentrations of total mercury measured in groundwater samples exceeded the specified maximum guideline limit established by most regulatory agencies for drinking water, it is likely that people living in the areas surrounding the Thohoyandou landfill site, in particular, and who depend on groundwater for their livelihood may be prone to the deleterious effects of mercury.

CHAPTER 5

RESULTS AND DISCUSSION

ANION AND CATION ANALYSIS AND THEIR POSSIBLE RELATIONSHIP WITH MERCURY

5.1 PREAMBLE

This chapter contains the results of the study and a discussion of the potential influence of cations and anions on the behaviour of mercury in leachate, sediment and groundwater samples. Results from the Pearson correlation test between mercury and cations are also discussed.

5.2 EXPERIMENTAL PROCEDURE

5.2.1 Materials and methods

The materials and methods that were employed are described in Chapter 3, with the materials and sample preparation procedures described in Sections 3.2.2 and 3.3.3, respectively. Leachate, sediment and groundwater samples were collected during summer and winter from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites in Gauteng and Limpopo Provinces.

5.3 RESULTS AND DISUSSION

5.3.1 The effect of cations on the behaviour of mercury

The concentrations of selected cations, namely manganese (Mn), chromium (Cr), copper (Cu), cobalt (Co), lead (Pb), zinc (Zn) and iron (Fe) in leachate, sediment and groundwater samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites were determined along with the determination of total mercury. The determination of these parameters was of importance since they are more likely to influence the behaviour, mobility, bio-availability and the toxicity of mercury in the environment. The presence of cations in leachate, soils and sediments may facilitate the mobilisation of mercury from the natural environment into streams, lakes and groundwater.

Figure 5.1 shows the concentrations of selected cations that were determined in leachate samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites during winter and summer. Higher concentrations of cobalt that ranged from 159 ± 1.83 – 896 ± 0.32 µg/L were determined in leachate samples from Hatherley, Onderstepoort and Soshanguve landfill sites in winter than in summer, and only Hatherley landfill site showed the highest concentrations of cobalt during summer. The concentrations of manganese in leachate samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort during winter and summer ranged from 73.9 – 738 µg/L, ND – 916 µg/L, ND – 574 µg/L and ND – 564 µg/L, respectively. The concentrations of manganese in leachate samples were higher in summer compared to winter. The concentrations of cobalt in leachate samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites during winter and summer ranged from ND – 2.17 µg/L, ND – 896 µg/L, 159 – 707 µg/L and ND – 837 µg/L, respectively, and the concentrations of lead ranged from 228 – 447 µg/L, ND – 170 µg/L,

78.8 – 219 µg/L and 102 – 157 µg/L, respectively. Elevated concentrations of cations were determined in sediment samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites during summer and winter compared to concentrations in leachate samples (Figure 5.2). A high concentration of manganese that reached 912 µg/L was detected in Thohoyandou sediment samples during winter.

The concentrations of iron in sediment samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites were higher during winter and summer. This may be attributed to the natural abundance of iron in the earth's crust. The concentrations of iron determined in sediment samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort ranged from 31.9 – 395 µg/g, 31.9 – 337 µg/g, 443 – 508 µg/g and 348 – 633 µg/g during winter and summer, respectively. The concentrations of chromium in sediment samples ranged from 50.5 – 364 µg/g, ND – 260 µg/g, 119 – 261 µg/g and ND – 328 µg/g during winter and summer, respectively, and the concentrations of zinc ranged from 49.2 – 77.5 µg/g, 154 – 210 µg/g, 1.38 – 288 µg/g and 53.8 – 104 µg/g during both winter and summer, respectively.

Figure 5.3 shows the concentrations of cations in groundwater samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites. The highest concentrations of manganese were determined in Thohoyandou landfill site during winter compared to Soshanguve, Hatherley and Onderstepoort during winter and summer. The concentrations of chromium in groundwater samples from Thohoyandou and Soshanguve landfill sites ranged from 378 – 460 µg/L and ND – 632 µg/L during winter and summer, respectively. The concentrations of lead in groundwater samples from Thohoyandou, Soshanguve and

Onderstepoort ranged from 318 – 482 µg/L, ND – 167 µg/L and 125 – 283 µg/L, respectively. The concentrations of manganese in Thohoyandou, Soshanguve and Onderstepoort ranged from 161 – 879 µg/L, ND and ND – 7.90 µg/L during winter and summer, respectively.

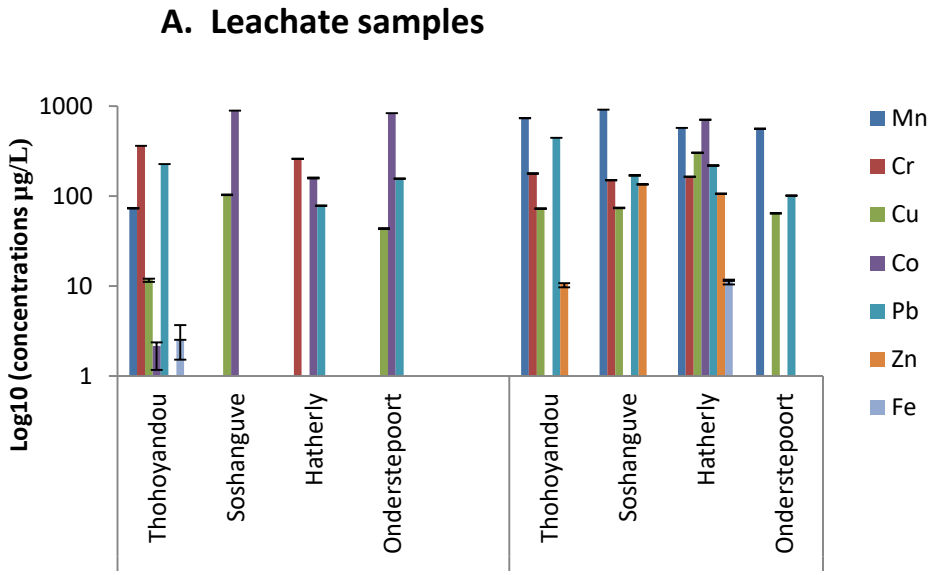

FIGURE 5.1: Concentrations of selected cations in leachate samples in winter and summer

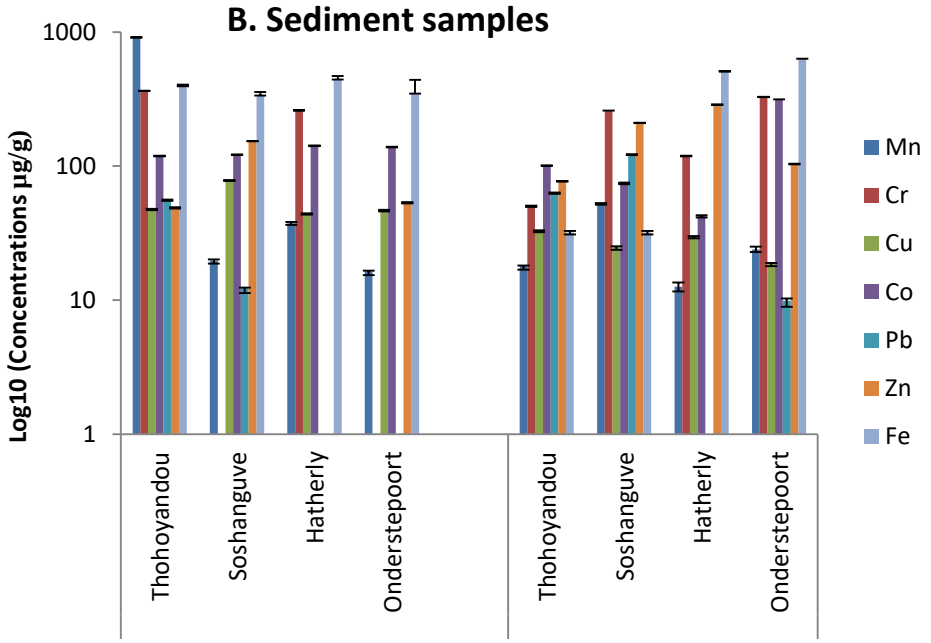

FIGURE 5.2: Concentrations of selected cations in sediment samples in winter and summer

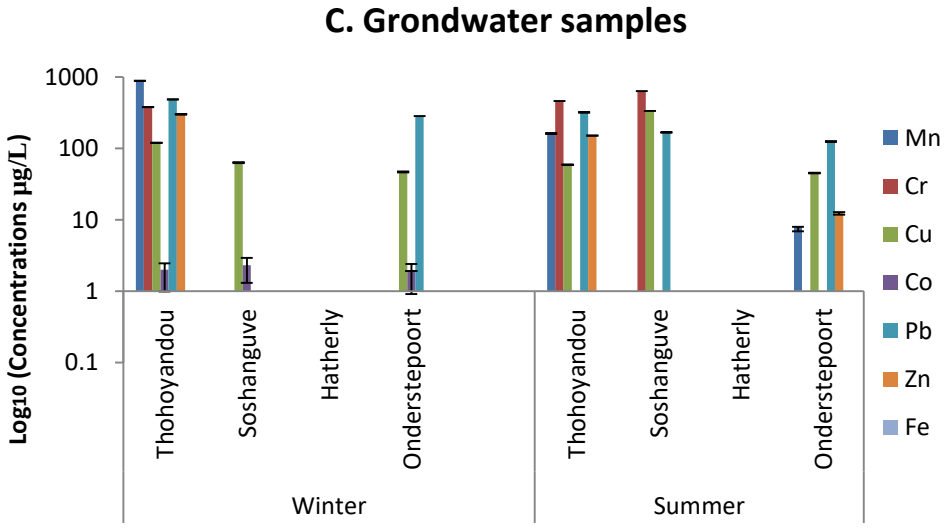

FIGURE 5.3: Concentrations of selected cations in groundwater samples in winter and summer

Pearson correlation coefficients of mercury with cations in leachate, sediment and groundwater samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites are shown in Tables 5.1 and 5.2, respectively. Strong positive correlations (r = 1.00) were observed between mercury and chromium, mercury and copper and between mercury and lead in leachate samples from Thohoyandou and Onderstepoort during winter (Table 5.1), possibly suggesting similar sources of these metals. The association of mercury with those cations was significant (p-value = 0.00). A moderate positive correlation (r = 0.67) between mercury and cobalt was also observed in Hatherley but this was not significant (p-value>0.05), and moderate negative correlations (r = -0.66, -0.66 and -0.78) were observed between mercury and copper, mercury and lead and between mercury and zinc in Thohoyandou and Soshanguve (p-value>0.05) respectively. Strong negative correlations (r = -0.90, -0.87, -0.99, -0.93) were also observed between mercury and manganese, mercury and cobalt and between mercury and chromium in Thohoyandou, Hatherley and Onderstepoort, respectively, but these were not significant (p-value>0.05). A negative correlation was observed between mercury and lead but it was not significant (p-value = 0.052). During summer, a moderate positive correlation (r = 0.65) was observed between mercury and lead (p-value = 0.55) in Thohoyandou and strong positive correlations (r = 0.95, 0.84, 0.86 and 0.98) between mercury and manganese, mercury and zinc, mercury and cobalt and between mercury and lead were observed in Soshanguve, Hatherley and Onderstepoort, respectively.

With respect to the sediment samples (Table 5.2), moderate negative correlations (r = -0.76 and r = 0.81) between mercury and lead and between mercury and zinc were observed in Thohoyandou, Soshanguve and Hatherley during winter. Moderate positive and negative correlations (r = 0.88, 0.98, -0.94, 0.80 and -0.95) were also observed between mercury and iron in Thohoyandou, Soshanguve, Hatherley and Onderstepoort during winter and summer

(*p*-value>0.05), respectively. The geochemistry of mercury and iron are closely related and mercury can be adsorbed by iron oxides in soils. According to Barringer and Szabo (2006), the sorption of mercury to iron hydroxides in soils is its major mechanism for attenuation but the presence of sulphide can reduce dissolved iron(II) hydroxides, thereby facilitating the release of the sorbed mercury thus leading to groundwater contamination. Elevated concentrations of total mercury that exceeded drinking water standards were determined in groundwater samples from Thohoyandou and Soshanguve landfill sites. The presence of iron in sediment samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites may have facilitated the mobilisation of mercury into groundwater.

The chemistry of mercury, particularly in aqueous systems, needs to be fully understood in order to be able to provide a clear explanation about its state, distribution and occurrence in such environments. Mercury showed strong positive correlations (r = 1.00) with manganese and zinc in summer (p-value = 0.009), and strong positive and negative correlations also occurred between mercury and manganese, mercury and lead, mercury and zinc, mercury and cobalt and between mercury and chromium. According to Fernandez-Martinez *et al*. (2005) the influence of manganese on the mobility of mercury in soil was due to the fact that the presence of manganese oxides is known to promote the solubility of mercury sulphide (HgS) in hydrochloric acid solutions. This may further explain the strong correlation between mercury and manganese in sediment samples which may have facilitated the mobilisation of mercury from sediment samples into groundwater in the present study. Strong positive and negative correlations (r = -0.97, 0.085, -0.89, 0.99, -0.98, 0.98, -0.93) between mercury and lead, mercury and zinc, mercury and cobalt and between mercury and iron were observed in groundwater samples (Table 5.3) from Thohoyandou and Onderstepoort (p-value<0.05) during summer and winter, respectively.

The concentrations of cations in groundwater samples from Thohoyandou, Soshanguve, and Onderstepoort landfill sites were further compared to the maximum contaminant level (MCL) for cations in drinking water (Table 5.4). Lower concentrations of certain cations are essential for human health but once they exceed their specified threshold limits, they can be toxic to human health. The concentrations of lead, manganese, zinc and chromium exceeded the specified maximum contaminant levels for drinking water set by WHO, EU, NL and SA. The presence of these toxic metals in drinking water can pose serious health problems to consumers. For instance, lead is known to affect children's mental development, and lead in children's blood can lead to a decreased intelligence quotient (IQ) (Chen *et al.*, 2007). It has also been established that it can cause hearing, balance and attention impairments. In pregnant women, exposure to high levels of lead can cause miscarriage (Kessel & O'Connor 2001). Studies conducted by He *et al*. (1994) on children indicated that children who ingested manganese in drinking water (≥241 µg/L) for a minimum of three years performed more poorly in school compared to non-exposed children. Chronic exposure to chromium can cause damage to liver, kidney circulatory and nerve tissue and the intake of higher concentrations of zinc in drinking water is known to cause nausea, vomiting and diarrhoea.

TABLE 5.1: Pearson correlation of mercury with cations in leachate samples in two seasons

Winter					**Summer**				
	Thohoyandou	**Soshanguve**	**Hatherly**	**Onderstepoort**		**Thohoyandou**	**Soshanguve**	**Hatherly**	**Onderstepoor**t
	Hg	Hg	Hg	Hg		Hg	Hg	Hg	Hg
Hg	1	1	1	1	Hg	1	1	1	1
Cu	0.91	-0.66		1.00*	Cu	-0.43	-0.63	0.15	
Pb	-0.66		-1.00*	1.00*	Pb	0.65	0.35	0.04	0.98
Mn	-0.90				Mn	-0.51	0.95	0.93	-0.83
Zn	-0.78				Zn		-0.44	0.84	
Co	-0.87	-0.79	0.67	-0.99	Co			0.86	
Fe	0.43				Fe			-0.31	
Cr	1.00*		-0.93		Cr	0.11	0.17	0.31	-0.61

Degree of significance (*p-value<0.05)

TABLE 5.2: Pearson correlation of mercury with cations in sediment samples in two seasons

Winter						**Summer**			
	Thohoyandou	**Soshanguve**	**Hatherly**	**Onderstepoort**		**Thohoyandou**	**Soshanguve**	**Hatherley**	**Onderstepoort**
	Hg	Hg	Hg	Hg		Hg	Hg	Hg	Hg
Hg	1	1	1	1	Hg	1	1	1	1
Cu	0.84	0.20	-0.53	-0.05	Cu	0.58	0.0090	-0.95	0.23
Pb	-0.76	-0.84			Pb	0.09	0.99		0.94
Mn	-0.96	-0.99*	0.23	-0.14	Mn	1.00*	-0.30	-0.99*	0.43
Zn	-0.81	0.29	0.62	-0.93	Zn	0.73	-0.48	0.94	1.00*
Co	0.63	-1.00*	-1.00*	-0.53	Co	0.80	-0.62	0.82	0.68
Fe	0.88	0.98		-0.19	Fe	-0.94	0.04	0.80	-0.95
Cr	-1.00*	-0.88	0.75		Cr	0.33	-0.90	0.99*	0.81

Degree of significance (*p-value<0.05)

TABLE 5.3: Pearson correlation of mercury with cations in groundwater samples in two seasons

Winter				**Summer**			
	Thohoyandou	**Soshanguve**	**Onderstepoort**		**Thohoyandou**	**Soshanguve**	**Onderstepoort**
	Hg	Hg	Hg		Hg	Hg	Hg
Hg	1	1	1	Hg	1	1	1
Cu	0.28	0.70	0.16	Cu	0.96	0.0090	0.93
Pb	-0.97		0.085	Pb	-0.89	0.99*	-0.99*
Mn	0.33		-0.49	Mn	0.98	-0.032	-0.55
Zn	-0.98			Zn	0.63	-0.48	-0.48
Co	0.93	0.87	-0.47	Co		-0.62	
Fe	-0.93		0.19	Fe			
Cr	0.68			Cr	-0.94	-0.90	0.50

Degree of significance (*p-value<0.05)

TABLE 5.4: Maximum contaminant level (MCL) of cations in drinking water compared to concentrations obtained in groundwater samples

						Present study Thohoyandou		**Soshanguve**		**Onderstepoort**	
Trace metal	**Unit**	**WHO Max limit**	**EU Max limit**	**NL Max limit**	**SA Max limit**	**Win**	**Sum**	**Win**	**Sum**	**Win**	**Sum**
Cu	µg/L	2 000	2 000	2 000	1 000	120 ± 0.02	59.5 ± 0.01	63 ± 0.06	334 ± 0.45	47 ± 0.01	45.5 ± 0.008
Pb	µg/L	10	10	10	20	482 ± 0.10	318 ± 1.37	ND	167 ± 0.98	283 ± 0.12	283 ± 0.33
Mn	µg/L	500	50	50	100	879 ± 0.12	161 ± 0.08	ND	ND	ND	7.9 ± 0.06
Zn	µg/L	3		3	5	300 ± 0.02	151 ± 0.04	ND	ND	ND	12.7 ± 0.01
Co	µg/L					1.99 ± 0.44	ND	2.31 ± 0.62	ND	1.91 ± 0.48	ND
Fe	µg/L	300	200	200	200	ND	ND	ND	ND	ND	ND
Cr	µg/L	50	50	50	100	378 ± 0.09	460 ± 0.27	ND	632 ± 0.06	ND	ND

*Source: Adapted from Mamba *et al*. (2008). Data from World Health Organization, European Union, The Netherlands, United States Environmental Protection Agency and South Africa

ND: not detected

5.3.2 The effect of anions on the behaviour of mercury

Figures 5.4, 5.5 and 5.6 show the mean concentrations of selected anions, namely fluoride (F), chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^-) in leachate, sediment and groundwater samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites during winter and summer. The concentrations of chloride in leachate, sediment and groundwater samples from all the selected landfill sites ranged from 121 – 759 µg/L, 104 – 734 µg/g and 185 – 392 µg/L during winter and summer, respectively. The behaviour and fate of mercury soil, sediment and aquatic media is normally controlled by adsorption and desorption processes. Mercury has a high affinity for ligands such as OH^- and Cl^- and forms strong complexes with these ions (Schuster, 1991). Mercury(II) chloride ($HgCl_2$) and mercury(II) hydroxide ($Hg(OH)_2$) have high solubility in water and the affinity of mercury for OH^- and Cl^- increases its mobility. The occurrence of chloride in leachate and sediment samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort may have influenced the mobilisation of mercury into groundwater resulting in the high concentrations of total mercury that were determined in the present study.

The concentrations of sulphate in leachate, sediment and groundwater samples from all the selected landfill sites ranged from ND – 675 µg/L, ND – 820 µg/g and ND – 862 µg/L in winter and summer, respectively. Mercury tends to bind strongly to sulphur in soils and aquatic organic matter to form mercuric sulphide (HgS) which is a stable and less soluble compound. Mercury is known to have a strong affinity for sulphur which normally results in the binding of mercury to soil organic matter. The strong complexation between mercury and sulphur may have contributed to the bio-availability of mercury in leachate and sediment

samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites. Fluoride is known act as ligands in the complexation reactions with mercury (Ochoa-Gonzalez *et al*., 2013). The concentrations of fluoride in leachate, sediment and groundwater samples from the selected landfill sites ranged from ND – 734 µg/L, 513 – 894 µg/g and 618 – 891 µg/L during winter and summer, respectively. The concentrations of nitrate in leachate, sediment and groundwater samples ranged from ND – 621 µg/L, 117 – 909 µg/g and 102 – 875 µg/L, respectively.

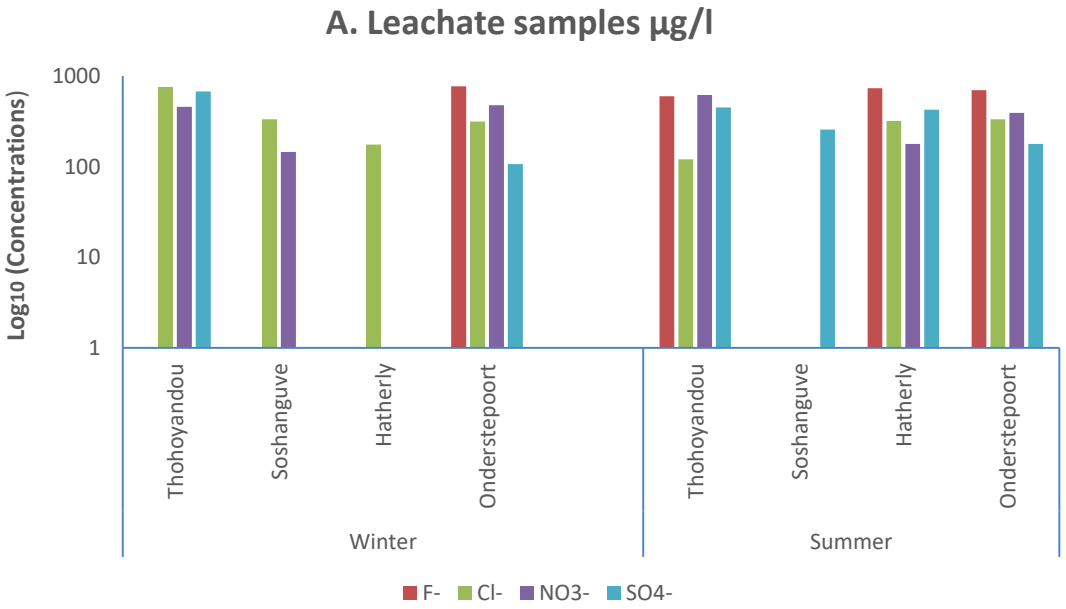

FIGURE 5.4: Concentrations of selected anions in leachate samples in winter and summer

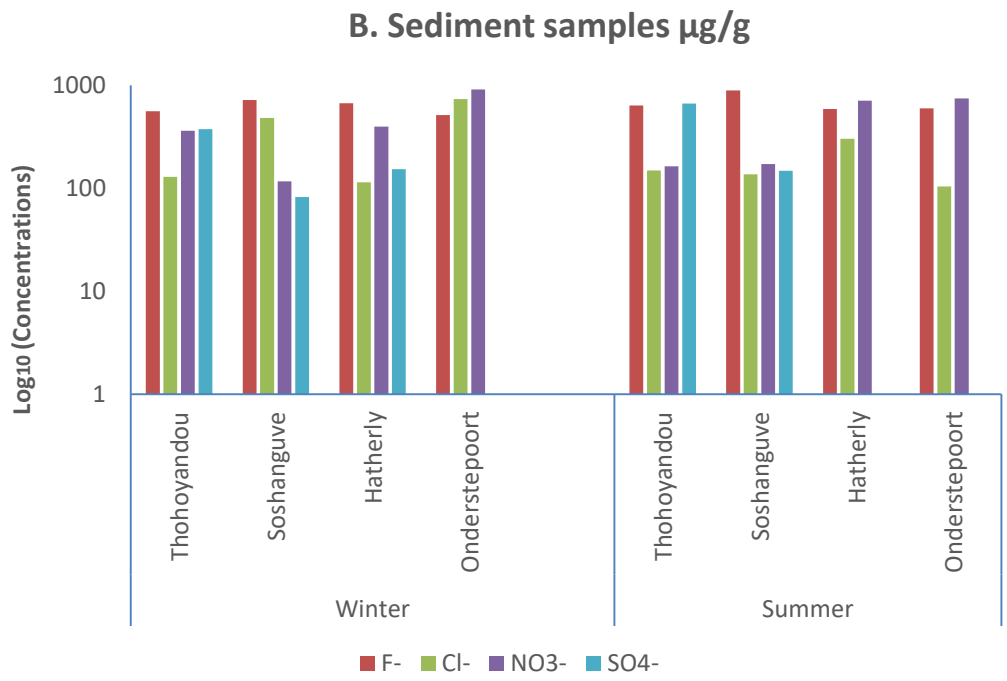

FIGURE 5.5: Concentrations of selected anions in sediment samples in winter and summer

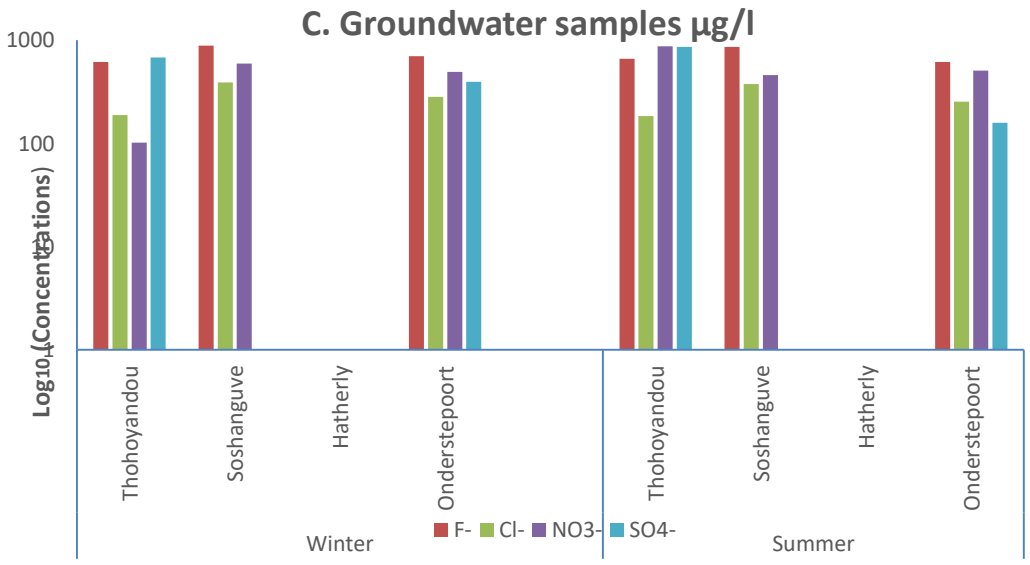

FIGURE 5.6: Concentrations of selected anions in sediment samples in winter and summer

5.3.3 The effect of pH on mercury

The pH of landfill leachate is one of the factors that can influence the toxicity, bioavailability and mobility of mercury in landfill leachate. The pH values that were determined in leachate samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites during winter were 7.78, 8.25, 8.37 and 8.67, respectively, and 7.87, 8.35, 6.69 and 7.22 during the summer season, respectively. Higher leachate pH normally increases the concentration of negatively charged hydroxyl ions (OH^-), which might attract and retain divalent mercury (Xu *et al*., 2014). However, low leachate pH is characterised by high positively charged hydrogen (H^+) ions which play a direct role in several reactions. According to Mahapatra *et al*. (2011), dissolved material in landfill leachate can shift the pH of neutral water either to the acidic or the alkaline side. At a pH that is greater than 7, a greater load of dissolved substances is expected to occur in leachate including dissolved metals. The alkaline nature of landfill leachate is an indicator of the mature stage of the landfill site (Jorstad *et al*., 2004). The alkaline pH determined in Thohoyandou, Soshanguve, Hatherley and Onderstepoort leachate samples may have contributed to the high concentrations of cations, anions and mercury determined in the present study.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

- This study has shown the occurrence and concentrations of total mercury in landfill leachate, sediment and groundwater samples from selected landfill sites in winter and summer seasons.
- The concentrations of total mercury were markedly higher in winter compared to summer in all analysed samples; this might possibly have been due to the dilution effects caused by the high precipitation in summer.
- It can be concluded that the possibility of landfill leachate contaminating groundwater exists, especially where the landfills are not lined with geomembrane material.
- Although Thohoyandou landfill site is located in Limpopo Province, a typical developing area, the concentrations of total mercury measured were relatively higher compared to the concentrations determined at landfills located within the Gauteng Province.
- Considering the fact that the concentrations of total mercury measured in groundwater samples exceeded the specified maximum contaminant level (MCL) established by most regulatory agencies for drinking water, it is likely that people living in the areas surrounding the Thohoyandou landfill site, in particular, and who depend on groundwater for their livelihood may be prone to the deleterious effects of mercury.

- Correlation of mercury with cations suggests that some cations may have an effect on the concentrations of total mercury obtained in leachate, sediment and groundwater samples.
- The occurrence of anions in leachate and sediment samples from Thohoyandou, Soshanguve, Hatherley and Onderstepoort landfill sites may have influenced the mobilisation of mercury into groundwater.
- The alkaline pH determined in the landfill leachate from Thohoyandou, Soshanguve, Hatherley and Onderstepoort may have contributed to the high concentration of mercury, cations and anions that were determined.

6.2 RECOMMENDATIONS

- Due to the higher concentrations of total mercury determined in groundwater samples that exceeded the drinking water standards for mercury, it is suggested that a household solid waste sorting and recycling scheme should be implemented in order to control hazardous waste such as mercury-containing waste from entering waste streams.
- Considering the toxicity of mercury to human health and that most people in the communities depend on groundwater as a source of drinking water, it is recommended that borehole water in the areas surrounding the landfill sites should be monitored for mercury regularly.

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