ASSESSMENT OF MUNICIPAL SOLID WASTE LEACHATE POLLUTION ON SOIL AND GROUNDWATER SYSTEM AT ONDERSTEPOORT LANDFILL SITE IN PRETORIA

By

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DECLARATION

Rudzani Tshibelo, hereby declare that the research study entitled "Assessment of municipal solid waste leachate pollution on soil and groundwater system at Onderstepoort landfill site in Pretoria" is my own work and has never been submitted to any other institution.

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I would also like to acknowledge and express my gratitude to Mr Thabo Mosia who provided guidance and words of encouragement towards the development of this thesis.

My family, words cannot express my appreciation and thank you is not enough for the support you have given me. To my younger brother, Mr Ndivhudzannyi Tshibalo, thank you for support and advice. My deep sense of gratitude to my father, Mr Ndivhudzannyi Tshibalo; my elder brother (Mr Mashudu Tshibalo); my elder sister (Ms Ndivhuho Rabambi); and my grandmother (Mrs Makwarela Tshililo Tshibalo).

TO GOD BE THE GLORY, GREAT THINGS HE HATH DONE.
This study focuses on determining the quality of soil and groundwater at the Onderstepoort Municipal Solid Waste (MSW) landfill site. The study area is situated in Pretoria North, a jurisdiction of City of Tshwane Metropolitan Municipality (CTMM). Samples were collected from three different spheres (i.e. leachate, soil and water) in the study area, to determine the concentration of metals accumulated in each sphere. The three spheres provided an overview of the contaminants found in leachate, soil and water.

The laboratory analyses using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) indicated that soils in the site have been severely contaminated with heavy metals. Higher concentrations of heavy metals occurred in the soils compared to the groundwater surrounding the landfill site and this may be due to the ability of the soil strata to absorb the contaminants caused by the landfill leachate. In essence, the measurements indicated that leachate soil has very high pollutant levels (0.21 to 2505.61 mg/kg); soil was characterised by fairly-high pollutant levels (0.03 to 638.27 mg/kg); leachate solution has given rise to moderate pollutant levels (0.01 to 2.296 mg/L) and water resources have low-moderate pollutant levels (<0.0001 to 0.456 mg/L) depending on the location.

Furthermore, the findings indicated that the soil was contaminated with lead, cadmium, copper, zinc and nickel, and the concentration increases particularly where the generation of leachate is taking place. Groundwater, particularly in Borehole 2 has been moderately contaminated with nitrite, calcium and manganese. The findings also indicated that the concentrations of contaminants become high in borehole located close to the waste dump and decrease further away from the waste dump. The chemical analysis of this groundwater indicated that the concentrations of chemical properties have increased since the year 2009. This was determined through the comparison of groundwater study undertaken in 2009 to the current study results obtained. The site geological formation, Rustenburg Layered Suite is known to contain the anomalies of nickel, chromium, vanadium, copper, arsenic, lead and zinc but these are less toxic and less distributed. Therefore, the primary source of pollution at the study area could be the landfill operation through the generation of leachate affecting both soil and water.
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<td>ARC</td>
<td>Agricultural Research Council</td>
</tr>
<tr>
<td>ATSDR</td>
<td>Agency for Toxic Substances and Disease Registry</td>
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<tr>
<td>BOD</td>
<td>Biochemical Oxygen Demand</td>
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<tr>
<td>BIC</td>
<td>Bushveld Igneous Complex</td>
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<tr>
<td>CGS</td>
<td>Council for Geoscience</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>CRM</td>
<td>Certified Reference Material</td>
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<tr>
<td>CTMM</td>
<td>City of Tshwane Metropolitan Municipality</td>
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<tr>
<td>DEFRA</td>
<td>Department of Environment, Food and Rural Affairs</td>
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<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Content</td>
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<tr>
<td>DWAF</td>
<td>Department of Water Affairs and Forestry</td>
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<td>EC</td>
<td>Electrical Conductivity</td>
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<tr>
<td>EIA</td>
<td>Environmental Impact Assessment</td>
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<td>EPA</td>
<td>Environmental Protection Agency</td>
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<tr>
<td>GIS</td>
<td>Geographical Information System</td>
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<tr>
<td>GPS</td>
<td>Geographical Position System</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma-Mass Spectrometry</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Emission Spectrometry</td>
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<tr>
<td>IRRI</td>
<td>International Rice Research Institute</td>
</tr>
<tr>
<td>ISCW</td>
<td>Institute for Soil, Climate and Water</td>
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<tr>
<td>MAD</td>
<td>Microwave Assisted Digestion</td>
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<tr>
<td>MSW</td>
<td>Municipal Solid Waste</td>
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<tr>
<td>NEMA</td>
<td>National Environmental Management Act</td>
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<tr>
<td>NFLG</td>
<td>Newfoundland and Labrador Government</td>
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<tr>
<td>NNS</td>
<td>National Norms and Standards</td>
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<tr>
<td>NRCS</td>
<td>Natural Resources Conservation Service</td>
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<td>NSW</td>
<td>New South Wales</td>
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<tr>
<td>PMT</td>
<td>Photo Multiplier Tube</td>
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<tr>
<td>PPE</td>
<td>Personal Protective Equipment</td>
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<tr>
<td>RLS</td>
<td>Rustenburg Layered Suite</td>
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<tr>
<td>SANS</td>
<td>South African Norms and Standards</td>
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<tr>
<td>SOP</td>
<td>Standard Operating Procedure</td>
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TDS  Total Dissolved Solids
TECC  Tshikovha Environmental and Communication Consulting
UNEP  United Nations Environment Programme
USDA  United States Department of Agriculture
USEPA  United States Environmental Protection Agency
USGS  United States Geological Survey
WHO  World Health Organisation
XOC  Xenobiotic Organic Compounds
# LIST OF CHEMICAL NOTATIONS

<table>
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<th>Chemical</th>
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<td>Arsenic</td>
<td>As</td>
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<td>Cadmium</td>
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<td>Calcium</td>
<td>Ca</td>
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<tr>
<td>Chloride</td>
<td>Cl</td>
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<tr>
<td>Chromium</td>
<td>Cr</td>
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<td>Cobalt</td>
<td>Co</td>
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<td>Copper</td>
<td>Cu</td>
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<td>Fluoride</td>
<td>F</td>
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<td>Lead</td>
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<td>Magnesium</td>
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<td>Manganese</td>
<td>Mn</td>
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<td>Mercury</td>
<td>Hg</td>
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<tr>
<td>Nitrate</td>
<td>NO₃</td>
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<tr>
<td>Nitrite</td>
<td>NO₂</td>
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<tr>
<td>Nickel</td>
<td>Ni</td>
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<tr>
<td>Phosphate</td>
<td>PO₄</td>
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<td>Potassium</td>
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<tr>
<td>Sodium</td>
<td>Na</td>
</tr>
<tr>
<td>Sulphate</td>
<td>SO₄</td>
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<tr>
<td>Zinc</td>
<td>Zn</td>
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CHAPTER ONE: INTRODUCTION AND BACKGROUND

1.1 Background

The main purpose of undertaking this research study was to be able to determine the impact of the municipal solid waste (MSW) leachates on soil and groundwater system within the Onderstepoort MSW landfill site. For decades, MSW landfills have been regarded as the main source of pollution and major threats to groundwater resources (Fatta et al., 1999). The project area, Onderstepoort MSW landfill site was established nearly two decades ago (TECC, 2016), with no proper leachate management systems (Du Plessis, 2010). This landfill site caters and accommodates approximately 600 tons of MSW per day and incorporates building rubble, garden refuse, industrial as well as domestic waste (Du Plessis, 2010). Other types of waste such as electronic devices (computer systems and cell phones) are also dumped in the site, which could escalate environmental risks due to mercury, lead and cadmium heavy metals found in these devices (Fatta et al., 1999).

The Onderstepoort landfill site, being outdated in terms of current technology, was designed in the absence of leachate collection systems and geo-membranes that prevent leachate migration towards groundwater system (Du Plessis, 2010). According to Al Raisi et al. (2014), the absence of leachate collection systems together with geo-membranes is suspected to escalate the migration of leachate to groundwater system. Al Raisi et al. (2014) further pinpointed that the landfill leachates become more active as a consequence of unavailability of sufficient, appropriate bottom liner or collection system. This increases the chances of leachate migration through the medium of landfill layers leading to groundwater contamination.

The method used to manage landfill leachate within the study area is based on the national legislative framework which is the “Minimum Requirements for Waste Disposal by Landfills” developed by the then Department of Water Affairs and Forestry (DWAF). This also included the use of the chemical detergents/treatment to solidify generated leachate either through neutralisation oxidation, precipitation and wet-air oxidation (DWAF, 1998). Regardless of the points already mentioned, it has been reported that if the landfill leachate is not collected and treated in an appropriate manner, major pollution of the water table is likely to result (Rout & Sharma, 2010). There are two leachate management strategies currently being used by modern MSW landfills i.e.
leachate reticulation and single pass leachate (Scott et al., 2005); however, none of these methods were found to be practiced at the study area. This leads to the question, whether the current chemical method used in the study area to manage generated leachate is sufficient to prevent leachate percolation towards groundwater resources.

Nonetheless, the landfill is located within the vicinity of areas marked as protected and reserved, such as De Onderstepoort Private Nature Reserve, Bon Accord Dam, Apies River known to be the city’s backbone, plus a range of other wetlands. Du Plessis (2010) highlighted that one of the disadvantages of the Onderstepoort MSW landfill site is that it is located near sensitive areas such as De Onderstepoort Nature Reserve and Magaliesberg protected natural environment. These natural resources could be at risk of being contaminated by leachate migration from the area. Galape and Parilla (2014) have indicated that poorly managed landfill leachate could result in further ecological as well as health related risks to persons residing in the vicinity of these areas.

Wuana and Okieimen (2011) are of the view that human beings together with ecosystem are liable to risks and hazards from heavy metal contamination of soil and drinking water. Al Raisi et al. (2014) also backed Wuana and Okieimen by stating that the landfill leachate produced could cause major environmental problems when it finds a way to the surrounding soil, surface and groundwater. Hence, landfill leachate may incorporate large amounts of organic matter, ammonia-nitrogen, together with heavy metals (iron, lead, chromium, cadmium, copper, zinc, nickel and arsenic) which have been reported to be present in these kinds of soil and groundwater systems (Renou et al., 2008). After these, heavy metals have become concentrated in soils and water resources, they may also be taken up by plants and subsequently taken up by human beings and animal species (Salem et al., 2000).

The remaining life span of the Onderstepoort landfill site is estimated at less than one and a half year (TECC, 2016) which could be 2016/2017; however, it is known that MSW landfill site will continue to generate leachate even after closure which could last for 30 to 50 years of age (Bhalla et al., 2012). As the Ondersteppoort landfill site is about to reach the end of the life span, it cannot be stressed enough for the research project to cover the gap in knowledge in terms of the closure of MSW landfill sites designed without proper leachate management systems, including that of post-closure leachate management. This research was therefore aimed at assessing and investigating the leachate pollution which could potentially cause land (soil) and water contamination
which affects the physical and chemical condition of the study area and also of the surrounding environment. After the successful investigation, appropriate remedial and remediation options were provided to assist in preventing, minimising and eliminating negative environmental impacts due to leachate movements through soil into the subsurface water environment.

1.2 Statement of the problem

The main cause of the problem in the study area is the discharge of leachate into the environment leading to soil and groundwater contamination. The study undertaken by Akinbile and Yusoff (2011) revealed that the concentration of wastes in the landfill site causes soil and groundwater pollution. Lack of adequate, strategised leachate collection system and management thereof, forms part of the factors that may cause, influence and facilitate the spread and increase of negative environmental impacts in the study area (Du Plessis, 2010). The impact of the leachate could be extensive and affect not only communities and environment, but also the economic and social well-being of the surrounding communities, including loss of property value and/or ecotourism interests in the nearby nature reserve.

1.3 Research Justification

The lack of effective and efficient leachate management tools in the study area is predicted to influence groundwater pollution (Du Plessis, 2010). In this regard, there are on-going engagements regarding closure and rehabilitation plan for the Onderstepoort MSW landfill site (TECC, 2016). However, there are difficulties associated with the rehabilitation process to be effected during imminent landfill closure, especially since the original design did not make provision for landfill liners that separate landfill leachate and groundwater (Du Plessis, 2010).

The study aims at addressing current and potential negative environmental impacts due leachate discharge by systematically examining the quality and condition of both soil and water which forms part of the study area and the surrounding environment. This is done to preserve the state of nature, tourists and the public. Therefore, this research study escalated the soil and water quality issue, thereby providing remedial actions for the study.
1.4 Research Questions

1.4.1 Can the leachate produced in the Onderstepoort MSW landfill site infiltrate into the groundwater system?

1.4.2 Do the chemical properties of soil and water indicate any toxic chemicals/heavy metals concentration?

1.4.3 Is the method used to manage leachate in the site efficient to eliminate soil and groundwater pollution?

1.4.4 What is the best methodology to eliminate leachate infiltration into the underlying groundwater system, now and in the future considering the rehabilitation and landfill post-closure care?

1.5 Aim of the Research

The main aim of the research study was to determine the impacts of leachate from Onderstepoort MSW landfill site on soil and groundwater systems.

1.6 Specific Objectives

1.6.1 To analyse the heavy metals in soils and establish the impact of leachate on soil quality.

1.6.2 To determine water quality, investigate the presence of heavy metals and inorganic macro-components within the surface and groundwater systems.

1.6.3 And thereafter; to develop appropriate proposals for solving and managing resultant or expected leachate generation and impacts putting in mind the affordable management strategies required for rehabilitation process and after the closure of the landfill site.
CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

This section will give a concise and detailed review on MSW waste classification, waste treatment and management, leachate generation, leachate characteristics, waste decomposition process, exposure to heavy metals and subsequent effect on human health, landfill leachates treatment and management, lastly leachate control policy framework.

2.2 Municipal Solid Waste Classification

With regard to MSW classification, the South African DWAF classified waste according to the type of material involved; the size of waste produced; and also according to the leachate production rate. In general, MSW occurs in the form of solids or semi-solids (DWAF, 1998). Hence National Environmental Management: Waste Act of 2008 defines this type of waste as waste material that has minimum hazards to human well-being and the environment. Types of general waste include domestic waste, demolition waste and commercial waste (NEMA: Waste, 2008).

New South Wales government has classified general waste as any waste material that excludes special waste, liquid waste, hazardous waste, restricted solid waste, chemical waste, radioactive waste, recyclable products, and organic products. These types of waste should not be composted, recycled, reprocessed or re-used (NSW Environmental Protection Authority, 2014).

2.3 Waste Treatment and Management

Waste management system within the MSW operation comprises of waste storage, collection, transportation, disposal, recovery and treatment (Agamuthu, 2011). According to Sholichin (2012), waste material is transformed from one stage to another. There are different phases and processes that waste undergoes which cover physical, biological, and chemical process. The discussion below only considers the physical process of waste management which involves waste compaction and cover application. As such, waste treatment and management involves the following:
2.3.1 Waste compaction

The United Kingdom Department for Environment, Food and Rural Affairs (DEFRA) stated that the practice of landfill involves the creation of waste cells which are then filled with waste, followed by the compaction process and cover application (DEFRA, 2004). The compaction process compresses waste and prevents wind from blowing waste. The parameters that affect the compaction process include the depth of the waste, weight of the compaction equipment and also the nature of waste (EPA, 1997). The operation of MSW landfill site in Newfoundland Labrador Government (NFLG) requires the use of heavy equipment which includes compactors and bulldozers. In this essence, properly placed waste materials are compacted and covered with approximately 150 mm of soil daily (NFLG, 2010).

2.3.2 Cover application

After waste compaction process, a cover is positioned over waste material, consisting of a layer of compacted clay which reduces and prevents water penetration as well as lowering leachate production rate (USEPA, 2012). Lee and Jones-Lee indicated that in a properly designed and constructed MSW landfill site, a plastic sheeting layer is used as a waste cover. The plastic sheeting layer prevents moisture from entering the processed waste, keeping waste dry. However, low-permeability soil layer allows moisture entering the waste and may influence generation of the landfill leachate (Lee & Jones-Lee, 2005). Newfoundland Labrador Government recommended that in areas where the waste disposal is placed on hold for a period of approximately six months, intermediate cover should be implemented within 30 days. The thickness of intermediate cover should be 450 mm when using soil and approximately 20 mils is required for geosynthetic cover. The final cover is applicable once the landfill working cell has reached its life span. This includes liners and vegetative layers to reduce and eliminate soil erosion, infiltration of precipitation and prevent landfill gas from escaping (NFLG, 2010). According to the Environmental Protection Agency (EPA), MSW cover materials include the low-permeability geosynthetic materials such as geotextiles. This type of waste cover is specifically useful on the side slopes and not suitable for heavy traffic movements; highly permeable geosynthetic textile-like material is not suitable for use as intermediate cover and should be used in combination with cover materials such as soils (EPA, 2014) and traditional cover consists of subsoil and industrial waste materials comprising bricks and concrete (EPA, 1997).
2.4 Leachates Generation

Leachate is produced due to percolation of water through processed waste, after which the compaction and covering of waste resulting in generation of this phenomenon (Sholichin, 2012). Morling (2007) and Bhalla et al. (2013) recorded number of factors generating landfill leachate, including rainfall, surface run-off, filtration as well as a number of biochemical processes. In addition, Jhamnani and Singh (2009) have indicated that there are different factors acting upon the rate and characteristics of leachate production. It was elaborated that the characteristics and rate of leachate produced are dependent upon the age of the landfill, temperature and moisture content. Furthermore, the climatic condition of the area where the landfill is situated also influences the kind of leachate subsequently (Aljarandin & Persson, 2012).

It has also been researched by DEFRA (2004) that leaching is influenced by the decomposition of waste and infiltration processes. In this regard, Lee and Jones-Lee (1993) are of the view that the MSW landfills during their life span produce leachate which causes surface and groundwater contamination. From experience acquired by the European Commission (2002), leaching of metals is known as a dominant passage of heavy metals released to the environment, which includes soil as well as surface and groundwater.

2.5 Leachate Characteristics and Composition

2.5.1 Leachate characteristics

The characteristics of leachate solution depend mostly on the waste type stored and processed in the landfill, together with hydrological and chemical properties of the landfill (Schiopu & Gavrilescu, 2010). In general, MSW leachate can be determined through the quantification of parameters such biochemical oxygen demand (BOD), chemical oxygen demand (COD) and dissolved organic carbon (DOC) (Bhalla et al., 2012).

However, Bundela et al. (2012) emphasized that leachate characteristics vary from site to site depending on the waste composition (chemicals) and time. Other factors which can contribute to leachate properties include waste processing method, landfill design
and operation (Reinhart & Grosh, 1998). This statement has been supported by Andreottola and Cannas (1992) who indicated that leachate composition depends upon factors such as waste composition, pH, redox potential, landfill age, waste mass, site location and also through the design and operation of the landfill site.

Furthermore, it has been demonstrated by Christensen et al. (2001) that the average heavy metal concentrations in landfill leachate are very low. Kamaruddin et al. (2013) studied that low pH characterising the landfill leachate during initial stage dependent upon high concentrations of volatile fatty acids.

2.5.2 Leachate composition

By way of definition, leachate is generally considered to result from the percolation of liquid through landfill waste material and contains both organic and inorganic compounds (Ramaiah et al., 2014). As such, the degree of precipitation, waste storage capacity, together with other biological, chemical and physical processes all contribute to the types of waste being treated (Stegmann et al., 2005; Andreottola & Cannas, 1992). Leachate composition is therefore sub-categorised into four groups of pollutants (Christensen et al., 2001), which are:

2.5.2.1 Dissolved organic content (DOC)

The dissolved organic content (DOC) involves chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD$_5$). The organic matters in leachate solution are measured using COD and BOD$_5$ (Reinhart & Grosh, 1998; Dvornic et al., 2011; Samudro & Mangkoedinhardjo, 2010). A standard period for determining BOD is 5 days, however the duration can be extended to 30 days (Samudro & Mangkoedihardjo, 2010). In this case, Raju (2012) has reported BOD and COD values between 9.2 mg/L to 10.4 mg/L and 80 mg/L to 91 mg/L. Furthermore, groundwater contaminated with landfill leachate contains BOD and COD values higher than 1.0 mg/L.

Other studies have indicated that leachate BOD and COD varies according to the season. BOD and COD reported values were 261.1 mg/L and 288.2 mg/L during dry season. During rainy season BOD value reported was 150.2 mg/L, whilst COD concentration reported was 288.2 mg/L (Nwabueze, 2011). During the month of May, the BOD and COD values have been found to be lower than the one acquired during January as a result of seasonal temperature and precipitations (Dvornic et al., 2011). The studies
undertaken in Serbia revealed that most contaminated areas were found to have BOD values ranging from 156 to 443 mg/L (Dvornic et al., 2011).

2.5.2.2 Inorganic macro-components

Landfill leachate normally includes dissolved organic matters as well as inorganic compounds such as ammonium, calcium, magnesium, sodium, potassium, iron, sulphates and chlorides (Bouzayani et al., 2014). Inorganic materials that act as pollutants include sulphate, chloride, ammonium, calcium, magnesium, iron and pH (Lee & Nikraz, 2014). However, Christensen et al. (2001) indicated that inorganic macro-components do not pose severe impacts to groundwater resources. Jhamnani and Singh (2009) stressed that soil and groundwater pollution may be caused by leachate migrations which do comprise chlorides and sulphides.

The World Health Organisation (WHO) indicated that fluorine is known to exist in different minerals such as fluorides, including cryolite, fluorspar and fluorapatite. These contents of fluorides are present in most waters wherein high concentrations are normally found in groundwater sources (WHO, 1996). A research study under taken by Bashir et al. (2012) contended that a major source of fluoride is water itself. Fluoride concentration below 1.5 mg/L could escalate the chances of dental caries. Furthermore, the study proved that the samples taken had excessive fluoride content which might cause dental fluorosis. With regard to sulphate, natural levels of sulphate in groundwater can be increased due to landfills. High concentrations of sulphate in drinking water can escalate gastrointestinal irritation in the presence of magnesium or sodium (Raju, 2012).

2.5.2.3 Heavy Metals

Zander (2012) defined heavy metals as metallic element represented by high atomic weight with a density greater than water. Apart from the dissolved organic content and inorganic macro-components that made up the landfill leachate, heavy metals also form part of the leachate composition discussed hereto.

According to the research studies undertaken recently, leachate composition comprises cadmium, chromium, copper, lead, nickel, zinc, arsenic, and mercury (Wuana & Okieimen, 2011). While many of these metals occur naturally in the environment (USDA & NRCS, 2000), subsequent leaching into surrounding soils aggravates the problem (Neustadt & Pieczenik, 2007).
To further compound this problem, some of the toxic metals found in MSW landfill leachate are caused by dumping electronic devices in the site; these include the cell phones and computer systems. These electronics contain trace metals such as lead, cadmium, mercury, arsenic, copper, zinc and others (Al Raisi et al., 2014). Despite the requirements for some heavy metals in our diet, such as zinc and copper (Haddad, 2012), extensive exposure to these toxic metals may result into illness and even death at the worst case (Zander, 2012).

Chromium mobility depends on soil adsorption characteristics, including clay and iron oxide content, and the amount of organic matter found therein (European Commission, 2002). This heavy metal may be transported by surface runoff to surface waters, which can result in soluble and un-adsorbed chromium complexes leaching from soil into groundwater (Wuana & Okieimen, 2011).

It has been studied that the discharge of heavy metals such as cadmium, chromium, copper, lead, zinc and nickel poses severe environmental threats to the surrounding resources including soil, surface and groundwater (Bouzayani et al., 2014). Therefore, the exposure to these toxic elements could cause chronic health threats, including the following:

- Ingestion of lead is known to cause mental lapse (USDA & NRCS, 2000);
- Exposure to cadmium may result into kidney and liver failure/problem; and
- Skin problems as well as certain central nervous system conditions are known to be caused by arsenic exposure (USDA & NRCS, 2000).

2.6 Landfill Classification and Waste Decomposition Process

The decomposition of waste within the MSW landfill site involves many phases/stages before a stable situation is attained (Altauqi, 2012). The municipal waste decomposition process depends upon stages that are characterised by distinct changes in both biological and chemical processes (Koc-Jurczyk & Jurczyk, 2011), which includes both organic and inorganic contaminants. Due to the biological, chemical and physical processes, both organic and inorganic leachate contaminants are released. According to Oliveira (2012), waste decomposition process is made up of four/five phases which are aerobic; anaerobic; initial methanogenic and stable methanogenic phase.
During stage 1 of waste decomposition process, aerobic bacteria oxidise carbohydrates, proteins and lipids into carbon dioxide. The gas emitted is made-up of nitrogen and oxygen. The amount of carbon dioxide increases with the improvements of the micro-organisms. In stage two, the acid increases in the landfill (Bialowiec, 2011). Initial methanogenic is the third stage of waste decomposition process within the MSW landfill site wherein the highest concentration of BOD$_5$ ranges from 1000 mg/L to 57 700 mg/L and COD values were determined to be between 1500 mg/L to 71 100 mg/L (Mor et al., 2006). In stage four, which could last for many years, the production of gas is constant (Bialowiec, 2011), and rise of methane producing bacteria occurs. At this phase, the organic acid produced is converted into methane and carbon dioxide (Aucott, 2006). Stage five is referred to as the maturation stage and excessive landfill gas emissions take place (Bialowiec, 2011).

**Table 2.1:** Leachate concentration variables between new, intermediate and matured landfill site (Adhikari & Khanal, 2015).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Young</th>
<th>Intermediate</th>
<th>Old</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age (Years)</td>
<td>&lt;5</td>
<td>5-10</td>
<td>&gt;10</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>6.5-7.5</td>
<td>&gt;7.5</td>
</tr>
<tr>
<td>COD mg/L</td>
<td>&gt;10 000</td>
<td>4 000-10 000</td>
<td>&lt;4 000</td>
</tr>
<tr>
<td>BOD$_5$ mg/L</td>
<td>&gt;2 000</td>
<td>150 -2 000</td>
<td>&lt;150</td>
</tr>
<tr>
<td>Heavy Metals</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Biodegradability</td>
<td>Important</td>
<td>Medium</td>
<td>Low</td>
</tr>
</tbody>
</table>

The matured landfill leachate is comprised of less COD and BOD concentration than in the young and intermediate landfill site as shown in Table 2.1. The decomposition of waste in the landfill site involves the following classifications:

**2.6.1  Young landfilling**

A young landfill (aerobic phase) site refers to landfilling that commences over a five year period. During this stage, excessive amounts of biodegradable matter include that giving rise to high COD concentrations of 20 000 mg/L (Sackey & Meizah, 2015). The available oxygen in the refuse pores is instantly used-up during the initial stage of decomposition, which produces carbon dioxide (CO$_2$) causing an increase in temperature to about 80-90°C (Kjeldsen et al., 2002).
Following waste deposition in the landfill site, this aerobic phase rapidly depletes the available oxygen, while the acetogenic fermentation is influenced by water infiltrated through processed waste material, thereby producing high BOD and COD leachate solution (Kjeldsen et al., 2002).

2.6.2 Intermediate landfilling

The intermediate landfilling occurs under acidic conditions which materialise after 5 to 10 years, being characterised by COD values between 3,000 mg/L to 15,000 mg/L (Sackey & Meizah, 2015). This is the transition phase wherein the condition of the landfill transforms from aerobic to an anaerobic environment (Aucott, 2006). Kjeldsen et al. (2002) concluded that the methanogenic bacteria might grow at this stage of waste decomposition in the landfill site. During the anaerobic acid phase, the hydrolytic, fermentative and acetogenic bacteria abound, causing accumulation of the carboxylic acids. The acid secreted is then converted to methane (CH₄) and carbon dioxide (CO₂), leading to the increase of the pH when the acids are consumed (Kjeldsen et al., 2002).

2.6.3 Old landfilling

An old landfill site (maturation phase) is above 10 years of age with fewer amounts of biodegradable matters with lower COD values of 2,000 mg/L (Sackey & Meizah, 2015). In this stage, the leachate is normally characterised by higher concentrations of humic and fulvic acids (Khalil et al., 2014).

2.7 Exposure to Heavy Metals and Subsequent Effect on Human Health

Health effects related to MSW operations include:

- Lead is known to accumulate in human brain leading to poisoning or death,
- Chromium compounds are known to cause cancer (European Commission, 2002).
- Cadmium on the other hand is related to renal failure as a result of drinking contaminated water (Salem et al., 2000).
- Copper is related to liver cirrhosis and chronic anemia (Salem et al., 2000).
- Neustadt & Pieczenik (2007) indicated that mercury of any sort is regarded toxic to the human body.
According to Wuana and Okieimen (2011) there are two ways of lead exposure which can be through inhalation and ingestion. Lead products are found in waste management facilities with major sources such as plastics, fishing tools and cathode ray tubes (European Commission, 2002). Mazumder (2000) indicated that human beings are exposed to arsenic basically through air, food and water. The most common route of exposure to arsenic is through the elevated inorganic arsenic in drinking water. Landfills may cause zinc concentrations in drinking water leading to health related problems. Water containing zinc absorbed by soils may also contaminate groundwater (Wuana & Okieimen, 2011).

2.8 Landfill Leachate Treatment and Management

Landfills are known to produce and release leachate solution (Regadio et al., 2015). The generated leachate continues to migrate through soil layers and if no preventive and remedial measures are considered, this will lead to aquifer contamination (Kanmani & Gandhimathi, 2013). With regard to the research study undertaken by Regadio et al. (2015) which was meant to determine leachate management in the old MSW landfill sites, clay soil was investigated in order to evaluate its performance and potential use as a landfill liner. A Researcher provided two methods that are useful in preventing the leachate migration to water bodies. These methods were categorised as the bottom and top scaling liners, and collection systems of the pollutants emission (Regadio et al., 2015).

On the other hand, DWAF has set guidelines applicable for the management of leachate in South African landfill sites. DWAF recommended that landfill owners or operators should design low-permeability lining systems which reduce the movement of leachate into the groundwater system. In many cases, liners are built from low-permeability clay soils or synthetic materials. The only leachate management method used in the study area has been the chemical treatment method. This method has been widely used in South Africa to treat and manage MSW leachate (DWAF, 1998). Taking into account South Africa's geological and hydrological makeup, including climatic conditions, various physico-chemical treatment methods can be applied to a landfill operation (Aljarandin & Persson, 2012); unfortunately this approach was not applicable in the study area as the landfill site is fully developed and is currently in the process of closure and rehabilitation.
2.8.1 Physical/chemical leachate treatment methods

This method is regarded as non-biological and preferred for leachate treatment. The method could be utilised both as pre-treatment and post-treatment of the landfill leachate (Liu, 2013). According to the South African DWAF, this method could be used to remove organic and inorganic compounds as well as the hazardous elements. The process includes neutralisation, oxidation, precipitation as well as wet-air oxidation (DWAF, 1998).

This leachate treatment method comprises a number of steps, including the coagulation-flocculation; chemical precipitation, flotation, activated carbon adsorption, ammonia stripping, ion exchange, electrochemical treatment, chemical oxidation and membrane filtration (Liu, 2013). Kilic et al. (2007) determined that the suspended solids together with COD and toxic metals found in landfill leachate could be eliminated or reduced in a serial manner during these chemical processes.

2.8.2 Biological treatment methods

Biological treatment methods have also been used for treating leachate around the globe. These methods make use of both aerobic and anaerobic process (Liu, 2013). The microbes are added to the leachate in order to destroy, eliminate and reduce the toxicity of the waste (DWAF, 1998). Biological leachate treatment methods incorporate recirculation, activated sludge, tricking filters, rotating biological contactors, stabilization ponds and wetlands (Poullot, 1999; Liu, 2013).

Many of the biological treatment processes are based on aerobic bio-degradation which is reliable and simple, but has unfortunately high cost of operation (Gotvajn & Pavko, 2015). The simplest biological leachate treatment method is the recirculation, which involves sending the leachate back to the original site for further decomposition with the landfill now acting as an anaerobic reactor (Poullot, 1999).

Liu (2013) indicated that for stabilized landfill leachate containing high concentrations of bio-toxic material and unable to degrade the organic matter, it is advisable to use a low cost efficient method. In this regard, leachate recirculation does provide low operating cost, being relatively simple to operate, and does result in reduction of the volume of leachate via evaporation (Poullot, 1999), as well as having a positive impact in reducing COD and stabilising pH (Rout & Sharma, 2010).
2.9 Leachate Control Policy Framework

The then Department of Water Affairs and Forestry (DWAF) has developed and implemented a document called “Minimum Requirements for Waste Disposal by Landfills”. The Concept document/strategy has been implemented to assist landfill operations within South African context which also apply to the study area which in this case is the Onderstepoort MSW landfill site. The strategy has been adopted by the Onderstepoort landfill site to assist and provide guidelines during the management of the landfill leachate.

The concept document, states that in order to eliminate water pollution within MSW landfills, generated leachate should be collected and treated using appropriate treatment systems incorporating the under-liners, drains and removal systems (DWAF, 1998). In commitment to reduce the impacts of landfill leachate to the environment, South Africa has previously developed awareness for leachate treatment. South Africa was one of the recipients of the sophisticated first world equipment (nitrification and denitrification), methods and ideas for leachate treatment. However, as a developing country in Southern Africa, it was studied that sophisticated equipment together with the developed methods were inappropriate due to lack of highly trained technical staff (Strachan et al., 2000). However, the South African landfill operation regulatory standards were based on techniques developed specifically for other countries (Ntsele et al., 2000). A recent work undertaken by Novella (2014) indicated that many landfills in South Africa produce less of landfill leachate due to dry environment; however most of the South African landfill sites are not complying with the developed Minimum Requirements.

Having compared with other international policies, it has been noted that the European Union waste management principles involved four approaches which are; the waste hierarchy which involves waste prevention, re-use, re-cycle and lastly recovery; to reduce the impacts related to waste operations; direct responsibility for contaminating the environment; and to secure appropriate infrastructure through treatment facilities integrated network (European Commission, 2012). Other policy frameworks/standards used to assess the quality of soil and water in the study area comprise World Health Organisation (WHO) and South African National Norms and Standard (SANS 241). The guidelines for drinking water quality and soil quality have been used to evaluate the contaminations among soil and water resources.
2.10 Summary

The bullet point summary of the literature review is as follows:

- MSW treatment involves compaction and cover application.
- Leachate is produced due to precipitation availability, surface run-off, infiltration; landfill age and biochemical process.
- Leachate composition is made-up of DOC, inorganic macro-components and heavy metals. During dry season, BOD and COD values are low as compared to rainy season. A high concentration of BOD$_5$ and COD is a good indicator of surface and groundwater contamination due to MSW leachate.
- MSW leachate could be determined through pH values, TDS, BOD$_5$, COD and heavy metals.
- Inorganic matters that act as pollutants include sulphate, chloride, ammonium, calcium, magnesium, and iron.
- The discharge of heavy metals such as cadmium, chromium, copper, lead, zinc and nickel are the roots to severe environmental threats to soil, surface and groundwater.
- The MSW decomposition process depends upon temperature, geologic condition, climatic condition and waste processing method.
- No matter how minimal toxic metals such as lead, cadmium and mercury together with inorganic arsenic can be toxic to the human body.
- The selection of the leachate treatment method is based on the characteristics and composition of the leachate and could be through the chemical; physical and biological process.
CHAPTER THREE: DESCRIPTION OF THE STUDY AREA

3.1 Introduction

The Onderstepoort landfill site is the only operative MSW landfill in Rosslyn, Pretoria North and accommodating 500-600 tons of MSW per day. The waste dumped and processed in this landfill site includes garden refuse, building rubble, commercial and domestic waste (TECC, 2016). Waste management process comprises compaction and cover application using clay soil in order to reduce precipitation and rainwater percolation. This landfill site was established in 1996 without considering advanced leachate management systems and collection. The leachate produced due to MSW operation is treated via chemical treatment centred on the use of chemical precipitation.

The study area is adjacent to De Onderstepoort Private Nature Reserve which is regarded as a protected area. The preliminary survey was undertaken in order to gain insight of the study area and to determine any aspect that could be useful to the study. This chapter provides information regarding the study area that includes land-use, climatic condition, surface and groundwater systems, geology and soil aspects, site waste management, leachate generation and management. The chapter provides both primary and secondary data collection of the study.

3.2 Description of Site

The Onderstepoort MSW landfill site was established 20 years ago (1996) and is still operational (TECC, 2016), with a landfill area of approximately 51.8 hectares (Stiff et al., 2013). The remaining life span of the site is expected to be less than a year and a half (TECC, 2016) and preparation for closure is expected to be implemented in due course. The site is located at 21 Kilometres (Km) north of Pretoria under the City of Tshwane Metropolitan Municipality (CTMM), in Rosslyn. Rosslyn is an industrial area located towards the North-West Province. The western boundary of the study area being the Rosslyn Railway Line and on the eastern boundary is formed by R556 Rosslyn Road and De Onderstepoort Private Nature Reserve as indicated in Figure 3.1. Soil samples were collected at sixteen (16) sampling sites (including leachate sediments) located at and away from the waste dump (Figure 5.3). Water samples were collected at three locations i.e. surface and groundwater systems (BH1 and BH2). The first sampling point (surface
water) is located approximately 100 m away from the waste dump. The second sampling point (BH2) is situated below the waste dump, east of the study area and the third is approximately 400 m from the waste dump (Figure 5.8). The Onderstepoort landfill site is located between the grid reference 25° 39’ 02” S (longitudes) and 28° 09’ 07” E (latitudes) (Stiff et al., 2013).

Figure 3.1: The location of the study area (Rison Groundwater Consulting, 2009).

Figure 3.1 shows the Onderstepoort MSW landfill site located adjacent to the R566 Rosslyn Road and De Onderstepoort Private Nature Reserve, north of the study area. More detailed pictures of the study area are given in Figure 5.1 (see page 60) and Figure 5.3 (see page 67).
3.3 Preliminary Survey

A preliminary survey was conducted in the study area in order to understand and gain knowledge of the area including pedology, topographical condition, geology and biodiversity. This survey was used as an Environmental Impact Assessment (EIA) tool to describe the environmental and project area setting during May 2015 to February 2016.

3.4 Land-Use and Man-Made Features

It is a concern that the landfill site was developed adjacent to a protected area such as De Onderstepoort Private Nature Reserve (Du Plessis, 2010). Furthermore, Rosslyn is known as a major industrial park within the region and is comprised of motor hub vehicle manufacturing companies being BMW and Nissan. Irrespective of the Industrial Park, the landfill is also surrounded by well-established residential and commercial areas. The Wonderboom Domestic Airport is located at approximately 5 km away.

On the south-eastern side of the study area, lies the agricultural land. The agricultural activities might be affected due groundwater contamination as a result of landfill leachate migration. Furthermore, a distinctive wetland resource complex is located adjacent to the Wonderboom Junction Shopping Centre which is a 3 Km away.

3.5 Climatic Condition

Regional climatic condition, is characterised by extremely hot summers with frequent rainfalls; whilst during winter season, it is dry and cold (TECC, 2016; Golder Associates Africa, 2013). The region has a humid subtropical climate with average annual temperature of 18.7 °C (Golder Associates Africa, 2013). The driest cold weather is in winter season with temperatures ranging from 04 °C to 19 °C; nonetheless, the area is too hot in summer season with average temperature from 18 °C to 29 °C. The region experiences average rainfall of 674 mm per annum, acquiring rain mainly during summer season between December and January (Gauteng Province Government, 2001). Gentle soaking rains occur mostly in the area, whilst thunderstorms normally occur during heavy rains (Golder Associates Africa, 2013).
3.6 Topography

The regional topography of Pretoria lies between Highveld steep slope and Lower-lying Bushveld, with an average elevation of 1330 metres above the sea level (Gauteng Province Government, 2001). The study area is surrounded by the Magaliesberg Mountain Range, which can be viewed north-western side of the study area. The general topography of the project area is flat; however, mountains and hills form part of the local topography (CTMM, 2008).

3.7 Biodiversity

The study area falls within the Savanna Biome of Southern Africa (TECC, 2016), comprising of grassy layer and woody akacia plant kingdom. As such, Rosslyn falls within this Savanna Biome, being characterised by warm summer temperatures, summer-rainfall and very dry-winters (TECC, 2016). The project site appears to be characterised by less natural plant species and is generally disturbed due to the waste management operation currently taking place. The site provides habitation to a number of scavenging bird species.

3.8 Hydrology

The study area lies next to Apies River known as the City’s backbone; the river is connected to Bon Accord dam approximately 15 Km north of Pretoria. The Apies River is also located at approximately 15 Km away from the study area (TECC, 2016). Within the vicinity of the project area there is a man-made pond with a critical element of dirty green-coloured water, as shown in Figure 3.2. This artificial water pond was formed as a result of rainwater collecting in the depression. Under these conditions, cyanobacteria can collect and produce toxins which are harmful to the health of both humans as well as animals (Matthews & Bernard, 2015). The water pond is used for dust suppression process during landfill operational activities. See also Figures 5.1 (see page 60) and 5.8 (see page 72) for aerial views of this water pond (surface water).
3.9 Hydrogeology

Two water boreholes used for groundwater quality assessments are operational in the site. Both boreholes were tested for leachate contamination, which in this case is the assessment of heavy metals, organic and inorganic compounds. Groundwater testing was performed as an assessment process to determine contaminations as a result of leachate migration through soil towards groundwater system.

A recent study undertaken by Kalele & Reddy (2011) for the BMW Production Plant in Rosslyn assisted in terms of determining the hydrogeological condition of the study area. As such, the area is underlain by Rustenburg Layered Suite (RLS) secondary fractured aquifer. The study revealed that two aquifers are located beneath the plant. It was further mentioned that the Rosslyn area wherein the study area is situated is comprised of norites of the Bushveld Igneous Complex (BIC) and known to contain a deep aquifer and shallow perched aquifer available within the weathered bedrock interface. The aquifer flowing direction is from south-west to north-east (Kalele & Reddy, 2011).

3.10 Pedology

The area is covered by 1 to 2 m of reddish clayey soil referred as vertic melanic clays (Kalele & Reddy, 2011). Due to the RLS being comprised of gabbro-norites, soils in the site are formed consequently due to weathering of the parent rock. In favour of the study,
soil profile was exposed due to quarry mining taking place, as shown in Figure 3.3, with four horizons.

Figure 3.3: Soil profile at the western side of the study area.

Figure 3.3, Horizon O is made up of the organic materials/plant residuals with dark brown colour; Horizon A is characterised of a very fine soil with light grey colour and in a powdery form; whilst Horizon B composed of a distinctive dark grey clay soil; and Horizon C is made up of the grabbonorites residuals characterised of reddish brown soil. Soil acquired from quarry mining activity was used as a waste cap or cover at the site.

In addition, referenced to BMW plant environmental assessment study, indicated that residual soil within Rosslyn is likely to be clayey and silty to gravelly. Furthermore, it was indicated that these soils may have impacts on geotechnical engineering properties of the material. Primarily; gabbronorite weathering results into acidic soils and noted to elevate heavy metals concentrations (Kalele & Reddy, 2011).

Das (2010) defined soil permeability as the ability of any liquid substance including water to flow through soil pores. Together with the permeability of clay soil being dependant on the thickness of the clay layers and ionic concentration, permeability to movement of leachate is also influenced by the availability of the interconnected voids that allow water to move from high energy to low energy. Compacted soil can be used as an artificial barrier, especially where the site is lacking a natural geological hindrance to the flow of
leachate. As such, the soil can be utilised as a landfill bottom liner which is enhanced by the compaction process (Stepniewski et al., 2011).

3.11 Geological Setting

3.11.1 Regional geology

The study area is located within the Bushveld Igneous Complex (BIC) and Transvaal Supergroup of Southern Africa, as indicated in Figure 3.4. The regional geology of the project area is divided into two geological formations; i.e. the BIC and Transvaal Supergroup.

The BIC is the World’s largest layered igneous intrusion and its thickness is approximately 7 to 9 Km. The BIC is made up of eastern, western and northern limbs/lobes (Shouwstra & Kinloch, 2000). Due to high content of iron and magnesium, the BIC rocks are classified mafic and ultramafic. The mafic and ultramafic rocks of the BIC comprise norite, gabbro and pyroxenite (Norman & Whitfield, 2006).

Moreover, the Transvaal Supergroup comprises a sequence of relatively underformed clastic sediments and volcanics with a thickness of 15,000 m. It has been well researched including a study by Cheney and Twist (1991) which states that the BIC intruded into the Transvaal Supergroup during the interruption of sedimentation (discontinuity in rock sequence) between the Rooiberg Group and the underlying Pretoria Group. This statement is in agreement with the results from a study by Cousins (1959), who indicated that BIC western belt reached and made contact with the Transvaal Supergroup western boundary. This complex lies on top of the Transvaal Supergroup sedimentary rocks, as shown in Figure 3.4. The norite and gabbro are the dominant rocks found within this basic zone.
3.11.2 Local geology

Considering that the geological formations within which a landfill site is placed influence the subsequent movement of leachate over time, it was deemed important to study and/or analyse the local geological setting. The local geology of the study area falls under the Rustenburg Layered Suite (RLS) of the BIC and Transvaal rock formation. These rock formations consist of peridot, pyroxene, gabbro, norite, anorthosite, troctolite, and diorite (Snyman, 1996).

The study area is regarded as a mixture between the BIC and Transvaal Supergroup. The aforementioned statement indicates that both the Transvaal Basin and BIC share a primary axis bearing east-northeast of Rosslyn (Kalele & Reddy, 2011). Hybrid gabbronorite found in the study area, as shown in Figure 3.5, is the most outer RLS formation towards South of Rosslyn. The gabbronorite rock formation is dipping at an angle above 20°. However; north of Rosslyn, gabbronorite is conformably overlain by ferrogabbro and diorite (Kalele & Reddy, 2011).
Figure 3.5: Bedrock formation of the study area.

Figure 3.5 illustrates the rock formation of the study area together with the type of soil that could have been formed due to weathering of the bedrock. The vertical distance between soil and bedrock formation was approximately 1 m to 3 m.

3.11.3 Structural geology

Figure 3.6 illustrates the regional geological structures. The RLS is characterised by faults trending from South-east to North-west direction. Aucott (2006) indicated that groundwater resources could be polluted by landfill leachate whenever landfill is sited above the fractured rock. Therefore, geological structures such as faults may influence groundwater pollution, particularly when leachate solution is easily able to percolate.

As is apparent in Figure 3.6, there are no faults running through the study site being good indication of the suitability of the landfill operation in this area. The unavailability of the geological structures such faults indicate that leachate produced from the landfill site cannot migrate through openings caused by these faults, thereby reducing chances of groundwater contamination. The red circle as indicated in Figure 3.6 shows the location of the study area with faults presented with the letter f. According to the figure, there are no geological structures or faults running across the area of interest.
3.12 Site Waste Management System

Daily MSW dumped in the Onderstepoort landfill ranges from 500-600 tons, being comprised of household, garden refuse, commercial and building rubble wastes. Unfortunately there are no reports and records stipulating the amount of waste received and reclaimed over the years in the site (TECC, 2016). Hazardous wastes dumped in the site include batteries, electronics as well as empty paint tins, shown in Figure 3.7, can collectively elevate heavy metals concentrations and contaminants.

Figure 3.7: Hazardous waste materials dumped in the site.
This landfill shown in Figure 3.8 is unlined (Du Plessis, 2010), with the inherent risk for the leachate to migrate towards the water level placed approximately 50 m below the base of the landfill dump. Arriving waste material is dumped into three different working cells, i.e. building rubble, garden refuse and domestic waste cells. The waste is confined and compacted to reduce its volume, then covered with a layer of clay soil on a daily basis. The liner soil used consists of clay soil formed from the weathering of gabbronorite rock formation.

Figure 3.8: Types of waste treated at the study area.

Figure 3.8: A) represents municipal solid wastes dumped at the site characterised of household wastes and B) is the garden refuse waste material dumped on separate working cells.

Clay soils mined in the site are used as a waste cap and the bulldozer shown in Figure 3.9 is used for compaction. Processed waste is completely covered with clay soil prior to vacating the working cell. Other than this, the landfill site is not equipped with a leachate collection area or landfill gas collection systems. Aucott (2006) illustrated that liners used to manage landfill leachate could be soils and bedrock located below the surface. After reducing the volume of the waste material using the caterpillar as shown in Figure 3.9, waste was covered with soil to reduce water infiltration into the processed waste.
Leachate Generation and Management

As previously stated, leachate has been noted to be the most likely source of environmental pollution on soil and groundwater resources in and around the area of interest. While leachate was seen to be flowing during winter, as indicated in Figure 3.10, it is more likely that maximal leaching would occur in the summer, due to periods of heavy precipitation (Aljarandin & Persson, 2012).

The management and preventive part of the leachate in the site is based on a chemical treatment method. This chemical treatment method is centred on neutralisation oxidation, precipitation and wet-air oxidation. In essence, this is cheap and cost effective to use chemical precipitation mainly lime (pre-treatment with lime) for leachate treatment (Kilic et al., 2007). Landfill leachate could also be collected and treatment in order to remove contaminants such as heavy metals, COD and BOD prior to discharging the leachate to surface water system (Aucott, 2006). As shown in Figure 3.10, following this kind of chemical treatment, the leachate dries out; however soil changes colour from reddish brown to khaki, as was observed in the present study.

Figure 3.9: Waste processing method used at the site.
Figure 3.10: Landfill leachate at the bottom of the waste dump.

The generation of leachate was detected at the study area during winter and summer season. This leachate is believed to escalate environmental contamination of the area. In addition, other factors, such as soil erosion also complicate the situation as shown in Figure 3.11, especially on the waste lift.

Figure 3.11: Gully soil erosion suspected to influence leachate migration.

Figure 3.11 indicates gully erosion as influenced by surface water runoff during heavy rainfalls. This could lead to waste cap failure particularly on the steep side of the waste
dump and could also influence contaminants to escape from the waste dump to the surrounding environment.

### 3.14 Summary

The overall summary of main points presented in Chapter Three includes the following:

- The Apies River is located approximately a few kilometres away from the site, the impact of the landfill operation on Apies River particularly leachate contaminants is minimal as compared to the surface water pond located within the site. The water pond could also be affected by runoff from the dumping site specifically during heavy rains. Soil and contaminants washed from the dumping site due to soil erosion could be deposited into the water pond as it is located below the waste fill.

- Waste management systems used in the site i.e. waste is confined, compacted and covered with a layer of clay soil have been widely used around the globe.

- In terms of the geological structures that may influence groundwater pollution due to cracks and openings: these were not active in the study area which could have minimised seeping of leachate towards the groundwater resources.

- The occurrence of leachate in the study area has been noticed during dry (winter) and rainy (summer) seasons.

- Lastly, unpermitted hazardous waste such as paints and petrochemical substances dumped in the site could lead to negative impacts on the environment specifically surface and groundwater. The chemicals within these substances may escalate further environmental contaminations and increase heavy metals concentration in soil and water resources.
CHAPTER FOUR: RESEARCH MATERIALS AND METHODOLOGY

4.1 Introduction

The Chapter is categorised into field investigations incorporating soil, water and leachate, with associated sampling methodology, which then leads into subsequent laboratory analysis. In the latter instance, laboratory analysis included soil samples preparations, dissolved organic content; inorganic macro-components and heavy metals analysis. For this research study, the pollutants were sub-divided into three groups as summarised in Table 4.1.

Table 4.1: Summarises selected pollutants for the study, laboratory analysis and instrument used.

<table>
<thead>
<tr>
<th>Group of Pollutants</th>
<th>Analysis Required</th>
<th>Instrumentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved organic content (DOC)</td>
<td>Biochemical oxygen demand (BOD)</td>
<td>Winkler method (Rounds et al., 2013)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chemical oxygen demand (COD)</td>
<td>Dichromate Open Reflux method (USEPA, 1993)</td>
</tr>
<tr>
<td>Inorganic macro-components</td>
<td>nitrite (NO₂⁻), nitrate (NO₃⁻), sulphate (SO₄²⁻), fluoride (F⁻) , chloride (Cl⁻).</td>
<td>Ion Chromatography (USEPA, 1993)</td>
</tr>
<tr>
<td></td>
<td>potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺), sodium (Na⁺),</td>
<td>ICP-OES (Rudel et al., 2007)</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), manganese (Mn), zinc (Zn), vanadium (V), nickel (Ni) and cobalt (Co)</td>
<td>ICP-MS (WHO, 2008)</td>
</tr>
</tbody>
</table>

The selected pollutants (dissolved organic content, inorganic macro-components and heavy metals) for the study were analysed using five laboratory methods and these methods were discussed separately throughout this chapter. The following laboratory
methods were used to determine the contaminants in three spheres of the research study, namely soil, water and leachate:

- **Soil**: In order to determine the quality and heavy metals level in soils, Microwave Assisted Digestion (MAD) together with the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) protocols were employed.

- **Water**: Both surface and groundwater samples were treated for inorganic macro-components and heavy metals. Applicable instrumentation included Ion Chromatography (ions analysis), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for cations analysis as well as Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for heavy metals analysis.

- **Leachate**: Leachate contaminants were determined using Winkler (BOD$_5$) and Dichromate Open Reflux (COD) methods.

### 4.2 Field Investigations and Sampling Methods

#### 4.2.1 Geotechnical investigations

The geotechnical factors of the study have already been discussed in Chapter Three. The research objective was based on investigating geotechnical parameters associated with soils used to process waste, as well as the potential to retain water and moisture entering this waste material. At such, the intention of this particular landfill study was to assist with better informed managerial decision making, particularly if it could be demonstrated that clay soils, such as shown in Figure 4.1, can be used to retain the leachate in percolating water. This soil type (Figure 4.1) is characterised by extremely fine texture and cracks when dry.
In order to determine the soil characteristics in the area, the “guideline for the field classification and description of soil and rock for engineering purposes” developed by the New Zealand Geotechnical Society (Read et al., 2005) was used to classify the soil strata. During the field work, soil structures were differentiated from each other using properties such as grittiness, smoothness, stickiness, and plasticity/elasticity (Read et al., 2005; Schoeneberger et al., 2011).
The western side of the study area comprised of four exposed soil horizons (Horizon O, A, B and C). On the eastern side, only one Horizon was exposed (Horizon C) and bedrock formation as illustrated by Figure 4.2.

4.2.2 Sampling methods

The sampling period and frequency involved a once off collection of soil, water and leachate samples. The samples were collected in February 2016 during post-monsoon/summer season of South Africa. Fifteen (15) soil samples; ten (10) water samples and two (2) leachate samples (sediments and solution) were collected from the study area. Leachate samples were collected at the bottom of the waste dump where seeping of leachate from processed waste was occurring. Soil samples were collected in and around the waste dump, whilst water samples were collected in three locations i.e. surface water pond, groundwater Borehole 1 and 2. In order to assess the accuracy of the laboratory analysis, replicate samples together with repeat analyses were undertaken. Samples that have yielded extremely high concentration and analysed after analysing a sample with high value were retested.

4.2.2.1 Soil sampling

The research objective was accomplished using both MAD and ICP-MS protocols to analyse trace metals in soils. As a baseline, dry soil sampling was undertaken during February 2016, because lack of rainfall at this time would not enhance leachate production via a water percolation process.

A Garmin Montana 650 Geographical Position System (GPS) was used to locate sampling points as well as places where field pictures were taken. Samples were collected using a hand-held Auger with a standard diameter of 20 cm. Soil samples were collected at a depth ranging from 0 cm to 20 cm. The samples were taken through turning a hand held Auger as shown in Figure 4.3. Soil samples were collected by downward pressure rotation of the Auger in an anti-clockwise direction.
Figure 4.3 shows soil sampling procedure used in the study area, this sampling area represents sample number RSS15 as shown in Figure 5.3 and the sampling point was hardly affected by the waste operation. Though the sampling point is located away from the waste dump, the soil at this point was disturbed due to soil excavation in the site.

In general, all sampling procedures were standardised, particularly with regard to geochemical sampling grids, which in this particular study was in a rectangular pattern of 1000 m by 100 m. Similarly, soil samples were collected using 200 m grid spacing, with occasional additional samples being collected, particularly where pockets of leachate accumulation were apparent. Soil samples were immediately transferred from the Auger to sampling bags which was sealed and marked according to its grid reference, as indicated in Table 4.2, also recorded in the field book as well.
Table 4.2: Soil sampling points (X and Y coordinates).

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Sample Position</th>
<th>Elevation (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X Coordinates</td>
<td>Y Coordinates</td>
<td></td>
</tr>
<tr>
<td>GROUP A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSS15</td>
<td>X: 25° 38' 54.9'' S</td>
<td>Y: 28° 08' 43.4” E</td>
</tr>
<tr>
<td>RSS1</td>
<td>X: 25° 38' 59.7'' S</td>
<td>Y: 28° 08' 43.3” E</td>
</tr>
<tr>
<td>RSS12</td>
<td>X: 25° 39' 00.6'' S</td>
<td>Y: 28° 08' 42.5” E</td>
</tr>
<tr>
<td>GROUP B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSS2</td>
<td>X: 25° 39' 00.7'' S</td>
<td>Y: 28° 08' 48.9” E</td>
</tr>
<tr>
<td>RSS11</td>
<td>X: 25° 39' 02.1'' S</td>
<td>Y: 28° 08' 50.5” E</td>
</tr>
<tr>
<td>RSS4</td>
<td>X: 25° 39' 01.3'' S</td>
<td>Y: 28° 08' 55.5” E</td>
</tr>
<tr>
<td>RSS3</td>
<td>X: 25° 39' 01.5'' S</td>
<td>Y: 28° 08' 56.6” E</td>
</tr>
<tr>
<td>GROUP C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSS5</td>
<td>X: 25° 39' 01.9'' S</td>
<td>Y: 28° 09' 04.8” E</td>
</tr>
<tr>
<td>RSS10</td>
<td>X: 25° 39' 04.6'' S</td>
<td>Y: 28° 09' 02.5” E</td>
</tr>
<tr>
<td>RSS13</td>
<td>X: 25° 39' 05.3'' S</td>
<td>Y: 28° 09' 03.6” E</td>
</tr>
<tr>
<td>RSS14</td>
<td>X: 25° 39' 05.1'' S</td>
<td>Y: 28° 09' 04.2” E</td>
</tr>
<tr>
<td>GROUP D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSS6</td>
<td>X: 25° 39' 02.4'' S</td>
<td>Y: 28° 09' 13.4” E</td>
</tr>
<tr>
<td>RSS9</td>
<td>X: 25° 39' 06.1'' S</td>
<td>Y: 28° 09' 10.5” E</td>
</tr>
<tr>
<td>RSS7</td>
<td>X: 25° 39' 03.3'' S</td>
<td>Y: 28° 09' 18.8” E</td>
</tr>
<tr>
<td>RSS8</td>
<td>X: 25° 39' 06.7'' S</td>
<td>Y: 28° 09' 18.8” E</td>
</tr>
<tr>
<td>LEACHATE SOIL SAMPLE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS1</td>
<td>X: 25° 38' 56.4” S</td>
<td>Y: 28° 08' 45.4” E</td>
</tr>
</tbody>
</table>

In total, 15 soil samples were collected in and around the waste dump considering extra leachate soil sample (TS1) taken after it has rained. The soil sampling sites were indicated in Figure 5.3 (see page 67), which shows specific grouping in relation to a location, dirt road and/or slope of the landfill site.

4.2.2.2 Surface water sampling

Table 4.3 indicates the water sampling locations, which were also recorded in the field. In each sampling point, a GPS was used to take and record sampling location. In
addition, sufficient quality-controls were also considered during the sampling process. This included the use of uncontaminated reagent water (deionised water).

Table 4.3: Indicates surface and groundwater sampling points.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Sample Position</th>
<th>Elevation (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X Coordinates</td>
<td>Y Coordinates</td>
</tr>
<tr>
<td>Surface Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RWS1</td>
<td>X: 25° 38’ 55.1” S</td>
<td>Y: 28° 08’ 49.4” E</td>
</tr>
<tr>
<td>RWS2</td>
<td>X: 25° 38’ 53.9” S</td>
<td>Y: 28° 08’ 49.2” E</td>
</tr>
<tr>
<td>RWS3</td>
<td>X: 25° 38’ 53.7” S</td>
<td>Y: 28° 08’ 49.7” E</td>
</tr>
<tr>
<td>Groundwater BH1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RWS4</td>
<td>X: 25° 39’ 04.5” S</td>
<td>Y: 28° 09’ 38.2” E</td>
</tr>
<tr>
<td>RWS5</td>
<td>X: 25° 39’ 04.5” S</td>
<td>Y: 28° 09’ 38.2” E</td>
</tr>
<tr>
<td>RWS10</td>
<td>X: 25° 39’ 04.5” S</td>
<td>Y: 28° 09’ 38.2” E</td>
</tr>
<tr>
<td>Groundwater BH2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSW6</td>
<td>X: 25° 39’ 05.9” S</td>
<td>Y: 28° 09’ 28.5” E</td>
</tr>
<tr>
<td>RWS7</td>
<td>X: 25° 39’ 05.9” S</td>
<td>Y: 28° 09’ 28.5” E</td>
</tr>
<tr>
<td>RWS9</td>
<td>X: 25° 39’ 05.9” S</td>
<td>Y: 28° 09’ 28.5” E</td>
</tr>
<tr>
<td>Municipal Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RWS8</td>
<td>X: 25° 39’ 05.8” S</td>
<td>Y: 28° 09’ 29.2” E</td>
</tr>
</tbody>
</table>

The locations of these water sampling points were indicated in Figure 5.8 (see page 72) and the grouping of samples was defined by the location (surface and groundwater). Water sampling was conducted based on the methodology of the United States Geological Survey (USGS, 2006), with the following steps outlined below:

- The workplace was cleaned and properly arranged as a safety protocol, and sampling tools were assigned.
- Sample containers were field rinsed several times with the sample prior to sampling commencement.
- GPS was used to locate all three sampling points; latitude and longitude coordinates were documented in the field book and also saved in the GPS.
- Vertical sections were developed and the depth of the sampling point was measured and recorded in a field notebook.
- A sterilised 250 ml plastic sample bottle was immersed carefully to a depth of 20 cm in such a manner that the bottle was allowed to fill without creating a column.
disturbance, as indicated in Figure 4.4. According to Boone et al. (1999) glass containers are not suitable for collection of water samples to be analysed for trace metals. Therefore, the apparatus (plastic sample container) used to collect water was found suitable for this research.

![Still-surface water sampling procedure](image)

**Figure 4.4: Still-surface water sampling procedure for the study (Bartram et al., 1996).**

- The sampling container was sealed immediately after the sample was collected.
- Thereafter, these samples were placed in an Ice Cooler Box prior to be stored overnight in the freezer.
- Finally, these samples were transported the following day to the ARC laboratory for further analysis within seven days after collection.

### 4.2.2.3 Groundwater sampling

Groundwater sampling was undertaken on two operational environmental monitoring boreholes located in the site. The schematic diagram as indicated in Figure 4.5, illustrates the monitoring borehole similar to the ones in the study area. As such, the monitoring well is used to monitor the groundwater environment.
This is an overview of the type of a well borehole used for groundwater sampling in the study area. The structure of the well comprised of a bottom plate, well screen which keeps sand and gravel out of the borehole, gravel pack, grout seal which protect well from contamination from caving materials. For consistency, all representative groundwater samples were collected on the same day (18 February 2016), at the Onderstepoort MSW landfill site, when the sun had reached its peak (12 pm). The Environmental Protection Agency (EPA, 2000) recommended purging of the well before groundwater sampling commenced in order to remove the static and stagnant water. Previous EPA (2000) studies have revealed that under most conditions low flow purging with bailing did not give false sampling results, provided that these were done in a vertical manner. Bailing was also reported to produce sampling results that were lower than the actual concentrations within the adjacent formation (Newell et al., 2000; Puls & Powell, 1997).

Groundwater sampling was undertaken on two monitoring wells instead of three as initially planned. The third borehole could not be sampled as it was not operative and could not be traced. Groundwater sampling was collected manually, meaning conventional well purging and pumping method was not applied due to unavailability of the pumping equipment in the study area, but well purging was conducted using bailing method (EPA, 2000) as shown in Figure 4.6.
Groundwater sampling differs from surface water sampling and involved the following procedure (USGS, 2006):

- Monitoring wells were identified and GPS was used to locate the wells.
- Sampling latitudes and longitudes were determined using Garmin Montana 650 GPS.
- Prior to sampling, hazards and environmental concerns were checked and considered including using of appropriate Personal Protective Equipment (PPE).
- Sediments covering the borehole were removed using a shovel.
- The borehole concrete cover was removed in order to access the borehole.
- The monitoring well was observed prior to sampling and documented in the field book.
- The sterilised sampling bottle was secured to the end with a clean rope and the weight was attached to the bottle as illustrated in Figure 4.6.
- Well purging was conducted using a clean bailer which was lifted carefully several times avoiding gross purging which may mixes the entire borehole. Vance (1997) indicated that the more vigorously a monitoring well is purged, the more the sample likely to under represent contamination level.
- After purging the standing water in the well, the bailer/sample container was lowered carefully to the bottom of the well and elevated carefully at an undisturbed rate, while considering keeping the suspension line clean off the ground. The purging water was disposed in an appropriate manner.

![Diagram of groundwater sampling procedure](image)

**Figure 4.6: Demonstrates groundwater sampling procedure used (Bartram et al., 1996).**
• A sample bottle was supported by a string and weight, the bottle was then directed towards borehole in order to collect a representative groundwater sample.
• Three samples were collected per monitoring well. Each sample was taken using a sterilised 250 ml sample bottle which was prepared at the laboratory and dried as a precaution measure.
• Duplicate samples were collected as a Quality Assurance/Control procedure.
• The unique sample number was documented on the sampling book.
• Finally, the sample container was closed tight and marked appropriately, before being placed in an Ice Cooler Box to keep it chilled until delivered to the freezer storage in the laboratory for further analysis.

Appropriate Personal Protective Equipment (PPE) was used at all times during sampling, which included the wearing of proper disposal powder-less gloves in every new sampling point. The sampling equipment including sampling containers/bottles were pre-washed, cleaned and rinsed according to the recommended procedures.

4.2.2.4 Leachate sampling

Due to the absence of percolating water in February 2016, it was deemed necessary to follow up this investigation after some rain had fallen. Following a period of rain during February 2016, dark grey leachate with a putrid smell was seen flowing in the study area, as indicated in Figure 4.7. As discussed previously, leachate collection was in sterile sample containers. A leachate solution was sampled at the bottom of the waste dump together with the leachate soil sample; the sampling point was represented as TS2 in Figure 5.8 (see page 72).
4.3 Laboratory Investigations and Materials

In order to determine the contaminants of leachate in soil and water in the site, laboratory investigations were conducted at the ARC Institute for Soil, Climate and Water (ISCW) and Waterlab (Pty) Ltd. Laboratory investigations were used to determine:

- Dissolved organic content (DOC) i.e. biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in landfill leachate solution.
- Inorganic macro-components in water samples.
- Heavy metals in soil, water and leachate.

4.3.1 Soil samples preparation

Soil samples were delivered to ARC: ISCW a day after sampling. As previously mentioned, soil samples prior to delivery, were stored in a cool dry place to maintain integrity, after which they were removed from sampling bags and disposed in non-corrosive sample dishes immediately after arrival at the laboratory. The soil processing involved drying, grinding and chemical related analyses. Soil samples were attached with the original sample number. The samples were sorted in a chronological order according to the field notebook list. Thereafter, these samples were registered for analyses and unique laboratory numbers were assigned.
4.3.1.1 Drying

Soil samples were transferred to oven trays to be oven dried at a maximum temperature of 50 ºC for a 24 hour drying period (Figure 4.8), and at all times ensuring that relevant number was placed with each sample tray.

4.3.1.2 Sieving and grinding

Soil sample should be crushed in order to obtain the particles of similar size (IRRI, 2011). Conventionally, large particles are crushed to reduce the size and grinding is used to further reduce the sample particles (Tan, 1996). In most cases, it is critical that soil samples for chemical analyses pass through a 2 mm sieve in order to recover a representative subsample (Boone et al., 1999). The main objective of sieving is to homogenize the sample after the grinding process (Tan, 1996).

![Figure 4.8: Soil preparations for chemical laboratory analysis.](image_url)

Each sample was placed in a non-corrosive sample dish together with the sample ticket as shown in Figure 4.8 and placed in an oven for drying purposes. After allowing a period to cool, these processed samples were prepared and then sent to the Grinder Room where 2 mm fraction was produced. The weight of each whole sample was noted prior to the grinding process, which involved a jaw crushing (Nasco-Asplin Soil Jaw Grinder), where crushed material was passed through 2 mm sieves, before being transferred into marked containers, as shown in Figure 4.9. To maintain the integrity of
crushed sample material, the crushing surface was subject to a blast of compressed air, which was then brushed, before the passage of the next sample.

Figure 4.9: 2 mm fraction soil samples ready for heavy metals analysis.

4.3.2 Dissolved organic content (DOC) analysis

The BOD and COD concentrations in leachate sample were determined at the Waterlab (Pty) Ltd, located 23B De Havilland Crescent, Persequor Techno Park, Meiring Naude Road, Pretoria.

4.3.2.1 Biochemical oxygen demand (BOD)

The determination of a five-day biochemical oxygen demand (BOD₅) was conducted using Winkler method (Rounds et al., 2013). The equipment components used during analysis include BOD bottles; BOD incubator; 300 mL glass stopper BOD bottles; 500 mL conical flask; pipette with elongated tip; wash bottles; burette and burette stand; glass beads; pump and compressor.

Reagents for the analysis comprise sodium azide; manganous sulphate; calcium chloride; magnesium sulphate; ferric chloride; di potassium hydrogen phosphate, ammonium chloride, potassium hydroxide, potassium iodide, concentrated sulphuric acid, starch indicator, sodium thiosulphate and distilled water. The reagents for BOD₅ analysis were prepared as shown in Figure 4.10.
Simplified biochemical oxygen demand analysis process used for analysing leachate solution sample. Steps 1-3 involve the preparation of reagent and Steps 4-5 involve the actual testing of sample (sample analysis).

Sample Analysis

Samples were incubated at a temperature of 20 °C for a period of 5 days. In this manner, the dissolved organic (DO) content within the samples was determined prior and after five days of incubation at a temperature of 20 °C. For the determination of the BOD after five days, the difference between initial and final DO was calculated to determine the BOD concentration of the samples.

As shown in Figure 4.10, steps 4-7 are therefore explained in detail. A maximum of four 300 mL glass stoppered BOD bottles were used. Two of these BOD bottles were for the sample solution, hence another two were for the blank solution. Therefore, 10 mL of the sample was added to the two BOD sample bottles and the remaining quantity was diluted with water. Dilution water was added to the two BOD bottles for the blank samples. The glass stoppers were placed over the BOD bottles immediately after addition. The identification numbers of the BOD bottles were noted down. Two BOD bottles, one containing blank and the other containing sample were preserved in a BOD incubator at 20°C for a period of five days. The remaining two bottles, for blank
and sample solution were analysed immediately. This experiment was conducted avoiding bubbles occurrence.

After five days of samples incubation at 20 °C, the BOD bottles were taken out of the incubator for further analysis. A 2 mL of manganese sulphate was added to the BOD bottles through insertion of the calibrated pipette below the surface of the liquid. A 2 mL of the alkali-iodide-azide reagent was added also using a calibrated pipette. Appropriate time was provided so that a brownish-orange cloud settles to the bottom and the contents were hand shaken thoroughly. A pipette was used to add 2 mL of concentrated sulphuric acid above the sample surface.

The titration process was initiated immediately after transferring the contents to the flask. The burette was rinsed with sodium thiosulphate and then filled with sodium thiosulphate. A 203 mL of the solution was measured from the solution and transferred to the flask. The standard sodium thiosulphate solution was used to titrate the solution until the yellow colour faded out. Then 1 mL of starch solution was added and titration continued until the blue colour became colourless. The volume of sodium thiosulphate solution added which gives the DO in mg/L was recorded.

**BOD\(_5\) Determination**

\[
\text{BOD}_5 \text{ (mg/L)} = (D_1 - D_2 - BC) \times \frac{\text{Volume of the diluted sample}}{\text{Volume of sample taken}}
\]

Where \(D_1 = \text{Initial DO of the diluted sample.}\)

\(D_2 = \text{Final DO of the sample after 5 days.}\)

BC = Blank Correction.

\(C_1 = \text{Initial DO of the blank.}\)

\(C_2 = \text{Final DO after 5 days.}\)

4.3.2.2 Chemical oxygen demand (COD)

In order to determine the COD concentration in leachate sample, COD Dichromate Open Reflux method was utilised. The method used was benchmarked with the Method 410.4 for the determination of COD as provided by the U.S Environmental Protection Agency, USEPA (1993).
For the functionality of the method, the components used were; COD digester, burette and burette stand, COD vials with stand, 250 mL conical flask, pipettes, wash bottle and pipette bulb. The analysis was performed under a formal quality control program which includes analysing blanks with each batch of samples. A series of at least three standards and blanks were processed as calibration check.

Sample Analysis

In this process, 1.5 mL of the sample was added to two of the three COD vials with a stopper. Distilled water was added to the remaining COD vial (blank). Then, in all three COD vials, 2.5 mL of potassium dischromate reagent (digestion solution) was added. Thereafter, 3.5 mL of sulphuric acid reagent (catalyst solution) was added to all three COD vials. The tubes were capped tightly, placed in a COD digester for 2 hours at a temperature of 150 ºC.

After 2 hours, the digester automatically switched off, the COD vials were removed and left to cool to the room temperature. The burette was filled with the ferrous ammonium sulphate solution, adjusted to zero and placed to the burette stand. The contents from the blank COD vial were transferred to the conical flask. Few drops of ferroin indicator was added to the conical flask containing blank contents and titrated with the ferrous ammonium sulphate from the burette.

A reddish brown colour appeared at the end of titration and the added volume of ferrous ammonium sulphate solution was recorded. Thereafter, the contents of the sample were transferred from COD vial to conical flask and few drops of ferroin indicator were added. The colour of the solution became green and the ferrous ammonium sulphate was used for titration. A reddish brown colour appeared at the end of the titration process. As such, the volume of ferrous ammonium sulphate solution added was recorded. The COD concentration was thereafter calculated.

4.3.3 Inorganic macro-components analysis

Research Objective 2: To determine water quality, investigate the presence of heavy metals and inorganic macro-components within the surface and groundwater system.
4.3.3.1 Ion Chromatography

The Ion Chromatography System: Dionex-1600 was used for the determination of the inorganic anions in liquid samples. The method was based on the USEPA (1993) method 300.0 for the determination of inorganic anions (i.e. phosphate, nitrite, nitrate, chloride, sulphate and fluoride) by Ion Chromatography. Instrumental conditions used to run Ion Chromatography included:

- Columns (Dionex ionpac AS22, 4 X 250 mm).
- Eluent (4.5 mM sodium carbonate, 1.4 mM sodium carbonate).
- Flow rate (1.2 ml/minute).
- Column temperature (30 ºC).
- Detection (suppressed conductivity).
- System backpressure (1800 psi).

Instrument Calibration and Standardisation

Prior to undertaking any analysis, the Ion Chromatography System was calibrated using a standard solution. The calibration standards were prepared for every analyte at a minimum of three concentration levels. The preparation of a blank solution was carried out by adding the volumes of stock standards to a volumetric flask. The contents of the volumetric flask were diluted with reagent water. The instrument was calibrated weekly and when a new eluent was being processed. The calibration curve was verified in a daily basis, after running a batch of 20 samples and when a new eluent was introduced. Water samples were filtered to remove sediments and particles prior to running the Ion Chromatography instrument. At the beginning of each batch, the reagent blanks were run and quality control was run after every 20 samples and at the end of every batch.

Instrumentation and Procedure

The process involved the use of liquid solvent, pump, injector, column, suppressor and conductivity detector as shown in Figure 4.11.
The introduction of eluent was delivered into the pump and the sample flows through the column for separation of the ion-exchange. After the suppressor of eluent, the analytes were introduced to the detector as indicated in Figure 4.11. The Ion Chromatography instrument uses six steps to detect inorganic anions in water samples. These include eluent delivery to the system, sample injection, separation, suppression, detection and the final step was based on data analysis as shown in Figure 4.12.
Step 1: eluent delivery, Step 2: sample injection to pump eluent at a constant level to the injector, Step 3: sample ions separation, Step 4: suppression, Step 5: detection and Step 6: data analysis using data processing device to evaluate the detector signals and produces a chromatogram.

A sample was introduced into a carbonate-bicarbonate eluent, which went through a pump, injector and columns. The ions were then separated using a separator column. The separated anions went through the suppressor where they were converted into highly conductive acid forms; hence the eluent was converted into weakly conductive carbonic acid. After the conversion process, the anions were measured by the conductivity detector and transmitted the signal to the data processing device. The Chromleon Chromatography Data System Software was used to produce a standard curve and standard responses against known concentration. Based on the response of the analytes of unknown sample, concentration was determined in order to develop a calibration curve.

4.3.3.2 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

The detection of Na$^{2+}$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ in water samples was conducted using ICP-OES instrument (Ultima JY Model). The ICP-OES instrument used to study water samples was also implemented for the study undertaken by Rudel et al. (2007) for the determination of the elemental content of environmental samples.

**Calibration**

Before analysing the samples, the instrument was calibrated and checked for wavelength accuracy. The calibration was undertaken using instrument programs and the standard solutions were diluted before analyses accordingly. The calibration validation was conducted continuously during samples analysis. The instrument before use was set based on the manufacturer instructions. The instrument remained switched-on for a period 30 minutes before starting with sample analysis process. Rudel et al. (2007) indicated that, for each element/ion being analysed by the ICP-OES, the determination of at least one straight calibration line with minimum of four concentrations should be implemented.

Therefore, the highest standard concentration received from the calibration process should be above the lowest concentration by a factor of 10-20. Whenever this
standard was not met, more calibration solutions should be conducted (Rudel et al., 2007). The instrument was also tested for functionality through using appropriate standard solutions containing the analysed of interest. The reagents used include water from a high-purity water supply system and nitric acid.

**Sample Analysis**

The standards together with a blank solution were introduced to the instrument in order to calibrate the instrument. A representative sample was introduced into the instrument as a liquid; a nebulisation process responsible for converting liquid into aerosol then took place. The aerosol was transported to the high-frequency plasma. Thereafter, the constituents of the sample solution were atomised and partially ionised. The atoms and ions produced radiation which turned into electronic signals. The electronic signals were converted into concentration information and sent to the computer as shown in Figure 4.13. The software in the emission spectrometry, evaluated the data produced.

![ICP-OES instrument for major cations detection](image)

**Figure 4.13**: ICP-OES instrument for major cations detection (Boss & Fredeen, 2004).

Figure 4.13 shows processes and stages involved during the cations scan, wherein the first stage involved sample introduction to the system and the last stage is the data processing using a computer. The method uses a pump to deliver the liquid to a nebuliser which then converts a liquid into aerosol, aerosol goes through the torch and
injected into the plasma through spray chambers. The photo multiplier tube (PMT) instrument component measured the intensity of the emission line. Electronics were used for signal processing and computer system to control the function of the ICP-OES instrument.

4.3.4 Heavy metals analysis

Research Objective 1: To analyse the heavy metals in soils and establish the impact of leachate on soil quality.

Research Objective 2: To determine water quality, investigate the presence of heavy metals and inorganic macro-components within the surface and groundwater system.

In order to determine the heavy metals in soil samples collected in and around the waste dump at the study area, Microwave Assisted Digestion (MAD) method was used to acid digest the samples and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technology was utilise to detect metals available together with their concentration levels.

4.3.4.1 Microwave Assisted Digestion (MAD)

In order to determine the available trace metals in soil samples, the digestion of the samples was conducted using the Microwave Assisted Digestion (CEM Model MARS Express). According to Mangum (2009), samples preparation using Microwave Assisted Digestion results into efficient and clean sample for undertaking the multi-element analytical techniques using ICP-MS. The MAD method was used to acid digest the organic matrices within the soil samples, thereby destroying the organic material in order to analyse the trace metals through ICP-MS.

Calibration and Standardisation

Prior to undertaking samples treatment, the instrument was evaluated for output power available in order for the microwave to transfer power from one system to another. The temperature sensing equipment was verified prior to samples treatment. The digestion vessels together with the volumetric flacks were acid washed, rinsed thoroughly and dried in a clean environment. The weighing machine was calibrated prior to weighing of 1.000 g of soil sample. The sample weighing machine was calibrated using precision mass standard (empty weighing dish) of a known accuracy.
Internal Standard and Solutions

Distilled-deionized water (18 MΩ-cm type 1 water), nitric acid (65 % Ensure grade), hydrogen peroxide (30% AR grade) and certified reference materials (CRMs) were used to prepare samples and standards. During the process, health and safety protocols were considered at all times including safe handling of the chemicals and supervision. Duplicate and blank samples were processed together with the batch of samples; by use of the same analysis and reagents quantities.

Instrumentation and Procedure

For the samples preparation, 1.000 g of soil sample was weighed and transferred to the inert polymeric microwave digestion vessels, the sample weighing was done keeping in mind the accuracy of the sample results. Thereafter, 9.00 mL of concentrated nitric acid (HNO₃) and 2.00 mL of hydrogen peroxide (H₂O₂) were added into the sample vessels. The sample mixes were then allowed to react inside the vessels before these were sealed and left to stand overnight.

![Microwave Assisted Digestion instrument](image)

Figure 4.14: Microwave Assisted Digestion instrument (Hewitt & Reynolds, 1990).

Figure 4.14 illustrates the microwave oven (left) and digestion vessels on a rotating turntable, venting nut, vent tubing, vessel cap, safety valve and vessel body (right). The sample vessels were hand shaken and put into the microwave carousel so that all
the digested samples obtain same treatment of the microwave energy. Thereafter, a set of digested vessels comprising of the vessels tray, vent tubing and vessel cap were placed into the microwave oven. The diagrams indicating the microwave oven and digestion vessel are shown in Figure 4.14.

After a successful microwave programme, the sample vessels were allowed to cool to room temperature and to decrease the internal pressure. The vessels were therefore removed from the microwave oven, opened individually, and the contents of the sample vessels were quantitatively transferred to 100 mL volumetric flasks. Each labelled sample extract was diluted to volume with deionized water as shown in Figure 4.15. Thereafter, for ICP-MS preparations, 3% of nitric acid was added to the samples, with indium solution as internal standard.

![Figure 4.15: Diluted soil sample extracts for trace metals analysis using ICP-MS.](image)

4.3.4.2 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The ICP-MS method used to analyse heavy metals for the research study was recommended by the World Health Organisation (2008) as the suitable-applicable technology. Bazilio and Weinrich (2012) indicated that ICP-MS is the most appropriate-quantitatively instrument for determining trace metals in water and extracted (soil) samples. ICP-MS, Agilent 7700x Model was used for the analysis of the heavy metals (As, Cd, Cr, Hg, Pb, Mn, V, Ni and Co) concentrations in soil and
water samples. ICP-MS method has been regarded as the most versatile and well proven method (Mangum, 2009), which makes it more suitable for this study.

![Diagram of the ICP-MS process](image)

**Figure 4.16: Five main stages employed for the ICP-MS process (Bailey et al., 2003).**

The grinding of the soil samples was the first step for ICP-MS analysis, representative samples were weighed and sample digestion then took place through MAD, followed by sample dilution prior to heavy metals scan as shown in Figure 4.16.

**Maintenance of Instrument**

The instrument used for analysis was regularly maintained including daily, monthly and annually. Standard tuning solution was used to daily check instrument performance, in order to determine the sensitivity or interference problem. Before undertaking any sample analysis, a performance check was run. Instrument performance report was obtained before starting with samples analysis.

**Calibration**

The calibration was carried out before analysing the samples and for every element analysed, one straight calibration line was determined and the validation of the calibration was verified using CRMs. The tuning solutions containing all required isotopes of elements were analysed sequential. The calibration standards together with the blank were run wherein the software created a calibration curve of the
measured element vs. element concentration within the standard. The standard mode performance and instrument calibration was taken into consideration during the analysis of the samples. The calibration standards were analysed and calibration report was produced.

The determination of the elements was through the use of elements atomic mass. The multi-element solution containing high concentration of low mass elements and low concentration of high mass elements and standard tuning solution was used for calibration. The samples analysed after analysing a sample with high concentration were retested. The elements atomic mass used were cobalt (59); vanadium (51); chromium (52); manganese (55); mercury (202); arsenic (75); cadmium (111); copper (65); zinc (66) and nickel (60). The samples were analysed with ICP-MS 7700x after 10x dilution with 3% nitric acid with indium as internal standard.

**Internal and External Standardisation**

The process involved measuring blank solutions to zero the instrument in order to subtract contribution of solvent matrix. The internal standard involved the diluent wherein deionised water together with nitric and hydrochloric acid was used. Blank samples were prepared using the same reagents used in the sample preparations. Per each batch of samples, duplicate samples were also processed to maintain sample integrity. The Standard Operating Procedure (SOP) developed by USEPA (2011) for ICP-MS method indicated that the objective of the duplicate samples is to validate the quality of the method used during the analyses and also on various matrices. Furthermore, USEPA (2011) pinpointed that at least one duplicate sample need to be analysed for a group of samples with homogeneous matrix type such as water or soil. The reagent blanks were run at the start of each batch; hence the quality control was run after every 20 samples and at the end of every batch. These include the use of CRMs regularly to assess the performance of the method.

**Instrument**

The Agilent 7700x ICP-MS instrument uses Sample Introduction System comprising of low-flow concentric nebuliser operating at 0.2 mL/minute in order to lower sample consumption and minimized matrix effects, spray chamber assists in removal of larger aerosol droplets, peristaltic pump, plasma, a high-frequency mass analyser, detector,
vacuum system and Agilent’s ICP-MS Mass Hunter Workstation Software which provides exhaustive functionality of the instrument.

**Quantitative Elemental Analysis**

The sample was introduced into the system in a form of a liquid, and then pumped at 1 mL/min using a peristaltic pump into a nebuliser. The nebuliser converted a sample into fine aerosol with argon gas. The aerosol fine droplets representing 1-2% of the sample were separated from large droplets using a spray chamber. The fine aerosol emerged from the spray chamber and was introduced into the plasma using an injector as shown in Figure 4.17. The plasma was then formed by the interaction of an intense magnetic field on a tangential flow of gas. When ionizing of gas seeded with a source of electrons from a high-voltage spark, formed a very-high-temperature plasma discharge at the open of the tube. The plasma torch produced positively charged ions; the generated ions were transported into the mass-spectrometry using the interface region. The metallic cones allowed the ions to pass through the ion optics and introduced into the mass separation device (Thomas, 2004; WHO, 2008).

![Figure 4.17: Basic components of the ICP-MS instrument (Thomas, 2004).](image)

The basic components of the ICP-MS instrument include nebuliser, spray chamber, plasma torch and a detector as shown in Figure 4.17. Thomas (2004) emphasized that one of the crucial stages of the ICP-MS is the interface region wherein the ions
are transported efficiently considering electrical integrity from the plasma to the mass spectrometry analyser region.

After the ions were extracted successfully from the interface region to the mass spectrometry analyser region, they were introduced into the main vacuum chamber by a series of ion optics. The ion optical region prevented the photons to reach a detector. The ion beam which contained analytes and matrix ions exits the ion optics into the mass spectrometry which is the mass separation device. The mass separation device allowed analyte ions of a particular mass-to-change ratio through the detector and filtered out all the non-analyte, interfering and matrix ions as shown in Figure 4.18. The ions were finally converted into an electrical signal with an ion detector. The electronic signal was then processed by the data handling system and lastly converted into the analyte concentration using ICP-MS calibration standard (Thomas, 2004).

![Diagram of ICP-MS instrument](image)

**Figure 4.18: ICP-MS instrument (Batsala et al., 2012).**

### 4.3.5 Other Parameters

The determination of the pH of the sample involved calibrating the pH meter first using buffer solutions of pH 4.0, 7.0 and 9.2. The calibration of the pH instrument involved the following procedure; the pH meter was switched on approximately 30 minutes before use, the pH meter was calibrated to the pH of 9.2, 7.0 and 4.0 using the buffers
and adjustment of the calibration knob. The apparatus required include the pH meter, standard flasks, magnetic stirrer, funnel, beaker, wash bottle and tissue paper.

The 50 mL of sample was placed into a clean dry 100 mL labelled glass beaker prior to inserting a teflon coated stirring bar. A glass beaker was placed on a magnetic stirrer and the probe was placed in a beaker considering that the sensor base was covered completely. The sample reading was allowed to stabilise before recording the pH value. The probe was always rinsed with de-ionised water between the samples and soft tissue paper was used to wipe the probe.
CHAPTER FIVE: RESEARCH RESULTS

5.1 Introduction

Bhalla et al. (2012) indicated that MSW leachate characteristics and contaminants could be determined through the measurement of the pH value; total dissolved solids (TDS); biochemical oxygen demand (BOD$_5$); chemical oxygen demand (COD); and heavy metal concentrations. The above mentioned parameters were used to determine the quality of soil and water in the study area. Therefore, this Chapter presents the results obtained on the dissolved organic content, inorganic macro-components and heavy metals. Surface and groundwater sampling process was undertaken on three locations i.e. surface water, Borehole 1 and Borehole 2 as shown in Figure 5.1.

![Figure 5.1: Water sampling locations at the study area (TECC, 2016).](image)

Borehole 2 of groundwater is located at the foot of the waste dump, whilst Borehole 1 is located further away from the waste dump as shown in Figure 5.1. The quality of groundwater in Borehole 1 and 2 could also be influenced by the distance/locality of the waste dump. Figure 5.8 (see page 72) illustrates in detail the surface and groundwater sampling points. The results for this study were organised in two formats
i.e. from lowest to highest value (Lohaka, 2007) and according to the location of the sampling sites.

5.2 Leachate Soil Sample

Leachate soil sample was analysed for heavy metal concentrations, the results are presented in Table 5.1. The metals were grouped from lowest to highest concentration, according to the *ordered array* method (Lohaka, 2007). The author, Lohaka (2007) stated that the raw/unorganised data is difficult to understand and interpret. Therefore, the raw data could be arranged in an *ordered array* method from lowest to highest value (ascending) or from highest to lowest value (descending). In contrast, the raw data for this study was classified into low, moderate, high and very high concentration range as presented in Table 5.1. According to Table 5.1, the concentrations of metals in leachate were classified into groups (Group A-D); low concentration range (0.214 to 0.314 mg/kg), moderate concentration range: (5.783 to 19.465 mg/kg), high concentration range (65.893 to 122.052 mg/kg) and very high concentration range (868.254 to 2505.611 mg/kg).

*Table 5.1*: Heavy metal concentrations detected in leachate soil sample vs. national (NEMA, 2008) and World Health Permissible Limits (Ekpete & Festus, 2013).

<table>
<thead>
<tr>
<th>Sample Label: TS1</th>
<th>Soil Quality Guidelines</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heavy Metals</strong></td>
<td><strong>Concentration</strong> (mg/kg)</td>
</tr>
<tr>
<td><strong>Group A</strong></td>
<td>Cadmium: 0.214</td>
</tr>
<tr>
<td></td>
<td>Mercury: 0.314</td>
</tr>
<tr>
<td><strong>Group B</strong></td>
<td>Arsenic: 5.783</td>
</tr>
<tr>
<td></td>
<td>Lead: 8.134</td>
</tr>
<tr>
<td></td>
<td>Cobalt: 19.465</td>
</tr>
<tr>
<td><strong>Group C</strong></td>
<td>Copper: 65.893</td>
</tr>
<tr>
<td></td>
<td>Nickel: 104.237</td>
</tr>
<tr>
<td></td>
<td>Zinc: 122.052</td>
</tr>
<tr>
<td></td>
<td>Vanadium: 183.279</td>
</tr>
<tr>
<td><strong>Group D</strong></td>
<td>Chromium: 868.254</td>
</tr>
<tr>
<td></td>
<td>Manganese: 2505.611</td>
</tr>
</tbody>
</table>
The leachate soil sample, TS1 as indicated in Figure 5.3 was collected at the bottom of the waste dump between sample RSS1 and RSS2. The grouping of heavy metals was defined by the level of contamination. In total, 30 trace metals were detected by the ICP-MS instrument. However, the research study focused on studying and analysing mercury; arsenic; cadmium; lead; copper; zinc; nickel; cobalt; vanadium; chromium and manganese.

i) **Group A: Low Concentrations**

The concentration level of mercury in leachate soil was found to be 0.314 mg/kg, whilst cadmium comprises a fraction of 0.214 mg/kg as shown in Table 5.1.

ii) **Group B: Moderate Concentrations**

The concentration levels of cobalt, lead and arsenic in leachate soil sample were 19.465 mg/kg, 8.134 mg/kg and 5.783 mg/kg respectively.

iii) **Group C: High Concentrations**

Under Group C of the trace metals; vanadium, zinc, nickel and copper were found to be active in leachate soil sample at high concentrations as compared to mercury, cadmium, cobalt, lead and arsenic. The highest concentration in Group C was 183.279 mg/kg (vanadium), while copper has the lowest value of 65.893 mg/kg as shown in Table 5.1.

iv) **Group D: Very High Concentrations**

The highest concentration levels of the selected metals in leachate soil sample were found to be manganese with an actual value of 2505.611 mg/kg and chromium (868.254 mg/kg).

### 5.3 Leachate Solution Sample

Bhalla et al. (2012) emphasised that for the determination of organic content, this could be achieved through measuring the COD, BOD and dissolved organic carbon. Therefore, leachate solution sample collected from the study area was analysed for BOD, COD and heavy metals. This was accomplished using Winkler method,
Dichromate Open Reflux method and ICP-MS technology. Figure 5.2 indicates the concentration levels of the COD and BOD determined in the leachate solution sample.

5.3.1 Dissolved organic content in leachate solution

Figure 5.2 shows the BOD and COD laboratory results obtained on the leachate solution sample. The BOD value obtained from the laboratory was 945 mg/L, whilst the COD concentration was 18 800 mg/L as shown in Figure 5.2.

![Figure 5.2: BOD₅ and COD concentration levels in leachate solution sample.]

5.3.2 Heavy metals in leachate solution

Table 5.2 summarises mercury, arsenic, cadmium, lead, copper, zinc, nickel, cobalt, chromium, vanadium, and manganese laboratory results obtained on leachate solution sample. In this case, metals were sub-divided into three groups of low; moderate and high concentrations.

As indicated previously, Lahaka (2007) pinpointed that the simplest method to organise raw data in a systematic format is through the ordered array method. This method assists in determining the minimum and maximum values and further provides the distribution of heavy metals concentrations over the range. For results presentation therefore, the metals were grouped from lowest to highest concentration (low, moderate and high). The data was classified into three groups; lowest
concentration (0.05 to 0.175 mg/L), moderate concentration (1.109 to 1.762 mg/L) and high concentration (2.309 to 6.296 mg/L).

**Table 5.2:** Measured concentrations of heavy metals in leachate solution sample vs. national and international water quality guideline values.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>Elements</strong></td>
<td><strong>Concentration</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(mg/L)</td>
<td>(mg/L)</td>
</tr>
<tr>
<td><strong>Group A</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.015</td>
<td>0.006</td>
</tr>
<tr>
<td>Lead</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.175</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Group B</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>1.109</td>
<td>2</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1.574</td>
<td>0.5</td>
</tr>
<tr>
<td>Vanadium</td>
<td>1.762</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Group C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>2.309</td>
<td>0.05</td>
</tr>
<tr>
<td>Zinc</td>
<td>3.303</td>
<td>5</td>
</tr>
<tr>
<td>Manganese</td>
<td>4.302</td>
<td>0.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>6.296</td>
<td>0.07</td>
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</tbody>
</table>

Leachate solution sample (TS2) was collected at the bottom section of the waste dump as shown in Figure 5.8 (see page 72). The concentration levels of metals in leachate solution sample were significant lower than in leachate soil sample as shown in Table 5.1.

i) **Group A: Low Concentrations**

Cadmium was determined to be characterised by the lowest concentration among the selected heavy metals as indicated in Table 5.2. The highest heavy metal concentration level in Group A of the leachate solution sample was determined to be arsenic with a concentration of 0.175 mg/L; hence the lowest concentration was 0.005 mg/L of cadmium as shown in Table 5.2. Characterisation and distribution of arsenic, mercury, lead and cadmium selected metals in the leachate solution sample were low as compared to other metals.
ii) **Group B: Moderate Concentrations**

Group B of heavy metals in landfill leachate was characterised by vanadium, cobalt and copper as shown in Table 5.2. These metals comprised of intermediate concentrations when compared to Group A and C. The detected concentration level of vanadium was 1.762 mg/L, cobalt 1.574 mg/L and copper 1.109 mg/L.

iii) **Group C: High Concentrations**

In Group C, a set of the selected heavy metals consisting of the highest concentrations in leachate solution sample were clustered together. The metals under Group C of the highest concentrations were nickel, manganese, zinc and chromium. The concentration levels of nickel, manganese, zinc and chromium were 6.296 mg/L, 4.301 mg/L, 3.302 mg/L and 2.309 mg/L respectively.

### 5.4 Soil Quality Results

In order to determine soil quality in the study area; arsenic, cadmium, chromium, copper, mercury, lead, manganese, zinc, vanadium, nickel and cobalt selected trace metals were analysed and the results as means were presented in Figure 5.4, 5.5, 5.6 and 5.7 (see page 68-70). The metals were categorised into four groups defined by the sampling location. The histograms were used to summarise data in a numerical system, from the highest to lowest concentration (descending). A histogram is defined as a graphical technique that summarises how quantitative data were distributed (Kaplan et al., 2014).

The sampling area was divided into four groups/sites. As indicated in Figure 5.3, sampling point number RSS15 is located further away from the waste dump, with a little less disruption. At this sampling point (RSS15), metals such as arsenic, cadmium, copper, lead, manganese, zinc and nickel were substantially lower than in other sampling points. Group A of the soil samples comprises sample number RSS15, RSS1 and RSS12. Group B is made up of sampling points RSS2, RSS11, RSS4 and RSS3; Group C (RSS5, RSS10, RSS13 and RSS14) and Group D consists of sampling points RSS9, RSS6, RSS7 and RSS8.
Soil samples RSS1 and RSS12 of Group A were located at the edge of the waste dump and characterised by sandy soil with khaki colour. Group B of the soil samples was located approximately 200 m away from Group A and composed of reddish brown colour. Group C was located at the centre of the landfill dump and characterised by very fine soils, whilst Group D was located far right of the waste dump as indicated in Figure 5.3. The visible haulage road between sampling points RSS6 and RSS9 was created by vehicles transporting waste material to the working-face. During this process, which is the transportation of waste, vehicles may also be source of contaminants/chemicals released to the soils. Therefore, some of the impacts at the study area may be accumulated due to the movements of haulage trucks and vehicles transporting waste into the site.

The map (Figure 5.3) illustrates soil sampling points in and around the waste dump. In total, 15 soil samples and leachate soil sample (TS1) were collected in the study area. Geographical Information System (GIS) ArcView Software was used to develop the map which included the sampling points. The sampling coordinates provided in Table 4.2 were used to locate the sampling points on the map.
Figure 5.3: Map indicating soil sampling areas at the study area.
i) **Group A: Heavy Metals in Soil**

Group A comprises soil sample number RSS15, RSS1 and RSS12 as indicated in Figure 5.3. The classification of soil samples into groups (Group A, B, C and D) was defined by the location of the sampling points.

![Figure 5.4: Average concentration levels of soil heavy metals in Group A.](image)

Figure 5.4 illustrates the average concentrations of the selected heavy metals in soil under Group A. According to the histogram, manganese concentration was detected at 727 mg/kg which was found to be the highest value under Group A of the selected metals. On the other hand, mercury was determined to be composed of the lowest concentration level of 0.02 mg/kg.

ii) **Group B: Heavy Metals in Soil**

Figure 5.5 demonstrates the average concentrations of the selected heavy metals in soil under Group B. Group B is made up of sampling points RSS2, RSS11, RSS4 and RSS3 as shown in Figure 5.3. As illustrated in Figure 5.5, manganese average value (566.8 mg/kg) was found to be higher than other selected metals under Group B. Chromium has the second highest average concentration level of 189.3 mg/kg, whilst mercury has the least concentration of 0.03 mg/kg.
Figure 5.5: Average concentration levels of soil heavy metals in Group B.

iii) **Group C: Heavy Metals in Soil**

Group C of the soil sampling points is composed of sample number RSS5, RSS10, RSS13 and RSS14 as shown in Figure 5.3. According to the figure, manganese as in Group A and B was characterised by the highest average concentration. The average concentration levels of chromium, copper and zinc were found higher than in Group A and B.

Figure 5.6: Average concentration levels of soil heavy metals in Group C.
iv) **Group D: Heavy Metals in Soil**

Sampling points RSS6, RSS9, RSS8 and RSS7 were categorised under Group C and located far right of the waste dump as shown in Figure 5.3.

![Figure 5.7: Average concentration levels of soil heavy metals in Group D.](image)

Figure 5.7 shows manganese with the highest average concentration, whilst chromium and vanadium average concentration levels were found to be moderate when compared with other selected metals in Group D. Cadmium was found to be characterised by the lowest average value of 0.04 mg/kg.

When comparing soil sample results under Group A, B, C and D, Group A was characterised by the highest concentration of chromium, manganese and cobalt. Under Group B, the metals which were determined to be higher than in Group A, C, and D were cadmium and nickel. Arsenic, copper, lead and zinc concentrations were determined to be high in Group C. Group D (RSS9, RSS6, RSS7 and RSS8) which is located far right (eastern-direction) as shown in Figure 5.3 was characterised by the highest concentration levels of mercury and vanadium when benchmarked to Group A, B and C.
5.5 Water Quality Results

Water samples were tested for inorganic macro-components, heavy metals and physicochemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), temporary and permanent hardness. Inorganic macro-components analysed for surface and groundwater include fluoride, nitrite, nitrate, chloride, sulphate, phosphate, sodium, potassium, calcium and magnesium as shown in Figure 5.9, 5.10 and 5.11 (see page 73-74).

Inorganic macro-components were detected using the Ion Chromatography methodology for anions and Inductively Coupled Plasma-Optical Emission Spectrometry method was used to determine the cations in surface and groundwater resources. The results obtained indicated that groundwater samples from Borehole 2 were characterised by the highest concentration of inorganic macro-components than in Borehole 1, particularly calcium and sulphate. Water sampling locations i.e. surface and groundwater (Borehole 1 and Borehole 2) were presented under Figure 5.8.
Figure 5.8: Map indicating water sampling points at the study area.

The map shows groundwater Borehole 1 (RSW 4, 5 and 10) located away from the waste dump; hence Borehole 2 (RSW 6, 7 and 9) is located at the foot of the waste dump. Surface water pond (RSW 1, 2 and 3) is located at the north-western side of the study area.
5.5.1 Inorganic macro-components

Inorganic macro-components in water samples were determined using Ion Chromatography for anions (i.e. chloride, sulphate, nitrate, nitrite and phosphate), whilst the ICP-OES instrument was used to detect cations (i.e. calcium, magnesium, sodium and potassium). Water samples were grouped based on the location and presented as follow:

i) Group A: Surface Water

Inorganic macro-components in surface water consist of calcium, chloride, magnesium, sodium, sulphate, potassium, nitrate, phosphate, fluoride and nitrite as presented in Figure 5.9. Calcium was detected to be composed of the highest value of 46.6 mg/L and nitrite with the lowest concentration of 0.247 mg/L as shown in Figure 5.9.

![Surface Water](image)

**Figure 5.9: Average concentrations of surface water inorganic macro-components.**

ii) Group B: Borehole 1

Figure 5.10 describes the concentrations of inorganic macro-components in Borehole 1 of the groundwater system. In groundwater Borehole 1, the highest amount was for magnesium (74.91 mg/L), whilst fluoride with lowest value of 0.203 mg/L as presented in Figure 5.10.
iii) **Group C: Borehole 2**

Group C comprised of inorganic macro-components from groundwater Borehole 2 (Figure 5.11). Sulphate was determined to have the highest value of 188.59 mg/L as compared to other inorganic macro-components in Group C, whilst fluoride was determined to have the least value of 0.803 mg/L.
5.5.2 Heavy metals in water

Heavy metals in water samples were determined using the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) instrument and 29 metals were detected. Selected metals for the study were arsenic, cadmium, chromium, copper, mercury, manganese, zinc, vanadium, nickel and cobalt, as shown in Figure 5.12, 5.13, 5.14 and 5.15 (see page 75-77). The highest concentrations were found in groundwater Borehole 2 specifically the concentration of copper, manganese, vanadium, zinc and nickel. Water samples were collected in three locations of the study area and also at the leachate migration area which was represented as TS2 on the map (Figure 5.8). Five samples including leachate and municipal water were collected from surface and six of the water samples were collected from groundwater Borehole 1 and 2. The selected heavy metals in water were categorised into four groups defined by the degree of contamination and sampling location.

i) Group A: Low Concentrations

Group A was characterised by the lowest values of the selected trace metals in water samples which included, cobalt, arsenic, cadmium and chromium. The selected trace metals under Group A were regarded as having the lowest concentrations in surface and groundwater systems. Arsenic and cadmium were characterised by the lowest values than cobalt and chromium as indicated in Figure 5.12.

![Figure 5.12: Mean concentrations of Co, As, Cd and Cr in surface and groundwater.](image-url)
ii) **Group B: Moderate Concentrations**

Figure 5.13 indicates mean concentrations of copper, vanadium and mercury as detected in water resources from the landfill site. As shown in Figure 5.13, the most common heavy metals with higher concentration levels were found in groundwater Borehole 2 than in surface and Borehole 1. Groundwater Borehole 2 consists of the highest concentrations of copper and vanadium, hence mercury concentration was found to be high in groundwater from Borehole 1.

![Figure 5.13: Mean concentrations of Cu, V and Hg in surface and groundwater.](image)

iii) **Group C: High Concentrations**

Group C is made up of the high concentration levels of the trace metals than in Group A and B presented above. This group comprises zinc and nickel trace metals. Figure 5.14 describes the relationship between surface and groundwater sample results with regard to zinc and nickel concentration levels. In this context, Borehole 2 is made up of the highest concentrations of zinc and nickel. Surface water together with Borehole 1 (groundwater) mean concentration levels of zinc and nickel were of equal value of 0.005 mg/L.
iv) **Group D: Very High Concentrations**

Figure 5.15 illustrates the manganese concentration variance in surface and groundwater systems. Manganese was hardly distributed in surface water samples but widely distributed in Borehole 2 of the groundwater resources, meaning the lowest concentration of manganese was found in surface water while the highest concentration was in groundwater Borehole 2.
5.5.3 Physicochemical data

The physical and chemical parameters of water such as pH, TDS, EC, Alkalinity, temporary hardness and permanent hardness were also analysed at ARC laboratory and the results were presented in Table 5.3. In this study, the pH of the water samples demonstrated no significant difference between surface and groundwater resources. The laboratory results indicated that municipal water was characterised by the lowest physico-chemical properties of substances such as TDS, EC, temporary and permanent hardness. On the other hand, water samples collected from surface and Borehole 1 were found to be characterised by moderate physico-chemical properties of substances. In particular, Borehole 2 of the groundwater system which is located at the foot of the landfill waste dump was characterised by the highest physico-chemical properties (See Table 5.3).
Table 5.3: Physicochemical parameters determined in water samples.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>pH</th>
<th>TDS</th>
<th>EC mS/m at 25°C</th>
<th>Alkalinity</th>
<th>Temporary Hardness</th>
<th>Permanent Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Water Samples: Water Pond</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSW 1</td>
<td>7.75</td>
<td>297.23</td>
<td>58</td>
<td>227.5</td>
<td>227.5</td>
<td>13.14</td>
</tr>
<tr>
<td>RSW 2</td>
<td>7.8</td>
<td>296.19</td>
<td>57</td>
<td>221</td>
<td>221</td>
<td>12.6</td>
</tr>
<tr>
<td>RSW 3</td>
<td>7.89</td>
<td>293.67</td>
<td>57</td>
<td>223.5</td>
<td>223.5</td>
<td>10.19</td>
</tr>
<tr>
<td><strong>Groundwater Samples: Borehole 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSW 4</td>
<td>7.58</td>
<td>270.17</td>
<td>52</td>
<td>203</td>
<td>203</td>
<td>12.45</td>
</tr>
<tr>
<td>RSW 5</td>
<td>7.72</td>
<td>325.01</td>
<td>65</td>
<td>259</td>
<td>259</td>
<td>13.26</td>
</tr>
<tr>
<td>RSW 10</td>
<td>7.6</td>
<td>315.42</td>
<td>61</td>
<td>248.5</td>
<td>248.5</td>
<td>0</td>
</tr>
<tr>
<td><strong>Groundwater Samples: Borehole 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSW 6</td>
<td>7.12</td>
<td>789.46</td>
<td>129</td>
<td>384.5</td>
<td>384.5</td>
<td>211.89</td>
</tr>
<tr>
<td>RSW 7</td>
<td>7.4</td>
<td>798.07</td>
<td>131</td>
<td>383.5</td>
<td>383.5</td>
<td>201.22</td>
</tr>
<tr>
<td>RSW 9</td>
<td>7.45</td>
<td>795.83</td>
<td>129</td>
<td>367.5</td>
<td>367.5</td>
<td>223.46</td>
</tr>
<tr>
<td><strong>Municipal Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSW 8</td>
<td>7.57</td>
<td>203.19</td>
<td>34</td>
<td>91.5</td>
<td>91.5</td>
<td>13.19</td>
</tr>
</tbody>
</table>

Groundwater Borehole 2 has shown excessive concentration levels of the total dissolved solids, electrical conductivity, alkalinity, temporary and permanent hardness when compared to Borehole 1 and surface water pond results.
CHAPTER SIX: ASSESSMENT OF STATE OF SOIL AND WATER QUALITY

6.1 Introduction

Chapter Six of the research study focused on analysing data obtained on three spheres i.e. leachate, soil and water. In order to evaluate the contaminants and chemical composition within the three spheres, national and international standards were used as the evaluation tools. These tools include the World Health Organisation (WHO), South African Norms and Standards and World Health Permissible Limits for water and soil quality.

6.2 Sphere 1: Leachate Analysis

6.2.1 Heavy metals analysis in leachate soil sample

The heavy metals determined in leachate sediments were compared to the national and international soil quality guidelines, i.e. South African National Norms and Standards (NNS) as prescribed by NEMA (2008) and World Health Permissible Limits (Ekpete & Festus, 2013). From Table 5.1 (see page 61), metals that have exceeded the South African National Norms and Standards for soil quality as prescribed by the National Environmental Management: Waste Act (2008) were; cobalt, copper, nickel, zinc, vanadium, chromium and manganese. These metals were found to be higher than the recommended concentrations for the quality of soil regardless of its use.

As mentioned previously, metals such as cadmium, chromium, copper, lead, nickel, zinc, arsenic and mercury were associated with leachate composition (Wuana & Okieimen, 2011). Therefore, high heavy metal contents were expected in this sampling point of the study area due to the generation of leachate. The factors that could have increased the concentration of heavy metals in soil include dumping of electronic devices which contain a number of heavy metals such as copper and zinc (Aucott, 2006). However, many of these metals were indicated to occur naturally in the environment (USDA & NRCS, 2000) and subsequent leaching into surrounding soil could also aggravate the problem (Neustadt & Pieczenik, 2007). The study area is known to contain mafic rock formation which is made up of these anomalies/metals (Maya & Cloete, 2011) and could also facilitate soil contamination but in less amount.
Cadmium, mercury and arsenic were determined to be within the required threshold value when benchmarked with the national norms and standards. These concentrations were also compared to the World Health Permissible Limits (Ekpete & Festus, 2013) for soil quality. It was determined that all the selected metals have exceeded the maximum permissible level in the sediment; these include cadmium, lead, copper, nickel, zinc and chromium. The distribution of nickel, zinc and copper in soil could be associated with the disposal of materials containing batteries, fluorescent lamps, paints and cosmetics in the site (Gendebien et al., 2002). These materials (i.e. batteries, fluorescent lamps, paints and cosmetics) end-up in the MSW landfill due to waste from residential areas (domestic wastes). Some of these wastes such as paints were also observed at the study area.

6.2.2 Heavy metals analysis in leachate solution sample

The South African National Norms and Standards (SANS 241, 2011) for drinking water quality together with the World Health Organisation (WHO, 2008/2011) drinking water standards were used to analyse heavy metals in leachate solution sample. As shown in Table 5.2 (see page 64), copper and zinc metals were determined to be below the SANS 241 and WHO guideline values; whilst cadmium, mercury, lead, arsenic, cobalt, vanadium, chromium and manganese were determined to be above the acceptable standard. In this particular instance, leachate solution was determined to be carrying trace metal contaminants in large amount. The level of lead in the landfill leachate could determine the disposal of batteries, paints and plastics in the site as indicated previously. Aucott (2006) indicated that increasing usage of batteries around the globe could be causing approximately 70% of cadmium to be present in MSW.

The concentration of heavy metals determined in leachate solution was moderate; this could be due to fresh leachate produced after it has rained at the study area. The percolation of rainwater through processed waste has resulted into leachate production in the site which has attributed to moderate concentration of heavy metals. The analysis of heavy metals in leachate solution was also based on Table 2.1 (see page 11) which summarises the leachate concentration in various stages/ages of the MSW landfill site. Adhikari and Khanal (2015) indicated that fresh landfill leachate is characterised by COD value of above 10 000 mg/L, BOD concentration level of 2 000 mg/L and moderate heavy metals availability. The leachate collected at the site comprises of these characteristics. Although the landfill site has been operating for almost two decades, waste materials were still processed in the site and still undergo a
biodegradability process. However, in this particular study, the heavy metal concentrations in leachate solution were found to be lower than the one obtained on leachate soil sample. For this reason, the study undertaken by Albright et al. (2012) found that the concentrations of heavy metals in digested samples were above the dissolved samples. This indicates that the contamination is highly taking place in the particulate phase than in the solution. Therefore, for this study, large quantities of heavy metals were most likely absorbed by sediments (clay soil) which resulted into high concentration of heavy metals deposited in the soil than in leachate solution.

6.2.3 Dissolved organic content analysis

SANS 241 (2011) and WHO (2008/11) do not give a clear guideline on the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) requirements for water quality. However, drawing from the previous similar studies undertaken, as indicated under Chapter Two of the Literature Review, the COD and BOD concentrations in the study area were found to be high as demonstrated under Figure 5.2 (see page 63).

Similarly, previous studies by other researchers indicated that the COD concentrations from possible contaminated soil and groundwater ranged from 155-714 mg/L (Dvornic et al., 2011), whilst the contaminated area in this study was found to be 18 800 mg/L which is equivalent to the findings of Renou et al. (2008). Renou et al. (2008) findings indicated that the landfill leachate was comprised of higher COD concentration of 20 000 mg/L. Furthermore, the contaminated area is normally characterised by the BOD concentration ranging from 156 mg/L to 443 mg/L, hence the sample taken in the study area determined the BOD value of 945 mg/L. This is a good indication that high values of BOD in the study area have high organic pollution of leachate (Dvornic et al., 2011). This observation suggests that higher values of BOD and COD were due to fresh landfill leachate at the sampling point. To elaborate more on this issue, Kyle-Baucom et al. (2013) described leachate as a liquid that has percolated through waste material and drained from waste material. Leachate generation is attributed to the precipitation, evapotranspiration and storage of waste.
6.3 Sphere 2: Soil Quality Analysis

The selected soil trace metals for this research study were benchmarked against the World Health Permissible Limits (Ekpete & Festus, 2013) and National Norms and Standards (NEMA, 2008) for soil quality as shown in Table 6.1.

Table 6.1: Summarises the quality of soil at the study benchmarked against the national (NEMA, 2008) and World Health Permissible Limits (Ekpete & Festus, 2013).

<table>
<thead>
<tr>
<th>Metals</th>
<th>World Health Permissible Limits (mg/kg)</th>
<th>NEMA Mean Concentration (mg/kg)</th>
<th>Degree of Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>-</td>
<td>5.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.01</td>
<td>7.5</td>
<td>0.052</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05</td>
<td>6.5</td>
<td>177.2</td>
</tr>
<tr>
<td>Copper</td>
<td>1.5</td>
<td>16</td>
<td>56.6</td>
</tr>
<tr>
<td>Mercury</td>
<td>-</td>
<td>0.93</td>
<td>0.03</td>
</tr>
<tr>
<td>Lead</td>
<td>0.1</td>
<td>20</td>
<td>1.85</td>
</tr>
<tr>
<td>Manganese</td>
<td>-</td>
<td>740</td>
<td>638.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>15.0</td>
<td>240</td>
<td>58.1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>-</td>
<td>150</td>
<td>65.6</td>
</tr>
<tr>
<td>Nickel</td>
<td>6.5</td>
<td>91</td>
<td>60.2</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-</td>
<td>300</td>
<td>25.8</td>
</tr>
</tbody>
</table>

Table 6.1 is linked to Figure 5.4; 5.5; 5.6 and 5.7 (see page 68-70). This table summarises average heavy metals concentration levels in soil. The soil quality at the study was assessed and evaluated using the South African National Norms and Standards (NNS) for the remediation of contaminated land and soil together with the World Health Permissible Limits (Ekpete & Festus, 2013) soil quality guidelines as indicated in Table 6.1. Trace metals that were determined to have been lower than the
national and international standards for soil quality include arsenic; mercury; cobalt; vanadium; chromium and manganese. However, metals such as lead; cadmium; copper; zinc and nickel were determined to have exceeded the standard required.

The presence of lead, cadmium, copper, zinc and nickel in soils could cause numerous environmental impacts due to percolation of leachate containing these metals through soil strata towards the groundwater system (Raman & Narayanan, 2008). A study undertaken by Kanmani and Gandhimathi (2013) indicated that high concentrations of these metals could be as a result of natural and anthropogenic activities such as the rock chemical composition and also attributed to the disposal of paints, plastics, batteries and computer systems in the landfill site.

The USDA and NRCS (2000) also indicated that heavy metals may occur naturally, however these are less toxic to the environment. According to the study undertaken by Council of Geoscience (CGS), metals such as nickel, chromium, vanadium, copper, arsenic, lead and zinc are found within the mafic rocks of the Rustenburg Layered Suite (Maya & Cloete, 2011). These anomalies have been found associated with the Rustenburg Layered Suite for the Bushveld Igneous Complex which forms part of the study area geological rocks. Kalele and Reddy (2011) indicated that the weathering of gabbro-norite which forms part of the study area is known to results into acidic soils that could increase heavy metals concentrations. Therefore, some these anomalies detected in the study area might have come about naturally but in fewer amounts.

Figure 6.1: Mean concentrations of heavy metals in soil per sampling group.
Figure 6.2 represents the average concentration of heavy metals in soil as per sampling groups i.e. Group A, B, C and D. Concentrations of heavy metals in Group C of the soil samples were generally higher than in Group A, B and D. This could have been caused by the leachate pockets observed in Group C. Another factor which could have influenced high concentration of heavy metals under Group C was the percentage of fine grained materials available in soil, unlike in Group A which comprised of large proportion of sandy particles. A research study undertaken by George (2014) indicated that the percentage of leachate concentration tend to increase as the fine particles increase. Group D located far right (eastern-direction) of the waste dump (see Figure 5.3, page 67) was characterised by the lowest concentration levels of the heavy metals, this could be attributed to the type of waste material being processed at the sampling location. Previously, garden refuse type of waste was processed at Group D portion of the waste dump which might have yielded low concentrations of heavy metals in soil due to lack of contaminants.

i) **Group A: Heavy Metals Analysis in Soil**

**Manganese:** Group A of the soil samples was characterised by the highest average value of manganese which was detected at an amount of 727 mg/kg as shown in Figure 5.4 (see page 68). However, the manganese concentration as per South African National Norms and Standards for soil quality was below the limit guideline value of 740 mg/kg as shown in Table 6.1. Approximately 65% of the sample results have demonstrated to be within soil quality standards as guided by NNS; whilst the remaining 35% were determined to have exceeded the guideline value of 740 mg/kg as shown in Appendix 1. However, the mean concentration of 638.266 mg/kg as calculated under Table 6.1 was found to be lower than the guideline value. WHO (2008) indicated that manganese is one of the most available metals in the Earth's crust, normally occurring with iron. Therefore, it could be expected that the presence of manganese as a heavy metal in the study area soil could be as a result of natural and anthropogenic sources.

**Chromium:** Another metal which was determined to be high in Group A than in Group B, C and D was chromium with a concentration of 229 mg/kg as indicated in Figure 5.4 (see page 68). The chromium overall (average of Group A, B, C and D) mean concentration level was 177.2 mg/kg as indicated in Table 6.1 which was above the national and international requirements. NNS stipulated that soil for any kind of use should contain chromium of less than 6.5 mg/kg (NEMA, 2008), and World Health
Permissible limit of 0.05 mg/kg as shown in Table 6.1. However, both of these standards were not met as chromium concentration in soil at the study area was detected above the guideline value. As discussed previously, chromium mobility depends on soil adsorption characteristics, including clay and iron oxide content, and the amount of organic matter found therein (European Commission, 2002). It can be transported by surface runoff to surface waters, which can result in soluble and un-adsorbed chromium complexes leaching from soil into groundwater (Wuana & Okieimen, 2011). From the analysis, it is suggested that high concentration of chromium could be due to run-off, as samples from Group A specifically RSS1 and RSS2 were located close to the area where gully erosion was taking place. Surface run-off, during heavy rains possibly transports contaminants to the edge of the waste dump.

**Cobalt**: Group A of the soil samples is located far left (western-direction) of the waste dump as illustrated by Figure 5.3 (see page 67), has the highest concentration level of cobalt when benchmarked to Group B, C and D. However, the amount of cobalt found in soil was lower than 300 mg/kg which is the maximum concentration required in soil according to the South African National Norms and Standards for soil quality. In this manner, the availability of cobalt in the study area soil was responsive but at an affordable level. Group A comprised largely of sandy soil particles with a khaki colour and it was studied by Eshanthini and Padmimi (2015) that a sandy soil lithology influences fast movement of landfill leachate towards the aquifer and increases the contamination level. It is therefore possible that the migration of leachate towards groundwater system containing heavy metal pollutants such as cobalt was occurring faster in Group A than in Group C which consists of fine grained soil.

ii) **Group B: Heavy Metals Analysis in Soil**

**Cadmium**: Group B of the soil samples was characterised by the highest concentration level of cadmium when compared to Group A, C and D. The average concentration of cadmium under Group B was 0.07 mg/kg as illustrated in Figure 5.5 (see page 69), which has exceeded World Health Permissible Limits (Ekpete & Festus, 2013) soil quality standard of 0.01 mg/kg but within the national guideline value of 6.5 mg/kg. The overall average concentration level of cadmium in soil samples collected at the study area was determined at a value of 0.052 mg/kg as shown in Table 6.1. However, this value has exceeded the World Health Permissible Limits required for soil quality.
In this essence, the availability of cadmium in the study area environment could be due to weathering of rocks and/or anthropogenic activities such as mobilization of waste materials containing cadmium (Perera et al., 2015). And again, the cadmium concentration level in the study area could have been escalated by natural activities or waste materials containing paints, plastics and electrical batteries (Haileslassie & Gebremendhin, 2015). Perera et al. (2015) indicated that cadmium is highly dangerous to some aquatic life and is regarded as the most toxic metal amongst 63 atomically stable heavy metals in the Periodic Table.

**Nickel:** When comparing nickel concentration levels in Group A, B, C and D, it was found that Group B of the soil samples consists of the highest level of nickel. Nickel concentration level under Group B was determined to be 100.3 mg/kg which was twice the amount of Group A, C and D. The overall average level (60.2 mg/kg) of nickel as shown in Table 6.1 was below 91 mg/kg of the NNS guideline value; however the overall value was higher than the World Health Permissible Limits (Ekpete & Festus, 2013) standard value of 6.5 mg/kg. It has been researched that large amounts of nickel compounds on the environment are adsorbed to soil. Through the adsorption process nickel compounds become more mobile and percolate towards groundwater systems (Wuana & Okieimen, 2011). The nickel concentration level in soil could be explained in two manners; 1) the concentration level obtained on soil samples could be lower than the actual concentration due to migration (mobility) of leachate to the subsurface or 2) the concentration could be higher as a result of nickel compounds being adsorbed to soil or retained by soil.

iii) **Group C: Heavy Metals Analysis in Soil**

**Arsenic:** The concentration level of arsenic heavy metal in Group C was higher than in Group A, B and D, but lower than 5.8 mg/kg of the required level in soil as per national standards. According to the South African soil quality requirements, arsenic average concentration of 0.6 mg/kg as indicated in Table 6.1 was found to be acceptable in the environment. A research undertaken by Haileslassie and Gebremendhin (2015) indicated that arsenic also occurs naturally in rock, soil, water and air, and the consumption of arsenic in large amount may cause gastrointestinal. Another possible reason for high levels of arsenic in Group C of the soil samples could be as a result of chemicals leaking from the trucks and vehicles transporting waste to the working cell.
Copper: The average amount of copper in Group C was determined to be 140.9 mg/kg (Figure 5.6, page 69) which was above the level detected in Group A, B and D. The overall average concentration of copper in soil samples was 56.6 mg/kg (Table 6.1) which was higher than the required level in soil. The World Health Permissible Limits (Ekpete & Festus, 2013) stipulated an amount of 1.5 mg/kg of copper in soil, whilst NNS determined that copper in soil should not exceed an amount of 16 mg/kg as shown in Table 6.1. Therefore, soils taken from the site have indicated copper contamination which could have been escalated by dumping of waste containing electronic devices such as cell phones and computer equipment (Aucott, 2006). In the study area, dumping of waste that could influence the concentration of copper in soil was common specifically waste from domestic areas which contains electronic devices and batteries. This could have attributed to high level of copper in soils at the study area.

Lead: The mean concentration of lead in Group C was above the level found in Group A, B and D. As shown in Figure 5.6 (see page 69), lead concentration level in Group C of soil samples was detected at 2 mg/kg which is above the World Health Permissible Limit (Ekpete & Festus, 2013) of 0.1 mg/kg as indicated under Table 6.1. However, according to Table 6.1 lead overall concentration level was determined to be 1.85 mg/kg and below 20 mg/kg of the maximum level required in soil as per South African standard. Fundamentally, the average lead concentration in soil has exceeded international standard for soil quality but met the South African requirement.

The combination of the geogenic (natural) and anthropogenic (man-made) sources could have influenced the amount of lead in the soil at the research area but, it should be noted that natural activities such as rock chemical composition brought less of the pollutants than landfill operation. Therefore sources of lead found in the study area can be divided into natural and anthropogenic activities. As indicated by Maya and Cloete (2011) previously, lead anomalies have been researched to be associated with the study area geological rocks. Additionally, anthropogenic activities such as dumping of waste containing batteries, fishing tools and plastics (European Commission, 2002) could have escalated lead concentrations in large amount than natural sources.

Zinc: Another metal which was found to be high under Group C was zinc with an average value of 143.3 mg/kg. The mean value of zinc in Group C was more than 5 times the concentration of Group A, B and D. The overall mean concentration of zinc in soil as shown in Table 6.1 (58.1 mg/kg) was determined to be above 15 mg/kg as
prescribed by World Health Permissible Limits (Ekpete & Festus, 2013), but within the national soil quality requirements. Maya and Cloete (2011) indicated that natural anomalies of lead and zinc have been associated with the Bushveld Igneous Complex and Transvaal Supergroup rocks. The study area therefore, lies between these two geological formations as discussed in Chapter Three, which could have also escalated zinc concentration levels in the study area.

iv) **Group D: Heavy Metals Analysis in Soil**

**Mercury:** Group D comprising samples RSS6, RSS9, RSS8 and RSS7 is located far right (eastern-direction) of the waste dump (see Figure 5.3, page 67) and characterised of 0.11 mg/kg of average mercury concentration. The level of mercury in Group D soil samples was above the one in Group A, B and C. However, the overall dissemination of mercury in soils at the site was at a very low concentration and below the maximum value of 0.93 mg/kg (Table 6.1) as determined by the South African National Norms and Standards. The low concentration of mercury in soils could indicate that rock formation at the study area lacks mercury anomalies which could influence mercury concentration levels. In this essence, the concentration of mercury as a heavy metal could be as a result of waste operation such as dumping of electrical switches, fluorescent bulbs and thermometers (UNEP, 2008). Irrespective of the negativity around heavy metals such as mercury, lead and cadmium associated with the landfill leachate, these metals could be used in certain industrial products (Aucott, 2006).

**Vanadium:** The concentration level of vanadium in the sediments was high in Group D of soil samples. This group consist of 73.4 mg/kg of vanadium which was above the concentration level detected under Group A, B and C. The overall mean concentration of vanadium in the study area sediments was calculated to be 65.6 mg/kg (Table 6.1) which was lower than the NNS guideline value of 150 mg/kg. The availability of vanadium metal in the study area could be as a result of magnetite gabbro of the Rustenburg Layered Suite which forms part of the study area rock formation (Maya & Cloete, 2011). It is therefore suggested that, natural phenomenon could have also played a role in the presence of vanadium in the soil of the study area. Another possible reason for low concentration of vanadium under Group D of soil samples could be that the sampling location was used previously as garden refuse working cell unlike a domestic waste working cell containing batteries and electronic devices.
6.4 Sphere 3: Water Quality Analysis

The national (SANS 241, 2011) and international (WHO, 2008) standards for drinking water quality were used to compare the research results as shown in Table 6.2. The quality analysis of surface and groundwater was defined by the inorganic macro-components and heavy metals results provided in Chapter Five of the research study.

Table 6.2: Indicates the SANS 241 and WHO guidelines for drinking water quality (Umgungundlovu District Municipality, 2015 and World Health Organisation, 2008).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heavy Metals (mg/L)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>&lt;0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Copper</td>
<td>&lt;2</td>
<td>2</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt;0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>Vanadium</td>
<td>&lt;0.2</td>
<td>-</td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt;0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Cobalt</td>
<td>&lt;0.5</td>
<td></td>
</tr>
<tr>
<td><strong>Inorganic Macro-Components (mg/L)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrite</td>
<td>&lt;0.9</td>
<td>3 (short-term exposure)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>&lt;11</td>
<td>50</td>
</tr>
<tr>
<td>Sulphate</td>
<td>&lt;250</td>
<td>0.009</td>
</tr>
<tr>
<td>Fluoride</td>
<td>&lt;1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Magnesium</td>
<td>&lt;70</td>
<td>-</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;150</td>
<td>-</td>
</tr>
<tr>
<td>Potassium</td>
<td>&lt;50</td>
<td>-</td>
</tr>
<tr>
<td>Sodium</td>
<td>&lt;200</td>
<td>-</td>
</tr>
<tr>
<td>Chloride</td>
<td>&lt;300</td>
<td>-</td>
</tr>
</tbody>
</table>
The table illustrates the South African National Standards (SANS 241) and World Health Organisation (WHO) Drinking Water Quality Guidelines used to evaluate pollution in water resources at the study area.

6.4.1 Inorganic macro-components analysis

**Fluoride:** When integrating surface and groundwater results, it was found that fluoride mean concentration was highest in Borehole 2 than in surface water and Borehole 1 as shown under Figure 5.11 (see page 74) and also in Appendix 2 (see page 120). Fluoride concentration levels in Figure 5.9 (0.357 mg/L) and 5.10 (0.203 mg/L) were lower than in Figure 5.11 (0.803 mg/L). This indicates that, Borehole 2 was fairly affected by the landfill leachate migration. However, the availability of fluoride in water resources were below 1.5 mg/L which is the maximum amount required in drinking water as per national and international standards as indicated under Table 6.2. A recent similar study demonstrated that fluoride content in groundwater was found to be within 1.1 mg/L to 1.2 mg/L which tend to increase during post monsoon season (Chavan & Zambane, 2014). And also, it was indicated that the presence of fluoride in high concentration level is associated with groundwater resources (WHO, 1996). The possible source of fluoride in the study area waters could be the surrounding geological formation which store groundwater and landfill leachate migration.

**Nitrite:** The average concentration levels of nitrite determined in surface (0.6 mg/L) and groundwater water (0.89 mg/L) systems were found to be within the national and international water quality requirements as indicated in Table 6.2. According to Figure 5.9, 5.10 and 5.11 (see page 73-74), the lowest concentration of nitrite was in surface water and the highest was in Borehole 2. The low contamination level of nitrite in surface water and groundwater Borehole 1 could be determined by the location. It is therefore suggested that surface water pond at the study area could be exposed to leachate contamination resulted from rainwater run-off from the waste dump as illustrated in Figure 3.11 (gully soil erosion, page 29). In comparison of the groundwater Borehole 1 and Borehole 2 results, Borehole 1 is located away from the waste dump and less contaminated, whilst Borehole 2 nitrite concentration was higher than in Borehole 1 as it is located next to the waste dump (see Figure 5.8, page 72).

**Nitrate:** The availability of nitrate as inorganic macro-component in the study area water resources as shown in Figure 5.9, 5.10 and 5.11 was low as compared to drinking water
Common groundwater pollutant is associated with nitrate and high concentration level of nitrate causes methemoglobinemia (Raman & Narayanan, 2008). However, Fawell (1993) indicated that nitrate is normally delayed reaching groundwater system, meaning the current nitrate concentration level in groundwater at the study area could be expected to increase in a later stage. In this essence, the possible cause of low nitrite in groundwater resources at the study area could be associated with the delay of nitrate reaching the aquifer.

**Calcium:** According to Borehole 2 as illustrated by Figure 5.11 (see page 74), calcium concentration level (165.74 mg/L) has exceeded national requirements for drinking water quality and was detected above 150 mg/L. On the other hand, calcium concentration level (44.73 mg/L) in groundwater Borehole 1 was found to be in a desirable limit. SANS 241 stipulated that calcium should be below 150 mg/L for drinking water purposes. The concentration of calcium as depicted in Figure 5.11 indicates that the concentration levels increase at the sampling site located next to the landfill waste dump and decrease away from the waste dump. These findings could also be elaborated a bit more through the results presented in Appendix 2.

**Sulphate, potassium, sodium and magnesium:** The average concentrations of sulphate, potassium, sodium and magnesium in surface and groundwater resources have been found to be within the required national and international standards for drinking water quality (Table 6.2). Although magnesium and sulphate were detected to contain the highest concentration as shown in Figure 5.10 and Figure 5.11 (see page 74), their concentrations were less than the maximum allowable level.

WHO (2008) indicated that sulphate is widely distributed in many minerals and mostly found in all natural water resources (Raman & Narayanan, 2008). In many circumstances, sulphate compounds in the environment originated from sulphate ores, shale formations and industrial wastes. The compounds of sulphate are mostly dissolved by rain and high concentrations in drinking water lead to laxative complications in combination with calcium and magnesium (Raman & Narayanan, 2008). Norman and Whitfield (2006) indicated that the Bushveld Igneous Complex rocks contain iron and magnesium. Nitrate occurs naturally in the environment as an important nutrient (WHO, 2008). With regards to sodium, Fawell (1993) indicated that sodium salts are normally high in water and can come from the salt bearing rock formation. In this particular instance, sodium levels in water resources could be
associated with coastal saline intrusion, underground salt deposits and sewage effluents. Furthermore, it was highlighted that sodium in supply water is below 20 mg/L; however it can be above 400 mg/L in some instances. Sodium impacts have been associated with heart and kidney diseases (Raman & Narayanan, 2008).

**Chloride:** WHO (2008) indicated that chloride in drinking water could originate from natural sources and can give unpleasant taste when the concentration is higher than 200 mg/L. When the chloride concentration escalates to 400 mg/L, water becomes salty, whilst more than 2 000 mg/L nausea and vomiting may be possible (DWAF, 1996). Chloride in surface and groundwater system at the study area was fairly low and found to be within 300 mg/L which is below SANS 241 guideline value.

It is therefore determined that groundwater Borehole 2 has shown higher concentration of the inorganic macro-components as compared to surface water and Borehole 1. This could have been caused by the fact that Borehole 2 is located (short distance) at the foot of the waste dump, whereas Borehole 1 is located (long distance) further away from the waste dump as shown in Figure 5.8 (see page 72).

### 6.4.2 Heavy metal analysis

The heavy metal concentrations in water samples were benchmarked to national and international drinking water standards in order to determine the degree of contamination as shown in Table 6.3. By way of a list of comparative results, Table 6.3 highlights that, arsenic and cadmium metals were hardly detectable within surface and groundwater resources. The overall analysis indicated that most of the toxic metals in surface and groundwater systems were lower than the recommended guideline values within national and International contexts. This research found that most of the toxic metals were fairly high in soil than in water resources. A study undertaken by Mor et al. (2006) revealed that heavy metals such as cadmium, chromium, copper, lead, zinc and mercury were detectable in leachate and groundwater samples. Similarly, these heavy metals were also detected in surface and groundwater water systems at the study area.
Table 6.3: Summarises the degree of contamination in surface and groundwater due to the presence of heavy metals.

<table>
<thead>
<tr>
<th>Heavy Metals (mg/L)</th>
<th>Surface Water</th>
<th>Groundwater Borehole 1</th>
<th>Groundwater Borehole 2</th>
<th>Degree of Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury</td>
<td>0.004</td>
<td>0.005</td>
<td>0.002</td>
<td>Low</td>
</tr>
<tr>
<td>Arsenic</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>Low</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>Low</td>
</tr>
<tr>
<td>Copper</td>
<td>0.002</td>
<td>0.001</td>
<td>0.006</td>
<td>Low</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.005</td>
<td>0.005</td>
<td>0.015</td>
<td>Low</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.003</td>
<td>0.004</td>
<td>0.02</td>
<td>Low</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>Low</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.003</td>
<td>0</td>
<td>0.001</td>
<td>Low</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>Low</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.007</td>
<td>0.237</td>
<td>1.275</td>
<td>High</td>
</tr>
</tbody>
</table>

Mor et al. (2006) indicated that the metals that are toxic for drinking water include lead, cadmium, chromium and nickel which are also discussed below:

i) **Group A: Low Concentrations in Water**

**Cobalt:** The occurrence of cobalt metal in surface and groundwater samples at the study area was very minimal as illustrated in Table 6.3, meaning the concentrations determined within the water samples were very low as compared to the SANS 241 stipulated maximum concentration. Although as shown in Figure 5.12 (see page 75), the highest concentration of cobalt was approximately 0.002 mg/L in groundwater Borehole 2. As in other discussions, groundwater Borehole 2 comprises higher concentration of cobalt than in Borehole 1. The occurrence of cobalt in the study area water systems was possibly caused by natural activities, however relatively small amounts of this metal are naturally found in most rocks, soil and water (ATSDR, 2004). Another possible source of cobalt in the study area environment was suspected to be anthropogenic activities through the disposal of coloured glasses and paints containing this metal. Kim et al. (2006) indicated that exposure or inhalation of cobalt can cause sensitisation and bronchial asthma.

**Arsenic:** SANS 241 (2011) and WHO (2008) standards stipulated that arsenic concentrations in drinking water should not exceed 0.01 mg/L (Table 6.2). In this study,
fairly low arsenic values were detected in surface and groundwater systems, as indicated in Figure 5.12 (see page 75). However, WHO (2008) highlighted that arsenic is widely distributed in the earth’s crust through an oxidation stage and mostly available in natural waters at concentrations of less than 0.001 to 0.002 mg/L. The mafic igneous rocks are known to contain a level of arsenic concentration (Albright, 2012), therefore the Bushveld Igneous Complex comprising of mafic igneous rocks together with waste operation possibly influenced arsenic concentration level in water resources at the site. The primary source and main player to arsenic contaminants in the study area water resources could be landfill operation through leachate generation.

**Cadmium:** The cadmium amount was hardly detectable in both surface and groundwater resources. The mean concentration determined in water samples was less than 0.057 ppb which is equivalent to 0.0001 mg/L. The weathering of rocks in the study area possible led to cadmium concentration in water resources and cadmium is also found associated with zinc compounds (Albright, 2012). When integrating soil and water quality findings, cadmium concentration level in soil was found to be higher than in water resources. This could be as a result of the ability of waste cover (clay soil) together with the underlying bedrock to reduce landfill leachate migration towards the groundwater system.

**Chromium:** The chromium concentrations in water samples were detectable, however, at a very low level. The highest concentrations were found in Borehole 2 of the groundwater system as shown in Figure 5.12 (see page 75), but have not exceeded the guideline value of 0.05 mg/L. The chromium concentration in the Onderstepoort MSW landfill site was likely caused by a combination of natural (minimal amount) and man-made activities. In order to determine the exact concentration of chromium due to geogenic (natural) contribution, future research work should focus on the geochemical analysis of the study area rock and soil formations.

ii) **Group B: Moderate Concentrations in Water**

**Vanadium:** This element was also found to have met the required concentration of <0.20 mg/L as stipulated under SANS 241. Rohrmann (1985) researched that the world’s largest vanadium ore reserves are contained within the Upper Zone of the Bushveld Igneous Complex situated within the Transvaal. The geological setting of the landfill site could possibly attributed to the concentration level of the vanadium metal in
water resources. Possible reason for low concentration of vanadium in surface and groundwater could be due to low concentrations detected in soil.

**Copper:** The average concentration of copper in surface water samples was 0.002 mg/L as shown in Table 6.3, but within the recommended level which is acceptable for drinking water purposes. The highest concentrations were discovered in Borehole 2 of the groundwater samples with a mean value of 0.006 mg/L. The distance between Borehole 2 and waste dump as shown in Figure 5.8 (see page 72) could have escalated copper concentration level in this borehole than in Borehole 1 which is located further away from the waste dump. The distance between Borehole 1 and Borehole 2 was approximately 300 m and the distance between Borehole 2 and waste dump was less than 50 m.

**Mercury:** The availability of mercury in the study area water resources was found at a low concentration and this was conducted using ICP-MS method. USGS (2009) indicated that inorganic mercury is deposited into the environment either directly or indirectly. Direct deposition of mercury into the environment includes landfill and mining operations, whilst the atmospheric deposition of emitted mercury is regarded as indirect deposition. It has been noticed that the development of industries has significant impacts on the level of mercury in the environment (UNEP, 2002; USGS, 2009). It was expected that mercury level in water resources could be lower as it is in soil. However, if the current situation persists, the concentration may increase, particularly in Borehole 1 which is characterised by the highest concentration of mercury as shown in Figure 5.13 (see page 76). The possible reason of high concentration of mercury in Borehole 1 than in Borehole 2 could be due to the particles suspension observed in this borehole. The source of mercury in the environment could be due to dental amalgam, thermometers, lamps and batteries as referenced previously. Therefore, dumping of waste containing these materials could influence mercury availability in surface and groundwater resources at the study area. However, it must also be noted that mercury is regarded not essential to the plants and animals survival (European Commission, 2002).

iii) **Group C: High Concentrations in Water**

**Nickel and Zinc:** The concentrations of nickel and zinc in all water samples were below the national and international guideline values for drinking water. However, samples (RSW7 and RSW9) from Borehole 2 yielded the highest nickel concentrations as shown
in Appendix 3 (see page 121), but within drinking water recommended standards. When integrating concentrations detected in soil and water, there are differences in terms of the concentrations. Soil was determined to be characterised by higher concentration levels of nickel and zinc. However, the concentration levels of these metals were lower in water resources. The possible reasons for these differences will be that; the high concentration levels of nickel and zinc in soil could be attributed to trucks leaking chemicals, lack of rainfall that could influence leachate generation and increases heavy metals transportation towards groundwater aquifer, and lastly clay soil together with the bedrock could have reduced the percolation of leachate containing these heavy metals towards groundwater system. Diseases such as renal failure, hair loss, and liver cirrhosis together with chronic anaemia were noted to be related with drinking water contaminated with heavy metals such as lead, cadmium, copper, nickel and chromium (Salem et al., 2000).

iv) Group D: Very High Concentrations in Water

Manganese: The World Health Organisation stipulated 0.4 mg/L of manganese concentration in drinking water. The South African drinking water is determined safe for consumption when the manganese concentration is lower than 0.1 mg/L; meaning the average concentration level in groundwater Borehole 2 has exceeded national and international water quality requirements. The average concentration of manganese in Borehole 2 was 1.275 mg/L which was above the drinking water quality requirements.

A similar study undertaken in Tamil Nadul, India revealed that the concentrations of contaminants were high in sampling sites located close to the landfill sites. The findings also indicated that leachate percolation was low further away from the landfill site and groundwater contamination becomes less with increase in the distance (Nagarajan et al., 2012). This particular study correlates very well with the current findings, in the study area it was determined that Borehole 2 is contaminated with manganese, whilst Borehole 1 is less contaminated. The contamination level in these two groundwater boreholes could be influenced by the distance from the waste dump. Borehole 2 is located at the bottom of waste dump as illustrated in Figure 5.8 (see page 72); whilst Borehole 1 is located further away from the landfill operation. Although it should be also noted that manganese as an element occurs naturally in rock, soil and water (WHO, 2008). In this particular instance, MSW landfill operation activities could have escalated the concentration of manganese in groundwater.
6.5 Physicochemical parameters analysis

Physicochemical properties tested for this study include pH, TDS, EC, temporary and permanent hardness amongst others; however this study focused around the inorganic macro-components together with the heavy metals. As shown in Table 5.3 (see page 67), all water samples indicated TDS of less than 1200 as stipulated by SANS 241 drinking water standards. Pande et al. (2015) indicated that values of EC and TDS give an indication of inorganic material availability in the samples and high TDS concentrations may cause gastro-intestinal problems in human (Pande et al., 2015).

In general, changes in the quality of groundwater are normally caused by the bicarbonate for temporary hardness whilst the permanent hardness is determined by the non-carbonate. The hardness of the water is mostly caused by calcium and magnesium; however cations such as manganese, barium and iron may contribute in small amount. In a normal instance, hardness of the drinking water is between 10 to 500 mg/L calcium carbonate/litre with less than 60 mg/L for soft water consideration. The overall occurrence of hardness in water resources is due to seeping of acid water through the sedimentary rocks (Fawell, 1993). South African National Norms and Standard (2011) and WHO (2008) drinking water guidelines do not specifically stipulate the amount of hardness suitable for drinking water purposes. However, groundwater data for Borehole 2 indicated high concentrations of temporary and permanent hardness as shown in Table 5.3 (see page 67).

The importance of the physicochemical parameters could be explained in the following; the pH of the water has impact on the solubility and availability of nutrients used by aquatic organisms (Osman & Kloos, 2010), the alkalinity of water indicates the concentration of carbonate and bicarbonate content (Saeed & Mohammed, 2012). Furthermore, Saeed and Mohammed (2012) pinpointed that pH, suspended matter and total alkalinity affects metals loadings in water. Electrical conductivity and hardness of water has an impact on zinc, cadmium and lead availability in aquatic species.

6.6 Comparison of this study with results of a previous study

The data obtained on groundwater was compared to the previous study conducted in the same study area as indicated in Table 6.4. Rison Groundwater Consulting Company was contracted by Tshwane Metropolitan Council in 2009 to undertake groundwater environmental monitoring programme in nine (9) landfill sites under its jurisdiction.
It is believed that this was the latest groundwater quality monitoring study undertaken in the study area. As shown in Table 6.4, some results indicate that the contaminant concentrations in groundwater resources were increasing since 2009. As indicated in Table 6.4, the concentrations of mercury, manganese and zinc have increased drastically since the year 2009, whilst cobalt availability remained stable. Most of the inorganic macro-components have also increased since the last sampling period.
According to the analysis, it is evident that seeping of leachate towards groundwater aquifer could be occurring further in the study area. Most of the heavy metals concentrations detected in 2009 were determined to be higher than the current concentrations (2016). According to Rison Groundwater Consulting (2009), there are three possible reasons for increase in concentrations of chemical parameters: reduction of static water level from 6.20 m to 37.08 m between 2006 and 2009, groundwater flow direction (easterly and north-easterly direction) and groundwater borehole is located in the contaminant flow path.

6.7 Summary

The leachate in the study area is characterised by high BOD and COD content which indicates high organic leachate pollution. The high concentrations of BOD and COD could lead to high risk of surface and groundwater contaminations. Heavy metals such as lead, cadmium, copper, zinc and nickel have exceeded the national soil quality guideline values. In essence, the quality of the soil was negatively impacted by this landfill operation. However, the added effect of this landfill being situated within a part of the Bushveld Igneous Complex could have also influenced the levels of some of these metals which were measured in the sample material. Overall, the moderate concentrations of nitrite, calcium and manganese in Borehole 2, were demonstrated to have exceeded the permissible limits within the country. The detection of lead, cadmium, copper, zinc, nickel (soil), nitrite, calcium and manganese (groundwater) in excess could be attributed to anthropogenic (landfill leachate migration) activities and less being attributed to natural sources.

Table 6.5 illustrates the degree of contamination in three spheres of this particular research study. Therefore, the results obtained for the study have indicated that leachate has a high impact on soils than water resources in the study area. The contaminations ranking in the study area could be explained as follows: Leachate Soil>Soil>Leachate Solution>Water.
This study in the Onderstepoort MSW landfill site has revealed that the concentration levels of heavy metals in soil (yellow colour) were almost a hundred times more than in water resources (green colour) as shown in Table 6.5. A study undertaken by Aderemi et al. (2011) has indicated that the soil stratigraphy of an area characterised by clay is capable of preventing large amounts of heavy metals moving towards groundwater systems. This finding could be positively correlated with the current research study as most of the metals in the study area were higher in soil than in water resources. Figure 6.3 indicates positively correlated heavy metals contamination levels in leachate, soil and water; from higher to lower level of contamination.
CHAPTER SEVEN: SUMMARY, RECOMMENDATIONS AND CONCLUSION

7.1 Summary

The Onderstepoort MSW landfill site is preparing for rehabilitation and closure process. Therefore, in order to reach closure consensus, it was deemed important for the research study to determine the current state of soil and water quality in the study area. The research study has determined that the MSW landfill operation has had a greater impact on the soil compared to the water resources. In addition, it has been demonstrated by analysed leachate that the soil quality has been affected by the present landfill operation. However, it should be noted that the chemical composition of the surrounding geological formation could have also influenced the heavy metals concentration levels but in less amount. The research summary is based on three spheres of the research study as discussed below:

7.1.1 Sphere 1: Leachate

Regarding leachate generation in the site, it has been found that approximately 70% of the analysed heavy metals in leachate solution sample have exceeded the maximum concentration levels as stipulated by national and international standards. Metals that have been found to be at a higher concentration are arsenic; chromium; mercury; selenium; lead; manganese; vanadium; nickel and cobalt as per South African National Standards (SANS 241) for drinking water quality.

7.1.2 Sphere 2: Soil

Research Objective 1: To analyse the heavy metals in soils and establish the impact of leachate on soil quality.

The research findings also indicated that supreme concentrations of heavy metals were deposited in sediments than in water resources, particularly where the generation of leachate is taking place. Soil sample taken at the leachate migration area has indicated very high pollution of trace metals and was ranked as the first degree of contamination. Leachate soil sample indicated a contamination of cobalt, copper, nickel, zinc, vanadium, chromium and manganese. The concentrations of these metals were extremely higher than the recommended guideline values for soil quality.
Hence the soil samples collected in and around the waste landfill have indicated high concentrations of lead, cadmium, copper, zinc and nickel. Therefore, soils have been adversely contaminated with leachate pollution and the quality of soil has been affected negatively, considering that the study area is located within the mafic rocks of the Rustenburg Layered Suite known to contain concentrations of nickel, chromium, vanadium, copper, arsenic, lead and zinc which could also escalate the pollution although in a very low concentration. The primary influence of soil contamination in the study area could be anthropogenic activities (landfill operation) and natural pollutants could be categorised as the secondary source.

7.1.3 Sphere 3: Water

Research Objective 2: To determine water quality, investigate the presence of heavy metals and inorganic macro-components within the surface and groundwater systems.

Sphere 3 is the lowest sphere in terms of inorganic macro-components and heavy metal concentrations. This sphere of the research study is rated third degree with respect to contaminations. The contamination is lower than in Sphere 1 and 2, the reason could be that a lot of pollutants were absorbed by clay soil used as waste cap in the site.

However, groundwater Borehole 2 has indicated high levels of inorganic macro-components and heavy metals than in groundwater Borehole 1. Nitrite and calcium concentrations in Borehole 2 have been determined to have exceeded South African requirements for drinking water quality. Furthermore, the research findings determined that the manganese concentration level in groundwater specifically Borehole 2 was higher than the required level, meaning groundwater in the study area has been contaminated with manganese. This borehole is more prone to contamination than Borehole 1 as it is located beneath/at the foot of the waste dump as indicated previously.

In 2009, CTMM through Rison Groundwater Consulting Company has undertaken an initiative to sample groundwater resources in its landfill sites as a monitoring strategy. For this reason, the groundwater monitoring results obtained in 2009 were compared to the current study results. The findings were that the concentration of inorganic macro-components particularly calcium, sodium, chloride, sulphate, nitrate and fluoride have increased drastically since the last monitoring programme undertaken in 2009.
The heavy metals that were evaluated to have increased in terms of their levels in study area groundwater include cobalt, mercury, nickel, selenium, zinc and manganese. The graph of these inorganic compounds in the study area groundwater has been getting steeper. This could indicate that inorganic macro-components together with heavy metals are subsequently seeping into groundwater system, escalating further groundwater contamination.

### 7.2 Recommendations

**Research Objective 3:** To develop appropriate proposals for solving and managing resultant or expected leachate generation and impacts putting in mind the affordable management strategies required for rehabilitation process and after the closure of the landfill site.

The Onderstepoort MSW landfill site was designed without geo-membranes/liners that could prevent landfill leachate migration towards surface and groundwater systems. The landfill site is about to reach a decommissioning stage, therefore appropriate leachate management process should be recommended for the remaining life span and after closure. The study recommended that:

- CTMM should develop an appropriate and effective Rehabilitation Plan considering post-closure monitoring strategy, this involves regular groundwater monitoring for the next two years after closure. The facility should be monitored of any environmental impacts for the next 30 years which include monitoring of the groundwater boreholes.
- Groundwater remediation should be implemented for use at farming and household activities in and around the study area. Some of the inorganic macro-components and heavy metals such as manganese were found to have exceeded the required concentrations therefore; this could have a serious impact on the quality of the nearby groundwater systems.
- It is also recommended that CTMM takes a responsibility and drill extra environmental monitoring boreholes in the study area.

For this reason, the research study has recommended three scenarios that will assist in the management of landfill leachate within the study area. These three recommended scenarios were based on the current and post-closure of the landfill site:
7.2.1 Scenario 1

The first scenario recommended that the landfill site be installed with an engineered cap cover to reduce water migrating towards processed waste. The landfill site should be capped with low permeability soil, effective geo-membranes and vegetative cover. The waste fill slope stability should be maintained at all times to avoid gully soil erosion.

7.2.2 Scenario 2

The second scenario involves the implementation of the landfill leachate collection and extraction system in the site. This will involve drilling of the well through processed waste, up to the bottom of the waste fill (MJCA, 2014). The leachate liquid will be removed from the well through pumping process. The leachate could be pumped into a designated tank or treatment facility. In this manner, the volume of leachate in waste will be reduced. This was regarded as the best methodology for landfill closure designed and constructed without leachate management systems such as the study area.

7.2.3 Scenario 3

The final scenario is based on the collection of the landfill gas/methane and leachate for energy generation. This reduces the impacts of leachate and methane on the environment and maximise economic benefits. The developed landfill gas collection systems are required to be maintained and monitored regularly. Biogas generation/bio-reactors should be considered at the lowest part of the landfill dump due to less oxygen and more organic materials available that increase methane production. Organic material could influence landfill gas recovery (Adhikari et al., 2015).

7.3 Conclusion

To this end, the study objectives have been met. The research study was meant to analyse the quality of soil and water, which could be affected by the project which in this case is the MSW landfill operation known to produce landfill leachate. The generated leachate is capable of contaminating both soil and groundwater resources. Therefore, in order to determine the impacts of the generated leachate on soil and water, various instruments were employed which include ICP-MS, ICP-OES, Ion Chromatography, Winkler method and COD Dichromate Open Reflux method. These instruments were able to determine inorganic macro-components and trace metals in soil and water.
resources. The research findings indicated that soil particularly where the waste processing is taking place has been contaminated by landfill leachate than surface and groundwater resources.

The geology of the study area, Bushveld Igneous Complex and Transvaal Supergroup rock formations could have influenced the concentration of heavy metals in soil and groundwater. The study area rock formation is known to contain the anomalies of nickel, chromium, vanadium, copper, arsenic, lead and zinc which could also escalate heavy metals concentration level in soil and water.

The research findings indicated that the current pollutants determined by the study results were higher than the last groundwater monitoring study undertaken in 2009 (Rison Groundwater Consulting, 2009) at the study area. The research study indicated that contamination has been taking place in groundwater since the last sampling which took place in 2009. The groundwater at Borehole 2 has been contaminated by manganese, nitrite and calcium. This borehole (Borehole 2) should be taken into consideration during the implementation of the remedial actions.

For this reason, in order to decrease and eliminate further contaminations of soil and water resources, the remedial actions were recommended for the study area. It is believed that these remedial actions indicated above will reduce and prevent pollution due to leachate migration within the Onderstepoort Municipal Solid Waste Landfill Site located in Pretoria, South Africa.
REFERENCES


hazardous household chemicals (HHC) (Report No.: CO 5089-2). Belgium: European Commission.


Farquhar, M. Mills, & A. Williams (Eds.), Field description of soil and rock (pp. 7-20). New Zealand: New Zealand Geomechanics Society.


### APPENDICES

**Appendix 1**: Selected heavy metals detected in soil samples using ICP-MS method.

<table>
<thead>
<tr>
<th>Metals (mg/kg)</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
<th>Group D</th>
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<tbody>
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<td></td>
<td>RSS15</td>
<td>RSS1</td>
<td>RSS12</td>
<td>RSS2</td>
</tr>
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<td>0.3</td>
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<td>&lt;0.02</td>
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<td>920</td>
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<td>Zn</td>
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<td>34.6</td>
<td>36.8</td>
<td>23.9</td>
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### Appendix 2: Inorganic macro-components in surface and groundwater resources at the site.

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<th>Sample</th>
<th>Fluoride</th>
<th>Nitrite</th>
<th>Nitrate</th>
<th>Chloride</th>
<th>Sulphate</th>
<th>Phosphate</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Calcium</th>
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<td></td>
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<td></td>
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<td></td>
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<td>14.87</td>
<td>0.09</td>
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<tr>
<td><strong>Groundwater</strong></td>
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<td></td>
<td></td>
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</tr>
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<td><strong>Samples: Borehole 2</strong></td>
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<td>RSW 6</td>
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<td>8.18</td>
<td>25.66</td>
<td>9.86</td>
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</table>
Appendix 3: Heavy metals concentration levels in surface and groundwater samples.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Surface Water: Water Pond</th>
<th>Groundwater: Borehole 1</th>
<th>Groundwater: Borehole 2</th>
<th>Municipal Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RSW1</td>
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</tr>
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<td>&lt;0.0001</td>
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<td>0.007</td>
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