A CRITICAL INVESTIGATION INTO THE EFFECTIVENESS OF SOIL AND WATER REMEDIATION EFFORTS IN STEEL VALLEY, VANDERBIJLPARK

by

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ABSTRACT

Post-remediation soil, ground and surface water monitoring is essential to assess the effectiveness of remediation efforts undertaken to eliminate or minimize the risk of pollution to human health and valuable ecosystems. In that regard, comparison of pollution levels pre- and post-remediation is an effective way of evaluating the effectiveness of the remediation techniques used. Thus, this study sought to measure concentrations of pollutants in the soil, ground and surface water post remediation in Steel Valley, Vanderbijlpark and compare them to concentration levels prior to remediation, as well as compare them to internationally accepted standards with respect to risk to humans and the environment. Water samples were collected from three locations within the study site, in both the dry and rainy seasons and their physio-chemical and organic properties were tested. Soil samples were collected from six different locations within the study site and analysed for metal concentrations. The data was compared against that of the Iron and Steel Corporation (ISCOR) Vanderbijlpark Environmental Master Plan (EMP), water and soil guidelines of the World Health Organization (WHO) as well as South African water and soil guidelines. The study found that groundwater is generally safe for domestic use but Aluminium (Al), Iron (Fe) and Manganese (Mn) concentrations were above South African water quality guideline levels – with their concentrations ranging from 0.54 to 0.91 mg/L, 1.01 to 1.86 mg/L and 0.24 to 0.53 mg/L respectively. There were no traces of organic pollution in the water samples. Soil samples had levels of Al ranging from 1106 mg/kg to 1 3621 mg/kg, Mn concentrations in the range of 202.8 to 966.4 mg/kg and Fe ranging from 1 1587 to 23 201 mg/kg. Thus, water and soil at the selected sites are safe in terms of physico-chemical and organic quality. Natural attenuation should be able, over time, to further reduce the levels of parameters that are currently above the target range. Thus, there has been considerable reduction in pollutant concentrations, but as this study was limited in scope, additional research is needed to verify the results.

Keywords: Remediation, Groundwater pollution, Soil pollution, Surface water pollution, Steel Valley, South Africa.

DECLARATION

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I am grateful to everyone that contributed to the success of this work.

LIST OF ABBREVIATIONS AND ACRONYMS

Al	Aluminium
AMD	Acid Mine Drainage
AMSA	ArcelorMittal South Africa (SA)
A.P	Atmospheric Pressure
As	Arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
B.A	Bicarbonate Alkalinity
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CA	Cluster Analysis
C.A	Carbonate Alkalinity
Cd	Cadmium
CEQGs	Canadian Environmental Quality Guidelines
CER	Centre for Environmental Rights
CH_4	Methane
CO_2	Carbon Dioxide
CN^-	Cyanide
Cu	Copper
Cr	Chromium
Cr^{+6}	Hexavalent Chromium
Cr^{+3}	Trivalent Chromium
CV	Coefficient of Variation
DEA	Department of Environmental Affairs
DI	Deionized (water)
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
EC	Electrical Conductivity
ECA	Environment Conservation Act
EMP	Environmental Master Plan
FID	Flame Ionization Detector
Fe	Iron
GC/MS	Gas Chromatography/Mass Spectrometry
H_2O	Water
H_2S	Hydrogen Sulphide
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
Hg^{2+}	Mercuric
Hg^{1+}	Mercurous
Hg	Mercury
HNO_3	Nitric Acid
ICP-OES	Inductively Coupled Plasma Optical Spectroscopy
ICV/CCV	Initial Calibration Verification/Continuing Calibration Verification Standard
ISCOR	Iron and Steel Corporation
IVS	ISCOR Vanderbijlpark Steelworks

K_{oc}	Carbon Sorption Coefficients
LCS	Laboratory Control Sample
MAHs	Mono Aromatic Hydrocarbons
MFI	Modified Fournier Index
Mn	Manganese
MS/MSD	Matrix Spike/Spike Duplication
Na_2CO_3	Sodium Carbonate
NAPL	Non-Aqueous Phase Liquid
NEMA	National Environmental Management Act
NEPA	National Environmental Policy Act
NH_3	Ammonia
NO_3	Nitrate
OECD	Organisation for Economic Co-operation and Development
PC	Principal Component
PCA/PCP	Principal Component Analysis
Pb	Lead
PCBs	Polychlorinated Biphenyls
PAHs	Polycyclic Aromatic Hydrocarbons
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RF	Radio Frequency
RPD	Relative Percent Difference
S1 –S6	Soil Sampling Points
SA	South Africa
SO_4	Sulphate
SOP	Standard Operating Procedures
SPE	Solid-Phase Extraction
SSV	Soil Screening Values
T.A	Total Alkalinity
TDS	Total Dissolved Solids
TF	Translocation Factor
Tl	Thallium
TPH	Total Petroleum Hydrocarbons
UNISA	University of South Africa
USA	United States of America
USEPA	United States Environmental Protection Agency
USNRC	United States Nuclear Regulatory Commission
VEJA	Vaal Environmental Justice Alliance
VOCs	Volatile Organic Compounds
V/V	Volume to Volume
W1,W2,W3	Water Sampling Points
WHO	World Health Organization

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CHAPTER 1: INTRODUCTION

1.1 Introduction

The iron and steel industry is characterized by the production of steel for both domestic and international markets and represents a significant contribution to the global economy due to the creation of jobs and its important role as a source of basic raw material for other manufacturing industries (Yellishetty, Ranjith, & Tharumarajah, 2010). It is also, however, known for its emission of pollutants into the air and water bodies, a significant problem for areas close to operation sites or plants (Wilson, 2008; Bilbao-Terol, 2009; Beagle, 2015). These pollutants include: metals, cyanide, hydrocarbons, polychlorinated biphenyls, asbestos, methane, ammonia, and hydrogen sulphide. They can be contained through the treatment of effluent and effective management of discharge channels. Poor or no management of the effluent is detrimental to the environment and its neighbouring communities (Van der Perk, 2006; Wilson, 2008). A case in point is South Africa's Vanderbijlpark Steelworks (owned by ISCOR/ArcelorMittal SA) whose historically poor waste management practices resulted in the significant pollution of groundwater sources and soil in Steel Valley, Vanderbijlpark (Munnik, 2012).

ISCOR (Iron and Steel Corporation) Vanderbijlpark Steelworks (IVS) started operating in 1947. At that time, legislation to control pollution was extremely limited. So, when the plant was commissioned there were few regulations governing effluent dams and canals. For example, containment dams and canals did not have to be lined. Consequently, pollutants began to percolate into the groundwater from 1961 onwards, a situation that the then Department of Water Affairs (DWA) was aware of but did not address (Munnik, 2012). Over a period of 40 years, ISCOR/ArcelorMittal SA discharged its wastewater into unlined effluent dams and the nearby Rietspruit River, a practice that impacted negatively on the quality of groundwater in Steel Valley (Cock, 2007; Munnik, 2012). Pollutants (including phenols and inorganics) released from the steelworks into the soil and water bodies were in quantities that exceeded tolerable limits. This persistent pollution eventually resulted in some residents of Steel Valley instituting legal action against ISCOR/ArcelorMittal SA in 2002 (Cock & Munnik, 2006).

After the 2006 takeover of ISCOR by ArcelorMittal SA (AMSA), major environmental rehabilitation of facilities and decommissioning took place to ensure compliance with South Africa's new pieces of environmental legislation (ArcelorMittal SA, 2014a). Since 2006, AMSA has spent over R 850 million in controlling emissions, treating water and rehabilitating landfills (ArcelorMittal SA, 2014a). All these measures were aimed at remedying the pollution within the steelworks and affected neighbouring communities. This study aims, independently of AMSA, to characterize soil and groundwater in Steel Valley, Vanderbijlpark in order to provide an independent assessment of the effectiveness of post-pollution rehabilitation and remediation. Although the effects of cumulative exposures and long latency times could hinder efforts to clean up polluted sites, nevertheless, polluted sites cannot be left to pose health risk to residents. Hence, the efforts and techniques to remedy polluted areas should be frequently reviewed and modified to counter the ever-changing properties of multiple accumulated pollutants (Hamby, 1996; Briggs, 2003). This study could, then, make recommendations concerning remedies for any pollution that is found.

1.2 Problem statement

Vanderbijlpark is an industrial town which has been exposed to pollution from ISCOR (now AMSA) for over forty years (Munnik, 2012). For example, storage and evaporation facilities were improperly managed, causing an accumulation of salt from the waste effluent, which then percolated into the soil. It was only in 2010 that the salts were removed to the Holfontein Hazardous Waste Disposal Site (ArcelorMittal SA, 2014b). Disposal of solid residues and sludge on an unlined 161 ha landfill also had adverse effects on soil and groundwater in Vanderbijlpark (Munnik, 2012). An Environmental Master Plan classified the water and soil pollution levels around the steelworks as unacceptable (Ockie Fourie Toxicologists (PTY) Ltd, 2002). Evidence of contamination of the soil and water bodies include deposits of tar found in smallholding wells in Steel Valley (Washington, Goodall, & Rosier, 2006). Tar, which can be absorbed through the skin, can be carcinogenic (Warshawsky & Landolph, 2005; Tongpool, Jirajariyavech, Yuvaniyama, & Mungcharoen, 2010). There have been various reported cases of cancer and kidney problems from residents of Steel Valley which have been attributed to the inorganic and organic contamination of water bodies (Washington et al., 2006). Livestock and poultry have died and some attributed this to pollution from the steelworks (Munnik, 2012). The mobile nature of water media means pollutants can spread from one point to the other which indicates that pollution from the plants within the premises of ISCOR is likely to spread to nearby communities such as Steel Valley and perhaps even further afield (Van der Perk, 2006).

Recommendations emanating from the Environmental Master Plan compelled AMSA to prevent further pollution and ensure remediation of the affected areas. However, the uniqueness of pollutants behaviour in different media and the extent of contamination could make remediation technologies fail, hence, there is a need to critically investigate the effectiveness of remediation technologies (Manahan, 2011). Thus, although environmental remediation serves to eliminate the source and potential sources of contaminations and restore sites or polluted areas to safety, remediation must be critically analysed to ensure its success (Wuana & Okieimen, 2011). So, characterization of soil and water resources in Steel Valley after remediation is therefore necessary in order to assess the current state of pollution, whether pollutants have been eliminated, reduced or still persist in the area.

1.3 Rationale/justification for the study

Long exposure of soil and water media to pollutants may not only lead to high concentrations of pollutants but also the spread of pollutants far from the point source of pollution. This can hamper the effectiveness of remediation technologies. This research aimed to ascertain if the soil, ground, and surface water in the area was still polluted, a significant issue considering that water flows underground through populated areas towards the Vaal River (a source of water for millions of South Africans) and supplies households in the form of boreholes, while the surface water (dam) is used for fishing and as drinking water for cattle. Steel Valley residents, neighbouring communities and AMSA can all benefit from this research such that the study can serve as an independent assessment of the effectiveness of implemented remediation techniques. Academically, the research will serve as a reference and literature for further studies in Steel Valley and areas with similar situations. In addition, the study will highlight on more useful information of bioremediation and phytoremediation in South Africa and internationally.

1.4 Aims and objectives

The aim of the study was to analyse water and soil samples from Steel Valley in Gauteng to determine the chemical profile of the area. The specific objectives of the project were to:

- Determine the physico-chemical properties and concentration of organic contaminants in the ground- and surface water (a dam) in Steel Valley;
- Determine the chemical profile of soils in Steel Valley by identifying any possible contaminants that can pose a threat to agriculture;
- Compare groundwater and soil quality in the area before and after remediation with data obtained from the laboratory, previous data from the Department of Water and

Sanitations' Resource Quality Information Services and from the Master Plan Integration Report;

- Compare the water quality indicators obtained with their respective national guideline values and discuss their possible impacts to public health and the environment.

1.5 Research questions

The study was conducted to address the following research questions;

Research Question 1: What are the concentrations of inorganic contaminants specifically Iron (Fe), Hexavalent Chromium (Cr^{+6}), Copper (Cu), Thallium (Tl), Cadmium (Cd), Trivalent Chromium (Cr^{+3}), Arsenic (As), Mercury (Hg), Sulphate (SO_4), Nitrate (NO_3), Aluminium (Al), Manganese (Mn) and organic contaminants (Hydrocarbons, Benzene, Toluene, Ethylbenzene, Xylene, Phenols) in Steel Valley's water bodies?

Research Question 2: What are the major, minor and trace elements in the soil samples, and their exact concentrations?

Research Question 3: What impact has the remediation had on the soil and groundwater in Steel Valley?

Research Question 4: Does the current chemical profile of the soil and groundwater pose any threat to end users?

1.6 Research design and methodology

The flow chart (Figure 1.1) summarizes the chosen research design and methodology used throughout the study. The methodology and research design were carefully chosen to address fully the research questions that this dissertation is centred around. Standard operating procedures on site and in the laboratory, were used to determine the concentrations of contaminants. Numerical data obtained were then analysed, discussed and concluded upon.

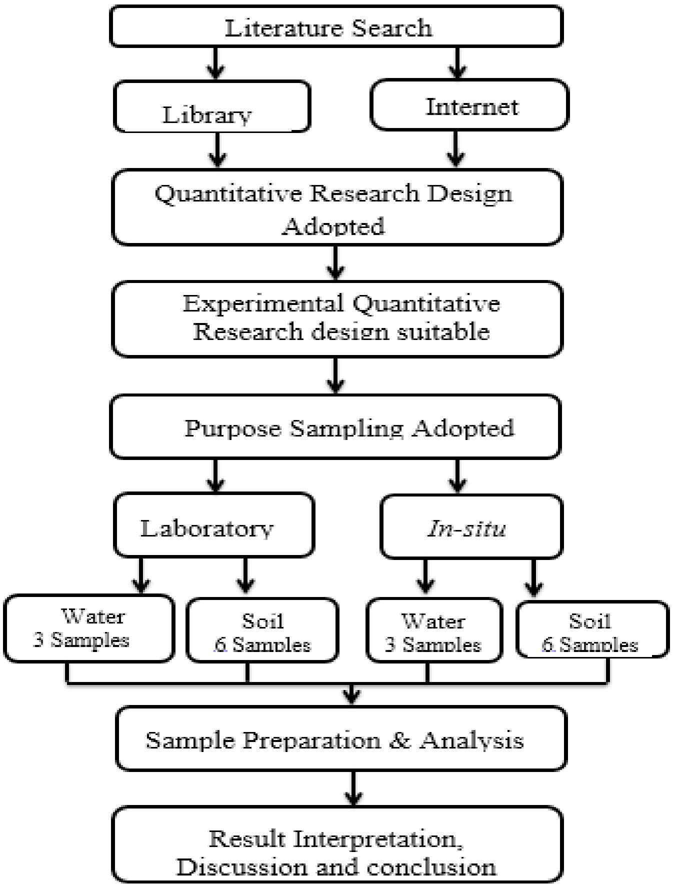


Figure 1.1. A flow chart of the research design and methodology used

1.7 Description of the study site

The study site, Steel Valley, is an outlying peri-urban suburb of Vanderbijlpark in Gauteng Province, South Africa. Steel Valley, is located in Emfuleni local municipality. Emfuleni, along with two other local municipalities, Midvaal and Lesedi form the Sedibeng District Municipality in Gauteng Province. Vanderbijlpark is historically an industrial town located on the banks of the Vaal River and forms part of a major industrial region of South Africa, commonly referred to as the 'Vaal Triangle' (Sasolburg and Vereeniging complete the triangle). Vanderbijlpark is approximately 70 km south of Johannesburg as shown in Figure 1.2. Chemical manufacturing and metal fabrication dominate the economic activities in the study area (Mtunzi, Dikio, & Moja, 2015). Due to the many industrial activities, the majority of the people work in the factories with only a few engaged in farming. Vanderbijlpark is made up of 30 892 households, with an average household size of 2.8 persons (StatsSA, 2011).

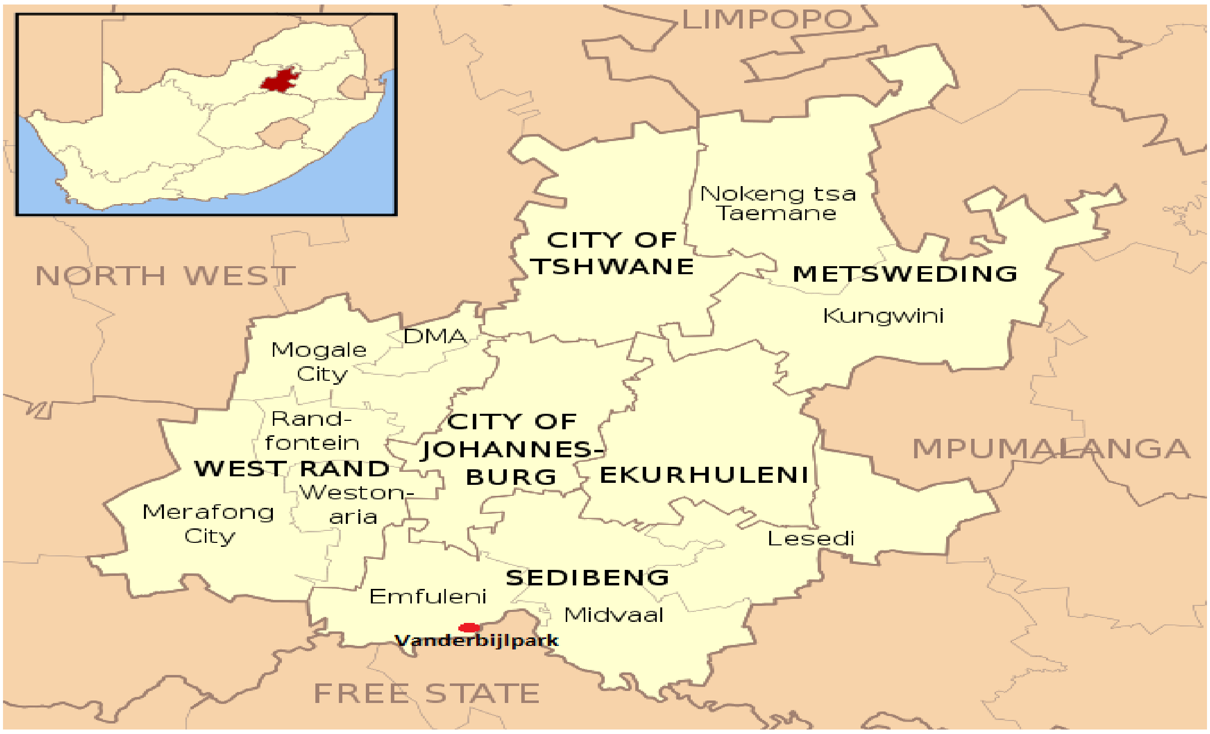


Figure 1.2 Map of Gauteng showing Vanderbijlpark. Inset: South Africa Map (Source: Gauteng Tourism Authority, 2011)

Steel Valley suburb is situated on latitude 26°42′42″ S and longitude: 27°50′16″ E. Steel Valley used to be a settlement of smallholdings, home to over 600 people and its located immediately west of the AMSA Plant in Vanderbijlpark (Lambert & Herod, 2016).

The climate at the study site is mild, generally warm and temperate. It is a summer rainfall region. Vanderbijlpark has an annual average rainfall of 550 mm per year with the highest of about 106 mm in December/January and the lowest recorded in June/July (Ochse, 2007). In June (winter), the average midday temperature for Vanderbijlpark is 17 °C and as low as 0 °C in the night. December/January (summer) receives the highest rainfall and records an average of 27.8 °C temperatures in the day.

The underlying geology of the area is mostly sedimentary Karoo Sequence, which is made up of sandy loam, clayey loam and clayey soil. The rocks identified in the area include sandstone, granite, mudstones and quartzite (Ochse, 2007).

The main drainage system is the Vaal River, which is a tributary of the Orange River (Thieme, 2005). The study site forms part of the Vaal ecosystem, which consists of a combination of grassland with moist types present towards the east and drier types towards the west and south.

Much of the area is covered by *Cymbopogon themeda* Veld (Bezuidenhout, Bredenkamp, & Theron, 1994). Trees and shrubs such as *Protea caffra* are common along the rocky hills and ridges. Farming activities were dominant at Steel Valley prior to families being relocated out of the area (as part of the rehabilitation plan). Currently, there are about five (5) small holdings with resident families still on the study site, with majority of the land used for maize cultivation. Steel Valley currently has less than ten (10) households who are involved in smallholder farming or subsistence farming.

1.8. A brief history of the Vanderbijlpark Steel Works

Vanderbijlpark Steel Works started as an expansion of the Iron and Steel Corporation's first plant in Pretoria, to meet the growing demand of steel around the world (ArcelorMittal SA, 2014). ISCOR first constructed a Plate Mill and started production in 1943, although it only started trading in 1947 (ArcelorMittal SA, 2014). Several production units were introduced in 1953 and subsequently major expansion schemes were undertaken (ArcelorMittal, 2014). Large extensions of electrolytic tinplating were added, and the steelworks was equipped with oxygen and electric arc furnaces (ArcelorMittal, 2014). A direct reduction plant was brought online in 1981, which increased productivity and subsequently also increased pollution at the Vanderbijlpark Plant (ArcelorMittal, 2014). Figure 1.3 shows the major sources of pollution within the steel works and locates the study site. Inorganic contamination plumes existed beyond the steelworks' perimeter, while residents reported tar deposits in their water wells, which could point to contamination transgression beyond the steelworks operational area.

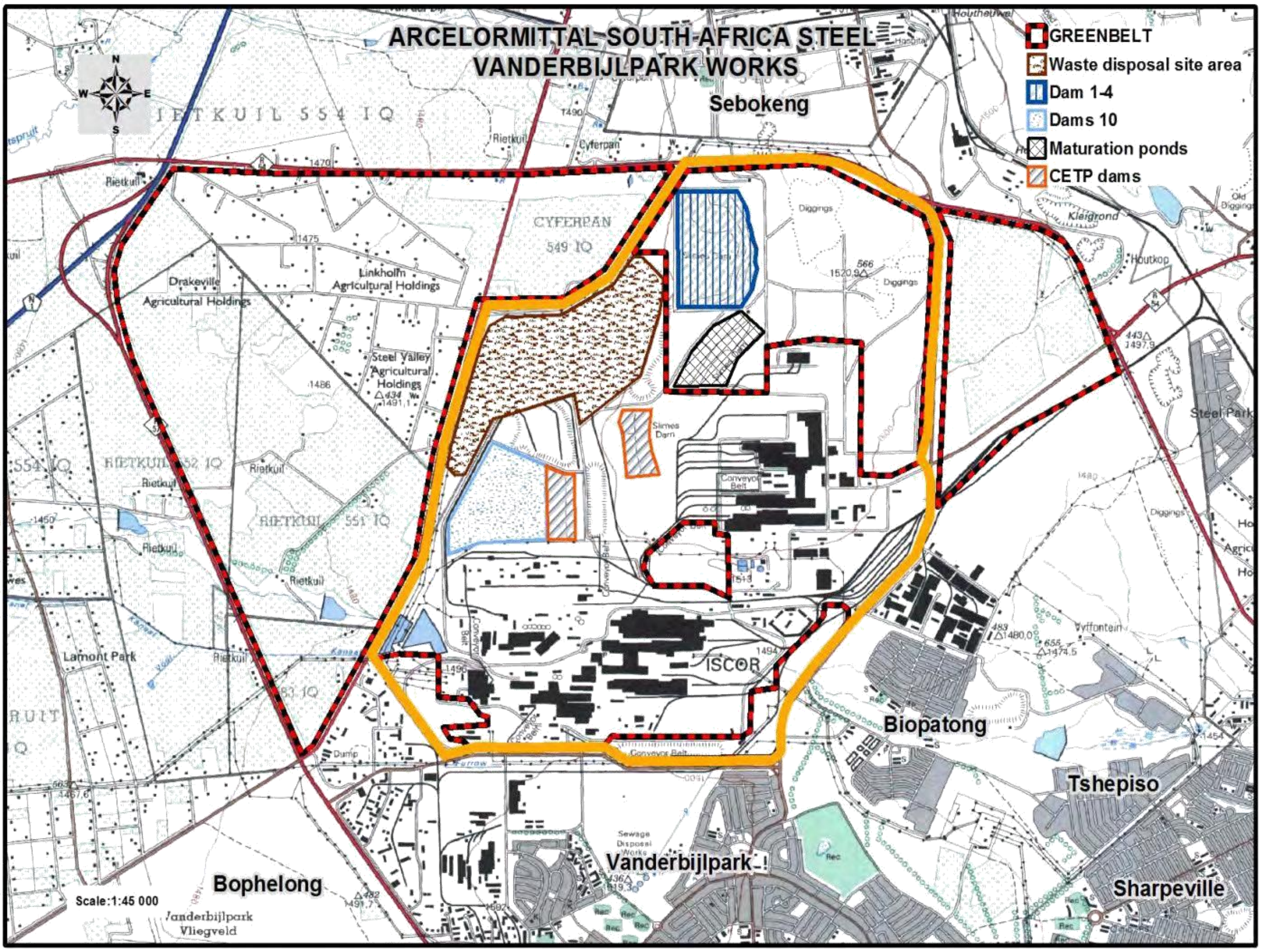


Figure 1.3 Map of ISCOR South Africa showing waste disposal sites, dams and ponds, and small holdings (Source: ArcelorMittal SA, 2014)

All these activities have had negative impacts on the surrounding areas (Munnik, 2012; Ockie Fourie Toxicologists (PTY) Ltd, 2002). The once vibrant community of Steel Valley has dissipated due to pollution from the steelworks. Figure 1.4 shows demolished housing and the sparsely distributed family homes left at Steel Valley.

(a) (b)

Figure 1.4 The current state of the once vibrant Steel Valley, Vanderbijlpark, 2016 (Source: E. Ahenkorah).

1.9 Overview of the chapters

Table 1.1 Overview of the chapters

Chapter	Content
Chapter 2 & 3	Literature review on pollution, remediation and legislation
Chapter 4	Methodology
Chapter 5	Dry season results
Chapter 6	Rainy season results
Chapter 7	Discussion
Chapter 8	Conclusion

1.10 Conclusion

The chapter has identified Steel Valley’s strive for environmental justice and the need to clean up polluted areas effectively as the main rational for the study. The next chapter will address pollution and remediation in South Africa and at international level, focusing but not confined to pollution from the steel and iron industry alone.

CHAPTER 2: LITERATURE REVIEW (POLLUTION & REMEDIATION)

2.1 Introduction

Water and soil have unique chemical and physical properties (Tchounwou, Yedjou, Patlolla, & Sutton, 2012). Such that, soil contains different types of minerals, as well as water and oxygen, all of which are essential for sustaining plant growth (Robert, 2014). The minerals that occur naturally in soil and water are mostly referred to as essential nutrients and they usually pose no threat to end users. They are, however, referred to as pollutants or contaminants if they occur in concentrations that pose health risks to living organisms and/or retard plant growth (Wuana & Okieimen, 2011).

In addition, both soil and water as media are susceptible to contamination when exposed to discharges, sludge and solid waste (Odiyo, Bapela, Mugwedi, & Chimuka, 2005). All solid waste is prone to disintegration and erosion into soil media, and subsequently to water bodies, even if they are not in direct contact with these media (Reinecke, Snyman, & Nel, 2003). One example is that of the waste generated by industrial processes. This is true for the iron and steel industry too (Naicker, Cukrowska, & McCarthy, 2003; McCarthy, 2011). Industrial waste takes the form of stones, slugs, sludge, ash, catalysts and mud (Cheng, Takahashi, Gao, Yoshikawa, & Li, 2016). The correct storage and treatment of the waste from industrial processes is vital if their ability to contaminate soil and water is to be controlled and limited (Aprilia, Tezuka, & Spaargaren, 2013). Thus, waste from industrial processes requires specific engineering solutions to ensure it is stored or landfilled correctly. Sludges, for example, are a combination of different industrial wastes, and their composition often causes reactions making remediation complex (Shamuyarira & Gumbo, 2014).

Pollution is not confined to solid waste, liquid industrial waste is also generated from the use of water during the industrial processes (Rajaram & Das, 2008). There is significant use of water in the steel industry as water is used for descaling, dust scrubbing and as part of the cooling processes. The water released after such use carries many pollutants which may contaminate soil and water bodies if not properly managed (Oelofse, Hobbs, Rascher, & Cobbing, 2004).

Before undertaking remediation of pollutants that has already entered the soil and water media, it is important to understand the fate and the mobility processes of these contaminants.

2.2 Contaminant fate and transport in the environment

The mobile or immobile tendency of pollutants and their ability to interact with each other and other particles either makes a pollutant more harmful, or less harmful over time. This affects remediation treatment processes (Evanko & Dzombak, 1997). Distance models must be used to estimate the impact of pollution and to construct mitigation procedures, but not as a standalone means, rather in combination with other well monitored factors (Heisterkamp, Doornbos, & Nagelkerke, 2000; Briggs, 2003; Chakraborty, Maantay, & Brender, 2011).

Advection, diffusion and dispersion are the main physical processes that carry pollutants away from their point of release (Wang, McMillan, & Chen, 1978; Padhye & Tezel, 2013). The movement and distribution of these pollutants in water and soil medium differ, even though the same remediation technique may be recommended for both soil and water contamination. Further studies and adjustment is required to suit each media. In water bodies, pollutants are more uniformly distributed than in soil due to the mixing ability of liquids (Shah et al., 2016). The movement of contaminant particles in water relates to the velocity of the water body (Wang et al., 1978). That being so, direct release of waste into surface waters may have impacts in a very short period of time and over a large area, whereas waste released into soil may take several months or years before its impacts are felt, although they are often more localised (Wuana & Okieimen, 2011). However, soil pollution is often associated with groundwater pollution (Konečný, Boháček, Müller, Kovářová, & Sedláčková, 2003).

The subsequent literature in this chapter reviews the fate of organic and inorganic chemicals in soil and water media with an indication when it applies to soil or water only. As the scope of the study was not that of a chemical research project, but a focus on management and containment, the review will therefore merely describe pollutants and remediation techniques along other vital aspects of environmental management.

2.3 The physico-chemical properties of water and soil media that influences the fate and transportation of contaminants

The properties of the media through which pollutants are introduced have a great influence on the way these pollutants behave and move (Oyerinde, Oluwasemire, & Oshunsanya, 2013; Klamerus-Iwan, Błońska, Lasota, Kalandyk, & Waligórski, 2015). In solids, after contaminants are released from the point source, contaminants can either dissolve, be adsorbed or be fixed chemically (Benjamin & Lawler, 2013). In groundwater, organic chemicals have a tendency to be transformed into inorganic chemicals (Dąbrowska, Kot-Wasik, & Namieśnik, 2004) as demonstrated in Figure 2.1.

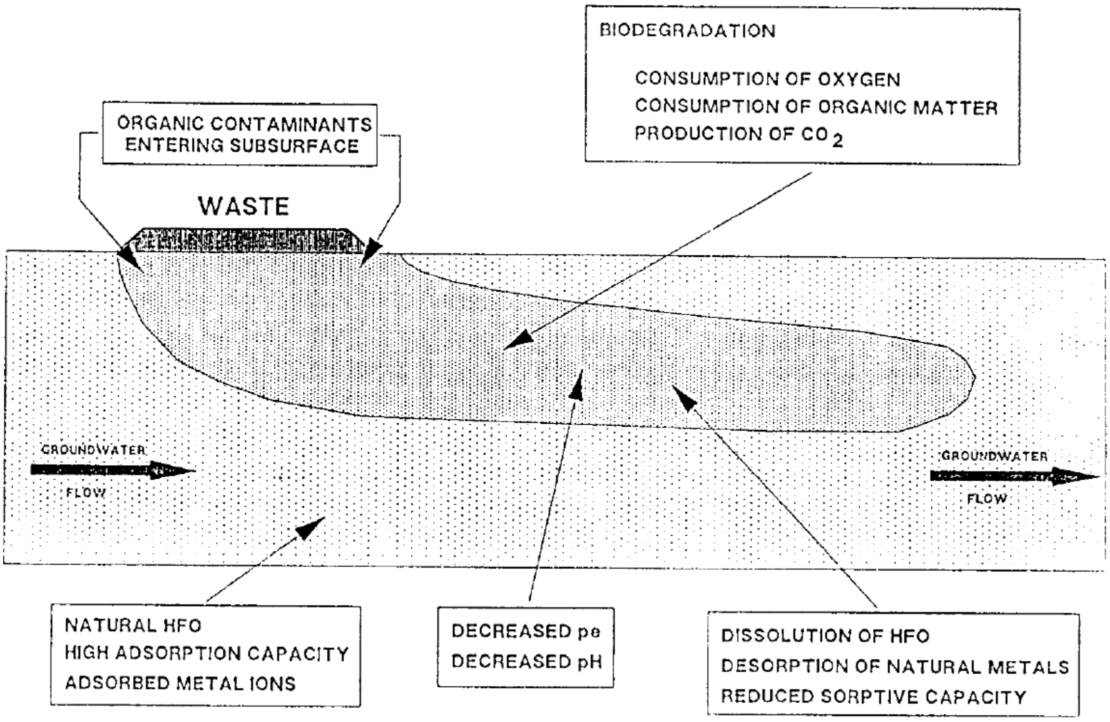


Figure 2.1 Fate, transport & transformation of organic pollutants (Source: Hashim, Mukhopadhyay, Sahu, & Sengupta, 2011; Mulligan, Yong, & Gibbs, 2001; Wuana & Okieimen, 2011).

The properties of water and soil that can alter the form in which contaminants exist can be grouped into physical and chemical.

2.3.1. Physical properties

Physical properties such as conductivity, types and level of dissolved minerals, the size and nature of soil particles, moisture content and temperature all impact on contaminants (Boulding & Ginn, 2003). For example, increasing the Electrical Conductivity (EC) of soil facilitates metal retention (Grobelak & Napora, 2015). Most trace elements other than lead and arsenic, see their concentrations levels increase when soil particle size is small (Qin, Ji, Li, Guo, Tang & Feng, 2014). Qin et al., (2014) further state that inorganic contaminants in soil correlate positively with dissolved minerals. Increasing organic matter in metal contamination studies have concluded on a decrease in the phytoavailability of the metals and so increases the potential risk they pose to plants and humans (Guo, Duan, Song, Xu, & Chen, 2008). Physical properties may also influence organic contaminants. In a study conducted on polycyclic aromatic hydrocarbons (PAHs), the organics exhibited negative correlations with physical properties such as pH and smaller sized soil particles, but showed positive correlations with sand and organic matter (Zhang et al., 2013). Volatile organic pollutants have a slow mobility rate if the soils they are located in have low levels of soil moisture (Ong, Culver, Lion, & Shoemaker, 1992). Other physical factors such as depth of the contaminated media and vapour diffusion may also alter the fate and mobility of organic pollutants, irrespective of the moisture content however (Ong et al., 1992).

In addition to the physical characteristics mentioned earlier, dispersion/dilution, filtration, density and movement also affect the fate of chemicals in groundwater. The mobility of pollutants in groundwater does not necessarily follow the steady flow pattern of the media itself (Bartram & Ballance, 1996). Water-soluble pollutants with similar densities as water tend to move at the same velocity as the flow of the water. Pollutants with lower density than water accumulate at the level of the water table, whilst dense and insoluble compounds accumulate at the bottom of an aquifer not far from the point source of pollution (Akowuah & Ampofo, 2016).

2.3.2. Chemical properties

Soil and water acidity, ions exchange and its adsorption abilities are interrelated chemical properties that either work together to reduce or increase toxicity, and also enhance or inhibit the rate at which the chemical is taken up by plants or animals (Mirsal, 2008). Toxic metals in a decreased pH soil medium are more likely to be retained in the soil (Rodriguez-Maroto, Gomez-Lahoz, Vereda-Alonso, Garcia-Delgado, & Garcia-Herruzo, 2001). Although the trend may not to be true for all toxic metals, it is very reliable for most metals in soil (Guo et al., 2008; Kazlauskaitė-Jadzevičė, Volungevičius, Gregorauskienė, & Marcinkonis, 2014). In groundwater, many chemical changes and reactions take place that retard the movement of contaminants, sorption and precipitation reactions (USNRC, 1984). The pollutants can remobilize or take different forms that can then facilitate movement or chelate. Chelating increases the mobility of metals and organic compounds in water, as does the presence of water miscible solvents (Boulding & Ginn, 2003).

2.4. Pollutants

Waste from steel mill may contain wide range of pollutants, including metals, cyanide (CN^-), polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), asbestos, methane (CH_4), ammonia (NH_3), and hydrogen sulphide (H_2S) (Van der Perk, 2006). The range and adaptability of the contaminants depends on the activities and disposal pattern of wastes at the point source of pollution (Wuana & Okieimen, 2011).

2.4.1. Inorganic pollutants: Metals

Unlike organic pollutants, most inorganic pollutants cannot be degraded in the environment, hence, the fate and transport of such chemicals are very important in weighing up remediation techniques (Hemond & Fechner, 2015). The fate and mobility of inorganic pollutants depend on several varying factors (Ashworth & Alloway, 2004). Inorganic chemicals consist of a wide range of metals and non-metals, and in this study, metals and anions were considered, due to their relevance to the production of steel.

Metals in soil are of great concern to remediation experts due to their ability to undergo speciation and/or become bioavailable to the food chain (Wuana & Okieimen, 2011). Another concern regarding heavy metals in the environment, especially in soils, is their ability to reduce the decomposition action of other pollutants (Chibuike & Obiora, 2014). Additionally, they are not easily degraded, so their impact is long lasting (Khan, Adil, & Al-Mayouf, 2015). Generally, metal complexation with organic compounds enhances pollutant transportation, whereas if pollutants are attached as metal sulphides, their mobility in water and soil decreases (ATSDR, 2004). From the point of pollution to other sections of water and soil media, there are several reactions that takes place (Silveira, Alleoni, & Guilherme, 2003). Known reactions that influence metal activities include: the precipitation of liquid waste and dissolution of solid waste (Bosbach, Hall, & Putnis, 1998; Wuana & Okieimen, 2011); complexation and ligand-exchange reactions (Hering & Morel, 1990); microbial mobilization/immobilization (Unz & Shuttleworth, 1996; Gadd, 2000), as well as, sorption (Alumaa, Kirso, Petersell, & Steinnes, 2002; Wuana & Okieimen, 2011) of metals.

2.4.1.1.Aluminium (Al)

Many studies concerning aluminum in soil, water bodies and the food chain have constantly pointed out pH as an important factor in the metal's toxicity and mobility (Coetzee, Du Preez,

& Van Vuren, 2002; Xiao, Reuter, & Boin, 2005; McCarthy, 2011; Dabrowski & de Klerk, 2013). Aluminum is not a plant nutrient and poses a threat to plant productivity. However, it usually poses less of a threat under neutral pH conditions. Aluminum is more toxic under acidic conditions, inhibiting root growth and restricting water uptake (Sparling & Lowe, 1996). Crops such as maize and groundnut are often the most affected (Merino-Gergichecich, Alberdi, Ivanov, & Reyes-Díaz, 2010). The inhibition of root growth is not the only concern. The ability of the metal to quickly move through acidic subsoils can make the problem more widespread (Sumner, 1970). There are also concerns about a high uptake of the metal by aquatic creatures (Oberholster, Myburgh, Ashton, Coetzee, & Botha, 2012). In terms of human impacts, the Department of Water and Sanitation (DWS) in South Africa notes that Al is inconclusively associated with chronic neurological disorders in terms of long-term exposure, while more than 10 mg/L may contribute to neurotoxicity in livestock. Thus, DWS has set a quantity limit of 0.15 mg/L in drinking water.

2.4.1.2. Arsenic (As)

Most of the anthropogenic release of Arsenic into water and soils in South Africa is related to Acid Mine Drainage (AMD), power plant residues and fly ash waste piles (Garelick, Jones, Dybowska, & Valsami-Jones, 2008). Arsenic sorption is influenced by the cation exchange capacity of the soil it is located in, with its solubility increasing as the pH decreases (Radloff et al., 2011). Another parameter affecting arsenic adsorption is the iron content of the soil (Elbaz-Poulichet et al., 2000). The transportation of arsenic is quite different from other metals. It is usually transported by air in the soil, although it can be leached. Under oxidizing conditions, leaching usually does not transport arsenic to any great depth (ATSDR, 2007). Since arsenic is toxic to humans, consumption of edible plant parts containing accumulated arsenic can be harmful (DWAF, 1996a). Chronic poisoning is characterized by skin lesions including hyperpigmentation and cancer, while acute poisoning can result in death from upper respiratory, pulmonary, gastrointestinal and cardiovascular failure (DWAF, 1996a). Thus, remediation of As is important in South Africa, hence a 5.8mg/kg is set as a target for already contaminated sites (see National Environmental Management Act: Draft National Norms and Standards for the Remediation of Contaminated Land and Soil Quality), while the water quality range for the metal is between 0 to 0.01 mg/L.

2.4.1.3. Cadmium (Cd)

Acidic conditions and low organic concentrations tend to enhance Cd concentrations in the environment (Bakshi & Henderson, 1998). Usually Cd released into soil remains in the topsoil, but may leach rapidly into water bodies under acidic conditions (ATSDR, 2012). According to the NEMA: Waste Act, 2008 (Act No. 59 of 2008): National Norms and Standards for the Remediation of Contaminated Land and Soil Quality, remediation of contaminated soil must be aimed at reducing Cd levels to below 7.5 mg/kg for all land uses. The target water quality range set by the South African Standards for Cd to not pose a significant health threat to humans is 0 – 0.05 mg/L (DWAF, 1996b). Cd has a long half-life in the human body, hence, even small amounts must be avoided (Godt et al., 2006). At elevated concentrations Cd is acutely toxic and can cause severe renal damage or even renal failure (ATSDR, 2012; Kim et al., 2015). Plants readily take up Cd due to its chemical similarity to zinc (an essential plant nutrient). Unfortunately, Cd can interfere with plant metabolic processes and is therefore toxic to many plants (DWAF, 1996a). Exposure of livestock to Cd during gestation results in adverse effects to the internal organ and size of the fetus (DWAF, 1996a; Castillo, Ibáñez, Guajardo, Llanos, & Ronco, 2012).

2.4.1.4. Chromium (Cr)

The different forms of chromium in the environment exhibit extremely different fates ranging from toxicity to mobility in water and soil medium (Oliveira, 2012). Among Cr (0), Cr (II), Cr (III) and Cr (VI), the latter is of utmost concern to researchers, policy makers and health experts as its regarded as highly soluble in water, very mobile and has a high rate of cell membrane permeability and toxicity (Oliveira, 2012; Guertin, Avakian, & Jacobs, 2016). This makes it easy to move from the point source of contamination to other points and therefore difficult to remediate. Oliveira (2012) describes Cr (VI) in soil and water bodies as a stronger oxidant which bioaccumulates in plants and livestock, and therefore poses a serious risk to humans via the food chain. Among the risks posed by Cr (VI) in small quantities include soil infertility, plant growth and seed germination inhibitions, mutagenicity, behavioural disorders, respiratory disorder, carcinogenicity, as well as teratogenicity in plants, livestock and humans (Wyszkowska, 2002; El Shafei, 2016). But, a reasonable amount of Cr (III) contributes to the reduction of type II diabetes and so has been used in the pharmaceutical industries to produce drugs (Vincent, 2007). That notwithstanding, Cr (III) must not be underestimated in the environment as it has the tendency to be transformed to Cr (VI) in favourable oxidation-reduction reaction conditions (Apte, Tare, & Bose, 2006). Although Cr (VI) can also be reduced to the less toxic Cr (III), Bartlett (1991) believes it is a complex and unreliable process, which makes natural attenuation a less viable option for Cr (VI) remediation. Bartlett (1991) argues that Cr (VI) has the tendency to become thermodynamically stable in water and soil media and stay this way for years. It is therefore appropriate to put emphasis on the total chromium in soil rather than just the toxic form of chromium. Water and soil regulatory bodies (both internationally and in South Africa) have strict quantity target values. Both set the target water quantity range for human consumption at between 0 – 0.05 mg/L and warn of irreversible effects above this range (DWAF, 1996a; WHO, 2011). Soil screening values for Cr, especially Cr (VI) has similar strict values. According to the DEA of South Africa, after chromium remediation, the contaminant levels in soil for all land uses must be below 46 mg/kg and 6.5 mg/kg for Cr (Ill) and Cr (VI) respectively (DEA, 2010).

2.4.1.5. Copper (Cu)

Copper easily and quickly adsorbs to organic constituents and clayey soil to form a complex of organic-Cu (ATSDR, 2004; Ashraf, Maah, & Yusoff, 2012). In water, it usually takes an hour for the metal to be adsorbed and less than 24 hours for it to be evenly distributed (ATSDR, 2004; Sharma, Sehkon, Deswal, & John, 2009). Just like the general behaviour of many metals in soil, Cu Sulfides experiences low solubility, hence low mobility but become more mobile after undergoing oxidation (Gray & Mclaren, 2006; Wuana & Okieimen, 2011). Apart from the oxidation-reduction effects on Cu, acidity also aids in leaching the metal in the soil (Gray & Mclaren, 2006). Copper is an essential plant micro-nutrient but plants may show symptoms of toxicity with concentrations greater than 1 mg/L (DWAF, 1996b). Copper levels of more than 200 mg/L in water may cause severe poisoning with possible fatalities (DWAF, 1996a). Thus, the difference between the amount of copper required as an essential nutritional micro-element and that which causes toxicity is marginal (Sonmez, Kaplan, Sonmez, Kaya, & Uz, 2006). The target concentration of copper in the soil after remediation per South African standards is 16 mg/kg for all land uses.

2.4.1.6. Iron (Fe)

Iron content in a polluted area may completely alter the water and soil chemistry along the path that it travels as the natural cycling of iron may result in the precipitation of trace metals such as As, Cu, Cd and lead (Pb) (Fruzińska, 2011; Moreno-Jiménez, Esteban, & Peñalosa, 2012).

Iron in water and soil media change its forms depending on pH and organic activities (Pezeshki & DeLaune, 2012). Anaerobiosis in soils lead to the reduction of Fe (III) and total Fe in water (Ammari & Mengel, 2006). However, Fe has a decreased ability to infiltrate into the food chain through plants in alkaline environments and travels at a very slow rate in loose soils (Ashraf et al., 2012). Plants grown in an iron contaminated area in Poland did not become contaminated with iron in alkaline loose soils (Fruzińska, 2011). South African water quantity range for iron concentration in domestic water ranges from 0 – 0.10 mg/L, while greater than 20 is deemed to have adverse chronic and acute effects such as diarrhoea, vomiting, acidosis, respiratory failure, liver and pancreas damage (DWAF, 1996a)

2.4.1.6. Manganese (Mn)

Manganese toxicity is a world-wide problem in areas with acidic soils (Millaleo, Reyes- Diaz, Ivanov, Mora, & Alberdi, 2010). A change in soil pH and redox potential caused by soil moisture conditions and organic amendments have a great influence on Mn solubility and subsequently its toxicity (Porter, Bajita-Locke, Hue, & Strand, 2004). Manganese levels are expected to be remediated to below 740 mg/kg for all soil use in South Africa (a relatively high target) although the target is expected to be kept as low as 0.05 mg/L by water quality standards in South Africa due to the adverse aesthetic effects that limit the acceptability of manganese-containing water for domestic use.

2.4.1.7. Mercury (Hg)

Mercury is very toxic, hence strict remediation targets are set in South Africa (0.93 mg/kg). It’s a chronic neurotoxin that takes the form of neurological (organic mercury) and renal (inorganic mercury) disturbances in humans (Papu-Zamxaka et al., 2010). The acceptable range for South African water standards is between 0 to 0.01 mg/L, as any level above this may result in acute and/or irreversible effects on human health (DWAF, 1996a). Mercury may exist in mercuric (Hg^{2+}) and mercurous (Hg^{1+}) states with different solubility in water, hence different mobility and toxicity (ATSDR, 1999b). In water, mercury may be methylated to its most toxic form, methyl-mercury (Hong, Kim, & Lee, 2012). Metallic mercury and dimethylmercury are volatile and evaporate easily, while Hg in its solid state forms partition to particulates in soil or water column and are transported downward in the water column to the sediments (ATSDR, 1999b).

2.4.1.8. Thallium (Tl)

This metal is highly soluble making it very mobile. Thus, although it is rare, it can become widely dispersed and very toxic (Peter & Viraraghavan, 2005). Tl in solid waste dissolves and travels faster in an acidic environment (Sangvanich et al., 2010). Tl easily undergoes sorption in the presence of organic matter, under reducing conditions and can be transferred from water to soils easily and from soils to crops readily (Peter & Viraraghavan, 2005). There is scant research on Thallium in South Africa, and the few studies that have undertaken report shown minimal or no levels in assessed areas. That notwithstanding, Tl is a growing concern with new discoveries of its sources (Saha, 2005).

2.4.2. Inorganic pollutants: Anions

The binding process of anions to soil and water particles are usually similar to that of metal cations, and are both mostly dependent on the same factor, namely pH (Sharpley, 1991). Unlike metal cations, the pH – adsorption dependence in anions is usually inversely related (Sharpley, 1991; Sherene, 2010). In anions such as sulphates and nitrates, high pH reduces the adsorption rate in soil and water (Nodvin, Driscoll, & Likens, 1986; Oburger et al., 2011).

2.4.2.1. Sulphates (SO_4)

SO_4 may occur as water-soluble salts, adsorbed by soil colloids, or as insoluble forms (Tabatabai, 1987). The concentration of adsorbable SO_4 in soils is dependent on the mineralization of organic sulphur and leaching, although the adsorbing capacity is also dependent on the type of soil. The capacity of soil to adsorb SO_4 depends upon clay content, nature of clay minerals, pH, temperature, associated cation, and the amount of hydrous Al and Fe oxides present (Tabatabai, 1987). The adsorption is readily reversible which is an important factor when considering remediation options (Martinson, Alveteg, & Warfvinge, 2003). Reduction reactions of SO_4 reduces the redox conditions and biogeochemical processes in groundwater; thus, the basics for most studies concerning remediation of SO_4 contamination and its practical application (Miao, Brusseau, Carroll, Carreón-Diazconti & Johnson, 2012). Soil screening levels may not exceed 4 000 mg/kg after remediation in South Africa (as per the NEMA; Waste Act), while acceptable concentrations in drinking water are set at 200 mg/L. It is known that high concentrations of sulphate exert predominantly acute health effects like diarrhoea, and may rather combine with other factors to make other elements more toxic (Davies, 2007).

2.4.2.2. Nitrates (NO_3)

Nitrates/nitrite levels must not exceed 120 mg/kg after remediation in soils according to the 2013 National Norms and Standards for the Remediation of Contaminated and Soil Quality. The target range for domestic water use is from 0 – 6 mg/L, as concentrations above 20 mg/L may cause Methaemoglobinaemia in infants and mucous membrane irritation in adults (DWAF, 1996a). Although highly soluble and highly mobile in soil and groundwater, they do not adsorb onto soil or aquifer geologic materials, but precipitate as a mineral under dry conditions. Nitrate and nitrite undergo oxidation-reduction reactions to interchange forms in water and as such cause health implications for fish and humans (Weiner, 2010).

2.4.3. Organic pollutants

The mobility of low-concentration organic contaminants with poor aqueous solubility in soil is very restricted, hence, contaminant mobility is negligible (Valentín, Nousiainen, & Mikkonen, 2013). Nevertheless, the Volatile Organic Compounds (VOCs) are relatively soluble and mobile (Gioia et al., 2011). Organic pollutants may dissolve in water, be sorbed on solid particles, transported by soil gas or form a non-aqueous phase liquid (NAPL) (Konečný et al., 2003). Petroleum hydrocarbons can be classified as aliphatic (in this study, alkanes) and aromatic (in this study Benzene, Toluene, Ethylbenzene and Xylene - BTEX/VOCs and Phenols) (Tolosa et al., 2005).

2.4.3.1. Alkanes

Low molecular weight aliphatics are more likely to leach from the point source of contamination to groundwater or biodegrade than the high molecular weight aliphatics, although the mobility is not as high as inorganic contaminants (ATSDR, 1999a; Konečný et al., 2003). The higher molecular weight compounds that are immobilized tend to sorb to the soil and persist at the point of release (ATSDR, 1999a). Alkanes categorized by the National Environmental Management: Waste Act (Act 59 of 2008) includes C_7-C_9, C_{10}-C_{14}, C_{15}-C_{36} with target levels after remediation in soil as 2 300 mg/kg, 440 mg/kg and 45 000 mg/kg respectively.

2.4.3.2. BTEX

BTEX is a group of the Mono Aromatic Hydrocarbons (MAHs) which comprises of benzene, toluene, ethylbenzene and isomers of xylene (arranged in order of decreasing mobility) and are the most water soluble of all petroleum organics (Pal, Gin, Lin, & Reinhard, 2010; Lapworth, Baran, Stuart, & Ward, 2012; Valentín et al., 2013). The primary source of BTEX in soil and water media is contamination with petroleum products (Mitra & Roy, 2011). Petroleum products are widely used in industrial plants (Day, Reinke, & Thomson, 2001). Among the BTEX group, benzene is singled out as the most harmful due to its solubility, and therefore, mobility in water. Benzene is known to be a carcinogenic pollutant (Jamall & Willhite, 2008). Among the aromatic hydrocarbons, BTEX contaminants are the most volatile hence the name VOCs and have the lowest soil organic carbon sorption coefficients (K_{oc}) (Atlas, 1981; Whelan et al., 2015). K_{oc} is the ratio of the amount of a chemical sorbed to the organic matter component of soil or sediment to the amount of the compound in the aqueous phase at equilibrium, and has been used as one variable in predicting the mobility of a compound from soil to ground water (Brown & Flagg, 1981; Mohr, Stickney, & DiGuiseppi, 2010).

2.4.3.3. Phenols

The coal tar, iron and steel and plastic industries are some of the inland anthropogenic sources of phenols (Dube & Delfino, 1976). Incomplete biodegradation or decomposition of other organic pollutants are also known source of phenol in the environment (Michałowicz & Duda, 2007). Phenol contributes to cell death in humans and has a deteriorating effect on the liver and kidneys. Thus, it is considered to be highly toxic (McCall et al., 2009; Gami, 2014). Sorption to soil particles by phenols and volatilization of the contaminant is very minimal, hence its mobility is negligible (Lapworth et al., 2012; Valentín et al., 2013). Phenols biodegrade quickly in small quantities in soil, leaving little or none to be leached into groundwater, unless they occur in high concentrations that cannot be biodegraded until leaching starts taking place (Guerin, 1999).

2.5. Remediation

Environmental remediation of media such as soil, sediment, groundwater and surface water involves the removal of contaminants and pollutants from sites with the aim of protecting the environment and human health (Yao, Li, Xie, & Yu, 2012). In the quest to remove or reduce anthropogenic contaminants in soil and water media, there are a number of concerns that need to be addressed. This includes the cost, the time to achieve clean-up goals, and, the efficacy of the remediation technology (Miller & Orbock Miller, 2007). Contaminated sites need to be remediated using suitable and cost-effective technologies. Due to the difficulty encountered with the degradation of metals, the remediation of sites contaminated by metals requires some form of manipulation such as exploiting, increasing or decreasing the mobility of the metal contaminants (Davydova, 2005; Wang, Hung, & Shammas, 2009).

Until recently, the remediation of contaminated sites involved the excavation of contaminated soil, replacing it with clean soil and landfilling the waste (Wang et al., 2009). This practice is criticised as the hazardous material can still find its way back into the environment; not to mention the limited availability of clean soil (Khan, Husain, & Hejazi, 2004). These issues led to the development of other remediation methods to remove, degrade or immobilize contaminants (Khan et al., 2004). Soil remediation technologies can be categorized using several criteria, ranging from the types of treatment processes (biological, chemical, physical, thermal, solidification and stabilization processes) to the place the remediation is done (Hamby, 1996). It is however very important to note that a particular technology can be applicable to an entire site, a specific geographical region of the site (operable unit) or a particular media. Decision makers may have a number of choices to pick from depending on the regions and media involved (Miller & Orbock Miller, 2007).

Compared to most other African countries, South Africa is advanced in terms of environmental remediation. South Africa deploys physico-chemical treatment processes, which are regarded as expensive to set up and may potentially generate hazardous waste due to the chemicals that are used. While some researchers believe it’s a step in the right direction, othersadvocate for more bioremedial techniques to be encouraged as it is a more environmentally friendly (Atagana, 2004; Teclu, Laing, & Wallis, 2009; Gitari, 2014; Masindi, Gitari, Tutu, & De Beer, 2015). According to Atagana, (2004) bioremediation also reduce the health risk for personnel and technicians, since *ex-situ* remediation may pose health risk in the evacuation process. Without a doubt, research into pollution (specific or group of pollutants), various remediation options and potentially exploitable techniques have played a vital role in pushing forward remediation in South Africa. This section will review some of the research done in the field of remediation in South Africa and other parts of the world, with emphasis on biological remediation processes.

Apart from bioremediation or phytoremediation, the idea of using passive remediation options over active techniques is gaining ground in South African academic circles (Masindi et al., 2015). Regarding heavy metals, most remediation techniques are developed based on their sorptive properties. However, the tolerance of biological films and systems used must be thoroughly assessed to know the limits as some of these techniques have been known to cause negative impacts on treatment efficiency when its tolerance capacity is reached (Azizi, Kamika, & Tekere, 2016). Neutralization and metal attenuation by magnesite has a promising potential in solving South Africa’s pollution issues (Gray, 1997; Johnson & Hallberg, 2005; Masindi et al., 2015). The batch experiment conducted by Masindi et al., (2015) proved amorphous magnesite’s ability to increase the pH of very acidic solutions to a strong basic solution and reduce EC as well as Total Dissolved Solids (TDS). The study however proposes post remediation treatments, as the technology efficacy on metals was not as successful as pH, TDS and EC.

Before remediation decisions are made, goals must be set based on a full characterisation of the study area. That is, the success of any remediation technique is rooted in a comprehensive physiochemical and biological characterization of the remediation site (Liu, Lee, Kitanidis, Parker, & Kim, 2012). This characterization, coupled with other factors, largely determines which technologies can be considered and which technology will be the most feasible (Liu et al., 2012). The remediation decisions are usually based on the properties of the contamination medium, contaminant characteristics and available resources to confine contaminants or trap contaminants in a zone, ‘paralyze’ contaminants or limit its movement. The remediation seeks to change the fate of pollutants to limit harm or excavate affected sites and directly extract the extractable contaminants.

2.5.1. Remediation by isolation & containment

It is possible to isolate and contain pollutants/chemicals in soil or water media to reduce its penetrating ability using barriers or reduce water filtration (Jankaite & Vasarevi, 2005). The permeability can be reduced by 1×10^{-7} m/s using various barriers and concrete materials such as grout, cement, montmorillonite and steel placed in either a horizontal or vertical orientation (Jankaite & Vasarevi, 2005). There are two types of isolation and containment techniques that will be reviewed in this chapter, that is capping and subsurface barriers.

Capping is a relatively cheap remediation technique and is able to prevent groundwater pollution by preventing seepage out from a waste heap or from contaminated soils (Lee & Jones-lee, 1997). The technique is a form of *in situ* containment that isolates contaminated media by limiting the water or liquid content that enters or leaves by using impermeable caps (Förstner & Apitz, 2007). The underlying principle behind this physical barrier is to limit chemical advection movement: movement of a contaminant within the seepage velocity or contaminants that diffuse (American Geological Institute, 1998).

The second option is the subsurface barrier technique which focuses on slowing down the velocity of fluid or sediment portion, so as to slow down the contaminant transfer process or redirect the contaminants pathway to a collectable source by using pollutant impermeable layers (Powell, Puls, Hightower, & Sabatini, 1995). This technology is often appropriate for buried or heap waste and so may not be able to properly remediate a long stretch of pollution (Pearlman, 1999). The challenge that most policy makers face in choosing a remediation method is finding environmental friendly materials that in themselves pose no additional threat to the environment. Research conducted on suitable materials in constructing the barriers tend to recommend humic organic materials due to their sorptive ability and environmental friendliness (Perminova, Hatfield, & Hertkorn, 2005). Research conducted in South Africa on *in-situ* denitrification techniques revealed that using permeable reactive barriers offers versatility in remediating different kinds of pollutants (Clarke, Tredoux, & Saayman, 2004). Clarke et al., (2004) concluded that, altering the reactive material used in constructing the barriers could make the technique useful not to only nitrate but to remediate metals including Cr (VI), hydrogenated organics and AMD.

2.5.2. Remediation by immobilization of pollutants

Chemical immobilization is considered an inexpensive remediation technology aimed at changing the redox states and restricting the flow of chemicals (Kobus, Barczewski, & Koschitzky, 1996; Basta, Gradwohl, Snethen, & Schroder, 2001). It is mostly used as a pre-remediation technique for very mobile or highly volatile contaminants (Maila, Randima, & Cloete, 2005). There are two forms of immobilization per the scope of this review, namely, solidification or stabilization and vitrification (Bolan et al., 2014).

Solidification/stabilization is aimed at minimizing contaminant solubility, leach ability and/or chemical reactivity using binders to hold the pollutants together physically (Tajudin, Azmi, & Nabila, 2016). This remediation option has proved unsuccessful for volatile and low solubility pollutants. Unfortunately, the procedure outlined produces air pollution especially when practised on organic pollutants (Ioannidis & Zouboulis, 2005). So, the procedure requires much attention to be paid in terms of temperature control and water content as these two factors could jeopardize the entire remediation process (Malviya & Chaudhary, 2006).

Most of the conditions required for vitrification remediation to thrive are directly opposite to solidification/stabilization conditions. High temperatures are used to convert highly soluble inorganic waste into vitreous contents, while less soluble and volatile contaminants are broken down due to the high amount of heat (Hamby, 1996). Unlike solidification/stabilization, vitrification is a suitable remediation option for organic contaminants, as it destroys organic waste rather than releasing it in the form of gas (Lichtfouse, Schwarzbauer, & Robert, 2013).

2.5.3. Remediation by toxicity reduction

Various chemical and biological processes can be used to decrease the mobility of contaminants, hence a reduction of the contaminant toxicity. The chemical processes and biological processes are reviewed briefly here. There are emerging studies that use permeable walls and combine both chemical and biological process (and sometimes physical processes) to treat contaminated water bodies (Skinner & Schutte, 2006; Israel, Engelbrecht, Tredoux, & Fey, 2009).

In terms of chemical processes, it has been demonstrated that for most contaminants changing their oxidation states or altering their acidity/basic state can render them less toxic (Tchounwou et al., 2012). This remediation phenomenon therefore capitalises on chemical processes such as oxidation-reduction reactions and neutralization reactions to reduce the toxicity of contaminants by changing their oxidation state (Wuana & Okieimen, 2011). But, *c*hanging oxidation states of contaminants may make either less toxic contaminants more toxic or toxic contaminant less toxic. So, this remediation option must be cautiously applied so as to avoid increasing the pollution problem, and usually requires a single pollutant or group of pollutants whose fate in soil and water media are the same in terms of oxidation-reduction and neutralization reactions (Evanko & Dzombak, 1997). Nonetheless, this treatment option has proven to be a good remediation option for chromium and arsenic (Hamby, 1996; Madhavi et al., 2013).

The use of living organisms to facilitate oxidation-reduction reactions, methylation and other physical process to treat waste is generally be termed as biological treatment (Gazsó, 2001). These processes have traditionally been used on organic pollutants (Kensa, 2011). Recent studies and applications have shown success in other fields, however, promising removal efficiencies and sustainability in removing a wide range of metal components from water and soil bodies (Juwarkar, Singh, & Mudhoo, 2010; Ahemad, 2012; Akhtar, Chali, & Azam, 2013;

Dixit et al., 2015). These biological processes encompass several sub strategies and will be categorized as bioremediation or phytoremediation under this review.

2.5.3.1.Bioremediation

Bioremediation utilizes microbial degradation processes to treat contaminated sites by altering the environmental conditions to favour microbial catabolism (or cometabolism) of contaminants leading to their breakdown and detoxification (Das & Chandran, 2011). This technique is applicable if the contaminants are mostly organic in which case they are degraded totally through mineralization to produce inorganic products such as H_2O and CO_2 or partially degraded through biotransformation (Rockne & Reddy, 2003). That notwithstanding, bioremediation is not restricted to only organic contaminants but can also be used for metal removal, since current techniques are able to alter the oxidation state of some elements, reducing or increasing their mobility and transforming them (Wang et al., 2009). Three bioreactors were used to evaluate the efficiency of bioremediation on metals, with water samples from the Plankenburg River, South Africa (Jackson et al., 2009). After bioremediation, Al concentrations had decreased from 0.41 mg/L to 0.06 mg/L, nickel (Ni) from 0.2 mg/L to 0.07 mg/L, while zinc concentrations had decreased from 75 mg/L to 0.02 mg/L, representing an efficiency rate of 85%, 65% and 97%, respectively. Another reactor also showed that Al, Cu, Fe and Mn concentrations had decreased by 75%, 57%, 44% and 57% respectively in the water samples.

Acid mine drainage has been one of South Africa’s environmental problems for decades and researchers believe it could even be worse if swift and long term measures are not put in place (Naicker et al., 2003; McCarthy, 2011). One of the most efficient models so far, used bioremediation to achieve a 99% and 80% removal rate for iron and sulphate, while converting an acidic medium to a less basic medium (Ramla & Sheridan, 2015). The underlying concept of the remediation model built by Ramla & Sheridan, (2015) has a basis similar to biomining which is been used in Chile and other parts of the world to reduce the chemical effect of copper, gold and uranium mining (Johnson, Kanao, & Hedrich, 2012; Schippers et al., 2014). The concept is based on oxidative dissolution of sulfidic minerals or the reduction of sulphate to sulphide using biological organisms specifically bacteria (Johnson et al., 2012; Ramla & Sheridan, 2015). Although the technique has not been tested on many pollutants, it is a boost for bioremedial studies and practical implementation on commercial basis considering the availability of the potential grass and plant species in the country. Additionally, research on the commercial implementation of this method needs to establish how by-products will be disposed of.

Bioremediation follows two main approaches: biostimulation and intrinsic bioremediation (Azubuike, Chikere, & Okpokwasili, 2016). Biostimulation optimises the activity of native microbes by creating a conducive environment to aid metabolism while intrinsic bioremediation does not generate external stimulation, it is a process of natural biodegradation (Adams, Fufeyin, Okoro, & Ehinomen, 2015; Van Bemmel, 2010). Natural attenuation often requires more time to achieve its goals and performance is difficult to predict.

2.5.3.2. Phytoremediation

Phytoremediation, also known as agro-remediation, vegetative remediation or green remediation is the technique that utilises green plants for partial or substantial remediation of organic and inorganic contaminated media (Hinchman, Negri, & Gatliff, 1998; Pilon-Smits, 2005). Depending on the processes that take place during this type of remediation technique, it could also be referred to as rhizofiltration, rhizodegradation, phytoextraction, phytodegradation, phytovolatilization and phytostabilization (Tangahu et al., 2011). The plants do this by immobilising the contaminants through absorption and accumulation into the roots. Research into phytoremediation and potential plant agent has intensified in South Africa in recent years, as most indigenous grasses show great promise in inorganic contaminant uptake. For example, research by Ochonogor & Atagana (2014) demonstrated that under greenhouse conditions *Psorelea pinata* accumulates iron and chromium from contaminated soils. The study went further to demonstrate phytoremediation with plants could tolerate high levels of metal contamination with minimal inhibition in growth processes. Hence, phytoremediation can be considered a degradation, extraction or containment technique.

In a study using the aquatic macrophyte *Eleocharis acicularis,* researchers monitored *E. acicularis'* ability to take up multiple heavy metals and its potential use at an abandoned mining area in Hokkaido, Japan (Sakakibara, Ohmori, Ha, Sano, & Sera, 2011). Elemental concentrations of Pb, Fe, Cr, Cu, Ni and Mn measured in samples of the plant, water and soil revealed an increased accumulation of Pb in the plant exceeding the initial concentrations. The result indicates that *E. acicularis* is a hyper accumulator of Pb. Other studies have highlighted the importance of phytoremediation, but some caution needs to be exercised. For example, it seems to work better when metal concentrations are low (Mellem, Baijnath and Odhav, 2009;

Paz-Alberto, 2013). Mellem (2008) used *Amaranthus dubius* as a metal accumulator on heavily contaminated sites in Durban and also evaluated the potential of plants for phytoextraction, using the translocation factor (TF). This ratio is an indication of the ability of the plant to translocate metals from the roots to the aerial parts of the plant (Marchiol, Assolari, Sacco, & Zerbi, 2004). Mellem (2008) found that the species can tolerate high Cr concentrations but can only translocate Cr to the aerial parts of the plant when Cr concentrations are below 25 ppm. Although *A. dubius*' rapid growth and great biomass makes it ideal for phytoremediation, Mellem (2008) concluded that the process shows limitations in its potential to remove Pb, Cu or Ni from contaminated sites.

2.5.4. Physical separation

This technique is an *ex-situ* technology that depends on the physical properties of both the pollutants and soil media (Hinton & Veiga, 2001). The process involves physical separation methods such as floatation (Veetil et al., 2014). Remediating by physical processes is cost effective and is efficient in terms of both organic and inorganic pollutant removal in sediments (Veetil et al., 2014). Laboratory models developed by Veetil et al., (2014) shows that the efficiency removal rate of organic pollutants is greater (80%) than the efficacy rate for metals (65%). The 80% maximum removal rate affirms the notion that the method must be combined with other methods for satisfactory remediation outcomes.

2.5.5. Extraction

The techniques used in extraction remediation are similar to that of physical separation, except that the 'separation process' in extraction uses chemical processes and can be implemented *in-situ* or *ex-situ*. Due to the broad nature of chemical processes, extraction can be grouped into four chemical processes:

(1) Physico-chemical *ex-situ* washing using aqueous suspension in the presence of extraction materials with the sole intention of leaching the contaminants sorbed on the soil particles (Evanko & Dzombak, 1997). The process is physical/chemical because after the leaching reactions. A particle size separation method is adopted to further 'sieve' contaminants in the leached solution (Wuana & Okieimen, 2011).

(2) Physico-chemical *in-situ* extraction, often called flushing, using aqueous extraction materials to mobilize and extract contaminants in the form of a solution on top of the

contaminated soil, which can then be collected and treated using particle separation methods or combined with other remediation techniques to treat the pollutant laced solution (Khan et al., 2004).

(3) Subjecting contaminated soil to high temperatures is effective when trying to deal with metal contaminants accumulated from slag waste (see Chen, Wang, Wang, Hung, & Shammas, 2016) and organic pollutants (see Barakat, 2011)

(4) Electrochemical soil processing with the help of a low-density current is used to remediate metals and organic pollutants (Acar et al., 1995). Electrochemical extraction is a preferred *in-situ* technique over many remediation options in areas identified as soil with low permeability with no or minimal chemical emissions (Huang, Xu, & Cheng, 2012).

In all the treatment options discussed, it can be inferred that pollutant mobility reduction, physical properties and chemical properties of the polluted media and the pollutants under consideration are key to the effectiveness of remediation. Pollutant persistence, biodegradation and mobility are also important in determining toxicity and the effects some of these waste pose to the environment and humans (Briggs, 2003).

2.6 Conclusion

Assessment of pollutant properties is the first step in determining the best remediation option for a polluted area. Physical and chemical properties affect the fate and transport of pollutants and subsequently the treatment methods. Treatment methods can be categorised in several ways; this study reviewed treatment methods based on how pollutants are reduced or removed, be it in soil, surface or groundwater. Apart from the major classifications of remediation discussed, there could be modifications that combines two or more of the techniques. For example, Arcelor Mittal SA modified its bioremediation by introducing excess carbon, lime and gypsum to stabilize inorganic contaminants and in its final stages using indigenous grass species for phytostabilization. While some of the techniques are pollutant, area or media specific, most of the techniques reviewed cut across media and environment. In all the methods reviewed, media alkalinity and pollutant mobility play a key role in the success of the chosen method. The relative benefit of these techniques depends on the cost involved and how efficient it is on a large scale.

CHAPTER 3: LITERATURE REVIEW (REMEDIATION & LEGISLATION)

3.1 Introduction

A country's ability to achieve sustainable development can be partially attributed to its environmental laws, its various Integrated Environmental Management Plans and whether it has a well-coordinated implementation policy that will prevent pollution or destruction to the ecosystems or not (Zhang & Wen, 2008; Qin, 2014). With that said, already polluted lands and water bodies also require similar approach so as to reclaim lands for productive purposes, as well as to protect the health of end users; be it humans, animals and plants. This chapter briefly looks at pollution, legislation and remediation as both the South African and international level.

3.2 International literature on pollution, legislation and remediation: an overview

Each step of the iron and steel manufacturing process is associated with particular types of waste and contaminants (Dong et al., 2013). The ore preparation procedure produces less aqueous pollutants but more solid waste, while the coke making process is associated with tar and ammoniacal liquid pollutants such as phenols, tar oil and sulphide (Yellishetty et al., 2010). Modern blast furnaces produce about 300 kg of blast furnace slag per tonne of iron produced (Kurunov, 2012). The pollutants are often emitted into the air and water bodies, especially in areas close to operation sites or plants (Wilson, 2008; Bilbao-Terol, 2009; Beagle, 2015). The type of emissions that find their way into soil and groundwater are dependent on the operation that occurs or has occurred (Wuana & Okieimen, 2011). These pollutants can be contained through treatment of effluent and effective management of discharge channels, whereas poor or no management of the effluent could be detrimental to the environment and its inhabitants (Wilson, 2008). Apart from the high cost involved in cleaning contaminated water and soil, the possibility of uptake/intake by plants and animals and the introduction of such elements into food chains could also mean that food safety is at risk (Mtunzi et al., 2015).

3.2.1 Industrial pollution trends and remediation on a global scale

Pollution poses significant health risks to humans, livestock and in some parts of the world is a threat to food security (Tai, Martin, & Heald, 2014). Due to industrialization, environmental pollution occurs in both developed and developing countries, with the later struggling to control or avert the possible negative consequences due to lack of investment in modern technology and poor environmental laws (Briggs, 2003). Waste from the steel and iron industry is a significant threat to the environment (Robins & Kumar, 1999; Yuan, Zhai, & Dornfeld, 2012). Industrial wastes have impaired water quality, plant growth and threatened soil fertility in most parts of the world (Briggs, 2003; Wuana & Okieimen, 2011).

In many developed countries, remediation has taken centre stage as laws now compel polluters to remediate and pressurize industries to 'green' their operations to reduce the emission of toxins into the environment. Developing countries however, often have industries that do not operate as per stipulated regulations or follow due environmental procedures when discarding waste or mitigating pollution. Nonetheless, such countries acknowledge such industrial activities that are problematic and so pollution control and mitigation measures are essential. In a developing country such as Indonesia, for example, there are over 700 documented small scale industrial zones that impact severely on the Kalimantan area of that country. Over 1 000 000 hectares of land in this area has been rendered sterile due to the roughly 150 kg per day of mercury deposited in its water bodies (Aspinall, 2001; Aryee et al., 2003; Kitula, 2006). Not only mercury but oil used in machinery also poses serious threat to water bodies in the area (Hentschel, Hruschka, & Priester, 2002; Spiegel & Veiga, 2010). Zambia's city of Kwabwe similarly faces serious pollution from lead smelting, which has caused the average lead concentration in the area to rise to between 60 µg/dl and 120 µg/dl (Kitula, 2006; Ikenaka et al., 2010). Rio Matanza in Argentina is another hub of industries, most of which do not adhere to environmental policies and are operating illegally (Mendoza, García, de Cabo, Weigandt, & Fabrizio de Iorio, 2015; Zabala, Martínez, Manzano, & Vives, 2016). The activities of these industries have contributed to heavy metal pollution of the Matanza-Riachuelo river basin and this now poses serious health threat to residents (Mendoza et al., 2015; Zabala et al., 2016). In all these cases, although there is an urgent need for remediation, it is especially hard to trace the pollution to specific companies, making it difficult to hold anyone directly responsible.

This is somewhat different when it comes to large companies or large industrial plants. Here the polluters are far more traceable, but they often have significant political clout, and so are not always held accountable for the pollution they cause. One such case is the tannery industry in Hazaribagh, Bangladesh (Bhowmik, 2013). This tannery industry is a huge source of Cr (VI) pollution (Azom, Mahmud, Yahya, Sontu, & Himon, 2012). This critical environmental problem has worsened over time as polluters continuously discard untreated waste and the lack of strict laws on remediation makes it difficult to hold them to account. The steps taken by the

Bangladesh government to relocate the industry so as to mitigate the situation has been criticized, with experts saying that this mitigation procedure is unsustainable (Bhowmik, 2013).

3.2.2 Environmental regulations

Industrialized countries that have had great success in terms of environmental pollution control and remediation have had to change their ways of dealing with pollution. They have moved from relying solely on regulations/Laws to active engagement citizens and stakeholders on what the underlying causes of pollution are, who is responsible, where to aim remediation efforts, and how to gauge success (Senge, 2008; Ahuti, 2015). Thus, strategic efforts by all stakeholders have helped to clean up the environment. Some notable and well-structured legislation on remediation is United States of America's (USA) superfund, the soil protection and surface water pollution acts of the Netherlands, Australia's contaminated site and land acts and Canada's Environmental Management Act. Among all these environmental laws, there is encouragement for firms to self-report their violations, rather than subject themselves to inspections, which in turn rewards self-reporters with less clean-up cost (Innes, 1999). Apart from the laws motivating self-reporting, there is also accountability for managing contamination as well as clear-cut roles for decentralized institutions to minimize legislation gaps. There is criminal enforcement of environmental laws in the European Union and in the United States resulting in much success in terms of environmental remediation in the last few decades (Gaynor & Bartmen, 1999).

It is often difficult to adopt a comprehensive regulatory infrastructure to protect the environment in the face of political obstacles and the vested interest of many organizations that contribute positively to the economy (Sorrell, 2015). In the early 1970s, the USA adopted one of its maiden environmental policies - the National Environmental Policy Act (NEPA), that would go a long way to make environmental protection part of the mission of all federal agencies who were directed to consider carefully the environmental effects of major actions in which they were involved (Black, 2004; Sabatier & Christopher, 2007). This legislation mandated comprehensive, national regulatory programmes to control air and water pollution, toxic substances and hazardous waste, which were all included in the Clean Air Act, the Clean Water Act, the Safe Drinking Water Act, the Toxic Substances Control Act, and the Resource Conservation and Recovery Act (RCRA) (Percival, 1998). In the same decade, the Environmental Protection Agency (EPA) was established to consolidate responsibility for environmental protection in an independent agency that would not be captive to any particular industry constituency, which was then given the responsibility for implementing the new, national regulatory legislation adopted (Percival, 1991; Bebchuk & Fried, 2003; Berrone & Gomez-Mejia, 2009). While the EPA struggled to implement these ambitious regulatory directives, the United States' Congress turned its attention to cleaning up the legacy of past contamination by creating the 'Superfund program' to remediate environmental contamination and make broad classes of parties strictly liable for the costs of any clean up (Percival, 1998). The success and durability of this legislation and its implementation has some of its roots in the broader civil rights and public interest movements of the 1960s. These movements also featured charismatic leaders who helped mobilize the public to press for enactment of landmark civil rights and consumer protection legislation.

3.2.3 Environmental legislation in developing countries

In most developing countries, environmental legislation is viewed as a normative response to discrete, specific problems such as pollution (Mayda, 1985; Singh & Rajamani, 2003). When this view prevails, legislators tend to concentrate on - and limit themselves to - the most pressing or immediate issues. Development banks, however, who often control the resources desperately needed by the developing countries for pollution management, promote the use of economic incentives and other market-based strategies to achieve environmental protection (Singh & Rajamani, 2003). However, the donors have rarely asked whether the approaches they are urging, which have recently had some success in Europe and the USA, can be implemented effectively in developing countries with limited resources and little experience with market-based policies of any kind. Although economists were developing incentive-based approaches to environmental control in the early 1970s, none of the early USA laws used economic instruments (Mayda, 1985). Market-based tools only began to make inroads in the 1980s when regulators at the EPA saw that they could be useful in dealing with the implementation of the Clean Air Act.

The primary problem with environmental legislation is that it is viewed as just another system of rules and agencies instead of being seen as part of ecomanagement of resources, that is, environmental management, informed by ecosystemic knowledge but integrated with economic development planning. Environmental laws should thus be used to achieve integrated decision-making and sustainability. There should however be priority in every country's judicial review to translate sustainability into specific legal principles, and addressing the gaps in existing laws (Dernbach & Mintz, 2011).

3.3 The South African experience

South Africa is still facing the consequences of the weak environmental legislation that prevailed during the apartheid era, with places like Steel Valley and Louisrus (both in Vanderbijlpark) still deserted due to pollution (Du Plessis, 2010; Mathee, 2011). Data paucity on individual contaminants have also contributed in the current environmental issues facing the country (Dalvie, Cairncross, Solomon, & London, 2003; Maboeta, Claassens, Van Rensburg, & Van Rensburg, 2006). An important industry that has had a significant impact on South Africa's pollution history is the metal manufacturing industry. Metal manufacturing in Vanderbijlpark has led to the contamination of water bodies, soils and sediments due to high concentrations of metal-rich waste. The contamination from the metal manufacturing industry has generally been as a result of leakages, spillages, improper disposal of industrial waste and other forms of negligence (Cock & Munnik, 2006; Munnik, 2012). The effects of metal manufacturing, coupled with inevitable ongoing pollution from other industries, are still felt today. In the long term this poses hazards to living organisms and the environment at large, inhibiting the achievement of sustainable development (Cock & Munnik, 2006).

The World Steel Association ranks South Africa as the highest producer of steel in Africa, at one stage responsible for about 45% of the total steel produced in Africa (Taylor, Page, & Geldenhuys, 1988). Worldwide, more than 1.6 billion tonnes of steel is manufactured and used every year, causing much environmental pollution (Worldsteel, 2010). Some environmental issues associated with the steel industry is the emission of greenhouse gases, spills and contamination of ground and surface water through the release of effluent into the soil or water bodies. While the industry is regarded as a job creator and one that helps to boost the economy by supplying steel to other industries, it is notorious for the emission of pollutants into the air and water bodies, especially close to operation sites or plants. Various chemical processes and subsequent emission of by-products and waste, which includes steel and iron slag, metallurgical dusts, and sludge, are common. Whereas these emissions can be contained by the treatment of effluent and well managed discharge channels, it is significantly worse in areas with little or no management of emissions.

Cock & Munnik (2006) allege that over a period of about 40 years, the steel mill of AMSA (formerly ISCOR) in Vanderbijlpark discharged its waste water into unlined effluent dams and the nearby Rietspruit River, while its chimneys spewed tons of poisonous sulphur dioxide and carbon dioxide into the air. At one stage some residents of Steel Valley filed a law suit against

ISCOR over pollution claims as research pointed to the possibility that the air and groundwater of the area had been polluted by the steel mill (Cock & Munnik, 2006). Residents claimed that effluent was discharged from the Vanderbijlpark Steel Works (ISCOR) through unlined canal into the Rietspruit River, which flows into the Vaal River. It was argued that as the steelworks lies at a slight elevation to the rest of the landscape, and this allows waste water drain away through the bottom of unlined effluent dams into the groundwater and tributaries of major river bodies (Cock, 2007; Munnik, 2012).

The steel works, which opened in 1952, was built before South African pollution legislation was created, hence there were almost no regulations governing effluent dams and canals (Cock & Munnik, 2006). Even when environmental legislation was passed, it was weak. Thus, pollutants have escaped through the bottom of unlined effluent dams into the groundwater since 1961, a fact well known to the then Department of Water Affairs (Cock & Munnik, 2006). These unlined dams prevailed until the year 2000. Although most of the facilities are no longer in use now or have been redesigned, the waste stayed long enough in these dams to have had an impact on soil and water bodies.

In 2000, ISCOR had bought the properties of some 400 nearby residents, mostly those residing in Steel Valley. Others remained because they wanted compensation to go beyond just buying them out of their property. For example, Martin Johannes Dewing, are resident in an interview with BBC said the situation was very bad such that, even people visiting them for a short period of stay felt the impact of the pollution after drinking the water (Dempster, 2002). Martin Johannes Dewing was offered R 50 000 but declined because he felt the compensation should include costs related to the medical care needed to deal with his exposure to pollution. Subsequently, sixteen residents of Steel Valley, including Mr. Dewing instigated legal action against the steel giant in 2002. This litigation against the company did not yield much unfortunately (Cock & Munnik, 2006). After the takeover of ISCOR, the new company, AMSA, agreed to rehabilitate facilities and decommission some old facilities to ensure compliance with the new environmental legislation. A compulsory Environmental Master Plan (EMP) was drawn up in this regard.

ArcelorMittal SA now claims that over R 850 million has been spent in controlling emissions, water treatment and landfill rehabilitation with a large portion of this spent on old legacy sites such as Steel Valley. ArcelorMittal SA has combined biodegradation and passive chemical mechanisms, as well as bioremediation at Steel Valley (ArcelorMittal SA, 2014a). With cost effectiveness an important factor in waste containment, the company was able to execute the project commercially at a cost of R 46 million, comparable less than many traditional remediation options and the company's own previous waste storage and disposal methods (ArcelorMittal SA, 2014b).

In 2004, the affected communities and groups, together with concerned organizations and individuals banded together to create the Vaal Environmental Justice Alliance (VEJA) and asked AMSA to make public a copy of the Steel Valley Environmental Master Plan. The company failed to do so, and the activists eventually turned to the courts in 2011. In September 2013, the Johannesburg High Court ruled that AMSA must release various environmental records to VEJA, a ruling that AMSA appealed. On 26 November 2014, the Supreme Court upheld the High Court judgement, additionally finding that AMSA must pay all legal costs. Thus, it can be said that it is now clear that industries in South Africa do have an obligation to stakeholders in terms of keeping them informed regarding contamination and pollution. For many years AMSA blocked the flow of vital information to the residents (and former residents) of Steel Valley despite the impacts on their health and legitimately acquired properties (Cock, 2006; Munnik, 2012).

3.3.1 Industries of notable mention in South Africa

South Africa once had a thriving synthetic chemical industry, but more recently, more than half of South Africa's plants have shut down or relocated to other parts of the world. However, their environmental impacts remain a major concern. An age long pollution problem that recent research suggests may not have been completely remediated is that of Thor Chemicals Pty Ltd.'s pollution of Mngceweni River in KwaZulu Natal (Williams, Leaner, Somerset, & Nel, 2011). Different studies have confirmed mercury levels in fish and hair (see Papu-Zamxaka, et al., 2010) as well the water, sediment and biota (see Williams et al., 2011).

3.3.2 Environmental legislature in South Africa

Over the years, South Africa environmental law has evolved with respect to environmental pollution and reclamation (Sowman, Fuggle, & Preston, 1995; Kotzé, 2007; Retief, 2010). The National Environmental Management Act (Act No. 107 of 1998) outlines norms and standards for the remediation of contaminated land and soil quality. There has also been a change to advocating for a systematic and hierarchical approach to waste avoidance, thus, waste disposal is now considered a last resort. Despite South Africa's commendable efforts to provide a mandatory right to clean environment, there are huge gaps between theory and practice. For example, there is often only a half-hearted approach on the part of authorities to enforcement, whilst environmental laws continually get changed and amended (Papu-Zamxaka, Harpham, & Mathee, 2010). The Organisation for Economic Co-operation and Development (OECD) assessment of the environmental policies and programmes in South Africa highlights the policy gaps in South Africa's environmental regulations with poorly regulated mining activities despite significant institutional changes and a massive overhaul of apartheid era environmental laws (OECD, 2013). According to the OECD, (2013) one particular problem is the decentralisation of enforcement to municipal levels.

Thus, the number of environmental laws passed is not a good measure of the effectiveness of South Africa's ecomanagement system. Importantly, legislation alone does not guarantee that the intent of the legislator will be implemented. There are major practical problems in terms of setting up control and enforcement mechanisms, and the capability of the public sector to enforce laws is limited (Brynard, 2010). When policy makers fear that environmental legislation may constrict economic decision-making, they sometimes resist the formulation of environmental laws or directives, which was the case of the very companies that contributed greatly to industrialization in South Africa during apartheid and the beginning of industrialization. The perceived conflict between environmental remediation directive and policy makers' ability to make unlimited economic choices can therefore not be ruled out in delayed clean up in polluted areas or laws that will lead to remediation (Mayda, 1985).

3.3.3 Environmental legislation history

A timeline for the implementation of legislation to protect the environment; controllable anthropogenic waste released into it as well clean up measures in South Africa is summarized in this section.

3.3.3.1 Environment Conservation Act – ECA (1989)

The ECA 1989 is regarded as South Africa's premier law focusing on environmental issues that seeks to protect and control the use of environmental resources. There have been various amendments on the act and portions of the act are still been enforced, but it has no clear policy on environmental remediation. The act introduced a policy for general environmental conservation, and in Part V and Part VI, touched on control of environmental pollution as well as the control of activities that may be detrimental to the environment.

3.3.3.2 Constitution Bill of Rights (1996)

Constitutional provisions on environmental issues elevates the environment to a fundamental justiciable human right; thus the 1996 Constitution Bill of Rights of South Africa created such atmosphere in section 24 that; Everyone has the right —

(a) to an environment that is not harmful to their health or wellbeing; and

(b) to have the environment protected, for the benefit of present and future generations, through reasonable legislative and other measures that—

  i. Prevent pollution and ecological degradation;
  ii. Promote conservation; and
  iii. Secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development.

Once again, this development in legislature concerning environment and pollution saw an improvement by adding equality and serving as a benchmark for the way in which South African courts approach (and should approach) all environmental cases but did not make any stand on reclamation of polluted resources (Davis, 2010).

3.3.3.3 National Environmental Management Act –NEMA (Act No. 107 of 1998)

This act presents framework legislation for environmental management and introduced remediation. The act also acknowledges the inevitable nature of environmental pollution or degradation, such that, in so far as it is authorized by law or cannot reasonably be avoided or stopped, must be minimized and rectified.

3.3.3.4 National Water Act (No. 36 of 1998)

Section 19 outlines responsibility of the polluter or contaminated site owners and task individuals or institutions to cease, modify or control any act or process causing the pollution. It also tasks polluters to eliminate any source of the pollution and remedy the effects of the pollution.

3.3.3.5 National Environmental Management: Waste Act (Act 59 of 2008)

The act points out the status and risk of contaminated sites and provides a legal mechanism for remediation activities to be instigated and controlled but lacked decision-support measures to remediation.

3.3.3.6 Framework for the Management of Contaminated Land (2010)

The Framework for Managing Contaminated Land was to compliment the 2008 National Environmental Management: Waste Act (Act 59 of 2008) to manage and remediate contaminated lands using compiled international standard methods and stipulated guideline values for site assessment. The framework also addressed setbacks in the previous legislature by outlining concise steps to be followed using the source-pathway-receptor model (Narayan et al., 2012)

i. Protocol for Site Risk Assessment

   This protocol seeks to establish as a first step that preliminary research has been done and results shows that there is a potential risk. Figure 3.1 summarizes the protocols used for site risk assessment based on accepted Soil Screening Values (SSV 1 and SSV 2)

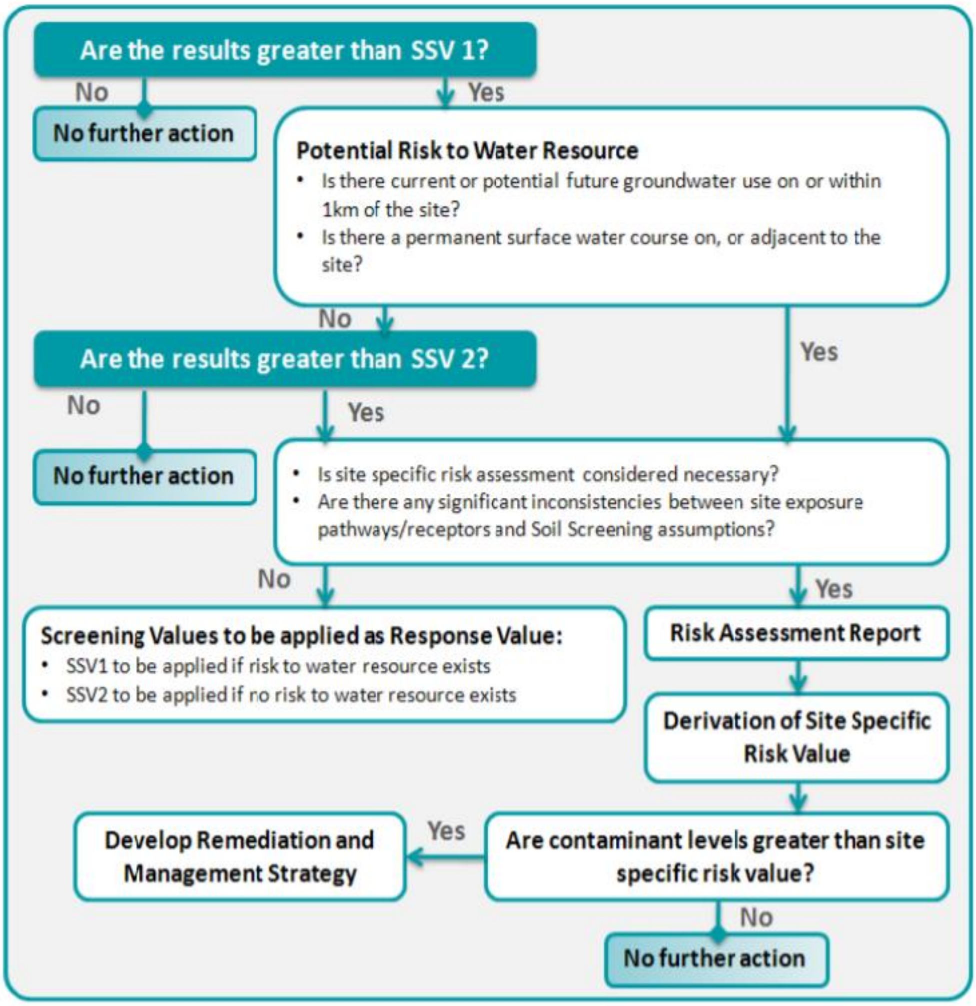


Figure 3.1 Protocols used for site risk assessment based on source-pathway-receptor model (Source: DEA, 2010)

ii. Reporting Norms and Standards for Contaminated Land

The aim is to investigate whether the land has been contaminated, and if contamination has occurred whether the contamination presents a significant risk of harm using a site assessment report that comply with any directions that may have been published or given and summarized in Figure 3.2.

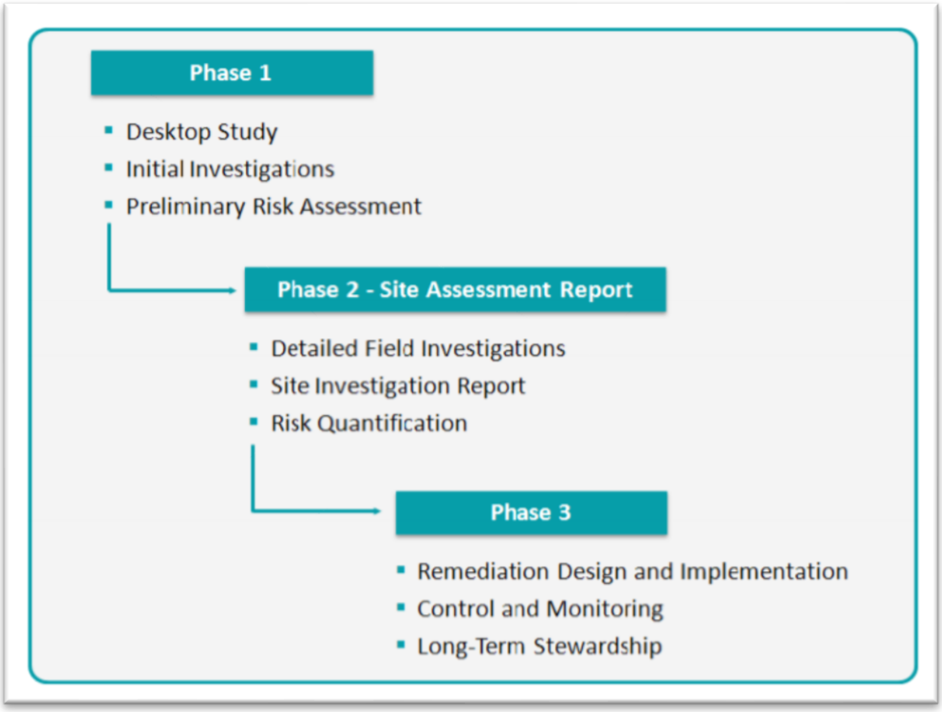


Figure 3.2 Procedures for Reporting Norms and Standards for Contaminated Land (Source: DEA, 2010)

iii. The Derivation and Use of Soil Screening Values

The framework puts together a set of target values derived from U.S. Environmental Protection Agency (USEPA) and Canadian Environmental Quality Guidelines (CEQGs) for selected pollutants, which are deemed as 'priority contaminants'. The values serve as initial points of reference for site assessment for authorisation of remediation activities and can be applied with discretion.

iv. Application of Site Specific Risk Assessment

The South African environmental law incorporates international best practices in the form of risk assessments that are aimed at making up for preliminary assessments. The legislature requires polluters with intention to remediate to do a thorough site-specific quantitative risk assessment to determine the state of pollutants and remediation options to be considered if there is a need for remediation at all. The law therefor provides guidelines for site specific risk assessment

v. Quality Control and Quality Assurance of Field Sampling and Laboratory Analysis. There is a section of the framework that highlight measures to maintain the integrity of field samples by applying simple and consistent routines that allow discrepancies in data to be traced and assessed, with the aim of attaining the minimum level of quality assurance (QA) / quality control (QC) expected for the undertaking of site investigations in South Africa (DEA, 2010, pp. 42 - 47).

3.3.3.7 National Waste Management Strategy (2011)

In 2011, a national waste management strategy was enacted to advocate a systematic and hierarchical approach in waste management, covering aspects of waste avoidance, reduction, re-use, recycling, recovery and safe disposal as a last resort (DEA, 2011). This document according to the DEA was passed to ‘achieve the objects of the 2008 National Environmental Management: Waste Act (Act 59 of 2008)’.

3.3.3.8 National Norms and Standards for the Remediation of Contaminated Land and Soil Quality (2013)

This document added on to the Framework for the Management of Contaminated Land (2010) by providing uniform methodologies, minimum standards to be targeted for contaminants and outline clear-cut criteria for remediation (Ngole-Jeme & Fantke, 2017). The document also built on the Section 8 of the 2008 National Environmental Management: Waste Act (Act 59 of 2008).

3.3.4 Framework for remediation in South Africa

Prior to the National Environmental Management: Waste Act (Act 59 of 2008), remediation was a voluntary activity on the part of the polluter or directives from the Department of Water Affairs (DWA) that could compel a polluter to clean up. The current National Norms and Standards read with previous legislation makes provisions for identifying and demarcating areas of interest for investigation by the polluter. Unlike the 2008 Waste Act, the 2013 National Norms and Standards gives the ministry the power to instigate investigations into suspected contaminated sites. In both cases, the polluter or the landowner will be liable for the cost involved in assessment and remediation. There is also a development of contaminated land register to help trace and document pollution history.

3.3.5 Research on remediation & performance of available commercial technologies

The concept of environmental remediation in Africa and developing countries at large has not been common due to lack of technical know-how, availability of the technology and logistics to execute, gaps in environmental law and poverty (Omanga, Ulmer, Berhane, & Gatari, 2014). Apart from the metal industry, there are abandoned gold mine tailings in South Africa that has also kindled the interest of scholars on remediation, with much emphasis on AMD (Ngole-Jeme & Fantke, 2017).

There has been remarkable progress on nitrate studies in the country, in terms of remediation. Nitrate contamination is one of the problems facing rural bore-hole water consumers in most parts South Africa, especially in Northern Cape and Limpopo (Schoeman & Steyn, 2003; Maherry, Tredoux, & Clarke, 2010). The causes of the high nitrate levels in underground in South Africa may be attributed to different factors with high concentrations been found in communities with open-pit mine sites (Bosman, 2009). Pilot studies into nitrate removal from water in South Africa have used eukaryotes in a reactor under aerated and un-aerated conditions (Angenent, de los Reyes, Oerther, & Mcmahon, 2005; Jahan et al., 2011). Nitrate removal in anaerobic bioreactors have shown up to 90% efficiency using fungal consortium (Greben, Joubert, Tjatji, Whites, & Botha, 2007). In another research involving protozoa, the nitrate levels were reduced from 19.31 mg/L to 0.10 mg/L (Akpor & Momba, 2010). These findings and other research in the academic circles prove the potential of some eukaryotes in remedying nitrate pollution. There is a common problem with remediation involving reactors, which is the effluent accumulated in the reactor needs a special attention, which if not handled properly, can find its way back into the environment. There are other conventional commercial nitrate treatment methods in South Africa with some accumulating high operational cost, there is currently no commercial *in-situ* nitrate removal technology tackling the worrying situation (Schoeman & Steyn, 2003).

CHAPTER 4: RESEARCH DESIGN AND METHODOLOGY

4.1 Introduction

This chapter describes the research design used in sampling and analysing data, the standard procedures that were followed to achieve reliable and valid data and the ethical issues concerning the whole research project. Propositions on the research questions were made and the limitations of the study are stated. Research methodology is a way to solve a research problem through a well-defined plan and strict procedures (Janjaroen et al., 2013). It is therefore essential to develop a research methodology according to the needs and expected output of a research.

4.2 Research design

The research design adopted was quantitative, using traditional scientific methods to generate data pertaining to natural phenomena (Borrego, Douglas, & Amelink, 2009). Quantitative research design was chosen as it was in alignment with the aim of determining the relationship between an independent variable and a dependent or an outcome variable to answer a research question (Brannen, 2005). According to Hopkins (2000) and Christensen, Johnson, & Turner (2011), quantitative research designs can be either descriptive or experimental. This was a descriptive study as it only sought to establish associations between variables. The observation of phenomena was undertaken in a strictly controlled setting in which one or more factors are varied and the others (samples) kept constant (Christensen et al., 2014). A controlled laboratory analysis of the samples collected was used to give a summary of the status of the study site. Extraneous variables were eliminated by taking only samples from carefully selected locations and following standard operating procedures.

The study made use of purposive sampling (Christensen et al., 2014). Purposive sampling, as sometimes referred to as judgmental sampling is a type of sampling based on a researcher’s judgement to target specific areas (Tongco, 2007). One of the unique characteristics of purposive sampling according to Teddlie & Yu (2007) is that, the technique aims at achieving representativeness and comparability. The targeted areas were those located close to the point source of pollution and close to where people were living or interacting with the environment. Results obtained from the sampling points close to the pollution source presented the highest contaminants, since pollutants concentration decrease away from their source (Kjellstrom et al., 2006). Thus, results were obtained at the highest possible concentrations outside of the actual industrial site. The entire Steel Valley was not sampled, for two reasons. Firstly, the whole area is not uniformly inhabited, as much of the area is under agriculture (maize in particular) and secondly the scope of the study would have become too large and costly for that of a master's thesis.

4.3 Ethics and ethical issues

The purpose of environmental research is to generate information that can be used to benefit the environment and protect it, either directly or indirectly. A very important aspect of ethical environmental research involves the prevention chemicals or non-environmental friendly waste to be released back into the environment. This was ensured by washing acids and soluble inorganic salts down the drain with excess water. Waste of reagents containing arsenic, cadmium, chromium, copper, mercury, thallium, cyanides and hydrocarbons were placed in designated containers as instructed by the technicians in charge of the laboratory. Further action was then taken by the laboratory managers to ensure safe disposal. Another aspect of ethical research is research undertaken in a manner that will uphold the integrity of the researcher and affiliated institutions. In this respect, the research was conducted with ethics clearance from UNISA (Ref: 2015/CAES/110) and all necessary considerations to ethical principles were adhered to. In particular, the seven pillars of ethics (Emanuel, Wendler, & Grady, 2015), namely; value, validity, objectiveness, favourable risk-benefit ratio, respect for enrolled subjects, informed consent and taking cognisance of the researcher's subjectiveness were all adhered to. The study followed the accepted procedures of UNISA's Code of Ethics.

The methodologies and operation procedures were standard, thoroughly assessed and carefully chosen to make the research scientifically valid. There was objectiveness and fair sampling throughout the data sourcing. There have been carefully laid out plan in the ethical clearance submitted and approved to ensure that UNISA, the study area, and all other institutions or people involved in this research are at no risk. The researcher also ensured that approval for the collection of samples was granted by the residents of the property.

4.4 Research questions and the consistency matrix

Research question 1: What are the concentrations of inorganic contaminants and organic contaminants in Steel Valley's water bodies?

The proposition of high or low metal contaminant levels in the water samples were achieved through Inductively Coupled Plasma Optical Spectroscopy (ICP-OES) analysis, which gave the exact concentration of Fe, Cu, Tl, Cd, Cr, As, Hg, Al, Mn. The colorimetric method was used for the speciation of Cr^{+6} (Vitale, Mussoline, & Rinehimer, 1997). Concentrations of SO_4 were determined by turbidimetric methods (Chesnin & Yien, 1951; Krug, Filho, Zagatto, & Jørgensen, 1977), NO_3 concentrations were determined using an automated hydrazine reduction method (Kamphake, Hannah, & Cohen, 1967). The concentrations of hydrocarbons and BTEX were quantified using a gas chromatography method and standard procedures adopted by Massachusetts Department of Environmental Protection and the USEPA (Seeley, Bandurski, Brown, McCurry, & Seeley, 2007). Phenols were also quantified using a direct photometric method from the USEPA.

Research question 2: What are the major, minor and trace elements in the soil samples, and their exact concentrations?

The inherent heterogeneity nature of soil and their composition of a wide range of contaminants and important minerals makes them complex to analyse (Voica, Dehelean, Iordache, & Geana, 2012). Using ICP-OES accounted for the variable and different mineral composition to display the quantity of the various elements that were targeted.

Research question 3: What impact has the remediation had on the soil and groundwater in Steel Valley?

Environmental remediation serves to eliminate the source and potential sources of contaminations and restore sites or polluted areas to safety (Wuana & Okieimen, 2011). Evaluation of the impact of any remediation technique will therefore depend on the constant reduction in concentration of pollutants over a proposed period. The study compared the findings of previous studies of the area to the current contaminants profile to arrive at the impact that remediation has had on Steel Valley. The data obtained from the soil analysis were also compared to the values stated in the National Norms and Standards for Remediation (see 2013 National Norms and Standards for the Remediation of Contaminated Land and Soil Quality) to ascertain whether the results are within targeted remediation values.

Research question 4: Does the current chemical profile of the soil and groundwater pose any threat to end users?

Assessment of the adequacy of chemical quality of drinking water relies on comparison of the results from water quality analysis with guideline values (Haloi & Sarma, 2011). A guideline value represents the concentration of a constituent that does not exceed tolerable risk to the health of the consumer over a lifetime of consumption (WHO, 2011). The water and soil analysis served to establish the portability and suitability of water bodies and soil use to the few end users left in Steel Valley and also people who will want to resettle in the area, through experimental data compared to data set of standards. The data obtained from the water analysis were compared to standard acceptable values from South Africa’s Department of Water and Sanitation’s water quality guidelines and that of the WHO to answer whether the data obtained are within limits to pose no threat to end users, or not (Gorchev & Ozolins, 2011).

4.5 Data collection

The essence of sampling is to select data from a group or population to make a generalization of the whole population (Marshall, 1996). It is therefore important to lay out a rigorous data collection plan for valid and reliable research.

4.5.1 Materials and equipment used

A portable multiparameter meter (Hanna Instruments HI 9828 meter with pH/EC/DO Probe/Kit) and glass thermometer were used to take the temperature of the various water samples on site immediately after sampling. The meter was also used to record pH and EC of the soil and water samples in the laboratory at 25 ^{o}C. Other materials and instruments used were a 15.24 cm stainless steel soil auger with handle, glassware, and logbook, trowel, measuring tape, trash bag, permanent marker and laboratory-cleaned sample containers. A clean stainless-steel rod was attached to sampling containers to fetch water samples. Ice cooler box with ice and distilled water were also used. Personal protective equipment such as boots, and disposable nitrile gloves were used for protection and also to prevent cross-contamination of samples.

4.5.2 Sampling points

W1, W2 and W3 indicated on the map in Figure 4.1 were the water sampling points. W1 and W2 were ground water samples, while W3 was from surface water (a groundwater-recharged dam). Point W1 is an old well pipe and W2 is an active well dug on the site.

The coordinates of the sampling points for water samples are shown on the map (Figure 4.1) and listed below:

W1: 26°38'23.52"S and 27°48'2.04"E
W2: 26°37'39.24"S and 27°47'47.73"E
W3: 26°39'36.54"S and 27°47'36.74"E

Figure 4.1 Map of the study site showing the sample points and ArcelorMittal SA, Vanderbijlpark (circled) (Source: Google Earth, December 29, 2015)

Soil samples were taken from point S1, S2, S3, S4, S5 and S6 as indicated on the map in Figure 4.1. Soil samples were all taken from a depth of 15.24 cm using an auger after the surface debris of the soil had been removed.

The coordinates of the sampling points for soil are shown on Figure 4.1 and listed below:

S1: 26°38'6.95"S and 27°48'7.03"E
S2: 26°37'53.28"S and 27°47'34.02"E
S3: 26°39'6.65"S and 27°47'37.51"E
S4: 26°39'25.22"S and 27°47'40.81"E
S5: 26°39'34.48"S and 27°47'24.74"E
S6: 26°39'48.30"S and 27°47'37.71"E

4.5.3 Sample regime and collection

Soil and water samples were collected from nine (9) different points, six (6) for soil, two (2) for ground water and one (1) for sampling surface water at various coordinates in Steel Valley, during two separate seasons:

1) Dry season, Winter (June 2016)
2) Rainy season, Spring (October 2016)

Personal observations were made on the sampling site concerning the state and the use of water and soil in the area. The study area currently houses less than ten (10) smallholdings. Most of the land is been used to cultivate maize. Prior to sampling, weather conditions were monitored and logged on a daily basis. Data received from the Accuweather station in Vanderbijlpark in June 2016 reveals that, the study site received a total of 4 mm rainfall with temperatures ranging from 2 °C to 19 °C for that month. The rainfall received in the area during the rainy season was 78mm with temperatures ranging from 11 °C to 29 °C in October 2016.

Table 4.1 shows the recorded temperatures and rainfall at the study site prior to sampling. The highest amount of rainfall was recorded in May, while there was no rainfall at all in August. The temperature reached its peak in October (29 °C, while May recorded as low as 0 °C.

Table 4.1 Climatic conditions of Vanderbijlpark before sampling (Source: Accuweather, 2016)

2016	**May**	**June**	**July**	**August**	**September**	**October**
Highest Temperature (°C)	21	19	9	23	26	29
Lowest Temperature (°C)	5	2	0	2	9	11
Average Temperature (°C)	13	11	9	12	17	20
Precipitation (mm)	96	4	31	0	12	78

4.5.3.1 Sampling of water

The three (3) points were selected based on purposive sampling, such that, they are relatively close to the point source of pollution. W2 was chosen as it is relatively far from the point source of pollution and close to a settlement, to record concentrations of pollutants that have travelled a relative distance across the study area. Collection of water samples was done using a discrete grab method, which does not account for variation in spatial environment or time (Byers, Lindgren, Noling, & Peters, 2010). The water grab sampling did not require any automated sampling device, but rather the hand and/or rod and a clean container, which was used to fetch the sample directly from the sampling points. The samples from each point and triplicate samples were collected in 1 litre pre-washed (in dilute nitric acid - HNO_3 and then rinsed in deionized water) sterile glass Schott bottles and were labelled accordingly using the code names in Tables 4.2 and 4.3.

Table 4.2 Labels for water sampled during the dry season

Dry Season (Winter) Water Sampling		
From W1 (WW1)	From W2 (WW2)	From W3 (WW3)
Triplicate samples a, b and c (WW1a, WW1b, WW1c)	Triplicate samples a, b and c (WW2a, WW2b, WW2c)	Triplicate samples a, b and c (WW3a, WW3b, WW3c)
A 1 litre sample container was used each for physical parameters, organic parameters and inorganic parameters	A 1 litre sample container was used each for physical parameters, organic parameters and inorganic parameters	A 1 litre sample container was used each for physical parameters, organic parameters and inorganic parameters

Table 4.3 Labels for water samples in the rainy season

Rainy Season (Spring) Water Sampling		
From W1 (SW1)	From W2 (SW2)	From w3 (SW3)
Triplicate samples a, b and c (SW1a, SW1b, SW1c)	Triplicate samples a, b and c (SW2a, SW2b, SW2c)	Triplicate samples a, b and c (SW3a, SW3b, SW3c)
A 1 litre sample container was used each for physical parameters, organic parameters and inorganic parameters	A 1 litre sample container was used each for physical parameters, organic parameters and inorganic parameters	A 1 litre sample container was used each for physical parameters, organic parameters and inorganic parameters

Samples that were analysed for metal contaminants were acidified with nitric acid in order to stabilize the metal ions and prevent bacteria activity. Samples for phenol concentrations were also acidified with concentrated sulfuric acid (H_2SO_4). The samples were stored at 4 °C during transportation to the laboratory at University of Johannesburg and Aquatico Scientific (Pty) Ltd. To maintain optimum temperatures, the samples were transported in ice coolers with dry ice so as to minimize loss of concentrations. Samples that were analysed the next day were properly stored in a refrigerator.

4.5.3.2 Sampling of soil

A hand auger sampler was used to collect grab samples of soil (Byrnes, 2008). A depth of 15.24 cm was reached using an auger and soil samples from six different points were sampled during the dry season and rainy season separately. The exact sampling points were cleared of loose debris, weeds, and foreign materials. A total of 5.08 cm of the outer soil was scooped aside before the actual sampling was done.

The handle of the auger was fitted into the 15.24 cm decontaminated stainless-steel auger and placed in an upright position into the soil. The handle was turned until soil filled up the whole capacity of the device. It was pulled gently, and the soil lowered into a clean plastic container. Wearing gloves and using the trowel, the soil was evenly and gently mixed and the 1 Litre sterile sample containers filled and labelled appropriately. Samples for analysis in the laboratory were logged, recorded (as shown in Appendix 1) and transported to the laboratory at University of Johannesburg and Aquatico Scientific (Pty) Ltd.

4.6 Data analysis

The samples were analysed in the laboratory and the data obtained was subject to statistical analysis. Physical, chemical and organic parameters were tested in water samples using various techniques on-site and in the laboratory. Each sample was analysed thrice, and the average recorded. Chemical determinations and analytical procedures were based on the American Standard Methods for Examination of Water and Wastewater (Rice, Baird, Eaton, & Clesceri, 2012), laboratory Methods from the USEPA, Soil & Plant Analysis Laboratory of the University of Wisconsin – Madison, and the Massachusetts Department of Environmental Protection’s standard operating procedures.

Listed below and in subsequent sub chapters is a summary of the parameters and the methods that were chosen for the various analyses:

4.6.1. Water samples

Over the years many institutions and national agencies have established laboratory standard operating procedures (SOP) to follow in laboratory analysis (Rice et al., 2012; University of Wisconsin – Madison, 2005). Carefully selected SOPs were chosen to analyse water samples at the study area and in the laboratory.

4.6.1.1. EC & TDS

A Hanna Instruments 9828 multimeter was used to measure the ability of the samples to conduct an electrical current, a physical property that is used as an indicator of water purity (Jones, 2002). Before analysis, the cell constant was calibrated using the HI9828-25 quick calibration standard solution and the probe rinsed with deionized water. At temperature of 25^{o}C, 50 mL of water sample was placed in a beaker, the probe was then inserted into the sample such that the temperature sensor was fully submerged and at the same time, making sure there were no bubbles in the probe. The read button on the probe was pushed and readings were taken after the measurement had stabilized. The probe was then rinsed with deionized water and the procedure repeated for all other samples.

TDS was calculated from conductivity values using;

$$\text{TDS (ppm)} = 6.40 \times \text{EC (in mS/m)}$$

4.6.1.2. Temperature

The clean and dry multimeter (Hanna Instruments 9828) was rinsed with sample water from W3 and then immersed into the water at source (at W3) to take readings after equilibration whereas a glass thermometer was used for water sample sites 1 and 2. The glass thermometer was immersed into the water at its source, after it had been rinsed with water from the same point. The temperature readings were recorded after equilibration.

4.6.1.3. pH

pH was measured at room temperature using a pH meter (Hanna Instruments 9828). The pH meter was initially calibrated by introducing the electrode into a pH buffer solution and the value adjusted to 4.00. The electrode was again placed in the pH 10 buffer solution and the value was adjusted to 10.00. 50 mL of the sample to be analysed was placed in a 250-mL beaker and the electrode dipped into the sample. The value on the meter was measured as the pH after readings had stabilized. The pH meter was cleaned, and the steps repeated for all other samples.

4.6.1.4. Alkalinity, Bicarbonates and Carbonates

Alkalinity, an index of the capacity of water to neutralize acidity is also a function of the concentrations of carbonates and bicarbonates (Boyd, Tucker, & Somridhivej, 2016). The standard operating procedures (SOP) used describes a titration procedure for alkalinity and subsequent calculation for carbonates and bicarbonates from alkalinity and pH values.

The following reagents and standards were used:

- Distilled water
- 11N Sulfuric acid: 310 mL of concentrated H_2SO_4 was transferred into a 1 L volumetric flask. Distilled water was added to fill the 1 L mark.
- 10% Sodium thiosulfate: 25 g of sodium thiosulfate was dissolved and diluted in a 1000 mL volumetric flask up to the mark.
- Sulfuric acid titrant (0.02N): 1.8 mL of the 11N H_2SO_4 was transferred into a 1 L volumetric flask and filled with distilled water to the mark.
- 0.02N Na_2CO_3: 1.0599 g of dried sodium carbonate (Na_2CO_3) was dissolved with distilled water and filled to the mark in a 1 L volumetric flask
- Methyl orange & phenolphthalein
- Sodium carbonate

A drying oven; burette (25 mL); pipette (20 mL); pH meter (Hanna Instruments 9828); glass beakers (50 mL, 100 mL, 150 mL); stop watch; Erlenmeyer flask; potassium iodide strip; graduated cylinder; magnetic stirrer; analytical balance and water bottles are among the equipment/apparatus that were used.

The test was conducted by manually and slowly titrating samples of water from Steel Valley against sulfuric acid to an indicator end-point and a specific pH. The average titre value was used to calculate total alkalinity. The alkalinity value obtained, together with the pH value was used to calculate the bicarbonate value. Carbonates were then calculated from the bicarbonate and pH values. A method blank was analysed before the sample analysis, analytical balance was checked for proper readings and the pH meter was calibrated before it was used as part of quality control measures. The pH probe was first cleaned with distilled water. 50 mL of 7.0 buffer was placed in a beaker and stirred. The probe was then inserted, and the calibration button pressed. After the reading had stabilized, the pH was recorded. The procedure was repeated for 4.0 buffer and 10.0 buffer. The probe then generated a slope which was within 95 – 105%. The pH of the sample to be analysed was recorded using a pH (Hanna Instruments 9828). Few drops of phenolphthalein indicator were added to 50 mL of water sample in an Erlenmeyer flask. The sample was titrated with standardized 0.02N H_2SO_4 until the colour disappeared and the burette volume recorded. Few drops of methyl orange indicator were added to the conical flask and the sample was titrated with standardized 0.02N H_2SO_4 until the colour changed. The final burette volume was then recorded. This was done in triplicate and repeated for the triplicate samples and all other samples.

Calculations:

- Alkalinity, mg $CaCO_3$ /L $= \frac{\mathrm{A} \times \mathrm{T} \times 50000}{\mathrm{mL\ of\ Sample}}$

    Where;

    T = Normality of titrant

    A = mL standard acid used

- Percent Relative Percent Difference (%RPD)

    $\%RPD = \frac{(V1-V2)}{(V1+V2)/2}$

    Where;

    V_1 = Observed value of sample

    V_2 = Observed value of duplicate sample

- Bicarbonate alkalinity, HCO_3^-

    HCO_3^- as mg $CaCO_3$/L $= \frac{T-5.0 \ X \ 10^{pH-10}}{1+ 0.94 \ X \ 10^{pH-10}}$

    Where;

    T = Total Alkalinity, mg $CaCO_3$/L

    pH = Recorded pH from alkalinity titration

- Carbonate alkalinity, CO_3^{2-}

    CO_3^{2-} as mg $CaCO_3$/L = $B \times 0.94 \times 10^{pH-10}$

    Where;

    B = Bicarbonate alkalinity, mg $CaCO_3$/L

    pH = Recorded pH from alkalinity titration

In terms of data validation, a log book was used to document all measurements and activities to make data retrievable and traceable. All control blanks and standards run were within control limits and calculations were rechecked for errors.

4.6.1.5. Inorganics (Fe, Cr^{+6}, Cu, Tl, Cd, Cr^{+3}, As, Hg, SO_4, NO_3, Al, Mn)

The analysis of inorganics in water samples was done using ICP-EOS. The method used includes calibration and quality control criteria defined by manufacturer and combined with SOPs from USEPA. The method measures element emitted light by optical spectrometry. Samples and standards are nebulized, and the resulting aerosol is transported to a plasma torch. Element - specific atomic - line emission spectra are produced by a radio frequency (RF) generated inductively coupled plasma. The plasma is then mounted radially, and the spectra are dispersed by a gratking spectrometer while photomultiplier tubes monitor the intensities of the lines. The intensities are calibrated using known concentrations and are used to quantify sample results. The analysis by ICP-OES followed the USEPA Method 6010b (US EPA, 2007).

Equipment/Apparatus

- An ICP Spectrometer connected to a computer system with a printer and an auto sampler.
- Microwave digestion system
- Electronic variable volume autopipettors
- Varying volumes class A volumetric flasks
- Digestion vessels
- Watch glasses
- Glass dispensers, 2 L and 1 L,
- 50 mL Class A graduated cylinder
- Analytical balance
- Plastic syringes
- 0.45 micron filters

Reagents

- Deionized water
- Concentrated nitric acid (trace metal grade)
- Nitric acid, 10% volume to volume (v/v)
- Concentrated hydrochloric acid, (trace metal grade)
- Hydrogen peroxide, 30%, reagent grade
- Argon plasma support gas
- Stock calibration standards
- Intermediate calibration standard, 100 mg/L – Prepared by diluting 10 mL of the 1000 mg/L stock calibration standards to 100 mL in a class A volumetric flask using 10% nitric acid.
- Working calibration standard
- Water reporting limit standard – Prepared by diluting 0.5 mL of the Water RL spiking solution to 500 mL in a class A volumetric flask using 10% nitric acid.
- Stock Initial Calibration Verification/Continuing Calibration Verification Standard (ICV/CCV).
- Working ICV/CCV containing all analytes at 2 mg/L except Al, Ca, Fe, Mg, K, Na at 20 mg/L – Was prepared by adding 10 mL of the stock 100 mg/L ICV/CCV and 1.8 mL of the stock 5 000 mg/L ICV/CCV to 500 mL using 10% nitric acid in a class A volumetric flask.
- Working ENDCCV containing all analytes at 2.5 mg/L except Al, Ca, Fe, Mg, K, Na at 12.5 mg/L – Was prepared by adding 12.5 mL of the stock 100 mg/L ICV/CCV and 1 mL of the stock 5 000 mg/L ICV/CCV to 500 mL using 10% nitric acid in a Class A volumetric flask.
- Matrix spike/spike duplication (MS/MSD) Solution
- Laboratory Control Sample (LCS)
- Stock Interference Check Standard (ICS)
- Working ICSA – Prepared by adding 20 mL of the stock INT-A1 standard to 200 ml using 10% nitric acid in a class A volumetric flask
- Working ICSAB – Prepared by adding 20 mL of the stock INT-A1 standard and 2 mL of the stock INT-B3 standard to 200 mL using 10% nitric acid in a class A volumetric flask

- Internal standard solution – Prepared by adding 5 mL of stock 1 000 mg/L yttrium (Y) and 9.93 g of stock Lithium Nitrate ($LiNO_3$) to 1 000 mL using 10% nitric acid in a 1-liter polyethylene bottle.

Procedure

Determination of pollutants using ICP-OES undergoes two procedures, the sample digestion and the main analysis on the ICP.

Sample Digestion

Each sample was mixed well and checked to ensure the pH was less than 2.45 mL each of DI, LCS and each sample to be analysed was measured with a 50-mL graduated cylinder and transferred into a digestion vessel with each marked and labelled accordingly. Two separate well-mixed 45-mL portions of each sample were transferred to separate digestion vessels and 0.5 mL of the MS and MSD spiking solution was added to each and mark the digestion vessels as the MS and MSD. 5 mL of concentrated HNO_3 was added to each vessel, made sure the pressure relief disks were in the caps and the caps tightened on the vessels. The vessels were evenly distributed in the microwave carousel according to the manufacturer's instructions and the samples subjected to 160 ± 4 ^{o}C for 10 minutes. The temperature was adjusted steadily to between 165 and 170 ^{o}C for another 10 minutes. The digestion vessels were allowed to cool and weighed to check if the weight of the digestate had not decreased by more than 10% of the original weigh. Each vessel was uncapped in a fume hood and the samples transferred to an acid-cleaned sample bottle.

Analysis using the ICP

After igniting the plasma, the instrument was allowed to thermally stabilize for an hour before calibration. After the plasma had stabilized, the instrument profile for Cu was verified and the spectrometer calibrated using the blank and the working calibration standard. The ICV standard was analysed with a recovery within ±10%. The ICB was analysed immediately and made sure its concentration was less than the reporting limit for each element to be analysed for. The RL, ICSA, ICSAB, CCV, and CCB standards were all analysed in that order. The method blank, LCS, and samples were then run, and the values recorded from the read-out device.

Speciation of Cr^{+6}

Dissolved hexavalent chromium may be determined colorimetrically by reaction with diphenylcarbazide in acid solution to produce a red violet colour of unknown composition. The absorbancy index per gram atom of Cr^{+6} being 40 000 at 540 nm makes it possible to measure the exact concentration of Cr^{+6} photometrically at 540 nm.

Reagents

- Reagent water
- Potassium dichromate stock solution – Prepared by dissolving 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and diluted to 1 litre (1 mL = 50 µg Cr).
- Potassium dichromate standard solution – Prepared by diluting 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 µg Cr).
- Sulfuric acid, 10% (v/v) – Prepared by diluting 10 mL of distilled reagent grade H_2SO_4, to 100 mL with reagent water.
- Diphenylcarbazide solution – Prepared by dissolving 250 mg 1,5-diphenylcarbazide in 50 mL acetone
- Acetone (analytical reagent grade)

Procedure

Some 95 mL of the sample was transferred into a 100-mL volumetric flask with 2.0 mL diphenyl carbazide solution added. Few drops of H_2SO_4 were added to give a pH of 2. The sample prepared was diluted to 100 mL with reagent water and allowed to stand 5 to 10 min for full colour development. A portion of the solution was transferred to a 1-cm absorption cell and measured at an absorbance of 540 nm using reagent water as a reference. To compensate for possible slight losses of chromium during digestion or other operations of the analysis, the chromium standards were treated by the same procedure as the sample.

4.6.1.6. Organics (BTEX, Hydrocarbons, Phenols)

The analysis of Organic compounds was done using gas chromatography/mass spectrometry (GC/MS) for BTEX and direct photometric method for phenols. The hydrocarbons were quantified by a solvent extraction, silica gel solid-phase extraction (SPE) /fractionation process, and GC analysis using a flame ionization detector (FID).

4.6.1.7. BTEX

Analysis for the levels of BTEX in the water samples followed USEPA's method 8260B (USEPA, 1996). The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method. The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with an MS interfaced to the gas GC. Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection (wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

<u>Apparatus/Materials</u>

- Purge-and-trap device
- Azeotropic distillation apparatus
- Vacuum distillation apparatus
- Injection port liners - Modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven. A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications
- Gas chromatography/mass spectrometer/data system
- Microsyringes
- Syringe valve
- Syringes
- Analytical balance
- Glass scintillation vials - 20-mL, with PTFE-lined screw-caps

Reagents

- Organic-free reagent water
- Hydrochloric acid (1:1 v/v)
- Certified stock solutions
- Secondary dilution standards
- Surrogate standards
- Internal standards
- 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol was prepared
- Premixed certified calibration standards - initial calibration standards and calibration verification standards.
- Matrix spiking and laboratory control sample (LCS) standards

Procedure

Prior to the analysis, the GC/MS operating conditions were established, and the system was tuned to meet the criteria identified by the manufacturer's manual. The sample introduction system was set up as instructed in the manual. Analysis of the calibration standards were done by injecting 2 µL of the standard into the GC/MS system. A system performance check, evaluation of retention times and calibration verification carried out in that order.

Sample screening was done to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds using an automated headspace-GC/FID. BFB tuning criteria and GC/MS calibration verification criteria were all met before the samples were analysed. The samples and standard solutions were allowed to warm to ambient temperature on the bench. The aqueous samples were composited. 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution were intermixed using the autosampler. 10 µL of the matrix spike solution was added to a 5-mL aliquot of the sample chosen for spiking. The various samples were analysed by injecting 2 µL into the GC/MS system and the readings. The resulting concentrations of the samples of interest were recorded.

4.6.1.8. Hydrocarbons

The analysis of hydrocarbons in the study was based on Massachusetts Department of Environmental Protection method for the determination of extractable petroleum hydrocarbons

(Herzfelder & Golledge, 2004; Seeley et al., 2007). This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil/sediment matrices. Extractable aliphatic hydrocarbons are collectively quantitated within two ranges: C_9 through C_{18} and C_{19} through C_{36}. Extractable aromatic hydrocarbons are collectively quantitated within the C_{11} through C_{22} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 265 °C.

The scope of the method is such that, a sample is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish apparatus. Sample clean-up and separation into aliphatic and aromatic fractions was accomplished using commercially available silica gel cartridges or prepared silica gel columns. The two individual fraction extracts produced are re-concentrated to a final volume of 1 mL (i.e., an aliphatic extract and an aromatic extract). The concentrated extracts are then separately analysed by a capillary column gas chromatograph equipped with a flame ionization detector. The resultant chromatogram of aliphatic compounds collectively integrates within the C_9 through C_{18} and C_{19} through C_{36} ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C_{11} through C_{22} range and is (optionally) used to identify and quantitate individual concentrations of Target PAH Analytes. Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture is used to calculate the collective concentrations of C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbons. An average calibration factor or response factor determined using a PAH standard mixture is used to calculate a collective C_{11} through C_{22} aromatic hydrocarbon concentration. Calibration factors or response factors determined for individual components of the PAH standard mixture are also used to calculate individual concentrations of Target PAH Analytes. This method is suitable for the analysis of waters, soils, sediments, wastes, sludges, and NAPL.

Apparatus/Materials

- Assorted glassware
- An analytical balance capable of accurately weighing 0.0001 g
- A gas Chromatographic System equipped with FID, an RTX-5 capillary column (30-m x 0.32-mm i.d., 0.25-µm film thickness, a data station and an autosampler
- Water bath

- Disposable pipets
- Microsyringes
- Boiling Chips
- An extractor
- Separatory Funnel
- Drying oven
- Desiccator

Reagents/Standards

- Reagent Water: organic free water
- Solvents: hexane, methylene chloride, and acetone
- Sodium sulfate: (ACS) granular, anhydrous. Purified by heating at 400 °C for 4 hours in a shallow tray
- Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.
- Silica Gel (10 grams) activated at 130 ºC for at least 16 hours, and heated to 150 – 160 ºC for several hours before use
- Stock standard solutions
- Petroleum reference spiking solution
- Surrogate standards
- Fractionation surrogate standards
- Internal standards (ISs)
- Matrix spiking solution
- Fractionation check solution

Procedure

The samples were extracted using methylene chloride and solvent-exchanged into hexane by using manual separatory funnel liquid-liquid extraction for aqueous samples. Silica Gel clean-ups and fractionation were then performed. Final sample extract concentration was obtained by transferring the contents of the 25.0 mL “aliphatics” (in hexane) and “aromatics” (in methylene chloride) volumetric flasks into separate labelled graduated concentrator tubes. Each of the tubes was concentrated to a final volume of 1 mL under a gentle stream of nitrogen. The final 1 mL extracts from each concentrator tube was transferred to labelled 2-mL glass autosampler vials with Teflon-lined rubber crimp caps and an internal standard added. The analysis was done in a group referred to as an analytical batch. The analytical sequence begun with instrument calibration (initial or continuing) followed by 20 samples interspersed with blanks and other QC samples and closed with a mid-range continuing calibration standard. Aliphatic and aromatic extracts were introduced into the gas chromatograph by direct injection. The sample extracts were injected using the solvent flush technique in volumes consistent with that of the sample and calibration standard.

4.6.1.8. Phenols

Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown antipyrine dye. The amount of colour produced is a function of the concentration of phenolic material.

Apparatus/Materials

- Distillation apparatus: All glass, consisting of a 1-liter Pyrex distilling apparatus with Graham condenser
- pH meter
- Spectrophotometer: For use at 460 or 510 nm
- Funnels
- Filter paper
- Membrane filters
- Separatory funnels: 500- or 1 000-mL
- Nessler tubes: Short or long form

Reagents

- ASTM Type II water
- Concentrated sulfuric acid solution
- Buffer solution – Prepared by dissolving 16.9 g NH_4Cl in 143 mL concentrated NH_4OH and diluted to 250 mL with Type II water. 2 mL of buffer should adjust 100 mL of distillate to pH 10.
- Aminoantipyrine solution – Prepared by dissolving 2 g of 4-aminoantipyrine (4-AAP) in Type II water and diluted to 100 mL
- Potassium ferricyanide solution – Prepared by dissolving 8 g of $K_3Fe(CN)_6$ in Type II water and diluted to 100 mL

- Stock phenol solution: Prepared by dissolving 1.0 g phenol in freshly boiled and cooled Type II water and diluted to 1 litre (1 mL = 1 mg phenol)
- Working solution A - Prepared by diluting 10 mL stock phenol solution to 1 litre with Type II water (1 mL = 10 µg phenol)
- Working solution B – Prepared by diluting 100 mL of working solution A to 1 000 mL with Type II water (1 mL = 1 µg phenol).
- Ferrous ammonium sulfate – Prepared by dissolving 1.1 g in 500 mL Type II water containing 1 mL concentrated H_2SO_4 and diluted to 1 litre with freshly boiled and cooled Type II water.

Procedure

During the distillation process, 500 mL of sample was measured into a beaker and the pH was lowered to approximately 4 with concentrated H_2SO_4 (1 mL/L), and then transferred to the distillation apparatus. 450 mL of the sample was distilled, and the procedure halted, when boiling had ceased. 50 mL of warm Type II water was added to the flask and distillation resumed until 500 mL have been collected.

Using working solution A, the following standards were prepared in 100-mL volumetric flasks:

Working Solution A (mL)	Concentration (µg /L)
0.0	0.0
0.5	50.0
1.0	100.0
2.0	200.0
5.0	500.0
8.0	800.0
10.0	1000.0

To 100 mL of distillate and standards, 2 mL of buffer solution was added and mixed at a pH of 10. 2.0 mL of aminoantipyrine solution was added, followed by 2.0 mL potassium ferricyanide solution. The solution was mixed, and absorbance read at 510 nm after 15 minutes.

4.6.2. Soil Samples

Soil analysis is important in many aspects of environmental and agriculture studies, ranging from sustainability evaluation of land use to the many soil management practices adopted in various sectors (Shukla, Lal, & Ebinger, 2006). Soil samples in this study were tested for pH, conductivity and various chemical components.

4.6.2.1. pH

5g of the soil sample was mixed with 50 mL of distilled water in a 250-mL beaker. The sample was stirred gently to mix well. A clean calibrated pH probe was then inserted, and readings taken while the particles were still suspended. The procedure was repeated for all other samples and readings recorded accordingly.

4.6.2.2. EC

A conductivity probe (Hanna Instruments 9828) was used to measure the ability of the soil to conduct an electrical current. Before analysis, the cell constant was calibrated using HI9828-25 quick calibration standard solution and the probe rinsed with deionized water. 5g of soil was weighed and mixed with 50 mL of distilled water in a beaker. The sample was mixed thoroughly with a stirrer before the cleaned (with distilled water and blot dry with lint-free tissue) probe was inserted into the sample in the beaker. Readings were taken after the measurement had stabilized. The probe was then rinsed with deionized water and the procedure repeated for all other samples.

4.6.2.3. Major, minor and trace elements

Metals can be extracted from soil by boiling aqua regia. The extraction solution is filtered and the concentration of metals in the filtrate determined by ICP-OES. The analysis by ICP-OES followed the USEPA Method 6010b while sample digestion followed Briggs & Meier method (Briggs & Meier, 1999). Many methods for the determinations of elements require that all element containing species are converted in one single form which is uniform and well defined; that is that all forms of binding present in a particular sample are converted into one or more simplified stages.

An aqueous sample is converted to aerosols via a nebulizer. The aerosols are transported to the inductively coupled plasma which is a high temperature zone (8 000– 10 000ºC). The analytes are heated (excited) too different (atomic and/or ionic) states to produce characteristic optical emissions (lights). These emissions are separated based on their respective wavelengths and their intensities are measured (spectrometry). The intensities are proportional to the concentrations of analytes in the aqueous sample. The quantification is an external multipoint linear standardization by comparing the emission intensity of an unknown sample with that of a standard sample. Multi-element calibration standard solutions are prepared from single- and multi element primary standard solutions. With respect to other kinds of analysis where chemical speciation is relevant (such as the concentration of ferrous iron or ferric iron), only total elemental concentration is analysed by ICP-OES.

Procedure

Determination of pollutants using ICP-OES undergoes two procedures, the sample digestion and the main analysis on the ICP.

Solid Sample Digestion

The samples were mixed thoroughly in its respective containers. 2 g of the sample to be analysed was weighed and transferred to a digestion vessel and marked the digestion vessel with the sample number. A separate digestion vessel was used and marked as the method blank. 1.0 g of the LCS was weighed and transferred to a digestion vessel and marked as the LCS.

Two separately well-mixed portions of the sample chosen for the MS/MSD were weighed and transferred to separate digestion vessels. 2.0 mL of the MS/MSD spiking solution was added to each and mark the digestion vessels as the MS and MSD accordingly. 10 mL of 1:1 HNO_3 was added to each digestion vessel and covered with a watch glass. The sample was heated to 95 ^oC and refluxed for 10 to 15 minutes without boiling. The sample was allowed to cool, and 5 mL of concentrated HNO_3 added. The cover of the sample was replaced and refluxed for 30 minutes. The sample was covered again with a watch glass and continued heating the digestate until the volume had been reduced to approximately 5 mL. The sample was allowed to cool and 10 mL of concentrated hydrochloric acid (HCl) added to sample digestate. After cooling, it was diluted to 100 mL with DI water. The particulates were removed by filtering prior to analysis.

ICP-OES Procedure

Five (5) working standard solutions were prepared from independent primary standard solutions. The newly prepared working standard solutions were confirmed against old working standard solutions and against other independent primary standard solutions. In daily operation, the ICP-OES instrument was started, brought to operation conditions and stabilized. The sample introduction system was checked, and the wavelengths tuned. The instrument was standardized with the five working standard solutions (multi-point linear fitting). Samples were measured with standardization blanks, other kinds of blanks, drift control samples, and quality control samples. After a batch of samples was measured, the data was downloaded to an Excel spreadsheet. The data were corrected in terms of standardization blanks, other relevant blanks, drift correction, and dilution factor application. The results were normalized to the internal reference standard.

4.6.3. Statistical analysis

The numerical data obtained from the laboratory and other sources were subjected to statistical analysis intended to show trends and changes in the variables.

4.6.3.1. Estimation of erosivity index

Thirty (35) year annual rainfall data (1977 - 2012) for Steel Valley was used for this analysis. The data was obtained from World Bank's Climate Change Knowledge Portal and AccuWeather. Using the data, rainfall distribution graph was plotted and moving average imposed on the graph. Rainfall erosivity of the study area was estimated using the Modified Fournier Index (MFI). MFI was calculated using the equation:

$$(\mathrm{MFI}) = \sum p^2/P$$

Where

p = rainfall amount for the wettest months of the year.

P = yearly rainfall amount.

4.6.3.2. Multivariate analysis

The standard deviation, mean and p values were determined using GenStat 12.1 software. The interrelationships among sample sites and the study parameters were analysed using correlation methods of the GenStat 12.1. Cluster analysis (CA) and principal component analysis (PCA) were also done using the software. Cluster analysis was useful in identifying sets of sites characterized by relatively high turnover of parameters (Trakhtenbrot & Kadmon, 2005). While principal component analysis was used to investigate the principles of interaction of the parameters (Kaplunovsky, 2005). Comparative graphs depicting the concentrations against guideline values were plotted with Microsoft Excel 2016.

4.7 Reliability and validity

Two (2) important tools that can be used to measure the confidence and truth of a quantitative research are reliability and validity. Reliability measures consistency over time and representativeness of samples as a generalization of a population, while validity is measures the truthfulness of research (Golafshani, 2003). The procedures used in the research to produce a replicable data were critically analysed and documented. Statistical analysis of the data was used to establish the required accuracy. Standards and calibrations were run for equipment accuracy. In monitoring precision, samples were analysed twice each, and the standard deviations and mean values calculated. Duplicate sample values and original sample values were also used to measure percent relative percent difference, a measure of consistency. Each standard operation used had results verified and documented.

4.8 Limitations

The major methodological limitation of the research was that only a few sample sites could be included for cost reasons. The research did not develop laboratory models of remediation technologies used at the study site. This method of analysis would have been ideal to measure the effectiveness of the technologies specific to the media of the study site. Instead, the research relied on available data and information, coupled with the physical, chemical and organic analysis to arrive at its findings.

4.9 Budget for the project

Table 4.4 Budget for the project

Item	No. of units	Price per unit(R)	Total (R)
Travel costs (Petrol)	1	3 000	3 000
Laboratory analysis cost	4	6 300	25 200
Statistical analysis	1	7100	7 100
Editing	1	5 000	5 000
Printing	1	500	500
Total			40 500

4.10 Conclusion

The research methodology addressed some of the objectiveness of the study as well as the basics of questions raised at the study. Subsequent chapters will use data from this section to fully address the research questions and aims to arrive at a final conclusion and possible recommendations.

CHAPTER 5: DRY SEASON RESULTS

5.1 Introduction

Soil and water samples were taken and analysed in June, when precipitation was low, for physical, inorganic and organic parameters. The total amount of rainfall received in the study area during the sampling month was 4 mm with a daily average temperature of 11 ^{o}C.

5.2 Soil samples

Al, As, Cd, Cr, Cu, Fe, Mn, Tl, Hg, EC, NO_3, SO_4, and pH were quantified in the laboratory and results statistically analysed. Soil samples were taken from site 1, site 2, site 3, site 4, site 5 and site 6 and labelled as WS1, WS2, WS3, WS4, WS5 and WS6 respectively.

5.2.1 Statistical summary

Soil sampled during the dry season had aluminium values that were significantly different from each other. The mean minimum Al concentration was recorded in WS1 (1263 ppb), while WS5 (12940 ppb) recorded the highest among all soil sampled during the dry season. Arsenic concentrations were significantly different across the sample site. The mean minimum concentration of Arsenic was in WS2 (1.740 ppb) and maximum levels in WS5 (3.247 ppb).

Both Cr 52 and Cr 53 were significantly different ($p < 0.05$) in the soils sampled from the six sites under study. The level of Cr 52 and Cr 53 were almost the same and the pattern of variation was similar in each soil sample. Both Cr 52 and Cr 53 recorded maximum concentration in WS3 and minimum in WS6. The same observations were made for Cu 63 and Cu 65. The mean maximum levels of Cu 63 (26.62 ppb) and Cu 65 (26.76 ppb) were recorded in WS3 and mean minimum level of Cu 63 (13.77 ppb) and Cu 65 (13.85 ppb) in WS4. Fe, Mn and Tl levels in the soils sampled were significantly different ($p < 0.05$) from each sampling point as shown in Table 5.1. Mercury levels in the soil samples were all below 0.004mg/L.

Table 5.1 Means of physico-chemical parameters measured in soil samples during the dry season

Sample ID	Al (ppb)	As (ppb)	Cd (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	Fe (ppb)	Mn 55 (ppb)	Tl (ppb)	EC (mS/m)	NO_3 (mg/L)	SO_4 (mg/L)	pH	Temp (°C)
WS1	1400	2.057	0.00333	126.2	124.5	16.09	16.32	14423	489.7	0.5267	887.7	0.4913	1183	8.89	13.04
WS2	8894	1.740	0.0433	121.3	120.1	14.72	14.77	12237	259.6	0.4733	920.7	0.338	1013	8.90	12.70
WS3	1263	2.440	0.0367	150.1	148.0	26.62	26.76	19921	864.4	0.5033	1317.3	0.3967	2564	8.65	12.16
WS4	10512	2.557	0.0367	132.9	130.1	13.77	13.85	13700	430.6	0.4467	1397	0.3503	1250	8.38	12.25
WS5	12940	3.247	0.0033	131.2	128.8	18.05	18.26	18840	691.2	0.5467	1330.7	0.419	1891	8.51	11.09
WS6	11119	2.153	0.0467	120.4	118.0	14.53	14.61	12128	212.2	0.4500	1523.3	0.4307	2307	8.15	12.04
Min	1106	1.66	0.00	112.2	110.4	13.4	13.49	11587	202.8	0.44	878	0.31	890	8.11	11.07
Max	13516	2.27	0.05	156.1	154.9	26.98	27.39	20133	933.2	0.57	1526	0.501	2791	8.99	13.09
P value	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
CV %	34.7	5.2	17.3	4.7	4.8	5.7	6.0	0.7	8.4	2.8	0.7	5.8	10.4	0.9	0.3

Soil sampled during the dry season revealed the presence of NO_3 and SO_4. These radicals were significantly different ($p < 0.05$) among soil samples as shown in Table 5.1. The mean maximum levels of NO_3, and SO_4 were recorded in WS1 and WS3 respectively. While the mean minimum values of NO_3 and SO_4 levels were recorded in WS2, thus 0.338 and 1013 mg/L respectively as shown in the Table 5.1. Electrical conductivity in WS3 and WS5 were similar and had no significant difference as shown in Table 5.1. The mean minimum electrical conductivity of the soils sampled was observed in WS1 (887.7 mS/m) and maximum conductivity in WS6 (1523 mS/m). Electrical conductivity was similar in WS3 (1317.3 mS/m) and WS5 (1330.7 mS/m) hence there was no significant difference between the soils as shown in Table 5.1. The pH recorded a minimum mean and a maximum mean in WS6 (8.15) and WS2 (8.90) respectively.

5.2.2 Multivariate analysis (PCA and CA)

The cluster analysis revealed that WS1 (a, b and c) were similar at a level of 0.982 and formed a distinct cluster (cluster 1). Soil WS2 had WS2a and WS2c closely related at the level of 0.979 and only merged with WS2b at the level of 0.934 to form an independent cluster (cluster 2) as shown in Figure 5.1. This implied that WS2b varied significantly from WS2a and WS2c. Soil WS1 and WS2 merged and had similarities at 0.909. WS 4 and WS 6 were similar at the point 0.962 to form cluster 3. WS1, WS2, WS4 and WS6 were merged at the point 0.907 to have close similarities as shown in Figure 5.1. WS5 samples were similar at the level of 0.991 and WS 6 formed similarities at the level of 0.983. It was observed that WS1, WS2, WS4 and WS6 were merged with WS 5 at the level of 0.863 to have similarities. Correlations among all the samples were obtained at the level of 0.839 as shown in Figure 5.1.

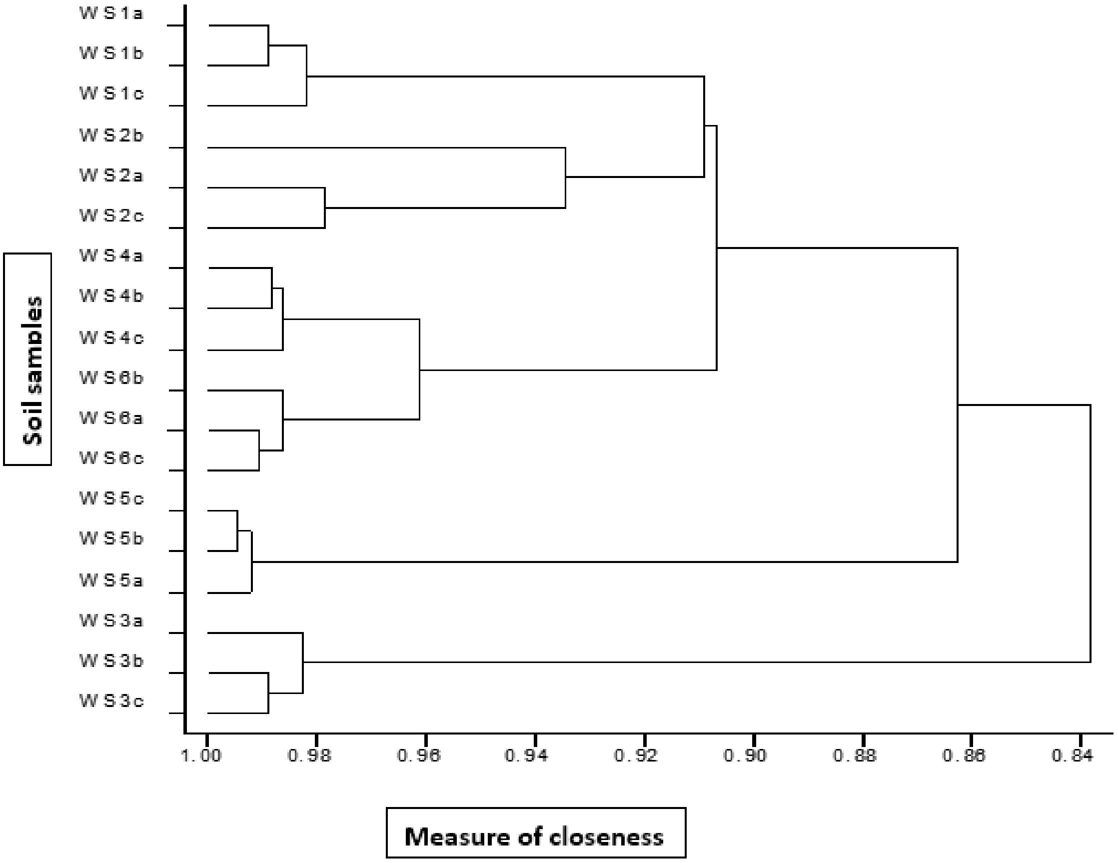


Figure 5.1 A dendrogram showing similarities in soil sampled during the dry season

In another statistical representation, a principal component analysis (PCP) biplot was used to show the correlation between the samples and parameters. The PCP biplot diagram shown in Figure 5.2 indicates that principal component (PC) 1 contributed the largest source of variation (43.55%), while PC-2 contributed 25.33% of the variation in data gathered. The two principal components contributed 68.88% of variation in data gathered. The PCP biplots indicated the correlations between the variables such that lines of variables in opposite direction indicated negative correlation. From the biplot, NO_3, Cr, Cu, Tl, Mn and Fe were positively correlated. EC, SO_4 and As were also positively correlated.

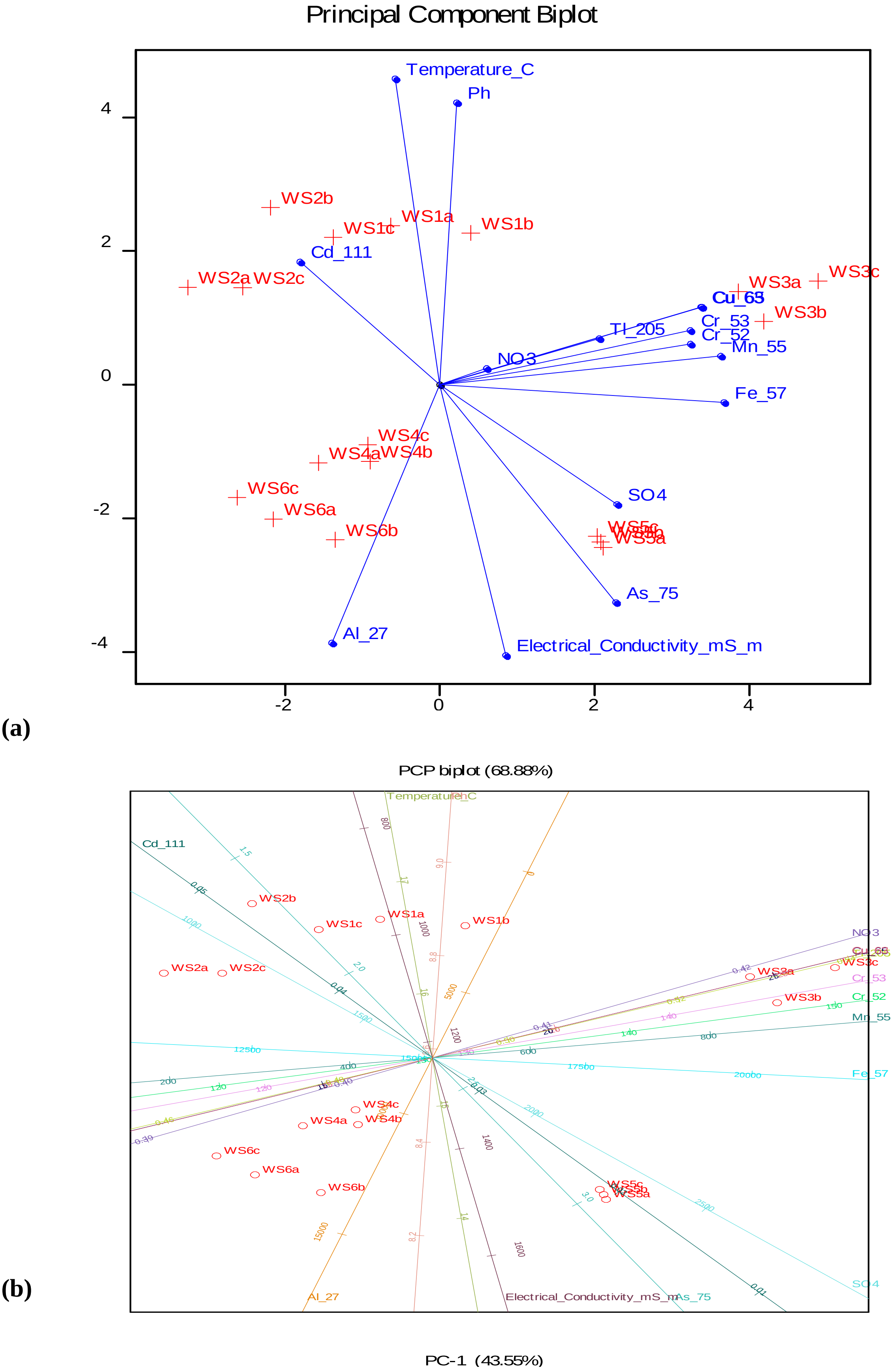


Figure 5.2 Principal component biplots of soil sampled during the dry season

5.2.3 Correlation matrix

The correlation matrix revealed the relationship between the various parameters and the level of correlation that exist between them. Values with * implies strong correlation either negatively or positively as presented in Appendix 2. Al and Cd correlated negatively with most of the metal parameters. As had negative correlation with the physical parameters and Cd and had a positive correlation with all the other parameters measured. Very strong positive correlation existed among Cu, Fe, Cr and Mn, while a very strong negative correlation exists between pH and temperature.

5.3 Water samples

The water samples were analysed for levels of BTEX, phenols, total petroleum hydrocarbons (TPH), total metal concentrations (Al, As, Cd, Cr, Cu, Fe, Mn, Tl, Hg), Cr^{3+}, Cr^{6+}, EC, NO_3, SO_4, temperature, alkalinity (Total, carbonate, bicarbonate) and pH. The sampling points 1, 2 and 3 have been labelled herein as WW1, WW2 and WW3 respectively.

5.3.1 Statistical summary

Al concentrations in WW3 were significantly higher than WW2 and WW1. There was no significant difference in Al concentration between WW2 and WW1. Aluminium concentrations recorded ranged from 543.062 ppb to 863.634 ppb in all the water samples as shown in Table 5.2. Different forms of chromium were measured in the water samples. Leachable chromium, Cr^{3+} and Cr^{6+} were all found to be below 0.01mg/L in all the samples. Cr 52 and Cr 53 were quantified in ppb, and both recorded low values of 3.557 and 3.463 respectively, with only one sample site (WW3) exceeding 6 ppb. WW3 was significantly higher than WW1 and WW2 in Cr concentrations. In Cu concentration, a maximum mean was recorded at WW1 and a minimum at WW2. The concentrations of Cu ranged from 15.97 ppb to 30.63 ppb. Cu recorded in the forms Cu 63 and Cu 65 were all except one below 30 ppb (mean of 22 ppb).

As, Cd and Tl all recorded a similar value pattern, that is, less than 1 ppb across all the water samples. Very low Tl values were recorded (range; 0.003 ppb – 0.012 ppb). Cd concentration varied significantly as well; WW3 (0.0847 ppb) was significantly higher than WW 1 and WW2. There was no significant difference between WW1 and WW2. Arsenic values varied among each other, WW3 (744 ppb) was significantly higher than WW2 and WW1. WW1 was also significantly higher than WW2. There was a highly significant difference in Tl, WW2 and

WW3 were higher than WW1 while there was no significant difference between WW2 and WW3. Iron concentrations fluctuated between the three sampling points; ranging from 1005.216 ppb to 1814.272 ppb. Iron varied significantly among the samples, WW3 was significantly higher than WW2 and WW1. WW1 was also significantly higher than WW2. There was a highly significant difference in Mn; WW 3 was higher in concentrations of Mn than WW2 and WW1. WW1 was also significantly higher than WW2. Manganese in the water samples were mostly less than 300 ppb, with only the triplicate samples from WW3 exceeding 500 ppb. Mercury level was also tested in the water samples, but very low quantities were recorded (<0.004 mg/L).

Table 5.2 Mean physico-chemical levels in water samples in Steel Valley during the dry season

Sample ID	Al (ppb)	As (ppb)	Cd (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	Fe (ppb)	Mn (ppb)	Tl (ppb)	EC (mS/m)	pH	Temp (°C)	B.A mg $CaCO_3$/L	C.A mg $CaCO_3$/L	T.A mg $CaCO_3$/L	NO_3 (mg/L)	SO_4 (mg/L)
WW1	644	0.548	0.046	4.408	4.288	28.12	27.81	1278	276.23	0.003	33.67	7.91	13.67	100.30	0.882	101.33	1.063	60.37
WW2	544	0.437	0.0467	3.654	3.474	16.44	16.97	1020	239.72	0.01	34.13	7.92	13.43	98.77	0.913	99.73	1.152	61.2
WW3	774	0.723	0.0847	6.554	4.690	23.30	23.58	1805	515.55	0.011	28.60	7.88	13.60	81.17	0.780	81.93	1.253	60.6
Min.	543.1	0.407	0.03	3.557	3.398	15.99	15.97	1005	238.2	0.003	28.1	7.88	13.1	80.5	0.701	81.7	1.01	60.1
Max.	863.6	0.779	0.094	6.891	4.891	30.63	29.1	1814	515.7	0.012	34.4	7.92	13.9	101	0.987	102	1.29	61.5
P value	0.002	0.001	0.015	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.727	0.001	0.347	0.001	0.004	0.021
CV%	6.9	6.9	21.5	6.0	4.2	6.0	4.3	2.5	0.7	8.2	1.2	0.1	2.6	0.8	12.4	0.8	3.6	0.4

Sulphate levels in water samples in Steel Valley average 60.7 mg/L while nitrate levels did not exceed 1.3 mg/L in water samples in the area. There was a significant difference in bicarbonate alkalinity among the sampling sites; WW1 had the highest bicarbonate alkalinity, which was significantly higher than WW3 and similar to WW2. Carbonate alkalinity did not vary significantly, WW2 recorded the highest carbonate alkalinity (0.913 mg $CaCO_3$/L) but this was not so different compared to WW1 and WW3. There was a significant difference in total alkalinity; WW1 had the highest total alkalinity (101.33 $CaCO_3$/L) which was higher than WW3 (81.93 $CaCO_3$/L) but not higher than WW2.

The temperatures in the water samples ranged from 13.1 °C to 13.9 °C with an atmospheric pressure around 853 mbar. The pH for all the water samples were less than 8.00, with a minimum pH of 7.88 measured from the lake sample (Standard deviation = 0.0169 for all the water samples). The mean EC for WW 1, 2 and 3 were 33.67 mS/m, 34.13 mS/m and 28.60 mS/m respectively. From the mean values, TDS was calculated for each sample; WW1 had a mean TDS of 215.488 ppm, while WW2 and WW3 had a calculated mean TDS of 204.78 ppm and 183.04 ppm respectively. Total alkalinity was highest in WW1, with a mean maximum alkalinity of 101.33 mg $CaCO_3$/L and lowest in WW3 (Mean alkalinity = 81.93 mg $CaCO_3$/L). The same pattern followed for bicarbonate alkalinity, with WW1 recording the mean highest (100.30 mg $CaCO_3$/L) and WW3 recording the mean lowest (81. 17 mg $CaCO_3$/L). Carbonate alkalinity was highest in samples from WW2 (0.913 mg $CaCO_3$/L) and recorded its lowest mean in WW3 (0.780 mg $CaCO_3$/L).

All organic parameters (BTEX, Phenols and Total hydrocarbons) were below detectable levels hence were not quantified as shown in Table 5.3.

Table 5.3 Mean values of organic parameter measured in water

Parameters	SW1	SW2	SW3	Min.	Max.
Cr (mg/L)	<0.003	<0.003	<0.003	<0.003	<0.003
Cr^{3+} (mg/L)	<0.010	<0.010	<0.010	<0.010	<0.010
Cr^{6+} (mg/L)	<0.002	<0.002	<0.002	<0.002	<0.002
Hg (mg/L)	<0.004	<0.004	<0.004	<0.004	<0.004
BTEX (µg/L)	< 2	< 2	< 2	< 2	< 2
Benzene (µg/L)	< 2	< 2	< 2	< 2	< 2
Toluene(µg/L)	< 2	< 2	< 2	< 2	< 2
Ethylbenzene(µg/L)	< 2	< 2	< 2	< 2	< 2
m + p Xylene (µg/L)	< 4	< 4	< 4	< 4	< 4
o-Xylene (µg/L)	< 2	< 2	< 2	< 2	< 2
TPH C10-C40 (µg/L)	< 10	< 10	< 10	< 10	< 10
C10 – C16 (µg/L)	< 10	< 10	< 10	< 10	< 10
C16 – C22 (µg/L)	< 10	< 10	< 10	< 10	< 10
C22 – C30 (µg/L)	< 10	< 10	< 10	< 10	< 10
C30 – C40 (µg/L)	< 10	< 10	< 10	< 10	< 10
Phenols (mg/L)	<0.020	<0.020	<0.020	<0.020	<0.020

5.3.2 Multivariate analysis (PCA and CA)

Principal component analysis carried out revealed that PC-1 contributed 57.49% of the total source of variation and PC-2 contributing 30.31% of variation. PC-1 and PC-2 are the two major sources of variation, which sums up to 87.79% of variation among the variables. The biplot in Figure 5.4 revealed that temperature, Tl, and SO_4 were correlated positively. Mn, Cr, Fe, As and Al also formed a cluster, signifying a positive correlation between the parameters. Positive correlation also existed between pH, EC and total alkalinity. The angle between the biplot axes represent the magnitude of correlation between the variables, and line in opposite directions indicate negative correlation.

The dendrogram displayed (Figure 5.3) revealed that water sampled from the three sites had no similarities at a level of 1. Sample WW1 (WW1a, WW1b, and WW1c) were similar at the level of 0.924 hence forming a cluster. It was noted that WW1a and WW1c were more closely related at the point of 0.962. At a level of 0.985, WW2 samples thus 'b' and 'c' had more similarities and merged at the point 0.96 to have similarity with WW2a. Samples of WW1 and WW2 were merged at a level of 0.814 to have close relation. It was only in samples of WW3 that had similarity within its triplicates at the level of 0.968 as shown in Figure 5.3.

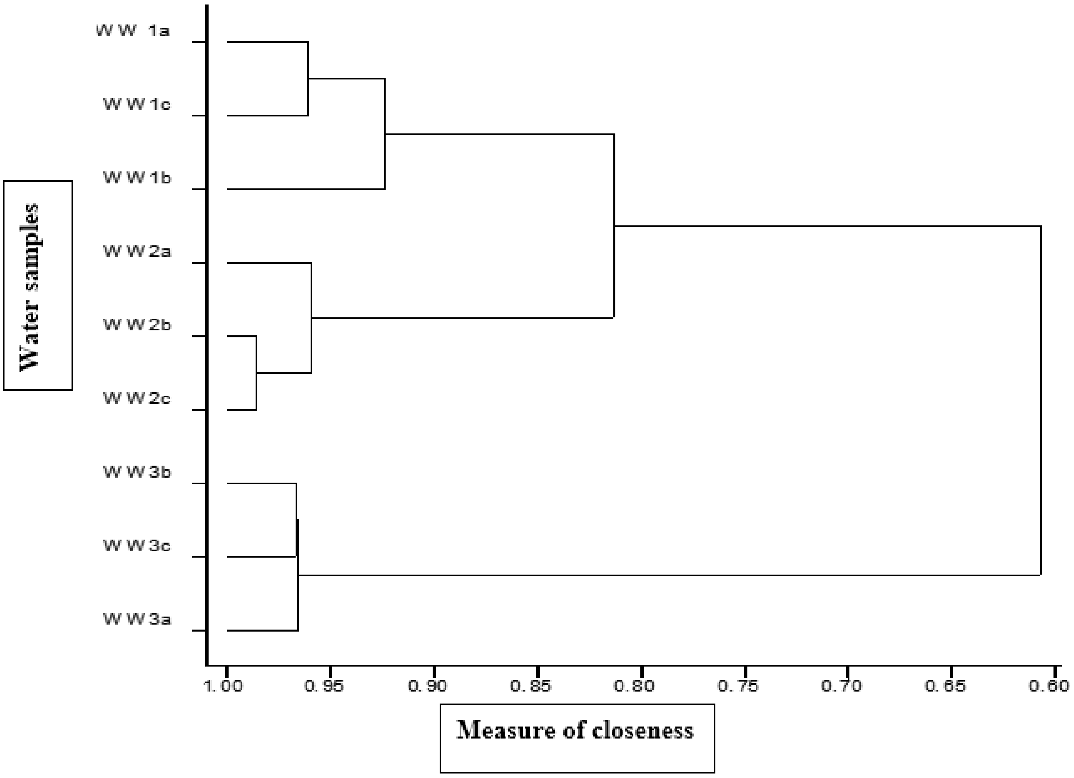
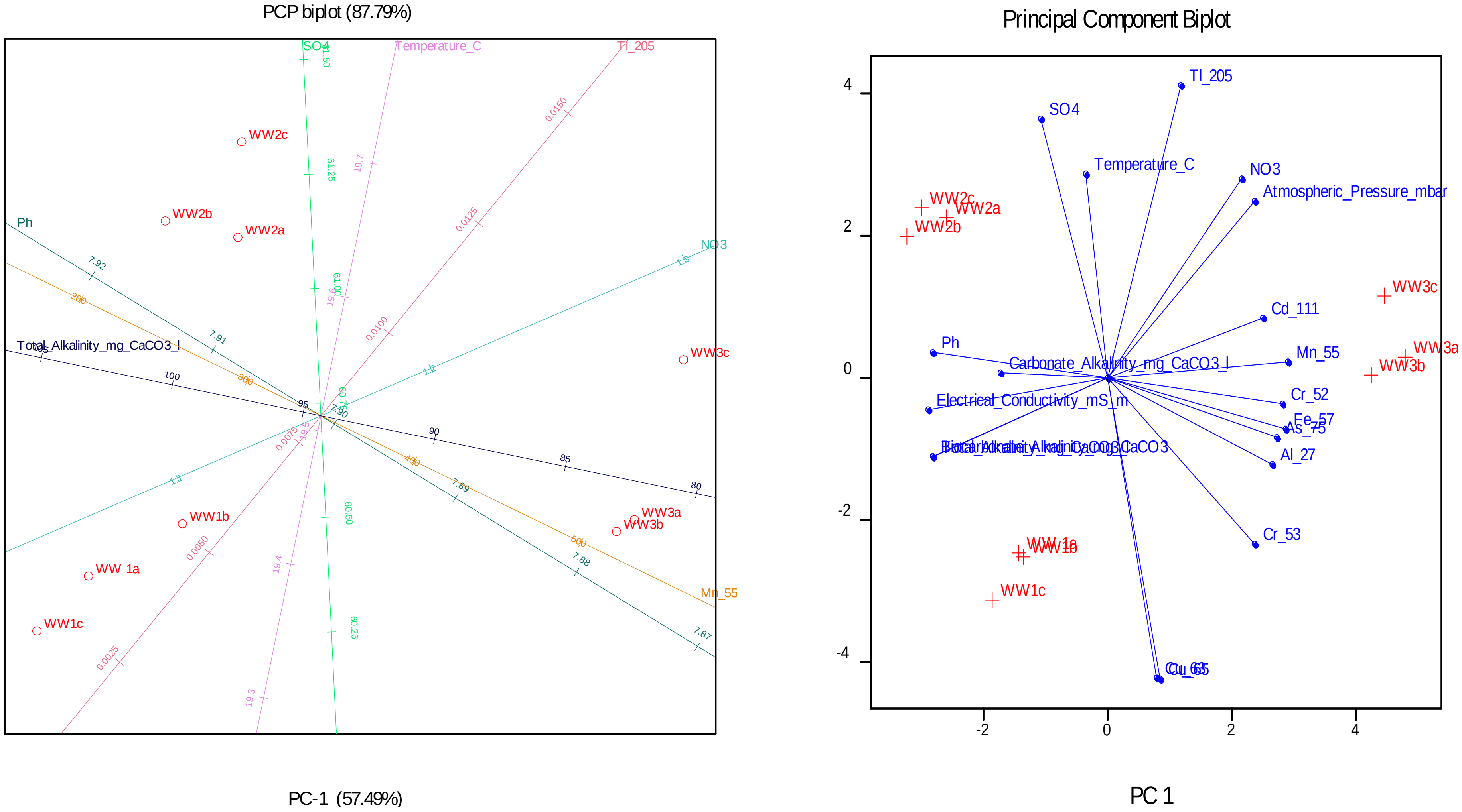


Figure 5.3 A dendrogram of water sample results during the dry season in Steel Valley



(a) **(b)**

Figure 5.4 Principal component analysis biplot of water sampled during the dry season in Steel Valley

5.3.3 Correlation matrix

The correlation matrix revealed the relationship between variables and the level of correlation significance that exist between the variables. Values with * implies strong correlation (negatively or positively) as shown in appendix 3. Positively correlated relationship implied that the two variables are directly proportional while negatively correlated variables implied inverse proportionality.

Al and As correlated negatively with physical parameters and SO_4 and showed a strong positive correlation with As, Cr, Fe and Mn. There was a trend of physical parameters correlating negatively with metals parameters. Cr, Mn, Fe and Al were strong positively correlated with among each other. Tl only had a strong positive correlation with atmospheric pressure and NO_3, while correlating negatively with all other parameters measured.

5.4 Conclusion

The results obtained during the dry season were summarized and tabulated in this chapter, with the detailed results presented in Appendix 4 (water samples) and Appendix 5 (soil samples). The results generally showed traces of some metal concentrations but did not record any organic concentrations in either the water or the soil samples. Metals concentrations were of notable concern. Al in water samples ranged from 863.634 to 863.634 ppb, Cr ranged from 3.557 to 6.891 ppb and Mn ranged from 238.159 to 515.735 ppb. Other results from the water samples were Fe (1005.216 - 1814.272 ppb), Cu (15.974 – 30.629 ppb), As (0.407 - 0.779 ppb), Cd (0.03 - 0.094 ppb) and Tl (0.003 - 0.012 ppb). The soil samples followed a similar pattern with the metals recording the highest of concentrations. Al, Cr, Mn, Fe, Cu, As, Cd and Tl in soil ranged from 1105.92 - 13516.16 ppb, 110.39 – 156.07 ppb, 202.83 - 933.23 ppb, 11586.51 - 20132.64 ppb, 13.4 – 27.39 ppb, 1.66 - 3.27 ppb, 0.00 - 0.05 ppb and 0.44 - 0.57 ppb respectively.

CHAPTER 6: RAINY SEASON RESULTS

6.1 Introduction

Soil and water samples were taken and analysed in October, when precipitation was high, for physical, inorganic and organic parameters. In 2016, the amount of rainfall received in the study area during the sampling period was 78 mm.

6.2 Soil analysis

Soil samples were collected from the study site in October 2016, analysed in the laboratory and the results here in from the laboratory analysed using statistical tools. SS1, SS2, SS3, SS4, SS5 and SS6 used in this chapter are names given to the rainy season samples.

6.2.1 Statistical summary

The mean of triplicate samples from each sampling point, the maximum and minimum values of the means for each parameter analysed, the respective p values (Gelman, 2013) for each parameter and coefficient of variation (CV) (Kendall & Costello, 2006) have been summarized in Table 6.1.

The physico-chemical characteristic of soil is a key factor to understand soil health over a period of time (Kibblewhite, Ritz, & Swift, 2008; Rahmanian et al., 2015). Hence, soil pH and EC were determined for all the soil samples. The pH of rainy season soils sampled were significantly different ($p = 0.001$) from each other. The minimum pH value was 7.78 and maximum of 8.13. The mean minimum pH value was observed in SS6 (7.79) and mean maximum pH in both SS2 and SS4 (8.11). The pH levels in the rainy season soils were similar in SS1, SS2, SS3, and SS4; hence, they were not significantly different as shown in Table 6.1. Electrical conductivity of soils sampled were significantly different ($p = 0.001$) from each other. The EC values varied among each soil sample; ranging from 1029 mS/m to 1595 mS/m. The mean least EC value was observed in SS1 (1031 mS/m) and the mean highest EC value observed in SS6 (1592.67 mS/m).

Soil samples obtained during the rainy season had Al concentrations significantly different ($p = 0.001$) from each other. Minimum and maximum levels of Al in the rainy season soils were 7706 ppb and 13621 ppb respectively. The mean concentration level obtained for Al was not significantly different between samples taken from point 1 (2510 ppb) and samples taken from point 2 (2743 ppb), similar observation was made for SS4 (12681 ppb) and SS6 (12824 ppb) when compared. SS3 and SS5 had no similarity when compared to each other or other Al concentrations of the rainy period soils sampled. SS3 recorded the least mean Al concentration (1870 ppb) whiles SS5 had the highest mean Al concentration (13608 ppb).

The minimum and maximum values of arsenic were 2.19 ppb and 4.01 ppb respectively. The means of SS2 and SS6 of arsenic show no significant difference, but all the other concentrations were different. The concentration levels of the rainy season soil samples obtained for cadmium at sampling site 1 (0.0467 ppb) and sampling site 2 (0.05 ppb) showed similarity. There were sampling points that recorded 0.00ppb for cadmium and a maximum of 0.06 ppb at other points. The concentration levels obtained for leachable chromium in the rainy season soil samples were highly significant. Mean concentrations of Cr 52 between SS1 (137.35 ppb) and SS4 (137.36 ppb) were similar and not significantly different, as shown in Table 6.1. Minimum concentration of Cr 52 was 129.6 ppb and maximum concentration level was 152.2 ppb. SS2, SS3, SS5 and SS6 varied significantly when compared to each other in terms of soil sampled for Cr 52 concentrations. Cr 53 concentration in soil the samples were significantly different from each other and had similar projections as Cr 52. The concentration level for Cr 53 was not significantly different between SS1 (138.64 ppb) and SS4 (138.10 ppb) while recording minimum and maximum concentration of Cr 53 at 130.4 ppb and 154.2 ppb respectively.

The minimum and maximum values of copper were 14.52 ppb and 28.61 ppb respectively. Cu 63 concentrations in the rainy season were statistically different ($p<0.05$) from each other. SS3 of Cu 63 recorded the highest concentration and SS2/SS4 recorded least concentrations of 14.70 ppb and 14.79 ppb respectively. Cu 65 concentrations in rainy season soil samples were statistically different ($p<0.05$). The minimum and maximum mean values of Cu 65 were 15.2 ppb and 29.32 ppb respectively. SS3 and SS5 recorded the highest concentration of 29.27 ppb and 21.97 ppb respectively, and the least concentrations were SS2 (15.35 ppb) and SS4 (15.57 ppb).

Iron concentrations in the rainy season soil samples were statistically different ($p<0.05$). The minimum and maximum concentration of iron was 14221 ppb and 23201 ppb respectively. SS3 recorded the highest concentration level of 23190 ppb while the least was 15244 ppb.

Table 6.1. Mean physico-chemical concentrations measured in soil samples during the rainy season

Sample ID	Al (ppb)	As (ppb)	Cd (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	Fe (ppb)	Mn (ppb)	Tl (ppb)	EC (mS/m)	NO_3 (mg/L)	SO_4 (mg/L)	pH	Temp ºC
SS1	2510	2.33	0.0467	137.35	138.64	17.79	18.04	16934	548.8	0.5833	1031.0	0.717	1312.7	8.07	16.28
SS2	2743	2.77	0.0533	140.26	143.01	14.70	15.36	14301	306.2	0.5033	1213.33	0.4977	1260.0	8.11	16.53
SS3	1870	3.127	0.0367	143.43	145.24	28.47	29.27	23190	962.5	0.5567	1200.33	0.4470	2870.3	8.06	16.14
SS4	12681	3.383	0.05	137.36	138.10	14.79	15.57	15528	464.5	0.4767	1476.67	0.4907	1831.7	8.11	15.33
SS5	13608	3.953	0.0033	129.98	131.70	21.10	21.97	21495	718.1	0.5733	1511.33	0.5823	2017.3	7.98	13.64
SS6	12824	2.810	0.0533	151.88	153.68	16.27	17.05	15244	242.6	0.4900	1592.67	0.6183	2555.3	7.79	14.67
Minimum	1706	2.19	0.00	129.6	130.4	14.52	15.2	14221	233.5	0.47	1029	0.44	1255	7.78	13.56
Maximum	13621	4.01	0.06	152.2	154.2	28.61	29.32	23201	966.4	0.59	1595	0.722	2901	8.13	16.85
P Value	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
CV %	1.6	2.7	13	0.5	0.5	1.1	0.6	0.3	1.1	3.5	0.2	1.6	1.2	0.3	1.6

Manganese concentrations in the soil samples were statistically different ($p<0.05$). The minimum concentration level was 966.4 ppb and the maximum concentration level was 966.4 ppb. 962.5 ppb was recorded as the highest concentration level for Mn in SS3, followed by SS5 (718.1 ppb) and the least was 242.6 ppb for SS6. The concentration level obtained for thallium was not significantly different between SS4 (0.4767 ppb) and SS6 (0.4900 ppb) as shown in Table 6.1. Similar observation was made for SS1 (0.5833) and SS3 (0.5567), thus, no significant difference observed.

Nitrate levels ranged between 0.44 mg/L and 0.722 mg/L, which were the minimum and maximum values, recorded respectively as shown in Table 6.1. The mean concentration of NO_3 were only similar in SS2 (0.4977 mg/L) and SS4 (0.4907 mg/L) whiles SS1, SS3, SS5 and SS6 had no similarities in their mean concentration. The least mean NO_3 concentration was recorded at SS3 (0.4470 mg/L) and with mean maximum concentration of NO_3 observed in sample SS1 (0.717 mg/L). SO_4 concentrations varied among the rainy season soils sampled. The minimum and maximum mean values of SO_4 concentration were 1255 mg/L and 2901 mg/L respectively. The rainy season soil samples SS1 and SS2 had mean SO_4 concentrations that were similar. The mean minimum and maximum concentration of SO_4 were recorded in SS2 (1260.0 mg/L) and SS3 (2870 mg/L) respectively as shown in Table 6.1.

Mercury levels were below detection (<0.004 mg/L) in all the soil samples analysed.

6.2.2 Multivariate analysis (PCA and CA)

The hierarchical data analysis method was used in carrying out cluster analysis for all the samples using the raw data, where a, b and c represent the triplicate samples. Clusters formed are defined according to similarity or dissimilarity measures (Murtagh & Contreras, 2011). From the dendogram in Figure 6.1, it was observed that all soil samples from SS1, SS22, SS3, SS4, SS5 and SS6 clustered at the point 0.98. There was close similarity among SS1a, SS1b, and SS1c at approximately point 0.996. Likewise, SS2a, SS2b, and SS2c have similarity at 0.997. Soil samples from site four (SS4a, SS4b and SS4c) were very much closely associated at 0.999; at a level of one, SS4a and SS4c were similar with SS4b. The cluster SS2 and SS4 were correlated at level of 0.916. SS2 and SS4 cluster merged with SS1 at the level of 0.915 (forming cluster 1). This implied that SS1, SS2, and SS4 had more similarities at 0.915 and were dissimilar compared to SS3, SS5 and SS6. Soil samples SS6a and SS6b were similar at 0.998 but merged with SS6c at a level of 0.997 to have similarity. Rainy season soils sampled from site six which were all clustering at a level of 0.997 had a correlation with SS1, SS2 and SS4 soil samples at a level of 0.846 (forming cluster 2).

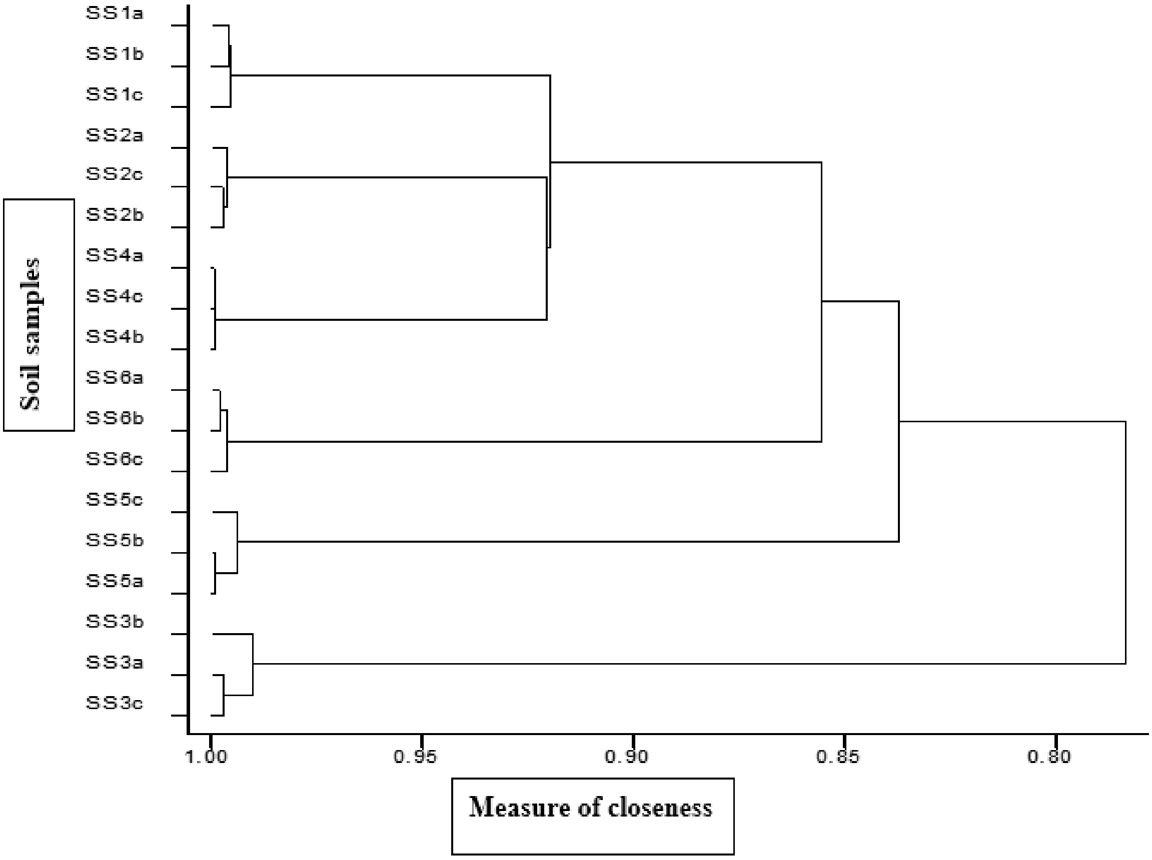
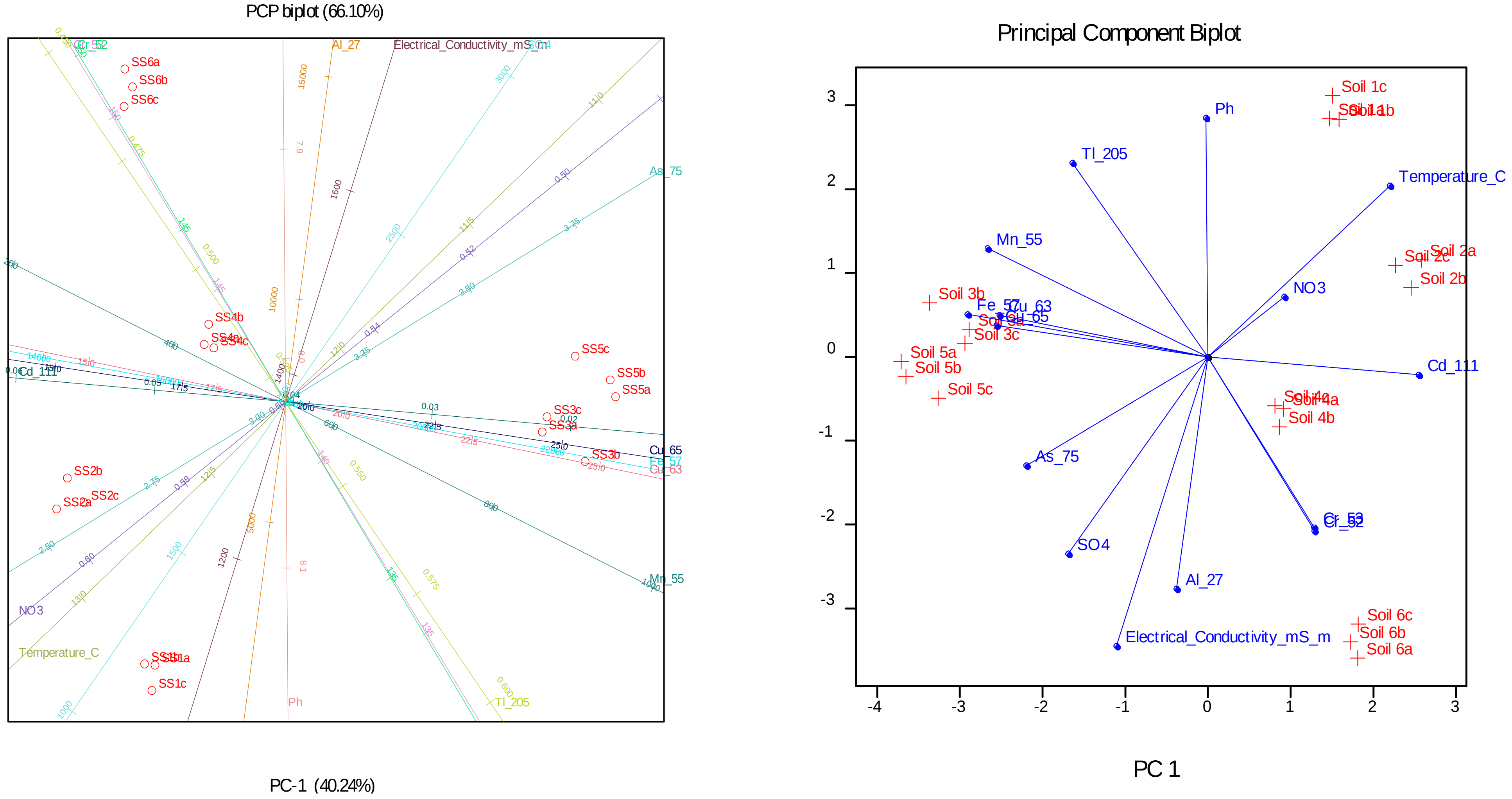


Figure 6.1 A dendrogram showing similarities in soil sampled during the rainy season

At a level of 0.99, SS5a and SS5b were similar with respect to the physico-chemical properties of the soils sampled but was dissimilar with SS5c at that same level. However, SS5a, SS5b and SS5c were only correlated at the level of 0.993 hence forming an independent cluster 3. The samples SS5 were similar to SS1, SS2, SS4 and SS6 at the level of 0.827. Soil samples SS3a and SS3c were similar at the level of 0.997. SS3b was only similar to SS3a and SS3c at the level of 0.989. The CA result presented all the 18 soil samples from six different sites based on similarities and dissimilarities into four statistically significant clusters. Cluster (group) 1 consists of SS1, SS2 and SS4 samples, cluster (group) 2 consists of SS6 soil samples, cluster 3 consist of SS5 soil samples and cluster 4 consist of only SS3 soil samples. The clustered group 1 (SS1, SS2 and SS4) and 2 (SS6) had similarities at a level of 0.845. While the next node of SS5 (cluster 3) samples were merged at 0.827 and that of SS3 (cluster 4) merged at 0.77.

From the biplot analysis in Figure 6.2, the angles between the biplots axes represent the correlation between the variables, and the lines in opposite directions indicate negative correlation. The principal component biplot indicated that first principal component (PC-1) contributed 40.24% of the variation whiles the second principal components (PC-2) contributed 25.86% of the variation. This implied that most of the variations were contributed by PC-1. The sum of PC-1 and PC-2 principal component variation resulted into a total variation of 66.1% of the variance. The biplot revealed that there was similarity between SS1a and SS1b than SS1c with respect to variables measured. Soils SS2a and SS2c were closely similar than SS2b. similar observations were made for soil from site 4 (SS4a, SS4b and SS4c). SS4 soils had similarities in physico-chemical among each replicate. Also did SS3 soils have close relation with some inorganic elements such as Cu 65, Cu 63, Mn and Fe. SS6 samples were closely similar in Cr 52, Cr 53 and Tl, and differed from the other soil sampled.

From the biplot in Figure 6.1, it can be seen that Cu, Mn and Fe cluster and show more similarity to each other and dissimilar to Cr and Cd. As, SO_4, Al and EC also showed similarities in terms of concentration levels and formed a cluster that is dissimilar to temperature and NO_3. SS1 samples showed similarities in terms of the parameters analysed with SS2, SS3 and SS5 were clustered while SS4 and SS6 had similar attributes in the parameters analysed.



(a) **(b)**

Figure 6.2 Principal component biplot of soil sampled during the rainy season

6.2.3 Correlation matrix

From Appendix 6, values with the negative sign implied that the variables of interest were negatively correlated while values that are positive signified positive correlation. From the correlation matrix below, values assigned with ** implied that there was a very strong correlation between the variables and the correlation between the variables were significant ($p < 0.05$). Values assigned with * imply a weak but significant correlation ($p < 0.05$).

The principal component biplot and correlation matrix revealed that As and Al; EC and Al ($p>0.05$), were positively and strongly correlated. EC and As; Fe and As; Cr and Cd; temperature and Cd; Fe and Cu; Mn and Cu; Tl and Cu; SO_4 and Cu; SO_4 and EC; Mn and Fe; SO4 and Fe; Tl and Fe; Tl and Mn were positively and strongly correlated. Strong negative correlation existed between pH and Al; temperature and Al; Cd and As; Cr and As; temperature and As; Fe and Cd; Mn and Cd; Tl and Cd; pH and Cr; pH and EC; temperature and EC; as well as temperature and Fe; the negative correlation between each of them was statistically significant ($p > 0.05$).

6.3 Water samples

Water samples from sites 1, 2 and 3 herein as SW1, SW2 and SW 3 respectively were sampled and analysed in October 2016. The water samples were analysed for levels of BTEX, phenols, total petroleum hydrocarbons (TPH), total metal concentrations (Al, As, Cd, Cr, Cu, Fe, Mn, Tl, Hg), Cr^{3+}, Cr^{6+}, EC, NO_3, SO_4, temperature, alkalinity (Total, carbonate, bicarbonate) and pH.

6.3.1 Statistical summary

Water samples collected from the three different sites during the rainy season revealed the presence of some total metal content and below detection levels of organic parameters with all data summarized in Table 6.2. Aluminium ranged from 600.2 ppb and 912.8 ppb. The concentration of Al had a mean minimum concentration of 602.4 ppb in SW2 and a mean maximum of 910.3 ppb was recorded in SW3. The concentration of Al was highly significantly different ($p < 0.05$) among water sampled. The concentration of As ranged from 0.417 ppb to 0.7 ppb. The mean minimum concentration of As was 0.421 ppb and observed in SW2 whiles the maximum concentration of As was 0.696 ppb and observed in SW3. Cd was significantly different ($p < 0.05$) from each other and had concentrations ranging from 0.052 to 0.098 ppb. The mean minimum concentration of Cd was 0.055 ppb and mean highest concentration was

0.96 ppb. There was no significant difference between SW 1 and SW2. Cr 52 was significantly different ($p < 0.05$) among SW1, SW2 and SW3. The minimum and maximum concentrations of Cr 52 were 5.449 ppb and 6.989 ppb respectively.

The concentration of Cr 53 was significantly different, with all samples varying significantly. The minimum and maximum concentrations of Cr 53 were 4.044 ppb and 5.125 ppb respectively. Each sample of Cu 63 and Cu 65 had similar variance in concentration values. Similar observation and pattern of Cu 63 and Cu 65 were similar for Fe and Mn. The Fe and Mn had the mean highest concentration in sample SW3 and mean minimum concentration in SW2. The Tl concentrations were significantly different among all samples and varied among each sample.

Physical parameters of water samples obtained during the rainy season (SW1, SW2 and SW3) were statistically insignificantly different ($p > 0.05$) with respect to atmospheric pressure, pH, and temperature. Values recorded for atmospheric pressure had no variation within water sampled. Maximum and minimum atmospheric pressure were 882.9 mbar and 882.1 mbar respectively. The pH had a minimum of 7.5 and maximum value of 8.9. EC was significantly different among water samples as shown in Table 6.2. Total dissolved solid was calculated from each mean of EC values of SW1, SW2 and SW3 as 298.88 ppm, 257.472 ppm and 226.368 ppm respectively. Temperature of the water samples ranged from 19.2 ^{o}C to 19.7 ^{o}C. Sulphate ion concentration, bicarbonate alkalinity, carbonate alkalinity and total alkalinity were significantly different ($p < 0.05$). Thus, means of sample varied and had no similarities with respect to the measured parameters as shown in the Table 6.2.

The levels of Cr^{3+}, Cr^{6+}, and Hg had no variation in all the water samples as they were below detection as shown in Table 6.3. All organic parameters analysed were also below detectable limits. Table 6.3 summarizes all parameters that were not quantified due to their low levels in water samples analysed from the study site.

Table 6.2 Mean physico-chemical levels in water samples in Steel Valley during the rainy season

Sample ID	Al (ppb)	As (ppb)	Cd (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	Fe (ppb)	Mn (ppb)	Tl (ppb)	EC (mS/m)	pH	Temp °C	B.A mg $CaCO_3$/L	C.A mg $CaCO_3$/L	T.A mg $CaCO_3$/L	NO_3 (mg/L)	SO_4 (mg/L)
SW1	694.3	0.487	0.065	5.492	5.079	20.93	21.58	1531	290.98	0.0023	46.70	8.02	19.4	140.1	0.634	140.90	2.063	48.53
SW2	602.4	0.421	0.055	5.777	4.082	18.93	19.02	1244	270.80	0.0163	40.23	8.30	19.63	109.0	0.841	110.07	2.240	55.37
SW3	910.3	0.696	0.096	6.675	4.958	25.84	26.04	1852	531.86	0.0093	35.37	8.73	19.5	114.3	0.913	115.53	2.170	46.50
Min.	600.2	0.417	0.052	5.449	4.044	18.66	18.53	1202	270	0.002	35.2	7.5	19.2	108.2	0.619	109.3	2.00	46.1
Max.	912.8	0.7	0.098	6.989	5.125	26.99	26.78	1856	532.2	0.017	47	8.9	19.7	142.1	0.921	142.9	2.32	55.7
P value	0.001	0.001	0.001	0.007	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.140	0.3	0.001	0.001	0.001	0.162	0.001
CV %	0.4	1	5.3	5.0	0.9	3.0	2.3	2.2	0.3	8.7	0.7	4.5	0.9	1.2	1.4	1.2	4.5	0.8

Table 6.3 Mean values of organic parameter measured in water

Parameters	SW1	SW2	SW3	Min.	Max.
Cr (mg/L)	<0.003	<0.003	<0.003	<0.003	<0.003
Cr^{3+} (mg/L)	<0.010	<0.010	<0.010	<0.010	<0.010
Cr^{6+} (mg/L)	<0.002	<0.002	<0.002	<0.002	<0.002
Hg (mg/L)	<0.004	<0.004	<0.004	<0.004	<0.004
BTEX (µg/L)	< 2	< 2	< 2	< 2	< 2
Benzene (µg/L)	< 2	< 2	< 2	< 2	< 2
Toluene(µg/L)	< 2	< 2	< 2	< 2	< 2
Ethylbenzene(µg/L)	< 2	< 2	< 2	< 2	< 2
m + p Xylene (µg/L)	< 4	< 4	< 4	< 4	< 4
o-Xylene (µg/L)	< 2	< 2	< 2	< 2	< 2
TPH C10-C40 (µg/L)	< 10	< 10	< 10	< 10	< 10
C10 – C16 (µg/L)	< 10	< 10	< 10	< 10	< 10
C16 – C22 (µg/L)	< 10	< 10	< 10	< 10	< 10
C22 – C30 (µg/L)	< 10	< 10	< 10	< 10	< 10
C30 – C40 (µg/L)	< 10	< 10	< 10	< 10	< 10
Phenols (mg/L)	<0.020	<0.020	<0.020	<0.020	<0.020

6.3.2 Multivariate analysis (PCA and CA)

The cluster analysis carried out and depicted with a dendogram in Figure 6.3 revealed the presence of three main clusters thus cluster 1 made of water sample 1 (Water 1a, water 1b and water 1c), cluster 2 (water 2a, water 2b and water 2c) and cluster 3 (water 3a, water 3b and water 3c). a, b and c are herein used as triplicate samples from the same site. Water sample (WS) 1b and 1c had similarities at a level of 0.973. WS1b and WS1c had similarities with WS 1a at the level of 0.938. All water samples fetched from site 2 were all closely associated at the level of 0.964. Water samples 3 had similarity between water 3a and 3b. Water sample 3c was distinct and has similarities with water 3a and 3b at a level of 0.921. Cluster 1 and cluster 2 merge at the point of 0.718 to a major cluster. Cluster 1, 2 and 3 only shared similarities at the level of 0.626. This implied that the distinct clusters were formed at 0.921 and at this point water samples varied significantly in similarities. It was worth noting that, water sample 2 had all its samples similar unlike water sample 1 and 3 which had variation within its samples with respect to the physico-chemical properties of water measured and analysed.

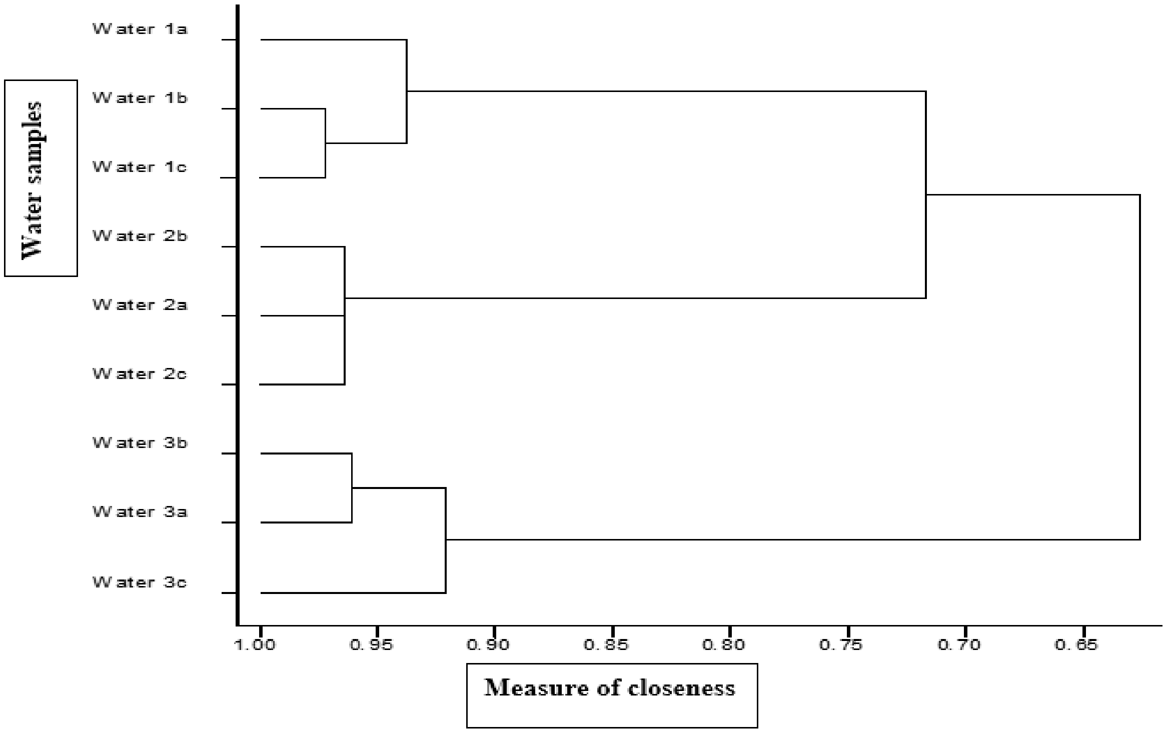


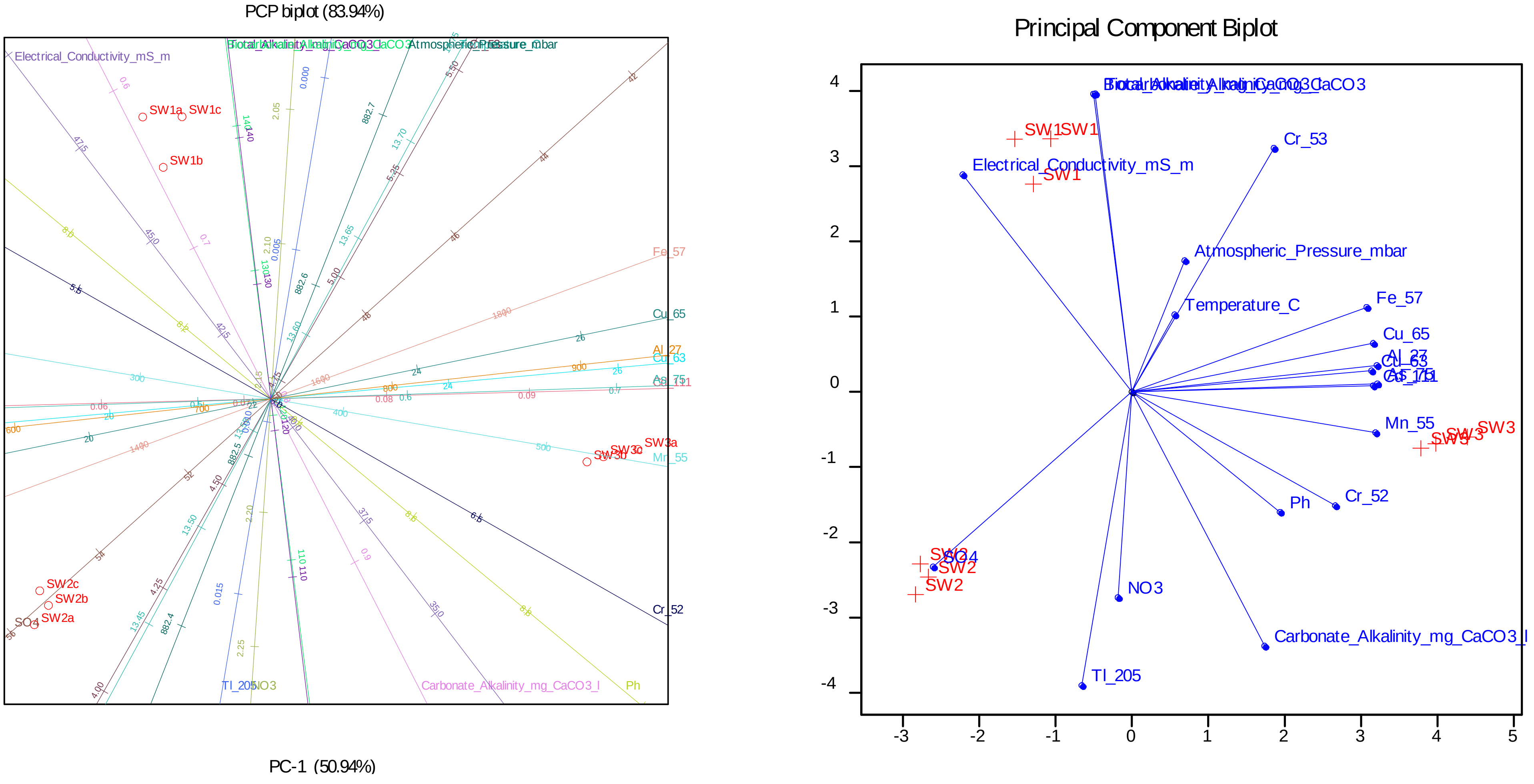
Figure 6.3 A Dendrogram for water sample results the rainy season in Steel Valley

The principal component biplot on the rainy season water samples revealed that, PC-1 (50.94%) contributed most of the variance and PC-2 contributed only 33% of the total variance. The total variation of PC-1 and PC-2 was 83.94%. The water samples plotted in the biplot indicate wide variation that exists between water sample sites. Most correlation between minerals was positive and strong.

The angle between the biplot axes in Figure 6.4 represents the correlation between variables, and lines in opposite directions indicate negative correlation. Hence, between any of the elements Fe, Cu, Al, Cu, Cd, Mn, Cr, and As, there was positive correlation. Similar observations were made for bicarbonate alkalinity and total alkalinity.

6.3.3 Correlation matrix

The correlation matrix in appendix 6 shows correlations between variables measured. Values with the negative sign implied that the variables of interest are negatively correlated while values that are positive signified positive correlation. From the correlation matrix, values assigned with * implied that there was strong correlation between the variables and the correlation between the variables.



(a) **(b)**

Figure 6.4 Principal component analysis biplot of water sampled during the rainy season in Steel Valley

From Appendix 7, it can be seen that Al, As, Cd, Cu, Fe and Mn all have strong positive correlation with each other. Physical parameters such as total alkalinity and bicarbonate alkalinity also showed strong positive correlation with each other. Carbonate alkalinity and bicarbonate alkalinity; Tl and bicarbonate alkalinity; total alkalinity and carbonate alkalinity; total alkalinity and Tl depicted a strong negative correlation while SO_4 and NO_3 mostly had a negative correlation with the metal parameters.

6.4 Conclusion

The results obtained during the rainy season were summarized and tabulated in this chapter, with the detailed results presented in Appendix 8 (water) and Appendix 9 (soil). The results generally showed traces of some metal concentrations but did not record any organic concentration in both water and soil samples. The results of the rainy season analysis followed a similar trend as the results obtained during the dry season, but concentrations were slightly elevated. Al in water samples ranged from 600.204 to 912.821 ppb, Cr ranged from 4.044 to 6.989 ppb and Mn ranged from 270.005 to 532.178 ppb. Other results from the water samples were Fe (1201.792 - 1855.668 ppb), Cu (18.528 – 26.986 ppb), As (0.417 - 0.7 ppb), Cd (0.052 - 0.098 ppb) and Tl (0.002 - 0.017 ppb). The soil samples followed a similar pattern with the metals recording the highest of concentrations. Al, Cr, Mn, Fe, Cu, As, Cd and Tl in soil ranged from 1861.89 - 13620.83 ppb, 129.66 - 154.22 ppb, 233.49 - 966.44 ppb, 14220.91 - 23201.4 ppb, 14.52 – 29.32 ppb, 2.19 - 4.01 ppb, 0.00 - 0.06 ppb and 0.47 - 0.59 ppb respectively.

CHAPTER 7: DISCUSSION

7.1 Introduction

This study sought to determine the physico-chemical properties and concentration of organic contaminants in ground and surface water around Steel Valley and also to determine the chemical profile of soils by determining some selected heavy metal of possible pollutants. The results are discussed in this chapter and compared to guideline values.

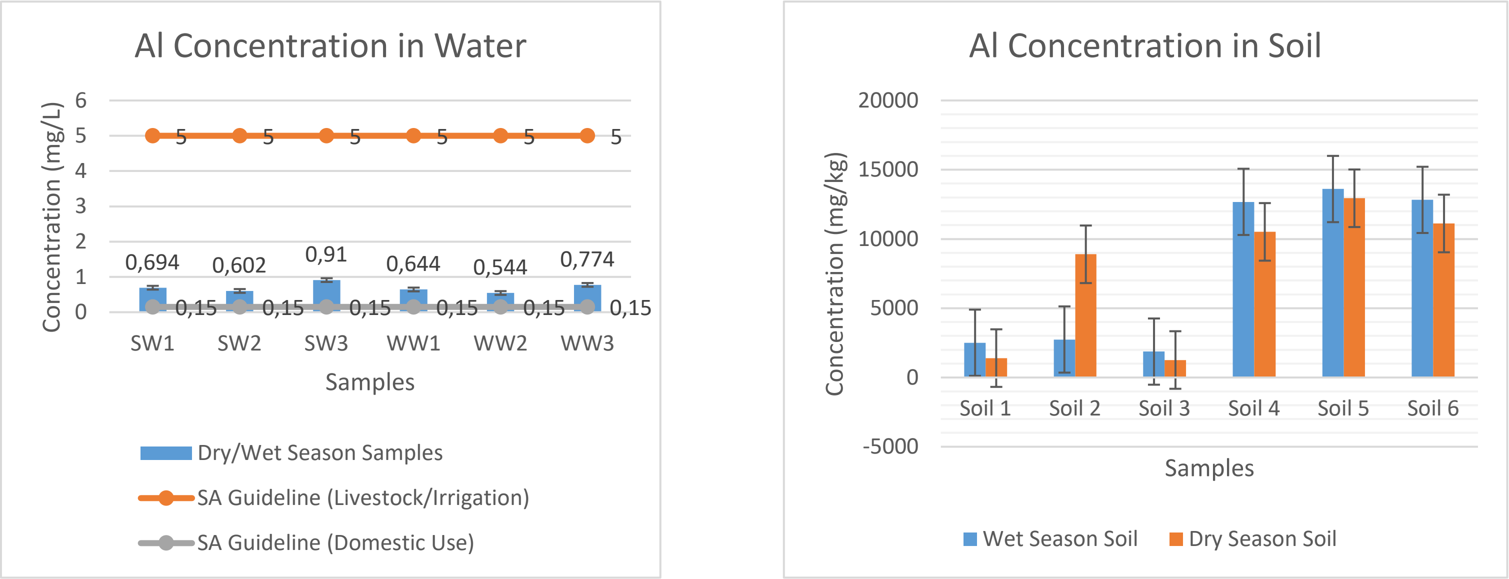
7.2 Statistical models adopted

The principal component analysis and cluster analysis was used as a pollution source identification. From the results of the principal component scores for water sample sites (both rainy and dry season), as indicated in Appendix 10, the principal component scores for sample site (3), was 4.79, 4.242 and 4.454, which signifies that this source site 3 is the greatest contributor of pollutants among the sample sites for water. The PCA performed and biplots from the dry season samples shows that PC-1 and PC-2 alone contributes over 87% (as shown in Figure 5.4 and Appendix 11 and 68.88% (as shown in Figure 5.2 and Appendix 12) of the total variance in water and soil samples respectively. Similarly, for the rainy season samples, both PC-1 and PC-2 accounted for 83.94% (as shown in Figure 6.4 and Appendix 13) and 66.10 % (as shown in Figure 6.2 and Appendix 14) of total variance in water and soil data respectively. The component vectors displayed in Appendix 15 explains the principal contributors of PC-1 and PC-2 in water samples. In the water samples, the greatest contributors (>0.3) to the 87.79 % and 83.94% variance were Mn, Fe, Cd, As, Al, and Cu. These parameters can be seen in Figure 5.4 and 6.4 clustering at the same quadrant as water sampling point (3). These parameters and site can also be seen as the main pollution source from the water data collected during the study. In Appendix 16, the principal contributors of PC-1 and PC-2 combined in soil samples are mainly Cr, Fe, Cu and Mn. These samples are thus the main contributors of pollution relative to other parameters analysed in soil samples. From the biplots in Figure 5.2 and 6.4, the sampling areas closely associated with the pollution source include soil site 3, 4, 5, and 6.

7.3 Concentrations of parameters

The concentrations of samples analysed varied between parameters and sampling points. Values obtained were compared to South African water guideline values, soil screening values and WHO standards for drinking water. Guideline or standard values provides appropriate estimations of acceptable levels of chemical and non-chemical constituents (be it from natural or anthropogenic source) that will pose less or no harm to end users (Carlon et al., 2007).

7.3.1. Aluminium



(a) **(b)**

Figure 7.1 Al concentration in water (a) and soil (b) samples from the study site compared to SA guideline values

All Al concentrations from the study site in water are above the water guideline value set for aluminium in domestic water use set by South African authorities as shown in Figure 7.1. This value however, pose no health threat but rather has aesthetic effects especially in the presence of other metals such as iron or manganese (DWAF, 1996a). The most significant aesthetic effect to consider in this case is discolouration caused by Al in the presence of iron or manganese. In this study, iron and magnesium were present in the water samples; therefore, some aesthetic effects will be seen or incurred when used for domestic purposes. However, presence of and exposure to aluminium in excess of 0.5 mg/L over a long period is discouraged by many researchers due to association with neurotoxicity and long severe aesthetic effects (Krewski et al., 2009; Qaiyum, Shaharudin, Syazwan, & Muhaimin, 2011). In this study all the water samples exceeding 0.5 mg/L for Al, with sample site (3) recording the most both in rainy and dry seasons. The levels of Al in this study - compared to studies conducted and recorded in the Environmental Master plan of ISCOR - have risen, although it is not clear if the sample sites are a direct match. Concentration of aluminium in water with near-neutral pH values usually range from 0.001 to 0.05 mg/L but rise to 0.5–1 mg/L in more acidic waters or water rich in organic matter. But, in this study, pH was generally near neutral with little or no organic matter; hence, aluminium should have been lower. Unfortunately, WHO does not have a clear guideline value for aluminium in drinking water but have health-based estimation that 0.9 mg/L will not cause any significant health effect to humans. It should be noted that levels of aluminium in water samples are below limits set for water used for irrigational and livestock feeding purposes.

Levels of Al in the last three (3) soil samples during both seasons are very high compared to the first three (3) samples as shown in Figure 7.1. Aluminium levels in soil could not be compared to soil screening values since it is not part of priority contaminants in the draft National Norms and Standards for the Remediation of Contaminated Land and Soil Quality of South Africa. The concentration levels and considering the fact that it is leachable into groundwater makes it a concern. It however important to note that leaching will not be favourable due to the near neutral pH levels of the study area.

7.3.2. Arsenic

Arsenic levels in the water samples were within acceptable levels of the South African guidelines and internationally recognized guidelines. Thus, arsenic levels do not pose any risk to human health, nor does it pose any threat to livestock. The water can also be used for irrigation. As levels in soil samples (Figure 7.2) were also below the soil screening values set for remediated soils and lands.

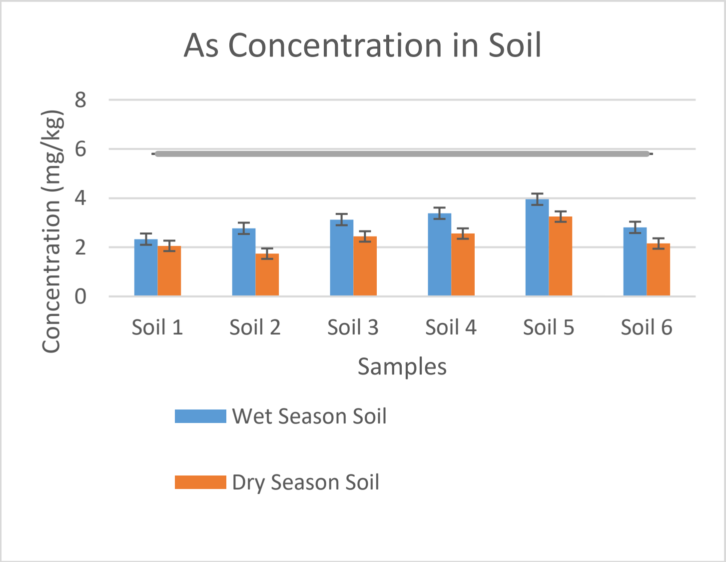


Figure 7.2 As concentration in soil samples from the study site compared to guideline values

7.3.3. Chromium

Chromium concentrations measured in water samples in the form of total chromium, Cr (III), Cr (VI) indicate that the water is suitable for domestic or agricultural purposes. Cr (VI) concentration in the water samples were <0.002 mg/L, within the 0.05 mg/L target set by South African regulatory authorities for water bodies. Total chromium levels for all the samples were below 0.003 mg/L, and, thus, favourably compared to WHO standards (0.05 mg/L). Thus, total chromium before speciation is a very good range and so poses no health effects. Total Cr in the form of Cr 52 and Cr 53 were also considered and again, their concentrations pose no significant health hazard.

Leachable chromium levels in the form of Cr 52 and 53 (averagely 120 mg/kg) in soil samples in Figure 7.3 is not alarming, considering the fact that the measured concentrations were total chromium which could be accounted for by the presence of Cr (III) (acceptable screening value in South Africa is 46 000 mg/kg) and not necessarily Cr (VI).

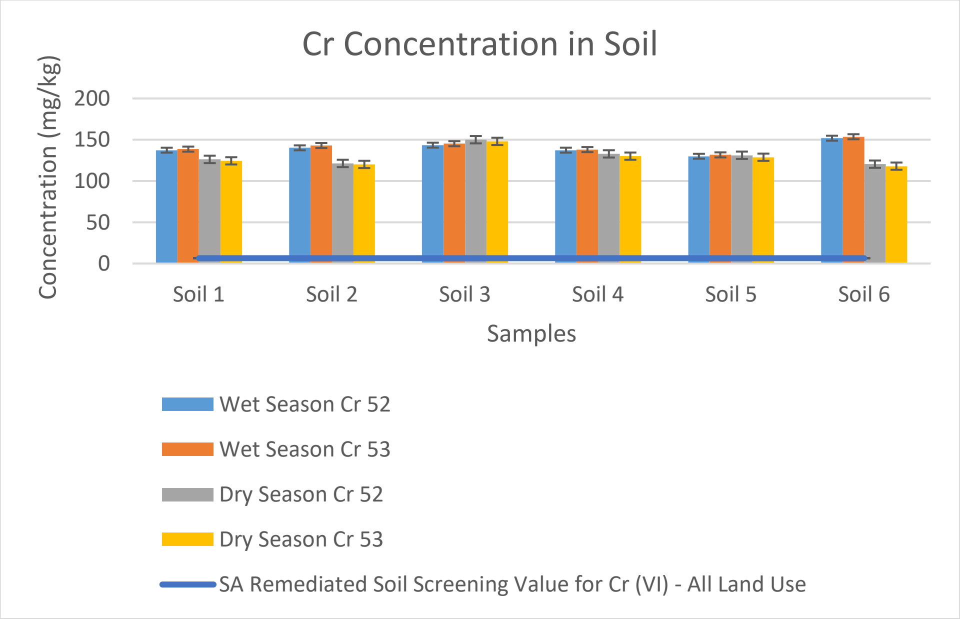
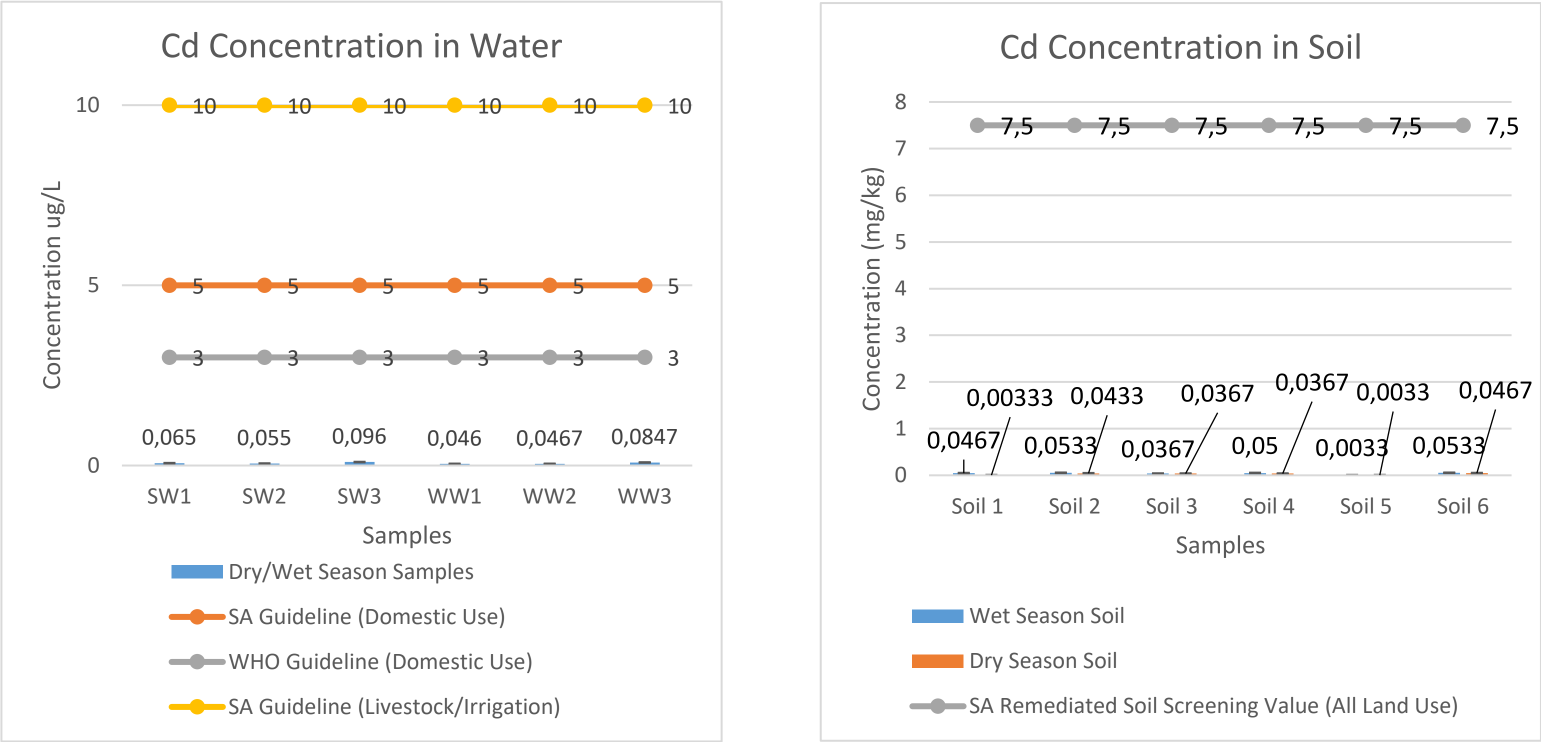


Figure 7.3 Cr concentrations in soil samples from the study site compared to soil screening values

7.3.4. Cadmium



(a) (b)

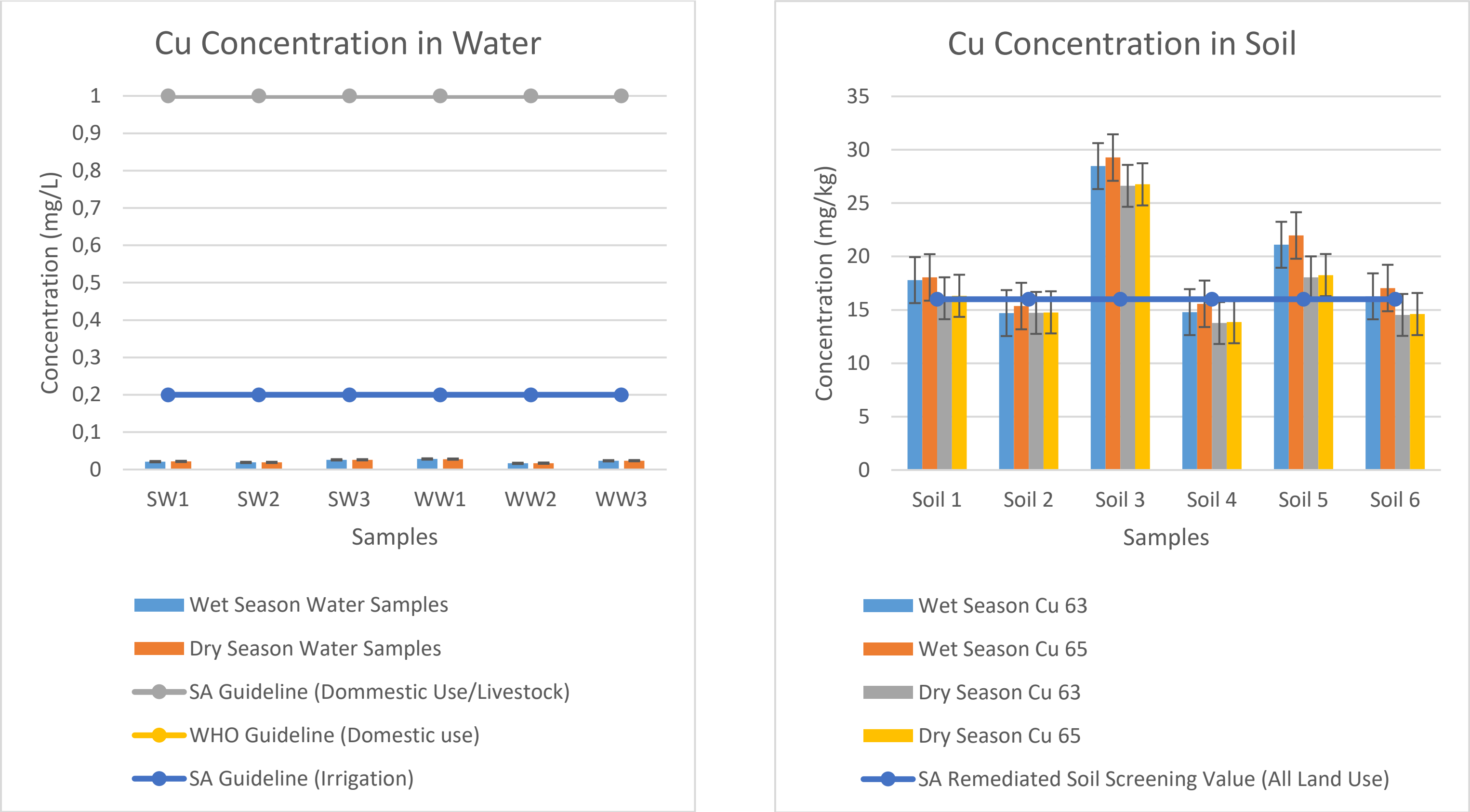
Figure 7.4 Cd concentration in water (a) and soil (b) samples from the study site compared to guideline values

Cadmium concentrations analysed in both water and soil were minimal compared to the SA guidelines and screening values as well as the WHO guidelines (Figure 7.4). The values obtained pose no health risk to humans and will have no effect in the soil for plant uptake looking at the concentrations recorded from all the study sites.

7.3.5. Copper

Apart from the target water quality range (0 – 1 mg/L) provided by South African authorities regarding water for domestic use, there are four other ranges that is provided on copper content in water samples with its effects. The copper content analysed in all water samples was well within the guideline values for South Africa and international standards (Figure 7.5).

Cu concentrations in soil were above the target values for remediated soils. In sample three (3) for instance, the value of Cu is twice the guideline. Soil copper toxicity is known for plant root damage and reduction in crop yield (Xu et al., 2006). According to Xu et al., (2006), copper levels of 100 mg/kg can reduce crop yield by 10%, and about 50% reduction in yield for Cu levels between 300 – 500 mg/kg. Copper levels in the soil, especially at site 3 (Figure 7.5) although above target levels, are not a serious course of concern.



(a) (b)

Figure 7.5 Cu concentration in water (a) and soil (b) samples from the study site compared to guideline values

7.3.6. Iron

Fe Concentrations in water samples from the study site have been summarized in Figure 7.6. The concentrations exceed the water quality target. The concentrations are however within the range for agricultural use such as irrigation.

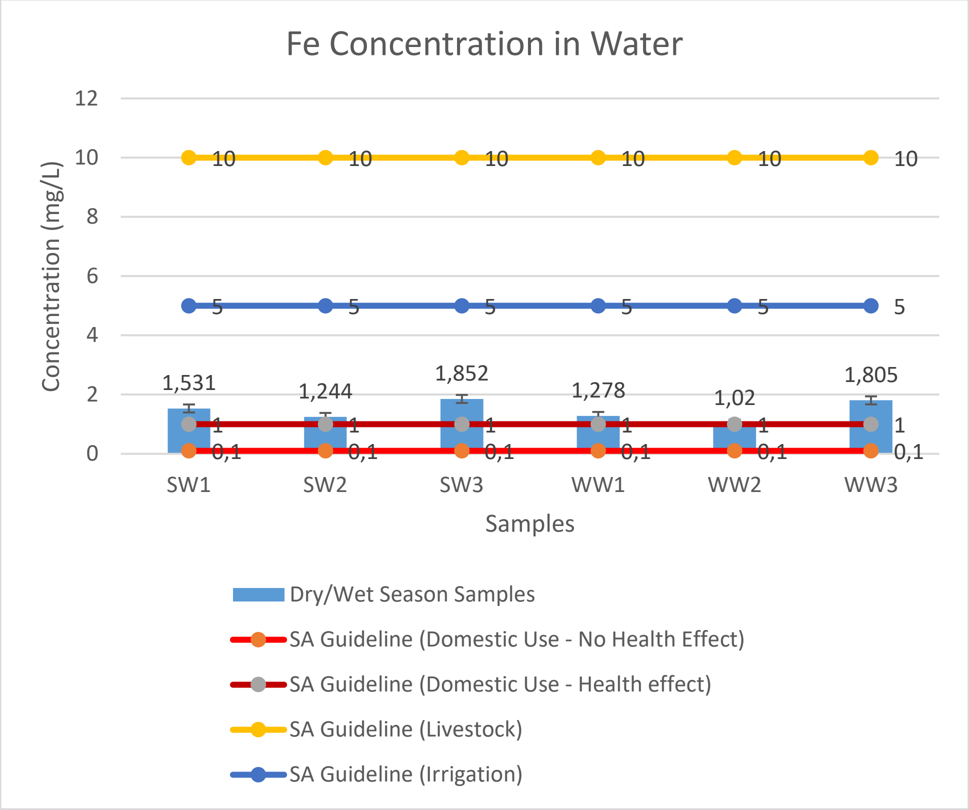


Figure 7.6 Fe concentration in water samples from the study site compared to guideline values

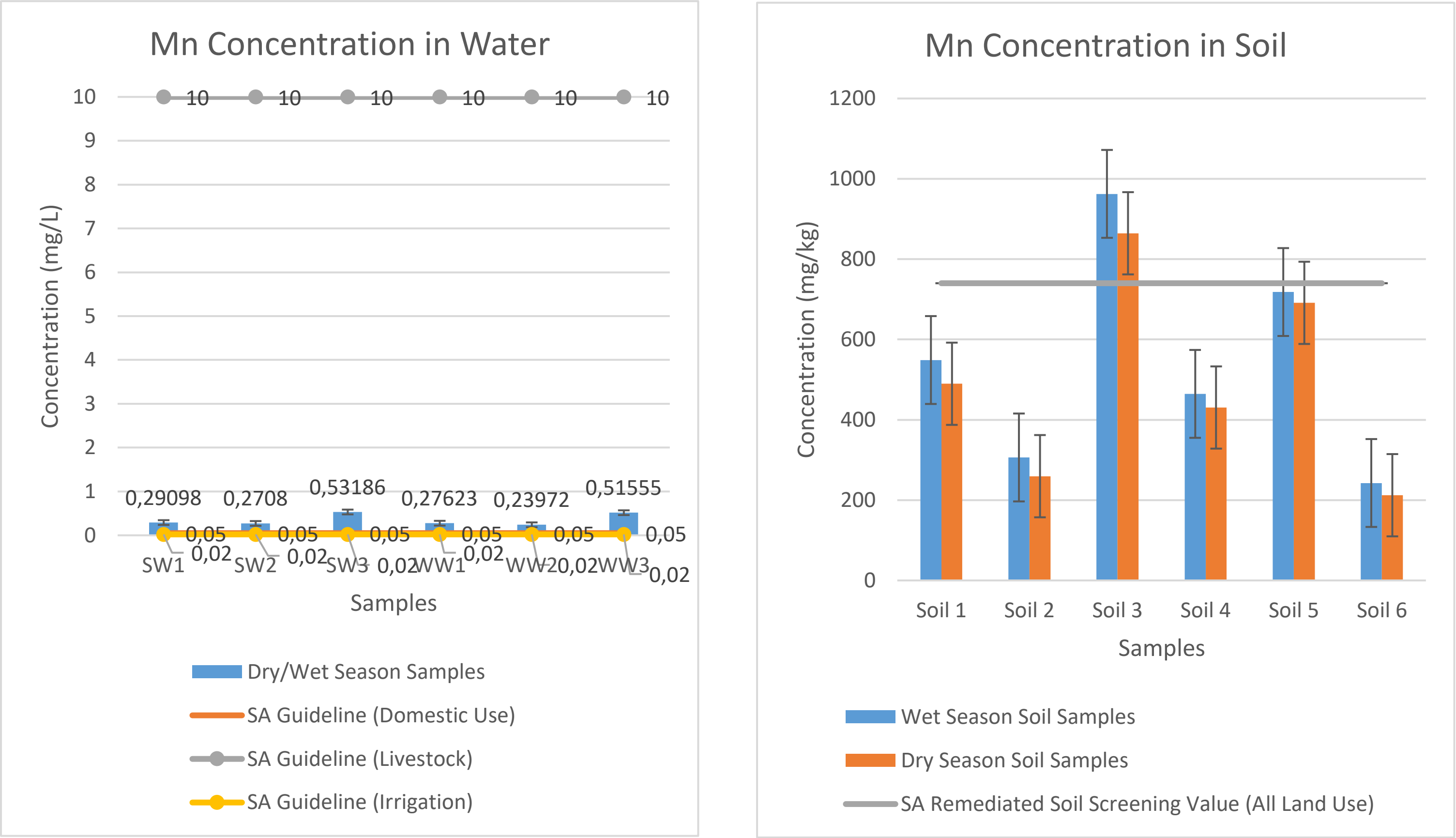
Iron concentrations classified by South Africa authorities' rates iron levels between 0 0.1 mg/L as ideal so as to pose no impact on taste, other aesthetics or health. The guidelines also state that levels between 0.1 - 0.3 mg/L will cause slight effects on taste and aesthetic quality but have no health implications. The authorities further indicate that levels between 1 – 10 mg/L of iron may have adverse health effects in young children, and sensitive individuals. Iron concentrations in the water samples, thus, indicate that the water may pose a health risk to children. Iron concentrations in the water was one of the parameters flagged as a serious concern by the Environmental Master plan of ISCOR, where concentrations of iron in dam water was as high as 57 mg/L and averaged around 0.8 mg/L in other sampling points.

Iron concentrations in the soil samples of this study ranged from 11,587 to 23201 mg/kg. Although there is no clear guideline value on iron in soil by South African authorities or WHO, the USEPA estimates typical iron concentrations in soil ranging from 20 000 mg/kg to over 500 000 mg/kg. These estimates therefore place the analysed iron levels at the study site as very low compared and unlikely to cause harm. However, it raises concerns as to whether this iron can be leached into underground water and possibly cause harm if used for domestic purposes.

7.3.7. Mercury

Mercury levels were below detection in all the samples from the study site.

7.3.8. Manganese



(a) **(b)**

Figure 7.7 Mn concentration in water (a) and soil (b) samples from the study site compared to guideline values

Manganese levels were reported in the Environmental Master plan as high (ranging 3.16 – 4.87 mg/L) and so were deemed a risk to humans. The current study shows that Mn pollution is still a problem, although concentrations are reduced. The Mn levels were highest in sample site (3) across both seasons and the overall concentration exceeds the water quality targets of both South Africa and WHO (Figure 7.7). In terms of soil, the Mn levels from the study ranged from 202 mg/kg to 966 mg/kg which means this is within the South Africa guidelines, except for sample site 3.

7.3.9. Nitrate as NO_3

Nitrate levels were all within SA guidelines and WHO guidelines (Figure 7.8). The nitrogen contents recorded in the soil samples were as low, as were the levels found in the water samples.

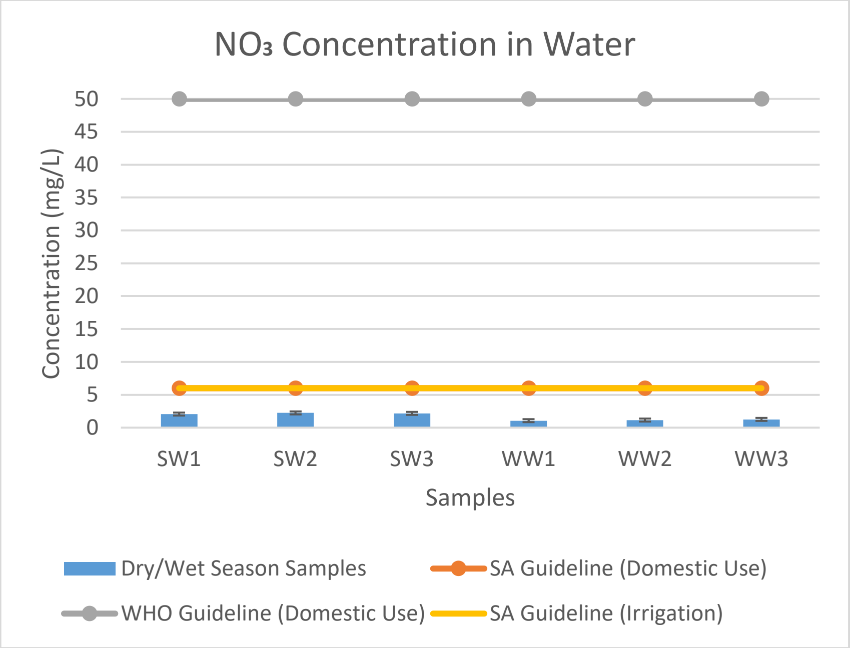


Figure 7.8 NO_3 concentration in water (a) samples from the study site compared to guideline values

Organic Parameters

Phenols, total petroleum hydrocarbons (C_{10}-C_{40}), Benzene, toluene, Ethylbenzene, m + p Xylene, and o-Xylene were all tested in water samples and were below detectable limits.

Physical indicators and rainfall pattern of the study area

Both the water samples and soil samples were near neutral pH levels, although the pH could rise to slightly alkaline, it didn't exceed 9.00. The impact of the near neutral soil could explain the reason behind less leaching of iron, considering the concentration in the soil samples and water samples. The levels of EC (@ 25 ^{o}C and TDS) throughout the study were within the acceptable 450 mg/L (for TDS) and 70 mS/m (for EC) laid out in the SA guidelines for drinking water. However, some samples of water sampled during rainy season recorded EC levels that exceeded the prescribed level for irrigation water (<40 mS/m). This could be attributed with the rise in EC and salinity levels during rainy season (Moore, Richards, & Story, 2008) rather than an indicator of pollution.

Rainfall characteristics and erosivity are of utmost importance in agriculture study areas like the case of Steel Valley, Vanderbijlpark because it plays a major role in soil transportation (Zorn & Komac, 2013). Figure 7.9 shows the annual rainfall for the study area, as well as the three-year moving average for the last thirty-five years.

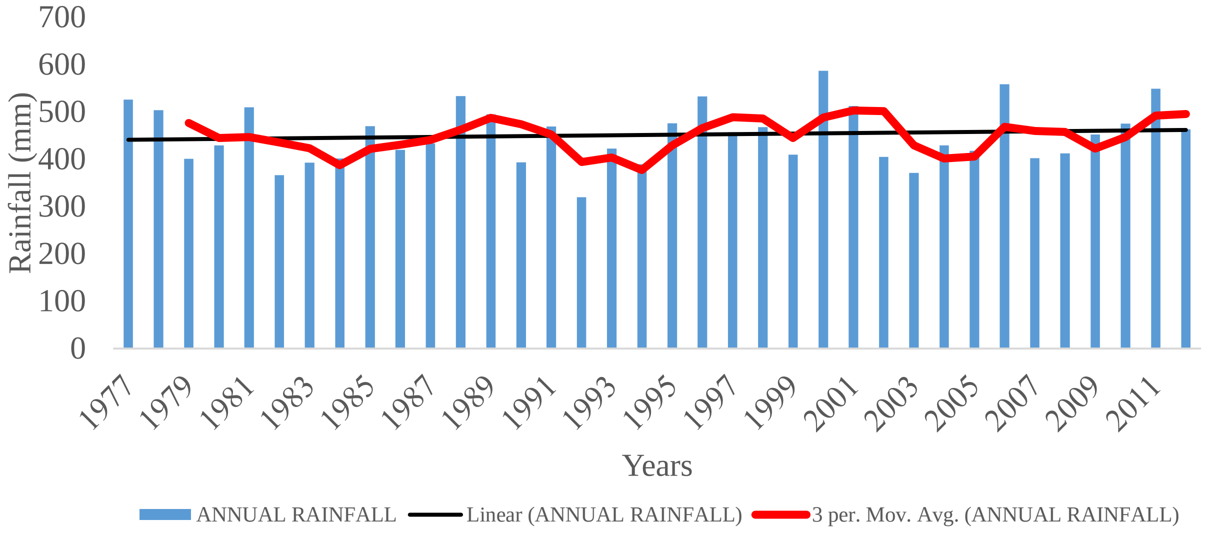


Figure 7.9 Annual Rainfall Variation and 3-year Moving Average for thirty-five years for Vanderbijlpark

The average annual rainfall for the last thirty-five years was 451 mm. During the period it revealed that the lowest rainfall recorded at the Steel Valley occurred in 1992, with an amount of 319 mm, followed by 2002 with an amount of 370 mm while the highest rainfall recorded during the period occurred in 2000 with an amount of 586 mm and the second highest occurred in 2006 with an amount of 558 mm (Figure 7.9). With an average of 450 mm rainfall, it implies there is adequate soil moisture to support crop production at Steel Valley hence plants susceptible to nutrient and heavy ions uptake.

Sulphate

Levels of sulphate in water samples were within range compared to South African standards (Figure 7.10).

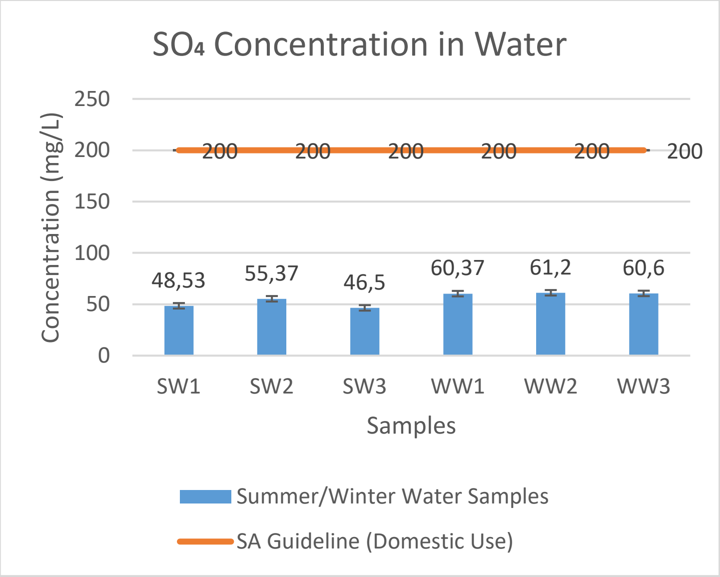


Figure 7.10 SO_4 concentration in water samples from the study site compared to guideline values

Thallium

Thallium concentrations were minimal with no significant threat to end users.

7.4 The impact of the remediation on soil and water bodies in Steel Valley

Prior to remediation, soil and water samples collected from the steelworks' premises and around the study site had metal and organic pollutants above guideline values, an account that was documented over a period in the Environmental Master plan. There has been significant change in concentrations, comparing the results obtained in this study to South African and WHO guideline values, which could either be attributed to natural attenuation or the remediation. The groundwater results were slightly higher in concentrations than the samples taken from the dam. This could either be because of the close proximity of the dam to the steelworks (point source of pollution) than the groundwater sampling points. It is however important to note that the remediation activities took place within the steelworks' yard only. This observation could also be because of the remediation targeting groundwater and soil, but not surface water specifically. Generally, metal concentrations found in the soil samples were higher than their respective concentrations in the water samples.

7.5 The impact of the remediation on agriculture and the Steel Valley community

Although the study did not conduct an investigation to establish a correlation between the remediation and its impact on agriculture, it could be observed that the remaining small holding farmers are focusing on maize cultivation and relying on fertilizer to boost the ‘contaminated’ soil. None of the farmers own livestock, possibly due to the fear that the animals will be become ill from the ‘contaminated’ underground water. Families at Steel Valley no longer rely on groundwater for domestic use, as the wells have been permanently sealed (by ISCOR) and their homes are now connected to the municipal water supply.

7.6 Conclusion

The statistical models discussed in this chapter placed emphasis on the pollution sources in relation to sample points and parameters. The pollutant concentration was higher in water sample point 3 and was slightly higher in soil sample points 4, 5 and 6. The charts used also demonstrated how the concentrations compare to guideline values. The physical properties of the study site and rainfall pattern were also discussed, shedding light on the adequate rainfall received in the study area over the years, and its potential to contribute to nutrient uptake by plants.

CHAPTER 8: CONCLUSION & RECOMMENDATIONS

8.1 Introduction

The study conducted an assessment of water and soil samples for organic and inorganic pollutants, using the results as yardstick against standard guideline values to ascertain quality. In addition, the results were also compared to the environmental master plan to ascertain the effectiveness of the soil and water remediation measures undertaken in Steel Valley, Vanderbijlpark. The study employed laboratory methods such as ICP-OES, colorimetric methods, turbidimetric methods, automated hydrazine reduction methods, gas chromatography and direct photometric methods. Due to cost constraints, the research was confined to three water and six soil samples over the course of two seasons; dry and rainy seasons.

8.2 Physico-chemical and organic assessment

Although thermal pollution may affect the biochemical characteristics of water bodies, especially dissolved oxygen in surface water, the temperatures recorded among the water samples in this study indicated that thermal pollution is not a problem. The range recorded for temperature in the dry season was 13.1 – 13.9 ^{o}C and in the rainy season 19.2 – 19.7 ^{o}C. Such ranges and temperatures would not have any significant impact on the biological and chemical characteristics of water in the area. Temperatures recorded during the rainy season were slightly higher than temperatures in the dry season, which could be attributed to the average amount of sunshine received during summer (which is the rainy season). Prior to sampling, the average atmospheric temperature in May (before dry season sampling) was 13 ^{o}C, while October (before rainy season sampling) recorded an average of 20 ^{o}C.

The study found no significant difference in pH levels between the two seasons, with the pH near neutral across both. The rainy season’s water sample results were slightly basic, which could be attributed to rain and runoff water entering the soil and water bodies. That said, it must be noted that the ideal pH levels of water and soil in the environment may vary. In the area under study, the recorded pH for the water samples falls within the range accepted by the WHO for drinking water, and so it can be concluded that, the water bodies tested in this study, with respect to pH, are suitable for drinking purposes. As with most remediation techniques, the remediation system adopted by Arcelor Mittal SA was pH dependent, that is, they sought to raise the pH levels from acidic to neutral. In particular, the ideal pH for nutrient uptake by plants differs from crop to crop but most soil nutrients are available for uptake when the soil pH range is from 5.5 to 6.5 (Ronan, 2007). As the pH recorded in this study was slightly above neutral, this indicates that the pH is slightly outside of the range for optimum nutrient uptake by plants.

The study found that Cr, Cr^{+6}, Cr^{+3}, As, Tl, SO_4, NO_3 and Cd were all within acceptable ranges and so pose no threat to domestic or agricultural users. In addition, Hydrocarbons, BTEX, phenols and Hg were not detected in any of the samples. However, Fe concentrations exceed water quality targets for domestic use, although they were within the acceptable range for agricultural use. Considering the pH levels in the area (>5.5) and the concentration of Fe in the soil samples, uptake of Fe by plants should not be negatively affected. That said, at this Fe concentration level, there may be adverse health effects in young children, and sensitive individuals if this water is consumed over a long period of time. But, importantly there has been drastic reduction in iron concentrations around the Steel Plant, if current results are compared to results prior to remediation.

Copper is an essential element for plant growth and healthy functioning of soil biological systems (Maderova, Watson, & Paton, 2011). However, in terms of posing a risk, concentrations of Cu are also related to the pH and conductivity (Ginocchio, Rodríguez, Badilla-Ohlbaum, Allen, & Lagos, 2002). On this basis, it was found that Cu concentrations are no longer a threat in water and soil in Steel Valley as concentrations of the metal were within guideline values for all the water samples. However, Cu concentrations in soil averaged above the accepted target values for remediated soils. As the target value used (16 mg/kg) is for all land use, this does not mean the excess copper will be a threat to plants. It was determined that the concentration of Cu in the soil, when taking pH levels and electrical conductivity into account does not contribute to Cu toxicity.

The study found that Al concentrations were in excess of 0.50 mg/L in all the water samples, therefore making its exposure in drinking water over a long period potentially harmful. However, the level Al in the water samples will not pose any health hazard if used for irrigation purposes. Aluminium concentrations close to the surface water source and steel works were higher than samples taken further away from the steel works and surface water source. Although Al is a naturally occurring element, the element in its ionic forms after solubilization in acidic soil (usually < 5 pH) can be very harmful to plants (Zheng, 2010). Naturally occurring Al in soil can range from 7 000 mg/kg to 100 000 mg/kg, based on these estimates, the research concluded that Al in soil is unlikely to pose a threat to plants.

It can be said, based on that data presented in this study that the remediation process has contributed positively to the drastic reduction of Mn concentrations around the steel works. Prior to remediation, the range was 3.16 – 4.87 mg/L, whereas it is now 0.24 – 0.53 mg/L. Despite this, concentrations still exceed acceptable limits for water. For example, the surface water source tested in this study, which was located very close to the steel plant, recorded over ten times the acceptable limit of Mn. Such levels of Mn exposed to humans directly or indirectly could lead to Mn neurotoxicity (Crossgrove & Zheng, 2004). Soil sampled close to the steel plant and the surface water body also had the highest levels of Mn pollution, also above acceptable levels of Mn.

The current concentration of parameters analysed in this research, stabilized and near neutral pH of water bodies in the area draws the conclusion that the remediation efforts by Arcelor Mittal SA were mostly successful. Adjusting an acidic pH to neutral or slightly basic is an essential part of all forms of chemical remediation and facilitates bioremediation. Apart from pH, mobility reduction is also an essential factor of efficient remediation.

8.3 Legislation & Remediation

During the early post-apartheid environmental struggles, researchers believed that the environmental movement in South Africa was fragmented. Organizations or societies either lobbied around the discourse of sustainable development or the discourse of environmental justice (Cock, 2006). These divisions were evident in the Steel Valley case. In particular, it became clear that one of the problems with the discourse of sustainable development was its vagueness while environmentalism seemed to focus on conservation but not social needs. Despite this, the environmental legislation and activists did manage to force ISCOR to undertake remediation of Steel Valley, with the importance of mass lobbying highlighted. In this regard the work of the Steel Valley Crisis Committee (SVCC) and the Vaal Environmental Justice Alliance (VEJA) stand out.

The SVCC started its mobilization in 2001 to indict ISCOR for the pollution of Steel Valley. The SVCC's strategy was to unite the local community around the environmental issues and so transcend racial and class divisions to unite behind a common cause (Cock, 2006). That said, the legal actions of the SVCC did not result in a successful judgment as thirteen out of the sixteen litigants had their properties bought out by ISCOR. Thus, while this resulted in justice for some, it was not justice for all and the pollution, at that stage was not cleaned up. In this regard, VEJA opted for mobilization of communities to lobbying against environmental racism, using the Bill of Rights Section 24 and the National Environmental Management Act to support their activities. The core of their argument was that people have rights of access to natural resources (such as groundwater and soil) and to be able to participate in decision making.

Local residents, with the help of VEJA, initially failed to force ISCOR to undertake any remediation or, later release the master environmental plan. As a result, they joined forces with the Centre for Environmental Rights (CER) and academics. On the basis of rights and responsibilities conferred in the Constitution of the Republic of South Africa (1996), the Promotion of Access to Information Act No 2 of 2000, the National Environmental Management Act No 107 of 1998, the Waste Act No 59 of 2008 and the National Water Act No 36 of 1998, the courts were once more approached and in the end the collaborative efforts of these stakeholders forced ISCOR to remediate Steel Valley.

There has been a laudable improvement in environmental legislation in South Africa. During the Steel Valley environmental 'battle' it became clear that the quest for environmental justice shifted away from a traditional authoritarian concept of 'environmentalism' which was far too concerned with the conservation of threatened species and resources, to include urban, health, labour and development issues. Environmental justice must be linked to social justice that values all forms of life, against the interests of wealth, power and technology. The case of Steel Valley demonstrated that mass lobbying for environmental justice can challenge the abuse of power where poor communities suffer the effects of environmental damage caused by industrial giants.

8.4 Research questions

The study took all necessary steps to answer all the research questions and summarized below:

Research Question 1:

What are the concentrations of inorganic contaminants specifically Fe, Cr^{+6}, Cu, Tl, Cd, Cr^{+3}, As, Hg, SO_4, NO_3, Al, Mn and organic contaminants (hydrocarbons, BTEX, phenols) in Steel Valley's water bodies?

The inorganic contaminants analysed for were mostly below guideline values except Fe, Mn, Al and Cu while organic contaminants (hydrocarbons, BTEX, phenols) were not detected in the water bodies. The mean concentration of Fe in water was 1814.272 ppb during the dry season and 1542.191 ppb during the rainy season. Cr^{+6}, Cr^{+3} and Hg were below 0.002 mg/L, 0.010 mg/L and 0.004 mg/L respectively. The mean concentration of 653.676 ppb and 735.685 ppb were recorded for Al during the dry season and rainy season respectively. Cu recorded mean values of 22.7 ppb (in rainy season) and 21.9 ppb (in dry season). Tl, Cd and Mn recorded highest mean concentrations during the rainy season, recording 0.009 ppb, 0.072 ppb and 364.547 ppb respectively. As concentrations was a little above 0.5 ppb in both seasons. SO_4 concentrations averaged 60.7 mg/L during the dry season and 50.13 mg/L during the rainy season. NO_3 in water was 2.16 mg/L during the rainy season and 1.16 mg/L during the dry season.

Research Question 2:

What are the major, minor and trace elements in the soil samples, and their concentrations?

Trace elements in soil are elements with low concentrations (usually 0.1%) and could be elevated from natural processes and human activities (Bañuelos & Ajwa, 1999). The inorganics analysed in the study were all below 100ppm hence they could be classified as trace elements. Cr, Mn, Cu, As, Cd, Tl and NO_3 all recorded less than 1 ppm in the soil samples. Al recorded 7.688 ppm during the dry season and 7.706 ppm during the rainy season. The average trace concentration of Fe in soil was 15.208 ppm and 17.782 ppb during the dry season and rainy season respectively. SO_4 concentrations averaged 1.701 ppm in June and 1.975 ppm in October.

Research Question 3:

What impact has the remediation had on the soil and groundwater in Steel Valley?

The study concluded that, remediation has had a positive impact on the soil and groundwater, considering the state of water being unacceptable prior to remediation. The comparative analysis between current concentrations and concentrations of pollutants prior to remediation suggests that remediation was able to drastically reduce the concentration of inorganic pollutants as well as reduce organic pollutants levels down to undetectable levels.

Research Question 4:

Does the current chemical profile of the soil and groundwater pose any threat to end users?

The study has demonstrated (using the results obtained and guideline values) that water in Steel Valley may not be ideal for domestic use and may have health implications if users are exposed to it for a long period of time. However, the water will not pose any threat when used for agricultural purposes and will pose no threat to plants. The soil contains the right concentration of trace elements to support plant growth.

8.5 Recommendations

Due to the current level of As, it will be necessary to monitor As in soil in future studies close to or in the same study area. There needs to be a natural attenuation focusing on Fe, Mn, Al in groundwater and Cu, Mn in soil to further reduce the concentrations. The study suggests that landowners can use the land for crop farming but should not use the water for household activities. Crop farming or planting on the land may further reduce the excess inorganics in the soil. Authorities should consider a more coherent and systematic approach to polluting activities, as this particular case was allowed to pollute the area for a very long time.

The study however, is limited as the entire site was not evaluated due to the significant cost involved. It is therefore recommended that further studies to assess the cost involved and also extend sampling to sediments of nearby rivers, soil and water samples within the Steel Works premises and other surrounding communities is undertaken.

8.6 Conclusion

Physico-chemical and organic assessments were done using analytical techniques and thereafter statistically analysed to give a fair representation of the current state of pollution at Steel Valley. Measured against the guideline values regarding allowable limits of soil and water pollution, meant that this study can state, within the scope of the study that remediation appears to have rendered the water and soil bodies tested safe in terms of their chemical profile. Generally, the remediation has had a positive impact on the soil and groundwater in Steel Valley. The water is safe for irrigation and the soil chemically safe for crop farming. Thus, it can also be said that the change in the environmental legislative regime post-apartheid in South Africa has, in this case, served its purpose.

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APPENDIX

APPENDIX 1

Appendix 1: Sample field log sheet

Project period:______________________________

Sampling Point/Number: ______________________

Location:___________________________________

Coordinates:________________________________

Date and time started: _______________________

Date & time completed: ______________________

Sampling method:____________________________

Size/Type of sample:_________________________

Weather Cond.: _____________________________

____

____

____

Sample Pack Amount__________________________

Triplicate Sample Number	Description	Notes

APPENDIX 2

Appendix 2: Correlation matrix of physico-chemical properties of soil sampled in Steel Valley during the dry season

Al	-														
As	0.33	-													
Cd	-0.22	-0.83*	-												
Cr 52	-0.44	0.42	-0.18	-											
Cr 53	-0.47	0.39	-0.17	1.00*	-										
Cu 63	-0.49*	0.25	-0.14	0.80*	0.81*	-									
Cu 65	-0.49*	0.25	-0.15	0.80*	0.81*	1.00*	-								
EC	0.44	0.52*	-0.06	0.22	0.19	0.11	0.11	-							
Fe	-0.27	0.69*	-0.61*	0.80*	0.79*	0.84*	0.84*	0.18	-						
Mn	-0.39	0.60*	-0.53	0.82*	0.82*	0.85*	0.86*	0.10	0.97*	-					
NO_3	-0.27	0.05	-0.14	-0.07	-0.07	0.11	0.12	-0.12	0.13	0.15	-				
pH	-0.56*	-0.37	-0.08	0.03	0.07	0.16	0.17	-0.92*	0.10	0.20	0.00	-			
SO_4	-0.07	0.33	-0.04	0.44	0.43	0.66*	0.66*	0.68*	0.53*	0.45	0.16	-0.51	-		
Temp	-0.69*	-0.79*	0.61*	0.08	0.12	0.13	0.13	-0.66*	-0.24	-0.08	-0.15	0.68*	-0.34	-	
Tl	-0.26	0.44	-0.77*	0.18	0.20	0.37	0.38	-0.35	0.63*	0.61*	0.45	0.46	0.06	-0.18	-
	Al	**As**	**Cd**	**Cr 52**	**Cr 53**	**Cu 63**	**Cu 65**	**EC**	**Fe**	**Mn**	**NO_3**	**pH**	**SO_4**	**Temp**	**Tl**

Appendix 3

Appendix 3 Correlation Matrix of the dry season water parameters

Al	-																		
As	0.85*	-																	
A.P	0.60*	0.63*	-																
B.A	-0.82*	-0.86*	-0.93*	-															
C.A	-0.61*	-0.37	-0.45	0.53	-														
Cd	0.78*	0.75*	0.73*	-0.85*	-0.58	-													
Cr 52	0.83*	0.95*	0.74*	-0.92*	-0.46	0.79*	-												
Cr 53	0.82*	0.86*	0.37	-0.66*	-0.45	0.64*	0.88*	-											
Cu 63	0.48	0.46	-0.29	-0.04	-0.13	-0.01	0.32	0.64*											
Cu 65	0.49	0.50	-0.28	-0.06	-0.08	0.04	0.36	0.68*	0.99*	-									
EC	-0.89*	-0.91*	-0.87*	0.99*	0.58	-0.85*	-0.94	-0.74*	-0.19	-0.20	-								
Fe	0.92*	0.96*	0.72*	-0.92*	-0.51	0.79*	0.98*	0.88*	0.42	0.44	-0.96*	-							
Mn	0.88*	0.93*	0.84*	-0.98*	-0.54	0.85*	0.97**	0.79*	0.22	0.24	-0.99*	0.98*							
NO_3	0.50	0.59	0.91*	-0.85*	-0.54	0.73*	0.64	0.25	-0.32	-0.33	-0.79*	0.62*	0.75*	-					
pH	-0.89*	-0.96*	-0.75*	0.93*	0.47	-0.73*	-0.94*	-0.80*	-0.39	-0.40	0.96*	-0.97*	-0.96*	-0.68*	-				
SO_4	-0.58	-0.39	0.10	0.16	0.47	-0.09	-0.37	-0.63	-0.87*	-0.82*	0.30	-0.48	-0.31	0.16	0.40	-			
Temp	-0.27	-0.16	0.25	-0.04	0.13	-0.18	-0.23	-0.59	-0.41	-0.48	0.03	-0.21	-0.11	0.43	0.04	0.40	-		
Tl	0.10	0.21	0.83*	-0.61*	-0.20	0.50	0.35	-0.11	-0.74*	-0.73*	-0.48	0.26	0.45	0.83*	-0.31	0.57	0.45	-	
T.A	-0.81*	-0.86*	-0.93*	1.00*	0.53	-0.84*	-0.92*	-0.66*	-0.04	-0.06	0.99*	-0.92*	-0.98*	-0.85*	0.93*	0.17	-0.04	-0.61*	-
	Al	**As**	**A.P**	**B.A**	**C.A**	**Cd**	**Cr 52**	**Cr 53**	**Cu 63**	**Cu 65**	**EC**	**Fe**	**Mn**	**NO_3**	**pH**	**SO_4**	**Temp**	**Tl**	**T.A**

APPENDIX 4

Appendix 4: Raw data for water samples during the dry season

Sample	pH	EC mS/m	Temp. °C	T.A mg CaCO3/L	B.A mg CaCO3/L	C.A mg CaCO3/L	A.P mbar	Al (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Mn (ppb)	Fe (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	As (ppb)	Cd (ppb)	Tl (ppb)	SO_4 (mg/L)	NO_3 (mg/L)
WW1a	7.91	33.8	13.2	102	101	0.77	853	644.045	4.384	4.437	273.127	1213.763	26.367	26.31	0.528	0.059	0.003	60.5	1.08
WW1b	7.9	33.2	13.9	100	99.1	0.89	853.1	643.365	4.308	4.025	280.529	1320.005	30.629	29.1	0.561	0.03	0.003	60.1	1.1
WW1c	7.91	34	13.9	102	100.8	0.987	853	644.111	4.531	4.402	275.03	1301.521	27.371	28.019	0.555	0.049	0.003	60.5	1.01
WW2a	7.92	34	13.5	99.4	98.6	0.764	853.3	543.627	3.583	3.463	240.013	1028.335	16.126	15.974	0.407	0.051	0.011	60.9	1.19
WW2b	7.92	34.4	13.7	100.5	99.4	0.987	853.3	543.062	3.823	3.56	240.995	1027.281	15.992	17.042	0.418	0.049	0.01	61.2	1.11
WW2c	7.91	34	13.1	99.3	98.3	0.987	853.3	543.923	3.557	3.398	238.159	1005.216	17.199	17.903	0.487	0.04	0.01	61.5	1.16
WW3a	7.88	28.1	13.9	81.7	80.5	0.701	853.7	863.634	6.011	4.535	515.326	1801.059	23.511	23.382	0.684	0.093	0.01	60.4	1.25
WW3b	7.88	28.9	13.7	82	81.8	0.789	853.7	728.557	6.891	4.891	515.594	1814.272	23.583	23.596	0.705	0.067	0.011	60.5	1.22
WW3c	7.88	28.8	13.2	82.1	81.2	0.851	853.6	728.761	6.759	4.643	515.735	1801.075	22.82	23.753	0.779	0.094	0.012	60.9	1.29
Min.	7.88	28.1	13.1	81.7	80.5	0.701	853	863.634	3.557	3.398	238.159	1005.216	15.992	15.974	0.407	0.03	0.003	60.1	1.01
Max.	7.92	34.4	13.9	102	101	0.987	853.7	863.634	6.891	4.891	515.735	1814.272	30.629	29.1	0.779	0.094	0.012	61.5	1.29
Mean	7.90	32.13	13.57	94.33	93.41	0.858	853.3	653.676	4.872	4.150	343.834	1368.059	22.622	22.787	0.569	0.059	0.008	60.7	1.16
St. Dev	0.017	2.677	0.328	9.350	9.232	0.1101	0.278	107.244	1.328	0.5576	129.771	347.8216	5.2202	4.807	0.129	0.022	0.004	0.438	0.09

Sample	Cr^{3+} (mg/L)	Cr^{6+} (mg/L)	Hg (mg/L)	BTEX (µg/L)	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	m + p Xylene (µg/L)	o - Xylene (µg/L)	TPH C10 - C40 (µg/L)	C10 - C16 (µg/L)	C16 - C22 (µg/L)	C22 - C30 (µg/L)	C30 - C40 (µg/L)
WW1a	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW1b	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW1c	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW2a	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW2b	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW2c	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW3a	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW3b	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
WW3c	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10

APPENDIX 5

Appendix 5: Raw data for soil samples during the dry season

Samples	pH	EC (mS/m)	Temp (°C)	Al (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Mn (ppb)	Fe (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	As (ppb)	Cd (ppb)	Tl (ppb)	SO_4 (ppb)	NO_3 (ppb)	Hg (mg/L)
WS1a	8.89	895	13.02	1309.59	125.82	124.55	499.31	14496.84	16.54	16.81	1.98	0.04	0.51	1197	0.501	<0.004
WS1b	8.9	890	13	1492.02	132.85	130.99	548.1	15637.12	17.44	17.62	2.25	0.03	0.52	1254	0.48	<0.004
WS1c	8.88	878	13.09	1399.67	119.93	117.95	421.83	13133.59	14.3	14.52	1.94	0.03	0.55	1099	0.493	<0.004
WS2a	8.92	921	12.72	12731.45	115.32	114.37	264.89	12069.62	13.69	13.63	1.76	0.04	0.48	912	0.329	<0.004
WS2b	8.99	921	12.69	1387.3	125.82	125.48	269.42	12519.49	13.88	13.87	1.8	0.04	0.48	1006	0.31	<0.004
WS2c	8.78	920	12.7	12564.38	122.84	120.46	244.5	12120.56	16.58	16.82	1.66	0.05	0.46	1120	0.375	<0.004
WS3a	8.8	1317	12.15	1105.92	142.88	140.33	862.43	19536.87	26.51	26.58	2.43	0.03	0.51	2399	0.387	<0.004
WS3b	8.5	1301	12.15	1389.25	151.39	148.74	797.57	20092.1	26.38	26.3	2.53	0.04	0.5	2501	0.399	<0.004
WS3c	8.65	1334	12.17	1292.7	156.07	154.88	933.23	20132.64	26.98	27.39	2.36	0.04	0.5	2791	0.404	<0.004
WS4a	8.37	1403	12.3	10624.25	126.02	124.01	392.83	13213.1	14	14.12	2.44	0.04	0.45	1589	0.333	<0.004
WS4b	8.4	1398	12.19	10339.54	135.43	131.25	446.77	13909.52	13.4	13.49	2.65	0.03	0.45	1272	0.328	<0.004
WS4c	8.38	1390	12.27	10572.75	137.29	135.08	452.07	13977.91	13.91	13.93	2.58	0.04	0.44	890	0.39	<0.004
WS5a	8.53	1327	11.07	13516.16	128.86	127.55	691.22	18802.17	18.03	18.25	3.24	0	0.57	1933	0.401	<0.004
WS5b	8.5	1335	11.09	12823.61	131.78	129.45	684.35	18594.26	18.03	18.23	3.23	0	0.54	1849	0.445	<0.004
WS5c	8.51	1330	11.1	12479.96	132.85	129.26	698.03	19122.49	18.1	18.3	3.27	0.01	0.53	1890	0.411	<0.004
WS6a	8.11	1526	12.02	11221.22	120.41	117.16	202.83	11909.44	14.02	14.12	2.18	0.05	0.46	2307	0.447	<0.004
WS6b	8.15	1524	12.04	11407.07	128.52	126.43	207.83	12888.41	14.4	14.47	2.33	0.04	0.45	2229	0.415	<0.004
WS6c	8.2	1520	12.05	10729.15	112.18	110.39	226.08	11586.51	15.17	15.23	1.95	0.05	0.44	2386	0.43	<0.004
Min.	8.11	878	11.07	1105.92	112.18	110.39	202.83	11586.51	13.4	13.49	1.66	0.00	0.44	890	0.31	<0.004
Max.	8.99	1526	13.09	13516.16	156.07	154.88	933.23	20132.64	26.98	27.39	3.27	0.05	0.57	2791	0.501	<0.004
Mean	8.58	1229.4	12.21	7688.111	130.35	128.24	491.29	15207.92	17.298	17.427	2.366	0.033	0.491	1701.33	0.4043	<0.004
St.Dev	0.28	246.69	0.627	5281.89	11.466	11.337	238.06	3205.799	4.5942	4.6230	0.499	0.015	0.0404	625.706	0.05642	

APPENDIX 6

Appendix 6: Correlation matrix of physico-chemical properties of soil sampled in Steel Valley during the rainy season

Al	-															
As	0.63*	-														
Cd	-0.31	-0.74**	-													
Cr52	-0.09	-0.52*	0.65*	-												
Cr53	-0.12	-0.52*	0.64*	0.99**	-											
Cu63	-0.32	0.26	-0.48*	-0.04	-0.04	-										
Cu65	-0.30	0.29	-0.49*	-0.04	-0.03	1.00**	-									
EC	0.79**	0.67*	-0.27	0.25	0.23	0.11	0.15	-								
Fe	-0.11	0.50*	-0.72**	-0.31	-0.31	0.94**	0.95**	0.19	-							
Hg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-						
Mn	-0.28	0.39	-0.59*	-0.38	-0.39	0.92**	0.92**	-0.01	0.95**	0.00	-					
NO3	0.08	-0.42	-0.01	-0.04	-0.07	-0.31	-0.33	-0.36	-0.24	0.00	-0.30	-				
pH	-0.52*	-0.04	0.07	-0.54*	-0.54*	0.03	0.02	-0.58*	0.04	0.00	0.30	-0.38	-			
SO4	0.22	0.32	-0.19	0.48*	0.46	0.67*	0.69*	0.71**	0.58*	0.00	0.44	-0.35	-0.51*	-		
Temp	-0.70**	-0.90**	0.78**	0.28	0.28	-0.32	-0.35	-0.79**	-0.53*	0.00	-0.32	0.20	0.42	-0.51*	-	
Tl	-0.36	0.01	-0.59*	-0.46	-0.47*	0.56*	0.54*	-0.42	0.64*	0.00	0.63*	0.39	0.13	-0.04	-0.09	-
	Al	**As**	**Cd**	**Cr52**	**Cr53**	**Cu63**	**Cu65**	**EC**	**Fe**	**Hg**	**Mn**	**NO3**	**pH**	**SO4**	**Temp**	**Tl**

Appendix 7

Appendix 7: Correlation matrix of the rainy season water parameters

Al	-																		
As	1.00*	-																	
A.P	0.21	0.20	-																
B.A	-0.07	-0.13	0.40	-															
C.A	0.46	0.51	-0.23	-0.92*	-														
Cd	0.98*	0.98*	0.18	-0.14	0.51	-													
Cr 52	0.78	0.80*	-0.08	-0.50	0.76	0.83*	-												
Cr 53	0.65	0.60	0.42	0.71	-0.37	0.57	0.15	-											
Cu 63	0.98*	0.98*	0.17	-0.08	0.46	0.95*	0.71*	0.63	-										
Cu 65	0.99*	0.98*	0.33	0.00	0.39	0.96*	0.72*	0.69*	0.97*	-									
EC	-0.62	-0.67*	0.15	0.82*	-0.98*	-0.67	-0.84*	0.19	-0.62	-0.56	-								
Fe	0.97*	0.96*	0.29	0.13	0.28	0.94*	0.68*	0.78*	0.96*	0.97*	-0.45	-							
Mn	0.97*	0.99*	0.13	-0.29	0.65	0.97*	0.86	0.46	0.96*	0.95*	-0.78*	0.91*	-						
NO_3	-0.12	-0.08	-0.01	-0.66	0.55	-0.14	-0.06*	-0.56	-0.01	-0.11	-0.44	-0.24	0.03	-					
Ph	0.53	0.55	0.20	-0.47	0.66	0.46	0.63	0.03	0.50	0.52	-0.66	0.43	0.61	0.35	-				
SO_4	-0.86*	-0.83*	-0.34	-0.45	0.06	-0.82*	-0.46	-0.93*	-0.83	-0.88*	0.14	-0.94*	-0.72*	0.49	-0.19	-			
Temp	0.17	0.12	0.36	0.24	-0.12	0.03	-0.11	0.33	0.21	0.26	0.13	0.22	0.09	0.29	0.43	-0.21	-		
Tl	-0.29	-0.23	-0.47	-0.93*	0.71*	-0.21	0.23	-0.91*	-0.27	-0.36	-0.56	-0.46	-0.07	0.63	0.24	0.72	-0.35	-	
T.A	-0.06	-0.12	0.40	1.00*	-0.91*	-0.13	-0.49	0.71	-0.08	0.01	0.81*	0.14	-0.28	-0.66	-0.47	-0.45	0.24	-0.93*	-
	Al	**As**	**A.P**	**B.A**	**C.A**	**Cd**	**Cr 52**	**Cr 53**	**Cu 63**	**Cu 65**	**EC**	**Fe**	**Mn**	**NO_3**	**pH**	**SO_4**	**Temp**	**Tl**	**T.A**

Appendix 8

Appendix 8: Raw data for water samples during the rainy season

Sample	pH	EC mS/m	Temp. °C	T.A mg CaCO3/L	B.A mg CaCO3/L	C.A mg CaCO3/L	A.P mbar	Al (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Mn (ppb)	Fe (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	As (ppb)	Cd (ppb)	Tl (ppb)	SO_4 (mg/L)	NO_3 (mg/L)
SW1a	7.5	46.2	19.3	141.7	140.9	0.619	882.6	691.691	5.55	5.011	292.932	1513.339	20.564	21.443	0.491	0.07	0.002	48	2
SW1b	8.1	47	19.7	138.1	137.3	0.654	882.4	699.22	5.449	5.125	290.156	1501.298	21.295	21.754	0.48	0.064	0.003	48.9	2.09
SW1c	8.45	46.9	19.2	142.9	142.1	0.63	882.9	692.067	5.476	5.1	289.842	1578.194	20.942	21.534	0.49	0.06	0.002	48.7	2.1
SW2a	8.05	40.1	19.6	109.3	108.2	0.844	882.1	602.119	5.911	4.044	270.431	1288.436	19.43	18.528	0.417	0.055	0.017	55.1	2.23
SW2b	8.76	40.3	19.6	110.4	109.3	0.839	882.5	604.879	5.643	4.097	270.005	1201.792	18.664	19.299	0.42	0.052	0.015	55.7	2.28
SW2c	8.1	40.3	19.7	110.5	109.5	0.84	882.6	600.204	5.778	4.105	271.967	1240.554	18.703	19.241	0.427	0.059	0.017	55.3	2.21
SW3a	8.9	35.2	19.5	115.5	114.3	0.921	882.8	910.002	6.934	4.921	531.501	1855.668	25.195	26.778	0.69	0.098	0.009	46.6	2.18
SW3b	8.54	35.4	19.4	115.2	114	0.911	882.6	908.163	6.101	4.981	531.908	1850.486	26.986	26.109	0.699	0.093	0.009	46.8	2.32
SW3c	8.76	35.5	19.6	115.9	114.6	0.906	882.3	912.821	6.989	4.971	532.178	1849.956	25.332	25.232	0.7	0.096	0.01	46.1	2.01
Min.	7.5	35.2	19.2	109.3	108.2	0.619	882.1	600.204	5.449	4.044	270.005	1201.792	18.664	18.528	0.417	0.052	0.002	46.1	2
Max.	8.9	47	19.7	142.9	142.1	0.921	882.9	912.821	6.989	5.125	532.178	1855.668	26.986	26.778	0.7	0.098	0.017	55.7	2.32
Mean	8.35	40.77	19.51	122.167	121.133	0.796	882.5	735.685	5.981	4.706	364.547	1542.191	21.901	22.213	0.535	0.072	0.009	50.13	2.16
St. Dev	0.45	4.93	0.176	14.3076	14.468	0.12554	0.245	136.924	0.594	0.473	125.795	265.302	3.1298	3.1085	0.125	0.019	0.006	4.036	0.114

Sample	Cr 3+ (mg/L)	Cr 6+ (mg/L)	Hg (mg/L)	BTEX (µg/L)	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	m + p Xylene (µg/L)	o - Xylene (µg/L)	TPH C10 - C40 (µg/L)	C10 - C16 (µg/L)	C16 - C22 (µg/L)	C22 - C30 (µg/L)	C30 - C40 (µg/L)
SW1a	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW1b	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW1c	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW2a	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW2b	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW2c	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW3a	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW3b	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10
SW3c	<0.010	<0.002	<0.004	<2	<2	<2	<2	<4	<2	<10	<10	<10	<10	<10

APPENDIX 9

Appendix 9: Raw data for soil samples during the rainy season

Samples	pH	EC (mS/m)	Temp (°C)	Al (ppb)	Cr 52 (ppb)	Cr 53 (ppb)	Mn (ppb)	Fe (ppb)	Cu 63 (ppb)	Cu 65 (ppb)	As (ppb)	Cd (ppb)	Tl (ppb)	SO_4 (ppb)	NO_3 (ppb)	Hg (mg/L)
SS1a	8.02	1034	16.2	2511.33	136.27	138.23	552.4	16976.22	17.64	17.98	2.42	0.05	0.59	1302	0.722	<0.004
SS1b	8.08	1030	16.35	2517.18	137.71	138.68	550.65	16906.45	17.94	18.12	2.38	0.05	0.57	1311	0.71	<0.004
SS1c	8.1	1029	16.25	2500.39	138.08	139.02	543.33	16920.64	17.8	18.02	2.19	0.04	0.59	1325	0.719	<0.004
SS2a	8.13	1215	16.55	2753.02	141.02	142.18	301.75	14310.48	14.52	15.63	2.71	0.06	0.51	1265	0.512	<0.004
SS2b	8.09	1211	16.85	2764.22	140.84	143.62	311.14	14371.55	14.61	15.2	2.79	0.05	0.49	1260	0.501	<0.004
SS2c	8.11	1214	16.2	2710.87	138.93	143.22	305.75	14220.91	14.96	15.25	2.81	0.05	0.51	1255	0.48	<0.004
SS3a	8.07	1402	16.08	1877.54	143.79	145.85	956.25	23190.65	28.51	29.29	2.98	0.04	0.55	2899	0.44	<0.004
SS3b	8.06	1400	15.9	1861.89	143.21	144.6	964.95	23201.4	28.29	29.19	3.19	0.03	0.59	2811	0.449	<0.004
SS3c	8.06	1399	16.45	1869.53	143.29	145.27	966.44	23177.03	28.61	29.32	3.21	0.04	0.53	2901	0.452	<0.004
SS4a	8.11	1476	15.32	12341.13	137.39	138.49	460.93	15547.65	14.89	15.52	3.33	0.05	0.48	1824	0.491	<0.004
SS4b	8.1	1475	15.41	12891.7	137.56	138.36	463.34	15502.99	14.78	15.57	3.39	0.05	0.47	1831	0.482	<0.004
SS4c	8.13	1479	15.25	12809.01	137.13	137.44	469.19	15532.08	14.69	15.61	3.43	0.05	0.48	1840	0.499	<0.004
SS5a	7.98	1510	13.56	13620.83	129.66	130.38	710.48	21432.37	21.5	21.98	3.91	0.01	0.59	2001	0.58	<0.004
SS5b	7.98	1515	13.7	13590.47	130.01	131.75	718.25	21450.77	20.91	22.04	4.01	0.01	0.58	2041	0.588	<0.004
SS5c	7.97	1509	13.65	13611.38	130.27	132.97	725.66	21603.01	20.88	21.9	3.94	0.00	0.55	2010	0.579	<0.004
SS6a	7.78	1592	14.8	12810.1	151.39	154.22	233.49	15201.93	16.18	17.09	2.84	0.05	0.47	2543	0.61	<0.004
SS6b	7.79	1591	14.25	12780.89	152.2	153.65	243.42	15289.54	16.25	17.17	2.8	0.05	0.49	2562	0.619	<0.004
SS6c	7.81	1595	14.97	12881.33	152.06	153.18	250.93	15239.25	16.38	16.89	2.79	0.06	0.51	2561	0.626	<0.004
Min.	7.78	1029	13.56	1861.89	129.66	130.38	233.49	14220.91	14.52	15.2	2.19	0.00	0.47	1255	0.44	
Max.	8.13	1595	16.85	13620.83	152.2	154.22	966.44	23201.4	28.61	29.32	4.01	0.06	0.59	2901	0.722	
Mean	8.02	1370.9	15.43	7705.712	140.05	141.73	540.46	17781.94	18.85	19.54	3.062	0.041	0.531	1974.56	0.55883	
St.Dev	0.12	197.63	1.0672	5501.834	6.8924	7.0596	251.81	3448.953	4.958	5.011	0.53	0.019	0.046	610.63	0.0943	

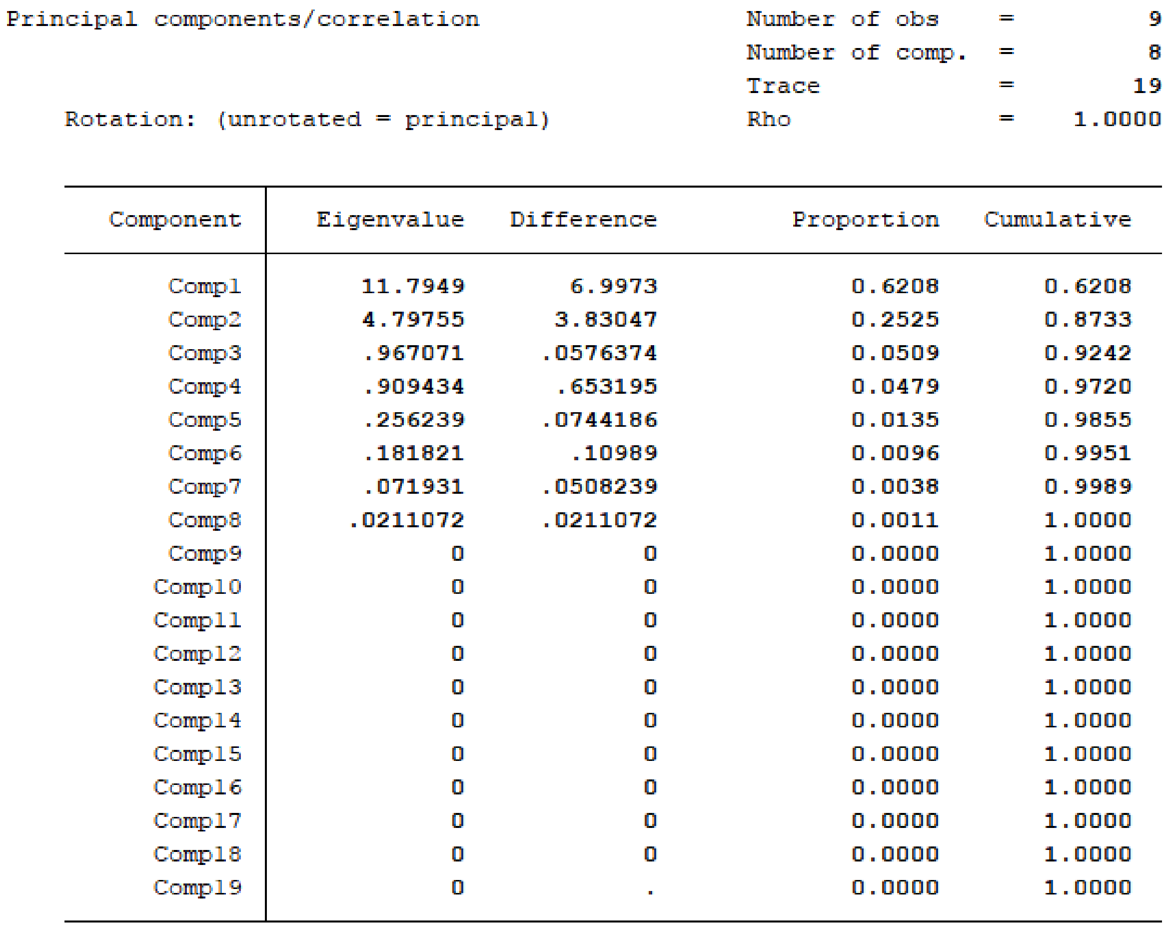
APPENDIX 10

Appendix 10: Principal component scores for the water sample sites

	1	2	3	4
Water 1a	-1.437	2.465	-1.269	-0.248
Water 1b	-1.358	2.52	1.773	-1.387
Water 1c	-1.859	3.128	-0.318	1.413
Water 2a	-2.598	-2.252	-1.092	-1.175
Water 2b	-3.235	-1.987	-0.009	0.65
Water 2c	-3	-2.394	0.908	0.473
Water 3a	4.79	-0.291	-0.583	-0.809
Water 3b	4.242	-0.036	-0.124	0.427
Water 3c	4.454	-1.154	0.712	0.656

APPENDIX 11

Appendix 11: Eigenvalues of the principal components in the water samples during the dry season

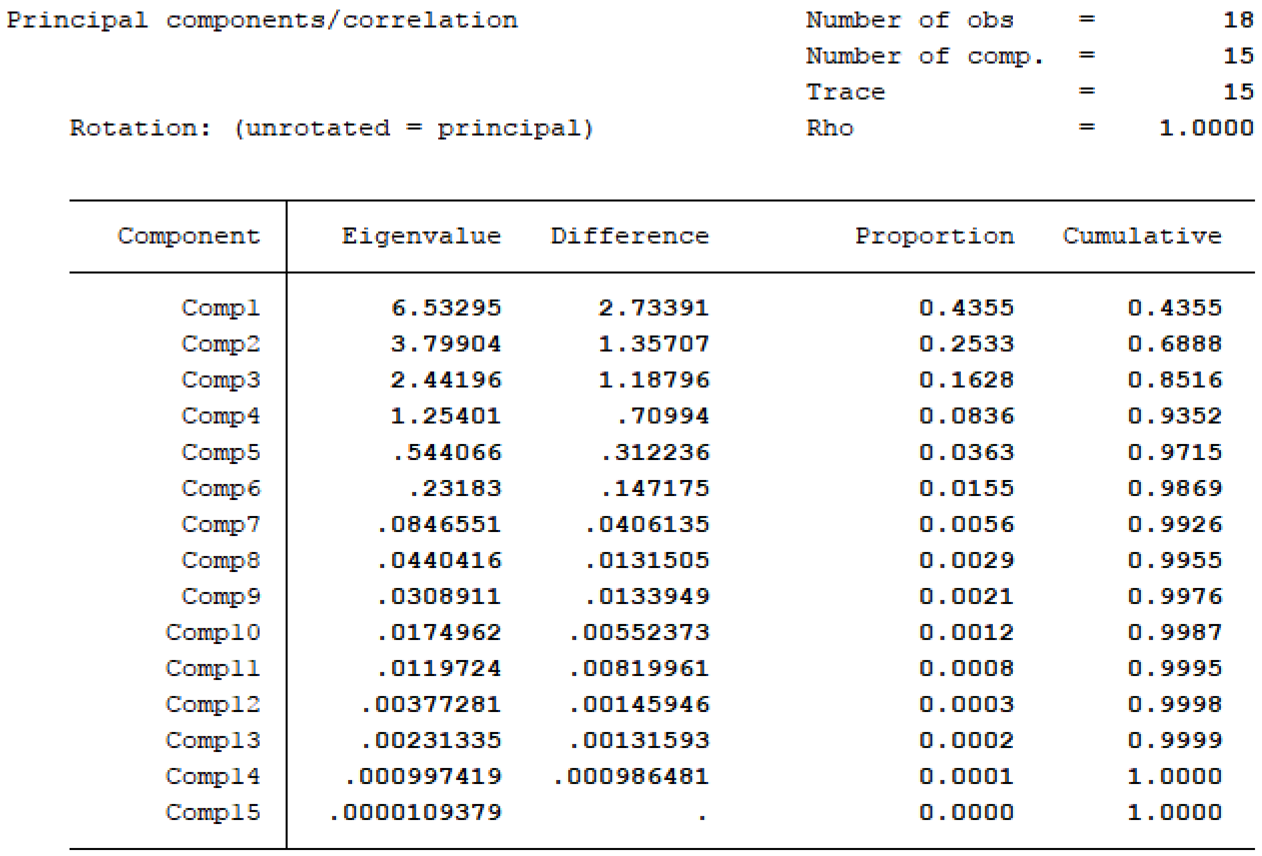


```
Principal components/correlation                  Number of obs    =          9
                                                  Number of comp.  =          8
                                                  Trace            =         19
    Rotation: (unrotated = principal)             Rho              =     1.0000

    --------------------------------------------------------------------------
       Component |   Eigenvalue   Difference         Proportion   Cumulative
    -------------+------------------------------------------------------------
           Comp1 |      11.7949       6.9973             0.6208       0.6208
           Comp2 |      4.79755      3.83047             0.2525       0.8733
           Comp3 |      .967071     .0576374             0.0509       0.9242
           Comp4 |      .909434      .653195             0.0479       0.9720
           Comp5 |      .256239     .0744186             0.0135       0.9855
           Comp6 |      .181821       .10989             0.0096       0.9951
           Comp7 |      .071931     .0508239             0.0038       0.9989
           Comp8 |     .0211072     .0211072             0.0011       1.0000
           Comp9 |            0            0             0.0000       1.0000
          Comp10 |            0            0             0.0000       1.0000
          Comp11 |            0            0             0.0000       1.0000
          Comp12 |            0            0             0.0000       1.0000
          Comp13 |            0            0             0.0000       1.0000
          Comp14 |            0            0             0.0000       1.0000
          Comp15 |            0            0             0.0000       1.0000
          Comp16 |            0            0             0.0000       1.0000
          Comp17 |            0            0             0.0000       1.0000
          Comp18 |            0            0             0.0000       1.0000
          Comp19 |            0            .             0.0000       1.0000
    --------------------------------------------------------------------------
```

APPENDIX 12

Appendix 12: Eigenvalues of the principal components in the soil samples during the dry season

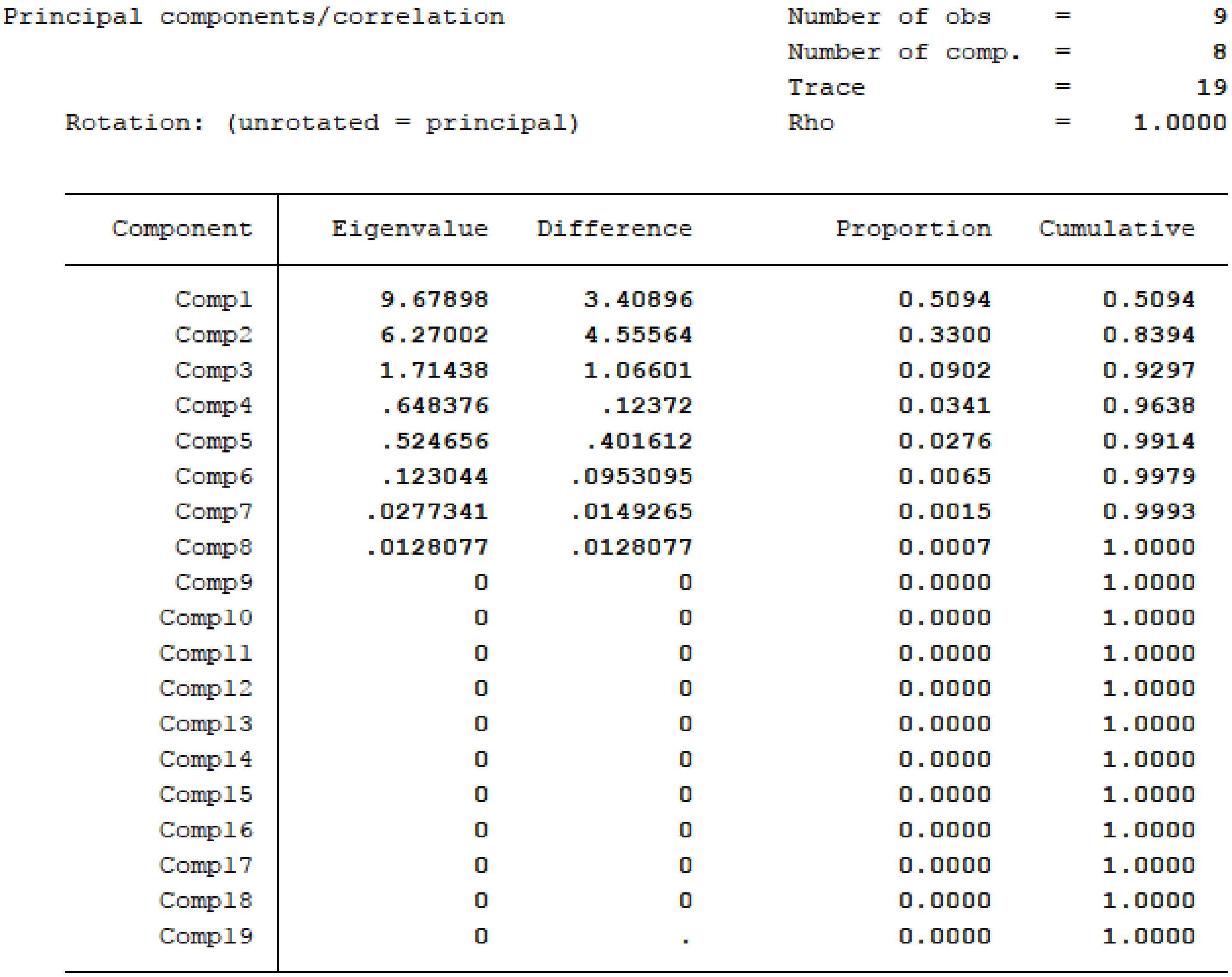


```
Principal components/correlation                 Number of obs    =        18
                                                 Number of comp.  =        15
                                                 Trace            =        15
    Rotation: (unrotated = principal)            Rho              =    1.0000

    --------------------------------------------------------------------------
       Component |   Eigenvalue   Difference         Proportion   Cumulative
    -------------+------------------------------------------------------------
           Comp1 |      6.53295      2.73391             0.4355       0.4355
           Comp2 |      3.79904      1.35707             0.2533       0.6888
           Comp3 |      2.44196      1.18796             0.1628       0.8516
           Comp4 |      1.25401       .70994             0.0836       0.9352
           Comp5 |      .544066      .312236             0.0363       0.9715
           Comp6 |       .23183      .147175             0.0155       0.9869
           Comp7 |     .0846551     .0406135             0.0056       0.9926
           Comp8 |     .0440416     .0131505             0.0029       0.9955
           Comp9 |     .0308911     .0133949             0.0021       0.9976
          Comp10 |     .0174962    .00552373             0.0012       0.9987
          Comp11 |     .0119724    .00819961             0.0008       0.9995
          Comp12 |    .00377281    .00145946             0.0003       0.9998
          Comp13 |    .00231335    .00131593             0.0002       0.9999
          Comp14 |   .000997419   .000986481             0.0001       1.0000
          Comp15 |  .0000109379            .             0.0000       1.0000
    --------------------------------------------------------------------------
```

APPENDIX 13

Appendix 13: Eigenvalues of the principal components in the water samples during the rainy season

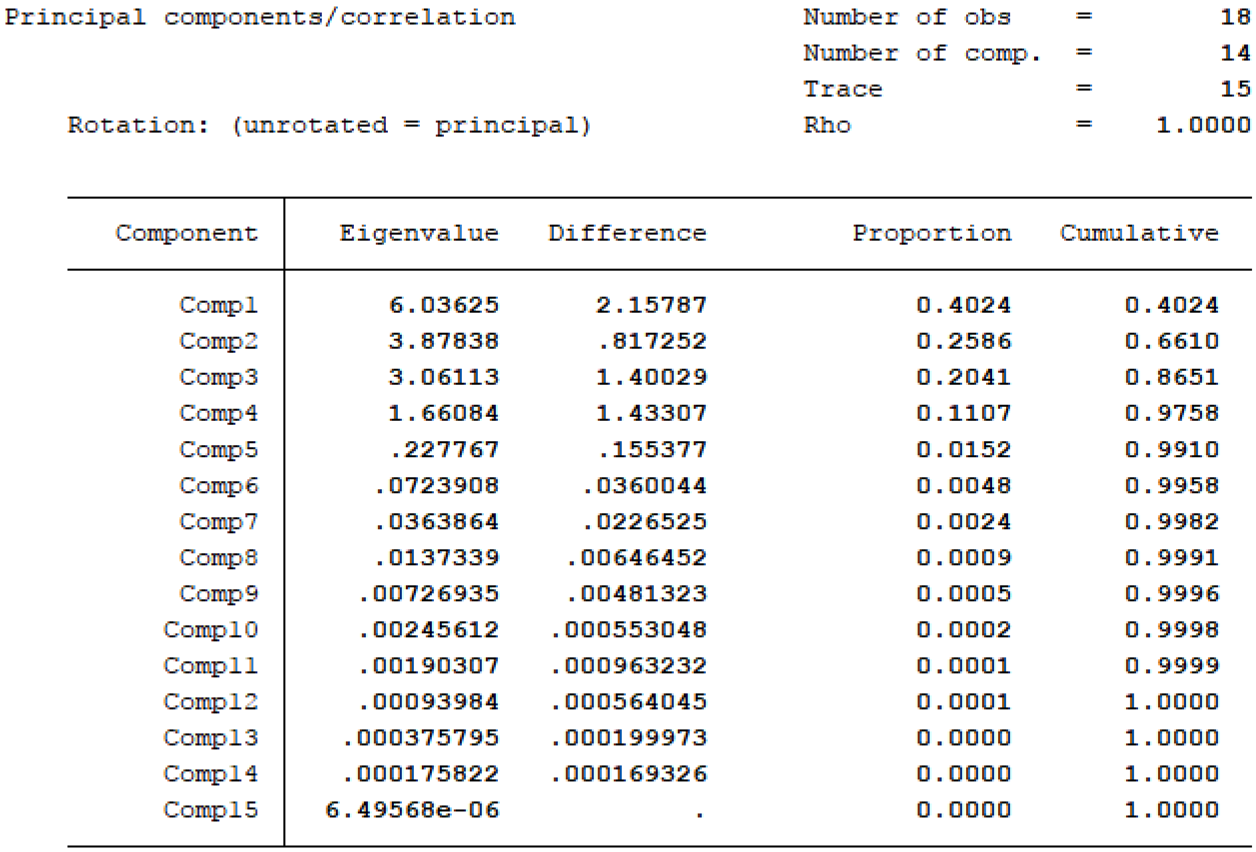


```
Principal components/correlation                  Number of obs    =          9
                                                  Number of comp.  =          8
                                                  Trace            =         19
    Rotation: (unrotated = principal)             Rho              =     1.0000

    --------------------------------------------------------------------------
       Component |   Eigenvalue   Difference         Proportion   Cumulative
    -------------+------------------------------------------------------------
           Comp1 |      9.67898      3.40896             0.5094       0.5094
           Comp2 |      6.27002      4.55564             0.3300       0.8394
           Comp3 |      1.71438      1.06601             0.0902       0.9297
           Comp4 |      .648376       .12372             0.0341       0.9638
           Comp5 |      .524656      .401612             0.0276       0.9914
           Comp6 |      .123044     .0953095             0.0065       0.9979
           Comp7 |     .0277341     .0149265             0.0015       0.9993
           Comp8 |     .0128077     .0128077             0.0007       1.0000
           Comp9 |            0            0             0.0000       1.0000
          Comp10 |            0            0             0.0000       1.0000
          Comp11 |            0            0             0.0000       1.0000
          Comp12 |            0            0             0.0000       1.0000
          Comp13 |            0            0             0.0000       1.0000
          Comp14 |            0            0             0.0000       1.0000
          Comp15 |            0            0             0.0000       1.0000
          Comp16 |            0            0             0.0000       1.0000
          Comp17 |            0            0             0.0000       1.0000
          Comp18 |            0            0             0.0000       1.0000
          Comp19 |            0            .             0.0000       1.0000
    --------------------------------------------------------------------------
```

APPENDIX 14

Appendix 14: Eigenvalues of the principal components in the soil samples during the rainy season



```
Principal components/correlation                  Number of obs    =        18
                                                  Number of comp.  =        14
                                                  Trace            =        15
    Rotation: (unrotated = principal)             Rho              =    1.0000

    --------------------------------------------------------------------------
       Component |   Eigenvalue   Difference         Proportion   Cumulative
    -------------+------------------------------------------------------------
           Comp1 |      6.03625      2.15787             0.4024       0.4024
           Comp2 |      3.87838      .817252             0.2586       0.6610
           Comp3 |      3.06113      1.40029             0.2041       0.8651
           Comp4 |      1.66084      1.43307             0.1107       0.9758
           Comp5 |      .227767      .155377             0.0152       0.9910
           Comp6 |     .0723908     .0360044             0.0048       0.9958
           Comp7 |     .0363864     .0226525             0.0024       0.9982
           Comp8 |     .0137339    .00646452             0.0009       0.9991
           Comp9 |    .00726935    .00481323             0.0005       0.9996
          Comp10 |    .00245612   .000553048             0.0002       0.9998
          Comp11 |    .00190307   .000963232             0.0001       0.9999
          Comp12 |    .00093984   .000564045             0.0001       1.0000
          Comp13 |   .000375795   .000199973             0.0000       1.0000
          Comp14 |   .000175822   .000169326             0.0000       1.0000
          Comp15 |  6.49568e-06            .             0.0000       1.0000
    --------------------------------------------------------------------------
```

APPENDIX 15

Appendix 15: Latent Vectors (loadings) of parameters analysed from the water samples

	PC-1	PC-2	PC-3	PC-4
Al	0.31947	0.03497	-0.02794	0.04045
As	0.32008	0.01073	-0.03919	-0.01267
Bicarbonate Alkalinity	-0.05014	0.39420	0.00911	0.00650
Carbonate Alkalinity	0.17299	-0.33632	0.00763	-0.01917
Cd	0.31473	0.00823	-0.11889	-0.07004
Cr 52	0.26527	-0.15060	-0.17799	-0.05893
Cr 53	0.18517	0.32254	0.00779	0.10357
Cu 63	0.31244	0.02795	0.00790	0.14048
Cu 65	0.31474	0.06420	0.04875	-0.03108
EC	-0.22066	0.28755	0.03511	0.07579
Fe	0.30617	0.11202	-0.02264	0.04209
Mn	0.31772	-0.05399	-0.03287	-0.00218
NO_3	-0.01814	-0.27222	0.45368	0.05657
Ph	0.19325	-0.15914	0.37312	0.00750
SO_4	-0.25922	-0.23157	0.07777	-0.04812
Temperature	0.05568	0.10220	0.64958	0.46768
Tl	-0.06536	-0.38846	-0.04817	-0.05630
Total Alkalinity	-0.04794	0.39459	0.00826	0.00771

APPENDIX 16

Appendix 16: Latent Vectors (loadings) of parameters analysed from the soil samples

	PC-1	PC-2	PC-3	PC-4
Al	0.05083	-0.37066	-0.35522	0.09280
As	0.29419	-0.17346	-0.30363	-0.20356
Cd	-0.34170	-0.02861	0.23695	-0.18381
Cr 52	-0.17265	-0.27801	0.40664	0.06070
Cr 53	-0.17233	-0.27255	0.40916	0.05200
Cu 63	0.33784	0.06659	0.30864	0.01397
Cu 65	0.34270	0.05014	0.30219	0.00016
EC	0.14814	-0.46203	-0.07301	-0.09200
Fe	0.38943	0.06812	0.13611	0.05535
Mn	0.35721	0.17341	0.15344	-0.06700
NO_3	-0.12383	0.09606	-0.10587	0.69343
pH	0.00302	0.38193	-0.06318	-0.48814
SO_4	0.22610	-0.31468	0.30484	0.00608
Tl	0.21958	0.30994	0.03612	0.41298