Spatio-temporal characterization of water quality and pollution sources apportionment in the Klip River catchment, South Africa.

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By

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DECLARATION

I, **TAFADZWA MARARA** (student number: **22082905**), hereby declare that this research is my original work. Furthermore, unless specifically stated, all the references listed have been consulted. The work of this thesis is a record that has been done by me and has not been previously accepted for any higher degree or professional qualification at any other educational institution.

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MISS TAFADZWA MARARA

Date ....

SUPERVISOR

This thesis has been submitted with my authorization as a university supervisor and I declare that the requirements for the applicable Philosophy Doctorate degree in Environmental Science rules and regulations have been fulfilled.

Signed..

PROF L.G. PALAMULENI

Date...

ABSTRACT

The Klip River wetland is one of the most economically important ecological river system in South Africa as it plays two roles: water purification in the Vaal River system and is also a source of water. However, several studies have demonstrated that the wetland is extremely degraded and has lost capability to perform the two functions. As a large catchment river system, the Klip River runs through different land uses and is subsequently prone to high water quality variability along its course and over time. The main aim of this research was to determine the spatial and temporal mechanisms influencing water quality, sources of pollution and the associated risks in the Klip River catchment. Thus informing the process of developing a framework for the monitoring and management of water quality in the catchment.

The methodology was centered on data collected from water quality monitoring activities from February 2016 to January 2017. Water samples were collected along the profile of the Klip River and analyzed for Al, As, Ca, Cd, Co, Cu, Cd, Fe, K, Mg, Mn, Na, Ni, Pb, U, V and Zn using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and nitrates and phosphates using Spectrophotometry. Water quality results were compared against South African water quality guidelines (SAWQG) for aquatic ecosystem protection, agricultural and domestic uses. To assess the seasonal and spatial dynamics of the water quality, multivariate statistics were employed. Furthermore, to classify seasonality and spatial level of pollution in the catchment, various environmental indices were computed; there included heavy metal pollution index, Potential ecological risk index, Comprehensive Pollution Index. In addition, analysis into the river's ability to self-purify was conducted using River Recovery Capacity and Capacity for self-purification per unit length calculations.

Findings revealed that the Klip River water quality is not in compliance with the SAWQG for aquatic ecosystem protection, agricultural and domestic uses thereby rendering the water unsuitable for its designated uses. Consequently, water quality in the Klip River Catchment (KRC) poses significant ecological and health risks. Furthermore, water quality in the Klip is influenced by spatial and seasonal factors. As such the KRC was grouped into two homogenous water quality zones, i.e. the upstream and downstream zones, and this was attributed to the influence of land use activities. Furthermore water quality in the KRC displayed homogenous characteristics in the 2015/16 season comprising of the period from February to June, and 2016/17 season comprising of the months from July to January. This was attributed to the effects of El Niño Southern Oscillation (ENSO) and La Niña phenomena phenomena respectively. Critical pollution was recorded in the upstream zone, in the 2015/16 season relative to the downstream and the 2016/17 season respectively. This was attributed to the evaporation and consequently low volume of water in the river. The main sources of pollution in the KRC included lithological, traffic, mining, point discharges from industries and sewage effluents. These sources varied between seasons and spatial locations. It was also observed that the Klip River possesses a natural capability even though limited, to self-purify for some heavy metals (Cd, Cr, Mn, Ni and Zn).

A surface water quality management plan was developed which highlighted the most impaired designated water uses and overall priority pollutants in the KRC. The management plan was used to identify appropriate water quality management measures specific to the KRC. Furthermore a framework for monitoring and evaluation of water quality was developed which outlines the pollutants to monitor per site and the specific uses for which to monitor. Findings from this research demonstrated the adeptness of applying multivariate statistics in dimension reduction, understanding of complex water quality monitoring data and identification of pollution sources in the Klip River Catchment. In addition, findings from this study serve as a guideline for developing strategies for monitoring, evaluating and managing surface water quality in other catchments. These findings can also be used to inform policy makers and various stakeholders to enable the design of efficient mechanisms for water quality management.

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DEDICATION

To my mother, Felistas Evelyn Marara.

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CHAPTER 1

INTRODUCTION

1.1 Synopsis

Water drives life. However challenges of water resources access; equitable distribution, quality and management continue to plague the globe. Most of the issues surrounding water security and safety have been largely attributed to anthropogenic activities associated with economic development, climate change and to a lesser extent, natural phenomena. The nature of these challenges varies between developed and developing countries. South Africa is a semi-arid country and it experiences highly variable rainfall patterns which lead to acute water shortages. Moreover, as a developing economy, various activities associated with economic development in South Africa have led to water pollution thus threatening the security of water resources. In this chapter, the challenges with regards to water resources safety and security from the global to local scales are presented. Furthermore, there is a discussion on the various factors which influence water quality, particularly in the Klip River catchment area. This is preceded by the objectives of this research, the hypothesis and the various research questions.

1.2 Background

Water is the most indispensable natural resource sustaining social and economic development as well as environmental diversity (Ashton, 2002). However, the quality of the world's water resources depicts a deteriorating trend.Ashton and Haasbroek (2002) submitted that water quality was fast declining because of resource depletion and pollution; and likewise suggested that the demand for water was increasing due to population growth coupled with rapid economic development; industrialization, mechanization and urbanization (UNESCO, 2006; Falkenmark, 1994) and anthropogenic induced climate change (Bates, 2009). Therefore, the resultant is transformation in water systems in terms of quality and quantity, emanating from land use and land cover changes associated with urbanization, industrialization and agricultural development.

On a global scale, the last decade has been characterized by exponential increases in population. In Africa alone, the urban population was noted to have more than doubled and from 1990, it was further forecasted that by 2030, approximately 50% of the population in Africa will be living in urban areas (WATER-UN, 2015). This growth in population has been characterized by an increase in the demand for water resources. The resultant is the amplified risk of pollution of water resources. Rand Water (2005) alluded that there is an exponential relationship between demand for water and pollution loads and subsequently, an inverse impact on the water quality. This results in the reduction of amounts of water available for various uses such as domestic consumption, agriculture, industrial and recreational purposes. As such, WATER-UN (2006) forecasted that approximately 1.8 billion people will be living in countries or regions with absolute water scarcity, and two-thirds of the world population could be under water stress conditions by year 2025. This has ramifications on public health, environmental sustainability, food and energy security, and economic development (WATER-UN, 2015).

UNESCO (2011) identified climate change as a challenge for global water resources management because of its influence not only on the availability but also the quality of water (Larsen, 2012; Carlisle et al., 2011). Climate change has resulted in significant increases in surface temperatures of rivers (Zietsman, 2011) and as such, this has a ripple effect on the aquatic ecosystems as well as the biogeochemical processes which occur in river systems. Climate change has also led to higher occurrences of heavy rainfall events which consequently, results in high sediments discharges and increased surface runoff and combined sewer overflows (Bates et al., 2008). This poses dire implications for arid countries like South Africa, which are plagued by acute water scarcity further worsened by pollution (Ashton, 2002). Parry et al. (2007), identified climate change and variability as potential factors, which would impose additional pressures on water availability in Africa. Despite the fact that Africa has an abundance of water resources, these are however erratically distributed. Therefore, the impacts of climate change such as rainfall variability coupled with population increase and land use changes, contribute to water scarcity and impairment of its quality in Africa.

Economic development activities have to some extent negatively impacted the quality of water resources through industrial processes and mining activities, whereby waste products containing toxic compounds are discharged directly into water bodies. Indirectly, industrial waste products that are disposed of in landfills may release chemical elements that find their way into adjacent watercourses (Oberholster and Ashton, 2008). A major problem related to mining in many parts of the world, particularly South Africa, where intense mining activities spanning hundreds of years have been ongoing, is acid mine drainage (AMD) (McCarthy, 2011). Acid mine drainage is classified as the most adverse impact of mining to the environment especially on water resources. Abandoned and active mining activities, result in the uncontrolled discharge of contaminated water (Banks et al., 1997; Pulles et al., 2005). AMD usually contains elevated levels of heavy metals (Akcil and Koldas, 2006).

The progression of agricultural practices with economic development has resulted in the use of fertilizers and pesticides, which by way of leaching, can be introduced to surface water bodies (Walmsley, 2000). This is because rigorous agricultural development involves the extensive use of inorganic fertilizers, which increase nutrient concentrations (Wu and Chen, 2013) as well as the widespread use of pesticides. This in turn results in nutrient enrichment of rivers (Rosemond et al., 2015) and eutrophication causing rapid and uninhibited growth of algae, which subsequently alters the biological equilibrium in the aquatic ecosystems (Wiik, 2012). Agriculture may also affect water quality by way of irrigation practices, whereby over-irrigation can trigger nutrient and chemical runoff as well as perched water tables which may lead to increased salinity (McKergow et al., 2003).

Urbanization, on the other hand, weighs down on the water supply, drainage systems, water infrastructure and sanitation services, leading to the deterioration of water quality in water bodies running through, downstream of and in proximity with urban areas. Urbanization results in an increase in impervious surfaces (Paul and Meyer, 2001; Sponseller et al., 200;, Walsh et al., 2001; Kearns et al., 2005; Chadwick et al., 2006). This intensifies erosion, elevates sediment discharges to rivers, and disrupts channel morphology thus reducing habitat for organisms such as fish and benthic macro invertebrates (ACCWP, 2004). Additionally, sedimentation affects water chemistry, whereby high concentrations of heavy metals and nutrients in sediments were recorded in various catchments in South Africa (Singh, 2015, Binning and Baird, 2001). This has detrimental implications such as eutrophication and other effects on aquatic life as well as human health.

The quality of water in streams and rivers is not only dependent on the anthropogenic activities taking place in the particular catchment, but the natural catchment characteristics such as hydrology, geology and geomorphology. Geology, for instance, influences water quality characteristics as a result of the chemical water-rock interactions depending on the structural and chemical composition of rocks found in the river bed as well as the weathering patterns of the bedrock (Khatri and Tyagi, 2015). Furthermore, natural processes such as leaching of organic matter and nutrients from the soil, hydrological factors leading to runoff and biological processes within the aquatic environment bring about changes in the physical and chemical composition of water (Khatri and Tyagi, 2015).

Water quality concerns have evolved and as such, there is an introduction of an ever increasing array of complex toxic compounds to water, such as synthetic organic compounds, heavy and or trace metals, nutrients and radionuclides (Larsen et al., 2013). The effects of heavy metals on aquatic ecosystems is well documented in literature (Solomon 2009; Singh et al., 2011; Prasad 2013; Fu et al., 2014; Aydoğan, et al., 2016). Heavy metals present a significant problem to aquatic systems because of their environmental persistence as well as their non-biodegradable and toxic nature. When discharged in water, heavy metals accumulate and are biomagnified along the food chain. This in turn endangers, not only the aquatic ecosystems but the dependent terrestrial ecosystems.

Larsen et al. (2013) demonstrated that water quality of a stream or river mirrors a composite of land uses, catchment processes, development activities, climate as well as the natural processes, which are usually specific to an area. Consequently, the responses to anthropogenic influences on river systems vary between spatial and time scales. As such, despite the fact that there is an understanding of the impact of anthropogenic activities on river water quality, this understanding is limited owing to the lack of long term water quality data, which are pertinent in the study of water quality behavior in river systems (Burt et al., 2011; Myroshnychenko et al., 2015). Larsen et al. (2013) suggested that long term monitoring of water quality trends enables the identification of variations between natural and anthropogenic effects on the quality of water. Chapman et al. (2016), reiterated that monitoring water quality is important for the determination of the magnitude of the impacts of anthropogenic activities on water quality and the suitability of water for various uses.

Various studies have been conducted to assess the various spatial and temporal trends of water quality in rivers in different countries and different regions of the world using multivariate statistical techniques (Zhang et al., 2012; David et al., 2013; Wang et al., 2014; Mei et al., 2014; Palma et al., 2014; Bhat and Pandit, 2014; Ogwueleka 2015 ; Phung et al., 2015; Barakat et al., 2016; Zipper et al., 2016; Chepchirchir et al., 2017; Zhang, et al., 2017). The use of multivariate statistical techniques is extensive in these assessments because the data from long term monitoring of water quality is voluminous and complex making it difficult to gain an understanding of the relationships between the various factors.

South Africa is a semi-arid country and is faced with a scarcity of freshwater resources (Kongolo, 2011). On average, it receives 8.6% run off per annum thus reducing the per capita availability of water to 109.9 m^3/yr., which is slightly above the 100.0 m^3/yr^{-1} for water stressed regions as illustrated by Makhaye et al. (2002). The inverse side of the water scarcity involves pollution of natural water systems especially rivers and streams, impacted by industrial and mine effluents and other anthropogenic activities like agriculture and urbanization. A majority of South African metropolitan cities are situated on the headwaters of river catchments which play multiple vital roles (Oberholster et al., 2010) including resources for domestic consumption, fishing, agricultural, industrial, ecological, and recreational and conveyance of wastewater (UNEP, 2010). As such, the water quality of rivers running through or downstream of metropolitan areas has deteriorated considerably over the years (Oberholster and Ashton 2008). In agreement Meyer et al. (2005) stated that rivers flowing through urbanized landscapes have high contaminant concentrations.

The Klip is one such river passing through the Gauteng metropolitan area. The Klip River catchment is very diverse in terms of land use; the upper part of the catchment is characterized by urban development and mining activities; the midsection comprises mainly of urban areas, industries and wastewater treatment plants and the lower section is mostly agriculture. The river catchment experiences pressure from anthropogenic activities in the form of point and diffuse pollution. Consequently, the Klip River and its tributaries (particularly Klipspruit and Rietspruit) were observed to be degraded by acid mine drainage and silt run-off from mine dumps (Humphries et al., 2017).

Table 1: Summary of wastewater treatment plant discharge volumes for the Klip River.

Wastewater treatment plant	Discharge/day(Ml/day)
Goudkoppies	105
Olifantsvlei	120
Bushkoppies	170
Dekema	36
Rondebult	36
Vlakplaats	53
Waterfall	105

(Source; Orange River IWRMP 2007).

Additionally, the Klip River catchment (hereon referred to as KRC) houses 7 wastewater treatment plants (WWTPs) shown in Table 1 and they discharge approximately 75% of discharge coming from all WWTPs in the Upper Vaal water management area. Furthermore, there have been reports of eutrophication within the Klip River, recording unacceptable levels of pollution particularly nutrients (McCarthy et al., 2007; Sibande, 2013). The Klip River is an important tributary of the Vaal River and, as such, the problem of pollution from the Klip River adds to current constraints in ensuring a good supply of clean water (DWAF, 2007).

1.3 Problem Statement

DWAF (1999), described the Klip River as one of the most impacted rivers in South Africa as it is subjected to every plausible type of pollution. Kruger (2004), reported that the Klip River is prone to diffuse pollution as it flows through residential, industrial, mining and commercial land use, thus diffuse pollution is the principal contributor of water quality degradation in this catchment. The Klip River is a large river system, and it runs through different land uses, which means that it is characterized by high water quality variability along its course and over time. As such, understanding the magnitude of the impacts of anthropogenic activities, and the various spatial and temporal dynamics on the water quality in this catchment is difficult. This information is important because it will help in designing a water quality monitoring programme and strategies to manage the water quality in the KRC effectively. The Klip River is vital because it serves all the categories of water use in the catchment, including domestic (Kotze, 2008), agriculture, recreational, industrial and natural environment, this is despite the Rand Water being the supplier of potable water to these users. This can be attributed to the increasing demand for water resources in the area. Therefore, the main aim of this study was to evaluate the spatial and temporal patterns of water quality characteristics in the KRC so as to inform the designing of accurate and efficient water quality assessment and management programs.

1.4 Justification

Several studies have been conducted on the quality of water in the Klip River and its tributaries. Silberbauer and Moolman (1993) assessed the rate of expansion of formal and informal housing in the Rietspruit (which is a sub-catchment of the Klip River catchment) and its influence on water quality, and observed elevated dissolved N, P and fecal coliforms concentrations, consequently leading to eutrophication and other related health risks. The authors concluded that there was an association between the rate of urban expansion and water quality. DWAF (1999) also alluded that informal settlements like Kagiso, Durban Roodepoort Deep and Soweto are diffuse sources of pollution to the Klip River. Showalter et al. (2000) re-examined the link between urban expansion and water quality, and established that urban expansion was still impacting the aquatic resources in the Rietspruit and consequently the Klip River.

Another study was carried out looking at the long term trends of water quality in the KRC with the purpose of ascertaining the ecological integrity of the Klip River (Kotze, 2005). Findings revealed that the water quality in the KRC had highly deteriorated. However, this study had limitations in terms of data as it was looking at long term trends (1973-2001), and in some cases, the data was missing. Furthermore, the water quality parameters which were used in this study were not representative of the nature of anthropogenic activities impacting this river (De Kock, 2008) and the choice of sampling points did not consider land use practices and tributaries' contributions.

McCarthy et al. (2007) studied the Klip wetland and concluded that tracts of the wetland had disappeared and as such, the water quality in this catchment was rapidly deteriorating. Kruger (2009) postulated that the urbanized environment, existence of mines (active and abandoned) and local industries could be the predominant contributors of the non-point source pollution in the KRC, and as such, cited the need for further investigation. As such, it can be concluded that the *status quo* of literature on water quality in the KRC is limited and not up to date. Therefore, this study aims to fill that research gap by identifying and describing the pollution sources, and analyzing the spatial and temporal mechanisms governing water quality in the KRC so as to formulate efficient methods of control and remediation of water quality.

1.5 Aim and Objectives

The main aim of this study was to evaluate the spatial and temporal dynamics governing water quality, sources of pollution and consequently the associated environmental risks so as to develop a framework for the monitoring and management of water quality in the Klip River catchment.

Specific Objectives

- To assess the environmental risks associated with water quality characteristics (physicochemical, nutrients and heavy metals) in the Klip River catchment,
- To analyze the spatial and temporal trends of water quality in the Klip River catchment,
- To identify the critical sources of pollution in the Klip River catchment,
- To evaluate the self-purification capacity of the Klip River,
- To develop a framework for the monitoring and management of surface water quality in the Klip River Catchment.

1.6 Research Hypothesis

H_1: Water quality in the Klip River catchment varies spatially and seasonally.

H_2: Spatial and seasonal factors influence sources of pollution.

H_3: Water quality in the Klip River is not suitable for domestic, agricultural and aquatic uses.

1.7 Research questions

1. What is the status of the water quality in the Klip River ?
2. What are the environmental risks associated with water quality in the Klip River catchment?
3. What are the point and non-point sources of pollution in the Klip River catchment?
4. To what extent do spatial and seasonal factors influence sources of pollution and consequently water quality?
5. What are the significant NPS variables in the Klip River catchment? When and where do they occur?
6. Which pollutants cause variations between and within seasons?
7. What are the existing mechanisms of NPS source pollution control and management in the Klip River catchment?
8. What can be done to improve the existing mechanisms to control NPS source pollution problems in the Klip River catchment?
9. What are the spatial and seasonal factors governing the self-purification capacity of the Klip River catchment?

1.8 Description of the study area

Location

The Klip River is located in the Gauteng province, South Africa (Figure 1). It originates from the Witwatersrand springs; and flows in a southerly direction thereby draining the southern Witwatersrand region, until its confluence with the Vaal River in Vereeniging. The river is characterized by many impoundments like the Florida Lake, the Fleurhof dam, New Canada and Orlando dams, which are responsible for trapping silt and pollutants, thus improving the quality of water to a certain extent (Johannesburg State of the Environment Report, 2003). The Klip River is a perennial river as a result of interference from activities like the consistent discharge of effluent (Johannesburg State of the Environment Report, 2003).

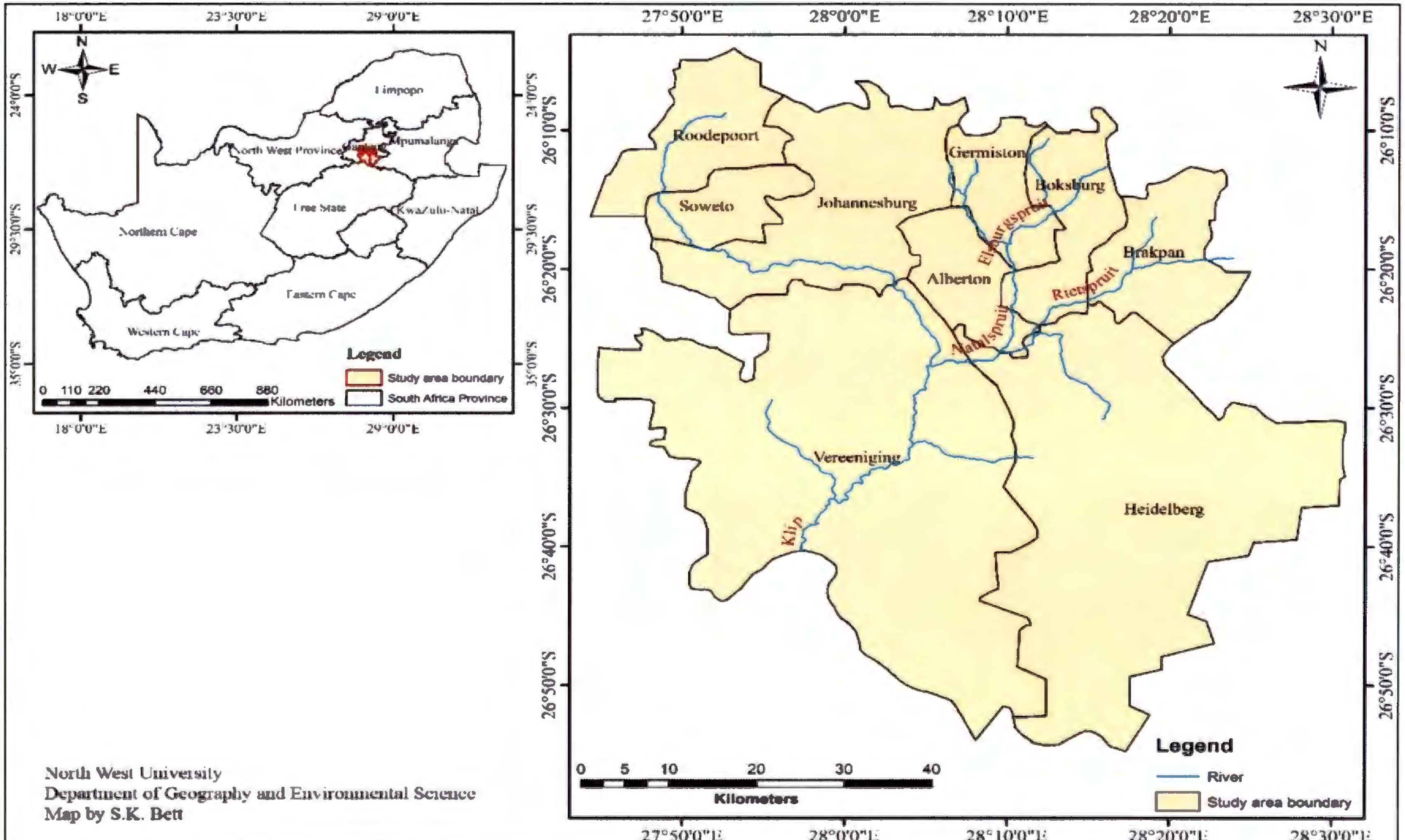

Figure 1: Map of the Klip River catchment.

RandWater (2005) divided the Klip catchment into three sub-catchments, namely: the Upper Klip, Rietspruit and Lower Klip. The Upper Klip drains Krugersdorp East and Roodepoort West. Tributaries in this sub-catchment include Klipspruit, Harringtonspruit, Glenvistaspruit, Diepkloofspruit, and the Bloubosspruit and Russel streams, and Robinson and Fordsburg canals. The middle section (the Rietspruit sub-catchment) drains Alberton, Boksburg and Germiston. Its tributaries include Natalspruit, Foriespruit, Varkensfonteinspruit, Elsburgspruit and Valsfontein. The Lower Klip sub-catchment is the area drained by the river between its confluences with the Rietspruit and the Vaal River.

1.9 Catchment characteristics

Hydrology

For the first 10-40km from the source, the Klip River is very steep, but flattens towards its lower section. Scott et al. (1998) revealed that the mean annual runoff in the Klip catchment was approximately 111 x $10^6 m^3/yr$ and the return flow average of about 200 x $10^6 m^3/yr$, which is an indicator of the significant influence of effluent onto the flow regime of the Klip River. The return flow consists of effluents from irrigation, mining and industrial activities which returns to the river. This results in the deterioration of water quality, loss of aquatic habitat and such an increased flow may result in the eroding of river bank material. Nevertheless, this has guaranteed the perpetual flow of the Klip River, thus supporting water uses like irrigation and recreation all year round.

Topography

The Klip River source is located in the Witwatersrand Hills. Therefore, it is steep at the source until its confluence with the Rietspruit. This range of hills runs in an East-West alignment across the urban complex, forming a drainage border between the Vaal and Crocodile catchments. Altitude ranges from 1800 m at the source to 1420 m, where the Klip River joins the Vaal River. Mining activities have altered the topography especially of the upper Klip, whereby the mine dumps have led to the characteristic steep ridges. Prominent examples of these features in the upper Klip catchment include the Gatsrand and Klipriviersberg. On the contrary, the Lower Klip is generally featureless, characterized by the widening of the floodplain as well as the narrowing of the catchment at the river's confluence with the Vaal River.

Climate

Davidson (2003) described temperature in the Klip catchment to be generally a highveld climate, sub-humid with a tendency towards semi-aridity (Vermaak, 2010). The area experiences warm to hot summers between October and March (Davidson, 2003). The mean maximum temperatures occur in January at approximately 26°C to the lowest in June (16°C). Rainfall averages between 600 and 750 mm per year. Rainfall is high in the east and decreases towards the west and this can be attributed to topography, whereby the Witwatersrand ridges cause the greatest degree of atmospheric convergence. Evaporation varies between 1600-1700 mm and is much higher than the rainfall leading to the recurrence of drought and water shortages.

Geology

Generally, the geology in the Klip catchment is complex. This is because it comprises of basement complex granites, which in the north are overlain by the Hospital Hill sequences quartzite, shales and lavas, which are further covered by the Witwatersrand sequence shales characterized by conglomerates containing the gold bearing reefs. In the south, there is the Ventersdorp Supergroup Lavas of the Klipriviersberg which are overlain by the Malmani dolomites. Accordingly and throughout much of the catchment, depths ranging 0-50m dolomite are predominant. Consequently, considering the fact that the level and geochemistry of the groundwater influences the nature and weathering of these rocks, the occurrence of sinkholes is inevitable in the catchment (DWAF, 1999).

The Klip River catchment falls in the sub-humid climatic zone where geology is generally exposed to differential weathering. As such soils in the catchment are residual soils, varying considerably over short distances. Therefore, the soil profiles range from very fine soft silts to coarse, large, rock pinnacles. Sandy loams are predominantly found in the upper part of the catchment whereas clayey is atypical of the lower parts of the catchment.

Vegetation

Vegetation in the Klip River catchment can be categorized into three bioregions; Mesic highveld grassland; Dry highveld grassland and Central bushveld. The Mesic highveld grassland is the dominant biome in South Africa, found in the high precipitation parts of the highveld (Mucina and Rutherford, 2006). In the Klip River catchment the dominant vegetation type is the Randh grassland, which is characterized by the species rich, wiry, sour grassland alternating with the low, sour shrublands on rock outcrops and steeper slopes (Mucina and Rutherford, 2006). The grassland species include *Heteropogon contortus, Panicum natalensis, Loutetia simplex, Thameda triandra* and *Digutaria tricholaenoides.* Davidson (2003) further stated that the Highveld grassland is characteristic of the high inland plateau occurring along the ridges of the Witwatersrand and the dolomite plains of Gauteng mainly between 1 300 to 1 635 m in altitude.

1.10 Water uses in the Klip River

The following section provides a detailed description of the specific activities the reliance on the KRC for water and how they contribute to water pollution.

Domestic

The Rand Water is responsible for drinking water supply in the KRC, servicing over 10 million people. Groundwater usage in the catchment is restricted to the lower part of the catchment where small communities and individuals have boreholes. Due to the fact that the Rand Water is supplying water to an ever increasing population of water users, DWAF (1999) acknowledged that it might not be able to cater for the demand in the future. Kotze (2002) reiterated this notion postulating that informal settlements have already resorted to the use of the river for domestic consumption. Furthermore, Kotze (2002) suggested that potential anthropogenic sources of pollution in the KRC comprise of gold mining activities, wastewater treatment works and waste disposal sites, informal settlements and agricultural activities.

Mining and Industries

Rand Water, as was mentioned earlier, provides water to industries directly and indirectly but there is direct abstraction of water from the Klip River by a notable number of mines and industries (Kotze, 2002). However, DWAF (1999) reported that there was a decline in industrial water use, which was attributed to poor water quality and availability of potable water. Mining activities are mostly found in the Upper Klip catchment where there are two underground mining companies, the Durban Roodepoort Deep and East Rand Proprietary Mines.

Agriculture

Agricultural activities are confined to the area between the periphery of Johannesburg on the south and Vereeniging. The activities include livestock farming and crop cultivation. Crops under cultivation include maize, fodder and vegetables such as cabbage, carrots and potatoes. These crops are mainly irrigated. Irrigation of crops was noted to be vital to the economy of the KRC supplying the Johannesburg and surrounding area with produce.

Recreational

The KRC recreational activities include the non-contact, intermediate and full contact activities for example; the riparian home ownership, fishing, bird watching, boating, swimming, windsurfing and water skiing.

1.11 Research ethics

In maintaining the principles of ethics, applications were made to seek ethical clearance in fulfilment of a requirement of the Doctor of Philosophy with the North West University. Permission to collect water samples from the Klip River was sorted from the relevant authorities and also the fact that the findings from this study will be used for research purposes only was communicated. This research was guided by the four main ethical principles; respect and protection, transparency, scientific and academic professionalism and accountability.

1.12 Organization of Chapters

Chapter 1: **Introduction**

Comprising of the background information, description of the study area, objectives and research hypotheses for the study. It also highlights the conceptual framework of the study.

Chapter 2: **Assessment of water quality in the Klip River catchment, South Africa**

Consists of the contemporary knowledge on issues of water quality at the global, regional, national and local scales. It also gives details with regards to the sampling strategy, from the selection of sampling sites, rationale, methods of analysis and results. The results are presented in the form of tables, graphs, and statistical tests are used to illustrate the relationships between the different variables.

Chapter 3: **The spatio-temporal characterization of water quality in the Klip River catchment, South Africa**

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Consists of the background on the importance of spatial and temporal characterization of water quality and the various techniques used in literature. Furthermore, background on pollution source apportionment research techniques is described. The methodology used in this setting as well as results are presented in the form of tables, graphs, and statistical analyses results are used to illustrate the relationships between the different variables. There is a discussion with regards the implications of these findings using literature.

Chapter 4: **Assessment of the self-purification capacity of the Klip River (Gauteng), South Africa**:

Consists of a background on self-purification, the factors influencing and processes governing self-purification are discussed; the significance thereof and methods applied in this particular chapter are presented. The results are presented and discussed with reference to findings from other similar or related research studies.

Chapter 5: **Framework for Monitoring, evaluating and managing water quality in the Klip catchment**

Consists of an analysis of literature studies on water resources management, particularly the water quality management component. Based on literature and findings from this study, a strategical framework to monitor, evaluate and manage pollution in the Klip River catchment is presented.

Chapter 6: **Conclusion and Recommendations**

Consists of a summary of the whole research, the significant findings, as well as the recommendations for water quality management in the Klip River catchment.

1.13 Summary

This chapter has demonstrated the state of water quality and related concerns over the various spatial scales. It is apparent that the quality of water resources is in direct peril as a result of various anthropogenic activities. In order to develop an in-depth understanding of the extent to which anthropogenic and natural factors interact to influence the behaviour of water quality characteristics in rivers, there is a need to monitor water quality over time. The next chapter is an assessment of the water quality characteristics and their impacts on the aquatic systems in the Klip River catchment from monitoring activities, which were conducted from February 2016 to January 2017.

CHAPTER 2

ASSESSMENT OF WATER QUALITY IN THE KLIP RIVER CATCHMENT, SOUTH AFRICA

2.1 ABSTRACT

In the previous chapter, challenges associated with water quality, emanating from anthropogenic activities; economic development, industrialization, urbanization, agriculture, climate variability, population growth as well as natural processes, have been discussed. The questions that this research seeks to answer have also been indicated. In this chapter, some of the research questions i.e. implication of the poor water quality on the aquatic and terrestrial ecosystems, and the suitability of the Klip River water for its uses, are discussed. In addition, background on water quality assessments and the environmental risks associated is given, making reference to contemporary literature. There is also a presentation of the approaches used in evaluating water quality and the associated risks, the findings thereon and the implications.

2.2 Introduction

The inability to provide sufficient safe drinking water and adequate sanitation services to all people has been referred to as the greatest developmental failure of the 20th century (Cooley et al., 2013). This is because there is an understanding of the connection between water and sustainable development. Water drives sustainable development. Therefore, poor water quality can limit economic productivity and the developmental opportunities of a country. However, there is a paradox whereby poor economies are unable to develop because of water stress and contrastingly, economic instability prohibits the development of programs that abate water problems. Water quality is critical for sustaining basic human and environmental needs. Nonetheless, the quality of the world's water resources is in direct peril from growth, expanding industrial and agricultural activities, climate change and climate variability, pollution, unsustainable land use and poor institutional arrangements that govern water management practices.

The National Water Act (NWA) (Act 36 of 1998) defines water quality as the quality of all aspects of a water resource including its in-stream flow (quantity, pattern, timing, water level and assurance), water quality (physical, chemical and biological characteristics, in stream and riparian habitat characters and conditions) and aquatic biota (characteristics, condition and distribution). Rockström et al. (201 4) defined water quality as the appropriateness of water to maintain various uses or processes depending on its physical, chemical and biological properties. There is a relationship between ecosystem and the water quality found within its corresponding water bodies (UNEP, 1996). Furthermore, the water quality of rivers at any point is also influenced by the proportion of surface runoff and ground water reactions within the river system governed by internal processes, the mixing of water from tributaries of different quality and inputs of pollutants (Chapman and WHO, 1996). The uses of water: drinking, recreational, industrial and agricultural also have an impact on the quality of water. Human activities on the other hand, can induce acidification from industrial effluents, mine drainage and acid rain which will alter the pH, leading to degradation of the water quality and mobilization of Fe, Al, Co, Mn, Pb, Zn, which may accumulate in crops and plants (Oberholster et al., 2010).

The United Nations World Water Assessment Programme (UNWWAP) (2006) reported that globally, an estimated 2 million tons of sewage, industrial and agricultural wastes is discharged daily into water resources. Moreover, in developing countries, 90% of the sewage and 70% industrial waste discharges were found to be untreated and as such they contaminate existing water supplies (WATER-UN, 2006). Cooley et al. (2013) identified the lack of sanitation as a causal factor of contamination. UNICEF WHO (2008) reported that 2.5 billion people have no sanitation; 70% of them are in Asia. In Africa, most of the water quality problems are associated with the lack of and improper sanitation which leads to human and animal waste finding its way into fresh water systems (Tatlock, 2006). Another factor is the improper management of industrial waste emanating from mining and manufacturing activities, which are atypical of Africa. These pump toxic waste into streams and because there is limited environmental regulation and no resources to enforce environmental legislation, this leads to an ineffective control and remediation of the effects of wastewater discharges into water (Oelofse, 2008). The Sub Saharan Africa was observed to be the most afflicted region in Africa with water stress because of the inadequate sanitation infrastructure (with only 31% reported to have improved sanitation in 2006) and disproportionate quantities of stored water (Tatlock, 2006).

Water quality problems are particularly widespread in South Africa because the country experiences acute water stress. These poor water supplies are a product of a synergy of factors. This can be attributed to the meteorological characteristics of the country which is semi-arid and thus experiences highly variable rainfall patterns and high evaporation rates. Furthermore, South Africa has an expanding economy and as such, there is an array of anthropogenic activities, which impact the quality of water resources. Consequently, it was concluded that pollution will hinder the ability of water resources to sustain the patterns of water use in South Africa (Oberholster et al., 2010; Knüppe, 2011).

The contamination of rivers with heavy metals in particular, has been identified as a problem in growing cities, owing to failure of sanitation and water infrastructure to cater for the increasing population and urbanization (Ahmad et al., 2010; Reza and Singh et al., 2010). Jarup (2003) defined heavy metals as metals having a specific density more than that of water. Duffus (2002) further stated that these metallic elements induce toxicity at low levels of exposure. Heavy metals can also be referred to as trace metals, owing to their occurrence in trace amounts (Kabata-Pendia, 2010). Heavy metal sources are both natural and anthropogenic in origin. However, in unaffected aquatic environments, heavy metal concentrations are low, largely emanating from mineralogy and weathering processes (Karbassi et al., 2008). The anthropogenic sources of heavy metals include untreated and partially treated wastewater discharges, industrial effluents, agricultural runoff, mining effluents and storm runoff (Nouri et al., 2006; 2008; Reza, 2010). In surface water, heavy metals are present in soluble and particulate forms. Furthermore, there are dynamic fluxes between the dissolved ion and particulate-bound forms of heavy metals (Yao et al., 2014) and as such, depending on the form, heavy metals may display varying biological toxicities and environmental behaviours (Yao et al., 2014). For instance, Atli and Canli (2008) and Manyin and Rowe (2009), reported that the hydrated ions of many metals cause chronic toxicity in aquatic organisms.

Water quality problems have an implication on the aquatic ecosystem and human health. Palaniappan et al. (2010) suggested that poor water quality threatens human and ecosystem health, increases treatment costs and reduces the availability of safe water for drinking and other uses. Heavy metals particularly, owing to their non-degradable nature, accumulate in the body and food chain, unveiling chronic toxicity (Jaishankar et al., 2014). The effects of metals in drinking water on humans and wildlife have been widely documented in literature, and these include genotoxicity (Jomova and Valko, 2011; Poręba et al., 2011), teratogenesis (Branch, 2004) as well as carcinogenesis (Martin and Griswold, 2009). In addition Halder and Islam (2015) reported the occurrence of health problems which are possibly related to the quality of water for example gastric ulcers, skin problems, diarrhea and dysentery. Patterson and Johnson

(2003) studied the effects of water quality on cattle and found that highly saline water could lead to trace mineral deficiencies, reduced water intake and toxic sulphur ingestion. Nutrient enrichment associated with nitrogen and Phosphates from agricultural runoff could also deplete oxygen levels and eliminate species with higher oxygen requirements, thus affecting the structure and diversity of both the aquatic and terrestrial ecosystems.

WATER -UN (2011) estimated that approximately two-thirds of the fresh water species of fish are endangered due to water quality degradation. Any sudden changes in temperature, salinity, and turbidity can lead to fish mortalities (James et al., 2013). On the other hand, consumption of fish loaded with toxic chemicals presents serious health risks for the human populations (Ahmed et al., 2016). Another problem associated with water pollution is eutrophication which is the increased rate of primary production and accumulation of organic matter as a result of elevated nutrient concentrations in water, which in turn, may result in the proliferation of harmful algal blooms and dead zones in coastal marine environments (Rabalais et al., 2009; Nixon, 1995). These harmful algal blooms in turn cause oxygen depletion in water and thus impact on the local aquatic ecology, and also in some cases, releasing toxins, which are harmful to plants and animals consuming the water.

2.3 Water quality parameters

In this section, a comprehensive discussion based on the existing literature on water quality parameters, which were considered in this assessment are presented.

Temperature

Temperature is an important water quality parameter because it determines the physical and chemical properties of water and thus the rate of chemical and biological reactions. It determines the solubility of certain toxic chemical elements in water. Consequently, temperature governs other parameters such as compound toxicity, conductivity, salinity oxidation reduction potential, and pH and water density (Reddy and DeLaune, 2008). It regulates the dissolved oxygen and gaseous concentrations of the water and also influences the tolerance limits of aquatic organisms to the toxic compounds.

pH

One of the most important parameters of water quality is pH, which is a logarithmic measure of its acidity or basicity (Kornblum, 2010). The level of pH is determined by carbon dioxide reactions and the organic and inorganic solutes in water. This parameter is important because it governs the solubility and bioavailability of nutrients, trace and heavy metals in water. As such, it determines the nature of biochemical activities, which occur in aquatic ecosystems, and subsequently, the concentrations of chemical parameters in water.

Electrical conductivity (EC)

Electrical conductivity (EC) can be defined as the ability of water to pass an electrical current. It is governed by the presence of ions coming from dissolved salts and inorganic materials. Therefore, the measure of water conductivity is influenced by the concentration of ions, mobility of the ions, oxidation state and temperature of the water (Simeonidis et al., 2016). Furthermore, the physical characteristics of the catchment, particularly the geology and soil types determine the EC.

Total dissolved solids (TDS)

Total dissolved solids (TDS) comprise of organic dissolved matter as well as inorganic salts found in water. As such, TDS concentration in water represents a qualitative measure of the amount of dissolved ions (cations and anions) in the water. It can thus be deduced that the TDS as a water quality parameter is simply an indicator of the general quality, but is limited in terms of providing an insight into the nature of ionic interactions in the water. Total dissolved solids sources vary from natural such as geological and soil characteristics in a catchment to anthropogenic sources such as sewage, urban run-off and industrial wastewater discharges. Changes in TDS concentrations influence density of the water and also determine the flow of water into and out of an organism's cells and consequently, the growth of many aquatic life can be limited, or even result in death (Mitchell and Stapp, 1992). High concentrations of TDS may also, reduce water clarity, contribute to a decrease in photosynthesis, combine with toxic compounds and heavy metals, leading to an increase in water temperature.

Aluminum (Al)

Aluminum (Al) is the most abundant metal and the third most common element constituting approximately 8% of the earth's crust. In aquatic systems, it emanates from both the natural and anthropogenic sources. Natural sources include the weathering and erosion of rocks and soils (ASTDR, 2008), and volcanic activity (Kockum et al., 2006). Aluminum is widely used in the manufacturing and construction industries as well in water treatment plants. Aluminum salts such as alum have coagulative characteristics, which enable the removal of nutrients from water and subsequently, preventing or reducing eutrophication (Niquette et al., 2004; Smeraldi, 2012), and furthermore, reducing organic matter, colour, turbidity and microbial concentrations. Aluminum concentration in water is governed by pH because it influences the solubility and speciation of this metal molecule (Driscoll and Postek, 1996; Howells et al., 1990; Spry and Wiener, 1991). At neutral pH (ranges 6.0 - 8.0), Al is relatively insoluble, but soluble at acidic and alkaline conditions (pH <6 or >8).

Arsenic

Arsenic (As), is a naturally occurring ubiquitous element in the shallow crust of the eEarth and its hydrosphere (Even et al., 2017). It normally exists as a principal component of over 200 minerals. Arsenic finds its way into the environment through natural processes such as weathering, biological activities and volcanic emissions (Smedley et al., 2002). Relative to other heavy metals, As is distinctive owing to its sensitivity to pH. Arsenic can be mobilized at pHs ranging between 6.5-8.5 and under both oxidizing and reducing conditions.

Calcium

Calcium (Ca) finds its way into the aquatic environment from carbonate rocks, whereby carbonic acid in water dissolves the rocks (WHO, 2009). At low carbon dioxide concentrations, there is precipitation of Calcium carbonate. Ca dominates in concentration relative to other cations in rivers where there is low mineralization (WHO, 2009).

Cadmium

Cadmium (Cd) is a naturally occurring element in the environment (Förstner and Wittmann, 2012). Cadmium in fresh water is present primarily as a hydrated ion or ionic complexes i.e. Cd (+2) and $CdCO_3$ respectively (Vrhovnik et al., 2013). Cadmium is highly mobile in its soluble form. It may be introduced to water through natural processes like weathering and also through anthropogenic activities such as industrial and sewer effluent discharges, and seepage from mine tailings into adjacent streams (Vrhovnik et al., 2013; Murtaza et al., 2014). A large proportion of the Cd concentration in the aquatic environment is due to diffuse pollution originating from many different sources rather than from point sources.

Cobalt

Cobalt (Co) was reported to be highly mobile in acidic oxidizing environments, but owing to its affinity to hydroxides of iron, manganese and silty minerals, its aqueous migration is limited (Smith and Huyck,1999). The occurrence of cobalt in the earth's surface varies greatly. This element does not exist in its native form is only encountered in meteorites (Barałkiewicz and Siepak, 1999) Cobalt is most often found in the form of arsenides and sulphides. The most important cobalt minerals are cobaltite, linnaet, smaltyn and karrolit. The source of cobalt pollution (apart from industrial waste) is the burning of cobalt. Cobalt may occur at oxidation levels of -1 to +4, but in nature it occurs usually as a double-valenced cation Co^{2+} (cobalt compounds) (Barałkiewicz and Siepak, 1999). In erosive environments Co, easily undergoes oxidation from Co^{2+} to Co^{3+} and creates the complex anion $Co(OH)_3$.

Chromium

Chromium (Cr) is a rare and naturally occurring metal present in the Earthearth's crust (Jacobs and Testa, 2005). Its abundance ranges from 0.1 to 0.3 mg/L (Mohammed and Abdalrahim, 2007). Cr is also an essential trace nutrient required in small amounts for carbohydrates metabolism, but becomes toxic at higher concentrations. The trivalent Cr (III) and hexavalent form Cr (VI) forms of this metal occur naturally whereas the elemental Cr is not naturally occurring (Tchounwou et al., 2012). The major anthropogenic contributor of Cr to the environment are industries. Cr (VI) is from anthropogenic sources and has been reported to be detrimental to fauna; flora and human beings (Abdalrahim, 2007). The toxicity of Cr is generally dependent on the oxidation state and solubility. In particular, the toxicity of the hexavalent form Cr (VI) to living organisms has been attributed to the fact that it possesses a greater ability to diffuse through cell tissues (ATSDR, 2012a). Furthermore, the toxicity of Cr to aquatic organisms is directly proportional to water temperature and inversely proportional to pH and water hardness.

Copper

Copper (Cu) is a reddish metal that occurs naturally in rocks soil, water and sediments. It is also an essential trace nutrient required for carbohydrate metabolism and enzymes functioning in humans, other mammals, fish and shellfish (Solomon, 2009). Copper acts as a cofactor for oxidative enzymes including catalase, superoxide dismutase, peroxidase, cytochrome C oxidases, ferroxidases, monoamine oxidase, and dopamine β- monooxygenase (Harvey and

McArdle, 2008; Ramos, 2012) as well as in metalloenzymes involved in hemoglobin formation, carbohydrate metabolism and catecholamine biosynthesis, as well as in the cross-linking of collagen, elastin and hair keratin. The anthropogenic sources of Cu include activities such as mining, waste dumps, domestic wastewater, combustion of fossil fuels and wastes, wood production, phosphate and fertilizer production (ATSDR, 2004a). Owing to its solubility in water, Cu binds easily to sediments and organic matter (Solomon, 2009). Copper toxicity is influenced by the physico-chemical parameters of water such as hardness, alkalinity, naturally occurring organic and inorganic ligands, pH and temperature. Although pH has been shown to influence toxicity of many metals (De Schamphelaer and Janssen, 2010), for Cu, it actually decreases its toxicity at pH ranging from 3.0-7.0 (Schubauer-Berigan et al., 1993;De Schamphelaer et al., 2002; Janssen et al., 2003). The ability of copper to cycle between an oxidized state, Cu(II), and a reduced state, Cu(I), makes it potentially toxic as this can result in the generation of superoxide and hydroxyl radicals (Harvey and McArdle, 2008; Stem, 2010).

Iron

Iron (Fe) occurs naturally and is abundant in the Earth's crust. It is an essential nutrient for algal and other aquatic organisms (Vuori, 1995). It is also an important constituent of enzymes and proteins. Iron was noted to have an impact on the structure and functioning of river ecosystems. The spatiotemporal variability of Fe was observed to be great (Davison and DeVitre, 1992, Kimball et al., 1992) and this was attributed to variations in flow conditions, pH and redox conditions, and the nature and concentrations of dissolved organic matter (Mladenov, et al., 2009). In rivers, Fe is transported in the particulate fraction and depending on the pH levels and redox conditions, the metal can be released into the water column. The toxicity of Fe is high in acidic conditions (Gerhardt, 1992), particularly for aquatic invertebrates (Vuori, 1995).

Potassium

Potassium (K) is a biogenic metallic element, which is found in nature and mostly in its ionic form. The primary natural source of K is the weathering of silicate. Potassium occurs in lower concentrations in surface water owing to its weak migratory ability (Dinka et al., 2015). The low migratory ability is a result of its bioavailability, therefore, it is absorbed by flora and fauna (Li et al., 2014a). Potassium concentrations in water are generally very low relative to other cations, and such concentrations are not variable.

Magnesium

Magnesium (Mg) is less abundant relative to Ca in the earth's crust. It enters surface water as a result of the processes of chemical weathering and dissolution of dolomites and other rocks (Yuen et al., 2016). However, its concentration in rivers is influenced by the composition of ions and not by the geology (WHO, 2009). Magnesium ions occur in all natural waters but very seldom dominate. Its concentration in river water ranges from 1 to tens of mg/L (WHO, 2009). The weaker biological activity of Mg compared with Ca and also the higher solubility of $MgSO_4$ and hydrocarbonate as compared to the equivalent compounds of Ca favour the increase of Mg concentration in water (WHO, 2009). The concentration of Mg increases in conditions of high mineralization. Magnesium is highly soluble and has a high migratory ability in pH, redox and conductivity conditions, which are atypical of rivers.

Manganese

Manganese (Mn) is a naturally occurring redox sensitive metal which makes up to 0.1 % of the Earth's crust. It exists in water in the form of Mn ion or in the oxidized state. It is in more than 100 minerals such pyrolusite, rhodonite and rhodocrosite fossil fuel combustions and the erosion of Mn containing soils (Grygo-Szymanko et al., 2016). Anthropogenic sources of the environmental Mn include municipal waste water discharges, sewage sludge and mining and mineral processing (Howe et al., 2004). Generally, Mn salts are soluble in water but the oxides are insoluble, and as such, they form precipitates. In rivers, Mn is transported by suspended sediments and is released to water through diffusion (Howe et al., 2004). Manganese speciation is governed by pH and redox conditions with Mn ions dominating at low pH and redox potential and the Mn oxide at pH of above 5.5 (Scott et al., 2002).

Sodium

Sodium (Na) has a high migratory ability. The Na concentration is determined by the level of mineralization of water, whereby the concentration increases at higher levels of mineralization (WHO, 2009). A high proportion of Na is balanced by Cl ions forming a stable mobile combination that migrates with high velocity in solutions (Odhiambo and Muthiso, 2014). The sources of Na in water are deposits of various salts (rock salt weathering), products of limestone rocks and its displacement from the absorbed complex of rocks and soils by Ca and Mg.

Nickel

Nickel (Ni) is a ferromagnetic, and nutritionally essential metal found in rocks such as alkaline magma and silty sedimentary rocks. It occurs naturally and is the 24^{th} most abundant element making up 3% of the Earth's crust (Stanhard et al., 2017). It usually exists in a combined form with other elements and has five isotopic forms (Ratié et al., 2016). The natural source of Ni in rivers is usually the dissolution of nickel ore bearing rocks (Ratié et al., 2016). Nickel concentrations in rivers are general very low usually not exceeding 10 mg/L (ATSDR, 2005a). Owing to its unique physical and chemical properties, Ni has an extensive use such as in electroplating, production of stainless steel and as a food supplement. In natural water, Ni exists as Ni $(H_2O)_6^{2+}$ (ATSDR, 2005a). However, Ni is sulfophillic and as such, combines with As and S to form various minerals of its own. As a result of the natural processes, for instance weathering, Ni is activated. A large proportion of Ni found in the environment has anthropogenic origins, particularly the burning of diesel oil containing this specific metal (ATSDR, 2005a). It easily forms quite stable chelate compounds. In rivers, Ni is transported mainly as a precipitated coating on particles and in association with organic matter.

Lead

Lead (Pb) like many other metals is naturally occurring in the Earth's crust although its component found in the environment is largely from the anthropogenic activities such as mining and manufacturing activities. The largest source of aquatic releases of Pb are from the steel and iron industries, Pb production and processing operations (Sparling, 2016). Other significant indirect sources of Pb to the aquatic environment include urban runoff and atmospheric depositions (Sparling, 2016). Owing to its nature that it exists in multiple forms in aqueous solution, the chemistry of Pb is complex; it forms compounds of low solubility with the major anions found in natural waters. The concentration of Pb in surface waters is a function of the pH and the dissolved salts concentration in water.

Uranium

Uranium (U) is a naturally occurring heavy metal found in the earth's crust. It finds its way into the environment as a result of leaching from natural deposits, releases in mill tailings, emissions from the nuclear industry, combustion of coal and other fuels, and the use of phosphate fertilizers that contain this metal (Winde, 2010). Of all the heavy metals, U has the highest geochemical mobility in aquatic environments. The U decay series releases primarily alpha radiation along with some gamma radiation. It has a half-life of 4.5 billion years and can persist in the human body for varying lengths of time, depending on the affected organs and various exposure pathways. The toxicity of U is as a result of its radioactive and chemical properties (Taylor and Taylor, 1997; Brugge et al., 2011).

Vanadium

Vanadium (V) is the 22nd most abundant element in the earth's crust and at mean concentrations of 100 mg/L (Baroch, 2006). The natural sources of V releases to water include wet and dry deposition, soil erosion as well as weathering and leaching from rocks. The release of V through water erosion from land surfaces presents the largest contribution of V to water. Anthropogenic releases to water and sediments are far smaller than natural sources. The anthropogenic sources include leaching from residue of ores and clays, vanadium–enriched slags, urban sewage sludges and certain fertilizers (Harita et al., 2005). Vanadium concentration and bioavailability is a function of pH as well as the concentrations of Fe and Mnoxyhydroxides and redox reactions (Wang and Sanudo-Wilhelmy, 2009) hydrogen sulfide (Wanty and Goldhaber, 1992), and organic content (Szalay and Szilagyi, 1967; Shiller and Mao, 2000). Vanadium exists in oxidation states of -1 to +6 but the pentavalent form is the most environmentally toxic as it mimics phosphate and binds on enzyme sites in the cell.

Zinc

Zinc (Zn*)* found in the earth's crust with sources being mainly both natural and anthropogenic although the latter exceeds the former. The primary anthropogenic sources of Zn are mining industry, urban runoff, municipal and industrial effluents. Zinc primarily occurs in the oxidation state and forms complexes with ligands. The transport of Zn in water is governed by biological activity, pH and anion species. Zinc bioconcentrates moderately in aquatic organisms but not in plants and cannot be biomagnified along terrestrial food chains. This is because the decomposition of biota produces ligands which by way of precipitation and adsorption, reduce Zn's migratory ability. Zinc increases with decreases in pH.

Nitrates

Nitrates (NO_3^-) are naturally occurring ions, which can be found in igneous and volcanic rocks. The NO_3^- is the stable form of combined nitrogen for oxygenated systems. These compounds are utilized in the manufacturing of proteins in plants and animals. Furthermore, a principal source of nitrates is the decomposition of plants and animals. Nitrates accounts for the majority of the total available nitrogen in surface waters. The solubility of NO_3^- has presented serious environmental problems, as these molecules will still find their way into streams and lakes. Contamination of waters is a result of agricultural runoff (use of chemical fertilizer or animal manure) and discharges from septic systems and municipal waste water treatment facilities. Although chemically unreactive, it can be reduced by microbial action into different forms, which present risks to the environment.

Phosphates

Phosphates (P) occurs in dissolved organic and inorganic forms or attached to sediment particles. Phosphates, the inorganic form, are preferred for plant growth, but other forms can also be used when phosphates are unavailable. Phosphates builds up in the sediments of a lake or water body. When it remains in the sediments, it is generally not available for use by algae; however, various chemical and biological processes can allow sediment phosphates to be released back into the water (MPCA, 2008). Phosphates in water are not considered to be directly toxic to humans and animals and as such, no drinking water standards have been established for P (U.S. EPA, 1990).

2.4 Chapter Objective

The water quality from the KRC is impacted upon by discharge from mines, industry, urban runoff and the wastewater treatment plants, which are located in the urban areas. The Klip River, owing to the diverse nature of land use activities in the catchment area, has been classified as the most heavily impacted river in South Africa (Durgapersad, 2005). Miller (1998) reported that the KRC experienced high incidents of vandalism of sewer networks and problems of poor sanitation infrastructure. The presence of informal settlements, which lack sanitation, compounds the situation because there is leakage and spillage of raw untreated sewage into the Klip River resulting in fecal contamination of the water (Miller, 2000). However, the Klip River serves all categories of water use (domestic, industrial, agricultural and recreational), hence, knowledge of its water quality is required to ascertain whether the water is suitable for these uses. Therefore, the main aim of this chapter was to assess the trends in water quality characteristics in the Klip River catchment.

2.5 Methodology

This section outlines the research approach for this objective. A detailed account of the sources and types of data, the methods of collection as well as the various analytical techniques employed in the study are specified. Validation is given regarding use of these techniques and their underlying principles.

2.5.1. Identification of Sampling Sites

The sampling sites were chosen taking into consideration accessibility for sampling and that they should be representative of the 3 sub-catchments in the Klip River catchment, also paying attention to the land use patterns.

The main land uses identified were urbanization, mining, agriculture and industrial areas. These land uses were acting as reference points for sampling. Figure 2 shows the sampling points for this study as well as the locations of mines and mine dumps, and wastewater treatment plants.

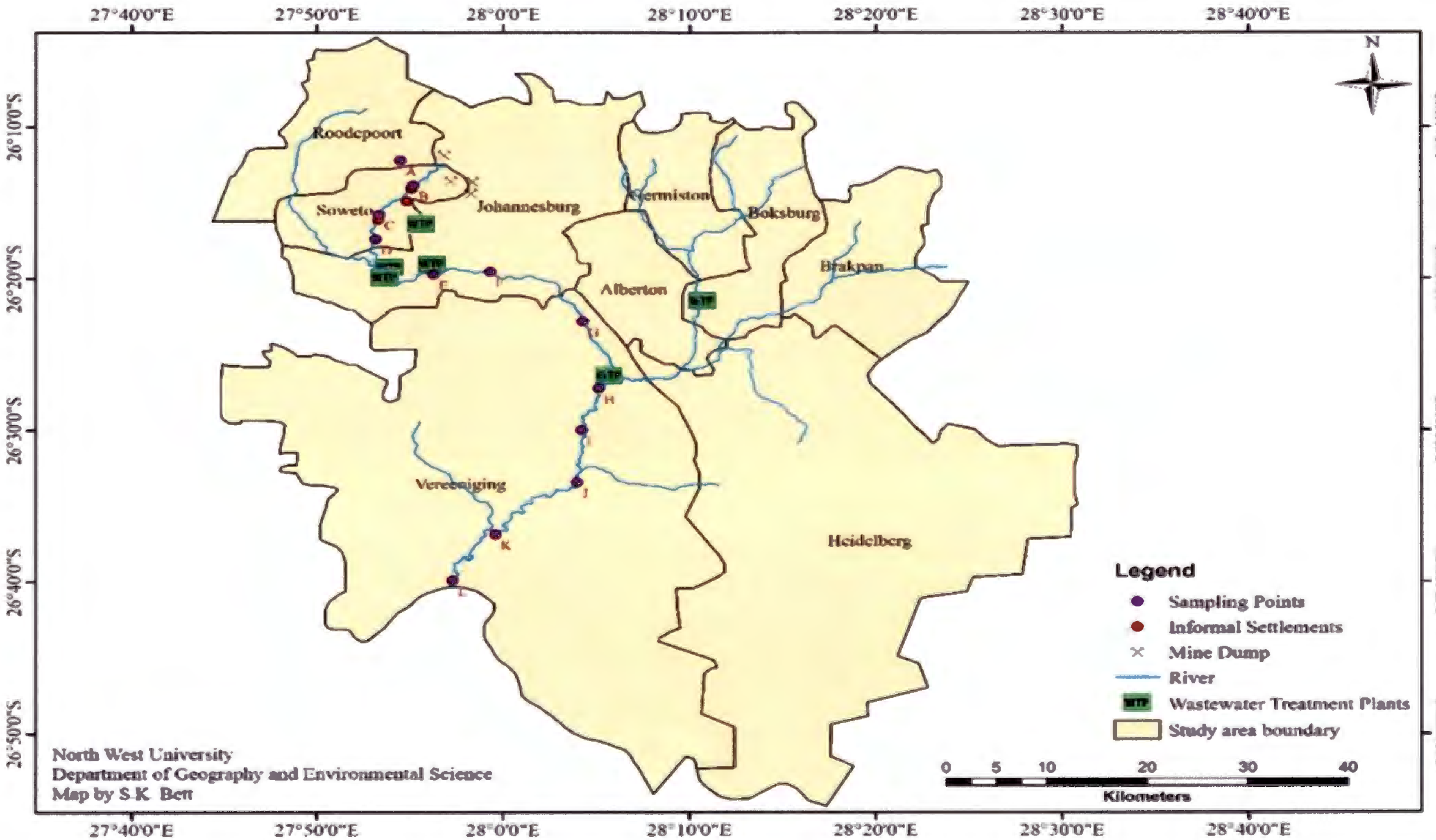

Figure 2: Map showing the sampling points in the Klip River catchment.

Figure 3 shows the sampling points located upstream of the Klip River denoted A, B, C and D. This section of the river runs through Soweto, where there is a concentration of settlements (both formal and informal), industries, mines and tailings dumps and a WWTP located adjacent to sampling point D. The sampling points are near tarred roads thus traffic which contribute metal availability in water bodies. This stretch of the river also represents the Upper Klip River in terms of the sub-catchment classification done by the Rand Water (2005).

Figure 2: Sampling points located upstream of the Klip River.

Figure 4 shows the sampling points located in the middle section of the river, denoted E, F, G and H. These points represent predominantly the industrial land uses and there are four WWTP located adjacent to this stretch of the river. Furthermore, this section aligns with the Rietspruit sub-catchment based on the Rand Water (2005) classification. The Rietspruit joins the Klip upstream of the sampling point G and as such, its influences on the Klip are incorporated.

Figure 3: Sampling points located in the midsection of the Klip River.

Figure 5 shows the sampling points located downstream of the Klip River, denoted I, J, K and L. These points represent agricultural activities and this section aligns with the lower Klip sub-catchment based on classification done by the Rand Water (2005).

Figure 4: Sampling points located in the lower reaches of the Klip River.

2.5.2. Water Sample Collection

From the identified sampling points, water samples were collected to determine contaminant concentrations. The samples were collected as follows:

Water samples were collected on a monthly basis for 12 months between February 2016 and January 2017 from 12 sampling sites. Samples were collected in triplicate sets to increase accuracy and precision of findings. Using 1 L High-density polyethylene (HDPE) bottles washed in 1% HNO_3, water samples were drawn from the different identified water sources. It should be noted that the bottles were rinsed with the sample water for three times before any sample was collected. The rinsing of the bottles with the sample was done for acclimatization purposes. The reason for using HDPE bottles was that they are good at preservation and have a high ability of reducing contamination of the samples.

2.5.3. Water Samples Analysis

The water samples were analysed for physicochemical parameters, nutrients, heavy metals, and radionuclides. The rationale for determining the above mentioned variables in particular was because this catchment is very diverse in terms of its land uses and subsequently, the potential sources of NPS pollution. The methods of analysis varied depending on the categories of parameters under study as shown in

Table 2: Parameters and methods of analysis of water samples.

Category of parameters	**Specific parameters**	**Method of analysis**
Physico/chemical	Temperature, pH Electrical Conductivity TDS	pH/TC/EC Field meters (Mettler Toledo Education Portable EL2-FIELD)
	Al, As, Ca, Cd ,Co, Cu, Cd, Fe, K, Mg, Mn, Na ,Ni Pb U,V, Zn	Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
Nutrients	Nitrates and Phosphates	Spectrophotometry

The determination of physicochemical parameters was done in two categories, the *in-situ* measurements and the *ex-situ* analysis. *In-situ* analysis involved measurements for temperature, pH (hydrogen potential), TDS (total dissolved solids) and EC (electric conductivity) which were done using standard procedures (Hemond and Fechner-Levy, 2000) by way of field meters. The information was then captured onto field data sheets. The rest of the parameters outlined in Table 2, formed the *ex-situ* analysis. The water samples were analyzed in the lab using ICP-MS and Spectrophotometry. As such, the water samples were then placed in cooler bags with ice to maintain a temperature of 4°C and immediately transported to the laboratory for analysis.

2.5.4. Inductively coupled plasma mass spectrometry (ICP-MS)

This technique employs an inductively coupled plasma (ICP) as an ionizing source and mass spectrometry (MS) is used to determine the elements. The samples are atomized to aerosol droplets. These droplets are transported to an argon plasma torch where excitation occurs. Firstly the plasma dries the aerosol, then separates the molecules thereby separating the electrons from the components. Singly-charged ions are formed and they are directed to a mass filtering device known as the mass spectrometer. Then the detector counts the number of ions passing through the quadrupole.

The ICP-MS method is advantageous in that the use of high temperatures enables the almost complete decomposition of the sample into constituent atoms thus enabling multi-element analysis (Ebdon et al., 1998). Furthermore and relative to other trace elemental analysis techniques, for example the atomic absorption spectrometry, it has advantages of high speed, precision and sensitivity. ICPMS has better sensitivity in such a way that it can be used for the determination of ultra-low levels of impurities in semi-conductors and long lived radionuclides in the environment (Falciani et al., 2000). However, prior to ICP-MS analysis, the water samples had to undergo several preparation procedures.

Sample Digestion

The samples were shaken vigorously to achieve homogeneity. 50 mL per sample was placed into a disposable digestion tube. One mL of (30%) HNO_3 and 0.5 mL of (1+1) HCl was added to the samples using micropipettes. The samples were placed in the hot block and heated for 2.5 hours at 85°C. The digestion tubes were removed from the hot block and were left to cool to room temperature. Distilled water was added to bring the sample volume back to 50mL. The digestion tubes containing the samples were then allowed to sit overnight before analysis, to allow any particulate material to settle out. Most of the samples still had some particulates and had to be filtered before the analysis.

2.5.5. Spectrophotometric determination of nitrates and phosphates

Nitrates

The spectrophotometer was calibrated using distilled water as a blank. A level micro spoon of NO_3 (-1) was placed into a test tube, then 5 mL of NO_3 (-2) was pipetted into the test tube. This mixture was then vigorously shaken for 1 minute after which 1.5 ml of the sample was gradually added to the test tube and allowed to stand for 10 minutes. The mixture was then poured into a 10 mm cuvette. The cuvette was then placed into the spectrophotometer to determine the absorbance. This procedure was repeated for the remaining samples.

Phosphates

The spectrophotometer was calibrated using distilled water as a blank. A level micro spoon of PO_4 (-1) was placed into a test tube, then 15mL of PO_4 (-2) was pipetted into the test tube. This mixture was then vigorously shaken for 1 minute after which 1.5 ml of the sample was gradually added to the test tube and allowed to stand for 5 minutes. The mixture was then poured into a 10 mm cuvette. The cuvette was then placed into the spectrophotometer to determine the absorbance. This procedure was applied for the remaining samples.

2.5.6. Water quality indices

Elshemy and Meon (2011) identified 4 approaches in the assessment of water quality of rivers namely; water quality indices, trophic status, statistical analyses and biological analyses. Bharti and Katyal (2011) stated that water quality assessments are complex owing to the multiple parameters under consideration. In a review of water quality indices used in various surface water quality assessments, Poonam et al. (2013) highlighted the necessity of using indices to resolve multi-parameter water quality data. As such, water quality indices reduce the volume of data making it simple to assign water quality status (Poonam et al., 2013). Therefore, this study used the Heavy Metal Pollution Index and Comprehensive Risk Index.

Heavy Metal Pollution Index (HPI)

Heavy metal pollution index (HPI) is a method of ranking that provides the compound influence of discrete heavy metals on the overall quality of water. The ranking ranges between 0 and 1 in value, thereby indicating the relative importance of individual quality considerations and the HPI is inversely proportional to the recommended standard (S_i) for each parameter (Prasad and Sangita 2008; Reza and Singh 2010). In this study the S_i values were taken from the South African Water Quality Guidelines.

1. Calculation of weightage of the *i*th parameter

$$W_i = \frac{K}{S_i} \qquad 1$$

Where W_i is the unit weightage and S_i is the recommended standard for the ith parameter and K is the constant of proportionality.

2. Quality ranking for each of the heavy metals

$$Q = 100\frac{V_i}{S_i} \qquad 2$$

Where V_i is the monitored value for a particular parameter and S_i is the standard permissible limit.

3. Calculation of the index

$$HPI = \sum_{i=1}^{n} Q_i W_i / \sum_{i=1}^{n} W_i \qquad 3$$

The HPI index was calculated per site on a monthly basis and also the yearly value, for 3 categories of water use: domestic, aquatic ecosystem protection and agriculture. This is because the Klip River satisfies all categories of water use, however recreational and industrial uses were excluded owing to unavailability of standards for many metals which were also incorporated in the study. The computations were done using the South African Water Quality Guidelines (SAWQG) for Domestic Water Use (Volume 1), Agricultural Water Use: Irrigation (Volume 4) and Aquatic Ecosystems (Volume 7) which were all published in 1996. It should also be noted that for Cr, Fe, Ni and V where there were no South African Water Quality Guidelines for Aquatic Ecosystems, the USEPA standards and the Canadian water quality standards were adopted.

Environmental risk Assessment

The environmental risk assessment was done using the Potential Ecological Risk Index (PERI). This index was devised to evaluate the heavy metal contamination based on characteristics of the heavy metals and its environmental behavior. PERI method has an advantage over other methods for instance the geoaccumulation index, pollution index as well as the regression analysis because it takes cognizance of the toxic response factor for a given contaminant whereas other indices look at the contaminant concentration disregarding their toxicity to humans and other biota (Huang et al., 2009; Ravankhah et al., 2016). Yuan et al. (2014) concluded that PERI is wide-ranging and as such, can be used to assess the synergistic effect of multiple types of heavy metals on the ecosystem.

The PERI method calculation was done in four stages: (i) Single contamination coefficient, (ii) Toxic response factor for heavy metals, (iii) Comprehensive contamination measure and (iv) PERI.

Comprehensive Risk Index (CRI) which is the sum of environmental risk ratios was calculated as follows:

$$R_i = T_i \times \frac{OC_i}{NOEC_i} \quad 4$$

$$CRI = \sum_{i=1}^{n} R_i \quad 5$$

Where OC_i is the observed concentration for the metal *I*; $NOEC_i$ is the highest concentration for the metal *i* which does not affect an aquatic ecosystem; T_i is the toxicity coefficient of metal *i* which could mirror the potential hazard posed by a metal to the aquatic ecosystem (Hakanson 1980). The classification of the CRI and the PERI is as shown in Table 3.

Table 3 : Classification of water based on the CRI and the PERI.

Ecological risk of single metal (E)	Grading	PERI (RI)	Grading
E<40	Low risk	**RI<150**	Low risk
40<E<80	Moderate risk	**150<RI<300**	Moderate risk
80<E<160	Considerable risk	**300<RI<600**	High risk
160<E<320	High risk	**>600**	Very high risk
E>320	Very high risk		

2.5.7. Data Analysis

Statistical analyses are used to describe, explain, understand and prove concepts under investigation. In this study, various statistical techniques were used in assessing and analyzing the various data that had been collected. These techniques varied from descriptive statistics (means and standard deviations) to inferential statistics (correlation analysis and the independent *t* test). Each of the various statistical techniques was applied to serve a particular purpose. The following section, describes these statistical analysis methods, how they were used and the rationale behind their use.

Mean and standard deviation was computed for each sampling point since the samples were collected in triplicate set per site. The formula for mean and standard deviation are as follows;

$$\bar{x} = \frac{\sum \bar{x}}{N} \quad (6)$$

$$S_x = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})}{n-1}} \quad (7)$$

One-way repeated measures ANOVA

A one-way repeated measures ANOVA was conducted to determine whether there were statistically significant differences in mean concentrations of water quality parameters recorded during the study period.

$$F = \frac{\sum_{j=1}^{s}\sum_{i=1}^{n_j} w_{ij}\,(\bar{x}_j-\bar{x})^2/(j-1)}{\sum_{j}^{s}\sum_{i=1}^{n_j} w_{ij}\,(\bar{x}_j-\bar{x}_{ij})^2 \Big/ \left(\left(\sum_{j=1}^{s}\sum_{i=1}^{n_j} w_{ij}-1\right)(j-1)\right)} \qquad 8$$

Where $\bar{x}_{ij}$ is the value of the i th of $n_j$observations in the jth of S groups, where $\bar{x}_{ij}$ has been centered' such that,

$$\sum_{j=1}^{s} x_{ij} = 0 \forall i \qquad 9$$

Where $\bar{x}_j$ is the Mean in the jth group and $\bar{x}$ is the overall mean, w_{ij} is the calibrated weight and $p \approx Pr\left(F_{(s-1)\epsilon\left(\sum_{j-1}^{s}\sum_{i=1}^{n_j} w_{ij}-1\right)(s-1))\epsilon} \geq F\right)$ and ϵ is computed using the Greenhouse-Geisser method.

Multiple linear regression

Multiple linear regression (MLR) is a statistical tool which is widely used in developing forecasting models. In this research, MLR was used to develop a predictive model that identified the metals, which could be used to predict the HPI for domestic uses, agricultural uses and aquatic ecosystem protection in the KRC. The general equation for MLR is as follows:

$$y = c + \sum_{i=1}^{n} a_i x_i + \varepsilon, \qquad 10$$

Where Y is the response variable in this case the HPI for domestic uses, agricultural uses and aquatic ecosystem protection, C is the intercept and a_i $i = 1, 2,...,n$ are the regression coefficients $x_i i = 1, 2,...,n$ are the independent predictor variables which in this case are the various metals and ε is the residual error.

2.6. Results and Discussion

2.6.1. Temperature

The water temperature recordings at all the sampling sites in the KRC depicted a cyclic trend during the study period as is shown in Figure 6. Wherein at the beginning of the sampling period in February, the temperatures at the various sampling sites, ranged from 22.5- 24°C along the profile of the river. The water temperatures then showed a declining trend in the preceding months until June synonymous with effects of winter. The lowest temperature recordings at all the sites except for site A, were in June. From July the water temperatures steadily increased, reaching peak temperatures in November at 9 of the sites (D, E, F, G, H, I, J, K and L). Overall the temperature ranged from 10.3- 27°C (Table 4).The lowest temperature was recorded at site L in June and the highest at site I in November.

Table 4: Annual mean, maximum and minimum temperature values (°C).

Site	*Mean ± SD*	*Maximum*	*Minimum*
A	20.2 ± 10.50	25.0	12.1
B	20.5 ± 10.62	24.8	16.6
C	19.7 ± 10.29	24.6	12.4
D	19.5 ± 10.22	26.6	11.3
E	19.5 ± 10.35	26.9	11.5
F	19.6 ± 10.31	26.8	11.7
G	19.0 ± 10.22	26	11.0
H	19.2 ± 10.21	26.5	11.3
I	**19.1 ± 10.24**	**27**	11.0
J	19.0 ± 10.16	26.4	10.5
K	19.1 ± 10.16	26.3	**10.4**
L	18.8 ± 10.14	26.4	**10.3**

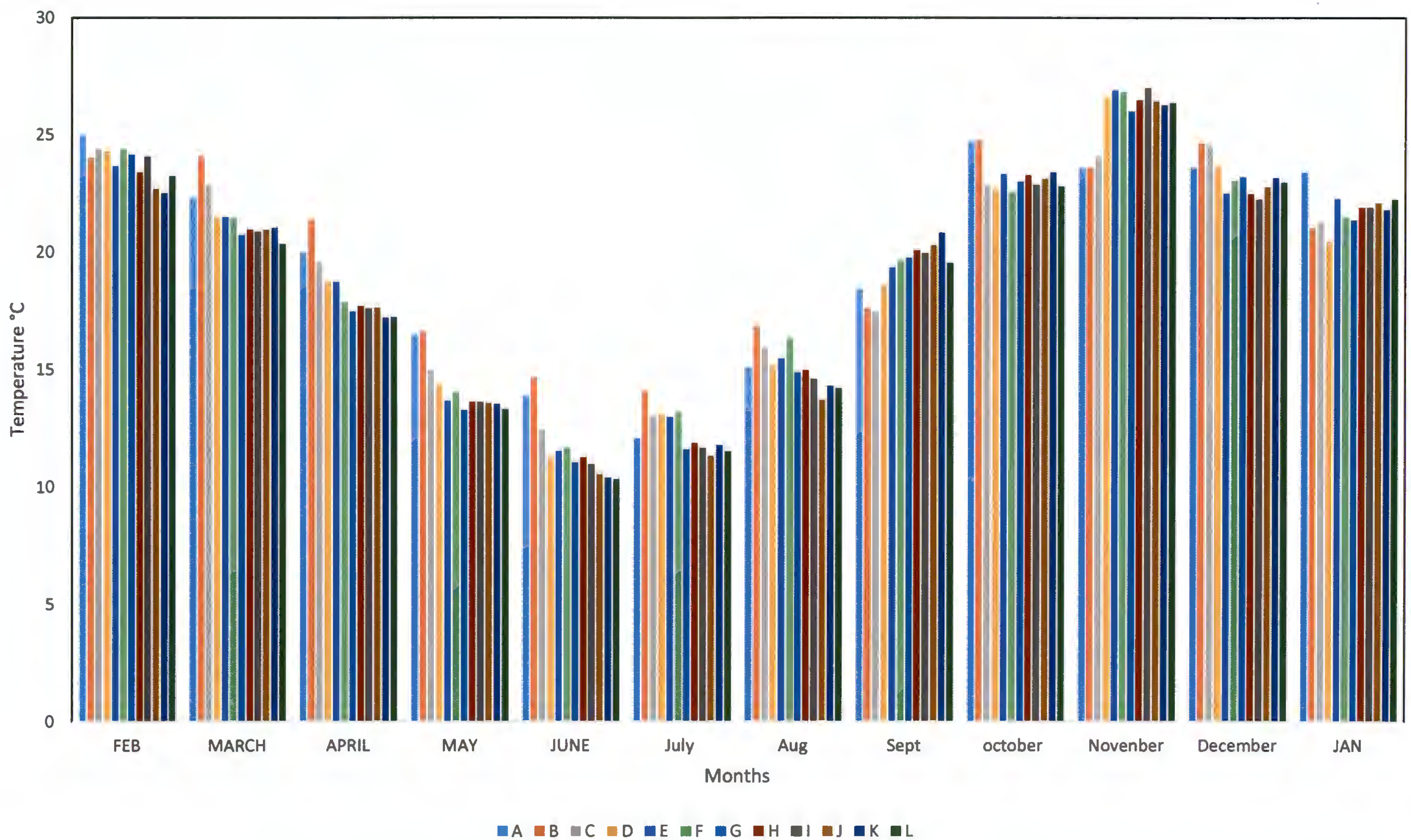

Figure 5: The trends in temperature in the KRC.

The Mauchly's test $\chi 2$ (65) = 199.028 p = 0.000 violated the assumption of sphericity (Field 2013).The one-way repeated measures ANOVA results indicated that at 95% confidence interval F (1.805, 19.856) = 310.303, p = 0.000), there were statistically significant differences in temperature in the various months from February 2016 to January 2017.The differences can be attributed to seasonal changes from summer to winter. Air temperature and tree shading can also influence water temperature. Although there w no SAWQG for temperature for various uses, it is important because it wields significant influence on biological activity and growth. For instance aquatic organisms are ectothermic, thus temperature governs their physiology, bioenergetics, behaviour, and biogeography (Rahel, 2002). High temperatures may increase the virulence of non-native parasites such as *Myxobolus cerebralis* and pathogens to native species such as salmonid resulting in lowering of the populations of fish (Rahel and Olden, 2008).Furthermore temperature is also important because it governs chemical reactions in water. At high temperatures, there is dissolution of minerals, thereby elevating the concentrations of ions in water.

2.6.2. pH

Overall, the pH values ranged in the neutral to alkaline categories all year round. For 11 of the sites except for Site A, the pH depicted similar trends, whereby it was relatively lower in the first 2 months and only increased in the third month (Figure 7) which can be linked to the Nernst equaton correlating water temperature and pH. Site A however, had the highest pH recorded in the month of February relative to the other sites. As is shown in Table 5, the pH ranged between 6.81 and 9.05. The lowest pH value during the study period was recorded at Site A in May and the highest, at site K in November. Sites E, F, G, H, I and J also had maximum pH recordings in November. Most minimum pH recordings were in February (sites D, G, H, I, J, K and L). The one-way repeated measures ANOVA results indicated that at 95% confidence interval, F (1.716, 18.877) = 13.076, p = 0.000) there were statistically significant differences in pH in the various months from February 2016 to January 2017.

Table 5: Annual mean, maximum and minimum pH values.

Site	*Mean*	*Maximum*	*Minimum*
A	7.45 ± 3.70	8.17	**6.81**
B	7.25 ± 3.66	7.38	7.03
C	7.26 ± 3.67	7.39	7.03
D	7.46 ± 3.72	7.99	7.06
E	7.55 ± 3.79	7.94	7.14
F	7.62 ± 3.85	8.16	7.15
G	7.79 ± 3.93	8.65	7.12
H	7.71 ± 3.87	8.77	7.1
I	7.77 ± 3.92	8.69	7.19
J	7.83 ± 3.95	8.72	7.22
K	7.92 ± 4	**9.05**	7.25
L	8.09 ± 4.04	8.91	7.31
SAWQGDomestic = 6-9			
SAWQGAquatic = 7-8			
SAWQGAgriculture = 6.5-8.4			

Generally the pH recorded in the KRC was in line with the SAWQG for domestic, aquatic and agricultural uses with the exception of site K (9.05) where there were agricultural activities taking place this site exceeded all the guidelines. Highly alkaline pH of freshwater > 9 affects fish by inducing gill damage, reduction of metabolic wastes disposal and consequently death (Wilkie and Wood, 1994; Tucker and D'Abramo 2008). High pH elevates drinking water hardness, thereby making wastewater disposal more difficult, and exacerbates the salinization of fresh water. Valdez-Aguilar et al. (2009) observed impacts of alkaline irrigation water on Marigold plants for pH value of 7.8 which many sampling sites in the KRC exceeded in various months during the study. The pH is important because it influences toxicity of heavy metals in water such as Cu (Woody and O'Neal, 2012).

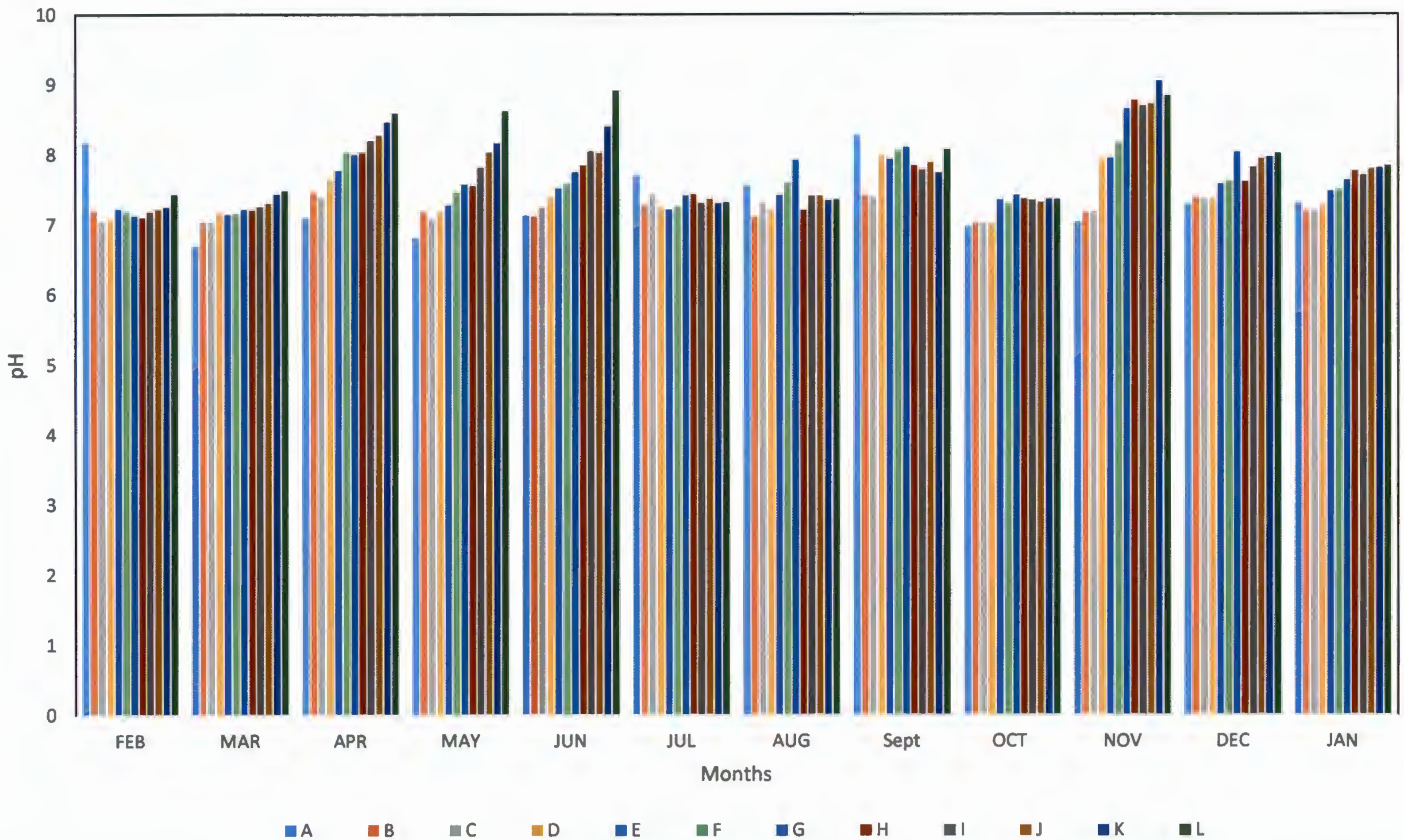

Figure 6: pH trends in the KRC.

2.6.3. Electrical Conductivity

Electrical conductivity can be defined as the ability of water to pass an electrical current. It is governed by the presence of ions coming from dissolved salts and inorganic materials. Therefore, the measure of water conductivity is influenced by the concentration of ions, mobility of ions, and the oxidation state and temperature of the water. Furthermore, the physical characteristics of the catchment, particularly the geology and soil types determine the concentration and nature of ions present in the water.

Table 6: Annual mean, maximum and minimum electrical conductivity values (µS/cm).

Site	*Annual Mean*	*Maximum*	*Minimum*
A	342.02 ± 184.52	457.33	**74.17**
B	516.89 ± 272.83	668	179.03
C	431.40 ± 225.74	497	181.43
D	452.92 ± 221.22	512.50	182.10
E	427.32 ± 219.49	521	248.67
F	440.12 ± 225.27	499	272.33
G	438.01 ± 225.08	510.33	261.33
H	612.49 ± 319.69	764.67	372.5
I	625.76 ± 314.98	**765**	411.67
J	615.88 ± 318.93	731	408.67
K	630.14 ± 318.34	738.67	470
L	613.99 ± 309.87	759.67	307.5
SAWQGDomestic = 400 (µS/cm)			
SAWQGAgriculture = 700 (µS/cm)			

As illustrated in Figure 8, sites H, I, J, K and L showed similar trends in EC over the period of the study with maximum EC values at these sites recorded in April and October and the lowest recorded in January and February. Site A recorded the lowest EC in all the months with the lowest reading in February. The highest EC was recorded at site I in October. The EC ranged between 74.17 and 765 (µS/cm) (Table 6).The one-way repeated measures ANOVA results indicated that at 95% confidence interval $F(2.006, 22.061) = 17.313$, $p = 0.000$) there were statistically significant differences in EC in the various months from February 2016 to January 2017. The EC recorded in the KRC exceeded the SAWQG for agriculture at a majority of the sampling sites and throughout the year. However, the sampling points A to G were in line with SAWQG for agriculture in some months.

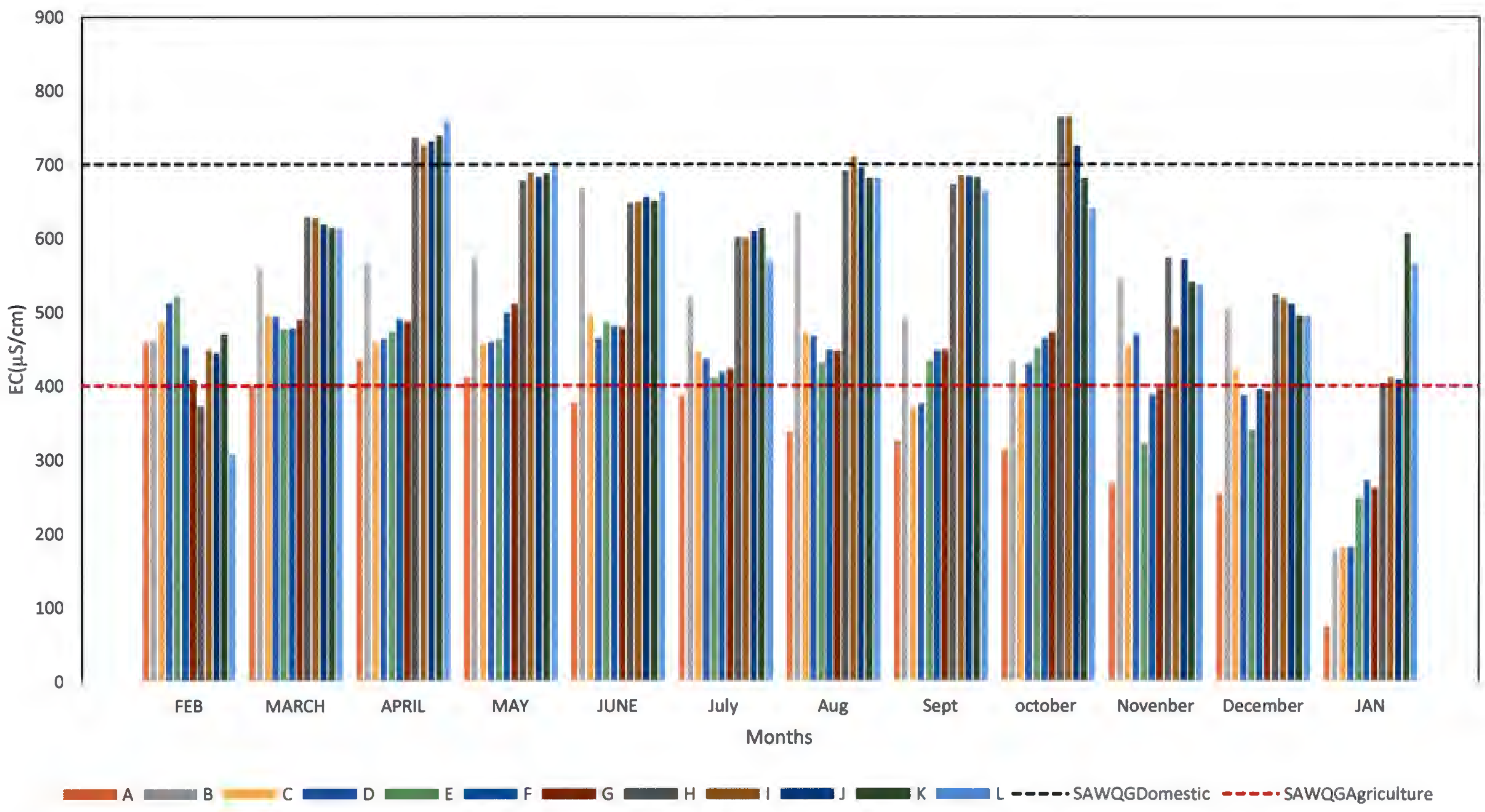

Figure 7: Electrical conductivity trends in the KRC.

The effects of high EC in irrigation water on crop productivity is physiological drought which is a result of the failure of plants to compete with ions in the soil solution for water (Bauder et al., 2011). However EC was mostly in line with the SAWQG for domestic uses with an exception of the months of April, August and October where sampling points H, I, J, K and L exceeded the SAWQG. It can be concluded that the EC values recorded in the KRC render the water unsuitable for agricultural uses.

2.6.4. Total Dissolved Solids

Generally, the TDS ranged between 47.5 and 1549.67 mg/L (Table 7) of which the lowest TDS was recorded at site A in January and the highest at site L in April. The TDS concentrations were generally above the mean concentration of 120 mg/L recorded in the world's rivers (Weber-Scannell and Duffy, 2007). Sites H, I, J, K and L depicted similar trends during the study period, and were relatively higher in concentration relative to the other seven sites which depicted a slightly different trend, particularly in the first five months. It is important to note that the lowest TDS concentrations were recorded in January for ten of the sites with the exception of sites K and L, whose lowest TDS recordings were in December.

Table 7: Annual mean, maximum and minimum total dissolved solids values (mg/L).

Site	*Annual Mean*	*Maximum*	*Minimum*
A	544.93 ± 368.49	960.67	**47.5**
B	769.08 ± 493.76	1362.67	114.6
C	655.54 ± 420.78	1014	116.1
D	670.21 ± 419.09	1045.5	116.43
E	658.47 ± 425.67	1063.5	159.13
F	667.40 ± 425.71	1029.33	174.43
G	662.28 ± 424.03	1041	167.27
H	910.70 ± 586.17	1500.67	258.33
I	923.29 ± 591.54	1481	263.67
J	916.74 ± 584.40	1491	261.33
K	926.47 ± 577.79	1506.33	317
L	905.73 ± 559.12	**1549.67**	312
SAWQGDomestic = 400 mg/L			

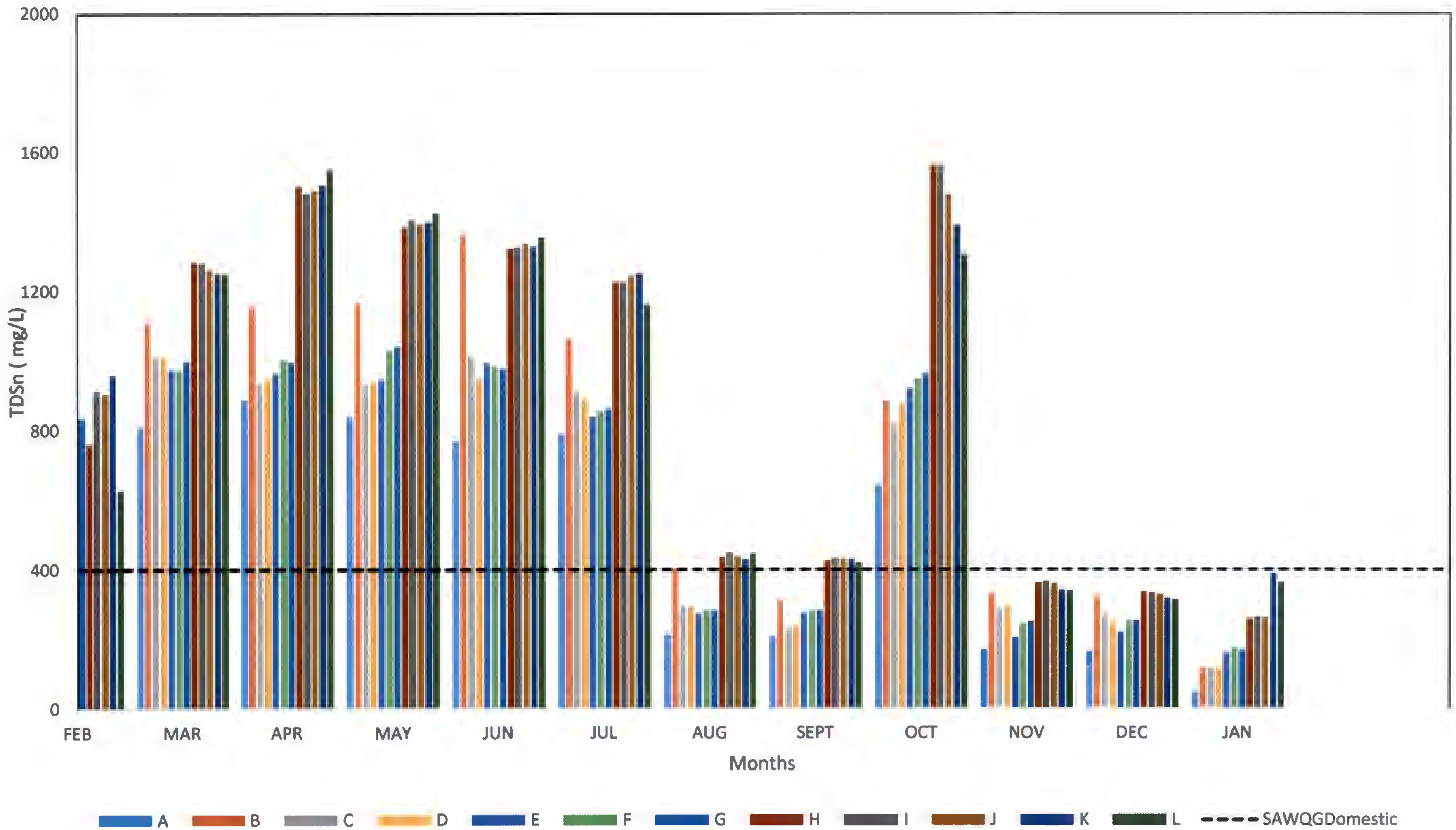

Figure 8: The trends in TDS concentrations in the KRC.

The one-way repeated measures ANOVA results indicated that at 95% confidence interval F (1.441, 15384) = 2.322, p = 0.000) there were statistically significant differences TDS in the various months from February 2016 to January 2017. Total dissolved solids concentrations in the KRC exceeded the SAWQG for domestic uses at all sites between February and June; and in October as well (Figure 9). WHO, (2003) reported that there was no data to substantiate health effects associated with the ingestion of TDS in drinking water.

Conversely, Kozisek (2005) had reported associations between various health effects and individual mineral salts that make up TDS. The palatability of water with TDS levels of less than 600 mg/L is generally considered good (Bruno et al., 2008). Drinking water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/L (Bruno et al., 2008). Total dissolved solids values greater than 1200 mg/L may be objectionable to consumers and could have impacts for those who need to limit daily salt intake e.g. severely hypertensive, diabetic, and renal dialysis patients (Mebrahtu and Zerabratu, 2011). Total dissolved solids toxicity results in increased salinity and consequently alterations in the ionic composition of water and toxicity of individual ions (Weber-Scannell and Duffy, 2007). As such it can be concluded that the KRC is not suitable for domestic uses based on the concentrations of TDS. Although there are no standards for aquatic ecosystem protection for TDS, increased salinity was shown to impact on aquatic ecosystems through loss of biodiversity (Weber-Scannell and Duffy, 2007). Furthermore, it can also cause acute or chronic effects at specific life stages of aquatic organisms.

2.6.5. Aluminum

Aluminum concentrations ranged between 0 and 4.226 mg/L of which the lowest recording was observed at sites A, B, K (Table 8) in February, site E in July and site H in December (Figure 10). The flow of water from soils into streams and rivers results in a gradual build-up of Al in the Klip River. The highest recording was at site A in September. The highest yearly mean Al concentration was recorded at site B (1.097 mg/L), and this is supported by the fact that for site B many peak concentrations were recorded relative to other sites over the duration of the sampling period in June, July, August and November (Figure 10).Sites A and B are located in the upstream section which is largely influenced by mining activities. The lowest yearly mean Al concentration was at site E (0.247 mg/L). Correspondingly, the values recorded between February 2016 and January 2017 at this site were generally low ranging between 0 and 0.385 mg/L.

Table 8: Annual mean, maximum and minimum aluminum concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0.640 ± 0.850	**4.226**[a]	**0**
B	1.097 ± 0.825	2.810	**0**
C	0.856 ± 0.536	1.354	0.126
D	0.448 ± 0.307	1.286	0.018
E	0.247 ± 0.131	0.385	**0**
F	0.466 ±0.643	3.228	0.035
G	0.324 ±0.227	0.881	0.009
H	0.379 ±0.200	0.624	**0**
I	0.420 ±0.238	0.916	0.136
J	0.446 ±0.24	0.654	0.042
K	0.392 ±0.232	1.035	**0**
L	0.654 ±0.704	3.543	0.153
SAWQGDomestic = 0.015mg/L			
SAWQGAquatic = 0.005 mg/L			
SAWQGAgriculture = 5 mg/L			

The low Al concentrations could be attributed to the dilution effect rainfall. One-way repeated measures ANOVA was conducted to determine if there were differences in Al concentrations recorded in the different months during the study period. The results indicated that at 95% confidence interval, (F (2.832, 31.151) = 1.752, $p = 0.179$) there were no statistically significant differences in mean Al concentrations from February 2016 to January 2017 and the values were below the permissible limits.

Guibaud and Gauthier (2003) observed an inverse relationship between Al concentrations in water and pH, whereby Al concentrations increased with a decrease in pH. Therefore, Guibaud and Gauthier (2003) concluded that Al solubility is elevated at acidic pH levels. However, the pH levels of the Klip River were mostly neutral to alkaline, but the Al concentrations were higher than those recorded in acidic rivers. Nonetheless, this aligns well with the findings from Driscoll and Postek (1996), whereby Al solubility was observed to be high at pH levels as high as 9.5. Wang et al. (2013) reported similar results in Xi'an City, China that at alkaline pH levels, Al concentrations were high. These elevated Al concentrations could be attributed to the usage of Al salts as a flocculent during wastewater treatment (Wang et al., 2013).

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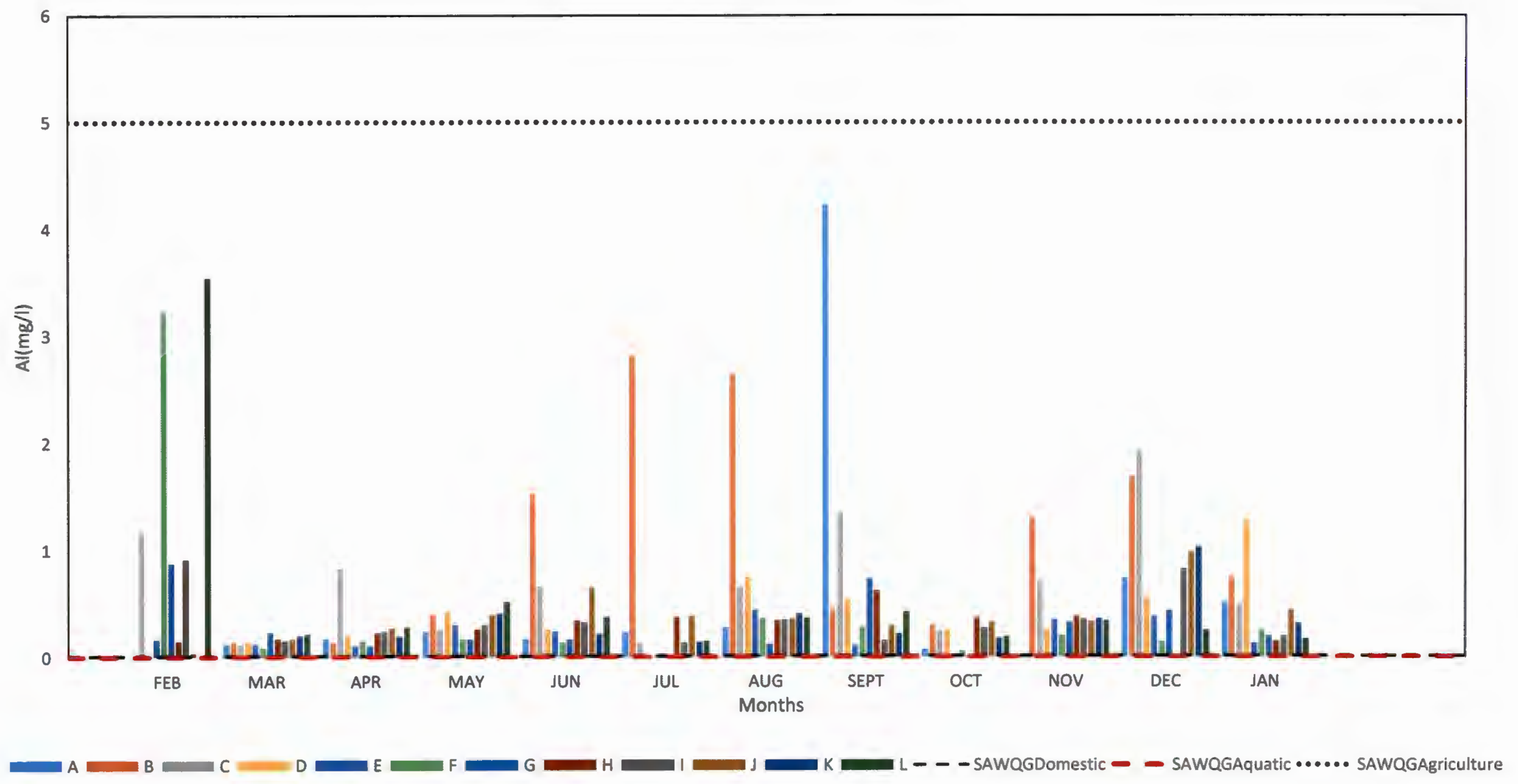

Figure 9: The trends in aluminium concentrations in the KRC.

Aluminum concentrations in the Klip River were in line with the SAWQG for agriculture at all sites throughout the year suggesting that the river water is suitable for agricultural uses. High concentrations of Al fertilization in maize and consequently decreased crop yields, increasing the threat to national food security. Conversely, the Al concentrations were mostly in excess of the SAWQG for domestic water and aquatic uses.

Martin et al. (1989) studied the risks of Alzheimer's disease in drinking water and established that the risk was 1.5 times higher in areas where Al concentrations were in excess of 0.11 mg/L of which the values recorded in the Klip, were above this. However, although Krewski et al. (2007) alluded that the association between Al and Alzheimer's disease, had been established (McLachlan 1995; Huang et al., 1997; Cucarella et al., 1998) owing to large disparities in the findings, they suggested that there should be further investigations. Galar-Martinez et al. (2010); Garcia-Medina et al. (2010) reported on an association between Al concentrations with gill damage in fish. Although toxicity of Al to fish had been previously linked to acidic environments, Poléo and Hytterød (2003) reported some physiological changes to elevated Al concentrations in alkaline environments.

2.6.6. Arsenic

Arsenic concentrations ranged between 0 and 17.124 mg/L (Table 9) of which the lowest concentration was recorded at all sites except G in various months between February and June and the highest having been recorded at site F in December. Arsenic depicted similar trends at all the sites whereby the concentrations were relatively low between February and June only to increase in July then fluctuate in the preceding months until January (Figure 11). The highest mean As concentration was 12.043mg/L at site F, which congruently recorded the highest monthly As concentrations relative to the other sites for six out of the twelve months duration of the study.

Even et al. (2017) reported that the distribution of As in river waters is strongly correlated with the distribution of the subsurface geology. High As concentrations in rivers can also be attributed to mineralization associated with mining activities which dominate land use activities in the Upper Klip River (Even et al., 2017). Furthermore the neutral and alkaline pH and availability of Fe enhance the dissolution and availability of As (Even et al., 2017). The lowest annual Mean was 8.994 mg/L at site K. Based on the one-way repeated measures ANOVA at 95% confidence interval ($F (4.498, 49.482) = 25.854$, $p = 0.000$) there was a statistically significant difference in As concentration in the various months from February 2016 to January 2017. Multiple pairwise comparisons with a Bonferroni adjustment revealed that the differences were particularly statistically significant between mean As concentrations in the first five months (From February to June) which were lower relative to the last seven months (from July to January).

Table 9 : Summary of annual mean, maximum and minimum arsenic concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	9.079 ± 3.597	12.845	**0**
B	11.153 ± 4.118	14.698	**0**
C	10.698 ± 4.096	12.609	**0**
D	10.436 ± 4.267	13.450	**0**
E	10.171 ± 3.205	10.323	**0**
F	12.043 ± 5.035	**17.124**	**0**
G	10.638 ± 3.946	13.123	1.624
H	10.234 ± 3.844	15.517	**0**
I	9.574 ± 4.036	12.137	**0**
J	9.966 ± 4.892	15.618	**0**
K	8.994 ± 3.845	11.272	**0**
L	10.734 ±3.681	11.358	**0**
SAWQGDomestic = 0.01 mg/L			
SAWQGAquatic = 0.01 mg/L			
SAWQGAgriculture = 0.1 mg/L			

The period between July and January was characterized by winter months and many irregular stormy events in the Klip River catchment, leading to the contribution of solutes from the soils and thus a high EC. These stormy events are liable for the sudden increase in solute chemistry, leading to weathering products being exposed to runoff (Sultan and Dowling, 2005), as is indicated by the levels of As in water during the period. Contrastingly, Giouri et al., (2012); (2013) associated high As concentrations with low flow of the river. Arsenic concentrations in the Klip River were mostly in excess of SAWQG for domestic, aquatic and agricultural uses (Figure 11). However, between February and June some sites complied with the SAWQG for domestic, aquatic and agricultural uses. Effects of As on aquatic organisms have been reported at concentrations as low as 0.019 to 0.048 mg/L (Eisler 1988), of which the values recorded in the Klip River where higher.

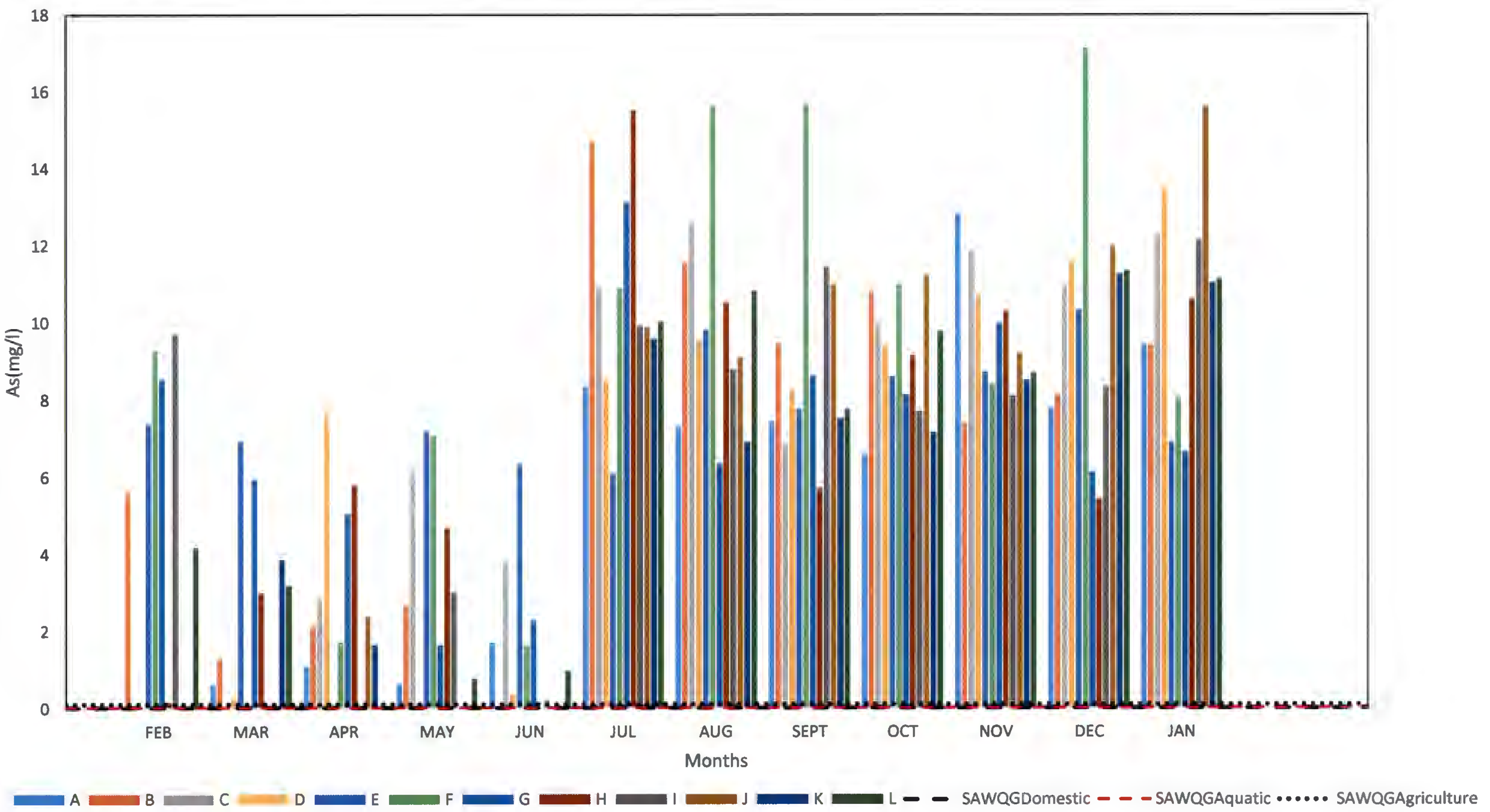

Figure 10: The trends in arsenic concentrations in the KRC.

Furthermore, there is extensive literature evidence of the impacts of As on fish (Ouédraogo and Amyot, 2013; Noël et al., 2013; Magellan et al., 2014).

Long term exposure of fish to low concentrations of As results in bioaccumulation, in the liver and kidney and consequently induced hyperglycemia, depletion of enzymatic activities, causing various acute and chronic toxicities as well as some immune system dysfunctions (Kumari et al., 2016). Chen et al. (2009) reported effects of consumption of water contaminated by As at concentrations ranging between 0.01-0.3 mg/L, such as skin lesions, circulatory disorders, neurological complications, diabetes, respiratory complications, hepatic and renal dysfunctions including mortality due to chronic diseases. Meharg and Rahman (2003) and Williams et al. (2005) also demonstrated the dangers associated with irrigation of crops (Vietnamese rice) with water contaminated with elevated As concentrations. Therefore, it can be concluded that the Klip River is not suitable for domestic, agricultural as well as sustaining aquatic life.

2.6.7. Calcium

The Ca concentrations ranged from 141.896-1094.183 mg/L (Table 10), wherein the lowest concentration was recorded at site A in January and the highest at site L in the same month.

Table 10: Annual mean, maximum and minimum calcium concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	368.369 ± 201.128	536.931	**141.896**
B	460.596 ± 266.253	953.859	254.647
C	370.823 ± 199.605	533.747	247.926
D	372.709 ± 199.226	531.271	246.89
E	362.844 ± 191.941	494.745	206.457
F	351.176 ± 183.267	458.845	274.811
G	386.993 ± 204.997	545.959	289.081
H	677.348 ± 360.977	1032.795	514.83
I	701.016 ± 373.806	1042.85	530.062
J	708.600 ± 375.518	1010.94	482.477
K	673.331 ± 357.505	1015.307	510.852
L	658.640 ± 363.235	**1094.183**	477.847
SAWQGDomestic = 32 mg/L			
SAWQGAquatic = 150 mg/L			

The majority of the minimum Ca concentrations were recorded in January at sites A, B, C, D, G and H followed by December at sites I, J and K. Calcium concentrations, generally displayed 2 sets of trends that grouped the sites into two clusters. In one group, comprising of sites H, I, J, K and L, there were generally higher concentrations relative to the other group (sites A, B, C, D, E, F, and G) suggesting an increase in calcium concentrations towards the downstream of the Klip River (Figure12). The bulk of the maximum Ca concentrations were recorded in April at sites A, H, I, J, K and L and in March at sites D, E and F. The highest annual mean Ca concentration was at site J which notably consistently recorded high Ca concentrations throughout the study period, ranging from 482.477-1010.94 mg/L. Contrastingly, the lowest annual mean Ca concentration was at site F, whose monthly Ca concentrations ranged from 274.811-458.845 mg/L.

A one-way repeated measures ANOVA, indicated that at 95% confidence interval (F (2.572, 28.293) = 16.205, p = 0.000) there were statistically significant differences in Ca concentrations in the various months from February 2016 to January 2017.

A further analysis of the multiple pairwise comparisons with a Bonferroni adjustment revealed that the differences were particularly statistically significant between Ca concentrations recorded in March to June (which were higher) and those recorded in February and from July to January (which were lower). The high concentrations of Ca during the March to June period can be attributed to higher evaporation rates of water (Ojok et al., 2017) as well as the mineralization of the carbonate containing rocks (Garizi et al., 2011).

Calcium concentrations were in excess of the SAWQG for domestic uses and aquatic ecosystem protection. Elevated Ca concentrations have been associated with acute myocardial infarction (Rubenowitz et al., 1999; Meride and Ayenew, 2016) and impacts on the reproductive system (Chandra et al., 2012; Dutta et al., 2013; Sengupta 2013). In fish, elevated Ca concentrations may affect the osmoregulation process. Therefore, it can be concluded that the Klip River, based on Ca concentrations only, is not suitable for domestic, and sustaining aquatic life.

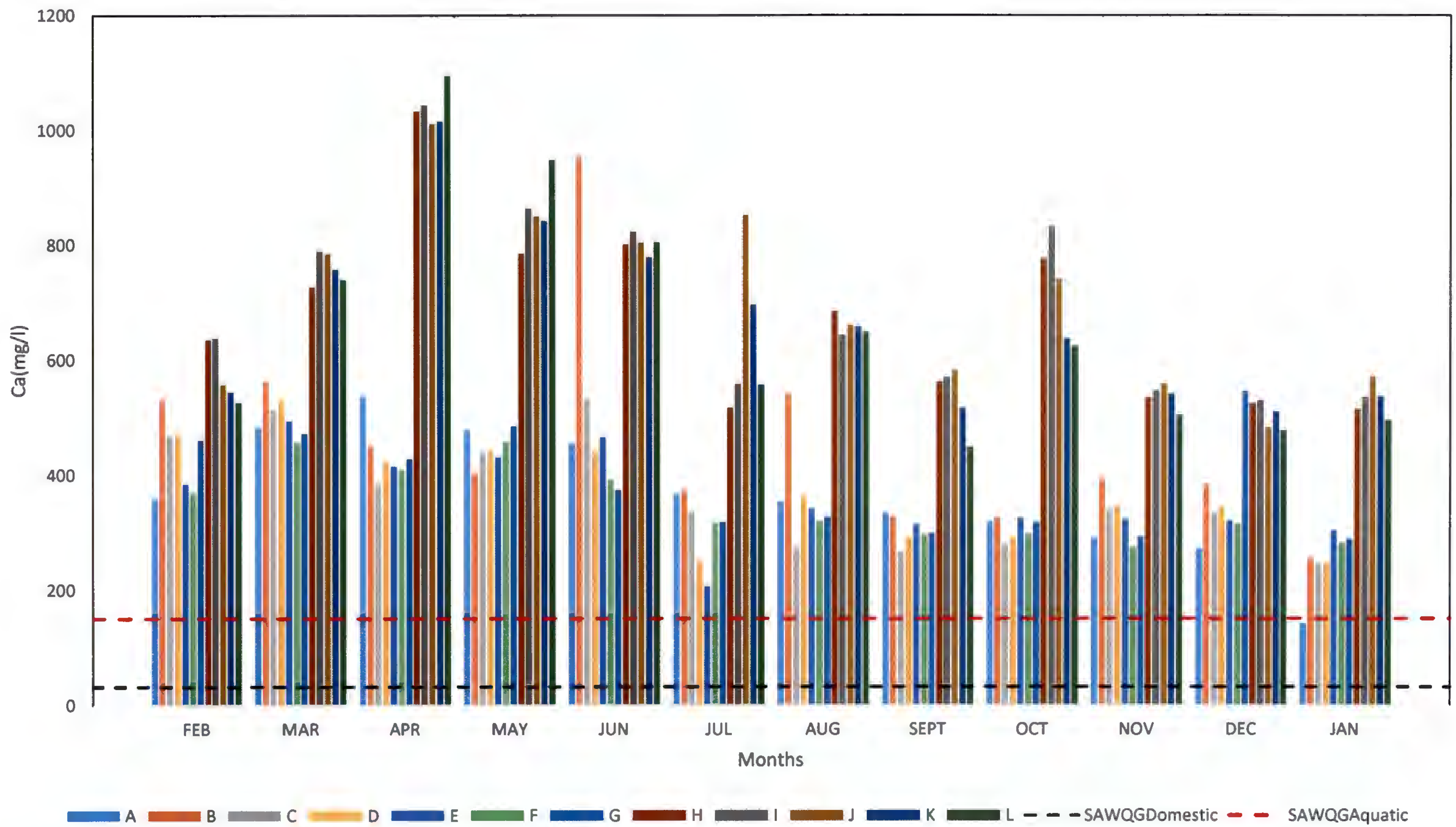

Figure 11: The trends of calcium concentrations in the KRC.

2.6.8. Cadmium

Cadmium concentrations recorded during the study period were generally very low ranging from 0 to 0.110 mg/L (Table 11) with the highest concentration recorded at site B in March. Coincidentally, the highest mean Cd concentration recorded at site B could be attributed to the highest Cd concentrations recordings in the first 4 months relative to the other sites.

Table 11: Annual mean, maximum & minimum cadmium concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0.071 ± 0.049	0.043	**0**
B	0.110 ± 0.059	**0.110**	**0**
C	0.054 ± 0.031	0.044	**0**
D	0.072 ± 0.040	0.017	**0**
E	0	0	**0**
F	0.071 ± 0.046	0.017	**0**
G	0.074 ± 0.043	0.050	**0**
H	0.064 ± 0.036	0.046	**0**
I	0.054 ± 0.033	0.025	**0**
J	0	0	**0**
K	0.087 ± 0.052	0.064	**0**
L	0.059 ±0.038	0.053	**0**
SAWQGDomestic = 0.005 mg/L			
SAWQGAquatic = 0.004 mg/L			
SAWQGAgriculture = 0.01 mg/L			

At sites E and J there was no Cd detected in the samples throughout the duration of the sampling period consequently these sites recorded the lowest mean Cd concentration. The non-detection of Cd at sites E and J may be attributed to a combination of high discharge emanating from an influx of wastewater discharges there by leading to dilution, and the presence of inorganic ligands to which Cd binds (Salomons and Kerdijk, 1986).

Cadmium concentrations along the Klip River displayed a fluctuating pattern in the first six months whilst in the last six months there was no recording of Cd at any of the sampling sites (Figure 13). Correspondingly a one-way repeated measures ANOVA indicated that at 95% confidence interval (F (2.241, 24.647) = 3.421, $p = 0.044$) there was a statistically significant difference in Cd concentrations in the various months from February 2016 to January 2017.

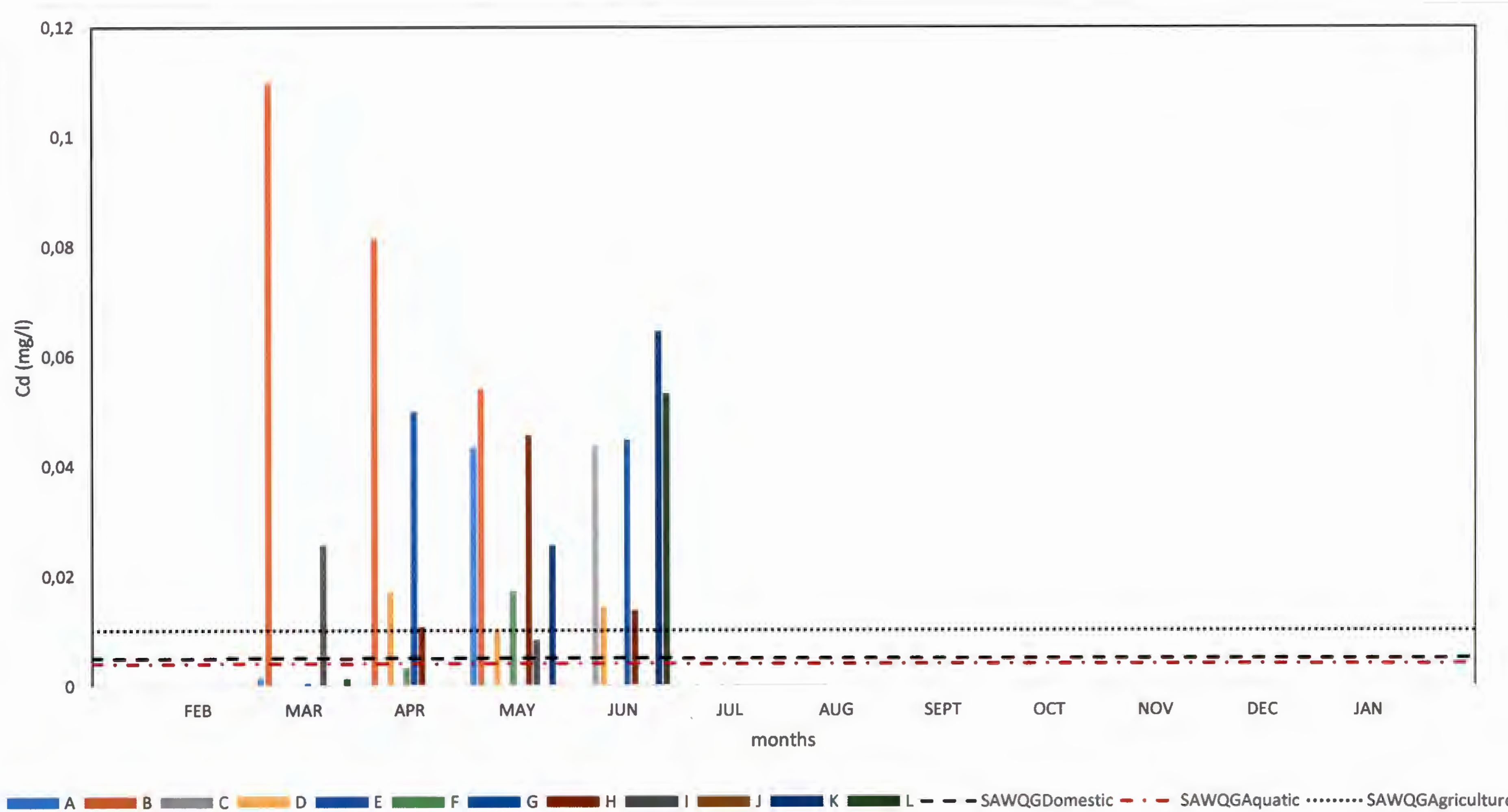

Figure 12: The trends of cadmium concentrations in the KRC.

The multiple pairwise comparisons with a Bonferroni adjustment revealed that Cd concentrations recorded in March to June were higher relative to those recorded in February and from July to January whereby no Cd was detected in any of the samples. The high Cd concentrations in the first six months can be attributed to the low volume of water atypical during this period with the residual effects of the 2015/2016 drought season. Cadmium concentrations were largely in line with the SAWQG (allowable limits for domestic uses, aquatic ecosystem protection and agricultural uses). However, in the few months where Cd was detected at some of the sampling sites, it exceeded the SAWQG for domestic uses, aquatic ecosystem protection and agricultural uses.

Chronic Cd exposure has been associated with kidney failure (Unisa et al., 2011; Johri et al. 2010). Furthermore, WHO (2011) reported cases of osteomalacia among Japanese people exposed to cadmium through drinking water. Cadmium accumulates in the kidney, liver, and gills of fish (Chowdhury et al., 2004). However, Cd toxicity is largely dependent on water hardness in particular the concentration of Ca (Niyogi et al., 2008). Calcium competes with Cd at the gill surface, thereby reducing the toxicity (Niyogi et al., 2008).

2.6.9. Cobalt

Cobalt concentrations ranged from 0-2.357 mg/L with the lowest concentration recorded at all sites in various months between March 2016 and January 2017. The highest Co concentration was recorded at site D in February. Correspondingly, the highest annual mean Co concentration was recorded at site D (0.490 mg/L). At all the sites the maximum Co concentrations were recorded in February. It should also be noted that from July to January at all the sampling sites, Co was not detected owing to the highly alkaline pH which could have resulted in Co adsorption and removal from the water column. Site H had the lowest annual mean cobalt concentration of 0.270 mg/L and this can be attributed to the fact that Co concentration at this site were only recorded in February, April and May. The concentrations at site H ranged from 0-0.938 mg/L (Table 12).

A one-way repeated measures ANOVA revealed at the 95% confidence interval (F (1.429, 15.715) = 22.858, $p = 0.000$) statistically significant differences in Co concentrations in the various months from February 2016 to January 2017.The multiple pairwise comparisons with a Bonferroni adjustment revealed that Co concentrations recorded from March to June were higher relative to those recorded from July to January, whereby no Co was detected in any of the samples.

Table 12: Annual mean, maximum and minimum cobalt concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0.285 ± 0.189	0.648	**0**
B	0.465 ±0.409	1.940	**0**
C	0.332 ±0.315	1.449	**0**
D	0.490 ±0.490	**2.357**	**0**
E	0.288 ±0.198	0.763	**0**
F	0.299 ±0.160	0.440	**0**
G	0.287 ±0.166	0.677	**0**
H	0.270 ±0.210	0.938	**0**
I	0.333 ±0.202	0.786	**0**
J	0.305 ±0.147	0.436	**0**
K	0.303 ±0.210	0.677	**0**
L	0.335 ±0.159	0.453	**0**
*SAWQGA*griculture = 0.05 mg/L			

The high Co concentrations recorded from March to June may be due to the low flow conditions as a result of evaporation and also as a result effluent discharges from metal alloys industries (Caruso and Bishop, 2009; Reza and Singh, 2010).Cobalt concentrations were in excess of the SAWQG for agricultural use from February to June, suggesting that the Klip River is not suitable for irrigation use during this period (Figure 14). Although Co is essential in maintenance of some plants at low concentrations, at elevated levels, it is toxic to human and aquatic ecosystems (Nagpal, 2004). There are no guidelines for protection of aquatic life for Co in South Africa, USA and Canada. However based on an interim chronic (30-day mean) guideline of 0.004 mg/L recommended by Nagpal (2004) and based on toxicity testing it can be concluded that the Klip River does not meet the criteria for protection of aquatic life in terms of its Co concentrations from February to June. Furthermore, there are no SAWQG for domestic uses for Co, however, the SANS 241 prescribes the limit of 0.5mg/L of Co in drinking water, of which the concentrations recorded in the Klip River were in excess at some of the sampling points between the months of February and June.

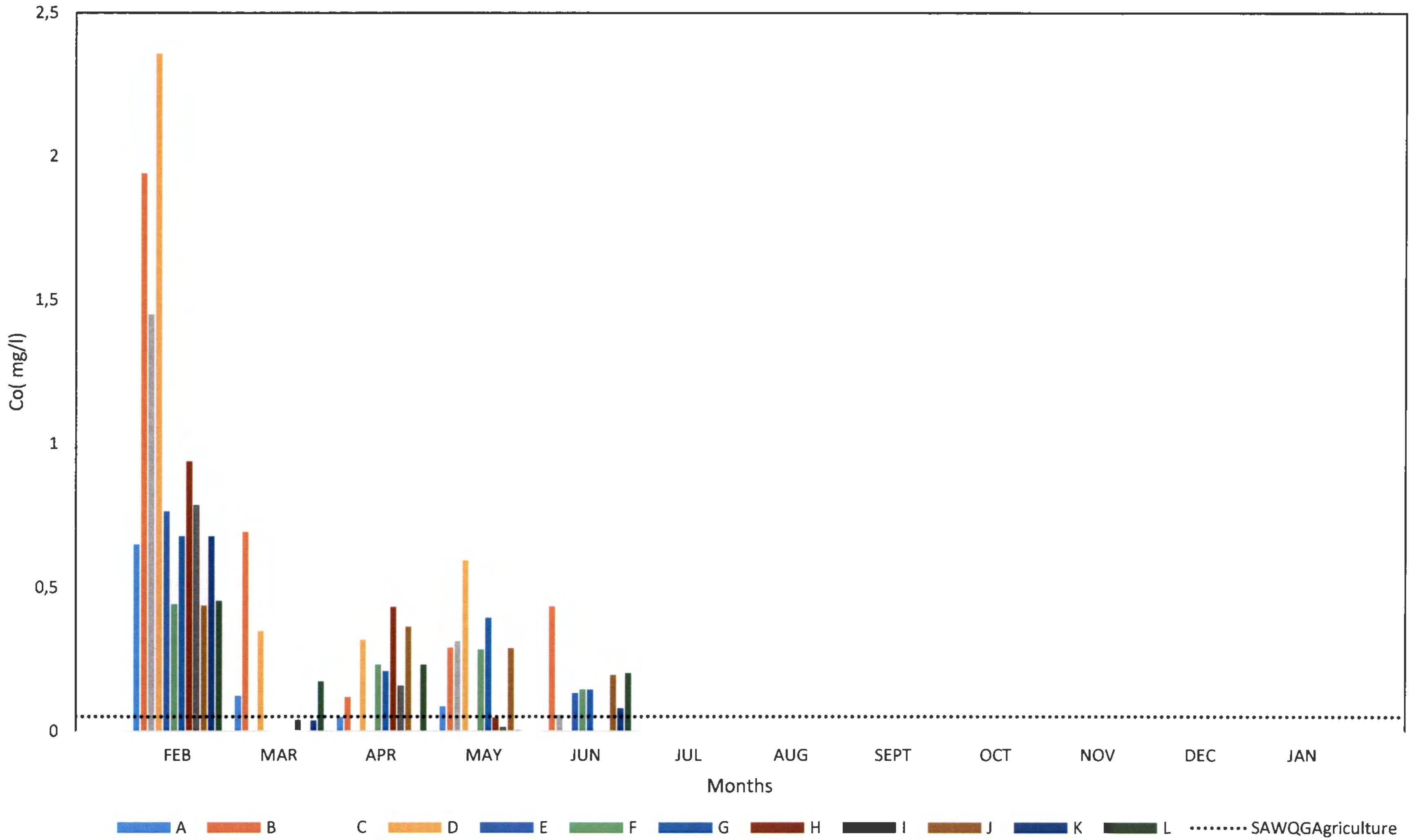

Figure 13: The trends of Cobalt concentrations in the KRC.

2.6.10. Chromium

Chromium concentrations in the KRC ranged from 0 to 1.263 mg/L, with the lowest concentration recorded at all the sites in various months between March and January and the highest at site B in September. Correspondingly, the highest annual mean was recorded at site B (0.194 mg/L) and the lowest at site L (0.07 5mg/L) (Table13).

Table 13: Annual mean, maximum and minimum chromium concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0.093 ± 0.074	0.313	0
B	0.194 ± 0.265	**1.263**	0
C	0.082 ± 0.073	0.343	0
D	0.096 ± 0.082	0.373	0
E	0.090 ± 0.080	0.368	0
F	0.096 ± 0.089	0.406	0
G	0.087 ±0.077	0.354	0
H	0.107 ±0.087	0.407	0
I	0.103 ±0.081	0.360	0
J	0.124 ± 0.102	0.369	0
K	0.116 ± 0.073	0.303	0
L	0.075 ± 0.055	0.225	0
SAWQGDomestic = 0.05 mg/L			
USEPAAquatic = 0.016 mg/L			
SAWQGAgriculture = 0.10 mg/L			

The maximum concentrations at the other sites except site J were recorded in February, whereas the maximum concentration for site J was recorded in June (Figure 15). A one-way repeated measures ANOVA indicated that at 95% confidence interval ($F(1.216, 13.377) = 9.900$, $p = 0.006$) there were statistically significant differences in Cr concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni adjustment revealed that Cr concentrations recorded in February were statistically different from concentrations in all the months whereby the former was higher and the latter mean Cr concentrations ranged from below detection limit to 0.1 mg/L.

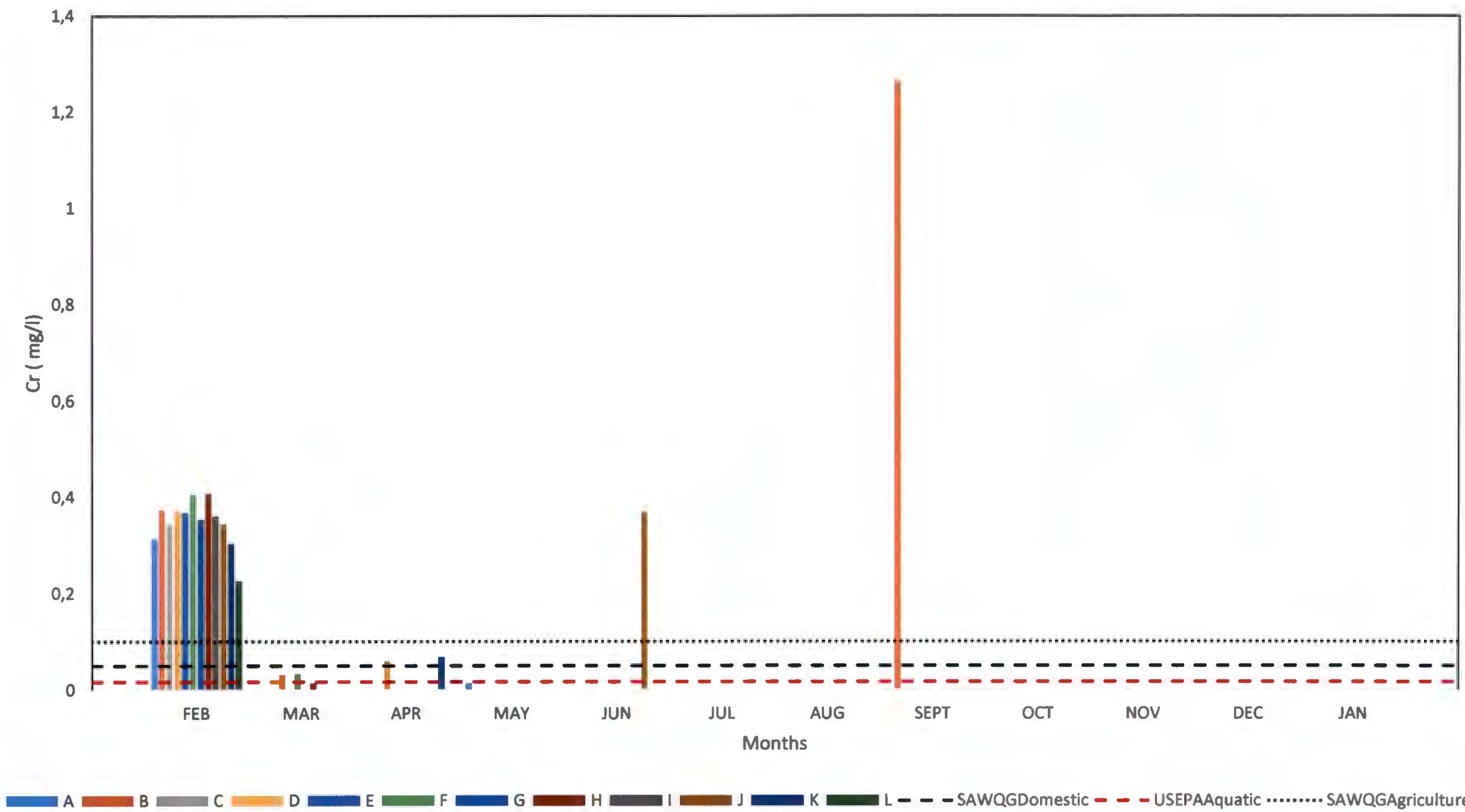

Figure 14: The trends of chromium concentrations in the KRC.

Correspondingly, the Cr concentrations recorded in February at all the sampling points were in excess of the SAWQG for domestic uses, agricultural uses and protection of aquatic life. Furthermore sites B and J were also in excess of the SAWQG for domestic uses, agricultural uses and protection of aquatic life in September and June respectively. Smith and Steinmaus (2009) revealed that there were knowledge limitations with regards to the human health effects of exposure to Cr through ingestion. However, Beaumont et al. (2008) found stomach cancer high mortality rates in the Chinese population in exposed to elevated Cr concentrations in drinking water relative to regions without contaminated water. Chromium toxicity spans across not only fish species but also different functional levels (Aslam and Yousafzai, 2017). Chromium concentrations as low as 0.005 mg/L were reported to have impacts on fertilization of the *Salmo gairdneri (*Billard and Roubaud, 1985) and at 0.098 mg/L, Cr was reported to have decreased the blood clotting time in *Tilapia sparrmani* (Gey Van et al., 1992). Acute exposure of fish to Cr alters enzyme activities in the kidneys, brain, and liver of fish while chronic exposure induces irregular behavioural responses in various species of fish (Aslam and Yousafzai, 2017). Chromium is toxic for agronomic plants at about 0.0005 to 0.005smg/ l (Hossner, 1996). In the Klip River, the Cr concentrations recorded, particularly in February at all the sampling sites render the water unsuitable for its prescribed uses and as such poses serious human health and environmental problems.

2.6.11. Copper

Copper concentrations ranged from 0 to 1.342 mg/L (Table 14), with the lowest concentration recorded at all the sites in different months throughout the sampling period and the highest at site J in May. The highest annual mean Cu concentration was recorded at site J (0.227 mg/L) whereas site G recorded the lowest annual mean Cu concentration of 0 mg/L due to the fact that at the aforementioned site, there was no Cu detected in any of the samples throughout the sampling period (Figure 16). Low Cu concentrations atypical of alkaline conditions which were reported in the KRC.

A one-way repeated measures ANOVA indicated that at 95% confidence interval (F (1.021, 11.228) = 1.050, p = 0.329), there were no statistically significant differences in Cu concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni also revealed no statistically significant differences in Cu concentrations in the various months.

Table 14: Annual mean, maximum and minimum copper concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0.003 ± 0.074	0.030	0
B	0.048 ± 0.086	0.056	0
C	0.014± 0.059	0.014	0
D	0.0003 ± 0.065	0.004	0
E	0.001 ± 0.075	0.006	0
F	0.007± 0.061	0.037	0
G	0 ± 0	0	0
H	0.001 ± 0.067	0.008	0
I	0.001 ± 0.045	0.014	0
J	0.227 ± 0.397	**1.342**	0
K	0.0001± 0.070	0.002	0
L	0.006 ± 0.055	0.055	0
SAWQGDomestic = 1 mg/L			
SAWQGAquatic = 0.0014 mg/L			
SAWQGAgriculture = 0.2 mg/L			

Copper concentrations were generally in line with the SAWQG for domestic uses, agricultural uses and protection of aquatic life at many sites throughout the year, this is because the Cu concentrations recorded were mostly below the detection limit. However, at sampling site J, in May Cu concentrations were in excess of the SAWQG for domestic uses, agricultural uses and protection of aquatic life. This can be attributed to the use of pesticides containing heavy metals such as Cu; site J is downstream of some agricultural activities. Furthermore, some of the sampling sites (A, B, F and L) were in excess of SAWQG for domestic uses in various months. Woody and O'Neal (2012) reported that aquatic organisms are sensitive to high Cu concentrations in water. Conversely, Cu toxicity is a function of pH, water hardness and anions concentrations (Woody and O'Neal, 2012). Copper is not classified as a carcinogen by the EPA, nonetheless, consumption of drinking water with elevated Cu concentrations has serious health effects; liver and kidney damage and even death (ATSDR, 2004a). So, results from the Klip River indicate that there are generally no risks for domestic and agricultural consumers as well as aquatic life in the catchment emanating from Cu with the exception of site J.

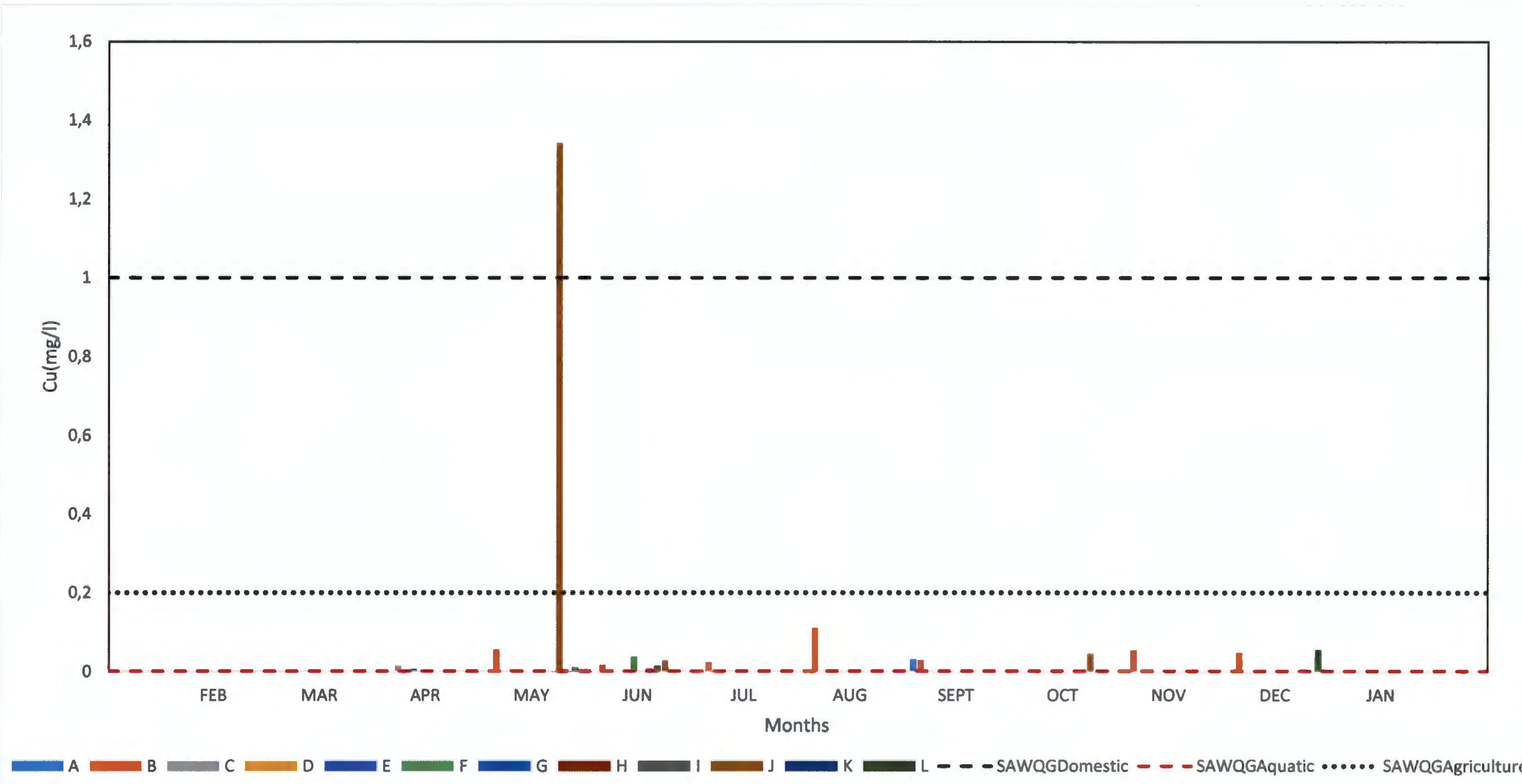

Figure **15**: The trends of copper concentrations in the KRC.

2.6.12. Iron

Iron in the Klip River displayed a decreasing trend from the upstream to the downstream (Figure 17). Iron concentrations ranged between 0 and 32.233 mg/L throughout the study period (Table 15).

Table 15: Annual mean, maximum and minimum iron concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	2.908 ± 6.031	29.17	0.086
B	11.174 ± 10.211	**32.233**	0.403
C	7.438 ± 6.769	25.515	0.004
D	4.735 ± 4.032	15.539	**0**
E	1.533 ± 1.390	2.4405	0.103
F	1.191 ± 0.748	2.131	0.078
G	1.003 ± 0.582	2.719	**0**
H	1.187 ± 0.786	2.719	0.030
I	1.103 ± 1.037	4.975	**0**
J	1.282 ± 1.132	5.448	**0**
K	0.697 ± 0.419	1.187	0.006
L	1.070 ± 0.784	3.424	0.166
SAWQGDomestic = 0.1 mg/L			
USEPAAquatic = 1 mg/L			
SAWQGAgriculture = 5 mg/L			

The highest Fe concentration was recorded at site B in July and the lowest at sites D, G, I and J in March and April. The highest annual mean Fe concentration was recorded at site B (11.174 mg/L) and concentrations at this site ranged between 0.403 mg/L and 32.233 mg/L. The lowest annual mean Fe concentration was recorded at site K (0.697 mg/L) of which concentrations at this site ranged from 0.006 to 1.187 mg/L.

The one-way repeated measures ANOVA, results revealed that at 95% confidence interval (F (2.738, 30.120) = 1.999, p = 0.140) there were no statistically significant differences in Fe concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni correction also revealed no statistically significant differences in Fe concentrations.

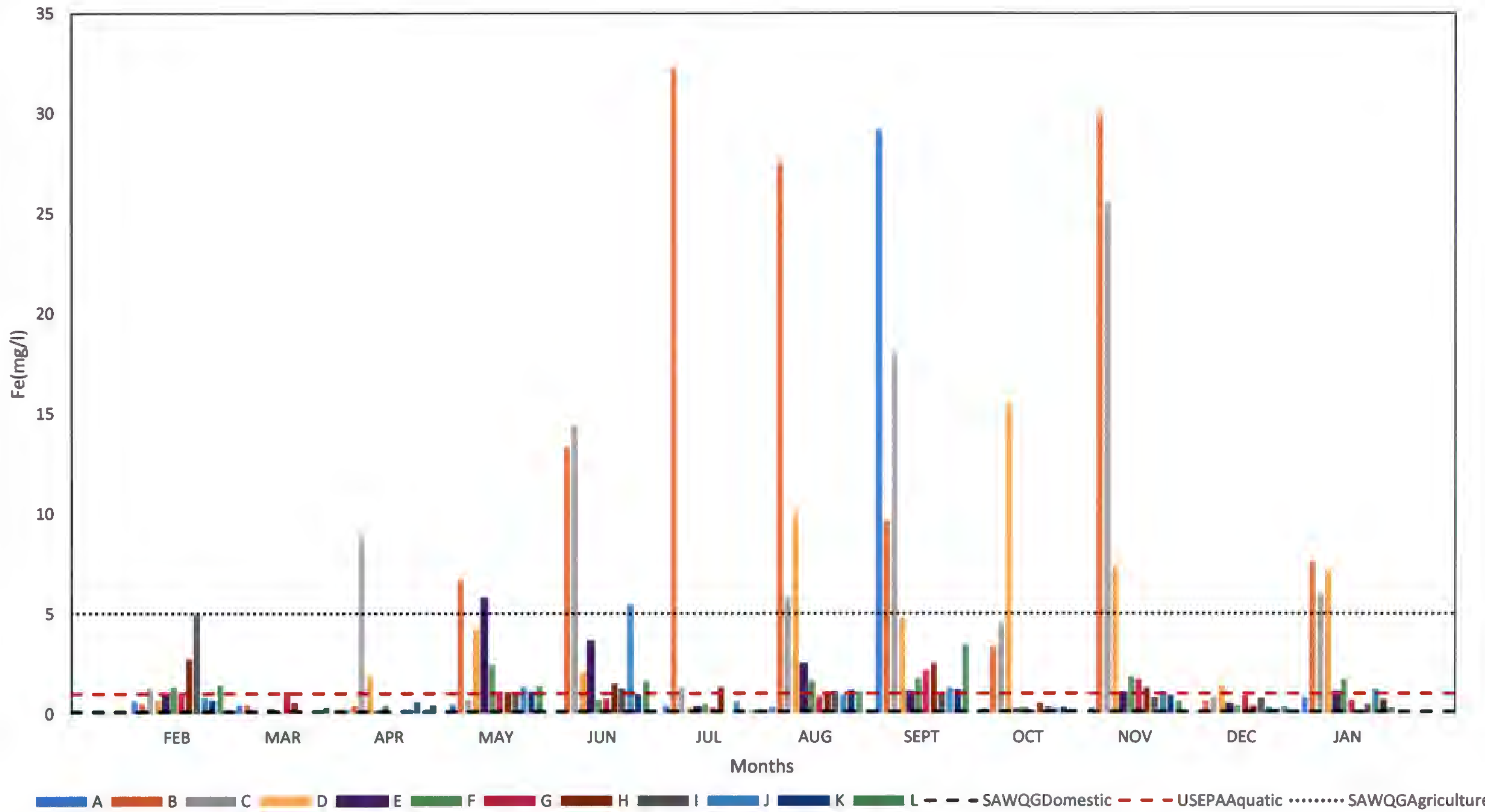

Figure 16: The trends of iron concentrations in the KRC.

Iron concentrations were generally in line with the SAWQG for agricultural use at many sites throughout the year with the exception of sites A, B, C and D which were in excess suggesting that only the mid to downstream section of the Klip River water quality is suitable for agricultural purposes. Furthermore, Fe concentrations were also mostly in line with the USEPA standards for protection of aquatic life, although various sites (B, C, D E, F, H and J) were in excess of the standards in some months during the study period. Iron toxicity in aquatic plants, alters their physiology and ecology and consequently, species composition and community dynamics in aquatic ecosystems (Xing and Liu, 2011). Phippen et al. (2008) studied Fe toxicity on aquatic rice, and observed inhibited growth at concentrations exceeding 1 mg/L of which the values recorded in the Klip River surpass such. As such, it can be concluded that water in the upper part of the KRC is not suitable for domestic and agricultural uses as well as sustaining aquatic life.

2.6.13. Potassium

The K concentration ranged between 6.693 mg/L to 162.401 mg/L of which both the highest and lowest concentrations were recorded at site B in June and May respectively. The highest annual mean K concentration was recorded at site J (92.180 mg/L). The concentrations at site J ranged from 59 mg/L-116 mg/L.

Table 16 Annual mean, maximum & minimum potassium concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	50.892 ±30.182	106.431	21.637
B	78.767 ± 47.863	**162.401**	**6.693**
C	61.285 ± 33.426	89.021	14.410
D	64.467 ± 33.229	82.860	42.644
E	70.491 ± 35.921	84.900	57.862
F	79.233 ± 40.259	92.935	62.262
G	77.874 ± 39.545	92.219	61.414
H	87.925 ± 45.233	107.482	61.246
I	88.270 ± 45.177	107.811	62.366
J	92.180 ± 47.611	116.073	59.809
K	85.997 ± 44.187	106.263	63.533
L	90.619 ± 47.769	121.87	61.341
SAWQGDomestic = 50 mg/L			

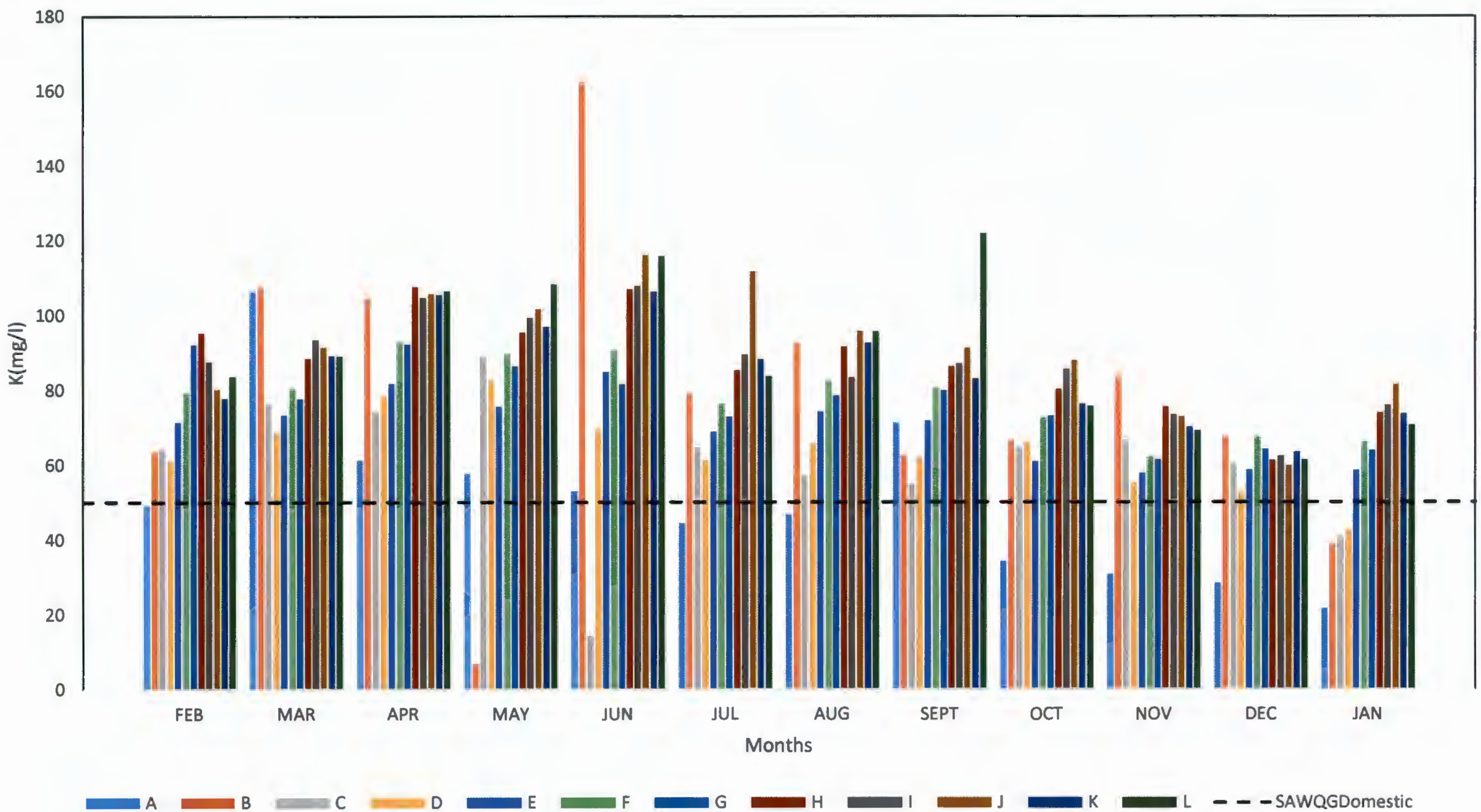

Figure 17: The trends of potassium concentrations in the KRC.

The lowest annual mean K concentration was recorded at site A 50.892 mg/L (Table 16). Results from a one-way repeated measures ANOVA indicated that at 95% confidence interval (F (2.515, 27.662) = 13.555, p = 0.000) there were statistically significant differences in K concentrations in the various months from February 2016 to January 2017.

The multiple pairwise comparisons with a Bonferroni adjustment revealed that K concentrations recorded in February, April, July, August and September were statistically different. K concentrations were mostly in excess of the SAWQG for domestic uses. However, it is noteworthy to mention that K concentrations at the upstream sampling sites (A, B, C and D) were in line with the SAWQG for domestic uses in some months (Figure 18). Although there are no SAWQG for aquatic ecosystem protection for K, Talling (2010) examined the growth and distribution of aquatic organisms with respect to K concentrations and concluded that high K concentrations limited the growth and distribution of the species of Crustacea.

2.6.14. Magnesium

Magnesium concentrations ranged from 41.568-317.685 mg/L of which the lowest concentration was recorded at site A in January and the highest at site J in July.

Table 17 Annual mean, maximum and minimum magnesium concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	119.729 ± 71.566	268.325	41.568
B	143.343 ± 75.229	184.281	100.313
C	126.631 ± 67.077	177.918	87.626
D	132.632 ± 9.640	186.337	94.275
E	139.131 ± 72.413	182.787	96.216
F	130.368 ± 67.962	175.128	84.922
G	145.773 ± 82.505	300.841	94.582
H	218.360 ± 113.133	288.454	158.046
I	224.486 ± 116.644	287.709	157.171
J	231.227 ± 122.296	317.685	144.118
K	218.468 ± 115.140	290.548	170.3
L	225.418 ± 117.843	268.325	142.484
SAWQGDomestic =30 mg/L			

Correspondingly, site A had the lowest yearly mean concentration of 119.729 mg/L while site J recorded the highest yearly mean concentration of 231.227 mg/L. At the majority of the sites (B, C, D, E, F, G, H and I), maximum Mg concentrations were recorded in December whereas the site minimum concentrations were recorded in February (H, I, J and L), October (B, C and D) and November (E, F and G) (Table 17). The temporal trend in Mg concentrations depicted a similar trend at all the sites, however, the spatial trend shows slightly higher Mg concentrations for the sites which are downstream of the river (H, I, J, K and L) relative to the upstream sites suggesting that Mg concentration increase towards the downstream of the river (Figure 19).

ANOVA results indicated that at 95% confidence interval (F (2.515, 27.662) = 13.555, p = 0.000) there were statistically significant differences in Mg concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni adjustment revealed that Mg concentrations recorded in February, April, July, August and September were statistically different. The Mg concentrations in the Klip River were in excess of the SAWQG for domestic water uses at all sampling points throughout the sampling period. Rapant et al. (2017) suggested that the Mg concentrations ranges of 28–54 mg/L are ideal for optimum health of which most of the concentrations recorded in the Klip River did surpass this range. Consumption of water with a high Mg concentration has been associated with hypomagnesaemia gastrointestinal disorders (WHO, 2009, Sengupta, 2013). As such, it can be concluded that, based on Mg alone, the Klip River is not suitable for domestic uses.

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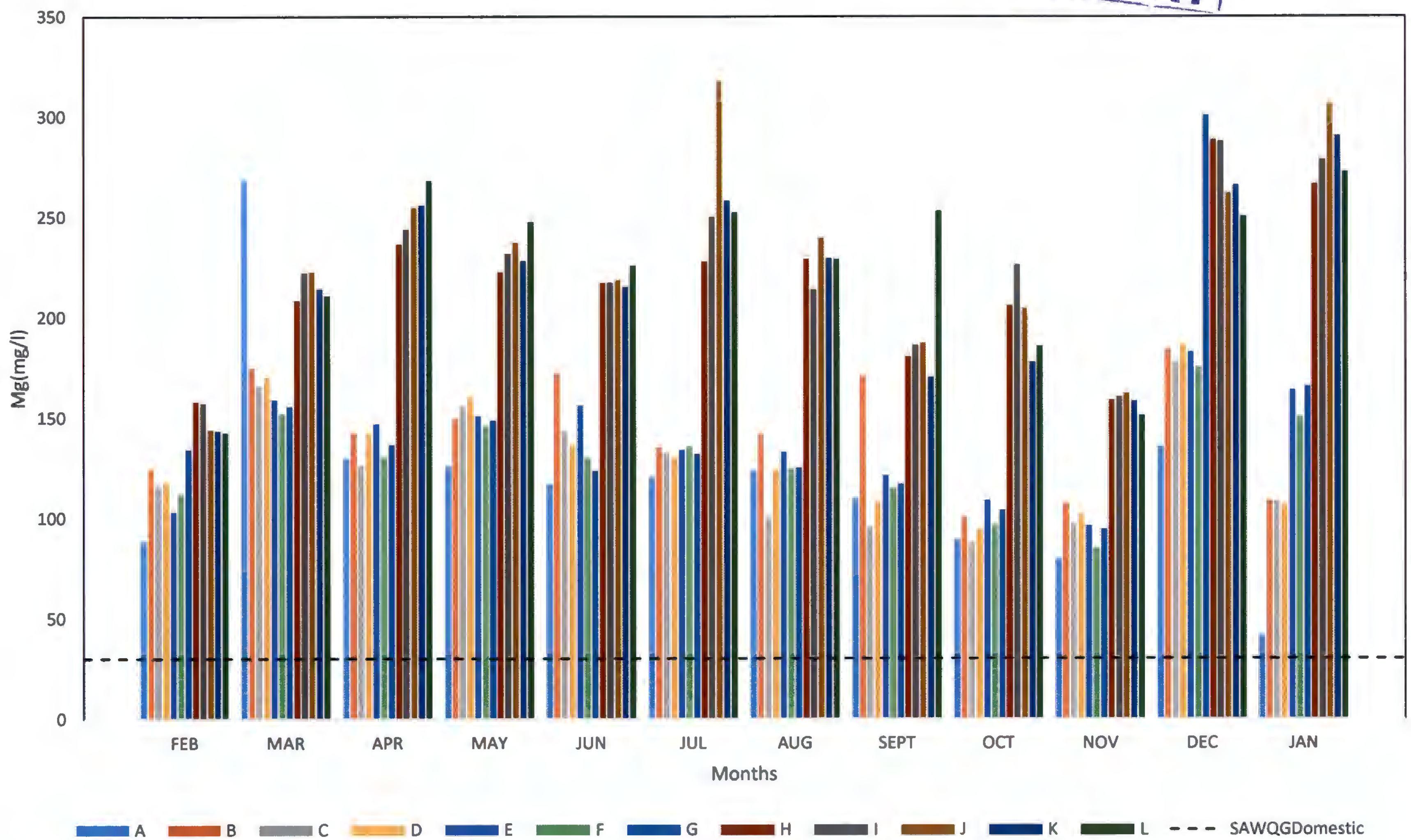

Figure 18: The trends of magnesium concentrations in the KRC.

2.6.15. Manganese

Manganese concentrations in the Klip River ranged from 0-31.900 mg/L of which the lowest was recorded at site K in various months and the highest at site B in June (Table 18). Site B recorded the highest Mn concentrations for ten months with the exception of February and September and consequently had the highest annual mean Mn concentration (17.02 mg/L).

Table 18: Annual mean, maximum and minimum manganese concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	3.721 ± 3.863	16.319	0.0334
B	17.202 ±10.147	31.900	4.775
C	7.632 ± 5.147	15.054	0.055
D	6.088 ± 4.972	19.647	0.069
E	1.855 ± 2.141	8.070	0.006
F	1.012 ±0.983	3.074	0.017
G	1.258 ±1.187	3.856	0.036
H	0.700 ± 0.700	2.462	0.018
I	0.574 ±0.574	2.320	0.018
J	1.024 ±0.940	3.441	0.015
K	0.919 ±0.854	2.650	0
L	1.289 ±1.352	5.415	0.057
SAWQGDomestic = 0.05 mg/L			
SAWQGAquatic = 0.18 mg/L			
SAWQGAgriculture = 0.02 mg/L			

The lowest annual mean Mn concentration was at site I (0.574 mg/L). At the majority of the sites (A, H, J, K and L) the maximum Mn concentrations were recorded in September, whereas the majority of minimum Mn concentrations were recorded in March at sites (C, D, E, F, J and K).

However, a one-way repeated measures ANOVA indicated that at 95% confidence interval ($F(3.301, 36.307) = 2.197$, $p = 0.100$), there were no statistically significant differences in Mn concentrations in the various months between February 2016 to January 2017. Generally the Mn concentrations for the upstream sites (A, B, C and D) were higher relative to sites downstream, whose concentrations ranged between 0 and 4 mg/L (Figure 20).

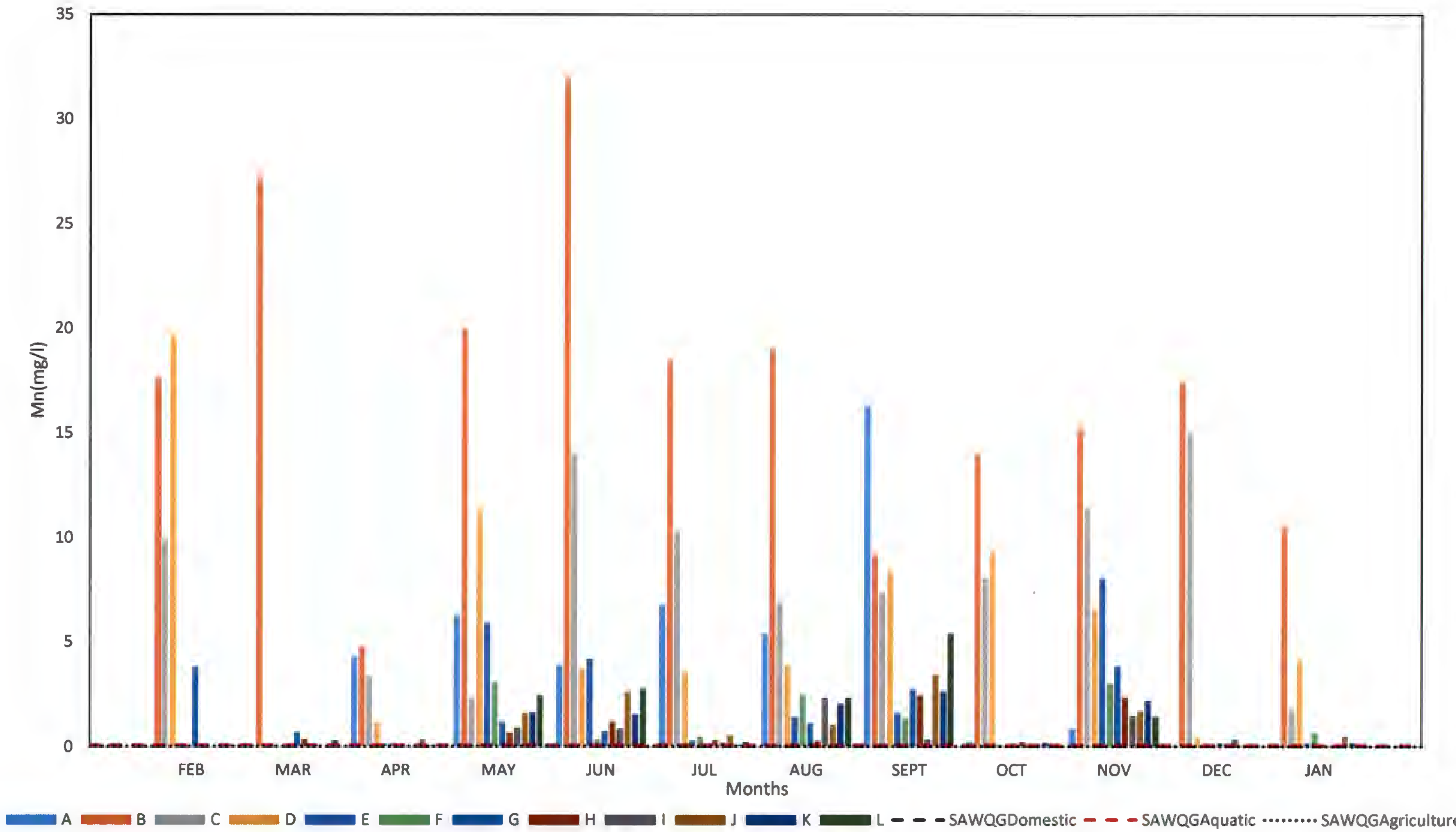

Figure 19: The trends of manganese concentrations in the KRC.

Manganese concentrations were generally in excess of the SAWQG for domestic water, aquatic ecosystem protection and agricultural uses with the exception of some sites in various months (February, March April and December), where Mn was detected at very low concentrations. Manganese in water can be significantly bioconcentrated by aquatic biota at the lower trophic levels. The uptake by aquatic invertebrates and fish greatly increases with temperature and decreases with pH but is not significantly affected by the dissolved oxygen. Therefore, based on the high water temperatures and pH in the KRC, it can be concluded that there is an imminent risk of Mn accumulating in fish, thereby posing a significant health risk to those who consume the fish. Toxic effects in aquatic organisms were reported for the dissolved Mn concentration of about 1 mg/L (Howe et al., 2004). The concentrations recorded in the Klip River catchment were mostly in excess of 1 mg/L suggesting that the aquatic ecosystem in the Klip is at high risk of Mn toxicity. In humans, long term exposure to Mn has been associated with neurological diseases (Normandin and Hazel, 2002; Takeda, 2003).

2.6.16. Sodium

Sodium concentrations ranged from 44.072mg/L to 780.94mg/L (Table 19) of which the lowest was recorded at site A in January and the highest at site L in September. The lowest Na concentration recordings were distributed recorded in January (sites A, B, C, D, E, F and G) and December H, I, J, K, and L whereas the highest Na concentration for the sites were mostly recorded in April (D, F, G, H, I, J and K) (Figure 21). The trends in Na concentration for all the sites except A depict an increase in concentrations from February to April. The concentrations for site A however, depicted an almost constant trend between April and August as well as October and November with peak concentrations recorded in March and September.

Based on a one-way repeated measures ANOVA at 95% confidence interval, (F (2.815, 30.961) = 16.050, p = 0.000) there were statistically significant differences in Na concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni adjustment revealed that the mean Na concentrations recorded in March, April, May and June were statistically different to those recorded during the rest of the year which were lower.

Table 19: Annual mean, maximum and minimum sodium concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	210.945 ± 173.066	776.312	44.0724
B	396.445 ± 220.593	654.484	123.578
C	308.660 ± 160.764	369.948	139.28475
D	302.975 ± 159.769	386.405	118.31725
E	360.320 ± 191.231	491.884	220.249
F	411.711 ± 213.732	489.588	280.937
G	412.360 ± 212.638	449.886	283.4885
H	545.956 ± 287.381	691.026	353.58675
I	554.758 ± 292.237	711.341	344.89825
J	569.232 ± 301.212	719.348	320.4895
K	534.392 ± 284.559	696.393	334.93075
L	552.538 ± 300.402	780.94	308.919
SAWQGDomestic = 100 mg/L			
SAWQGAgriculture = 70 mg/L			

The Na concentrations in the Klip River were in excess of the SAWQG for domestic water use. Sodium concentrations above 20 mg/L have been reported to cause health problems in hypertensive individuals of which the Na concentrations recorded at all the sites throughout the study period in the Klip River, were above this value. Water with $NaCl_2$ creates a higher water density and will settle at the deepest part of the water body where current velocities are low leading to chemical stratification and consequently dissolved oxygen cannot reach the lower layers while nutrients within the bottom layers cannot reach the top layers (Lampert and Sommer, 2007). Furthermore, salts like Na alter the ecological health status of rivers by enhancing flocculation of suspended material, thereby allowing more sunlight to penetrate rivers leading to uncontrolled growth of algal blooms (Ally, 2013).

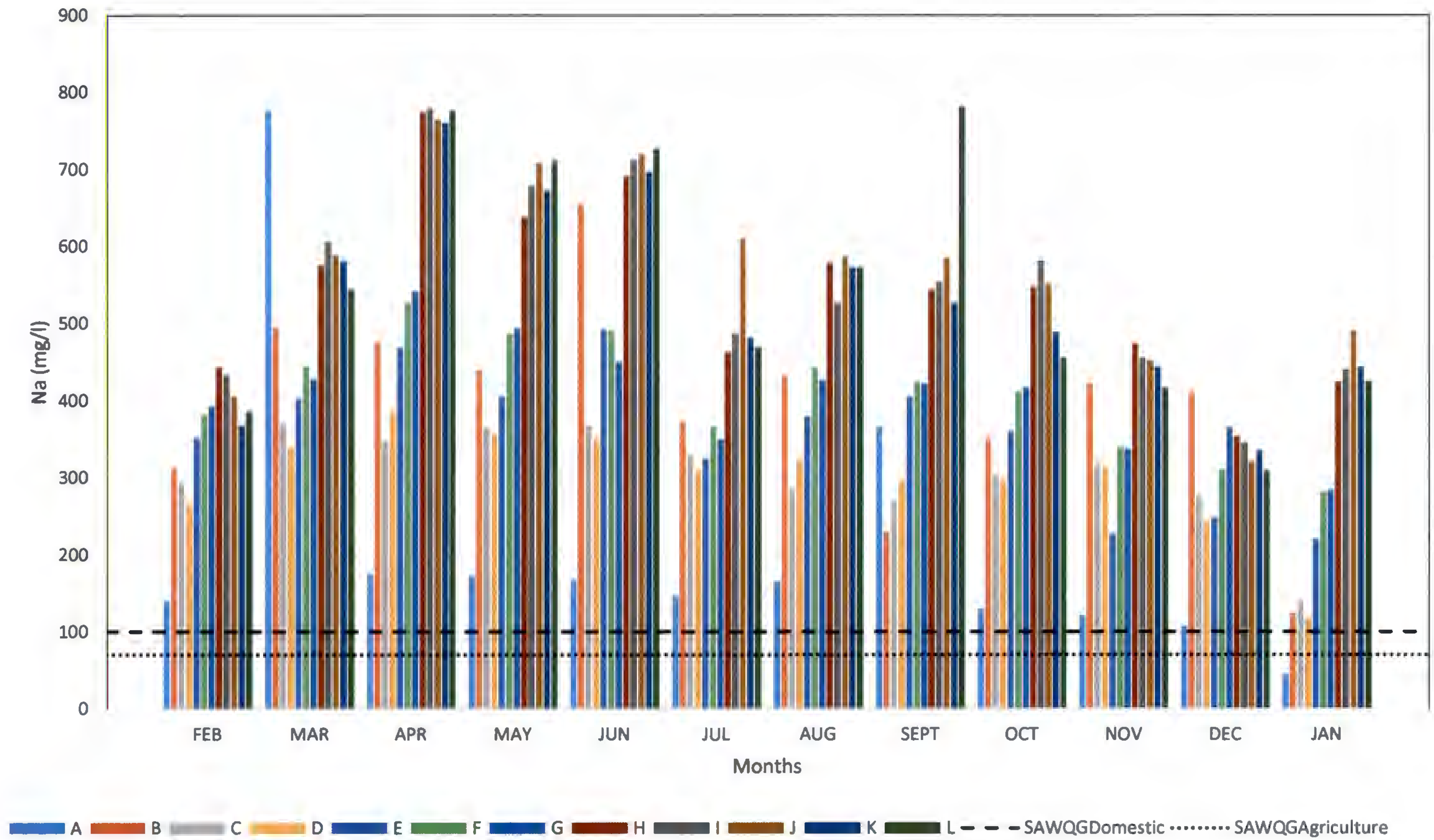

Figure 20: The trends of sodium concentrations in the KRC.

2.6.17. Nickel

Ni concentrations ranged from 0 to 2.9 mg/L with the highest recorded at site D in February and minimum recorded at all the sites in various months throughout the year (Table 20). The site maximum Ni concentration were mostly recorded in March at sites B, E, F, H, I and K. The highest annual site mean Ni concentration was recorded at site B (1.229 mg/L) and the lowest was at site J (0.460 mg/L). In terms of the trends in Ni concentration over the year between the months of July to June, at all the sites excluding sites A and J there was no Ni detected in any of the samples suggesting a temporal trend in Ni concentrations (Figure 22).

Table 20: Annual mean, maximum and minimum nickel concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	1.196 ± 0.847	2.75	0
B	1.229 ± 0.697	2.33	0
C	0.939 ± 0.526	1.86	0
D	1.086 ± 0.669	2.9	0
E	0.976 ± 0.545	1.97	0
F	0.882 ± 0.507	1.76	0
G	0.924 ± 0.528	1.71	0
H	0.847 ± 0.563	1.68	0
I	0.837 ± 0.510	1.66	0
J	0.460 ±	1.69	0
K	0.861 ± 0.465	1.39	0
L	0.778 ± 0.555	1.86	0
SAWQGDomestic = 0.02 mg/L			
USEPAAquatic = 0.47 mg/L			
SAWQGAgriculture = 0.2 mg/L			

The one-way repeated measures ANOVA results indicated that at 95% confidence interval ($F (2.494, 27.858) = 23.858$, $p = 0.000$) there were statistically significant differences in Ni concentrations for the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni adjustment revealed that there were statistically significant differences, particularly in Ni concentrations recorded in March, April, May, and June relative to those recorded in February, and from July to January which were relatively lower.

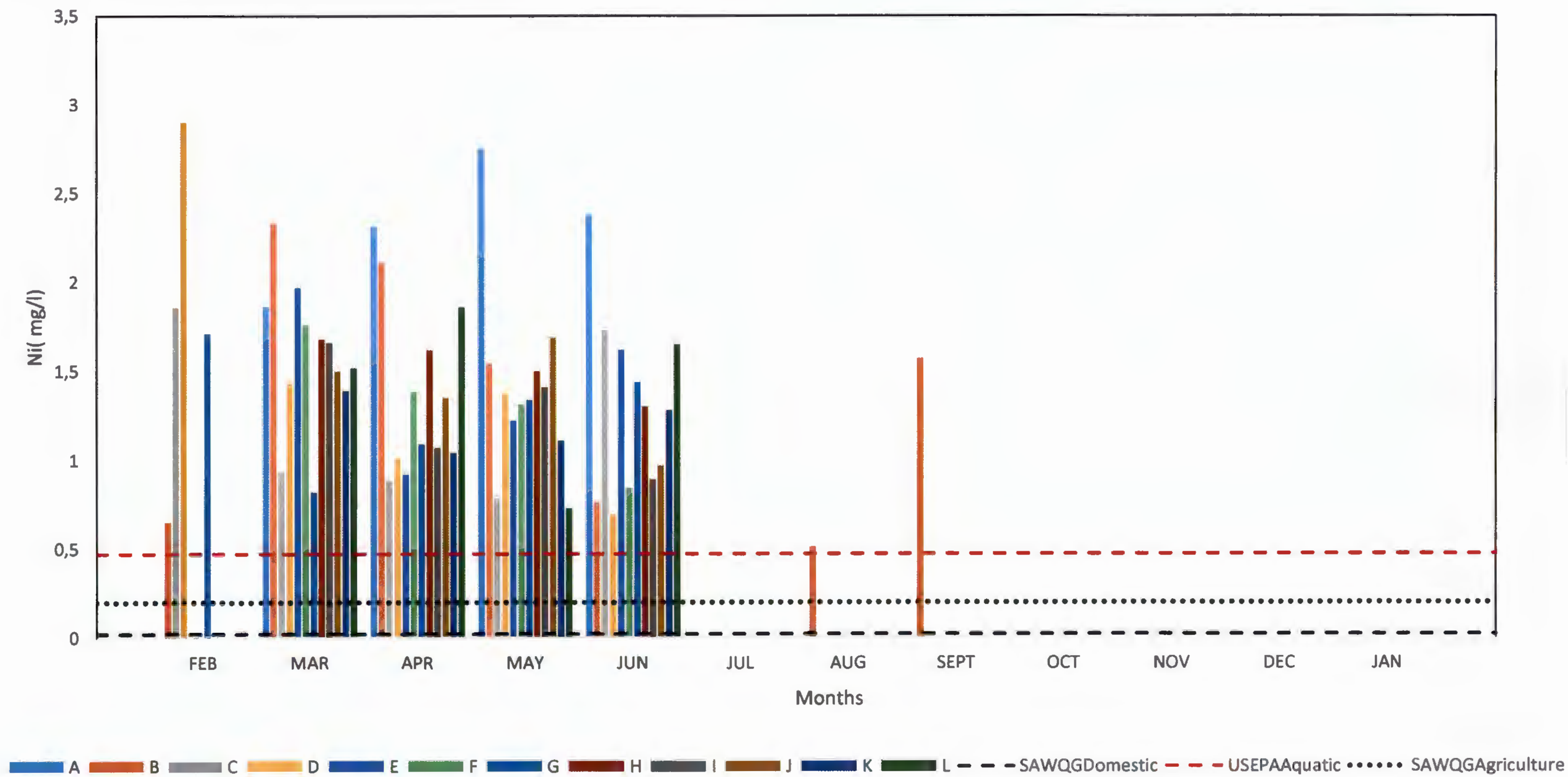

Figure 21: The trends of nickel concentrations in the KRC.

This temporal trend also aligned with the suitability of the Klip River water for domestic water, aquatic and agricultural uses, whereby between the months of July to June at all the sites, excluding sites A and J, the water was suitable for the aforementioned uses, and from March to June the water was in excess of the SAWQG for domestic water, aquatic and agricultural uses. Nickel tends to bioaccumulate in phytoplankton and other aquatic plants (Cempel and Nikel, 2006). It was shown to have toxic effects on the immune system of mammals (Eisler, 1998; Svecevičius, 2010; Min et al., 2015) and fish (Zelikoff et al., 1996). Ni impacts on human health include skin dermatitis, carcinogenicity and oral hypersensitivity (Duda-Chodak and Blaszczyk, 2008).

2.6.18. Lead

Lead concentrations in the Klip River ranged from 0-6.155 mg/L at site I in May while the lowest concentration (0 mg/L) was recorded at all the sites in the various months throughout the year. The highest mean concentration was recorded at site H (2.557 mg/L) (Table 21), whereby the concentrations at this site ranged between 0 and 4.038 mg/L whereas the lowest site mean was computed at site J (1,243 mg/L) whose concentrations ranged between 0 and 1.369 mg/L.

Table 21: Annual mean, maximum and minimum lead concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	1.587 ± 0.995	4.546	0
B	1.439 ± 1.086	2.065	0
C	2.172 ± 1.720	5.493	0
D	2.057 ± 1.358	5.142	0
E	1.378 ± 1.053	1.117	0
F	2.350 ± 1.656	5.206	0
G	1.537 ± 0.954	2.449	0
H	2.557 ± 1.331	4.038	0
I	2.225 ± 1.741	6.155	0
J	1.243 ± 0.754	1.369	0
K	1.886 ± 1.091	3.972	0
L	1.775 ± 1.323	4.786	0
SAWQGDomestic = 0.01 mg/L			
SAWQGAquatic = 0.0012 mg/L			
SAWQGAgriculture = 0.2 mg/L			

At all the sites, Pb concentrations showed a decreasing trend from July to January relative to the first five months, where the concentrations were high, suggesting a temporal influence on the Pb concentrations (Figure 23). The one-way repeated measures ANOVA results confirmed the temporal trend, and at 95% confidence interval, $F (3.326, 36.586) = 35.017$, $p = 0.000$), there were statistically significant differences in Pb concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni adjustment revealed that there were statistically significant differences particularly in Pb concentrations recorded in March, April, May and June relative to those recorded in February, and from July to January which were relatively lower.

Pb concentrations were in excess of the SAWQG for domestic water, aquatic and agricultural uses in the first five months at a majority of the sites, and at a few sites between July and January.This suggests that the water quality in the Klip River was not suitable for domestic, aquatic and agricultural uses between February and June relative to the time period between July and January. High Pb concentrations in excess of 0.5 mg/L were noted to result in the inhibition of enzymes for photosynthesis in algae and consequently leading to the increased algal growth, which may affect the ecological balance of aquatic ecosystems (Solomon, 2009).

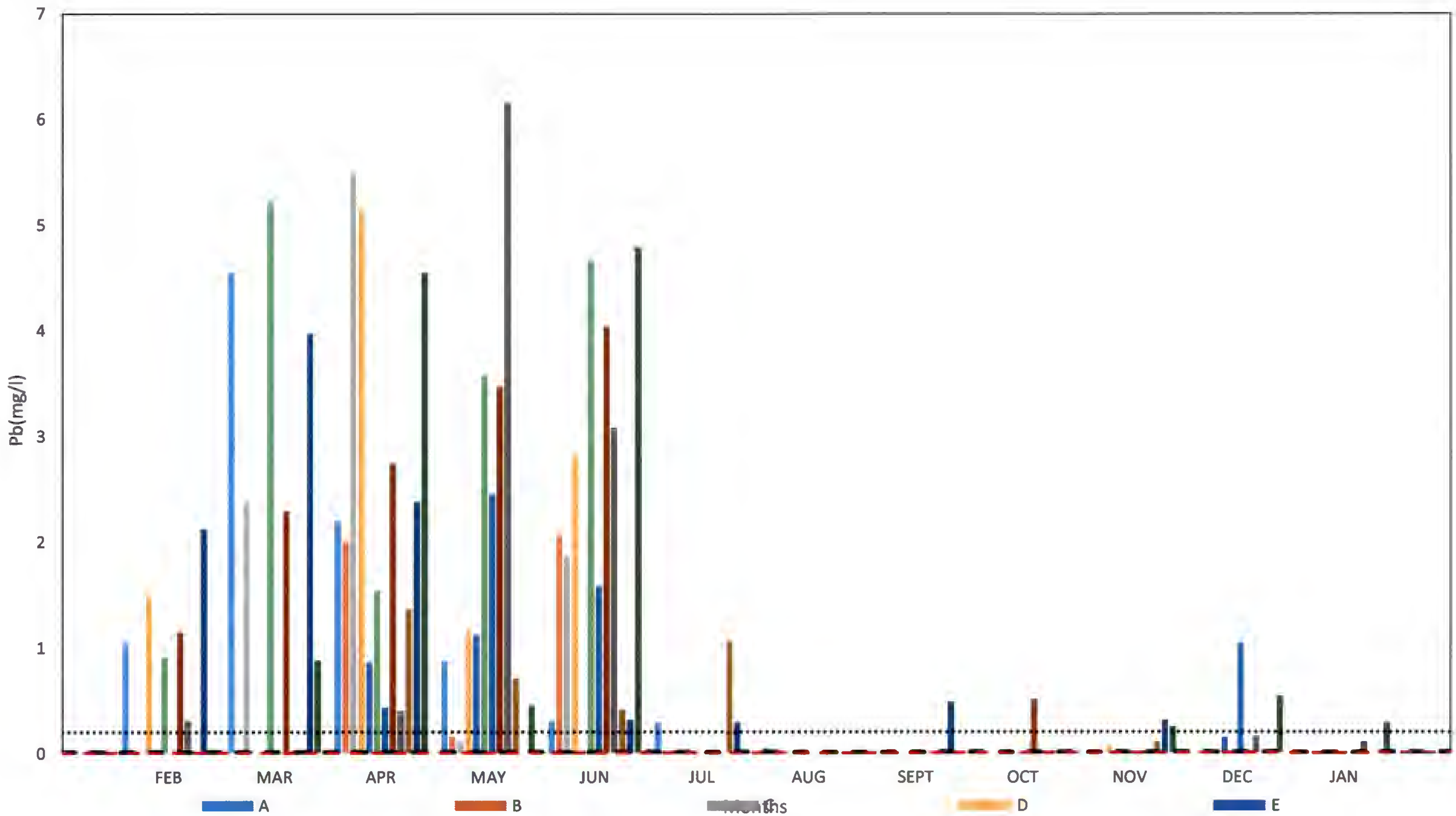

Figure 22: The trends of lead concentrations in the KRC.

2.6.19. Uranium

Uranium concentrations ranged from 0 to 0.211 mg/L of which the lowest was recorded at 10 of the sites excluding C and D, while the highest was recorded at site C in December. The highest annual mean U concentration was recorded for site J (0.552 mg/L). Uranium concentration at this site ranged between 0-0.143 mg/L (Table 22). The lowest annual mean U concentration was recorded at site H and ranged between 0 and 0.163 mg/L.

Table 22 Annual mean, maximum and minimum uranium concentrations.

Site	*Mean*	*Maximum*	*Minimum*
A	0.087 ± 0.029	0.099	0
B	0.112 ± 0.044	0.152	0
C	0.162 ± 0.046	0.211	0.031
D	0.122 ± 0.026	0.129	0.009
E	0.083 ± 0.039	0.150	0
F	0.084 ± 0.037	0.119	0
G	0.089 ± 0.035	0.121	0
H	0.064 ± 0.037	0.163	0
I	0.104 ± 0.049	0.189	0
J	0.552 ± 1.164	0.143	0
K	0.080 ± 0.042	0.137	0
L	0.094 ± 0.043	0.143	0
SAWQGDomestic = 0.03 mg/L			
USEPAAquatic = 0.03 mg/L			
SAWQGAgriculture = 0.01 mg/L			

Uranium concentration depicted a highly fluctuating pattern and as such no temporal or spatial variation could be deduced. The one-way repeated measures ANOVA results indicated that at 95% confidence interval $F(4.742, 52.165) = 3.541$, $p = 0.009$) there were statistically significant differences in U concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni adjustment revealed particularly statistically significant differences in the mean U concentrations recorded in May (lowest) and December (highest).

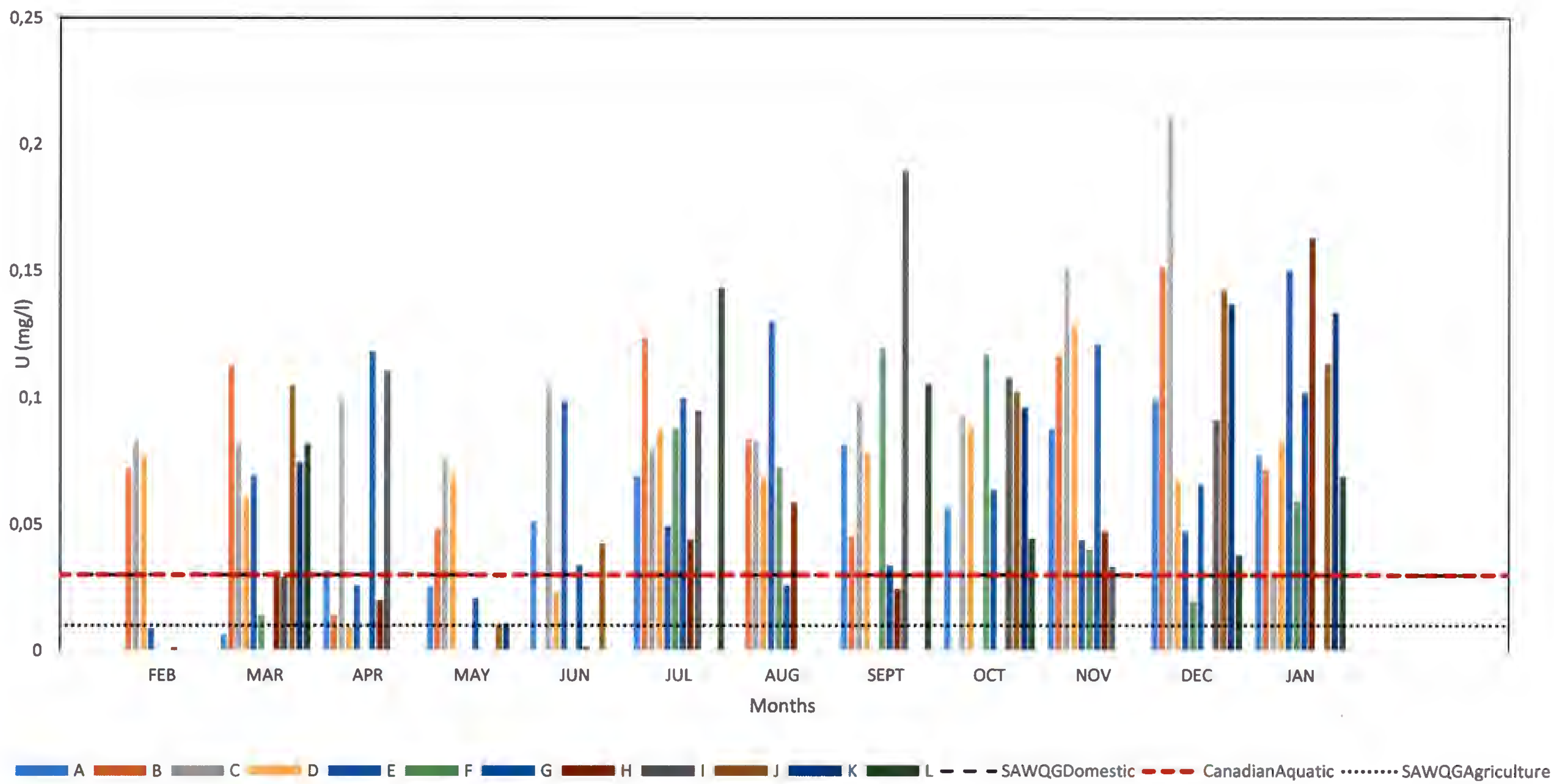

Figure 23: The trends of uranium concentrations in the KRC.

Uranium concentrations in the Klip River were in excess of the SAWQG for agricultural use (Figure 24), at all sites in the various months,but excluding some sites between the months of February and May. In terms of the SAWQG for domestic and aquatic ecosystem protection, the U concentrations were in excess, particularly between July and January where the concentrations were generally higher at a majority of the sites relative to the first five months which had lower concentrations. However, between February and June some sites were in excess of the SAWQG for domestic uses and aquatic ecosystem protection. There is a lot of literature on human health effects after exposure to uranium in drinking water; nephrotoxicity (ATSDR, 2013; Brugge and Buchner 2011), carcinogenicity, (although U is no longer classified as carcinogenic by the IARC and EPA) (Radespiel-Tröger and Meyer 2012), genetic problems (Dinocourt et al., 2015) and developmental problems (Arfsten et al., 2001; Bourrachot et al., 2008) have all been reported. In one study, uranium in drinking water depicted estrogenic effects in mice at concentrations below the EPA and WHO drinking water standards (Raymond-Whish et al., 2007). Lourenço et al. (2017) proved that U altered the normal development of fish's early life stages by significantly affecting important parameters such as growth, hatching and morphogenesis. Irrigation with uranium contaminated water was reported to have negative effects on lettuce varieties although the concentrations in that study were far above those recorded in this study (Abreu et al., 2014). As such, it can be concluded that the Klip River water is not suitable for domestic, agricultural and protection of aquatic life in terms of U.

2.6.20. Vanadium

The highest V concentration was recorded at site I in October. Correspondingly, Site I also had the highest annual mean V concentration of 0.138mg/L. The lowest annual mean V concentration was recorded at site D (0.051 mg/L), whereby the concentrations at this site were generally very low ranging from 0 to 0.027 mg/L (Table 23).

The V concentrations depicted a highly fluctuating trend throughout the year at all the sites. The one-way repeated measures ANOVA results confirmed this that at 95% confidence interval $F(5.440, 59.836) = 4.002$, $p = 0.003$), there were statistically significant differences in V concentrations in the various months from February 2016 to January 2017. The multiple pairwise comparisons with a Bonferroni adjustment revealed that there were statistically significant differences particularly in V concentrations recorded in March, April, May, and

June relative to those recorded in February, and from July to January which were relatively lower.

Table 23: Annual mean, maximum and minimum vanadium concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0.078 ± 0.037	0.111	0
B	0.086 ±0.032	0.112	0
C	0.069 ±0.032	0.107	0
D	0.051 ±0.021	0.027	0
E	0.081 ±0.038	0.123	0
F	0.086 ±0.030	0.108	0
G	0.082 ±0.043	0.158	0
H	0.103 ±0.037	0.125	0
I	0.138 ±0.048	0.197	0
J	0.107 ±0.040	0.138	0
K	0.101 ±0.038	0.116	0
L	0.112 ±0.040	0.127	0
SAWQGDomestic = 0.1 mg/L			
USEPAAquatic = 0.080 mg/L			
SAWQGAgriculture = 0.1 mg/L			

Vanadium concentration in the Klip River were generally in line with the SAWQG for domestic water as well as agricultural uses at a majority of the sites. However, some sites (C and E, in July; G in February, July and December; H in February and October; I in October; J in February and September; K in May; L February, October and December) were in excess of the SAWQG for domestic water as well as agricultural uses (Figure 25). Elevated levels of V may cause anemia, fertility problems and birth defects (ATSDR, 2012b). Vanadium concentration in the Klip River were mostly in line with the SAWQG for aquatic uses at a majority of the sites throughout the sampling period except for February, whereby from 8 sites they were in excess of the SAWQG for aquatic uses. Costigan et al. (2001) reported that V can cause toxicity to aquatic organisms. Schiffer (2016), also reported that *Daphnia* and *Ceriodaphnia* species were sensitive to V concentration < 1 mg/L. As such, it can be concluded that water quality in the KRC in terms of V is unsuitable for domestic uses, agricultural uses as well as protection of aquatic life.

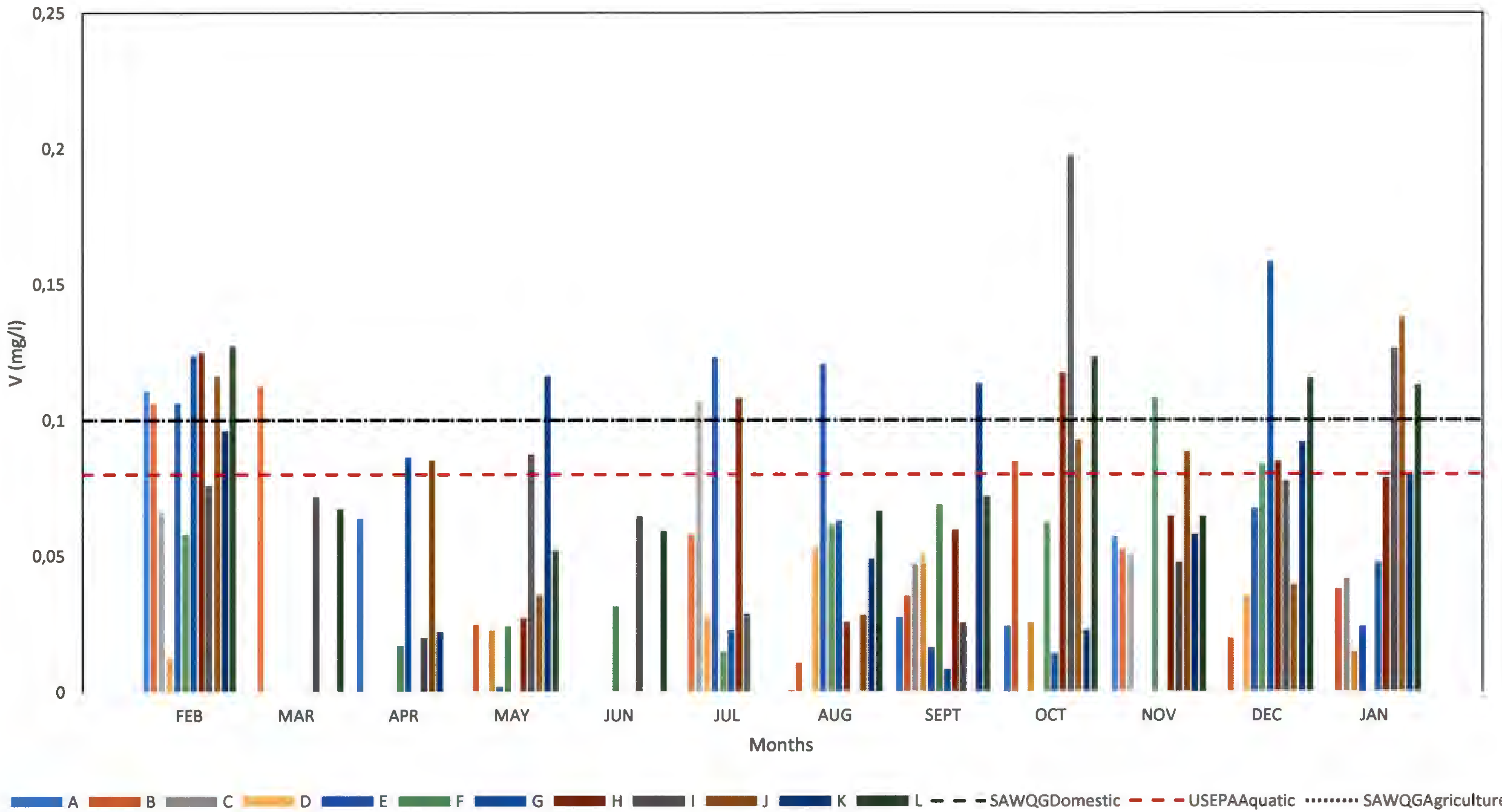

Figure 24: The trends of vanadium concentrations in the KRC.

2.6.21. Zinc

Zinc concentrations ranged from 0 to 10.18 mg/L of which the lowest, was recorded at all the sampling sites while the highest was recorded only at site B in September. Correspondingly, site B had the highest annual mean Zn concentration of 1.371 mg/L and the lowest was at site E (0.225 mg/L) (Table 24). The Zn concentrations at site E were relatively low ranging between 0 and 0.795 mg/L. At a majority of the sites, the maximum Zn concentration recordings were in February for sites (C, D, E, F, G, H, and I).

Table 24: Annual mean, maximum and minimum zinc concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0.855 ± 0.462	1.693	0
B	1.371 ± 2.104	1.559	0
C	0.335 ± 0.307	1.513	0
D	0.520 ± 0.424	1.957	0
E	0.225 ± 0.178	0.795	0
F	0.267 ± 0.158	0.589	0
G	0.323 ± 0.419	2.049	0
H	0.311 ± 0.305	1.280	0
I	0.278 ± 0.178	0.835	0
J	0.404 ± 0.264	0.968	0
K	0.287 ± 0.183	0.616	0
L	0.855 ± 0.379	0.612	0
SAWQGDomestic = 3 mg/L			
USEPAAquatic = 0.020 mg/L			
SAWQGAgriculture = 1 mg/L			

Figure 26 displays a temporal trend in Zn concentration, whereby the Zn concentrations recorded in February were high after which the concentrations decrease between April and May for all sites except site D. The concentrations increased again between June and September while between October and November, they were low low and only increased in December to January. The Zn concentrations depicted a highly fluctuating trend throughout the year at all the sites. However, a one-way repeated measures ANOVA indicated that at 95% confidence interval $F(1.204, 13.247) = 2.817$, $p = 0.112$) there were no statistically significant differences in Zn concentrations in the various months from February 2016 to January 2017.

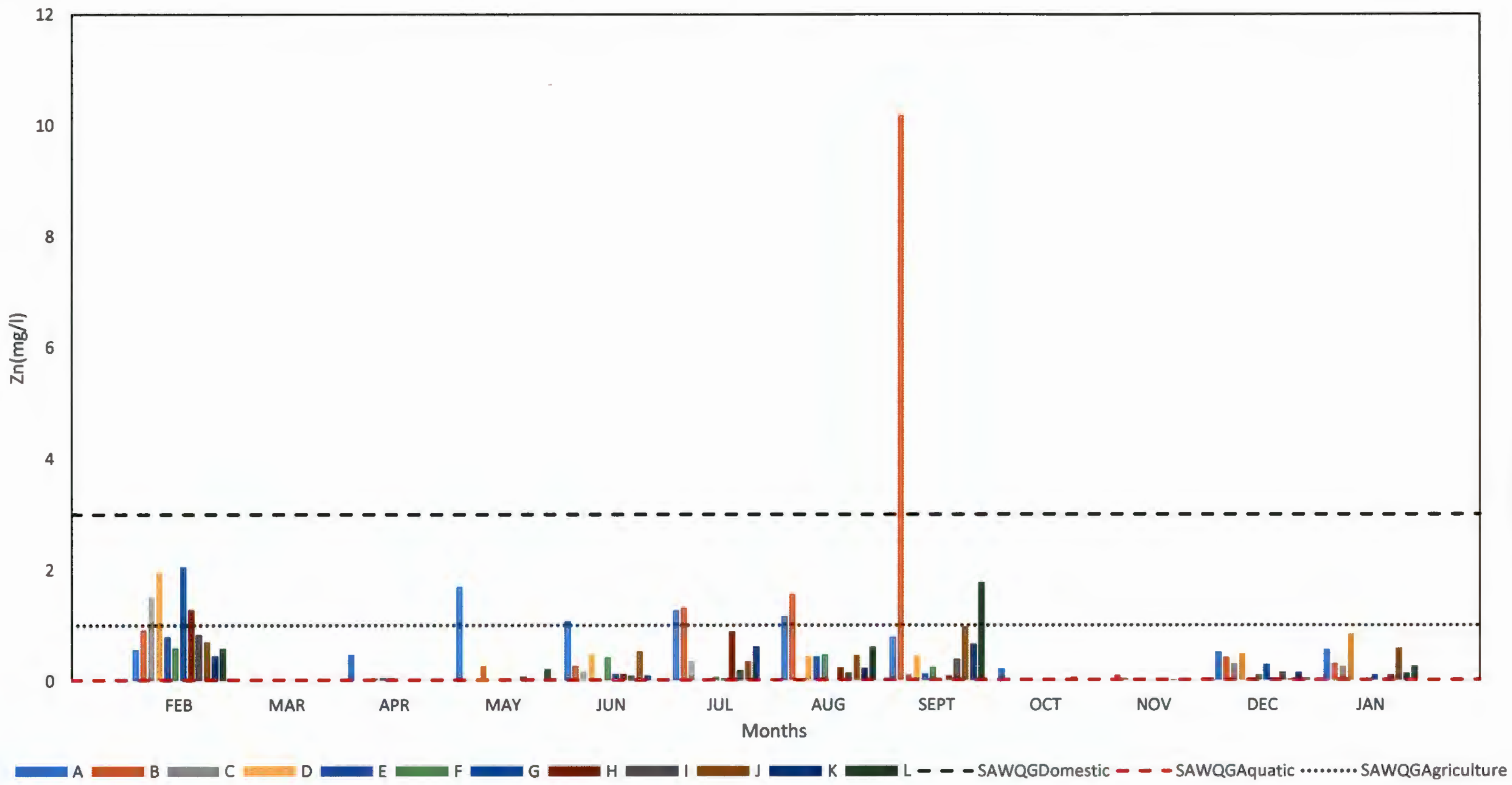

Figure 25: The trends of zinc concentrations in the KRC.

The multiple pairwise comparisons with a Bonferroni adjustment revealed that there were however, statistically significant differences between the mean Zn concentrations for February and those for March, April, May, and November, December and January, relative to those recorded in February, and from July to January, which were relatively lower. The observed Zn concentrations were in line with the SAWQG for domestic uses at all the sites throughout the year except for site B in September. However, for the SAWQG for agricultural uses, although there is evidence of compliance with the standards at many of the sites throughout the sampling period, some sites (A, B, G, F, and L) were in excess of the SAWQG for agricultural uses suggesting that water at these sites is not suitable for any agricultural uses.

The Zn concentrations in the Klip River were mostly in excess of the SAWQG for aquatic ecosystem uses at all sites throughout the study period except for March, April, October and November. Monteiro et al. (2011), reported the toxicity of Zn on species of algae at elevated concentrations. Furthermore, excess Zn was shown to inhibit metabolism of the pancreas, bone, gall bladder and kidney in mammals and the gills in fish (Eisler et al., 1977).

2.6.22. Nitrates

Nitrates concentrations depicted a highly fluctuating spatial trend throughout the year. NO_3^- concentrations ranged from 0.88-83.747 mg/L of which the highest and lowest concentrations were recorded at sites C and F respectively (Table 25). The highest and lowest annual mean NO_3^- concentrations were recorded at sites L (42.643±25.652 mg/L) and C (25.178±25.220 mg/L) respectively. NO_3^- concentrations at some of the sampling sites (B, C, D, F and K) depicted a temporal trend whereby the concentrations recorded between February and June were higher compared to those recorded in some months (between July and January). However, for the rest of the sampling points, no trend was observed, instead, there were high fluctuations in NO_3^- concentrations throughout the study period at those sites (Figure 27).

The one-way repeated measures ANOVA results indicated that at 95% confidence interval ($F(2.182, 24.005) = 5.793$, $p = 0.008$) there were statistically significant differences in NO_3^- concentrations in the various months from February 2016 to January 2017. The statistically significant differences in NO_3^- concentrations based on multiple pairwise comparisons with a Bonferroni adjustment were particularly observed between February and March annual mean NO_3^- concentrations and the September and October recordings.

Table 25: Annual mean, maximum and minimum nitrate concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	36.948±24.162	73.670	7.040
B	37.73±29.213	68.053	1.760
C	25.178±25.220	65.120	0.880
D	34.332±29.215	77.000	1.173
E	41.248±20.760	65.707	10.56
F	37.156±28.724	83.747	3.667
G	28.466±18.550	66.293	1.173
H	37.816±26.237	71.720	2.640
I	37.424±23.690	66.000	5.720
J	36.104±14.458	55.147	11.44
K	30.299±28.703	70.840	1.467
L	42.643±25.652	79.347	2.640
SAWQGDomestic = 6 mg/L			
MPCAAquatic = 13.7mg/L			

In this study, the slightly higher NO_3^- concentrations recorded between February and June can be attributed to lower rainfall volumes (as a result of drought) which had a limited dilution capacity on the agricultural sourced NO_3^- (Neal et al., 2004). Neal et al. (2006) alluded and attributed the higher NO_3^- concentrations to elevated within-river NO_3^- uptake during summer months which are characterized by low flows, river water residence times and water column volumes and high biological activity.

Conversely, in a study assessing the mechanisms which induce variations in NO_3^- concentrations, NO_3^- concentrations were higher in a wet winter relative to the dry summer and this was attributed to hydrological and biochemical processes (Reynolds et al., 1992). Sigleo and Frick (1998) alluded and attributed an increase in dissolved NO_3^- concentrations to stormy events. NO_3^- concentrations were to a greater extent higher than the SAWQG for domestic uses at many sites throughout the study. However, at some of the sampling sites (B, C, D, E, G, H and K) the concentrations were in line with the SAWQG for domestic uses mostly between the months of July and January. Drinking water with high levels of NO_3^- causes methemoglobinemia in infants (<6 months of age) and consequently infant mortality (ATSDR, 2017).

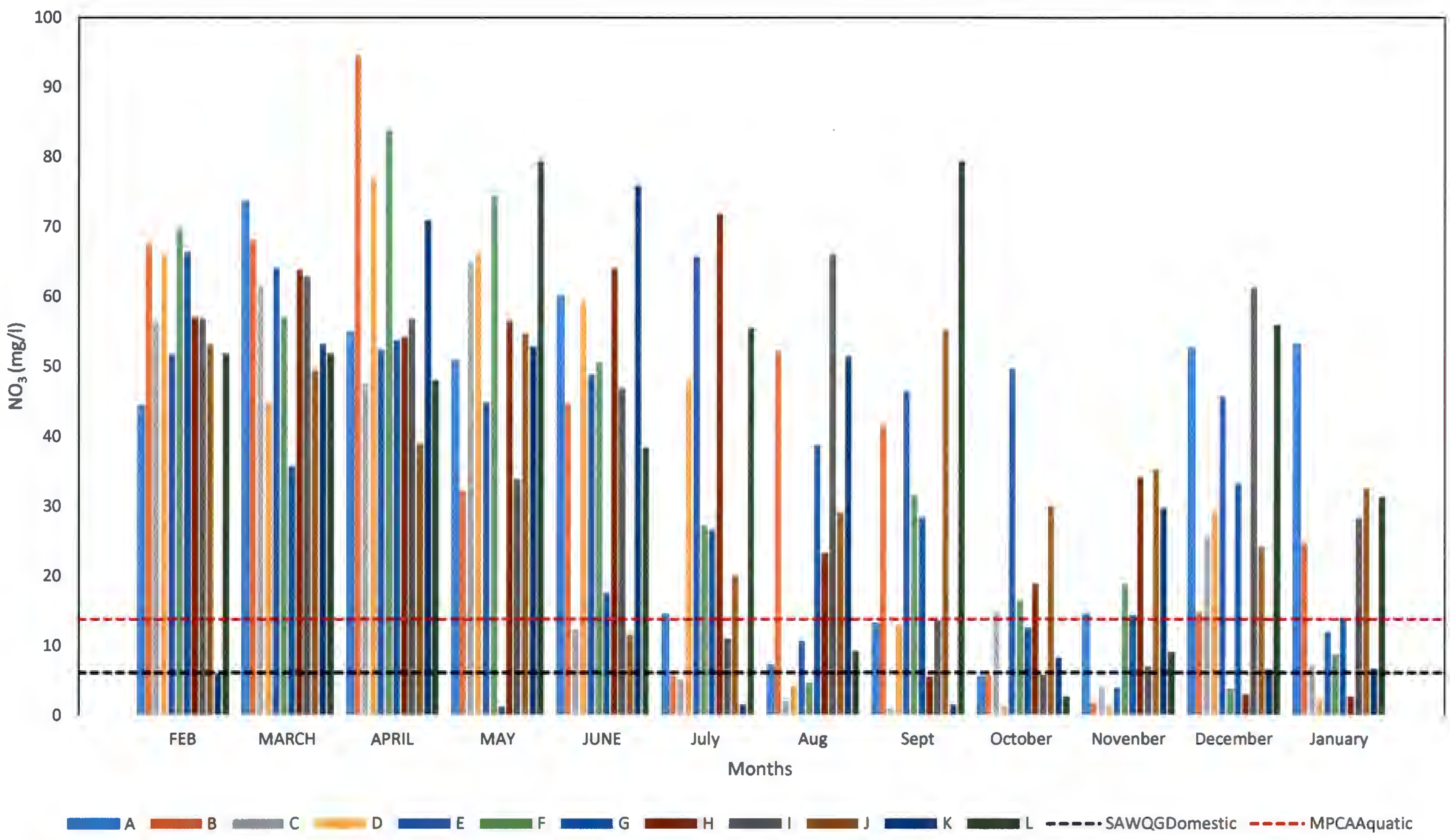

Figure 26: The trends of nitrate concentrations in the KRC

However, IARC (2010) reported that there was insufficient evidence to suggest that NO_3^- are carcinogenic with the exception of cases where it is converted to NO_2^- and then it is classified as class 2A carcinogen. NO_3^- concentrations were in excess of the Minnesota Pollution Control Agency (MPCA) aquatic ecosystem protection guideline at a few sites from February to September. Cheng and Chen (2002) observed that nitrate toxicity to aquatic animals is as a result of the conversion of oxygen-carrying pigments to forms that are incapable of carrying oxygen. Camargo et al. (2005) reported that long-term exposures to NO_3-N concentrations of 10 mg /l (44 mg/l NO_3^-) has some serious effects to freshwater invertebrates (*E. toletanus*, *E. echinosetosus*, *Cheumatopsyche pettiti*, *Hydropsyche occidentalis*), fishes (*Oncorhynchus mykiss*, *Oncorhynchus tshawytscha*, *Salmo clarki*), and amphibians (*Pseudacris triseriata*, *Rana pipiens*, *Rana temporaria*, *Bufo bufo*). In agreement, James et al. (2005) and Barker et al. (2008) observed the loss of aquatic species richness as a result of the dominance of the competitive free-floating species associated with the high NO_3^- concentrations. As such and based on the values recorded in the Klip River, it can be concluded that the water is unfit for sustaining aquatic life.

2.6.23. Phosphates

Phosphates concentrations in the KRC ranged between 0,007-5,447 mg/L of which the lowest was recorded at site A in February and the highest at site B in October. It is important to note that site B also recorded the highest P concentration relative to all the other sites from March to August and as such this site (B) also recorded the highest annual mean P concentration (1,433±1,586 mg/L) (Table 26).The lowest annual mean P concentration was recorded at site A (0,029±0,072 mg/L) which correspondingly recorded the lowest P concentration relative to all the sites throughout the study period (Figure 28). The P concentrations depicted a highly fluctuating trend throughout the year at all sites. As such, the one-way repeated measures ANOVA results indicated that at 95% confidence interval $F(5.687, 62.558) = 9.686$, $p = 0.000$) there were statistically significant differences in P concentrations in the various months from February 2016 to January 2017.

Table 26: Annual mean, maximum and minimum phosphates concentrations (mg/L).

Site	*Mean*	*Maximum*	*Minimum*
A	0,029±0,072	0,257	0,007
B	1,433±1,586	5,447	0,060
C	0,660±0,664	2,57	0,041
D	0,447±0,204	0,85	0,050
E	0,376±0,198	0,687	0,108
F	1,170±0,829	2,77	0,434
G	1,278±1,116	3,65	0,248
H	0,633±0,277	1,082	0,14
I	0,605±0,199	0,896	0,282
J	0,732±0,624	2,567	0,295
K	0,532±0,309	1,032	0,008
L	0,725±0,611	2,593	0,320
SAWQGAquatic = 5 mg/L			

The recorded P concentrations were generally in line with the SAWQG for aquatic ecosystem protection with the exception of site B, whereby the concentrations recorded in October exceeded the guideline and based on this the water was mesotrophic. In fresh water systems, P toxicity is indirect. It stimulates the growth of toxic algal blooms. Bornette and Puijalon (2011) reported that an increase in P concentrations can lead to competition between macrophytes and phytoplankton, thereby altering the composition of aquatic plant communities. Phosphates are not directly toxic to humans and animals (Amdur et al., 1991), and as such no drinking water standards for it have been established (U.S. EPA, 1990).

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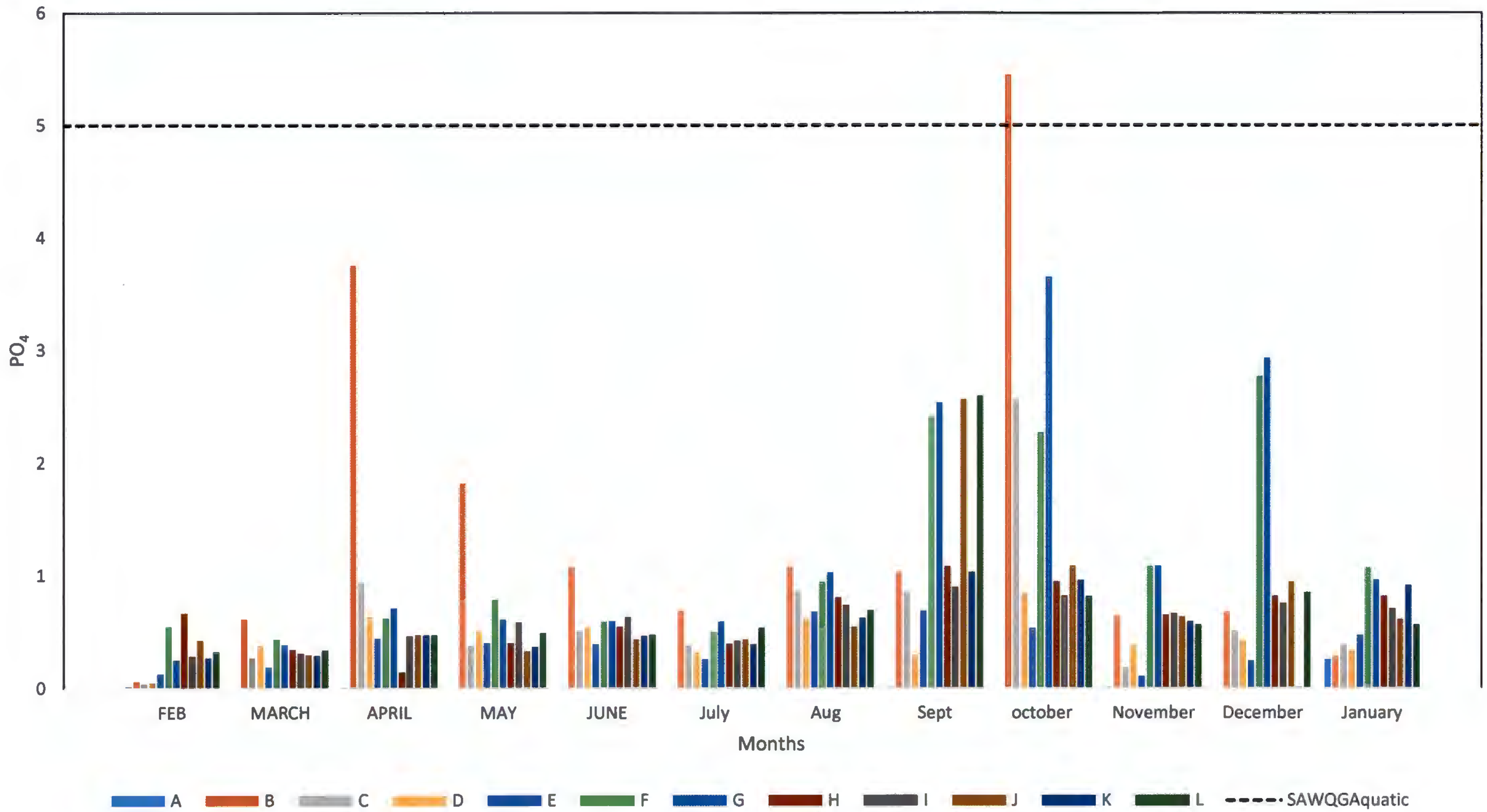

Figure 27: The trends of phosphates concentrations in the KRC.

2.6.24. Heavy metal pollution index

HPI is a rating reflecting the composite influence of different dissolved metals (Sirajudeenet et al., 2014). It is used to evaluate the suitability of water for its various uses. Table 27 shows the mean, maximum and minimum HPI for domestic uses. The HPI for domestic water uses was generally very high ranging from 71.527 to 32901.840 of which the highest was computed for site H in July and the lowest at site J in February. The highest annual mean HPI for domestic uses was recorded at site F (18 010.211).

Table 27: Annual mean, maximum & minimum heavy metal pollution index for domestic uses, in the KRC

Site	*Mean*	*Maximum*	*Minimum*
A	11158.026	21085.46	1736.504
B	14775.720	32410.52	5694.774
C	15280.604	22606.58	2332.852
D	13790.422	23339.78	1110.514
E	12957.307	17432.66	1877.107
F	**18019.211**	28136.9	6023.023
G	12970.634	16885.69	7434.384
H	14060.429	**32901.84**	2303.526
I	13168.437	21806.3	965.2703
J	11943.140	25948.09	**71.52657**
K	11103.891	18336.29	1050.594
L	13830.025	25208.12	2837.407
Critical index value =100			

It is important to note that all the values of HPI for domestic water uses were above the critical index value of 100 with the exception of site J in February (Figure 29). This suggests that in terms of heavy metals, the Klip River is not suitable for domestic uses

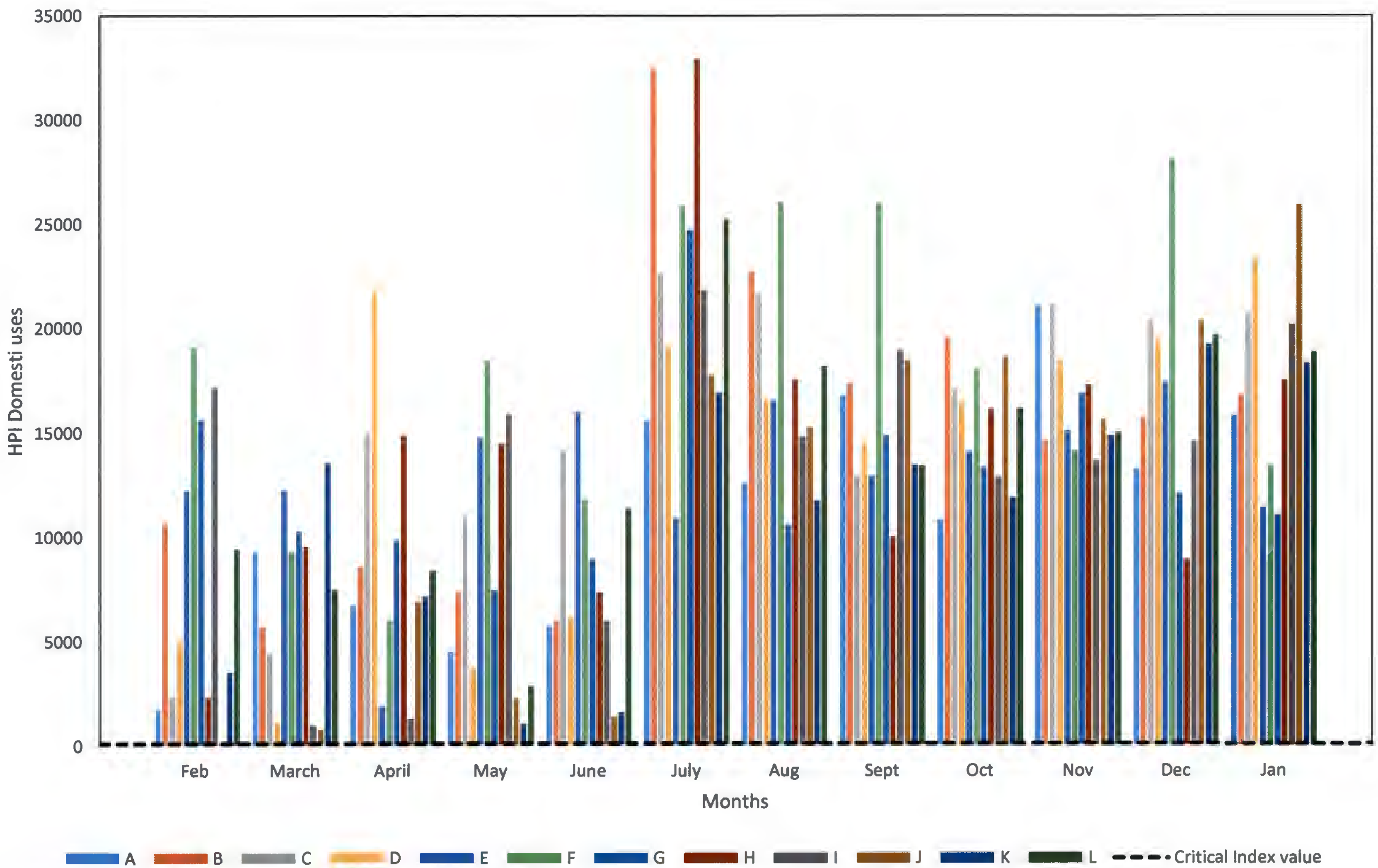

Figure 28: Heavy metal pollution index along the Klip River domestic for uses.

A multiple regression was conducted to determine which metals could predict the HPI for domestic uses. As and Pb were statistically significant in predicting the HPI for domestic water uses at 95% confidence interval, F [2, 9] = 89.679, p= 0.000 $R^2 = 0.952$. The 95.2% of the variability in the HPI for domestic water uses could be accounted for by the heavy metals. The tolerance >0.1 and VIF<5 revealed that the data had no multicollinearity and as such the predictive model was a good one (Hossain et al., 2010). The P-P plot in Figure 30 indicates that the MLR predictive model had no multicollinearity and the model was effective in predicting the metals which influence the HPI for domestic uses.

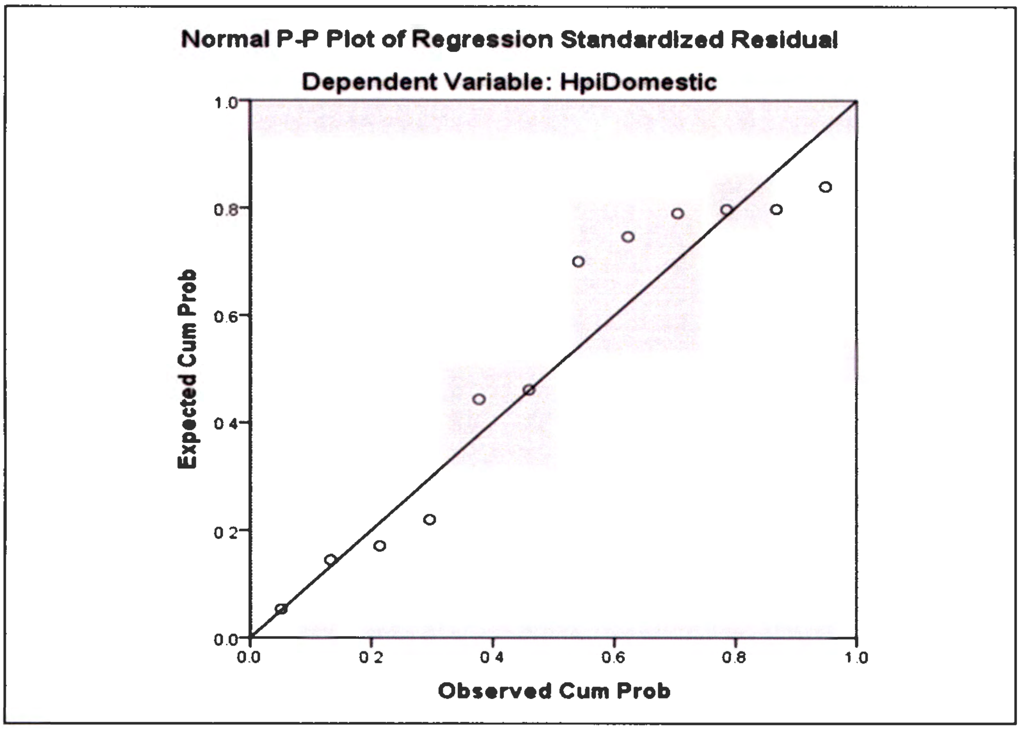

Figure 29: The P-P plot: HP1 for domestic uses.

Equation 11 shows the estimated multiple linear regression (MLR) model for domestic uses

$$HPI\ (\ domestic\ Uses) = 1885.824(As) + 1564.57(Pb) - 8750.834 \quad \textit{(11)}$$

The HPI for aquatic ecosystem protection was generally very high ranging from 45.312 to 22490.18 (Table 28). The highest was computed for site D in April and the lowest at site J in February. The highest mean concentration was recorded at site E (3951.010). It is important to note that all the values of HPI for aquatic ecosystem protection were above the critical index value of 100 with the exception of site J in February (Figure 31).It can be concluded that in terms of heavy metals, the Klip River is not suitable for sustaining aquatic life.

Table 28: Annual mean, maximum and minimum heavy metal pollution index for aquatic ecosystem protection, in the KRC.

Site	*Mean*	*Maximum*	*Minimum*
A	5562.188	17079.81	1989.082
B	5104.771	8665.370	1046.128
C	6746.232	21987.82	778.0829
D	6498.394	**22490.18**	205.1564
E	**3951.010**	7493.414	2689.092
F	9056.158	19222.1	3706.878
G	4920.892	9843.921	2769.945
H	7519.963	15106.19	2398.85
I	6273.230	11619.63	155.596
J	4324.566	8479.175	**45.31232**
K	5717.931	16452.19	314.4797
L	6854.973	18400.28	2323.655
Critical index value =100			

A multiple linear regression (MLR) was conducted to determine which metals could predict the HPI for aquatic ecosystem protection. Pb and As in decreasing order, were statistically significant in predicting the HPI for domestic water uses at 95% confidence interval $F [2, 9] = 30.510$, $p = 0.000$ $R^2 = 0.850$; 85% of the variability in the HPI for domestic water uses could be accounted for by the heavy metals. The tolerance >0.1 and VIF<5 revealed that the data had no multicollinearity and as such the predictive model was a good one (Hossain et al., 2010) . The P-P plot in Figure 32 further substantiates that the MLR predictive model had no multicollinearity and the model was effective in predicting the metals which would influence the HPI for aquatic uses.

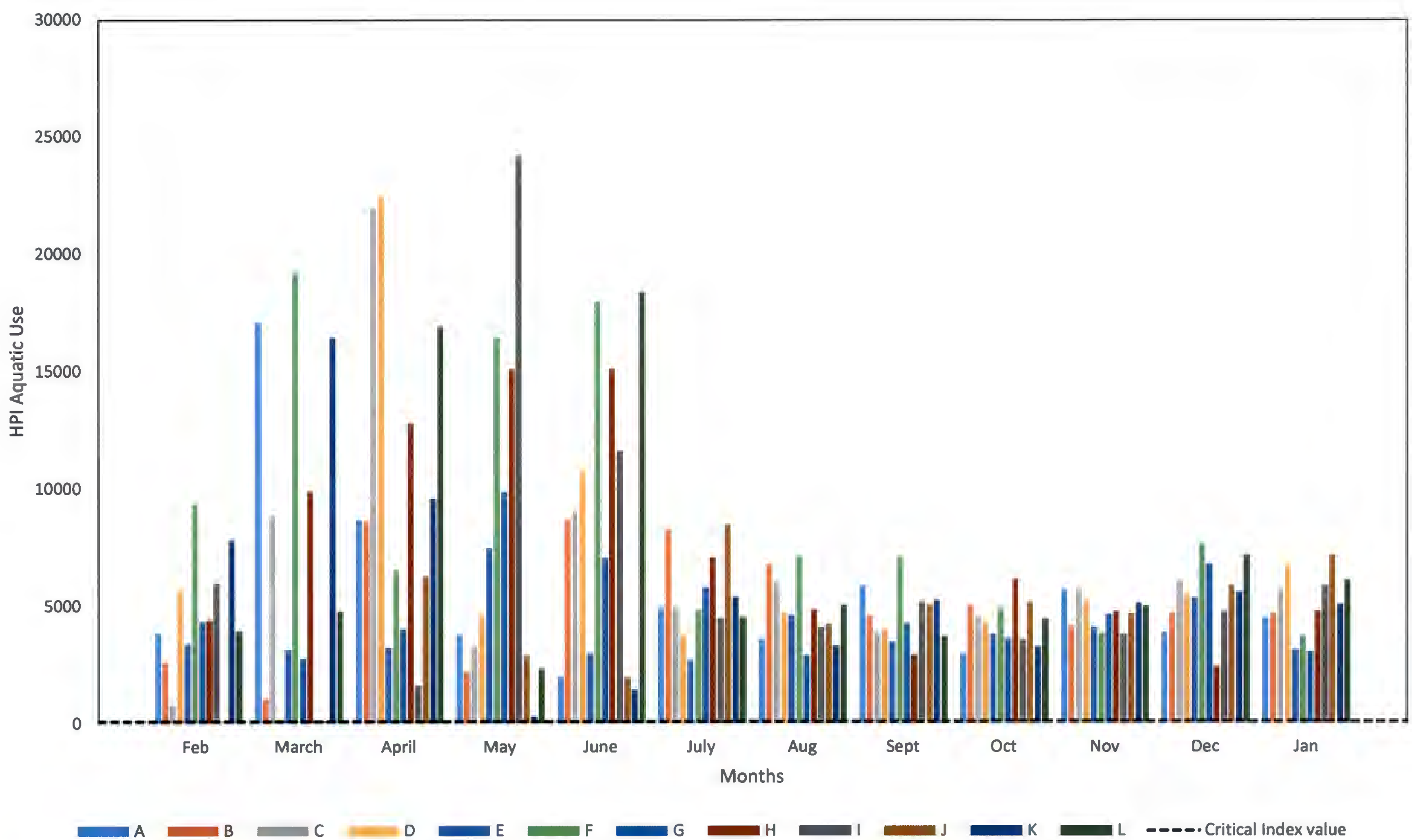

Figure 30: Heavy metal pollution index along the Klip River for aquatic uses.

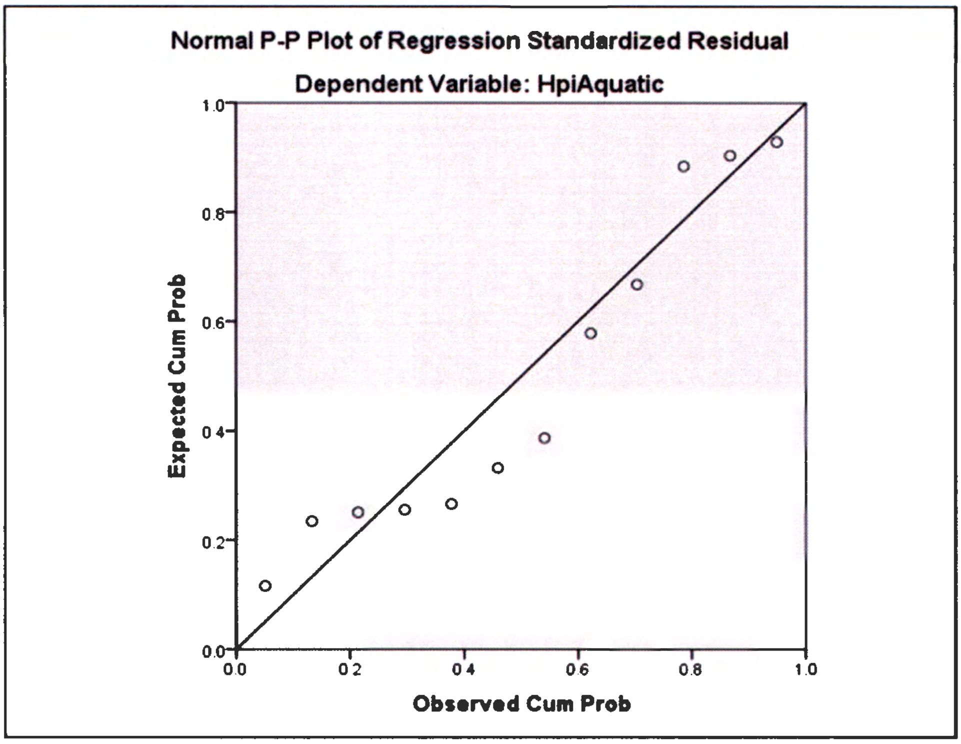

Figure 31: The P-P plot: HP1 for aquatic ecosystem protection

Equation 12 shows the estimated multiple linear regression (MLR) model for aquatic ecosystem protection.

$$HPI\ (\,Aquatic\ protection) = 2727.722(Pb) + 531.548(As) - 4484.807 \qquad (12)$$

Table 29: Annual mean, maximum and minimum heavy metal pollution index for Agricultural uses, in the KRC.

Site	*Mean*	*Maximum*	*Minimum*
A	3264.648	8054.699	212.136
B	**8476.076**	**11190.9**	3407.872
C	5361.045	9025.074	593.549
D	4586.894	7237.9	298.171
E	3170.707	5719.66	295.074
F	3654.413	6203.674	1034.564
G	2979.498	4810.982	1498.971
H	2819.904	5393.19	302.860
I	2686.041	4148.735	288.909
J	2746.641	5570.228	45.727
K	2473.125	3941.262	396.953
L	2927.461	4568.204	950.225

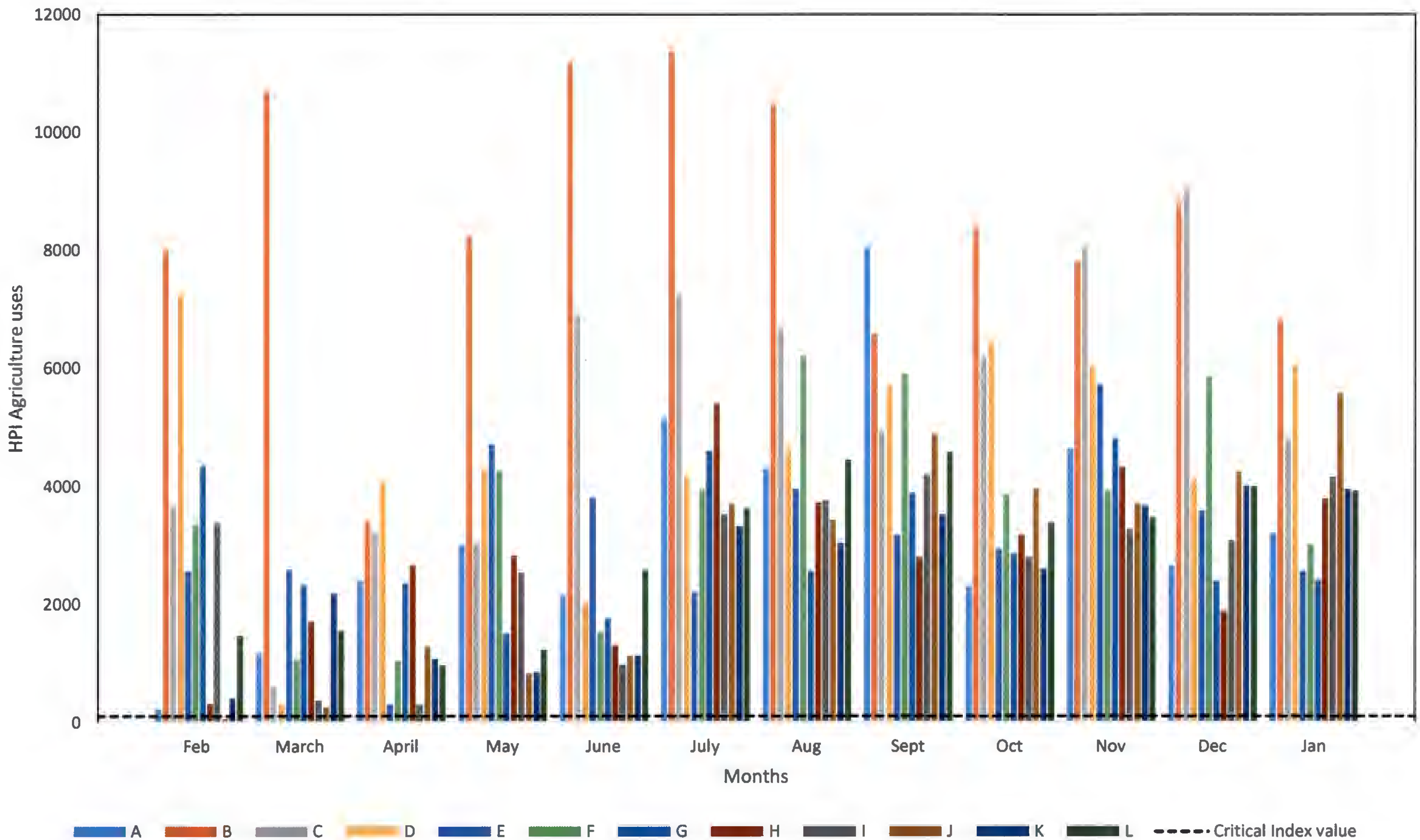

Figure 32: Heavy metal pollution index along the Klip River for agricultural use.

The HPI for agricultural uses was generally very high ranging from 45.727 to 11190.9 (Table 29) of which the highest was computed for site D in April and the lowest at site J in February (Figure 33). The highest mean concentration was recorded at site B (8476.076). Furthermore, all the values of the HPI for agricultural uses were above the critical index value of 100 with the exception of site J in February. Therefore and in terms of heavy metals, the KRC is not suitable for agricultural uses.

Results of the MLR revealed that As and Mn in decreasing order, were statistically significant in predicting the HPI for Agricultural uses at 95% confidence interval F [2, 9] = 280.017, p = 0.000 R^2 = 0.995. 99.5% of the variability in the HPI for agricultural uses could be accounted for by the heavy metals. The tolerance >0.1 and VIF<10 revealed that the data had no multicollinearity and as such the predictive model was a good one. Figure 34 indicates that the data had no multicollinearity and the predictive model is a good one.

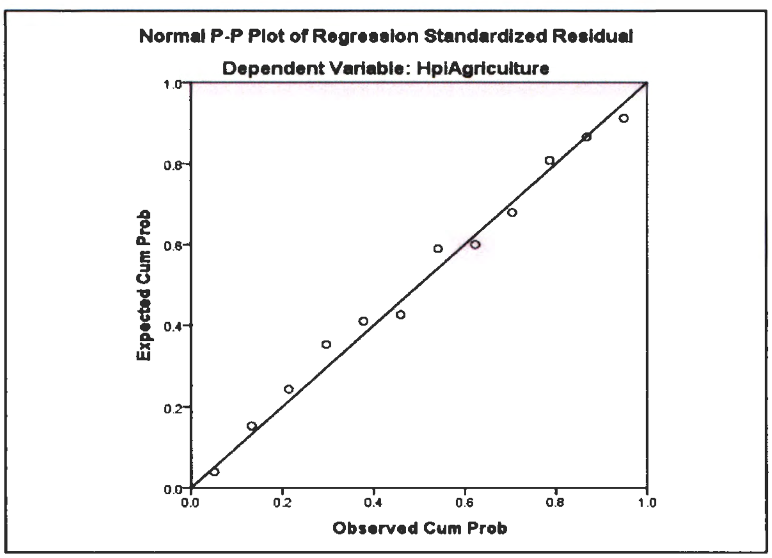

Figure 33:The P-P plot: HPI for agriculture uses.

Equation 13 shows the estimated multiple linear regression (MLR) model for agriculture uses

$$HPI\ (Agriculture\ uses\ ) = 360.136.183(As) + 326.183(Mn) - 1127.132 \quad (13)$$

2.6.25. Comprehensive Risk Index (CRI) and Potential Ecological Risk Index

The mean CRI for the

2.6.26. Comprehensive Risk Index (CRI) and Potential Ecological Risk Index

The mean CRI for the different metals was in this order; Cd >As>Pb>Ni>Zn.>Mn>Cu>Fe>Cr (Table 30). As such, Cd poses the most significant ecological risk in the KRC, with the CRI ranging from 0 to 3604.999 and Cr the lowest ecological risk ranging from 0.114 to 0.826

Table 30: The CRI for different metals and PERI for the sampling sites and risk classifications in the KRC

	CRI									PERI	PERI Category
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn		
A	102.160	656.731	0.165	0.576	0.630	4.497	129.167	129.047	9.910	1032.882	Very high
B	133.356	3604.999	0.826	6.369	2.514	20.861	131.528	58.656	17.940	3977.049	Very high
C	141.415	641.116	0.173	0.266	1.658	9.221	85.833	136.812	3.299	1019.794	Very high
D	127.788	604.495	0.234	0.077	1.053	7.346	102.778	148.738	5.921	998.429	Very high
E	137.852	0	0.186	0.114	0.329	2.236	79.583	29.539	1.676	251.516	Moderate
F	170.509	298.485	0.221	0.803	0.249	1.210	73.472	220.703	2.358	768.013	Very high
G	132.132	1396.876	0.179	0	0.202	1.504	88.889	76.453	3.131	1699.366	Very high
H	129.578	1026.293	0.212	0.147	0.249	0.828	84.722	197.199	3.112	1442.339	Very high
I	127.193	495.561	0.182	0.261	0.223	0.683	69.861	141.694	2.386	838.043	Very high
J	128.834	0	0.360	26.805	0.263	1.228	76.528	50.673	4.448	289.138	Moderate
K	108.182	1322.793	0.187	0.035	0.139	1.099	66.944	137.003	2.768	1639.15	Very high
L	126.041	800.282	0.114	1.269	0.216	1.547	80	163.129	4.148	1176.747	Very high
Mean	130,420	903,969	0,253	3,060	0,644	4,355	89,109	124,137	5,091	1261,039	Very high
Min	102.160	0	0.114	0	0.139	0.828	66.944	29.539	1.676	251.516	Moderate
Max	170.509	3604.999	0.826	26.805	2.514	20.861	131.528	163.129	17.940	3977.049	Very high
CRI class	Considerable	Very high	Low	Low	Low	Low	Moderate	Considerable	Low	Low	

The highest CRI for Cd was recorded at site B with sites G, H and K also recording very high CRI values. However, the CRI for Cd at sites E and J was the lowest (0). Other metals whose individual ecological risks were low include Cu, Fe, Mn and Zn whereas As and Pb fell in the considerable risk category and Ni in the moderate risk category. The PERI was in decreasing order; B>G>K>H>L>A>C>D>I>F>J>E. The PERI aligned with the CRI, with a maximum at site B and a minimum at site E. Most of the sites were in the very high risk category in terms of PERI with the exception of site E and J which fell in the moderate PERI category. It can be concluded that the KRC potentially poses moderate to very high risk to the ecological communities in its aquatic ecosystem.

2.7. Chapter summary

Most of the water quality parameters in the Klip River depicted statistically significant differences in mean concentrations except for; Al, Cu, Fe, Mn and Zn whose monthly mean concentrations variations were not statistically significant. Furthermore, based on the HPI for aquatic, domestic and agricultural uses which were far above the critical index, it can be concluded that the water in the KRC is not fit for domestic and agricultural uses and also for sustaining aquatic life. Cr, As and Pb were each individually shown to pose significant ecological risks to aquatic life in the Klip River. Furthermore, at the majority of the sampling sites along the profile of the Klip River, PERI was very high suggesting that there is a serious threat to ecological communities from heavy metals. In the next chapter, the water quality parameters are assessed in a holistic manner to identify and demystify the seasonal and temporal dynamics as well as the correlation between the various parameters.

CHAPTER 3

SPATIO-TEMPORAL CHARACTERIZATION OF WATER QUALITY IN THE KLIP RIVER CATCHMENT, SOUTH AFRICA

3.1 ABSTRACT

The previous chapter has provided more insight on the trends of individual water quality parameters during the study period (February 2016 to January 2017) and the potential risks. However, the spatial and temporal patterns and the mechanisms governing these dynamics still needed to be explained. Understanding the spatial and temporal patterns of water quality is central to water quality management as it provides information essential to the restoration as well as protection of water resources. The main objective of this chapter was to characterize the spatial and temporal trends of water quality in the Klip River catchment and to identify the variables responsible for the spatio-temporal dynamics. Literature on the processes (natural and anthropogenic-induced) which influence water quality are discussed. Furthermore, the approaches used in the contemporary spatio-temporal water assessments, which were applied in this particular study, the findings and implications thereof are presented.

3.2 INTRODUCTION

The quality of water in any catchment at any particular time is influenced by natural processes atypical of that catchment (Khalil and Ouarda, 2009; Pejman et al., 2009), as well as the anthropogenic activities (Huang et al., 2014). Natural processes such as precipitation, weathering, soil erosion, hydrological processes, nutrient leaching as well as the biogeochemical cycling coupled with natural factors such as geology, topography, meteorology, hydrology and biology, influence surface and ground water quality. Therefore it can be deduced that the composition of surface and ground water is reflective of the local geological, topographical, meteorological, hydrological as well as biological factors. The most significant natural influences to water quality in particular, are hydrology, geology and climate as they impact both the quality and quantity of water (Singh et al., 2004). Figure 35 shows some of the natural (hydrological, physical, biological and chemical) processes which govern water quality within a catchment.

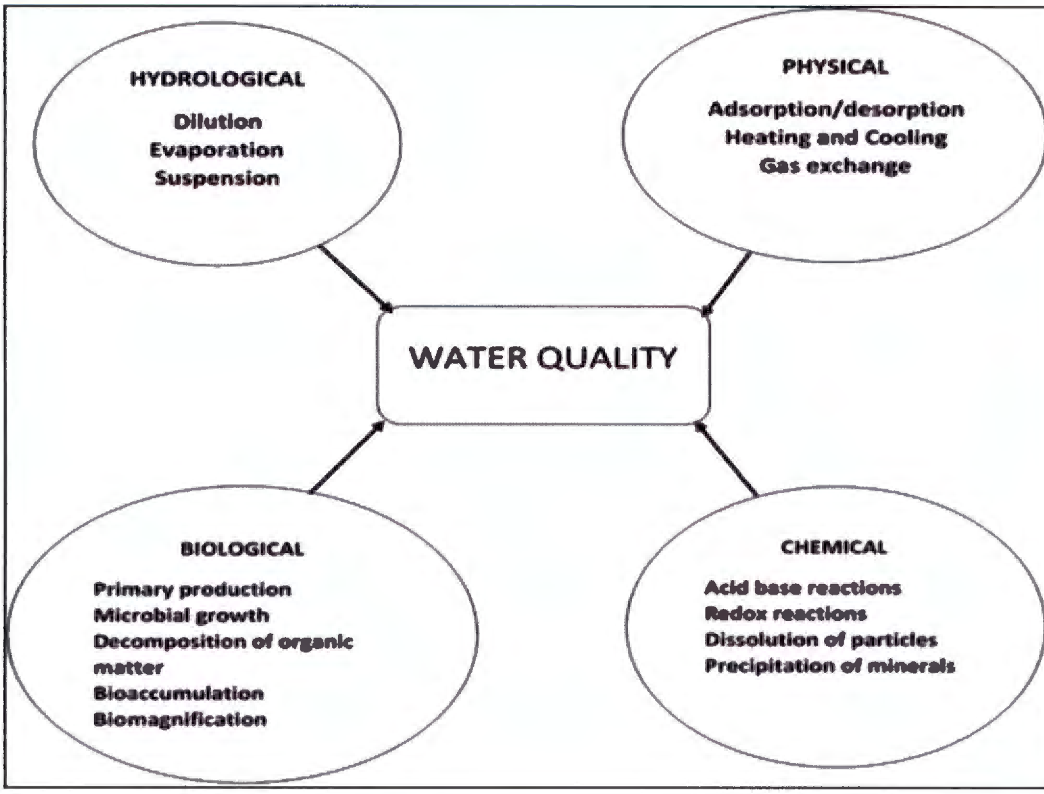

Figure 34 : Hydrological, physical, biological and chemical processes which influence water quality.

Source: (World Health Organisation, 1996).

The influence that these factors have on water quality is subject to the nature of environmental factors brought about by climatic, geographical and geological conditions. Environmental factors such as vegetation (terrestrial and aquatic), climate and rock composition control the natural processes occurring in a catchment and subsequently the water quality (Khatri and Tyagi, 2015). Climate and vegetation regulate the occurrence of soil erosion, weathering and dissolved materials concentration through evaporation and evapotranspiration (Bartram et al., 1996; Khatri and Tyagi, 2015). The decomposition of aquatic plants alters the levels of N, P, pH, CO_3, dissolved oxygen in water, and additionally, those elements and compounds which respond to oxidation and reduction reactions (Khatri and Tyagi, 2015). Furthermore, the decomposition of plants in terrestrial settings influences the carbon and nitrogenous compounds concentration in water. However, water quality is also influenced by anthropogenic activities (Nouri et al., 2008; Noori et al., 2010) as there is adequate evidence to the effect that human induced alterations on the landscape have resulted in deterioration of water quality (Khatri and Tyagi, 2015).

The catchment characteristics which influence spatial variation comprise of topography and geology (Whigham et al., 2003; Chen and Lu 2014; Wang et al., 2014b). Physiography determines the rate of erosion which ultimately controls the discharge of sediments (Sliva and Williams, 2001). Geology influences the chemical characteristics of water based on the mineral make-up of the bedrock as well as the weathering and other biogeochemical processes (Jarvie et al., 2002; Mosher and Findlay 2011). For example, if the bedrock is made of limestone, the water would predominantly be comprising of calcium and bicarbonate ions (Banks and Jones, 2014). Vörösmarty et al. (2010) and Duan et al. (2013) concluded that it is very pertinent to establish the catchment processes which govern water quality under increasing anthropogenic alterations coupled with pressure from natural processes.

Mitchell et al. (2001), Ouyang et al. (2006) and Martin et al. (2004) observed that the hydrological and biogeochemical processes account for the seasonal variation in water quality. Seasonal variations in weather conditions, for instance, precipitation as well as runoff and water level (Vega et al., 1998) were shown to influence water quality characteristics in different seasons (Pathak et al., 2015) because these processes have an influence on the water pollution pathways. For instance, Martin et al. (2004) attributed seasonal variations in nitrate concentrations to hydrological and biogeochemical processes. Furthermore, the movement of nutrients between the ground and surface water is largely controlled by precipitation. Prathumratana et al. (2008) and Van Vliet and Zwolsman (2008) demonstrated the impact of flow rate on the concentration of dissolved substances and dissolved oxygen particularly where temperatures are high. Extreme weather events such as floods and droughts were identified as having an influence on the concentrations of contaminants in water. Wo and Burt (2001) and Duan and Kaushal (2013) alluded that the biogeochemical processes associated with the hydro-meteorological regimes, for instance, denitrification and mineralization processes also influence the temporal variability of stream water quality. Climate change also greatly impacts the water quality by way of temperature and rainfall characteristics.

Other processes like immobilization, denitrification, mineralization and bedrock weathering, associated with the hydro-meteorological regime, also determine the temporal veniality of stream water quality (Worall and Burt, 2001; Martin et al., 2004). Other biogeochemical processes which were found to determine the geochemical composition of water bodies are diagenesis, adsorption/desorption of organic matter and precipitation - dissolution of Fe Mn[6] oxyhydroxides (Solai et al., 2010). Salomons and Förstner (1984), Wang and Chen (2000), Ackay et al. (2003) and Abdel-Ghani and Elchaghaby (2007), demonstrated the various changes that metals in water undergo as a result of precipitation, sorption, dissolution and complexation. Khatri and Tyagi (2015) concluded that natural factors which influence water quality in both rural and urban areas are the same, whereas the anthropogenic influences vary between rural and urban settings. In urban settings, more water pollution occurs relative to rural areas, due to industrialization, sewage discharge and domestic activities (Khatri and Tyagi, 2015). During heavy rainfall events there is delivery of high NPS discharges from agricultural activities and roads to aquatic systems (Servais et al., 2007).

In order to carry out the spatial and seasonal characterization of water quality, long term water quality monitoring data is required so as to determine the sources and factors influencing these dynamics (Pathak et al., 2015). Data from this long term monitoring is voluminous, thus it requires analytical tools which have an ability to reduce its multidimensionality and complexity hence the use of multivariate statistical techniques. Multivariate statistical techniques are useful in water quality assessment, identification and apportionment of pollution sources and factors. Dixon and Chiswell (1996) justified using multivariate statistics because of the non-linear nature of water quality data and as such these multivariate statistics provide a reliable, and easy method of analysing water quality data (Zhang et al., 2012). Manoj and Padhy (2014), reviewed the multivariate statistical techniques employed in water quality assessments and revealed that owing to the large and complex water quality monitoring data, multivariate statistical techniques help reveal hidden information in the data. Moreover, Kanade and Gaikwad (2011) reiterated that multivariate statistics are very helpful in the pattern recognition and exploratory data analysis thereby driving hidden information from the data set.

Different types of multivariate statistical analysis techniques have been used in various studies. Cluster Analysis (CA) and Principal Component Analysis (PCA) for instance have been extensively used in the spatio-temporal analysis of environmental data because of their ability to identify relationships between samples and variables (Wenning and Erickson, 1994). Helena et al. (2000) and Alberto et al. (2001) noted that PCA identifies significant variables which are representative of a large data set thereby reducing the dimensionality of the data, without compromising the original information. As such, PCA employs correlation to reduce variables and can therefore assist in the establishment of hydrological and geochemical factors which influence the spatial characteristics of water quality (Olsen et al., 2012). Fitzpatrick et al. (2007) carried out a study in the USA where multivariate statistics were used to explore the effects of urban and agricultural land use. The study identified biogeochemical fingerprints for the various land uses using CA, from which they were able to assess the behaviour of nutrients relative to land use. Furthermore, there were observations of associations of trace elements as well as P in an urban setting which they could not explain.

Spatial variability is driven by anthropogenic activities as well as catchment characteristics (Huang et al., 2014). The anthropogenic activities in form of different land uses impact water through PS and NPS discharges. Ndungu (2014) concluded that in order to achieve the optimal management of water resources, both seasonal and spatial considerations should be incorporated in pollution reduction strategies, and an appreciation of the water quality dynamics (spatial and temporal) is required. Don-Pedro et al. (2004), stated that spatio-temporal analysis is a crucial stage in the protection and conservation of water. Furthermore, Shrestha and Kazama (2007) and Mustapha et al. (2013) alluded and demonstrated the importance of spatial and temporal characterization of water quality in ecological environmental protection as well as water resources management. Wu et al. (2015) reiterated that to enhance our knowledge on the anthropogenic impacts to water, an understanding of the spatio-temporal variations of pollution and its sources is crucial.

The characterization of seasonal changes in surface water quality is pertinent in the understanding of temporal dynamics of river pollution relative to the influence of natural processes as well as anthropogenic inputs of point and non-point sources (Ouyang et al., 2006). Yang et al. (2013) suggested that carrying out spatial characterization of pollution is also important, since information on the pollution critical zones is determined, and as such any remediation programs designed using this information can allow for efficient water management programs to be enacted thus improving water quality. Simeonov et al. (2003) suggested that source apportionment is an essential approach which purposes to establish the concentrations of the identified sources to the concentration of each parameter. Huang and Liu (2014) cited the need for integrating the multiple parameters of water quality and their spatio-temporal variations, as they are necessary in the identification of pollution characteristics and potential pollution sources.

Rothwell et al. (2010) and Alberto et al. (2010) highlighted the significance of long term water quality monitoring programs in water resources management, so that information on the spatio-temporal variability in water quality characteristics can be obtained. Despite the fact that water quality monitoring techniques have greatly improved over the years, there remains a challenge of representativeness as well as reliability of surface water quality data particularly in large river systems (Mustapha et al., 2013). Large river systems possess vast heterogeneity in water quality characteristics spatially and temporally, thus making these kinds of systems difficult to monitor (Soininen et al., 2004; Chen et al., 2012; Wang, 2014).

The Klip River is a large system which runs past a diverse array of land uses and as such is atypical of water quality heterogeneity. This makes designing a water quality monitoring programme for the Klip River, which has representative sampling points, difficult. An appreciation of the influence of anthropogenic and natural factors on water quality, taking into consideration the temporal and spatial dynamics, is critical in water resource management because it enables the targeting of appropriate scales and factors for the improvement of water resources management (Huang et al., 2014). Therefore, an assessment of the spatial and temporal dynamics of water quality is important in this catchment as it enables the design of accurate water quality assessment programs. The main objectives addressed in this chapter were (i) to analyze the spatial and temporal trends of water quality and (ii) subsequently to identify the critical sources of pollution in the Klip River catchment.

3.3 Methodology

3.3.1 Delineation of homogenous pollution zones and seasonality

Cluster Analysis is a statistical tool which uses the similarities within a class of samples to group them. Vega et al. (1998) and Singh et al. (2004) suggested that CA helps in the interpretation of data as well as assessment of patterns within the data. In this study, CA was used to analyse similarities and dissimilarities between sampling sites, thus sampling sites (described in section 2.5.1 of this thesis) with similar water quality characteristics were grouped into homogenous clusters. Results are presented as dendrograms, whereby the linkage distance D_{link}/D_{max}, which represents the quotient between the linkage distance for a particular case divided by the maximal distance, multiplied by 100 as a way to standardize the linkage distance, isrepresented on y-axis (Alberto et al.,2001; Simeonov et al., 2003; Singh et al., 2004).

Discriminant Analysis (DA): the main aim of this statistical analysis is to determine discriminatory variables between the identified groups. In this study, the DA was used to assess the temporal variations in river water quality. The identified seasonal clusters were subjected to DA to identify variables that discriminate between the seasons. Temporal variables were used as the grouping (dependent) variables, while all the measured parameters constituted the independent variables. In essence, DA was used to explore the statistically significant disparities in the various parameters between the samples derived from areas subject to various types of land use (Li et al., 2014).

The discriminant analysis linear equation is as follows:-

$$D = v_1X_1 + v_2X_2 + v_3X_3 = \cdots v_1X_1 + a \qquad (14)$$

Where D = discriminate function

V = the discriminant coefficient or weight for that variable

X = score for the Variable

a = constant

I = number of the predictor variables

The Wilk's lambda statistical test was used in the multivariate analysis of variance to test whether there were differences between means of the identified groups of subjects on a combination of dependent variables. It is a direct measure of proportion of variation in the combination of dependent variables that is unaccounted for by the independent variable (Everitt and Dunn, 2001).

3.3.2 Identification of pollution sources

Principal Component Analysis (PCA) and **Factor Analysis** (FA) was used for sources apportionment in that it explains the variance of a large set of inter-correlated variables and transforms them into a smaller set of variables which are termed principal components. Principal component analysis provides information on the most significant parameters which are sufficiently representative of the whole data set. This reduction of data therefore does not result in the loss of the original information. In this study, PCA was applied to the identified individual groups from the temporal cluster analysis to determine factors that could influence compositional patterns in the water samples. The principal components are expressed as in Equation 15:

$$Z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + a_{i3}x_{3j} + \cdots + a_{im}x_{mj} \qquad (15)$$

Where a is the component loading, z the component score, x *is* the measured value of a variable, i the component number, j the sample number, and m the total number of variables.

Factor Analysis

Factor analysis explains the correlation present in the common factor portion (Praus, 2007). It adds valuable qualitative information about the pollution sources by reducing the contribution of less significant variables to further simplify the data structure extracted from PCA. This is done by rotating the axis defined by PCA, according to well established rules, and constructing new variables, also called varifactors (VF). Unlike the principal components (PC), VF can include unobservable, hypothetical, latent variables (Vega et al., 1998; Helena et al., 2000). Factor analysis is expressed as in Equation 16.

$$z_{ij} = a_{f1}f_{1i} + a_{f2}f_{2i} + ...a_{fm}f_{mi} + e_i \tag{16}$$

Where, z = determined value of a variable; a = factor loading; f = factor score; e = residual term accounting for errors or other sources of variation; i = sample number; j = variable number, m = total number of factors.

To quantify the various source contributions, the Absolute Principal Component Source (APCS)-Multi Linear Regression **(MLR)** was used. APCS-MLR was shown to be effective in supplying information regarding contributions of each source type (Pekey et al., 2004; Song et al., 2006).

Comprehensive Pollution Index

To evaluate the qualitative and quantitative aspects of water quality and determine the spatial variations in the water quality, the Comprehensive Pollution Index was used. In this study, the single factor index (Si) and the Comprehensive pollution index (P_i) were used to evaluate the spatio-temporal patterns of water quality based on Equations 17 and 18 (Ma et. al., 2015).

$$S_i = \frac{C_i}{C_o} \tag{17}$$

$$P_i = \frac{1}{n} S_i \tag{18}$$

Where C_i = actual concentration of a particular surface water pollutant

C_o = pollutant concentration according to water quality standards

n = number of monitoring parameters

Ma et al. (2015) used the parameters which were responsible for the significant difference between clusters to calculate the comprehensive pollution index (CPI) however in this study all the parameters were used depending on the availability of water quality standards. Figure 36 is a flow diagram, which summarizes the methodology used in this chapter.

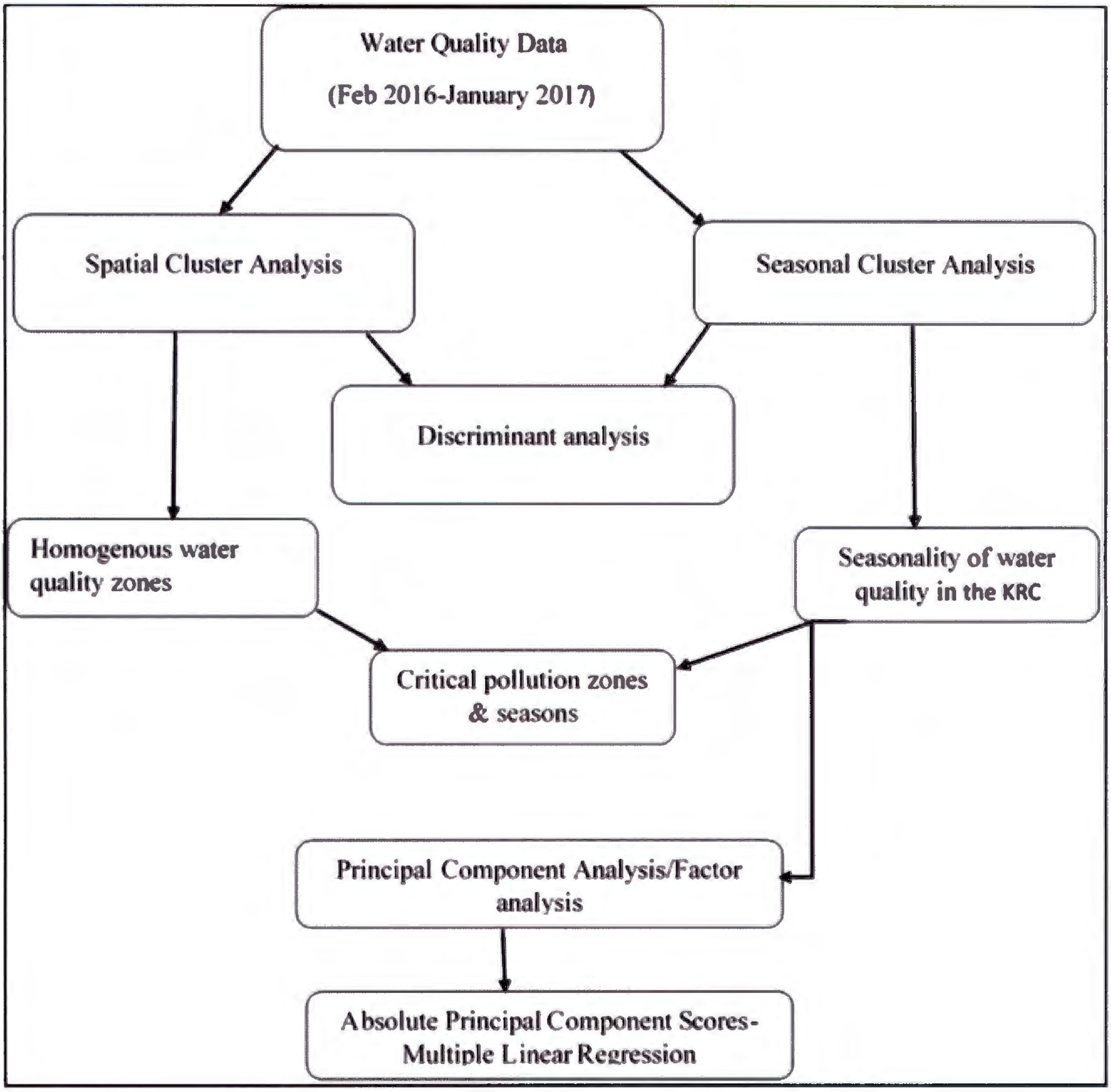

Figure 35: The analytical framework for this chapter.

3.4 Results

3.4.1. Homogenous water quality zones

The spatial cluster analysis grouped water quality characteristics into two homogenous water quality zones as is illustrated in Figure 37. **Cluster 1** comprised of sampling points A, B, C, D, E, F and G, which are located in the upper to the midsection of the Klip River and **Cluster 2** consisted of sampling points H, I, J, K and L which are located in the downstream section. Within Cluster 1 the sampling point A displayed close proximity to points B and D, however, the sampling points F and E were more closer to Cluster 2 point K.

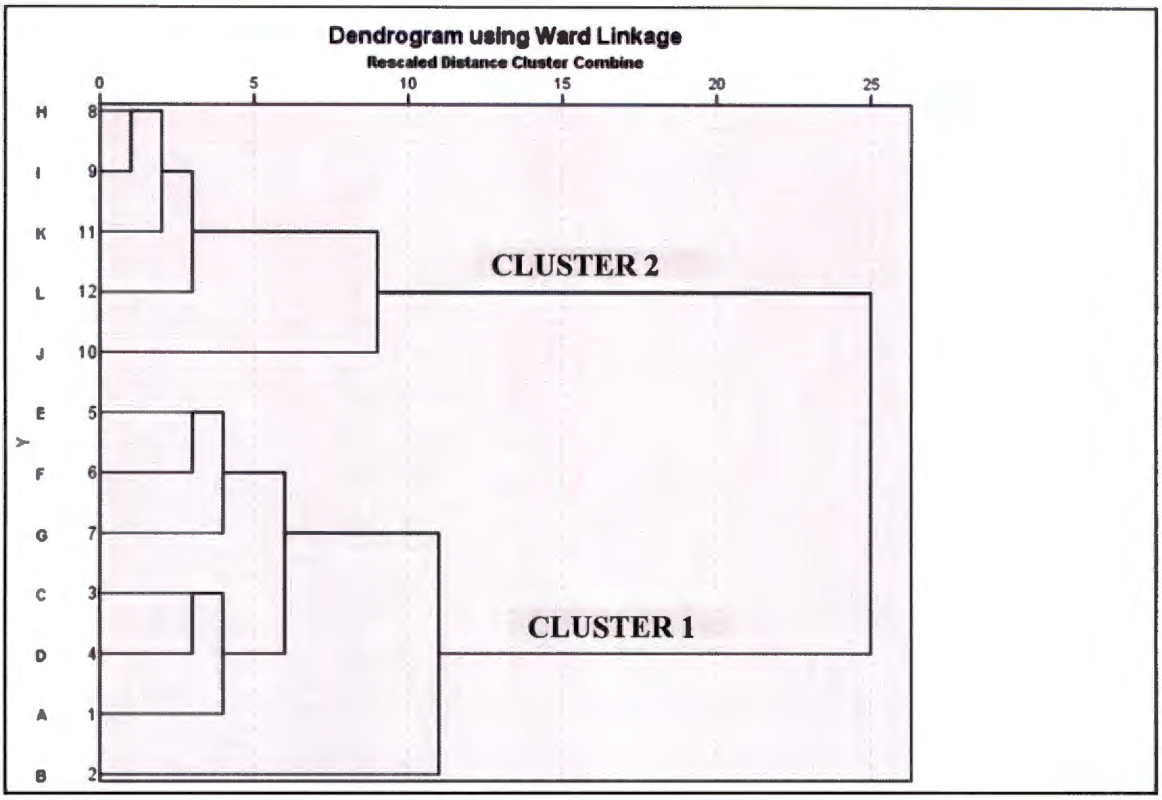

Figure 36: Dendrogram showing spatial distribution of sampling points in the Klip River catchment.

The rationale for the spatial grouping was as follows; Cluster 1 which is the upstream section of the river is characterized by mining activities, industries, urban areas and WWTP. There are mine dumps and numerous mines which are located in the vicinity of the sampling points A and B hence their close proximity on the dendrogram. Furthermore, between sampling sites C, D and E there are 3 WWTPs (Bushkoppies, Goudkoppies, Olifantsvlei and Dekema) which all discharge in this part of the Klip River. Whereas Cluster 2 comprised of sampling sites located in the downstream section of the Klip River. The anthropogenic activities in the downstream segment are predominantly agriculture and residential settlements. Although sampling site H is influenced by discharges from the Vlaakplats WWTP which discharges in the Rietvlei tributary and the Rondebult WWTP, which discharges directly into the Klip River, the volume of the discharges are low relative to the upstream WWTPs, as is shown in Table 1.

Discriminant Analysis (DA) was conducted to determine the water quality parameters which were responsible for discriminating the spatial clusters as well as the proportion of cases which were correctly classified using CA (Table 31). Firstly, the results indicate that 100% of the predicted values of the discriminant functions of the original group cases for Group 1 (Cluster 1) and 100% for Group 2 (Cluster 2) variables were correctly classified. Therefore and overall, 100% of the cross-validated grouped cases were correctly classified which is an indication of the accuracy of the model. As such, it can be deduced that water quality characteristics in the Klip River catchment can be distinguished based on two homogenous water quality zones i.e. the Upstream and Downstream. This matrix is important as it evaluates the effectiveness of the DA (Smeti and Golfinopoulos 2015).

Table 31 : The confusion matrix for the spatial CA.

		Ward Method	Predicted Group Membership		Total
			1	2	
Original	Count	1	7	0	7
		2	0	5	5
	%	1	100.0	.0	100.0
		2	.0	100.0	100.0

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The DA (Wilk's lambda value 0.004, $p<0.002$) resulted in one discriminant function. Discriminant function coefficients identified the predictor variables which were highly correlated with the discriminant function. In this case, these included As, Ca, Cd and Mg, which were largely responsible for discriminating spatial differences in water quality characteristics. This model was validated as being a good model based on the value of the Wilk's lambda and p values (Table 32).

Table 32: Standardized Canonical Discriminant Function Coefficients.

	Function
	1
Al	-.666
As	2.736
Ca	2.086
Cd	.796
Co	-.578
Cr	-.234
Cu	-.442
Fe	-1.243
K	-4.237
Mg	1.950

Figures 38-41 depict the mean concentrations of the discriminant variables for the spatial CA. Overall, the concentrations of metal discriminant variables i.e. As and Cd were higher in the upstream relative to the downstream. However, the concentrations of the cationic discriminant variables i.e. Ca and Mg were higher in the downstream part of the KRC relative to the upstream. Elevated concentrations of metals in the upstream section of the KRC, particularly As can be associated with the mining activities, the presence of 5 WWTPs and several industrial activities which dominate land use activities in this river reach. This aligns with findings from Hudson-Edwards et al. (2008); Hajalilou et al. (2011); McCarty et al. (2011) and Patowary (2016), where water bodies located in close proximity to mines, mining dumps, and industrial activities recorded elevated As and Cd concentrations.

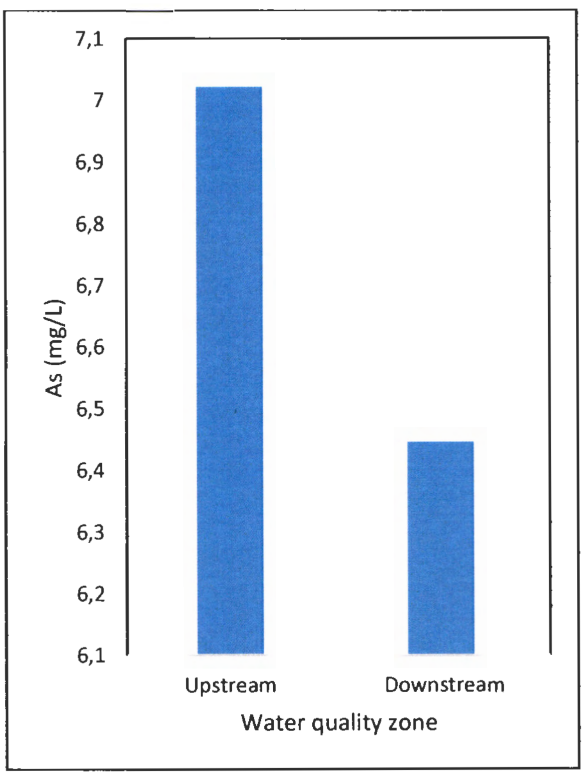

Figure 37: Mean As concentration in water quality zones.

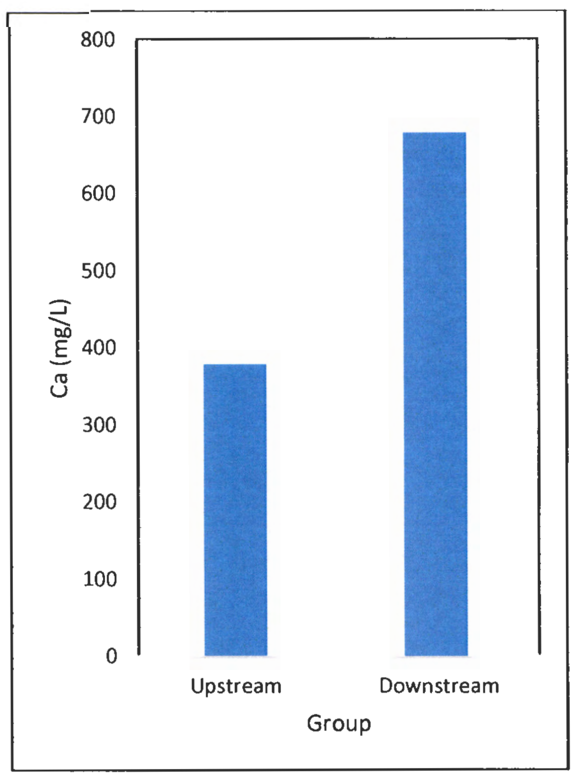

Figure 38: Mean Ca concentration in different water quality zones.

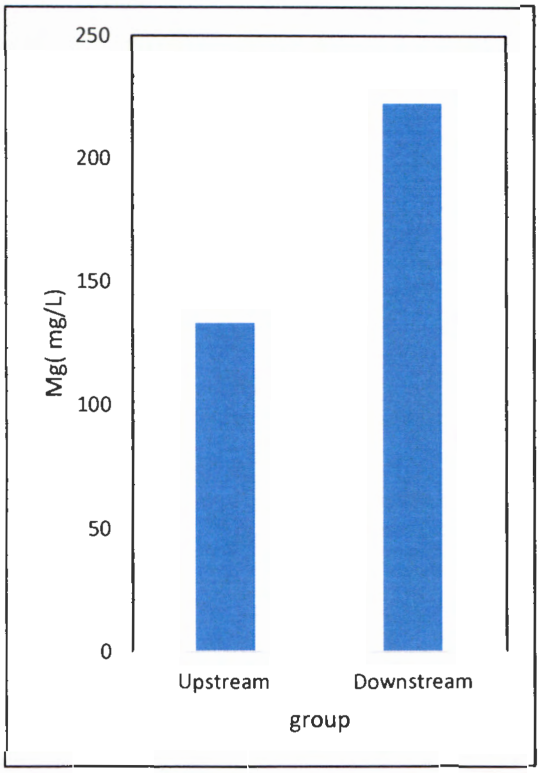

Figure 39: Mean Mg concentration in water quality zones.

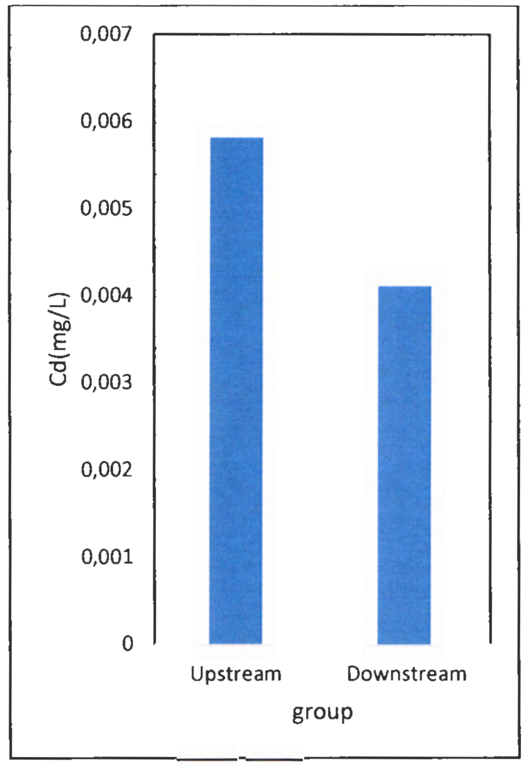

Figure 40: Mean Cd concentration in different water quality zones.

3.4.2 Seasonality of water quality in the KRC

Seasonal CA

Figure 42 is an illustration of results of the seasonal cluster analysis of water quality characteristics in the Klip River catchment. The cluster analysis grouped water quality into two clusters. The first cluster comprised of 5 months i.e. February, March, April, May and June (2016) and as such was referred to as the 2015/16 season. This cluster was clearly influenced by the residual effects of the 2015/2016 season, which as a result of the El Niño Southern Oscillation (ENSO) phenomenon, was declared a drought rainfall season in South Africa (Archer et al., 2017 ; Baudoin et al., 2017; Ikeda et al., 2017). The other cluster comprised of July, August, September, October, November, December (2016) and January (2017) and was referred to as the 2016/2017 season. This cluster was influenced by La Niña which brought about heavy rainfall and caused flooding in the Gauteng province (South African Weather Services, 2017).

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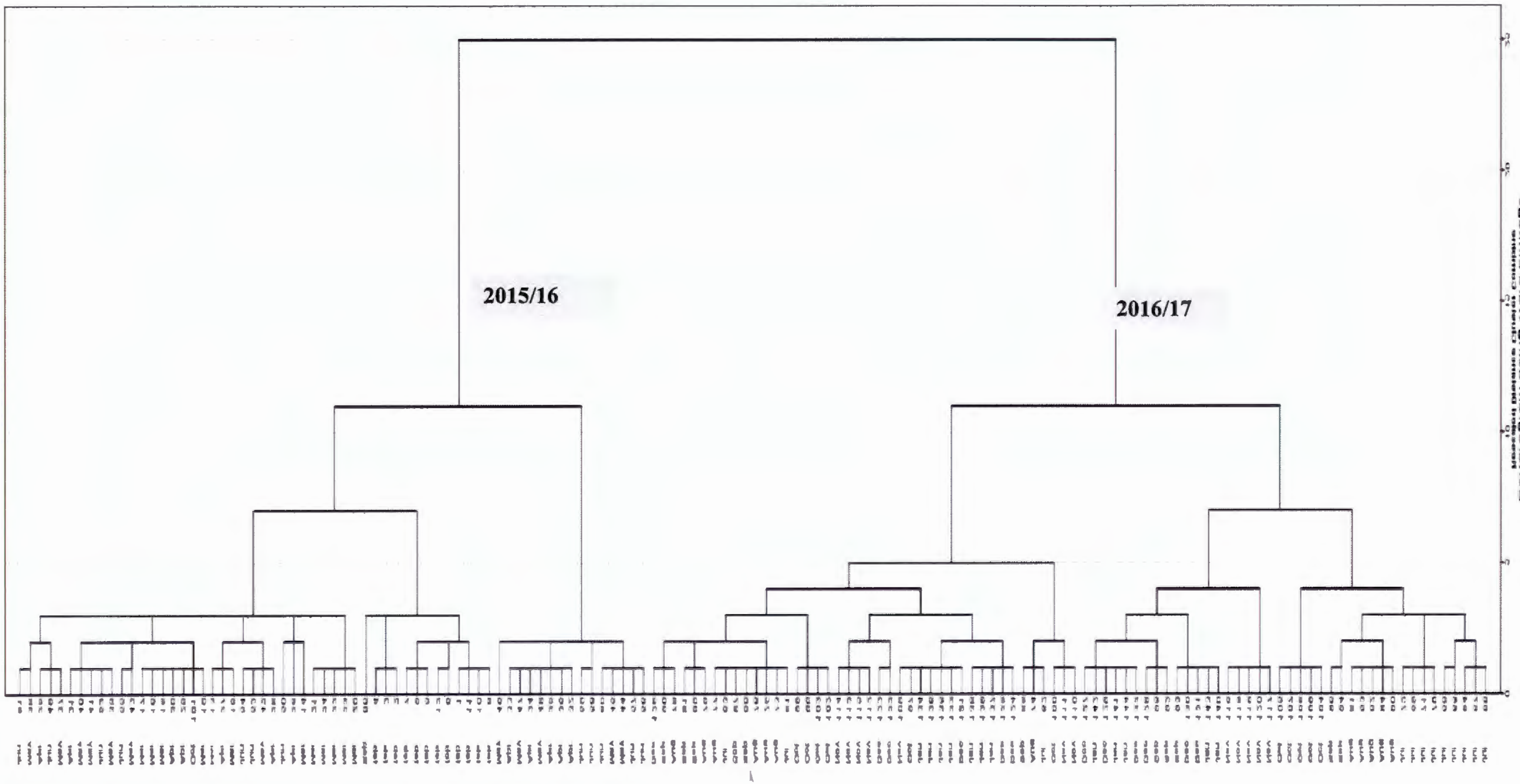

Figure 41: Dendrogram showing the seasonality of water quality in the Klip River catchment.

An analysis into the classification of results to determine the proportion of cases which were correctly classified using CA (Table 33) indicated that 96.8% of the predicted values of the discriminant functions of the original group cases for group 1 and 100% for group 2 variables were correctly classified. Overall, 98.1% of the cross-validated grouped cases were correctly classified which is an indication of the accuracy of the model, and as such, it can be deduced that the water quality characteristics in the Klip River catchment could be distinguished based on two seasons. This matrix is important as it evaluates the effectiveness of the DA (Smeti and Golfinopoulos 2015).

Table 33: The Confusion Matrix for the seasonal CA.

		Ward Method	Predicted Group Membership		Total
			1	2	
Original	Count	1	62	0	62
		2	0	42	42
		Ungrouped	5	35	40
	%	1	100.0	.0	100.0
		2	.0	100.0	100.0
		Ungrouped	12.5	87.5	100.0
Cross-validated	Count	1	60	2	62
		2	0	42	42
	%	1	96.8	3.2	100.0
		2	.0	100.0	100.0

2015/16 season

In the 2015/16 season, the mean concentrations of metals were as follows in descending order: Mn>As>Fe>Pb>Ni>Al>Co>Zn>Cr>V>U>Cu>Cd (Table 34). Therefore the three most abundant metals were Mn, As and Fe. Similar findings were also observed by Montalvo et al. (2014), Nwadinigwe et al. (2014) and Pandey and Singh (2017) in which Fe and Mn were amongst the most abundant metals. The abundance of Fe has been linked to natural processes such as weathering and erosion as well as anthropogenic sources such as industrial and municipal waste water discharges; construction and agricultural activities (Singh et al., 2005; Mora et al., 2013; Ghrefat et al., 2011; Pandey and Singh, 2017). Mn and As abundance particularly in the dry season could be attributed to high evaporation rates and low flow rates of water during the season (Montalvo et al., 2014).

Table 34: Summary of chemical parameters in the 2015/16 season.

Sample ID	U	AL	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	V	Zn	NO_3-	P
A	0.023	0.143	0.801	462.693	0.009	0.181	0.065	0	0.367	65.484	145.860	2.917	285.837	1.86	1.792	0.035	0.761	12.887	7.176
B	0.049	0.442	2.340	580.266	0.049	0.695	0.075	0.014	4.270	88.933	152.694	20.293	475.612	1.478	0.845	0.049	0.238	13.94	7.195
C	0.089	0.613	2.564	467.961	0.009	0.364	0.069	0.003	5.044	63.707	141.671	5.954	348.962	1.236	1.970	0.013	0.338	11.04	7.158
D	0.047	0.211	1.658	462.355	0.008	0.723	0.093	0.001	1.758	72.193	145.368	7.178	339.945	1.48	2.126	0.007	0.554	14.24	7.288
E	0.040	0.191	5.563	438.579	0	0.179	0.074	0.001	2.111	77.417	143.319	2.061	424.118	1.146	0.395	0.022	0.171	11.887	7.384
F	0.003	0.757	3.933	417.503	0.004	0.220	0.088	0.008	0.991	86.620	134.148	0.737	465.492	1.058	3.178	0.026	0.214	15.233	7.480
G	0.035	0.314	4.687	444.382	0.019	0.284	0.071	0	0.793	86.000	139.714	1.298	461.025	1.28	0.893	0.042	0.434	7.92	7.529
H	0.011	0.233	2.722	796.403	0.014	0.284	0.084	0.002	1.167	98.665	208.600	0.466	623.998	1.22	2.738	0.030	0.280	13.413	7.543
I	0.028	0.388	2.584	831.670	0.007	0.199	0.072	0.003	1.439	98.552	214.523	0.365	641.626	1.006	1.987	0.064	0.202	11.673	7.698
J	0.031	0.309	0.474	801.969	0	0.256	0.142	0.274	1.636	99.022	215.549	0.932	637.459	1.102	0.497	0.047	0.254	9.433	7.768
K	0.017	0.207	1.101	787.736	0.018	0.159	0.074	0.0004	0.565	95.077	211.439	0.661	615.473	0.964	1.756	0.047	0.108	11.747	7.938
L	0.016	0.988	1.814	822.673	0.011	0.211	0.045	0.002	1.030	100.599	219.024	1.125	628.75395	1.152	2.133	0.061	0.158	12.233	8.205
Mean	0.032	0.400	2.520	609.516	0.012	0.313	0.079	0.026	1.764	86.022	172.659	3.666	495.692	1.249	1.693	0.037	0.309	12.137	7.530
Std dev	0.023	0.261	1.550	179.894	0.013	0.194	0.023	0.078	1.449	13.397	36.666	5.684	130.515	0.252	0.870	0.018	0.189	2.049	0.325

Table 35: A Correlation Matrix for the 2015/2016 season.

	U	**AL**	**As**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**V**	**Zn**	**NO_3N**	**P**	**pH**	**temp**	**EC**	**TDS**
U	1.000																						
AL	-.043	1.000																					
As	.057	.067	1.000																				
Ca	-.374	.107	-.494	1.000																			
Cd	.152	.015	-.063	.024	1.000																		
Co	.481	-.069	-.121	-.273	.550	1.000																	
Cr	-.026	-.330	-.265	.117	-.274	.140	1.000																
Cu	-.015	-.091	-.413	.333	-.265	-.067	**.856**	1.000															
Fe	**.849**	.196	.093	-.230	.375	.544	-.006	.000	1.000														
K	-.605	.225	-.114	**.824**	.123	-.256	.178	.313	-.353	1.000													
Mg	-.412	.087	-.494	**.990**	-.094	-.350	.135	.358	-.314	**.806**	1.000												
Mn	.496	.007	-.082	-.260	**.798**	**.818**	-.064	-.113	.695	-.245	-.369	1.000											
Na	-.499	.207	-.163	**.899**	.012	-.354	.183	.344	-.283	**.967**	**.890**	-.337	1.000										
Ni	.214	-.310	-.245	-.478	.278	.414	-.164	-.182	.071	-.628	-.497	.456	-.723	1.000									
Pb	-.362	.386	-.114	.065	-.170	-.074	-.252	-.432	-.227	.029	.064	-.271	.030	-.082	1.000								
V	-.420	.242	-.247	**.707**	.277	-.345	-.158	.184	-.289	**.744**	.674	-.089	**.716**	-.287	-.180	1.000							
Zn	.182	-.395	-.238	-.511	-.062	.252	-.016	-.108	-.133	-.677	-.491	.101	-.733	**.877**	.045	-.400	1.000						
NO_3	-.252	.160	-.079	-.150	.146	.340	-.147	-.392	.049	-.125	-.185	.323	-.208	.220	.607	-.292	.031	1.000					
P	-.554	.374	-.214	**.756**	-.193	-.490	-.051	.216	-.511	**.794**	**.803**	-.531	**.822**	-.640	.083	.664	-.587	-.257	1.000				
pH	-.554	.374	-.214	**.756**	-.193	-.490	-.050	.217	-.511	**.794**	**.803**	-.531	**.822**	-.640	.083	.664	-.587	-.256	**1.000**	1.000			
Temp	.463	-.114	-.065	-.527	.524	.514	-.174	-.231	.566	-.619	-.609	.784	-.679	**.741**	-.112	-.268	.477	.379	-.817	-.816	1.000		
EC	-.315	.128	-.352	**.948**	.141	-.151	.202	.350	-.093	**.884**	**.920**	-.127	**.944**	-.629	-.009	.664	-.701	-.121	**.724**	**.725**	-.524	1.000	
TDS	-.323	.127	-.355	**.951**	.130	-.162	.203	.351	-.104	**.885**	**.925**	-.140	**.946**	-.631	-.003	.665	-.698	-.123	**.730**	**.730**	-.532	**1.000**	1.000

However, the low abundance of metals such as U, Cu and Cd particularly during the dry season, could be as a result of the atypical high pH values, which facilitate the formation of insoluble metal hydroxide compounds and consequently, the metals precipitating into the sediment (Wang et al., 2005).

The mean concentrations of macro-minerals were as follows in descending order: Ca>Na>Mg>K of which similar results were also previously obtained in a related study in Bangladesh (Bodrud-Doza et al., 2016). The strongest positive correlation was observed between pH and P (1.00) and EC and TDS (1.00). The latter confirms the direct proportionality which exists between EC and TDS hence either can be used to estimate the concentration of the other. Furthermore, strong positive correlations were observed between Ca and K (0.824); Mg (0.990); Na (0.899); V (0.707); P (0.756); pH (0.756); EC (0.948) and TDS (0.951) (Table 35). There were also very strong positive correlations between K and Mg (0.806); Na (0.967); V (0.744); P (0.803); pH (0.803); EC (0.920) and TDS (0.925). Overall, it can be concluded that Ca, Na, Mg and K in descending order, influenced salinity in the 2015/16 season. Furthermore, the strong positive correlation between these major cations suggests a similar lithological source (Bodrud-Doza et al., 2016).

2016/17 season

In the 2016/17 season, the mean concentrations of metals were as follows in descending order: As >Fe>Mn>Al>Zn>U>Pb>V>Ni>Cr>Cu>Cd>Co (Table 36) and as such As, Fe and Mn were the most abundant metals. Similar results were also obtained in the 2015/16 season although the order of abundance was not the same. In particular, the mean concentrations for As and Fe were higher in the 2016/17 season relative to the 2015/16 season; however, Mn slightly decreased in the 2016/17 season. The higher As concentrations in the 2016/17 season can be attributed to the multiple stormy events which occurred during this period which resulted in the sudden increase in solute chemistry, leading to weathering products being exposed to runoff (Sultan and Dowling, 2005). The lower Mn concentrations can be linked to the high rainfall during the 2016/17 season which ultimately diluted the Mn. The mean concentrations of macro-minerals were as follows in descending order: Ca>Na>Mg>K of which similar results have also been previously reported in a similar study in Bangladesh (Bodrud-Doza et al., 2016) as well as in the 2015/16 season. The strongest positive correlation was observed between Ni and Cr (1.00) in the 2016/17 season.

Table 36: Summary chemical parameters in the Klip 2016/17 season.

Sample ID	U	AL	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	V	Zn
A	0.067	0.870	8.535	297.01	0	0	0	0.004	4.469	39.645	99.983	4.238	154.191	0	0.048	0.016	0.645
B	0.084	1.423	10.217	371.621	0	0	0.180	0.038	15.827	70.179	135.412	14.829	334.468	0.297	0	0.043	1.983
C	0.107	0.788	10.775	297.378	0	0	0	0	8.844	58.537	114.250	8.709	274.584	0	0	0.035	0.155
D	0.086	0.525	10.207	305.428	0	0	0	0	6.651	57.978	121.685	5.199	272.216	0	0.011	0.029	0.315
E	0.061	0.204	8.315	305.511	0	0	0	0	0.962	64.477	134.292	1.670	309.382	0	0.022	0.050	0.079
F	0.074	0.194	12.390	300.318	0	0	0	0.001	1.163	72.623	126.086	1.174	368.072	0	0	0.057	0.130
G	0.073	0.264	8.431	341.564	0	0	0	0	0.948	70.592	148.494	1.187	371.461	0	0.149	0.045	0.065
H	0.048	0.322	9.607	587.784	0	0	0	0	1.037	79.154	222.465	0.831	483.464	0	0.073	0.077	0.174
I	0.074	0.329	9.493	602.043	0	0	0	0	0.645	79.545	228.981	0.699	483.871	0	0.038	0.072	0.142
J	0.051	0.450	11.1463	635.704	0	0	0	0.006	0.809	85.863	240.003	1.060	513.516	0	0.166	0.055	0.352
K	0.052	0.382	8.858	585.283	0	0	0	0	0.642	78.238	221.458	1.073	470.213	0	0.155	0.059	0.255
L	0.057	0.274	9.9401	536.655	0	0	0	0.008	0.884	82.574	227.766	1.372	489.907	0	0.154	0.079	0.385
Mean	0.070	0.502	9.826	430.525	0	0	0.015	0.005	3.573	69.950	168.406	3.503	377.112	0.025	0.068	0.051	0.39
Std dev	0.0173	0.362	1.226	143.537	0	0	0.0520	0.011	4.731	13.100	54.183	4.310	112.990	0.086	0.0686	0.019	0.527

Table 37 : Correlation Matrix 2016/2017 season.

	U	AL	As	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	V	Zn	NO3N	P	pH	temp	EC	
U	1.000																				
AL	.478	1.000																			
As	.277	.057	1.000																		
Ca	-.654	-.275	-.002	1.000																	
Cr	.264	**.802**	.100	-.129	1.000																
Cu	.161	**.792**	.137	-.045	**.967**	1.000															
Fe	.671	**.925**	.183	-.437	**.816**	**.761**	1.000														
K	-.497	-.419	.268	**.789**	.005	.055	-.394	1.000													
Mg	-.676	-.409	-.007	**.979**	-.192	-.100	-.525	**.860**	1.000												
Mn	.661	**.928**	.163	-.432	**.827**	**.778**	**.995**	-.378	-.515	1.000											
Na	-.581	-.468	.174	**.889**	-.119	-.059	-.494	**.976**	**.943**	-.482	1.000										
Ni	.264	**.802**	.100	-.129	**1.000**	**.967**	**.816**	.005	-.192	**.827**	-.119	1.000									
Pb	-.668	-.390	-.261	.634	-.312	-.175	-.559	.536	.685	-.537	.611	-.312	1.000								
V	-.548	-.539	.122	.744	-.138	-.094	-.514	**.882**	**.828**	-.495	**.902**	-.138	.395	1.000							
Zn	.193	**.879**	.072	-.110	**.951**	**.971**	**.814**	-.120	-.199	**.820**	-.206	**.951**	-.244	-.248	1.000						
NO_3^-	-.627	-.314	-.297	.410	-.066	.085	-.435	.393	.485	-.404	.406	-.066	.449	.443	-.028	1.000					
P	.144	-.048	.389	-.039	.323	.294	.081	.463	.041	.095	.321	.323	.149	.263	.140	-.055	1.000				
pH	-.716	-.794	-.181	.608	-.549	-.473	-.877	.645	.706	-.869	.716	-.549	**.804**	.645	-.570	.492	.237	1.000			
temp	-.171	.073	.051	-.262	.395	.301	.113	-.047	-.269	.124	-.147	.395	-.417	.012	.310	-.020	.091	-.201	1.000		
EC	-.547	-.271	.115	**.950**	-.013	.045	-.334	**.895**	**.960**	-.326	**.949**	-.013	.561	**.840**	-.056	.311	.130	.559	-.186	1.000	
TDS	-.565	-.303	.091	**.967**	-.063	-.008	-.380	**.881**	**.972**	-.375	**.948**	-.063	.552	**.841**	-.102	.330	.088	.579	-.199	**.995**	1.000

Similar results were also previously reported in the Gomti river basin whereby in the rainy season there was a strong correlation (0.97) between Ni and Cr (Gaur et al., 2005) (Table 37). Strong positive correlations were observed between Al and Cr (0.802); Cu (0.792); Fe (0.925); Mn (0.928); Ni (0.802) and Zn (0.879) suggesting a common source of these metals i.e. industrial activities. Calcium also had strong positive correlations with K (0.789); Mg (0.979); Na (0.889); EC (0 .950) and TDS (0.967): Cr had strong correlations with Cu (0.967); Fe (0.816); Mn (0.827) and TDS (0. 951) and K had strong positive correlations with Mg (0 .860); Na (0.976); V (0.882); EC (0.895) and TDS (0.881). Consequently, a similar deduction to that of the 2015/16 season is that Mg, Ca, Na, and K in descending order, influenced salinity in the 2016/17 season. The strong positive correlation between these major cations suggests a similar lithological source (Bodrud-Doza et al., 2016).

Discriminant Analysis

Discriminant analysis was conducted on the 2015/16 and 2016/17 seasonal clusters to determine the variables that could discriminate between the seasons. The tests of equality of group means which determines the existence of statistically significant differences between the mean concentrations of predictor variables between clusters, revealed that there were statistically significant differences in mean concentrations between the identified seasons for: Al, As, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Na, Ni, Pb ,U, NO_3-N, T°C, TDS and EC. However, there were no statistically significant differences in the mean concentrations of Cu, V, Zn, P and pH between the identified seasonal clusters.

The DA (Wilk's lambda value = 0.082, $p<0.001$) resulted in one discriminant function whereby the discriminant function coefficients identified the predictor variables which were highly correlated with the discriminant function, of which in this case, these included Cr, TDS, Ni, and P. Furthermore from the structure matrix, the predictor variables which were largely responsible for discriminating seasonal differences in water quality characteristics included in decreasing order of importance, TDS, Ni, P and Cr (Table 38). This model was validated as being a good model based on the Wilk's lambda value.

Table 38: Standardized Canonical Discriminant Function Coefficients.

	Function
	1
Al	.150
As	-.330
Ca	-.154
Cd	.091
Co	-.273
Cu	-.069
Cr	**1.748**
Fe	-.063
K	.008
Mg	-.143
Mn	-.113
Na	.157
Ni	**.716**
Pb	.136
V	-.014
Zn	-1.090
U	-.183
Nitrates	-.395
P	**.458**
pH	-.248
Temp	-.288
TDS	**.812**
EC	-.146

Figures 43-46 depict the mean concentrations of the discriminant variables in the 2015/16 and 2016/17 seasons. Overall, the concentrations of all the discriminant variables were higher in the 2015/16 relative to the 2016/17 season. TDS concentrations in the Klip River were high during the 2015/16 season, which was a drought year with little or no rainfall experienced, however in 2016/17 season which was characterized by high rainfall and flooding, the TDS concentration decreased. Similar findings were also previously reported in other catchments (Islam et al., 2015; Ondieki and Kitheki, 2017), whereby the lowering of TDS concentrations was attributed to the dilution effect of rainfall. The trend was the same for the metals Ni and Cr which were higher in the 2015/16 relative to the 2016/17 season. Similar results were reported, where high metal concentrations were observed in hot dry summers relative to the wet winters (Reza and Singh, 2010). The high metal concentrations in summer were attributed to the low flow condition of rivers as a result of high evaporation rates coupled with high temperatures; therefore metal concentrations become elevated (Abdel-Satar and Elewa, 2001). For P concentration, Conkright et al. (2000) reported higher concentrations in summer than in winter in the Southern Hemisphere which somewhat correspondingly alludes to findings in this study.

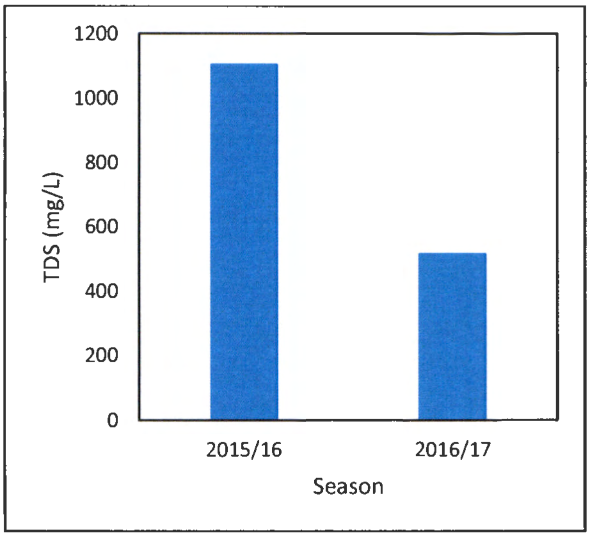

Figure 42: Seasonal TDS concentrations.

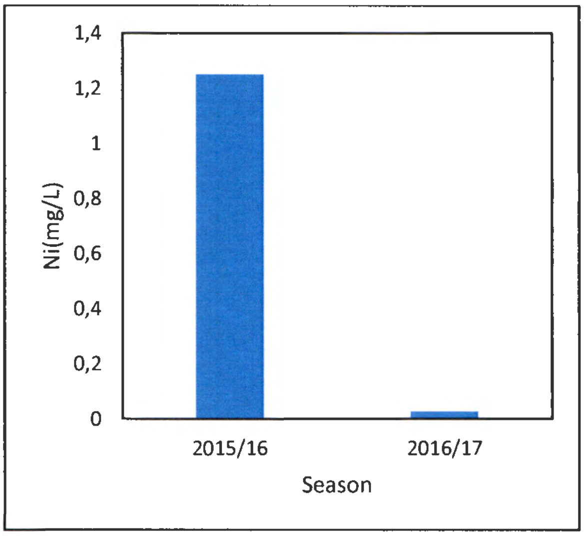

Figure 43: Seasonal P concentration.

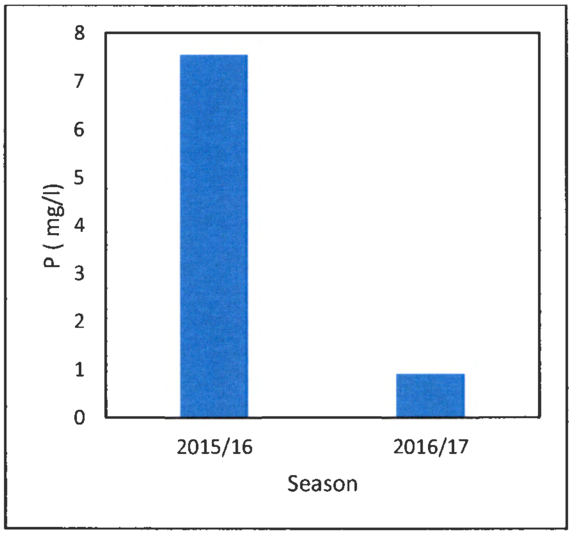

Figure 44: Seasonal Ni concentrations.

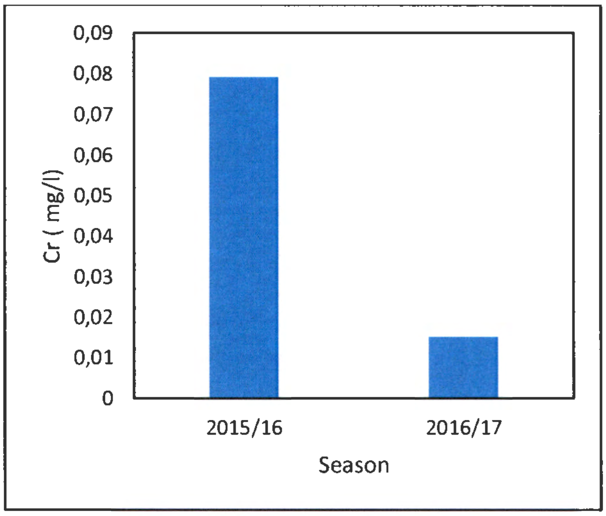

Figure 45: Seasonal Cr concentrations.

3.4.3 Sources of Pollution of the Klip River catchment

In the 2015/16 season, 6 principal components (PC) were initially extracted and the resultant is the scree plot in Figure 47.

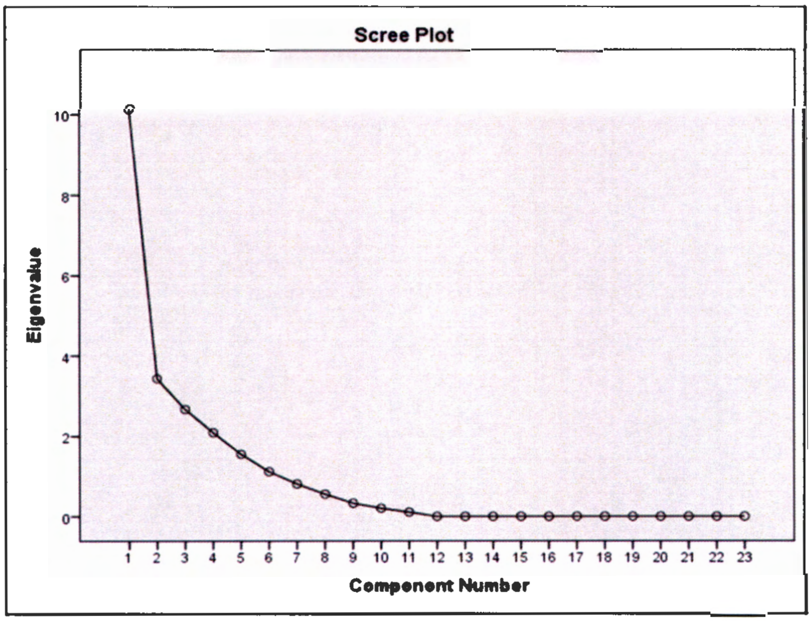

Figure 46: Scree plot for the 2015/16 season

These components explained 91% of the variance as is indicated in the Appendix, Table 50. However, after conducting a Monte Carlo PCA Parallel Analysis (Appendix Table 51), only 3 components were retained (Table 39), which cumulatively explained 71% of the variance. The communalities (Appendix Table 52) were >0.50 for almost all the variables with the exception of Al, As, Pb and NO_3^-, suggesting that this model could explain the variability of a majority of the variables. The classification for loading values shown in Tables 39 and 40 is as follows: strong>0.75, moderate 0.50–0.74 and weak 0.30–0.49 (adopted from Liu et al., 2003; Li and Zhang, 2010; Yao et al., 2014).

Principle component 1 explained 44% of the variance and had strong positive loadings for TDS, EC, Na, Mg, Ca, K, pH and P and a weak loading for Al. Principle component 1 was indicative of the influence of major cations and as such reflected the process of bedrock weathering owing to high loadings for Na, Mg, Ca, K (Mirza et al., 2017). Calcium and Mg reflect silicate weathering and carbonate dissolution depending on the lithological characteristics of the catchment (Mirza et al., 2017). In the KRC, the underlying geology is predominanlty dolomite comprising of Ca, Mg and carbonate, ideally $CaMg(CO_3)_2$ (Azimi et al., 2016). Sodium and K also substantiate the source as being bedrock weathering (Taiwo et al., 2011; Taiwo, 2012). Furthermore, EC, which is indicative of high ion concentrations, had high loadings during the dry season which can be attributed to the mineralization process and also dissolution of soluble inorganic salts constituting the riverbed in the KRC (Wang et al., 2013).

Table 39: Rotated Component Matrix 2015/2016 season .

	Component		
	1	**2**	**3**
EC	**.967**	.017	.150
TDS	**.967**	.004	.150
Na	**.952**	-.221	.090
K	**.925**	-.174	.024
Ca	**.916**	-.106	.144
Mg	**.886**	-.224	.174
pH	**.810**	-.478	-.054
P	**.810**	-.479	-.054
V	**.768**	-.030	-.014
Zn	-.740	.031	.132
Ni	-.634	.367	.004
Mn	-.118	**.971**	-.052
Cd	.199	**.797**	-.226
Co	-.193	**.789**	.033
Fe	-.136	**.777**	.072
temp	-.526	**.735**	-.113
U	-.389	**.569**	.263
Cu	.274	-.066	**.845**
Cr	.061	-.047	**.794**
Pb	.023	-.245	-.660
NO_3-	-.109	.246	-.582
AL	.315	.023	-.515
As	-.294	-.162	-.313

Principle component 2 explained 14% of the variance and had strong positive loadings for Mn , Cd, Co and Fe; moderate loadings for temperature and U and a weak loading for Ni. This component reflected influences from industrial activities (Ahamed and Loganathan, 2017). Manganese, Cd, Co could be attributed to industrial activities (Hanh, et al., 2010; Sakan et al., 2011) while Fe also was attributed to the mixing of industrial wastewater. Also, Ni presence, could be associated with industrial effluents as well as metallurgical operations, burning of fossil fuels, and atmospheric deposition (Qadir et al., 2008). However the loading for Ni was weak in this PC suggesting an alternative source. Nickel could also attributed to soil leaching (Simeonov et al., 2003).

Principle component 3 explained11% of the variance and had strong positive loadings for Cu and Cr. Cu and Cr are usually associated with industrial activities ,but in this case ,these two metals were in their own PC suggesting an alternative source. Zeng et al. (2015) attributed Cu and Cr to natural processes such as erosion, mineral exploitation activities and non-point agricultural sources. There has been a reported increase in the use of pesticides containing heavy metals such as Cu and Cr (Zeng et al., 2015).

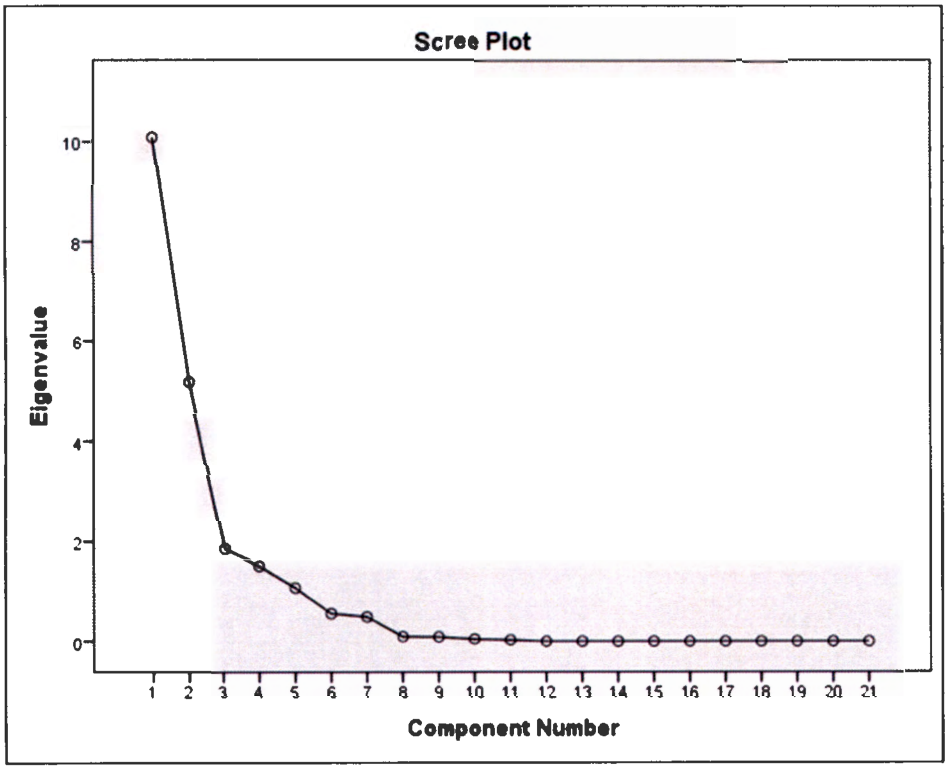

Figure 47: Scree plot for the 2016/2017 season.

In the 2016/2017 season, 5 principal components were extracted and the resultant is the scree plot in Figure 48. These components explained 93.763 % of the variance as indicated in the Appendix Table 54. However after conducting a Monte Carlo PCA Parallel Analysis only 4 components were retained (Table 40), which cumulatively explained 88.658% of the variance (Appendix Table 54).

Principle component 1 explained 48.035% of the variance, and had strong positive loadings for EC. Total dissolved solids ,Na , Mg,Ca,K, Pb, pH and V and weak loadings for NO3- (Table 40). In this case PC 1 for the 2015/16 season was similar to the PC1 for the 2016/17 season, which indicated the influence of natural processes such as mineralization and bedrock weathering (Taiwo et al., 2011; 2012; Wang et al., 2013; Mirza et al., 2017). The weak loading for NO3- showed that there was an alternative source, to PC1As NO3- can emanate from both point and non point sources such as sewage discharges and agricultural runoff respectively.

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Table 40: Rotated Component Matrix 2016/2017 season.

	Component			
	1	2	3	4
EC	**.975**	.012	.042	-.102
Na	**.972**	-.159	.132	.084
TDS	**.970**	-.033	.013	-.116
Mg	**.970**	-.154	-.132	-.096
Ca	**.942**	-.061	-.162	-.177
K	**.931**	-.074	.247	.204
V	**.851**	-.211	.128	.239
Pb	**.657**	-.274	-.352	-.075
pH	**.651**	-.623	-.176	.213
U	-.610	.279	**.543**	-.349
Zn	-.043	**.973**	-.057	.127
Ni	-.005	**.959**	.104	.243
Cr	-.005	**.959**	.104	.243
Cu	.083	**.957**	.026	.216
Al	-.303	**.904**	-.010	-.237
Mn	-.373	**.877**	.215	-.162
Fe	-.386	**.867**	.230	-.183
As	.101	.068	**.820**	.013
P	.238	.125	**.615**	**.431**
NO_3	**.452**	-.080	-.554	**.352**
Temp	-.199	.218	.013	**.809**

Principle component 2 explained 24.668% of the variance and it had positive loadings for Zn, Ni, Cr, Cu, Al, Mn and Fe. This component reflects influences from industrial activities, domestic sewage effluent discharges and traffic (Yao et al., 2014; Roshinebegam et al., 2014). In particular, Zn and Cu were attributed to traffic (Yang et al., 2013) owing to the high Zn and Cu concentrations in brake linings. Davis et al. (2001) alluded, but attributed Cu concentrations to emissions from vehicles. Ni presence was associated with industrial effluents as well as metallurgical operations, burning of fossil fuels, and atmospheric depositions (Qadir et al., 2008).

Principle component 3 explained 8.808% of the variance and it had strong positive loadings for As and moderate positive loadings for P and U. As and U are atypical of areas where there are gold mining activities and tailings dumps, of which in the KRC such activities are dominant particularly in the upper part of the catchment. Phosphates were attributed to the use of phosphate-based fertilizers.

Principle component 4 explained 7.147% of the variance and it had positive loadings for Temperature, P and NO_3 only. This component reflected influences from anthropogenic activities and non-point sources. NO_3 is an indicator of anthropogenic pollution with its sources being sewage effluents which are a PS and agricultural discharges which are NPS (Kura et al., 2013; Ishaku et al., 2011). The strong loading for temperature was attributed to the seasonal effects (Singh et al., 2005; Zhou et al., 2007). Phosphates are also from phosphate-based fertilizers and sewage effluents.

3.5 Comprehensive Pollution Index

Domestic Use

The CPI, in terms of SAWQG for domestic uses indicates that the upstream water quality zone is critically polluted relative to the downstream section (Table 41). For both zones, the CPI values were higher in the 2016/17 season relative to the 2015/16 season in both the upstream and downstream sections. In the 2015/16 season, As, Pb and Mn (in decreasing order) recorded the highest single factor indices in the upstream, while the lowest was for V, Zn and Cu. However in the downstream section, Pb, As and Ca recorded the highest single factor indices in the 2015/16 season and similar to the upstream section, the lowest single factor indices were for V, Zn and Cu. In the 2016/17 season As, Mn and Fe recorded the highest single factor indices in the upstream while the lowest were recorded for V, Ni and Cd. In the downstream, As, Pb and Al recorded the highest single factor indices in the 2016/17 season, while the lowest values were recorded for Cd, Cr and Ni. Higher single factor indices were recorded for U, Al, As, Cd, Cr, Fe, K, Mn, Ni, Pb, Zn and U in the upstream, and as such, it can be concluded that there are risks associated with domestic use of the Klip River water. However, these elements decreased towards the downstream in the 2015/16 season. Incidentally the 2016/17 season depicted a similar trend, for all parameters with the exception of Pb, which was higher in the downstream section.

Table 41: Comprehensive pollution index for domestic uses in the KRC.

	Cluster 1(Upstream)		*Cluster 2 (Downstream)*	
	2015/16	**2016/17**	**2015/16**	**2016/17**
U	9.560	18.369	3.443	9.413
Al	178.018	284.571	141.646	117.095
As	2154.446	6887.003	869.414	4904.311
Ca	102.304	69.338	126.264	92.108
Cd	19.591	0	9.914	0
Cr	10.663	3.608	8.352	0
Cu	0.027	0.0426	0.281	0.015
Fe	153.341	388.630	58.381	40.179
K	10.807	8.681	9.838	8.108
Mg	33.426	29.340	35.638	38.022
Mn	808.794	740.157	70.983	100.673
Na	28.010	20.844	31.473	24.410
Ni	476.9	14.857	272.2	0
NO_3	63.908	42.9	23.225	22.010
Pb	1119.897	22.878	911.055	58.649
V	1.934	2.747	2.495	3.423
Zn	0.903	1.124	0.334	0.436
CPI	323.283	162.1632	532.2135	338.6782

Aquatic ecosystem protection

The CPI for aquatic ecosystem protection in the KRC was very high relative to that computed for domestic uses (Table 42). The CPI was higher in the upstream relative to the downstream section and in the 2015/16 relative to the 2016/17 season. In the 2015/16, season Pb, As and Al (in decreasing order) recorded the highest single factor indices in the upstream, while the lowest was for V, U and Fe. Similarly, Pb, As and Al (in decreasing order) recorded the highest single factor indices downstream of the Klip River in the 2015/16 season.

Table 42: Comprehensive Pollution Index for aquatic uses in the KRC.

	Cluster 1 (Upstream)		*Cluster 2 (Downstream)*	
	2015/16	**2016/17**	**2015/16**	**2016/17**
U	9.560	18.369	3.443	9.413
Al	534.052	853.714	424.937	351.284
As	2154.446	6887.003	869.414	4904.311
Ca	21.825	14.792	26.936	19.650
Cd	24.489	0	12.393	0
Cr	33.321	11.276	26.101	0
Cu	19.270	30.441	200.523	10.416
Fe	15.334	38.863	5.838	4.018
Mn	224.665	205.599	19.718	27.965
Ni	20.294	0.632	11.583	0
NO_3	27.989	18.788	10.171	9.640
P	17.429	11.7	6.334	6.002
Pb	9332.472	190.652	7592.121	488.744
V	2.41770	3.434	3.119	4.278
Zn	135.519	168.606	50.128	65.365
CPI	837.094	617.697	562.324	393.060

The lowest single factor indices were recorded for Fe, U and Zn. In the 2016/17 season; As, Al and Mn recorded the highest single factor indices in the upstreamwhile the lowest were recorded for V, Ni and Cd. In the downstream; As, Pb and Al recorded the highest single factor indices in the 2016/17 season, whilst the lowest values were recorded for Cd, Cr and Ni. As such, it can be concluded that in terms of aquatic ecosystem protection, water in the KRC particularly the upstream was critically polluted relative to the downstream, and particularly in the hot dry season (2015/16) relative to wet season (2016/17). Higher single factor indices in the upstream were recorded for U, Al, As, Cd, Cr, Fe, K, Mn, Ni, Pb, Zn and U.Consequently, it can be concluded there is a high risk for aquatic life in the upstream section of the Klip River especially in the dry season.

Agriculture

The CPI for agricultural uses in the KRC was very low relative to that computed for domestic uses and aquatic ecosystem protection (Table 43). The CPI for agricultural uses was higher in the downstream section relative to the upstream, and in the 2015/16 season relative to the 2016/17. During the 2015/16 season, Mn, As and Pb (in decreasing order) recorded the highest single factor indices in the upstream, while the lowest was for V, Al and Zn.

Table 43: Comprehensive Pollution Index for agricultural uses in the KRC.

	Cluster 1 (Upstream)		*Cluster 2 (Downstream)*	
	2015/16	**2016/17**	**2015/16**	**2016/17**
U	28.679	10.329	55.107	28.240
Al	0.534	0.425	0.854	0.351
As	215.445	86.941	688.700	490.431
Cd	9.796	4.957	0	0
Co	52.913	22.165	0	0
Cr	10.662	8.352	11.276	0
Cu	0.135	1.404	0.213	0.073
Fe	3.067	1.168	7.773	0.804
Mn	2021.986	177.459	1850.394	251.683
Na	40.014	44.962	29.777	34.871
Ni	47.69	27.22	1.486	0
Pb	55.995	45.553	1.144	2.932
V	1.934	2.495	2.747	3.423
Zn	2.710	1.003	3.372	1.307
CPI	177.969	31.031	189.489	58.151

The highest single factor indices for agricultural uses in the KRC, were recorded for Mn, As and U (in decreasing order) downstream of the Klip River in the 2015/16 season. The lowest single factor indices were recorded for Cu, Cd and Co. In the 2016/17 season; Mn, As, and Pb recorded the highest single factor indices in the upstream while the lowest were recorded for Fe, Zn and Al. In the downstream, As, Mn and U recorded the highest single factor indices in the 2016/17 season, while the lowest values were recorded for Cd, Co, Cr and Ni. In the 2015/16; U, Al, As, Cr, Cu, Fe and V, had higher single factor indices in the downstream thereby rendering this section of the river critically polluted for agricultural uses. However, in the 2016/17 season, a majority of the parameters recorded higher single factor indices in the upstream; Al, Cr, Cu, Fe, Na, Ni and Pb. Therefore, it can be concluded that in terms of agricultural uses, the water quality in the downstream section of the KRC was critically polluted relative to the upstream and particularly in the hot dry season (2015/16) relative to the 2016/17 (wet season).

3.5 Chapter Summary

In this chapter, water quality characteristics were grouped spatially and temporally using CA. The spatial grouping yielded two homogenous water quality zones, i.e. the upstream zone, which comprised of sampling points A, B, C, D, E, F, G and H; and the downstream zone comprising of the remaining sampling points. This spatial grouping could be explained by the anthropogenic activities which are distinct between the two zones, with the upstream zone predominantly associated with mining, industrial and domestic wastewater discharge while the downstream is characterized by agricultural activities and residential areas. Based on DA, this spatial grouping was validated at 100% and the parameters responsible for discriminating between the homogenous water quality zones included As, Ca, Cd and Mg. Arsenic and Cd were higher in the upstream relative to the downstream zone however the opposite was true for Ca and Mg.

Temporal CA yielded two clusters, the 2015/16 season comprising of months starting from February to June and the 2016/17 season comprising of the months from July to January 2017. Discriminant Analysis validated this seasonal classification at 98.1%. The discriminant parameters included TDS, P, Ni and Cr which were all higher in the 2015/16 season relative to the 2016/17 season due to the high evaporation rates and low flow conditions of the river. The sources of pollution in the 2015/16 season were mainly lithological, traffic, point discharges from industries and sewage effluents; and agricultural NPS from pesticide applications. In the 2016/17 season, the sources of pollution were lithological processes, industrial, mining and agricultural NPS from the use of phosphate and ammonia based fertilizers.

The CPI revealed that the KRC was critically polluted in the upstream with regards to domestic and aquatic uses in both the 2015/16 and 2016/17 seasons. Furthermore, in the upstream the parameters which recorded the higher single factor indices relative to the downstream were heavy metals with the exception of V, Pb and Cu which were higher in the downstream. The heavy metals in the upstream can be attributed to mining and industrial activities; and the concentration of WWTPs whereas in the downstream, the heavy metals are associated with agricultural activities such as pesticide application. Furthermore, the major cations such as Ca, Mg and Na were also higher in the downstream suggesting an influence of natural processes such as bedrock weathering which aligns with findings from the PCA. Water quality in the downstream section of the KRC recorded high CPI values for agricultural uses, rendering it unsuitable for such related activities. In the next chapter and to enable the design of efficient water quality management mechanisms, an understanding of the capability of the river to naturally recover from its heavily polluted state is investigated.

CHAPTER 4

ASSESSMENT OF THE SELF-PURIFICATION CAPACITY OF TRACE METALS IN THE KLIP RIVER (GAUTENG), SOUTH AFRICA

4.1 Abstract

In the previous chapters, more insight has been presented with regards the individual water pollution characteristics in the Klip River, their spatial and temporal trends and factors influencing them. In this chapter the Klip River's natural ability to restore its background water quality concentrations is evaluated. Furthermore an analysis of the spatial and temporal variability of this self-purification processes in the Klip River is also conducted. An understanding of the self-purification capacity process of a river is very crucial as it will contribute towards the development of river restoration programs which are effective.

4.2 Introduction

Rivers have a capability (although limited) to recycle, organic and inorganic waste through various processes (Groot et al., 2002). This capability is termed self–purification. Benoit (1971) defined self-purification as "the partial or complete restoration by natural processes of a stream's pristine condition following the introduction of foreign matter sufficient in quantity and quality to cause a measurable change in physical, chemical and biological characteristics of the stream". Thus, self-purification is an important process in that it is pivotal in the maintenance of aquatic ecosystems (Oustroumov, 2005; Vagnetti et al., 2003; Wei et al., 2009; Demars and Manson, 2013) and can thus be used as an indicator of river health (Tian et al., 2011). Furthermore and in light of the increasing anthropogenic inputs to rivers, which are associated with economic development, urbanization, and changing land uses, it is important to understand the process of self-purification and the role it can play in the process of river restoration. River restoration involves implementation of structural measures and exclusion of anthropogenic activities that contribute to water quality degradation, to return ecosystems to their original pristine condition (Bradshaw, 1996; Roni, 2005).

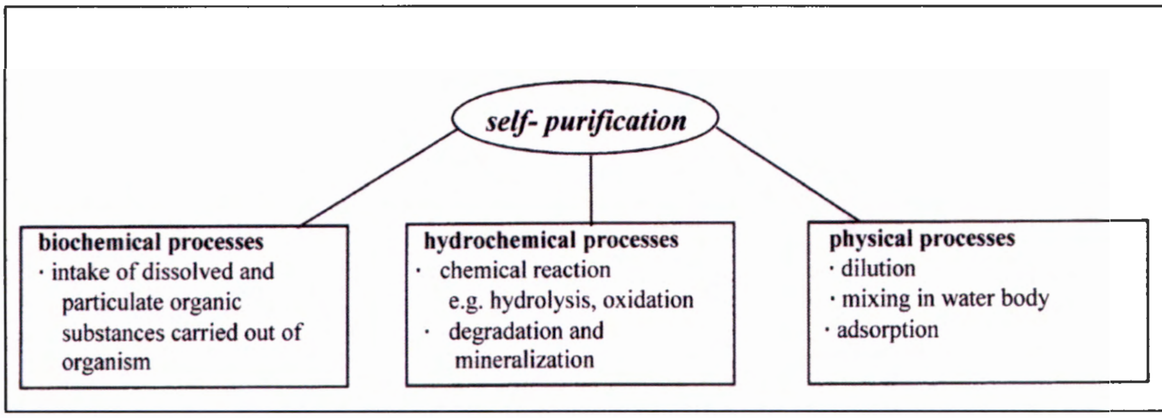

Figure 48: Various processes governing self-purification in rivers.

(Source: Heidenwag et al., 2001).

The process of self-purification however is very complex because it involves an interaction of a myriad of chemical, physical and biological processes as is shown in Figure 49 (Gonzalez et al., 2014). The physical processes which result in the removal of pollutants include dilution and mixing, adsorption by sediments, diffusion, and precipitation of the pollutants (Ifabiyi, 2008; Hanelore, 2013; Thu et al., 2015). Other physical processes identified include the volatilization of pollutants from water into the atmosphere (Keqiang et al., 2012). The biochemical processes of self-purification lead to degradation by bacteria, and decomposition of organic wastes by organisms in the water. The biological processes include oxidation, reduction, hydrolysis, neutralization and the nitrification and denitrification of ammonia and nitrate, respectively (Hily, 1991; Beyers and Odum, 1993; Mandi et al., 1996; Stimson et al., 1996; Drinan and Spellman, 2001). Koichi and Hong (2002) suggested that biological processes play the most important role among the mechanisms of self -purification in natural water bodies relative to the other process. As such the biological removal of pollutants is termed "true self-purification" whereas the total purification by physical, chemical and biological processes is called "apparent self-purification".

The extent of self-purification in any stream depends on certain factors; some of which are: river characteristics such as flow discharge, flow rate, level of river sediment-load and aquatic organisms, distribution and types of aquatic weeds along the channel, amount of inorganic compound in the stream and temperature (Tian et al., 2011). In the assessment of self-purification of rivers, various methods have been employed in different parts of the world.

Throughout literature, there has been more focus on the biological self-purification processes of organic pollutants (Mandi et al., 1996; Stimson et al., 1996; Oustromov, 1999; Drinan and Spellman, 2001) rather than the inorganic pollutants particularly trace metals. Fisenko (2013) studied the natural purification of inorganic pollutants in the Niagra river and in this study, it was observed that rivers self-purify inorganic pollutants by way of frothing.Consequently, nutrients and trace metals are collected at the surface of the water (Fisenko, 2013; 2006). However the spatial dynamic was not investigated in this study. Therefore ,Fisenko (2013), recommended that a follow up study should include samples collected upstream and downstream of the Niagra falls to incorporate spatial analysis of self-purification.

An evaluation of the self-purification capacity of a river is important in that it enables the development of sound strategies for river recovery programmes (Brierley and Fryirs, 2008). Wohl et al. (2005) suggested the use of a river reach-scale approach, in geomorphic river rehabilitation, to improve the health of aquatic ecosystems and as such it is only logical to use river segments in the study of self-purification of rivers. Therefore, the main objective of this chapter was to evaluate, using River Recovery Capacity and the Capacity of the Self-Purification per Unit Length, the natural ability of the Klip River to purify trace metals.

4.3 Methodology

To evaluate the self-purification capacity of the KRC two indices were used i.e. capacity of the self-purification per unit length and river recovery capacity. The capacity of self-purification per unit length (CSUL) was developed to determine the changes in contaminant concentrations with distance (Tian et al., 2011). It can be defined as the change in pollutant concentration in the river per unit length (Tian et al., 2011). The CSUL also enables the identification of not only the stretches of river where self-purification is high, but also the spatial points of influx of pollution. The CSULwhich was calculated for individual water quality characteristics was computed using the Equation 14 stated below;

Capacity of the self-purification per unit length (P) $P_X = \frac{S_0 - S_i}{D}$ 19

Where P_X is the CSUL for parameter x, and S_0 is the concentration at the downstream point, S_i is concentration at the upstream point and D is the length along the river between the two points. The CSUL is expressed as mg/ (L•km). Negative P values revealed the active removal of a particular pollutant, however positive P values were an indication of addition of pollutants. The distance along the river was measured using google earth maps based on the sampling points described in Section 2.5.1 of this thesis (Table 44).

Table 44: Length of river segments in the KRC.

River Segment	***Distance (km)***
AB	4.57
BC	5.84
CD	3.85
DE	12
EF	6.12
FG	13
GH	10.94
HI	7.44
IJ	8.13
JK	14.5
KL	11.03

River recovery capacity (RRC) determines the proportion of river restoration based on its downstream conditions relative to the initial and unpolluted state. Negative RRC values revealed the percentage recovery of a particular pollutant, however positive RRC values were an indication of the percentage by which a particular pollutant has increased relative to the initial and unpolluted state of the river. RRC computation is expressed using Equation 20.

River recovery capacity (RRC) $$RRC = \frac{S_0 - S_i}{S_0} \times 100\% \qquad 20$$

Where S_0 is the concentration at the downstream point, S_i is the concentration at the upstream point and the RRC is expressed as percentage.

The rationale for using both the CSUL and the RRC was that the former only represents the change in concentration in a river segment, but is limited in terms of the holistic recovery of the river in relation to a particular pollutant, which the latter does. RRC however does not reveal the spatial points of influx which can be generated using the CSUL.

4.4 Results and Discussion

Self-purification for Aluminum

The Klip River rate of self-purification for Al was at its maximum along the river segment AB where the highest negative CSUL was recorded in September (-0.824 mg/ (L•km)) indicating the active removal of Al. Other segments such as BC, CD and DE also recorded significant CSUL in various months (Figure 50). The highest positive CSUL was recorded along the river segment AB in July whereby the river was gaining Al at 0.563 mg/ (L•km) followed by the segment EF in February (0.5 mg/ (L•km). Aluminum is used in WWTPs for the process of flocculation and coagulation (Wang et al., 2013; Saritha et al., 2017). This process is driven by high temperatures atypical of September, whereby the highest removal of Al was recorded, suggesting that Al was absent in the water column.

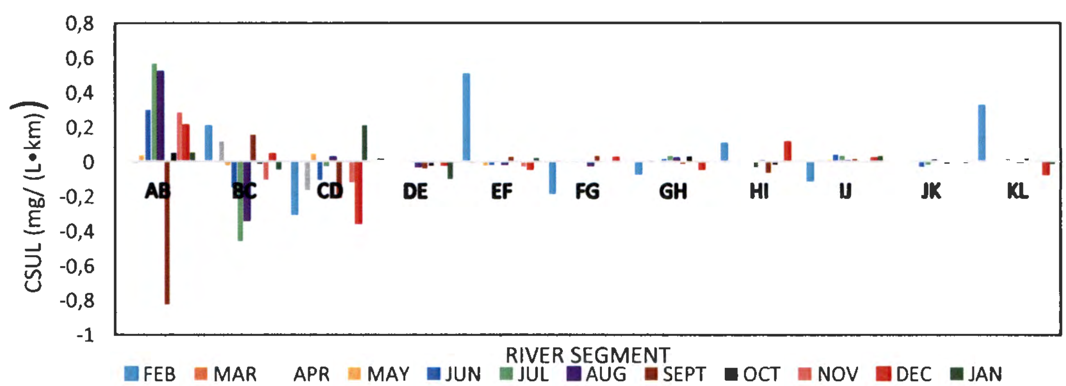

Figure 49: The CSUL of aluminium in the Klip River.

It should also be noted that along the segment AB, the river was gaining more Al relative to other segments of the river in the months between June and December. This suggests that the source of Al, is influenced by temporal factors. The low CSUL could thus be attributed to the Al residuals in WWTPs discharges in river segment AB and the temporal variability coincides with the lowering of nutrients concentrations in the upstream sampling points during the June and December period which Al removes through coagulation.

Overall, the RRC of the Klip for Al was at its highest recovery in September (-887.571%) (Figure 51). This also aligns with the CSUL which was at the maximum in September. High negative RRCs were also recorded in the months of July (-53.89%), December (-186.382%) and January (-198.158%), which generally shows the removal of Al beyond the initial concentrations. However, the lowest RRC was recorded in February (100%). From the months of February to June, August, October and November the Klip River displayed low RRC suggesting some temporal influence on the process of river recovery.

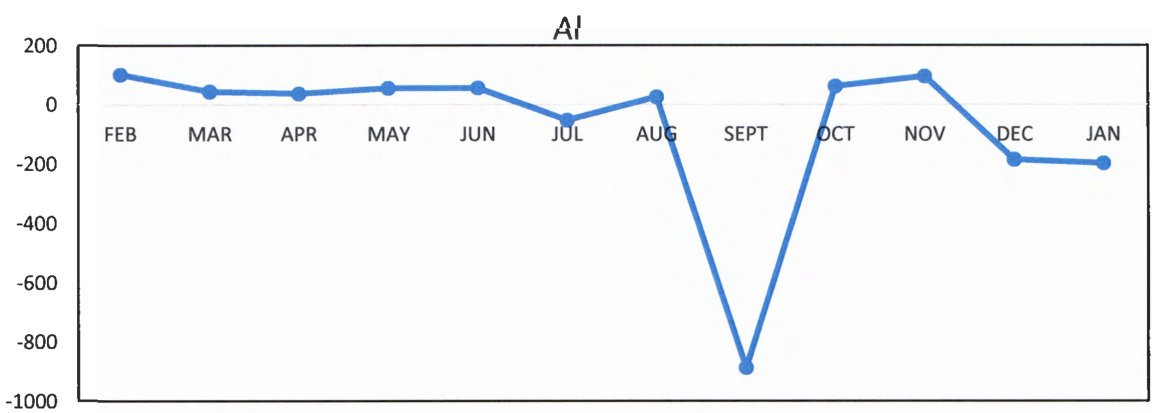

Figure 50: The RRC of aluminium in the KRC.

Self-purification for Arsenic

The maximum rate of self-purification of As in the KRC was along the segment CD where the highest negative CSUL (-1.606 mg/ (L•km) was recorded in May. The lowest CSUL was recorded along segment AB where the river was gaining As at 1.391 mg/ (L•km) in July (Figure 52).

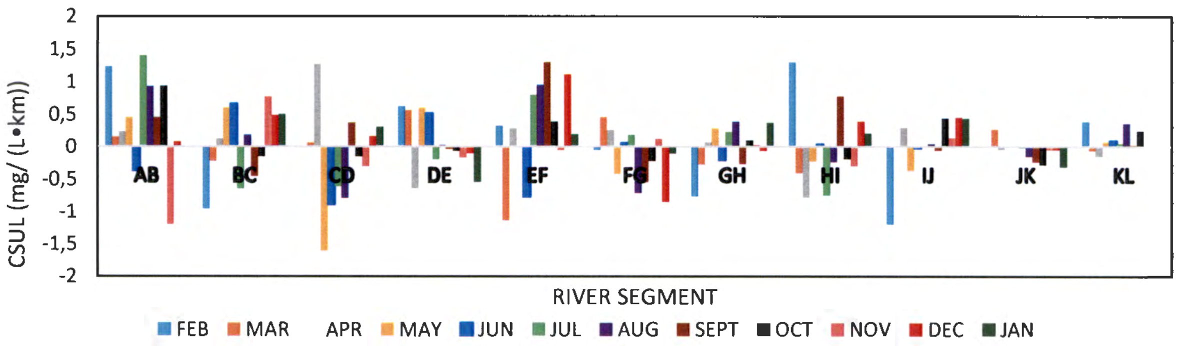

Figure 51 : The CSUL of arsenic in the Klip River.

Although the Klip River depicted high CSULs in all segments in various months, it largely displayed significant gains in As owing to the frequency of low (positive) CSULs in the various months and at all the segments except for JK. As inputs to rivers emanate from a variety of sources including mining activities, industries and agricultural chemicals (Illeperuma, 2010; Jayasumana et al., 2011). These activities are found along the profile of the KRC, and as such in many months there are inputs of As making it difficult for the river to recover.

Overall the RRC of the Klip River for As was at its highest recovery in June (-75.173%) (Figure 53). High RRCs were also recorded in the months of April and September (0%) and November (-47.528%). These findings are similar to the study by Ogbuagu and Samuel (2014) which recorded RRC of 0% for As in sand mine ponds of the Otamiri River. In their study As removal was attributed to adsorption to sand (Ogbuagu and Samuel, 2014). In this study high RRC can be attributed to by-products of industrial activities such as chars and coals, which act as adsorbents for heavy metals such as As (Brown et al., 2000; Sneddon et al., 2005 and Mohan and Chander, 2006). However the lowest RRC was recorded in February (100%) followed by March which recorded 81.128%.

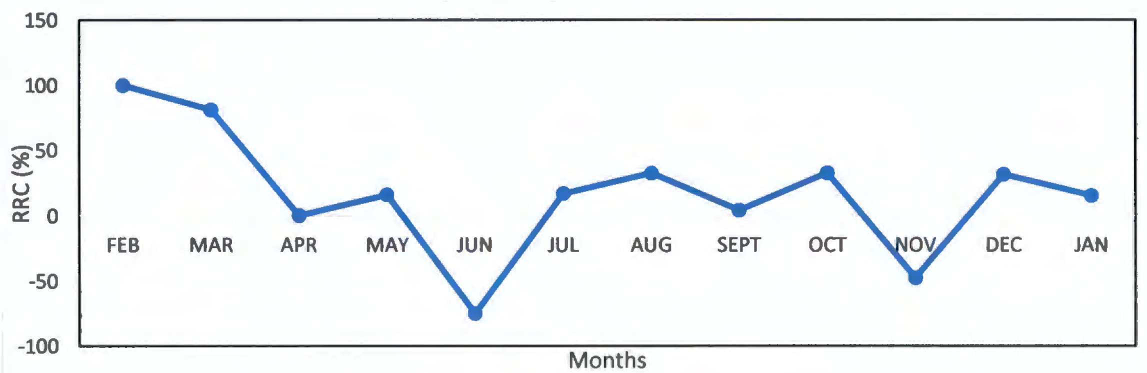

Figure 52: The RRC of arsenic in the KRC.

Self-purification for Cadmium

The self-purification of the Klip for Cd was at its maximum in March along the river segment BC where the highest negative CSUL (-0.019 mg/ (L•km) was recorded (Figure 54). Segment BC receives effluent discharges from various WWTPs (refer to Figure 2). This discharge from the WWTPs contains organic matter (Aristi et al., 2015), to which Cd strongly adsorbs (Yang et al., 2015), and as such, it was absent in the water column. The lowest CSUL was recorded along segment AB where the river was gaining Cd at 0.024 mg/ (L•km) in March and this can be attributed to inputs of Cd emanating from seepage from mine tailings which are located in the vicinity of this river segment.

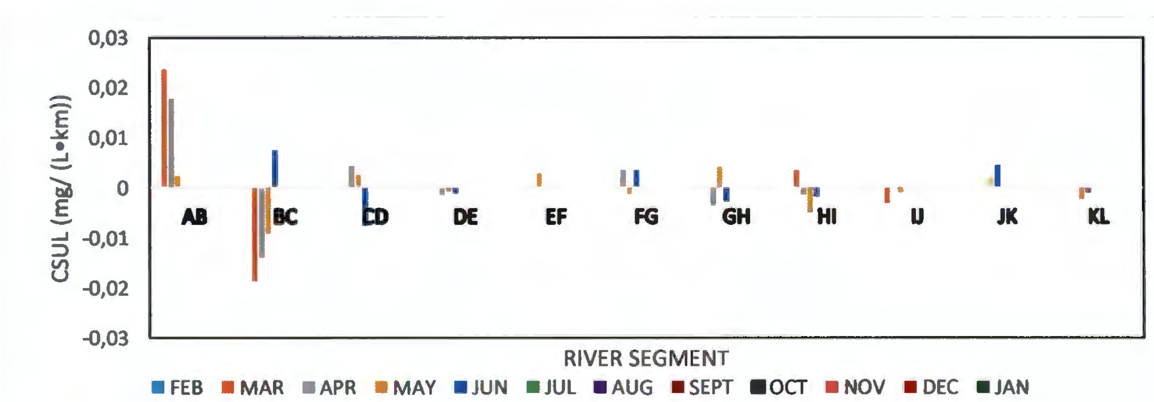

Figure 53: The CSUL of cadmium in the Klip River.

Overall, the RRC of the Klip for Cd was at its highest in the months of February, March, and from July to January, whereby the RRC was 0% (Figure 55). This means that the river managed to recover to its exact Cd concentrations at the river head. As was indicated in Chapter 2, Cd was not detected in any of the samples between July and January, which might suggest that the activities that contribute to Cd in the Klip are seasonal. In this case the application of heavy metal containing pesticides and fertilizers, was associated with an increase in Cd concentration between March and June (Parent et al., 2009; Schwartz and Reis, 2000). As such the lowest RRC was recorded in April and June (100%) followed by May, which recorded 56.639%, suggesting that instead of purification, the river had actually gained from inputs of Cd along the profile of the Klip River.

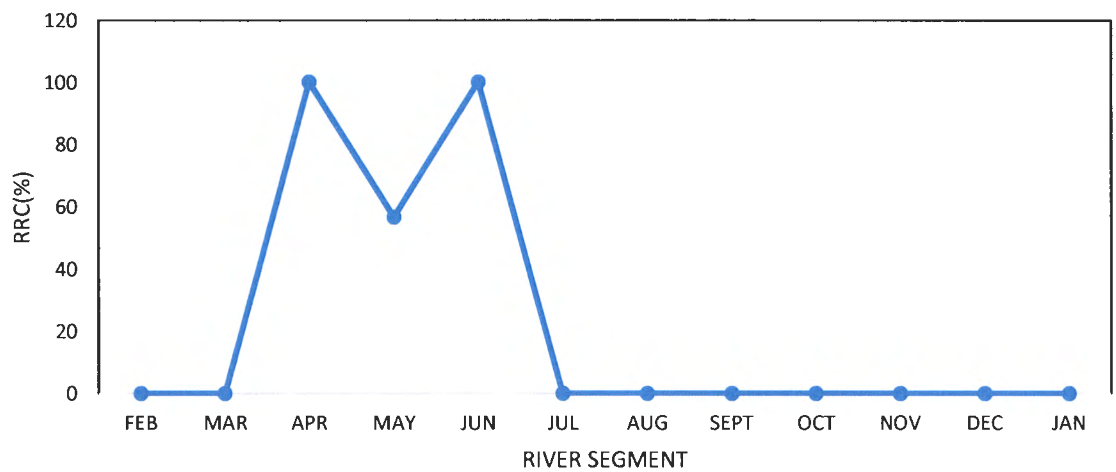

Figure 54:The RRC of cadmium in the KRC.

Self-purification for Cobalt

The self-purification of the Klip River for Co was at its maximum along the segment DE where the highest negative CSUL (-0.133 mg/ (L•km)) was recorded in February. The lowest self-purification for Co was along the segment AB in February, where the highest positive CSUL was recorded (Figure 56). Along this segment AB, the Klip River was gaining Co at a rate of 0.283 mg/ (L•km). The low CSUL in the segment AB can be attributed to an influx of effluents from mine tailings, which contain elevated Co concentrations (Kagambega et al., 2014), and these tailings are located in the vicinity of segment AB. In other segments along the profile of the Klip River, there were Co inputs though relatively lower to inputs in segments AB and BC, suggesting sources other than mine tailings e.g. industrial discharges.

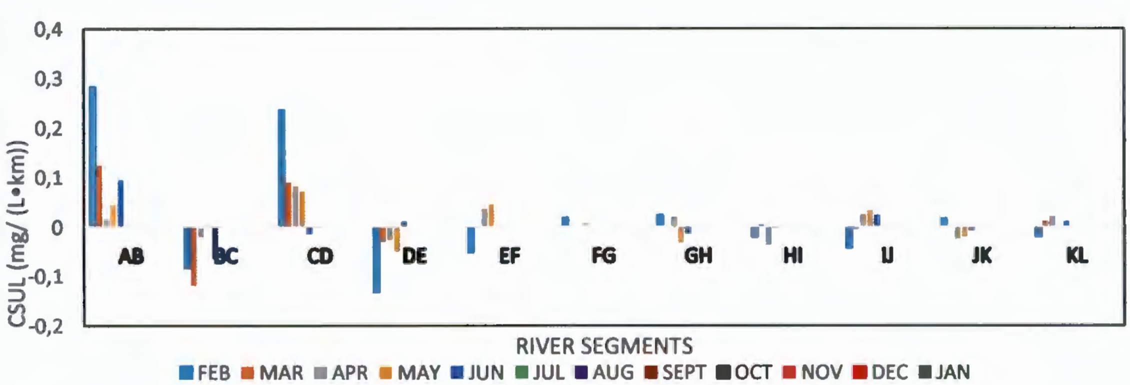

Figure 55: The CSUL of cobalt in the Klip River.

The RRC of the Klip was at its highest in the month of February, whereby the river managed to recover beyond its initial quality by 40% (Figure 57). In other months i.e. in May and from July to January, the Klip River managed to recover to its initial unpolluted state, where the RRC was 0%. However, the RRC was at its lowest in the month of June, where it recorded 100%, and similarly, the months of March and April displayed low RRCs of 28.754% and 79.098% respectively. This suggests that in these months the river failed to recover to its less polluted state, rather it was gaining Co which could be attributed to the continuous seepage of mine tailings (ATSDR, 2004b) into the Klip River.

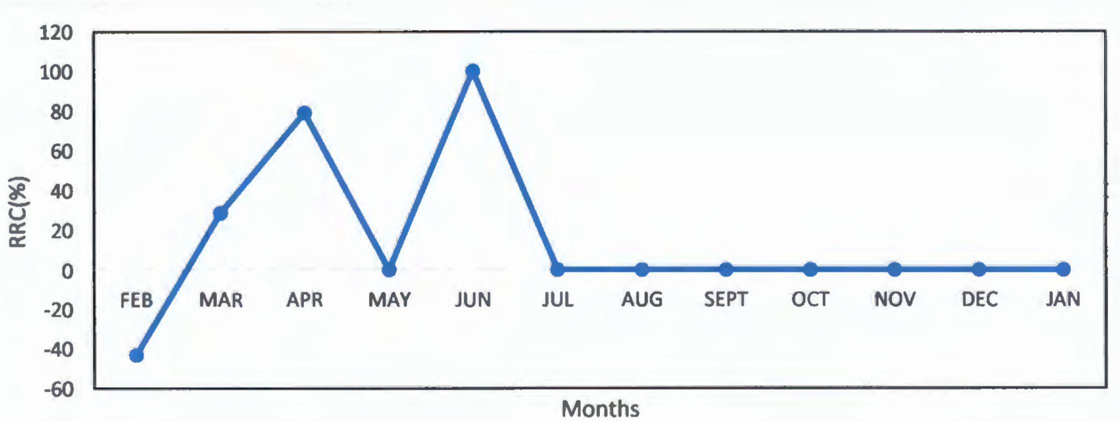

Figure 56: The RRC of cobalt in the KRC.

Self-purification for Chromium

The rate of self-purification of the Klip River for Cr was at its highest along the river segment BC, where the highest negative CSUL (-0.216 mg/ (L•km)) was recorded in September (Figure 58). This suggests that the rate of Cr removal was at its highest in this segment. This coincides with the lowest CSUL which was recorded in the segment AB of the river in September (0.276 mg/ (L•km)), which suggests the active input in Cr concentrations in this segment during the study period. However, based on the results of water quality monitoring, Cr was detected at various sites between the months of February and June, but in September, it was only detected at one site (B), suggesting NPS discharges. The high removal can be attributed to the fact that the highest input was recorded at a segment upstream of BC in the same month of September. Removal mechanisms for Cr involve its interaction with organic and suspended matter to which it adsorbs and thus its mobility is limited (Zhitkovich, 2011).

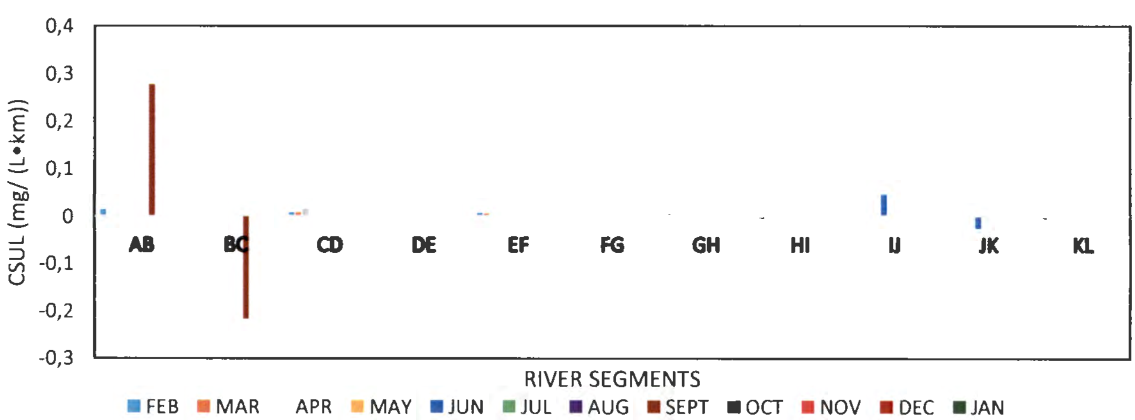

Figure 57: The CSUL of chromium in the Klip River.

The RRC of the KRC for Cr was at its maximum in the month of February (-39.110%) (Figure 59). This suggests that during this month, the river managed to recover beyond its initial Cr concentrations in the upstream by 39.110%. From March to January, the Klip River managed to recover to its initial state and maintain its 0% recording for RRC. As such it can be concluded that the Klip River has a high capacity of recovery for Cr.

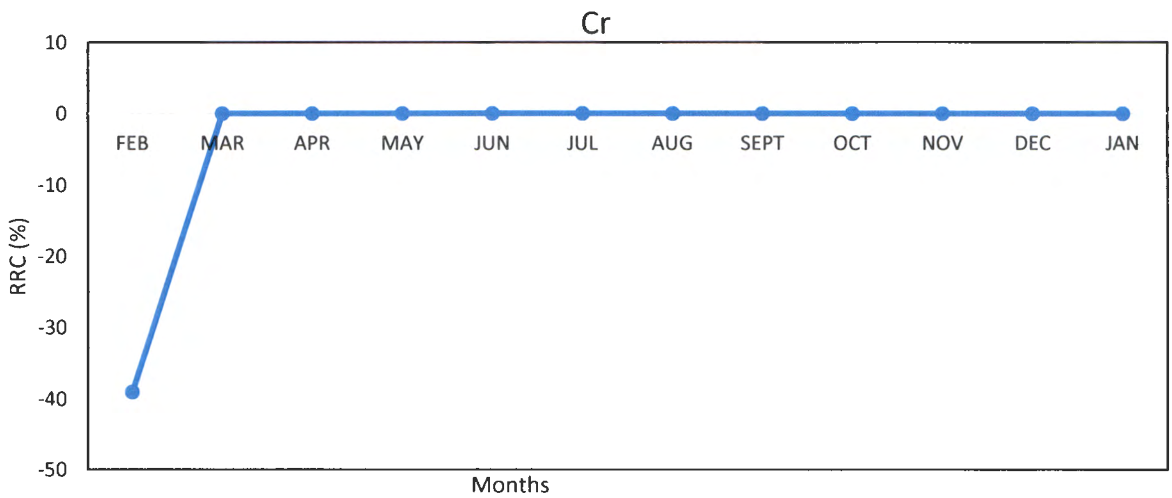

Figure 58: The RRC of chromium in the KRC.

Self-purification for Copper

The rate of self-purification of the KRC for Cu was at its maximum along the river segment JK, whereby the highest negative CSUL was recorded in May (-0.093 mg/ (L•km)) (Figure 60). This could be attributed to the fact that JK is the longest segment, and as such, the process of dilution influenced the Cu concentration and consequently, the CSUL. Davidson (2003) illustrated that water quality in the Witwatersrand basin deteriorates in the proximity of mine tailings and improves in the distal regions, and thereby justifying dilution as a mechanism for removal of Cu in this case. The lowest CSUL was recorded in the segment IJ in May, whereby the Klip River was gaining Cu at a rate of 0.165 mg/ (L•km). This segment is located in the downstream, where agricultural land use is predominant, and as such, the inputs of Cu can be attributed to application of pesticides containing heavy metals and non-point discharges (Ottesen et al., 2015; Willis and Bishop, 2016).

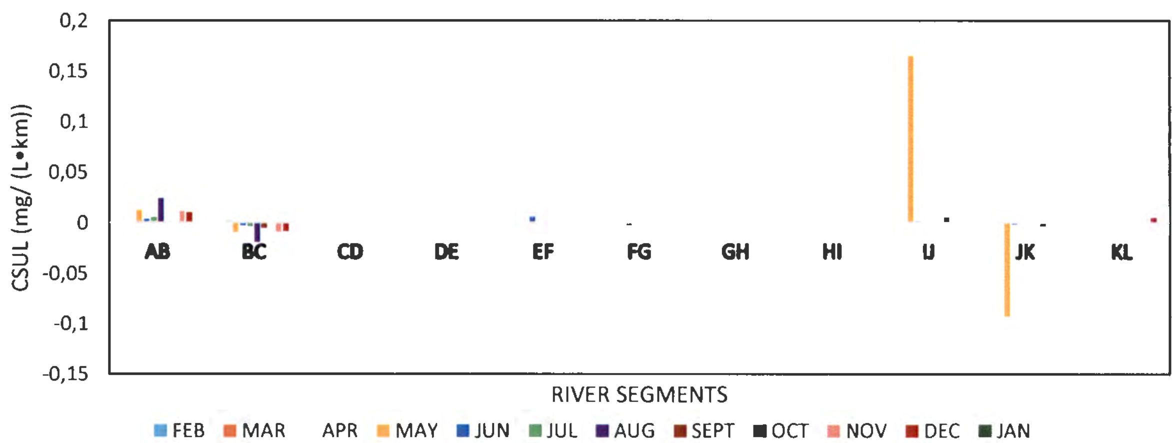

Figure 59: The CSUL of copper in the Klip River.

The RRC in the months of February to April, June to September, November and January was 0% (Figure 61), which suggests that the river managed to recover to its initial Cu concentrations recorded at site A. The lowest recovery, denoted by the highest positive RRC (100%) was in the months of May, October and January. This suggests that the river deteriorated in terms of Cr concentrations by 100% from its initial state. As such, it can be concluded that the Klip River had a high capacity to self-purify Cu throughout the year with an exception of the months of May, October and January. The low capacity for recovery in the months of May, October and January could be attributed to pesticide transfers which is a function of many factors; floods (Boithias et al., 2010;2011), rainfall intensity and irrigation (Vryzas et al., 2009), hence the lack of temporal pattern.

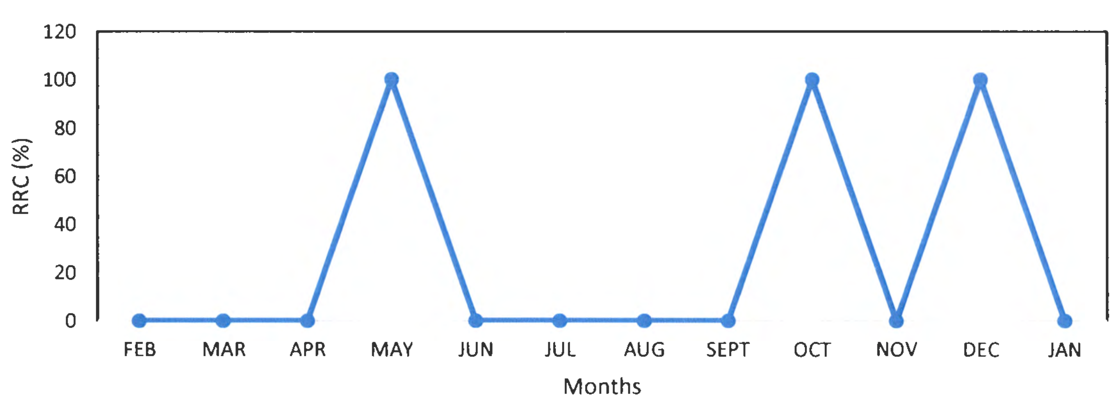

Figure 60: The RRC of copper in the KRC.

Self-purification for Iron

The rate of self-purification of the KRC for Fe was at its maximum along the river segment BC where the highest negative CSUL was recorded in July (-5.296 mg/ (L•km)) (Figure 62). Other segments (AB, CD and DE) also recorded high negative CSUL in various months between April and December. The lowest CSUL was recorded in the segment AB in July (6.967 mg/ (L•km)) suggesting that Fe was being added into the KRC at a rate relatively higher than its removal downstream of this segment. Significant inputs of Fe were also recorded in this segment in other months and other segments (BC and CD) in the upstream section of the river.

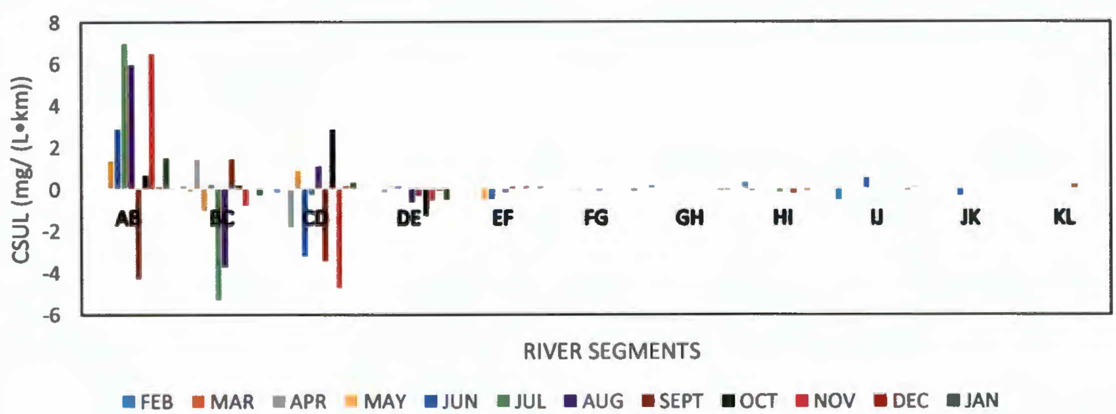

Figure 61: The CSUL of iron in the Klip River.

Sources of Fe in these segments can be attributed to industrial effluents (Ado et al., 2014) and acid mine drainage (Florence et al., 2016) atypical of the land use activities in the upstream. Minor inputs ranging from 0.15 to 0.518 mg/ (L•km) were recorded in the downstream segments where agriculture is the predominant land use activity. Boxall et al. (2012) in a study on new and emerging pollutants to water from agriculture, identified metallic elements as emerging pollutants from the application of pesticides. Iron is one such element contained in pesticides (Boxall et al., 2012). As such, the minor inputs of Fe can be attributed to leaching of agricultural soils in the downstream segments.

The RRC of the Klip River for Fe was at its highest in September with a recording of -751.961% (Figure 63). This suggests that during this month the Klip River managed to self- purify for Fe beyond the concentrations recorded at the upstream. The river also managed to recover like this in

March, July and January. The lowest RRC for Fe in the KRC was recorded in June (91.926%). Similarly in various other months the Klip River's rate of self-purification was lower (Figure 63).

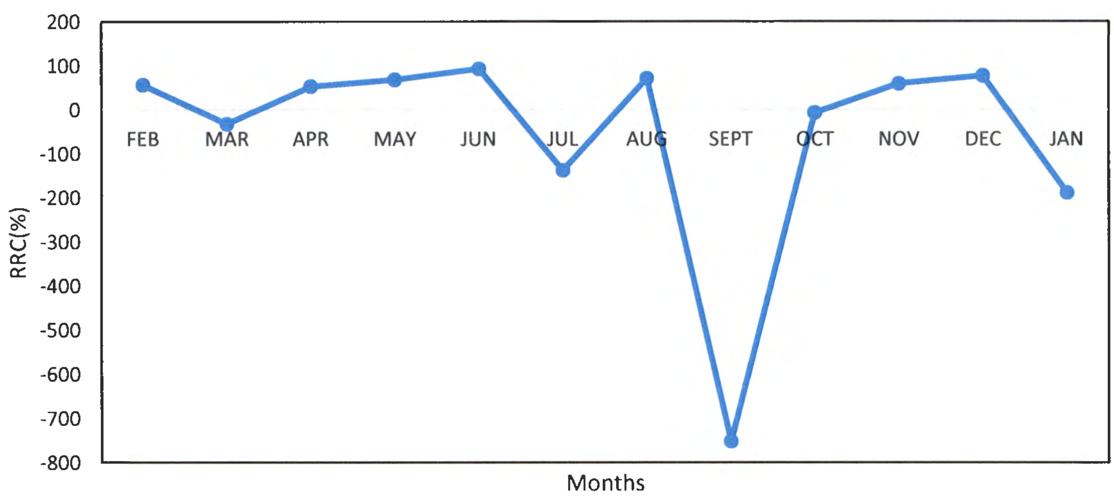

Figure 62: The RRC of iron in the KRC.

Self-purification for Manganese

The rate of self-purification of the KRC for Mn was at its maximum along the river segment BC in March, which recorded the highest negative CSUL (-4.650 mg/ (L•km)) (Figure 64). It should be noted that in the segment BC, the CSUL was high throughout the year. This suggests that along this segment, there was active removal of Mn. This can be explained by the fact that Mn is transported in rivers adsorbed to suspended sediments (Howe et al., 2004), especially at high pH ranges such as those recorded in the Klip River. The influx of municipal wastewater discharges result in the unsettling of sediments to which the Mn adsorbed. Other segments (CD and DE) also recorded high CSUL in various months. The lowest self-purification was recorded in the segment AB in July, where the highest positive CSUL (6.967 mg/ (L•km)) was recorded. Furthermore the segment AB displayed the lowest CSUL relative to other segments throughout the year with the exception of the month of September. These findings suggests that the largest Mn inputs are located in the vicinity of this segment (AB). In the segment AB, the source of Mn is attributed to seepage from tailings dumps (Johnson and Hallberg, 2005; Freitas et al., 2013) coupled with industrial discharges (Howe et al., 2004).

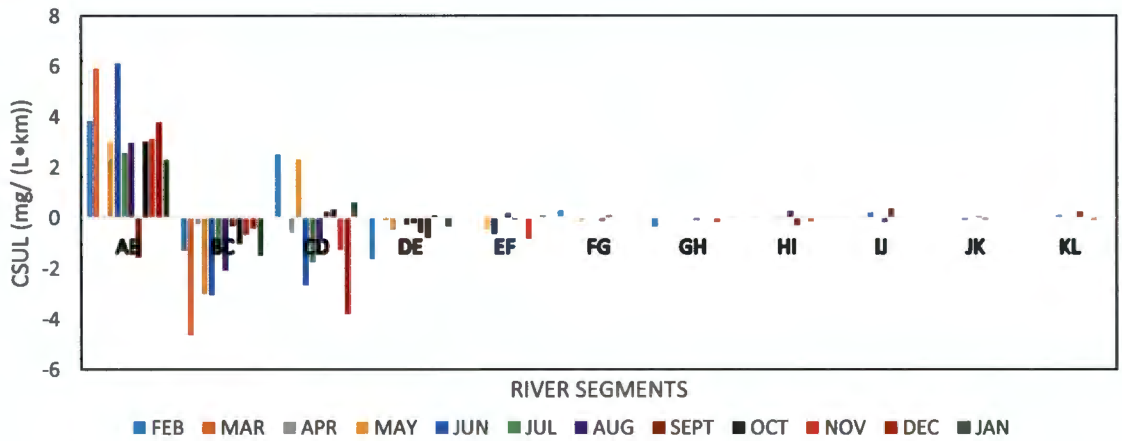

Figure 63: The CSUL of manganese in the Klip River.

The highest RRC for Mn was recorded in April (-5752.611%) followed by July (-2830.980%) (Figure 65). This suggests that in these months, the river was able to recover to its quality in terms of Mn concentrations and beyond its initial state. The lowest RRC for Mn was recorded in the months of February, March, June, November, December and January (0%). An RRC of 0% means that the Klip River managed to recover to its initial state in terms of Mn concentrations. As such it can be concluded that the Klip River displayed a high capacity to recover from Mn pollution throughout the year.

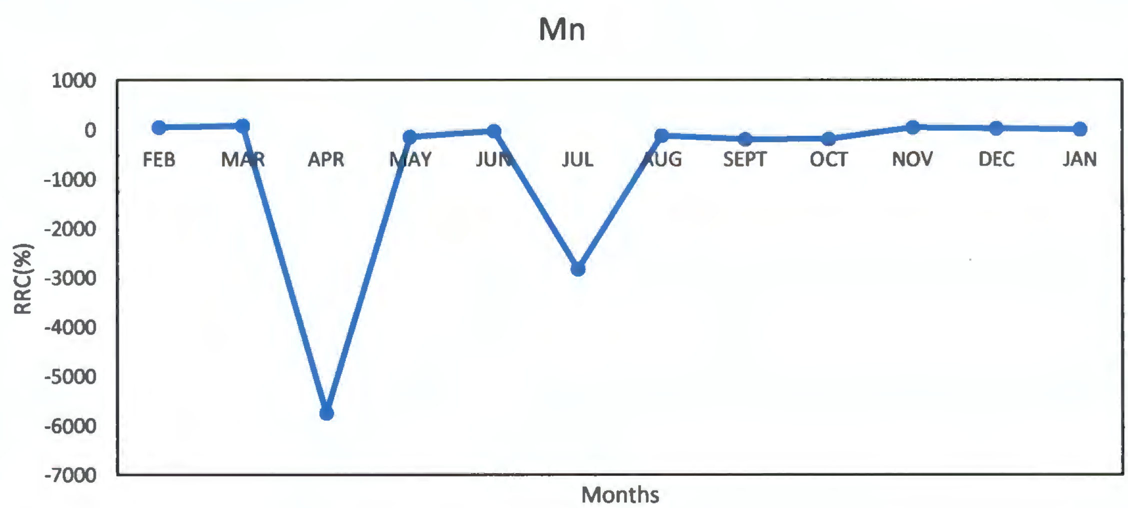

Figure 64: The RRC of manganese in the Klip River.

Self-purification for Nickel

The self-purification of the KRC for Ni was at its maximum along the river segment AB in June where the highest negative CSUL (-0.354 mg/ (L•km)) was recorded (Figure 66). In this segment, the upper point is a dam outlet and the lower point a river, as such the Ni concentrations in the dam outlet were higher relative to the river as was previously demonstrated by Hansen and Gonzalez-Marquez (2010). This can be attributed to the trapping of elevated concentrations of metals in the dam, which are then lowered by dilution as water flows downstream.

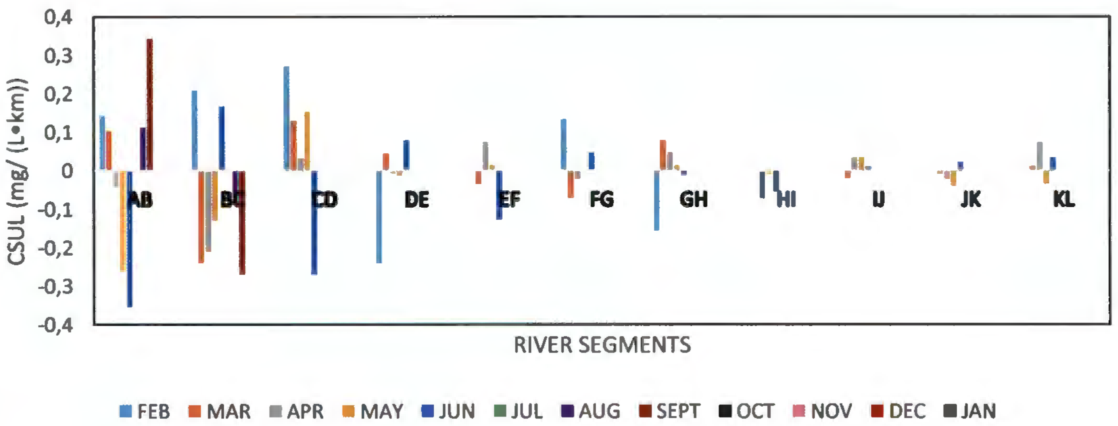

Figure 65: The CSUL of nickel in the Klip River.

It should be noted that other segments also displayed high CSUL for Ni in the KRC and these included BC, CD, DE, EF, FG, GH and HI in various months throughout the year,thus further substantiating the process of dilution as the removal mechanism for Ni. The lowest CSUL was recorded in the segment AB in September (0.344mg/ (L•km)), suggesting the input of Ni along this segment to be from mining, industrial and municipal discharges. There are however, inputs of Ni along the whole profile of the Klip River, which can be attributed to the natural erosion of soil and rocks, and leaching (ATSDR 2005a).

The Klip River displayed a high capacity to recover Ni throughout the year (Figure 67). The highest RRC for Ni was recorded in May (-276.712%) followed by June (-44.242%). This suggests that the river managed to recover the Ni concentrations to lower than those recorded in the upstream. The lowest RRC for Ni was recorded in the months of February and from July to January (0%). This means that the Klip River managed to recover to its initial state in terms of Ni concentrations. Overall, it can be concluded that Klip River had a high capacity to self-purify for Ni throughout the year.

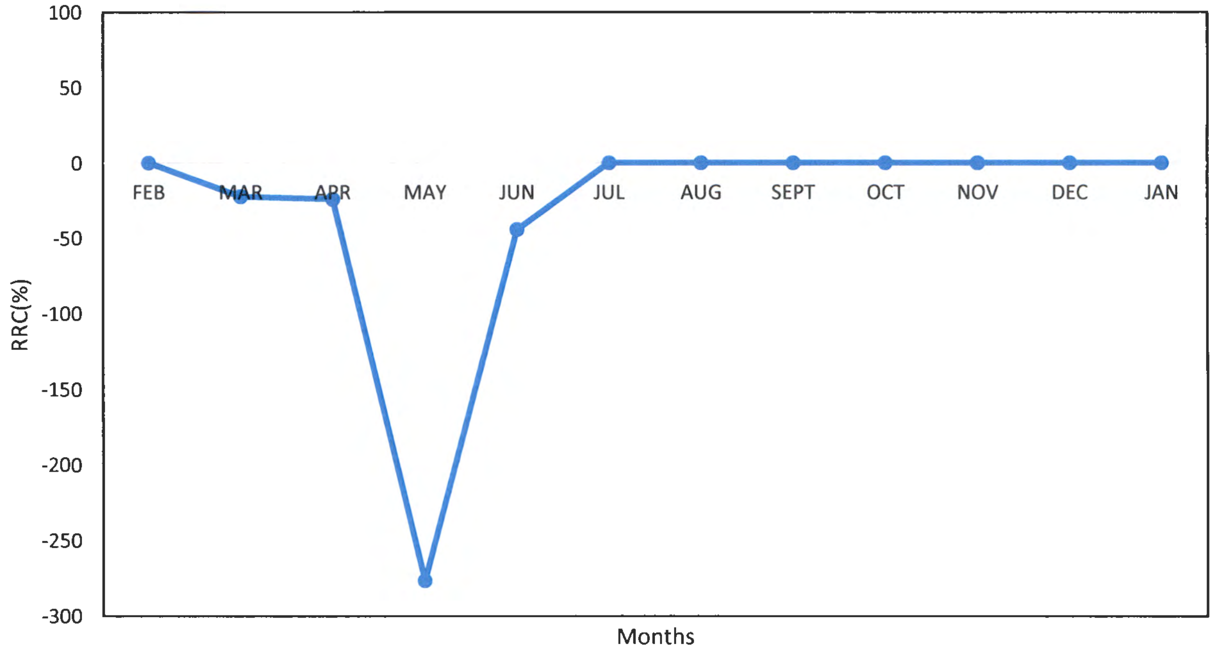

Figure 66: The RRC of nickel in the Klip River.

Self-purification for Lead

The self-purification of the KRC for Pb was at its maximum along the river segment AB in March, where the highest negative CSUL (-0.995 mg/ (L•km)) was recorded (Figure 68). This can be attributed to the dilution of elevated concentrations of Pb in the trapped sediments of the Fleurhof dam (Ndasi, 2008). High CSUL values were also recorded in other river segments in the month of March, and these include CD (-0.622mg/ (L•km)), FG (-0.400mg/ (L•km)), HI (-0.309mg/ (L•km)) and KL (-0.280 mg/ (L•km)), which also substantiates the decrease in Pb concentrations with distance from the source and attributed to dilution (Changnon, 2016). The lowest CSUL was recorded in the segment EF in March (0.851 mg/ (L•km)), suggesting an input of Pb from land use activities in proximity to this segment. The source of Pb in this segment can be attributed to its extensive use in various industries as well as mining activities (Karrari et al., 2012), which are characteristic of this segment.

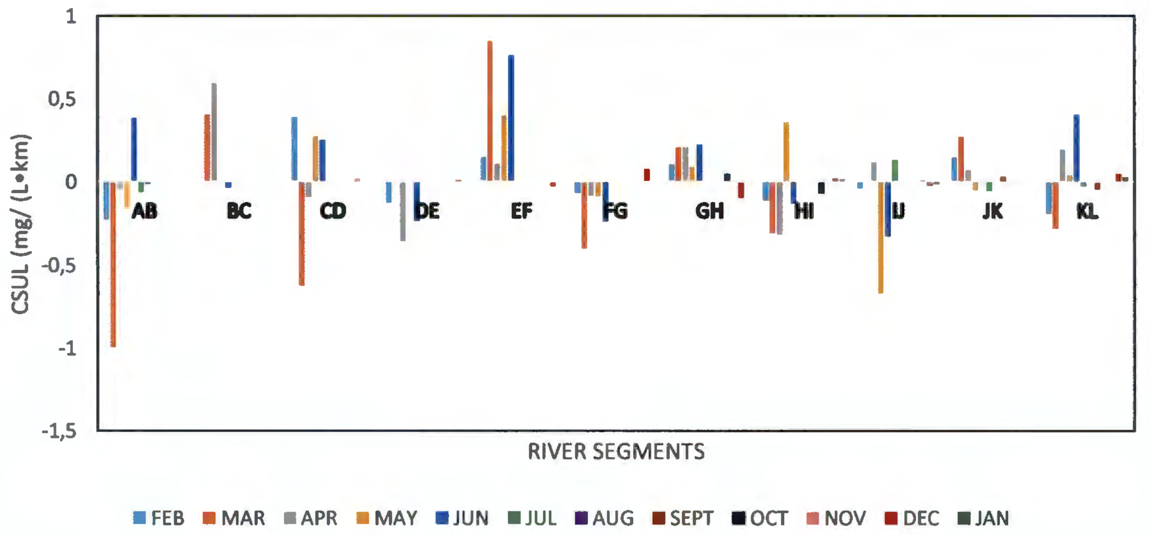

Figure 67: The Rate of removal of lead in the Klip River.

The highest capacity to recover Pb in the Klip River was in March (-417.369%) (Figure 69) which meant that during this month the Klip River managed to self-purify Pb concentrations to lower levels beyond those that were recorded in the upstream. The lowest RRC for Pb was recorded in the months of November, December and January (100%). From July to October, the RRC was 0% suggesting that the Klip River managed to recover to its initial state in terms of Pb concentrations. As such, it can be concluded that the KRC has considerable capacity to recover its quality in terms of Pb concentrations.

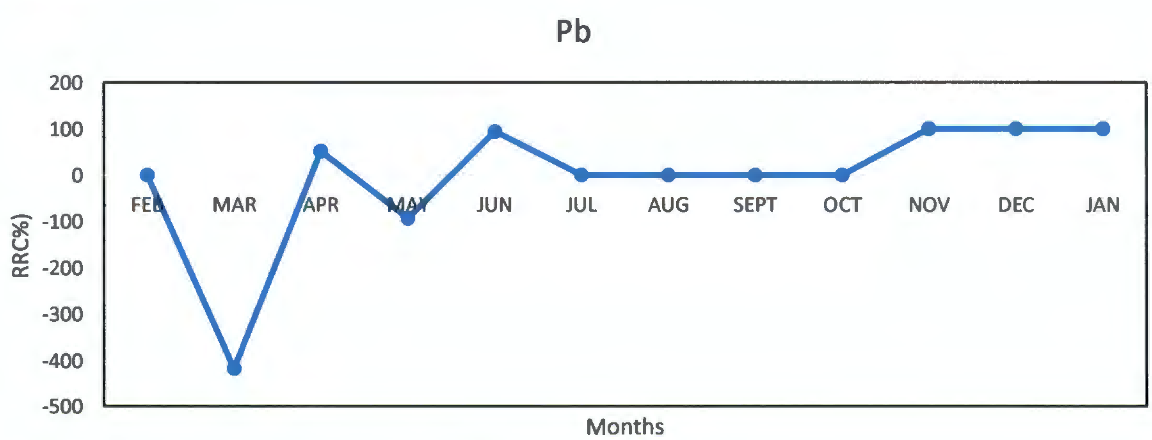

Figure 68: The RRC of lead in the Klip River.

Self-purification for Vanadium

The self- purification of the KRC for V was at its maximum along the river segment CD in July where the highest negative CSUL (-0.021 mg/ (L•km)) was recorded (Figure 70). High CSUL values were also recorded in all the other river segments in various months. The lowest CSUL was recorded in the segment AB in March (0.025 mg/ (L•km)) which meant that in this segment there were significant inputs of V. It should be noted that the Klip River largely depicted low CSUL for V at all the segments in various months throughout the year suggesting multiple sources of V inputs along the profile of the Klip River. The sources of V include anthropogenic sources; hydrocarbon fuel combustion, and the industrial production of V (Mejia et al., 2007), which are characteristic of the upstream section of the Klip River. In addition, V can originate from natural sources such as soil erosion, and leaching from rocks and soils, a situation which is substantiated by findings in Chapter 3, which suggests that the dominant source of pollution in the downstream section of the KRC is bedrock weathering. The findings in Chapter 3 indicated that V was higher in the downstream, thereby alluding to findings from Van Zinderen Bakker and Jaworski (1980), who suggested that the anthropogenic inputs of V to water are far less relative to natural sources.

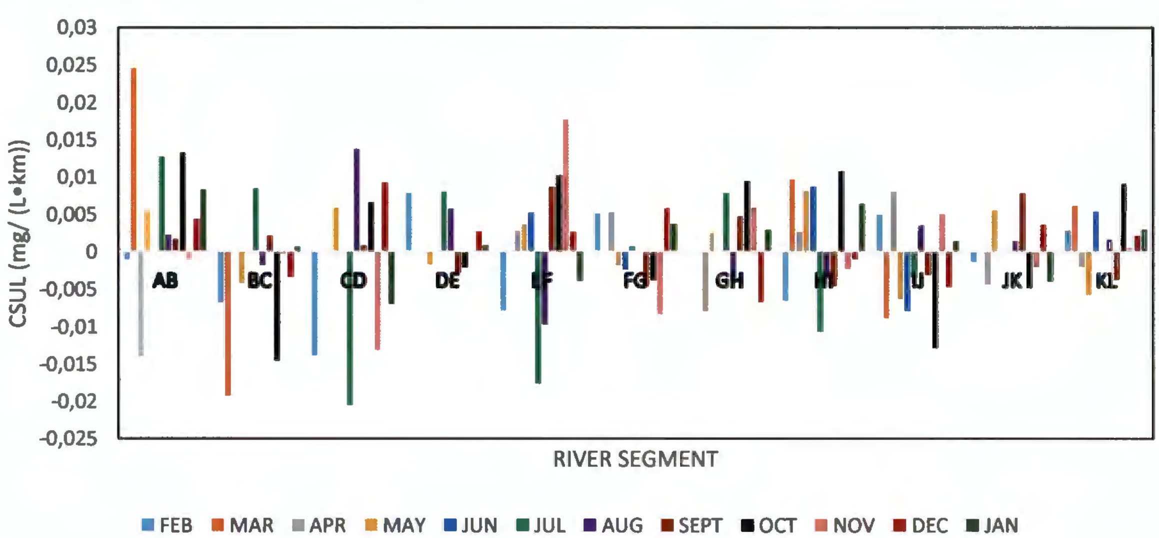

Figure 69: The CSUL of vanadium in the Klip River.

The highest capacity to recover V in the Klip River was recorded in the months of April and July (0%) (Figure 71). An RRC of 0% means that the Klip River managed to recover to its initial state in terms of V concentrations. The lowest RRC for V was recorded in the months of March, May, June, December and January (100%). It can be concluded that, generally the ability of the Klip River to recover its quality in terms of V concentrations is very low, and this can be attributed to the multiple sources along the whole profile of the KRC.

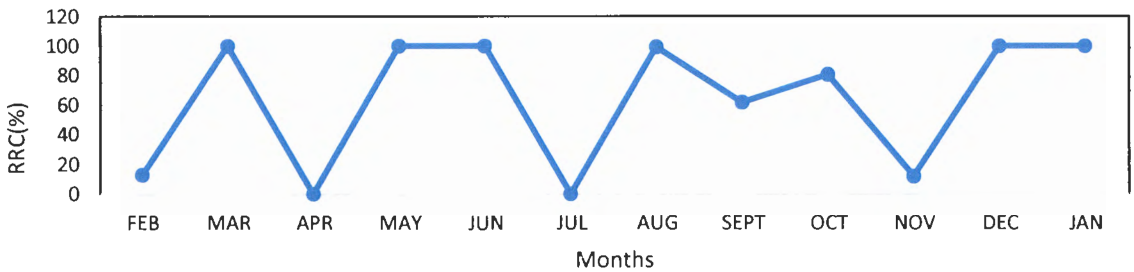

Figure 70: The RRC of vanadium in the Klip River.

Self-purification for Zinc

The rate of self-purification of the KRC for Zn was at its maximum along the river segment BC in September, which recorded the highest negative CSUL (-1.723 mg/ (L•km)) (Figure 72). This suggests that Zn removal was high along this segment. Atanassova et al. (2000) studied the mechanism of self-purification of Zn and other heavy metals in mine effluents. In that study, self-purification which was highest for Zn, was attributed to an algae-driven process of mineral crystallization (Atanassova et al., 2000). Similarly in this study Zn removal can be attributed to the process of mineral crystallization triggered by algae associated with mine tailings. The lowest CSUL was recorded in the segment AB in September (2.055 mg/ (L•km)) suggesting inputs of Zn along this segment. Zinc inputs can be attributed to mining activities atypical of this segment (ATSDR, 2005b). Although very minimal, there were several inputs of Zn in all the other segments of the Klip River, which can be attributed to natural sources. ATSDR (2005b) postulated that Zn releases from anthropogenic sources are greater than those from natural sources.

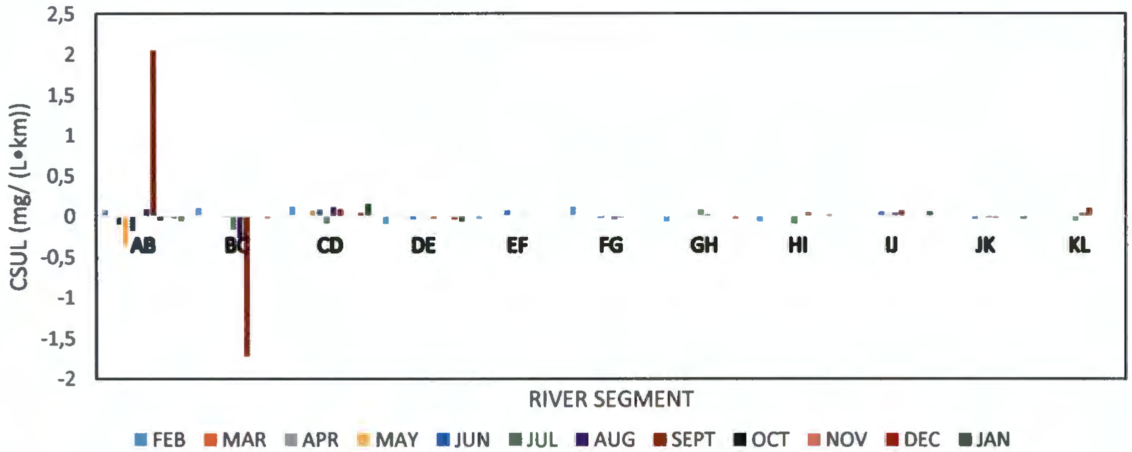

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Figure 71: The CSUL of zinc in the Klip River.

The highest capacity to recover Zn in the Klip River was recorded in December (-956.567%) which means that the river managed to recover beyond the initial water quality state (Figure 73). From the months of February to March, June and July, the KRC recorded RRCs of 0% for Zn, which means that the Klip River managed to recover to its initial state in terms of Zn concentrations. The lowest RRC for Zn was recorded in September (55.570%). Overall it can be concluded that the capacity for recovery of water quality in the KRC with respect to Zn was considerably high.

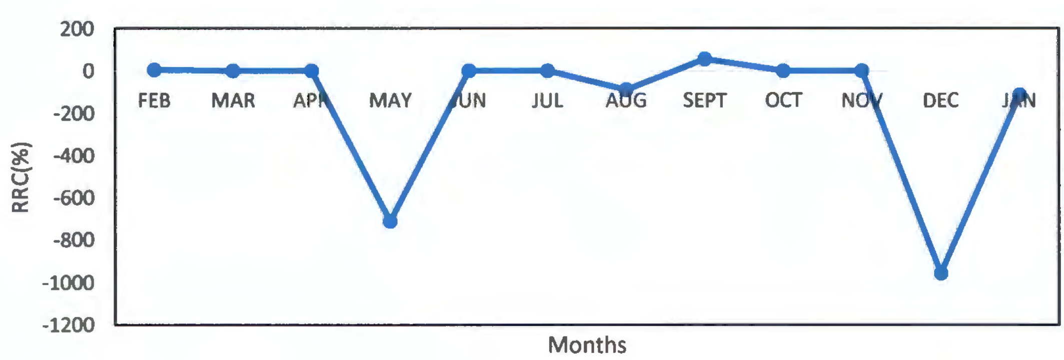

Figure 72: The RRC of zinc in the Klip River.

Self-purification for Uranium

The rate of self-purification of the KRC for U was at its maximum along the river segment CD in July, where the highest negative CSUL (-0.037 mg/ (L•km)) was recorded (Figure 74). High CSUL values were also recorded in all the other river segments in various months. The lowest CSUL was recorded in the segment HI in March (0.022 mg/ (L•km)) suggesting inputs from agricultural activities located in the downstream. The solubility of U is influenced by bedrock in the Klip River, which is dolomite and whose dissolution may result in the formation of complexes with sulphate (Hockley et al., 2006). There were several inputs of U along the profile of the Klip River suggesting multiple sources, such as mining activities (Winde, 2009; 2013); the production of phosphate fertilizers and natural processes that result in the resuspension of soils containing uranium through water erosion (ATSDR, 2013).

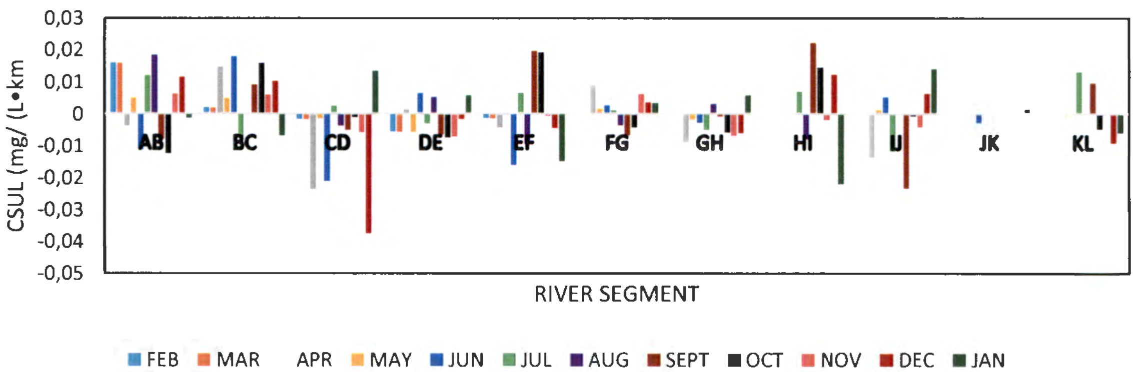

Figure 73: The CSUL of uranium in the Klip River.

The highest capacity to recover U in the Klip River was recorded in December (-165.290%) which means that the river managed to recover beyond the initial U concentrations (Figure 75). The KRC recorded RRCs of 0% for U in February and August which means that the river managed to recover to its initial state in terms of U concentrations. The lowest RRC for U was recorded in March (92.214%).

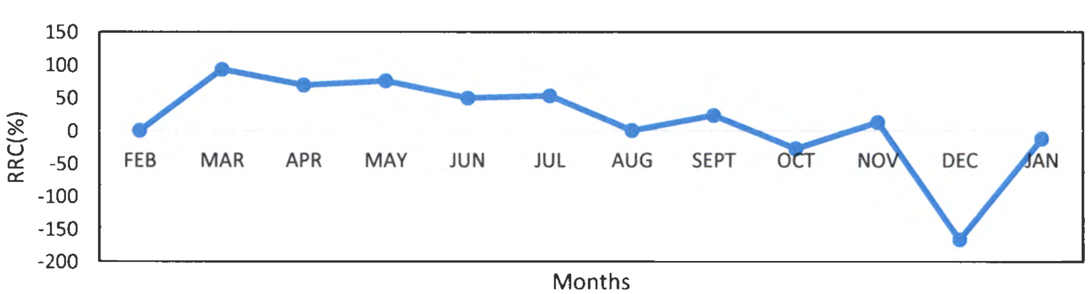

Figure 74: RRC of uranium in the Klip River.

4.5 Chapter summary

Most heavy metals i.e. Cd, Cr, Fe, Mn and Zn recorded the maximum CSUL in the river segment BC in various months (March, July and September). The minimum CSUL was however recorded in the river segment AB for Al, As, Cd, Co, Cu, Fe, Mn, Ni and V. The maximum RRC was mostly recorded in the months between February and June for As, Cd, Co, Cu, Cr, Mn, Ni, Pb and V. Metals such as Al, As, V and U depicted a trend whereby the KRC failed to recover to its initial state for majority of the months during the course of the year. However, the KRC managed to recover to its initial water quality state and beyond for Cd, Cr, Mn, Ni and Zn in a majority of months during the course of the sampling period. Previous studies which employed the RRC disregarded positive or negative recovery and its implication thereof, which has been demonstrated in this chapter. In the following chapter, based on a synthesis of findings from the previous chapters, a water quality management plan for the KRC was developed.

CHAPTER 5

SURFACE WATER QUALITY MANAGEMENT PLAN IN THE KLIP RIVER CATCHMENT

5.1 Abstract

The preceding chapters have provided an in depth understanding of water quality characteristics, the seasonal and spatial factors governing the trends, the associated risks, and the sources of pollution and the natural ability of the Klip River to remove these pollutants. As previously stated, the natural capacity of the river to self-purify is not sufficient to deal with the water quality problems. Therefore, the main aim of this chapter was to develop a water quality management plan for the Klip River catchment informed by the findings discussed in the previous chapters. This will enable the sustainable use of water resources that optimizes water quality and incorporates the inextricable link between water quality and quantity.

5.2 Introduction

Water quality management is the preservation of the suitability for use of water resources on a continuous basis, by ensuring a balance between socio-economic development and environmental protection (Krenkel, 2012). Consequently, water quality management involves identifying water quality problems associated with its uses so that its utilization at any location will not be unfavourable to designated use at other locations (Krenkel, 2012). For that reason, water quality management introduces a new facet to water resources management whereby there is optimization of water quality (Krenkel, 2012).

Water quality management is riddled with many challenges which vary between developing and developed countries. In developing countries, owing to poor financial capability and planning, water quality management barriers are characterized by substandard water and wastewater treatment infrastructures as well as poor water quality monitoring programs, which consequently results in the unavailability of reliable water quality data (Huang and Xia, 2001). However, Somlyody (1995), identified the problem of an increasing array of chemical toxicants introduced to aquatic environments through non-point sources (NPS) as a challenge to water quality management in developed countries.

In order to ensure the effective management of water quality, there is a need for reliable information on the status quo of water quality, pollution sources, natural processes and anthropogenic influences; socio-economic factors and water uses (Helmer and Hespanhol, 1997; Huang and Xia, 2001). However, there are problems with regards to the availability and the quality of information making the development of effective decision support impossible. Huang and Xia (2001), noted that there was insufficient knowledge in the area of water quality effects and this can be attributed to the poor water quality detection abilities. For the management of point-sources, information constraints include accuracy of pollutant-emission inventories, effectiveness of monitoring programs, and uncertainties that exist in the configurations, processes, efficiencies, and costs of pollution abatement actions.

In South Africa, water quality management has progressed over time initially targeting pollution sources control, through general and special effluent standards but now it also includes the receiving environment (DWS, 2015). This was owing to the realization that the aggregate impacts of many effluent sources surpassed the assimilative capacity of the receiving water bodies. Consequently there was introduction of the source directed controls and resources directed measures in the National Water Act (NWA) (DWS, 2015). Source directed controls involve the use of regulatory measures such as registration and permits to enable the achievement of resource quality objectives (Allanson et al., 2010). Whereas resources directed measures are aimed at the protection of water resources, by safeguarding ecosystem functions and preserving a state of health for aquatic and groundwater dependent ecosystems (Allanson et al., 2010). However, water quality management continues to be riddled with problems whereby there are challenges with regards to striking a balance between protecting the water resources and utilization of water for socio-economic development (DWS, 2015).

South Africa developed a Water Quality Management (WQM) Policy and an Integrated Water Quality Management (IWQM) Strategy to enable this balance between protection and use, and also to ensure that impacts on the environment and the functions it performs are effectively remediated (DWS, 2015). DWAF (2003), reiterated that water quality management in South Africa is designed in such a way that it takes place at a local level; as such, water quality management plans, decisions and actions are generally at a sub-catchment scale. The main objective for this chapter was to develop a surface water quality management plan in the Klip River. The water management plan for the Klip River will be incorporated into the Water Quality Management Framework-Plan which details the institutional arrangements for water quality management at the Water Management Area (WMA) level. Furthermore this plan may also be adopted in other river catchment areas experiencing similar pollution challenges as the KRC.

5.3 Methodology

The methodology to attain this objective is as is presented in Figure 76 adopted and modified from Brown et al. (2000). This methodology, relied heavily on data and findings generated in the previous chapters.

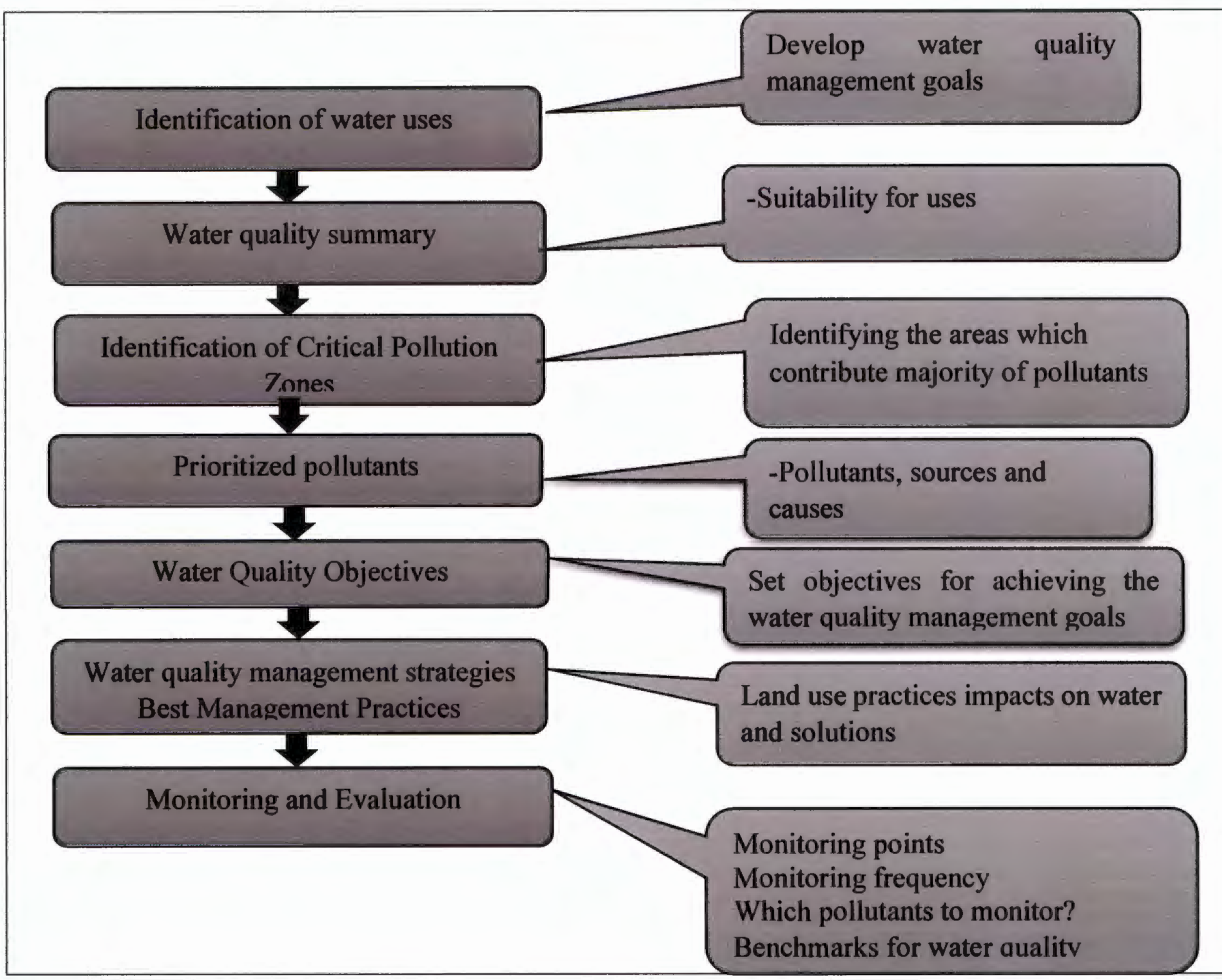

Figure 75: Framework for developing a water quality management plan (adopted and modified from Brown et al., 2000).

It also included a rigorous search of literature particularly in identifying the management options for water quality management in the Klip River catchment.

The first step involved the ***identification of designated water*** uses in the Klip River. This was done so as to inform the process of developing water quality management goals in the KRC. The ***water quality summary*** was then compiled, which involved an assessment of the suitability of the Klip River water quality for its designated uses. This was done using parameter by parameter, in the identified seasons i.e. the 2015/16 and the 2016/17 seasons. The most impaired designated use was identified based on the number of parameters which were unsuitable for that use. There was also ***identification of priority pollutants, critical pollution zones and seasons.*** Priority pollutants are those pollutants, which were identified as impairing all the water uses at all the points along the whole profile of the Klip River. Critical pollution zones and seasons were identified, by assessing from the identified clusters, the regions and seasons respectively, which had the highest comprehensive pollution indices. Furthermore, using findings from the self-purification assessment, the segments which were receiving high inputs of various pollutants were identified as critical pollution zones. In order to develop an optimal water quality management plan, ***water quality management objectives,*** which outline specific targets for achieving pollution reduction and remediation were formulated. Consequently, ***water quality management measures and best management practices (BMPs)*** were identified which could ameliorate the problem of PS and NPS pollution in the Klip River catchment. A framework for monitoring and evaluation of surface water quality in the Klip, in both the dry and wet season was then developed. This framework, outlines the parameters to be monitored per sampling site for designated use(s).

5.4 Results and Discussion

5.4.1 Water uses in the Klip River

Brown et al. (2000) described designated uses as those water uses which are recognized and established by state and federal water quality programs. As was discussed in section 1.10 of this thesis, the designated water uses in the Klip River include domestic, industrial, agricultural and recreational. The purpose of identifying these uses was to conduct an evaluation of which uses were directly at risk from human activities so as to formulate efficient methods of pollution control.

The evaluation was conducted using the SAWQG for aquatic ecosystem protection, domestic and agricultural uses. However, because there is a lack of standards for many pollutants with regards water quality, for the industrial and recreational uses, these uses were therefore not included in the evaluation.

5.4.2 Water quality summary

The following section is a summary of the water quality in the Klip River, based on the water quality parameters and suitability for various uses. In the dry season, the designated use which was most threatened based on the number of parameters which were not suitable was domestic use followed by aquatic ecosystem protection and agricultural uses (Table 45).

Table 45: Suitability of water quality parameters for use in the dry season.

	Water uses		
	Domestic	**Aquatic**	**Agriculture**
pH	√	√	√
EC	√	**X**	**X**
Temp	√	√	√
TDS	**X**	√	√
Al	**X**	**X**	√
As	**X**	**X**	**X**
Ca	**X**	**X**	√
Cd	√	√	**X**
Co	√	√	**X**
Cr	**X**	**X**	**X**
Cu	√	√	√
Fe	**X**	**X**	**X**
K	**X**	√	√
Mg	**X**	√	√
Mn	**X**	**X**	**X**
Na	**X**	**X**	√
Ni	**X**	**X**	**X**
Pb	**X**	**X**	**X**
U	**X**	**X**	**X**
V	**X**	**X**	**X**
Zn	√	√	√
NO_3	**X**	**X**	√
P	√	√	√

Key

√	Suitable
X	Not Suitable

The non-suitability for various uses of the Klip River, can be largely attributed to heavy metals with the exception of Cd, Co, Cu and Zn. This aligns with the findings in Chapter 2 whereby high HPI was recorded for domestic, aquatic ecosystem protection and agricultural uses.

Similarly, in the wet season, the designated use which was most impaired based on the number of parameters which were not suitable was domestic use, followed by aquatic ecosystem protection and agricultural uses (Table 46).

Table 46: Suitability of water quality parameters for use in the wet season.

	Water uses		
	Domestic	**Aquatic**	**Agriculture**
pH	√	√	√
EC	√	√	X
Temp	√	√	√
TDS	X	√	√
Al	X	X	√
As	X	X	X
Ca	X	X	√
Cd	√	√	√
Co	√	√	√
Cr	√	√	√
Cu	X	√	√
Fe	X	X	X
K	X	√	√
Mg	X	√	√
Mn	X	X	X
Na	X	√	X
Ni	√	√	√
Pb	X	X	X
U	X	X	X
V	X	X	X
Zn	X	X	X
NO_3	X	X	√
P	√	√	√

However, some parameters such as Cr and Ni which threatened all the designated uses under this study in the dry season were suitable for these uses in the wet season. The unsuitability of the Klip River for domestic uses in particular, can be largely attributed to heavy metals with the exception of Cd, Co, Cr and Ni. Similarly, the number of metal parameters which were suitable for aquatic and agricultural uses was high.

5.4.3 Priority Pollutants

Based on the analysis done in Tables 45 and 46, the priority pollutants in the KRC are heavy metals, listed as follows: As, Cr, Fe, Mn, Ni, Pb, U, V and Zn which have to be monitored for all the uses along the whole profile of the Klip River. As, Mn and Pb were shown to contribute significantly in HPI for domestic, aquatic ecosystem protection and agricultural uses, thus they are a priority. Furthermore, based on the CRI, an additional metal Cd, which was detected in a few months, represented a significant ecological risk in the KRC and equally requires continuous monitoring.

5.4.4 Water quality management goals

The main goals for surface water quality management in the Klip River would therefore be to achieve compliance with SAWQG for domestic and agricultural uses as well as aquatic ecosystem protection. This will be done:

- To reinstate water quality in the Klip River for domestic uses by reducing the levels of heavy metals, major cations and nutrients,
- To restore water quality in the Klip River for aquatic ecosystem protection by reducing the levels of heavy metals and nutrients,
- To restore water quality in the Klip River for agricultural uses by reducing the levels of heavy metals.

5.4.5 Critical pollution zones and season

Based on the CPI calculations, the upstream zone of the Klip River was the most critically polluted particularly with reference to domestic and aquatic uses, in both seasons. In the upstream, the majority of metals registered high single factor coefficients of pollution. Furthermore, based on the findings from the assessment of river recovery and a majority of water parameters having low CSUL, the segment AB located in the upstream zone, is the most critically polluted. However, the downstream was critically impaired for agricultural uses with some metals, V, Pb and Cu and macrominerals Ca, K, Mg and Na, registering high single factor coefficients of pollution in both seasons.

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5.4.6 Pollutants, Sources and Causes

Table 47 shows the sources and associated causes of priority pollutants finding their way into the Klip River. The contribution of heavy metal pollutants from industrial sources was attributed to both the illegal and legal dumping of industrial effluents in the Klip River (Humphries et al., 2017; Sibanda et al., 2015).

Table 47: Pollutants their sources and causes in the Klip River catchment.

POLLUTANTS	SOURCES	CAUSE
Trace/heavy metals	Industrial	Discharge of industrial effluents (illegal and legal)
	Traffic	Elevated number of traffic using petroleum fuels
	Agriculture	Improper application of fertilizers and pesticides
	Mining	Poor mine closure procedures, and rehabilitation hence seepage of tailings
	WWTPs	-Effluent discharges -Collapse of WWTPs due to growing population
	Runoff from paved surfaces	Poor Urban stormwater systems
Nutrients	Agriculture	Improper application of fertilizers
	Livestock	Uncontrolled access for livestock watering
	Informal settlements	-Inadequate sanitation facilities -Discharge of domestic waste into the River
	Domestic waste	Phosphates used in detergents
Major Cations	Lithology	Bedrock weathering

The contributions from traffic can be attributed to an increase in traffic using various petroleum products in the area. The poor mine closure management in the Witwatersrand was identified as a source of heavy metals in the KRC (Rosner, 2007). Sibanda et al. (2015) attributed effluent discharges and contaminated runoff from larger cities, smaller urban centres and informal settlements for the heavy metal concentrations in the Vaal River system. Nutrients' sources from agriculture were associated with the improper application of fertilizers as well as the uncontrolled access of livestock to the river.

5.4.7 Water Quality objectives

In this section the specific targets and measures for achievement of water quality management are listed.

Objectives

- ***To decrease heavy metal concentrations***
    - Ensure compliance with industrial effluent discharges,
    - Regulate the application of fertilizers and pesticides,
    - Upgrading wastewater infrastructure
    - Improving the stormwater systems in the urban areas
    - Ensure proper mine closure procedures
    - Rehabilitation of tailings dump
- ***To decrease major ion concentrations***
    - Reducing agricultural runoff
- ***To decrease nutrient concentrations***
    - Regulate the application of fertilizers
    - Provide adequate sanitation for informal settlements
    - Regulate livestock access to the river
    - Identifying and correcting failing septic systems

5.4.8 Water quality management in the Klip River catchment

In this section, various water quality management measures are presented. These measures align with the identified sources, causes and priority pollutants and overall the achievement of the main goal for water quality management in the KRC.

Waste and Wastewater management

The findings in this study revealed the significant impact and contribution of wastewater discharges to the water quality of the KRC particularly in the upstream where a majority of WWTPs are located. These WWTP discharge effluents which contain elevated concentrations of residual nutrients and heavy metals into the Klip River (McCarthy et al., 2007). Furthermore, there is evidence that industries located in the area discharge their wastewater in the Klip River. Therefore, there is need to enforce compliance, through monitoring of effluent discharges from the WWTPs as well as industries.

Mine closure management

Based on the results in the previous chapters, in the upstream section of the Klip River, there is evidence of significant inputs of heavy metals from mines and tailings dumps located in the vicinity. Mine closure in South Africa was historically inexpedient, with the South African government now owning thousands of derelict mines and facing liabilities worth billions of rands for rehabilitation as a consequence (Milaras, 2015). However, this historical ineptness was removed by the Mineral and Petroleum Resources Development Act 28 of 2002 (MPRDA), the National Environmental Management Act (107 of 1998) and the National Water Act (36 of 1998) wherein legally mines are mandated to plan for rehabilitation after decommissioning of their mining activities and to allocate funds for implementation of the environmental rehabilitation. Conversely, there are still challenges with mine closure, with Feris and Kotze (2014) calling for a strict environmental impact assessment regime with particular reference to mine rehabilitation. So,the management strategy in this case will be for the competent authorities that issue environmental authorization for mining projects, to ensure that sufficient funds are set aside for rehabilitation. Furthermore, these competent authorities are to ensure that sound plans for mine closure are laid out and are strictly adhered to during the rehabilitation implementation.

Stormwater management

Armitage et al. (2013) observed that stormwater management in the urban areas of South Africa is largely centred on runoff collection and channelling it to water bodies; consequently impacting the environment through erosion, siltation and pollution of water courses. Storm water management can improve the quality of water by reducing the quantity of the stormwater and also managing the quality of the stormwater. The quantity of stormwater can be controlled by rainwater harvesting, infiltration, detention, conveyance, long term storage and extended attenuation storage (Armitage et al., 2013). The quality of stormwater can be managed through several processes such as sedimentation, filtration and biofiltration, adsorption, biodegradation, volatilization, precipitation, plant uptake, nitrification and photosynthesis (Armitage et al., 2013). It is therefore suggested that stormwater management plans be developed for the Klip River catchment.

Wetland rehabilitation and restoration

McCarthy et al. (2007) stated that the Klip River wetland was one of the most economically important wetlands in South Africa as both a source of water and a purifier of urban-industrial-mining pollutants in the Witwatersrand region. McCarthy et al. (2007) carried out a geomorphological study of the wetland and concluded that the wetland had lost its purifying abilities, and postulated that the end result will be heavy metal sequestration and eutrophication in the Vaal River system. Vermaak (2010) conducted a similar study and observed that large tracts of wetland had disappeared, the remaining ones were not functioning optionally and concluded that The Klip River wetland was at the brink of collapse. The levels of pollution recorded in this study allude to these findings and as such, strategies to deal with water quality wetland rehabilitation are suggested.

Wetland rehabilitation refers to the implementation of a series of measures to reverse impacts of certain activities on a wetland area, so that it reverts to a condition that is ecologically similar its former ('pre-activity natural state') or desired ecosystem structure, function, biotic composition and associated ecosystem services (DEA et al., 2013). The Klip River system is impacted by a diverse range of anthropogenic activities and as such the wetland rehabilitation strategy should be able to cater for all these activities. Macfarlane et al. (2016) alluded that wetland rehabilitation using a landscape approach, and such rehabilitation of wetlands within the mining landscape for example, requires an ecosystem (as opposed to a species) approach. Wetland rehabilitation should therefore, recognise the interdependence between biodiversity, ecosystems and the benefits they provide for people (Cadman et al., 2010). Vermaak (2010) suggested that the water should be forced into the wetland by way of damming the water upstream of the weir, so as to flood the wetland again. It is suggested that rehabilitation plan be developed for the Klip River wetland. Other methods of rehabilitation include; draining of central channels, re-vegetation, and the control of alien vegetation (Macfarlane et al., 2016).

Best Management practices

Best Management Practices (BMPs) are structural and non-structural measures, operational and maintenance procedures and prohibition of practices, which can be implemented at any stage of the pollution producing activities to prevent and reduce water pollution (Ashley et al., 2011). These control the conveyance of NPS pollutants to rivers by: reduction at the source, reduction of the rate of delivery of pollutants to a water body and remediation (Ashley et al., 2011). In the following section, various BMPs selected based on the priority NPS pollutants and associated causes in the KRC are described.

- The use of an Integrated Pesticide Management (IPM) which involves the monitoring of pesticide use. This approach employs Prevention, Avoidance, Monitoring and Suppression (PAMS) to manage pests, whereby there is use of preventative measures to maintain pests below the threshold whilst using the minimum amount of pesticides (Waskom et al., 2017),
- Conservation tillage which results in the decrease in the volume and velocity of agricultural runoff and also reduces erosion (Waskom et al., 2017),
- Pesticide use licensing and education
    - Understanding of pesticide properties; chemical, pathway and rate of degradation, volatility, solubility, absorptivity and solubility.
    - Education on soil properties and corresponding pesticide loss potential
    - Best Application Practices

- Nutrient Management- involves putting in place mechanisms that capitalizes nutrient uptake and simultaneously decreases nutrient waste and reduce nutrients losses to water. This can be achieved through:
    - o Reducing soil compaction, by avoiding wheel traffic and tillage of wet soils,
    - o Increasing surface water infiltration,
    - o Irrigation management - decreasing runoff.
    - o Efficient application of fertilizers and implementation of leaching practices
    - o Proper fertilizer handling, transportation and storage
    - o Education of farm owners on application of fertilizers and implementation of leaching practices
- Creation and restoration of riparian and buffer zones: - Stringham and Repp (2010) defined riparian zones as physical barriers to sediment-bound nutrients and furthermore riparian vegetation also takes up nutrients, thereby reducing nutrient contributions to water bodies (Uusi-Kämppä, 2000; Sharpley et al., 2006).

5.4.9 Monitoring and evaluation

Monitoring of water quality is important for the continuous improvement of water resources management. Thus a framework for monitoring water quality in both the dry and wet seasons was developed. This framework identifies priority pollutants for monitoring per site and the specific uses for which to monitor those pollutants.

In the dry season, the pollutants of priority were As, Mn, Cr, Fe, Ni, Pb, U and V (Table 48). These pollutants were in excess of the SAWQG for aquatic ecosystem protection, domestic and agricultural uses along the whole profile of the Klip River in the 2015/16 season. Consequently, it is suggested that these pollutants be monitored for aquatic ecosystem protection, domestic and agricultural uses at all sites along the river in the dry season. Other pollutants such as NO_3, Na and Ca are of considerable priority since they exceeded the SAWQG for aquatic ecosystem protection and domestic uses along the whole profile of the Klip River and as such should be monitored for those uses in both the downstream and upstream zones..

Table 48: Framework for monitoring the upstream section water quality in the KRC (dry season).

Sites →	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
Variables↓												
pH												
EC												
Temp												
TDS												
Al												
As												
Ca												
Cd												
Co												
Cr												
Cu												
Fe												
K												
Mg												
Mn												
Na												
Ni												
Pb												
U												
V												
Zn												
NO_3												
P												

Key

	Domestic
	Aquatic Ecosystem Protection
	Agricultural uses –irrigation
	Not a priority

Electrical conductivity should be monitored for agricultural uses only, at all points in the upstream, whilst in the downstream it should be monitored for both domestic and agricultural uses. Total dissolved solids, K and Mg are of priority in terms of domestic uses along the whole profile of the Klip River. Cadmium is of priority with regards to agricultural uses in the Klip River at points A, B, C, F, G, K and L. However, points D, H and I should be monitored for aquatic ecosystem protection, domestic and agricultural uses. Furthermore, at sites E and J, Cd were in line with the SAWQG for aquatic ecosystem protection, domestic and agricultural uses are therefore not priority pollutants Other parameters which are predominantly not a priority for monitoring in the dry season include pH, temperature and Cu. However, for Cu, it should be monitored for all uses at site J and for domestic uses at site B.

In the wet season, the priority pollutants were As, Fe, Mn, U and Zn (Table 49). These pollutants were in excess of the SAWQG for aquatic ecosystem protection, domestic and agricultural uses along the whole profile of the Klip River in the 2016/17 season. As such, in the proposed framework, these pollutants are to be monitored for aquatic ecosystem protection, domestic and agricultural uses along the whole profile of the Klip River. Other pollutants of priority include Al, Ca and NO_3 which are to be monitored for both domestic and aquatic uses, and Na which should be monitored for domestic and agricultural uses.

Similar to the dry season TDS, K and Mg are of priority in terms of domestic uses along the whole profile of the Klip River. Temperature, Cd and Co are not a priority for monitoring at any point along the Klip River. Phosphates, Cr and Ni are not a priority at all points with the exception of sampling site B which has to be monitored for these pollutants for all the uses.

Table 49: Framework for monitoring the upstream section water quality in the KRC (Wet season).

	UPSTREAM							*DOWNSTREAM*				
Sites → **Variables** ↓	**A**	**B**	**C**	**D**	**E**	**F**	G	**H**	**I**	**J**	**K**	**L**
pH												
EC												
Temp												
TDS												
Al												
As												
Ca												
Cd												
Co												
Cr												
Cu												
Fe												
K												
Mg												
Mn												
Na												
Ni												
Pb												
U												
V												
Zn												
NO_3												
P												

Key

	Domestic
	Aquatic Ecosystem Protection
	Agricultural uses –irrigation
	Not a priority

5.5 Chapter summary

In this chapter, a synthesis of the findings from the previous objectives have been used to formulate a surface water quality management plan for the Klip River catchment. The surface water quality management plan highlighted the most impaired designated water use in the KRC as domestic uses in both seasons. The water in the Klip River is rendered unfit for domestic uses largely by heavy metals; nutrients and macrominerals in both seasons. This surface water quality management plan also identified the overall priority pollutants in the KRC as follows; As, Cr, Fe, Mn, Ni, Pb, U, V and Zn. These pollutants recorded elevated concentrations, which exceeded the SAWQG for aquatic ecosystem protection, domestic and agricultural uses throughout the study period and along the whole profile of the Klip River. As such, the main goal for water quality management was derived: to enforce compliance with SAWQG for domestic and agricultural uses as well as aquatic ecosystem protection in the Klip River through the reduction of heavy metal, nutrient and macromineral contributions. A management framework was presented for dealing with PS and NPS through the development and implementation of stormwater management, wetland rehabilitation and restoration; and BMPs amongst other strategies. Furthermore, a monitoring framework for the dry and wet season was developed. This outlines the parameters of priority per season, site and designated use. In the following chapter, a summary of the significant findings from this research and the contributions to contemporary studies in the area of water quality dynamics and management, as well as recommendations, are presented.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Synopsis

In this chapter, a synthesis of the significant findings from this research is presented. Furthermore, significant contributions to contemporary knowledge in the area of environmental chemo-metrics arising from this research are highlighted and the implications of the research findings are discussed. This then culminates into suggestions and recommendations for further research.

6.2 Introduction

The principal aim of this study was to monitor water quality trends in the Klip River so as to identify and describe the pollution sources, and to assess the spatial and temporal mechanisms governing water quality in the KRC and consequently formulate efficient methods of control and remediation of water quality. The specific objectives were (i) to assess the environmental risks associated with water quality characteristics (physicochemical, nutrients and heavy metals) in the Klip River catchment, (ii) to analyze the spatial and temporal trends of water quality in the Klip River catchment, (iii) to identify the critical sources of pollution in the Klip River catchment (iv) to evaluate the self-purification capacity of the Klip River and (v) to develop a framework for the monitoring and management of water quality in the Klip River catchment.

6.3 Research Summary

In this section a summary of the significant findings is presented.

6.3.1 Water quality in the KRC

The Klip River water quality is highly degraded. A majority of the water quality parameters in this study exceeded the SAWQG for domestic uses, aquatic ecosystem protection and agricultural use. Based on the HPI for aquatic, domestic and agricultural uses which were far above the critical index, it can be concluded that the heavy metal concentrations in the KRC render the water unfit for domestic and agricultural uses and also for sustaining aquatic life. In terms of the CRI, Cd poses a very high ecological risk, followed by As and Pb which pose considerable ecological risk. The rest of the metals pose moderate (Ni) to low ecological risks (Cr, Cu, Fe, and Zn). However, all the sampling points along the profile of the Klip River had very high PERI values, with the exception of sites E and J which had moderate PERI. As such, it can be concluded that, there is a significant threat to ecological communities in the Klip River from heavy metal pollution.

6.3.2 The spatio-temporal dynamics of water quality in the Klip River catchment

An analysis into the spatial and temporal characteristics for the Klip River resulted in the identification of homogenous water quality zones and seasons. Spatial Cluster Analysis yielded 2 zones; the upstream (A, B, C, D, E, F and G) and downstream (H, I, J, K and L). The rationale for the spatial grouping was attributed to land use activities atypical of these two zones. The upstream is characterized by mines, tailings dumps, WWTPs, informal settlements, industries and urban areas whereas the downstream section comprises of agriculture, urbanization and WWTP. Discriminant Analysis validated this classification at 100% and identified the discriminant parameters: As, Ca, Cd and Mg. The metal discriminants were higher in the upstream and the cations in the downstream.

The seasonal CA yielded 2 groups; 2015/16 comprising of the months February to June and 2016/17 comprising of the months July to January, of which the grouping was attributed to the El Nino and La Nina phenomena respectively. Discriminant Analysis validated this seasonal classification at 98.1%. The discriminant parameters; TDS, P, Ni and Cr were all higher in the 2015/16 season relative to the 2016/17 season, owing to the high evaporation rates and low flow conditions of the Klip River during this drought period. The high percentage of validation of DA aligns well with findings in contemporary literature that suggest CA is an efficient tool to study spatio-temporal dynamics of water quality.

6.3.3 Sources of pollution

The main sources of pollution during the 2015/16 season were mainly lithological, traffic, point discharges from industries and sewage effluents; and agricultural NPS from pesticide application. In the 2016/17 season, the sources of pollution were lithological processes, industrial, mining and agricultural NPS from use of phosphate and ammonia based fertilizers. Therefore, it can be concluded that the sources of pollution in the KRC vary with season i.e. the variables responsible for influencing water quality in one season differ in other seasons, which aligns well with findings from previous studies in other catchments. Furthermore, the CPI revealed that the KRC was critically polluted in the upstream with regards to domestic and aquatic uses in both the 2015/16 and 2016/17 seasons. The major contributors to this pollution were shown to be heavy metals with the exception of V, Pb and Cu, which were higher in the downstream. However, water quality in the downstream section of the KRC recorded high CPI for agricultural uses, rendering it unsuitable for any related activities.

6.3.4 Self-purification of the Klip River

The Klip River depicted high capacity for recovery for parameters such as Cd, Cr, Mn, Ni and Zn. This was attributed to self-purification processes such as adsorption to organic matter (Cd, Cr and Mn) dilution (Ni) and mineral crystallization (Zn). However, the Klip River failed to recover for metals such as Al, As, V and U, owing to inputs along the profile of the river from multiple sources of pollution. Using the CSUL, a spatial point of influx for many pollutants was identified as segment AB. This segment recorded the lowest CSUL for Al, As, Cd, Co, Cu, Fe, Mn, Ni and V. Pollution in this segment was attributed to seepage from tailing dumps and effluent from mining activities, which are located in the Witwatersrand region. However, in segment BC, the river managed to self-purify for majority of the metals and this was attributed to the dilution effect, owing to the influx of wastewater from treatment plants located in the vicinity of this segment.

6.3.5 Surface water quality management in the Klip River catchment

The most impaired designated water use in the KRC was domestic uses in both the 2015/16 and 2016/17 seasons owing to the majority of water quality parameters having exceeded the SAWQG for this use. The majority of these water quality parameters which impaired the Klip River with reference to domestic uses were heavy meals; nutrients and macrominerals in both seasons. Overall, priority pollutants in the KRC were identified as follows; As, Cr, Fe, Mn, Ni, Pb, U, V and Zn. The rationale being that these parameters exceeded the SAWQG for aquatic ecosystem protection, domestic and agricultural uses throughout the study period and along the whole profile of the Klip River. The goal for water quality management was identified as: reinstating the water quality in the Klip River for domestic and agricultural uses as well as aquatic ecosystem protection. Subsequently, a framework for monitoring and evaluation of water quality, as well as management measures for ameliorating PS and NPS pollution in the KRC was developed.

6.4 Limitations

Owing to limited financial resources, the microbial quality of the Klip River was not included in this study and also the length of period for collection of samples was limited to one year. However, coincidentally the period during which the samples were taken, was affected by the El Niño Southern Oscillation (ENSO) and La Niña phenomena which are associated with extreme dry temperature and heavy flooding respectively. Therefore the findings of this study represent a worst case scenario which is ideal for optimized water quality management. Also, the SAWQG for industrial and recreational uses have no information particularly with regards to a majority of the trace and heavy metals thus an analysis of the level of impairment of the Klip River with reference to uses was excluded in this study.

6.5 Research contribution to contemporary knowledge

The contribution of this study to contemporary knowledge is in respect of catchment classification, a methodology of CSUL and RRC in self-purification capacity and the development of a framework for managing water quality.

This research has contributed to contemporary knowledge on the *status quo* of water quality in the KRC as well as the associated risks to domestic, agricultural uses and the environment. Furthermore, the Klip River is a large river system and as such an undertaking to understand the spatial and temporal mechanisms governing its water quality had not been done before. *This research has closed that gap by classifying the catchment into homogenous water quality seasons and zones. The approach used can be applied in other catchments, for classification of pollution sources based on seasonal and spatial factors. This will enable an optimized approach to water quality management and it is ideal, as it enables the efficient utilization and distribution of resources for water quality management at the catchment level and other spatial spheres.*

Furthermore, this research has contributed to knowledge on the PS and NPS pollution in the KRC. *The successful use of both the CSUL and RRC in evaluating the self-purification capacity of the*

KRC for heavy metals is a contribution to contemporary knowledge. Previous studies which employed the RRC, did not consider the concept of positive or negative recovery and its implication thereof. But, in this study the concept has been clearly explained. This study has successfully demonstrated the ability of the CSUL in the identification of the spatial points of pollution influx, PS or NPS into the Klip River.

A surface water quality management plan was developed which identified the most impaired uses, pollutants of priority and the critically polluted areas. Consequently, *a framework for monitoring water quality in the KRC was developed which identifies priority pollutants per site, use and season*. Findings in this study can thus be used to inform the process of restoration and rehabilitation of the Klip River wetland, as well as manage its water quality. Additionally, this framework can be used as a guideline for monitoring and evaluation of water quality in catchments similar to the KRC. The surface water quality management framework for the KRC developed in this study, is unique in that it has a framework for monitoring and evaluating water quality, which specifies the parameters for monitoring, the use for which to monitor and the corresponding sampling sites. In doing so, water quality management strategies can be specific, based on the priority pollutants and zones and impaired use. Furthermore, this simplifies the efficient evaluation of the water quality management strategies. This approach can be systematically implemented in various other catchments and as such can be used for the formulation of policy and water quality management at the national level.

6.6 Conclusion

Based on the findings from this research, it can be concluded that the Klip River water quality is highly degraded, and poses significant risks to agricultural and domestic uses and is not suitable for aquatic ecosystem protection. Wetlands are areas of significant ecological importance, with the Klip River wetland playing a role of supplying water for various uses as well as purifying water in the Vaal River system. Nonetheless, the findings from this study have aligned well with findings from previous studies that observed that the wetland had lost its functionality and is headed for collapse owing to the elevated levels of heavy metals, nutrients and macrominerals in the Klip River. As such, there is an urgent need for wetland rehabilitation and restoration in this catchment.

Furthermore, seasonal and spatial factors influence water quality in the KRC as well as the sources of pollution. Consequently, water quality in the Klip River is generally poor overally, though its quality improves, although to a limited extent, towards the downstream. Additionally, water quality is more deteriorated during the dry season relative to the wet season. Subsequently, it can also be concluded that pollutants which influence water quality in the Klip River in one season and or location may not necessarily be the same in the other season or location. This assertion is true except for As, Mn, Fe and U, which remained pollutants of priority throughout the study period and along the whole profile of the Klip River. Although limited, the Klip River, has a capability to self-purify for certain parameters, by way of dilution, adsorption and mineral crystallization amongst other processes. However, there is an urgent need for human intervention, through the strict and systematic enforcement of environmental compliance for waste and wastewater management, environmentally sustainable mine closure planning and implementation and wetland conservation for any developmental activities in this catchment.

6.7 Recommendations

It is therefore recommended that:

- There should be a systematic and stringent enforcement of environmental and water resource management laws in the KRC: - the granting of environmental authorizations for development projects and monitoring of industrial and WWTPs effluent discharges into the Klip River,
- There should be the development of programs to rehabilitate and restore the Klip River wetland. Wetlands are sites of significant ecological importance and as such they should be conserved,
- The Catchment Management Agency (CMA) should initiate and implement programs on environmental education to conscientize farmers in the area on BMP and with regards to pesticide and fertilizers in terms of handling, transportation and storage. This study recommends training and monitoring of pesticide and fertilizer application.
- There should be stakeholder involvement in the design and implementation of water quality management in the KRC i.e. farmers, mining companies, informal settlements dwellers, competent authorities (Department of Environmental Affairs), relevant government

departments, so that there is commitment from their part, in their different capacities, to reduce pollution in the KRC.

- There should be development of SAWQG for industrial and recreational uses which incorporate the standards for heavy metals, nutrients and macrominerals. Furthermore for the other uses (domestic, agricultural and aquatic ecosystem protection) there were some parameters whose standards were not specified, warrantying an update of the current standards.

6.8 Areas of further research

Further research is recommended in the following areas:-

- River recovery capacity: further analysis into the processes driving self-purification.
- Spatio-temporal dynamics of microbial pollution in the KRC.
- An assessment of risks associated with industrial and recreational uses of water in the KRC, which were not included in this study because of the non-availability of standards.

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APPENDIX 1

Table 50: Total Variance Explained 2015/2016 season.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	10.130	44.044	44.044	10.130	44.044	44.044	9.099	39.560	39.560
2	3.434	14.931	58.975	3.434	14.931	58.975	4.150	18.042	57.602
3	2.668	11.601	70.575	2.668	11.601	70.575	2.243	9.753	67.354
4	2.091	9.090	79.666	2.091	9.090	79.666	2.036	8.851	76.205
5	1.552	6.748	86.414	1.552	6.748	86.414	1.781	7.742	83.947
6	1.115	4.847	91.261	1.115	4.847	91.261	1.682	7.313	91.261
7	.811	3.525	94.786						
8	.557	2.422	97.207						
9	.331	1.438	98.646						
10	.204	.889	99.535						
11	.107	.465	100.000						
12	1.144E-15	4.974E-15	100.000						
13	4.175E-16	1.815E-15	100.000						

14	3.851E-16	1.674E-15	100.000
15	2.520E-16	1.096E-15	100.000
16	1.199E-16	5.212E-16	100.000
17	-2.931E-17	-1.274E-16	100.000
18	-1.338E-16	-5.819E-16	100.000
19	-1.654E-16	-7.189E-16	100.000
20	-2.364E-16	-1.028E-15	100.000
21	-2.981E-16	-1.296E-15	100.000
22	-6.801E-16	-2.957E-15	100.000
23	-7.532E-16	-3.275E-15	100.000

Extraction Method: Principal Component Analysis.

Table 51 : Monte Carlo PCA for Parallel Analysis.

Eigenvalue #	Random Eigenvalue	Standard Dev
1	1.8245	.0817
2	1.6619	.0556
3	1.5541	.0403
4	1.4655	.0411
5	1.3835	.0367
6	1.3137	.0355
7	1.2430	.0329
8	1.1802	.0321
9	1.1184	.0299
10	1.0588	.0317
11	1.0040	.0351
12	0.9502	.0303
13	0.8959	.0281
14	0.8488	.0254
15	0.8019	.0252
16	0.7531	.0249
17	0.7029	.0248
18	0.6577	.0253
19	0.6144	.0283
20	0.5681	.0270
21	0.5204	.0282
22	0.4687	.0301

23	0.4102	.0308

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Table 52 : Communalities 2015/2016 season.

	Initial	Extraction
U	1.000	.544
AL	1.000	.365
As	1.000	.210
Ca	1.000	.871
Cd	1.000	.726
Co	1.000	.662
Cr	1.000	.636
Cu	1.000	.793
Fe	1.000	.627
K	1.000	.887
Mg	1.000	.866
Mn	1.000	.959
Na	1.000	.963
Ni	1.000	.537
Pb	1.000	.496
V	1.000	.590
Zn	1.000	.566
NO3N	1.000	.412
PO4	1.000	.888
pH	1.000	.888
temp	1.000	.830
EC	1.000	.958
TDS	1.000	.957

Table 53: Communalities 2016/2017 season.

	Initial	Extraction
U	1.000	.879
AL	1.000	.965
As	1.000	.713
Ca	1.000	.974
Cr	1.000	.991
Cu	1.000	.983
Fe	1.000	.988
K	1.000	.975
Mg	1.000	.998
Mn	1.000	.981
Na	1.000	.994
Ni	1.000	.991
Pb	1.000	.889
V	1.000	.875
Zn	1.000	.970
NO_3	1.000	.663
P	1.000	.973
pH	1.000	.972
temp	1.000	.937
EC	1.000	.989
TDS	1.000	.991

Table 54: Total Variance Explained 2016/2017 season.

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	10.087	48.035	48.035	10.087	48.035	48.035	7.468	35.562	35.562
2	5.180	24.668	72.703	5.180	24.668	72.703	6.706	31.935	67.497
3	1.850	8.808	81.511	1.850	8.808	81.511	2.503	11.921	79.418
4	1.501	7.147	88.658	1.501	7.147	88.658	1.589	7.568	86.986
5	1.072	5.105	93.763	1.072	5.105	93.763	1.423	6.777	93.763
6	.557	2.652	96.415						
7	.491	2.339	98.754						
8	.096	.456	99.210						
9	.091	.432	99.642						
10	.046	.219	99.861						
11	.029	.139	100.000						
12	1.290E-15	6.141E-15	100.000						
13	6.282E-16	2.992E-15	100.000						
14	4.373E-16	2.082E-15	100.000						
15	1.561E-16	7.434E-16	100.000						
16	5.901E-17	2.810E-16	100.000						

17	-1.438E-16	-6.848E-16	100.000
18	-2.932E-16	-1.396E-15	100.000
19	-4.550E-16	-2.167E-15	100.000
20	-7.339E-16	-3.495E-15	100.000
21	-8.831E-16	-4.205E-15	100.000

Extraction Method: Principal Component Analysis.

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APPENDIX 2: Ethical clearance

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Institutional Research Ethics Regulatory Committee

Tel: +27 18 299 4849

Email : Ethics@nwu.ac.za

ETHICS APPROVAL CERTIFICATE OF PROJECT

Based on approval by the Health Science Ethics Committee (FAST-HSEC) on 15/05/2017 after being reviewed at the meeting held on 09/05/2017, the North-West University Institutional Research Ethics Regulatory Committee (NWU-IRERC) hereby **approves** your project as indicated below. This implies that the NWU-IRERC grants its permission that, provided the special conditions specified below are met and pending any other authorisation that may be necessary, the project may be initiated, using the ethics number below.

Project title: Spatio-temporal dynamics of pollution and sources apportionment in the Klip River catchment (Gauteng), South Africa.

Project Leader/Supervisor: Prof L.G Palamuleni
Student: MARARA, T

Ethics number: N W U - 0 0 4 0 6 - 1 7 - A 9

Application Type: New Single Application

Commencement date: 01/06/2017 **Expiry date:** 31/05/2020 **Risk:** **No Risk**

Special conditions of the approval (if applicable):

- Translation of the informed consent document to the languages applicable to the study participants should be submitted to the HSEC (if applicable).
- Any research at governmental or private institutions, permission must still be obtained from relevant authorities and provided to the HSEC. Ethics approval is required BEFORE approval can be obtained from these authorities.

General conditions:

While this ethics approval is subject to all declarations, undertakings and agreements incorporated and signed in the application form, please note the following:

- *The project leader (principle investigator) must report in the prescribed format to the NWU-IRERC via HSEC:*
  - *annually (or as otherwise requested) on the progress of the project, and upon completion of the project*
  - *without any delay in case of any adverse event (or any matter that interrupts sound ethical principles) during the course of the project.*
  - *Annually a number of projects may be randomly selected for an external audit.*
- *The approval applies strictly to the protocol as stipulated in the application form. Would any changes to the protocol be deemed necessary during the course of the project, the project leader must apply for approval of these changes at the HSEC. Would there be deviated from the project protocol without the necessary approval of such changes, the ethics approval is immediately and automatically forfeited.*
- *The date of approval indicates the first date that the project may be started. Would the project have to continue after the expiry date, a new application must be made to the NWU-IRERC via HSEC and new approval received before or on the expiry date.*
- *In the interest of ethical responsibility the NWU-IRERC and HSEC retains the right to:*
  - *request access to any information or data at any time during the course or after completion of the project;*
  - *to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process.*
  - *withdraw or postpone approval if:*
    - *any unethical principles or practices of the project are revealed or suspected,*
    - *it becomes apparent that any relevant information was withheld from the HSEC or that information has been false or misrepresented,*
    - *the required annual report and reporting of adverse events was not done timely and accurately,*
    - *new institutional rules, national legislation or international conventions deem it necessary.*
- *HSEC can be contacted for further information via Mvsanchi.Sichembe@nwu.ac.za or 018 299 2319.*

The IRERC would like to remain at your service as scientist and researcher, and wishes you well with your project. Please do not hesitate to contact the IRERC or HSEC for any further enquiries or requests for assistance.

Yours sincerely

Prof LA Du Plessis — Digitally signed by Prof LA Du Plessis Date: 2017.05.26 10:12:08 +02'00'

Prof Linda du Plessis
Chair NWU Institutional Research Ethics Regulatory Committee (IRERC)

APPENDIX 3: PROOF OF LANGUAGE EDITING

NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
NOORDWES-UNIVERSITEIT
MAFIKENG CAMPUS

DEPARTMENT OF BIOLOGICAL SCIENCES

Tel: +27 18 389 [illegible] Fax: 018 389 [illegible]
Cell: +27 72 626 84 [illegible] E-mail: [illegible]

Date: [illegible] November, [illegible]

To Whom It May Concern.

REF: Language Editing and Proof reading of Dissertations/Theses

Dear Sir or Madam,

This serves to confirm that I have proof-read and edited the PhD thesis of **Taladzwa Marara (22082905; Orcid.org/0000-0002-0776-0261)** entitled: **Spatio-temporal Characterization and Pollution Sources Apportionment in the Klip River Catchment, South Africa**. The candidate then later corrected all the identified language and technical errors to my utmost satisfaction. Thus the document presented here is of sufficient and acceptable academic standards.

Thank you.

Prof. O Ruzvidzo