

**SEASONAL AND SPATIAL DISTRIBUTION OF
HEAVY METALS IN SURFACE WATER AND
SEDIMENTS OF MSUNDUZI RIVER,
KWAZULU-NATAL, SOUTH AFRICA**

By

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Submitted in fulfilment of the academic requirement for the degree of Master of Science in the School of Chemistry and Physics, College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Durban, South Africa

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As the candidate's supervisor I have approved this thesis/dissertation for submission

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Part of this work has been presented in a National conference:

Conference attended: 42nd National Convention of the South African Chemical Institute held at the Southern Sun Elangeni Hotel in Durban, South Africa from 29th November 2015 – 4th December 2015.

Title of the poster presented: Seasonal assessment of heavy metals and spatial distribution in surface water and sediments of Msunduzi River, KwaZulu-Natal, South Africa.

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ABSTRACT

Some physicochemical parameters and heavy metal concentrations of surface water as well as sediments in the Msunduzi River were investigated to provide information on the spatial and seasonal characteristic patterns of surface water quality, concentrations, chemical speciation and environmental risks of heavy metals in surface sediments. The physicochemical properties of surface water were determined following standard analytical procedures as described by the American Public Health Association (APHA). The levels of total metals in water and sediments were quantified by inductively coupled plasma-mass spectrometry (ICP-MS) after digestion with a mixture of acids, while the chemical speciation of heavy metals in the sediment was evaluated following the Community Bureau of Reference (BCR) sequential chemical extraction method.

The physicochemical, concentrations and chemical speciation patterns of heavy metals in the investigated samples showed significant ($p < 0.05$) spatial and seasonal variations. The value ranges for the measured physicochemical properties of water were: temperature 12.9 - 28.7 °C, pH 5.08 - 9.02, EC 84.0 - 1165 $\mu\text{S cm}^{-1}$, TDS 60.9 - 952 mg L^{-1} , DO 3.08 - 6.18 mg L^{-1} , Cl^- 8.73 - 102 mg L^{-1} , NO_3^- nd - 7.96 mg L^{-1} and SO_4^- 0.27 - 103 mg L^{-1} . Total metal concentrations in surface water for all seasons ranged from 0.22 - 5.44, 0.00 - 1.35, 0.80 - 50.2, 0.16 - 21.9 and 0.03 - 658 $\mu\text{g L}^{-1}$ for As, Cd, Cr, Pb and Zn, respectively while those of the sediment varied from 1.5 - 2.79, 42.26 - 246, 8.3 - 63.7 and 36.9 - 402 mg kg^{-1} for Cd, Cr, Pb and Zn, respectively.

The water quality index (WQI) for surface water based on physicochemical and heavy metal characteristics were 50, 85, 134 and 155 for autumn, winter, spring and summer, respectively. The WQI values for this river system fell within the “very poor quality” to “unsuitable for drinking” water categories. The ecological risk index indicated that there is low ecotoxicological risk associated with exposure to heavy metals in these sediments. The speciation patterns indicated that Cd, Pb and Zn were found mostly in the residual and Fe-Mn oxide phases while Cr existed mainly in the residual and oxidisable phases.

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LIST OF ABBREVIATIONS

DWAF: Department of Water Affairs and Forestry

ICP – OES: Inductively Coupled Plasma – Optical Emission Spectrometer

ICP – AES: Inductively Coupled Plasma – Atomic Emission Spectrometer

ICP – MS: Inductively Coupled Plasma – Mass Spectrometry

AAS: Atomic absorption spectrometry

MARS: Microwave Accelerated Reaction System

HPLC: High Pressure Ion Chromatography

IC: Ion Chromatography

ICP: Inductively Coupled Plasma

WHO: World Health Organisation

EPA: Environmental Protection Agency

XRF: X-ray fluorescence

SA: South Africa

CCME: Canadian Council of Ministers of the Environment

USEPA: United States Environmental Protection Agency

ZECC: New Zealand Environment and Conservation Council

TWQR: Target Water Quality Range

DWWW: Darvill Waste Water Works

WWTP: Wastewater Treatment Plant

COD: Chemical Oxygen Demand

EC: Electrical Conductivity

BCR: Community Bureau of Reference

CRM: Certified Reference Material

I_{geo} : Geoaccumulation index

RI: Ecological Risk Index

ER: Estimated Ecological Risks

WQI: Water quality index

SQG: Sediment Quality Guideline

PLI: Pollution Load Indexes

TEL: Threshold Effect Level

PEL: Probable Effect Level

TDS: Total Dissolved Solids

DO: Dissolved Oxygen

ND: Not detected

ANOVA: Analysis of Variance

CHAPTER ONE: INTRODUCTION

1.1 Background of the Study

Environmental contaminants and are found virtually in all environment compartments such as soil, air, water, sediment and biota. The occurrence of metals in the environment reflects the existence of natural or anthropogenic sources. The occurrence of high concentrations of toxic metals can adversely affect human health and the aquatic ecosystem through species loss, fishing restrictions and dietary restrictions on seafood. The concentrations of heavy metals in the water are relatively low compared to those found in the sediment. Low discharge of contaminant into water bodies may not adversely affect the water quality but long term process could lead to accumulation of the pollutant in the sediment (Iwegbue, 2007).

In aquatic ecosystems, sediments play indispensable roles as geochemical sinks of contaminants, and as natural media for the distribution of chemical materials and elements. These functions are influenced by changes in the environmental conditions including pH, and the redox potentials of the sediments. Sediment is a very sensitive indicator of contamination of the aquatic environment, and can provide a record of the history and sources of river pollution (Iwegbue, 2011) because of its role in the fate and transport of contaminants (Zhao *et al.*, 2010). Therefore, chemical fractionation is necessary to evaluate the behaviour and the impact of different phase associations of metals on the environment.

Metals present environmental and human health concerns because a number of them exhibit a wide spectrum of toxic and long-term health effects. They are resistant to degradation under natural conditions, and can be mobilized through a wide range of natural processes (such as

weathering and erosion of geological formations) and anthropogenic activities. Anthropogenic activities are by far the most important contributor to the metal burden in sediments rather than natural processes. During the mobilization process, metals may be adsorbed by clays and colloids or complexed with organic matter or co-precipitate with oxides or hydroxides (Liaghati *et al.*, 2004). Metals enter into the aquatic food chain via absorption from the water and sediment, by benthic feeding habits, and subsequently become biomagnified along the food chain, and attain highest level in higher consumer fish tissues at the top of the aquatic fish chain (Atalar *et al.*, 2013).

The potential contamination of aquatic ecosystem can be assessed through the chemical analysis of surface sediments given the fact that it represents the contemporary environmental conditions (Prudencio *et al.*, 2007; Pradit *et al.*, 2010). Metals exist in different geochemical forms or phases in the sediments, which include those that are (i) water soluble or participate in ion-exchange reactions, (ii) precipitated as carbonates, (iii) occluded in Fe, Mn and Al oxides/hydroxides, (iv) complexed with organic matter and (v) incorporated in the crystalline lattice of clay. Metals in water soluble/exchangeable forms and those that are precipitated as carbonates are very mobile and readily available to plants, whereas those that are incorporated in the crystalline lattice of clay are relatively inactive (Sungur *et al.*, 2014). However, metals bound in Fe-Mn oxides/hydroxides or complexed with organic matter can be relatively active or firmly bound depending upon the prevailing physicochemical properties of the soils (Iwegbue, 2007). The sequential extraction method provides detailed information on the origin, mode of occurrence, biological and physicochemical availability, mobilization and transportation of metals (Sungur *et al.*, 2014).

A number of sequential chemical extraction schemes have been applied for the partitioning of metals in various solid phases in soils and sediments (Gupta and Chen, 1975; Stover *et al.*, 1976; Tessier *et al.*, 1979; Sposito *et al.*, 1982; Rauret *et al.*, 1989; Rauret, 1998; Rauret *et al.*, 1999; Ma and Rao 1997; Salbu *et al.*, 1998). The European Community Bureau of Reference (BCR) standard sequential extraction provides reliable results as compared to other sequential extraction methods (Usero *et al.*, 1998; Rauret *et al.*, 1999; Soylak *et al.*, 2004; Sysalová and Száková, 2007; Doelsch *et al.*, 2008; Saracoglu *et al.*, 2009). The BCR sequential extraction method has three steps to recover metals that are: exchangeable and bound to carbonates; reducible (bound to Fe–Mn oxides) and oxidizable (bound to organic matter and sulphides). The last step concerns those metals bonded to minerals that can only be liberated by using strong acid solutions.

1.2 Research Motivation

The Msunduzi River is a stream of the Umgeni River, which runs into Inanda Dam that is Durban's primary water supply and flows out into the Indian Ocean in Durban, South Africa (Neysmith and Dent, 2010). The Msunduzi River suffers from disposal of solid and liquid waste into the river system. A number of previous studies have examined the organic pollutants in Msunduzi River (Matongo *et al.*, 2015, Agunbiade and Moodley, 2015, Gemmell and Schmidt, 2013, Manickum *et al.*, 2011). Shoji, 2015 was the first to conduct a study to analytically examine the spatial distribution and seasonal variation of heavy metals in the aquatic column and sediment of this tributary. The focus area of this work is mainly based on inorganic pollutants such as heavy metal pollution (As, Cd, Cr, Pb and Zn).

1.3 Aims and Objectives of the Study

The purpose of this work was to examine spatial and seasonal variation on heavy metal distribution, anions and physicochemical properties in surface water and sediments from nine locations along the Msunduzi River in South Africa.

The objective of this work was to:

- Quantify the levels of anions in surface water for all four seasons.
- Determine the total and bioavailable content of heavy metals in sediments along the Msunduzi River as a function of season.
- Determine the total concentration of heavy metals in surface water of the Msunduzi River as a function of seasonal variation.
- Apply different statistical techniques and pollution indices or factors to assess for metal pollution or contamination.
- Discuss possible sources of heavy metals.

1.4 Significance of the Study

This study provides information on the concentrations of metals in the surface water and sediments of Msunduzi River. The data obtained in this study complements the array of data currently available on the pollution status of rivers in South Africa. Such information is necessary in designing strategies for surveillance programmes, pollution control measure, risk and local environmental quality management.

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CHAPTER TWO: LITERATURE REVIEW

2.1 Climate Change

Climate change is caused by both natural and anthropogenic activities, which affect processes such as volcanic eruptions, rising of an oceans temperature and leads to melting of ice in the poles. As a result there is variation in rainfall patterns which causes floods and droughts. Anthropogenic activities include combustion of fossil fuels (coal, gas and oil), and deforestation because of urban growth and agriculture. These activities release greenhouse gases into the atmosphere. Greenhouse gases are carbon dioxide, methane, nitrous oxide, chlorofluorocarbons and ozone (Change, 2007, Houghton, 2005). Greenhouse gases at an acceptable level are needed to keep the planet warm and stable. However, above acceptable levels, these gases in the atmosphere lead to global warming which causes instability of our planet. The world is faced with the persistent threat of climate change. Global temperatures and warming rate have increased worldwide over the last 100 years (Adger *et al.*, 2003, Power *et al.*, 2005).

2.2 South African Water Shortage

South Africa is faced with water shortage; the available water resources cannot meet the needs of South Africans. The country has a mean rainfall of 450 mm annually, which is lower than the worldwide mean of 860 mm (Strydom, 2010). In addition, South Africa has relatively few free standing natural water bodies (lakes and pans), which naturally store water for future usage, during dry seasons and drought. Yearly evaporation surpasses rainfall through a factor of 1.2 to 4, and approximately 8% of annual rainfall becomes available as surface runoff. Large areas of South Africa experience unpredictable extremes of drought and floods (Miller, 2002). For instance, the Cape Town area goes through a ‘Mediterranean’- type of weather pattern where rainfall occurs throughout the year with maximum rainfall in winter

(New, 2002). On the contrary, the weather pattern of Johannesburg shows a wet period during summertime (October – April) with the province being arid for the rest of the year (ARUP, 2009).

South Africa's freshwater resources including rivers, lakes and groundwater are excessively enriched and are considered to be moderately to highly eutrophic (Oberholster and Ashton, 2008). Contaminated water can have a harmful effect on the wellbeing of humans; river systems and has negative financial implications for different divisions of the economy as well as farming and other industries. (Oberholster and Ashton, 2008, Sharma *et al.*, 2014). Industrialisation and urbanisation has a major impact in deterioration of the country's water resources. The demand for water in South Africa has grown such that the major rivers have been modified with dams. The water resources are developed to supply the majority of the urban, industrial and agricultural needs.

Water usage in South Africa by irrigation accounts for 62%, by means of household and municipal use (as well as water used for industries delivered by water boards) accounts for 27% by mining, big industries and power production accounts for 8%, and by marketable forestry farms account for less than 3% of water used by decreasing overflow into rivers and tributaries (DWAF, 2004). Agricultural development also increases as pollution increases which in turn leads to an increased demand for irrigation water. It is projected that South Africa's water resources will be completely exhausted and incapable of meeting the requirements of societies and businesses by 2030 (Jackson *et al.*, 2009b, Oberholster and Ashton, 2008). By 2025, two thirds of the world's inhabitants are expected to live in nations with severe water availability (Azizullah *et al.*, 2011).

Water is essential for existence; it is a vital component of all living organisms. It is crucial for economic development, is needed in industries such as power generation and mining operations. Furthermore, humans need safe water for drinking, health, sanitation and agriculture. The right to use non-toxic water is described in South Africa's constitution as a simple human right (Murthy *et al.*, 2014). The natural features that contribute to aquatic contamination are gases, soil, minerals and waste from wildlife. (Begum *et al.*, 2009). Chemical industries, domestic waste and agricultural activities are responsible for poor water quality. Some chemical industries discharge their untreated waste products directly into the river systems. Even the waste goods that are discarded by landfill sites release substances that could leach into groundwater systems. Fertilisers used in agriculture prepared from sludge and animal waste is contaminated with minerals, which are washed off into river systems during rainy seasons. Contaminated runoff water enters the rivers and contaminants partition to sediments and soil (Gambhir *et al.*, 2012).

2.4 Chemical Composition of river water

2.4.1 Physicochemical parameters

The elemental composition of water and sediments consist of the physical factors, anions, total metals and extractable metals as these describe the quality of river water (Singovszka and Balintova, 2012). The chemical composition of an aquatic system is dependent on many aspects, including the weathering of rocks, strength and conformation of the precipitation in that region, chemical reactions that take place between the water and sediment, and contamination from different causes (Murthy *et al.*, 2014). Physicochemical factors such as pH, electrical conductivity (EC), total dissolved solids (TDS) and dissolved oxygen (DO) are important parameters that influence accumulation of heavy metals. For that reason, in order

to comprehend the ecological chemistry of metals, it is essential to take account of the physicochemical factors, particularly the quantity of free metal ions (Okonkwo and Mothiba, 2005). The contamination of water by metals brings noticeable deviations in physicochemical properties and makes the water poisonous to several life forms (Rai, 2010).

The pH of an aquatic system regulates the chemical species of many metals as well as changes their accessibility and toxicity in a water environment. Speciation and bio-availability of metals in aquatic systems are dependent on pH (Fatoki and Awofolu, 2004). Low pH (acidic range) values, of less than 4, typically raise the harmfulness of most metals because they are stable at this pH. The temperature of water has an effect on the chemical and biological reactions that take place in aquatic forms. The increased temperatures raise the toxicity of heavy metals and insecticides, and furthermore increase the sensitivity of existing organisms to poisonous materials (Akiya and Savage, 2002). The sample temperature and the temperature at which physicochemical measurements are taken are significant for information correlation and elucidation purposes. Low DO, temperature and pH also affect the diversity and population of aquatic organisms in surface water other than heavy metals.

Electrical Conductivity (EC), is the of ability of a water sample to carry an electric current and it is associated with the concentration of ionised substances in the water (Radojević and Bashkin, 1999). The conductivity of water is influenced by the presence of H^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and HCO_3^- . Other ions such as Fe^{2+} , Fe^{3+} , Mn^{2+} , Al^{3+} , NO_3^- and $H_2PO_4^-$ have minor influences on the conductivity (Radojević and Bashkin, 1999). Conductivity is sensitive to temperature, as the temperature increases the conductivity also increases thus increasing the toxicity of metals in water. Temperature affects the solubility and availability of oxygen in aquatic environments.

The low DO conditions decrease redox potential and thus alter the conformation of metal complexes and may discharge metal ions into the overlying water (Okweye and Golson-Garner, 2012). Oxygen deficiency is fatal to fish, and many types of aerobic bacteria. Fish kills occur when exposed for a few hours to DO concentrations below 3 mg L⁻¹ (Okweye and Garner, 2013, Haddad and Jackson, 1990, Neysmith and Dent, 2010).

2.4.2 Anions

Anions provide nutrients in aquatic systems (Ashraf *et al.*, 2012). Generally, ground water and surface water have low concentrations of nitrates (Azizullah *et al.*, 2011). Nitrogen is released into environmental water through different sources such as animal and chemical fertilizer run-off and sewage. Sulfate occurs naturally in surface water as SO₄²⁻ ions. The source of sulfate in surface water include atmospheric deposition of oceanic aerosols and leaching of sulfur compounds, also sulfate minerals like gypsum or sulfide mineral such as pyrite, from sedimentary rocks. Industrial discharges and atmospheric precipitation which is produced by the burning of fossil fuels and in metallurgical roasting practices, may possibly contribute to the amount of sulfate in surface water.

The high levels of nitrate and sulfate in aquatic systems are usually used as indicators of contamination status and anthropogenic capacity. Increased amounts of nutrients in aquatic systems cause a process called eutrophication. Eutrophication is a form of water pollution, whereby the aquatic environment becomes enriched with nutrients mainly nitrogen and phosphorus. Nutrient pollution often causes algae growth and aquatic plants which reduces the levels of DO in aquatic systems. These result in death of various aquatic creatures like fish which require the oxygen in the water to survive (Morrison *et al.*, 2001, Oluyemi *et al.*, 2010, Chigor *et al.*, 2012, Suthar *et al.*, 2010).

2.4.3 Metals and metalloids

Metals are good conductors of electricity and heat. Metals are elements that contain silvery luster (Jayaraju *et al.*, 2011). Arsenic and selenium are metalloids, they have both properties of metals and non-metals. However, they are often classified as heavy metals. Metals can occur in a positively charged form and can bind onto negatively charge organic molecules to produce complexes (Appenroth, 2010). Heavy metals are defined as those elements that consist of large atomic mass plus a specific density of more than 5 g cm⁻¹ (Fernández-Luqueño *et al.*, 2013, Yahaya *et al.*, 2012). They are inorganic elements which can exist in surface water as soluble form (free ions) or as particulate form (adsorbed to suspended solids).

The total metal concentration is defined as the sum of the concentrations of the dissolved and particulate forms. The particulate metals often fall to the bottom of the river, lakes and additional aquatic forms (Tao *et al.*, 2012). The behaviour of metals in aquatic environments is influenced by their different types and binding state (complexed by the organic complexes), which effect their mobility, bioavailability and harmfulness to animals and plants. The potential effects of contaminated compounds are also determined by their physicochemical forms (Al Obaidy *et al.*, 2014, Jiang *et al.*, 2013, Yahaya *et al.*, 2012, Papafilippaki *et al.*, 2008, Tao *et al.*, 2012).

2.4.3.1 Arsenic

Arsenic (Ar) occurs naturally in rocks, soil, water and air. The main anthropogenic sources of arsenic are manufacturing of non-ferrous metals, the manufacture and use of arsenical insecticides, timber stabilisers and the production of energy from fossil fuel (MacDonald *et al.*, 2000, Chakravarty and Patgiri, 2009). Inorganic arsenic exists in groundwater used for drinking in certain countries, whereas organic arsenic compounds are mainly found in fish

(Wang *et al.*, 2011). The arsenic concentration in natural waters is usually less than $10 \mu\text{g L}^{-1}$, and ranges from 1 to 40 mg kg^{-1} in soils (Järup, 2003). The challenges encountered by existing water investigations is dealing with increased levels of arsenic in drinking water, of which, it has been a worldwide problem (Smith *et al.*, 1996).

2.4.3.2 Cadmium

Cadmium (Cd) is a soft, silverish metal that has an atomic number of 48 and an atomic mass of 112. The main stable oxidation state of most cadmium compounds is +2. It is commonly known for the mineral called Greenock (cadmium sulfide, CdS) (Connell, 1845). Cadmium minerals are usually associated with zinc, lead and copper minerals, since it is manufactured as a by-product from heat up and purifying of zinc, lead and copper ores. Cd occurs naturally in the environment by erosion of rocks and soil. It enters the environment anthropogenically through wastes from manufacturing practices such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining (Rino *et al.*, 2008, Mohiuddin *et al.*, 2016, Haribhau, 2012).

In aquatic environments, Cd is more transportable in acidic environments in pH below 5.5. The average concentration in surface water has been reported to be $< 0.5 \mu\text{g L}^{-1}$ (Kamala-Kannan *et al.*, 2008). Cadmium is very toxic to living organisms even if present in low concentrations. Humans are exposed to Cd through ingestion of food and tobacco smoke. Smokers have higher concentrations of cadmium in their blood and kidneys as compared to non-smokers (Satarug and Moore, 2004). Cadmium tends to accumulate in the kidneys as later causes kidney disease. Health effects of cadmium exposure include cancer risk, renal injuries and bone problems (Järup *et al.*, 1998).

2.4.3.3 Chromium

Chromium (Cr) is a white, hard and brittle metal, it is odourless and tasteless. It belongs to group six and has an atomic number of 24. The name chromium was derived from a Greek name *chroma* meaning colour, due its coloured compounds. Chromium is amongst the seventh most abundant elements in the earth's layer and its commonly known for its mineral called Crocoite (PbCrO_4) (Islam *et al.*, 2016). Chromium exists in many oxidation states, from -2 to +6. Although many different oxidation states of Cr occur in the environment, Cr^{3+} and Cr^{6+} are the most stable. Cr^{6+} being the most toxic form and carcinogenic (Katz and Salem, 1993). Trivalent chromium occurs naturally in many vegetables, fruits, meats, yeasts and grains. A number of ways of food preparation and storage may change the chromium contents of food. When food is stored in steel tanks or cans, chromium concentrations may increase (Haribhau, 2012).

Chromium is used in stainless steel, chromium plating e.g. cars, and can also be used as a catalyst. Chromium occurrence in the environment is due to discharge of waste (gaseous, liquid and solid) from industrial processes such as pigment, tannery waste, leather manufacturing waste and municipal sewage waste (Nzeve *et al.*, 2015). In aquatic systems, Cr enters natural waters through natural sources such as weathering of rocks and leaching from soils. The concentration range of Cr in natural waters is up to 0.117 mg L^{-1} with an average of 0.0097 mg L^{-1} (Hakanson, 1980, Yi *et al.*, 2011). Chromium is an essential trace element for functioning of living organisms. It has been reported in human nutrition to be responsible for glucose metabolism (Turekian and Wedepohl, 1961). Inhalation of Cr^{6+} can cause asthma, bronchitis, pneumonitis and liver problems while skin contact may cause skin allergies and dermatitis (Guo *et al.*, 2010).

2.4.3.4 Lead

Lead (Pb) is a non-essential metal that is harmful even at low concentrations in aquatic systems (Cude, 2001). The elevated levels of lead in the ecosystem are mainly owed to man-made activities. Lead releases to ambient air have contaminated the atmosphere. However, lead emissions in developed countries have reduced over the past few decades due to the introduction of unleaded gasoline (Järup, 2003). The possible sources of lead in river systems are soil erosion, municipal and industrial wastes and runoff. Studies have revealed that elevated Pb quantities in natural aquatic resources are attributed to anthropogenic activities (Nelson, 2015). The typical levels of Pb in river water is less than 0.010 mg L^{-1} (DWAF, 1996a).

2.4.3.5 Zinc

Zinc is an essential nutrient for body growth and development. However, drinking water containing high levels of Zn may lead to stomach cramps, nausea and vomiting.. Zinc is introduced into aquatic systems through leaching from fertilisers, effluent from industries during mining and smelting, urban runoff, municipal sewage, by-product of steel production and coal fired power stations (Nelson, 2015, Nzeve *et al.*, 2015, Iwegbue *et al.*, 2012b). Zinc concentrations can range from 0.02 to 1000 mg L^{-1} in river systems closer to mining activities (Ryan *et al.*, 2002).

2.5.1 Heavy metals in aquatic environments

Heavy metals that originate from anthropogenic activities are often detected in sediments than water column. Contamination by these heavy metals can be expressed by their high concentrations in water, as well as in sediments and aquatic organisms (Zhang *et al.*, 2015, Nzeve *et al.*, 2015, Okweye and Garner, 2013).

Some heavy metals can cause death to aquatic animals. The presence of metals in water becomes harmful when the concentrations present rise above that of the background concentrations found in water and sediment (Greenfield *et al.*, 2012). Therefore, it is crucial to quantify the levels of metals in both surface water and surface sediments. Heavy metals are present in low concentrations of up to nanogram to microgram per litre in natural aquatic ecosystems (Aliyu *et al.*, 2015). Quantification of heavy metal in both surface water and sediments and comparison with reference levels is a reliable indicator of aquatic environmental health.

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years due to their toxicity. They accumulate in aquatic river systems and are able to reach toxic levels in short period. These metals are usually found in agricultural and industrial liquid waste which are discharged into river systems (Murthy *et al.*, 2014, Haribhau, 2012). Their removal from the aquatic environment is quite difficult and sometimes impossible since they are very persistence. They can cause long-term irreversible effects if present above the normal concentration limit. As the metal levels in many aquatic environments increase due to anthropogenic activities, they raise concerns on metal bioaccumulation through the food chain and related human health hazards such as development retardation, kidney damage and cancer (Nzeve *et al.*, 2015, Wei and Yang, 2010, Bichi *et al.*, 2013).

During their transportation, heavy metals undergo various changes in their chemical speciation because of their dissolution, sorption, precipitation and complexation occurrences which affect their behavior and bioavailability (Islam *et al.*, 2015, Akcay *et al.*, 2003, Nicolau

et al., 2006). The concentration of heavy metals in aquatic systems varies seasonally depending on their distribution. Seasonal variations have a huge influence on metal distribution in aquatic ecosystems. Seasonal deviations in agricultural activity, storm water runoff, interflow and atmospheric deposition also has strong impact on river water quality (Li and Zhang, 2010, Jin *et al.*, 2012). Therefore, characterization of seasonal variability in surface water quality is an important characteristic for assessing variations of aquatic ecosystem pollution. The heavy metal concentration is generally higher in wet season as compared to dry season due to seasonal differences of river discharge and rainfall (Zhang *et al.*, 2015).

Excessive build-up of heavy metals in agricultural soils may result in high heavy metal uptake by crops, which may affect food quality and safety (Hakanson, 1980). Heavy metals in aquatic systems accumulate in living organisms such as fishes, thus providing a pathway into the human food chain (Murthy *et al.*, 2014). They enter the human body through the food chain via contaminated water and food, and are known to have serious health implications. They can also accumulate in the human body via inhalation and skin contact. Plants such as fruits and vegetables, and water are the medium of passage of heavy metals into human systems.

2.5.2 Speciation and bioavailable metals

Sediments are important material of river systems, they provide nutrients for aquatic organisms. The chemistry of sediment is normally regulated by natural and anthropogenic factors such as regional geology, biology, climate, mining and cultivation. They can be indicators for monitoring pollutants in aquatic environments and are important for the water quality (Ajibola and Ladipo, 2011, Sankar *et al.*, 2010, Jiang *et al.*, 2013, Ko *et al.*, 2012).

Sediments act as a potential sink for various contaminants (Dumčius *et al.*, 2011; Bai *et al.*, 2011; Fatoki and Awofolu, 2003; Turki, 2007). They are polluted with different kinds of hazardous and toxic substances including heavy metals. Heavy metals enter the sediments through complex physical and chemical adsorption mechanisms which depend on the nature of the sediment matrix and the properties of adsorbed compounds (Raulinaitis *et al.*, 2012, Iwegbue *et al.*, 2012b).

Study of sediments allows contaminants that are adsorbed by particulate matter, which could not be detected by water analysis, to be identified (Pejman *et al.*, 2015, Ajibola and Ladipo, 2011, Iwegbue *et al.*, 2012b). High concentrations of metals often deposit in the river sediments, and can be a good indication of anthropogenic influence rather than natural influence. Heavy metals that are present in surface sediments are inert, and are often considered as the conservative pollutants. However, they may return to surface water in a much more toxic form once fluctuations in environmental state such as pH occur, which then introduces possible environmental hazards to aquatic organisms (Bai *et al.*, 2011; MacDonald *et al.*, 2000; Long *et al.*, 1995; Cude, 2001).

The possible environmental threat of heavy metals in sediment is determined by total concentration and speciation. The information on total metal concentration alone is not sufficient for the assessment of environmental impact of sediment contamination which leads to the particular concern of chemical fractionation of sediment. The knowledge of the total concentration and chemical forms of metals in soils are necessary to characterize their behaviour, mobility, and bioavailability. Metals in the soil, exist in different chemical forms, which influences their reactivity, mobility and bioavailability (Muruvu and Tekere, 2013) .

Table 2.1 The effects of heavy metals on human health.

<i>Heavy Metal</i>	<i>Exposure route</i>	<i>Causes</i>	<i>Reference</i>
<i>Arsenic</i>	Ingestion, and smoking cigarettes	Wounds on skin, heart and liver, respiratory complications, chronic renal failure, cytogenic damage, hypertension, lung function failure, coughing and chest problems	(Osman and Kloas, 2010, Oguzie and Okhagbuzo, 2010, Nawiri <i>et al.</i> , 2013, Lokeshwari and Chandrappa, 2006, Greenfield <i>et al.</i> , 2012)
<i>Cadmium</i>	Ingestion	Kidney failure, lasting renal breakdown and it is absorbed through the alimentary tract, enters over placenta for the period of pregnancy, dangers of miscarriage, and damages membranes and DNA	(Jackson <i>et al.</i> , 2009a, Oguzie and Okhagbuzo, 2010, Nawiri <i>et al.</i> , 2013,)
<i>Chromium</i>	Inhalation, skin contact and ingestion	Cancer	(, Malik <i>et al.</i> , 2014)
<i>Lead</i>	Ingestion	Blood composition, chronic renal failure, Parkinsons disease and neurodegenerative disorders	(, Chatterjee and Raziuddin, 2002, Yogendra and Puttaiah, 2008, Oguzie and Okhagbuzo, 2010)
<i>Zinc</i>	Ingestion	Accumulation in muscle and liver	(Fu <i>et al.</i> , 2013, Wojtkowska, 2011)

The behaviour and availability of heavy metals depends on their chemical form and their speciation. The chemical speciation of heavy metals plays an important role in its bioavailability. Metals can be separated into different chemical forms that are associated with a variety of organic and inorganic phases which influence their bioavailability, mobility and toxicity to organisms. These forms are water soluble, exchangeable, carbonate bound, Fe-Mn oxides bound, organic matter bound, and residual (Yang *et al.*, 2009, Turki, 2007, Jiang *et al.*, 2013, Iwegbue *et al.*, 2016, Arimoro *et al.*, 2007).

Generally, the mobility of heavy metals decreases in the order of extraction sequence. The exchangeable and carbonate bound fractions are considered to be weakly bounded metals which may equilibrate with the aqueous phase and become more bioavailable. The Fe-Mn oxides and organic matter fractions have been identified as the main components that play a major role in the control and transport of heavy metals. These fractions may be affected by a change in physicochemical parameters and be transformed back to exchangeable or carbonate bound fractions (Theurillat *et al.*, 2014, Huong *et al.*, 2012).

The distribution of pollutants is among most essential information for environmental research. Chemical speciation and distribution of heavy metals in the specific chemical fraction has been used in predicting their potential contamination, mobility and bioavailability. Heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Sn and Zn are of major interest in bioavailability and toxicology studies because of the potential for increased environmental and health risk.. Heavy metals from anthropogenic activities are usually introduced into river systems as inorganic complexes which are easily adsorbed on the surfaces of sediment particles through relatively weak physical or chemical bonds. Thus,

heavy metals of anthropogenic origin are found mostly in the labile extractable fraction of sediment (Vuković *et al.*, 2014, Vuković *et al.*, 2011).

The choice of sediment grain size is very important in assessing metal concentrations in sediments. The recommended sediment particle size is fraction $< 63\mu\text{m}$ for heavy metals since this fraction can be easily carried in suspension and is the most important system for transport of sediments (Jayaraju *et al.*, 2011). Sediment grain size followed by a complete digestion plays an important role in bonding of heavy metals in size fractions.

2.6 State of the Rivers

2.6.1 The Asian continent

Asia is the biggest continent in the world with a population of over four billion population (Rino *et al.*, 2008). The continent suffers from environmental issues such as large amounts of heavy metals that have been found in drinking water (Fernández-Luqueño *et al.*, 2013). The heavy metal contamination in Bangladesh is a challenge. The river systems in the country receives large amount of untreated industrial wastes and heavy metal enriched with suspended solids coming down from India through the Teesta and the Brahmaputra Rivers (Ghosh, 2002). The Korotoa River, which is linked to river Teesta and Brahmaputra, has raised public attention due to its high pollution (Islam *et al.*, 2016).

The river Korotoa is situated in the capital city of Bangladesh. Islam *et al.* (2015) conducted a study to evaluate the contamination status of the Korotoa River by measuring the concentrations of heavy metals in water and sediment. The quantification of heavy metals such as Cr, Ni, Cu, As, Cd and Pb was done by ICP-MS in surface water and sediment. The results showed a decreasing trend of metals in water as $\text{Cr} > \text{Cu} > \text{As} > \text{Ni} > \text{Pb} > \text{Cd}$ and in

sediment as $Cr > Ni > Cu > Pb > As > Cd$. The concentrations of Cr, As, Cd and Pb were greater than the safe restrictions for water consumption, which made the water from this river unsafe for human consumption. The heavy metal pollution in this study was credited to anthropogenic activities such as municipal sewage, house hold waste and manufacturing waste from nearby inhabitation (Islam *et al.*, 2015).

Peifang *et al.*, (2014) did a study that focused on seasonal and spatial distribution of total amounts and chemical forms of heavy metals and the pollution assessments in Taihu lake. Taihu lake is the third biggest freshwater lake in China, and is located in the most developed areas with high population. The lake is used as an important source of drinking water by cities such as Wuxi and Suzhou. However, the lake suffers from water pollution that is due to industrial wastewater and sewage discharged from a nearby industrial zone which contains huge amounts of heavy metals such as Cd, Zn and Cu (Ibanez *et al.*, 2008, Reichle *et al.*, 1975). The aquatic plant life that grows in the lake, especially in summer, results in eutrophication which affects the quality of available drinking water.

The heavy metals such as Cd, Cr, Cu, Ni, Pb, and Zn studied in this lake were analysed in surface sediment by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). The study showed that Cd and Zn were high while Cu, Pb and Cr were within background concentration ranges. The concentration of Pb, Zn, Cu, Cr, and Cd were highest in spring and Pb, Cd, and Cr were lowest during autumn. The fractionated metals, Zn and Cd, were observed to be bioavailable which could have possible mobility in the water system. The I_{geo} values revealed that almost all the sediment was strongly contaminated by Cd. They concluded that the sediment of Taihu Lake was polluted by Cd (0.70 - 6.23 mg kg⁻¹), Zn (40.54 - 456.63 mg kg⁻¹), and Cu (20.52 - 78.8 mg kg⁻¹) (Peifang *et al.*, 2014).

The Yamuna River is one of the most contaminated rivers in India owing to discharge of raw domestic and industrial effluents into the river. The river suffers from organic and inorganic pollution. A study done by Sen (2011) for quantification of heavy metals in fish types revealed that the concentration of heavy metals found in the fish samples were higher than the maximum acceptable limits of the World Health Organisation (WHO) (Ma and Rao, 1997). A research of heavy metals was conducted by Sehgal (2012) in water and soil of Yamuna basin. The main outcomes of the study were: mean heavy metal concentration at different locations in the river water differed in the manner of $Fe > Cr > Mn > Zn > Pb > Cu > Ni > Hg > As > Cd$ and the average heavy metal concentration at different locations in soil varied in the order of $Fe > Mn > Zn > Cr > Pb > Ni > Hg > Cu > As > Cd$ (Feng *et al.*, 2006). The industries which discharge directly into the river are the possible cause of the heavy metals in the Yamuna, leading to serious harmful effects on humans, aquatic species and plants (Malik *et al.*, 2014).

Al Obaidy *et al.* (2014) examined the heavy metal concentration status of surface water of the Mahrut River. The Mahrut River is located in Diyala City of Iraq, and is mainly used for irrigation. The concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were measured by Atomic absorption spectrometry (AAS). The concentrations of heavy metals in the surface water samples were found to be in the order: $Cr > Pb > Fe > Ni > Mn > Cu > Cd > Zn$ for the wet season and $Cr > Fe > Ni > Mn > Cu > Pb > Cd > Zn$ for the dry season. The detected levels of Cd, Cr, and Pb exceeded the recommended value for river sustaining systems whereas Cd, Cr, Cu and Pb levels were above the guidelines values for protection of aquatic life. According to Al Obaidy *et al.* (2014) the heavy metal pollution in Mahrut River was mainly influenced by anthropogenic activities rather than natural activities (Al Obaidy *et al.*, 2014).

The Xiawangang River is located near a smelting and chemical industrial region. The river is considered to be the one of the most contaminated regions in China. The assessment of heavy metal pollution of surface sediments and nearby soils of Xiawangang River was done by Jiang *et al.* (2013). The contents and fractions of Cd, Cu, Pb and Zn were investigated by AAS. The concentrations of the studied heavy metals were greater in soil samples compared to sediment samples, with Zn and Pb being the highest. Pollution evaluation according to I_{geo} revealed that Cd, Cu, Pb and Zn contaminated both soil and sediment. Correlation analysis showed that Cd, Cu, Pb and Zn possibly originate from comparable contamination pollution sources such as human activities especially industrial inputs (Jiang *et al.*, 2013).

2.6.2 The African continent

Africa is the second biggest and second most-populous continent in the world, following Asia. This continent experience many environmental problems including deforestation, degradation, desertification, air and water pollution, the loss of soil fertility, a dramatic decline and loss of biodiversity (Iwegbue *et al.*, 2007a, De Wit and Stankiewicz, 2006, Iwegbue *et al.*, 2012a).

Nzeve *et al.* (2015) studied the Tana River, the longest river in Kenya. The river drains into the Masinga Reservoir. The main environmental issues affecting Tana River are pollutions from agro-based industries, agro-chemicals, urban effluent, car washing, soil erosion (siltation), river bank encroachment and industrial discharge (Ghrefat and Yusuf, 2006). The study was based on valuation of heavy metal pollution in the water of the Masinga reservoir. The concentration of Cu, Zn, Pb, Cr, Mn and Cd in water was quantified by AAS. The concentrations of metals were in sequence of $Zn > Mn > Cu > Cr > Pb > Cd$. Studied heavy

metals were below WHO recommended limits for drinking water. It was concluded that the Masinga Reservoir was not polluted by heavy metals (Nzeve *et al.*, 2015).

The River Kaduna functions as a main source of irrigation for most of the farming activities in Kaduna Metropolis, Nigeria. However, the river suffers from water quality issues as a result of industrial activities and other anthropogenic sources of contamination. An examination of the effects of heavy metal pollutants to aquatic ecosystems was performed by Aliyu *et al.* (2015). The concentrations of Pb, As, Fe, Cr, Cu and Zn were measured using X-ray fluorescence (XRF) on water samples. The results indicated that the levels of most of the heavy metals exceeded acceptable limits (Lambert *et al.*, 2007). Heavy metal pollution was attributed to urban, municipal, industrial effluents and other anthropogenic sources (Aliyu *et al.*, 2015).

The Nile River, Egypt is the longest river, globally. Research was conducted by Dahshan *et al.* (2013) on the Nile River to determine the levels of Ag, Al, Cd, B, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, St, V, Zn, and As in surface water, sediments plus fish species by ICP. The findings of this study indicated that the highest metal concentrations were noted in sediments and fish species. Heavy metals in water were at the acceptable range according to Egyptian criteria. The high levels of metals detected at the River Nile were due to effluent runoff from the nearby industrial estate, as well as from derelict ships within the bay and from agricultural activities (Dahshan *et al.*, 2013).

A study was done by Iwegbue *et al.* (2016) to evaluate the quality of Orogo River (Nigeria). This river is fed by municipal wastes, surface overflow and precipitation from the nearby societies. It also suffers from high sedimentation which ought to significantly decreased the river depth and width (Lambert *et al.*, 2007, Schoeman and Steyn, 2003). The

metal chemical forms were studied in the sediment column during different seasons. Sequential extraction on sediments was performed following a procedure by Tessier (1979). The quantification of Cu, Ni, Mn, Fe, Pb, Cr, and Zn levels in sediments was done using AAS. The results of this study showed significant variation in metal concentrations with respect to depth and period of the year. The concentrations of Fe, Cu and Ni were found in Fe–Mn oxide and residual fractions, while nickel was mainly in the residual form. Iwegbue concluded that the metal speciation forms indicated that most of the metals are present in the Fe–Mn oxides or residual form, and that metal mobility and availability identifies possible pollution hazards by Fe, Zn, Mn, and Pb in the Orogodo River sediment system (Iwegbue *et al.*, 2016).

2.6.3 Rivers in South Africa

Previous studies have been conducted in South African river systems, including the Mvudi River, Nyl River, Plankenburg River, Diep River, Berg River, Tyume River, uMtata River and Buffalo River. The outcome of these studies showed that one of the biggest pollutant threats to river health are heavy metals such as Cr, Pb, Cd and Zn. Typically, metal pollutants exceed river quality limits set by South African Department of Water affairs and Forestry (DWAF) and Environmental Protection Agency (EPA).

Edokpayi *et al.* (2015) conducted a study on water and sediments of the Mvudi River, Limpopo Province, South Africa to evaluate the concentrations of heavy metals and the quality of sediment. The river is a major source of water to the Nandoni Dam that is used for drinking water distribution to nearby Thohoyandou. It is also used for domestic, recreational and agricultural activities. The levels of Al, Cd, Cr, Cu, Fe, Mn, Pb, Zn and Cd were measured by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP – OES) after acid digestion. The results showed metals in decreasing order of Fe > Al > Mn > Cu >

Cr > Zn > Pb > Cd. The mean concentrations of Al, Cr, Fe, Mn and Pb in the water samples surpassed the recommended DWAF and WHO standard for domestic water use. The levels of Cd, Cr and Cu in sediment samples exceeded the Canadian Council of Ministers of the Environment (CCME) sediment ranges for freshwater sediments. The main pollution sources for this river were the release of partially-treated wastewater effluents from Thohoyandou wastewater treatment plant, runoffs from agricultural soil, landfill sites very close to the river and other non-point sources such as atmospheric deposition (Murthy *et al.*, 2014).

Previous studies have been conducted on the Nyl River, Limpopo Province, South Africa to assess the quality of water. Greenfield *et al.* (2010) did a microbiological assessment of the river and discovered that the bacteria levels made the water unsuitable for human consumption. A similar study revealed that metals in the sediments were not actually bioavailable and was primarily from lithogenic sources (Murthy *et al.*, 2014). Water samples were quantified by ICP-MS to measure Zn, Cu, Fe, Se, Cd, Pb, Al, As, Cr, and Mn concentrations. The results showed that all concentrations of Al, Zn, As, Cr, Pb and Cd exceeded the Target Water Quality Range (TWQR). The heavy metal pollution in Nyl River was attributed to natural sources (Greenfield *et al.*, 2012).

Jackson *et al.* (2009) investigated spatial and temporal variation on pollution by metals in the Plankenburg and Diep Rivers in South Africa (Western Cape). The two rivers are located near industrial areas, residential areas, agricultural areas and informal settlements. Al, Cu, Fe, Pb, Mn, Ni and Zn levels in water as well as sediment samples were determined by ICP-AES. The metals studied in Plankenburg River indicated that all concentrations of Al and Cu in water were above the DWAF guideline and Al, Fe, Cu, Ni concentrations were above CCME values, while Mn and Zn concentrations fell within the DWAF values. Water samples in Diep River revealed that Al, Zn and Cu exceeded the recommended DWAF limits and Al, Zn, Cu

and Ni exceeded CCME standards while Mn concentrations fell within the DWAF values. The concentration of Zn in sediment for both rivers exceeded the guidelines stipulated by CCME. Heavy metal pollution in the Plankenburg River was possibly due to the discharge of household waste into the river from the informal settlements, as well as the discharge of industrial waste from a number of industries along the river banks (Jackson *et al.*, 2009b).

The Berg River is located in South Africa (Western Cape). The river is the main source of water to urban areas, rural communities, farms and recreational users in the area. A deterioration in water quality of this river led to a study on metal contamination in the rivers which was conducted by Jackson *et al.* (2007). Water, sediment and biofilm samples were measured for Al, Zn, Cu, Fe, Pb, Ni and Mn by means of ICP – AES. The results of water samples for Al and Fe surpassed the limit recommended by DWAF and CCME. The levels of Cu and Zn in sediments exceeded the recommended guidelines for freshwater sediment (CCME, 2001). The increased availability of Al and Fe was attributed to anthropogenic activities (Jackson *et al.*, 2007).

2.6.4 Rivers in KwaZulu-Natal Province (South Africa)

Olaniran *et al.* (2014) evaluated the effects of periodic fluctuations on the physicochemical parameters and heavy metal levels of Umgeni and Umdloti Rivers in South Africa (Durban, KwaZulu-Natal Province). The quality of river water in these rivers has been considerably affected by many contaminating sources including agricultural drainage, urban wash-off, effluent reappearance, industries, mining, inadequate hygiene services, leachate from landfills and human settlements (Sugiyama and Tanoshima, 2007). The study involved analysing river water samples for temperature, pH, turbidity, electrical conductivity, biological oxygen demand, chemical oxygen demand, phosphates, sulfates, ammonium ions, nitrates, Pb^{2+} ,

Hg^{2+} , Cd^{2+} , Al^{3+} , and Cu^{2+} . The physicochemical parameters were measured in the field using portable meters while metals and anions were analysed using ICP-OES and Ion Chromatography (IC), respectively.

The findings of this study revealed that the spatial and seasonal variations of the physical and chemical ecological variables varied considerably between the water samples. The levels of many of the studied factors surpassed the acceptable limits set by DWAF and WHO for freshwater quality. Olaniran *et al.* (2014) concluded that the water pollution in these rivers was due to anthropogenic activities (Olaniran *et al.*, 2014).

In 1990, concerns were raised concerning mercury contamination of the river systems below the mercury processing plant (Thor Chemicals) in South Africa (KwaZulu-Natal). Thor Chemicals processed mercury waste from international as well as local sources. It was reported that drums containing used mercury waste were emptied directly into the Mngceweni River which joins the Umgeni River, which in turn flows into the Inanda Dam. An investigation conducted from the Mngceweni River nearly downstream from the plant presented elevated mercury levels in sediment ($50 \text{ mg L}^{-1} \text{ Hg}$) and fish samples (Zhao *et al.*, 2010, Liaghati *et al.*, 2004). Papu-Zamxaka *et al.* (2010) conducted a study two decades after the incident to assess the downstream ecological mercury levels and their effects in selected villages neighbouring the Inanda Dam.

Sediment samples, fish species and hair samples from villagers were determined for total mercury by ICP-MS. The levels of mercury in hair samples varied from < 0.1 to $54.8 \text{ } \mu\text{g g}^{-1}$, of which 17 % of samples surpassed the WHO guideline of $7 \text{ } \mu\text{g g}^{-1}$. The mercury concentration in the sediment samples varied from <0.1 to $897.5 \text{ } \mu\text{g g}^{-1}$. Approximately 22%

of the sediment samples contained mercury levels that surpassed the severe effect level of $2 \mu\text{g g}^{-1}$ implemented by the Ontario Ministry of the Environment (Iwegbue *et al.*, 2007b). Total mercury levels in fish samples varied from 0.26 to $1.78 \mu\text{g g}^{-1}$, of which, 50 % surpassed the WHO limit of $0.5 \mu\text{g g}^{-1}$. The high exposure to mercury observed in this study was attributed to the Thor Chemicals incident that took place in 1990 (Zamxaka *et al.*, 2010).

2.7 Methods for analysis of metals

2.7.1 Sample handling and pre-treatment

Polyethylene containers are used to collect samples that required metals analysis. These containers are rinsed a seven times with double-distilled water and nitric acid before use. Surface water samples are passed through 0.45 micron filters then acidified using nitric acid to $\text{pH} \leq 2$ for preservation purposes. The acidification minimise absorption of metals into the wall of the sample containers. The prepared samples are generally stored approximately at 4°C prior to analysis (Okweye and Golson-Garner, 2012).

2.7.2 Quantification methods

The different quantification methods of heavy metals in previous studies in summarised on table 2.2.

Table 2.2 Previous studies showing methods of heavy metal analysis

Method	Matrix	Metals analysed	Reference
Anode stripping voltammetry using micro - electrode	surface water	Zu, Cd, Pb and Cu	(Yahaya <i>et al.</i> , 2012)
Spectrograph using graphite electrode	surface water	Cd, Cr, Pd, V, Zn Fe and Mn	(Yahaya <i>et al.</i> , 2012)
X-Ray fluorescence	sediments	As, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Sn and Zn	(Raulinaitis <i>et al.</i> , 2012)
	surface water	Pb, As, Fe, Cr, Cu and Zn	(Aliyu <i>et al.</i> , 2015)
Inductively Coupled Plasma – Optical Emission Spectrometer	Surface water, sediments and fish species	Al, Cd, Bo, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, St, V, Zn, and As	(Dahshan <i>et al.</i> , 2013)
Inductively Coupled Plasma – Optical Emission Spectrometer	surface water	Al, Co, Ni, Cu, Fe, Mn, Cd, As, Se, Zn, Pb, and P	(Okweye and Golson-Garner, 2012)
Atomic absorption spectrometry	surface water and sediments	Cd, Pb, Cr, Ni, Fe, Mn, and Zn	(Iwegbue <i>et al.</i> , 2012b)
Inductively Coupled Plasma – Mass Spectrometry	surface water	Zn, Cu, Fe, Se, Cd, Pb, Al, As, Cr and Mn	(Greenfield <i>et al.</i> , 2012)
	surface water and sediments	Cr, Cu, As, Ni, Pb and Cd	(Islam <i>et al.</i> , 2015)

2.7.2.1 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

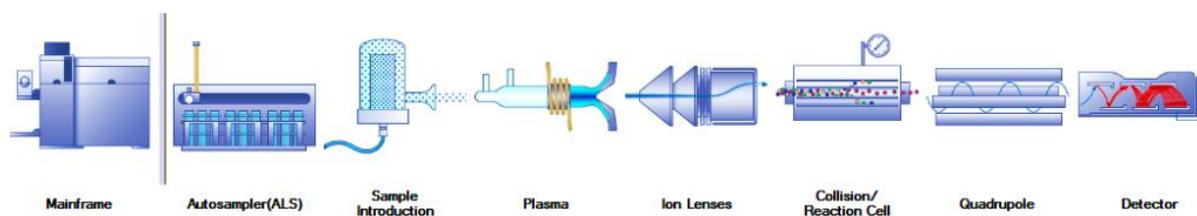


Figure 2.1 Schematic diagram of ICP-MS (Deekae *et al.*, 2010)

ICP-MS is a widely used analytical technique for elemental analysis. This instrument is used in routine analysis and research in a range of areas. There are six main components of the instrument used in ICP-MS namely: Introduction of the sample, ion generation – plasma, interface, ion focusing, and ion separation – mass spectrometer and ion measurement – detector. The liquid sample is pumped from an auto sampler into a nebuliser using a peristaltic pump where it is converted into a fine mist called an aerosol. The liquid sample that was not converted into aerosol is sent to the spray chamber. This aerosol is carried to the plasma by means of argon gas via the sample injector. Plasma is located at the central canal on the torch that is surrounded by a cooled coil. The temperature of the plasma is around 10 000K (Shanbehzadeh *et al.*, 2014).

The plasma decomposes, atomises and ionises the sample. Ions that are formed in the plasma are focused into the mass spectrometer through the interface area. The interface comprises of two metal plates called cones namely, sampler cone and skimmer cone. These cones have small holes to allow the ions to pass through. The mass spectrometer operates under a high vacuum with a mechanical roughing group. A quadrupole mass analyser is the commonly used mass spectrometer. Quadrupole consists of direct current and alternating current electric field that is used to disperse ions according to their mass to charge ratio. After separation, the ions are transferred to the detector. The detector converts the analytical signal to electrical

signal. It also counts and stores signal of the ion mass thus creating a spectrum. The magnitude of each peak is directly proportional to the concentration of the analyte (Shanbehzadeh *et al.*, 2014).

2.7.2.2 Ion Chromatography (IC)

Chromatography is a physicochemical method of separation that enables components to separate between two phases, the stationary phase and mobile phase. IC is a kind of chromatography that separates up ions and polar molecules based on their similarity to the ion exchanger (Schmid, 1997). It is commonly used as an analytical method for determination of inorganic ions in environmental samples, and includes all separations of ionic species within IC.

IC is an analytical technique for the separation and determination of ionic solutes. This technique falls into the classification of liquid-solid chromatographic methods, in which a liquid (called the eluent) is passed through the solid stationary phase and then to a flow-through injector. The stationary phase particles are packed uniformly into the column and are retained by means of porous frits located at each end of the column. A high pressure pump is required to force the eluent through the column at typical flow-rate of 1 to 2 mLmin⁻¹. The sample to be separated is introduced into the flowing eluent stream by means of an injection device inserted into the flow-path prior to the column. The detector usually contains a low volume cell through which eluent flows (Haddad and Jackson, 1990).

The IC is operated in the elution mode. That is, a discrete amount of the sample is applied to the top of the column. The sample components progress through the column at different rates and therefore enter the detector at different times. The detector senses the sample components

and produces the chromatogram. The anions are identified on the basis of retention time as compared to known standards. Quantification is achieved by measuring peak area or peak height.

2.8 Statistical analysis and quality assurance

2.8.1 Principal Component Analysis (PCA)

PCA is applied to simplify data that has a large number of correlated variables. This technique has been used for determining the distribution and source apportionment of metals in the environment. The principal components consist of the linear combination of the original variables that accounts for most of the variability in the dataset. The first component explains the greatest variability while the successive components explain the lesser trends in a decreasing order of importance (Stout *et al.*, 2001; DeMott *et al.*, 2010). PCA can be used to visualize the relationships between multivariate samples in a simple 2 or 3-dimensional PCA score plots (Johnson and Erhlich, 2002). PCA has been implemented by Ayari *et al.*, 2016, Zhang *et al.*, 2015, Nelson, 2015, Yao *et al.*, 2014 and Peifang *et al.*, 2014 in literature to evaluate the trace metal concentration relations, and identify potential natural and anthropogenic sources of trace metals.

2.8.2 Water Quality Index of the water samples

Water quality index (WQI) is an important parameter for communicating water quality information to policy makers and concerned citizens (Bano and Ahmad, 2014). WQI is a ranking indicating the composite effect of various water quality factors used for calculation of WQI (Bano and Ahmad, 2014). WQI shows the water quality in terms of index number which signifies overall quality of water for any anticipated usage (equation 1). The WQI in

this study was evaluated using the equation as defined by (Cude, 2001). WQI values have five categories as shown in Table 2.3. Murthy *et al.*, (2014) applied WQI to Lingambudhi Lake, Kukkarahalli Lake, Yennehole Lake and Yemaehole Lake to assess the water quality state of these lakes. He concluded that the rating of water quality for Lingambudhi Lake and Kukkarahalli Lake was between marginal and acceptable, while it was marginal in Dalvoi Lake, but acceptable in Yenmehole Lake.

$$W_{QI} = \frac{\sum Q_i W_i}{\sum W_i}$$

..... equation 1

Q_i = Quality rating of each parameter =

$$\frac{V_{actual} - V_{ideal}}{V_{standard} - V_{ideal}} \times 100$$

V_{actual} = Actual value of the water quality parameter obtained from laboratory analysis

V_{ideal} = Ideal value of that water quality parameter can be obtained from the standard Tables

V_{ideal} for pH = 7 and for other parameters it is equal to zero

$V_{standard}$ = Recommended WHO standard of the water quality parameter

W_i = Unit weight = $\frac{1}{S_i}$

S_i = Standard permissible value for nth parameter

Q_i = Quality rating of i^{th} parameter for a total of n water quality parameters

Table 2.3 Water quality index categorisation (Ramakrishnaiah *et al.*, 2009, Bano and Ahmad, 2014).

Category	Description
<0-25	Excellent water quality
26-50	Good water quality
51-75	Poor water quality
76-100	Very poor water quality
>100	Unsuitable for drinking

2.8.3 Ecological Risk Assessment for Metals in Sediment

The ecological risk assessment index for metals was originally introduced by Hakanson (1980). The index has been used to assess the ecological risk of metals in sediment, soil and dust samples. The potential ecological risk index (RI) is given by the equation 2. The potential ecological risk index was applied by Fu *et al.*, 2013 to assess the degree of heavy metal pollution in sediments of Yangtze River and Taihu Lake in China. Ecological risk evaluation showed that the heavy metal contaminants in sediments from the Yangtze River posed higher risk of adverse ecological effects, while sediments from the study areas of Taihu Lake were relatively safe.

$$RI = \sum_{i=1}^n E_r^i \dots\dots\dots\text{equation 2}$$

where $E_r^i = T_r^i \times C_f^i$

and $C_f^i = \frac{C_s^i}{C_b^i}$

Also, $C_d = \sum_{i=1}^n C_f^i$

C_s^i is the concentration of a particular metal in the sediment sample and C_r^i represents the regional background level of the particular metal in the sediment. The crustal abundance values for the investigated elements were used as the background levels (Table 3.6). C_f^i is the contamination factor for a particular metal. E_r^i is the ecological risk factor for a particular metal and RI is the potential ecological risk factor for multiple metals. T_f^i represents the toxicity factor for a particular metal. Guo et al. (2010) found the toxicity factors for Cd, Cr, Pb and Zn to be 30, 2, 5 and 1, respectively. The E_r^i and RI factors have been classified into five and four categories, respectively depending on their values. C_d is the degree of contamination and is based on four classification categories (Table 2.4)

Table 2.4 Indices and potential ecological risk factors for metal pollution (Yi *et al.*, 2011, Hakanson, 1980, Guo *et al.*, 2010)

Contamination factor (C_f^i)	Contamination factor for an individual metal	Degree of contamination (C_d)	Degree of contamination of the environment	E_r^i	Ecological risk factor for an individual metal	Potential ecological risk index (RI)	Pollution Degree
$C_f < 1$	Low	$C_d < 5$	Low contamination	$E_r < 40$	Low risk	$RI < 65$	Low risk
$1 \leq C_f < 3$	Moderate	$5 \leq C_d < 10$	Moderate contamination	$40 \leq E_r < 80$	Moderate risk	$65 \leq RI < 130$	Moderate risk
$3 \leq C_f < 6$	Considerable	$10 \leq C_d < 20$	Considerable contamination	$80 \leq E_r < 160$	Considerable risk	$130 \leq RI < 260$	Considerable risk
$C_f \geq 6$	High	$C_d \geq 20$	High contamination	$160 \leq E_r < 320$	High risk	$RI \geq 260$	Very high risk
				$E_r \geq 320$	Very high risk		

2.8.4 Index of Geoaccumulation

Geoaccumulation index (I_{geo}) is a principle that is used to assess the heavy metal contamination in sediments. I_{geo} was originated by Muller to measure metal pollution in sediments by relating current levels with pre-industrial levels. In order to evaluate the amount of pollution in sediments, I_{geo} values are calculated using equation 3. According to Muller, (1969), the classification of I_{geo} is based on Table 2.5 (Saha and Hossain, 2011, Wei and Yang, 2010, Alagarsamy, 2006, Islam *et al.*, 2015, Jiang *et al.*, 2013, Weber-Scannell and Duffy, 2007).

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right] \dots\dots\dots \text{equation 3}$$

Where C_n is the measured concentration of the test metal in the sediment sample and B_n is the background concentration of the test metal. In this case, the crustal abundance values of the test metals were used as the background concentrations (Turekian and Wedepohl, 1961). The factor, 1.5, modifies for potential lithological deviations in the background concentrations (Rogan *et al.*, 2010). The Muller index of geoaccumulation (I_{geo}) has seven classes ranging from unpolluted to extremely pollute as shown in Table 2.5. Mohiuddin *et al.*, 2016 used the geoaccumulation principle to assess toxic metals pollution in sediments of the Buriganga River. The I_{geo} of the studied sediments for Cu were greater than 3.0, which exhibited strongly polluted sediment quality in Buriganga River.

Table 2.5 Muller’s classification for the Geoaccumulation index (Saha and Hossain, 2011, Dumčius *et al.*, 2011, Peifang *et al.*, 2014)

I_{geo} value	Class	Sediment Quality
≤ 0	0	Unpolluted
0 -1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly polluted to extremely polluted
> 6	6	Extremely polluted

2.8.5 River Water Quality Guidelines

South African river water quality guidelines for aquatic ecosystems are national standards that are set to provide data on water quality requirements. These guidelines are meant to maintain the fitness of water for specific uses, identify the problems associated with river water quality, define the water quality constituents and protect the health of the aquatic ecosystem (DWAF, 1996b). The international guidelines values are derived from many chemical constituents of water. These values normally represent the concentration of a constituent that does not result in any significant risk to health over a life time (Table 2.6).

Table 2.6 South African river water quality guidelines (DWAF, 1996b).

Metal	Domestic use ($\mu\text{g L}^{-1}$)	Aquatic ecosystems ($\mu\text{g L}^{-1}$)
As	10	10
Cd	5	0.15
Cr	50	7
Pb	10	0.2
Zn	3000	2

2.8.6 Sediment Quality Guidelines

Gordon and Muller (2010) reported that there was no South African sediment quality guideline as it was still under development. Therefore for sediment quality the international guidelines will be used to monitor the state of Msunduzi River. The Canadian Environmental Quality Guidelines (CCME, 1999) for freshwater sediments are used to determine the possible toxic effects of the metals on aquatic organisms (Table 2.7). Edokpayi *et al.*, 2016 used CCME guidelines to evaluate the extent of pollution of Mvudi River sediment.

Table 2.7 CCME for freshwater sediment guidelines (CCME, 2001).

Metal	Guideline (mg kg^{-1})
Cd	0.6
Cr	37.3
Pb	35.0
Zn	123

2.9 References

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CHAPTER 3: EXPERIMENTAL

3.1 Study Area

3.1.1 The Msunduzi River

The Msunduzi River is situated in Pietermaritzburg, the capital city of KwaZulu-Natal, South Africa (Figure 3.1). It is located between the latitudes 29°32 to 29°47 S and longitudes 30°05 to 30°41 E. The river is 115 km long, flows from Midlands through Edendale Valley and stretches through Pietermaritzburg (heavily industrialised city) up to rural developing areas. It is the largest tributary of Umgeni River that joins the Nagle Dam and flows through Inanda Dam. Inanda dam is the Durban's primary water supply, and flows out into the Indian Ocean in Durban (South Africa). The Msunduzi River is commonly known as Duzi or Dusi, and is famous for rowing and canoeing activities at Camps Drift where used as the starting point of the annual Duzi Canoe Marathon (Pole, 2002). The catchment of Msunduzi River covers an area of 540 km², an area with large amount of informal settlements next to the surface water sources. Most of the people living in this catchment are from disadvantaged communities (Edokpayi *et al.*, 2016, Matongo *et al.*, 2015, Gemmell and Schmidt, 2013).

3.1.2 Water quality in the Msunduzi River

The increasing population and economic development have contributed to deterioration in the quality of water in the Msunduzi catchment regions. The catchment has been exposed to increases in population, industrial activities and agricultural activities. The river is mainly used for household, recreation, agricultural and industrial activities in the Msunduzi municipality. The study locations were mainly located upstream of Pietermaritzburg, through the city, and immediately upstream and downstream of the Darvill Waste Water Works which is situated along Msunduzi River. DWWW is the biggest sewage treatment plant in

Pietermaritzburg, receiving about 75 mLday⁻¹ of raw municipal sewage and treated industrial wastewater. The plant operates through activated sludge process (hydraulic capacity 110 ML/day) has Solids Retention Time (SRT) of ± 8 days, and mean Hydraulic Retention Time (HRT) of 7 h. Typical effluent values are: 75 mg/L for Chemical Oxygen Demand (COD), 10 mg L⁻¹ for ammonia (NH₃), 15 mg L⁻¹ for nitrate anion (NO₃⁻) and 1000 µg L⁻¹ for Soluble Reactive Phosphate (SRP) (Manickum and John, 2014, Radojević and Bashkin, 1999). The treated effluent from DWWW is discharged back into the Msunduzi River (Sivparsand and Wray, 2010, Matongo *et al.*, 2015, Arimoro *et al.*, 2007b). It is of great concern to determine whether the discharge of DWWW contributes to the contamination of Msunduzi River. The main environmental issues in Msunduzi catchment include contamination from industrial activity, urban effluent, car washing, soil erosion and agricultural activities. These influences caused by anthropogenic activities in the catchment are transferred to Msunduzi River.

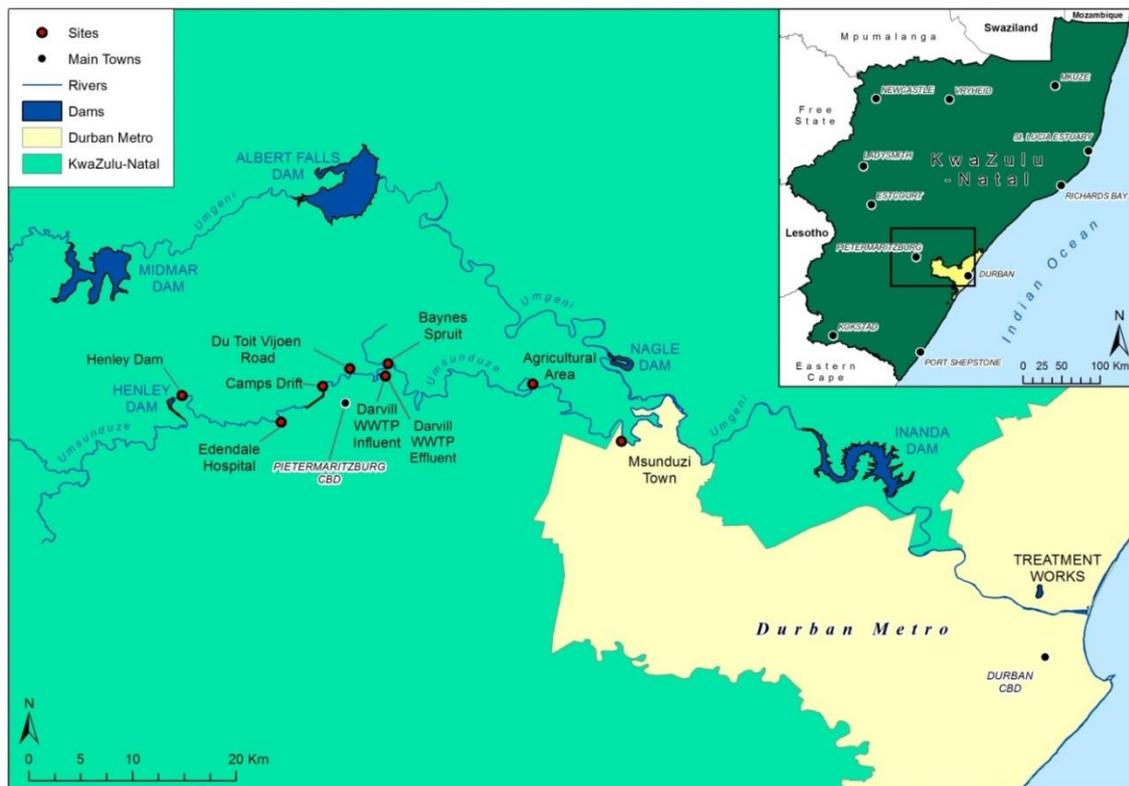


Figure 3.1 Map of the study Area

Table 3.1 Geographical coordinates and activities of the sampling sites in the Msunduzi River

Site	Co-ordinates		Activities at sampling site
	Latitude(S)	Longitude(E)	
Henley Dam	29.6211	30.2545	Domestic
Edendale Hospital	29.6443	30.3407	Commercial, Domestic and Industrial
Camps Drift	29.6131	30.3767	Commercial, Industrial and Recreational
Du Toit Viljoen Road	29.5978	30.4002	Domestic and Industrial
Baynespruit	29.5934	30.4335	Agricultural, Commercial, Domestic and Industrial
Darvill WWTP Influent	29.6042	30.4311	Industrial
Darvill WWTP Effluent	29.6042	30.4311	Industrial
Agricultural Area	29.6111	30.5589	Agricultural and Domestic
Msunduzi Town	29.6611	30.6361	Agricultural and Domestic

3.2 Sampling and procedure

The surface water and sediment samples were collected from nine different locations alongside the Msunduzi River (Figure 3.1) across four seasons: winter, spring, summer and autumn during 2014 to 2015. The 1 L polypropylene bottles used for sampling and storage were conditioned. The bottles were washed with soapy water, rinsed three times with double distilled water, soaked overnight in 10 % HNO₃ and finally cleaned three times using double distilled water.

3.3 Sample Collection

At the sampling location the bottles were washed three times using water before a grab sample was taken. Individual samples were taken by means of submerging the sample bottle into the river at approximately 100–300 mm lower than the surface with the open end facing against the existing flow direction (Panduranga Murthy, 2014 and Hosmani, Nzeve *et al.*, 2015, Zhang *et al.*, 2015). Two water samples were collected per sampling location, one used for metal determination and the other for anion determination. The samples for metal determination were acidified with 1:1 HNO₃ on site to pH < 2 for preservation purposes, to reduce the adsorption of metals onto the walls of the plastic bottles (Okweye and Garner, 2013).

Sediment samples were taken from surface sediment (0–10 cm) using a plastic scoop, homogenised and transferred into two litre polypropylene bags. Sample bottles and bags were then labelled with the sampling site and sampling date for identification (Murthy *et al.*, 2014). The physicochemical parameters were measured and the GPS co-ordinates recorded at each sampling location. All samples were transported in a cooler box to the research laboratory and kept at 4°C until further investigation.

3.4 Physicochemical Parameters

The physicochemical parameters investigated were pH, electrical conductivity (EC), dissolved oxygen (DO) as well as temperature which were measured *in situ* using Hanna portable pH/EC/DO/temperature combined water proof meter. Analysis was carried out in the field following a standard method as set out by the United States Environmental Protection Agency (US-EPA) (2001).

3.5 Chemicals

All chemicals and reagents used were obtained from Merck (Germiston, South Africa):

HCl \approx 37%, acetic acid, HNO₃ \approx 69%, hydroxylammonium chloride, H₂O₂, ammonium acetate, and 1000 mg L⁻¹ stock solutions for As, Cd, Cr, Pb and Zn. Working metal standards for calibrations were prepared from stock standard solutions. All chemicals were analytical grade and used directly without further purification. Double distilled water was used throughout the experiments.

3.6 Water Sample Preparation and Analysis

3.6.1 Metals

All glassware, ICP tubes and microwave digestion vessels were washed and soaked overnight in 10 % HNO₃ and cleaned using ultra-pure water before usage. Water samples were digested using the Microwave Accelerated Reaction System (MARS) before analysis to reduce organic matter interferences. A volume of 10 mL aliquot of the well-mixed acidified sample was transferred to a 100 mL microwave digestion vessel, and 3 mL of aqua regia (3HCl:HNO₃) was added. The digestion vessels were closed and positioned in the microwave digester as per the manufacturer's instruction. The microwave system was allowed to run for fifteen minutes under the conditions stated in Table 3.2. By the completion of the microwave program, the vessels were permitted to cool for five minutes before removing them from the microwave system. The digested solution was quantitatively transferred to a 50 mL volumetric flask filled up to the mark with ultra-pure water. The samples were analysed for heavy metals using ICP-MS under the conditions stated on Table 3.3 (USEPA, 1992, Virha *et al.*, 2011).

Table 3.2 Microwave digester instrument settings

Parameter	Setting
Microwave Model	CEM MARS 6
Temperature	180 °C
Power	800 watts
Ramp Time	20 minutes
Hold Time	20 minutes

Table 3.3 ICP-MS instrument settings

Parameter	Setting
Instrument model	ICP-MS Agilent 7900
Tune mode	He: HMI
Internal standard (ISTD)	Scandium
Radio-frequency power (W)	1600
Flow rate of carrier gas (L/min)	0.28
HMI dilution gas (L/min)	0.67
Sample uptake rate (mL/min)	0.17
ISTD uptake rate (mL/min)	0.17
Total nebuliser flow (mL/min)	0.34
Sample cone	Nickel Skimmer
Mass analyser	Quadrupole
Detector	Electron multiplier

3.6.2 Anions

Unacidified samples were filtered through 0.45 µm filters and analysed for anions using Ion Chromatography. The settings for the IC Dionex ICS-5000+ instrument conditions are shown in Table 3.4.

Table 3.4 IC instrument settings

Parameter	Setting
Column	IC PAK A Anion column
Detector	Dione CD 20 Conductivity detector
Pump	Waters dual piston pumps
Flow Rate	1.2 mL/min
Nitrogen Gas	20 kPa
Pressure	20.0 psi

3.7 Sediment Sample Preparation and Analysis

3.7.1 Total Metal Determination

The samples were air dried at room temperature, homogenised and ground with an agate mortar, sieved to fine particles (<75 µm clay fraction) and stored in polyethylene bags. The sieved samples were kept at room temperature (25°C) prior to sequential extraction and total heavy metal analysis. Sequential extraction was done according to the Community Bureau of Reference (BCR) sequential extraction process (Rauret *et al.*, 2001). A volume of 10 mL of aqua regia was added to a 0.5 g sieved sample in a 100 mL microwave digestion vessel, the same procedure was followed for the certified reference material (CRM). The microwave digestion method stated in 3.6.1 was followed. The digested solution was then filtered by a

Whatman No. 1 filter paper into a 50 mL volumetric flask and the filtrate was filled up to a mark with ultra-pure water. The concentrations of metals in the digested samples were analysed by ICP-MS (USEPA, 2007, USEPA, 1996, Lin *et al.*, 2004, Deekae *et al.*, 2010, Sugiyama and Tanoshima, 2007).

3.7.2 BCR Extraction

3.7.2.1 Exchangeable Metals

A volume of 20 mL of 0.11 mg L⁻¹ acetic acid was added to 0.5 g of prepared sediment and CRM (BCR 701) in a 50 mL centrifuge tube. The mixture was shaken for 16 h at 22 ± 5°C (overnight). The extract was separated from the solid residue by centrifugation at 3800 rpm for 20 minutes. The supernatant liquid was decanted into a polypropylene ICP vial and stored in the refrigerator at 4°C prior to analysis. The residue was rinsed by adding 10 mL of double-distilled water, shaken for 15 minutes and then centrifuged. The second supernatant liquid was thrown away without any loss of solid residue.

3.7.2.2 Metals bound to iron and manganese oxide

Metals bound to iron and manganese oxides were extracted by adding 20 mL of 0.5 mg L⁻¹ hydroxylammonium chloride (adjusted to pH 2 ± 0.1 with 2 mg L⁻¹ HNO₃) onto the residue from the first step. The mixture was shaken for 16 h at 22 ± 5°C (overnight). The extract was separated from the solid residue by centrifugation at 3800 rpm for 20 minutes. The supernatant liquid was transferred into a polypropylene ICP vial and kept in the refrigerator at 4°C prior to determination. The residue was washed by adding 10 mL of double-distilled water, shaken for 15 minutes and then centrifuged. The second supernatant liquid was thrown away without any loss of solid residue.

3.7.2.3 Metals bound to organic matter and sulfides

Metals bound to organic matter and sulfides were extracted by adding 5 mL of 8.8 mg L⁻¹ hydrogen peroxide to the residue from the second step. The mixture was digested at room temperature for 1 hour with random manual shaking. The process was continued for 1 h whilst heating in a water bath at 85 ± 2 °C and then the volume was reduced to 0.5 mL. A second aliquot of 5 mL of 8.8 mg L⁻¹ hydrogen peroxide was added and the digestion procedure was repeated and the solution was heated to near dryness. A volume of 25 mL of 1 mg L⁻¹ ammonium acetate (adjusted to pH 2 ± 0.1 with HNO₃) was added onto the cool moist residue. The mixture was shaken for 16 h at 22 ± 5 °C (overnight). The extract was separated from the solid residue by centrifugation at 3800 rpm for 20 minutes. The supernatant liquid was transferred into a polypropylene ICP vial and kept in the refrigerator at 4 °C prior to the analysis (Igbinosa and Okoh, 2009).

3.8 Statistical analysis and evaluation methods

3.8.1 Analysis of Variance (ANOVA)

The analytical data was tested using one-way (ANOVA) to analyse the significant differences among sampling sites and seasons. Data analyses were performed using Microsoft Excel 2010.

3.8.2 Pearson Correlation Analysis

The correlation coefficients between the quality parameter pairs of the water samples were calculated by the application of Pearson correlation analysis in order to indicate the nature and the sources of the polluting pollutants.

3.9 References

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CHAPTER FOUR: RESULTS AND DISCUSSION

In the discussion below, the water and sediment quality of the Msunduzi River and the impact of the wastewater works on the river is discussed, separately.

4.1 Physicochemical characteristics of Surface water

4.1.1 Temperature

The temperature of a water body has significant influence in the rate of chemical reactions, stability of the water column and toxicity. The mean temperature of the water measured on site across the sampling locations ranged from 17.2 to 23.1 °C and 21.7 to 23.2 °C for the Msunduzi River and Darvill Wastewater Works (DWWW) respectively (Table 4.1). Matongo *et al.* (2015) reported similar temperature range of 21 to 22 °C for the DWWW. On average, the temperature of the water bodies was higher during the summer than the other season (Table 4.2). There was no significant difference ($p>0.05$) in the mean temperature of the water bodies during all seasons. The observed temperature range corresponds to those found in some river systems in Nigeria (Egobueze *et al.*, 2011, Arimoro *et al.*, 2007) and South Africa, Umgeni River and Umdloti River (Olaniran *et al.*, 2014).

4.1.2 pH

The mean pH values observed in these water bodies ranged from 7.14 to 8.37 and 7.28 to 7.56 for the Msunduzi River and DWWW respectively (Table 4.1). The previous study on Msunduzi River conducted by Gemmell and Schmidt (2013) also showed a pH range of 7.18 to 8.47. The recorded pH values for the DWWW were lower than those reported by Morrison *et al.* (2001) for the Keiskammahoek Sewage Treatment Plant, South Africa. The highest mean pH was observed during winter. Virha *et al.* (2011) reported high pH values during

winter for surface water. Similar pH results of range 5.52 to 9.52 were reported for a South African river by Greenfield *et al.* (2012) who did a study on the Nyl River, Limpopo Province. The pH mean values obtained in this investigation are similar to the range of 7.2 to 7.7 as stated for the Mvudi River, South Africa (Edokpayi *et al.*, 2016). The pH values observed in this river system are within the range of 6.5 to 8.5 as specified by the Department of Water Affairs and Forestry (DWAF) and World Health Organisation (WHO) for domestic water use (DWAF, 1996a).

4.1.3 Conductivity

The mean conductivity values of the water bodies ranged from 118 to 428 $\mu\text{S cm}^{-1}$ and 696 to 939 $\mu\text{S cm}^{-1}$ for the Msunduzi River and DWWW, respectively (Table 4.1). The EC mean values detected in this study are comparable to the ranges 15.8 to 5180 mS m^{-1} , stated by Olaniran *et al.* (2014) in KwaZulu-Natal Rivers, South Africa. There was no significant difference ($p>0.05$) in the mean conductivity concentrations of the water bodies during all seasons.

4.1.4 Total Dissolved Solids

Total dissolved solids (TDS) consist mainly of inorganic salts, some organic compounds and dissolved gas. The TDS content of drinking water varies between 20 and 100 mg L^{-1} (Radojević and Bashkin, 1999). The mean TDS values of these water bodies varied from 85.2 to 327 mg L^{-1} and 591 to 728 mg L^{-1} for the Msunduzi River and DWWW respectively (Table 4.1). The observed TDS mean concentrations were within the range of 1.29 to 350 mg L^{-1} reported by De Villiers (2007) for the KwaZulu-Natal Rivers, South Africa. The DWWW TDS concentrations exceeded the concentrations of 118 to 350 mg L^{-1} reported by Igbinsosa and Okoh (2009) for the wastewater treatment facility in the Eastern Cape, South Africa. The TDS values showed significant ($p<0.05$) variations in all seasons.

Table 4.1 Mean values of some physicochemical properties of water samples.

	Temperature	pH	EC	TDS	DO	Chloride	Nitrate	Sulfate
Henly Dam Outlet	17.2±5.51 (12.9-25.0)	7.82±0.16 (7.60-7.99)	118±28.0 (84.0-151)	85.2±27.0 (60.9-121)	4.41±0.43 (3.97-4.96)	9.67±1.44 (8.73-11.8)	1.08±0.37 (0.46-1.46)	4.80±4.90 (0.27-11.7)
Edendale Hospital	19.6±3.30 (17.1-24.4)	7.14±1.37 (5.08-7.96)	335±109 (226-482)	248±46.8 (205-290)	4.38±0.80 (3.26-5.03)	26.4±2.60 (23.0-28.5)	2.12±0.37 (1.63-2.45)	8.54±3.95 (4.00-13.1)
Camps Drift	21.3±4.46 (16.3-27.1)	7.75±0.23 (7.42-7.94)	256±105 (133-384)	188±49.3 (28-230)	5.20±0.48 (4.64-5.80)	21.3±2.26 (17.9-22.7)	1.27±0.85 (0.45-2.46)	7.69±4.42 (1.26-10.6)
Dutoit	19.8±3.16 (15.5-23.1)	7.63±0.17 (7.39-7.76)	177±44.0 (125-232)	134±27.5 (110-171)	5.26±0.30 (4.98-5.67)	16.8±6.95 (7.00-22.4)	0.73±0.41 (0.23-1.23)	11.6±7.36 (1.84-17.7)
Baynespruit	21.6±2.83 (18.5-25.3)	7.61±0.13 (7.50-7.76)	265±48.0 (194-296)	204±54.7 (172-286)	4.65±1.29 (3.08-6.07)	27.9±6.10 (21.9-35.8)	0.91±0.87 (ND-1.79)	10.8±7.86 (0.82-20.0)
Darvil Inlet	23.2±3.87 (19.7-28.7)	7.28±0.10 (7.18-7.39)	939±166 (778-1165)	728±205 (465-952)	2.27±0.31 (1.99-2.72)	79.5±16.4 (62.8-101)	0.63±1.13 (ND-2.32)	49.1±29.2 (10.7-81.2)
Darvil Outlet	21.7±4.55 (16.7-27.7)	7.56±0.21 (7.37-7.77)	696±168 (543-928)	591±172 (363-741)	4.95±0.96 (4.08-6.18)	74.8±30.5 (45.7-102)	2.99±3.81 (ND-7.96)	55.6±39.3 (7.09-103)
Agriculture	22.6±4.89 (17.8-27.9)	8.37±0.47 (7.68-8.69)	334±69.0 (254-396)	289±68.9 (236-389)	5.12±0.13 (5.02-5.31)	38.9±4.48 (33.2-43.2)	2.76±1.29 (1.23-4.26)	31.5±9.72 (21.4-44.4)
Msunduzi Town	23.1±4.71 (18.8-27.8)	7.99±1.34 (6.13-9.02)	428±68.0 (329-485)	327±76.1 (274-440)	5.19±0.25 (4.98-5.52)	42.4±7.76 (37.4-53.9)	3.92±1.43 (1.93-4.98)	24.6±7.96 (20.0-36.5)

ND – Not Detected

Table 4.2 Physicochemical parameters for all seasons

Site	Season	Water temperature (°C)	pH	Conductivity ($\mu\text{S cm}^{-1}$)	TDS (mg L^{-1})	DO (mg L^{-1})
Henly Dam Outlet	Spring	17.0	8.0	120.4	121.0	4.0
	Summer	25.0	7.6	83.9	60.9	4.5
	Autumn	13.8	7.9	114.4	68.4	5.0
	Winter	12.9	7.8	151.3	90.5	4.2
Edendale Hospital	Spring	17.9	8.0	288.0	290.0	4.9
	Summer	24.4	5.1	226.2	210.5	5.0
	Autumn	18.9	7.8	342.6	205.2	4.3
	Winter	17.1	7.8	481.6	287.6	3.3
Camps Drift	Spring	21.5	7.9	225.0	227.0	5.1
	Summer	27.1	7.4	132.9	127.5	5.8
	Autumn	20.3	7.9	281.2	168.2	4.6
	Winter	16.3	7.8	384.2	229.5	5.2
Dutoit	Spring	20.6	7.8	169.4	171.0	5.0
	Summer	23.1	7.4	125.3	117.1	5.7
	Autumn	19.9	7.8	182.3	109.7	5.1
	Winter	15.5	7.6	231.7	138.6	5.3
Baynespruit	Spring	21.7	7.7	283.0	286.0	5.2
	Summer	25.3	7.8	193.7	181.0	6.1
	Autumn	20.8	7.5	287.6	171.5	3.1
	Winter	18.5	7.5	296.1	177.9	4.3
Darvil Inlet	Spring	22.3	7.3	946.0	952.0	2.0
	Summer	28.7	7.4	865.5	799.9	2.2
	Autumn	21.9	7.2	777.6	465.1	2.7
	Winter	19.7	7.2	1165.0	694.7	2.2
Darvil Outlet	Spring	21.8	7.4	703.0	706.0	4.3
	Summer	27.7	7.8	543.0	741.4	4.1
	Autumn	20.6	7.7	608.6	363.2	6.2
	Winter	16.7	7.4	928.2	554.0	5.2
Agriculture	Spring	25.5	8.7	387.0	389.0	5.3
	Summer	27.9	7.7	300.3	278.5	5.1
	Autumn	19.1	8.5	395.9	236.4	5.0
	Winter	17.8	8.6	253.5	252.1	5.1
Msunduzi Town	Spring	26.5	8.9	438.0	440.0	5.3
	Summer	27.8	7.9	329.0	305.5	5.5
	Autumn	19.3	6.1	458.2	274.4	5.0
	Winter	18.8	9.0	485.0	289.8	5.0

The highest TDS value was observed in the water sample collected from the Darvil inlet during spring which may be due to disturbances of salts and water balance. The average TDS values of this water body were in decreasing order of: spring > summer > winter > autumn which might be caused by more solubility of ions as the temperature and rainfall generally

increases moving from autumn to summer. The TDS values observed surpassed the DWAF and WHO guideline for domestic water usage (DWAF, 1996a, WHO, 2011). The TDS values recorded for this river system was lower than 333 to 1384 mg L⁻¹ reported for water bodies in the combined Main Reef Area, Roodepoort, South Africa (Muruvu and Tekere, 2013).

4.1.5 Dissolved Oxygen

Dissolved oxygen (DO) is the gaseous oxygen that is dissolved in water. All aerobic life, as well as aquatic ones, requires oxygen for breathing. A warm-water aquatic environment ought to have DO concentration of at least 5 mg L⁻¹ in order to sustain a diversified biota (Radojević and Bashkin, 1999). DO depends on temperature, pressure, salinity and biological activities within the water body. As temperature increases, less oxygen can be dissolved in water since oxygen is less soluble in warm water than in cold water. The mean concentration of DO in this river system ranged from 4.38 to 5.26 mg L⁻¹ and 2.27 to 4.95 mg L⁻¹ for the Msunduzi River and DWWW, respectively (Table 4.1).

The recorded DO mean values were similar to those reported by Deekae *et al.* (2010) (5.17 to 6.43 mg L⁻¹) for a Nigerian River, and Greenfield *et al.* (2012) (3.4 to 10.75 mg L⁻¹) for Nyl River, South Africa. Lower DO values were observed at the Darvil inlet than other sites throughout the study period (Table 4.2). The seasonal differences in the DO concentrations for these sites were not significant ($p > 0.05$). The DO values were within the acceptable range for aquatic ecosystems except the water sample from Darvil inlet. The observed low DO concentration at the Darvil inlet (influent sample) was attributed to high amounts of organic contamination from different industries and municipal sewage. Excess nutrients in water can increase growth of phytoplankton that is decomposed by bacteria that consume DO during the process, thus decreasing DO concentration in water (Ibanez *et al.*, 2008).

4.1.6 Nitrate

The mean nitrate concentrations of the flowing water bodies in this project varied from 0.73 to 3.92 mg L⁻¹ and 0.63 to 2.99 mg L⁻¹ for the Msunduzi River and DWWW respectively (Table 4.1). The mean NO₃⁻ concentration observed in this study fell within the ranges of 0.05 to 4.21 mg L⁻¹ and 0.24 to 4.26 mg L⁻¹ as reported by Olaniran *et al.* (2014) and Arimoro *et al.* (2007), respectively. On average, the highest concentration of nitrate was found detected at the Msunduzi Town section of the river (Table 4.1). The high value from Msunduzi Town was attributed to local run-off from the nearby crop field in the region where agronomists used nitrogen fertilisers. Nitrate ions in water was a major environmental concern due to high concentrations, eutrophication enhancement and human health effects (blue-baby syndrome).

The current nitrate drinking water guideline is 50 mg L⁻¹ and 6 mg L⁻¹ according to the WHO and DWAF guidelines for domestic water usage respectively (DWAF, 1996a, WHO, 2011). The concentrations of nitrate ions in water from this river system for all sites and seasons were below the maximum allowed value of NO₃⁻ in drinking water.

4.1.7 Sulfate

The mean levels of sulfate in water samples from this river system ranged from 4.8 to 31.5 mg L⁻¹ and 49.1 to 55.6 mg L⁻¹ for the Msunduzi River and DWWW, respectively (Table 4.1). The highest concentration of sulfate (103 mg L⁻¹) was observed in the sample collected from the Darvill outlet followed by the Agriculture sampling station. The DWWW uses potassium aluminum sulfate dodecahydrate for coagulation during the treatment process (WHO, 2011, Schmid, 1997). The increased levels of sulfate in the Darvill outlet sample may be due to insufficient removal of SO₄²⁻ from the wastewater. The release of inefficiently

treated municipal wastewater into the Msunduzi River has been recognised as the main route of surface water pollution (Matongo *et al.*, 2015). DWWW contributed to the elevated SO_4^{2-} concentrations at the Agriculture sampling station along with some agricultural runoff having leachates of gypsum (CaSO_4) (Matongo *et al.*, 2015).

The concentrations of sulfate in this water body showed no significant spatial and seasonal variation ($p>0.05$). The concentrations of sulfate were high during summer compared to other seasons. The higher levels of sulfate during wet season could be the results of inputs from runoff. The concentrations of sulfate in all the studies locations including DWWW were below the maximum allowed value of $200 \text{ mg L}^{-1} \text{ SO}_4^{2-}$ in domestic water usage (DWAf, 1996a).

4.1.8 Chloride

Chloride (Cl^-) is one of the main ions in surface waters and wastewater and concentrations in natural waters vary extensively (Fatoki *et al.* 2003). Higher levels of chloride are associated with water from saltwater lakes while mountain streams have low levels. Chloride is not considered as being harmful to human health. The concentrations of chloride in the water samples ranged from 9.67 to 42.4 mg L^{-1} and 74.8 to 79.5 mg L^{-1} for the Msunduzi River and DWWW, respectively (Table 4.1). Fatoki *et al.* (2003) reported similar chloride concentrations in Keiskamma River, South Africa.

In this study water, samples from the Darvil inlet and outlet had significantly higher concentrations of Cl^- than other sites. Sewage water and industrial effluents are rich in Cl^- and therefore the release of these wastes result in elevated chloride concentration in surface waters downstream (Ravindra and Kaushik, 2003). Higher mean levels of chloride ions were observed in the water during summer and spring. The high chloride values obtained during

the wet season can be attributed to rainfall, which lead to increased surface runoff carrying industrial effluents into the river.

Virha *et al.* (2011) observed similar distribution patterns of Cl^- in surface water of the Upper Lake of Bhopal. The observed Cl^- concentrations were lower than the range 3.64 to 184.04 mg L^{-1} reported by Oluyemi *et al.* (2010) and 7.5 to 181 mg L^{-1} reported by Chigor *et al.* (2012) in Nigerian waters. Chloride in water provisions are limited to 250 mg L^{-1} as at high concentration chloride imparts a salty taste which makes the water undrinkable (WHO, 2011). The concentrations of Cl^- in water samples from this river were below the maximum allowable concentration of Cl^- in drinking water and 100 mg L^{-1} Cl^- in domestic water usage (DWAF, 1996a).

4.2 Heavy Metals in surface water

The mean concentration of As in this river ranged from 0.75 to 2.33 $\mu\text{g L}^{-1}$ and 0.39 to 2.14 $\mu\text{g L}^{-1}$ for the Msunduzi River and DWWW, respectively (Table 4.3). Huntsman-Mapila *et al.* (2006) reported similar As concentration ranges of 1.1 to 3.1 $\mu\text{g L}^{-1}$ in Okavango Delta, Botswana. There was no significant spatial and seasonal changes ($p < 0.05$) in the concentration of the metals studied in this water body, except for Cd. The highest mean concentration of As was observed in the water samples from the Baynespruit (Figure 4.3) and this could be attributed to the nearby wood chemical industry that use copper arsenate during wood treatment. The mean concentration of As in this river system for summer was higher than that of other seasons could be caused by surface runoff during short rainfall. The observed As values were below the WHO limit of 10 $\mu\text{g L}^{-1}$ in drinking water (Table 4.3) (WHO, 2011).

Table 4.3 Mean concentrations ($\mu\text{g L}^{-1}$) of metals in water

	As	Cd	Cr	Pb	Zn
Henly Dam Outlet	0.75±0.42 (0.29-1.30)	0.12±0.15 (0.03-0.29)	8.24±7.52 (2.49-18.5)	2.84±1.74 (0.98-4.86)	11.1±10.8 (0.03-25.9)
Edendale Hospital	1.64±1.50 (0.45-3.77)	0.46±0.75 (0.02-1.57)	18.0±19.1 (0.88-39.1)	10.9±13.3 (0.78-29.2)	19.8±21.1 (0.33-49.5)
Camps Drift	1.88±1.51 (0.71-4.09)	0.38±0.67 (0.03-1.38)	20.1±21.2 (3.67-50.2)	7.66±7.62 (2.58-18.7)	17.0±15.5 (0.12-37.6)
Dutoit	0.80±0.92 (0.24-2.17)	0.20±0.23 (0.01-0.50)	7.81±6.48 (0.80-13.6)	5.59±4.42 (1.36-11.7)	54.5±87.7 (0.03-186)
Baynespruit	2.33±2.12 (0.70-5.44)	0.70±0.91 (0.01-0.50)	13.5±16.3 (1.32-35.8)	7.12±9.97 (0.93-21.9)	200±310 (0.20-658)
Darvil Inlet	2.14±1.39 (1.11-4.11)	0.83±0.89 (0.24-2.12)	40.3±12.5 (28.1-57.7)	0.29±0.12 (0.16-0.40)	241±175 (0.18-412)
Darvil Outlet	0.39±0.13 (0.22-0.55)	0.06±0.11 (0.00-0.22)	11.9±8.01 (3.92-23.0)	1.85±1.58 (0.59-3.95)	17.9±15.7 (0.06-37.5)
Agriculture	1.49±1.11 (0.80-3.16)	0.25±0.41 (0.03-0.86)	16.9±16.3 (3.20-40.0)	5.64±3.08 (3.14-10.1)	20.8±19.7 (0.04-47.3)
Msunduzi Town	1.58±1.51 (0.73-3.85)	0.28±0.39 (0.04-0.73)	13.4±16.4 (3.04-37.7)	4.62±4.68 (1.31-11.5)	19.6±25.5 (0.04-57.1)

The mean concentrations of cadmium in these sites varied from 0.12 to 0.7 $\mu\text{g L}^{-1}$ and 0.06 to 0.83 $\mu\text{g L}^{-1}$ for the Msunduzi River and DWWW respectively (Table 4.3). The highest mean concentration of Cd was observed in winter in the water sample from the Darvil inlet (Figure 4.2). The results indicate that water bodies for the proposed study area contained higher amounts of some of the heavy metals investigated. Higher mean levels of Cd were recorded in winter than other seasons. Winter is a dry season and usually elevated metal concentrations are observed because there is no dilution from the rainfall (Lokeshwari and Chandrappa, 2006).

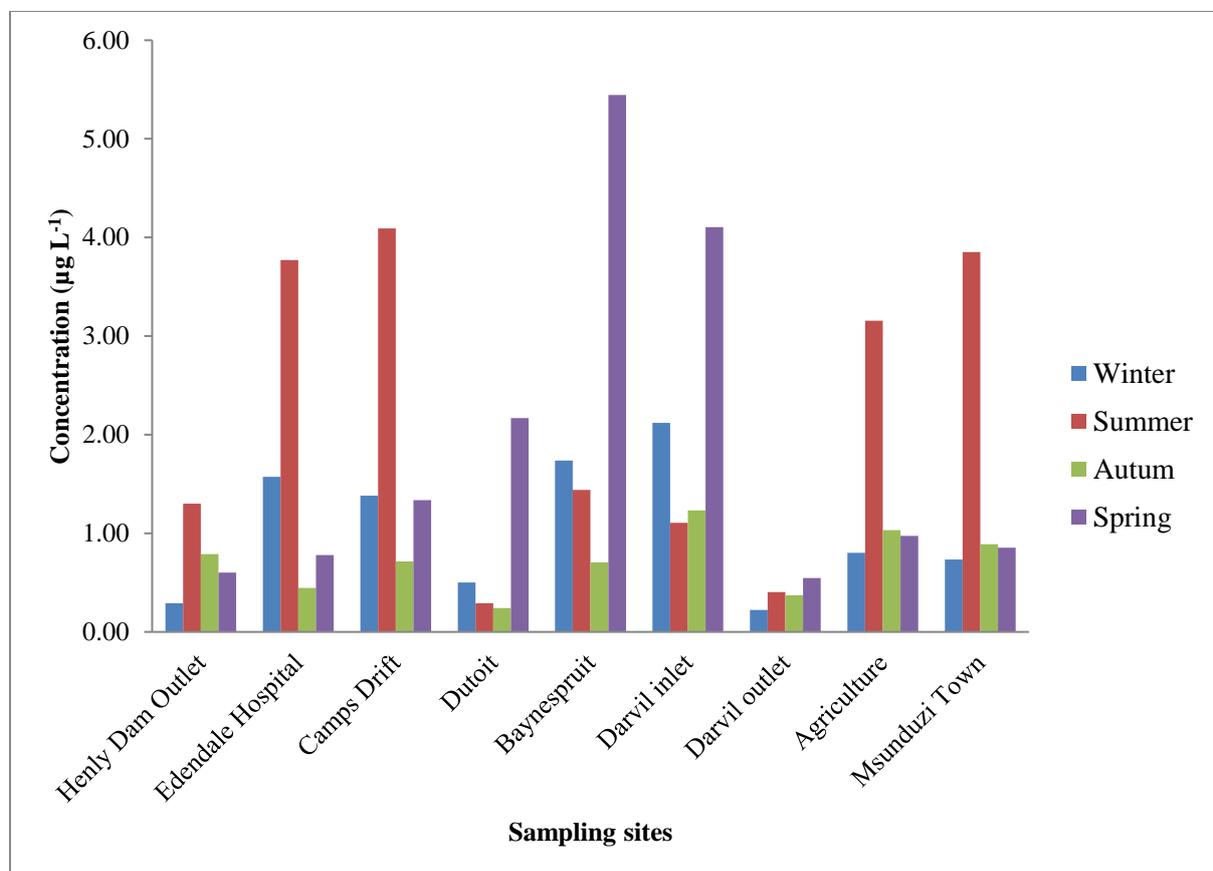


Figure 4.1 Seasonal total As concentrations in water samples

The concentration of Cd in this river system were above the DWAF standard for the protection of aquatic life (1.5×10^{-4} mg L⁻¹) but were below the WHO (0.003 mg L⁻¹) and DWAF (0.005 mg L⁻¹) standards for Cd in drinking water and domestic use, respectively (DWAF, 1996a, DWAF, 1996b, WHO, 2011). The observed Cd values are lower than the range of 1 to 10 µg L⁻¹ and 10 to 1000 µg L⁻¹ reported by Nawiri *et al.* (2013) and Fatoki *et al.* (2001), respectively.

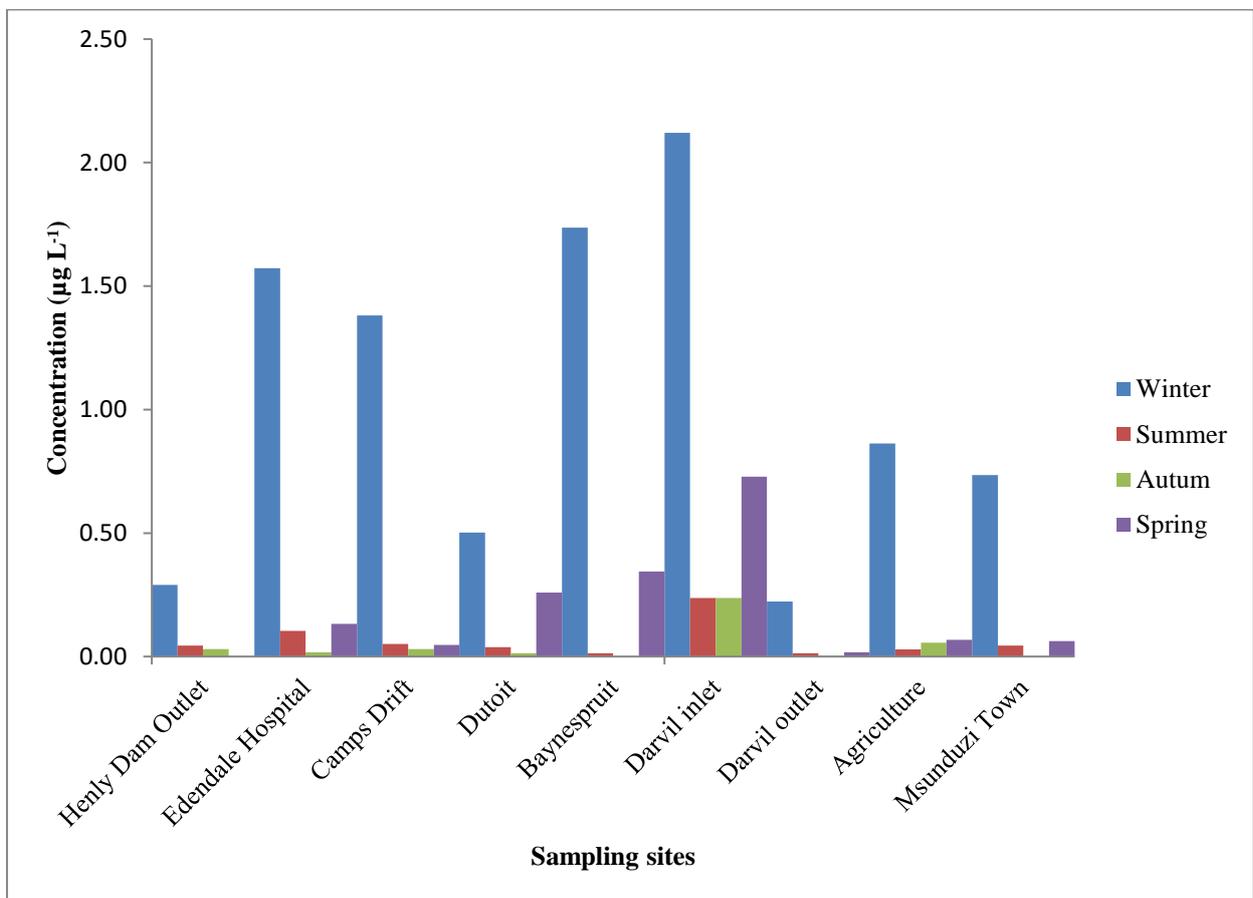


Figure 4.2 Seasonal total Cd concentrations in water samples

Pb is toxic and has no known biological function in plants and animal metabolism. Lead is considered unsafe even at trace levels in drinking water (Edokpayi *et al.*, 2016). The mean concentrations of Pb in the river water varied from 2.84 to 10.9 $\mu\text{g L}^{-1}$ and 0.29 to 1.85 $\mu\text{g L}^{-1}$ for the Msunduzi River and DWWW, respectively (Table 4.3). The highest mean concentration of Pb was detected in the water sample collected at Edendale Hospital (Figure 4.3), which may be credited to man-made activities such as traffic emission and medical waste near the site. Although Pb free gasoline has been introduced, there are vehicles that still use leaded gasoline (Edokpayi *et al.*, 2016). The mean concentration of Pb in Edendale hospital was higher during the winter months than the other months. These results show the effect of the dry season and water evaporation resulting in an increase in concentration of the heavy metal in the water.

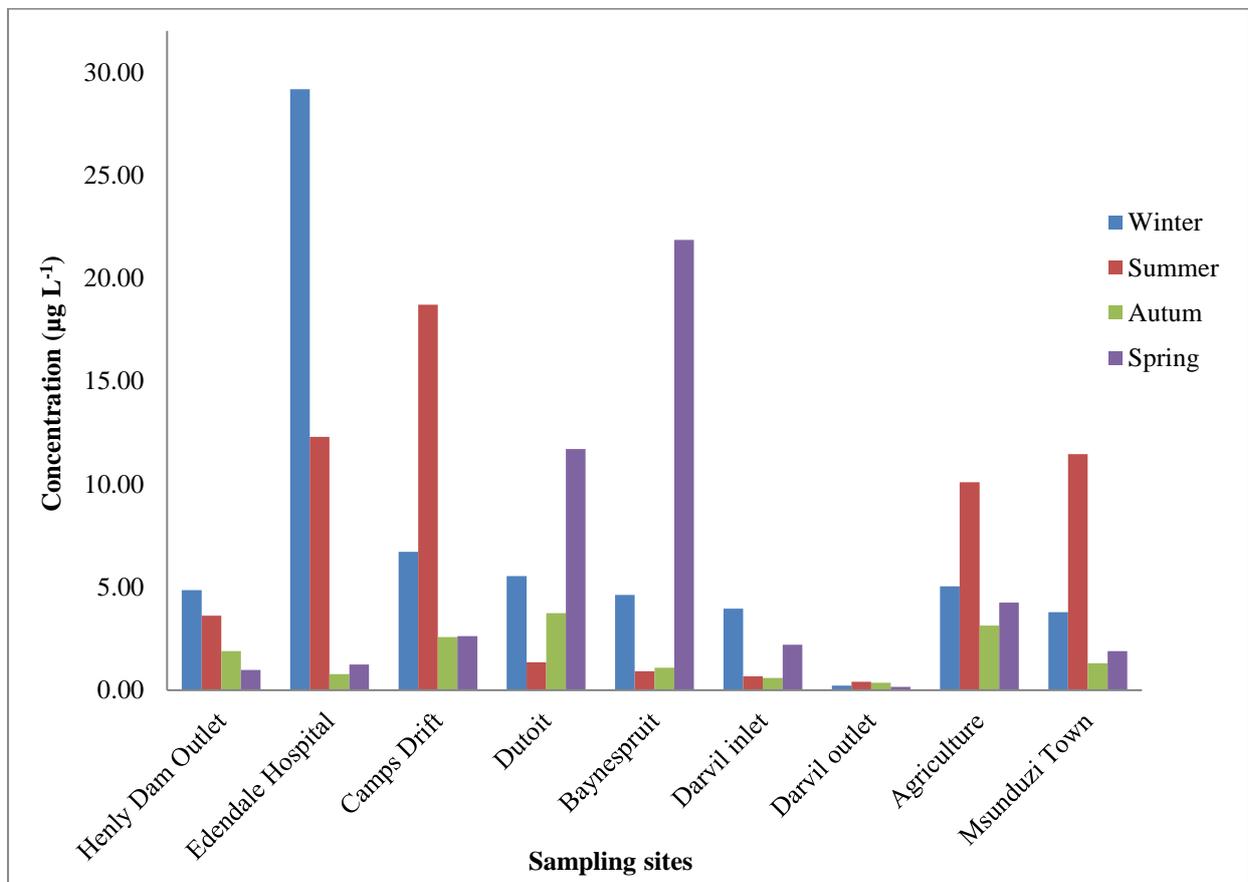


Figure 4.3 Seasonal total Pb concentrations in water samples

The WHO guideline for drinking water and South African target water quality range (TWQR) for Pb in river water for domestic use is 0.01 mg L⁻¹ (DWAF, 1996a). The DWAF guideline for protection of aquatic ecosystems is 2×10⁻⁴ mg L⁻¹. The concentrations of Pb in the water samples for all sites and seasons surpassed the DWAF guideline for protection of aquatic ecosystems but were lower than the TWQR value for Pb in water for domestic use except for the sample collected at Edendale Hospital in winter (29 µg L⁻¹) and Baynespruit in spring (22 µg L⁻¹). The concentrations of Pb obtained in this study were less than 0.042 mg L⁻¹, 0.9 mg L⁻¹ and 1,11 mg L⁻¹ for Mvundi, Plankenburg and Mtata rivers respectively in South Africa (Edokpayi *et al.*, 2016, Jackson *et al.*, 2009, Fatoki *et al.*, 2002).

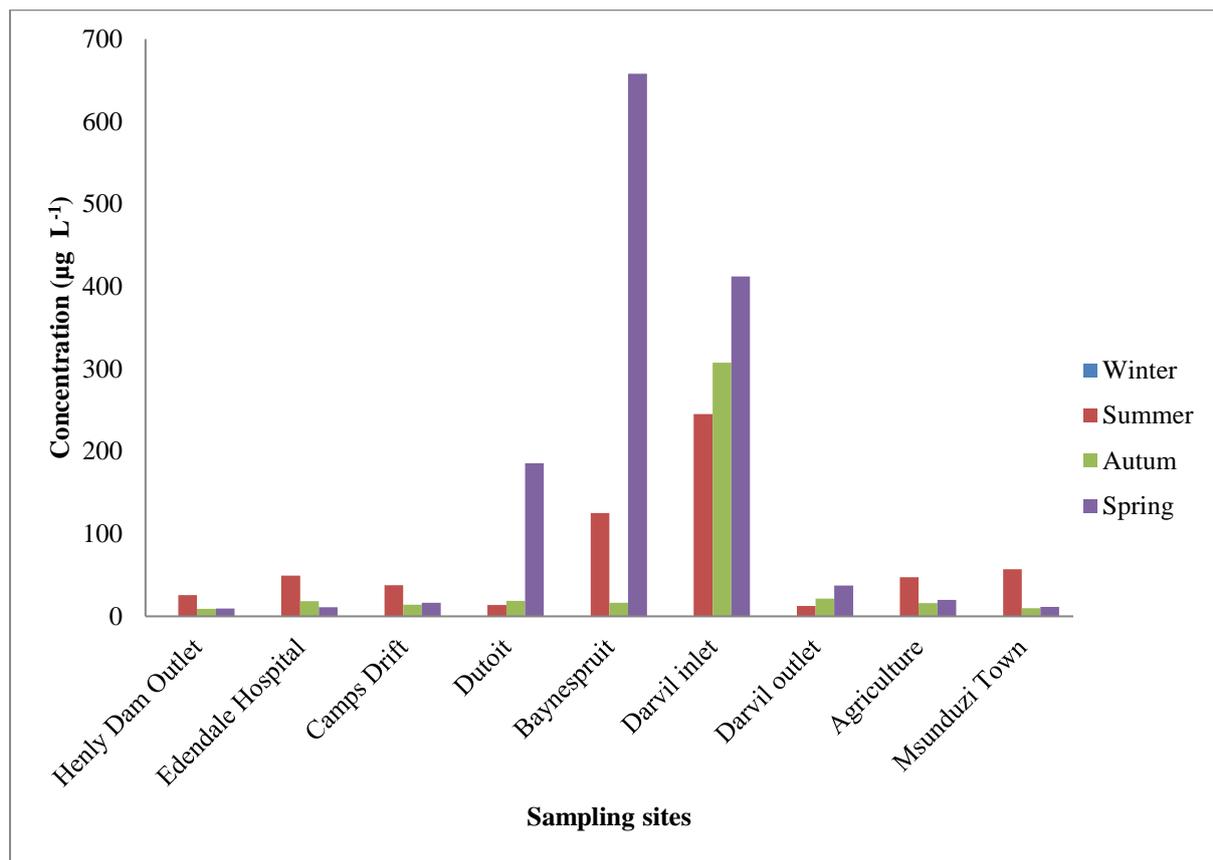


Figure 4.4 Seasonal total Zn concentrations in water samples

The mean concentrations of Zn in the surface water samples varied from 11.1 to 200 $\mu\text{g L}^{-1}$ and 17.9 to 241 $\mu\text{g L}^{-1}$ for the Msunduzi River and DWWW, respectively (Table 4.3). The mean concentrations of Zn in water samples collected at Baynespruit and the Darvill inlet were higher than those of the other locations (Figure 4.4). The increased levels of Zn may be attributed to the release of heavy metal loaded industrial wastewater. The concentrations of Zn in this water body were higher during spring than the other seasons. This increased Zn level could be due to rainfall during spring, which could increase the metal content of water by washing down industrial waste. The concentrations of Zn observed in the sites were lower than the South African TWQR of 3.0 mg L^{-1} for Zn in water for domestic use (DWAF, 1996a). The concentrations of Zn observed in this river system are comparable to levels reported for Dzindi, Umtata, Plankenburg, Diep and Mvudi Rivers in South Africa (Edokpayi *et al.*, 2016, Jackson *et al.*, 2009, Fatoki *et al.*, 2002).

Chromium is a required trace element for functioning of living organisms. However, it can cause human poisoning if consumed from drinking water at levels higher than 50 $\mu\text{g L}^{-1}$ (WHO, 2011). The mean concentrations of Cr in the studied water varied from 7.81 to 20.1 $\mu\text{g L}^{-1}$ and 11.9 to 40.3 $\mu\text{g L}^{-1}$ for the Msunduzi River and DWWW, respectively (Table 4.3). Oguzie and Okhagbuzo (2010) reported similar Cr levels of up to 75 $\mu\text{g L}^{-1}$ in Nigerian wastewater. High mean concentrations of Cr were observed in summer, which was due to seasonal differences of the river discharge and rainfall. The highest mean concentration of Cr was detected in the Darvill inlet followed by Camps Drift (Figure 4.5). The elevated Cr levels in Camps Drift are probably due to the nearby steel chemical industry.

The concentrations of Cr observed at all the sites were lower than the South African TWQR of $50 \mu\text{g L}^{-1}$ for Cr in water for domestic use and the range of 3 to $88 \mu\text{g L}^{-1}$ reported by Osman and Kloas (2010) in the Nile River, Egypt (DWAF, 1996a). The mean Cr levels found in this study did not exceed the recommended limit of $50 \mu\text{g L}^{-1}$ for Cr in drinking water (WHO, 2011). Chromium concentrations in river water failed to comply with the South African TWQR of $7 \mu\text{g L}^{-1}$ for protection of aquatic ecosystem for all four seasons (DWAF, 1996b), which means that the Msunduzi River is highly polluted with Cr.

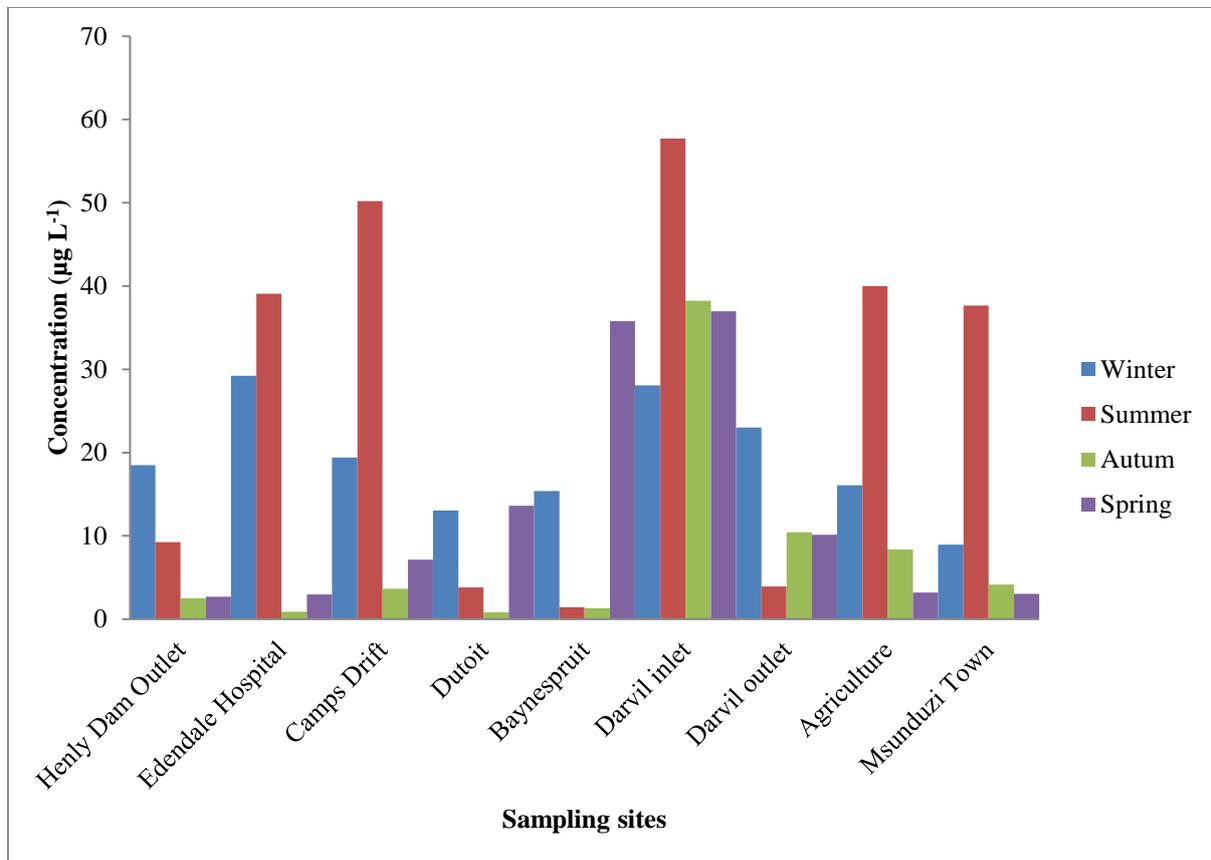


Figure 4.5 Seasonal total Cr concentrations in water samples

4.3 Water Quality Index

The results for the calculation of water quality indices for the different seasons are displayed in Tables 4.4 to 4.7. The significance of the water quality index (WQI) as shown in Table 3.7 in chapter 3 of thesis, suggests categories of water quality index levels (Chatterjee and Raziuddin, 2002, Yogendra and Puttaiah, 2008). The WQI is a measure of the water quality as expressed in terms of index number that represents the overall quality for any of the intended uses. The WQI values for this water body were 50, 85, 134 and 155 for autumn, winter, spring and summer respectively. This means that the studied river water was of good water quality in autumn, very poor water quality in winter and unsuitable for drinking in both spring and summer (Murthy *et al.*, 2014).

Spring and summer had relatively higher WQI values than that of winter and autumn. This suggests that water quality of this river system was poorer during spring and summer than autumn and winter, which could be attributed to surface runoffs from different accomplishments in the catchment such as agriculture, industries and informal settlements. Overall, WQI values for this river system fall within the very poor quality to inappropriate for drinking water categories. This indicates that the quality of the Msunduzi River has deteriorated and the water is not suitable to support and protect the aquatic life. The higher values of As, Cd and Pb contributed to the high values of WQI, therefore they are the key factors responsible for deterioration of water quality of this river system.

Table 4.4 Water Quality Index during the spring season

Determinant	Observed values	Standard values (S_n)	Unit Weight (W_n) = 1/S_n	Quality Rating (Q_n)	W_nQ_n
pH	7.96	8.5	0.1176	64.296	7.564
Conductivity (μS cm ⁻¹)	396	250	0.0040	158.213	0.633
TDS (mg L ⁻¹)	398	500	0.0020	79.600	0.159
DO (mg L ⁻¹)	4.56	6	0.1667	75.944	12.657
Chloride	41.9	250	0.0040	16.771	0.067
Nitrate	1.50	50	0.0200	3.008	0.060
Sulfate	25.0	250	0.0040	9.993	0.040
As	0.0019	0.001	1000	187	187000
Cd	0.0002	0.003	333.33	7.000	2333.333
Cr	0.0128	0.05	20	25.680	513.600
Pb	0.0052	0.01	100	52.100	5210
Zn	0.1512	3	0.3333	5.041	1.680
			∑W_n = 1454		
				∑W_nQ_n = 195080	
				WQI = 134	

Table 4.5 Water Quality Index during the summer season

Determinant	Observed values	Standard values (S_n)	Unit Weight (W_n) = 1/S_n	Quality Rating (Q_n)	W_nQ_n
pH	7.33	8.5	0.1176	22	2.588
Conductivity (μS cm ⁻¹)	311	250	0.0040	124.4	0.498
TDS (mg L ⁻¹)	314	500	0.0020	62.7	0.125
DO (mg L ⁻¹)	4.88	6	0.1667	81.3	13.543
Chloride	41.3	250	0.0040	16.5	0.066
Nitrate	2.44	50	0.0200	4.9	0.098
Sulfate	31.1	250	0.0040	12.4	0.050
As	0.00216	0.001	1000	216	216000
Cd	0.0001	0.003	333	3.333	1111
Cr	0.0270	0.05	20	54.02	1080.4
Pb	0.0066	0.01	100	66.2	6620
Zn	0.0683	3	0.3333	2.275	0.758
			∑W_n = 1454	∑W_nQ_n = 224829	
			WQI = 155		

Table 4.6 Water Quality Index during the autumn season

Determinant	Observed values	Standard values (S_n)	Unit Weight (W_n) = 1/S_n	Quality Rating (Q_n)	W_nQ_n
pH	7.59	8.5	0.1176	39.19	4.610
Conductivity (μS cm ⁻¹)	383	250	0.0040	153.26	0.613
TDS (mg L ⁻¹)	229	500	0.0020	45.83	0.092
DO (mg L ⁻¹)	4.56	6	0.1667	75.98	12.664
Chloride	34.0	250	0.0040	13.61	0.054
Nitrate	2.12	50	0.0200	4.23	0.085
Sulfate	15.8	250	0.0040	6.34	0.025
As	0.0007	0.001	1000	70	70000
Cd	0.0001	0.003	333	3.333	1111
Cr	0.0078	0.05	20	15.64	312.8
Pb	0.0017	0.01	100	17.2	1720
Zn	0.0479	3	0.3333	1.60	0.533
			∑W_n = 1454	∑W_nQ_n = 73162	
				WQI = 50	

Table 4.7 Water Quality Index during the winter season

Determinant	Observed values	Standard values (S_n)	Unit Weight (W_n) = 1/S_n	Quality Rating (Q_n)	W_nQ_n
pH	7.84	8.50	0.1176	56.30	6.62
Conductivity (μS cm ⁻¹)	401	250	0.0040	160.58	0.64
TDS (mg L ⁻¹)	302	500	0.0020	60.33	0.12
DO (mg L ⁻¹)	4.42	6	0.1667	73.67	12.28
Chloride	32.8	250	0.0040	13.11	0.05
Nitrate	1.24	50	0.0200	2.48	0.05
Sulfate	18.8	250	0.0040	7.54	0.03
As	0.0010	0.001	1000	100	100000
Cd	0.0011	0.003	333.33	35.00	11667
Cr	0.0191	0.05	20.00	38.14	763
Pb	0.0071	0.01	100.00	71.00	7100
Zn	0.0001	3.00	0.33	0.0038	0.0013
			∑W_n = 1454	∑W_nQ_n = 119549	
			WQI = 82		

4.4 Total metal concentrations in sediments

The results for determination of total concentrations of Cd, Cr, Pb and Zn in sediment are presented in Figures 4.6 to 4.9. The results indicated that there was no significant difference ($p>0.05$) in the concentration of Cd in the sediments from a given site during the study period. However, there were significant differences ($p<0.05$) in the concentration of Cr, Pb and Zn collected within a given location during the study periods due to various types of activities (Table 3.1 in Chapter 3 of thesis) along the river. Gordon and Muller (2010) reported that there was no South African sediment quality guideline as it was still under development. Therefore for the assessment of the state of Msunduzi river sediments, the international guidelines were used. . The extent of pollution of investigated sediments was assessed by comparison with the Canadian Environmental Quality Guideline for freshwater sediments (CCME, 2001). A comparison with these guidelines suggested that sediment from the majority of sites were heavily polluted with Cd which was from anthropogenic inputs including nearby metal plating and plastic fabrication industries.

The seasonal concentrations of Cd for all four seasons are displayed in Figure 4.6 and they ranged from 1.5 mg kg^{-1} to 2.79 mg kg^{-1} . The concentrations of Cd in the sediments collected from the Msunduzi town were slightly higher than those observed in the other sampling stations. The increased Cd levels in Msunduzi town may be due to runoffs from agricultural soil near the river. There were differences in the mean concentration of Cd in sediments from Edendale Hospital, Camps drift and Msunduzi town. The concentrations of Cd in the sediments were all above Canadian Environmental quality guidelines of 0.60 mg kg^{-1} for freshwater sediments.

The concentration of Cd observed at these sites corresponds to the ranges of 0.07 to 2.47 mg kg⁻¹ and 1.25 to 2.52 mg kg⁻¹ recorded by Fu *et al.* (2013) and Wojtkowska (2011) respectively, in areas, with significant anthropogenic activities. Cadmium pollution in this study was possibly caused by anthropogenic activities such as agricultural runoff containing phosphate fertilizers and pesticides which have Cd (Ghrefat and Yusuf, 2006, Lambert *et al.*, 2007).

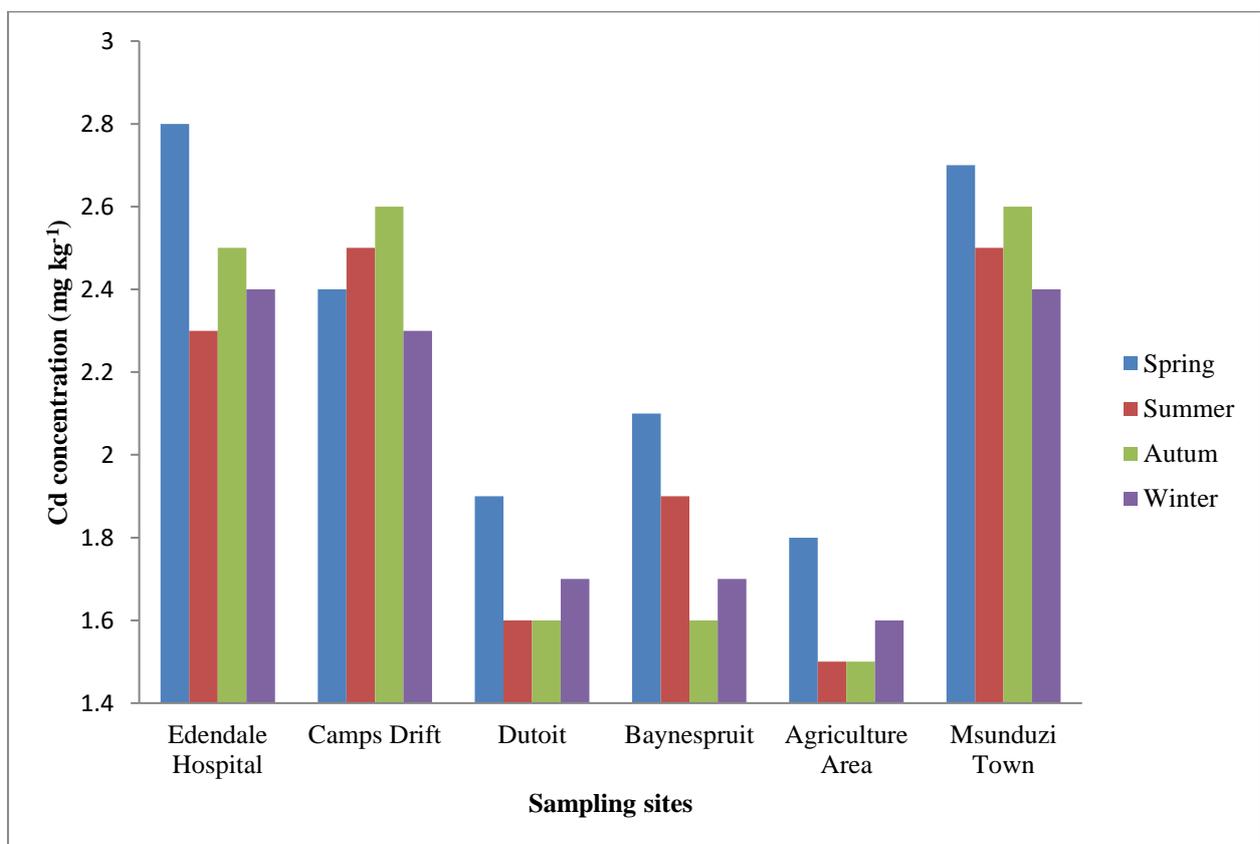


Figure 4.6 Seasonal total Cd concentrations (mg kg⁻¹) in sediment

The concentration of Cr in the sediment samples varied from 42.6 to 246 mg kg⁻¹ (Figure 4.7). The highest concentrations of Cr were observed in sediments collected at Edendale Hospital and Baynespruit sections of the river. This could be due to the nearby paint industry and domestic waste discharge from the informal settlements. For most sites, the sediment samples collected during spring and summer showed higher concentrations of Cr except for the Agricultural area and Msunduzi town. Elevated Cr levels during spring and summer may be attributed to increased rainfall which washes surface soil into the river system.

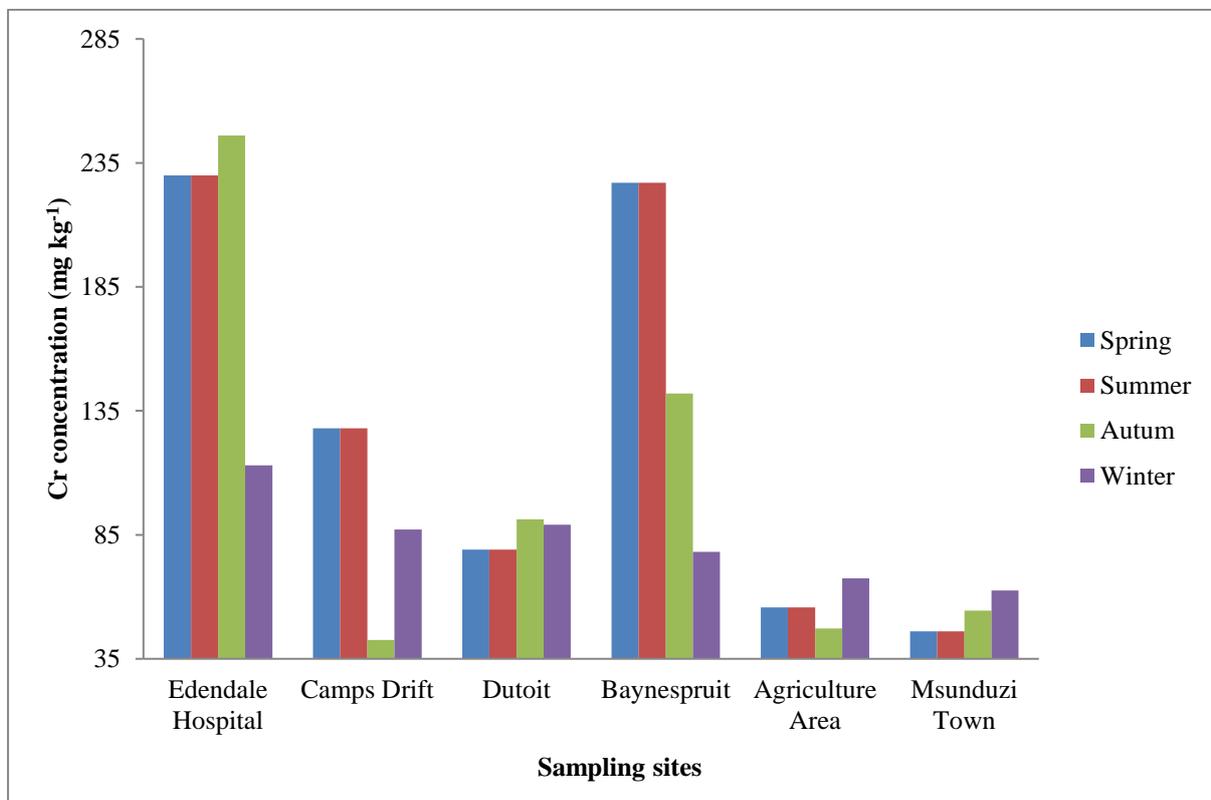


Figure 4.7 Seasonal total Cr concentrations (mg kg⁻¹) in sediment

Chromium concentrations at all study sites during all seasons exceeded the CCME guideline of 37.3 mg kg⁻¹ and were higher than levels reported for the Swartkop River and estuary (Binning and Baird, 2001) and other African river systems (Iwegbue *et al.*, 2012, Chukwujindu *et al.*, 2007). This implies that the sediments of the studied river are contaminated with Cr which may be caused by anthropogenic activities. Similar to this study Cr ranges of 43.28 mg kg⁻¹ to 106.64 mg kg⁻¹ were reported by Peifang *et al.*, (2014) in Gonghu Bay sediments in Taihu Lake, China (Peifang *et al.*, 2014).

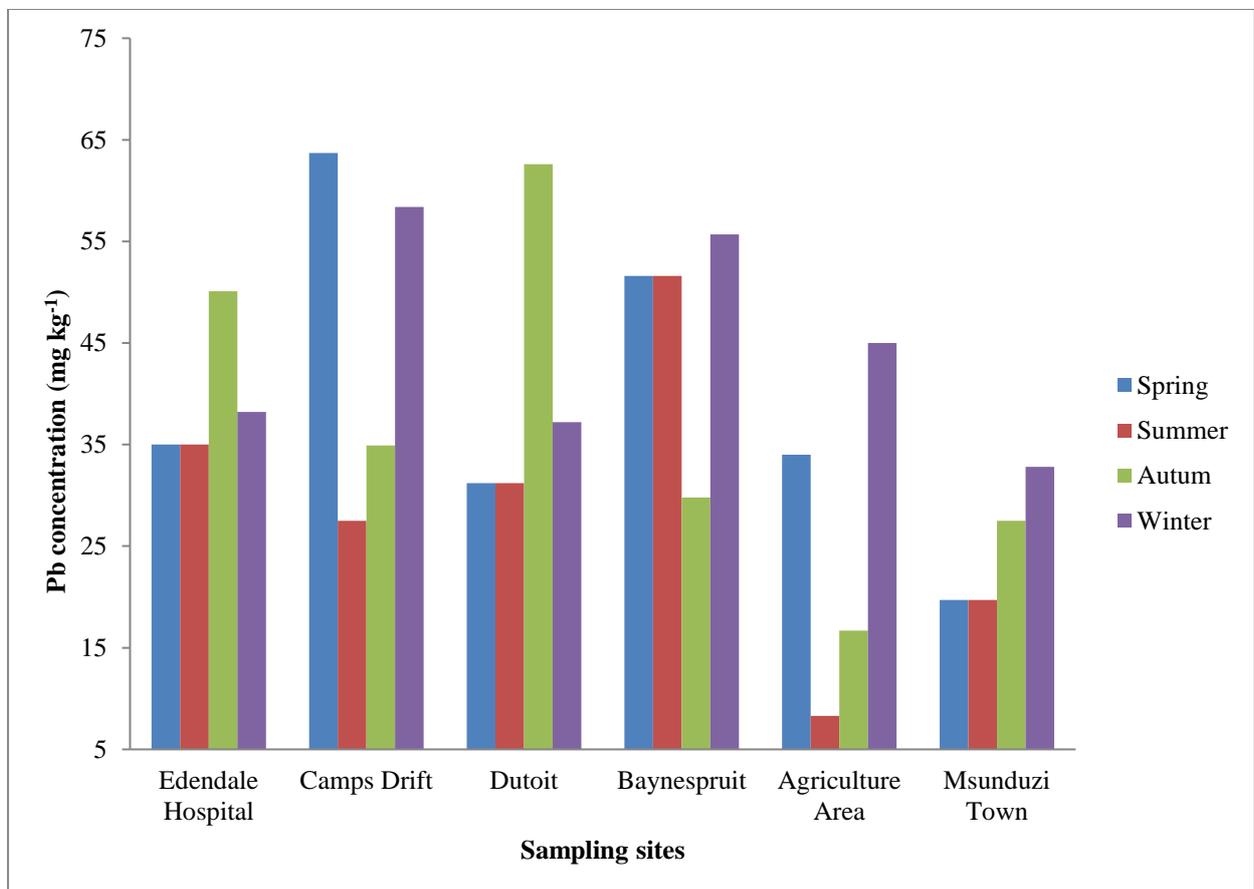


Figure 4.8 Seasonal total Pb concentrations (mg kg⁻¹) in sediment

The Pb concentration in the sediment samples varied from 8.3 to 63.7 mg kg⁻¹ (Figure 4.8). The guideline value for Pb in freshwater sediment is set at 35.0 mg kg⁻¹ (Smith *et al.*, 1996). The concentrations of Pb observed in the majority of the samples were above the guideline value of 35.0 mg kg⁻¹. The highest Pb concentration was observed at Camps Drift during spring, probably because the temperature, pH, conductivity in the river are moderate during the spring (Table 4.2). These conditions are favourable for sediment to be adsorbed and combined with heavy metals (Peifang *et al.*, 2014). The sources of Pb in the river system were due to emissions from leaded gasoline vehicle. The concentration of Pb observed in the study sites were lower than that found in sediments of the Guangzhou section of the Pearl River, Southern China (Wang *et al.* (2011) and Qued El Maadene basin, Northern Tunisia (Ayari *et al.* (2016).

The concentration of Zn in the sediment throughout the study period ranged from 36.9 to 402 mg kg⁻¹ (Figure 4.9). The highest concentration of Zn was observed in the Agricultural area during the winter period. This indicates that upstream industrial and municipal wastewater discharges along the river bank are major sources of Zn pollution. The Zn concentrations varied significantly with the seasons. The concentrations of Zn observed in this study were higher than those reported by Edokpayi *et al.* (2016) which ranged from 14.48 to 39.88 mg kg⁻¹ for sediments of the Mvudi River and Awofolu *et al.* (2005) which ranged from 0.08 to 0.491 mg kg⁻¹ for sediments of the Tyume River, South Africa.

The levels of Zn obtained in the investigation were below the Canadian Sediment Quality Guideline (123 mg kg⁻¹), the Australian and New Zealand Environment and Conservation Council Guideline (200 mg kg⁻¹) (ZECC, 2000) and the United State Environmental Quality Guidelines (120 mg kg⁻¹) (MacDonald *et al.* (2000) except for sediment samples obtained in the Agricultural area and from Baynespruit.

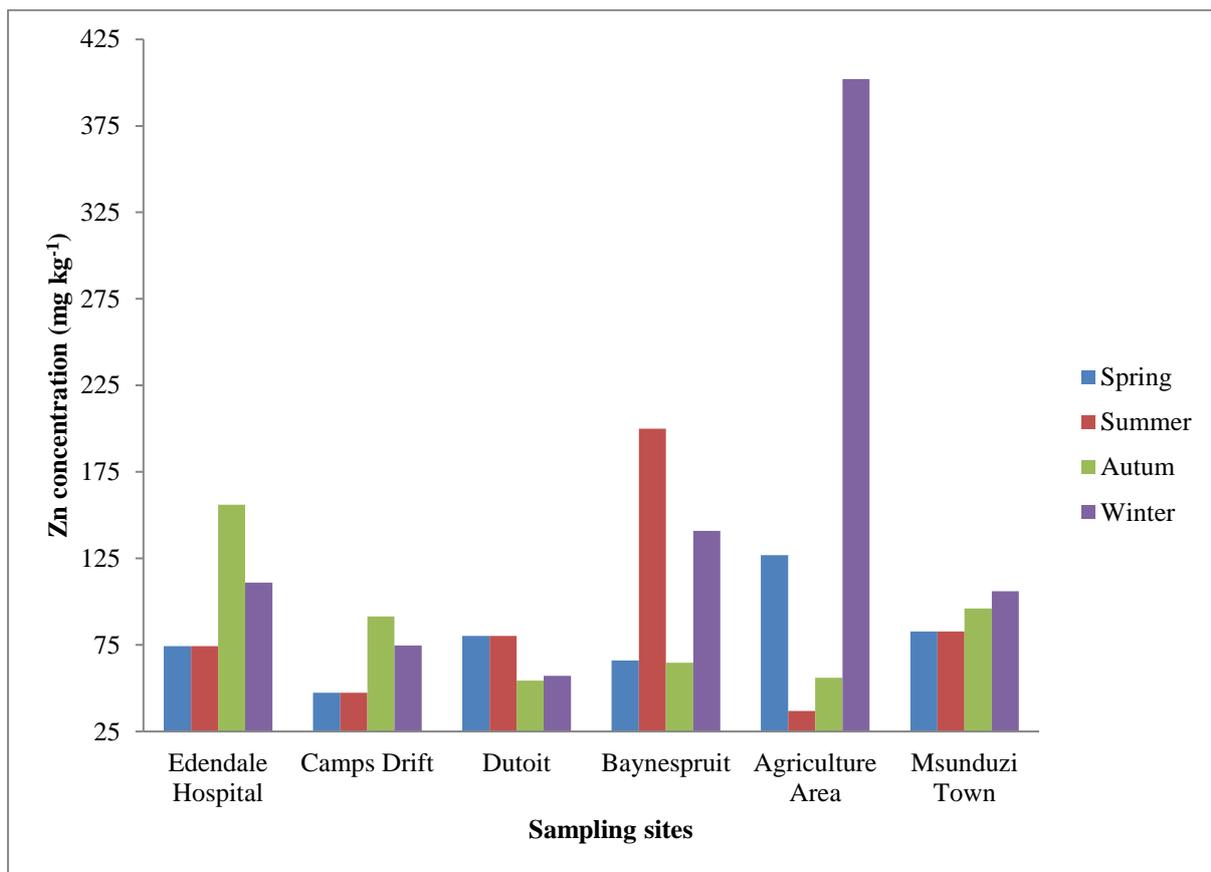


Figure 4.9 Seasonal total Zn concentrations (mg kg⁻¹) in sediment

The levels of Zn obtained in the investigation were below the Canadian Sediment Quality Guideline (123 mg kg⁻¹), the Australian and New Zealand Environment and Conservation Council Guideline (200 mg kg⁻¹) (ZECC, 2000) and the United State Environmental Quality Guidelines (120 mg kg⁻¹) (MacDonald *et al.* (2000) except for sediment samples obtained in the Agricultural area and from Baynespruit.

Zinc can enter aquatic systems from numerous sources including industrial discharges, municipal sewage and runoff (Alagarsamy, 2006). The high levels of Zn in this study were attributed to the galvanizing metal industry near Baynespruit. The increased Zn concentration at the Agricultural site indicated that inputs of Zn are probably from the waste treatment plant situated upstream. The contribution of organic waste from municipal sewage add to elevated levels of Zn in sediments (Alagarsamy, 2006).

4.5 Index of Geoaccumulation

The index of geoaccumulation (I_{geo}) is a criterion that is used to assess for heavy metal contamination in sediments. The I_{geo} of Cd, Cr, Pb and Zn in the sediment samples from the study sites are displayed in Table 4.8. The I_{geo} values for Cd in the sediments ranged from 1.91 to 2.63. According to the Muller classification (Saha and Hossain, 2011), the investigated sites fall within the moderately polluted to strongly polluted categories with Cd.

4.6 Pollution load factor

The estimated pollution load indices (PLI) for the studied metals are displayed in Table 4.9. The significance of the PLI values is defined as follows, PLI values >1 indicates pollution while PLI values <1 indicate no pollution (Chakravarty and Patgiri, 2009, Seshan *et al.*, 2010). The calculated PLI values as shown in Table 4.9 for most sites were greater than 1 which indicated that the studied sites were polluted. In this study, Cd had the greatest contribution to the pollution load values.

4.7 Ecology Risk Assessment of metals in sediments

The estimated ecological risks (ER) associated with exposure to metals in the studied sediments are presented in Table 4.10. The ecological risk of metals in the sediment was evaluated by ecological risk indices (RI) originated by Hakanson (1980) as well as comparing with the numerical Sediment Quality Guideline (SQG) of the USEPA derived for coastal sediment of Florida (Long *et al.*, 1995, MacDonald *et al.*, 2000). The SQG can be useful for the assessment of the ecological effect of sediments in terms of Threshold Effect Level (TEL) less than which no adverse effect is anticipated to occur and probable effect level (PEL) above which adverse effects are anticipated to occur (MacDonald, 1994).

The ER values are shown in Table 4.10 for the difference sites. The ER values for the investigated metals in these sites were less than 20 except for Cd which indicates that negligible ecological risk is associated with exposure to Cr, Pb and Zn in these sediments. However, in the case of Cd, the ER values ranged from 147 to 279. The sediment samples from Edendale Hospital and Msunduzi town sections of the river had higher ER values than the other sites. This indicates that these sections of the river are polluted with Cd which may be attributed to domestic waste entering from informal settlements and the use of fertilisers from agricultural activities. The potential ecological risk for metals in the sediments followed the decreasing order of $Cd > Pb > Cr > Zn$. In this study, Cd has the highest ER value which suggests that Cd was the main contributing factor to ecotoxicological risk associated with exposure to the sediments. The RI value of these sites ranged from 152 to 294 which suggest considerable to very high ecological risk (Table 3.6 in Chapter 3 of thesis).

Table 4.8 Geoaccumulation index

Sites	Season	Cd	Cr	Pb	Zn
Edendale Hospital	Spring	2.63	0.77	0.22	-0.94
	Summer	2.37	0.77	0.22	-0.94
	Autumn	2.48	0.87	0.74	0.13
	Winter	2.41	-0.26	0.35	-0.36
Camps Drift	Spring	2.42	-0.08	1.09	-1.59
	Summer	2.45	-0.08	-0.13	-1.59
	Autumn	2.51	-1.66	0.22	-0.64
	Winter	2.37	-0.63	0.96	-0.93
Dutoit	Spring	2.11	-0.77	0.06	-0.83
	Summer	1.85	-0.77	0.06	-0.83
	Autumn	1.83	-0.56	1.06	-1.39
	Winter	1.91	-0.60	0.31	-1.32
Baynespruit	Spring	2.21	0.75	0.78	2.11
	Summer	2.07	0.75	0.78	0.49
	Autumn	1.81	0.07	-0.01	-1.14
	Winter	1.94	-0.79	0.89	-0.01
Agriculture Area	Spring	1.97	-1.28	0.18	-0.17
	Summer	1.76	-1.28	-1.86	-1.95
	Autumn	1.70	-1.52	-0.85	-1.35
	Winter	1.82	-1.00	0.58	1.50
Msunduzi Town	Spring	2.57	-1.55	-0.61	-0.78
	Summer	2.48	-1.55	-0.61	-0.78
	Autumn	2.53	-1.31	-0.13	-0.57
	Winter	2.43	-1.11	0.13	-0.43

Table 4.9 Pollution Load Index

Sites	Season	Cd	Cr	Pb	Zn	PLI
Edendale Hospital	Spring	9.30	2.56	1.75	0.78	2.39
	Summer	7.73	2.56	1.75	0.78	2.28
	Autumn	8.36	2.74	2.51	1.65	3.12
	Winter	7.99	1.25	1.91	1.17	2.17
Camps Drift	Spring	8.03	1.42	3.19	0.50	2.06
	Summer	8.17	1.42	1.38	0.50	1.68
	Autumn	8.53	0.47	1.75	0.96	1.61
	Winter	7.78	0.97	2.92	0.79	2.04
Dutoit	Spring	6.48	0.88	1.56	0.84	1.65
	Summer	5.42	0.88	1.56	0.84	1.58
	Autumn	5.34	1.01	3.13	0.57	1.76
	Winter	5.63	0.99	1.86	0.60	1.58
Baynespruit	Spring	6.94	2.52	2.58	6.48	4.13
	Summer	6.30	2.52	2.58	2.11	3.05
	Autumn	5.25	1.57	1.49	0.68	1.70
	Winter	5.77	0.87	2.79	1.48	2.13
Agriculture Area	Spring	5.86	0.62	1.70	1.34	1.69
	Summer	5.10	0.62	0.41	0.39	0.84
	Autumn	4.89	0.52	0.83	0.59	1.06
	Winter	5.31	0.75	2.25	4.23	2.48
Msunduzi Town	Spring	8.90	0.51	0.98	0.87	1.41
	Summer	8.39	0.51	0.98	0.87	1.39
	Autumn	8.68	0.61	1.37	1.01	1.64
	Winter	8.08	0.70	1.64	1.12	1.79

Table 4.10 Ecological risk of metals

Sites	Season	Cd	Cr	Pb	Zn	RI
Edendale Hospital	Spring	279	5.11	8.75	0.78	294
	Summer	232	5.11	8.75	0.78	247
	Autumn	251	5.47	12.53	1.65	271
	Winter	240	2.50	9.56	1.17	253
Camps Drift	Spring	241	2.83	15.93	0.50	260
	Summer	245	2.83	6.88	0.50	255
	Autumn	256	0.95	8.74	0.96	267
	Winter	233	1.94	14.59	0.79	251
Dutoit	Spring	195	1.76	7.80	0.84	205
	Summer	163	1.76	7.80	0.84	173
	Autumn	160	2.03	15.64	0.57	178
	Winter	169	1.98	9.31	0.60	181
Baynespruit	Spring	208	5.04	12.89	6.48	232
	Summer	189	5.04	12.89	2.11	209
	Autumn	157	3.15	7.45	0.68	169
	Winter	173	1.74	13.93	1.48	190
Agriculture Area	Spring	176	1.24	8.50	1.34	187
	Summer	153	1.24	2.07	0.39	157
	Autumn	147	1.05	4.16	0.59	152
	Winter	159	1.50	11.24	4.23	176
Msunduzi Town	Spring	267	1.02	4.92	0.87	274
	Summer	252	1.02	4.92	0.87	259
	Autumn	260	1.21	6.87	1.01	269
	Winter	242	1.39	8.19	1.12	253

4.8 Chemical Speciation

The speciation patterns of Cd, Cr, Pb and Zn in the river bed sediment are displayed in Figures 4.10 to 4.13. The speciation patterns of these metals in the sediments showed spatial and seasonal differences. The speciation pattern of Cd in these sediment samples was dominant in the residual fraction (29.8 to 47.4%) (Figure 4.10). Metals related with residual fractions generally form part of the crystalline structure of minerals, remain comparatively stable and inert, and they are not simply released into the mobile and bioavailable phases (Jiang *et al.*, 2013, Rogan *et al.*, 2010, Turki, 2007). The existence of Cd in the residual phase has been documented in the literature (Shaheen *et al.*, 2013). Cadmium in the Fe-Mn oxide phase constituted 21.3 to 41.1% of the total Cd content in the sediment surface.

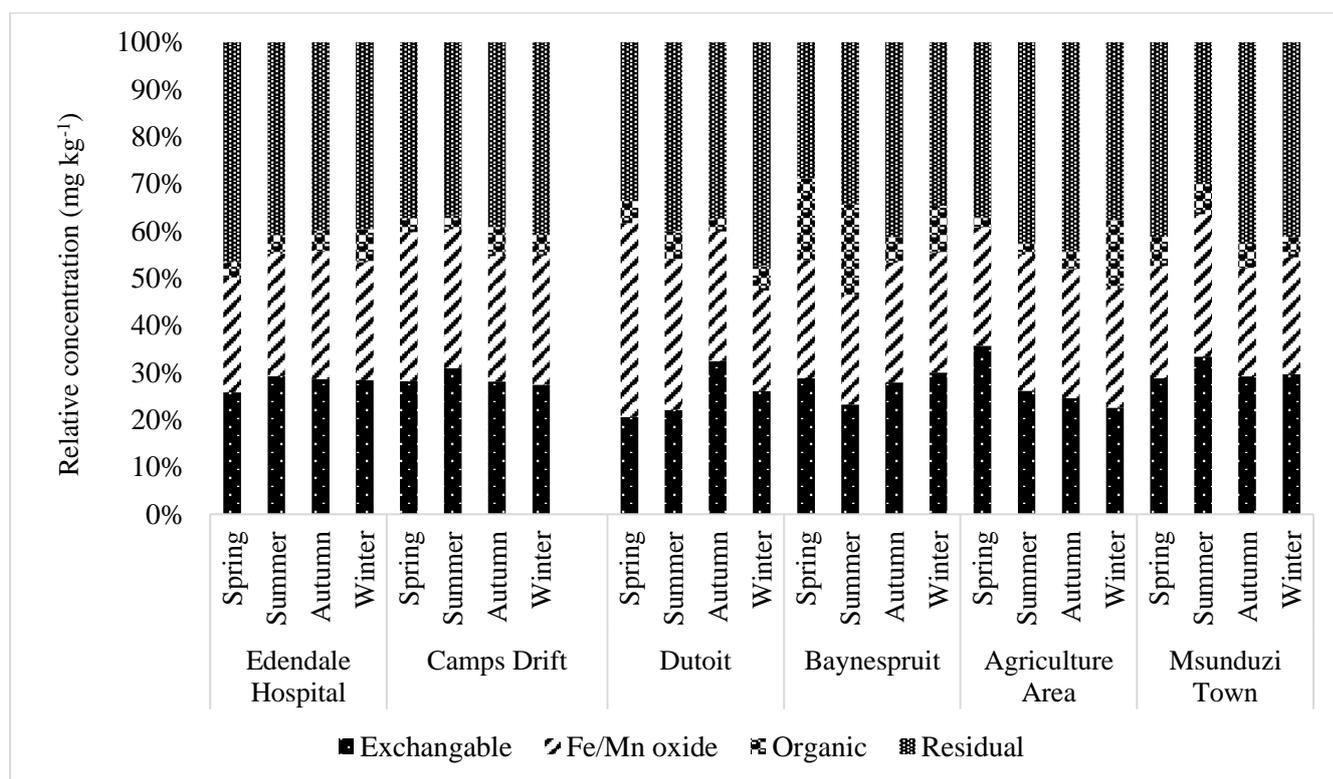


Figure 4.10 Speciation of Cd concentrations in sediment

The association of Cd with the Fe-Mn oxides phase (reducible phase) suggests that Cd can be easily released and made available to the surrounding biota under reducing conditions. In these sediments, lower amounts of Cd were found in the oxidisable phase which ranged from 2.2 to 19.5%.

The exchangeable and acid soluble phase constituted 22.6 to 32.5% of the total Cd concentrations in the sediments. The existence of significant amounts of Cd in this phase suggests that Cd is potentially available to biota. However, the association of Cd with the exchangeable/acid soluble phase is due to Cd having special affinity for clay mineral structures due to its ionic radius and tends to associate with carbonate minerals at high pH (Jiang *et al.*, 2013).

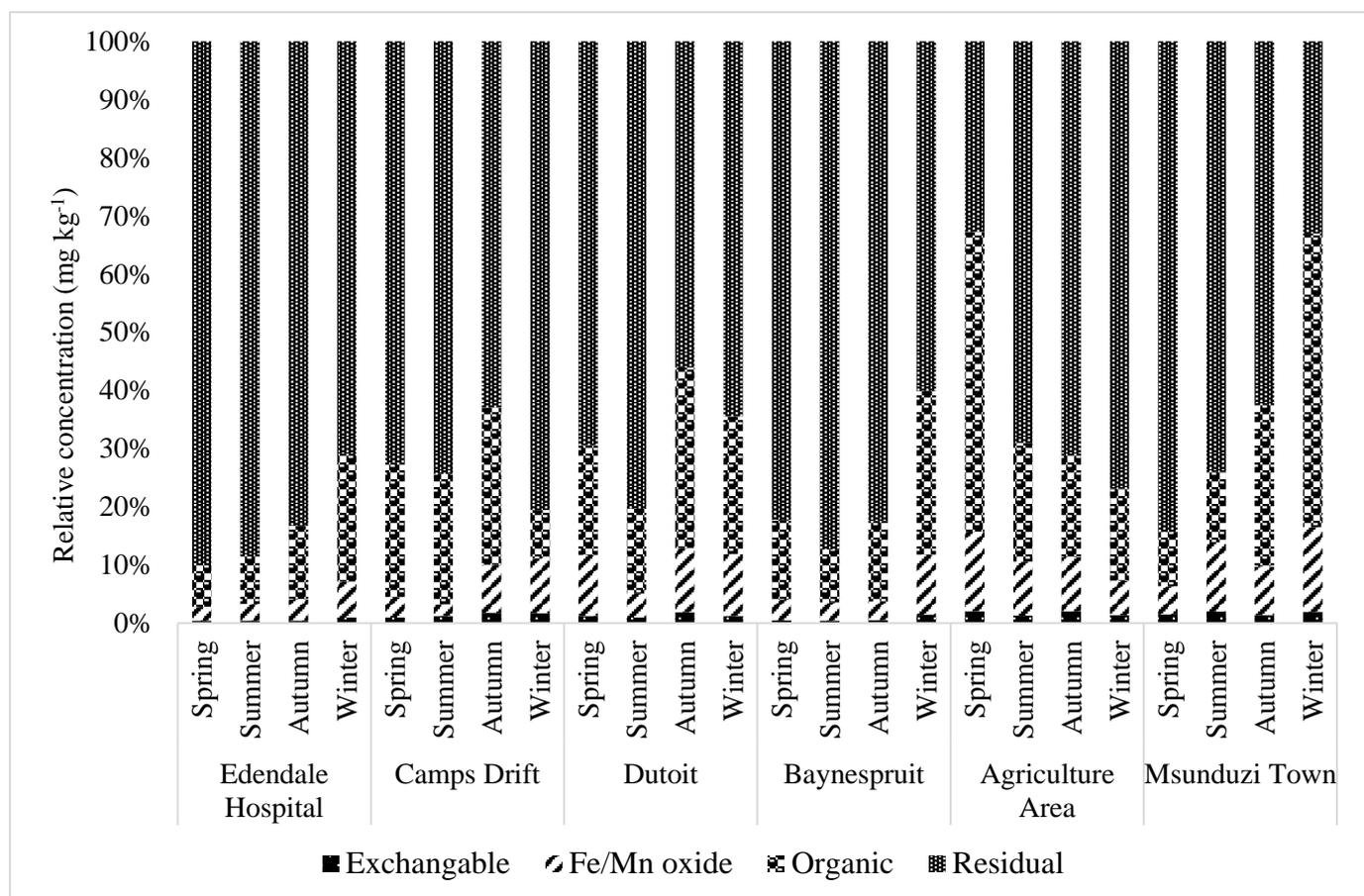


Figure 4.11 Speciation of Cr concentrations in sediments

The speciation patterns of Cr followed the order residual > organic > Fe-Mn oxides > exchangeable (Figure 4.11). The residual fractions constituted 33 to 89.7 % of the total Cr concentrations at these sites. The dominance of Cr in the residual fraction indicates that Cr is not soluble in this type of sediment. Low solubility of Cr in sediment has been documented in the literature by Yang *et al.* (2009), Iwegbue (2011) and Iwegbue *et al.* (2007) who reported >75%, 62.3% and 65%; respectively. In this study, the organic bound fraction constitutes another important phase of Cr in the sediment. The organic bound Cr constituted 7.5 to 51.5% of the total Cr concentrations. The occurrence of significant amounts of Cr in the organic bound fraction in sediment systems has been reported in the literature ranging from 18 to 44% (Iwegbue, 2011). The occurrence of Cr in the organic fraction indicated that it occurred in the form of Cr³⁺ oxides bound to organic matter (Kotoky *et al.*, 2003, Tokalioglu *et al.*, 2000).

Cr appeared to be linked with the Fe-Mn oxide fraction ranging from 2.0 to 14.6% of the total Cr content in these sediments. This is probably due to the fact that the existing pH of the sediment does not encourage the formation of dichromate and decreases the affinity of sorption by the hydrous metal oxides (Fe-Mn). pH influences the oxidation of Cr(III) primarily by varying the redox potential in the system i.e. the concentration of H⁺, the species of Cr(III) and their distribution in the system (Feng *et al.*, 2006). Nevertheless, at low pH and concentration, where solubility of Cr (III) is higher, strong precise adsorptions on Fe-Mn oxides occur. This is possibly the reason why there is a variance in the percentage of chromium associated with the Fe-Mn oxide (Kotoky *et al.*, 2003, Iwegbue, 2011). The amount of Cr (0.4 to 2.0%) in the exchangeable fraction was lower compared with the other geochemical phases of Cr in the sediment. The existence of low amounts of Cr in the exchangeable phase indicates that Cr is available at low concentrations in these sediments.

The partition scheme (Figure 4.12) for Pb suggests that this metal is associated with all the fractions that make up the sedimentary material. The residual and Fe-Mn oxide fractions of Pb are the most important phases in the investigated sediments. The elements strongly bound to Fe-Mn fractions are thermodynamically unstable in reducing conditions and hence easily discharged and accessible for the surrounding biota (Rogan *et al.*, 2010). The amount of Pb in residual and Fe-Mn oxide phases varied from 5.8 to 77.5% and from 17.6 to 79.9%, respectively. This suggests that Pb is kept in the easily-to-moderately reducible oxide or hydroxide phase (Ryan *et al.*, 2002). The Pb in the Fe-Mn oxides show that Pb^{2+} is able to substitute Fe^{2+} in Fe-Mn oxide because of the adsorption capacity and surface area (Rogan *et al.*, 2010). This indicates that Pb could form stable complexes with Fe and Mn oxides (Turki, 2007, Iwegbue, 2011).

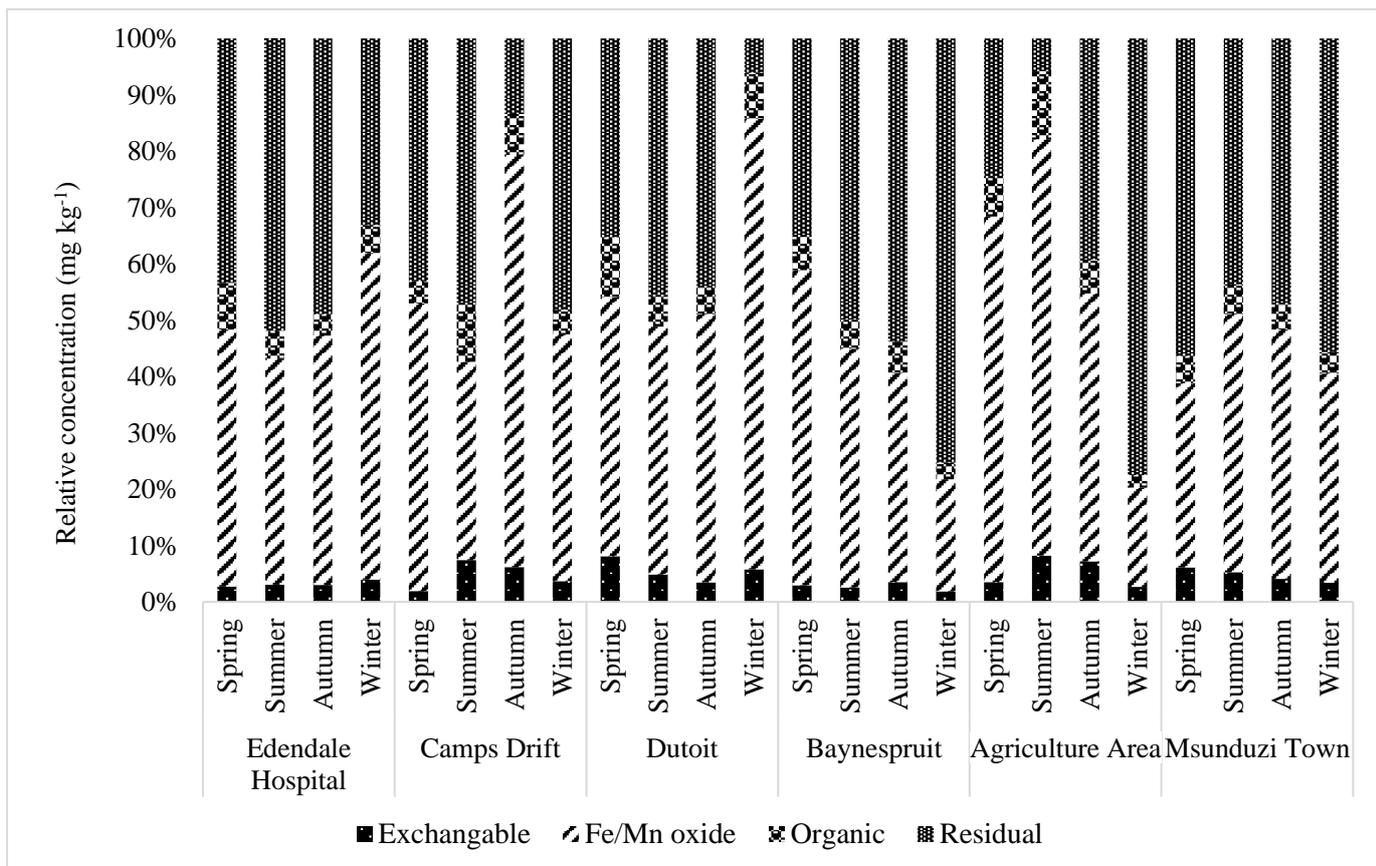


Figure 4.12 Speciation of Pb concentrations in sediment

Lower amounts of Pb in the residual fraction were observed in sediments from the Agriculture area (5.8%) in summer and the Dutoit areas (6.1%) during winter. Jiang *et al.* (2013) also established that Pb was mostly associated with Fe/Mn oxides and residual fractions in the Xiawangang river sediments, China. Relatively low amounts (2.2 to 12.1%) of Pb were found in the organic phase. The results obtained for Pb in organic phase reported by Shaheen *et al.* (2013) was also less than 53%. The results of Pb in the exchangeable fraction (1.9 to 8.1%) indicate that Pb is not readily available in this sediment system.

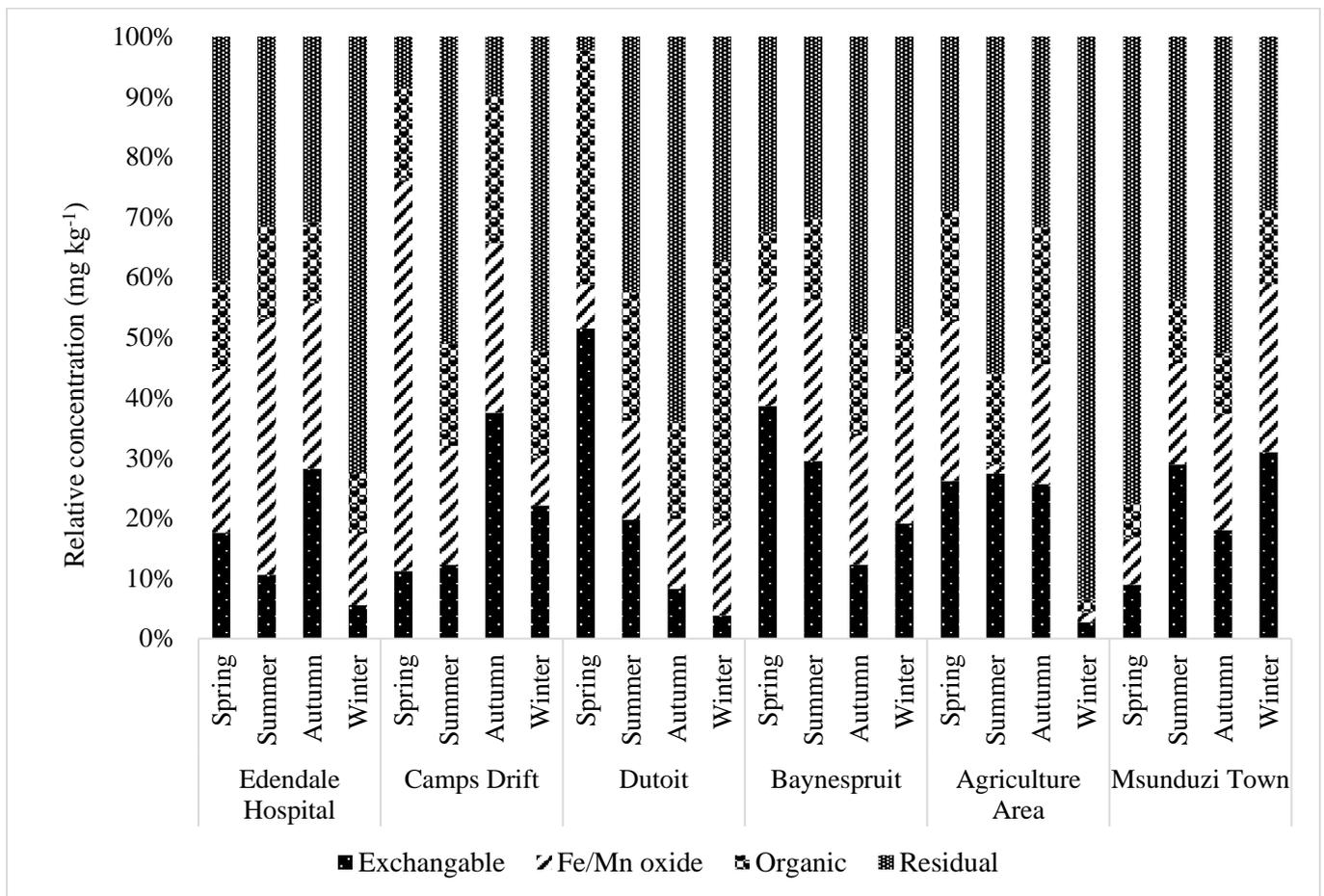


Figure 4.13 Speciation of Zn concentrations in sediment

The percentage of Zn in different extraction fractions ranged from 2.4 to 93.4%, 2.3 to 43.7%, 1.3 to 64.9% and 2.7 to 51.5% in the residual, organic, Fe-Mn oxide and exchangeable phases, respectively. Soluble Zn attaches to Fe-Mn oxides or organic matter and the mobility and availability is dependent on pH (Singovszka and Balintova, 2012). The fractionation patterns (Figure 4.13) suggest that a significant proportion of Zn in these sediments exist in the residual and Fe-Mn oxide phases. The occurrence of significant amounts of Zn in the residual and Fe-Mn oxide fractions have been reported to be 25.3 to 46.8%, 53% and 66.25% by Iwegbue (2011), and Ashraf *et al.* (2012), respectively.

The presence of Zn in the residual fraction suggests that Zn occurred mainly as stable silicate while Zn associated with the Fe-Mn oxide phase is linked to the high stability constant ($\beta = 1.46 \times 10^6$ at 25 °C) of Zn oxides (Turki, 2007, Li *et al.*, 2011, Reichle *et al.*, 1975, Ma and Rao, 1997). In this study, significant proportions of Zn (37.5-51.5%) were found in the exchangeable phase in sediments from Dutoit and Baynespriut during spring and Camps Drift during autumn. The results suggest that Zn was readily available to the surrounding biota during these periods.

The exchangeable fraction holds weakly bound heavy metal species which can be released by ion-exchange processes, and metals which are precipitated by carbonates (Rogan *et al.*, 2010). In other sites and seasons, the percentages of Zn associated with the exchangeable fractions were less than 30% (Figure 4.13). The percentages of Zn in the oxidisable phase (38.9-43.7%) in sediments from Dutoit were higher than the other sites during spring and winter (Figures 4.13). The occurrence of high amounts of Zn in the oxidisable phase in this site indicates that Zn may be readily available to the biota upon changes in the pH of the sediments.

4.9 Statistical Analysis

4.9.1 Analysis of variance (ANOVA)

Analysis of variance (ANOVA) between the all sampling seasons (winter, spring, summer, and autumn) and locations indicate that there were seasonal variations in the concentrations of TDS, Cd and Cr. In addition the differences observed in the TDS, Cd and Cr concentrations among the different sampling stations were also significant ($p < 0.05$). However, in the case of pH, conductivity, temperature of the water and in the concentrations of DO, As, Cl^- , NO_2^- , SO_4^- , Pb and Zn, the observed seasonal changes and differences among the various sampling points were not significant ($p > 0.05$). The outputs of the analysis of variance are given in the appendix.

4.9.1 Principal Component Analysis (PCA)

The PCA results for some physicochemical properties of the surface water of Msundzi River are given in Table 4.10. The results of PCA of metals in the surface water of Msunduzi River are displayed in Table 4.8. The PCA was resolved into 2 components accounting for 74.1% of the total variability in data set. Factor 1 explained 50.1% of the total variance and was dominated by metals such as Cr, Pb, Zn and As. Metals in factor 1 are anthropogenic metals associated with agrochemicals (As and Zn), industrial and traffic emissions (e.g. Pb and Zn). Factor 2 accounted for 24.0% of the total variance and have positive loading in Cd. Factor 2 suggested that sources of Cd in the surface is different from that of other metals. The PCA of metals in the riverbed sediments are shown in Table 4.9 and was resolved into two components accounting for 68.1% of the total variance. Factor 1 accounted for 37.1% of the variability in the data set and has metals such Cr and Pb while Factor 2 accounted for 30.7% of the total variance and was heavily weighted by Cd and negative bipolar loading in Zn. The

results of the PCA suggest that the Cd and Zn in the riverbed sediments come from a common source.

Table 4.11 Water samples: varimax rotated component loadings of five metals on two significant components explaining 74.1% of the total variance

	PCA1	PCA2
Cr	.799	.270
Pb	.622	.453
Zn	.804	-.268
Cd	.033	.914
As	.911	.128
Eigen values	2.503	1.201
% of Variance	50.053	24.020
Cumulative %	50.053	74.073

Table 4.12 Sediment samples: varimax rotated component loadings of four metals on two significant components explaining 68.1% of the total variance

	PCA1	PCA2
Cd	.281	.760
Cr	.812	.255
Pb	.804	-.265
Zn	.316	-.725
Eigen values	1.485	1.238
% of Variance	37.117	30.960
Cumulative %	37.117	68.077

Table 4.13 Physiochemical data: varimax rotated component loadings of eight physiochemical parameters on three significant components explaining 83.01% of the total variance

	PCA1	PCA2	PCA3
Water Temperature	-.065	-.902	.135
pH	-.042	.910	.134
Conductivity	.781	.004	-.158
TDS	.958	-.027	-.121
DO	-.528	.084	.678
Chloride	.969	-.002	-.059
Nitrate	.126	-.050	.920
Sulphate	.860	.083	.299
Eigen values	3.508	43.851	43.851
% of Variance	1.659	20.731	64.582
Cumulative %	1.474	18.426	83.008

4.9.2 Pearson Correlation Analysis

Pearson correlation analysis was employed to establish the relationship between some of the physicochemical characteristics and metals in the surface water of the Msunduzi River, South Africa. The correlation matrix obtained is displayed in Table 4.11. Temperature had significant positive correlation ($p=0.01$) with EC, TDS, Cl^- , SO_4^- and Cd while pH showed significant positive correlation ($p=0.05$) with dissolved oxygen (DO). TDS has significant positive correlation ($p=0.05$) with Cl^- , SO_4^- and Cr. The results suggest that TDS levels of the river were controlled by the presence of Cl^- , SO_4^- and Cr. As shown in Table 4.11, As showed positive significant correlation with Cd ($p=0.05$) and positive correlations with Cr and Zn at $p=0.01$. The results of correlation analysis suggest that these metals have a common source or similarity in chemical properties. Pb has no significant correlation with any physicochemical properties and other metals investigated, which suggests that the sources of Pb in the surface water are entirely from that of other metals.

Table 4.14 Pearson's correlation coefficient of physicochemical properties and metals in water samples

	Temperature	pH	EC	TDS	DO	Chloride	Nitrate	Sulphate	As	Cd	Cr	Pb	Zn
Temperature	1.00	0.18	0.65*	0.65*	-0.16	0.69*	0.39	0.64*	0.48	0.41	0.54*	-0.22	0.39
pH		1.00	-0.37	-0.32	0.56*	-0.22	0.42	-0.04	-0.13	-0.47	-0.37	-0.09	-0.40
EC			1.00	1.00**	-0.68	0.97**	0.14	0.89**	0.15	0.40	0.75**	-0.60	0.49
TDS				1.00	-0.63	0.99**	0.17	0.93**	0.10	0.34	0.70**	-0.62	0.45
DO					1.00	-0.53	0.44	-0.38	-0.38	-0.70	-0.83	0.46	-0.73
Chloride						1.00	0.27	0.96**	0.05	0.26	0.61*	-0.62	0.40
Nitrate							1.00	0.33	-0.24	-0.46	-0.25	0.03	-0.55
Sulphate								1.00	-0.15	0.04	0.46	-0.69	0.26
As									1.00	0.89**	0.61*	0.30	0.64*
Cd										1.00	0.76**	0.07	0.87**
Cr											1.00	-0.28	0.64*
Pb												1.00	-0.30
Zn													1.00

*Pearson Correlation is significant at 0.01 levels (1 tailed)

**Pearson Correlation is significant at 0.05 levels (1 tailed)

4.9 References

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CHAPTER FIVE: SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary of Important Findings

The total metal concentrations, speciation patterns and physicochemical parameters investigated showed significant spatial and seasonal changes. The high metal concentrations reveal that increased urbanisation and industrialisation might be the main source of contamination along the Msunduzi River. The industries situated alongside the studied river which are the possible sources of pollution include chemical industries, wastewater treatment plant, medical industries, steel manufacturers, electrical industries and bakeries.

The BCR sequential extraction method was used to indicate metal partitioning in the sediments and to assess bioavailability of metals. The residual fraction is the most important phase of cadmium, chromium, lead, and zinc in the river bed sediments. Significant amounts of cadmium were found in the readily and potentially available fractions. This means that the Msunduzi River is in poor health for both aquatic organisms and humans who use this water for consumption.

The water quality index values for the river system for the different seasons falls within the very poor quality to unsuitable for drinking categories. The ecological risk values indicate that there is low ecotoxicological hazard associated with exposure to the levels of metals in the river bed sediment.

5.2 Conclusions & Recommendations

The results of this study revealed that the surface water and sediment from the Msunduzi River were moderately contaminated with the investigated metals. The levels of metals in surface water and sediments investigated by following different digestion procedures and instrumental methods are within the ranges reported in contemporary literature for African rivers affected by a variety of anthropogenic activities. Therefore, further studies should be conducted to determine the concentrations and forms of other metals including Hg, As, Sb, Cu, Ni, Co, Fe, Al, Mn and Ba as well as organic pollutants such as petroleum hydrocarbons, polycyclic aromatic hydrocarbons and halogenated hydrocarbons in order to present a complete picture of the pollution status of the Msunduzi River.

APPENDIX: ANOVA DATA

ANOVA for Temperature

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	51.60028	1	51.60028	3.17	0.084	4.13
Within Groups	553.1894	34	16.27028			
Total	604.7897	35				

ANOVA for pH

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	2.1505	3	0.716833	1.59	0.21	2.90
Within Groups	14.3944	32	0.449825			
Total	16.5449	35				

ANOVA for Conductivity

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	139603	3	46534.33	0.63	0.60	2.90
Within Groups	2359755	32	73742.34			
Total	2499358	35				

ANOVA for TDS

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	548759.9	1	548759.9	16	0.00036	4.13
Within Groups	1188100	34	34944.11			
Total	1736860	35				

ANOVA for DO

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1.006811	3	0.335604	0.28	0.84	2.90
Within Groups	38.83731	32	1.213666			
Total	39.84412	35				

ANOVA for chloride

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	617.6334	3	205.8778	0.29	0.83	2.90
Within Groups	22959.29	32	717.4777			
Total	23576.92	35				

ANOVA for nitrate

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	8.154831	3	2.718277	0.87	0.47	2.90
Within Groups	100.3073	32	3.134604			
Total	108.4622	35				

ANOVA for sulfate

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1241.78	3	413.9267	0.72	0.55	2.90
Within Groups	18448	32	576.5			
Total	19689.78	35				

ANOVA for arsenic

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	12.44970324	3	4.1499	2.75	0.059	2.90
Within Groups	48.2134483	32	1.50667			
Total	60.66315155	35				

ANOVA for cadmium

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	6.199685865	3	2.066561955	15.7	1.89E-06	2.90
Within Groups	4.217567518	32	0.131798985			
Total	10.41725338	35				

ANOVA for chromium

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1852.106331	3	617.3687769	2.83	0.054	2.90
Within Groups	6983.39232	32	218.23101			
Total	8835.49865	35				

ANOVA for lead

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	159.4887732	3	53.1629244	1.26	0.30	2.90
Within Groups	1347.847008	32	42.120219			
Total	1507.335781	35				

ANOVA for zinc

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	107412.6274	3	35804.20914	2.07	0.12	2.90
Within Groups	553955.7655	32	17311.11767			
Total	661368.3929	35				

Abbreviations

SS: sum of squares

df: degrees of freedom

MS: mean squares (varians)

F: F calculated

F crit: F critical