

# SEASONAL ANALYSIS OF WATER AND SEDIMENT ALONG THE UMGENI RIVER, SOUTH AFRICA

---

Mothusi Dikole

Submitted in fulfilment of the academic requirements for the degree of Master in the School of Chemistry and Physics, University of KwaZulu-Natal, South Africa

May 2014

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

Signed ..... Name ..... Date .....

Signed ..... Name ..... Date .....

## Abstract

Increased pollution caused by industrialization, urbanization, afforestation and agriculture has resulted in severe reductions to the health of rivers in South Africa. Numerous studies carried out on South African rivers show that one of the biggest pollutant threats to the river health are heavy metals (*e.g.* Cr, Pb, Cd and Zn). Typically, metal pollutants exceed river quality limits set by the South African Bureau of Standards (SABS) and international standards including Environmental Protection Agency (EPA). The Umgeni River is the major river in the province of KwaZulu- Natal. It suffers from heavy pollution due to effects of industrialization and increasing urban population. Research was carried out to investigate the impact of these industries on the ecosystem by measuring the total and bioavailable concentrations of Cd, Cr, Cu, Pb and Zn in water and sediments over the four seasons.

Seasonal sampling of water and sediment was done at nine sites. The total and bioavailable metal concentrations (Pb, Zn, Cr, Cd and Cu) were measured using ICP-OES. To ensure the validity of the data, certified reference materials were used; NIST 2702 for total metals and BCR 701 for the bioavailability study. Both CRM's showed high recoveries. Metal concentrations in water ranged from 1.0 – 6.0  $\mu\text{g L}^{-1}$  Cd, 1.0 – 11.0  $\mu\text{g L}^{-1}$  Cu, 0.3 – 82.7  $\mu\text{g L}^{-1}$  Cr, 2.7 – 65  $\mu\text{g L}^{-1}$  Zn and 0.3 – 16  $\mu\text{g L}^{-1}$  Pb. The total metal content of sediments ranged from 0.07 – 264.5  $\text{mg kg}^{-1}$  Cd, 11.9 – 168.5  $\text{mg kg}^{-1}$  Cu, 28.6 – 135.1  $\text{mg kg}^{-1}$  Cr, 29.5 – 602.1  $\text{mg kg}^{-1}$  Zn and 12.1 – 601.7  $\text{mg kg}^{-1}$  Pb.

Analysis of Variance (ANOVA) was used for statistical evaluation. This data showed that there was a significant difference between the dry (autumn/winter) and the wet seasons (spring/summer).

Considering the total metal concentration the river is typically in poor health as defined by the SABS and EPA. All the metals, except Cd, were above the stipulated limited in both the sediment and water. The sequential extractions showed all metals primarily in the residual fraction (unavailable). However, very little Cd and Cr has potential of mobility. Cu has high affinity to partition in the Fe/Mn oxide and organic fraction indicating that the presence of reducing agents and microorganisms would avail the metal pollutant. Zn was associated with carbonates, and is highly mobile and bioavailable. This bioavailability data shows that any change in the environment condition may result in the release of the metal pollutants and would adversely affect the environment.

## **Preface**

The experimental work described in this dissertation was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, South Africa, from February 2012 to January 2014, under the supervision of Dr. Letitia Pillay and Dr. Patrick Ndungu.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

## Declaration

I, Mothusi Dikole, declare that

1. The research reported in this dissertation, except where otherwise indicated, and is my original research.
2. This dissertation has not been submitted for any degree or examination at any other university.
3. This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
4. This dissertation does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:
  - a. Their words have been re-written but the general information attributed to them has been referenced.
  - b. Where their exact words have been used, then their writing has been placed in italics and inside quotation marks, and referenced.
5. This dissertation does not contain text, graphics or tables copied and pasted from the internet, unless specifically acknowledged, and the source being detailed in the dissertation and in the references sections.

Signed: .....

## Conference contribution

1. Research day 2013, Durban, South Africa: poster presentation on seasonal analysis of total and bioavailable metals along Umgeni River, South Africa
2. South African Chemical Institute (SACI) 2013, East London, South Africa: oral presentation on the chemical composition of water and sediment along the Umgeni River, South Africa

Signed: .....

## Table of Contents

SEASONAL ANALYSIS OF WATER AND SEDIMENT ALONG THE UMGENI RIVER, SOUTH AFRICA.....	i
Abstract.....	i
Preface .....	ii
Declaration.....	iii
Conference contribution.....	iv
Table of Contents.....	v
Abbreviations.....	viii
Acknowledgements.....	ix
 CHAPTER 1: INTRODUCTION .....	 1
1. Rivers and heavy metals .....	1
1.1. State of rivers: selected examples in Asia.....	2
1.2. Overview on the state of rivers within Africa.....	4
1.3. Overview on the state of rivers within South Africa.....	5
1.4. Problem statement.....	7
1.5. Objectives .....	7
1.6. Rationale .....	7
1.7. Scope and limitations of the study .....	8
 CHAPTER 2: LITERATURE REVIEW .....	 9
2. Theory.....	9
2.1. Study area: The Umgeni River.....	9
2.2. Physico-chemical and chemical composition of river water.....	12
2.2.1. Physico-chemical parameters.....	12
2.2.2. Anions .....	14
2.2.3. Total metals.....	16
2.3. Bioavailable metals .....	18
2.4. Certified reference materials.....	21
2.4.1. National Institute of standard and technology (NIST) 2702 .....	22
2.4.2. Community Bureau of Reference (BCR) 701 .....	22
2.5. Water and sediment quality guidelines .....	22

2.5.1.	South African river quality guidelines .....	23
2.5.2.	International guidelines.....	23
2.6.	Analysis techniques .....	25
2.6.1.	Decomposition techniques .....	25
2.6.2.	Inductively Coupled plasma- Optical Emission Spectrometry (ICP-OES).....	26
2.6.3.	Ion Chromatography (IC).....	26
2.6.4.	Statistical analysis.....	27
CHAPTER 3: EXPERIMENTAL WORK .....		28
3.	Sampling and procedure.....	28
3.6.	Water collection and analysis .....	28
3.7.	Sediment collection and analysis .....	29
References.....		30
CHAPTER 4: PAPER 1 .....		42
Rationale: Total metals in Umgeni River water and sediments and their spatial distribution .....		42
Abstract.....		43
1.	Introduction.....	44
2.	Experimental .....	47
2.1.	Chemicals.....	48
2.2.	Instrumentation .....	48
2.3.	Sampling and procedure.....	48
3.	Results and discussion .....	49
3.1.	Quality assurance .....	49
3.2.	Total metals in water.....	50
3.3.	Total metals in sediments.....	53
4.	Conclusion .....	59
5.	Acknowledgement .....	60
6.	References.....	60
CHAPTER 5: PAPER 2.....		64
Rationale: Seasonal bioavailability of heavy metal contaminants from Umgeni River, South Africa .....		64

Abstract.....	65
1. Introduction.....	66
2. Experimental.....	70
2.1. Chemicals.....	70
2.2. Sampling.....	70
2.3. Procedure.....	71
3. Results and discussion.....	72
3.1. Quality Assurance.....	72
3.2. Physico-chemical parameters.....	72
3.3. Extractable metals.....	73
4. Conclusion.....	79
5. Acknowledgement.....	79
6. References.....	79
 CHAPTER 6: CONCLUSION.....	 94
FUTURE WORK.....	95
APPENDICES.....	96



## Abbreviations

ANOVA: Analysis of Variance

BCR: Community Bureau of Reference of the European Commission

CRM: Certified Reference Material

DO: Dissolved Oxygen

DWAF: Department of Water affairs and Forestry

EC: Electrical conductivity

EPA: Environmental Protection Agency

FDEP: Florida State Department of Environmental Protection

IC: Ion Chromatography

ICP-OES: Inductively Coupled Plasma- Optical Emission Spectrometry

KCV: Known Certified Value

NIST: National Institute of Standard and Technology

NRC: National Research Canada

OV: Observed Value

SABS: South African Bureau of Standards

SPSS: Statistical Package for Social Scientists

SQAG: Sediment Quality Assessment Guideline

TDS: Total Dissolved Solids

US EPA: United States Environmental Protection Agency

WHO: World Health Organisation

## Acknowledgements

I would like to extend my sincere thanks to the following people/ parties for being part of this success story:

- Heartfelt gratitude to my supervisor Dr. Letitia Pillay for many fruitful discussions, assistance, encouragements, guidance and support.
- Sincere appreciation to my co-supervisor Dr. Patrick Ndungu for his interest and support in my work.
- The University of KwaZulu-Natal, College of Agriculture, Science and Engineering for bursary and project funding.
- Thanks to the Analytical laboratory technicians for their assistance; Mrs Anita Naidoo and Mr Neil Broomhead.
- Appreciation to Ms. Caroline Reid from the Department of Environmental Sciences, UKZN for assistance with the GIS map.
- Thanks to my friends Mr E Oseghe, Mr B Gumbi and Ms C Naicker who assisted during sampling.
- Professor G. Matthews and Mr K. Molebatsi for helping out with statistical analysis.
- To Dr Foluso, Mr S Akpotu and Mr S Sewpersad for proof reading some sections in my work.
- Thanks to all members of my writing room; Doctor, Adey, Lawy, Sammy, Jerry, Emmy, Mendy and Solomon for helping me maintain the momentum in difficult times.
- Many thanks to all my friends in South Africa and Botswana for the encouragements, prayers and motivations throughout my research. Thank you friends!
- Thanks to my family in particular Mrs Samo, Carol Dikole and Phemo Dikole for the unconditional love and support
- Above all to the God Almighty for the love and grace.

# CHAPTER 1: INTRODUCTION

---

## 1. Rivers and heavy metals

River quality is described by the physical, chemical and biological properties of water and sediments which protect the health of the ecosystem. These properties are influenced by constituents which are either dissolved or suspended within the river including metals, anions, organics, coliforms and various other organic or inorganic based materials (DWAF, 1996a). Heavy metals as major pollutants in the environment can occur as a result of natural processes and most can be found in the rocks and soil (Coetzee *et al.*, 2002). These metals are released from weathering, veld fires, and biogeochemical processes and depend on the natural geologic structure of an area (Bartoli *et al.*, 2012; Davis *et al.*, 2009; Nriagu, 1989).

Seasonal changes affect the rate of weathering of rocks both physically and chemically. This is due to variations in temperature, rainfall and wind pressure. For example high wind pressure and river flow rate favour the transport of metals from the point source to other localised area (Sultan *et al.*, 2011). Heavy metals also occur from anthropogenic sources. Metal inputs occur from a wide range of activities and these include release of domestic effluent, construction activities, burning of fossil fuels (*e.g.* coal and forest fires) and industrial activities such as paint, oil, electrical and battery manufacture (Audry *et al.*, 2004; Wuana *et al.*, 2011). The river may still recover naturally through dispersion of pollutants at low levels but high pollutant levels may not be naturally remediated (Prabhakar, 2012; WRC, 2002). The ecosystem removes excessive amounts of dissolved salts that are introduced annually by floods from the surface water (Mmualefe *et al.*, 2011).

High concentrations of metals in the river system can be unsafe, thus metal analysis measures the extent of pollution. Heavy metals can be toxic at certain levels while some are not required in any amount, for example Hg. Total metal studies may suggest the possible sources of metal pollutants so that monitoring may be done (Coetzee, 1993). The levels and forms in which metals enter the system of an organism may determine if it will cause a severe effect (Adriano, 2001). There is a limitation in these studies as high concentration does not necessarily mean that the metals are toxic (Coetzee, 1993). For a metal to be toxic it has to be in high concentration, harmful and easily taken up by an organism.

Information on the toxicity and mobility of a metal rather than its total concentration is determined by bioavailability using extraction procedures (Akçay *et al.*, 2003). Bioavailability is a portion of the total metal pollutant that is available for organism uptake in an environment (Adriano, 2001). Bioavailability studies are undertaken to investigate the phases in which the metals are in and to estimate the fraction of metal that is bioavailable. Chemical extraction procedures are commonly used which partition the metals. Extraction procedures are used to explain the distribution of metals as exchangeable, bound to carbonates, Fe/Mn oxides, organic matter and residual. The uses of different extractants which expose the sediment sample to chemicals show the solubility and bioavailability of metals. The weakly held (readily soluble) metals are bioavailable while the strongly held are not bioavailable (Adriano, 2001).

Studies on total metal concentration and bioavailability in rivers have been done worldwide (Klavinš *et al.*, 2000). This is so as rivers are sources of water to living organisms and the assessment of the river helps in safeguarding the environment. There are several factors that justify the need to measure the distribution of heavy metals within a riverine system. Rivers are used recreationally and add value to the economy through tourist attractions. They are sources of food for example fish, a plant called waterblommetjie bredie (found in the Western cape, South Africa) and water lilies (SANB, 2013). There is arable and livestock farming for subsistence and commercial purposes benefit from river water. Rivers help in overcoming the problem of scarcity not only in South Africa but the world as a whole.

### **1.1. State of rivers: selected examples in Asia**

All countries irrespective of socio-economic status are affected by river pollution (Abdul-Kareem *et al.*, 2011). Most of the various highly industrialised countries especially in the American and Asian continents, for example China and the USA, face high levels of river pollution from various effluents (Sponza *et al.*, 2002). The Yangtze River in China is the third largest river in the world. It was reported to be receiving  $5 \times 10^6$  tons of industrial and domestic sewage daily from the Chinese city of Shanghai (Zhang *et al.*, 2007). Shanghai is one the largest cities in the world, and it is full of industries and over populated which accounts for the high rates of metal pollution from industrial and domestic wastes. Factories or industries use water from the river for cooling and operation of machines, and contaminated water is usually returned to the river. Lin *et al.* (2002) sampled 59 stations; the metal concentration exceeded the Marine Sediment Quality issued by China State Bureau of Quality and Technical Supervision. High concentrations of heavy metals (Cd, Cr, Cu, Pb and Zn) were reported. Fine grained sediments had high metal concentrations due to the high surface area and that the enrichment was mainly due to surface adsorption and ionic attraction (Lin *et al.*, 2002).

Kaohsiung Harbour is situated along the south western coast, and it is the largest international port in Taiwan and a study indicated that it received water flows from four contaminated rivers, including the Love River, Canon River, Jen-Gen River, and Salt-water River. Results from the investigation pointed out that the Kaohsiung Harbour was heavily polluted, and the Salt-water River was one of the major pollution sources (Chen *et al.*, 2007). Water quality and sediment investigation results showed that river water contained high concentrations of organics and ammonia–nitrogen, and sediments contained high concentrations of heavy metals and organic contaminants. The main pollution sources were municipal and industrial wastewaters.

Lin *et al.* (2011) did a study on the same site (Kaohsiung River) on heavy metal pollution and results showed high concentrations of Al and Fe, mostly in the downstream sediments. They concluded that it was an indication that the Salt-water River was heavily polluted. Therefore, since 2007 there has not been any improvement on the levels of heavy metals in the river. The contaminated river water and sediments would threaten the environmental quality and ecological balance of Kaohsiung Harbour. Thus it was concluded that effective pollution control strategies should be applied in the watershed and improve the quality of river water and sediments (Lin *et al.*, 2011).

From Chen *et al.* (2012) rapid agriculture, industrial, urban development and the heavy use of chemicals since the late 1970's the Pearl River Estuary (China) region had degenerated as efforts were made to investigate the trace metal pollution in sediments and pollution control measures were put in (Chen *et al.*, 2012). Therefore the past data was used to assess the current situation regarding the trace metal pollution, the spatial distribution in sediments and identification of the transport of contaminants as control measures was done. The study showed that the mean concentration in the surface sediments increased over the last decade while for the Pb, Ni and Zn there was a decrement. The decrease in mean concentration of Pb was that anthropogenic release of Pb into the environment attributed to the widespread of use of leaded gasoline therefore leaded gasoline was gradually phased out in the region. Deposition of wastewater into the rivers and atmospheric emissions when reduced were found to reduce contamination level of the region (Chen *et al.*, 2012).

Similar studies have been conducted in other countries including Spain, Sri Lanka, Turkey, India, France and others (Akçay *et al.*, 2003; Alagarsamy, 2006; Bandara *et al.*, 2010; Farkas *et al.*, 2007; Jose *et al.*, 2005). Their studies were conducted to assess the seasonal levels of pollution, sources of contamination, environmental implications and developing proper management practices (Jose *et al.*, 2005). The results showed high total and bioavailable concentrations of metals Cd, Cr, Cu, Pb and Zn.

Most of these studies identified the possible sources of pollution being areas characterised by intense shipping traffic, effluent outfalls from the city emissions, households, drainage water and businesses, industries, domestic waste and agriculture which have increased the pollution levels of rivers (Akca *et al.*, 2003). For example, a study that was done in the Seine River (France) showed different patterns of contamination at different time scales (Meybeck *et al.*, 2007). All metals (Cd, Cr, Cu, Pb and Zn) were recorded to have decreased at least since 1955/65 (Meybeck *et al.*, 2007).

## **1.2. Overview on the state of rivers within Africa**

Supplying adequate water to small scattered rural communities and/or large fast growing settlements in remote areas is a challenge in undeveloped or developing countries. Mahmood (2006) estimated that more than 50 countries in the world with an area of 20 000 000 hectares are exposed to polluted or partially treated polluted river water (Mahmood, 2006). Africa, which has both undeveloped and developing countries, most studies showed high levels of water and sediment pollution (Jaji *et al.*, 2007; Report, 2005; Sahli *et al.*, 2011). These studies covered North African countries; Algeria, Morocco, Tunisia, Western and Eastern and Southern African countries including Zimbabwe, Botswana, Angola and Swaziland. Studies included work on river water and sediment samples which were collected and analysed for physico-chemical parameters and heavy metal concentrations.

Generally, the values obtained for Pb, Cd, total dissolved solids, dissolved oxygen, chloride, phosphate and nitrate from the sites in wet and dry seasons were compared to the international standard. The metal concentrations and physico chemical parameters were above the maximum acceptable limit for water and sediments set by the international standard. This confirmed that the rivers were polluted. The main sources of contamination were from non-point sources such as diffuse pollution from agriculture, urbanization, logging, effluents and construction (covering dry season and rainy season) (Jaji *et al.*, 2007). Runoff from small scale mining operations, solid waste disposal, urban storm water and runoff from agricultural livestock and poultry operations impair the quality of the river especially in the Southern African region (Masamba *et al.*, 2008; Sahli *et al.*, 2011).

The US EPA assembled a report pertaining to countries that were affected by river pollution (USEPA, 1996). It showed that countries are affected by pollution due to the discharge of industrial and municipal effluent. Rivers received sewage from informal settlements because of breakdown of pumps and stabilisation ponds. As a result, rivers were heavily polluted with high levels of poisonous metals and substances which are affecting the river's ecology.

For example Angola was also affected by river pollution from rural areas settling in the coastal region, urban areas also resulting in overpopulation, overburdening of sanitation facilities and localised pollution. The polluted water poses a severe health risk to communities located near the river who use it for domestic activities, such as cooking, washing and bathing (USEPA, 1996).

### **1.3. Overview on the state of rivers within South Africa**

Previous studies have been conducted in South African river systems, namely the Vaal, Jukskei/Crocodile, Umgeni, Orange, Modder and Buffalo Rivers are the most polluted rivers in South Africa (Metropolitan, 2011). The water quality of the rivers has reduced due to increased pollution caused by industrialization, urbanization, afforestation, mining and agriculture. Toxic and radioactive substances generated from industries is polluting rivers and causing long term contamination of the aquatic ecosystems (USEPA, 1996).

Large areas of South Africa are arid to semi-arid and experience erratic and unpredictable extremes of drought and floods. Lakes and reservoirs that receive point source nutrient inputs also experience high rates of evaporation as well as long periods when river inflows and outflows decline. River monitoring is an important aspect in assessing environmental quality and if a river is deemed as polluted then municipalities make efforts to remediate them. The results of remediation may show a significant decrease in pollutant concentrations due to reduction in anthropogenic inputs.

Heavy metals in sediments pose a threat to the ecosystem due to accumulation and bioavailability of metals (Serife *et al.*, 2001). Pollutants may cause death and diseases to organisms in the river or people dependent on those organisms. The sources of these metals are anthropogenic as studies have shown. Metals disrupt the functioning of the ecosystem as they are more hazardous than organic pollutants (da Luz Lopes *et al.*, 2009). It is very crucial to study the behaviour of metals, their possible sources and health effects in order to safeguard the ecosystem (Adriano, 2001). Rivers, dams and reservoirs located along developed areas need special attention as they are sources of water to humans. Many of the major rivers are highly polluted and are in need of increased monitoring and improved management. Numerous studies carried out on South African rivers showed that one of the biggest pollutant threats to river health are heavy metals (*e.g.* Cr, Pb, Cd and Zn). Typically, metal pollutants exceed river quality limits set by the South African Bureau of Standards (SABS) and international standards including Environmental Protection Agency (EPA).

A study was done in the Swartkops River measuring concentrations of Cr, Pb, Zn and Cu. Results showed high concentration at sampling sites where there were informal settlements and industries indicating that they were possible sources of pollution (Binning *et al.*, 2001). The Swartkops River in South Africa was found to be polluted by metals from settlements and industries. The results were compared to a study done at the same points 20 years ago and they yielded an increase in concentrations of Cr, Pb, Zn, Ti, Mn, Sr, Cu and Sn (Binning *et al.*, 2001). Some rivers in the north-east of South Africa were analysed for metal concentrations. The rivers were highly polluted with Cd and Pb as the concentration values were exceeding the international standards. Bioavailability data then showed that the Cd was highly bioavailable and could pose a threat to the environment (Okonkwo *et al.*, 2004). Other studies have been carried out in South Africa to investigate the impacts of pollution sources in the environment (Table 1).

Table1: Studies undertaken in some of the major rivers in South Africa

River	Water/ sediment	Parameters measured	Reference
Limpopo	Soil	Metal analysis: Cd, Pb, Mn, Zn, Fe & Ca. Physico chemical: pH and texture. Phthalate esters	(Adeniyi <i>et al.</i> , 2008)
	Water	Physico chemical, microbiological and metal analysis	(Chilundo <i>et al.</i> , 2008)
Vaal	Water, sediment and fish	Metals, organics and physico chemicals (pH, EC, DO)	(Wepener <i>et al.</i> , 2011)
	Water	Physico chemical (Salinity, EC, TDS) and metals (Ca, Na, K and Mg)	(Roos <i>et al.</i> , 1995)
Orange	Sediments	Rb, Sr, U, Th and Pb	(Reid, 1979)
Umtata	Water and sediment	Metal analysis: Fe, Mn, Al, Cd, Cu, Zn and Pb. Physico chemical parameters: pH and total hardness	(Fatoki <i>et al.</i> , 2002)



#### **1.4. Problem statement**

The Umgeni River is a major river in the province of KwaZulu-Natal; it is situated along informal settlements and industries. It appears to suffer from heavy metal pollution due to the effects of industrialization, agricultural activities and increasing urban population on this region. There is limited data on the total metal concentration and thus far no study has been identified on the bioavailability of metals in the Umgeni River. Therefore, it is vital to investigate the potentially toxic metal concentration and if the activities negatively affect the quality of the Umgeni River. Seasonal variability and spatial distributions are used in assessing the probable influence of activities on the pollution of the ecosystem.

#### **1.5. Objectives**

The main objective of this study is to assess the distribution of heavy metals in water and sediment samples along a specific section of the Umgeni River within the province of KwaZulu-Natal. The specific objectives include:

- To identify and select suitable sampling points along the Umgeni River
- To measure the total concentrations of metals Cd, Cr, Cu, Pb and Zn in water and sediments.
- To assess the river quality by comparing the data with the accepted values from South African guidelines and international guidelines for river water and sediments.
- To ascertain metal partitioning and bioavailability of Cd, Cr, Cu, Pb and Zn in sediments.
- To investigate the seasonal variations of metals and possible impacts of polluted river water on the environment.

#### **1.6. Rationale**

Heavy metals in high enough concentrations are toxic. The water from the Umgeni River is a vital source of water for agricultural use, industrial and various commercial processes, domestic purposes and recreational activities. There is little data on the seasonal variation of heavy metals within the Umgeni River system. The aim of this work is to provide crucial data on the distribution of heavy metals and the seasonal variation using well established analytical protocols and certified reference materials. ICP-OES was used to screen a selection of water and sediment samples for most transition metals, including Ca, Al, Fe, Mn, Mg, As, Hg, Co and Ni. The five investigated metals Cd, Cr, Cu, Pb and Zn were selected due to their environmental impact and their presence in most samples. The other toxic metals *viz.* As and Hg were below the detection limits of the ICP-OES.

### **1.7. Scope and limitations of the study**

The study aimed at seasonally assessing the total and bioavailable metals along the Umgeni River. This was done by measuring the chemical and physico-chemical parameters in water and sediments. Studies have shown that assessing heavy metals in water and sediments are critical in determining river quality. Plants and fish can be analysed for bioaccumulation studies but this is outside the aims and objectives of this study as plants and other marine life are key to studies dealing with phytotoxicity, bioaccumulation and toxicity studies on organisms, and not necessarily with river quality. There was no direct monitoring as it was difficult to pin point the sources of pollution along the river. This was due to varying activities along the Umgeni River. Some of the activities were not constant for example construction and around informal settlements.

# CHAPTER 2: LITERATURE REVIEW

---

## 2. Theory

The Umgeni River is situated in KwaZulu-Natal, Durban, South Africa. The river is approximately 4441 km<sup>2</sup> with a length of 225 km from source (Midmar Dam) which exits into the Indian Ocean, Durban, KwaZulu-Natal. It receives annual precipitation of 410-1450 mm, mean annual runoff of 72-680 mm and mean annual evaporation is 1360-2040 mm (CSIR., 2011). The river passes three dams including Albert Falls which consists of pastoral landscape where stock farming and forestry are practiced, Nagle Dam passing through informal settlements with thin vegetation and the catchment passes through the Inanda Dam to the Indian Ocean which is the study area for this research (Figure 1). It is an area accompanied by residential and it is highly industrialised.

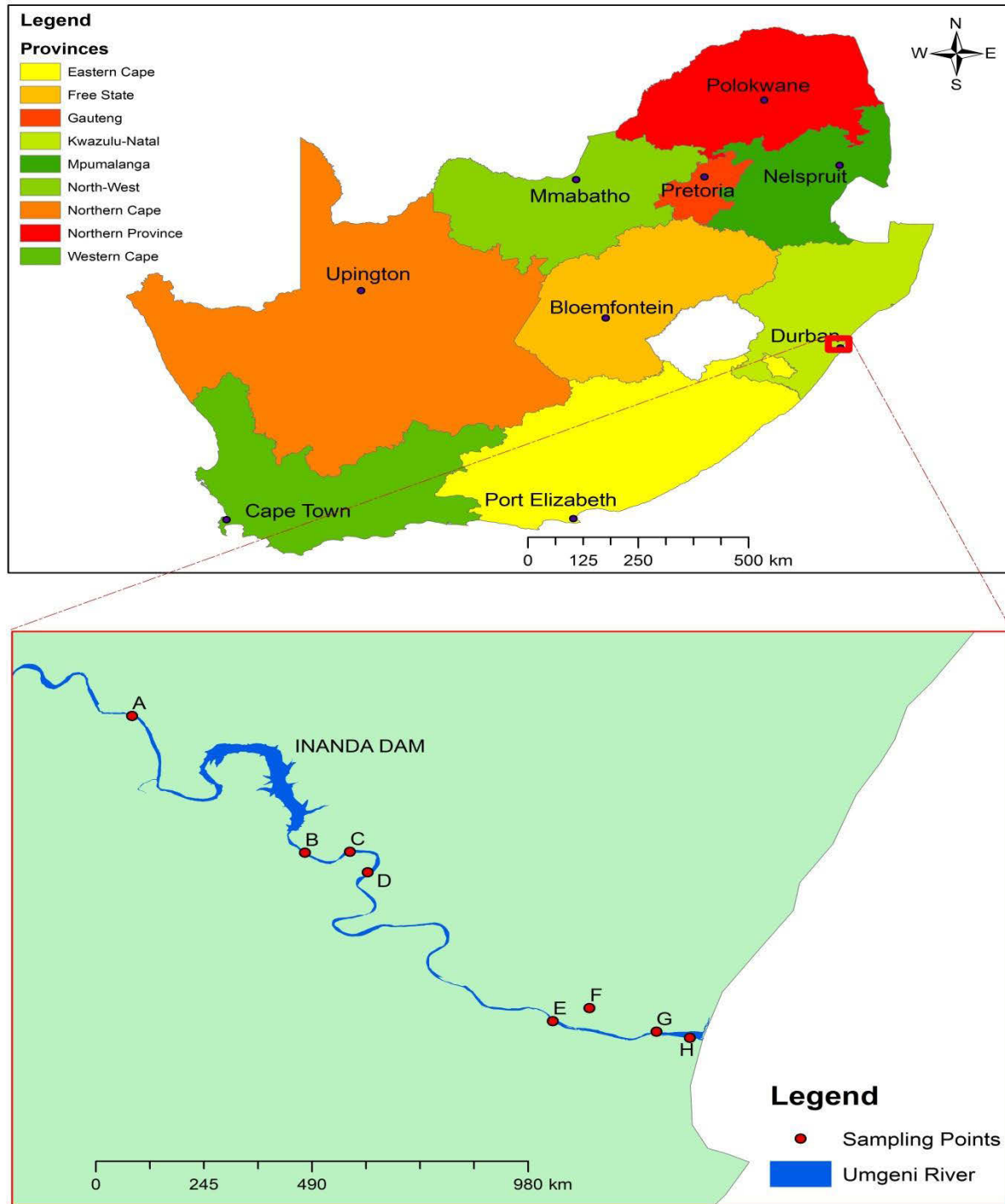
### 2.1. Study area: The Umgeni River

History plays an important role in research as it views the past and therefore dictates what answers to offer for existing problems. Few studies on total metal concentration have been done in the Umgeni River while bioavailability studies are not well documented. Some of these studies include a study done in 1990 on Hg spillage from a mercury recovery plant into two river systems which included the Umgeni River. Subsequently there have been studies investigating the degree of Hg up to the year 2002 (Barratt, 2002). Their results showed that Hg levels in sediment below the Hg plant were of similar magnitude to those detected 8 years previously. A 98% increase in Hg sediment levels was noted at a sample located 10 km downstream from the plant which may suggest that a degree of biomagnification may have taken place (Barratt, 2002). This showed that river systems need to be monitored for pollution.

The sediment plays an important role in the aquatic ecosystem as it provides a home to other organisms. Therefore, any form of disturbance to sediment will affect the ecosystem and this can be chemical and physical contamination (DWAF, 1996a). Another unpublished study was conducted in 2011 on the chemical and pathogenic status of the Umgeni Estuary. The study also focused on heavy metals, physical (including TDS, EC and pH) and other biological parameters *e.g.* coliforms (Shozi, 2011).

Results indicated that the river was affected by metal pollution as metal concentrations exceeded the South African limit set by Department of Water Affairs and Forestry (DWAF). It was recommended that more frequent monitoring should be done on the chemical pathogenic levels in the river (Shozi, 2011).

The eThekweni municipality and Umgeni Waters do routine monitoring by performing a water quality analysis (WRC, 2002). This is done by measuring the chemical and biological parameters including EC, TDS, nitrates and phosphorus. The results indicated that the Umgeni River quality in the upper catchment (Inanda am section) has reduced due to the poor quality of uMsunduze River which is one of the tributaries of the Umgeni River. After the Inanda Dam the water quality was mostly fair because of the purification that takes place in the Inanda Dam, but in the lower catchment the water quality was poor because of city pollutants (WRC, 2002).



*A: Before Inanda Dam, B: After Inanda Dam1, C: After Inanda Dam2, D: After Inanda Dam3, E: Start of industries, F: After waste management, G: End of industries, H: Estuarine site*

Figure 1: Map showing the study area and sampling sites

River quality measurements entails the analysis of chemical parameters such as concentrations of metals, organic pollutants, physical parameters as dissolved oxygen, turbidity, total suspended solids, conductivity, pH and biological as faecal coliforms and bacterial concentrations (Olaniran *et al.*, 2013). These parameters should fall between a specified guideline values for the river to be deemed safe for use and if they do not fall within the stipulated range therefore monitoring will have to be done to reduce the effects. Heavy metal accumulation in sediments may persist as a source of pollutants. This is because sediments are good absorbers of nutrients, when the water is flowing in a river the elements are deposited in sediment and will stay there for a long period of time. Heavy metals and physico-parameters are explained in this chapter.

## **2.2. Physico-chemical and chemical composition of river water**

Typically, natural water contains dissolved gases, metals and organic substances from gases, dust and other substances in the atmosphere. The chemical composition of water and sediments include the physical parameters, anion determination, total metals and extractable metals as these define river quality (Mathis *et al.*, 1973).

### **2.2.1. Physico-chemical parameters**

There are factors in the environment that affect the availability of metal pollutant. These changes in the environment can facilitate the release of metals from sediments.

The **pH** of an aquatic system determines the concentrations, accumulations and bioavailability of metals, phosphates, nitrates and organic materials dissolved in the water, which are essential for various metabolic processes in primary producers such as plants and algae (Serife *et al.*, 2001). Alkaline environment could alter the toxicity of other pollutants. For example ammonia is more toxic in alkaline water than in acidic because free ( $\text{NH}_3$ ) at high pH values ( $\text{pH} > 8.5$ ) is more toxic to aquatic biota than when oxidised from  $\text{NH}_4^+$ . Precipitation of cations, sorption into Fe/Mn oxide and complexation of cations with other dissolved ligands occurs due to high alkaline (Adriano, 2001). All these factors at alkaline pH show a decrease in the mobility and bioavailability of metals.

A more acidic pH could decrease the solubility of some essential elements (Olaniran *et al.*, 2013). In acidic environments there are complexation of cations and anions whilst in an alkaline environment it is complexation of carbonates (Serife *et al.*, 2001). A decrease in sorption of cations into the Fe/Mn oxide at low pH increase the mobility and bioavailability of metals (Adriano, 2001). Metal pollution in aquatic systems is related to pH. When the pH of water decreases, the solubility and speciation of some metals are enhanced thus increasing their toxicity (Blighnaut *et al.*, 2007). The pH linked to availability of metals is a cause of mobilisation for some if not most of the elements (Olaniran *et al.*, 2013). The pH between 5 to 8, can lead to low levels of Mn. Cu precipitates at pH approximately 4 and total precipitation then occurs at approximately pH 6 (Balintova *et al.*, 2012). The increasing pH due to dissolution by surface water increases the precipitation or accumulation of metals in sediments as metal hydroxides (Rios-Arana *et al.*, 2004). If the pH of water is not within the neutral range (6- 8) then the water may not be safe for other living organisms (DWAf, 1996b).

**Redox** potential is one of the main constituents of metal pollutants in the ecosystem (Chuan *et al.*, 1996). It affects the solubility, mobility and bioavailability of most metals including Cd, Cr, Cu, Pb and Zn. However, the activity of redox potential is always coupled with pH (Du Laing *et al.*, 2009). In reduction process the protons are used up while in oxidation there is acidification of which leads to changes in pH affecting the metal bioavailability. At low redox potential there is a decrease in metal solubility which decreases the mobility of metals, whereas a decrease in solution complexation leads to an increase in the bioavailability of metals in sediments (Adriano, 2001). A positive redox potential (oxidising condition) facilitates the metals to be in their free ionic form thus increasing their solubility (Olaniran *et al.*, 2013). This high redox potential leads to higher bioavailability of the metal.

**Dissolved oxygen (DO)** concentration depends on oxygen sources which deliver oxygen into water including water absorbing air from the atmosphere and through the action of photosynthesis which release pure oxygen directly into the water during daylight hours (Greve *et al.*, 2003). Photosynthesis has a greater effect on dissolved oxygen than does atmospheric diffusion because the oxygen is produced by algae (Mack, 2003). Dissolved oxygen is higher in freshwater than in saltwater and also higher in cold water than warm water because oxygen gas solubility increases with temperature decrease. Low dissolved oxygen indicates demand has outstripped supply and can accelerate the toxicity of metals for example low dissolved oxygen makes Cr more toxic (DWAf, 1996b).

**Electrical conductivity (EC)** is the measure of dissolved ions or inorganic materials including calcium, bicarbonate, nitrogen, phosphorus, iron and sulphur. High EC is attributed to the dissolution of dried salts from the previous flooding season by approaching floods. However, EC is reduced as the flood passes and the water is further diluted by local rainfall (Masamba *et al.*, 2008). High EC coupled with high temperatures increase the toxicity of metals. At low temperatures the EC tends to be low which reduces the scattering of metal bound in sediments.

**Salinity** is the measure of salt in the water body and it is a component of conductivity. Most species can survive only within certain salinity ranges (Austin *et al.*, 1979). Salinity can affect the metal bioavailability and mobility and an increase in salinity is associated with an increase in concentrations of elements like Ca, Na, K and Mg. Studies also showed that increase in salinity lead to increase in availabilities of Zn, Fe and Mn but with a smaller effect (Du Laing *et al.*, 2009). Changes in salinity levels result in changes to the variety and types of species found for example salinity in a river system occurs where deep rooted vegetation is removed from the surface and through irrigation practices (Du Laing *et al.*, 2009). This means more water can infiltrate the soil and water can move towards the surface bringing with it large amounts of salt from underground storage. As water evaporates, high concentrations of salt remain in sediments.

### 2.2.2. Anions

Anions, at permissible levels, provide nutrients (Tandon, 2005). High levels of these nutrients degrade the water for drinking, industry, recreation and agriculture of which is a major source of nitrates and phosphates. In agriculture, pesticides and fertilizers are used on crops and are washed away from the soil by rain and deposited in rivers. These fertilizers are sources of anions for example NPK which produce nitrates, phosphates and potassium metal in dissolved form. Their entry into rivers causes algal blooms which are harmful as they destroy or compromise the biota.

Anions do not adsorb equally for example, phosphates are more highly adsorbed than nitrates. The concentrations are used to explain the behaviour of the different phases of metals as they affect the bioavailability of metals (Lokeshwari *et al.*, 2006). Typically no metals complex in the presence of nitrates and thus the bioavailability of metals will be reduced. Conversely the high concentration of chloride will avail some metals as a result of their complexing ability.



**Nitrates ( $\text{NO}_3^-$ )** occur in trace quantities in surface water. It is an essential nutrient for many photosynthetic autotrophs and has been identified as the growth limit nutrient. It is found in small amounts in fresh domestic wastewater, but may be found in concentrations up to  $30 \text{ mg L}^{-1}$  in biological treatment plants (Howard *et al.*, 1995). Nitrate is a less serious environmental problem and it can be found in relatively high concentrations where it is relatively nontoxic to aquatic organisms. Eutrophication is an increase in chemical nutrients-compounds containing nitrogen or phosphorus in an ecosystem and may occur in land or in water. This may be as a result of nutrient pollution, such as the release of sewage effluent, urban storm water runoff and runoff carrying excess fertilizers into natural waters (Chen *et al.*, 2009).

High levels of nitrates ( $\text{NO}_3^-$ ) are common pollutants associated with fertilisers. Nitrates are highly toxic to aquatic life as they easily convert to the even more toxic nitrites ( $\text{NO}_2^-$ ). The ammonium ion ( $\text{NH}_4^+$ ) tends to leach slowly but may be converted by soil bacteria to  $\text{NO}_3^-$  or  $\text{NO}_2^-$  which spreads more rapidly through the soil if not taken up by plants. Nitrates at high concentrations can lead to loss of oxygen, odour and taste problems and death of aquatic animals. In aquatic environments, enhanced growth of choking aquatic vegetation or phytoplankton (algal blooms) disrupts the normal functioning of the ecosystem, causing a variety of problems such as a lack of oxygen in the water, needed for fish. For human society it decreases the resource value of rivers, lakes and estuaries with respect to recreation, hunting, fishing and aesthetic appeal (Balintova *et al.*, 2012).

**Chloride ( $\text{Cl}^-$ )** is mostly found in water as a result of industries including chlorination, bleaching which are mostly found in wastewater treatment plants. It can be threat to life if present in high amounts especially where waters containing ammonia or organic matter may convert chlorine to chloramines which are less toxic but persistent (DWAf, 1996b). The toxicity of chlorine is increased by reduction in dissolved oxygen.

**Sulphates ( $\text{SO}_4^{2-}$ )** are present from industrial applications including paint, rubber and paper (Moret *et al.*, 2003). The solubility of sulphates is high and they tend to accumulate in one area at high concentrations. Sulphates form salts with metals and some salts are highly soluble and mobile while others are not (DWAf, 1996a). For example the Pb- sulphate salt is very insoluble while K, Ca and Mg- sulphates are highly soluble. They have an additive toxic effect in the environment. A high amount of sulphate can accelerate the toxicity of Cd thus making it bioavailable to aquatic plants and animals like fish (if the metal is in soluble state) (DWAf, 1996b).

High concentration of sulphates in the organism system may lead to laxative effects (diarrhoea) and the taste of the water may turn bitter (Abdul-Kareem *et al.*, 2011; DWAF, 1996a).

### 2.2.3. Total metals

Heavy metals are found naturally but may come from different types of anthropogenic sources *e.g.* fertilizers and pesticides, fuel burning, steel, leathering, electrical appliances, metal surface treatments, electroplating, mining, smelting ferrous ores and other industries (Wuana *et al.*, 2011). These metals flow with the water or settle in sediments and act as sinks for pollutants (da Luz Lopes *et al.*, 2009). The effects of metals in water and wastewater range from beneficial to dangerously toxic. Heavy metals are highly persistent and can easily enter a food chain and accumulate until they reach toxic levels (USEPA, 1996).

Water, sediments and biota are generally metal reservoirs in aquatic environment. Nearly all metal content in aquatic environment reside in water sediments. Bower (1979) reported that sediments are the major depository of metals, in some cases holding up to 99% of the total amount of metal present in the system. The concentration of harmful and toxic substances is of many orders of magnitude higher in water sediments (Maitera *et al.*, 2011). Human exposure to pollutants can occur through ingestion of contaminated water, food or through dermal absorption *via* water or air. There are some known health risks associated with exposure to chronic and toxic levels of the individual pollutants that are commonly associated with water-borne pollutants (Colvin *et al.*, 2011).

**Cadmium (Cd)** is naturally found in the ecosystem from weathering. It is considered one of the hazardous and a toxic element listed by the United States Environmental Protection Agency (USEPA) (Sultan *et al.*, 2011). The anthropogenic sources of Cd are atmospheric deposition, smelting and refining of non-ferrous metals and it is mobilized to the water phase by acidification. It is also discharged from paint and agricultural industries (Friberg *et al.*, 1992). In sediments Cd is less mobile than other metals in alkaline media (Shirkhanloo *et al.*, 2011). A high concentration of Cd shows that there is a high potential of toxicity which can result in permanent depletion of some aquatic species (DWAF, 1996b). Cd interferes with the renal regulation of the calcium and phosphate balance (DWAF, 1996a).

**Chromium (Cr)** is a low mobility element at pH of 7 and is considered less toxic compared to other metals *e.g.* Cd, Cu and Ag (Craford *et al.*, 2011). The sources for Cr are natural weathering, burning of fuel and domestic waste, oil drilling operations, and metal plating. Different species of Cr are extensively released from high amounts of industrial effluents which are disposed into rivers (de Castro Dantas *et al.*, 2001). Common oxidation states of Cr are Cr (III) which is found naturally and the most toxic is Cr (VI) which is mostly from industries.

Accumulation of Cr (III) in the system of an organism causes renal failure and acidosis (EPA). It also causes ulcers and nasal problems especially from inhalation of high amounts of Cr in the environment.

**Copper (Cu)** is a nutrient for living organisms but becomes toxic when it is present in higher levels (Shirkhanloo *et al.*, 2011). Cu exists naturally as a result of erosion of mineralized rocks, however, the major contributions also include man-made sources for example fossil fuel combustion, agriculture and industries. These include electric wastes disposed into the river, copper and brass used in water pipelines, fertilizers and effluents. It is known to be toxic in aquatic ecosystems especially with changes in pH, temperature and water hardness (Mathis *et al.*, 1973). High concentrations of Cu lead to respiratory problems, retarded growth, fatigue and breathless palpitations causing nausea and diarrhoea.

**Lead (Pb)** is known as a hazardous inorganic pollutant that enters the environment mostly from anthropogenic activities such as lead-acid batteries, pipes, leaded paints, building construction, weights and alloys (Mathis *et al.*, 1973) (Dekov, Komy, Araujo, *et al.*, 1997) (Sultan *et al.*, 2011). Pb is usually in high concentrations at locations in close proximity to bridges or roads due to motor vehicle emissions<sup>50</sup>. The combustion of leaded petrol is the main cause of such pollution (Agarwal, 2009; Mutia *et al.*, 2012). This metal is usually concentrated in phosphates and is associated with oxides of manganese, iron, clay minerals, organic matter and aluminium hydroxides. This takes place in alkaline conditions because of the high concentration (Gale *et al.*, 2002).

Pb when detected in water or sediments can easily be absorbed by aquatic life as there is a link with the aquatic. It causes poisoning through inhalation of Pb polluted environment, ingestion and drinking of contaminated food and water (Duruibe *et al.*, 2007). It is a toxic metal may cause health problems in animals and humans as it affects the kidneys, brain cells, liver membrane and the reproductive system. It accumulates in the body and leads to nausea, anorexia, vomiting, sweating, convulsion, coma and death (Shirkhanloo *et al.*, 2011; Wuana *et al.*, 2011).

**Zinc (Zn)** is one of the essential elements for the formation of enzymes and nucleic acid (Mathis *et al.*, 1973). This element is dangerous when in high concentrations and appears in sediments as carbonate, oxide and sulphate (Olaniran *et al.*, 2013). Zn occurs naturally from weathering but may also be from anthropogenic sources. The sources of Zn are manure from agrochemicals (including pesticides and insecticides), industries, domestic waste and metal plating (Adriano, 2001).

The metal is mostly adsorbed to oxides, clays and organic material. Zn availability to the ecosystem may cause toxicity in high concentration. The toxicity arises from overdose and therefore disturb cholesterol metabolism in humans.

Thus, the levels of Cd, Cr, Cu, Pb and Zn in an ecosystem should be monitored to prevent adverse effects in the environment. The impact of these metals on the environment can be better understood by examining their mobility in the environment (Adriano, 2001).

### **2.3. Bioavailable metals**

Total metal concentrations give no information on the interaction, the bioavailability and toxicity of the metal with sediments. Thus, it is crucial to carryout bioavailability studies to assess the effect of the metal contaminants (Du Laing *et al.*, 2009; Okonkwo *et al.*, 2004). Bioavailability is the identification of different forms or phases in which an element occurs (Tessier *et al.*, 1979). Different states of metals are more bioavailable than others (Olaniran *et al.*, 2013). The higher the concentration of bioavailable metals in sediments the greater the potential for plant uptake and animal consumption which may lead to toxicity.

Sediments act as sinks for metal pollutants and influence the pollution level of the river. These metal pollutants are bonded into the sediment matrix through adsorption, precipitation and reaction with carbonates, oxides, hydroxides, acids, and clays (Perin *et al.*, 1997). Physico-chemical parameters including pH, temperature, redox potential, dissolved oxygen and organic matter govern the release of metals from the sediments (See section 3.1.1). The binding and availability of metals in sediments can be determined by performing chemical extractions. The extractable metal is the fraction of the total metal that is released from sediment and can be linked to how bioavailable that metal will be to the environment (Adriano, 2001). Therefore, unlike total metals, which only give an indication on the level of contamination, extractable metals provide insight on element mobility and the manner which the metals partition (Divvela, 2010).

Extraction procedures are used to partition the metal into fractions. These fractions are either available (toxic) or unavailable (potentially non-toxic) for uptake by living organisms (Olaniran *et al.*, 2013). There are various chemical methods used to measure bioavailability of metals *viz.* single and sequential extraction procedures (Ivezić *et al.*, 2013). Single extraction methods estimate bioavailability by displacement or chelating effects using acids or complexing agents. The most commonly used extractants for single extractions are ammonium acetate, calcium chloride and EDTA. Ammonium acetate and calcium chloride use displacement methods where the metals preferentially displace the ammonium ion or the calcium ion. EDTA is a chelating agent and will complex metals in solution (Ivezić *et al.*, 2013).

Single extraction techniques may over-extract metals and therefore cause an over-estimation of results. Sequential extraction procedures are step wise methods of extraction which partition metals into different fractions (Adriano, 2001). The methods selected for sequential extractions differ in chemicals used to extract the bound metals. Each extracting solution is able to extract metals that are bound as different complexes thus estimating potential availability. They are widely used and the preferred method for estimating bioavailability. The Tessier *et al.* (1979) is the first extraction procedure developed for metal fractionation and it is mostly applied in sediment samples (Tessier *et al.*, 1979). The procedure uses different chemicals to partition metals into five fractions *i.e.* metals associated with the exchangeable, carbonates, Fe/Mn oxides, organic matter and residual fractions (Table 2).

Metals bound to the exchangeable and carbonate fractions are easily mobilised and bioavailable. This is because these metals are held by a weak electrostatic force. Metals bound to oxides of Fe and Mn have lower mobility than those in the exchangeable phase. The Fe/Mn oxide fraction acts as an adsorber of heavy metals during co-precipitation. These metals complexes can be mobilised by reducing agents in the environment (Kazi *et al.*, 2005). Metals bound to the Fe/ Mn oxyhydroxide are biologically unavailable.

Other similar sequential extraction procedures were developed for example the Zeine and Brummer method (1989) which partitioned metals into five fractions (exchangeable, carbonate bound, Fe/Mn, organic and residual) (Conesa *et al.*, 2008). The Community Bureau of Reference (BCR) method developed a sequential extraction technique in an attempt to standardise the procedure for comparable results (Rauret, *et al.* 2000). The original BCR was introduced which partitions metals into four fractions by combining the exchangeable step with the carbonate (Farkas *et al.*, 2007; Mossop *et al.*, 2003).

The modified BCR sequential extraction procedure (Table 2) was optimised by to improve the reproducibility of the results (Rauret *et al.*, 2000). This is today the most used and preferred sequential extraction procedure. It is preferred because of good reproducibility, sensitivity of the method and there is no redistribution of analytes between the fractions (Kartal *et al.*, 2006). In addition, there is a reference material; BCR 701 (Lake sediment) for this process, making it ideal.

Table 2: The sequential extraction procedures (Rauret *et al.*, 2000; Tessier *et al.*, 1979)

Extraction fraction	The Tessier <i>et al.</i> 1979 extraction	Modified BCR sequential extraction
Exchangeable	1M MgCl <sub>2</sub> buffered at pH 7 Shake for 1 hour	N/A
Carbonate	1M NaOAc at pH 5 Shake for 5 hours	0.11M NH <sub>4</sub> OAc Shake for 16 hours
Fe/Mn oxide	0.004M NH <sub>2</sub> OH·HCl dissolved in 25% (v/v) HOAc Occasional stirring for 6 hours	0.5M NH <sub>2</sub> OH·HCl at pH 1.5 Shake for 16 hours
Organic	0.02M HNO <sub>3</sub> and 30% H <sub>2</sub> O <sub>2</sub> at pH 2. After cooling: 3.2M NH <sub>4</sub> OAc in 20% (v/v) HNO <sub>3</sub> Continuous mixing for 30 minutes	30% (m/m) H <sub>2</sub> O <sub>2</sub> , Followed by 1M NH <sub>4</sub> OAc at pH 2 Shake for 16 hours
Residual	4:1:1:1 (HNO <sub>3</sub> : HF: HClO <sub>4</sub> : HCl)	HNO <sub>3</sub> / HCl

N/A- Not Applicable

Heavy metals may be bound to organic matter which includes microorganisms and may become bioavailable under oxidising conditions. Under oxidising conditions, organic matter has a high mobility and bioavailability (Olaniran *et al.*, 2013). Generally metals held by organic matter and sulphides are unavailable for uptake. The residual fraction is the unavailable fraction. The metals are held by the crystalline structure of primary and secondary minerals (Tessier *et al.*, 1979). In an attempt to standardise sequential extractions to obtain meaningful and comparable data, a standardised and commonly used sequential extraction procedure is the Community Bureau of Reference (BCR) (Table 2). The BCR sequential extraction involves use of strong acids to extract exchangeable metals from sediments without extracting also the Fe/Mn oxide and organic bound metals (Mossop *et al.*, 2003; Rauret *et al.*, 2000; Tessier *et al.*, 1979; Zimmerman *et al.*, 2010).

These extraction procedures are important in studying the bioavailability of metals. They give an indication of how metals partition and therefore the mobility of metals if the conditions change. These extraction procedures also give an indication of metal speciation. (Naidu *et al.*, 2002). Speciation identifies the metal oxidation state and can be used to estimate toxicity of metals towards living organisms. Speciation and bioavailability is usually influenced by redox condition in sediment as metals are found in different oxidation states (Akçay *et al.* 2003). Environmental monitors and risk assessors recognise bioavailability more than speciation and that physicochemical- dependent speciation characteristic for example pH may be used to for bioavailability studies. This is so as they are controllers of bioavailability (Naidu *et al.*, 2002).

#### 2.4. Certified reference materials

A certified reference material (CRM) is an important aspect in analytical measurements to ensure method validation. They are essential for achieving traceability and comparability of measurements between laboratories. They are usually accompanied by certificates which have instructions for handling, storage and use, preparation of that certified reference material and the certified values with their uncertainties. The selection of CRMs for trace metal analysis includes target concentrations of the analytes of interest, the method used to obtain the reference values and how well the CRM matrix matches that of routine samples. Certified reference materials are used for quality control. Percentage recovery for metals should be between 80%-120% and the values for percentage recovery are calculated using the equation 1 (FAO, 2011; USEPA, 2012a):

$$\% \text{ Recovery} = (\text{OV}/\text{KCV}) \times 100 \dots\dots\dots \text{Equation 1}$$

OV- Observed Value (Experimental value)

KCV- Known Certified Value

The choice of CRM is important and should be made after considering the sample being analysed. This is to avoid matrix interferences and to prevent a CRM with vastly different concentration ranges to the samples from being used. There are a range of different CRM's for metal analysis in water and sediments. Some of them include PACS-2 (marine sediment), SRM 2710 (Montana soil), SRM 2702 (Buffalo river sediment), SRM 1084a (metals in oil), NIST 2702 (marine sediment), BCR 701 and BCR 601.

The marine sediment PACS- 2 is from the national research council of Canada (NRC- CNRC) and it is collected from the harbor of Esquimalt. It is commonly used in determination of total metal concentration in river, lake and marine soils and sediments (da Silva *et al.*, 2002; Mandiwana *et al.*, 2004). The BCR 601 certified reference material is from the Commission of the European Community, Brussels, Belgium. The certified reference material is extracted by the BCR procedure and is routinely used in analyses where chemical extractions to measure bioavailability are made (Giacomelli *et al.*, 2002). Several papers have evaluated these CRM's and given good recoveries (USEPA, 2007b). Mostly used and recommended CRM's are NIST and BCR for total metal determination and fractionation studies respectively.

#### **2.4.1. National Institute of standard and technology (NIST) 2702**

NIST 2702 is the certified reference material for Inorganics in marine sediment. It was produced by the National Research Canada (NRC). It was issued in 2002 as a replacement for the CRM 2704 (Zeisler, 2004). This CRM was selected for quality control in total metal analysis in sediments and it contains the metals of interest in the study. The certification of the CRM contains specific instruments recommended for analysis of these metals. Procedures have been validated using the NIST 2702 in a number of studies (Breslin *et al.*, 2005; dos Santos *et al.*, 2005; Greenberg, 2005).

#### **2.4.2. Community Bureau of Reference (BCR) 701**

The BCR 701 is sourced from the European Commission joint research centre. It is sediment from Lake Orta Piemonte, Italy (Sutherland, 2010). The certified reference material contains the metals of analysis that is Cd, Cr, Cu, Pb and Zn. They are extracted in three steps; acid extractable, reducible and oxidizable. This certified reference material was selected to validate the BCR sequential extraction procedure. Once the BCR sequential procedure is optimised, it can be applied on the sediment samples. This CRM has been applied on numerous studies and good recoveries are reported (Farkas *et al.*, 2007; Obbard, 2006; Pueyo *et al.*, 2001).

### **2.5. Water and sediment quality guidelines**

Assessment of the adequacy of the chemical quality of the river relies on comparison of the results of water and sediment quality analysis with guideline values. These are to protect the ecosystem from effects associated with metal pollutants (Farkas *et al.*, 2007). The guidelines used are the South African guidelines on water and sediment quality from Department of Water Affairs and Forestry (DWAF) and international ones from the Environmental Protection Agency (EPA).



### 2.5.1. South African river quality guidelines

South African water quality guidelines for aquatic ecosystems are national standards set to give information on water quality requirements. This is to safeguard the health of local (South African) aquatic ecosystems. These guidelines are meant to identify the problems associated with river quality, define the water quality constituents and protect the most sensitive species (DWAF, 1996b).

DWAF is the national institution for the promotion and maintenance of quality standards (DWAF, 1996a). It offers certification, testing, consignment inspection and other services mostly to industry to ensure a healthy ecosystem as there are still uncontrolled effluent discharges into the river systems from industries, municipalities, home and agricultural works. Numerous studies reported the high levels of constituents that were above the South African guidelines values (Fatoki *et al.*, 2003; Igbinosa *et al.*, 2009; Morrison *et al.*, 2001).

Gordon and Muller (2010) reported that there was no South African sediment quality guideline as it was still under development (Gordon *et al.*, 2010). Therefore for sediment quality the international guidelines will be used to monitor the state of sediments in Umgeni River. The DWAF limits for metals in river water and proposed sediment guideline values are shown in Table 3.

**Table 3: South African river water and sediment guidelines**

Element	DWAF value for river water/ mg L <sup>-1</sup> (DWAF, 1996b)
Cd	0.1500
Cr	0.0070
Cu	0.0003
Pb	0.0002
Zn	0.0020

### 2.5.2. International guidelines

The international guidelines values are derived for many chemical constituents of drinking water and sediments (USEPA, 2012b). The water and sediment quality guideline that were of vital interest in this study is the EPA. Guideline values normally represent the concentration of a constituent that does not result in any significant risk to health over a lifetime of consumption (Table 4).

A number of provisional guideline values have been established at concentrations that are reasonably achievable through practical treatment approaches or in analytical laboratories; in these cases, the guideline value is above the concentration that would normally represent the calculated health-based value.

The FDEP forms part of the nationally used sediment quality assessment guidelines (SQAG's) from the USEPA (USEPA, 2012b). The areas are reported not to be affected by extensive industrial developments but it is vital to assess sediment as they are sinks for pollutants. The FDEP developed a SQAG for main pollutants that may be released into water systems and stored in sediments (FDEP, 1994). These pollutants were provided by FDEP (1994), Long and Morgan (1990), Trefry *et al.* (1983), Leslie (1990) and Long *et al.* (1991) include Cd, Cr, Cu, Pb and Zn and they affect the sediment quality. The Umgeni River has possible sources of metal input including agriculture, manufacturing industries, residential and effluents from waste water treatment. This makes this guideline to be selected as best for this research as it incorporates almost the same possible sources of pollutants. Studies have been carried out and results compared to the SQAG (Cesar *et al.*, 2007; Lewis *et al.*, 2001; Sigua *et al.*, 2000).

Table 4: Guideline values for river water and sediments (FDEP, 1994; FDEP, 2013)

Element	Water guideline value in mg L <sup>-1</sup>	Sediment guideline value in mg kg <sup>-1</sup>
Cd	0.0088	0.676
Cr	0.05	52.3
Cu	0.0037	18.7
Pb	0.0085	30.2
Zn	0.086	124.0

## 2.6. Analysis techniques

This section includes all methods of analysis in the laboratory. The theory behind each of the analytical techniques used is discussed.

### 2.6.1. Decomposition techniques

There are different types of decomposition techniques to transform sediment samples to aqueous solution. The most commonly used are a hot plate and microwave assisted digestion (Sastre *et al.*, 2002). The hot plate digestion is the first basic method of decomposition. A known volume of acid, typically HNO<sub>3</sub> and/or HCl is added to the accurately weighed sediment sample in the beaker. The beaker is placed on a hotplate and heated until the acid is mostly evaporated. Optimum temperature is adjusted to less than 85 °C which is given in the EPA standard procedure for digestion of sediment samples using the hot plate digestion method (USEPA, 1994b). The solution is quantitatively transferred into a volumetric flask ready for analysis using an appropriate instrument.

Studies have used hot plate digestion (Creed *et al.*, 1992; Martin *et al.*, 1992) but microwave assisted digestion method has been shown to be a more effective tool for trace metal concentration measurements (Bettinelli *et al.*, 2000a; Chatreewongsin, 2000; Chen *et al.*, 1998; Sastre *et al.*, 2002). The microwave is used for digestion of samples which may have a matrix of clay, minerals, silicates, organic and oxides (Sandroni *et al.*, 2003). It offers efficient methods of digestion before analysis of metals as they give good recoveries and short digestion times (Bettinelli *et al.*, 2000b; Sakan *et al.*, 2011). Furthermore, they reduce contamination and loss of sample as closed vessels are used at regulated temperature and pressure.

The digested samples are analysed using one or more instruments including flame atomic absorption spectrophotometry (FAAS), graphite furnace atomic absorption spectrophotometry (GFAAS), cold vapour- atomic absorption spectrophotometry (CV-AAS), inductively coupled plasma- optical emission spectrometry (ICP-OES) and inductively coupled plasma- mass spectrometry (ICP-MS). The choice of instrument is dependent on the levels of analyte present in the sample and the sample matrix. Currently ICP- OES is the preferred choice of instrument as it has low detection limits; it offers wide linear dynamic range and provides simpler spectral interpretation (Batista *et al.*, 2008). Studies have shown that ICP- OES is the dominantly used instrument for analysis of metals because of its availability and sensitivity (Bettinelli *et al.*, 2000a; Ivezić *et al.*, 2013)

### **2.6.2. Inductively Coupled plasma- Optical Emission Spectrometry (ICP-OES)**

ICP-OES is an instrument that qualitatively and quantitatively measures the elemental composition of samples. The instrument is used in a large variety of applications because of its high specificity, multi-element capability and good detection limits (PerkinElmer, 2008). It uses a plasma source to dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level of which they return to their ground state by emitting photons of a characteristic wavelength depending on the element present (PerkinElmer, 1998).

This light is recorded by an optical spectrometer so when calibrated against standards the technique provides a quantitative analysis of the original sample. The plasma source can have axial and radial configuration for low and high concentrations (PerkinElmer, 1998). The detection limit of the instrument varies depending on the type of metal. ICP-OES has lower detection limits in mid-ppb range with wide elemental capabilities.

### **2.6.3. Ion Chromatography (IC)**

Ion chromatography (IC) is a separation technique used for ions and polar compounds. A water sample is injected into a stream of carbonate-bicarbonate eluent and passed through a separation column. Anions are then separated according to their affinity for the stationary phase of the separation column. In the anion determination, the stationary phase is positive and the negatively charged ions bind onto it. The basic anions are then passed through a suppressor column where they are converted to their highly conductive acid forms and the carbonate-bicarbonate eluent is converted to weakly conductive carbonic acid.

A conductivity detector then measures the conductivity of the acidic anions against the carbonic acid, which is taken as the zero baseline (Bettinelli *et al.*, 2000b) (Rocklin, 1991). The anions are identified on the basis of retention time as compared to known standards. Quantitation is achieved by measuring peak area or peak height.

#### **2.6.4. Statistical analysis**

Statistical analysis was done using Statistical Package for Social Scientists (SPSS), version 18. Seasonal variability of sediment was done using one-way Analysis of Variance (ANOVA). The null hypothesis stated that there was no significant difference between the seasons for a particular metal at different sampling sites. The alternative stated that there was a significant difference between the seasons for a particular metal at different sampling sites. If the p-value was greater than 0.05 the null hypothesis was accepted and rejected otherwise.

# CHAPTER 3: EXPERIMENTAL WORK

---

## 3. Sampling and procedure

Water and sediment samples were collected from the field in specialised containers and taken to the laboratory for analysis. Physical parameters were measured in the field. Sampling was done in April, July, October 2012 and January 2013, representing autumn, winter, spring and summer respectively. Below are the methods explained in detail.

### 3.6. Water collection and analysis

Polyethylene bottles were pre-cleaned with  $\text{HNO}_3$  and distilled water in a ratio of 4:1 that is water to  $\text{HNO}_3$ , soaked overnight and rinsed with de-ionized water. Bottles were rinsed 3 times with sample water before being filled and each sample bottle was dipped below the water surface projecting the mouth of the container against flow direction (Okoh *et al.*, 2007; Shoji, 2011). The other water samples were acid preserved with  $\text{HNO}_3$  in the field for metal determination and others were unacidified for anion determination then kept in the refrigerator before analysis.

Water samples were analysed using the EPA 200.8 method. About 10 mL of the sample was taken with a syringe and filtered through a 0.4  $\mu\text{m}$  filter into an acid pre cleaned ICP vial (USEPA, 1994a). Then samples were analysed with ICP-OES (Perkin Elmer, Optima 5300DV). The ICP-OES was calibrated with diluted commercial standards and blank solution having a similar matrix to the samples analysed. The wavelengths in Table 5 were selected because of detection limits and less interference (PerkinElmer, 2008). Analysis was done in triplicates.

Table 5: Wavelengths in ( $\mu\text{g L}^{-1}$ ) and detection limits for analysis

Element	Wavelength/ nm	Detection Limit/ $\mu\text{g L}^{-1}$
<b>Cd</b>	214.440	0.1
<b>Cr</b>	283.563	0.2
<b>Cu</b>	327.393	0.4
<b>Pb</b>	220.353	1
<b>Zn</b>	213.857	0.2

The unacidified samples were filtered using a  $0.4 \mu\text{m}$  and analysed using the ion chromatograph (Dionex ICS- 90) for anion determination. Ion chromatograph conditions were set as shown below (Table 6). Dionex conductivity column was used.

Table 6: Conditions set for the IC

Parameter	
Flow rate	2.0 mL/min
Nitrogen gas	20 kPa
Conductivity	17-19 $\mu\text{S}$
Pressure	20.0 psi

The remaining sample solutions were stored in plastic containers in the refrigerator in case an error was encountered they would be used for analysis.

### 3.7. Sediment collection and analysis

Sediment samples were collected in polyethylene bags and air dried at room temperature for a period of 1 week. Each sample was slightly ground to break the moulds and then passed through sieves to  $90 \mu\text{m}$  for total and bioavailable heavy metals analysis.

For total metal determination, the sediment samples including the certified reference material NIST 2701 were put in acid-cleaned petri dishes and placed in an oven at 60 °C overnight to ensure complete dryness. About 0.5 g of sample was placed in different digestion vessels and microwave digested with 10 mL aqua-regia ratio 3:1 (HCL: HNO<sub>3</sub>) (USEPA, 2007b).

Digestion vessels were capped and placed in an autoclave, then microwaved following the EPA 3051a method. The MARS 6, CEM was used in this study for digestion of sediment samples. The procedure involved ramping at 60 °C for 15 minutes, then held for 15 minutes at 180 °C (USEPA, 2007b). At the end of the program, the vessels were allowed to cool for about 15 minutes in the microwave. The solution was filtered into an acid cleaned 50 mL volumetric flask then made to the mark with double distilled water. Samples were analysed using ICP-OES (Perkin Elmer, Optima 5300DV) as set in table 5.

The BCR sequential procedure was used for bioavailable metals. Sediment samples were oven dried at 70 °C overnight. About 0.5 g of sediment samples, certified reference material BCR 701 and sample blank (one without sample) were extracted (Rauret, 2001). All extracts from each step were analysed using ICP-OES (Perkin Elmer, Optima 5300DV) for Cd, Cr, Cu, Pb and Zn.

## References

- Abdul-Kareem, B. M., Rabee A.M., & Al-Fatlawy Y.F. (2011). Monitoring heavy metals, cations and anions levels and its possible health risks in Tigris River at Baghdad region. *Iraqi Journal of Science*, 52(3), 306-316.
- Adeniyi, A., Dayomi, M., Siebe, P., & Okedeyi, O. (2008). An assessment of the levels of phthalate esters and metals in the Muledane open dump, Thohoyandou, Limpopo Province, South Africa. *Chemistry Central Journal*, 2(9).
- Adriano, D. C. (2001). *Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals* (2 ed.). New York, USA: Springer.
- Agarwal, S. K. (2009). Heavy metal pollution Vol. 4. (pp. 37-71). Retrieved from [http://books.google.co.za/books?hl=en&lr=&id=nmputzkzWWkC&oi=fnd&pg=PR5&dq=Heavy+metal+pollution+by+Agarwal+S+K&ots=SdHT21I2dY&sig=S7U\\_BhEnnbDnDrULAQPoQdDrWrk#v=onepage&q=Heavy%20metal%20pollution%20by%20Agarwal%20S%20K&f=false](http://books.google.co.za/books?hl=en&lr=&id=nmputzkzWWkC&oi=fnd&pg=PR5&dq=Heavy+metal+pollution+by+Agarwal+S+K&ots=SdHT21I2dY&sig=S7U_BhEnnbDnDrULAQPoQdDrWrk#v=onepage&q=Heavy%20metal%20pollution%20by%20Agarwal%20S%20K&f=false)
- Akçay, H., Oguz, A., & Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Research*, 37(4), 813-822.



- Alagarsamy, R. (2006). Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. *Estuarine, Coastal and Shelf Science*, 67(1–2), 333-339.
- Audry, S., Schäfer, J., Blanc, G., & Jouanneau, J.-M. (2004). Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environmental Pollution*, 132(3), 413-426.
- Austin, R., & Rhoades, J. (1979). A compact, low-cost circuit for reading four-electrode salinity sensors. *Soil Science Society of America Journal*, 43(4), 808-810.
- Balintova, M., Petrlikova, A., & Singovszka, E. (2012). Study of Metals Distribution between Water and Sediment in the Smolnik Creek (Slovakia) Contaminated by Acid Mine Drainage. *Chemical Engineering*, 28.
- Bandara, J. S., Wijewardena, H. P., Bandara, Y. Y., Jayasooriya, R. T., & Rajapaksha, H. (2010). Pollution of River Mahaweli and farmlands under irrigation by cadmium from agricultural inputs leading to a chronic renal failure epidemic among farmers in NCP, Sri Lanka. *Environ Geochem Health*, 33(439-453).
- Barratt, G. J., Combrink, J., (2002). *An assessment of the degree of mercury (Hg) bio-transformation in two river systems following discharges from a mercury recovery plant*. Technikon Natal, Durban, South Africa.
- Bartoli, G., Papa, S., Sagnella, E., & Fioretto, A. (2012). Heavy metal content in sediments along the Calore river: Relationships with physical–chemical characteristics. *Journal of Environmental Management*, 95, Supplement(0), S9-S14.
- Batista, B. L., Rodrigues, J. L., Nunes, J. A., Tormen, L., Curtius, A. J., & Barbosa Jr, F. (2008). Simultaneous determination of Cd, Cu, Mn, Ni, Pb and Zn in nail samples by inductively coupled plasma mass spectrometry (ICP-MS) after tetramethylammonium hydroxide solubilization at room temperature: comparison with ETAAS. *Talanta*, 76(3), 575-579.
- Bettinelli, M., Beone, G., Spezia, S., & Baffi, C. (2000a). Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. *Analytica Chimica Acta*, 424(2), 289-296.
- Bettinelli, M., Beone, G. M., Spezia, S., & Baffi, C. (2000b). Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. *Analytica Chimica Acta*, 424(2), 289-296.
- Binning, K., & Baird, D. (2001). Survey of heavy metals in the sediments of the Swartkops River Estuary, Port Elizabeth South Africa. *Water SA*, 27(4), 461-466.

- Blighnaut, J. N., Marais, C., & Turpie, J. K. (2007). Determining a charge for the clearing of invasive alien plant species (IAP's) to augment water supply in South Africa. *Water SA*, 33(1).
- Breslin, V. T., Clough, D., Cucchiarelli, D., Dart, P., Detelich, C., Guandal, S., . . . Loman, P. (2005). Sediment Metal Contamination in the Branford River and Harbor.
- Cesar, A., Choueri, R. B., Riba, I., Morales-Caselles, C., Pereira, C. D. S., Santos, A. R., . . . DelValls, T. A. (2007). Comparative sediment quality assessment in different littoral ecosystems from Spain (Gulf of Cadiz) and Brazil (Santos and São Vicente estuarine system). *Environment International*, 33(4), 429-435.
- Chatreewongsin, U. (2000). *Metal Extraction From Soil Samples By chelation in a Microwave System*. Virginia Polytechnic Institute and State University.
- Chen, B., Liang, X., Xu, W., Huang, X., & Li, X. (2012). The changes in trace metal contamination over the last decade in surface sediments of the Pearl River Estuary, South China. *Science of the total environment*, 439, 141-149.
- Chen, C. W., Kao, C. M., Chen, C. F., & Dong, C. D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor. *Chemosphere*, 66(1431–1440).
- Chen, F., Jia, G., & Chen, J. (2009). Nitrate sources and watershed denitrification inferred from nitrate dual isotopes in the Beijiang River, south China. *Biogeochemistry* 94, 163-174.
- Chen, M., & Ma, L. Q. (1998). Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. *Journal of Environmental Quality*, 27(6), 1294-1300.
- Chilundo, M., Kelderman, P., & O'keeffe, J. H. (2008). Design of a water quality monitoring network for the Limpopo River Basin in Mozambique. *Physics and Chemistry of the Earth, Parts A/B/C*, 33(8–13), 655-665.
- Chuan, M., Shu, G., & Liu, J. (1996). Solubility of heavy metals in a contaminated soil: effects of redox potential and pH. *Water, Air, and Soil Pollution*, 90(3-4), 543-556.
- Coetzee, L., Du Preez, H. H., & Van Vuren, J. H. J. (2002). Metal concentrations in *Clarias gariepinus* and *Labeo umbratus* from the Olifants and Klein Olifants River, Mpumalanga, South Africa: Zinc, copper, manganese, lead, chromium, nickel, aluminium and iron. *Water SA*, 28(4), 433-448.
- Coetzee, P. P. (1993). Determination and speciation of heavy metals in sediments of the Hartbeespoort Dam by sequential chemical extraction. *Water S. A.*, 19(4), 291-300.
- Colvin, C., Burns, A., Schachtschneider, K., Maherru, A., Charmier, J., & De Wit, M. (2011). Coal and water futures in South Africa: The case for protecting headwaters in the Enkangala grasslands: South Africa. [www.wwf.org.za](http://www.wwf.org.za)

- Conesa, H. M., Robinson, B. H., Schulin, R., & Nowack, B. (2008). Metal extractability in acidic and neutral mine tailings from the Cartagena-La Unión Mining District (SE Spain). *Applied Geochemistry*, 23(5), 1232-1240.
- Crafford, D., & Avenant-Oldewage, A. (2011). Uptake of selected metals in tissues and organs of *Clarias gariepinus* (sharp-tooth catfish) from the Vaal River System - Chromium, copper, iron, manganese and zinc. [Article]. *Water SA*, 37(2), 181-200.
- Creed, J., Martin, T., Lobring, L., & O'Dell, J. (1992). Minimizing chloride interferences produced by combination acid digestion using palladium and hydrogen as a matrix modifier in graphite furnace atomic absorption spectrometry. *Environmental Science & Technology*, 26(1), 102-106.
- CSIR. (2011). South African river health programme *uMngeni River and Neighbouring Rivers and Streams*. Durban: Council for Scientific and Industrial Research. <http://www.dwa.gov.za>
- da Luz Lopes, W., Santelli, R. E., Oliveira, E. P., de Carvalho, M. d. F. B., & Bezerra, M. A. (2009). Application of multivariate techniques in the optimization of a procedure for the determination of bioavailable concentrations of Se and As in estuarine sediments by ICP OES using a concomitant metals analyzer as a hydride generator. *Talanta*, 79(5), 1276-1282.
- da Silva, A. F., Welz, B., & Curtius, A. J. (2002). Noble metals as permanent chemical modifiers for the determination of mercury in environmental reference materials using solid sampling graphite furnace atomic absorption spectrometry and calibration against aqueous standards. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 57(12), 2031-2045.
- Davis, H. T., Marjorie Aelion, C., McDermott, S., & Lawson, A. B. (2009). Identifying natural and anthropogenic sources of metals in urban and rural soils using GIS-based data, PCA, and spatial interpolation. *Environmental Pollution*, 157(8-9), 2378-2385.
- de Castro Dantas, T., Dantas Neto, A., de A. Moura, M., Barros Neto, E., & de Paiva Telemaco, E. (2001). Chromium adsorption by chitosan impregnated with microemulsion. *Langmuir*, 17(14), 4256-4260.
- Dekov, V., Komy, Z., Araujo, F., Van Put, A., & Van Grieken, R. (1997). Chemical composition of sediments, suspended matter, river water and ground water of the Nile (Aswan-Sohag traverse). *Science of the total environment*, 201(3), 195-210.
- Divvela. (2010). Sequential extraction procedure, *Lab Science News*.
- dos Santos, E. J., Herrmann, A. B., Frescura, V. L. A., & Curtius, A. J. (2005). Simultaneous determination of As, Hg, Sb, Se and Sn in sediments by slurry sampling axial view inductively

- coupled plasma optical emission spectrometry using on-line chemical vapor generation with internal standardization. *Journal of Analytical Atomic Spectrometry*, 20(6), 538-543.
- Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. (2009). Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review. *Science of the total environment*, 407(13), 3972-3985.
- Duruibe, J., Ogwuegbu, M., & Egwurugwu, J. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2(5), 112-118.
- DWAF. (1996a). Domestic water use *South African Water Quality Guidelines* (2 ed.). South Africa: Department of water affairs and forestry
- DWAF. (1996b). South African water quality guidelines *Aquatic ecosystems*. Pretoria: Department of Water Affairs and Forestry. [http://www.capetown.gov.za/en/CSRM/Documents/Aquatic\\_Ecosystems\\_Guidelines.pdf](http://www.capetown.gov.za/en/CSRM/Documents/Aquatic_Ecosystems_Guidelines.pdf)
- EPA, U. Environmental Protection Agency.(2000). *EPANET 2" Users Manual*.
- FAO. ( 2011). Quality assurance for animal feed analysis laboratories *FAO Animal Production and Health Manual* (Vol. 14). Rome
- Farkas, A., Erratico, C., & Vigano, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. *Chemosphere*, 68(4), 761-768.
- Fatoki, O. S., Lujiza, N., & Ogunfowokan, A. O. (2002). Trace metal pollution in Umtata River. *Water SA*, 28(2), 183-190.
- Fatoki, S. O., Cogwana, P., & Ogunfonokan, A. O. (2003). Pollution assessment in the Keiskamma River and in the impoundment downstream. *Water SA*, 29(3), 183-187.
- FDEP. (1994). Numerical Sediment Quality Assessment Guidelines for Florida Coastal Waters. USA: USEPA. [www.dep.state.fl.us/water/monitoring/docs/seds/vol1/chapter6.pdf](http://www.dep.state.fl.us/water/monitoring/docs/seds/vol1/chapter6.pdf)
- FDEP. (2013). Surface water quality standards. In USEPA (Ed.), *Sections of Florida Administrative code addressing water quality standards*. USA. [http://water.epa.gov/scitech/swguidance/standards/wqslibrary/fl\\_index.cfm](http://water.epa.gov/scitech/swguidance/standards/wqslibrary/fl_index.cfm)
- Friberg, L., Elinder, C. G., & Kjellstrim, T. (1992). International programme on chemical safety. In W. H. Organisation (Ed.), *Environmental health criteria for cadmium*. New Zealand: Karolinska Institute, Sweden and University of Auckland, New Zealand

- Gale, N. L., Adams, C. D., Wixson, B. G., Loftin, K. A., & Huang, Y. (2002). Lead concentrations in fish and river sediments in the Old Belt of Missouri. *environmental Science and Technology*, 36(20), 4262-4268.
- Giacomelli, M. B. O., Lima, M. C., Dias, L. F., Welz, B., & Curtius, A. J. (2002). Fractionation of Cd and Pb in BCR No. 601 sediment reference material following the BCR protocol for sequential extraction and determination by electrothermal atomic absorption spectrometry using permanent modifiers. *Journal of Analytical Atomic Spectrometry*, 17(10), 1339-1343.
- Gordon, A. K., & Muller, W. J. (2010). Developing sediment quality guidelines for South Africa. *PHASE 1: Identification of international best practice and applications for South Africa to develop a research and implementation framework* Retrieved 09/10/2013, 2013, from <http://www.wrc.org.za/Pages/DisplayItem.aspx?ItemID=8754&FromURL=%2FPages%2FAllKH.aspx%3F>
- Greenberg, R. R. (2005). CCQM-K13. 1 Subsequent Key Comparison Cadmium and Lead in Sediment. *Metrologia*, 43(1A), 08004.
- Greve, T. M., Borum, J., & Pedersen, O. (2003). Meristematic oxygen variability in eelgrass (*Zostera marina*). *Limnology and Oceanography*, 48(1; NUMB 1), 210-216.
- Howard, J. R., Ligthelm, M. E., & Tanner, A. (1995). The development of a water quality management plan for the Mgeni River catchment. *Water Science and Technology*, 32(5-6), 217-226.
- Igbiosa, E. O., & Okoh, A. I. (2009). Impact of discharge wastewater effluents on the physico-chemical qualities of a receiving watershed in a typical rural community. *Environmental Science & Technology*, 6(2), 175-182.
- Ivezić, V., Lončarić, Z., Engler, M., Kerovec, D., & Singh, B. R. (2013). Comparison of different extraction methods representing available and total concentrations of Cd Cu, Fe, Mn and Zn in soil. *PoljoPrivreda*, 19(1), 53-58.
- Jaji, M. O., Bamgbose, O., Odukoya, O. O., & Arowolo, T. A. (2007). Water quality assessment of Ogun river, South West Nigeria. *Environ Monit Assess*, 133(473-482).
- Jose, M., Guerra-Garcia, & Carlos Garcia-Gomez, J. (2005). Assessing pollution levels in sediments of a harbour with two opposing entrances. Environmental implications. *Environmental Management*, 77(1-11).
- Kartal, Ş., Aydın, Z., & Tokaloğlu, Ş. (2006). Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *Journal of Hazardous Materials*, 132(1), 80-89.

- Kazi, T., Jamali, M., Kazi, G., Arain, M., Afridi, H., & Siddiqui, A. (2005). Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test. *Analytical and bioanalytical chemistry*, 383(2), 297-304.
- Klavinš, M., Briede, A., Rodinov, V., Kokorite, I., Parele, E., & Klavina, I. (2000). Heavy metals in rivers of Latvia. *Science of the total environment*, 262(1–2), 175-183.
- Lewis, M. A., Moore, J. C., Goodman, L. R., Patrick, J. M., Stanley, R. S., Roush, T. H., & Quarles, R. L. (2001). The effects of urbanization on the chemical quality of three tidal bayous in the Gulf of Mexico. *Water, Air, and Soil Pollution*, 127(1-4), 65-91.
- Lin, C. E., Chen, C. M., Kao, A., Hong, A., & Wua, C. Y. (2011). Development of the sediment and water quality management strategies for the Salt-water River, Taiwan. *Marine Pollution Bulletin*, 63(528-534).
- Lin, S., Hsieh, I. J., Huang, K. M., & Wang, C. H. (2002). Influence of the Yungtze River and grain size on the spatial variations of heavy metals and organic carbon in the East China sea continental shelf sediments. *Chemical Geology*, 182, 377-394.
- Lokeshwari, H., & Chandrappa, G. (2006). Impact of heavy metal contamination of Bellandur Lake on soil and cultivated vegetation. *Current science*, 91(5), 622-627.
- Mack, P. (2003). Dissolved oxygen and the three S's: Sources, Sinks and Solubility. Retrieved from
- Mahmood, S. (2006). Wastewater irrigation: issues and constraints for sustainable irrigated agriculture. *Basic and applied sciences*.
- Maitera, O. N., Ogugbuaja, V. O., & Barminas, J. T. (2011). Determination of trace metal levels in water and sediments of River Benue in Adamawa state, Nigeria. *Ecology and the Natural Environment*, 3(4), 149-156.
- Mandiwana, K. L., & Panichev, N. (2004). Electrothermal atomic absorption spectrometric determination of vanadium (V) in soil after leaching with  $\text{Na}_2\text{CO}_3$ . *Analytica Chimica Acta*, 517(1), 201-206.
- Martin, T. D., Creed, J. T., & Long, S. (1992). Sample preparation procedure for spectrochemical determination of total recoverable elements. *Methods for the Determination of Metals in Environmental Samples*, 15-24.
- Masamba, W. R. L., & Mazvimavi, D. (2008). Impact on water quality of land uses along Thamalakane-Boteti River: An onlet of the Okavango Delta. *Physical Chemistry. Earth*, 33, 687-694.
- Mathis, B., & Cummings, T. (1973). Selected metals in sediments, water, and biota in the Illinois River. *Journal (Water Pollution Control Federation)*, 1573-1583.

- Metropolitan, D. (2011). *Fresh water state*. Durban.
- Meybeck, M., Lestel L., Bonté P., Moilleron R., Colin J. L., Rousselot O., . . . Thévenot, D. R. (2007). Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950–2005). *Science of the total environment*, 375, 204-231.
- Mmualefe, L. C., & Torto, N. (2011). Water quality in the Okavango. In W. R. Commission (Ed.), (Vol. 37). Pretoria: Grahamstown. [www.wrc.org.za](http://www.wrc.org.za)
- Moret, A., & Rubio, J. (2003). Sulphate and molybdate ions uptake by chitin-based shrimp shells. *Minerals engineering*, 16(8), 715-722.
- Morrison, G., Fatoki, O. S., Persson, L., & Ekberg, A. (2001). Assessment of the impact of point source pollution from the Keiskammahoek sewage treatment plant on the Keiskamma River pH, electrical conductivity, oxygen demanding substance and nutrients. *Water SA*, 27(4), 475-480.
- Mossop, K. F., & Davidson, C. M. (2003). Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. *Analytica Chimica Acta*, 478(1), 111-118.
- Mutia, T., Virani, M., Moturi, W., Muyela, B., Mavura, W., & Lalah, J. (2012). Copper, lead and cadmium concentrations in surface water, sediment and fish, C. Carpio, samples from Lake Naivasha: effect of recent anthropogenic activities. *Environmental Earth Sciences*, 67(4), 1121-1130.
- Naidu, R., Gupta, V. V. S. R., Rogers, S., Kookana, R. S., Bolan, N. S., & Adriano, D. C. (2002). *Bioavailability, toxicity and risk relationships in ecosystems*. United States of America: Science Publishers Inc.
- Nriagu, J. O. (1989). A global assessment of natural sources of atmospheric trace metals. [10.1038/338047a0]. *Nature*, 338(6210), 47-49.
- Obbard, J. P. (2006). Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. *Applied Geochemistry*, 21(8), 1335-1346.
- Okoh, A. I., Odjadjare, E. E., Igbinosa, E. O., & Osode, A. N. (2007). Water treatment plants as a source of microbial pathogens in the receiving watershed. *African Journal Of Biotechnology*, 6(25), 2932-2944.
- Okonkwo, J. O., & Mothiba, M. (2004). Physico-chemical characteristics and pollution levels of heavy metals in the rivers in Thohoyandou, South Africa. *Journal of Hydrology*, 308(1–4), 122-127.

- Olaniran, A. O., Balgobind, A., & Pillay, B. (2013). Bioavailability of Heavy Metals in Soil: Impact on Microbial Biodegradation of Organic Compounds and Possible Improvement Strategies. *International journal of molecular sciences*, 14(5), 10197-10228.
- Perin, G., Fabris, R., Manente, S., Wagener, A. R., Hamacher, C., & Scotto, S. (1997). A five-year study on the heavy-metal pollution of Guanabara Bay sediments (Rio de Janeiro, Brazil) and evaluation of the metal bioavailability by means of geochemical speciation. *Water Research*, 31(12), 3017-3028.
- PerkinElmer. (1998). Optima 8X00 ICP-OES Spectrometers Retrieved 05/04/2013, 2013, from [www.perkinelmer.com/catalogue/product](http://www.perkinelmer.com/catalogue/product)
- PerkinElmer. (2008). World leader in AA, ICP-OES and ICP-MS 2011. Retrieved 26/08/2013, 2013, from [www.perkinelmer.com/PDFs/Downloads/BRO\\_WorldleaderAAICPMSICPMS.pdf](http://www.perkinelmer.com/PDFs/Downloads/BRO_WorldleaderAAICPMSICPMS.pdf)
- Prabhakar, C. (2012). Seasonal Variation of Heavy Metals Distribution and Sediments in Palar River in and Around Vaniyambadi Segment, Vellore District, Tamil Nadu, India. *International Journal of Pharmaceutical & Biological Archive*, 3(1).
- Pueyo, M., Rauret, G., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, P., & López-Sánchez, J. (2001). Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. *Journal of Environmental Monitoring*, 3(2), 243-250.
- Rauret, G. (2001). *The Certification of the Extractable Contents (mass Fractions) of Cd, Cr, Cu, Ni, Pb and Zn in Freshwater Sediment Following a Sequential Extraction Procedure-BCR-701*: Directorate-General for Research.
- Rauret, G., López-Sánchez, J.-F., Sahuquillo, A., Barahona, E., Lachica, M., Ure, A., . . . Bacon, J. (2000). Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. *Journal of Environmental Monitoring*, 2(3), 228-233.
- Reid, D. L. (1979). Total rock RbSr and UThPb isotopic study of Precambrian metavolcanic rocks in the lower Orange River region, southern Africa. *Earth and Planetary Science Letters*, 42(3), 368-378.
- Report, D. B. C. W. (2005). Preparation of the African water development report. In U. ECA (Ed.). Botswana



- Rios-Arana, J., Walsh, E., & Gardea-Torresdey, J. (2004). Assessment of arsenic and heavy metal concentrations in water and sediments of the Rio Grande at El Paso–Juarez metroplex region. *Environment International*, 29(7), 957-971.
- Rocklin, D. R. (1991). Detection in ion chromatography. *Journal of Chromatography A*, 546, 175-187.
- Roos, J. C., & Pieterse, A. (1995). Salinity and dissolved substances in the Vaal River at Balkfontein, South Africa. *Hydrobiologia*, 306(1), 41-51.
- Serife, T., Senol, K., & Gökhan, B. (2001). Application of a Three-Stage Sequential Extraction Procedure for the Determination of Extractable Metal Contents in Highway Soils. *Journal of Chemistry*, 27(2003), 333-346.
- Sahli, L., Afri-Mehennaoui, F.-Z., Okki, M. E. H. E., Blaise, C., & Mehennaoui, S. (2011). Spatial and seasonal variations and ecotoxicological significance of sediment trace metal concentrations in Kebir-Rhumel basin (Northeast of Algeria). [Article]. *Water Science & Technology*, 64(8), 1759-1766.
- Sakan, S., Đorđević, D., Dević, G., Relić, D., Anđelković, I., & Đuričić, J. (2011). A study of trace element contamination in river sediments in Serbia using microwave-assisted aqua regia digestion and multivariate statistical analysis. *Microchemical Journal*, 99(2), 492-502.
- SANB. (2013). *Healthy wetlands, healthy people*. South Africa: South African Biodiversity Institute Retrieved from [http://wetlands.sanbi.org/articles2/File/R\\_HealthyWetlandsPeople.pdf](http://wetlands.sanbi.org/articles2/File/R_HealthyWetlandsPeople.pdf).
- Sandroni, V., Smith, C. M. M., & Donovan, A. (2003). Microwave digestion of sediment, soils and urban particulate matter for trace metal analysis. *Talanta*, 60(4), 715-723.
- Sastre, J., Sahuquillo, A., Vidal, M., & Rauret, G. (2002). Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. *Analytica Chimica Acta*, 462(1), 59-72.
- Shirkhanloo, H., Mousavi, H. Z., & Rouhollah, A. (2011). Preconcentration and determination of heavy metals in water, sediment and biological samples. *Serbian Chemical Society*, 76(11), 1583-1595.
- Shozi, M. (2011). *A study of the chemical and pathogenic status of Umgeni Estuary, Durban*. Environmental Science. University of Kwazulu Natal. Durban, South Africa.
- Sigua, G. C., Steward, J. S., & Tweedale, W. A. (2000). Water-quality monitoring and biological integrity assessment in the Indian River Lagoon, Florida: Status, trends, and loadings (1988–1994). *Environmental Management*, 25(2), 199-209.
- Sponza, D., & Karaoğlu, N. (2002). Environmental geochemistry and pollution studies of Aliğa metal industry district. *Environment International*, 27(7), 541-553.

- Sultan, K., Shazili, N. A., & Peiffer, S. (2011). Distribution of Pb, As, Cd, Sn and Hg in soil, sediment and surface water of the tropical river watershed, Terengganu (Malaysia). *Journal of Hydro-environment Research*, 5(3), 169-176.
- Sutherland, R. A. (2010). BCR®-701: A review of 10-years of sequential extraction analyses. *Analytica Chimica Acta*, 680(1–2), 10-20.
- Tandon, H. L. S. (2005). *Methods of analysis of soils, plants, waters, fertilisers & organic manures*: Fertiliser Development and Consultation Organisation.
- Tessier, A., Campbell, P. G., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7), 844-851.
- USEPA. (1994a). Determination of trace elements in waters and wastes by Inductively Coupled Plasma-Mass Spectrometry *Method 200.8*. United States
- USEPA. (1994b). Sample preparation procedure for spectrochemical determination of total recoverable elements *Method 200.2*. Ohio, USA
- USEPA. (1996). The metal translator: Guidance for calculating a total recoverable permit limit from a dissolved criterion
- USEPA. (2007). Microwave assisted acid digestion of sediments, sludges, soils and oils *Method 3051A*. United States
- USEPA. (2012a). Analytical control facility. In U. S. F. a. w. service (Ed.), *Division of environmental quality*. Shepherstown, West Virginia: U.S. Fish and wildlife
- USEPA. (2012b). Water: contaminated sediments *Technical resources-guidelines*. <http://water.epa.gov/polwaste/sediments/cs/guidelines.cfm>
- Wepener, V., van Dyk, C., Bervoets, L., O'Brien, G., Covaci, A., & Cloete, Y. (2011). An assessment of the influence of multiple stressors on the Vaal River, South Africa. *Physics and Chemistry of the Earth, Parts A/B/C*, 36(14), 949-962.
- WRC. (2002). State of rivers report uMngeni River and neighbouring rivers and streams (W. A. a. Forestry & E. A. a. Tourism, Trans.). In U. Water, e. Municipality, C. Environmentek & U. o. Natal (Eds.), *Product of the river health*. Pretoria, South Africa
- Wuana, R. A., & Okieimen, F. E. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecology*, 2011, 20.
- Zeisler, R. (2004). New NIST sediment SRM for inorganic analysis. *Analytical and bioanalytical chemistry*, 378(5), 1277-1283.

- Zhang, W., Yu, L., Lu, M., Hutchinson, S. M., & Feng, H. (2007). Magnetic approach to normalizing heavy metal concentrations for particle size effects in intertidal sediments in the Yangtze Estuary, China. *Environmental Pollution*, 147(1), 238-244.
- Zimmerman, A. J., & Weindorf, D. C. (2010). Extraction: A review of procedures. *Analytical Chemistry*, 20.

# CHAPTER 4: PAPER 1

---

## **Rationale: Total metals in Umgeni River water and sediments and their spatial distribution**

Heavy metals arise naturally or through anthropogenic inputs. Naturally metals are from mineral breakdown and anthropogenic sources are mostly from human activities. These metal pollutants accumulate in sediment from where they can pose a threat to the ecosystem. Metal pollutants may cause death and diseases to organisms in the river or people dependent on those organisms. Heavy metals disrupt the functioning of the ecosystem as they are more hazardous than organic pollutants. It is crucial to study the behaviour of metals, their possible sources and health effects in order to safeguard the ecosystem. Seasonal analysis of total metals in the Umgeni River was done as follows:

- Water and sediment samples were analyzed for total metals using the ICP-OES.
- The water data was compared to the South African river quality guideline while sediment data was compared to the Sediment Quality Assessment Guidelines (SQAG's).
- Sampling sites were categorized into pristine, informal settlements and highly industrialized areas. These were used to investigate the possible impacts of metal pollution along the Umgeni River.

# TOTAL METALS IN UMGENI RIVER WATER AND SEDIMENTS AND THEIR SPATIAL DISTRIBUTION

---

Mothusi Dikole, Letitia Pillay & Patrick Ndungu

*School of Chemistry and Physics, University of KwaZulu-Natal, P/Bag X54001, Durban 4000, South Africa*

## **Abstract**

Rivers are carriers of metals and organic pollutants from natural and anthropogenic sources. Studies have shown that sediments are sinks for these pollutants as they carry more than 99% of the total amount of metals which are released as soluble metals into the water. The Umgeni River, located in KwaZulu-Natal, South Africa runs along a highly industrialised and residential area. This paper reports the total metal concentrations in water and sediment and their seasonal variations. Water and sediment samples were collected for four seasons in 8 sampling sites. The certified reference material NIST 2702 was used for quality assurance with recoveries ranging from 80% to 120%. Results showed water data having lower concentrations of metals as compared to sediments. Winter had higher concentrations of metals as compared to other seasons. Total concentrations in water were Cd (1.0-6.0), Cu (1.0-11.0), Cr (0.3-82.7), Zn (2.7-65.0) and Pb (0.3-16.0) all in  $\mu\text{g L}^{-1}$  respectively. Statistical analysis showed that there was a significant difference between the winter and autumn dry seasons and spring and summer wet seasons for sediments. Cd was the only metal at acceptable levels while Cr, Cu, Pb and Zn concentrations all exceeded levels deemed acceptable by the SABS and the EPA. Therefore, the river is in poor health.

**Keywords:** heavy metals, seasonal variability, pollution, NIST 2702, industries

## 1. Introduction

Heavy metals, such as lead and cadmium are considered pollutants because of their potential toxicity to plants, animals and human life (Banerjee *et al.*, 2012). Anthropogenic and natural activities, from the surrounding environment are the main sources of river pollution (Kankılıç *et al.*, 2013; Mutia *et al.*, 2012). Direct influxes from industrial and agricultural activities are common and may be further supplemented by natural weathering. Physical parameters of river water and sediments are pH, redox, electrical conductivity, dissolved oxygen and temperature. These contribute to the availability of heavy metals in the river system, and these parameters are often included in various guidelines to monitor and control anthropogenic pollution of rivers. Metal concentration and physical parameters are compared to river quality guidelines to protect the ecosystem (Farkas *et al.*, 2007). Within South Africa, the local guideline used for aquatic ecosystems is Department of Water Affairs and Forestry (DWAF) from South African Bureau of Standards (SABS) (DWAF, 1996b), while comparative international guidelines are provided by the Environmental Protection Agency (EPA) (FDEP, 1994).

The rate of water pollution varies seasonally, depending on discharge, flow rates and interactions with the environment (Tsai *et al.*, 2007; USEPA, 2001). Seasons in South Africa may be classified as dry or wet; the dry seasons are Autumn (February- April) and Winter ( May- July), while the wet seasons are Spring (August- October) and Summer (November- January). Studies have shown that water and sediments have varying concentrations per season depending on the type of pollution and region (Kamau *et al.*, 2008; Lokeshwari *et al.*, 2006). Water usually shows high concentrations of metals during the dry season as there is no rapid movement, mixing and/or dilution caused by rainfall. In the dry season water levels reduce due to lower rainfall and evaporation, and precipitation of the metals leads to sediments accumulating most of the metals. Conversely during wet season, previously accumulated metals are released as a result of increased water flow, this is dependent on the physico chemical conditions present in the river (Kamau *et al.*, 2008).

The Umgeni River is located in KwaZulu-Natal, a province within South Africa. This area is host to many activities which are industrial (paint, machinery, and waste management) and agricultural (arable and livestock farming) based; these make extensive use of natural water resources. Water in the area is also used for recreational and domestic purposes. The aforementioned industrial activities are possible sources of heavy metals particularly (Cd, Cr, Cu, Pb and Zn) contamination (Fatoki *et al.*, 2002).

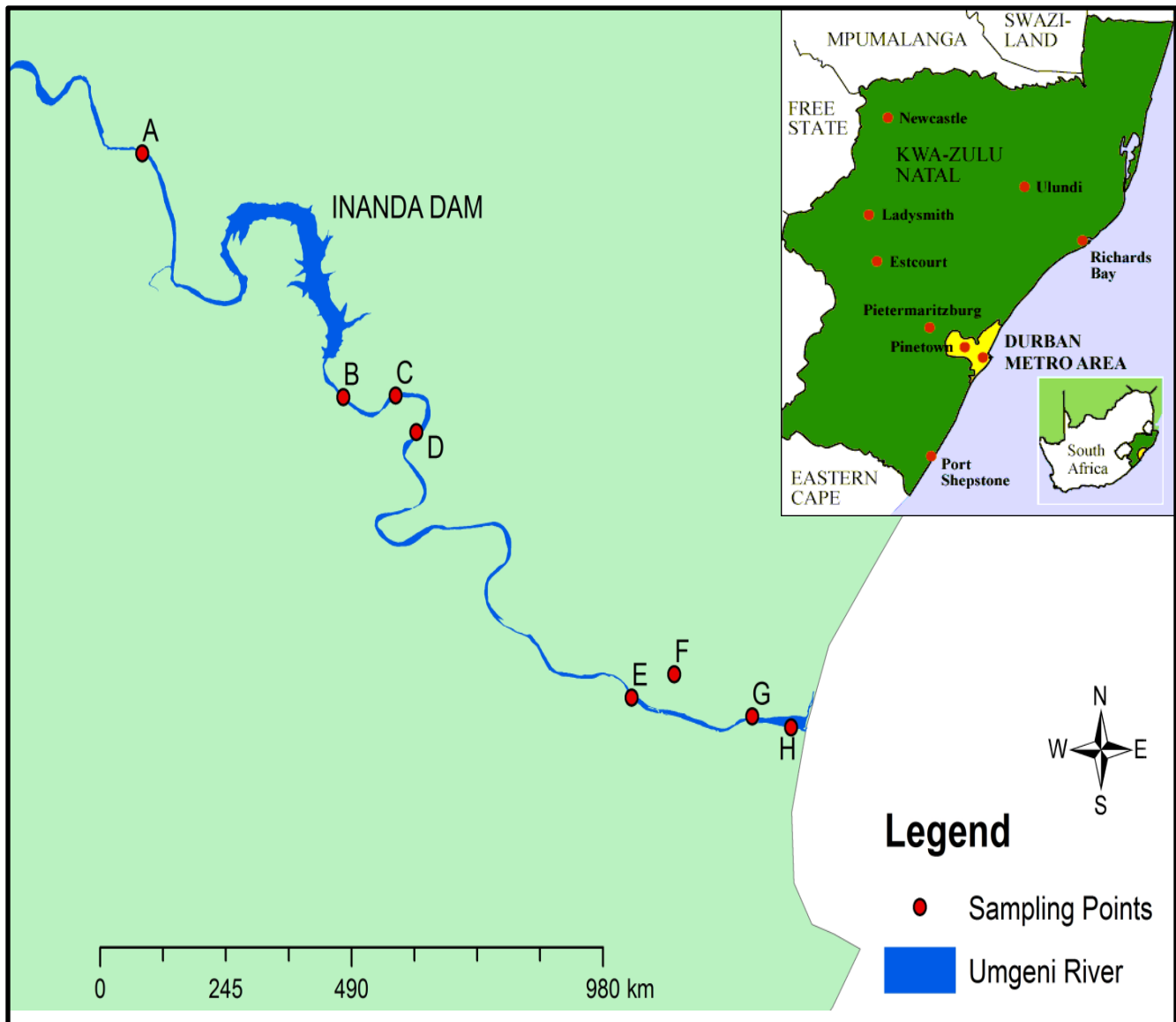
Investigations on organic pollutants within the system have previously been conducted while metal determination studies have been very limited and are not widely documented for possible pollutant inputs (Barratt, 2002; Dickens *et al.*, 1998; Ramjatan *et al.*, 2000).

One study was carried out in the Olifants River for a period of one year. The results showed high concentration of Zn, Pb and Cr accumulated in different fish species at varying localities (Coetzee *et al.*, 2002). The river had industries and sewage treatment works alongside it which were reported to affect its water quality. Okonkwo and Mothiba (2005) conducted a study on trace metals from Dzindi, Madanzhe and Mvudi rivers in South Africa. The concentrations of Cd and Pb among other measure metals exceeded the international guideline for drinking water (Okonkwo *et al.*, 2004). This study measures the total concentrations of metals in the Umgeni River water and sediments. A range of metals were screened in both water and sediment samples and Cd, Cr, Cu, Pb and Zn were selected based on their toxicity, essentiality and detectability in samples. Arsenic and mercury for example, while highly toxic, were present at levels below the detection limits and hence were excluded from the list of the studied metals. Spatial distribution will be used to assess the impact of industries on metal input.

## Study area

Figure 1 shows the study area that is 30 km long and includes the Inanda Dam which is a local water source. Sampling locations highlighted in red have been chosen because they represent a mixture of pristine areas (A) informal settlements, (B- D) and heavily industrialized areas (E- H). H represents the estuary. Seasonal sampling was done in autumn (April 2012), winter (July 2012), spring (October 2012) and summer (January 2013)

The Umgeni River as mentioned earlier is characterised by varying activities and can be sub divided into a pristine, residential and industrial zones. Sampling sites and the area description are shown in Table 1.



*A- Before Inanda Dam, B- After Inanda Dam 1, C- After Inanda Dam 2, D- After Inanda Dam 3, E- Start Of Industries, F- After Waste Management, G- End Of Industries, H- Estuarine Site*

*Figure 1: Study area showing sampling sites*



Table 1: Description and location of the sampling sites

SITE CODES	DESCRIPTION
<b>A</b>	Pristine area: Upper Inanda Dam with varying activities around the area at different times of the year. Some of the activities include fishing, livestock farming and road construction.
<b>B</b>	Informal settlement site situated South of the Inanda Dam. There are not many activities around the area. There are isolated houses at some distance from the river.
<b>C</b>	Informal settlement site after the Inanda Dam with fishing as an activity.
<b>D</b>	Informal settlement site
<b>E</b>	Represents the industrial region known as the Umgeni Business Park. The industries range from steel, paint manufacture, iron works, brick tiles manufacture to power heating systems. A railway transport is present south of the sampling area.
<b>F</b>	Discharge site for the eThekweni waste water treatment works which treats waste water from municipal sources before discharging into the river. An informal settlement is present and domestic waste is evident in the system.
<b>G</b>	This marks the end of industries. Residential on the right side and railway station on the left side of the sampling area.
<b>H</b>	Site underwent construction during the dry season. The activities in this area include fishing and rowing.

A- Before Inanda Dam, B- After Inanda Dam 1, C- After Inanda Dam 2, D- After Inanda Dam 3, E- Start Of Industries, F- After Waste Management, G- End Of Industries, H- Estuarine Site

## 2. Experimental

This section encompasses the chemicals and instruments used in analysis of metals in water and sediments.

## 2.1. Chemicals

The following chemicals were used; Nitric acid  $\geq 69\%$  (Merck), Hydrochloric acid  $\geq 37\%$  (Merck), 1000 ppm Cd standard (DLD Scientific), 1000 ppm Cr and 1000 ppm Pb standards (Fluka), 1000 ppm Cu and 1000 ppm Zn standards (Merck). All chemicals were of analytical grade and used directly without further purification.

The multi element standards were prepared based on the concentration ratio of the sample. Certified reference material NIST 2702 was from the NIST, Canada. Double distilled water was used throughout the study as blank and for making up standards and sediment samples

## 2.2. Instrumentation

This involves all the apparatus that were used including the ICP-OES and microwave.

### 2.2.1. Microwave

Microwave digestion was done with a pressurised microwave (MARS 6, CEM) equipped with rotor that holds the vessels.

### 2.2.2. Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES)

Analysis of Cd, Cr, Cu, Zn and Pb was done using ICP-OES (Perkin Elmer, Optima 5300DV). The elements wavelengths were optimised in the instrument before calibration. These were Cd: 214.440; Cr: 283.563, Cu: 327.393, Pb: 220.353, Zn: 213.857 nm. Blanks and standards were used for calibration at the accepted correlation coefficient of greater than 0.995.

## 2.3. Sampling and procedure

Water samples were collected in pre cleaned polyethylene bottles and preserved with 0.5 mL concentrated  $\text{HNO}_3$  on site and put in an ice box (Singh *et al.*, 2005). They were refrigerated at  $4^\circ\text{C}$  before analysis in the laboratory. Surface sediment samples were collected using a plastic scoop and placed directly into plastic bags and air dried.

Water samples were filtered through a  $0.45\ \mu\text{m}$  filter and analysed using Perkin Elmer ICP-OES. The dried sediment samples were ground using a pestle and mortar and sieved to  $90\ \mu\text{m}$  and stored in plastic bags before analysis.

The sediment samples and certified reference material were oven dried overnight at 60 °C to ensure complete dryness. Approximately 0.5 g of the sample was weighed into a microwave vessel. The samples were acid digested in the vessels using 10 mL aqua regia 1:3 (HNO<sub>3</sub>: HCl) using MARSXpress, CEM microwave.

The microwave was set to ramp to 180 °C for 15 minutes, hold at 180 °C for 15 minutes and cool for 15 minutes. This method was adapted from EPA methods (USEPA, 2007a). The vessels were allowed to cool at room temperature to further reduce the pressure as part of the operation procedure to avoid leaking of the solution. Digests were filtered and made to volume with double distilled water. Elemental analysis was made using ICP-OES. Statistical analysis was done using Microsoft Excel and Statistical Package for Social Scientists (SPSS) version 18.

### 3. Results and discussion

Results show the certified reference material recoveries and total metals in water and sediments.

#### 3.1. Quality assurance

Certified reference materials were used for quality assurance. Table 2 shows experimental values as compared to certified values and the relative percentage recovery. Percentage recovery of metals between 80-120% are generally acceptable (FAO, 2011; USEPA, 2012a).

Table 2: Experimental values for concentration of metals as compared to certified values and percentage recoveries<sup>n</sup>

Analyte name	Experimental concentration (mg kg <sup>-1</sup> )	Certified value (mg kg <sup>-1</sup> )	% Recovery
Cd	0.975 ± 0.12	0.817 ± 0.011	119 ± 14
Cr	281 ± 5.0	352 ± 22	80 ± 1.5
Cu	107.7 ± 1.1	117.7 ± 5.6	92 ± 0.96
Pb	107 ± 3.5	132.8 ± 1.1	81 ± 2.6
Zn	449.7 ± 11	485.3 ± 4.2	93 ± 2.2

*n* (number of replicate analysis of the certified reference material)= 3

The percentage recoveries are within the accepted range hence it validates the procedure for the metal analysis (Table 2).

### 3.2. Total metals in water

Water typically has lower metal concentrations compared to sediments. This is due to constant mixing and flow (Mutia *et al.*, 2012). This trend was also observed in the Umgeni River, wherein the concentration of metals in water are lower than  $0.100 \text{ mg L}^{-1}$  with Cd, Cr, Cu and Zn below the detection limit at some of the sites. The ranges for these metals in water are Cd (1.0-6.0), Cu (1.0-11.0), Cr (0.3-82.7), Zn (2.7-65.0) and Pb (0.3-16.0) all in  $\mu\text{g L}^{-1}$ .

#### 3.2.1. Cadmium, Chromium and Lead

These three metals showed the highest concentrations during winter. Thus, winter as the dry season usually has the highest concentration of metals because there are no dilutions from rain (Lokeshwari *et al.*, 2006). Autumn is also classified as a dry season but unlike winter dry season; there were rains during the sampling period. The SABS value from DWAF for Cd is  $150 \mu\text{g L}^{-1}$  and from EPA is ( $8.8 \mu\text{g L}^{-1}$ ) (DWAF, 1996b; FDEP, 2013). All the sites for Cd are below SABS limit indicating it is in the permissible level. Though Cd has a lower concentration, it is still a toxic element and not essential to aquatic life (Fianko *et al.*, 2007). Autumn and summer samples showed fluctuations with sites A, C and H in autumn having Cd below the detection limit. Generally no specific spatial trend was observed in winter and spring concentrations especially at the upper catchment.

The SABS accepted value for Cr is  $7.0 \mu\text{g L}^{-1}$  and the respective EPA value is ( $50.0 \mu\text{g L}^{-1}$ ) (DWAF, 1996b; FDEP, 2013). All sites exceed the SABS limit in winter but other seasons are below the standard (Figure 2). Compared to the EPA standard, autumn, spring and summer are below the limit and sites B, D, E and G also exceed this limit. Mutia *et al.* (2012) reported that high concentration of metals in surface water indicates that the pollution is recent, as the water exhibit high mobility (Mutia *et al.*, 2012). Thus high winter values indicate that there was a recent input of Cr into the river at the start of industries. The industries most likely responsible for the elevated Cr concentration may be chemical and textile.

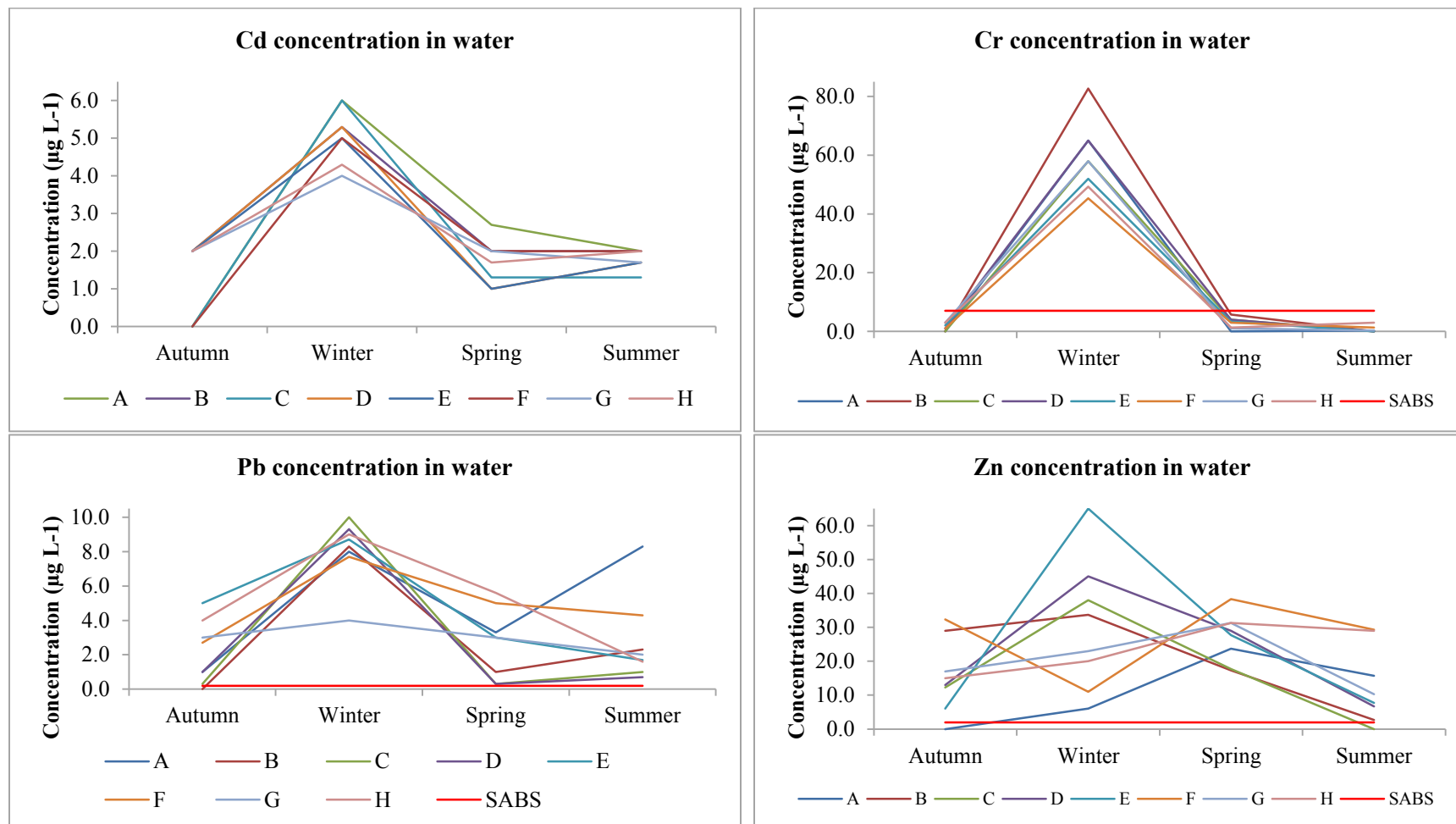
Pb in B (autumn) was below the detection limit, Figure 2 shows that all sites for all seasons are exceeding the SABS limit and also exceed the EPA limit in the winter season. The SABS limit is  $0.2 \mu\text{g L}^{-1}$  while the EPA is ( $8.5 \mu\text{g L}^{-1}$ ) (DWAF, 1996b; FDEP, 2013). Seasonal variation shows winter having the highest concentration in all sites except A and H in summer.

### 3.2.2. *Copper and Zinc*

Cu and Zn showed distinct seasonal fluctuations. Winter had the highest concentration among other seasons. Cu showed no trend in the settlement, township or industrial zones. Sites exceeded the SABS Cu limit of ( $0.3 \mu\text{g L}^{-1}$ ) (DWAF, 1996b) except for A, B, C and H in winter which had concentrations below the detection limit. All sites were below the EPA limit which is ( $3.7 \mu\text{g L}^{-1}$ ) (FDEP, 2013).

Zn does not follow any seasonal or spatial trend, but its concentrations compared to the SABS limit all sites exceeded the recommended limits except sites A (autumn and summer) and B (summer) which were below detection limit. Figure 2 shows concentration of Zn in all sites compared to the SABS values. Comparing the concentration of Zn in samples to the standards of  $2.0 \mu\text{g L}^{-1}$  and  $86 \mu\text{g L}^{-1}$  for SABS and EPA respectively, all sites had concentration below the SABS and EPA standards (DWAF, 1996b; FDEP, 2013).

Most sites are above the stipulated limit, thus the ecosystem of the Umgeni River water may have been negatively affected by the various activities around it. These metals may be from natural sources especially in the upper catchment immediately after the Inanda Dam or from industries in the lower catchment. The eThekweni waste management plant receives waste-water from households and industries which is treated and disposed into the river. The input of pollutants from the waste management brings a change to the dynamics of the metals in the river. The water discharged is not free from pollutants, as the concentrations in those areas are very high. This is observed in the three preceding sites; thus it explains the increase in concentration of metals just after the connection with the waste management. Moreover, in autumn and winter there was construction at H and it is observed that there is high concentration of Pb, Cu and Zn in that area for spring and summer.



A- Before Inanda Dam, B- After Inanda Dam 1, C- After Inanda Dam 2, D- After Inanda Dam 3, E- Start Of Industries, F- After Waste Management, G- End Of Industries, H- Estuarine Site

Figure 2: Cd, Cr Pb and Zn concentrations in water

### 3.3. Total metals in sediments

Total metals refer to individual concentrations of metals in the sediments and their measurement plays an important role in the environment. They indicate the level of pollution by providing individual concentrations at different sampling points (Divvela, 2010). High concentrations of metals accumulate in the sediments, and later be dispersed into the environment. Therefore, this study investigates the concentrations Cd, Cr, Cu, Pb and Zn to determine toxicity and seasonal variability. Statistical analysis for variability of sediment was done using one-way ANOVA.

Statistically there were no significant differences between Autumn and Winter. There was also no significant difference between Spring and Summer. The significant differences were between the dry season and the wet season hence the data presented will show winter which had the lowest amount of rainfall received in 2012 representing the dry season and summer which had the highest rainfall will represent the wet season. After the wet season, the turbidity decreases due to reduced mixing from rainfall; hence metal concentrations decrease in the dry season as metals have been washed away. The spatial distribution of each of the metals shows the trend at which the metal was following from the upper catchment till the lower catchment. There is no South African sediment guideline therefore the EPA standard was used to determine if metal concentrations were within the acceptable limit (Gordon *et al.*, 2010).

#### 3.3.1. Cadmium

There were high values of Cd in the wet season hence there is higher input in the wet season than in the dry season. Winter showed Cd concentration below the detection limit  $0.1 \mu\text{g L}^{-1}$  (PerkinElmer, 2008) in D, E, F and G. High concentrations were expected during dry season because of lower rainfall. Table 3 shows a comparison of sites to the EPA guideline value of  $0.676 \text{ mg kg}^{-1}$ ; all concentrations obtained for Cd in summer and spring exceeded the limit. Sites A, C, F and H in winter and autumn also exceeded the EPA limit.

Table 3: Cd concentration ( $\text{mg kg}^{-1}$ ) in sediments compared to the EPA guideline value,  $n=3$ 

	A	B	C	D	E	F	G	H
<b>Summer</b>	133.84 ( $\pm 0.92$ )	166.40 $\pm$ 0.37	117.34 $\pm$ 1.4	199.22 $\pm$ 0.41	207.91 $\pm$ 1.8	351.36 $\pm$ 0.79	156.10 $\pm$ 1.3	191.57 $\pm$ 1.1
<b>Winter</b>	*0.23 $\pm$ 0.42	1.98 $\pm$ 0.32	5.23 $\pm$ 1.7	*0.00	*0.00	*0.00	*0.00	*0.46 $\pm$ 0.17
<b>EPA</b>	0.676	0.676	0.676	0.676	0.676	0.676	0.676	0.676

(standard deviation), \*Below EPA limit

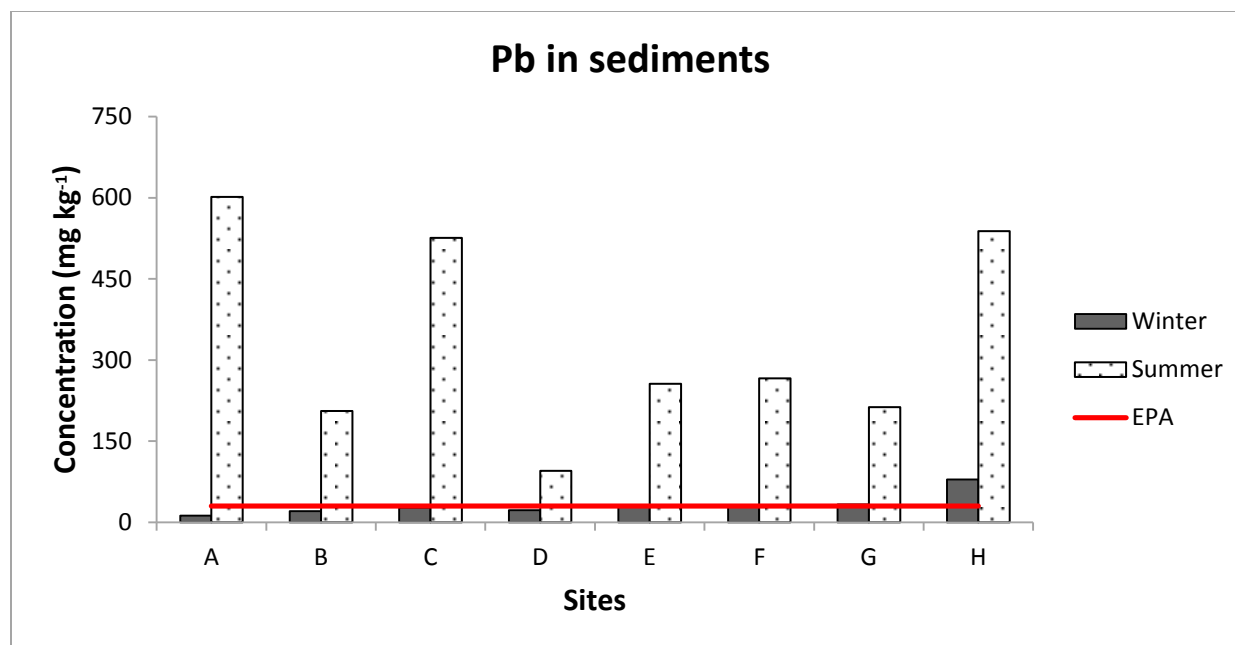
Cd concentrations showed fluctuations at the upper catchment of the river, especially in the wet season, with an increase at the settlement to industrial zone. The wet season showed an increased input of Cd at the industries; E and F had an increase in concentration. The increase in concentration of Cd at F reflected that inputs of Cd are likely to be from the waste management plant or domestic waste entering from the informal settlement. Concentration of Cd may be due to concentration effects from inputs of discharge from industries, landfills and use of fertilizers. Use of phosphate fertilizer in agriculture may pollute the river as Cd binds into organic matter, phosphate, sulphate, hydroxide and carbonate (Fianko *et al.*, 2007).

It is stated that Cd may be adsorbed into sediments immediately or be transported in aqueous solution to a distance of 50 km and later settle back into the sediments (Friberg *et al.*, 1992). It can be assumed that Cd from the upper sites settled in the estuarine site as the water is almost stagnant. The river may be impacted by industries along it such as battery, steel and paint industries which are sources of Cd. The high concentration of Cd accumulated in sediments is to the aquatic life as Cd is a toxic metal. The possible impacts of this high Cd concentration on humans are brain damage and pains in the bones (Fatoki *et al.*, 2002). These happen when Cd is released from sediments in dissolved form into the water and taken up by fish and other aquatic animals which are then consumed by humans.

### 3.3.2. Lead

Spatial distribution shows the industrial sites having lower amount of Pb as compared to the upper catchment (Figure 3). This suggests that the pollution in that area was not anthropogenic. It may be from chemical weathering during high temperatures in the wet season releasing Cd (Dekov, Komy, Araújo, *et al.*, 1997). Compared to the EPA limit  $30.2 \text{ mg kg}^{-1}$ ; spring and summer had high concentration of Pb which exceeded the EPA limit, whereas in autumn and winter, concentrations were low and were below the limit as shown in Figure 3. The concentration of Pb in A, B, C, D, E and F in autumn and winter were below the EPA stipulated limit.





A- Before Inanda Dam, B- After Inanda Dam 1, C- After Inanda Dam 2, D- After Inanda Dam 3, E- Start Of Industries, F- After Waste Management, G- End Of Industries, H- Estuarine Site

Figure 3: Pb compared to the EPA guideline value

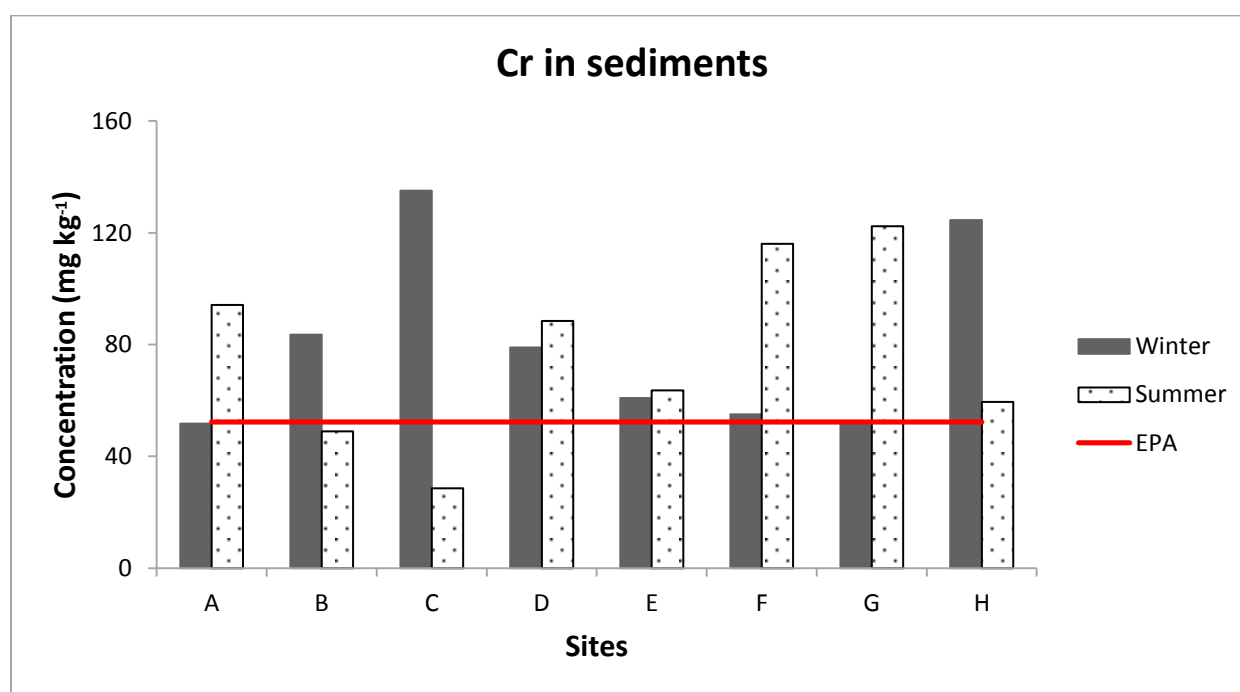
The spatial distribution for Pb in the wet season shows high concentrations in A, then fluctuation after Inanda Dam to D. Sources of Pb along Umgeni River may include paint and battery manufacturing present along the Umgeni River at the start of industries (Agarwal, 2009). Agricultural activities may also contribute to the concentration of Pb at the start of industries as Pb is found in some fertilizers (Maroulis *et al.*, 2007; McLaughlin *et al.*, 1996). The minor increase in Pb concentration in F may be due to the waste management plant or the informal settlement located near the area. The effluent discharge from the waste plant and the runoff from the settlement may increase the concentration of Pb (Fatoki *et al.*, 2002).

Closer to the informal settlement there is litter composed of cans and other metal materials which rust and may have added to the amount of contamination. When deposited in solid form such as ash, few Pb compounds readily dissolve in water but will be precipitated as solid into sediments. Generally the industrial site has lower concentrations and only an immediate increase at H. Wright *et al.* (1999) explained this increase that high concentrations of metals in estuaries are caused by the feeding river and direct discharges (Wright *et al.*, 1999). It could therefore be expected that Pb from the upper catchments was trapped in the estuary and accumulated in the sediments, or may be as a result of construction works.

Trace metals are from natural source like weathering of bedrock and also from corrosion of metal pipes (Sherman, 1998). There is likelihood that the increase in concentration of Pb may be from corrosion of metal pipes which take water into the river.

### 3.3.3. Chromium

A comparison of the Cr concentrations to the EPA value shows that site A (winter), B and C (summer) were below the EPA stipulated limit (Figure 4). Cr in sediments exhibits almost the same trend as water; there was an increase in concentration at the start of industries.



*A- Before Inanda Dam, B- After Inanda Dam 1, C- After Inanda Dam 2, D- After Inanda Dam 3, E- Start Of Industries, F- After Waste Management, G- End Of Industries, H- Estuarine Site*

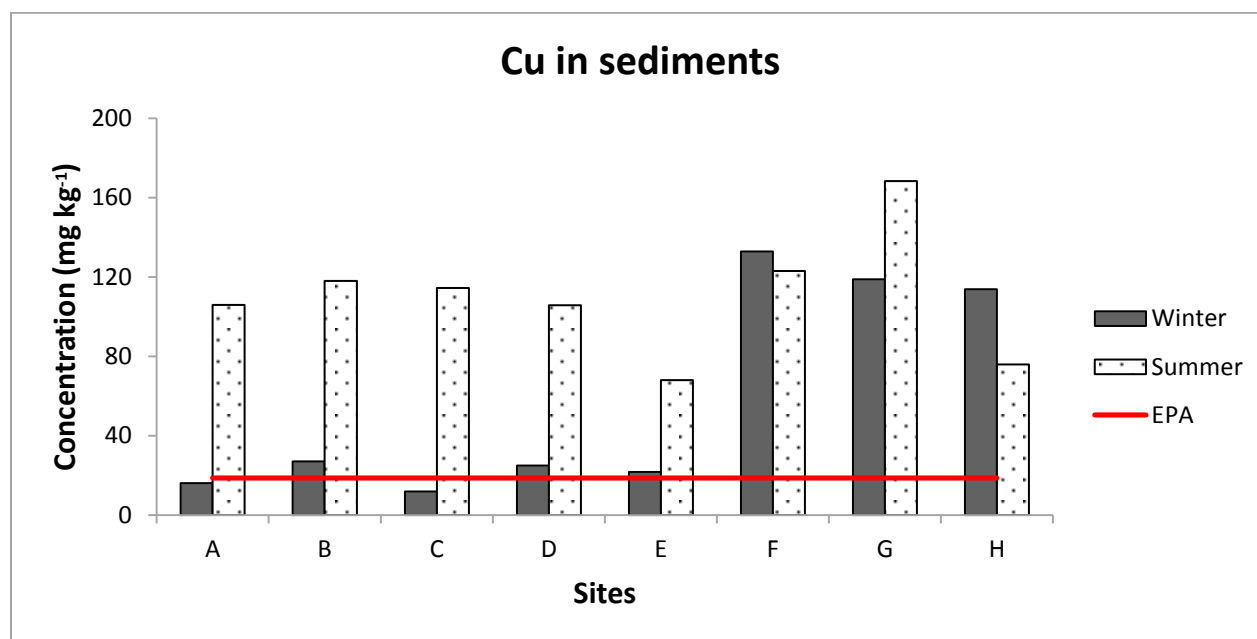
*Figure 4: Cr compared to the EPA guideline value*

The dry season has an increase in concentration from A to C with the wet season having an inverse trend. This may suggest a high input of Cr moving downstream in the dry season while a decrease in activities leading to reduced pollution in the wet season. Both dry seasons show a slight increase at H hence the construction might have had an effect. All seasons except for winter show an increase at F hence the area may have had input into the river.

Cr inputs into the river are highly likely from paint industries as it is used as constituent of certain pigments (Tabari S. *et al.*, 2010). Other industries Cr sources are metal plating and rubber (Agarwal, 2009).

### 3.3.4. Copper

All concentrations for Cu as shown in Figure 5 exceed the EPA limit of ( $18.7 \text{ mg kg}^{-1}$ ) except for A in and C in winter.



A- Before Inanda Dam, B- After Inanda Dam 1, C- After Inanda Dam 2, D- After Inanda Dam 3, E- Start Of Industries, F- After Waste Management, G- End Of Industries, H- Estuarine Site

Figure 5: Cu compared to the EPA guideline value

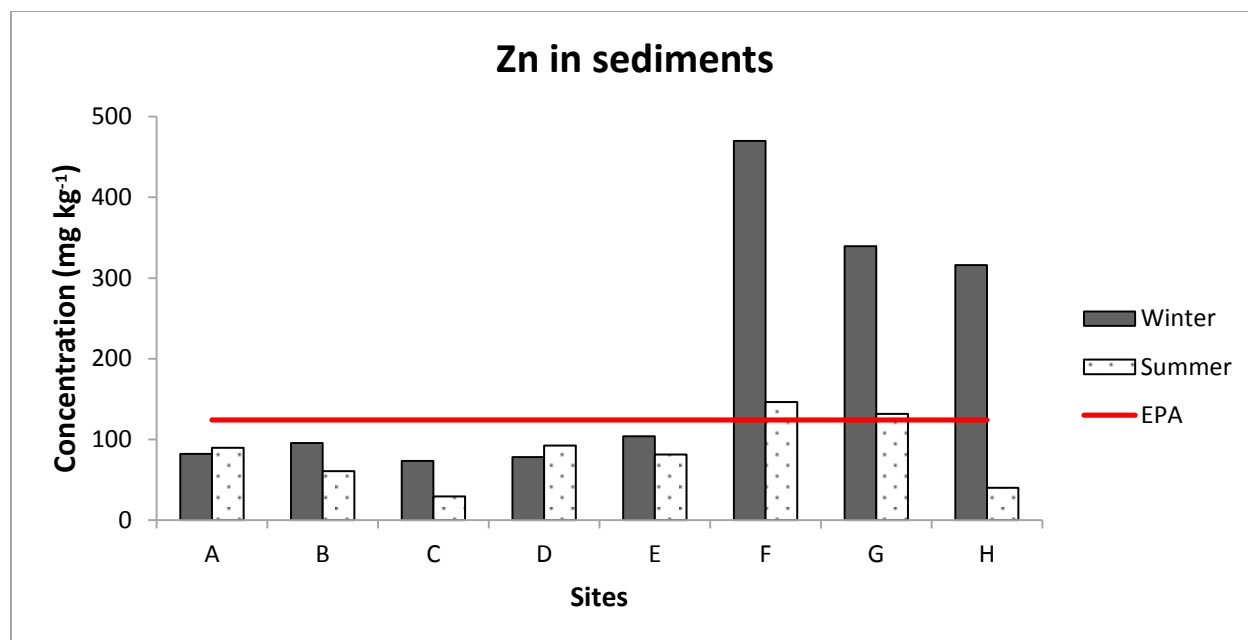
Cu has not shown any specific trend with regard to seasonal variance, but there is a lower concentration of Cu in both seasons from C to E. Samples from sites C- E were obtained after the Inanda Dam moving downstream to industries which shows that industries are not influencing the increase of Cu in the preceding sites. The Umgeni business park has steel industries, waste management, factory and others. Some industries are permitted to discharge effluent into the river by Umgeni Water; some are meeting the required standards but there are some who do not have permission but also discharge (UmgeniWater, 2013).

Cu sources from this area may be electrical in origin. Due to informal settlement at F, there are accumulations of refuse including cans, plastic and domestic waste, all of which may increase the concentration of Cr (Mondol *et al.*, 2011).

### 3.3.5. Zinc

Spatial distribution shows significant increase in concentration of Zn in F, G and H. The same variations were noticed also in the water data. From Figure 6, Zn shows a huge fluctuation in summer where there is an increase in concentration from E to F. This large difference can be noted and furthermore the distribution shows both seasons having decreasing Zn concentration after F. As F is after the waste management, study done by Alagarsamy (2006) indicated that input of organic waste from municipal sewages adds to high concentrations of Zn in sediments (Alagarsamy, 2006).

Zn is the only metal that has most sites within the EPA limit. All sites from F to H were above EPA limit in winter and autumn as shown in Figure 6, while in summer F and G were above the accepted value. Zn is an essential element but toxic in high concentrations (Ye *et al.*, 2012). Possible sources of Zn along the Umgeni River include plating, galvanising, steel and iron industries. Zn and Cd are used in conjunction in electroplating, thus it may be assumed that they would follow similar trends of industrial input into the river (Friberg *et al.*, 1992). This however is not so as the distribution of metals in sediments is not uniform across the river because of changes in the environment. There are variations in physico chemical conditions, reactions depending on the binding of metals to the sediment and processes that release them into the environment.



A- Before Inanda Dam, B- After Inanda Dam 1, C- After Inanda Dam 2, D- After Inanda Dam 3, E- Start Of Industries, F- After Waste Management, G- End Of Industries, H- Estuarine Site

Figure 6: Zn compared to the EPA guideline value

#### 4. Conclusion

The concentration of Cd, Cr, Cu, Pb and Zn in water and sediments, seasonal variations and their distribution along the Umgeni River has been found. Concentrations were compared to the SABS and EPA water and sediment quality guidelines. Water data showed Cr, Cu, Zn and Pd above the stipulated SABS limit while for sediments Cd, Cr, Cu, Pb and Zn were above the EPA limit. In the wet season Cd in water was below the SABS limit and above for sediments. Based on this, use of water directly from the river may pose health problems like kidney disease, bone disease, brain damage and other illnesses (Fatoki *et al.*, 2002).

The results showed there was a significant difference in concentration of metals in sediments between the dry seasons (winter and autumn) and the wet seasons (spring and summer). The study shows a variation in the amounts of metals at different sampling points due to varying types of activities along the river. The spatial distribution showed an increase in concentration of Cd, Cr, Cu, Pb and Zn at the start of industries moving down to the end of industries, with Cd, Cr and Pb mostly at the estuarine site; ES.

Construction was conducted near site H during these seasons which ceased before spring hence detectable in the wet seasons, this may have been due to dredging of sediments from the land. The upper catchment which is A to C shows an increase in concentration of Cd, Cr, Cu and Pb in the dry season but a decrease in the wet season. Unlike other metals; Zn showed a decrease from A to C but only in the wet season with fluctuations in the dry seasons. Most of the metals increase in concentration at the waste management facility and decrease down the preceding sites. Sediment samples particularly those taken during the wet season showed the highest levels of contamination while the water showed a peak in contamination during the dry season. The highest contamination is in the industrial site. Generally the river shows that it is in poor health as most of the metals in water and sediment are exceeding the SABS and EPA limits respectively. There is a need for increased environmental monitoring along the Umgeni River.

## 5. Acknowledgement

This research was made possible by the University of KwaZulu-Natal, College of Agriculture, Science and Engineering funding.

## 6. References

- Agarwal S.K. (2009). Heavy metal pollution Vol. 4. (pp. 37-71). Retrieved from [http://books.google.co.za/books?hl=en&lr=&id=nmputzkzWWkC&oi=fnd&pg=PR5&dq=Heavy+metal+pollution+by+Agarwal+S+K&ots=SdHT21I2dY&sig=S7U\\_BhEnnbDnDrULAQP0QdDrWrk#v=onepage&q=Heavy%20metal%20pollution%20by%20Agarwal%20S%20K&f=false](http://books.google.co.za/books?hl=en&lr=&id=nmputzkzWWkC&oi=fnd&pg=PR5&dq=Heavy+metal+pollution+by+Agarwal+S+K&ots=SdHT21I2dY&sig=S7U_BhEnnbDnDrULAQP0QdDrWrk#v=onepage&q=Heavy%20metal%20pollution%20by%20Agarwal%20S%20K&f=false)
- Alagarsamy, R. (2006). Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. *Estuarine, Coastal and Shelf Science*, 67(1–2), 333-339.
- Barratt, G. J., Combrink, J., (2002). *An assessment of the degree of mercury (Hg) bio-transformation in two river systems following discharges from a mercury recovery plant*. Technikon Natal, Durban, South Africa.
- Coetzee., Du Preez, H. H., & Van Vuren, J. H. J. (2002). Metal concentrations in *Clarias gariepinus* and *Labeo umbratus* from the Olifants and Klein Olifants River, Mpumalanga, South Africa: Zinc, copper, manganese, lead, chromium, nickel, aluminium and iron. *Water SA*, 28(4), 433-448.

- Dekov V. M., Komy Z., Araújo F., Van Put A., & Van Grieken R. (1997). Chemical composition of sediments, suspended matter, river water and ground water of the Nile (Aswan-Sohag traverse). *Science of the total environment*, 201(3), 195-210.
- Dickens, C. W. S., & Graham, P. M. (1998). Biomonitoring for effective management of wastewater discharges and the health of the river environment. *Aquatic ecosystem health and management*, 1(2), 199-217.
- Divvela. (2010). Sequential extraction procedure, *Lab Science News*.
- DWAF. (1996b). South African water quality guidelines *Aquatic ecosystems*. Pretoria: Department of Water Affairs and Forestry.
- FAO. ( 2011). Quality assurance for animal feed analysis laboratories *FAO Animal Production and Health Manual* (Vol. 14). Rome.
- Farkas, A., Erratico, C., & Vigano, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. *Chemosphere*, 68(4), 761-768.
- Fatoki, O., Lujiza, N., & Ogunfowokan, A. (2002). Trace metal pollution in Umtata River. *Water SA*, 28(2), 183-190.
- FDEP. (1994). Numerical Sediment Quality Assessment Guidelines for Florida Coastal Waters. USA: USEPA.
- FDEP. (2013). Surface water quality standards. In USEPA (Ed.), *Sections of Florida Administrative code addressing water quality standards*. USA.
- Fianko, J., Osae, S., Adomako, D., Adotey, D., & Serfor-Armah, Y. (2007). Assessment of heavy metal pollution of the Iture Estuary in the central region of Ghana. *Environmental monitoring and assessment*, 131(1-3), 467-473.
- Friberg L., Elinder C. G., & Kjellström T. (1992). International programme on chemical safety. In W. H. Organisation (Ed.), *Environmental health criteria for cadmium*. New Zealand: Karolinska Institute, Sweden and University of Auckland, New Zealand.
- Gordon, A. K., & Muller, W. J. (2010). Developing sediment quality guidelines for South Africa. *PHASE 1: Identification of international best practice and applications for South Africa to develop a research and implementation framework* Retrieved 09/10/2013, 2013, from <http://www.wrc.org.za/Pages/DisplayItem.aspx?ItemID=8754&FromURL=%2FPages%2FAllKH.aspx%3F>
- Kamau, J. N., Gachanja, A., Ngila, C., Kazungu, J. M., & Zhai, M. (2008). Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya. *Lakes & Reservoirs: Research & Management*, 13(2), 145-154.

- Kankılıç, G. B., Tüzün, İ., & Kadioğlu, Y. K. (2013). Assessment of heavy metal levels in sediment samples of Kapulukaya Dam Lake (Kirikkale) and lower catchment area. *Environmental monitoring and assessment*, 1-12.
- Lokeshwari, H., & Chandrappa, G. (2006). Impact of heavy metal contamination of Bellandur Lake on soil and cultivated vegetation. *Current science*, 91(5), 622-627.
- Maroulis, M., Economou, A., & Voulgaropoulos, A. (2007). Determination of Cd and Pb in phosphorites and phosphate fertilizers by means of a portable voltammetric analyzer based on “Virtual Instrumentation”. *Electroanalysis*, 19(19-20), 2149-2154.
- McLaughlin, M. J., Tiller, K., Naidu, R., & Stevens, D. (1996). Review: the behaviour and environmental impact of contaminants in fertilizers. *Soil Research*, 34(1), 1-54.
- Mondol, M., Chamon, A., Faiz, B., & Elahi, S. (2011). Seasonal variation of heavy metal concentrations in Water and plant samples around Tejgaon industrial Area of Bangladesh. *Journal of Bangladesh Academy of Sciences*, 35(1), 19-41.
- Mutia, T., Virani, M., Moturi, W., Muyela, B., Mavura, W., & Lalah, J. (2012). Copper, lead and cadmium concentrations in surface water, sediment and fish, C. Carpio, samples from Lake Naivasha: effect of recent anthropogenic activities. *Environmental Earth Sciences*, 67(4), 1121-1130.
- Okonkwo, J. O., & Mothiba, M. (2004). Physico-chemical characteristics and pollution levels of heavy metals in the rivers in Thohoyandou, South Africa. *Journal of Hydrology*, 308(1–4), 122-127.
- PerkinElmer. (2008). World leader in AA, ICP-OES and ICP-MS 2011. Retrieved 26/08/2013, 2013, from [www.perkinelmer.com/PDFs/Downloads/BRO\\_WorldleaderAAICPMSICPMS.pdf](http://www.perkinelmer.com/PDFs/Downloads/BRO_WorldleaderAAICPMSICPMS.pdf)
- Ramjatan, A., Ahmed, F., Hodgson, K., Simpson, D., & Quinn, N. (2000). The Potential Impacts of Water Fluoridation: A Case Study of the Umgeni Water Operational Area, KwaZulu-Natal.
- Saleh Tabari., Seyed Soheil Saeedi Saravi., Gholamali A Bandany., Atena Dehghan., & Mohammad Shokrzadeh. (2010). Heavy metals (Zn, Pb, Cd and Cr) in fish, water and sediments sampled from Southern Caspian Sea, Iran. *Toxicology and Industrial Health*, 26(10), 649-656.
- Sherman, H. M. (1998). *The assessment of groundwater quality in rural communities : two case studies from KwaZulu-Natal*. Masters, University of KwaZulu-Natal, Durban, South Africa.
- Singh, K. P., Mohan, D., Singh, V. K., & Malik, A. (2005). Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India. *Journal of Hydrology*, 312(1–4), 14-27.
- Tsai, L.-j., Yu, K.-c., & Ho, S.-T. (2007). Cadmium distribution in sediment profiles of the six main rivers in southern Taiwan. *Journal of Hazardous Materials*, 148(3), 630-639.



- Udaysankar Banerjee, & Gupta, S. (2012). Source and distribution of Lead, Cadmium, Iron and Manganese in the river Damodar near Asansol Industrial Area, West Bengal, India. *International journal of Environmental Sciences*, 2(3).
- UmgeniWater. (2013). How people affect our water quality. *Water for growth and sustainable development* Retrieved 17/10/2013, from [http://www.umgeni.co.za/water\\_education/wpwq.asp](http://www.umgeni.co.za/water_education/wpwq.asp)
- USEPA. (2001). Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: technical manual. Washington: United States Environmental Protection Agency.
- USEPA. (2007). Microwave assisted acid digestion of sediments, sludges, soils and oils *Method 3051A*. USA: Environmental Protection Agency.
- USEPA. (2012). Analytical control facility. In U. S. F. a. w. service (Ed.), *Division of environmental quality*. Shepherstown, West Virginia: U.S. Fish and wildlife.
- Wright, P., & Mason, C. F. (1999). Spatial and seasonal variation in heavy metals in the sediments and biota of two adjacent estuaries, the Orwell and the Stour, in eastern England. *Science of the total environment*, 226(2–3), 139-156.
- Ye, F., Huang, X., Zhang, D., Tian, L., & Zeng, Y. (2012). Distribution of heavy metals in sediments of the Pearl River Estuary, Southern China: Implications for sources and historical changes. *Environmental Sciences*, 24(4), 579-588.

# CHAPTER 5: PAPER 2

---

## **Rationale: Seasonal bioavailability of heavy metal contaminants from Umgeni River, South Africa**

Heavy metal pollution and toxicity is one of the main challenges to human health. Total metal concentration gives information on the abundance of the metal pollutant but toxicity may be dependent on the extent to which the organism uptake the metal pollutant. Bioavailability is the potential availability of pollutant to be taken up from the sediment by an organism. It is used as an indicator of toxicity to the environment. Metals have to be in a particular form to be assimilated by the system of an organism. Partitioning of metals into fractions is done using chemical extractions. The partitioning includes the carbonate, Fe/Mn oxide, organic and residual (unavailable) fraction. Mobility and bioavailability of metals is highest in the carbonate and lowest in the organic fraction. Physico-chemical parameters are measured as they may also influence the bioavailability of metals. This is what was seasonally carried out:

- The BCR sequential extraction was used to partition metals into different fractions.
- Bioavailability of metals was analysed using the ICP-OES and metals partitioned into the carbonate, Fe/Mn oxide, organic and residual fractions.
- Physico chemical parameters measured in the field were used to explain some of the behaviour of metal partitioning. Some parameters may indicate that the presence of acidic, oxidising and reducing environment the metal pollutants may be available to the environment.

# SEASONAL BIOAVAILABILITY OF HEAVY METAL CONTAMINANTS FROM THE UMGENI RIVER, SOUTH AFRICA

---

Mothusi Dikole, Letitia Pillay & Patrick Ndungu

*School of Chemistry and Physics, University of KwaZulu-Natal, P/Bag X54001, Durban 4000, South Africa*

## **Abstract**

Heavy metals have been implicated as river pollutants from sources such as agriculture, mining and manufacturing industries and waste water treatment works. A study was carried out in the Umgeni River South Africa to investigate the seasonal bioavailability of the heavy metal contaminants Cd, Cr, Cu, Pb and Zn. The physical parameters pH, redox potential, temperature, TDS and conductivity were measured on site. Dried sediment samples were extracted using the Community Bureau of Reference (BCR) sequential procedure and analysed by ICP-OES. A certified reference material (CRM), BCR 701 (lake sediment) was used for quality assurance with recoveries ranging between 80-120%. Statistical analysis (ANOVA) showed that there was a significant difference between metal distribution in the dry and wet seasons. Cr and Cd were partitioned in the residual fraction (unavailable for uptake). Cu, Pb and Zn were in the available fractions (carbonate, Fe/Mn oxide and organic). Cu was highest in the Fe/Mn oxide and organic fractions. This indicated that an increase in reducing agents and organic matter will avail the Cu. Zn was distributed in all fractions while Pb was found in the Fe/Mn oxide fraction (3.93- 21.3 %). Results showed that the bioavailability of Cu, Pb and Zn was high. Metal bioavailability by BCR indicates a potential risk of pollution in Umgeni River sediments as the available metals exceeded the permissible Sediment Quality Assessment Guidelines (SQAG's) from Environmental Protection Agency (EPA).

Keywords; bioavailability, heavy metals, BCR extraction, Umgeni River, sediments

## 1. Introduction

Heavy metals (Cd, Cr, Cu, Pb, Hg) are toxic at elevated concentrations and may cause health problems to users of water from rivers, reservoirs, dams and wells which has been exposed to metal input (Musyoka *et al.*, 2013). Sources of metal pollutants include weathering of soil, waste water discharge, solid waste deposited into the river by surface runoff transporting pollutants (Grabowski *et al.*, 2001; Jain, 2004; Singh *et al.*, 2005). Metals settle in sediments and bind through processes of adsorption, ion exchange and precipitation (Filgueiras *et al.*, 2002). They are released depending on a number of factors, that include pH, conductivity, salinity, total dissolved solids, temperature and turbidity (Ramirez *et al.*, 2005) (Calmano *et al.*, 1993). For example a slightly acidic environment may increase the availability of metals, as most metals are soluble in acid more than alkaline, however Cr is reported to have high mobility in alkaline environments (Babale *et al.*, 2011).


It is well established that total metal concentration is not an indicator of mobility or toxicity to living organisms. Bioavailability studies are used to measure metal mobility and bioavailability in the environment (Adriano, 2001). This involves fractionation of the total metal contaminant using chemical extraction procedures (Jain, 2004). To assess how metals are partitioned and their availability for uptake, single or selective extractants are used (Adriano, 2001). The extractants are chosen based on selectivity, precipitation and adsorption. Chemical sequential extractions are most commonly used to evaluate metal partitioning and mobility in sediment (Davidson *et al.*, 1998; Margui *et al.*, 2004).

The most common and widely used sequential extraction was first developed by Tessier *et al.* (1979) (Baffi *et al.*, 1998; Tessier *et al.*, 1979). This method involves exposing the sample to the selected extractants in order to leach out the metals depending on their partitioning. The Tessier sequential procedure releases metals from five fractions. The fractions are metals bound to the exchangeable, carbonates, Fe/Mn oxides, organic matter and residual. A standardised sequential extraction procedure, the BCR sequential extraction is used for extraction of metals in soils and sediments (Ho *et al.*, 1997). The BCR sequential extraction assists in identifying and quantifying different defined species, forms or phases in which an element occurs in the material (Van Herreweghe *et al.*, 2003).

The procedure exposes sediment to different reagents which partition metals into fractions: carbonates, oxides of Fe and Mn, organic and residual phases as shown in Table 1.

Table 1: The BCR sequential extraction procedure (Rauret *et al.*, 2000)

Chemical extractants	Metal partition
NH <sub>4</sub> OAc	Carbonate
NH <sub>2</sub> OH·HCl	Fe/Mn oxide
H <sub>2</sub> O <sub>2</sub> / 1M NH <sub>4</sub> OAc	Organic
HNO <sub>3</sub> / HCl	Residual



Decreasing mobility

Metals bound to carbonates are in the exchangeable phase where mobility is high. There may be the release of the metals due to ion exchange as these weakly adsorbed metals are held by weak electrostatic force. Low pH accelerates the mobility as it breaks the carbonate structure and increases the solubility of metals making them bioavailable to the living organisms (Atwell *et al.*, 1999; Kazi *et al.*, 2005). Metals bound to other fractions typically require a change in environmental conditions to become available.

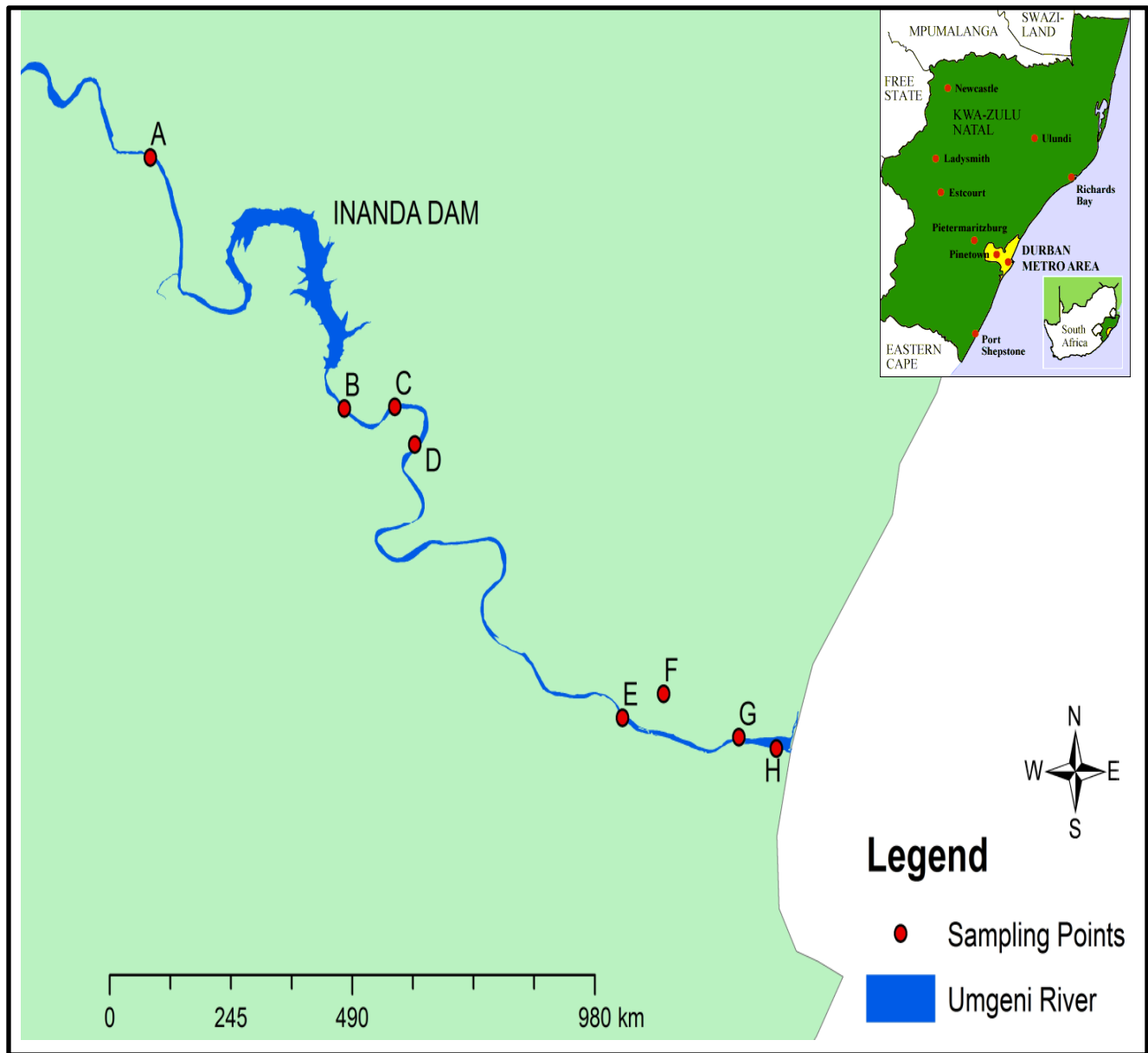
Constant deposition of the metal onto the surface of most minerals causes co-precipitation. The metals can be mobilised by an influx of reducing conditions in the environment (Kazi *et al.*, 2005). Metals bound to the organic phase are more difficult to mobilise as a result of metals forming strong complexes with organic compounds in an oxidising environment (Atwell *et al.*, 1999). The residual phase is the unreactive or the non-available phase, which is mostly bound to the silicate and can be made available from weathering (Filgueiras *et al.*, 2002) (Farkas *et al.*, 2007; Ianni *et al.*, 2000; Ianni *et al.*, 2001).

Numerous studies have been carried out using the BCR sequential extraction procedure for measuring the mobility of Pb, Cd, Cr, Cu and Zn (Coetzee, 1993; Filgueiras *et al.*, 2004; Singh *et al.*, 2005). In South Africa sediment quality studies have been carried out in some rivers, dams and estuaries. These were done by analysis of the physical parameters, particle size distribution and metal pollutants. The amount of metal contaminant that is bioavailable was measured by the amount accumulated in an organism (especially fish) and this was used as a measure of toxicity (Wepener *et al.*, 2011). There is limited data on the bioavailability of metals in South African river sediments. Analysis must be undertaken to understand the chemical behaviour of metals and their impact on the environment.

One of the major rivers in KwaZulu-Natal is the Umgeni River which is a water source to the local population. It flows along informal settlements and industries and their input may affect the river health. Therefore, it will require study into its pollution status and potential impact using bioavailable metal information (Howard *et al.*, 1995). This study investigates the seasonal bioavailability of Cd, Cr, Cu, Pb and Zn. To the best of our knowledge, no data is available in literature on the bioavailability of these metals in the Umgeni River.

### **Study Area**

The study location lies between the coordinates 29 39' 6.87'' S, 30 48' 4.59'' E and 29 48' 40.85'' S, 31 02' 7.58'' E (Figure 1) with descriptions (Table 2). The sampling area covers a length of 32 km from upper Inanda Dam to the mouth of the river (Garland *et al.*, 2000). Sampling was done in eight sites and they were divided into three categories; pristine site, informal settlement and the industrial zone.



*A- Before Inanda Dam, B-After Inanda Dam 1, C-After Inanda dam 2, D-After Inanda Dam 3, E-Start Of Industries, F- After Waste Management, G- End Of Industries, H-Estuarine Site*

*Figure 1: Map of Umgeni River showing sampling sites*

Table 2: Sampling sites description

Site	Description
A	Located before the Inanda Dam and was selected as the clean site. Activities included agriculture, fishing and road construction.
B	Sampling site directly south of the Inanda Dam.
C	Informal settlement after the Inanda Dam with distributed housing away from the river.
D	Informal settlement with fishing as one of the major activities.
E	Umgeni Business Park which marks the start of industries. Industries vary and include paint, steel, chemical, electrical and plastic manufactures.
F	The eThekweni municipality wastewater management works treats waste from homes and discharges into the Umgeni River. Before the effluent reaches the river, it passes through a sampling point coded F which also had domestic waste estimated to have come from the nearby informal settlement.
G	End of industries which had a railway line on the south and residential on the north of the river.
H	Umgeni River discharges into the Indian Ocean (estuarine site). This site was under construction.

*A- Before Inanda Dam, B-After Inanda Dam 1, C-After Inanda dam 2, D-After Inanda Dam 3, E-Start Of Industries, F- After Waste Management, G- End Of Industries, H-Estuarine Site*

## 2. Experimental

### 2.1. Chemicals

The extracting chemicals used were purchased from Merck; Glacial Acetic acid, hydroxylammonium chloride, nitric acid  $\geq 69\%$ , hydrogen peroxide, ammonium acetate and hydrochloric acid  $\geq 37\%$ . The certified reference material, BCR 701 was purchased from European Commission, Canada.

### 2.2. Sampling

Eight locations were sampled in four seasons; autumn (April, 2012), winter (July, 2012), spring (October, 2012) and summer (January, 2013). On site measurements were pH, redox potential (Eh) and temperature using a combined Hanna<sup>TM</sup> digital pH meter. An electrical conductivity (EC), total dissolved solids (TDS) and salinity were measured using a WTW<sup>TM</sup>, Oxi 320 oximeter was used for the dissolved oxygen. Water and surface sediment samples were collected.



### 2.3. Procedure

Sediment samples were air-dried, ground and sieved to 90  $\mu\text{m}$ . A mass of approximately 0.5 g of the samples and the certified reference material (BCR 701) was dried prior to analysis and sequentially extracted using the adapted BCR procedure (Rauret, 2001). The sediment samples and extraction blank were extracted as shown in table 3.

Table 3: The modified BCR sequential extraction procedure (Rauret, 2001)

Steps (fractions)	Procedure
1. Exchangeable	20mL of $0.11 \text{ molL}^{-1}$ HOAc, was added to the samples and shaken overnight for 16h at $25^{\circ}\text{C}$ . The samples were centrifuged at SPEED and supernatant was refrigerated for analysis.
2. Fe/Mn oxide	The residue from step 1 was treated with 20mL of $0.5 \text{ molL}^{-1}$ $\text{NH}_2\text{OH.HCL}$ and shaken overnight for 16h at $25^{\circ}\text{C}$ . Centrifuging was done as in step 1.
3. Organic	5mL of $\text{H}_2\text{O}_2$ at $85^{\circ}\text{C}$ was added to the residue from step 2: then first hour manual shaking with uncovered vessel and last hour with a covered vessel, 25mL of $1.0 \text{ molL}^{-1}$ $\text{NH}_4\text{OAc}$ was later added and the samples were shaken for 16h at $25^{\circ}\text{C}$ . Centrifuging was done
4. Residual	Samples were digested with aqua regia 3:1 ( $\text{HCl}:\text{HNO}_3$ )

The extracts from each step were analysed using ICP-OES (Perkin Elmer 5300 DV). Analysis of variance (ANOVA) was done for seasonal variations,  $p < 0.05$ .

### 3. Results and discussion

Statistical analysis (one way-ANOVA) for the total metals showed that there was no significant difference between spring and summer and between winter and autumn. However, there is a significant difference between the dry season (autumn and winter) and wet season (spring and summer). Therefore we present data from 1 season from each grouping. The data presented shows winter and summer extractions to represent the dry and wet season respectively.

#### 3.1. Quality Assurance

The method was validated (Table 4) with the CRM. The percentage RSD was typically <3%.

Table 4: Experimental and certified (bold) values for the certified reference material BCR 701

Metal	Step 1	Step 2	Step 3
Cd	8.1 ± 0.1 <b>7.3 ± 0.4</b>	3.65 ± 0.01 <b>3.77 ± 0.28</b>	0.24 ± 0.03 <b>0.27 ± 0.06</b>
Cr	2.29 ± 0.02 <b>2.26 ± 0.16</b>	38.2 ± 0.2 <b>45.7 ± 2</b>	114 ± 1 <b>143 ± 7</b>
Cu	59.0 ± 1.3 <b>49.3 ± 1.7</b>	108 ± 0.4 <b>124 ± 3</b>	49 ± 2 <b>55 ± 4</b>
Pb	3.50 ± 0.09 <b>3.18 ± 0.21</b>	107 ± 2 <b>126 ± 3</b>	7.6 ± 0.1 <b>9.3 ± 2</b>
Zn	233 ± 2 <b>205 ± 6</b>	96 ± 0.1 <b>114 ± 5</b>	53 ± 0.6 <b>46 ± 4</b>

*Values in mg kg<sup>-1</sup>*

#### 3.2. Physico-chemical parameters

The results (Table 5) show the physico- chemical parameters. The pH ranges from 6 to 8 which is typical for river water (Babale *et al.*, 2011).

Table 5: Physico- chemical parameters

Site code	Seasons	pH	Temperature/ °C	Eh/ mV	TDS/ mg L <sup>-1</sup>	DO/ mg L <sup>-1</sup>	EC/ µS cm <sup>-1</sup>	Salinity/ mg L <sup>-1</sup>
A	Winter	6.02	14.8	80	440	11.2	860	0.2
	Summer	6.04	24.2	35	18	6	31.2	0
B	Winter	6.79	15.3	49	395	10.5	772	0.1
	Summer	6.84	26	74	26	6.6	45.4	0
C	Winter	6.47	16.4	73	396	9.6	774	0.1
	Summer	6.6	25.6	130	26	6.75	45.4	0
D	Winter	6.38	16.3	79	400	10.7	702	0.1
	Summer	6.77	25.7	115	26	6.9	48.6	0
E	Winter	6.38	15	158	48	2	1000	0
	Summer	6.59	25.3	97	28	5.8	47	0
F	Winter	7.1	16.1	55	562	2.9	1269	0.3
	Summer	7.38	26.2	60	44	6.1	75.8	0
G	Winter	7.25	17.3	59	1594	3.7	5690	1.5
	Summer	7.47	26.3	58	88	6.6	151.7	0
H	Winter	6.6	15.4	44	820	1.2	1440	0.6
	Summer	7.24	24.4	8	69	6.6	118.5	0

*A- Before Inanda Dam, B-After Inanda Dam 1, C-After Inanda dam 2, D-After Inanda Dam 3, E-Start Of Industries, F- After Waste Management, G- End Of Industries, H-Estuarine Site*

### 3.3. Extractable metals

The BCR extraction showed Cd and Cr mostly in the residual fraction. The behaviour has been shown to be typical for these two metals (Babale *et al.*, 2011; Kartal *et al.*, 2006). Seasonally winter had the highest number of metals in the potentially available fractions and when exposed to changes in the environment these metals will become available.

High temperatures in the wet season increase the rate of chemical weathering which in turn release metals and through runoff are deposited in solubilised form into the river (Dekov, Komy, Araújo, *et al.*, 1997). Some data presented will be explained using the physical parameters as studies have shown that they influence the bioavailability of metals (Sauve *et al.*, 2000).

### 3.3.1. Cadmium

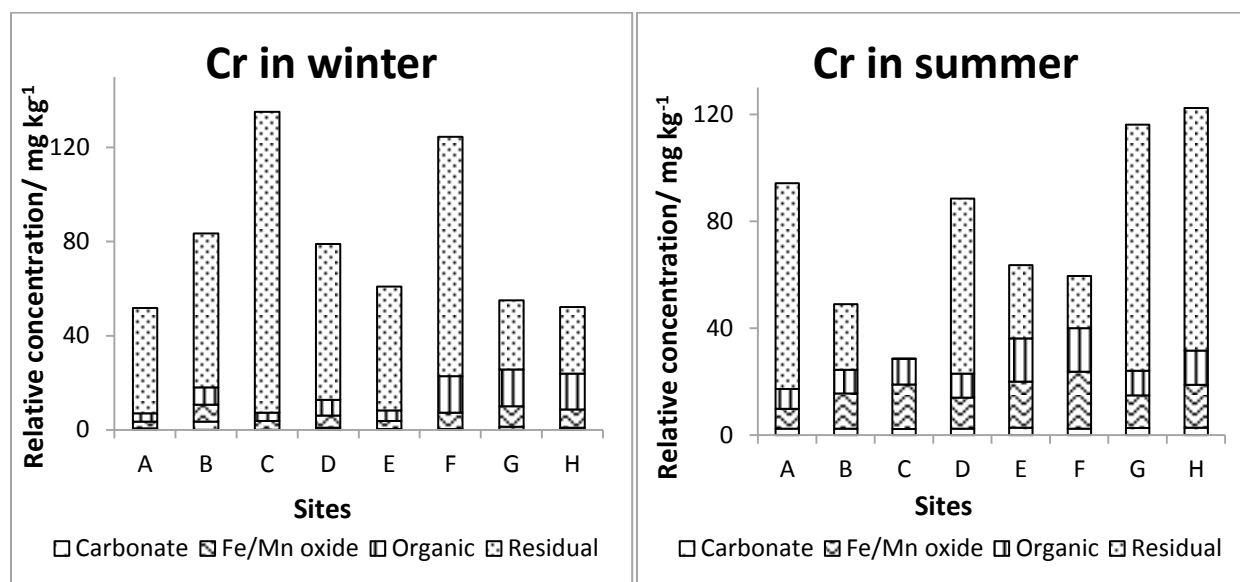
The distribution of Cd was in the following order; residual > organic > exchangeable ~ Fe/Mn oxide. This was observed in the wet season where Cd was in high concentration whereas in the dry season most of the measurements were below the detection limit. Though the Cd concentration was high in the wet season, it was mostly in the residual fraction (not available). The Cd concentration that was in the available fractions (carbonate, Fe/Mn oxide and organic) were consistent throughout ranging from 2.0 to 3.0 mg kg<sup>-1</sup>. All sites showed Cd input from residential to industrial areas as Cd ions immediately discharged from point sources are absorbed into the sediment as they are not mobile over long distances. When the ions are detected in high concentrations in the carbonate phase, it generally implies that a nearby source had some influence (Tsai *et al.*, 2007).

Cd in the exchangeable fraction meant that it was held by weak electrostatic forces and can be removed by ion exchange (Babale *et al.*, 2011). The EPA Sediment Quality Assessment Guideline (SQAG) value for Cd in river sediment is 0.676 mg kg<sup>-1</sup> (FDEP, 1994). This indicates that Cd in the exchangeable fraction has a possibility of negatively impacting the biological processes of the ecosystem as it is exceeding the limit value (Klavinš *et al.*, 2000). It has also been shown in other bioavailability studies that even though Cd exists in low concentrations, it is found mostly in the exchangeable phase and is bound to carbonates (Gunther *et al.*, 2005; Tsai *et al.*, 2002). Metals bound to carbonates (acid soluble fraction) are susceptible to pH changes but in this case Cd bioavailability will not be highly influenced by pH because it is in the optimum level (6- 8).

### 3.3.2. Chromium

Cr was found mostly in the residual fraction meaning that it is retained in the crystalline structure and not bioavailable (Kazi *et al.*, 2005). It has relatively low amounts in the Fe/Mn oxide fraction, followed by organic and finally exchangeable fractions for all seasons (Figure 2). The available fractions do not exceed the EPA SQAG permissible value of 52.3 mg kg<sup>-1</sup> therefore there is low toxicity. As shown in Figure 2, Cr in winter from the industrial zone was predominantly in the organic fraction whereas in summer it was in the Fe/Mn oxide fraction.

Cr is used in industries and if deposited as hazardous waste into the river, the metal oxides that is  $\text{CrO}_2$  will flow with the water and some particulates settle in the sediments (Metze *et al.*, 2005). There is a possibility of Cr input entering from the waste sludge which flushes down the catchment until it reaches the ocean. The presence of reducing agents in the river will release the Cr bound to the Fe/Mn oxide from the sediment in the summer season.



A- Before Inanda Dam, B-After Inanda Dam 1, C-After Inanda dam 2, D-After Inanda Dam 3, E-Start Of Industries, F- After Waste Management, G- End Of Industries, H-Estuarine Site

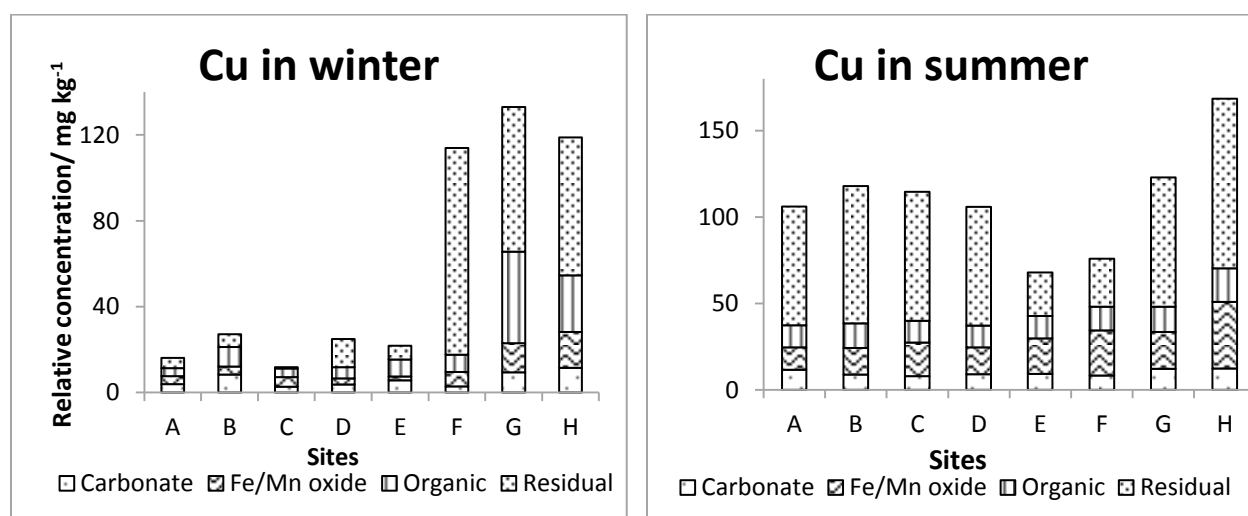
Figure 2: Cr bioavailability in summer

Cr exists as Cr (III) and Cr (VI) states and its bioavailability is dependent on the chemical state. The highly soluble, more toxic and bioavailable form of Cr is Cr (VI) (Dirilgen *et al.*, 2002). Both of them are predominant and highly available in humic environments, but Cr (VI) in acidic solution has a high redox potential which shows that it is strongly oxidising and unstable in the presence of electron donors for example organic matter (Metze *et al.*, 2005). The pH in summer is approximately 6.0 which is weakly acidic and high redox potential up to 130 mV, therefore these can avail Cr (VI) that is bound to the Fe/Mn oxide phase.

### 3.3.3. Copper

Sediments typically have high concentrations of Cu in the wet season (Dekov, Komy, Araújo, *et al.*, 1997). Cu was predominantly in the organic and residual phase in the dry season (Figure 3) making its potential mobility to be limited. In addition these partitioned stable complexes are highly mobile and toxic (Artiola, 2005). Cu bound to the organic fraction in the dry season has the highest percentage (32% of the total concentration). The stable Cu organic complex can be described by anion exchange from binding with hydroxyl and carbonyl functional groups (Iwegbue, 2011) (Coetzee, 1993).

Cu in the dry season has a possibility of being bioavailable under oxidising conditions and can be toxic to the ecosystem. The metals bound to organic matter will be released into the environment by oxidising agents (decomposition processes) (Artiola, 2005).  $\text{Cu}^{2+}$  is usually adsorbed onto clays especially Fe/Mn oxide while the stable Cu is mostly in organic soils. In the wet season Cu was consistently associated with the Fe/Mn oxide fraction. The EPA SQAG permissible limit for Cu in river sediments is  $18.7 \text{ mg kg}^{-1}$  (FDEP, 1994). For highly mobile soluble Cu the levels are below the permissible EPA SQAG limit which indicates less toxicity.



A- Before Inanda Dam ,B-After Inanda Dam 1, C-After Inanda dam 2, D-After Inanda Dam 3, E-Start Of Industries, F- After Waste Management, G- End Of Industries, H-Estuarine Site

Figure 3: Bioavailability results of Pb, Zn and Cu in winter and summer

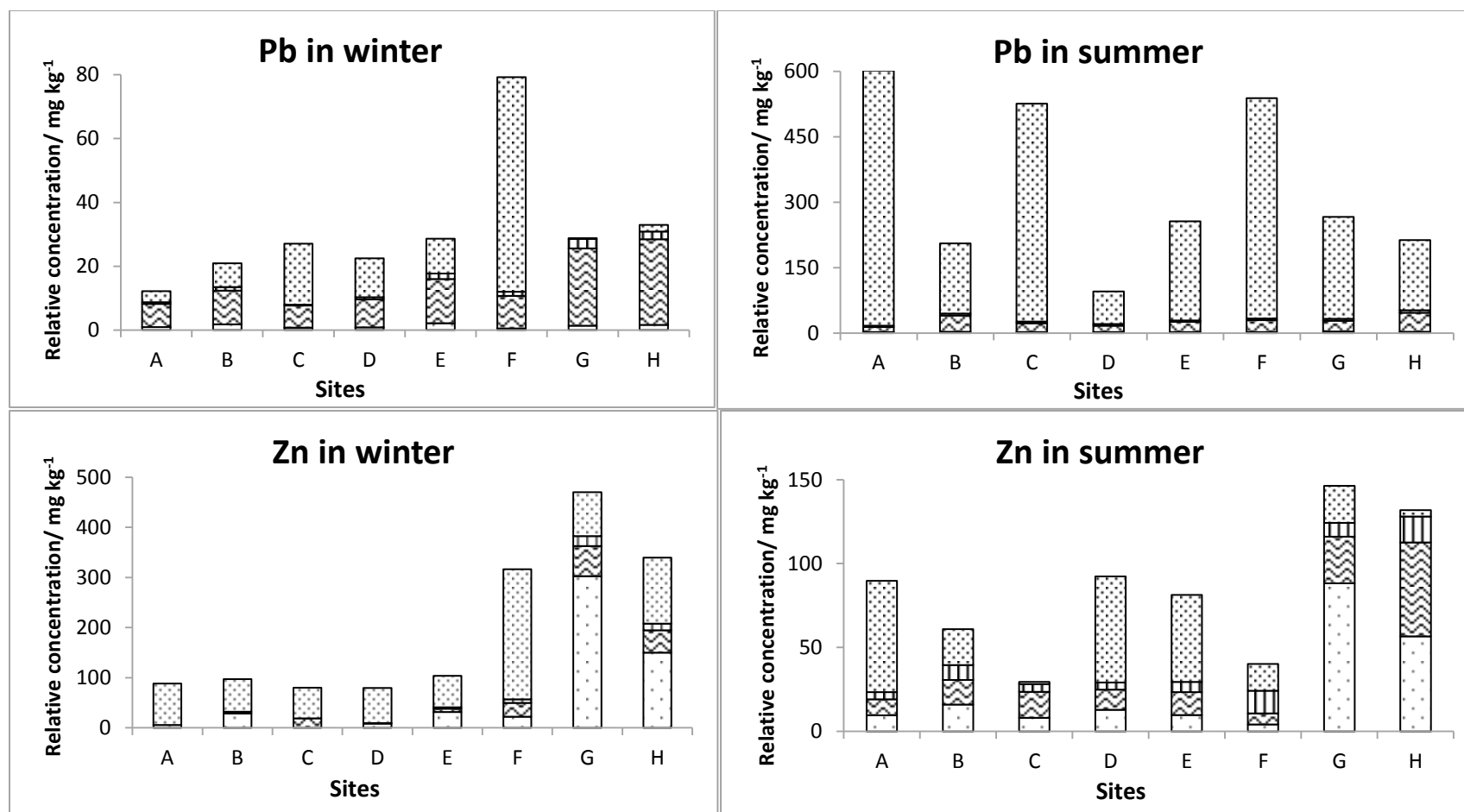
### 3.3.4. Lead

Pb is predominantly in the Fe/Mn oxide phase (Figure 4) in the winter season and mostly unavailable in summer. This shows that in winter  $\text{Pb}^{2+}$  is able to replace  $\text{Fe}^{2+}$  in the Fe/Mn oxide because of the adsorbing capacity and surface area (Iwegbue, 2011). High concentrations of Pb will be bioavailable depending on the reducing conditions and changes in redox conditions. Our data follows the reported trend that Fe/Mn oxide fraction has a high affinity of Pb in the dry season (Fonseca *et al.*, 2013). The available Pb partitioned to carbonates in the dry season is below the EPA SQAG permissible limit ( $30.2 \text{ mg kg}^{-1}$ ) hence there is low toxicity threat.

In the wet season Pb was in the residual fraction indicating that it is not bioavailable. However if the Pb-Fe-Mn-oxide phase become available; the concentration of Pb would be above the permissible levels and would pose a threat to the environment. These results are in agreement with another study on seasonal bioavailability of Pb in sediments which showed that Pb was mostly in the Fe/Mn oxide phase in the dry season as compared to the wet season (Iwegbue, 2011).

### 3.3.5. Zinc

Zn is distributed in all the fractions (Figure 4). Soluble Zn attaches to Fe/Mn oxides or organic matter and the mobility and availability is dependable on pH (Balintova *et al.*, 2012). When the pH is basic the metal is likely to be mobile and bioavailable. Concentrations of Zn range from; 3.48- 302 (exchangeable), Fe/Mn oxide (1.08- 95.51), organic (1.09- 23.62) and residual phases (1.05- 259.35)  $\text{mg kg}^{-1}$ , the year through. In the dry season Zn was consistently unavailable until sites G and H where Zn was primarily bound to the carbonate fraction. The percentage of Zn in the carbonate fraction was 64.4% and 44.2% of the total metal concentration for sites G and H respectively. This indicated that a high amount of Zn in the lower catchment was bioavailable. The same trend was observed in the wet season except that from A to F Zn had an association with the Fe/Mn oxide and organic fractions. The abundance of Zn in the carbonate (easily mobilised) fraction in site G and H shows that there may be influence from the waste sludge management and on-going construction. This flushed down in summer yielding a decrease in total concentration but not percentage contribution. It can be concluded that Zn is a pollutant and primarily from anthropogenic sources. The concentrations are exceeding the EPA SQAG value of  $124 \text{ mg kg}^{-1}$  (FDEP, 1994) which shows that the Zn will be toxic to the ecosystem. Zn will be highly bioavailable as the pH and redox in the sediment changes (Iwegbue, 2011).



A- Before Inanda Dam ,B-After Inanda Dam 1, C-After Inanda dam 2, D-After Inanda Dam 3, E-Start Of Industries, F- After Waste Management, G- End Of Industries, H-Estuarine Site

Figure 4: Bioavailability results of Pb, Zn and Cu in winter and summer



#### 4. Conclusion

Due to the nature of the areas along the river, it is difficult to point out the reasons for the variations. Many activities may be affecting the natural balance of the river and these include informal settlements, industries, illegal dumpsites and commercial zones. Heavy metals Cd, Cr, Cu, Pb and Zn were extracted and bioavailable in different seasons and sampling sites. Cd and Cr were mostly in the residual fraction; this meant that the metals were not available. Low traces of Cr were found in the Fe/Mn oxide phase in summer while Cd was in the exchangeable phase only in winter. Generally seasonal variability of these metals showed winter having more metals that is Cd, Cu, Pb and Zn in the available fractions. Metals in the exchangeable fraction like Cd and Zn which is predominant in most sampling sites are toxic to organisms. This is so as they can easily be moved, therefore, bioavailable to organisms in the ecosystem. The organic phase is also toxic as the metals are easily solubilised when the environmental conditions change. Change in the environment pH, redox potential, conductivity and anion concentration will solubilise the metals making them bioavailable thus subjecting Umgeni River to be a danger zone to living organisms.

#### 5. Acknowledgement

This research was made possible by the University of KwaZulu-Natal, College of Agriculture, Science and Engineering through their funding.

#### 6. References

- Abdul-Kareem, B. M., Rabee A.M., & Al-Fatlawy Y.F. (2011). Monitoring heavy metals, cations and anions levels and its possible health risks in Tigris River at Baghdad region. *Iraqi Journal of Science*, 52(3), 306-316.
- Adeniyi, A., Dayomi, M., Siebe, P., & Okedeyi, O. (2008). An assessment of the levels of phthalate esters and metals in the Muledane open dump, Thohoyandou, Limpopo Province, South Africa. *Chemistry Central Journal*, 2(9).
- Adriano, D. C. (2001). *Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals* (2 ed.). New York, USA: Springer.

- Agarwal, S. K. (2009). Heavy metal pollution Vol. 4. (pp. 37-71). Retrieved from [http://books.google.co.za/books?hl=en&lr=&id=nmputzkWWkC&oi=fnd&pg=PR5&dq=Heavy+metal+pollution+by+Agarwal+S+K&ots=SdHT21I2dY&sig=S7U\\_BhEnnbDnDrULAQPoQdDrWrk#v=onepage&q=Heavy%20metal%20pollution%20by%20Agarwal%20S%20K&f=false](http://books.google.co.za/books?hl=en&lr=&id=nmputzkWWkC&oi=fnd&pg=PR5&dq=Heavy+metal+pollution+by+Agarwal+S+K&ots=SdHT21I2dY&sig=S7U_BhEnnbDnDrULAQPoQdDrWrk#v=onepage&q=Heavy%20metal%20pollution%20by%20Agarwal%20S%20K&f=false)
- Akcay, H., Oguz, A., & Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Research*, 37(4), 813-822.
- Alagarsamy, R. (2006). Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. *Estuarine, Coastal and Shelf Science*, 67(1-2), 333-339.
- Artiola, J. F. (2005). Speciation of Copper. In H. C. R. Cornelis, J. Caruso, K. G. Heumann (Ed.), *Handbook of elemental speciation II: Species in the environment, food, medicine and occupational health*. England: John Wiley and sons.
- Atwell, B. J., Kriedemann, P. E., & Turnbull, C. G. N. (1999). Plants in Action: Adaptation in Nature, Performance in Cultivation. In D. P. E. K. Dr Brian J. Atwell., Dr. Colin G.N., Associate Prof. Derek Eamus ., Dr Roderick L ., Bielecki Prof. Graham Farquhar (Series Ed.) M. E. AU (Ed.) Retrieved from <http://plantsinaction.science.uq.edu.au/edition1/?q=content/title-page>
- Audry, S., Schäfer, J., Blanc, G., & Jouanneau, J.-M. (2004). Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environmental Pollution*, 132(3), 413-426.
- Austin, R., & Rhoades, J. (1979). A compact, low-cost circuit for reading four-electrode salinity sensors. *Soil Science Society of America Journal*, 43(4), 808-810.
- Babale, A., Uzairu, A., Kagbu, J., Okunola, O., & Abba, H. (2011). Assessment of Cd and Cr Bioavailability in Sediment of River Challawa, Nigeria. *British J. Appl. Sci. Technol*, 1(3), 116-130.
- Baffi, F., Ianni, C., Ravera, M., Soggia, F., & Magi, E. (1998). Evaluation of the acetate buffer attack of a sequential extraction scheme for marine particulate metal speciation studies by scanning electron microscopy with energy dispersive X-ray analysis. *Analytica Chimica Acta*, 360(1), 27-34.
- Balintova, M., Petrilakova, A., & Singovszka, E. (2012). Study of Metals Distribution between Water and Sediment in the Smolnik Creek (Slovakia) Contaminated by Acid Mine Drainage. *Chemical Engineering*, 28.
- Bandara, J. S., Wijewardena, H. P., Bandara, Y. Y., Jayasooriya, R. T., & Rajapaksha, H. (2010). Pollution of River Mahaweli and farmlands under irrigation by cadmium from agricultural inputs leading to a chronic renal failure epidemic among farmers in NCP, Sri Lanka. *Environ Geochem Health*, 33(439-453).

- Banerjee, U., & Gupta, S. (2012). Source and distribution of Lead, Cadmium, Iron and Manganese in the river Damodar near Asansol Industrial Area, West Bengal, India. *International journal of Environmental Sciences*, 2(3).
- Barratt, G. J., Combrink, J., (2002). *An assessment of the degree of mercury (Hg) bio-transformation in two river systems following discharges from a mercury recovery plant*. Technikon Natal, Durban, South Africa.
- Bartoli, G., Papa, S., Sagnella, E., & Fioretto, A. (2012). Heavy metal content in sediments along the Calore river: Relationships with physical–chemical characteristics. *Journal of Environmental Management*, 95, Supplement(0), S9-S14.
- Batista, B. L., Rodrigues, J. L., Nunes, J. A., Tormen, L., Curtius, A. J., & Barbosa Jr, F. (2008). Simultaneous determination of Cd, Cu, Mn, Ni, Pb and Zn in nail samples by inductively coupled plasma mass spectrometry (ICP-MS) after tetramethylammonium hydroxide solubilization at room temperature: comparison with ETAAS. *Talanta*, 76(3), 575-579.
- Bettinelli, M., Beone, G., Spezia, S., & Baffi, C. (2000a). Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. *Analytica Chimica Acta*, 424(2), 289-296.
- Bettinelli, M., Beone, G. M., Spezia, S., & Baffi, C. (2000b). Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. *Analytica Chimica Acta*, 424(2), 289-296.
- Binning, K., & Baird, D. (2001). Survey of heavy metals in the sediments of the Swartkops River Estuary, Port Elizabeth South Africa. *Water SA*, 27(4), 461-466.
- Blighnaut, J. N., Marais, C., & Turpie, J. K. (2007). Determining a charge for the clearing of invasive alien plant species (IAP's) to augment water supply in South Africa. *Water SA*, 33(1).
- Breslin, V. T., Clough, D., Cucchiarelli, D., Dart, P., Detelich, C., Guandal, S., . . . Loman, P. (2005). Sediment Metal Contamination in the Branford River and Harbor.
- Calmano, W., Hong, J., & Foerstner, U. (1993). Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Water Science & Technology*, 28(8), 223-235.
- Cesar, A., Choueri, R. B., Riba, I., Morales-Caselles, C., Pereira, C. D. S., Santos, A. R., . . . DelValls, T. A. (2007). Comparative sediment quality assessment in different littoral ecosystems from Spain (Gulf of Cadiz) and Brazil (Santos and São Vicente estuarine system). *Environment International*, 33(4), 429-435.

- Chatreewongsin, U. (2000). *Metal Extraction From Soil Samples By chelation in a Microwave System*. Virginia Polytechnic Institute and State University.
- Chen, B., Liang, X., Xu, W., Huang, X., & Li, X. (2012). The changes in trace metal contamination over the last decade in surface sediments of the Pearl River Estuary, South China. *Science of the total environment*, 439, 141-149.
- Chen, C. W., Kao, C. M., Chen, C. F., & Dong, C. D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor. *Chemosphere*, 66(1431–1440).
- Chen, F., Jia, G., & Chen, J. (2009). Nitrate sources and watershed denitrification inferred from nitrate dual isotopes in the Beijiang River, south China. *Biogeochemistry* 94, 163-174.
- Chen, M., & Ma, L. Q. (1998). Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. *Journal of Environmental Quality*, 27(6), 1294-1300.
- Chilundo, M., Kelderman, P., & O'keeffe, J. H. (2008). Design of a water quality monitoring network for the Limpopo River Basin in Mozambique. *Physics and Chemistry of the Earth, Parts A/B/C*, 33(8–13), 655-665.
- Chuan, M., Shu, G., & Liu, J. (1996). Solubility of heavy metals in a contaminated soil: effects of redox potential and pH. *Water, Air, and Soil Pollution*, 90(3-4), 543-556.
- Coetzee, L., Du Preez, H. H., & Van Vuren, J. H. J. (2002). Metal concentrations in *Clarias gariepinus* and *Labeo umbratus* from the Olifants and Klein Olifants River, Mpumalanga, South Africa: Zinc, copper, manganese, lead, chromium, nickel, aluminium and iron. *Water SA*, 28(4), 433-448.
- Coetzee, P. P. (1993). Determination and speciation of heavy metals in sediments of the Hartbeespoort Dam by sequential chemical extraction. *Water S. A.*, 19(4), 291-300.
- Colvin, C., Burns, A., Schachtschneider, K., Maherru, A., Charmier, J., & De Wit, M. (2011). Coal and water futures in South Africa: The case for protecting headwaters in the Enkangala grasslands: South Africa. [www.wwf.org.za](http://www.wwf.org.za)
- Conesa, H. M., Robinson, B. H., Schulin, R., & Nowack, B. (2008). Metal extractability in acidic and neutral mine tailings from the Cartagena-La Unión Mining District (SE Spain). *Applied Geochemistry*, 23(5), 1232-1240.
- Crafford, D., & Avenant-Oldewage, A. (2011). Uptake of selected metals in tissues and organs of *Clarias gariepinus* (sharp-tooth catfish) from the Vaal River System - Chromium, copper, iron, manganese and zinc. [Article]. *Water SA*, 37(2), 181-200.
- Creed, J., Martin, T., Lobring, L., & O'Dell, J. (1992). Minimizing chloride interferences produced by combination acid digestion using palladium and hydrogen as a matrix modifier in graphite furnace atomic absorption spectrometry. *Environmental Science & Technology*, 26(1), 102-106.

- CSIR. (2011). South African river health programme *uMngeni River and Neighbouring Rivers and Streams*. Durban: Council for Scientific and Industrial Research. <http://www.dwa.gov.za>
- da Luz Lopes, W., Santelli, R. E., Oliveira, E. P., de Carvalho, M. d. F. B., & Bezerra, M. A. (2009). Application of multivariate techniques in the optimization of a procedure for the determination of bioavailable concentrations of Se and As in estuarine sediments by ICP OES using a concomitant metals analyzer as a hydride generator. *Talanta*, 79(5), 1276-1282.
- da Silva, A. F., Welz, B., & Curtius, A. J. (2002). Noble metals as permanent chemical modifiers for the determination of mercury in environmental reference materials using solid sampling graphite furnace atomic absorption spectrometry and calibration against aqueous standards. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 57(12), 2031-2045.
- Davidson, C. M., Duncan, A. L., Littlejohn, D., Ure, A. M., & Garden, L. M. (1998). A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land. *Analytica Chimica Acta*, 363(1), 45-55.
- Davis, H. T., Marjorie Aelion, C., McDermott, S., & Lawson, A. B. (2009). Identifying natural and anthropogenic sources of metals in urban and rural soils using GIS-based data, PCA, and spatial interpolation. *Environmental Pollution*, 157(8-9), 2378-2385.
- de Castro Dantas, T., Dantas Neto, A., de A. Moura, M., Barros Neto, E., & de Paiva Telemaco, E. (2001). Chromium adsorption by chitosan impregnated with microemulsion. *Langmuir*, 17(14), 4256-4260.
- Dekov, V., Komy, Z., Araujo, F., Van Put, A., & Van Grieken, R. (1997). Chemical composition of sediments, suspended matter, river water and ground water of the Nile (Aswan-Sohag traverse). *Science of the total environment*, 201(3), 195-210.
- Dekov, V. M., Komy, Z., Araújo, F., Van-Put, A., & Van-rieken, R. (1997). Chemical composition of sediments, suspended matter, river water and ground water of the Nile (Aswan-Sohag traverse). *Science of the total environment*, 201(3), 195-210.
- Dickens, C. W. S., & Graham, P. M. (1998). Biomonitoring for effective management of wastewater discharges and the health of the river environment. *Aquatic ecosystem health and management*, 1(2), 199-217.
- Dirilgen, N., & Doğan, F. (2002). Speciation of chromium in the presence of copper and zinc and their combined toxicity. *Ecotoxicology and Environmental Safety*, 53(3), 397-403.
- Divvela. (2010). Sequential extraction procedure, *Lab Science News*.

- dos Santos, E. J., Herrmann, A. B., Frescura, V. L. A., & Curtius, A. J. (2005). Simultaneous determination of As, Hg, Sb, Se and Sn in sediments by slurry sampling axial view inductively coupled plasma optical emission spectrometry using on-line chemical vapor generation with internal standardization. *Journal of Analytical Atomic Spectrometry*, 20(6), 538-543.
- Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. (2009). Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review. *Science of the total environment*, 407(13), 3972-3985.
- Duruibe, J., Ogwuegbu, M., & Egwurugwu, J. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2(5), 112-118.
- DWAF. (1996a). Domestic water use *South African Water Quality Guidelines* (2 ed.). South Africa: Department of water affairs and forestry
- DWAF. (1996b). South African water quality guidelines *Aquatic ecosystems*. Pretoria: Department of Water Affairs and Forestry. [http://www.capetown.gov.za/en/CSRM/Documents/Aquatic\\_Ecosystems\\_Guidelines.pdf](http://www.capetown.gov.za/en/CSRM/Documents/Aquatic_Ecosystems_Guidelines.pdf)
- EPA, U. Environmental Protection Agency.(2000). *EPANET 2" Users Manual*.
- FAO. ( 2011). Quality assurance for animal feed analysis laboratories *FAO Animal Production and Health Manual* (Vol. 14). Rome
- Farkas, A., Erratico, C., & Vigano, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. *Chemosphere*, 68(4), 761-768.
- Fatoki, O. S., Lujiza, N., & Ogunfowokan, A. O. (2002). Trace metal pollution in Umtata River. *Water SA*, 28(2), 183-190.
- Fatoki, S. O., Cogwana, P., & Ogunfonokan, A. O. (2003). Pollution assessment in the Keiskamma River and in the impoundment downstream. *Water SA*, 29(3), 183-187.
- FDEP. (1994). Numerical Sediment Quality Assessment Guidelines for Florida Coastal Waters. USA: USEPA. [www.dep.state.fl.us/water/monitoring/docs/seds/vol1/chapter6.pdf](http://www.dep.state.fl.us/water/monitoring/docs/seds/vol1/chapter6.pdf)
- FDEP. (2013). Surface water quality standards. In USEPA (Ed.), *Sections of Florida Administrative code addressing water quality standards*. USA. [http://water.epa.gov/scitech/swguidance/standards/wqslibrary/fl\\_index.cfm](http://water.epa.gov/scitech/swguidance/standards/wqslibrary/fl_index.cfm)
- Fianko, J. R., Osae, S., Adomako, D., Adotey, D. K., & Serfor-Armah, Y. (2007). Assessment of heavy metal pollution of the Iture Estuary in the central region of Ghana. *Environmental monitoring and assessment*, 131(1-3), 467-473.

- Filgueiras, A. V., Lavilla, I., & Bendicho, C. (2004). Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: a case study. *Science of the total environment*, 330(1–3), 115-129.
- Filgueiras, A. V., Lavilla I., & Bendicho C. (2002). Chemical sequential extraction for metal partitioning in environmental solid samples. *Journal of Environmental Monitoring*, 4(6), 823-857.
- Fonseca, E. M., Baptista Neto, J. A., Silva, C. G., McAlister, J. J., Smith, B. J., & Fernandez, M. A. (2013). Stormwater impact in Guanabara Bay (Rio de Janeiro): Evidences of seasonal variability in the dynamic of the sediment heavy metals. *Estuarine, Coastal and Shelf Science*, 130, 161-168.
- Friberg, L., Elinder, C. G., & Kjellström, T. (1992). International programme on chemical safety. In W. H. Organisation (Ed.), *Environmental health criteria for cadmium*. New Zealand: Karolinska Institute, Sweden and University of Auckland, New Zealand
- Gale, N. L., Adams, C. D., Wixson, B. G., Loftin, K. A., & Huang, Y. (2002). Lead concentrations in fish and river sediments in the Old Belt of Missouri. *environmental Science and Technology*, 36(20), 4262-4268.
- Garland, G., & Moleko, L. (2000). Geomorphological impacts of Inanda Dam on the Mgeni estuary, north of Durban, South Africa). *Bulletin of Engineering Geology and the Environment*, 59(2), 119-126.
- Giacomelli, M. B. O., Lima, M. C., Dias, L. F., Welz, B., & Curtius, A. J. (2002). Fractionation of Cd and Pb in BCR No. 601 sediment reference material following the BCR protocol for sequential extraction and determination by electrothermal atomic absorption spectrometry using permanent modifiers. *Journal of Analytical Atomic Spectrometry*, 17(10), 1339-1343.
- Gordon, A. K., & Muller, W. J. (2010). Developing sediment quality guidelines for South Africa. *PHASE 1: Identification of international best practice and applications for South Africa to develop a research and implementation framework* Retrieved 09/10/2013, 2013, from <http://www.wrc.org.za/Pages/DisplayItem.aspx?ItemID=8754&FromURL=%2FPages%2FAIHKH.aspx%3F>
- Grabowski, L. A., Houppis, J. L., Woods, W. I., & Johnson, K. A. (2001). Seasonal bioavailability of sediment-associated heavy metals along the Mississippi river floodplain. *Chemosphere*, 45(4), 643-651.
- Greenberg, R. R. (2005). CCQM-K13. 1 Subsequent Key Comparison Cadmium and Lead in Sediment. *Metrologia*, 43(1A), 08004.
- Greve, T. M., Borum, J., & Pedersen, O. (2003). Meristematic oxygen variability in eelgrass (*Zostera marina*). *Limnology and Oceanography*, 48(1; NUMB 1), 210-216.

- Gunther, K., & Kastenholz, B. (2005). Speciation of Cadmium. In H. C. R. Cornelis, J. Caruso, K. G. Heumann (Ed.), *Handbook of elemental speciation II: Species in the environment, food, medicine and occupational health*. England: John Wiley and Sons.
- Ho, M. D., & Evans, G. J. (1997). Operational speciation of cadmium, copper, lead and zinc in the NIST standard reference materials 2710 and 2711 (Montana soil) by the BCR sequential extraction procedure and flame atomic absorption spectrometry. *Analytical Communications*, 34(11), 363-364.
- Howard, J. R., Ligthelm, M. E., & Tanner, A. (1995). The development of a water quality management plan for the Mgeni River catchment. *Water Science and Technology*, 32(5-6), 217-226.
- Ianni, C., Magi, E., Rivaro, P., & Ruggieri, N. (2000). Trace metals in Adriatic coastal sediments: distribution and speciation pattern. *Toxicological & Environmental Chemistry*, 78(1-2), 73-92.
- Ianni, C., Ruggieri, N., Rivaro, P., & Frache, R. (2001). Evaluation and comparison of two selective extraction procedures for heavy metal speciation in sediments. *Analytical Sciences*, 17(11), 1273-1278.
- Igbinsosa, E. O., & Okoh, A. I. (2009). Impact of discharge wastewater effluents on the physico-chemical qualities of a receiving watershed in a typical rural community. *Environmental Science & Technology*, 6(2), 175-182.
- Ivezić, V., Lončarić, Z., Engler, M., Kerovec, D., & Singh, B. R. (2013). Comparison of different extraction methods representing available and total concentrations of Cd Cu, Fe, Mn and Zn in soil. *PoljoPrivreda*, 19(1), 53-58.
- Iwegbue, C. M. (2011). Chemical fractionation of metals in core sediments of Orogon River, southern Nigeria. *Toxicological & Environmental Chemistry*, 93(7), 1341-1358.
- Jain, C. K. (2004). Metal fractionation study on bed sediments of River Yamuna, India. *Water Research*, 38(3), 569-578.
- Jaji, M. O., Bamgbose, O., Odukoya, O. O., & Arowolo, T. A. (2007). Water quality assessment of Ogun river, South West Nigeria. *Environ Monit Assess*, 133(473-482).
- Jose, M., Guerra-Garcia, & Carlos Garcia-Gomez, J. (2005). Assessing pollution levels in sediments of a harbour with two opposing entrances. Environmental implications. *Environmental Management*, 77(1-11).
- Kamau, J. N., Gachanja, A., Ngila, C., Kazungu, J. M., & Zhai, M. (2008). Anthropogenic and seasonal influences on the dynamics of selected heavy metals in Lake Naivasha, Kenya. *Lakes & Reservoirs: Research & Management*, 13(2), 145-154.



- Kankılıç, G. B., Tüzün, İ., & Kadioğlu, Y. K. (2013). Assessment of heavy metal levels in sediment samples of Kapulukaya Dam Lake (Kirikkale) and lower catchment area. *Environmental monitoring and assessment*, 1-12.
- Kartal, Ş., Aydın, Z., & Tokaloğlu, Ş. (2006). Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *Journal of Hazardous Materials*, 132(1), 80-89.
- Kazi, T., Jamali, M., Kazi, G., Arain, M., Afridi, H., & Siddiqui, A. (2005). Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test. *Analytical and bioanalytical chemistry*, 383(2), 297-304.
- Klavinš, M., Briede, A., Rodinov, V., Kokorite, I., Parele, E., & Klavina, I. (2000). Heavy metals in rivers of Latvia. *Science of the total environment*, 262(1-2), 175-183.
- Lewis, M. A., Moore, J. C., Goodman, L. R., Patrick, J. M., Stanley, R. S., Roush, T. H., & Quarles, R. L. (2001). The effects of urbanization on the chemical quality of three tidal bayous in the Gulf of Mexico. *Water, Air, and Soil Pollution*, 127(1-4), 65-91.
- Lin, C. E., Chen, C. M., Kao, A., Hong, A., & Wua, C. Y. (2011). Development of the sediment and water quality management strategies for the Salt-water River, Taiwan. *Marine Pollution Bulletin*, 63(528-534).
- Lin, S., Hsieh, I. J., Huang, K. M., & Wang, C. H. (2002). Influence of the Yungtze River and grain size on the spatial variations of heavy metals and organic carbon in the East China sea continental shelf sediments. *Chemical Geology*, 182, 377-394.
- Lokeshwari, H., & Chandrappa, G. (2006). Impact of heavy metal contamination of Bellandur Lake on soil and cultivated vegetation. *Current science*, 91(5), 622-627.
- Mack, P. (2003). Dissolved oxygen and the three S's: Sources, Sinks and Solubility. Retrieved from
- Mahmood, S. (2006). Wastewater irrigation: issues and constraints for sustainable irrigated agriculture. *Basic and applied sciences*.
- Maitera, O. N., Ogugbuaja, V. O., & Barminas, J. T. (2011). Determination of trace metal levels in water and sediments of River Benue in Adamawa state, Nigeria. *Ecology and the Natural Environment*, 3(4), 149-156.
- Mandiwana, K. L., & Panichev, N. (2004). Electrothermal atomic absorption spectrometric determination of vanadium (V) in soil after leaching with  $\text{Na}_2\text{CO}_3$ . *Analytica Chimica Acta*, 517(1), 201-206.

- Margui, E., Salvadó, V., Queralt, I., & Hidalgo, M. (2004). Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes. *Analytica Chimica Acta*, 524(1), 151-159.
- Maroulis, M., Economou, A., & Voulgaropoulos, A. (2007). Determination of Cd and Pb in phosphorites and phosphate fertilizers by means of a portable voltammetric analyzer based on “Virtual Instrumentation”. *Electroanalysis*, 19(19-20), 2149-2154.
- Martin, T. D., Creed, J. T., & Long, S. (1992). Sample preparation procedure for spectrochemical determination of total recoverable elements. *Methods for the Determination of Metals in Environmental Samples*, 15-24.
- Masamba, W. R. L., & Mazvimavi, D. (2008). Impact on water quality of land uses along Thamalakane-Boteti River: An onlet of the Okavango Delta. *Physical Chemistry. Earth*, 33, 687-694.
- Mathis, B., & Cummings, T. (1973). Selected metals in sediments, water, and biota in the Illinois River. *Journal (Water Pollution Control Federation)*, 1573-1583.
- McLaughlin, M. J., Tiller, K., Naidu, R., & Stevens, D. (1996). Review: the behaviour and environmental impact of contaminants in fertilizers. *Soil Research*, 34(1), 1-54.
- Metropolitan, D. (2011). *Fresh water state*. Durban.
- Metze, D., Jakubowski, N., & Klockow, D. (2005). Speciation of Chromium. In H. C. R. Cornelis, J. Caruso, K. G. Heumann (Ed.), *Handbook of elemental speciation II: Species in the environment, food, medicine and occupational health*. England: John Wiley and sons.
- Meybeck, M., Lestel L., Bonté P., Moilleron R., Colin J. L., Rousselot O., . . . Thévenot, D. R. (2007). Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950–2005). *Science of the total environment*, 375, 204-231.
- Mmualefe, L. C., & Torto, N. (2011). Water quality in the Okavango. In W. R. Commission (Ed.), (Vol. 37). Pretoria: Grahamstown. [www.wrc.org.za](http://www.wrc.org.za)
- Mondol, M., Chamon, A., Faiz, B., & Elahi, S. (2011). Seasonal variation of heavy metal concentrations in Water and plant samples around Tejgaon industrial Area of Bangladesh. *Journal of Bangladesh Academy of Sciences*, 35(1), 19-41.
- Moret, A., & Rubio, J. (2003). Sulphate and molybdate ions uptake by chitin-based shrimp shells. *Minerals engineering*, 16(8), 715-722.
- Morrison, G., Fatoki, O. S., Persson, L., & Ekberg, A. (2001). Assessment of the impact of point source pollution from the Keiskammahoek sewage treatment plant on the Keiskamma River pH, electrical conductivity, oxygen demanding substance and nutrients. *Water SA*, 27(4), 475-480.

- Mossop, K. F., & Davidson, C. M. (2003). Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. *Analytica Chimica Acta*, 478(1), 111-118.
- Musyoka, S. M., Ngila, J. C., & Mamba, B. B. (2013). Remediation studies of trace metals in natural and treated water using surface modified biopolymer nanofibers. *Physics and Chemistry of the Earth, Parts A/B/C*, 66(0), 45-50.
- Mutia, T., Virani, M., Moturi, W., Muyela, B., Mavura, W., & Lalah, J. (2012). Copper, lead and cadmium concentrations in surface water, sediment and fish, C. Carpio, samples from Lake Naivasha: effect of recent anthropogenic activities. *Environmental Earth Sciences*, 67(4), 1121-1130.
- Naidu, R., Gupta, V. V. S. R., Rogers, S., Kookana, R. S., Bolan, N. S., & Adriano, D. C. (2002). *Bioavailability, toxicity and risk relationships in ecosystems*. United States of America: Science Publishers Inc.
- Nriagu, J. O. (1989). A global assessment of natural sources of atmospheric trace metals. [10.1038/338047a0]. *Nature*, 338(6210), 47-49.
- Obbard, J. P. (2006). Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. *Applied Geochemistry*, 21(8), 1335-1346.
- Okoh, A. I., Odjadjare, E. E., Igbinosa, E. O., & Osode, A. N. (2007). Water treatment plants as a source of microbial pathogens in the receiving watershed. *African Journal Of Biotechnology*, 6(25), 2932-2944.
- Okonkwo, J. O., & Mothiba, M. (2004). Physico-chemical characteristics and pollution levels of heavy metals in the rivers in Thohoyandou, South Africa. *Journal of Hydrology*, 308(1-4), 122-127.
- Olaniran, A. O., Balgobind, A., & Pillay, B. (2013). Bioavailability of Heavy Metals in Soil: Impact on Microbial Biodegradation of Organic Compounds and Possible Improvement Strategies. *International journal of molecular sciences*, 14(5), 10197-10228.
- Perin, G., Fabris, R., Manente, S., Wagener, A. R., Hamacher, C., & Scotto, S. (1997). A five-year study on the heavy-metal pollution of Guanabara Bay sediments (Rio de Janeiro, Brazil) and evaluation of the metal bioavailability by means of geochemical speciation. *Water Research*, 31(12), 3017-3028.
- PerkinElmer. (1998). Optima 8X00 ICP-OES Spectrometers Retrieved 05/04/2013, 2013, from [www.perkinelmer.com/catalogue/product](http://www.perkinelmer.com/catalogue/product)
- PerkinElmer. (2008). World leader in AA, ICP-OES and ICP-MS 2011. Retrieved 26/08/2013, 2013, from [www.perkinelmer.com/PDFs/Downloads/BRO\\_WorldleaderAAICPMSICPMS.pdf](http://www.perkinelmer.com/PDFs/Downloads/BRO_WorldleaderAAICPMSICPMS.pdf)

- Prabhahar, C. (2012). Seasonal Variation of Heavy Metals Distribution and Sediments in Palar River in and Around Vaniyambadi Segment, Vellore District, Tamil Nadu, India. *International Journal of Pharmaceutical & Biological Archive*, 3(1).
- Pueyo, M., Rauret, G., Lück, D., Yli-Halla, M., Muntau, H., Quevauviller, P., & López-Sánchez, J. (2001). Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. *Journal of Environmental Monitoring*, 3(2), 243-250.
- Ramirez, M., Massolo, S., Frache, R., & Correa, J. A. (2005). Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile. *Marine Pollution Bulletin*, 50(1), 62-72.
- Ramjatan, A., Ahmed, F., Hodgson, K., Simpson, D., & Quinn, N. (2000). The Potential Impacts of Water Fluoridation: A Case Study of the Umgeni Water Operational Area, KwaZulu-Natal.
- Rauret, G. (2001). *The Certification of the Extractable Contents (mass Fractions) of Cd, Cr, Cu, Ni, Pb and Zn in Freshwater Sediment Following a Sequential Extraction Procedure-BCR-701*: Directorate-General for Research.
- Rauret, G., López-Sánchez, J.-F., Sahuquillo, A., Barahona, E., Lachica, M., Ure, A., . . . Bacon, J. (2000). Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. *Journal of Environmental Monitoring*, 2(3), 228-233.
- Reid, D. L. (1979). Total rock RbSr and UThPb isotopic study of Precambrian metavolcanic rocks in the lower Orange River region, southern Africa. *Earth and Planetary Science Letters*, 42(3), 368-378.
- Report, D. B. C. W. (2005). Preparation of the African water development report. In U. ECA (Ed.). Botswana
- Rios-Arana, J., Walsh, E., & Gardea-Torresdey, J. (2004). Assessment of arsenic and heavy metal concentrations in water and sediments of the Rio Grande at El Paso–Juarez metroplex region. *Environment International*, 29(7), 957-971.
- Rocklin, D. R. (1991). Detection in ion chromatography. *Journal of Chromatography A*, 546, 175-187.
- Roos, J. C., & Pieterse, A. (1995). Salinity and dissolved substances in the Vaal River at Balkfontein, South Africa. *Hydrobiologia*, 306(1), 41-51.
- S,erife, T., S,enol, K., & G,okhan, B. (2001). Application of a Three-Stage Sequential Extraction Procedure for the Determination of Extractable Metal Contents in Highway Soils. *Journal of Chemistry*, 27(2003), 333-346.

- Sahli, L., Afri-Mehennaoui, F.-Z., Okki, M. E. H. E., Blaise, C., & Mehennaoui, S. (2011). Spatial and seasonal variations and ecotoxicological significance of sediment trace metal concentrations in Kebir-Rhumel basin (Northeast of Algeria). [Article]. *Water Science & Technology*, 64(8), 1759-1766.
- Sakan, S., Đorđević, D., Dević, G., Relić, D., Anđelković, I., & Đuričić, J. (2011). A study of trace element contamination in river sediments in Serbia using microwave-assisted aqua regia digestion and multivariate statistical analysis. *Microchemical Journal*, 99(2), 492-502.
- SANB. (2013). *Healthy wetlands, healthy people*. South Africa: South African Biodiversity Institute Retrieved from [http://wetlands.sanbi.org/articles2/File/R\\_HealthyWetlandsPeople.pdf](http://wetlands.sanbi.org/articles2/File/R_HealthyWetlandsPeople.pdf).
- Sandroni, V., Smith, C. M. M., & Donovan, A. (2003). Microwave digestion of sediment, soils and urban particulate matter for trace metal analysis. *Talanta*, 60(4), 715-723.
- Sastre, J., Sahuquillo, A., Vidal, M., & Rauret, G. (2002). Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. *Analytica Chimica Acta*, 462(1), 59-72.
- Sauve, S., Hendershot, W., & Allen, H. E. (2000). Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environmental Science & Technology*, 34(7), 1125-1131.
- Sherman, H. M. (1998). *The assessment of groundwater quality in rural communities : two case studies from KwaZulu-Natal*. Masters, University of KwaZulu-Natal, Durban, South Africa.
- Shirkhanloo, H., Mousavi, H. Z., & Rouhollah, A. (2011). Preconcentration and determination of heavy metals in water, sediment and biological samples. *Serbian Chemical Society*, 76(11), 1583-1595.
- Shozi, M. (2011). *A study of the chemical and pathogenic status of Umgeni Estuary, Durban*. Environmental Science. University of Kwazulu Natal. Durban, South Africa.
- Sigua, G. C., Steward, J. S., & Tweedale, W. A. (2000). Water-quality monitoring and biological integrity assessment in the Indian River Lagoon, Florida: Status, trends, and loadings (1988–1994). *Environmental Management*, 25(2), 199-209.
- Singh, K. P., Mohan, D., Singh, V. K., & Malik, A. (2005). Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India. *Journal of Hydrology*, 312(1–4), 14-27.
- Sponza, D., & Karaoğlu, N. (2002). Environmental geochemistry and pollution studies of Aliaga metal industry district. *Environment International*, 27(7), 541-553.

- Sultan, K., Shazili, N. A., & Peiffer, S. (2011). Distribution of Pb, As, Cd, Sn and Hg in soil, sediment and surface water of the tropical river watershed, Terengganu (Malaysia). *Journal of Hydro-environment Research*, 5(3), 169-176.
- Sutherland, R. A. (2010). BCR®-701: A review of 10-years of sequential extraction analyses. *Analytica Chimica Acta*, 680(1–2), 10-20.
- Tabari S., Saravi S. S. S., Bandany G. A., Dehghan A., & Shokrzadeh M. (2010). Heavy metals (Zn, Pb, Cd and Cr) in fish, water and sediments sampled from Southern Caspian Sea, Iran. *Toxicology and Industrial Health*, 26(10), 649-656.
- Tandon, H. L. S. (2005). *Methods of analysis of soils, plants, waters, fertilisers & organic manures*: Fertiliser Development and Consultation Organisation.
- Tessier, A., Campbell, P. G., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7), 844-851.
- Tsai, L., Yu, K., & Ho, S. (2007). Cadmium distribution in sediment profiles of the six main rivers in southern Taiwan. *Journal of Hazardous Materials*, 148(3), 630-639.
- Tsai, L., Yu, K. C., Huang, J. S., & Ho, S. T. (2002). Distribution of heavy metals in contaminated river sediments. *Environmental Science Health Part A Toxic/Hazard*, 37(8), 1421-1439.
- UmgeniWater. (2013). How people affect our water quality. *Water for growth and sustainable development* Retrieved 17/10/2013, from [http://www.umgeni.co.za/water\\_education/wpwq.asp](http://www.umgeni.co.za/water_education/wpwq.asp)
- USEPA. (1994a). Determination of trace elements in waters and wastes by Inductively Coupled Plasma-Mass Spectrometry *Method 200.8*. United States
- USEPA. (1994b). Sample preparation procedure for spectrochemical determination of total recoverable elements *Method 200.2*. Ohio, USA
- USEPA. (1996). The metal translator: Guidance for calculating a total recoverable permit limit from a dissolved criterion
- USEPA. (2001). Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses: technical manual. Washington: United States Environmental Protection Agency
- USEPA. (2007a). Microwave assisted acid digestion of sediments, sludges, soils and oils *Method 3051A*. USA: Environmental Protection Agency
- USEPA. (2007b). Microwave assisted acid digestion of sediments, sludges, soils and oils *Method 3051A*. United States
- USEPA. (2012a). Analytical control facility. In U. S. F. a. w. service (Ed.), *Division of environmental quality*. Shepherstown, West Virginia: U.S. Fish and wildlife

- USEPA. (2012b). Water: contaminated sediments *Technical resources-guidelines*. <http://water.epa.gov/polwaste/sediments/cs/guidelines.cfm>
- Van Herreweghe, S., Swennen, R., Vandecasteele, C., & Cappuyns, V. (2003). Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. *Environmental Pollution*, 122(3), 323-342.
- Wepener, V., van Dyk, C., Bervoets, L., O'Brien, G., Covaci, A., & Cloete, Y. (2011). An assessment of the influence of multiple stressors on the Vaal River, South Africa. *Physics and Chemistry of the Earth, Parts A/B/C*, 36(14), 949-962.
- WRC. (2002). State of rivers report uMngeni River and neighbouring rivers and streams (W. A. a. Forestry & E. A. a. Tourism, Trans.). In U. Water, e. Municipality, C. Environmentek & U. o. Natal (Eds.), *Product of the river health*. Pretoria, South Africa
- Wright, P., & Mason, C. F. (1999). Spatial and seasonal variation in heavy metals in the sediments and biota of two adjacent estuaries, the Orwell and the Stour, in eastern England. *Science of the total environment*, 226(2-3), 139-156.
- Wuana, R. A., & Okieimen, F. E. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecology*, 2011, 20.
- Ye, F., Huang, X., Zhang, D., Tian, L., & Zeng, Y. (2012). Distribution of heavy metals in sediments of the Pearl River Estuary, Southern China: Implications for sources and historical changes. *Environmental Sciences*, 24(4), 579-588.
- Zeisler, R. (2004). New NIST sediment SRM for inorganic analysis. *Analytical and bioanalytical chemistry*, 378(5), 1277-1283.
- Zhang, W., Yu, L., Lu, M., Hutchinson, S. M., & Feng, H. (2007). Magnetic approach to normalizing heavy metal concentrations for particle size effects in intertidal sediments in the Yangtze Estuary, China. *Environmental Pollution*, 147(1), 238-244.
- Zimmerman, A. J., & Weindorf, D. C. (2010). Extraction: A review of procedures. *Analytical Chemistry*, 20.

## CHAPTER 6: CONCLUSION

---

The results show that the Umgeni River is in poor health as all metals investigated exceeded the set standards by SABS and EPA SQAG limits except Cd. Higher concentrations of Cd, Cr, Cu, Pb and Zn accumulated in sediments than in water. The seasonal variability in the water data showed high concentrations of metals in winter. The water data was compared to SABS guideline value and all metals except Cd exceeded the limit. Metal concentrations in sediments also varied seasonally. In sediments there was a significant difference between the wet (Spring and Summer) and dry (Autumn and Winter) seasons, with most metals present in high concentration during the wet season.

The spatial distribution of metals along the river showed a marked increase in concentrations in sites E to G (industrial area). These sites showed the highest concentration of Cd, Cr, Cu, Pb and Zn. The metal pollutant levels suggest that high urbanisation and industrialisation may be the cause of pollution along the Umgeni River. Types of industries along Umgeni River which may be potential sources of these metals are electrical, plastic, paint, furniture manufactures, chemical industries, building materials, cleaning and steel industries.

Physico-chemical parameters which affect the behaviour of metal pollutants in the environment were analysed. Conductivity, pH, salinity, redox, temperature, total dissolved solids and dissolved oxygen were measured. These parameters were in the optimum levels but differed per season. The BCR sequential extraction was used to show metal partitioning in sediment and was used to measure bioavailability. Cd and Cr were mostly unavailable (residual fraction). Other metals; Cu, Pb and Zn were bioavailable. This indicated that reducing agents will avail the toxic Cu and can lead to health problems including retarded growth and breathless palpitations.

From the bioavailable and partitioning data, most metals were present in the residual fraction and unavailable. However, Zn and Pb were present in exchangeable form *i.e.* bioavailable at levels which exceed those stipulated by EPA for total metals thus indicating that these pollutants will adversely affect the environment.



Generally, the partitioning data shows that changes to the environment (*e.g.* changes in pH or redox) could lead to the release of metals held by Fe/Mn oxyhydroxides or sulphides. This would result in an increase of these metals in a bioavailable form which would have an adverse impact on the environment.

High metal concentrations may negatively impact the survival, health and reproduction of living organisms hence remediation processes should be investigated for the Umgeni River. There needs to be a much stringent monitoring of both water and sediment at regular intervals to ensure that pollutants are not continually released. This may include removing heavy metals in waste water from industries and treatment plants before deposition into the river to avoid further decline of the Umgeni River quality.

## **FUTURE WORK**

This study has assessed the quality of the Umgeni River in terms of heavy metals. However, there are some suggestions for future work. As explained in Chapter 2 the Umgeni River starts from beyond the Midmar Dam to the Indian Ocean. These locations (before Inanda Dam) have three other dams which are Midmar Dam, Albert Falls and Nagle Dam. In these areas the river passes along informal settlements and agricultural activities. Therefore, the quality of the river basin before Inanda dam would need a similar study by extending the sampling sites to assess river quality for the whole of the river catchment area. In addition, it has been shown that there is an increase in concentration of metals along the industrial sites, which suggest that industries along the Umgeni River may be adding to the pollution of the river. The study can investigate techniques used for remediation/treating the contaminated water from industrial effluents, monitoring industrial effluents, and identifying illegal dump sites. There should also be investigation of the metals in biological organism (plant and marine) within the water system.

## APPENDICES

### Appendix 1: Average total concentrations for water data

Site code	Seasons	Autumn	Winter	Spring	Summer
A	Cd	<DL	0.0060	0.0027	0.0020
	Cr	<DL	0.0650	<DL	0.0003
	Cu	<DL	<DL	0.0087	0.0097
	Mn	0.0327	0.0190	0.1257	0.1777
	Pb	0.001	0.0080	0.0033	0.0083
	Zn	<DL	0.0060	0.0237	0.0157
B	Cd	0.0020	0.0053	0.0020	0.0020
	Cr	<DL	0.0827	0.0057	<DL
	Cu	0.0090	<DL	<DL	0.0020
	Mn	0.0930	0.0543	0.0380	0.1996
	Pb	<DL	0.0083	0.0010	0.0023
	Zn	0.0290	0.0337	0.0173	0.0027
C	Cd	<DL	0.006	0.0013	0.0013
	Cr	<DL	0.058	0.0040	<DL
	Cu	0.0007	<DL	0.0010	0.0010
	Mn	0.0867	0.456	0.0537	0.0346
	Pb	0.0003	0.010	0.0003	0.0010
	Zn	0.0123	0.038	0.0177	<DL
D	Cd	0.002	0.0053	0.0010	0.0017
	Cr	0.001	0.0653	0.0040	<DL
	Cu	0.0050	0.0023	0.0067	0.0010
	Mn	0.0830	0.0407	0.0710	0.0463
	Pb	0.0010	0.0093	0.0003	0.0007
	Zn	0.0130	0.0453	0.0290	0.0067
E	Cd	0.002	0.0050	0.0010	0.0017
	Cr	0.002	0.0520	0.0033	<DL
	Cu	0.0120	0.0043	0.0013	0.0013
	Mn	0.1800	0.0963	0.0766	0.0866
	Pb	0.0050	0.0087	0.0030	0.0017
	Zn	0.0060	0.0650	0.0277	0.0077
F	Cd	0.0010	0.0050	0.0020	0.0013
	Cr	0.0020	0.0480	0.0043	0.0033
	Cu	0.0050	0.0013	0.0307	0.0110
	Mn	0.1880	0.1107	0.1517	0.1033
	Pb	<DL	0.0060	0.0063	0.0017
	Zn	0.0150	0.0147	0.1953	0.0596
G	Cd	0.0020	0.0040	0.0020	0.0017
	Cr	0.0030	0.0580	0.0010	0.0003
	Cu	0.0070	0.0040	0.0053	0.0030
	Mn	0.2320	0.0343	0.1030	0.1030
	Pb	0.0030	0.0040	0.0030	0.0020
	Zn	0.0170	0.0230	0.3130	0.0103
H	Cd	0.0020	0.0043	0.0017	0.0020
	Cr	0.0030	0.0493	0.0013	0.0030
	Cu	0.0080	<DL	0.0063	0.0110
	Mn	0.2330	0.2393	0.1050	0.1663
	Pb	0.0040	0.0090	0.0056	0.0160
	Zn	0.0150	0.0200	0.0313	0.0290

<DL: Below Detection Limit

## Appendix 2: Average total concentrations for sediment data

Site code	Seasons	Autumn	Winter	Spring	Summer
A	Cd	1.32	0.23	197.39	133.84
	Pb	12.87	12.13	536.75	601.70
	Cu	13.47	16.13	84.72	106.02
	Cr	57.75	51.75	67.07	94.16
	Zn	62.25	81.95	104.05	89.75
	Mn	537.39	632.76	80.83	89.87
B	Cd	0.07	1.98	126.00	166.40
	Pb	19.62	20.88	430.79	205.60
	Cu	22.87	27.11	82.54	118.01
	Cr	72.46	83.50	54.04	48.93
	Zn	109.95	95.75	61.94	60.86
	Mn	5012.82	9822.15	46.70	62.45
C	Cd	1.25	5.23	164.67	117.34
	Pb	21.07	27.07	528.37	525.83
	Cu	33.03	11.86	62.22	114.54
	Cr	86.27	135.06	45.92	28.61
	Zn	80.57	73.47	82.90	29.51
	Mn	1040.02	2189.52	45.50	56.53
D	Cd	0.18	<DL	250.79	199.22
	Pb	15.28	22.51	304.21	95.39
	Cu	21.00	24.92	165.71	105.81
	Cr	57.39	78.95	78.14	88.50
	Zn	84.41	77.96	80.43	92.41
	Mn	474.74	687.58	72.83	62.87
E	Cd	0.20	<DL	264.46	207.91
	Pb	55.04	28.60	225.54	256.21
	Cu	37.55	21.75	154.26	67.99
	Cr	81.94	60.86	91.99	63.62
	Zn	176.50	103.89	96.90	81.31
	Mn	499.54	497.57	81.11	64.18
F	Cd	0.73	0.99	205.18	151.81
	Pb	136.13	53.82	186.02	144.73
	Cu	133.49	81.21	128.53	119.99
	Cr	126.35	111.94	98.14	102.86
	Zn	602.12	246.20	57.98	103.25
	Mn	737.18	1052.19	48.60	85.70
G	Cd	0.13	<DL	207.90	351.36
	Pb	65.88	28.81	211.16	266.26
	Cu	80.88	132.99	123.95	123.01
	Cr	127.45	55.08	82.71	116.10
	Zn	420.65	469.92	59.20	146.33
	Mn	649.32	284.25	54.80	117.70
H	Cd	<DL	<DL	211.95	156.10
	Pb	51.15	32.98	174.83	212.95
	Cu	65.97	118.92	164.00	168.47
	Cr	98.83	52.17	105.36	122.31
	Zn	262.63	339.37	81.24	131.85
	Mn	472.56	389.46	82.09	107.57

&lt;DL: Below Detection Limit

## Appendix 3: ANOVA data for Cd, Cr, Cu, Pb and Zn

Multiple Comparisons									
Dependent Variable	(I) Season	(J) Season	Sig. (Cu)	Sig. (Zn)	Sig. (Cd)	Sig. (Pb)	Sig. (Cr)	95% Confidence Interval	
								Lower Bound	Upper Bound
Site A	Autumn	Winter	.999	.764	1.000	1.000	.992	-63.06794	57.72799
		Spring	.022	.238	.027	.006	.971	-131.65398	-10.85805
		Summer	.005	.550	.141	.003	.390	-152.95403	-32.15810
	Winter	Autumn	.999	.764	1.000	1.000	.992	-57.72799	63.06794
		Spring	.027	.700	.026	.006	.891	-128.98401	-8.18808
		Summer	.006	.979	.137	.003	.277	-150.28406	-29.48813
	Spring	Autumn	.022	.238	.027	.006	.971	10.85805	131.65398
		Winter	.027	.700	.026	.006	.891	8.18808	128.98401
		Summer	.683	.890	.653	.932	.614	-81.69801	39.09791
	Summer	Autumn	.005	.550	.141	.003	.390	32.15810	152.95403
		Winter	.006	.979	.137	.003	.277	29.48813	150.28406
		Spring	.683	.890	.653	.932	.614	-39.09791	81.69801
Site B	Autumn	Winter	.987	.942	.999	1.000	.930	-93.19642	75.95947
		Spring	.152	.138	.000	.004	.755	-148.20951	20.94638
		Summer	.023	.291	.000	.172	.602	-183.67841	-14.52252
	Winter	Autumn	.987	.942	.999	1.000	.930	-75.95947	93.19642
		Spring	.237	.292	.000	.004	.432	-139.59104	29.56485
		Summer	.037	.551	.000	.175	.310	-175.05994	-5.90405
	Spring	Autumn	.152	.138	.000	.004	.755	-20.94638	148.20951
		Winter	.237	.292	.000	.004	.432	-29.56485	139.59104
		Summer	.564	.943	.116	.087	.992	-120.04685	49.10904
	Summer	Autumn	.023	.291	.000	.172	.602	14.52252	183.67841
		Winter	.037	.551	.000	.175	.310	5.90405	175.05994
		Spring	.564	.943	.116	.087	.992	-49.10904	120.04685



Multiple Comparisons									
Dependent Variable	(I) Season	(J) Season	Sig. (Cu)	Sig. (Zn)	Sig. (Cd)	Sig. (Pb)	Sig. (Cr)	95% Confidence Interval	
								Lower Bound	Upper Bound
Site E	Autumn	Winter	.977	.212	1.000	.957	.914	-107.07271	137.40471
			.060	.160	.099	.049	.989	-239.60839	4.86903
			.846	.083	.221	.022	.941	-153.33382	91.14360
	Winter	Autumn	.977	.212	1.000	.957	.914	-137.40471	107.07271
			.034	.997	.096	.025	.778	-254.77439	-10.29697
			.637	.904	.215	.011	1.000	-168.49982	75.97760
	Spring	Autumn	.060	.160	.099	.049	.989	-4.86903	239.60839
			.034	.997	.096	.025	.778	10.29697	254.77439
			.187	.965	.935	.936	.820	-35.96414	208.51328
	Summer	Autumn	.846	.083	.221	.022	.941	-91.14360	153.33382
			.637	.904	.215	.011	1.000	-75.97760	168.49982
			.187	.965	.935	.936	.820	-208.51328	35.96414
Waste management	Autumn	Winter	.831	.001	1.000	.734	.900	-105.68571	181.66366
			1.000	.000	.061	.920	.564	-141.79544	145.55394
			.995	.000	.187	1.000	.690	-133.25107	154.09830
	Winter	Autumn	.831	.001	1.000	.734	.900	-181.66366	105.68571
			.850	.033	.062	.399	.910	-179.78441	107.56496
			.925	.109	.188	.675	.971	-171.24005	116.10933
	Spring	Autumn	1.000	.000	.061	.920	.564	-145.55394	141.79544
			.850	.033	.062	.399	.910	-107.56496	179.78441
			.997	.835	.853	.952	.996	-135.13032	152.21905
	Summer	Autumn	.995	.000	.187	1.000	.690	-154.09830	133.25107
			.925	.109	.188	.675	.971	-116.10933	171.24005
			.997	.835	.853	.952	.996	-152.21905	135.13032

Multiple Comparisons									
Dependent Variable	(I) Season	(J) Season	Sig. (Cu)	Sig. (Zn)	Sig. (Cd)	Sig. (Pb)	Sig. (Cr)	95% Confidence Interval	
								Lower Bound	Upper Bound
Site F	Autumn	Winter	.213	.049	1.000	.976	.934	-163.32218	31.63470
		Spring	.103	.469	.002	.280	.179	-179.26627	15.69061
		Summer	.807	.137	.000	.008	.097	-124.79358	70.16330
	Winter	Autumn	.213	.049	1.000	.976	.934	-31.63470	163.32218
		Spring	.951	.006	.002	.456	.079	-113.42253	81.53435
		Summer	.607	.002	.000	.013	.043	-58.94985	136.00703
	Spring	Autumn	.103	.469	.002	.280	.179	-15.69061	179.26627
		Winter	.951	.006	.002	.456	.079	-81.53435	113.42253
		Summer	.344	.772	.005	.110	.969	-43.00575	151.95113
	Summer	Autumn	.807	.137	.000	.008	.097	-70.16330	124.79358
		Winter	.607	.002	.000	.013	.043	-136.00703	58.94985
		Spring	.344	.772	.005	.110	.969	-151.95113	43.00575
Site G	Autumn	Winter	.178	.192	1.000	.983	.032	-145.62802	24.03332
		Spring	.297	.000	.028	.526	.208	-135.36966	34.29168
		Summer	.311	.000	.001	.282	.943	-134.43455	35.22680
	Winter	Autumn	.178	.192	1.000	.983	.032	-24.03332	145.62802
		Spring	.979	.000	.027	.350	.562	-74.57230	95.08904
		Summer	.973	.000	.001	.175	.069	-73.63719	96.02415
	Spring	Autumn	.297	.000	.028	.526	.208	-34.29168	135.36966
		Winter	.979	.000	.027	.350	.562	-95.08904	74.57230
		Summer	1.000	.018	.134	.948	.416	-83.89556	85.76578
	Summer	Autumn	.311	.000	.001	.282	.943	-35.22680	134.43455
		Winter	.973	.000	.001	.175	.069	-96.02415	73.63719
		Spring	1.000	.018	.134	.948	.416	-85.76578	83.89556

Multiple Comparisons											
Dependent Variable	(I) Season		(J) Season		Sig. (Cu)	Sig. (Zn)	Sig. (Cd)	Sig. (Pb)	Sig. (Cr)	95% Confidence Interval	
										Lower Bound	Upper Bound
Site H		Autumn	Winter	.728	.030	1.000	.994	.097	-157.62667	79.92421	
			Spring	.186	.000	.037	.363	.980	-202.69938	34.85150	
			Summer	.158	.001	.130	.181	.547	-207.16990	30.38098	
		Winter	Autumn	.728	.030	1.000	.994	.097	-79.92421	157.62667	
			Spring	.635	.000	.035	.263	.057	-163.84815	73.70273	
			Summer	.568	.000	.123	.127	.014	-168.31867	69.23221	
		Spring	Autumn	.186	.000	.037	.363	.980	-34.85150	202.69938	
			Winter	.635	.000	.035	.263	.057	-73.70273	163.84815	
			Summer	.999	.164	.804	.947	.758	-123.24596	114.30492	
		Summer	Autumn	.158	.001	.130	.181	.547	-30.38098	207.16990	
			Winter	.568	.000	.123	.127	.014	-69.23221	168.31867	
			Spring	.999	.164	.804	.947	.758	-114.30492	123.24596	



## Appendix 4: Bioavailability data

<b>AUTUMN EXTRACTION</b>						
Site	Analyte	Carbonate	Fe/Mn oxide	Organic	Residual	Total
A	Cr	<DL	2.91	3.90	51.05	57.75
	Pb	0.21	5.48	0.13	7.05	12.87
	Cd	<DL	<DL	<DL	1.49	1.32
	Cu	<DL	3.69	0.55	10.42	13.47
	Zn	12.48	4.12	2.21	43.43	62.25
B	Cr	0.28	3.36	5.39	63.42	72.46
	Pb	0.75	5.82	0.89	12.16	19.62
	Cd	<DL	<DL	<DL	0.33	0.07
	Cu	3.25	3.36	9.25	7.01	22.87
	Zn	11.68	2.57	1.09	94.61	109.95
C	Cr	<DL	8.53	5.66	72.13	86.27
	Pb	0.37	10.61	0.20	9.89	21.07
	Cd	<DL	<DL	<DL	1.61	1.25
	Cu	<DL	5.23	0.58	27.83	33.03
	Zn	8.77	10.23	3.99	57.57	80.57
D	Cr	0.27	3.48	3.58	50.06	57.39
	Pb	0.77	5.92	0.58	8.00	15.28
	Cd	<DL	<DL	<DL	0.56	0.18
	Cu	4.99	4.57	6.53	4.91	21.00
	Zn	14.59	1.63	<DL	71.77	84.41
E	Cr	0.52	5.86	9.52	66.04	81.94
	Pb	3.55	36.26	2.09	13.14	55.04
	Cd	0.12	<DL	<DL	0.22	0.20
	Cu	6.50	7.54	9.72	13.78	37.55
	Zn	34.18	25.89	9.82	106.60	176.50
F	Cr	0.16	12.74	11.86	88.35	113.10
	Pb	0.29	23.07	0.76	10.44	34.56
	Cd	<DL	<DL	<DL	1.66	1.23
	Cu	<DL	8.98	1.88	38.76	48.66
	Zn	41.99	34.80	8.02	75.78	160.59
G	Cr	0.36	8.81	16.62	101.66	127.45
	Pb	0.87	39.42	2.98	22.61	65.88
	Cd	0.04	0.00	<DL	0.19	0.13
	Cu	7.19	5.12	27.09	41.48	80.88
	Zn	204.41	95.51	23.12	97.60	420.65

<b>AUTUMN EXTRACTION</b>						
<b>Site</b>	<b>Analyte</b>	<b>Carbonate</b>	<b>Fe/Mn oxide</b>	<b>Organic</b>	<b>Residual</b>	<b>Total</b>
H	Cr	0.68	5.63	10.03	82.48	98.83
	Pb	1.20	30.31	1.70	17.95	51.15
	Cd	0.00	<DL	<DL	0.20	<DL
	Cu	8.11	13.38	13.88	30.61	65.97
	Zn	123.20	35.66	4.69	99.07	262.63

<b>WINTER EXTRACTION</b>						
<b>Site</b>	<b>Analyte</b>	<b>Carbonate</b>	<b>Fe/Mn oxide</b>	<b>Organic</b>	<b>Residual</b>	<b>Total</b>
A	Cr	0.66	2.82	3.48	44.79	51.75
	Pb	0.93	7.27	0.53	3.41	12.13
	Cd	<DL	<DL	<DL	0.57	0.23
	Cu	3.94	3.63	3.82	4.74	16.13
	Zn	5.92	<DL	<DL	82.29	81.95
B	Cr	3.51	7.19	7.29	65.52	83.50
	Pb	1.80	10.54	1.10	7.44	20.88
	Cd	0.04	<DL	<DL	2.17	1.98
	Cu	8.34	3.71	9.08	5.97	27.11
	Zn	28.82	3.51	<DL	64.96	95.75
C	Cr	0.20	3.61	3.53	127.72	135.06
	Pb	0.79	6.91	0.25	19.12	27.07
	Cd	<DL	1.30	<DL	4.25	5.23
	Cu	2.71	4.48	4.03	0.65	11.86
	Zn	<DL	18.69	<DL	61.59	73.47
D	Cr	0.84	5.27	6.63	66.21	78.95
	Pb	0.84	8.78	0.65	12.24	22.51
	Cd	<DL	<DL	<DL	0.11	<DL
	Cu	3.79	2.75	5.19	13.19	24.92
	Zn	8.54	1.08	<DL	70.14	77.96
E	Cr	0.31	3.41	4.55	52.59	60.86
	Pb	2.17	13.83	1.74	10.86	28.60
	Cd	0.00	<DL	<DL	<DL	<DL
	Cu	5.69	1.82	7.84	6.39	21.75
	Zn	31.30	6.78	2.76	63.05	103.89

<b>WINTER EXTRACTION</b>						
<b>Site</b>	<b>Analyte</b>	<b>Carbonate</b>	<b>Fe/Mn oxide</b>	<b>Organic</b>	<b>Residual</b>	<b>Total</b>
F	Cr	0.36	6.97	15.48	101.72	124.53
	Pb	0.48	10.26	1.25	67.28	79.27
	Cd	<DL	<DL	<DL	0.81	0.46
	Cu	2.85	6.65	8.16	96.22	113.88
	Zn	22.48	27.41	6.96	259.35	316.20
G	Cr	1.27	8.68	15.63	29.49	55.08
	Pb	1.35	24.20	2.99	0.27	28.81
	Cd	0.12	<DL	<DL	<DL	<DL
	Cu	9.42	13.62	42.55	67.40	132.99
	Zn	302.39	60.09	20.17	87.26	469.92
H	Cr	0.88	7.75	15.28	28.26	52.17
	Pb	1.60	26.88	2.35	2.15	32.98
	Cd	0.04	<DL	<DL	<DL	<DL
	Cu	11.54	16.62	26.46	64.29	118.92
	Zn	150.07	44.62	12.98	131.70	339.37

<b>SPRING EXTRACTION</b>						
<b>Site</b>	<b>Analyte</b>	<b>Carbonate</b>	<b>Fe/Mn oxide</b>	<b>Organic</b>	<b>Residual</b>	<b>Total</b>
A	Cr	2.63	8.40	12.14	43.90	67.07
	Pb	3.03	10.75	3.73	519.25	536.75
	Cd	2.23	2.19	2.74	190.24	197.39
	Cu	9.32	14.13	14.23	47.04	84.72
	Zn	5.45	7.52	8.86	82.21	104.05
B	Cr	2.79	8.34	9.53	33.37	54.04
	Pb	3.27	9.06	3.24	415.21	430.79
	Cd	2.28	2.20	2.74	118.78	126.00
	Cu	9.70	11.90	11.78	49.17	82.54
	Zn	5.95	5.55	7.29	43.16	61.94
C	Cr	2.80	8.20	9.76	25.15	45.92
	Pb	3.08	9.58	3.06	512.66	528.37
	Cd	2.21	2.17	2.71	157.58	164.67
	Cu	9.58	12.78	11.93	27.93	62.22
	Zn	8.76	6.90	5.82	61.42	82.90
D	Cr	2.65	10.46	15.10	49.93	78.14
	Pb	2.93	15.41	4.90	280.96	304.21
	Cd	2.26	2.18	2.67	243.68	250.79
	Cu	8.91	14.06	20.25	122.48	165.71

	Zn	22.54	15.29	12.82	29.78	80.43
E	Cr	2.60	9.93	13.05	66.42	91.99
	Pb	4.41	34.19	5.12	181.82	225.54
	Cd	2.36	2.21	2.76	257.14	264.46
	Cu	12.01	22.17	16.79	103.29	154.26
	Zn	46.83	32.73	16.30	1.05	96.90
F	Cr	2.36	16.99	23.89	24.96	68.20
	Pb	2.48	16.03	4.95	225.40	248.86
	Cd	2.24	2.20	2.70	95.39	102.53
	Cu	8.28	20.19	20.54	81.44	130.45
	Zn	9.48	19.07	13.19	45.12	86.87
G	Cr	2.80	16.06	30.17	33.67	82.71
	Pb	3.40	51.19	12.49	144.09	211.16
	Cd	2.40	2.28	2.75	200.48	207.90
	Cu	12.47	31.97	45.35	34.16	123.95
	Zn	3.48	37.44	14.44	3.85	59.20
H	Cr	2.76	15.62	24.85	62.12	105.36
	Pb	3.43	51.52	9.32	110.56	174.83
	Cd	2.37	2.25	2.76	204.57	211.95
	Cu	13.37	31.20	35.65	83.77	164.00
	Zn	22.84	33.25	23.62	1.53	81.24

SUMMER EXTRACTION						
Site	Analyte	Carbonate	Fe/Mn oxide	Organic	Residual	Total
A	Cr	2.38	7.45	7.39	76.94	94.16
	Pb	2.62	11.22	3.37	584.49	601.70
	Cd	2.22	2.18	2.78	126.66	133.84
	Cu	11.58	13.05	12.69	68.71	106.02
	Zn	9.67	9.48	4.31	66.28	89.75
B	Cr	2.39	13.16	8.87	24.51	48.93
	Pb	3.35	37.36	4.04	160.85	205.60
	Cd	2.23	2.15	2.74	159.27	166.40
	Cu	8.93	15.23	14.30	79.54	118.01
	Zn	16.07	14.59	8.82	21.38	60.86
C	Cr	2.28	16.63	9.65	0.06	28.61
	Pb	2.44	20.39	3.90	499.10	525.83
	Cd	2.20	2.20	2.75	110.19	117.34
	Cu	7.92	19.47	12.59	74.56	114.54
	Zn	8.12	15.47	4.60	1.32	29.51

<b>SUMMER EXTRACTION</b>						
<b>Site</b>	<b>Analyte</b>	<b>Carbonate</b>	<b>Fe/Mn oxide</b>	<b>Organic</b>	<b>Residual</b>	<b>Total</b>
D	Cr	2.44	11.56	9.00	65.50	88.50
	Pb	2.84	14.56	3.45	74.54	95.39
	Cd	2.24	2.20	2.75	192.03	199.22
	Cu	9.00	15.64	12.60	68.57	105.81
	Zn	12.96	11.92	4.30	63.23	92.41
E	Cr	2.74	17.27	16.23	27.38	63.62
	Pb	2.86	22.83	3.47	227.05	256.21
	Cd	2.22	2.18	2.73	200.78	207.91
	Cu	9.13	20.64	13.00	25.21	67.99
	Zn	9.77	13.62	6.05	51.88	81.31
F	Cr	2.38	21.40	16.18	19.56	59.53
	Pb	2.50	27.44	3.87	504.51	538.32
	Cd	2.22	2.22	2.73	184.40	191.57
	Cu	8.38	26.05	13.70	27.85	75.98
	Zn	4.25	6.55	13.45	15.87	40.12
G	Cr	2.69	12.16	9.21	92.04	116.10
	Pb	3.60	25.11	4.31	233.24	266.26
	Cd	2.26	2.18	2.72	344.20	351.36
	Cu	12.16	21.31	14.70	74.85	123.01
	Zn	88.32	27.80	8.17	22.04	146.33
H	Cr	2.81	15.98	12.86	90.66	122.31
	Pb	3.44	43.52	5.44	160.55	212.95
	Cd	2.37	2.22	2.77	148.74	156.10
	Cu	12.30	38.62	19.39	98.16	168.47
	Zn	56.62	55.94	15.48	3.81	131.85

## Appendix 5: Physico- chemical parameters

Site code	Seasons	pH	Temperature/ °C	Eh/ mV	TDS/ mg L <sup>-1</sup>	DO/ mg L <sup>-1</sup>	EC/ µS cm <sup>-1</sup>	Salinity/ mg L <sup>-1</sup>
A	Winter	6.02	14.8	80	440	11.2	860	0.2
	Autumn	6.23	24.5	NM	17	NM	30.1	0
	Spring	6.00	19.5	105	3.2	6.1	57.6	0
	Summer	6.04	24.2	35	18	6	31.2	0
B	Winter	6.79	15.3	49	395	10.5	772	0.1
	Autumn	5.91	24.1	71	125	8	245	0
	Spring	7.42	21.0	70	29	9.8	52.1	0
	Summer	6.84	26	74	26	6.6	45.4	0
C	Winter	6.47	16.4	73	396	9.6	774	0.1
	Autumn	7.36	22.5	NM	72	NM	124.6	0
	Spring	8.00	21.2	69	29	9	51.5	0
	Summer	6.6	25.6	130	26	6.75	45.4	0
D	Winter	6.38	16.3	79	400	10.7	702	0.1
	Autumn	6.54	24.8	23	126	8	247	0
	Spring	7.33	20.6	35	29	6.5	50.9	0
	Summer	6.77	25.7	115	26	6.9	48.6	0
E	Winter	6.38	15	158	48	2	1000	0
	Autumn	6.53	22.5	55	137	4.9	253	0
	Spring	7.15	20.4	72	30	7.7	51.9	0
	Summer	6.59	25.3	97	28	5.8	47	0
F	Winter	7.1	16.1	55	562	2.9	1269	0.3
	Autumn	6.86	27.1	61	374	2.5	782	0.1
	Spring	7.14	20.0	92	69	7.7	120.7	0
	Summer	7.38	26.2	60	44	6.1	75.8	0
G	Winter	7.25	17.3	59	1594	3.7	5690	1.5
	Autumn	6.9	22.6	99	243	4.8	459	0
	Spring	6.48	20.7	13	43.0	7.5	74.9	0
	Summer	7.47	26.3	58	88	6.6	151.7	0
H	Winter	6.6	15.4	44	820	1.2	1440	0.6
	Autumn	6.7	23.5	85	764	6.3	1459	0.6
	Spring	7.45	20.6	80	48	8.1	83.5	0
	Summer	7.24	24.4	8	69	6.6	118.5	0

NM: Not measured

## Appendix 6: Anion data

Site code	Seasons	Autumn	Winter	Spring	Summer
A	Chloride	33.052	32.134	21.8908	35.91
	Nitrate	20.165	15.546	4.769	10.96
	Sulfate	19.354	21.237	12.8292	13.42
B	Chloride	3.47	28.36	20.57	56.64
	Nitrate	12.15	10.64	1.22	12.40
	Sulfate	15.27	17.33	10.22	31.71
C	Chloride	26.22	30.54	18.94	51.38
	Nitrate	16.27	0.92	0.81	7.93
	Sulfate	10.98	11.84	9.72	27.25
D	Chloride	31.78	30.99	19.13	55.44
	Nitrate	18.55	2.16	1.15	13.46
	Sulfate	17.46	18.26	9.07	26.36
E	Chloride	92.36	83.18	17.85	58.14
	Nitrate	5.21	6.16	1.15	13.90
	Sulfate	17.99	19.91	9.72	29.49
F	Chloride	53.26	62.99	49.63	166.39
	Nitrate	24.71	8.53	0.34	68.06
	Sulfate	33.27	34.97	22.62	73.34
G	Chloride	71.21	1304.61	38.28	111.26
	Nitrate	30.26	1.44	2.60	18.29
	Sulfate	105.36	91.90	17.38	40.61
H	Chloride	189.71	1543.4	4.7553	296.52
	Nitrate	19.64	177.5	0.2508	8.64
	Sulfate	158.40	555.8	1.7108	63.81