

ASSESSING THE DISTRIBUTION OF SEDIMENTARY HEAVY METALS IN THE MSUNDUZI RIVER CATCHMENT, KWAZULU- NATAL, SOUTH AFRICA

by

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MSc

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NOTE: This thesis has been prepared according to Format 3 as outlined in the guidelines from the College of Agriculture, Engineering and Science which states:

This is a thesis in which the chapters are written as a set of discrete research papers, with an Overall Introduction and a Final Conclusion. These research papers would not be published yet. The references are reformatted to a uniform standard.

As the candidate's supervisors, we have approved this thesis for submission.

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ABSTRACT

Heavy metal pollution of freshwater environments is a global and local crisis due to the toxic nature of metals. Elevated concentrations of heavy metals in sediments, in comparison to sediment quality guidelines (SQGs), are an indication of anthropogenic input into the environment. Concentrations of cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) were investigated in the water and sediments of Msunduzi River and two of its tributaries, the Bayne's Spruit and Slangspruit, in KwaZulu-Natal, South Africa. Macro-elements, aluminium (Al), iron (Fe) and manganese (Mn) were also investigated and compared to the distribution and partitioning pattern of the trace metal concentrations. Total metal concentrations in the water samples were below the detection limit of the Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) for most metals. In surface sediments, total metal concentrations were >Effects Range-Low (ERL) of the SQG. The Community Bureau of Reference (BCR) sequential extraction protocol was used to determine speciation of metals in the sediments and implications for potential bioavailability and overall metal toxicity. Results indicated that potentially mobile sediment fraction concentrations were >ERL for most of the metals. Fe-Mn oxyhydroxides, organic matter content and redox potential had an effect on the geochemical partitioning and possible remobilisation or precipitation of the metals in all three rivers. Negative redox values were indicative of reducing conditions that remobilised metals from the sediments. In the sediment core, the trace metals had the same deposition pattern and were correlated to organic matter content at depth. Normalisation with Al, at 95% confidence interval indicated that the sediment in the Msunduzi River Catchment is enriched with anthropogenic heavy metal input. In terms of particle size distribution in the sediment core, the sediment was mainly made up of fine sediment ($\leq 500 \mu\text{m}$). The sediment is a potential source of long-term heavy metal pollution in the catchment.

PREFACE

The experimental work described in this thesis was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, Durban, from February 2012 to January 2015, under the supervision of Dr J. Finch and Dr L. Pillay.

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.

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DECLARATION 1

Plagiarism

I, Mendy Shozi, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
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DECLARATION 2

Publications and conference contributions

DETAILS OF CONTRIBUTION TO PUBLICATIONS that form part and/or include research presented in this thesis (include publications in preparation, submitted, *in press* and published and give details of the contributions of each author to the experimental work and writing of each publication).

Conference contributions

1.

Poster presentation, *Assessing the distribution of sedimentary heavy metals in the Msunduzi River Catchment, KwaZulu-Natal, South Africa*, College of Agriculture, Engineering and Science Research Day, Howard College, Durban, South Africa, 2013

2.

Poster presentation, *Assessing the distribution of sedimentary heavy metals in the Msunduzi River Catchment, KwaZulu-Natal, South Africa*, 9th Biennial SSAG Conference, Bloemfontein, South Africa, 2013

3.

Oral presentation, *Assessing the distribution of sedimentary heavy metals in the Msunduzi River Catchment, KwaZulu-Natal, South Africa*, 10th Biennial SSAG Conference, East London, South Africa, 2014

4.

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LIST OF ABBREVIATIONS AND UNITS

Abbreviations

Al	Aluminium
AMS	Accelerator mass spectrometry
ANOVA	Analysis of variance
As	Arsenic
Ba	Barium
BCR	Community of Bureau of Reference
Cd	Cadmium
CI	Confidence Interval
Co	Cobalt
Cr	Chromium
CRM	Certificate Reference Material
Cu	Copper
DWAF	Department of Water Affairs and Forestry
ERL	Effects range-low
ERM	Effects medium-range
Fe	Iron
HCl	Hydrogen chloride
Hg	Mercury
HNO ₃	Nitric acid
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
Li	Lithium
LOI	Loss on Ignition
Mg	Magnesium
Mn	Manganese
Na	Sodium
Ni	Nickel
NOAA	National Oceanic and Atmospheric Administration
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead

PSD	Particle Size Distribution
Redox	Reduction-oxidation
RHP	River Health Programme
SEP	Sequential Extraction Procedure
Si	Silicon
SQG	Sediment Quality Guidelines
V	Vanadium
Zn	Zinc

Units

°C	Degrees Celsius
cm	Centimetre
g.cm ⁻³	Grams per cubic centimetre
km	Kilometres
km ²	Square kilometres
m	Metres
mg.kg ⁻¹	Milligrams per kilogram
mol.L ⁻¹	Moles per litre
ppm	Parts per million
µg.L ⁻¹	Micrograms per Litre
µm	Micrometres
µS.cm ⁻¹	Micro Siemens per centimetre

1 INTRODUCTION

Heavy metal¹ pollution is one of the major problems facing freshwater systems worldwide. Heavy metals do not naturally bio-degrade, thus they remain one of the most persistent environmental pollutants associated with anthropogenic activities(Callender, 2003; Osman and Kloas, 2010; Sekabira *et al.*, 2010; Bednarova *et al.*, 2013).In the past, water sample analysis was the main technique used to assess the level of heavy metal pollution on the receiving environment(Fangueiro *et al.*, 2002; Dalvie *et al.*, 2003; Bosman and Kidd, 2009; Nel *et al.*, 2013). However, water analysis results may be inconclusive due to fluctuations in dissolved heavy metals in the water column within short time intervals. In addition, heavy metal concentrations found in water are usually very low, resulting in analytical difficulties (Förstner and Wittmann, 1979; Förstner, 1980; Burton, 1991; Binning and Baird, 2001; Botes and van Staden, 2005). Sediment quality, as a method to measure freshwater quality, has been widely studied on a local and global scale (Burton, 1991; Biney *et al.*, 1994; Thomas and William, 2003; Aprile and Bouvy, 2008). Within freshwater systems, bottom sediments are regarded as heavy metal sinks due to the densities and chemical properties of metals. Long-term partitioning within the sediments make them more useful for measuring heavy metal pollution than water analysis (Burton, 2002; Ayas *et al.*, 2007; Chen *et al.*, 2007; Osman and Kloas, 2010; Qiao *et al.*, 2013; Shanbehzadeh *et al.*, 2014). However, heavy metals are naturally present in the environment, thus distinguishing between natural and enriched concentrations is important (Callender, 2003).

The distinction between natural and enriched heavy metals is achieved by comparing measured concentrations to background values in a region. Background levels are determined by measuring the vertical distribution or historical deposition of heavy metals in the sediments on the assumption that the natural levels can be found at certain depths (Chapman *et al.*, 1999; Grosbois *et al.*, 2006; Meybeck *et al.*, 2007;

¹ The term ‘**heavy metal**’ will be used to refer to a group of stable elemental metals and/or metalloids with an atomic density greater than 6 g.cm⁻³ (aluminium is the exception in this research). These are often classified as Potential Toxic Elements (PTEs) (Callender, 2003).

Birch and Olmos, 2008; Bednarova *et al.*, 2013). The low solubility of heavy metals, coupled with reduced flow rates, causes materials suspended in the water column to settle and become incorporated in bottom sediments, thus forming a vertical profile and broad history of heavy metal pollution. Even without utilising dating techniques, vertical sediment profiles assist in portraying the historical accumulation of heavy metals (Valette-Silver, 1993; Aleksander-Kwaterczak and Prosowicz, 2007; Cantwell *et al.*, 2007; Karbassi *et al.*, 2008; Harikumar *et al.*, 2009; Zhang *et al.*, 2013). To guarantee reliable data, the cored material must ideally be undisturbed and fine-grained with a relatively rapid sedimentation rate (Förstner and Salomons, 1980; Valette-Silver, 1993; Li *et al.*, 2001). Once background concentrations have been determined, it is easier to determine natural metal concentrations and concentrations from land use activities in the catchment.

The effects of land use practices put a strain on river catchments, therefore, monitoring and measuring metal pollutant levels in sediments is vital to inform freshwater management decisions (Singh *et al.*, 2005; Sekabira *et al.*, 2010; Akpor and Muchie, 2011; Bednarova *et al.*, 2013; Songca *et al.*, 2013; Olaniran *et al.*, 2014). Land uses impacting freshwater environments release different forms of metal compounds into river water and this is when the metals become associated with the bottom sediments (Binning and Baird, 2001; Bednarova *et al.*, 2013). Early studies on heavy metals in sediments focused on rapid assessments of overall heavy metals in freshwater environments. Rapid assessments only determine the exchangeable forms and total concentrations of heavy metals in sediments (Förstner and Wittmann, 1979; John and Leventhal, 1995; Matusiewicz, 2003; Okoro and Fatoki, 2012). To fully understand the role of sediments as sources of heavy metal pollution in freshwater systems, their geochemical partitioning within the sediment fractions should also be taken into account (Tessier *et al.*, 1979; Jain, 2004). The forms in which metals are found bound in sediment fractions determines the potential mobility and bioavailability of the metal, should it remobilise into the overlying water column (John and Leventhal, 1995; Kartal *et al.*, 2006). The remobilisation of metals is controlled by physico-chemical parameters such as pH, reduction and oxidation (redox) potential and organic matter content (Gambrell *et al.*, 1991; Calmano *et al.*, 1993).

Several baseline studies on total heavy metal accumulation, in freshwater sediments and water column, have been conducted in South Africa (Greichus *et al.*, 1977; Watling, 1981; Watling and Watling, 1983; Watling *et al.*, 1985; Roux *et al.*, 1994; Allanson and Read, 1995). In KwaZulu-Natal, where the study area, the Msunduzi River Catchment is located, heavy metal research on the total metal content in freshwater systems has been investigated (Wepener and Vermeulen, 2005; Malherbe *et al.*, 2010; Papu-Zamxaka *et al.*, 2010; Mthembu *et al.*, 2012; Sukdeo *et al.*, 2012; Olaniran *et al.*, 2014). Msunduzi River is a tributary of the Umgeni River (figure 1.1). There have been a variety of water management research conducted on the Msunduzi River Catchment, Pietermaritzburg (Bartholomew and Sivparsand, 2013; Gemmell and Schmidt, 2013). However, there has been no comprehensive heavy metal research conducted on the catchment.

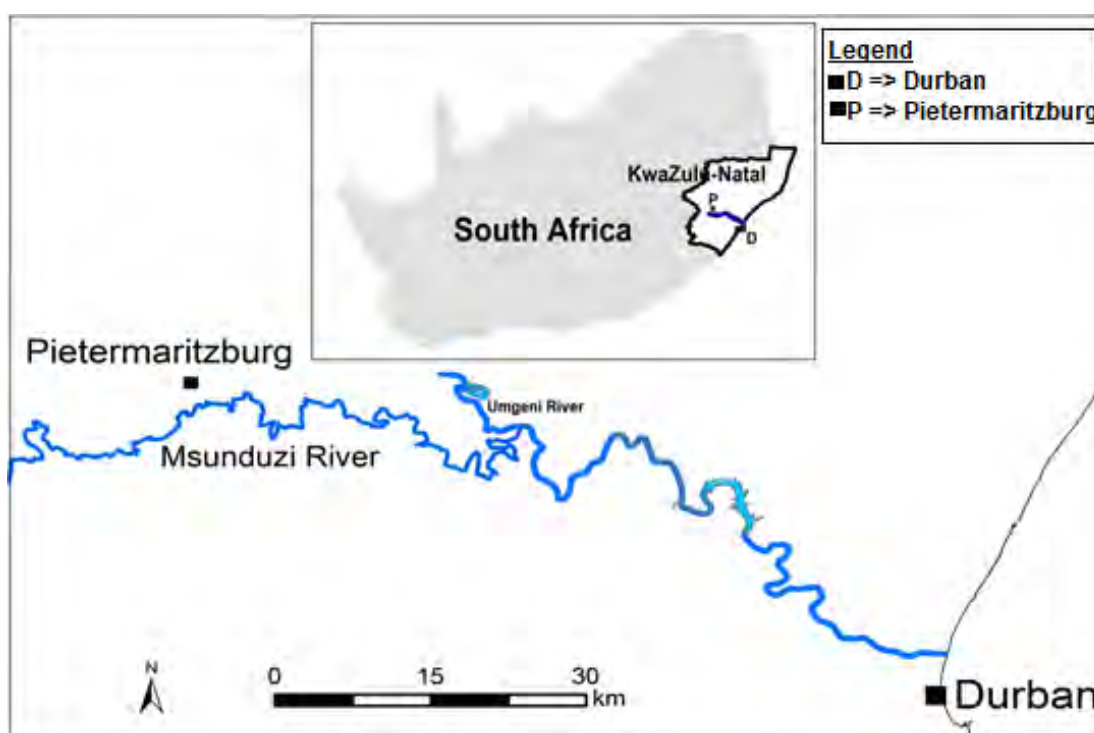


Figure 1.1: Overview of the Msunduzi River Catchment in KwaZulu-Natal, South Africa

There have been studies conducted on the water quality, in terms of microbiological contamination and on water management in the Msunduzi River Catchment (Rivers-

Moore and Hay, 1998; Salter and De Vos, 2002; Neysmith and Dent, 2010; Gemmell and Schmidt, 2013). However, there have been no comprehensive studies conducted on heavy metal accumulation in the sediments and the factors that determine their remobilisation from the sediments, thus polluting the overlying water column.

Cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) are the most frequently researched heavy metals in bioaccumulation and environmental toxicity studies. Nickel (Ni) and chromium (Cr) were considered for this research because they have been found to be in high concentrations in areas impacted by urban and industrial runoff (Novotny, 1995; Goodyear and McNeill, 1999; Grosbois *et al.*, 2006; Wallinder *et al.*, 2006; Meybeck *et al.*, 2007; Turki, 2007; Marchand *et al.*, 2012). Aluminium (Al), iron (Fe) and manganese (Mn) were the macro-elements considered for correlation purposes. These metals will be focused on in this research, although other heavy metals, arsenic (As), barium (Ba), cobalt (Co), lithium (Li), silicon (Si), sodium (Na) and vanadium (V), were analysed in the course of the research as possible pollutants in the study area.

1.1 AIM AND OBJECTIVES

The aim of the research was to establish heavy metal baseline concentrations in the Msunduzi River and two of its tributaries, the Bayne's Spruit and Slangspruit, by assessing the spatial and vertical distribution of the metals, as well as the potentially mobile metal species in the sediments and water.

Specific objectives were as follows:

1. To characterise total metal content in the sediment and water samples;
2. To determine the fractionation pattern of the metals in the sediment;
3. To determine particle size distribution in the core sediment sample;
4. To investigate the historical deposition of heavy metals in the sediment
5. To interrogate the sources of heavy metals and their implications; and
6. To quantify heavy metal concentrations in the water and sediment samples using ICP-OES.

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2 LITERATURE REVIEW

This chapter will provide a brief background, as well as cited literature, on heavy metals, their sources and their behaviour in the environment. The chapter will also discuss the theory behind the chosen methods.

2.1 HEAVY METALS

Heavy metals cannot be broken down or bio-degrade like organic pollutants. They tend to accumulate in the water and sediments in freshwater systems where they are sequestered from one medium to the other (Burton, 1991; Duffus, 2002; Callender, 2003; Bosman and Kidd, 2009; Sekabira *et al.*, 2010). Some metals, such as iron (Fe) and manganese (Mn), are essential biological micronutrients required for organism growth. Non-essential heavy metals, such as mercury (Hg), are not required for growth and are considered to be most harmful to humans and freshwater biota (Corbett, 1995; Wasik and Namiesnik, 2001; Ouyang *et al.*, 2002; Jarup, 2003; Fasinu and Orisakwe, 2013). Beyond their optimum threshold, low concentrations of non-essential metals are as harmful as high concentrations of the essential metals (Newman and Clement, 2008; Hariprasad and Dayananda, 2013). Cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) are commonly classified as trace heavy metals.

2.2 TOTAL METALS

2.2.1 TRACE METALS

The term ‘trace metals’ is used when referring to heavy metals of low natural concentrations (less than 0.01%) in the environment and may be toxic at relatively high concentrations (Alloway, 1995; Duffus, 2002; Callender, 2003; Jarup, 2003; Yao and Gao, 2007; Appenroth, 2010). Trace metal toxicity can be defined as the concentration level required to exhibit acute (may lead to death) or a sub-lethal biological response in organisms (Smith, 1985). Zn is an essential nutrient for the human body and thus is important for human health (Ohnesorge and Wilhelm, 1991). Zn also has a prominent role in determining the outcome of pregnancies and

supporting neurobehavioral development. However, like other essential heavy metals, Zn can be toxic in high concentrations (Jarup, 2003). In humans, health effects of zinc poisoning include gastrointestinal distress, diarrhoea, slow reflexes, anaemia and metabolic disorder. Zn is unusual in that it has low toxicity in humans, but relatively high toxicity to fish (Eisler, 1993; Hemat, 2004). Unlike Zn, Cu is as biologically essential as it is toxic to organisms. Cu is naturally widely distributed in the environment and plants and animals have the ability to rapidly absorb the metal (Jarup, 2003). Cu binds to certain enzymes, mutating their physiological functioning and is known to cause brain damage in mammals (Scheinberg, 1991). Unlike Zn and Cu, Pb is hazardous to most forms of life at any concentration and is relatively bioavailable to freshwater organisms (Jarup, 2003). The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system (Jackson *et al.*, 2009).

Similar to Pb, Cd is a rare mineral in the Earth's crust and is highly toxic to humans, animals and freshwater organisms even at concentrations as low as $1\mu\text{g.L}^{-1}$ (Callender, 2003; Jarup, 2003). The effect of Cd toxicity in humans includes kidney damage and bone pains. Cd also has mutagenic (changes in genetic make-up), carcinogenic (cancer-causing) and teratogenic (causing developmental malformations) effects (Johri *et al.*, 2010; Nawrot *et al.*, 2010). Ni is a non-essential and toxic heavy metal which occurs as Ni(II) in the environment. In some aquatic invertebrate populations, Ni can cause death even in small concentrations ($\mu\text{g.L}^{-1}$) (Di Toro *et al.*, 1992; John and Leventhal, 1995). Cr, on the other hand, is a relatively common element found in many minerals in the Earth's crust (Callender, 2003; Guertin *et al.*, 2004). The eastern part of South Africa harbours the largest reservoirs of chromium in the world (as chromite) (Callender, 2003). Cr can exist as Cr(III) and as Cr(VI) but Cr(VI) is 100 to 1000 times more toxic than chromium(III) as it causes severe skin damage in humans (Sharma *et al.*, 2012).

2.2.2 MACRO-ELEMENTS

Aluminium (Al), iron (Fe) and manganese (Mn) are macro-elements that are also naturally present in the environment, but in relatively higher concentrations than trace

metals (Alloway, 1990). Al is the most abundant metallic element in Earth's outer crust but is highly insoluble in freshwater environments, therefore, most organisms have not adapted to elevated concentrations of bioavailable forms and cannot survive high concentrations of intracellular accumulation (Alloway, 1995; Allin and Wilson, 2000). The absorption of Al into the bodies of animals and humans occurs to only a slight extent. Inputs of Al to surface waters occur through a variety of processes and exhibit many forms, but the metal is mainly associated with bottom sediments (Driscoll and Schecher, 1990; Allin and Wilson, 2000; Fatoki *et al.*, 2002). Fe, one of the most abundant metals on Earth, is essential to most life forms and to normal human physiology (Callender, 2003). A deficiency of Fe limits oxygen delivery to cells, resulting in fatigue, poor work performance, and decreased immunity (Heubers, 1991; Jarup, 2003). On the other hand, excess concentrations of Fe in humans can result in toxicity and even death because very little Fe is excreted from the human body (Corbett, 1995). Mn is widely distributed in Earth's crust and is also an essential macro-element for both animals and humans (Schiele, 1991). Mn can be concentrated in the tissue of humans at factors of up to 10, whereas freshwater biota concentrate Mn by factors of up to 100 000 thereby reaching toxic levels (Schiele, 1991; Jarup, 2003; Matoka *et al.*, 2014). Symptoms of Mn toxicity in humans includes dullness, weak muscles, headaches and insomnia (Martin and Griswold, 2009).

2.2.3 SOURCES

There are a multitude of natural heavy metal emissions into the environment from terrestrial and atmospheric sources (Callender, 2003; Issa *et al.*, 2011). Heavy metals from weathered and eroded crustal material and from volcanic activities account for approximately 80% of natural heavy metal sources on Earth (Smith, 1985; Alloway, 1995; Callender, 2003; Obasohan *et al.*, 2008; Hariprasad and Dayananda, 2013). Elements such as Al and silicon (Si) contribute approximately 90% of the Earth's crust (Alloway, 1995; Dinelli *et al.*, 2005; Sekabira *et al.*, 2010). The chemical composition of freshwater sediments may depend on the lithology, morphology and structural settings of the catchment. Heavy metals may be divided into lithogenic, geochemical and anthropogenic with relation to their source. Geochemical and lithological sources, also referred to as detrital minerals, are governed by processes such as geological weathering. Weathering of underlying rocks provides baseline or

background levels of metal concentrations that are specific to that region (Smith, 1985; Alloway, 1995; Reitermajer *et al.*, 2011; Hariprasad and Dayananda, 2013). Forest fires and biogenic sources account for 20% of the remainder of natural heavy metal sources (Nriagu, 1990; Callender, 2003). Heavy metals from anthropogenic sources, are one of the major problems facing freshwater ecosystems worldwide (Osman and Kloas, 2010). Most heavy metal concentrations deposited to the Earth's surface by anthropogenic activities are many times greater than depositions from natural sources (Battarbee *et al.*, 1988; Nriagu, 1989; Connell *et al.*, 1999; Bosman and Kidd, 2009). Research has been directed towards understanding the transportation route of heavy metals in the freshwater environments by investigating the pathways used by metals to enter freshwater systems (Dominik *et al.*, 2007; Sakultantimetha *et al.*, 2009).

2.2.4 THE FATE OF HEAVY METALS IN FRESHWATER ENVIRONMENTS

In the water column, trace metals may exist as free or complexed ions or they may be adsorbed onto solids. Some trace metals are incorporated within insoluble organic or inorganic matter in bottom sediments where they are partitioned within the geochemical fractions (Filipek and Owen, 1979; John and Leventhal, 1995). One of the main processes that governs distribution and partitioning of heavy metals between phases is sedimentation (Förstner and Salomons, 1980; Forstner *et al.*, 1986). Sedimentation is not a simple or straightforward process and it allows heavy metals to be removed from surface water as they become trapped in the bottom sediments (Ayoub *et al.*, 2001; Peijnenburg and Jager, 2003; Yao and Gao, 2007). Heavy metals become incorporated into bottom sediments by means of the following sedimentation processes:

1. **Cation and anion (ion) exchange** is a process that occurs between a negatively and positively charged ion at a constant charged surface of sediment colloids and overlying water (Yao and Gao, 2007). Ion exchange occurs on sediments with surface areas large enough for selective adsorption of ions from solution, normally onto fine-grained sediments (John and Leventhal, 1995; Peijnenburg and Jager, 2003; Violante *et al.*, 2010). Hydrous Fe and Al oxides tend to be positively charged under acidic conditions as a

result of their relatively high isoelectric points. Under alkaline conditions, clay and organic colloids remain negatively charged majority of the time (Alloway, 1990; Thomas and William, 2003; Yao and Gao, 2007).

2. **Adsorptive** interactions are associated with clays and oxide surfaces. The surfaces control the dissolved metal concentrations in freshwater environments. Fe-Mn oxyhydroxides, including organic matter, play an important role in adsorptive processes (Sposito, 1984). Heavy metals may also be associated with organic substances such as organic ligands (humic acids). The metal-organic ligand complexes either precipitate onto the sediment or are adsorbed (Förstner and Wittmann, 1979; Elder, 1989). Alternatively, heavy metal adsorption onto hydrous forms of Fe-Mn oxyhydroxides limits solubility on the surfaces of clays (John and Leventhal, 1995; Peijnenburg and Jager, 2003; Violante *et al.*, 2010).
3. **Precipitation** reactions (includes co-precipitation and occlusion) occur when heavy metals react with anions, thus precipitating out of the water column. Ligands that are involved in precipitation reactions include carbonate, hydroxide, silicate, phosphate, and sulphide (in anoxic environments). The precipitation processes may determine the activity, and therefore, the environmental bioavailability of heavy metals when they are in the aqueous phase (Noller *et al.*, 1994; John and Leventhal, 1995; Yao and Gao, 2007). In effect, the formation of insoluble heavy metal precipitates is a limiting factor in bioavailability potential of heavy metals in freshwater ecosystems. Heavy metals form compounds with low solubilities and the degree of solubility is controlled by pH. That is, acidic conditions will result in increased solubility of the metal complexes thus releasing metals in the environments (Förstner and Wittmann, 1979; Fergusson, 1990; John and Leventhal, 1995; Peijnenburg and Jager, 2003; Violante *et al.*, 2010). Cu, Mn, Ni and Zn are co-precipitated in Fe-oxides whereas cobalt (Co), Fe, Ni and Zn are co-precipitated in Mn-oxides. The process is not important in terms of long-term transport as well as retention of heavy metals (Förstner, 1982; Forstner *et al.*, 1986; Otte *et al.*, 1995; Sheoran and Sheoran, 2006; Yao and Gao, 2007).
4. **Biological activities** occur when heavy metals are taken up by aquatic biota and then the metals later enter the sediment through decomposition of these organisms. Micro-organisms can reveal the extent of heavy metal present in a

freshwater system because micro-organisms uptake and store heavy metals during metabolic processes (Ye *et al.*, 2001; Russell *et al.*, 2003; Hallberg and Johnson, 2005; Yao and Gao, 2007). Metals, such as chromium may become immobilised when reduced through biologically-catalysed processes (Yao and Gao, 2007). Chemically-reducing conditions prevail in freshwater environments causing heavy metals to be associated with sulphide minerals. The sulphide-metal compounds are relatively immobile, provided the environment remains chemically reducing (John and Leventhal, 1995; Peijnenburg and Jager, 2003).

2.2.5 HISTORICAL DEPOSITION AND SPATIAL DISTRIBUTION OF HEAVY METALS

The brief review of Valette-Silver (1993), indicates that sediment cores can be used to reconstruct historical anthropogenic contamination in a region. There are certain criteria that a site must meet in order to be suitable for historical core analysis (Heim and Schwarzbauer, 2013). Such conditions can be found in marine and estuarine environments. The majority of sediment core studies have been concentrated in coastal environments (Chow *et al.*, 1973; Bruland *et al.*, 1974; Tanner *et al.*, 2000; Li *et al.*, 2001; Spencer and MacLeod, 2002). Heavy metal pollution of sediments increased in the late 1800s. The pollution rapidly accumulated in the 1940s before reaching its maximum between the 1960s and 1970s (Goldberg and Arrhenius, 1958; Goldberg, 1976; Valette-Silver, 1993). A decrease in certain heavy metals occurred in the 1980s, when new environmental laws and regulations were implemented (Valette-Silver, 1993).

A historical perspective of mismanagement and lack of legislation to protect freshwater environments can be highlighted by using sediment cores to reconstruct pollution history (Valette-Silver, 1993). Catallo *et al.* (1995) studied sediment cores deposited between 1950 and 1991. Sediments deposited between 1955 and 1980 were due to widespread industrial and agricultural activities because of uncontrolled point source discharge of contaminants (Catallo *et al.*, 1995). However, a typical sediment core would show decreasing concentrations dating back to pre-industrial eras. Abu-Rukah and Ghrefat (2001) studied the distribution of heavy metals (Cd, Co, Cr, Ni,

Mn and Pb) in six sediment cores at two locations along the Yarmouk River, Jordan. The concentrations of the heavy metals decreased with depth in all sediment cores (Abu-rukah and Ghrefat, 2001). Zhao and Marriott (2013) investigated heavy metals in floodplain sediments of the River Severn, United Kingdom. Concentrations of heavy metals increased with depth and then decreased, with peak values reached at varying points affected by translocation and hydroperiod. The peaks also corresponded with the change of historical mining output upstream (Zhao and Marriott, 2013).

Implementation of stringent regulatory laws and acts have also shown a decreasing trend in sediment accumulation of heavy metals and other contaminants as you move up the sediment core (Zhang *et al.*, 2013). Santschi *et al.* (2012) reconstructed historical inputs of Cu and Pb in the Mississippi River using sediment cores. Similarly Ye *et al.* (2012) investigated the accumulation of metals in sediments of the Pearl River, China. Spatial distribution of metals was consistent with anthropogenic input into the river basin. In terms of vertical deposition, there was a decline in pollution from the mid-1990s consistent with efficient pollution management in the basin (Santschi *et al.*, 2001; Ye *et al.*, 2012). Studies conducted in the late 1980s found that anthropogenic heavy metal emissions into the atmosphere, mainly due to mining, smelters and steel manufacturing, are in the order of two times (for Cu and Ni), five times (for Cd and Zn), and thirty-three times (for Pb) greater than the natural emissions of metals to the atmosphere (Smith, 1985; Hart and Lake, 1987; Nriagu, 1988; Nriagu and Pacyna, 1988). Similarly, Beck *et al.* (1990) investigated sediments in the Calcasieu River, Louisiana. The extent of pollution and transport of certain heavy metals exceeded background concentrations (Beck *et al.*, 1990). Ramesh *et al.* (1990) investigated heavy metal distribution in suspended and bed sediments of the Krishna River in India. There was substantial variation in the concentration of metals towards downstream sites which may be due to various degrees of human impact in the basin (Ramesh *et al.*, 1990).

Understanding the distribution of pollutants is critical for environmental management of spatially distributed heavy metals in sediments (Raulinaitis *et al.*, 2012).

Once heavy metals have entered the freshwater environment, they pose a risk to biota and human health (John and Leventhal, 1995; Jarup, 2003). Studies have been performed to investigate heavy metal pollution in Florida rivers and estuaries in the United States (Schropp and Windom, 1987; Alexander *et al.*, 1993; Campbell *et al.*, 1993). Ouyang *et al.* (2002) investigated the characteristics and spatial distributions of Cd, Cu, Pb and Zn in sediments from the lower St. Johns River basin, Florida. Most of the metal concentrations exceeded the background levels by factors of 2–10 (Ouyang *et al.*, 2002). A great deal of effort was invested to reduce the heavy metal pollution of the Keelung River, Taiwan. A set of sediments was analysed for heavy metal concentrations and grain size content in order to understand the spatial variations of sediment heavy metal concentrations as well as to evaluate the effectiveness of pollution control that had been implemented in the region (Huang and Lin, 2003). In Turkey, Ayas *et al.* (2007) conducted a study on the accumulation of Cd, Pb and Ni in water and sediment samples. Results showed that spatial distribution of the three heavy metals was extensive throughout the study area. In the water samples, heavy metal concentrations were below the respective detection limits of the metals. Expectedly, metal concentration levels in the sediment samples were higher than that of the water samples (Ayas *et al.*, 2007).

The distribution and enrichment of heavy metals (Cd, Cr, Cu, Mn, Pb, Ni and Zn) in sediments in the Tapacurá River basin, Brazil, were examined by Aprile and Bouvy (2008). Metal concentrations in the industrial and agricultural areas were higher than those in the urban areas. Particle size and anthropogenic influences were dominating factors controlling the spatial variations of heavy metals (Aprile and Bouvy, 2008). The Smolnik Creek, Slovakia, was impacted on by acid mine drainage and was known to contain high concentrations of sulphates and heavy metals. Decreasing pH caused remobilisation and release of historically deposited metals from the sediments into the overlying water column (Santschi *et al.*, 2001; Balintova *et al.*, 2012). Bednavora *et al.* (2013) studied the spatial distribution of heavy metals in the Morava River and Drevnice River, Czech Republic. The analysis was based on heavy metal enrichment factors and their concentrations were benchmarked using sediment quality guidelines (SQGs). The use of enrichment factors which include grain size proxy normalisation and heavy metal background levels, along with the comparison of the

detected concentrations to guidelines, proved an efficient way to identify pollution from anthropogenic sources (Bednarova *et al.*, 2013).

A more recent study was carried out by Shanbehzadeh *et al.* (2014) where they examined heavy metal concentrations in water and sediment, upstream and downstream of the entry of the sewage to the Tembi River, Iran. Results indicated that the average concentrations of the metals in water and sediment in downstream sites was higher than that of the upstream sites (Shanbehzadeh *et al.*, 2014). Even though land-use activities influence the vertical and spatial distribution of heavy metals in freshwater environments (dependant on the source and the location of the source), the sediment, water and sediment-water interactions also influence the behaviour of heavy metals in any freshwater system. Moreover, the macro-elements previously mentioned, mainly Fe and Mn, also play a critical role in the partitioning and release of heavy metals from bottom sediments. Thus, it is also important to investigate the factors that control the behaviour of heavy metals in sediments. Particularly since metals are found in different chemical forms in the environment.

2.3 BIOAVAILABLE METALS

2.3.1 PARTITIONING OF HEAVY METALS WITHIN SEDIMENTS

Within sediments, heavy metals are partitioned into various fractions, namely exchangeable², Fe-Mn oxyhydroxides, organic matter/sulphides and residual fractions³. Collectively, these fractions constitute the total metal concentration in a sediment sample (table 2.1) (John and Leventhal, 1995; Salomons, 1995).

2.3.2 REMOBILISATION OF HEAVY METALS

Heavy metals are not permanently bound within the sediment fractions, but are remobilised when environmental conditions change (Fergusson, 1990; Connell *et al.*, 1999). Once in the water column, the heavy metals remain in dissolved and mobile

² The term ‘**exchangeable fraction**’ will be used to describe those metals bound within the exchangeable, carbonates and acid-soluble sediment fractions.

³ The term ‘**residual**’ will be used to describe those metals bound within the crystalline sediment fraction.

Table 2.1: Relative mobility and availability of trace metal from the different sediment fractions [adapted from (John and Leventhal, 1995; Salomons, 1995)]

Sediment fractions	Degree of mobility	Implications
Exchangeable	High	Changes in major cationic composition lead to ion exchange that causes the associated metals to be released.
Fe-Mn oxyhydroxides	High to medium	Occurs with changes in redox potential. Associated metals may be released, but some may precipitate if the sulphide mineral present does not re-dissolve.
Organic matter/sulphides	Medium to low	The decomposition and/or oxidation of organic matter take place over time. Under oxic conditions, the oxidation of sulphide minerals in the sediment causes the release of associated heavy metals.
Residual	Low	Metals associated with the fraction are released after weathering or decomposition events.

Forms that are significant enough to exert toxic effects if bioavailable to organisms. Fe and Mn are examples of released heavy metals that are rapidly re-precipitated and deposited as insoluble oxyhydroxides where newly mobile trace heavy metals can become adsorbed (Di Toro *et al.*, 1992; Saulnier and Mucci, 2000). In terms of toxicity effects, humans become affected when they consume contaminated animals or when they come into contact with contaminated water or sediments (Jarup, 2003; Papu-Zamxaka *et al.*, 2010). Some of the most important environmental factors that affect metal remobilisation are changing pH and redox conditions of surface waters and the presence of Fe-Mn oxyhydroxides (John and Leventhal, 1995).

2.3.2.1 CHANGING pH AND REDOX CONDITIONS

Natural or man-made disturbances to the sediment in a freshwater system alter the redox potential and pH. The change in chemistry causes remobilisation of heavy metals from the sediments thus contaminating the water column (Förstner and Wittmann, 1979; Forstner *et al.*, 1986; Calmano *et al.*, 1993; Fytianos and Kotzakioti, 2005; Belzunce Segarra *et al.*, 2007; Kumar *et al.*, 2010). Oxic (oxidising) sediment

conditions lead to a positive redox potential of the sediment, among other chemical properties. In the anoxic (reducing) layer of the sediment, the redox potential of the sediment is reduced and the metals in these conditions are normally in the stable, sulphidic form. In large rivers, periodical oxidation and reduction of sediments may also take place. Change of redox potential of water changes the heavy metal-binding forms in the surface sediments in contact with the water (Förstner and Wittmann, 1979; Tessier *et al.*, 1979; Förstner and Salomons, 1980; Forstner *et al.*, 1986; Tessier and Campbell, 1987; Calmano *et al.*, 1993; John and Leventhal, 1995). The pH affects both the solubility and adsorption-desorption processes of metal-hydroxide minerals (Förstner and Wittmann, 1979; White *et al.*, 1979; Calmano *et al.*, 1993). Under a reducing environment, metal-carbonates, metal-hydroxides and metal-sulphides are precipitated due to changing pH. Oxidated Fe-oxide surfaces have a positive charge when the pH is lowered, but become negatively charged when the pH is increased (Calmano *et al.*, 1993; Eggleton and Thomas, 2004; Jain, 2004; Yao and Gao, 2007; Dordio *et al.*, 2008).

Alterations in redox potential lead to decreases in pH causing most metals to become increasingly mobile and potentially bioavailable. The extent to which pH is reduced is dependent on the sulphide matter content in the sediment and how much of the sulphide matter is oxidised (Forstner *et al.*, 1986; Calmano *et al.*, 1993; Delaune and Smith, 1995; Petersen *et al.*, 1997; Simpson *et al.*, 1998). Most metal-hydroxide minerals are not readily soluble under naturally occurring freshwater pH. The solubility of the hydroxides increases with decreasing pH thus increases the chances of their potential bioavailability (John and Leventhal, 1995; Osman and Kloas, 2010). However, alkaline conditions allow for co-precipitation of heavy metals into the sediment and the metals are not mobile (Thomas and William, 2003; Yao and Gao, 2007).

2.3.2.2 PRESENCE OF FE-MN OXYHYDROXIDES

Fe-Mn oxyhydroxides are significant sinks for heavy metals in sediments. In the water column, Fe and Mn are in their reduced states as Fe(II) and Mn(II) where they are present as insoluble oxyhydroxides. Recently released heavy metals become adsorbed onto Fe-Mn oxyhydroxides at varying rates and extent (Calmano *et al.*, 1993; Dong *et al.*, 2000; Eggleton and Thomas, 2004). Dissolved oxygen in the water oxidise the

metals and Fe-Mn oxyhydroxides precipitate out of solution as insoluble compounds due to their relative solubility in oxic (oxygenated) conditions. Heavy metals co-precipitate with these oxides or become adsorbed to their surface which are then bound to the surface sediments (Förstner and Wittmann, 1979; Fytianos and Laurantou, 2004). Most metal-hydroxide compounds have low solubilities under pH between 6 and 8, but their solubility increases with decreasing pH thus increases the chances of their incorporation in biological processes (Calmano *et al.*, 1993; John and Leventhal, 1995; Caetano *et al.*, 2002). The slower oxidation kinetics associated with sulphide-bound metals causes them to be more stable and less likely to be momentarily oxidised (Saulnier and Mucci, 2000; Eggleton and Thomas, 2004).

2.3.3 POTENTIAL MOBILITY AND BIOAVAILABILITY LITERATURE

Heavy metal speciation, utilising different sequential extraction procedures on lake, river and marine sediments, has been assessed in the past (Tessier *et al.*, 1979; Forstner *et al.*, 1986; Allen *et al.*, 1990; Pardo *et al.*, 1990; Davidson *et al.*, 1994; Ngiam and Lim, 2001). Toxic metals such as arsenic and mercury may accumulate in sediments. If released, due to changing environmental processes, the metals can move up the biological food chain where they may be ingested by humans (Förstner and Wittmann, 1979; Yao and Gao, 2007). The partitioning behaviour of toxic heavy metals has received increasing attention due to growing concerns of human health impacts and freshwater quality issues. Technological advancement has allowed for identification and comparison the spatial distribution of heavy metals within sediments (Li *et al.*, 2001; Jarup, 2003). An understanding of the partitioning behaviour of divalent metals provides an understanding of the physico-chemical factors influencing their potential toxicity and bioavailability in freshwater systems (Dong *et al.*, 2000).

In the 1960s and early 1970s, few studies had attempted to assess the speciation of particulate forms of metals (Tessier *et al.*, 1979). Total metal concentration values were used as a proxy to assess the potential effects that contaminated sediments may have. However, assessing the concentrations of metals in their entirety implied that all forms of a heavy metal have a uniform impact on the environment (Holmgren, 1967;

Chow *et al.*, 1973; Gibbs, 1973; Bruland *et al.*, 1974). In the late 1970s and early 1980s, authors theorised that solid material can be partitioned into various fractions which can be selectively extracted by using certain reagents (Ngiam and Lim, 2001). Jackson (1958) conceptualised that one can borrow or adapt extraction procedures used for soils and use them in sediment extraction procedures due to similarities between sediments and soil (Jackson, 1958). Förstner (1982) investigated accumulative fractions for heavy metals in freshwater sediments, in Hamburg, Germany, with the use of a selective extraction procedure. Clay-rich sediments are the major carriers of heavy metals where exchangeable, Fe-Mn oxyhydroxides and sulphide fractions predominantly accumulate heavy metals in sediments. Freshwaters affected by acid precipitation release Co, Ni and Zn from the reducible fraction and Cd from the organic fraction (Jackson, 1958; Förstner, 1982).

Tessier *et al.* (1979) examined a sequential “selective” extractions method that would allow for the partitioning of particulate trace metals into species, from geochemical fractions, that may be released under varying environmental conditions. The metal chemical forms were: exchangeable-metals, metals-carbonates, metals bound to Fe-Mn oxyhydroxides, those metals bound to organic matter and metals bound to the residual fraction (Sobolewski, 1999). Fe-Mn oxyhydroxides and sulphide/organic matter fractions of the scavenged metals in sediments in concentrations that exceed their own concentrations thus, Fe-Mn oxyhydroxide and sulphide/organic fractions are important sources of potentially mobile metals (Salomons and Förstner, 1984; Kersten and Förstner, 1986).

Following this, Tessier *et al.* (1985) investigated the role of Fe-Mn oxyhydroxides in controlling the heavy metal concentrations in natural freshwater systems. They concluded that the adsorption of Cd, Cu, Ni and Zn onto iron-oxides is an important mechanism in the lowering of heavy metal concentrations in oxygenated pore waters (Tessier *et al.*, 1985; Callender, 2003). Tessier and Campbell (1987) conducted a review study on the geochemical partitioning of trace heavy metals in sediment fractions and how this related to bioavailability. The accumulation of trace metals by freshwater organisms is influenced by various physico-chemical and biological factors. The partitioning of heavy metals among various fractions obtained by

experimental techniques, such as sequential extraction, provided an insight into the physico-chemical factors influencing bioavailability of particulate trace metals (Tessier and Campbell, 1987). In a subsequent study, Tessier *et al.* (1989) concluded that Zn is adsorbed onto Fe-Mn oxyhydroxides, organic matter and clay (Sigg, 1987; Tessier *et al.*, 1989). Finally, the authors expanded their studies to include adsorbed organic matter. pH was shown to play an important role in determining which types of particle surface binding sites predominate in the sorption of heavy metals in freshwater sediments (Tessier *et al.*, 1996; Callender, 2003).

The problem of post-extraction readsorption of Cd, Ni, Pb and Zn was addressed by Belzile *et al.* (1989) who found that by using an extraction procedure on trace-element spiked natural sediments it is possible to recover the added trace elements within the limits of experimental error (Belzile *et al.*, 1989; Callender, 2003). Despite the drawbacks of sequential extraction techniques, the method remains one of the most widely used technique when gaining a better insight of geochemical processes that affect sediment-bound metals (Tipping *et al.*, 1985; Rapin *et al.*, 1986; Martin *et al.*, 1987; Belzile *et al.*, 1989; Allen *et al.*, 1990; Pardo *et al.*, 1990; Yao and Gao, 2007). The effects of the water column chemistry on remobilisation of heavy metals from contaminated sediments have also been studied (Deurer *et al.*, 1978; Lerman, 1978; Calmano *et al.*, 1993; Eggleton and Thomas, 2004). Gambrell *et al.* (1991) provide information on factors affecting the mobilisation/immobilisation of metal contaminants under conditions of various possible remediation alternatives (Gambrell *et al.*, 1991). Calmano *et al.* (1993) investigated the precipitation and remobilisation of heavy metals in sediments affected by changing pH and redox potential, in Hamburg, Germany. During sediment oxidation, the pH value decreased, leading to the mobilisation of heavy metals. Cd and Zn were more strongly released compared to Cu and Pb. The reducible fraction (Fe-Mn oxyhydroxides) increased during oxidation while the organic matter/sulphide fraction decreased. At constant pH more metals are mobilised in oxidised sediment compared to sediments in the reducing state. The changing reduction and oxidation of the sediments show that redox potential also plays a role in the mobilisation of sediments (Calmano *et al.*, 1993).

Sediments are an important storage compartment for metals that are released to the water column in freshwater systems. Their ability to sequester metals allows sediments to reflect water quality and record the effects of anthropogenic emissions (Förstner, 1990; Callender, 2003). Lim and Kiu (1995) investigated the impacts of domestic and industrial waste discharge on the speciation of heavy metals in sediments of the Juru River, Malaysia. To ascertain the extent of heavy metal pollution, total and non-residual concentrations of Cu, Mn, Fe, Pb and Zn in sediment samples were determined. Both total and non-residual metal concentrations in sediments can successfully be used to identify heavy metal pollution sources (Lim and Kiu, 1995). Perin *et al.* (1997) conducted a five year study on heavy metal pollution and potential bioavailability in Rio de Janeiro, Brazil. Lin and Chen (1998) investigated the relationship between adsorbed heavy metals and organic matter in Lau-Che River sediments. Whereas, Traina and Laperche (1999) observed the effects that dissolution and precipitation have on sediment-bound metals (Perin *et al.*, 1997; Lin and Chen, 1998; Traina and Laperche, 1999).

As Tessier *et al.* (1979) determined that the toxicity of metals is dependent on its chemical forms. Jain (2004) also noted that it is more meaningful to quantify the different forms rather than using total metal concentrations. Fytianos and Lourantou (2004) performed a five-step extraction on sediment samples collected from lakes Volvi and Koronia in Greece, concluding that readily extractable metals were Cd, Cr, Cu, Mn and Pb. In Lake Volvi, the metal distribution followed a pattern that was expected as typical background levels in the sediments as more than 30% of the heavy metals were bound to the residual fraction (Fytianos and Lourantou, 2004). Fe-Mn oxyhydroxides, together with organic matter content scavenge metals in environmentally oxidising sediments and this is in agreement with results found by Tessier *et al.* (1979) upon development of their extraction procedure.

Particle size can also govern the distribution of heavy metals in a system. Sediment particle size has an effect on the geochemical partitioning of heavy metals (Filipek and Owen, 1979; Huang and Lin, 2003). Lin *et al.* (2003) assessed sediment toxicity by metal speciation in different particle-size fractions the sediments in two rivers in Taiwan. Heavy metals were subject to accumulation in the silt/clay (<25 μm) and

coarse sand (420 to 2000 μm) fractions. The potential toxicity to the river was caused by the fine sediments as well as coarse sediments (Lin *et al.*, 2003). In contrast, a study by Rangel *et al.* (2011) the authors showed that sand fractions did not accumulate, nor did they have a distinctive fractionation pattern of heavy metals as much as finer particles (Rangel *et al.*, 2011).

More recently, sequential extraction schemes have been applied to a number of different freshwater systems. Silva *et al.* (2012) studied the distribution of heavy metals in surface sediments of the Sergipe River, Brazil. Enrichment factor values indicated that some sites could be considered contaminated by Cr, Cu and Pb (Silva *et al.*, 2012). A study in Kenya determined spatially distributed and accumulated trace metals in two freshwater lakes. Variable accumulated levels were found in the analysed sediments. The residual fractions retained relatively higher concentrations of metals. Relatively higher concentrations of Cr, Cu and Pb were found in Lake Victoria sediments. Cd, Ni, Mn and Pb are of concern because a higher percentage of these metals were retained in the more bioavailable fractions in Lake Naivasha (Mwamburi, 2013).

2.4 THE STATE OF HEAVY METAL RESEARCH IN SOUTH AFRICA

Despite being seen as a region of limited industrial activity there is growing need for increased management and protection of Africa's freshwater environments. Proper management becomes that much more vital in light of an expected increase in industrial as well as urban activities in most regions of Africa (Idowu *et al.*, 2004; Ogoyi *et al.*, 2011; Okoro and Fatoki, 2012). South Africa is an example of such a region where the quality of natural water resources are declining from increased industrialisation and urbanisation (Crafford and Avenant-Oldewage, 2010; Gordon and Muller, 2010; Gemmell and Schmidt, 2013; Olaniran *et al.*, 2014). Approximately 20 – 40 % of South Africa's available freshwater is extracted from rivers and freshwater stress is likely to increase, making knowledge of water quality that much more vital (Holmes, 1996a, 1996b, 1996c, 1996d; Jackson *et al.*, 2009; Olaniran *et al.*, 2014). Any activities that degrade or adversely contaminate natural water resources require a water use license issued by the Department of Water Affairs. Therefore, routine freshwater quality monitoring forms an essential part of the conditions of

aforementioned licences (Holmes, 1996a, 1996b, 1996c, 1996d). In South Africa, water chemistry has been seen as a suitable proxy for some human disturbances, such as heavy metal pollution. However, heavy metal concentrations fluctuate greatly in river water and only represent the water quality at the time of sampling, thus interpreting the extent of heavy metal pollution status is difficult (Botes and van Staden, 2005; Bosman and Kidd, 2009). High concentrations of metals usually accumulate in river sediments as sediments act as important sinks for heavy metals (MacDonald *et al.*, 2003; Zhao and Marriott, 2013). The impact of human activities on the quality of South Africa's freshwater systems is demonstrated when referring to the River Health Programme.

2.4.1 SOUTH AFRICAN RIVER HEALTH PROGRAMME

The design of the River Health Programme (RHP) began in 1994 by DWAF and is intended to produce information regarding the ecological condition of riverine ecosystems in South Africa (Roux *et al.*, 1999; WRC, 2002; Strydom *et al.*, 2006; Osman and Kloas, 2010). Its overall goal was to expand the ecological basis of information on freshwater systems for effective management of the systems (Roux *et al.*, 1999; Dallas, 2000; WRC, 2002; Strydom *et al.*, 2006). Assessment tools with different indicator organisms have been developed for assessment of environmental water quality within the RHP. These tools utilise the responses of freshwater biota to characterise impacts of anthropogenic activities on in-stream biota. The rationale is that the health status of the biota provides an all-inclusive and integrated measure of the overall health status of the river in which they live, often referred to as biological monitoring (or biomonitoring) (Hamer and Soulsby, 1980; Charles, 1996; Karr and Chu, 1997; Barbour *et al.*, 1999; Kleynhans, 1999; Blinn and Bailey, 2001; Dickens and Graham, 2002; Strydom *et al.*, 2006; Oberholster *et al.*, 2008; Arimoro, 2009; Hermoso *et al.*, 2010).

Biomonitoring is based on the assumption that measurements of the integrity of biota can be used to assess the ecological integrity of an ecosystem, thus inferring the water quality. This is due to ecosystem pollution and other perturbations that might result from anthropogenic activities (Rosenberg and Resh, 1993; Karr and Chu, 1997;

Novotny *et al.*, 2005; Bonada *et al.*, 2006; Ollis *et al.*, 2006). The use of macro-invertebrates in biomonitoring of South Africa's water resources became popular with the development of the South African Scoring System (SASS), and was later incorporated into the river health programme as one of its biological indices. SASS is a biotic index based on the presence of selected families of aquatic macro-invertebrates and their apparent sensitivity to changes in water quality (Rosenberg and Resh, 1993; Chutter, 1998; Strydom *et al.*, 2006; De la Rey *et al.*, 2008a, 2008b).

Benthic macro-invertebrates have the advantage of being visible to the naked eye, easily identifiable, have rapid seasonal life cycles and are largely sedentary (Dallas, 2000; Ollis *et al.*, 2006; Strydom *et al.*, 2006; Hermoso *et al.*, 2010). However, Round (1991) listed some disadvantages of using macro-invertebrates as measures of ecosystem integrity. Their seasonality, distribution, food resources and choice of substratum limit the use of aquatic invertebrates as a measure of water quality. They also have complex reproductive cycles causing them to sometimes change habitats making them difficult to sample. Many freshwater macro-invertebrates are actively grazed, mostly have specific habitat niches and are closely linked to flow regimes meaning they only reflect the impact of physical habitat destruction and certain chemical changes (Round, 1991; Charles, 1996; De la Rey *et al.*, 2004; Bonada *et al.*, 2006; De la Rey *et al.*, 2008a, 2008b). Sediment quality, as a protocol for monitoring the quality and potential long-term pollution in South African freshwater systems should be added to the RHP.

2.4.2 PREVIOUS HEAVY METAL RESEARCH IN SOUTH AFRICA

Some of the earliest work on the analysis of South African freshwater systems was conducted by Greichus *et al.* (1977), who determined levels and distributions of heavy metals, in the Hartbeespoort Dam and Voëlville Dam, Johannesburg. Both dams were impacted on by a variety of human activities. The levels of arsenic (As), mercury (Hg), Cd, Cu, Mn, Pb and Zn were investigated in water and sediment samples. There were higher metal levels in Hartbeespoort Dam compared to Voëlville Dam (Greichus *et al.*, 1977). Watling and Emmerson (1981) investigated areas of heavy metal input in the Papenkuils River, Port Elizabeth. The study served as a preliminary survey of

the pollution status of the river. Results revealed that the level of pollution had caused extensive ecological modification in the river (Watling and Emmerson, 1981). In contrast, the Swartkops River estuary was generally unpolluted with regards to heavy metal pollution (Watling and Watling, 1982a). Similar studies by the same author indicated that the estuaries of Knysna, Bushmans, Kariega, Kowie and Great Fish rivers were not as severely polluted as the Swartkops (Watling and Watling, 1982b, 1983). A series of survey studies then ensued in South Africa.

Watling *et al.* (1985) studied the distribution of selected heavy metals in the Buffalo River as well as the Mzoniana and Ncabanga streams from August 1982 – August 1983. Surface water and sediment samples along with sediment cores were collected and analysed. Results indicated widespread anthropogenic input of Co, Cd, Cr, Cu, Hg, Pb, Ni and Zn, throughout the study area (Watling *et al.*, 1985). Background concentrations were exceeded by 100 fold when compared to a 1981 study in the same area (Watling, 1981). Talbot *et al.* (1985) investigated heavy metals in the Blind, Ihlanza, Nahoon and Quinera Rivers, near East London. Samples were analysed for up to sixteen heavy metals. Results revealed that the Blind, Ihlanza and Nahoon Rivers were enriched with Cu, Hg, Pb, Ni and Zn from unrestricted land-use in the river catchments. Only the Quinera River was found to be relatively unpolluted, in terms of heavy metal contamination (Talbot *et al.*, 1985).

While Greichus *et al.* (1977) determined total metal concentrations in the Hartbeespoort Dam, Coetzee (1993) employed a sequential extraction technique to determine the distribution of vanadium (V), Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in sediments collected from the dam. The observed metal distribution patterns in the different sediment fractions indicated that major proportions of most metals seemed to be associated with the inert fraction and could therefore be classified to be of geochemical origin (Greichus *et al.*, 1977; Coetzee, 1993). A survey of heavy metals in the Swartkops River, Eastern Cape Province was conducted by Binning and Baird (2001), nearly twenty years after the first published survey by Watling and Watling (1982a). The authors concluded that the continuous increase in heavy metal contamination was a cause for concern as the metals studied had the ability to

bioaccumulate (Watling and Watling, 1982a; Binning and Baird, 2001). Dissolved heavy metals, Al, Cd, Cu, Fe, Mn, Pb and Zn, in the Umtata River, Eastern Cape Province were determined by Fatoki *et al.* (2002). High levels metals that may affect the health of freshwater biota and communities that use the untreated river water were observed. Anthropogenic sources such as rural, urban and agricultural activities may have caused the elevated metal concentrations. Although it cannot be concluded that natural sources did not contribute to the observed high metal levels (Fatoki *et al.*, 2002).

Metal concentrations were observed in the Mooi River sediments from mining activities on a tributary of the river (Wade *et al.*, 2000). Van Aardt and Erdmann (2004) took sediment core samples from three dams within the Mooi River Catchment, namely Klerkskraal, Potchefstroom and Boskop. The dams had elevated concentrations of Cd, Cu, Pb and Zn (Van Aardt and Erdmann, 2004). Both studies were based on the original baseline study conducted decades before (Wittmann and Förstner, 1977), where the concentrations of Cu and Zn were reported in the water and sediments. Similarly, Okonkwo and Mothiba (2005) determined baseline data for trace metals in surface waters and sediments from the Dzindi, Madanzhe and Mvudi Rivers in Thohoyandou, Limpopo Province. Speciation studies revealed that Pb was mainly found in the particulate form while Cu and Zn were mainly found in the non-mobile fraction. Cd was equally distributed between the mobile and non-mobile sediment fractions. The three rivers were polluted by Cd and Pb when using international SQGs (Okonkwo and Mothiba, 2005). Greenfield *et al.* (2007) conducted a similar study on baseline metal study on sediments from the Nyl River flood plain, within the Waterberg catchment area, Limpopo. Al, As, Cd, Cu, Cr, Mn, Pb and Zn in the sediments revealed that the sediment was of a fair quality when compared to international SQG values. Most of the metals were found to be bound in the fourth and fifth geochemical fraction when using a sequential extraction technique. Despite being subject various potential impacts via anthropogenic activities, the quality of the sediment posed little potential threat to the system (Greenfield *et al.*, 2007).

There have been a number of published heavy metal studies in marine and estuarine environments, including harbours, in KwaZulu-Natal. Vermeulen and Wepener (1999) conducted a study on the heavy metal status of water, sediments and biota of Richards Bay Harbour (Vermeulen and Wepener, 1999). In a subsequent study, Wepener and Vermeulen (2005) investigated heavy metal concentrations in the harbour 20 years after its construction. The authors observed bioavailable metal concentrations in the harbour sediments (Wepener and Vermeulen, 2005). Mzimela *et al.* (2003) investigated the accumulation of metals in water, sediment and fish from the Mhlathuze Estuary. Metal concentrations were found to be higher when there was high freshwater inflow from the Mhlathuze River (Mzimela *et al.*, 2003). More recently, Pillay *et al.* (2014) investigated heavy metal pollution in the Isipingo River Estuary, KwaZulu-Natal (Pillay *et al.*, 2014). Similarly, Sukdeo *et al.* (2014) studied the Mvoti River Estuary, KwaZulu-Natal, which is known for its poor water quality due to agricultural, industrial and domestic water uses.

In one of KwaZulu-Natal's freshwater environments, Mthembu *et al.* (2012) studied the effect of human activities, such as agricultural and industrial, on the Mhlathuze River water quality, similar to that of Mzimela *et al.* (2003) (Mthembu *et al.*, 2012). Whereas Papu-Zamxaka *et al.* (2010) investigated the effect of mercury exposure on communities living close to the Hg-polluted Umgeni River in the Inanda Dam area. Sukdeo *et al.* (2012) assessed the presence of heavy metals in the lower Mvoti River. Results show that the river and estuarine sites closest to industrial effluent discharge sites and informal settlements had the highest levels of heavy metal pollution (Sukdeo *et al.*, 2012). Olaniran *et al.* (2014) conducted an assessment of the physico-chemical and heavy metal status of two rivers, Umgeni and Umdloti. However, the authors only analysed water samples. Moodley *et al.* (2014) investigated the seasonal variation of heavy metal concentrations in the water and sediments of the Palmiet River, a tributary of Umgeni River, KwaZulu-Natal (Moodley *et al.*, 2014). Results indicated that industrial activities and the winter season yielded higher metal concentrations. One of the few water quality studies in the Msunduzi River Catchment was conducted by Gemmell and Schmidt (2013). However, the authors only assessed the microbiological quality of the Msunduzi River Catchment.

The previous cited literature indicates that heavy metals from anthropogenic sources have detrimental impacts on the receiving water body, depending on the nature of the activities and proximity to the river environment. Once the metals have entered the system, they become assimilated into the bottom sediments where they can remain for several decades. Thus, sediments may be used to demonstrate the historical heavy metal input in a particular region. The spatial and vertical distribution as well as mobility and potential bioavailability of sediment-bound heavy metals are influenced by biological, physical and chemical processes. A number of analytical procedures can be applied in order to determine chemical characteristics that will assist in estimating total metals and metal bioavailability.

2.5 THEORETICAL METHODOLOGY

This sub-section will provide a background to the techniques that were applied in this research to determine total metal concentrations and potentially mobile metals in the water and sediments of the Msunduzi River Catchment.

2.5.1 WATER AND SEDIMENT QUALITY GUIDELINES

Water chemistry has long been used to measure river health and water quality in South African freshwater systems (Botes and van Staden, 2005). Pollution levels measured in water quality studies are compared against South African water quality guidelines published by the Department of Water Affairs and Forestry (DWAF) in 1996 (Holmes, 1996a, 1996b, 1996c, 1996d; Hallberg and Johnson, 2005). A series of guidelines for the different water uses, ranging from Water Quality Guidelines for Agricultural Use, to Water Quality Guidelines for Recreational Use, were developed and are still in use. The South African Water Quality Guidelines for Aquatic (freshwater) Ecosystems are used by the DWAF as the principal source of reference data and decision-making tool for the management of freshwater systems (Holmes, 1996a, 1996b, 1996c, 1996d; Bosman and Kidd, 2009). The current South African water quality guidelines are being revised, but judging from their criteria, they only reflect the effects of dissolved chemicals in the water column on biota. The chemicals associated with suspended and settled sediments, as well as the sediments themselves, are not taken into account. As particulate matter acts as a binding site for

contaminants, they ultimately accumulate in the bottom sediments (Chen *et al.*, 2007; Gordon and Muller, 2010; Osman and Kloas, 2010; Shanbehzadeh *et al.*, 2014).

Benthic organisms in intimate contact with the sediments are exposed to any chemical contamination adsorbed onto the sediment particles, thus introducing the contaminant into the food chain (Loring and Rantala, 1992; Gordon and Muller, 2010). Currently, South African legislation does not provide a definition for contaminated sediment and there is no universally accepted definition for contaminated sediment. The only applicable definition comes from Palermo (2001) in which contaminated sediment is defined as: “sediments containing chemical concentrations that pose a known or suspected threat to the environment or human health” (Palermo, 2001). Sediments are essential to the functioning of a healthy aquatic ecosystem and any form of anthropogenic disturbance may have an ecosystem level effect (Förstner and Wittmann, 1979; Burton, 2002; MacDonald *et al.*, 2003). The development of sediment quality guidelines (SQG) for freshwaters, much like the water quality guidelines, could be an important step towards the management and protection of freshwater ecosystems (Newman and Watling, 2007). There has been some work in deriving and, ultimately, implementing sediment quality guidelines in South Africa, but the study has not been conducted to date (Gordon and Muller, 2010).

The National Oceanic and Atmospheric Administration (NOAA) collect and analyses marine sediment samples on a yearly basis. A set of guidelines were developed by Long and Morgan (1990) which were derived by matching chemical concentrations and biological effects from saltwater and freshwater sediments. These biological effects mainly comprised the effects on benthic communities (Long and Morgan, 1990; Gordon and Muller, 2010). The guidelines were later revised by Long *et al.* (1995) and they included nine trace elements [arsenic (As), Cd, Cr, Cu, Pb, Hg, Ni, silver (Ag) and Zn], total polychlorinated biphenyls, two pesticides, thirteen polycyclic aromatic hydrocarbons and three classes of polyaromatic hydrocarbons (PAHs) (Long *et al.*, 1995; NOAA, 1999). The SQGs are intended to be used as an informal guideline for the interpretation of chemical data from sediment analyses and for use in classifying chemicals in terms of potential adverse health effects. With

regards to the trace elements, the NOAA SQGs work by deriving effects range-low (ERL) and effects range-median (ERM) values. ERLs represent concentrations below which effects were rarely observed (NOAA, 1999; Newman and Watling, 2007). That is, any concentration values below the ERL would have less adverse biological effects on benthic biota. Whereas, the ERM denotes concentration values above which adverse biological effects frequently occur. It was found that the ERM values better indicated health effects compared to the ERL values (Long and Morgan, 1990; Long *et al.*, 1995; NOAA, 1999; MacDonald *et al.*, 2003). Consequently, NOAA (1999) sediment quality guidelines were used in this study as they followed the mechanistic approach adopted by the upcoming South African guidelines.

2.5.2 TOTAL METAL ANALYSIS

Chemical extraction procedures are used to extract metals from sediments into aqueous solution for easier analysis in analytical equipment. Extraction methods may be in the form of single or sequential extractions. Different reagents are used to selectively dissolve metals associated with the different fractions within the sediments (Bakircioglu *et al.*, 2011). The single extraction technique used in the research was acid extraction. Wet acid digestion is a preparative analysis step used for the determination of total metal concentrations in sediments (Kotz *et al.*, 1972; Bakircioglu *et al.*, 2011). Microwave-assisted digestion is a type of closed wet acid digestion procedure used in determining elements in a solid sample by transferring the analytes into solution form (Matusiewicz, 2003; Sakan *et al.*, 2011). The principal advantage of a closed vessel system is the speed of digestion. In comparison with open digestion, such as the traditional “hot plate” method, closed microwave digestion is faster and can achieve higher temperatures. Microwave digestion is safe, fast and reliable. As sample preparation consumes the largest share of time for any analysis, this technique has economic significance (Kotz *et al.*, 1972; Förstner and Wittmann, 1979; John and Leventhal, 1995; Matusiewicz, 2003; Okoro and Fatoki, 2012).

It has been suggested that for pollution studies it is not necessary to obtain full digestion of all sediment components since the pollution effects are associated with the surface of the sediment particles. Therefore, it is not necessary to dissolve metals

bound into the internal structures of silicates and other detrital minerals (Chand and Prasad, 2012). Total metal concentrations reflect the geological origins of sediments and may also reveal anthropogenic input into a system. Determining the total metal concentrations in sediments in environmental monitoring ensures that total metal levels are within the range of natural background levels (Sastre *et al.*, 2002; Sakan *et al.*, 2011; Chand and Prasad, 2012). Despite being rapid and simple, this technique suffers from the time-consuming effort of having to transform the solid sediment sample into solution (Kazi *et al.*, 2009). Additionally, one has to find a single reagent effective enough in quantitatively dissolving the non-residual (mobile) forms of heavy metals (Chand and Prasad, 2012). Aqua regia (in the form of nitric acid:hydrochloric acid (1:3) decomposition of sediments is sufficient for trace heavy metal analysis as it is strong enough to extract metals associated with all sediment fractions, including silicates (Förstner and Wittmann, 1979; Tessier *et al.*, 1979; Förstner, 1980; Förstner and Salomons, 1980; Nriagu, 1990). Primarily, mixtures of commercially available acids are used, along with acid-resistant vessels, such as Teflon vessels, used to ensure chemical and temperature stability (Kotz *et al.*, 1972; Förstner and Salomons, 1980; Matusiewicz, 2003).

In addition to the task of transforming the solid sample into an aqueous solution, the acid extraction technique suffers from the fact that the fraction of the total metal extracted by any partial technique will depend on the reagent used (Sabra *et al.*, 2011). Re-adsorption of metals can occur at neutral pH and the use of a single reagent does not permit the dissolution of all the organic and inorganic labile forms without also attacking the detrital minerals (Tessier *et al.*, 1979; Martin *et al.*, 1987; Tessier and Campbell, 1987; Sabra *et al.*, 2011). Sample preparation is the most critical in environmental analysis studies and microwave-assisted digestion to determine total metal concentrations with the use of an additional technique (Velez, 2009). In effect, single extraction is only useful to provide a preliminary scan or idea of the heavy metal levels in sediments and should be considered in conjunction with other data, including sequential extraction procedures, when undertaking the task of predicting potentially mobile, bioavailable and toxic metal species in sediments (Tessier *et al.*, 1979; Tessier and Campbell, 1987; Thomas *et al.*, 1994).

2.5.3 SEQUENTIAL EXTRACTION

The use of total metal concentrations to assess sediment contamination implies regardless of the form in which a metal is found, all forms exert an equal impact on the receiving environment (Chand and Prasad, 2012). Using sequential extraction procedures, although more time consuming than total metal determination, provides information on the physical and chemical factors affecting bioavailability, mobilisation and transport of heavy metals in sediments (Bernhard *et al.*, 1986; Ure *et al.*, 1993). Sequential extractions are based on the notion that heavy metals can be partitioned or fractionated into specific fractions in sediments. The metals in the fractions can be selectively extracted using the appropriate reagent and the metal concentrations are related to the extractant used instead of the simulated environmental conditions (Förstner and Wittmann, 1979; Tessier *et al.*, 1979; Förstner and Salomons, 1980; Förstner, 1982; Forstner *et al.*, 1986; Tessier and Campbell, 1987; Quevauviller *et al.*, 1997; Baeyens *et al.*, 2003; Jain, 2004).

Numerous sequential extraction procedures have been proposed, with the initial extraction procedures were largely a combination of single extractions originally used by soil scientists (Goldberg and Arrhenius, 1958; Jackson, 1958; Martin *et al.*, 1987; Bettinelli *et al.*, 2000; Fernandez *et al.*, 2004). Considering the similarities between sediments and soils, research has shown that extraction techniques may be adapted from soil chemical analysis methods (Jackson, 1958; Tessier *et al.*, 1979; Sposito, 1984; Tessier and Campbell, 1987; Nriagu and Pacyna, 1988). The sediment fractions used in early partitioning studies were the exchangeable, carbonate-bound, easily reducible, labile organics, oxides, oxidisable oxides/sulphides, crystalline iron-oxides and the residual minerals (Tessier *et al.*, 1979). Early research saw the successful application of a variety of reagents to selectively extract metals from all these fractions. The exchangeables were extracted with compounds such as magnesium chloride, calcium chloride, barium chloride and weak acetates as the fraction holds easily soluble metals (Jackson, 1958; Gibbs, 1973; Engler *et al.*, 1977; Gibbs, 1977). The carbonate bound fractions were extracted with acidified acetates (pH = 5) (Deurer *et al.*, 1978; Filipek and Owen, 1979).

Labile organic bound metals were extracted with phosphate and carbonate compounds, acidified with HCl. The easily reducible fractions were extracted with hydroxylamine hydrochloride (at pH = 2) whilst the oxide fractions were extracted with a mixture of hydroxylamine hydrochloride and a weak acetate (Jackson, 1958; Gibbs, 1973; Cooper and Harris, 1974; Gupta and Chen, 1975; Engler *et al.*, 1977; Gibbs, 1977). The oxidisable oxides/sulphides were almost exclusively extracted with a hydrogen peroxide/ammonium acetate solution. The crystalline Fe-oxides were extracted in only a few studies with acids such as nitric acid and hydrochloric acid compounds (Chester and Hughes, 1967; Holmgren, 1967; Filipek and Owen, 1979; Förstner and Salomons, 1980). Finally, the residual minerals were extracted with concentrated acids, such as hydrofluoric acid, nitric acid and hydrogen perchlorate mixtures (Förstner and Wittmann, 1979; Ure, 1996; Bettinelli *et al.*, 2000).

In an early study, Tessier *et al.* (1979) aimed to develop an extraction scheme and examine its ability to partition sediment-bound trace heavy metals into chemical forms likely be released into the overlying water column, under changing environmental conditions. The authors proposed a five-step procedure, known as the Tessier extraction scheme, which partitioned selected heavy metals to distinguish between metals bound in five sediment fractions: exchangeable, carbonates, iron-manganese oxides, organic matter and residual. The Tessier extraction scheme is the most widely used extraction scheme in the world, even in recent studies (Tessier *et al.*, 1979; Rauret *et al.*, 1989; Allen *et al.*, 1990; Eslokkary and Muller, 1990; Pardo *et al.*, 1990; Zhang *et al.*, 1990; Coetzee, 1993; Fytianos and Laurantou, 2004; Hlavay *et al.*, 2004; Jain, 2004; Silveira *et al.*, 2006; Sharmin *et al.*, 2010). However, one of the disadvantages of using this method was that it does allow results to be compared worldwide as the procedure cannot be validated (Rauret *et al.*, 1989; Rauret *et al.*, 2001; Hlavay *et al.*, 2004).

2.5.3.1 DEVELOPMENT OF THE BCR PROTOCOL

The European Community Standards Measurement and Testing Programme (BCR) (formerly the Community of Bureau of Reference) launched a project aimed at harmonising and standardising single and sequential extractions for the determination

of metals in sediments and soils (Rao *et al.*, 2007; Okoro and Fatoki, 2012). An initial study of the literature and consultation with European experts was conducted by Ure *et al.* (1993). The following recommendations were made at a meeting of representatives of leading European soil and sediment laboratories:

1. Single and sequential extraction procedures for the analysis of soil and sediments were designed;
2. An inter-laboratory trial analysis of three different extraction schemes was carried out. Namely, the Tessier *et al.* (1979) scheme, the short method of Förstner and Salomons (1980), and the method of Meguellati (1983);
3. The elements to be included were Cd, Cr, Cu, Ni, Pb and Zn;
4. The sediment was selected from materials available from the Joint Research Centre in Ispra, Italy; and
5. The reference material, whose extractable contents were certified by an extraction procedure, was then developed.

Thus, a three-step extraction protocol was developed based on an acetic acid extraction in step 1, a hydroxyl ammonium chloride extraction in step 2 and a hydrogen peroxide attack followed by an ammonium acetate extraction in step 3 (Tessier *et al.*, 1979; Förstner and Salomons, 1980; Meguellati *et al.*, 1983; Ure *et al.*, 1993; Rauret *et al.*, 2001). This three-step procedure was first tested in 1992 in an inter-laboratory trial in which the extraction was conducted on sediment samples from the Netherlands (Ure *et al.*, 1993). Subsequent studies resulted in the improvement and validation of this protocol, as well as the preparation of certified reference material 601 (CRM 601) for the three-step BCR protocol (Davidson *et al.*, 1994; Quevauviller *et al.*, 1994; Quevauviller *et al.*, 1997).

The three-step BCR protocol was then modified, in the late 1990s, from the findings of the validation of CRM 601, which had some discrepancies at the 95% confidence interval (Rauret *et al.*, 2001). This modified procedure, along with the addition of the

aqua regia stage, was used to certify the newly developed CRM 701: for lake sediments. The aqua regia extracts were considered to be an important tool for internal control, and this is now the preferred protocol and CRM according to the European Community Standards Measurement and Testing Programme (Rauret *et al.*, 2001). Researchers have used some variation of the BCR protocol in their speciation studies (Lopez-Sanchez *et al.*, 1993; Davidson *et al.*, 1994; Thomas *et al.*, 1994; Whalley and Grant, 1994; Fernandez *et al.*, 2004; Yuan *et al.*, 2004; Kartal *et al.*, 2006). More recently, a fourth step was added to the BCR protocol, in which the residual (crystal lattice) is extracted by means of aqua regia (HNO₃/HCl; 1:3). The aqua regia acts a strong oxidising agent which is able to destroy the remaining minerals and resistant oxidisable material. The data from the first three steps is deducted from this data to obtain the residual fraction of the sediment (Rauret *et al.*, 2001).

2.5.3.2 LIMITATIONS AND ASSUMPTIONS OF SEQUENTIAL EXTRACTION PROCEDURES

Although sequential extraction procedures (SEPs) are routinely used in environmental monitoring, many methodological problems remain unresolved. They include non-selectivity of extractants, redistribution of trace elements and matrix effects (Goldberg and Arrhenius, 1958; Jackson, 1958; Tessier *et al.*, 1979; Tessier and Campbell, 1987). Extractant selectivity requires that the targeted sediment fraction is entirely solubilised, while the remaining fractions resist extraction. If extractants are not selective, the specific origin of a metal in a particular fraction cannot be determined and it would not be justified to interpret results by assigning a pollutant to a particular sediment fraction. However, this is exactly the way in which sequential extraction results have been generally interpreted and published in the past. Moreover, different mineralogical compositions can lead to different efficiencies of extraction (Goldberg and Arrhenius, 1958; Jackson, 1958; Tessier *et al.*, 1979; Förstner and Salomons, 1980; Tessier and Campbell, 1987).

Table 2.2: The chemistry of the extractants in the BCR protocol [adapted from (Tessier *et al.*, 1979; Rauret *et al.*, 2001)]

Step	Sediment phase	Chemistry of extractant
1	Water and acid soluble; exchangeable (bound to exchangeable cations and carbonates)	<u>Acetic acid</u> The acetic acid dissolves exchangeable carbonate minerals and their associated metals.
2	Reducible (bound to Fe-Mn oxyhydroxides)	<u>Hydroxylamine hydrochloride (pH = 2)</u> Brings reducible species of iron and manganese oxides into solution
3	Oxidisable (bound to organic matter and sulphides)	<u>Hydrogen peroxide</u> Used to extract the oxidisable material and includes any organic matter or metal sulphides in the sediments. The hydrogen peroxide therefore acts as an oxidising agent. <u>Ammonium acetate</u> Used to complex the extracted and dissolved metal ions and prevent readsorption onto the sediment.

Readsorption of extracted species onto the next sediment fraction, during the extraction process, can result in a particular pollutant being allocated to a different fraction. This effect may be reduced by buffering each extractant to an optimal pH (Baeyens *et al.*, 2003). Matrix effects may hinder the instrumental analysis of the samples, depending on the geochemical make-up of the sediment (Tessier *et al.*, 1979). Despite all these problems, SEPs seem to fulfil an important need in environmental sciences. With extensive validation of the procedures and the proper appreciation of the chemistry of reagents used, SEPs may prove useful.

2.5.4 INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETRY

Inductively Coupled Plasma Optical (ICP) – Optical Emission Spectrometry (OES) is an analytical technique that uses inductively coupled plasma as an excitation source. The “plasma” is a luminous volume of partially ionised gas (Skoog *et al.*, 2004; Velez, 2009). ICP-OES is a type of emission spectroscopy that is based on the fact

that atoms from different elements emit electromagnetic radiation at characteristic wavelengths. This allows for simultaneous, quick, accurate detection of a broad range of elements metals. It not only measures major macro-elements, but can also detect trace elements, therefore, a large number of samples may be analysed using ICP-OES. The most commonly used plasma gas is argon as it can simultaneously excite and ionise most elements (Huang *et al.*, 2006). Liquid samples are introduced by means of a peristaltic pump and then go through a nebuliser which forms a fine aerosol. The aerosol is transported to the centre of the plasma which decomposes the sample into atoms, at temperatures in excess of 7000°C. Some of the atoms are ionised and excited and electrons from the ground state are excited to vacant higher energy levels (Skoog *et al.*, 2004). As they revert to their ground state the atoms they emit light at a wavelength characteristic to that element and this emission is measured with an optical spectrometer. The intensity of the emission has a direct relationship with the concentration of that element in the sample being analysed (Skoog *et al.*, 2004; Huang *et al.*, 2006; Ojeda and Rojas, 2007).

ICP-OES is a widely-used and robust trace element technique that provides accurate, precise results with low detection limits. Due to its multi-element capabilities, it is ideal for a large number of samples for routine analysis. ICP-OES requires minimal dilution, even in samples high in salt content (Skoog *et al.*, 2004; Velez, 2009; Dospatliev *et al.*, 2012). However, the technique has its limitations. It consumes a larger volume of the introduced sample than other ICP techniques and cannot determine isotopic ratios. The absence of self-absorption in the argon plasma results in linear calibration lines over a large concentration range (Dams *et al.*, 1995; Ojeda and Rojas, 2007). Although the high temperature of the plasma reduces interferences, it cannot eliminate all spectral and non-spectral interferences (Dams *et al.*, 1995). When electrons revert to their ground state an emission spectral line is generated. If the electrons move to more than one vacant energy level a series of spectral lines may be produced. A sample containing a number of different elements may then produce complex emission spectra (Dams *et al.*, 1995; Hill *et al.*, 2004; Skoog *et al.*, 2004; Huang *et al.*, 2006; Ojeda and Rojas, 2007).

2.5.5 PARTICLE SIZE ANALYSIS

When undertaking heavy metal analysis in sediments it is imperative that a standardised procedure is adopted with regard to particle size. This can be done by means of normalisation using linear regression (Newman and Watling, 2007). Normalisation is the process of compensating for the mineralogical and granulometric factors that influence the natural variation in the heavy metal concentrations (Lin *et al.*, 2003; Wei and Wen, 2012). Granulometric normalisation refers to the isolation of the <90 μm fraction (or less) of all sediment samples as it aims to reduce the diluting effects of the non-metal bearing coarser particles. This is because heavy metals tend to be associated with the finer sediment particles (<90 μm) due to their higher surface area (Herut and Sandler, 2006; Newman and Watling, 2007). Small particles with a large surface area to mass ratio allow more adsorption of heavy metals than larger particles (Förstner and Salomons, 1980; Lin *et al.*, 2003; Jain, 2004). Particle size distribution (PSD) is vital in characterising water and sediment samples. Physico-chemical parameters, as well as heavy metal distribution, are closely correlated to PSD (Sabra *et al.*, 2011; Sadeghi *et al.*, 2012).

There are a number of methods available to determine the particle size distribution of a sediment sample and these include dry sieving, sedimentation, microscopy as well as laser diffraction. The laser diffraction technique has gained increasing popularity as the method of choice for particle size analysis as it is simple and rapid, yet accurate (Eshel *et al.*, 2004; Rawle, 2005). Laser diffraction is based on the diffraction angle of spherically-shaped particles being indirectly proportional to the size of the particle (Eshel *et al.*, 2004). Laser diffraction instruments, such as the Malvern Mastersizer 2000, use a laser as a source of intense light at a fixed wavelength, an apt detector and a manner in which the sample can be passed through the laser beam (Kiurski *et al.*, 2010). The latest laser diffraction instruments use the Mie theory which allows for completely accurate results over a large size range (normally 0.02 to 2000 μm). The light pattern scattered from particles at different angles is recorded and an analytical procedure is used to determine the size distribution (Rawle, 2005). This is based on the spherically shaped particles that create the light patterns. The results are depicted as the relative distribution of volume (or number) of particles in the range of classes. The volume distribution is generated directly and is equal to the weight of

distribution, provided that the density is kept constant. This is why the solvent of choice is water for measuring the solids as a liquid suspension, and is one of the advantages of using this technique (Eshel *et al.*, 2004; Rawle, 2005; Kiurski *et al.*, 2010; Stojanović and Marković, 2010).

According to Allen (1965) the particle size characteristics of river sediment is dependent on flow regime of the river. The flow rate, as well as the characteristics of the particles transported, strongly influences the rate of deposition of sediments in freshwater environments (Allen, 1965; Chakrabarti and Lowe, 1981). Taking into account particle size distribution (PSD) may reveal the flow strength and characteristics of heavy metal transport mechanisms in river systems as the metals are incorporated into the sediment as it is deposited down the river (Nilsson and Malm-Renöfält, 2008; Rahman and Plater, 2014). When considering particle size data as depicted by a laser instrument, the particle distribution pattern may reveal flow events in a freshwater system. Blanchard *et al.* (2011) studied the concentrations and particle size of sediments distributed in the Red River, North Dakota. Results showed that during high-flow events, there is an increase in pollutant loads at the settling point. The peak is sometimes directly proportional to the existence of smaller sediment particles that were easily transported by the rapidly flowing river water (Blanchard *et al.*, 2011). As particle size distribution is sensitive to flow strength spatial and vertical distribution patterns of sediments can indicate when there was increased (flood events) or decreased flow (drought) in a freshwater system (Nilsson and Malm-Renöfält, 2008; Okon and Asuquo, 2012; Rahman and Plater, 2014).

2.5.6 LOSS ON IGNITION

One of the most important components of river sediment deposits is organic matter. River sediment organic matter content may be estimated by measuring the concentration of weight lost in sub-samples subjected to different stages of heating (Heiri *et al.*, 2001). Loss on ignition (LOI) is a form of gravimetric methodology that is widely used to estimate the organic matter content of sediments (Cooper and Harris, 1974; Allen *et al.*, 1990; Lin and Chen, 1998; Heiri *et al.*, 2001). This technique is based on the different thermal conditions of materials in the sediment. Organic matter

ignites at 200 °C until the organic matter is completely depleted at 550 °C where the organic matter is oxidised to carbon dioxide and ash. Weight losses are quantified by recording the sub-sample weight before and after controlled heating (ignition at ~ 550 ° C) and this may be correlated with water and organic matter content. The ignition is typically done in a muffle furnace (Sutherland, 1998; Santisteban *et al.*, 2004; Wang *et al.*, 2011). The advantages of the LOI technique is that it is relatively simple, less costly and less labour-intensive compared to automated techniques and other chemical methods (Veres, 2002). However, the LOI method has its limitations. Higher temperatures can drive can lead to the decomposition of carbonates and hydrated salts, thus increasing errors and results in over-predicting organic matter content (Santisteban *et al.*, 2004; Konare *et al.*, 2010). Technical factors can also affect measurements, such as sample size, exposure time, location of the sample tube inside the furnace (Heiri *et al.*, 2001; Veres, 2002).

2.6 SYNTHESIS

Heavy metals are introduced into freshwater environments from natural and anthropogenic sources. Certain metals (e.g. Zn) are essential as biological nutrients, although they may be toxic when they exceed a certain threshold. Non-essential metals (e.g. Pb), are hazardous at any concentration. Historical anthropogenic activities enrich naturally present metal concentrations and pose a threat to freshwater environments, freshwater biota and potentially, humans. Due to the physical and chemical properties of metals and the receiving environment, the metals mainly become incorporated with the bottom sediments. Speciation (chemical forms) of metals involves understanding the distribution of metals over sedimentary fractions such as exchangeable, Fe-Mn oxyhydroxides, organic matter/sulphides and crystalline geochemical fractions. Under changing environmental conditions, metals are released from these geochemical fractions and pollute the overlying water column. Research on heavy metals in sediments is increasing in South Africa, and in KwaZulu-Natal, in particular. However, there has been no comprehensive research done on the heavy metal status of the Msunduzi River Catchment in Pietermaritzburg, KwaZulu-Natal. There are methods that can assist in providing a comprehensive overview of the heavy metal status in the catchment. Namely, total metal (of Cd, Cr, Cu, Pb, Ni, Zn, Al, Fe and Mn) and potentially bioavailable metal concentrations in the water and sediment.

The effect of physico-chemical factors (pH, redox potential, particle size and organic matter content) on the distribution, bioavailability and remobilisation of heavy metals can also be investigated.

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3 MOBILITY AND POTENTIAL BIOAVAILABILITY OF SEDIMENTARY HEAVY METALS IN THE MSUNDUZI RIVER CATCHMENT, KWAZULU- NATAL, SOUTH AFRICA

3.1 RATIONALE

Sediments represent an important reservoir of heavy metals in rivers, regardless of whether the metals are from natural or anthropogenic sources. Some physical and chemical disturbances, such as change in pH and redox potential, may cause the release of metals into the overlying water column. Thus, sediments can be seen as long term metal pollutants as disturbance can occur long after metals have been discharged into a river system. There is no published data on the metal pollution status of the Msunduzi River Catchment in KwaZulu-Natal. Simply determining the total metals present in the sediment is not sufficient, thus determining the chemical forms in which the metals occur is important. In addition, investigating the physical and chemical conditions that occur in freshwater systems that might affect the precipitation or remobilisation of metals is also important. The objective was to determine baseline levels of total concentrations and potentially mobile metal concentrations in the sediments of the Msunduzi River Catchment.

3.2 ABSTRACT

An evaluation of total metal [cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn)] concentrations within the sediments of the Msunduzi River and two of its tributaries was undertaken. The forms in which the metals occur were also investigated to measure the level of heavy metal pollution. The purpose of this study was to identify potential problem areas and possible sources of metal pollution in the Msunduzi River Catchment. It therefore serves as baseline study for sedimentary heavy metal levels in the Msunduzi River catchment from which informed future management decisions can be made. Total metal values were assessed against sediment quality guidelines to determine the potential toxicity level of the metals in the sediments. The Community Bureau of Reference (BCR) sequential

extraction method was used to analyse metals in the potentially mobile geochemical fractions of the sediment. The highest levels of heavy metal concentrations were recorded at points where the rivers flowed through dense residential and industrial regions. Total and potentially bioavailable concentrations of Cd, Cr, Cu, Ni and Pb did not exceed the Effects Range-Median (ERM) values but all metals exceeded the permitted Effects Range-Low (ERL). Pb was found to be the most potentially mobile metal. The level of potentially mobile heavy metals present in the sediment samples indicates the possibility for long-term pollution in the Msunduzi River Catchment.

Keywords: Sediment quality, BCR sequential extraction, partitioning, trace element toxicity, ERL, ERM

3.3 INTRODUCTION

Heavy metals cannot naturally bio-degrade and are one of the most persistent pollutants in freshwater systems as they become enriched in bottom sediments (Harris and Santos, 2000; Callender, 2003; Singh *et al.*, 2005; Osman and Kloas, 2010; Akpor and Muchie, 2011; Bednarova *et al.*, 2013). Heavy metals occur naturally in Earth's crust in trace concentrations and become enriched when they enter freshwater environments due to anthropogenic activities, such as mining, agricultural practices, municipal and urban waste and industrial discharge (Callender, 2003; Cempel and Nikel, 2006; Dominik *et al.*, 2007; Hariprasad and Dayananda, 2013). Sediments not only act as a sink for heavy metals, but also as a possible delayed source of long-term heavy metal pollution in freshwater systems (Turki, 2007).

In South Africa, water chemistry has been used as a proxy for some human disturbances, such as waste from industrial activities, agricultural practices and domestic sewage. There are water quality guidelines for the different water uses such as drinking water, recreational use, and agricultural use (Holmes, 1996d; Burton, 2002). However, chemical parameters in water fail to capture long-term changes in an environment as chemical features fluctuate greatly in freshwater (Holmes, 1996d; Bosman and Kidd, 2009; John and Trollip, 2009; Nel *et al.*, 2013). Since trace metals

are continuously sequestered in the water column and bottom sediments they remain environmentally significant due to their potential for future toxicity, mobility and biological availability (bioavailability) (Ramesh *et al.*, 1990; Yuan *et al.*, 2004; Singh *et al.*, 2005).

To fully understand sediments as potential pollution sources, and their potential toxicity to organisms, their chemical partitioning should also be assessed (Tessier *et al.*, 1979; Tessier and Campbell, 1987; John and Leventhal, 1995; Jain, 2004; Turki, 2007). Partitioning, or fractionation, refers to the distribution of heavy metals among the different binding phases of a complex substrate (Baeyens *et al.*, 2003; Lin *et al.*, 2003; Krupadam *et al.*, 2006). In substrates such as sediments, fractionation includes the successive application of selective extractants or reagents under increasingly harsh conditions. This is known as sequential extraction and the idea behind the method is that the selected extractant could stepwise liberate the metals associated with a specific sediment fraction. These include carbonates, iron-manganese (Fe-Mn oxyhydroxides), sulphides/organic material (these three fractions are known as the mobile forms) and the crystalline lattice (known as the non-mobile form) (Tessier *et al.*, 1979; Tessier and Campbell, 1987; Lim and Kiu, 1995; Baeyens *et al.*, 2003; Eggleton and Thomas, 2004; Kartal *et al.*, 2006; Dominik *et al.*, 2007). The mobile forms may be potentially available for uptake by freshwater biota if released in their respective sediment fractions. The metals bound in crystalline structures and silicates, are not bioavailable, unless they undergo geochemical weathering (Luoma, 1983; Forstner *et al.*, 1986; Calmano *et al.*, 1993; Goodyear and McNeill, 1999; Krupadam *et al.*, 2006; Ayas *et al.*, 2007).

The current South African water quality guidelines only reflect the potential biological effects of dissolved metals in the water column. These guidelines do not take into account for the chemicals associated with settled sediments that have the potential to be remobilised should environmental conditions change (Holmes, 1996a, 1996b, 1996c, 1996d; Gordon and Muller, 2010). There has been some work in developing and, ultimately, implementing local sediment quality guidelines (SQGs), but the study has not yet been concluded (Gordon and Muller, 2010). For this reason,

the National Oceanic and Atmospheric Administration (NOAA) SQGs were used in this study, as these are integral in the formulation of the South African SQGs (NOAA, 1999; Gordon and Muller, 2010). SQGs are used to interpret the contamination of heavy metals in sediment considering they exceed the set guideline values. Effects Range-Low (ERL) indicates concentrations below which adverse effects rarely occur, or are rarely observed, whilst Effects Range-Median (ERM) values represent concentrations above which adverse effects frequently occur (NOAA, 1999). The afore-mentioned effects are based on measures of potential biological effects associated with toxicants in freshwater sediments and their toxicity on the biota (Long and Morgan, 1990; Long *et al.*, 1995; NOAA, 1999). SQGs do not differentiate between natural and anthropogenic sources of metals, but define them at concentrations above which adverse biological effects may occur (Burton, 2002; MacDonald *et al.*, 2003). SQGs will be used to evaluate heavy metal concentrations in the sediments of the Msunduzi River Catchment, KwaZulu-Natal, South Africa (figure 1.1).

Human health risks associated with regular use and exposure to the Msunduzi River water has not been adequately documented. Microbiological testing has been the primary focus of water quality determination in the Msunduzi as the river is used for recreational, domestic and irrigation purposes (Bartholomew and Sivparsand, 2013; Gemmell and Schmidt, 2013). There have also been socio-economic studies on one of Msunduzi River's tributaries, the Bayne's Spruit (Rivers-Moore and Hay, 1998; Neysmith and Dent, 2010). However, there have been no published chemical studies, particularly, heavy metal testing, on the Msunduzi River or any of its tributaries. The heavy metals of interest, for bioavailability studies, are cadmium (Cd), copper (Cu), chromium (Cr) [as Cr(III) and Cr(VI)], nickel (Ni), lead (Pb), and zinc (Zn). These trace metals were selected because of their potential for human exposure and increased health risk (Trefry *et al.*, 1985; Daskalakis and O'Connor, 1995; John and Leventhal, 1995; Santschi *et al.*, 2001; Fleeger *et al.*, 2003; Powell and Alexander, 2003). Aluminium (Al), Fe and Mn were also assessed for correlation purposes. The overall aim of this study was to assess heavy metal concentrations in the water as well as metal partitioning patterns in the surface sediments of the Msunduzi River

Catchment and relate these to potential mobility, toxicity and bioavailability of the metals.

3.4 METHODS

3.4.1 SITE DESCRIPTION

The Msunduzi River Catchment flows through the city of Pietermaritzburg in the KwaZulu-Natal Province (figure 3.1). The topology of the catchment is mountainous with various hills, lowlands, wetlands, marshes and flat areas (Gericke *et al.*, 2004). In this study, a targeted sampling design was employed in which sites were intentionally selected for their location relative to suspected sources of contamination and for their accessibility. Sampling started downstream of Henley Dam and ended downstream of the wastewater treatment works.

3.4.2 SAMPLING AND ANALYSIS

A once-off sampling event occurred in September 2013. One 50 mL water sample and one sediment sample (shovel collection at a depth not more than 5cm) was collected at each chosen site. In total, 27 water and 27 sediment samples were collected (16 sites along the Msunduzi River, 8 sites along the Bayne's Spruit and 3 sites along the Slangspruit). Only certain samples were reported on in this study to make an observation on land use effect on the water and sediment quality (Figure 3.1). Concentrations for all metals at all sites can be found in Appendix A for water and Appendix B for surface sediments. Chemicals used were of analytical grade purchased from Sigma Aldrich. Water and sediment samples were quantified using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Optima 5300 DV with AS 90 plus Autosampler) with axial/radial view. Analysis was done in three replicates ($n=3$) for each sample. Where applicable, the mean, standard deviation and percentage relative standard deviation, were calculated. One-way analysis of variance (ANOVA) was used to determine statistical significance ($p<0.05$). One-way ANOVA is a statistical procedure used to determine whether there were any significant differences between the means of two or more independent sets of data and this is done by analysis of variance. The method is useful in revealing

important information, particularly in interpreting experimental outcomes and to determine the influence of some factors on other parameters (Ostertagova and Ostertag, 2013).

3.4.2.1 WATER SAMPLES AND PHYSICO-CHEMICAL PARAMETERS

The water sampling technique that was employed is a standard method as set out by the United States Environmental Protection Agency (US-EPA) (2001). Polyethylene bottles (50 mL) were rinsed with deionised water prior to sampling. At each sampling site, the bottles were rinsed with the surface water sample before collecting a sample. Three drops of nitric acid were added to each sample before being stored in ice. The *in situ* water quality parameters (temperature, total dissolved solids, pH, redox potential and electrical conductivity) were measured using hand-held pH and conductivity meters. In the laboratory, the water samples were passed through a 0.45 µm membrane filter and stored in 15 ml vials prior to ICP-OES analysis.

3.4.2.2 SURFACE SEDIMENT SAMPLES

All sediment sampling techniques used are those set out by the U.S. EPA (2001). In the laboratory, sub-samples from each site, were air-dried. The dry sediment sub-samples were sieved to <90 µm. The first step in total metal analysis involved weighing 0.5 ± 0.0001 g of sediment into Teflon vessels and digesting at room temperature by adding 10 mL aqua regia ($\text{HNO}_3\text{:HCl}$, 1:3) in a fume cupboard. The samples were then digested using a MARS 6 Microwave digestion unit. The final step involved decanting the supernatant into 50 mL volumetric flasks and making it up to the mark with Millipore water.

3.4.2.3 SEQUENTIAL EXTRACTION

Approximately 0.5 ± 0.0001 g of sieved sample was used for mobility and bioavailability studies, using the three-step BCR sequential extraction (Rauret *et al.*, 2001). The first step in the extraction procedure involved selective extraction of metals bound to the exchangeable/carbonate fraction where 20 mL of acetic acid

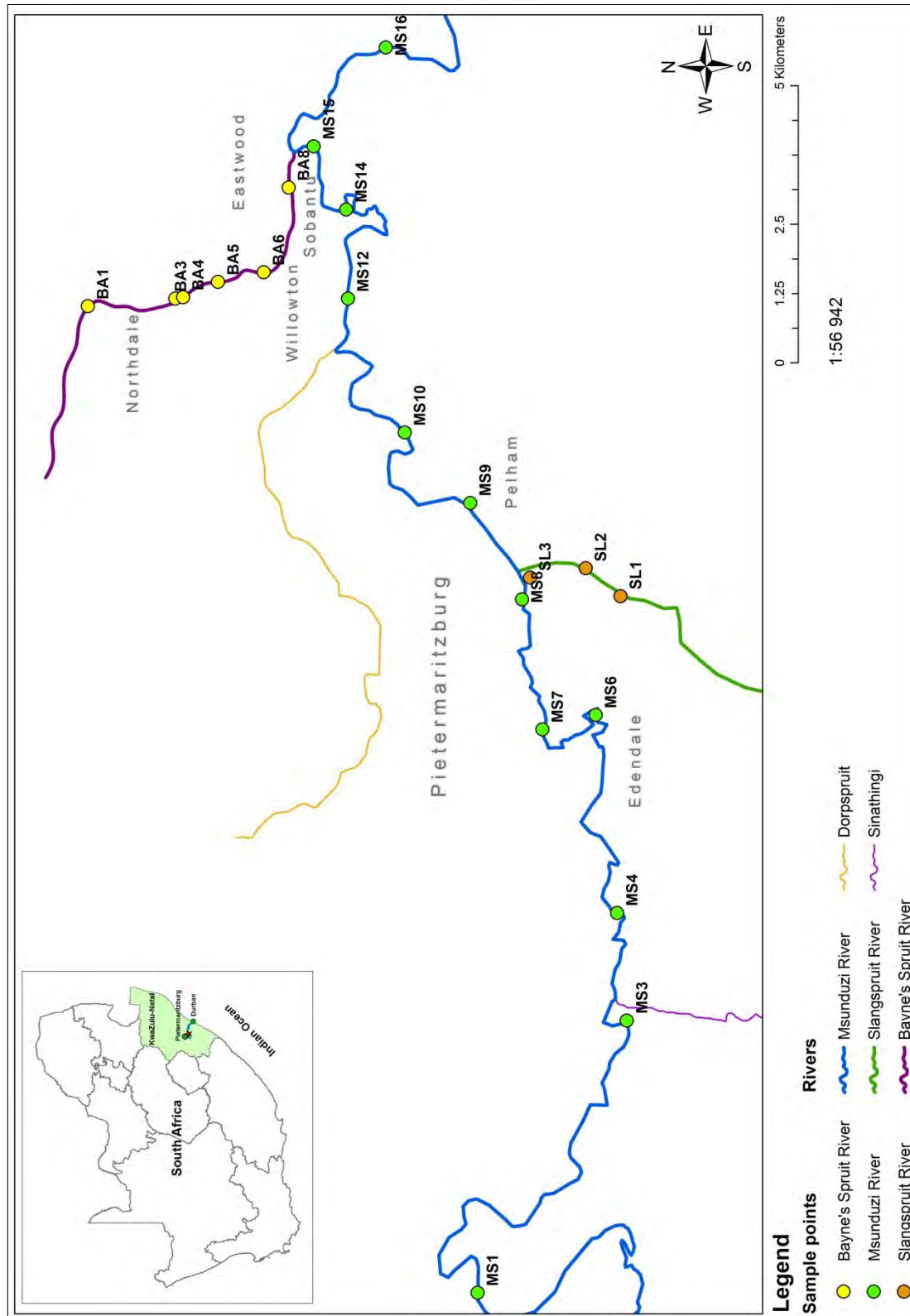


Figure 3.1: Distribution of sample sites on the Msunduzi, Slangspruit and Bayne's Spruit rivers

Table 3.1: Description of Msunduzi, Slangspruit and Bayne's Spruit sampling sites

River	Sampling site	Land use category	Site description
Msunduzi	MS1	Rural	Reference site for the Msunduzi River, downstream of Henley dam wall and rural areas of Chaewe and Ezibomvini
	MS3	Urban	Dense urban area of Edendale
	MS4	Urban	Dense urban area of Edendale and downstream of Sinathing Stream confluence with Msunduzi River
	MS6	Urban	Adjacent to existing tannery and old tannery ponds
	MS7	Urban/ Industrial	Downstream of tannery and urban area of Edendale A
	MS8	Industrial	Downstream of metal works factory
	MS9	Industrial/ Commercial	Camps Drift downstream of industrial complex and Slangspruit confluence; slowest river flow compared to upstream sites
	MS10	Urban	Dense urban area of Pelham and site was observed to be area of illegal dumping of waste during sampling trip
	MS12	Urban	Downstream of Dorpspruit River (which passes through an industrialised area) confluence with Msunduzi River
	MS14	Urban	Downstream of landfill site and adjacent to wastewater treatment works and adjacent to urban area of Sobantu
	MS15	Urban/ Industrial	Adjacent to wastewater treatment works and downstream of Sobantu
	MS16	Rural	Downstream of wastewater works and Hollingwood rural area
Slangspruit	SL1	Urban	Downstream of urban area of Edendale D
	SL2	Industrial	Adjacent to industrial area of Masons Mill and urban area of The Grange
	SL3	Industrial	Adjacent to industrial area of Camps Drift
	BA1	Urban	Reference site for Bayne's Spruit upstream of industrial area

River	Sampling site	Land use category	Site description
Bayne's Spruit	BA3	Urban	Dense urban area of Rosedale and industrial area
	BA4	Industrial	Dense urban area and industrial area, downstream from small stream coming from quarry near Panorama Gardens
	BA5	Industrial	Downstream and adjacent to industrial area
	BA6	Industrial	Dense urban settlement area of Eastwood and downstream of industrial area
	BA8	Industrial/ Residential	Dense urban areas of Eastwood and Sobantu and downstream of industrial area of Willowton

acetic acid (0.11 mol.L^{-1}) was added to the sample and shaken for 16 hours. The second step was carried out to selectively extract of metals bound to the Fe-Mn oxyhydroxides fraction where 20 mL hydroxyl ammonium chloride (0.5 mol.L^{-1}) was added to the sample shaken for 16 hours. The third step involved selective extraction of metals bound to the organic matter/sulphide fraction where 5 mL hydrogen peroxide (8.8 mol.L^{-1}) was added to the sample and digested at 85°C until almost dry, followed by 25 mL ammonium acetate (1.0 mol.L^{-1} , $\text{pH} = 2$) and shaken for 16 hours. The residual fraction was determined by extracting concentrations from steps one, two and three from the total metal concentration levels determined in a separate step. Analytical accuracy was determined using a certified standard reference material (CRM) BCR-701: Lake Sediment.

3.5 RESULTS AND DISCUSSION

3.5.1 WATER SAMPLES AND PHYSICO-CHEMICAL PARAMETERS

Cd, Cr and Ni were below the instrument detection limits in all samples and the results are omitted from this chapter. There were higher concentrations of Pb in the water, particularly in the Msunduzi and Bayne's Spruit, compared to Zn and Cu. The physico-chemical parameters are presented (table 3.2).

Table 3.2: In situ physical and chemical parameters measured in the water

Site	Temperature (° C)	Total Dissolved Solids (mg.L ⁻¹)	pH	Electrical Conductivity (µS.cm ⁻¹)
MS1	15.1	69	5.9	118
MS2	14.2	69	6.25	118
MS3	14.5	75	6.5	130
MS4	16	88	7.38	151
MS5	16.6	94	7.48	162
MS6	16.6	102	7.4	177
MS7	16.3	104	6.01	180
MS8	16.1	107	7.15	184
MS9	18.9	136	7.02	234
MS10	17.5	132	7.05	228
MS11	18.6	133	7.16	228
MS12	19.1	132	6.67	224
MS13	18.9	133	6.56	228
MS14	18.7	137	6.67	236
MS15	18.3	152	5.75	263
MS16	19.5	324	5.55	557
BA1	21.8	164	5.86	298
BA2	20.9	185	5.76	319
BA3	20.7	152	5.76	264
BA4	18.1	319	6.27	554
BA5	14.3	119	6.17	205
BA6	15.2	118	6.39	203
BA7	15.4	122	6.4	211
BA8	14.9	124	6.29	214
SL1	21.7	224	7.28	384
SL2	21.4	225	7.3	385
SL3	21.7	237	6.71	406

The water temperature increased due to the time of the day when samples were collected. The highest pH throughout the catchment was pH 7.48 at MS5 and the lowest was pH 5.55 at MS16. Total Dissolved Solids (TDS) increased along the

Msunduzi River where MS1 had a value of 69 mg.L⁻¹ and MS16 was 324 mg.L⁻¹. In the Bayne's Spruit, values were constant with a peak at BA4. Electrical Conductivity (EC) followed a similar trend in both rivers as the two parameters have a direct relationship with another and measurements are recorded as a ratio (TDS:EC) (Holmes, 1996b, 1996c; van Niekerk *et al.*, 2014). TDS:EC is a measure of the concentration of material dissolved in water and if TDS:EC values are too high or too low, it can affect biological organisms in the river (Holmes, 1996a; Murphy, 2007). Factors that may affect increased TDS:EC at the downstream Msunduzi sites and BA4 in the Bayne's Spruit, that led to increased TDS:EC readings, include urban run-off, agricultural activities and wastewater treatment effluent (Murphy, 2007).

3.5.2 CERTIFIED REFERENCE MATERIAL ANALYSIS (CRM)

In order to validate and evaluate the results, the extracted sample concentrations had to be correlated with the CRM data values (table 3.3). Heavy metal recoveries were within the acceptable ranges for steps two and three of the BCR 701 extraction, although there was over-recovery at some instances due to matrix effect and analytical errors. There may not have been complete destruction of all the metal-containing minerals in the sediment by the selected reagent. There may also have been precipitation of extracted zinc and copper as insoluble compounds. It is reasonable to expect a small loss of analyte due to the number of transfers of the sample residue between steps. Matrix effects may have hindered the instrumental analysis of the samples depending on the geochemical makeup of the sediment.

3.5.3 SEDIMENT SAMPLES

The Msunduzi River was the main focus of the partitioning and mobility study. The impacts of the two tributaries, Slangspruit and Bayne's Spruit, was also investigated (figures 3.2 to 3.7). Organic matter content, redox values and formation of Fe-Mn oxyhydroxides (depicted as total Fe and Mn) are important physico-chemical parameters that assist in evaluating the geochemical partitioning of metals within the four sediment fractions (table 3.4).

Table 3.3: Concentrations and recovery of heavy metals extracted from the certified reference material (BCR 701: Lake Sediment) where all values are represented as mean \pm standard deviation

	Element	Experimental values (mg.kg ⁻¹)	Certified values (mg.kg ⁻¹)	Recovery (%)
Step 1 (Exchangeable fraction)	Cd	8.19 \pm 1.26	7.34 \pm 0.35	112
	Cr	4.42 \pm 0.01	2.26 \pm 0.16	195
	Cu	57.7 \pm 0.89	49.3 \pm 1.7	117
	Ni	21.2 \pm 1.92	15.4 \pm 0.9	138
	Pb	3.72 \pm 1.22	3.18 \pm 0.21	117
	Zn	202 \pm 1.32	205 \pm 6.0	98.5
Step 2 (Reducible: bound to Fe-Mn oxyhydroxides)	Cd	7.42 \pm 0.1	3.77 \pm 0.28	197
	Cr	52.2 \pm 1.95	45.7 \pm 2.0	114
	Cu	121 \pm 4.13	124 \pm 3.0	97.6
	Ni	28.9 \pm 0.94	26.6 \pm 1.3	109
	Pb	130 \pm 1.98	126 \pm 3.0	103
	Zn	122 \pm 1.36	114 \pm 5.0	107
Step 3 (Oxidisable: bound to organic matter and sulphides)	Cd ⁴	3.89 \pm 0.04	0.27 \pm 0.06	-
	Cr	148 \pm 7.89	143 \pm 7.0	103
	Cu	60.1 \pm 3.15	55.2 \pm 4.0	109
	Ni	17.3 \pm 1.11	15.3 \pm 0.9	113
	Pb	10.5 \pm 0.34	9.3 \pm 2.0	113
	Zn	49.6 \pm 1.35	46.0 \pm 4.0	107

Table 3.4: Total Fe, total Mn and organic matter content in the surface sediments and redox potential in the water

Surface sediments				Water
Site	Total Fe (mg.kg ⁻¹)	Total Mn (mg.kg ⁻¹)	Organic matter (%)	Redox (mV)
MS1	45181	2329	12.0	27.5
MS3	35615	954.1	8.02	30.1
MS4	36625	953.5	7.92	22.1
MS6	34286	821.1	5.71	23.5
MS7	33856	101.7	6.41	60.6
MS8	29518	570.2	5.18	-1.5

⁴ There was also an over-recovery of Cd in **step three** by several orders of magnitude, which hindered the validation of those results.

Surface sediments				Water
Site	Total Fe (mg.kg ⁻¹)	Total Mn (mg.kg ⁻¹)	Organic matter (%)	Redox (mV)
MS9	32586	739.1	6.79	-3.6
MS10	31447	779.2	7.56	-0.5
MS12	31617	846.5	7.87	20.1
MS14	31567	955	5.78	20.8
MS15	38494	972.5	4.36	76.8
MS16	30037	638.3	5.32	85.6
BA1	37435	990.1	5.59	73.5
BA3	38324	1698	6.19	85.4
BA4	37634	1039	3.77	34.5
BA5	31517	1386	10.8	50.2
BA6	36105	629.6	10.0	37.7
BA8	42672	778.3	8.07	42.9
SL1	36415	2675	4.93	-20.7
SL2	37195	2999	3.9	-4.4
SL3	35255	2147	6.18	15.4

Results for Cd show that the total potentially mobile fraction in all three rivers was <ERM, apart from site MS1 (figure 3.2). Cd was largely partitioned in the residual fraction in all three rivers. Metals associated with the residual fraction have low mobility. The partitioning pattern changes at sites BA5, BA6 and BA8. While the total metal concentration is not significantly higher, compared to the other Bayne's Spruit sites, the partitioning pattern is different in that the oxidisable fraction is >ERL. Organic matter % in the Bayne's Spruit was highest (average of 7.4%) compared to most of the sites in all three rivers except for MS1 and MS12. The higher overall mobility at BA6 may indicate anthropogenic input at this site and the effects are seen downstream as well.

In freshwater systems, the redox potential controls the chemical association of Cd whereas the pH affects the stability of the metals chemical forms (Jain, 2004). However, remobilisation of Cd in the oxidisable fraction is unlikely as Cd mostly occurs as metal-sulphides. Also, positive redox values in the Bayne's Spruit favoured

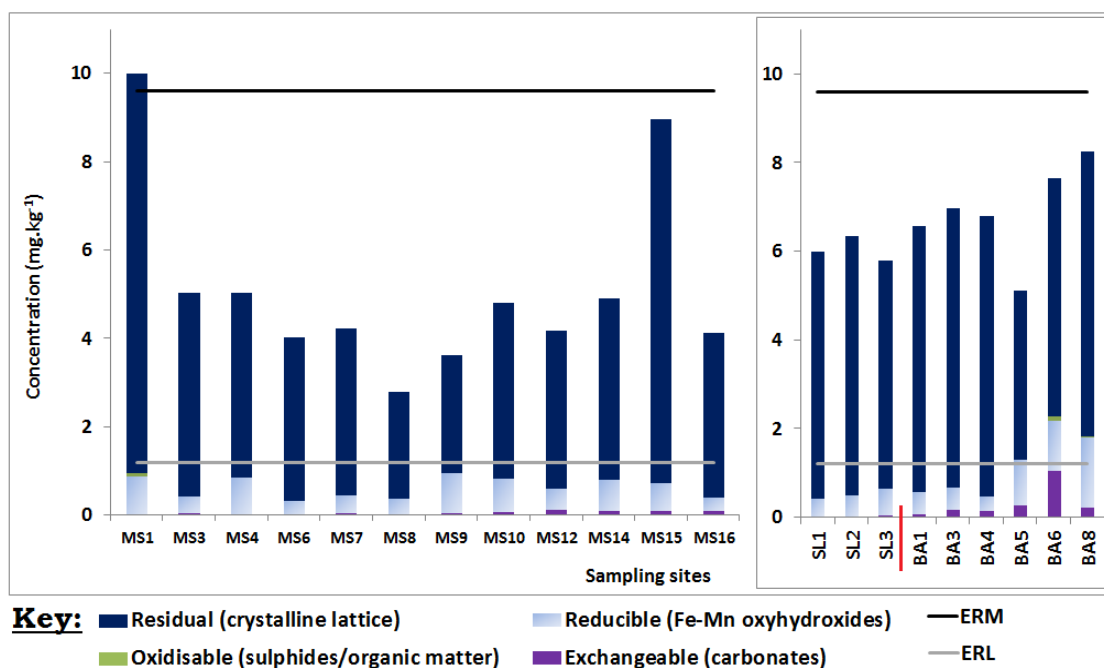


Figure 3.2: Fractionation of Cd in the sediment samples as determined by the three-step BCR procedure

the formation of stable metal complexes. Cd minerals are very rare in the Earth's crust and the metals sources in the rivers are likely to be associated with anthropogenic activities (Stoeppler, 1991). It is a highly toxic metal so any remobilised forms in the rivers would be harmful to freshwater biota and humans (Jarup, 2003).

The partitioning pattern of Cr was similar in all three rivers (figure 3.3). The total potentially mobile fraction did not exceed the ERL and ERM (value of 370 mg.kg^{-1}). Most of the Cr was associated with the residual fraction which is unavailable for biological uptake. The second most abundant form was Cr associated with sulphides/organic matter. The highest concentration of the oxidisable fraction was found at site MS7 (organic matter content was 6.4%) (Kotas and Stasicka, 2000). In waters of moderately acidic or neutral pH, Cr is found as non-toxic, but also relatively insoluble. Cr(III) hydroxy complexes. The pH values at all sites were neutral and redox potential was positive, meaning that conditions were oxidising and anaerobic, allowing for the formation of stable metal complexes.

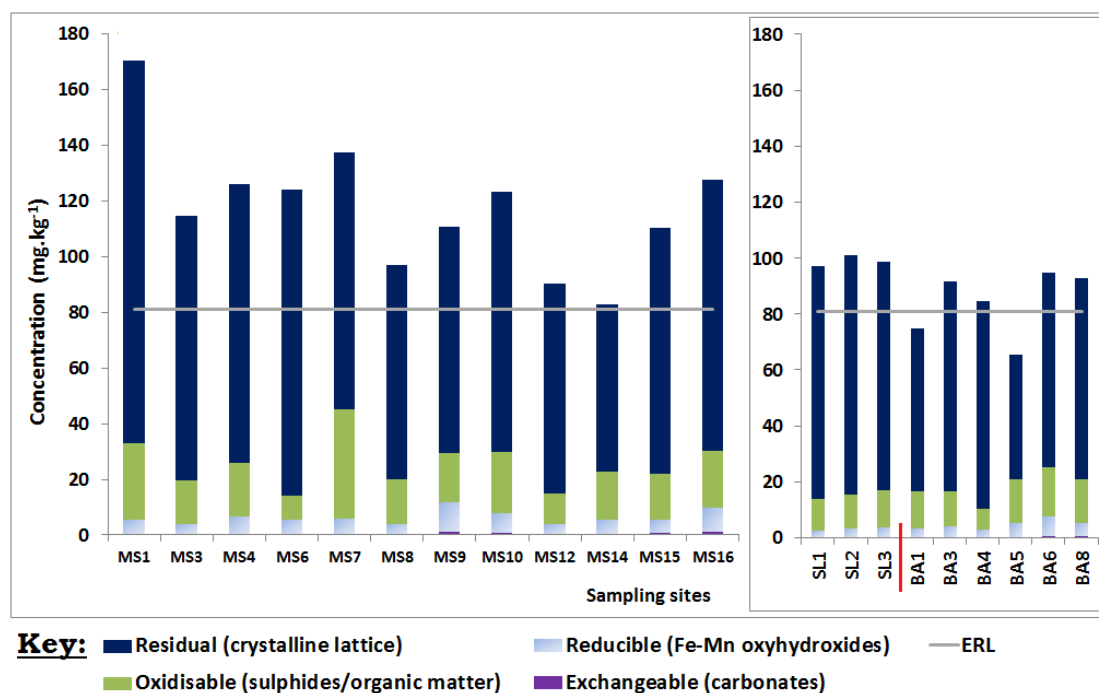


Figure 3.3: Fractionation of Cr in the sediment samples as determined by the three-step BCR procedure

The total potentially mobile forms of Cu were <ERM (value of 270 mg.kg⁻¹) (figure 3.4). Cu was associated with all geochemical fractions, but in all three rivers, the residual fraction was the primary association for Cu, followed by the reducible fraction, then the oxidisable fraction and lastly was the exchangeable fraction. At all three Slangspruit sites there was no significant difference ($p>0.05$) in the total Cu concentrations. In the Msunduzi, there was an increase in total, oxidisable and reducible Cu at MS12 (organic matter content of 7.9%), where a potentially mobile fraction is now >ERL, compared to upstream sites. This is linked to industrial activities from the tributary confluence upstream. In the Bayne's Spruit, BA3, BA6 and BA8 had higher total Cu compared to the other Bayne's Spruit sites. Cu was bound to sulphides/organic matter (oxidisable fraction) which was >ERL at sites BA3 and BA5, while reducible and oxidisable forms of Cu were >ERL at site BA6 and

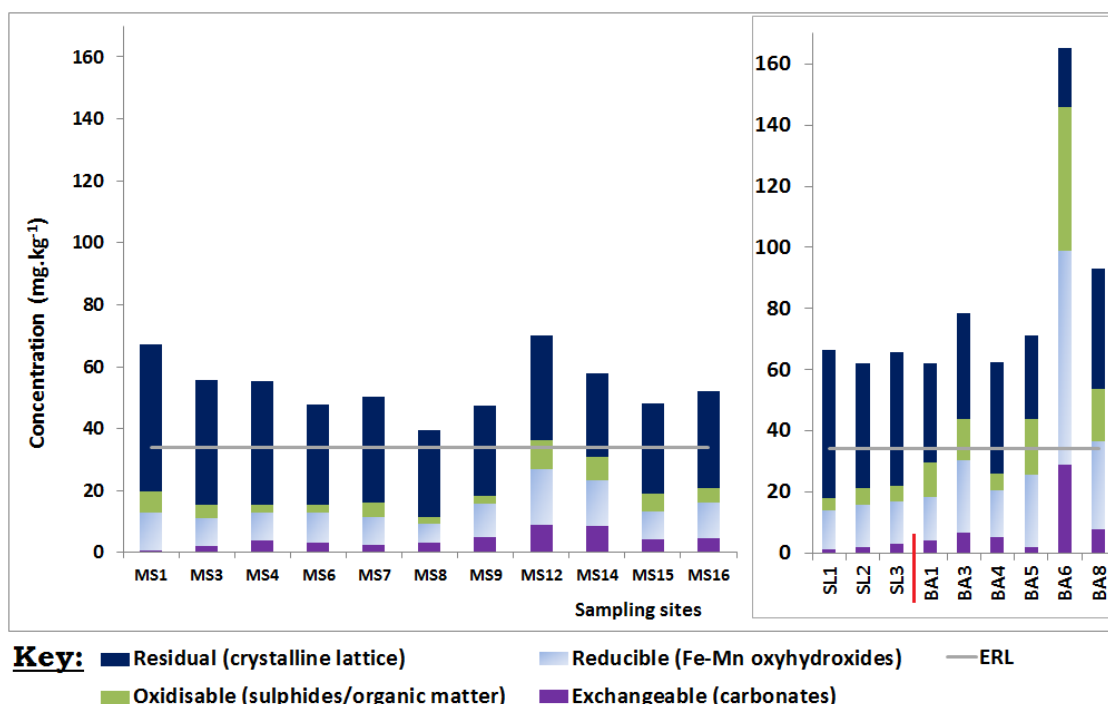


Figure 3.4: Fractionation of Cu in the sediment samples as determined by the three-step BCR procedure

BA8. Fe concentrations in the Bayne's Spruit were lowest at BA5 and were the highest at BA8, while Mn concentrations fluctuated with the lowest concentrations at BA8, when comparing Bayne's Spruit sites. The corresponding reducible fraction was not affected by the Fe-Mn content at all Bayne's Spruit sites. Metals in the reducible fraction can be released with a decrease in pH or if redox potential changes the sediment from oxic to anoxic conditions (Turki, 2007).

Redox values were positive in the Bayne's Spruit and the higher organic matter content at BA6 and BA8 and this corresponded with the increased concentration of the oxidisable fraction at these sites. Industries such as the combustion processes, refineries and the electric industry are possible Cu sources, particularly in the Msunduzi and Bayne's Spruit (Chen *et al.*, 2007).

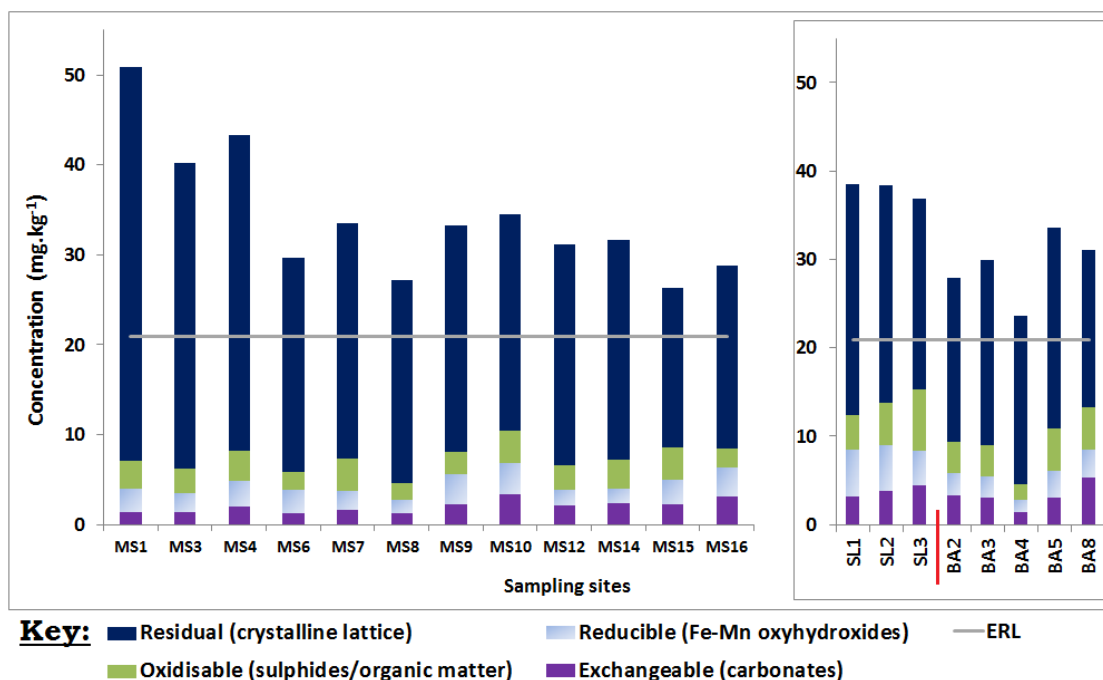


Figure 3.5: Fractionation of Ni in the sediment samples as determined by the three-step BCR procedure

Ni is a non-essential and toxic element which is mostly bound within the non-mobile crystal lattice in sediments (figure 3.5) (Sunderman and Oskarsson, 1991). Total potentially mobile forms of Ni were all <ERM (value of 51.6 mg.kg⁻¹) and the ERL in all three rivers. Ni displayed a similar partitioning pattern between the four geochemical phases in that the metal was mostly associated with the residual fraction. Concentrations of Ni bound in oxidisable, reducible and exchangeable fractions increased in the Slangspruit and Bayne's Spruit when compared to the Msunduzi. Similar to Cu, at all three Slangspruit sites there was no significant difference ($p>0.05$) in the partitioning pattern of the potentially mobile fractions as well as total Ni. Compared to the other Bayne's Spruit sites, BA4 (organic matter content of 3.8 % and redox value was 34.5 mV) had lower concentrations of total Ni and potentially mobile Ni. The reason may be is that BA4 is in an industrial area and the difference in partitioning could be due to changes in input to that system from industries such as smelters and refineries (Smith, 1985; Moore *et al.*, 2011). Additionally, physico-chemical parameters of the water at this site may account for the different geochemical pattern compared to the other sites.

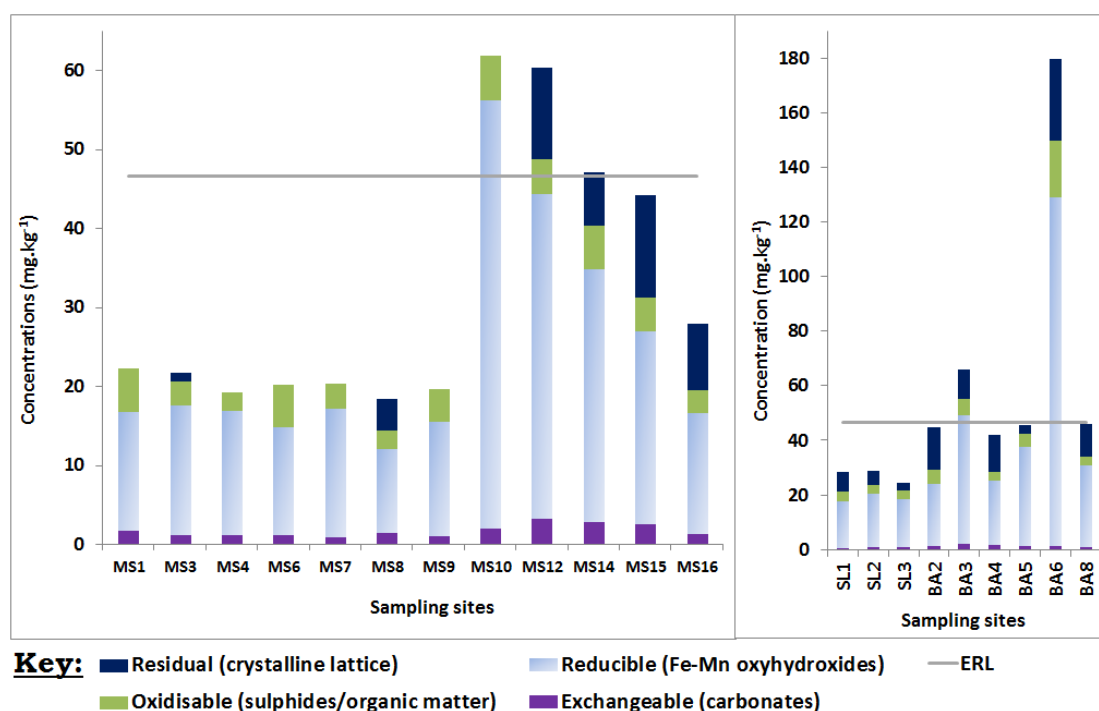


Figure 3.6: Fractionation of Pb in the sediment samples as determined by the three-step BCR procedure

The total potentially bioavailable forms of Pb were <ERM (value of 218 mg.kg⁻¹). Pb was mostly bound to Fe-Mn oxyhydroxides in the reducible fraction in all three rivers (figure 3.6). Fe-Mn oxyhydroxides are important scavengers of Pb in sediments and Pb is able to form stable complexes with Fe-Mn oxyhydroxides (Li *et al.*, 2001; Wong *et al.*, 2007). Metals in the reducible fraction can be released from the sediment if the pH decreases or if the redox potential changes (from oxidising to reducing) (Turki, 2007). In the Msunduzi, total Pb at sites MS10, MS12 and MS14 are >ERM. The reducing conditions at MS9, MS10 and MS12 (negative redox values) favours the release of metals from sediment fractions. Organic matter content was also higher at these sites compared to downstream sites. Sampling site MS10 is adjacent to a residential area and elevated concentrations may come from sewage or illegal dumping. Sampling site MS12 is downstream of a Dorpspruit River confluence where possible Pb sources include smelting processes, fertilisers and the paint and dye industry (Sheikh *et al.*, 2013). Slangspruit had the lowest total and potentially mobile Pb concentrations and all values were <ERM, although SL1 and SL2 had low redox values and conditions may favour metal remobilisation.

Most of the Bayne's Spruit sites had lower total Pb when compared to MS16 and the sites downstream. Site BA6, which is downstream from most industrial complexes, had significantly higher total Pb, as well as Pb associated with Fe-Mn oxyhydroxides, when compared to the Msunduzi and Slangspruit. Most probably from the nature of the Pb-based compounds discharged from industrial processes such as sewage effluent and the paint and dye industry (Zoumis *et al.*, 2001). Naturally occurring lead minerals are not very mobile under normal environmental conditions, the sources of Pb are likely anthropogenic in nature (Jain, 2004). Mn at BA6 was at lower concentrations compared to other Bayne's Spruit sites and Fe was not significantly higher compared to the other Bayne's Spruit sites.

Similar to Ni, the partitioning pattern of Zn was bound in all sediment fractions as the Zn has amphoteric properties (figure 3.7) (Grosbois *et al.*, 2006). There was higher total and exchangeable fraction concentrations of Zn compared to the other metals. The exchangeable fraction is the most mobile fraction and Zn may be released if pH is decreased (Turki, 2007). In the Msunduzi River, the total potentially bioavailable fraction did not exceed the ERL. Sites MS12, MS14 and MS15 had higher total and potentially mobile Zn concentrations compared to upstream sites. These sites are impacted by industrial activities (smelters and metal manufacturing) and wastewater effluent (Li *et al.*, 2001). The Zn in the Slangspruit sediments were mainly bound in the residual fraction and total potentially mobile fractions were <ERL. The pH values (table 3.2) in the Msunduzi were neutral so the remobilisation of the exchangeable fraction was unlikely.

In the Bayne's Spruit, concentrations of total, exchangeable and reducible forms of Zn were the highest total at BA5, BA6 and BA8 and concentrations were >ERL. BA5 is downstream from residential areas and is adjacent to dense industrial complexes, as is BA6. BA8 is downstream from all activities impacting the Bayne's Spruit. Most Zn compounds are insoluble in water and may account for the high total concentrations in the sediments. Metals with an anthropogenic source are mainly associated with the

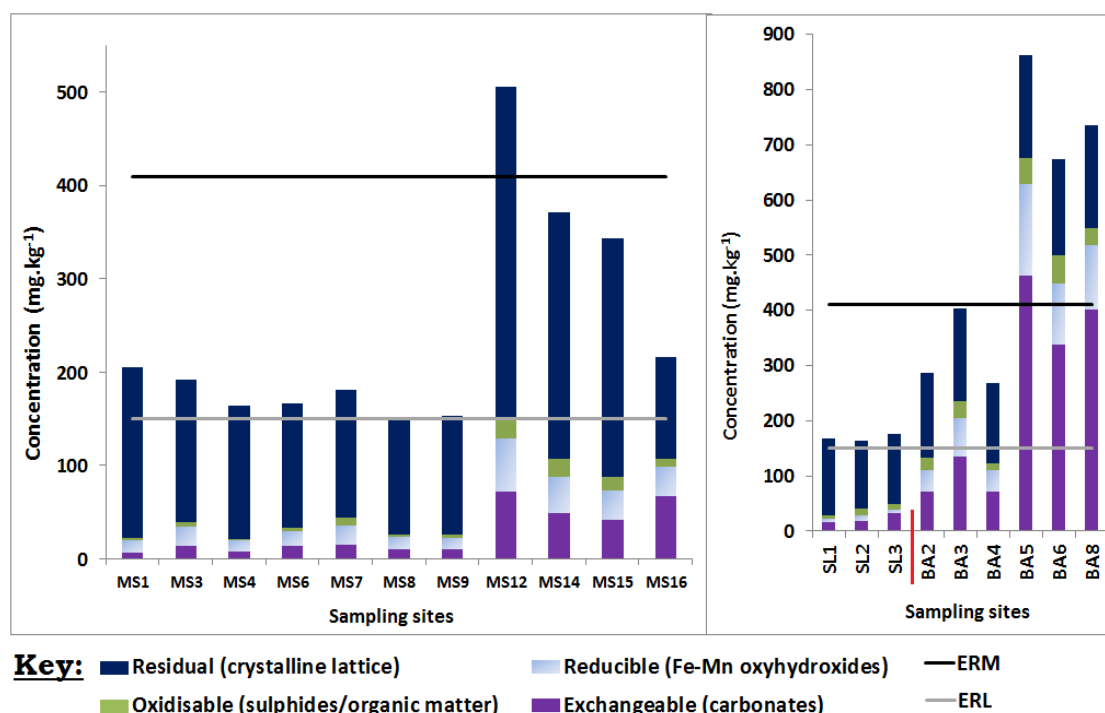


Figure 3.7: Fractionation of Zn in the sediment samples as determined by the three-step BCR procedure

exchangeable, reducible and oxidisable fractions (Turki, 2007). Fe-Mn oxyhydroxides in the reducible geochemical fraction, are major carriers of Zn in freshwater sediments and this may account for the increased concentration of Zn in this fraction compared to the Msunduzi and Slangspruit (Li *et al.*, 2001). The pH in the Bayne's Spruit was <6 and a decrease in the pH, due to industrial effluent, may result in the release of exchangeable Zn, which is present in higher concentrations at BA5, BA6 and BA8 compared to upstream sites. At BA5 and BA6, Fe concentrations were lower compared to the concentration at BA8, which was the highest in the river. Mn concentrations were constant. Organic matter content was the highest at BA5 (10.8%) and decreased at BA6 and BA8. Fe-Mn content and organic matter content may account for the increased concentration of potentially mobile Zn compared to the other Bayne's Spruit.

3.6 CONCLUSION

Total and mobile metal concentrations in the sediments were assessed against NOAA SQGs. With respect to ERL and ERM values of the SQG, Bayne's Spruit had poor sediment quality compared to Msunduzi and Slangspruit. The metals were primarily associated with the residual fraction except for Pb in all three rivers and Cu and Zn in the Bayne's Spruit. Sites impacted by industrial activities were areas of concern in the Msunduzi Catchment, particularly in the Bayne's Spruit. The metal of concern was Pb and the sediments are a potential source of long-term Pb pollution in the Catchment. The research served as a baseline study for total and bioavailable metal status of the Msunduzi River Catchment.

3.7 ACKNOWLEDGEMENTS

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4 SPATIAL DISTRIBUTION AND VERTICAL PROFILE OF SEDIMENTARY HEAVY METALS IN THE MSUNDUZI RIVER CATCHMENT, KWAZULU-NATAL, SOUTH AFRICA

4.1 RATIONALE

There is a gap in the knowledge in terms of heavy metal pollution in the Msunduzi River Catchment, KwaZulu-Natal. Determining the source of heavy metal pollution can be done by assessing the spatial distribution pattern of metals in the water and sediments. Vertical distribution patterns, coupled with particle size distribution analysis can be used to determine historical metal pollution and changes in flow regimes that may transport pollutants down a river system. The objective was to investigate the spatial and vertical distribution pattern of metals in the sediments of the Msunduzi River Catchment. Particle size distribution and organic matter composition can be used to infer relationships between the metals and physico-chemical parameters. Normalising with a metal such as aluminium assists in determining whether metal pollutants are from natural or anthropogenic sources.

4.2 ABSTRACT

Heavy metals are one of the most persistent and noxious pollutants in freshwater environments. Sediments in freshwater ecosystems act as a sink for heavy metals, where the metals are continuously sequestered between the sediment surface and overlying water column. As sediments accumulate on the river bed, they form a vertical profile of the trapped heavy metals in that system. Surface sediments illustrate the most recent anthropogenic inputs of heavy metals into freshwater systems, while undisturbed profiles are advantageous in that they preserve the historical sequence of pollution intensities. Surface sediments in the Msunduzi River and Bayne's Spruit, KwaZulu-Natal, South Africa, as well as a sediment core from the Msunduzi, were collected. The spatial distribution of heavy metals [cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn)], was determined by analysing the heavy metals in the $>90\ \mu\text{m}$ sediment fraction. In both the Msunduzi River and

Bayne's Spruit, spatial distribution of Cd and Ni was similar, while Cu, Pb and Zn had similar distribution patterns. Particle size distribution revealed that the flow regime of the river changed and the sediment eventually settled. Most of the heavy metal pollution from surrounding areas has been deposited downstream. This serves as a baseline study for heavy metal pollution in the Msunduzi River, Slangspruit and Bayne's Spruit. Further work on possible dating of the core sample, analysis of industrial effluent and comparison of other pollutants (organics and/or microbiological) with heavy metal pollution is needed.

Keywords: Vertical distribution, accumulation, normalisation, geochemical baseline, baseline study

4.3 INTRODUCTION

Pollution of freshwater environments has been intensively studied, with heavy metals recognised as being toxic to freshwater organisms even at moderate concentrations (Burton, 1991; Biney *et al.*, 1994; Connell *et al.*, 1999). Heavy metals may directly jeopardise the development and reproduction of an organism that absorbs and accumulates them (John and Leventhal, 1995; Aderinola *et al.*, 2009; Appenroth, 2010; Kumar *et al.*, 2010). As sediments can be particularly useful in detecting pollution sources they can be used in the selection of critical sites for routine water sampling (Förstner and Salomons, 1980; Salomons and Forstner, 1980; Valette-Silver, 1993). Sediments do not only behave as a sink for heavy metals, but may also act as source of heavy metal pollution in freshwater environments. This occurs when metals are remobilised from the bottom sediments when the chemistry of the overlying water column, and surrounding environments, changes (Tessier *et al.*, 1979; Tessier and Campbell, 1987; John and Leventhal, 1995; Jain, 2004; Turki, 2007). Depending on the dissolved metal concentrations present, heavy metals have an impact on the freshwater ecosystem, on humans using the river for recreational and domestic (Holmes, 1996a, 1996b, 1996c, 1996d).

Specific local sources such as discharge from smelters, metal-based industries, paint and dye formulators, petroleum refineries, as well as effluents from chemical manufacturing plants, may lead to heavy metal accumulation in sediments (Smith, 1985; Callender, 2003; Dinelli *et al.*, 2005). During periods of reduced flow rate, suspended material settles to the river bed, becoming partially incorporated into the bottom sediment. Thus, spatial distribution indicates local sources of heavy metal input and the sources can be determined and further investigated (Bednarova *et al.*, 2013; Qiao *et al.*, 2013; Shanbehzadeh *et al.*, 2014). Due to their large adsorption capabilities, fine-grained sediments tend to be a major repository for heavy metals, where metal pollutants are stored and can later be investigated as sediment cores (Fabbri *et al.*, 2001; Léopold *et al.*, 2012).

Undisturbed vertical sediment cores often preserve the historical sequence of pollution intensities, providing reasonable estimates of the background level and input variations of a pollutant over an extended period (Valette-Silver, 1993; Aleksander-Kwaterczak and Prosowicz, 2007; Cantwell *et al.*, 2007; Zhang *et al.*, 2013). In the 1970s, researchers began to use sediment cores to reconstruct the history of coastal pollution (Chow *et al.*, 1973; Bruland *et al.*, 1974; Aller and Cochran, 1976; Goldberg *et al.*, 1976; Goldberg *et al.*, 1977; Goldberg *et al.*, 1979). Sediment cores have also been used to study the behaviour of metals in different environments (Förstner and Salomons, 1980; Valette-Silver, 1993; Li *et al.*, 2001). Research expanded to freshwater lakes because the cored sediment material in lacustrine environments is usually undisturbed, fine-grained, and collected with a relatively rapid sedimentation rate (Beck *et al.*, 1990; Valette-Silver, 1993; Catallo *et al.*, 1995; Aleksander-Kwaterczak and Prosowicz, 2007; Wang *et al.*, 2012; Mwamburi, 2013). However, because of their low buffering capacity, lakes can be very sensitive to acidification processes (Valette-Silver, 1993). Studies of pollution, especially heavy metal pollution, in rivers has attracted attention for a long time because sediments are an important sink for pollutants (Ramesh *et al.*, 1990; Lim and Kiu, 1995; Mwamburi, 2003; Jain, 2004; Turki, 2007; Ogoyi *et al.*, 2011; Léopold *et al.*, 2012).

To better understand the data from sediment cores, dating techniques are often employed to provide a chronological framework for the observed trends (Valette-Silver, 1993; Bednarova *et al.*, 2013). However, dating techniques such as accelerator mass spectrometry (AMS) radiocarbon dating are costly, thus, particle size distribution (PSD) may also be used as an indicator of flow strength within the depositional freshwater environment (Rahman and Plater, 2014). It is imperative to base heavy metal analyses, particularly those from river sediments, on a standardised procedure with regard to particle size, as there is a marked decrease in the content of metals as sediment particle size increases (Callender, 2003; Mwamburi, 2003; Kiurski *et al.*, 2010; Sabra *et al.*, 2011; Sadeghi *et al.*, 2012; Mwamburi, 2013). PSD can reveal a relationship between the deposited sediment and metal concentrations associated with a certain sediment fraction. Sedimentation may be affected by anthropogenic activities that change the flow regime of the river at any given time. Such a phenomenon may be linked to natural variability, but may also be accelerated by anthropogenic activities (Walling, 1997; Zhang *et al.*, 2006; Sadeghi *et al.*, 2009; Sadeghi *et al.*, 2012).

Although heavy metal research has received increasing attention in South Africa, there is no data on the comprehensive state of heavy metal pollution in the Msunduzi River Catchment, KwaZulu-Natal, South Africa (figure 4.1). The Msunduzi River Catchment drains the Msunduzi Local Municipality, which includes the highly urbanised and industrialised city of Pietermaritzburg. Most of the research in the Msunduzi River Catchment has been focused on socio-economic issues as well as microbiological studies (Rivers-Moore and Hay, 1998; Gericke *et al.*, 2004; Bartholomew and Sivparsand, 2013; Gemmell and Schmidt, 2013). Due to recent and historical anthropogenic activities in the catchment, determining the heavy metal status is important. The main objective of this study was to investigate the spatial and vertical distribution of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in the sediment samples, as well as to investigate the heavy metal, organic matter content and particle size distribution in the sediment core.

4.4 METHODS

4.4.1 SITE DESCRIPTION

This study was conducted in the Msunduzi District Municipality, KwaZulu-Natal Province, South Africa, along the Msunduzi River and Bayne's Spruit River (figure 4.1). The main factor for sample site selection (16 sites on the Msunduzi River and 8 sites on the Bayne's Spruit River) was to investigate the impact of land use activities along the two rivers. Sampling site accessibility was a secondary factor.

4.4.2 SAMPLING

A once-off sampling event occurred in September 2013. One water and one surface sediment sample was collected at each site (figure 4.1). The water sampling technique that was employed is a standard method as set out by the United States Environmental Protection Agency (US-EPA) (U.S. EPA, 2001). Polyethylene bottles (50 mL) were rinsed with deionised water prior to sampling. At each sampling site, the bottles were rinsed with the surface water sample before collecting a final sample. Three drops of nitric acid were added to each sample before being stored in ice. In the laboratory, the water samples were passed through a 0.45 μm membrane filter and stored in 15 ml vials prior to ICP-OES analysis. The *in situ* water quality parameters were measured onsite using hand-held pH meter and conductivity meters. The surface sediment samples (0 – 15 cm deep) were collected with a plastic grab sampler along the Msunduzi and Bayne's Spruit Rivers and transferred to polyethylene bags, labelled and stored for further analysis in the laboratory. For the full metal concentration results at all sites for water and surface sediments, refer to Appendix A and B, respectively. One 1.5 m sediment profile was collected at site MS8 (figure 4.1) using a 5 cm diameter gouge auger. The sediment profile was stored horizontally in plastic tubes and wrapped with plastic and foil to minimise dehydration and prevent mixing of sediments. Site MS8 is downstream of a metal works and other industries.

4.4.3 SAMPLE ANALYSIS

All chemicals used were of analytical grade purchased from Sigma Aldrich. Water and sediment samples were quantified using Inductively Coupled Plasma-Optical

Emission Spectroscopy (ICP-OES) (Optima 5300 DV with AS 90 plus Autosampler) with axial/radial view. Analysis was done in three replicates ($n=3$) for each sample. Where applicable, the mean, standard deviation and percentage relative standard deviation, were calculated. One-way analysis of variance (ANOVA) was used to determine statistical significance ($p<0.05$). One-way ANOVA is a statistical procedure used to determine whether there were any significant differences between the means of two or more independent sets of data and this is done by analysis of variance. The method is useful in revealing important information, particularly in interpreting experimental outcomes and to determine the influence of some factors on other parameters (Ostertagova and Ostertag, 2013).

4.4.3.1 TOTAL METAL CONCENTRATIONS IN THE SURFACE SEDIMENTS AND SEDIMENT CORE

Surface sediment sub-samples from each site, were placed in plastic dishes to increase the surface area, and then air-dried in a fume cupboard. The dry sediment samples were ground with pestle and mortar to break down the larger particles and then sieved using mesh screens to the $<90\ \mu\text{m}$ fraction. The sediment profile from site MS8 was sliced at differing intervals into 60 sub-samples using a plastic spatula that was cleaned between each sub-interval to avoid cross contamination. Sediment core sub-sampling resolution was determined based on the focus of the study. From the top, the sediment core (0 cm) to a depth of 15 cm, the sediment core was sliced every 1 cm.

From a depth of 15 cm to a depth of 49 cm the sediment profile was sliced every 2 cm. From 49 cm to 100 cm the sub-samples were obtained by slicing every 3 cm. From 100 cm to 144 cm the sediment profile was sliced every 4 cm. The sub-samples were air dried in a fume hood and then sieved to the $<2000\ \mu\text{m}$ fraction. Acid digestion with 10 ml aqua regia ($\text{HNO}_3\text{:HCl}$, 1:3) was performed on $0.5\pm0.0001\ \text{g}$ of sub-sample. Samples were digested using a MARS 6 Microwave digestion unit. Total metal concentrations were quantified using ICP-OES. Correlations of spatial distribution with physico-chemical parameters, as well as comparisons of vertical distribution of metals (Cr, Cu, Ni, Pb and Zn) to aluminium (Al) concentrations were investigated. Correlation was computed to establish the existence of a significant

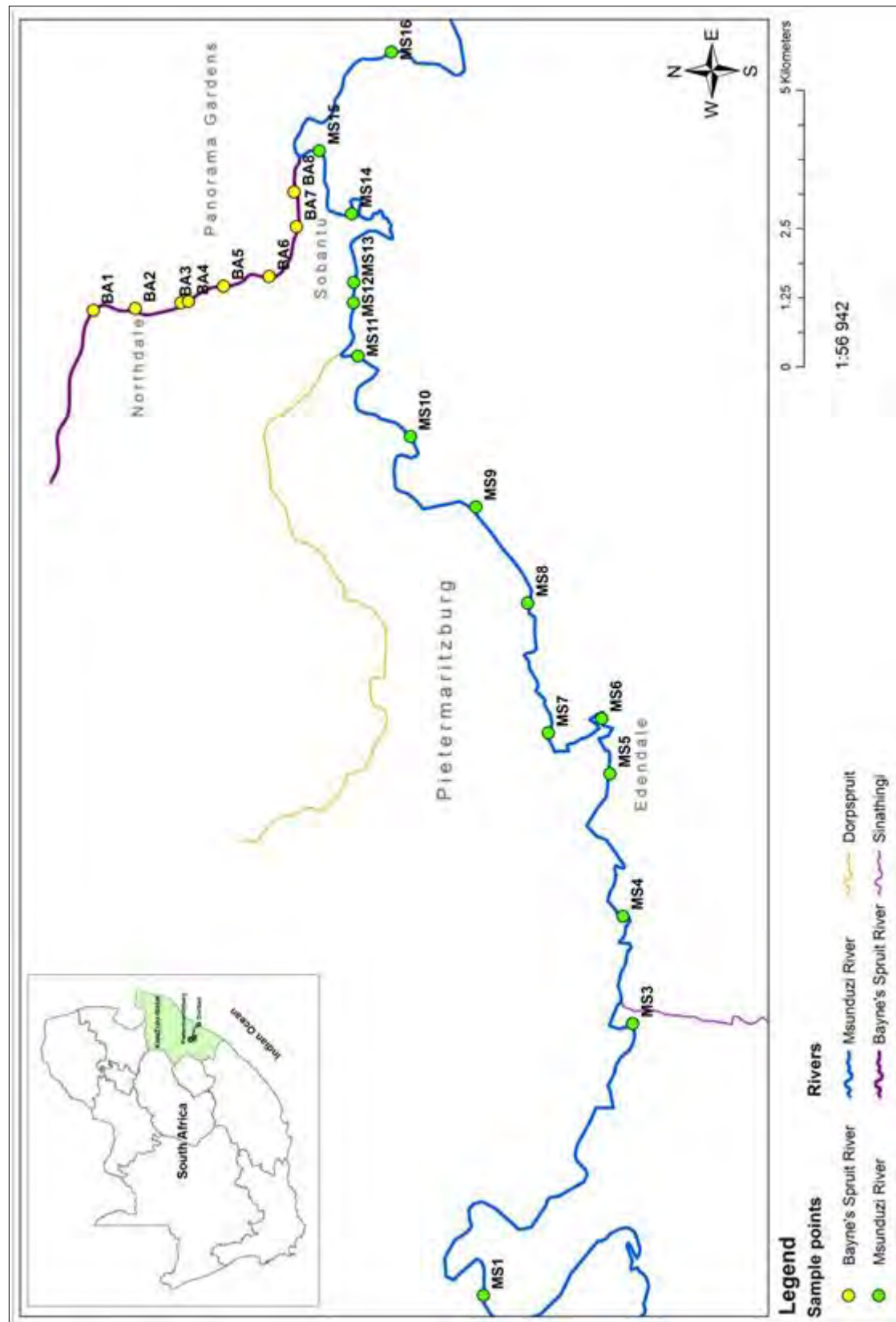


Figure 4.1: Map showing sample sites on the Msunduzi and Bayne's Spruit Rivers

linear relationship between spatially distributed heavy metals in the data sets and relate these to potential natural or anthropogenic sources.

4.5 RESULTS AND DISCUSSION

4.5.1 TOTAL METAL CONCENTRATIONS IN THE WATER

Cd, Cr and Ni were not detected by the ICP-OES instrument during water sample analysis and were omitted from the results (table 4.1). Below D/L means that the metals in that sample were below the detection limit of the instrument.

Targeted water quality guidelines for Cu, Pb and Zn for different uses are presented (table 4.2). Cu concentrations were less than the targeted water quality value in all three rivers. Pb concentrations were greater than the aquatic ecosystems guideline values in the Msunduzi and was at a level that may be harmful to organisms. In the Bayne's Spruit, metal concentrations at BA6, BA7 and BA8 were greater than the aquatic ecosystems guideline values and in the Slangspruit, metal concentrations were below the guideline values. In terms of domestic use, Cu and Zn were measured in mg.L^{-1} in the guidelines, but the metals still < targeted water guideline for domestic use at all sites. There are no targeted water quality concentrations for metals with respect to recreational use. Water used for agriculture has targeted water quality concentrations in mg.L^{-1} for all metals, and there were no metals, at any site, that exceeded the acceptable limits. The only guidelines that were exceeded were the targeted water quality guidelines for aquatic ecosystems.

Table 4.1: Heavy metals detected in the water samples

Site	Copper ($\mu\text{g.L}^{-1}$)	Lead ($\mu\text{g.L}^{-1}$)	Zinc ($\mu\text{g.L}^{-1}$)
MS1	0.0592	4.527	0.81
MS2	0.0564	1.697	0.796
MS3	0.0524	0.614	0.512
MS4	0.0293	0.559	0.215

Site	Copper ($\mu\text{g.L}^{-1}$)	Lead ($\mu\text{g.L}^{-1}$)	Zinc ($\mu\text{g.L}^{-1}$)
MS5	0.0286	0.714	0.37
MS6	0.0272	0.687	0.232
MS7	0.0195	3.149	0.254
MS8	0.019	1.384	0.223
MS9	0.0187	0.147	0.313
MS10	0.0145	0.687	0.457
MS11	0.0139	0.714	0.371
MS12	0.0146	1.025	0.693
MS13	0.0121	1.342	0.55
MS14	0.0236	1.284	0.197
MS15	0.0244	0.886	0.231
MS16	Below D/L	0.0565	Below D/L
BA1	0.0074	0.873	0.143
BA2	0.0071	0.851	0.146
BA3	0.0065	0.436	0.246
BA4	0.0079	0.339	0.478
BA5	0.0109	0.702	0.578
BA6	0.0112	1.602	0.662
BA7	0.011	1.403	0.204
BA8	0.0073	1.112	0.279

4.5.2 SPATIAL DISTRIBUTION OF HEAVY METALS IN SURFACE SEDIMENTS

Results of a one-way ANOVA showed that there was no significant difference ($p>0.05$) between the two rivers for each of the heavy metals sampled. The Slangspruit River was not considered in the spatial distribution results as the concentrations showed no trend (i.e. were constant at all three sites). In the Msunduzi River (figure 4.2), site MS1 is one of the most contaminated sites for all of the metals. The source of this pollution may be the Henley Dam, upstream from sites MS1 and MS2. The bottom waters of the dam may be anaerobic (reducing conditions) and thus sequester heavy metals from sediments into the water column which in turn are transported to sampling sites MS1 and MS2, before metals are incorporated into the bottom sediment (Audry *et al.*, 2010). Cd and Ni exhibited a similar distribution pattern. As both metals are not naturally common in the Earth's crust, the sources are

Table 4.2: DWAF targeted water quality guidelines for metal concentrations in water [adapted from (Holmes, 1996a; 1996b; 1996c; 1996d)]

Metal	Aquatic Ecosystems ($\mu\text{g.L}^{-1}$)	Domestic ($\mu\text{g.L}^{-1}$)	Recreational ($\mu\text{g.L}^{-1}$)	Agriculture (Irrigation) (mg.L^{-1})
Cu	0.3 – 1.4	In mg.L^{-1}	No data	≤ 0.2
Pb	0.2 – 1.2	0 - 10	No data	≤ 0.2
Zn	≤ 2	In mg.L^{-1}	No data	≤ 1.0

likely to be anthropogenic (*e.g.* waste from rural residential areas) (Issa *et al.*, 2011; Shanbehzadeh *et al.*, 2014). Cu and Pb also exhibited a similar distribution pattern where the two metals had the highest concentration at sampling site MS12.

Upstream of sampling site MS12 is the Dorpspruit River confluence with Msunduzi River. The Dorpspruit is flanked by industrial complexes on its banks and may account for the elevated metal concentrations at MS12. Cr and Zn were present in the highest concentrations in the sediments. Cr is a relatively common element in the Earth's crust, accounting for the higher concentration levels compared to Cd, Cu, Pb and Ni. Additionally, South African sediments are known to have the largest reservoirs of Cr in the world (Callender, 2003). Zn also had elevated concentrations at sampling sites MS10, MS12, MS14 and MS15, compared to the downstream sites. Zn sources at the four sites may attributed to wastewater treatment effluent, galvanizing and metal manufacturing (Grosbois *et al.*, 2006).

In the Bayne's Spruit (figure 4.3), metal concentrations at sampling site BA1 had expectedly lower concentrations than the downstream sites, as this was in an residential area. Within the manufacturing industry in Pietermaritzburg, the leading industrial sector is metal manufacturing, followed by agricultural (including food processing) and electronic industries (Gemmell and Schmidt, 2013). This may account for the increase in metal deposition in the sediments, at sites BA4 to BA7, compared to upstream sites. Sampling site BA6 is adjacent to and downstream from dense industrial areas from Willowton and Panorama Gardens. Zn concentrations

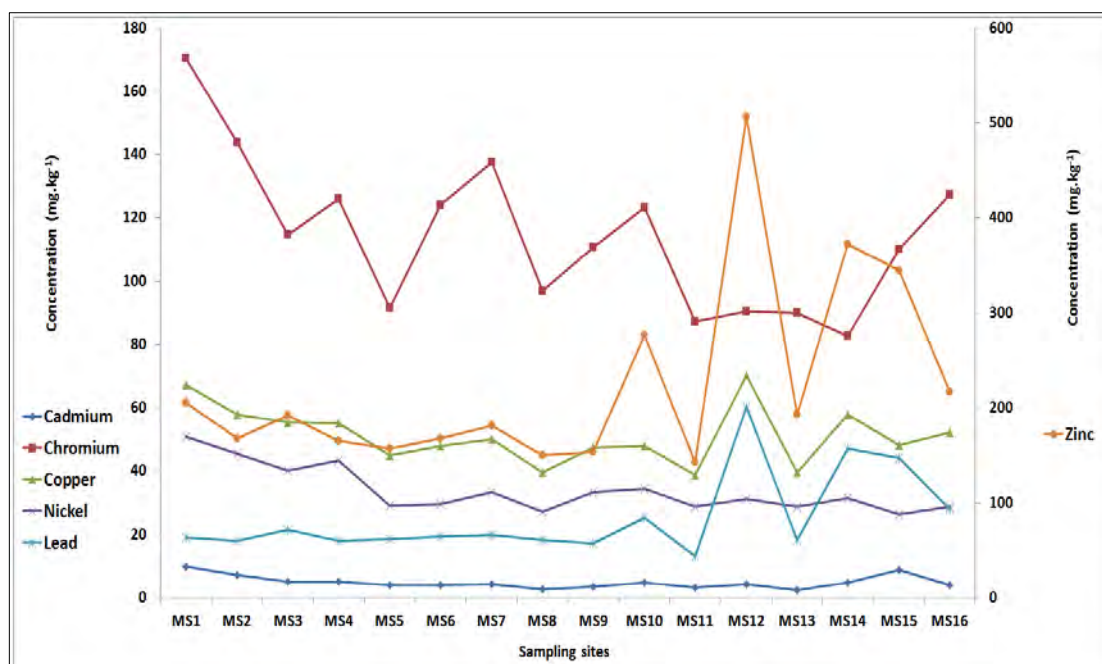


Figure 4.2: Spatial distributions of Cd, Cr, Cu, Ni, Pb and Zn in the surface sediments of the Msunduzi River

were the highest in both rivers and also had the same distribution as that of Cu and Pb where there were noticeable increases at sampling sites MS12 and BA6. This was not expected as the chemistry of Zn is similar to that of Cd, not to Cu and Pb (Connell *et al.*, 1999). Consequently it would be expected that the two metals follow similar spatial distribution patterns. Cr concentrations were variable in both rivers. Industrial and urban activities that historically and recently released metal compounds into the receiving environment are of concern in the catchment.

4.5.3 VERTICAL METAL DISTRIBUTION AND PARTICLE SIZE DISTRIBUTION IN THE SEDIMENT CORE

The sediment core was sampled at site MS8, which is downstream for a metal manufacturing plant. There was no correlation between metal concentrations in the water at MS8 and the sediment core as a high metal concentration in the water sample did not result in the sediments (table 4.3). Particle size distribution (as volume weighted mean), organic matter content and metal concentrations were analysed in the sediment core (figure 4.4). Volume-based results indicate the location of most of the

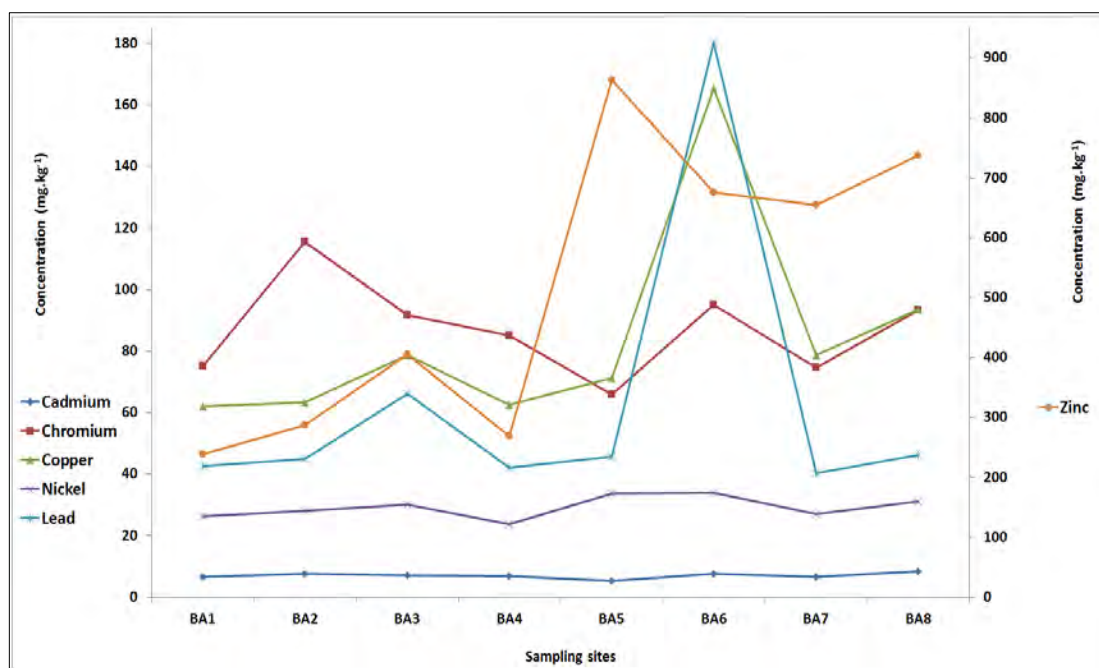


Figure 4.3: Spatial distributions of Cd, Cr, Cu, Ni, Pb and Zn in the surface sediments of the Bayne's Spruit River

mass, in terms of particle sizes, in the sediment core. Results for all metal concentrations and organic matter content % can be found in Appendix C and the raw data for the Volume-based results in Appendix F. The majority of the total particlemass or volume comes from the 500 - 150 μm size fraction. These grain size ranges belong to sand particles (fine to medium). Particle size and metal concentrations did not exhibit a similar trend in terms of distribution patterns. When metal peaked particle size decreased (between 43 – 37 cm) as metals have a greater affinity for small sediment particle sizes.

Table 4.3: Water and surface sediment concentrations at sediment core site MS8

	Cr	Cu	Pb	Ni	Zn
Water ($\mu\text{g.L}^{-1}$)	<0.3	0.019	1.384	<0.5	0.223
Surface sediments (mg.kg^{-1})	97.03	39.66	27.15	18.37	150.1

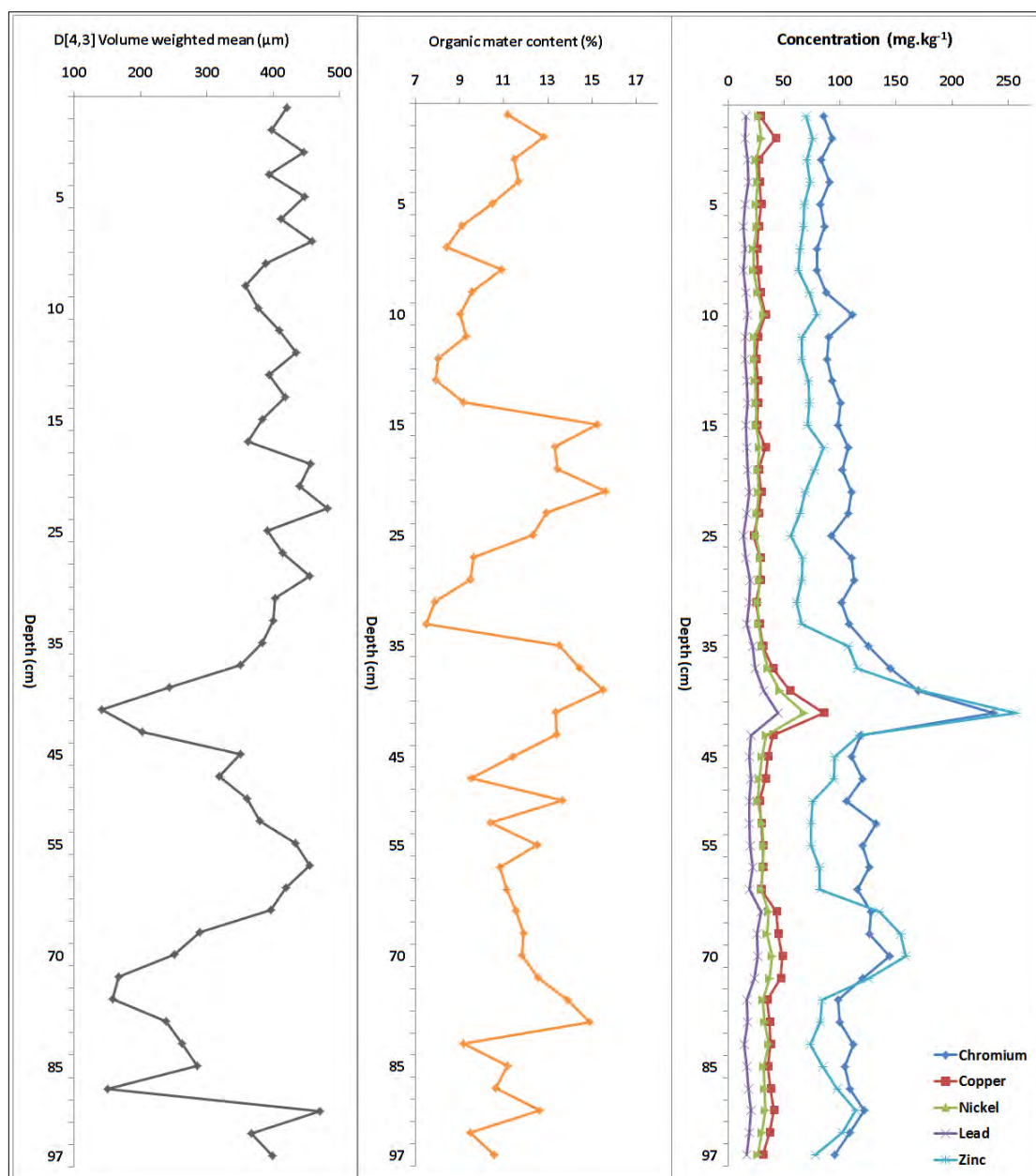


Figure 4.4: Particle size distribution (as volume weighted mean), organic matter content and vertical distribution pattern of Cr, Cu, Ni, Pb and Zn in the MS8 sediment core

Cd concentrations at all depths were $<0.5 \text{ mg.kg}^{-1}$ and results were omitted in the vertical distribution analysis. The metals exhibited a similar vertical distribution pattern (peaks between 76 and 61 cm and between 43 and 37 cm), possibly from industrial activities. Organic matter peaked at 79, 39 and between 23 – 17 cm depths). According to Lin and Chen (1998), organic matters are important scavengers

for metals in river sediments. One would expect the two parameters to have similar distribution patterns. However, the organic matter content fluctuated with depth. The reasons could be analytical error or there were other factors, such as industrial activities or natural environmental conditions, that may have affected organic matter content in the past.

Normalisation is the process of compensating for the granulometric and geochemical factors that influence the natural variation in the heavy metal concentrations (Newman and Watling, 2007). Granulometric analysis was conducted by sieving to the $<90\ \mu\text{m}$ sediment fraction. To determine whether the likely sources of the heavy metals in the sediment core are natural or anthropogenic, geochemical normalisation was performed by normalising metal concentrations (Cr, Cu, Ni, Pb and Zn) with Al (level of statistical inference set at 95%). At depth, normalised concentrations are expected to lie along or between the 95% confidence interval (CI) statistical inference. These concentrations are from metal input from natural sources and depict the natural geochemical and mineralogical makeup of the sediments. Outliers are points where metal concentrations are indicative of anthropogenic activities or where naturally present metals mixed with anthropogenic pollutants (Aleksander-Kwaterczak and Prosowicz, 2007; Newman and Watling, 2007).

The normalisation of Cr, Cu and Ni (figure 4.5) observed fewer outliers (37 – 25 cm) compared to Pb and Zn (figure 4.6). The outliers observed for Cr, Cu and Ni (7 – 1 cm) may be from recently released metals from anthropogenic sources, into the river catchment. Site MS8 is downstream from a tannery and adjacent to a metal manufacturing industry and this may account for the elevated metal concentrations. Particularly for Cu and Ni which are not as naturally abundant in Earth's crust as Cr. Pb and Zn normalised concentrations were mostly present as outliers (79 – 61 cm, 47 – 31 cm and 7 – 1 cm). Possible surficial Pb and Zn sources, and metals deposited at depth, were anthropogenic in nature. In this area, the possible sources may be industry, untreated residential effluent and run-off from land use in the Catchment at upstream sites (Callender, 2003). The rest of the metals that were not normalised were correlated with Al and visually represented in Appendices D and E.

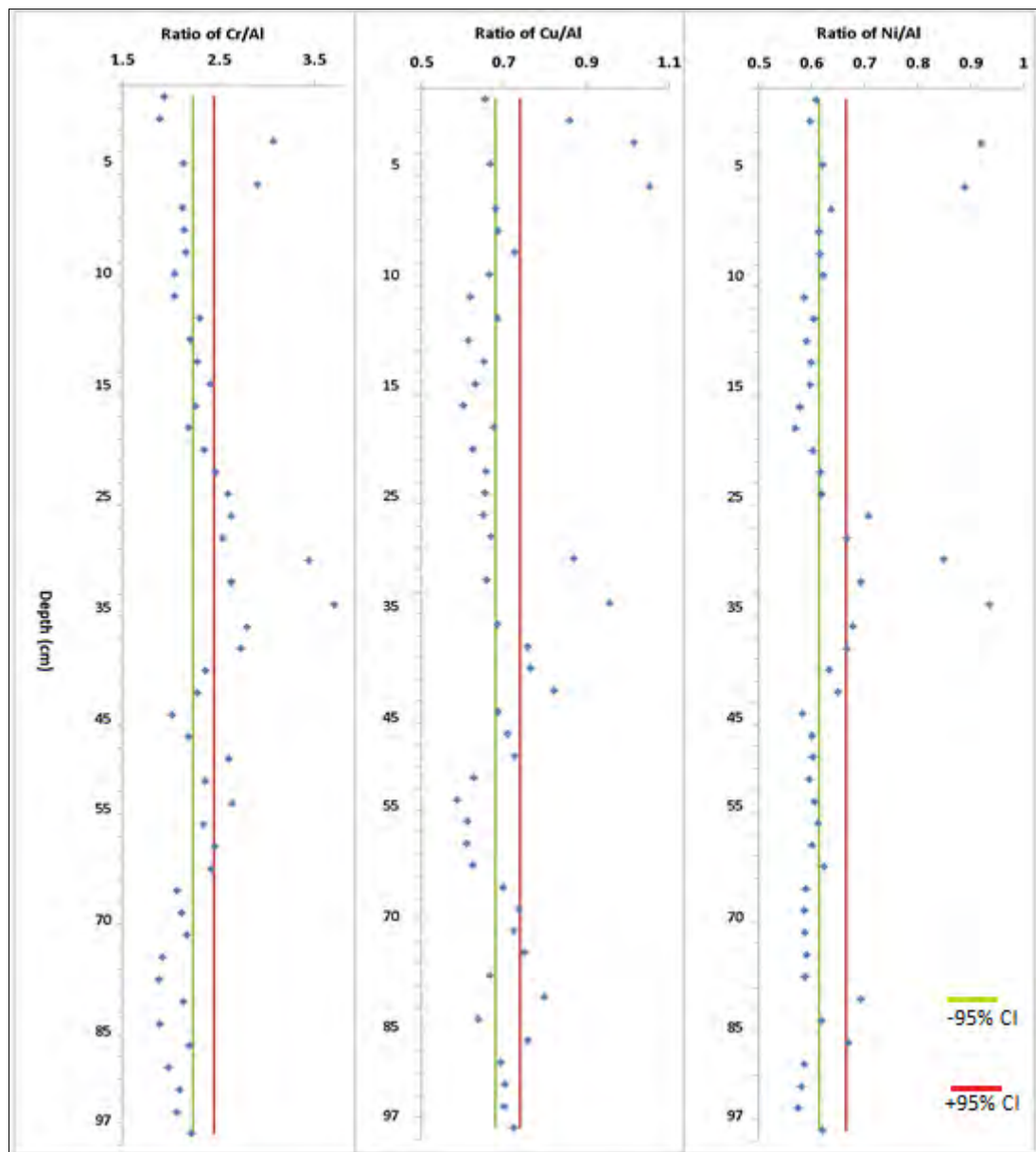


Figure 4.5: Ratio of Cr, Cu and Ni to Al in the MS8 sediment core (+/-95% CI)

4.6 CONCLUSION

Compared to aquatic ecosystem DWAF targeted water quality values, the Bayne's Spruit was the more polluted of the two rivers. This was expected as the catchment of the Bayne's Spruit has more industries compared to the Msunduzi. Metal concentration exceeded the water quality range targeted for a healthy aquatic ecosystem, in terms of heavy metal content. For the sake of the biota in the river,

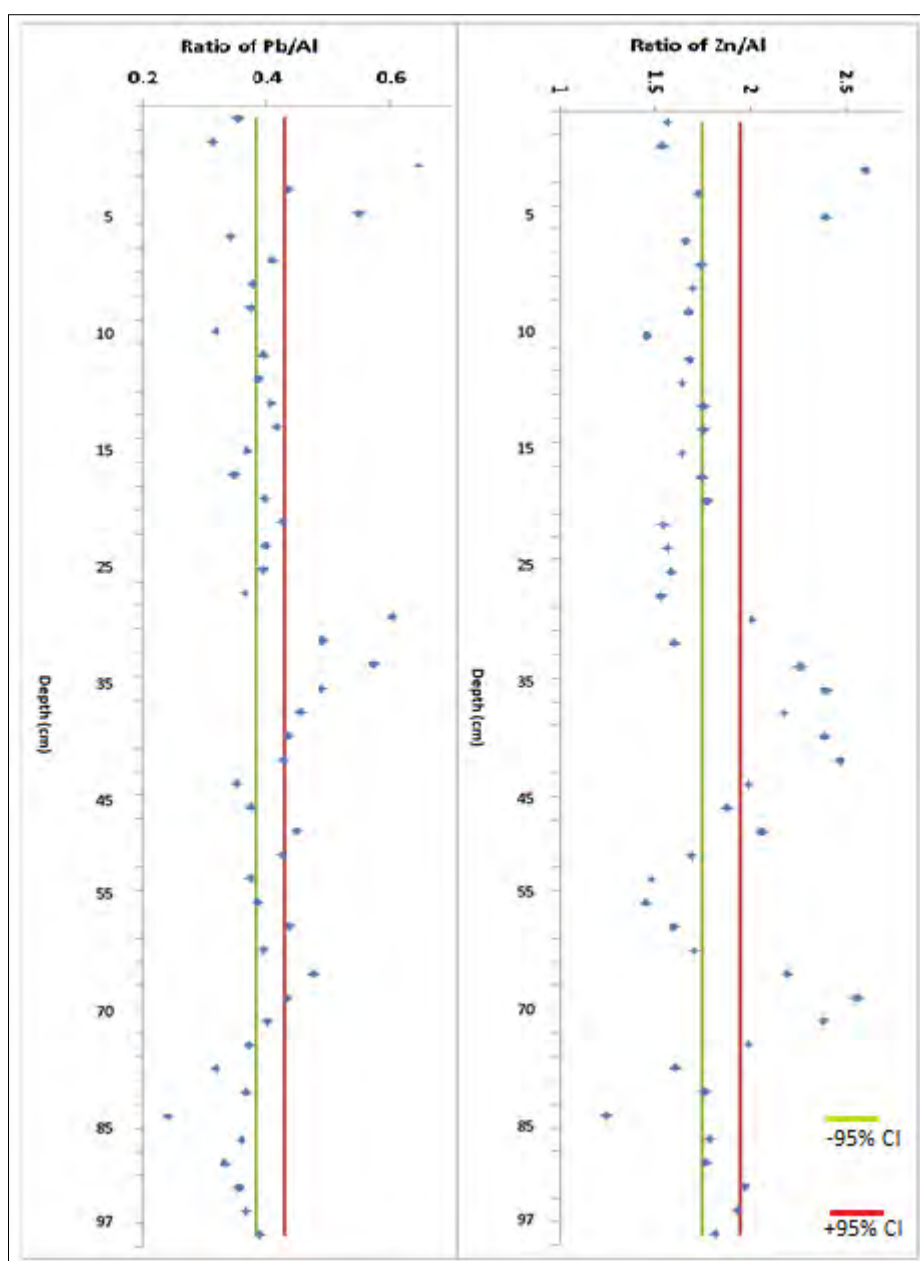


Figure 4.6: Ratio of Ni and Cu to Al in the MS8 sediment core (+/-95% CI)

metal concentrations would have to be decreased to improve ecosystem health. In the Msunduzi and Bayne's Spruit sediments, Zn, Cu and Pb had similar spatial distribution patterns. Cd and Ni had similar patterns while Cr had a different distribution pattern compared to the rest of the metals. However, MS1, MS12 and BA6 had the highest concentrations. The particle size distribution analysis revealed that the sediment core was mainly comprised of medium to fine sands. There was no correlation between organic matter content and vertical metal deposition. There was a

correlation between particle size in the sediment core and metal concentrations in that metals peaked in accordance with reduced particle sizes in the sediment core. Statistical analysis revealed that the sediment core was polluted with Pb and Zn and these were the metals of concern in the surficial sediments as well. The research served as a baseline study for the spatial distribution and vertical deposition heavy metal status of the Msunduzi River Catchment. As this was a result of a once-off sampling event, the measured concentrations only provide a snapshot of the heavy metal status of the catchment. Further research is needed to evaluate the significance of different seasons on metal distribution in the Catchment, and what implication this may have on the biota and of the land uses in the Catchment. Additionally, dating techniques may assist in determining when certain pollution events occurred and a possible reason why.

4.7 ACKNOWLEDGEMENTS

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5 CONCLUSION

Heavy metals concentrations are enriched to toxic levels in the water and sediments of freshwater environments due to anthropogenic activities. Even biologically essential heavy metals (e.g. Zn) can increase to concentrations that are as toxic as low levels of non-essential metals (e.g. Pb). Thus, monitoring heavy metal concentrations is vital to ensure ecosystem and human health. The spatial distribution and historical deposition of heavy metals, cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), as well as potentially mobile forms of the metals, in the Msunduzi River, KwaZulu-Natal, South Africa and two of its tributaries, the Bayne's Spruit and Slangspruit, were investigated. Distribution of metals in water and sediments is controlled by the dynamic interaction with specific physico-chemical, such as redox potential, pH, total dissolved solids (TDS), electrical conductivity (EC), particle size distribution and organic matter content). Metals such as aluminium (Al), iron (Fe) and manganese (Mn) are used for geochemical referencing.

In terms of the physico-chemical parameters, the pH ranged from 5.55 to 7.48 in the Msunduzi River Catchment. For surface waters, pH values typically range between 4 and 11 (Holmes, 1996a, 1996b, 1996c, 1996d). The pH values did not correspond to any increase or decrease in metal concentrations in the catchment. TDS increased along the Msunduzi River, but in the Bayne's Spruit the value only peaked at BA4. EC followed a similar trend to that of TDS as the two parameters have a direct relationship in the environment (van Niekerk *et al.*, 2014). Anthropogenic sources that may lead to increased TDS and EC readings are urban run-off and agricultural practices (Murphy, 2007). In the water, Pb was found to be the metal with the highest concentrations in the Msunduzi and Bayne's Spruit rivers. Zn was the second highest and the lowest was Cu. Cd, Cr and Ni were below the instrument detection limit in all samples. Compared to Department of Water Affairs and Forestry (DWAF) targeted water quality values, Cu concentrations were less than the targeted water quality value in all three rivers. Pb in the Msunduzi and Bayne's Spruit was greater than DWAF aquatic ecosystems guideline values. There are no metal guidelines for water used for

recreational purposes and metals did not exceed targeted water quality values for domestic and agricultural use (Holmes, 1996a, 1996b, 1996c, 1996d). Only the aquatic ecosystem water quality guidelines were exceeded. This may result in adverse effects on organisms in terms of heavy metal toxicity. Interventions are required in the form of improved natural resource management in the catchment, particularly for the industries in the catchment.

Heavy metals that are sequestered between the water column and surface sediments must also be analysed. Total metal concentrations in the surface sediments were compared to sediment quality guidelines (SQG) to investigate its pollution status. Effects Range-Low (ERL) indicates concentrations below which adverse effects rarely occur, or are rarely observed, whilst Effects Range-Median (ERM) values represent concentrations above which adverse effects frequently occur (NOAA, 1999). Total Cd, Cr, Cu, Pb, Ni and Zn were > than the ERL in all three rivers, but only Zn was > ERM. In the Msunduzi and Bayne's Spruit, Zn, Cu and Pb had similar spatial distribution patterns. Cd and Ni had similar distribution patterns. Sampling sites MS1, MS12 and BA6 had the highest metal concentration concentrations. Possible sources of increased concentrations at these sites include industrial and urban discharge into the river water (Moore *et al.*, 2011). Total metal concentrations only indicate the levels at which metals are present in the environment. Speciation analysis reveals the chemical forms that metals are present in. Mobile forms are potentially bioavailable and are toxic to organisms at elevated concentrations (Tessier *et al.*, 1979; Jain, 2004). Metals in the sediment fractions (exchangeable, reducible, oxidisable and residual) were extracted using a sequential extraction procedure. Extracted metal values were validated using a certified reference material (CRM) from the Community of Bureau of Reference (BCR). Organic matter content, redox values and formation of Fe-Mn oxyhydroxides (depicted as total Fe and Mn) are important physico-chemical parameters that assist in evaluating the geochemical partitioning of metals within the four sediment fractions. Metals were primarily associated with the residual fraction except for Pb in all three rivers and Cu and Zn in the Bayne's Spruit. These three metals were also partitioned within the mobile sediment fractions and can be released with decreasing pH, changing redox potential and presence of Fe-Mn oxyhydroxides that facilitate the precipitation of metals (Ure

et al., 1993; John and Leventhal, 1995). Speciation analysis revealed that the Bayne's Spruit is the most polluted river, compared to the Msunduzi and Slangspruit. The Bayne's Spruit had higher concentrations of metals partitioned in the potentially mobile fractions. Should environmental factors change, such as decrease in pH, a change in redox potential and a change in temperature, the metals may be released from these fractions and pollute the overlying water column. Organisms found in the catchment, as well as any humans that come in contact with the water, may be adversely affected.

Historical deposition trends were investigated by collecting a sediment core at site MS8. The vertical distribution pattern was assessed against particle size distribution (as volume weighted mean) and organic matter content of the sediment core. Cr, Cu, Pb, Ni and Zn had a similar vertical profile (peaks between 76 and 61 cm and 43 and 37 cm). There was no relationship between organic matter content and metal distribution (organic matter peaked at 79 cm, 39 cm and 23 – 17 cm depths). The majority of the sediment was composed of very fine to medium sand. The fine sand may account for the increased metal concentrations at certain depth as fine sand is associated with sediments that were transported from upstream sites due to increased flow rate in the river. Increased flow rate can be from a natural phenomenon (flood) or large concentrations of discharged effluent into the Msunduzi (Walling, 2005; Rahman and Plater, 2014). To investigate whether the metals present in the sediment core were from natural or anthropogenic sources, geochemical normalisation was performed by normalising metal concentrations (Cr, Cu, Ni, Pb and Zn) with Al (level of statistical inference set at 95%). Cr, Cu and Ni were from natural sources, but outliers at the 95% confidence interval (CI) revealed possible mixing of natural mineralogical makeup and anthropogenic inputs. Pb and Zn were from anthropogenic sources in the catchment, possibly from metal works and municipal discharge (Callender, 2003). Overall analysis indicated that Pb and Zn were the metals of concern in the catchment and industrial activities had an impact on heavy metal concentrations in the water and sediments. The sources of the metals at depth cannot be determined unless a dating technique is used to identify the exact date (in years) of the pollution events. Mixing of sediments, due to river flow, may also affect the results and this must be taken into account.

The results allowed for the determination of baseline heavy metal levels in the water and sediments of the Msunduzi River Catchment. Further work is recommended in the study area as there is lack of published literature with regards to the heavy metal status. Thus, the current research can add to the overall body of literature on heavy metal pollution in KwaZulu-Natal. Sampling during different seasons may reveal a relationship between seasonal variations in physico-chemical parameters and heavy metal concentration in the water and sediment. As there is possible vertical mixing of river sediments, dating techniques would not be advisable, but regular particle size distribution analysis, of surface sediments and sediment cores, at certain points down the river may reveal information on past and current hydrological and geological patterns of the Msunduzi River Catchment. The results given in this research may require routine water quality monitoring and overall improved catchment management of certain sites. Industrial and municipal effluents discharged into the river should also be monitored to determine the possible sources of anthropogenic heavy metals entering the Msunduzi River Catchment.

The overall aim of the research was to establish heavy metal baseline concentrations. The study of heavy metal distribution (spatial and vertical) and particle size through the Msunduzi River catchment has demonstrated to be a useful tool for gaining understanding about not only the distribution degree of metals but also about their possible pollution sources and the chemical properties that allow them to act as long-term pollutants in water and sediments.

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APPENDICES

Appendix A: Total heavy metal concentrations in the water samples

Site	(in $\mu\text{g.L}^{-1}$)								(in mg.L^{-1})			
	Aluminium (Al)	Barium (Ba)	Copper (Cu)	Iron (Fe)	Manganese (Mn)	Lead (Pb)	Vanadium (V)	Zinc (Zn)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Silicon (Si)
MS1	20.33	20.05	0.0592	24.45	2.035	4.527	2.271	0.81	7.182	4.669	2.17	7.094
MS2	8.533	18.64	0.0564	13.75	0.523	1.697	1.805	0.796	6.755	4.548	1.927	7.074
MS3	7.377	18.2	0.0524	12.05	0.569	0.614	1.909	0.512	7.536	4.879	2.154	7.064
MS4	6.69	20.35	0.0293	17.45	0.296	0.559	2.008	0.215	8.764	5.689	2.655	7.347
MS5	13.35	21.09	0.0286	13	0.826	0.714	1.865	0.37	9.224	5.908	2.812	7.504
MS6	5.677	22.18	0.0272	12.23	0.474	0.687	2.146	0.232	10.2	6.379	3.133	7.625
MS7	10.91	22.54	0.0195	19.52	2.838	3.149	2.232	0.254	10.18	6.37	3.249	7.476
MS8	12.34	23.54	0.019	16.59	1.594	1.384	1.85	0.223	10.63	6.501	3.348	7.386
MS9	11.14	25.6	0.0187	21.85	0.803	0.147	2.007	0.313	13.72	8.215	4.849	7.876
MS10	10.23	22.14	0.0145	13.98	0.555	0.687	2.925	0.457	13.63	8.307	4.42	7.839
MS11	31.27	30.02	0.0139	41.42	30.98	0.714	3.345	0.371	13.72	7.64	4.17	6.966
MS12	7.196	23.6	0.0146	13.98	0.661	1.025	2.955	0.693	13.5	7.781	4.238	7.397
MS13	6.854	23.71	0.0121	12.6	0.132	1.342	2.892	0.55	13.44	7.72	4.283	7.242
MS14	3.67	16.56	0.0236	5.724	3.183	1.284	2.739	0.197	8.573	4.918	2.843	4.483
MS15	20.98	22.56	0.0244	16.34	0.825	0.886	2.546	0.231	15.81	8.093	4.976	7.073
MS16	5.25	22.21	Below D/L	18.05	1.452	0.0565	2.846	Below D/L	27.18	7.323	4.652	5.771

	(in $\mu\text{g.L}^{-1}$)								(in mg.L^{-1})			
Site	Aluminium (Al)	Barium (Ba)	Copper (Cu)	Iron (Fe)	Manganese (Mn)	Lead (Pb)	Vanadium (V)	Zinc (Zn)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Silicon (Si)
BA1	3.741	19.13	0.0074	11.6	1.352	0.873	1.73	0.143	12.98	5.713	4.096	5.432
BA2	2.783	17.42	0.0071	15.01	2.702	0.851	1.84	0.146	12.54	5.274	4.031	4.965
BA3	3.075	19.17	0.0065	30.4	6.291	0.436	1.798	0.246	13.08	5.37	3.9	4.993
BA4	27.21	85.71	0.0079	4.828	2.327	0.339	2.209	0.478	24.95	8.739	6.351	7.515
BA5	2.424	14.12	0.0109	10.83	0.56	0.702	2.018	0.578	14.05	6.243	7.854	5.267
BA6	10.74	15.01	0.0112	114.3	1.38	1.602	1.851	0.662	14.84	6.473	8.522	5.545
BA7	5.489	16.22	0.011	38.77	1.458	1.403	2.065	0.204	15.27	6.66	7.538	5.609
BA8	9.06	22.72	0.0073	15.83	0.825	1.112	2.723	0.279	25.18	7.725	6.398	6.007
SL1	4.685	28.52	0.0098	10.97	0.813	0.657	2.899	0.105	23.12	14.05	2.368	11.73
SL2	3.561	19.53	0.0109	16.78	1.112	0.565	1.959	0.081	13.69	6.376	3.756	6.032
SL3	4.711	31.66	0.011	22.47	1.006	0.789	2.945	0.078	22.82	13.97	8.308	11.52

Note: Cadmium, chromium, cobalt and nickel in the water samples were below the detection limit of the ICP-OES.

Appendix B: Total heavy metal concentrations (in mg.kg-1) in the surface sediment samples

Site	Cd	Cr	Cu	Ni	Pb	Zn	Al	Fe	Mn	Ba	Li	Mg	Na	Si	Co	V
MS1	9.988	170.4	67.23	50.88	18.97	205.7	89026	45181	2329	66.14	49.1	4357	306.6	3.743	37.228	121.7
MS2	7.207	143.7	57.86	45.43	18.13	168.1	79201	40863	509.1	91.93	46.5	2586	260.8	423.5	33.56	418.9
MS3	5.034	114.7	55.56	40.23	21.64	192.1	59411	35615	954.1	83.62	36.5	2911	269	532	27.88	86.84
MS4	5.034	125.9	55.19	43.26	18.05	165.1	55725	36625	953.5	79.98	33.3	3535	287.1	428.8	29.24	84.19
MS5	4.086	91.51	45.08	28.97	18.55	157.4	43899	33226	595.9	48.25	26.5	2663	288.2	570.1	23.37	72.75
MS6	4.023	124.1	47.88	29.61	19.50	167.7	39126	34286	821.1	102.3	25	2998	286.4	516.9	24.67	87.30
MS7	4.213	137.6	50.18	33.48	19.80	181.4	49441	33856	101.7	68.47	31	3252	302.5	537.9	26.14	74.89
MS8	2.781	97.03	39.65	27.15	18.36	150.0	35738	29518	570.2	82.44	23.3	2503	237	538.8	19.92	60.44
MS9	3.611	110.7	47.41	33.27	17.17	153.4	46163	32586	739.1	63.57	30.7	2646	255.4	414.9	25.97	72.45
MS10	4.794	123.3	47.92	34.46	25.17	276.1	32388	31447	779.2	146.3	16.5	2560	168	180.2	25.74	58.41
MS11	3.275	87.34	38.70	28.66	13.28	142.8	45140	30597	940.5	47.26	34.6	2689	335	246.2	26.32	67.92
MS12	4.185	90.41	70.23	31.13	60.33	505.9	43051	31617	846.5	75.13	29.9	2627	262.7	447.9	21.31	61.03
MS13	2.402	89.95	39.46	28.72	18.41	192.64	45230	26199	438.3	42.18	32.5	2320	294.1	330.3	22.54	70.08
MS14	4.895	82.78	57.92	31.61	47.13	372.5	28244	31567	955	154.1	20.6	1900	101.9	87.7	21.64	56.69
MS15	8.954	110.1	48.27	26.35	44.21	344.3	34553	38494	972.5	69.83	22.9	2745	310.9	412.3	26.19	91.28
MS16	4.115	127.4	52.16	28.831	27.88	216.8	39099	30037	638.3	64.99	28	2583	303.9	413.7	21.52	60.63
BA1	6.588	75.18	62.06	26.22	42.52	237.9	29140	37435	990.1	162.5	16.4	2779	145.9	17.5	18.55	59.97
BA2	7.491	115.4	63.19	28.04	44.8	287.4	27780	39884	1644	184.4	21.1	3791	144.3	9.5	19.08	67.05
BA3	7.002	91.69	78.72	30.05	66.1	404.9	28610	38324	1698	175.8	16.1	2797	162.6	299.4	19.36	64.11

Site	Cd	Cr	Cu	Ni	Pb	Zn	Al	Fe	Mn	Ba	Li	Mg	Na	Si	Co	V
BA4	6.804	84.92	62.48	23.72	42.2	269.1	22560	37634	1039	133.2	18	1917	124.9	19.3	17.53	64.7
BA5	5.126	65.77	71.3	33.65	45.59	863.9	26210	31517	1386	162.9	20.3	2687	184.3	51.7	16.54	50.19
BA6	7.672	95.06	165.4	33.98	180.2	675.3	29850	36105	629.6	216	16.4	2549	178.3	32.3	22.44	63.2
BA7	6.491	74.5	78.56	27.05	40.4	654.7	26730	37445	1080	203.9	21.4	2539	151.6	17.5	22.38	62.52
BA8	8.27	93.11	93.48	31.17	46.06	737.5	28450	42672	778.3	421.2	17.2	2761	184.4	154.8	23.79	72.85
SL1	6.006	97.31	66.33	38.56	28.44	168.9	49270	36415	2675	48.89	40.9	3811	402.1	263.6	38.09	90.22
SL2	6.336	101	62.21	38.41	29.03	165.1	47730	37195	2999	38.83	38.8	3579	409.6	350.2	42.61	86.34
SL3	5.795	98.98	65.69	36.93	24.45	177.1	49070	35255	2147	53.47	40.9	3618	392.3	393.3	33.45	80.85

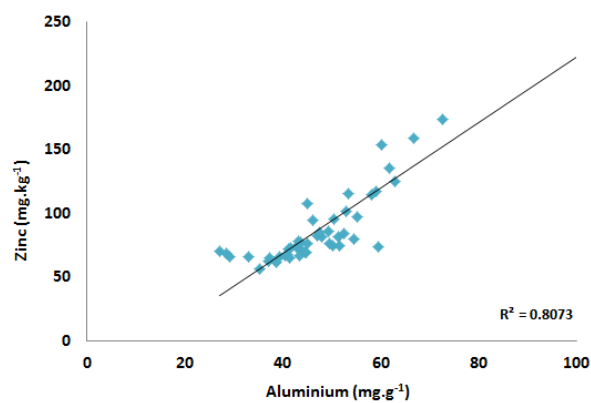
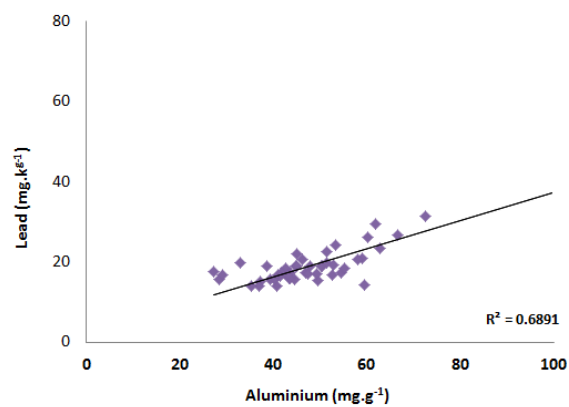
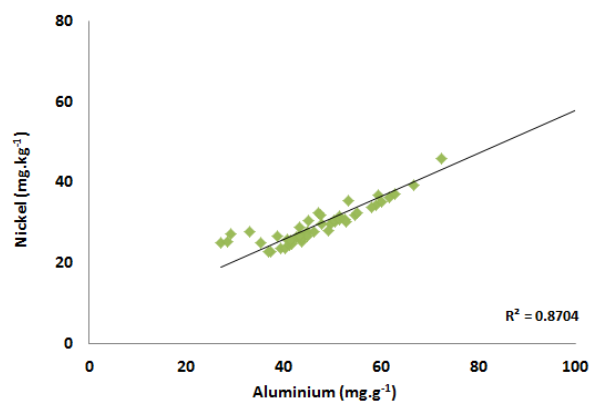
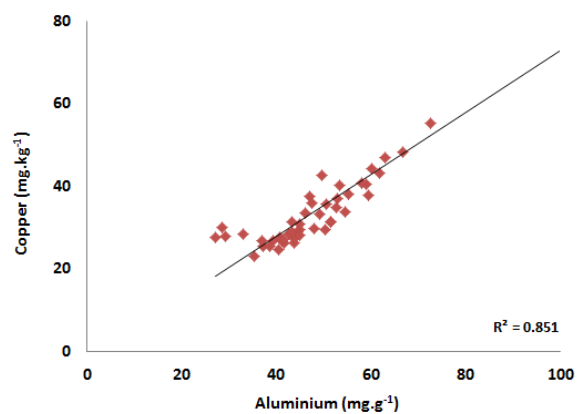
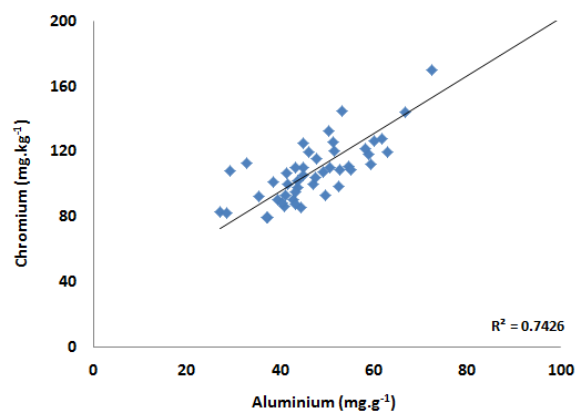
Appendix C: Total metal concentrations in the sediment core and organic matter content

(in mg.g ⁻¹)			(in mg.kg ⁻¹)											Organic matter (%)
Depth (cm)	Al	Fe	Al	Fe	Co	Cr	Cu	Ni	Pb	Zn	Mg	Mn	V	
0-1	44	41	44450	40590	17	86	29	27	16	70	2267	413	84	11.18
1-2	50	47	49530	47320	18	93	43	30	16	76	2428	441	87	12.81
2-3	27	36	27140	36270	16	83	28	25	18	71	1998	394	68	11.46
3-4	43	38	42650	38070	17	91	28	26	19	74	2208	409	80	11.68
4-5	28	36	28420	35600	16	82	30	25	16	68	2006	463	53	10.47
5-6	41	39	40780	38830	17	86	28	26	14	68	2165	459	79	9.099
6-7	37	34	37220	33620	16	80	26	23	15	65	2015	387	77	8.427
7-8	37	35	36960	34820	16	80	27	23	14	63	2005	387	74	10.92
8-9	43	40	43230	40120	18	88	29	27	16	72	2243	426	81	9.557
9-10	55	50	54580	50260	19	111	34	32	17	79	2547	458	88	9.045
10-11	39	38	39350	37830	16	90	27	24	16	66	2053	363	75	9.314
11-12	40	39	40330	38660	15	89	25	24	16	66	2057	368	77	8.025
12-13	41	40	41080	39570	16	93	27	25	17	72	2127	375	78	7.902
13-14	42	40	41620	39790	17	100	26	25	17	73	2127	377	82	9.178
14-15	44	41	43620	40660	17	98	26	25	16	72	2143	392	75	15.23
15-17	49	47	49190	47410	18	107	33	28	17	86	2229	446	80	13.32
17-19	44	41	43630	40980	17	102	27	26	17	77	2162	408	80	13.42
19-21	45	42	44840	42100	19	110	29	28	19	69	2185	437	86	15.62
21-23	41	40	41390	39960	18	107	27	26	17	65	2099	430	84	12.95
23-25	35	31	35320	31080	16	93	23	25	14	56	1956	372	70	12.33
25-27	43	42	43350	41960	18	110	29	29	16	66	2200	480	79	9.638
27-29	33	36	32870	35940	19	113	29	28	20	66	2024	543	70	9.495

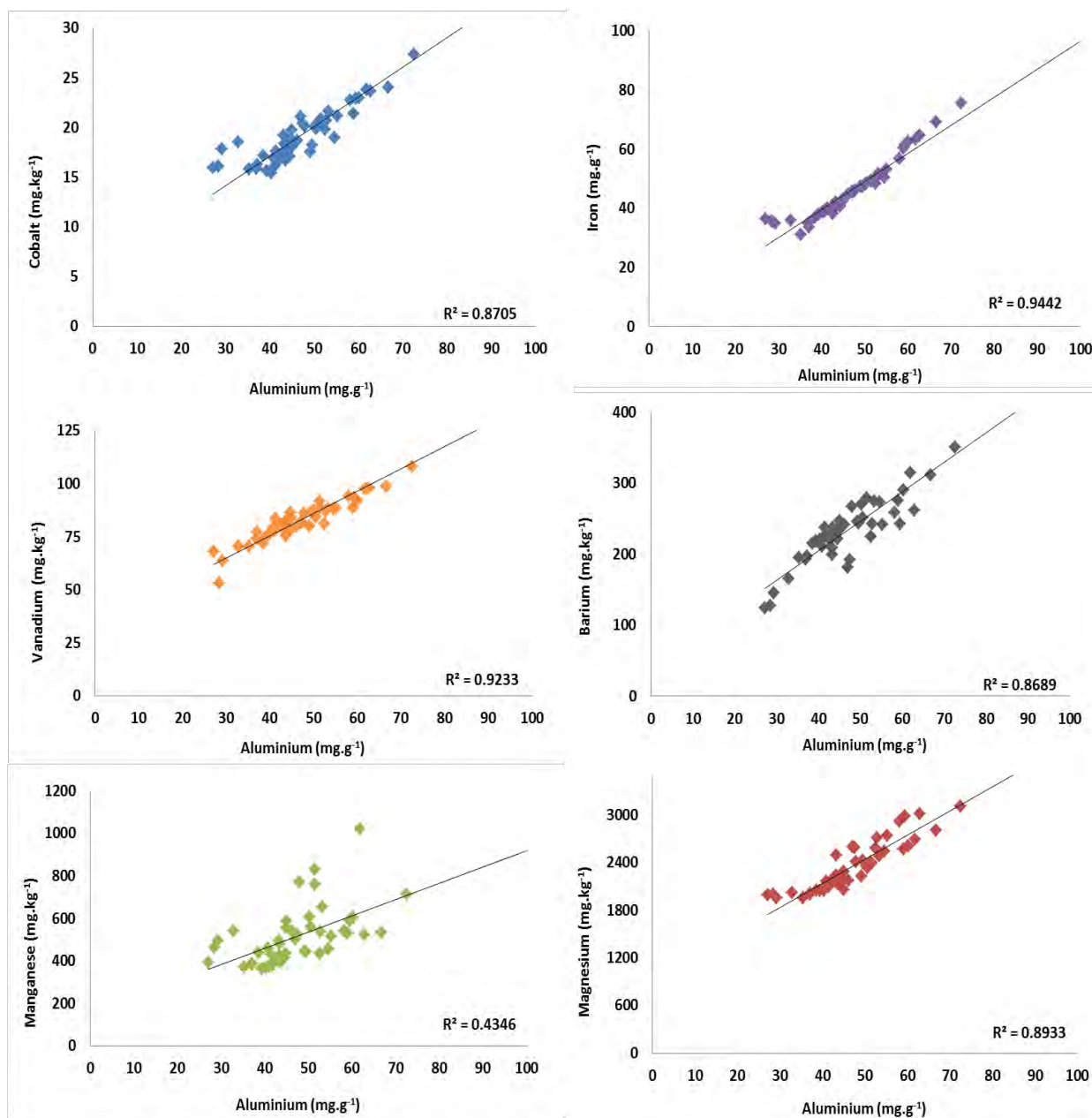
	(in mg.g ⁻¹)		(in mg.kg ⁻¹)											
Depth (cm)	Al	Fe	Al	Fe	Co	Cr	Cu	Ni	Pb	Zn	Mg	Mn	V	Organic matter (%)
29-31	39	37	38570	36800	17	101	25	27	19	62	2050	439	72	7.877
31-33	29	35	29200	34730	18	108	28	27	17	66	1960	495	64	7.511
33-35	45	43	44950	42980	20	126	31	31	22	108	2291	588	84	13.52
35-37	53	52	53280	51710	22	145	40	36	24	116	2490	655	88	14.41
37-39	72	75	72490	75420	27	171	55	46	32	173	3119	713	108	15.48
39-41	104	98	104300	97850	40	238	86	68	45	257	4230	956	153	13.36
41-43	59	60	58980	60350	21	119	41	34	21	117	2577	533	88	13.40
43-45	51	48	50500	48490	20	110	36	30	19	95	2335	561	84	11.41
45-47	46	44	46150	44390	19	120	34	28	21	95	2173	541	80	9.528
47-49	45	43	44920	42570	18	106	28	27	19	76	2064	555	78	13.67
49-52	50	48	50250	48170	20	133	30	31	19	75	2370	610	87	10.42
52-55	52	49	51510	49090	21	121	32	32	20	74	2393	761	92	12.51
55-58	51	49	51420	49250	21	126	31	31	22	82	2413	830	89	10.82
58-61	48	46	47840	45920	20	116	30	30	19	81	2414	772	86	11.14
61-64	62	63	61800	63260	24	128	43	36	29	135	2694	1023	97	11.55
64-67	60	62	60150	62470	23	127	44	35	26	154	2617	605	92	11.89
67-70	67	69	66670	69230	24	144	48	39	27	159	2814	533	99	11.82
70-73	63	65	62820	64660	24	120	47	37	23	125	3018	525	98	12.57
73-76	53	48	52520	48210	20	99	35	31	17	84	2583	435	81	13.91
76-79	47	46	47010	45520	21	100	38	33	17	82	2599	504	81	14.87
79-82	59	61	59380	61270	23	112	38	37	14	74	2989	592	94	9.186
82-85	47	45	47470	45430	20	104	36	32	17	85	2598	524	82	11.17
85-88	55	53	55170	53040	21	109	38	32	18	97	2744	515	88	10.65
88-91	58	57	58110	56750	23	122	41	34	21	114	2928	541	94	12.63

	(in mg.g ⁻¹)		(in mg.kg ⁻¹)											
Depth (cm)	Al	Fe	Al	Fe	Co	Cr	Cu	Ni	Pb	Zn	Mg	Mn	V	Organic matter (%)
91-94	53	50	52800	50390	21	109	37	30	19	102	2714	537	87	9.494
94-97	43	40	43200	40060	19	96	31	27	17	78	2494	496	80	10.58

Appendix D: Correlation of Cr, Cu, Ni, Pb and Zn with Al in the sediment core



Appendix E: Correlation of Co, Fe, V, Ba, Mn and Mg with Al in the sediment core



Appendix F: Volume-based particle size distribution analysis and parameters

Note: Particle absorption index = 1

Depth (cm)	d (0.1)	d (0.2)	d (0.5)	d (0.8)	d (0.9)	D [3,2] Surface weighted mean	D [4,3] Volume weighted mean	Obscuration
0-1	87.325	186.914	377.51	635.297	802.3	147.177	420.487	11.26
1-2	51.624	113.341	344.176	637.534	826.92	100.227	398.695	13.74
2-3	77.589	193.768	410.175	678.662	846.489	129.26	446.601	11.45
3-4	86.287	188.763	365.222	588.186	725.839	140.717	394.145	10.6
4-5	133.291	230.75	412.967	656.888	809.409	174.094	447.85	10.2
5-6	168.889	232.744	380.628	584.952	711.137	230.171	412.037	11.76
6-7	107.448	214.578	417.646	687.193	857.593	146.147	458.653	13.29
7-8	54.7	164.724	362.042	596.004	738.168	78.141	388.929	16.25
8-9	64.4	141.743	328.793	554.231	688.842	123.322	358.8	12.13
9-10	63.047	150.941	347.073	579.188	721.507	108.368	377.077	11.8
10-11	103.189	194.765	378.755	611.089	750.439	155.726	409.207	11.33
11-12	188.788	256.365	408.191	612.985	736.336	198.176	435.063	12.16
12-13	97.672	172.606	363.325	597.952	735.885	153.711	394.611	14.94
13-14	160.213	236.413	391.93	598.541	723.617	183.558	418.473	11.88
14-15	94.486	196.359	364.336	566.117	683.849	144.541	384.114	11.99
15-17	92.191	182.852	340.04	537.243	654.619	124.299	363.009	12.93
17-19	228.283	285.152	428.388	623.6	739.047	248.68	456.211	11.12
19-21	163.844	256.252	421.018	628.625	748.761	178.286	440.554	12.56
21-23	248.087	302.367	447.656	650.212	770.537	401.687	481.692	9.69
23-25	148.336	214.441	363.487	563.622	683.99	192.289	392.125	12.05
25-27	164.132	232.563	385.75	592.459	717.194	194.627	414.799	11.58
27-29	193.895	264.847	426.822	643.093	770.869	211.791	454.941	11.1
29-31	154.32	217.853	370.919	580.863	706.832	226.12	403.259	12.37
31-33	155.31	221.373	372.166	574.861	695.53	215.122	400.853	11.69
33-35	136.391	209.744	358.51	554.685	672.124	180.36	384.078	11.94
35-37	108.855	185.194	326.715	512.158	624.216	142.675	350.33	11.36
37-39	23.812	49.279	196.554	419.32	544.935	37.542	243.428	13.61
39-41	13.865	28.548	86.188	242.427	358.949	20.957	142.345	14.61

Depth (cm)	d (0.1)	d (0.2)	d (0.5)	d (0.8)	d (0.9)	D [3,2] Surface weighted mean	D [4,3] Volume weighted mean	Obscuration
41-43	21.451	41.083	137.755	358.634	484.043	33.048	203.155	14.57
43-45	72.963	160.861	328.851	528.054	645.733	122.208	350.695	10.35
45-47	83.992	145.975	288.199	478.487	596.15	137.799	318.52	11.1
47-49	115.936	181.84	330.164	529.814	652.576	177.556	361.123	10.32
49-52	157.954	217.08	354.103	539.86	651.224	217.975	380.613	11.77
52-55	199.686	262.826	409.55	602.898	715.709	282.709	434.236	10.03
55-58	211.344	278.306	432.123	630.659	744.092	272.842	454.84	9.75
58-61	91.229	207.243	396.471	626.344	761.227	119.388	419.997	13.34
61-64	39.536	140.404	354.11	615.712	790.204	55.414	397.108	12.07
64-67	19.851	41.815	237.397	507.074	662.149	30.664	290.14	14.42
67-70	17.342	35.661	153.901	458.455	628.256	28.416	251.995	13.87
70-73	11.346	24.141	80.24	296.107	473.399	17.951	167.889	20.7
73-76	15.609	30.846	87.585	232.73	403.859	23.079	159.007	11.36
76-79	33.859	69.237	186.098	387.894	523.513	57.088	238.415	10.7
79-82	30.378	68.197	199.015	447.406	591.06	44.773	262.441	12.23
82-85	34.385	74.78	236.123	471.364	617.751	56.398	286.135	11.38
85-88	24.139	42.51	101.244	225.408	338.62	34.869	150.416	11.58
88-91	179.671	262.447	437.683	674.797	820.741	222.346	471.023	10.47
91-94	59.886	142.701	338.333	566.57	704.946	108.3	367.107	10.66
94-97	44.165	159.266	383.723	613.825	749.813	68.623	399.783	13.41