CHEMICAL SPECIATION AND SPATIAL DISTRIBUTION OF HEAVY METALS AND THEIR ADSORPTION ONTO SEDIMENTS OF THE BERG RIVER, SOUTH AFRICA

Thesis Presented for the Degree of

DOCTOR OF PHILOSOPHY

By

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DEDICATION

To my family, I would never have gone this far without your concern and support.

DECLARATION

I, Mustafa Benamer hereby declare that the work on which this thesis is based is my original work (except where acknowledgements indicate otherwise) and that neither the whole work nor any part of it has been, is being, or is to be submitted for another degree in this or any other university, I authorise the University to reproduce for the purpose of research either the whole or any portion of the contents in any manner whatsoever.

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CONFERENCES

This work has been presented at the following conferences;

- South African Chemical Institute Conference; December 2013 in East London at WSU University; Chemical speciation, mobility and bioavailability of heavy metals in core sediments from the Berg River and its estuary, Western Cape, South Africa. The poster presentation won the first prize for the best poster presentation at the conference.

- Vertical distribution of heavy metals and sediment characteristics in core sediment from the Berg River and its estuary. East and Southern Africa Environmental Chemistry (ESAECC) and the 10TH Theoretical Chemistry in Africa (TCCA) Conference; April 2014 at University of Venda, Thohoyandou, South Africa.

  A poster was presented at this conference

- Chemical speciation of heavy metals and their adsorption onto sediments of the Berg River and its estuary. International conference in integrated Management of Environment (ICIME); September 2014, Hammamet, Tunisia.

  A poster was also presented at this conference

ABSTRACT

The Berg River, Western Cape, South Africa, is an example of a catchment region where human pressures and conservation of natural resources collide. The river receives effluents from two large settlements and several smaller adjacent villages, including that of industrial and extensive agricultural activity. The estuary is one of the largest in South Africa and rated as the third most important conservation zone in the country. In this study, the chemical speciation of heavy metals in the river sediment was determined in order to evaluate the extent of pollution.

Chemical speciation using sequential chemical extraction of sediment samples was used to measure the mobility and bioavailability of cadmium (Cd), lead (Pb), arsenic (As), chromium (Cr), nickel (Ni), cobalt (Co), iron (Fe), copper (Cu), zinc (Zn) and manganese (Mn). The metals Cd and Zn were found to be the most mobile and bioavailable.

The study also examined the vertical distribution of heavy metals in estuarine sediment cores to evaluate the extent of heavy metal contamination with time and the degree to which heavy metals are influenced by other sedimentological parameters such as grain size, sediment composition and organic matter. Three sediment cores, ranging from 160 to 240 cm long, were collected using a mechanical vibrating corer. The vertical distribution of metals in the cores showed that the metal concentration was higher at the top and middle of the cores. Based on the enrichment factor (EF) and anthropogenic factor (AF) values, it is suggested that the sediments of the estuary are not polluted with Co, Mn, Cu, Ni, Zn and Fe but moderately to highly polluted with Pb, As, Cd and Cr. The data reported provide a useful baseline for establishing heavy metal concentrations in the estuary and will be an important consideration in future sediment quality studies.

The spatial distribution of the metals was also studied to understand how location is linked to metal concentration. The average concentration of metals in the core sediment increased with increasing distance from the mouth of the river.

The adsorption behaviour of the estuary sediment with micro-pollutants has a significant influence on the environmental quality of estuary waters. For this reason, the absorption of Pb, Cr, Cu, Ni, and Zn onto sediment was study. It was found that the sediments of the Berg River estuary have a low potential for adsorbtion of Ni and Zn making these metals more mobile and bioavailable.

LIST OF ABBREVIATIONS

AF	Anthropogenic Factor
AMD	Acid Mining Drainage
ANZECC	Australian and New Zealand Environment and Conservation Council
BCR	Community Bureau of Reference
CAPE	Cape Action for People and the Environment
CBSQG	Consensus-Based Sediment Quality Guidelines
CCME	Canadian Council of Ministers of the Environment
DEAT	Department of Environmental Affairs and Tourism
DWAF	Department of Water Affairs and Forestry
EF	Enrichment Factor
GWP	Global Water Partnership
IAFA	International Atomic Energy Agency
ICP-OES	Inductive Coupled Plasma Optical Emission Spectroscopy
I_{geo}	Geochemical Index
ISQGs	International Sediment Quality Guidelines
LOI	Loss-On-Ignition
LOD	Loss-On-Drying
MP-AES	Microwave Plasma Atomic Emission Spectrometer United State
NAS	National Academy of Sciences
PTFE	Polytetrafluoroethylene
SA.EPA	South Australia Environment Protection Authority
SES	Sequential Extraction Scheme
US.EPA	United Nation Environmental Pollution
WHO	World Health Organization
WMA	Water Management Area
WRC	Water and Rivers Commission (South Africa)
$10^6\,m^3.y^{-1}$	million cubic per year

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THESIS OUTLINE

The thesis report is divided into the following chapters:

Chapter one presents the background of the thesis research about environment problems due to heavy metals and their chemistry, also the research hypothesis, and objectives of the study. The chapter also presents literature review of studies conducted by the other researches, in which this research problem was referred to.

Chapter two focuses on the methodology employed to achieve the objectives of the study. It discusses the experiments that were conducted and also describes the study area, sampling sites, samples collection, storage, procedures, apparatus, adsorption experiments and quality control.

Chapter three focuses on the results that were obtained from the determination of chemical speciation, vertical and spatial distribution of heavy metals in sediments of the Berg River and its estuary. It covers findings on the sediment characteristics and organic matter. It also covers the data obtained from the adsorption experiments.

Chapter four focuses on the discussion of the results that obtained from the determination of chemical speciation, vertical and spatial distribution of heavy metals in sediment. It also includes the analysis of the results obtained from adsorption experiments, and data from the isotherm models are discussed at the end of the chapter. In addition to this, the chapter presents correlation coefficient between heavy metals and sediment characteristics.

Chapter five gives a general conclusion of the present study. It provides observations, conclusions and recommendations for future work. It highlights the outcomes that were obtained from the study.

1.1 General problems of heavy metals

Rivers are a valuable freshwater resource, irreplaceable, and priceless asset providing critical habitats and corridors for nature conservation, recreation, amenity and economic growth. A river which comprises both the main course and the tributaries is a complex ecological system carrying a load of matter in dissolved and particulate phases from natural and anthropogenic sources (Bellos *et al.*, 2004).

The water quality in rivers may vary depending on the geological morphology, vegetation and land use (modification by human activities such as agriculture, industrialization and urbanization) in the catchment areas. Industries, agriculture and urban settlements produce nutrients (sewage effluent and fertilizers) and toxic substances, such as organic and inorganic pollutants, and other chemicals including heavy metals. Water pollution in rivers occurs when these substances, which degrade the water quality of the river, enter the waterway and alter their natural function (Water and Rivers Commission, 1997).

Environmental problems related to heavy metals have a long history. Many rivers and streams have become contaminated with heavy metals, as a result of human activities (Akcay *et al.*, 2003; Fatoki & Awofolu, 2003). Entry of heavy metals into rivers and streams can occur naturally from leaching of ore deposits and anthropogenic sources, such as atmospheric deposition, domestic wastewater effluents, and wash-off from urban areas, industrial sites, solid waste disposal units and agricultural materials. These sources tend to have high concentrations of metals particularly As, Cd, Cr, Cu, Mn, Ni, Pb and Zn (Nriagu & Pacyna, 1988; Alloway & Ayres, 1993; Pegram & Gorgens, 2001).

Agriculture activities contributes non-point sources of heavy metal pollutants, such as impurities in fertilizers (Cd, Cr, Pb and Zn), pesticides (As, Cu, Pb and Zn), desiccants, wood preservatives (As and Cu), wastes from intensive pig and poultry production (As and Cu), composts and manures (As, Cd, Cu, Ni, Pb and Zn), sewage sludge (Cd, Cu, Ni, Pb and Zn) and corrosion of metal objects (Cd and Zn) (Alloway and Ayres, 1993). In many African countries, heavy metal contaminants are now a significant health issue. As a result of the growth in agricultural and industrial development, African aquatic environments are in particularly experiencing increasingly heavy metal pollution, (Lwanga et al., 2003 and Berg et al., 1995). For this reason, many researchers have focused on and reported on the assessment of heavy metal concentrations in the environment (Zhai et al., 2008 and Razo et al., 2004). However, currently most data on heavy metals in African countries are the result of regional investigations that have been limited to the area around the source of the heavy metals (Aguilar et al., 2002). Surveys of heavy metals across the whole country and comprehensive analyses, which include economic activities, are needed to clarify the impact of these chemicals on humans and wildlife. This will further allow for the protection and management of the environment in African countries.

South Africa is rich in mineral resources such as ores of many metals (Thomas, 2007). The main environmental problem relating to mining is uncontrolled discharge of contaminated water from abandoned mines as well as acid mine drainage (Pulles et al., 2005). Acid mine drainage (AMD) is characterized by low pH and high salinity levels, and it can elevate concentration of toxic heavy metals such as Cd, Cr, Co, Mn, Ni, Zn and Fe (Akcil and Koldas, 2006). South Africa is a country that is predominantly semi-arid, with an average rainfall of about 450 $mm.y^{-1}$, well below the world average of about 860 mm. y^{-1}. South Africa's water resources are, in global terms, extremely scarce, with the combined flow of the entire rivers approximately 49000 $x10^6$ m^3. y^{-1}. This number is less than half of that of the Zambezi River, the largest river close to South Africa (DWAF, 2004-g). As a result, heavy metal pollution in South Africa's aquatic ecosystems, especially river systems, is a major environmental concern (Boocock, 2002).

As a result of the high fresh water demand in relation to supply, the water inflow (including floods) reaching South Africa's estuaries and adjacent marine environment has been markedly reduced. This poses a significant threat to the functioning of many estuarine systems and hence to life-cycles of many fish and invertebrate species with an obligate estuarine phase in their life cycles (Lamberth and Turpie, 2003). During the 1970s concern also grew regarding the conditions of estuaries in South Africa. Water abstraction, dam construction soil erosion and pollution also were clearly affecting more and more estuaries. The ecological functioning and sustainability of estuarine systems are affected by the reduction in fresh water inflows (CSIR, 1998; DWAF, 2002, 2003a, 2003b, 2003c, 2004e, 2004f, and 2004h). Effects include an increase in the frequency of mouth closure of temporarily open/closed estuaries, increase in the extent of saline intrusion in permanently open systems, and increase of siltation in estuaries.

In South Africa, there is increasing tendency for the disposal of sewage to the estuaries, surf zone and marine environment ranges from preliminarily treated sewage discharged offshore and where secondary treated effluent discharges to the surf zone and estuaries to untreated sewage entering the marine environment from informal settlements through storm water runoff (RSA DWAF, 1995). According to CSIR (1991) and DWAF (2004), the estimated annual volumes of sewage effluent discharges into estuaries to the marine environment of South Africa between 1991 and 2004 ranged from 21.4 to 55.5×10^6 $m^3.\ y^{-1}$ respectively. The estimated volumes for municipal wastewater (point sources) discharged into estuaries ranged from 35 500 to 152 123 $x10^6$ m^3 /day (Taljaard et al., 2006). Thus, total wastewater and sewage volumes discharged to estuaries and then to the marine environment almost doubled and tripled between 1991 and 2004. In a comparison of the health status of 27 South African estuaries, assessed in the 1990s according to Whitfield (1995 and 2000) and more recently by Turpie (2004), showed a decline in the health of six of the estuaries that were evaluated. However, it was also concluded that many of South Africa's estuaries are still considered to be in a relatively safe state.

In the past, water quality techniques assessment were the main tool used to assess the impact that humans have on the environment. However, soil and sediments are also prone to contamination from atmospheric and biological sources. In South Africa, this indicator of pollution is not intensively investigated in comparison to the water resources component. Poor water quality does not only affect associated sediments and aquatic life but also has an impact on terrestrial ecosystems and even on the economy.

1.2 The Berg River

The Berg River is one of the largest rivers in the Western Cape Province, is situated within the Berg Management Area (WMA), and lies in a region which is categorized as a biodiversity hotspot on the Southern African continent (Goldblatt and Manning, 2002). Due to human development, such as increasing agricultural activities and increasing urbanization, ecosystems in the area are steadily impacted upon by increasing anthropogenic pressures, such as higher nutrient inputs, unsustainable water management practices, and, as a consequence, reductions in biodiversity (Rouget et al., 2003). More details on the Berg River will explained in the Section 2.1.

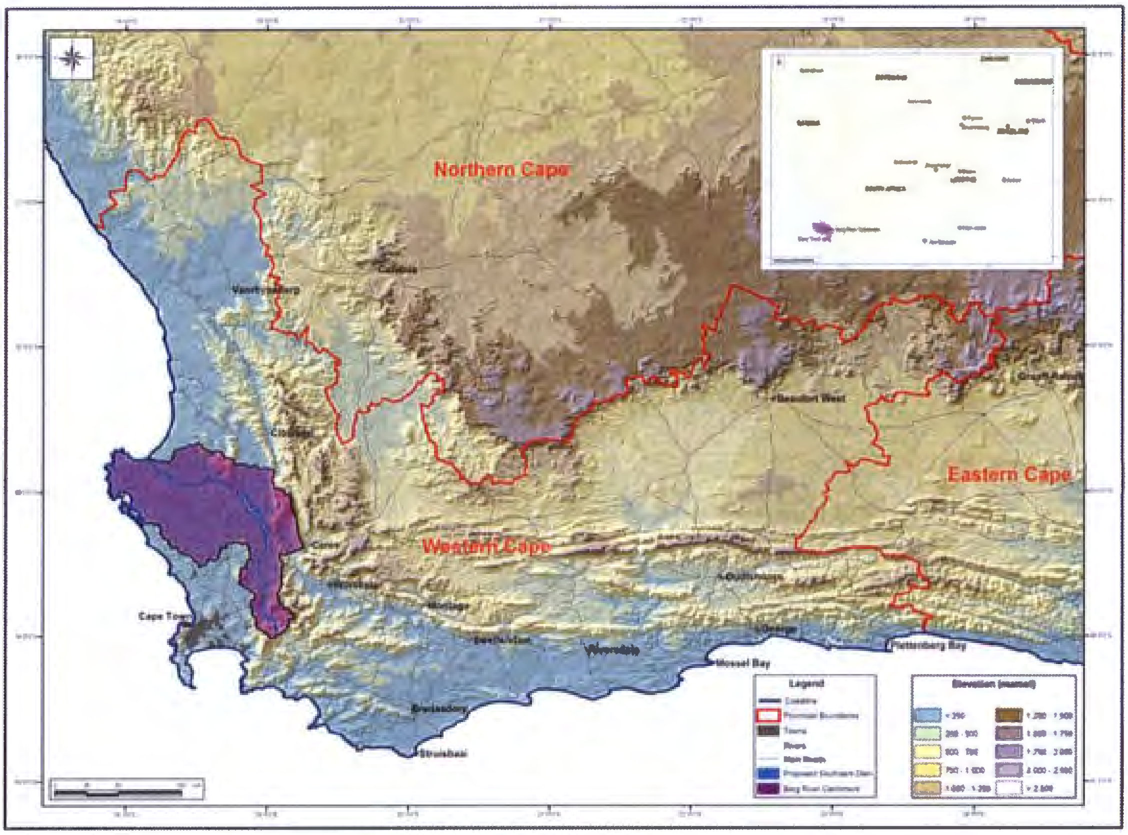

Figure 1.2 Location of the Berg River catchment (Source: Parsons 2007).

The natural runoff from the catchment amounts to 931 x10^6 $m^3.y^{-1}$, nearly half of which (45%) is generated in the top three quaternary catchments which cover 7% of the area. There are already two major dams in the catchment, the Wemmershoek Dam (66 x10^6 m^3) and the Voelvlei Dam (170 mm^3), and numerous small farm dams. These, together with forested areas of the catchment, have reduced the runoff to some 682 x10^6 $m^3.y^{-1}$ (DWAF, 2004b). Flow and quality features have been severely modified, with dry season releases, inter-basin transfers and agricultural return flows exacerbating the effects of abstraction from the system. Low flows in the Berg River vary from 0.2 to 2.0 $m^3.s^{-1}$ in summer (Nov-Feb) and 4 to 15 $m^3.s^{-1}$ in winter (May-Aug). During floods, flows reach 150 to 600 $m^3.s^{-1}$ along the river (DWAF, 2004b).

In this region, most of the rivers arise in the Table Mountain Group mountain watershed, with good water quality and with total dissolved solids concentrations of less than 60 $mg.L^{-1}$. The Berg River rises in the mountains near Franschhoek, and the runoff in this vicinity is characterized by good water quality (Bate and Snow, 2007). However, water quality deteriorates further in a downstream as a result of agricultural activities, urban storm water, discharges from wastewater treatment works, and runoff from low cost housing and informal settlements that often have no sanitation services or dysfunctional systems. Certain of the head waters of the Berg River are normally acidic and colored brown as a result of dissolved humic substances. Many of the lower Berg River tributaries are underlain by Malmesbury shale of marine origin, therefore have generally high salinity concentrations (DWAF, 2004b). The shale, coupled with agricultural return flows, introduces elevated salinity levels in the middle and lower reaches of the Berg River.

The river is nowadays impacted by both diffuse pollution from agricultural run-off and point-source pollution from urban and industrial wastewater. There are concerns that pesticide residue washed into the river through irrigation and leaching of fertilizers as a result of irrigation, are impacting on the water quality of the Berg River and its tributaries. Fortunately, there is no mining activity in the vicinity of the river although South Africa is among the World's largest producers of metals such as Cr and Mn. The construction of a dam on the headwaters of the Berg River in 2007 and other impoundments have the potential to change the hydrology of the upper catchment. It was reported that the volume of flow and flow characteristics would be most pronounced at Paarl, nearly 80 kms downstream from the dam, would be a significant effect on the sediment and water volumes between Paarl and Hermon (Clark and Ratcliffe, 2007).

The Berg River estuary, the site of interest research is one of only four perennial estuarine systems on the west coast of South Africa, and one of the largest of the country's approximately 258 functional estuaries. It is a river-dominated estuary and is one of only three estuaries in which muddy sediments are deposited seaward of the mouth (Cooper, 2001). It is also fairly unusual because it has a very large supratidal zone in association with the upper reaches of the estuary. The estuary is rated among the top three estuaries in South Africa in terms of its conservation value of the rarity in physical type, its large size and high diversity and abundance of biota (Turpie et al., 2002 and 2004). It is also recognised as one of the important estuaries in the country for avifauna (Turpie, 1995). It supports nationally important populations of several species (fish, invertebrates and vegetation). About 35 fish species from 30 families have been recorded in the Berg River estuary, and it also supports the highest recorded density of shore birds on the East Atlantic seaboard (Velasquez et al., 1991 and Hockey et al., 1992), while 92 water bird species have been recorded in the estuary over the past 10 years.

There is a scarcity of data on the sediments of the Berg River estuary or historical sedimentation processes such as geochemistry, sedimentation of the subsurface sediments and sedimentation record. Estuaries contain a mixture of river and marine sediments, the balance of which is determined by the size of the tidal prism (amount of water moving in and out of the estuary during a tidal cycle), riverine base flows and floods. The size of particles that can be transported from the catchment increases with increased velocity and larger particles are deposited first before small particles eventually precipitated with decreased flow. Base flows carry relatively little sediment, mostly fine silts, and this is deposited when fresh water flows are slowed by the incoming sea water.

The Berg River estuary waters are well-oxygenated during the year particularly in the winter. On average about 5 $mg.L^{-1}$ of dissolved oxygen concentration has been recorded in the summer and 9-10 $mg.L^{-1}$ in the winter (Schumann, 2007). Nutrients (phosphate, nitrate and silicate) enter the estuary from both the sea (inputs dominating in the summer) and the river (inputs dominating in the winter) as a result of agricultural inputs and runoff. The total nitrogen concentration was 300 $\mu g.L^{-1}$ in 1980 and 2000 $\mu g.L^{-1}$ in 2005 (Day, 2007). High concentrations of phosphate and silicate were observed in the estuary due to the anthropogenic inputs of nutrients along the estuary and catchment activities (domestic and industrial). These are the main factors influencing water quality of the Berg River and its estuary. River water quality integrates these anthropogenic influences at a catchment scale.

Organic matter also flocculates out of the fresh water when it mixes with salt water. These processes probably result in an accumulation of fine sediments in the lower to middle estuary, so that the channel and inter-tidal areas become muddier and shallower with time. Floods take much of silt from the catchment, and this is deposited wherever flood waters slow down significantly, such as on the flood plain. Floods scour away the sediments that have built up in the channel and the lower inter-tidal areas, and very large floods may scour the flood plain. The area of scouring versus deposition is likely to depend on the size of the flood (Clark and Ractliffe, 2007).

During the summer low-flow period, saline water penetrates the estuary up to 40 km from the mouth, this depending on the tidal state while the fresh water inflow to the estuary during winter is sufficient to push the salt water entering the estuary back to within

10 km from the mouth (Slinger and Taljaard, 1994). Salinity is assumed to decrease with increased flow, but there is little effect at low flows when the tidal flow is stronger. Higher flows push salt water out of the estuary. Salinity affects the species composition of all of the biotic components, with different species having different salinity tolerance ranges. When Fourie and Gorgens (1977) examined the mineralization of the Berg River, their study showed that the salinity increase of the river could be the result of increasing irrigation practices along the river.

Temperature is fairly uniform along the estuary during winter, typically 12-15 °C (Schuman, 2007). Maximum temperatures are experienced in January and minimum usually occur in July (DWAF, 1994). In the summer, the river water is warmer than the sea, and temperatures are typically above 20°C throughout the estuary except in the lowest reaches. Temperature in the lower estuary varies with tidal state, and can be as low as 12 °C after upwelling at sea.

Anthropogenic inputs of heavy metals along the estuary channel include runoff from adjacent farmland, waste water from human settlements along the banks of the estuary concentrated mostly around the mouth, and effluent from industries situated near the mouth of the estuary. Waste water (domestic and industrial) tends to be rich in toxic compounds and can act as an important contributor of these pollutants to the estuary (DWAF, 2007). Development around the Berg River over the last few decades has also taken its toll on the natural habitats of the estuary. In particular, salt marshes have been significantly transformed and threatened by anthropogenic disturbance (O'Callaghan 1994 and McDowell, 1993).

1.3 Heavy metals

Over the past two decades, the term "heavy metals" has been used increasingly in different literature and legislation related to toxic compounds and the safe use of chemicals. It is often used as a group name for metals and metalloids that have been associated with contamination and potential toxicity (Duffus, 2002). Usually the term "heavy metals" is used inconsistently to replace the name "trace metals."

There are many different definitions for the term "heavy metals" in the environmental literature. The term "heavy metals" is based on the density (specific gravity), atomic weight (relative atomic mass), atomic number and toxicity of the metals. According to the International Union of Pure and Applied Chemistry (IUPAC) the term "trace metals" defines metals in very low concentration, in mass fraction of a part per million or less, in some specified source (e.g. soil, sediment, plant, tissue and ground water).

One definition as given by Jennett et al. (1980) and Davies (1992) is that "heavy metal" is a term that includes any element with an atomic density greater than 5 g/cm^3 and may include some 39 elements. Within the context of this broad category, major metals such as Na, K, Ca, and Mg are not usually considered to be heavy metals due to their lighter atomic mass and prevalence within the natural environment. Metals such as Al, As, Cr, Co, Cu, Fe, Mn, Mo, Ni, Sc, Sn, V and Zn may be required by some organisms in small quantities and are sometimes referred to as trace metals or trace elements (Thornton, 1995).

The most useful definition for the purposes of this study is Thornton's (1995) definition of heavy metals, includes any metal or metalloid that is associated with contamination and potential toxicity. Heavy metals are most commonly associated with human-induced contamination of the aquatic environment including As, Cd, Pb, Hg, Cr, Cu, Ni, and Zn (Jennett et al., 1980). According to Jennett (1968), the term "trace metal" is used to denote those metals that are distributed in the earth's crust, in very low concentrations. The general elements of this group are Cd, Cr, Co, Cu, Pb, Ni and Zn. Fe and Mn also often find a place in the study of trace metals, as the environmental chemistry of the trace metals are closely related to that of heavy metals.

Aluminium falls outside most definitions of heavy metals due to its density (3 g/cm^3) but is often included in contamination studies because it can serve as an indicator of clay content (Daskalakis and O'Connor, 1995). It also has a high natural concentration that causes Al to exhibit conservative behaviour in estuarine systems (de Groot, 1995). Consequently, it tends to have relatively constant concentrations over space and time (Purton and Statham, 1990). This property makes Al useful in normalizing total metals according to natural levels of enrichment (Menon et al., 1998). Arsenic is technically considered a metalloid but is often regarded as a heavy metal due to its similarity in chemical properties and behaviour to other heavy metals.

Lastly, Fe and Mn are not usually considered as contaminants because of their high, naturally occurring concentrations (Chen et al., 1999). Under certain soil conditions, however, such as strong reducing, anoxic conditions, toxicity of these metals are a concern (Williams et al., 1994). A group of non-essential elements including Ag, Au, Cd, Hg and Pb also qualify as heavy metals (Furness and Rainbow, 1990). In this study, all the metals (As, Cd, Pb, , Cr, Cu, Mn, Co, Fe, Ni, and Zn) are considered as heavy metals rather than trace metals in order to avoid confusion.

1.4 Heavy metals-pollution and toxicity

Pollution from heavy metals began with the industrial revolution at the end of the 19th century resulting in the fluxes of many heavy metals from terrestrial and atmospheric sources to the aquatic environment have increased (Brannvall et al., 2007). The pollution by trace metals is a worldwide problem requiring attention at global and national levels. In recent years, there has been growing interest in studying the environmental turnover of metal species. Analytical techniques have been developed for the determination of inorganic turnover of metal species and organic forms of the metals in different environmental matrices (Haraldsson et al., 1994).

Not all metals have the same environmental impact. Some are potent toxins, and some are essential trace elements, and for some the eco-toxicological properties are not well known (Jonsson, 2000). The first of these categories includes metals such as Pb, Hg, As and Cd. These metals are considered to be among the severe pollutants under natural conditions because of their persistent and bioaccumulation properties, especially with respect to such ecosystems as rivers or other industrialized coastal areas that receive chronic inputs of these metals (Tam and Wong, 2000). They are also classified as priority pollutants because these metals are not necessary for metabolic activity, and can be toxic even in small concentrations (US-EPA, 1999).

The second category includes metals that are required for living organisms, and also includes these most widely used in society, such as Fe, Cu and Zn. These metals are major constituents of the so-called technosphere. The third category includes metals such as platinum (Pt), rhodium (Rh) and iridium (Ir), metals that are increasingly used in catalysts and electronic components, but whose effects on the environment are not well studied.

Contamination caused by heavy metals also affects the ocean waters and coastal zone, where, besides having a longer residence time, metal concentrations are higher due to the input and transport by river runoff. The impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to urban areas. Trace metals from incoming tidal water and fresh water sources are rapidly removed from the water body and are deposited onto the sediments (Guzman and Garcia, 2002).

Since heavy metals cannot be degraded biologically, they are transferred and concentrated into plant tissues from soil or sediments, and can have a long-term damaging effect on plants. Heavy metals, that accumulate in soils and sediment not only exert deleterious effects on plant growth, but also inhibit the soil microbial communities and soil fertility (Ong Che, 1999). Chemical pollution by heavy metals can also cause mass mortality of fish stocks, decline or changes in the composition of fish populations or an entire ecosystem, an increase in fish disease and decline in growth rates (UNEP, 1996).

This thesis focuses on total concentration of heavy metals and chemical speciation in sediments of the Berg River and its estuary. Ten heavy metals are investigated; these include Cd, , Pb, As, Cr, Cu, Co, Ni, Mn, Fe and Zn. This group includes very toxic three metals (Cd, As and Pb) that still constitute a dangerous to the environment and to public health, even though they have given rise to extensive concern environmental amongst for a long time (Abel, 1996).

1.5 Chemical speciation of heavy metals and their partitioning in sediment

Due to the presence of empty *d* orbital's in transition metal ions and *f* orbitals in lanthanides and actinides, these metals exist in various oxidation states. For this reason, the metal ions occur in the environment in different oxidation states, and form different species, for example, for chromium, Cr (III) and Cr (VI). The different oxidation states of a particular metal ion possess different physical and chemical properties. Speciation is a concept frequently used in biological science, and it was adopted by those in analytical chemistry, expressing the idea that the specific chemical forms of an element should be considered individually (Frank, 1997).

The term chemical speciation may be used to encompass both functionally defined speciation and that is, the determination of species that are, for example, available to plants or present as 'exchangeable' forms, and operationally defined speciation, which refers to the determination of 'extractable forms' of an element. Whilst it is often possible to define a particular compound or oxidation state when dealing with solutions, for example, natural waters, it is far more difficult to characterize the actual chemical form of an element in solids such as soils and sediments. Thus, speciation tends to be defined somewhat differently by workers to reflect this field of study. However, one of the most comprehensive formal definitions of speciation is the one recommended by the International Union of Pure and Applied Chemistry (IUPAC), which states that speciation, is the process yielding evidence of the atomic or molecular form of an analyte (Templeton et al., 2000).

The definitions of species and speciation of elements are based on many different levels of atomic and molecular structure where species' differences are manifest. Here, two levels were considered: electronic or oxidation state and inorganic and organic compounds. The chemical speciation of elements in aquatic environments is one of the most important topics in the fields of analytical chemistry, geochemistry, and environmental chemistry (Bernhard et al., 1986a). It is essential for discussing the chemical reactivity of trace constituents in the environment, such as biological availability and toxicity, and the geochemical behavior of chemical species. Chemical speciation analysis has also become important in heavy metal research to understand the different processes that control metal distribution in aquatic environments and the risks associated with metal pollution (Donat et al., 1994).

There are a number of important environmental factors which may affect the speciation of metals in the environment and these should be borne in mind during speciation research. One of the most important of these is the prevailing redox conditions which not only determine the oxidation state of some metals, but may also affect the bioavailability and toxicity of the element. For example, Fe (II) and Mn (II) are soluble in natural waters deficient in oxygen but will precipitate out at higher oxidation states.

Speciation studies are also important in estuary systems because metal speciation is affected by the change of environmental conditions such as salinity, pH, temperature, and sediment redox potential (Gambrell et al., 1980). High salinity gradients strongly affect the extent of chloride complexation to Cu (II), Cd (II) and Hg (II).

Hydrogen ion concentration (pH) is also a most important factor controlling chemical speciation of metals. pH affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubility under the pH conditions prevailing in natural water. Because the concentration of hydroxide ion is directly related to pH, the solubility of dissolved metal hydroxide minerals increases with decreasing pH, and more dissolved metals become potentially available for incorporation in biological processes as pH decreases. Ionic metal species also are the most toxic form to aquatic organisms (Salomons, 1995). Temperature exerts a significant influence on metal speciation, because most chemical reaction rates are highly sensitive to temperature changes (Elder, 1989).

Aquatic systems are physically and chemically dynamic. The ability to determine the chemical forms of metal ions in sediment is becoming increasingly important, in identifying sources and sinks for aquatic metal constituents. It is also important in the identification and quantification of the metal associations in sediments (suspended and bottom) and the reactions among sediment, water, and biota (Rauret et al., 1991).

A search of the literature on sedimentary chemical partitioning shows that two approaches have been used. The first approach aims at determining how trace metals are retained on or by sediments - the so-called mechanistic approach. According to Gibbs (1977), there are many mechanisms for inorganic accumulation in or on sediments; adsorption processes, precipitation, co-precipitation with hydrous iron and manganese oxides and carbonates and incorporation in crystalline minerals.

Adsorption will be discussed in Section 1.6. Precipitation and co-precipitation are readily understandable terms. Incorporation in crystal minerals is also called substitution. These entail the substitution of one element for another within a fixed crystal structure; substitution is governed by ionic radius and charge.

The second approach seeks to determine where inorganic constituents are retained on or by sediments (phase or site) - the so-called phase approach. This has been attempted because individual constituents such as Cd, Pb, Fe, Mn, Zn, Ni, Co, and Cu may be, and usually are associated with many phases. The term phase is used in the thermodynamic sense and incorporates categories like interstitial water, clay minerals, sulfides, carbonates, humic acid, manganese oxides, and so forth.

Despite this relatively simple division into two approaches, very few attempts to chemically partition complex sediment samples entail a purely mechanistic or phase approach; rather, they combine features of both.

One of the oldest and most commonly used methods of chemically partitioning sediments involves the use of partial chemical extractions. Much of the original work in different areas was carried out on marine material (Chester & Messiah-Hanna, 1970; Horowitz, 1974; Horowitz & Cronan, 1976; Tessier et al., 1979). The principle of this process is based on the selective extraction of trace metals in different physicochemical fractions of material using specific solvents (Bruder-Hubscher et al., 2002). These techniques have also been widely used in a range of environmental media, involving sediments (Tokalioglu et al., 2000; Petit & Ruccandio, 1999; Fytianos et al., 1995; Martin et al., 1998; Stephens et al., 2001; Steve et al., 2001; Tuzen., 2003; Guevara-Riba et al., 2004; Yuan et al., 2004) soil (Davidson et al., 1998; Mossop & Davidson, 2003; Fernandez et al., 2004) and waste materials (Alonso et al., 2002; Brudet-Hubscher et al., 2002).

In order to optimize sequential extraction of metals in relation to the characteristics of the sediments or to distinguish the two metal fractions in the oxidizable fraction, the methods have been modified by many researchers (Campanella et al., 1995; Zdenek., 1996; Gomez-Ariza et al., 2002). In order to harmonize the different sequential extraction methods used for sediment analysis, in 1992, the BCR 3-step, procedure was proposed (Sahuquillo et al., 1999). This method consists of three successive steps that allows one to associate the metals with one of the following fractions:

Fraction 1 (acid-soluble phase)

This fraction is comprised of exchangeable metals and others bound to carbonates that can easily enter the water column when, for example, the pH decreases. This is a fraction with the most labile union to the sediment and, therefore, the most dangerous for aquatic systems.

Fraction 2 (reducible phase)

This fraction is made up of metals associated with iron and manganese oxides that can free themselves if the conditions of the sediment change from oxic to anoxic. A change to anoxic conditions can be caused, for instance, by the activity of microorganisms present in sediments.

Fraction 3 (oxidizable phase)

This fraction shows the amount of metal bound to the organic matter and sulphides that can be freed under oxidizing conditions. These conditions occur, for example, as a result of sediment re-suspension (due to current and flooding) when the sediment particles come into contact with oxygen-rich water.

Furthermore, a fourth residual or inert phase was determined; this is the difference between the total content and the sum of the content in the three previous fractions. The metals that primarily correspond to this fraction are those associated with minerals, which form part of their crystalline structure, and which, as a result are unlikely to be released from the sediments.

In the study not only were the total amounts of ten metals (Cd, As, Pb, Hg, Cr, Co, Cu, Fe, Ni, and Zn) determined in sediment cores of the Berg River and its estuary, but metal fractionation was also determined. Fractionation studies the mobility and bioavailability of these metals in the sediments that affect their ability to enter the water under changes in the environmental conditions of the Berg River and its estuary.

1.6 Adsorption of heavy metals on to sediment

Conventionally, adsorption is accepted as a phenomenon where molecules of contaminants dissolve in water attach themselves the surface of individual sediment particles (Sparks, 2003). Adsorption process entails the condensation of atoms, ions, or molecules on the surface of another substance. Materials having large surface areas are good adsorbers (Jenne, 1976). In our case, the surface sediment is the 'adsorbent' and the metal ion concentrated or adsorbed on the surface of bed sediment is "adsorbate." On this basis, the sediment particles are referred to as "the adsorbent."

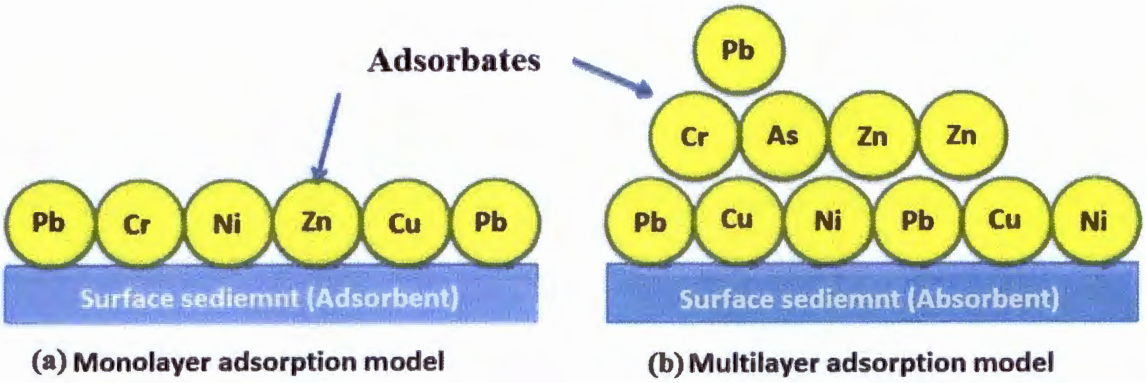

Figure 1.6 Adsorption models showing (a) the monolayer adsorption models assumed by Langmuir Theory and (b) the multilayer adsorption model assumed by BET Theory

Adsorption of heavy metals on sediment constituents is one of the most important reactions that determine the mobility and bioavailability of metals in aquatic environments. Adsorption properties of the sediment provide valuable information relating to the tolerance of the system to the added heavy metal load. Many rivers and estuaries highly populated areas contain anomalously high concentration of metals. The metal concentrations in river water vary with flow as well as sediment concentrations. The metal load of sediments reaches high levels that it is sudden desorption which poses a great danger to aquatic life (Salomons and Forstner, 1984). Therefore, adsorption and desorption processes influence the water quality to a considerable extent. Earlier studies have identified three of the most important geochemical components affecting bioavailability in aquatic systems: Mn oxides, Fe oxides and organic materials (Lion et al., 1982; Perret et al., 2000). These effects are crucial for binding and adsorption of metals onto the surface of sediments, indicated by different analytical methods that will be used in the research such as sequential extraction (Lion et al., 1982 and Chartier et al., 2000). Furthermore, correlation analysis will also be used (Wang and Chen, 2000). Lastly, the combination of chemical extraction and adsorption techniques have been used (Lion et al., 1982 and Fujiyoshi et al., 1994). Many technologies have also been developed to remove toxic metals from water using different material. The most important of these include adsorption, ion exchange and reverse osmosis.

In this thesis, adsorption studies were carried out on sediment of the Berg River estuary because adsorption plays an important role in the transport of metals in aquatic systems but no data is available regarding the adsorption of metals on to these sediments.

The primary factors controlling adsorption process include chemical speciation, sediment type and environmental parameter as pH.

1.7 Aquatic sediments

1.7.1 Sediment transport in riverine environment

Sediments are integral and inseparable parts of the river ecosystem, therefore any environmental program concerning river water quality would be incomplete without the proper study of its sediments. Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of a water body (US.EPA, 2002).

Consequently, bottom sediments act as both carrier and long-term source of contaminants in the aquatic environment. They not only play an important role in influencing river pollution but can be used to record the history of this pollution, and they also reflect the quality of an aquatic system (Mucha et al., 2003). Sediment contaminants can be passed to fish, birds, and mammals until they accumulate to levels that may be toxic. Such toxic effects may include neurological, developmental, and reproductive impacts. Toxic chemicals such as heavy metals come from point and nonpoint sources (US.EPA, 1998). These contaminants may pose a high risk to the environment on a large scale and hence need to be monitored at regular intervals.

Sediment is the most important reservoir of pollutants and acts as a source of trace contamination (Salomons and Forstner, 1984). Sediments give an indication of potential contamination on a temporal scale. The analysis of water indicates the contamination status at present, whereas sediment can provide information on the systems contamination history (Shine, 2004). Sediment is also an important component of coastal aquatic ecosystems since it provides a necessary habitat for communities of autotrophic and heterotrophic organisms, and bacteria (MacDonald et al., 2003). As such, sediment is essential to the functioning of 'healthy' coastal aquatic ecosystems (Burton, 1991). Coastal waters receive contaminants from local anthropogenic activities through riverine inputs, amongst other factors. Within these waters the contaminants partition between aqueous phase (pore water and overlying water) and solid phase (sediment, suspended particulate matter and organisms (Luoma, 1983).

1.7.2 Sediment transport in the Estuarine Environment

In general, estuaries are areas of accretion where sediment deposition and movement is driven by vertical and horizontal circulation patterns within the water body (Salomons and Forstner, 1984). The sediment distribution pattern in an estuary depends on several factors such as sediment sources, the texture (particle size) of the sedimentary material supplied, the bottom topography of the basin and salinity ranging from that of saltwater to freshwater (Seralathan, 1986) more details in the next paragraph.

The main characteristics responsible for sediment distribution are hydrodynamic regime of an estuary such as tidal action, river inflow, waves and wind. As a result of the complex relations between these factors, sediment distributions tend to be extremely variable on both spatial and temporal scale (Perillo, 1995 and Williams et al., 1994), although tides arguably exert the most significant control over an estuary's ability to transport sediment (Dyer, 1995). Estuaries can be classified according to their tidal range as microtidal (< 2 m), mesotidal (2-4 m) and macrotidal (> 4 m) (Dyer, 1994). With increasing tidal range, the whole of the estuarine water mass can move in response to tidal periodicity (Dyer, 1995). Sediment characteristics also control of sediment transport; sediments carried by estuary waters typically encompass the range of sizes from less than 0.002 mm to more than 0.004 mm, but the fine sizes dominate most estuaries. Cohesive sediments such as coarser sands and silts are transported as single grains in several modes by bouncing or creeping (Mehta, 1986).

In estuarine systems, the metals enter through river flow and can be distributed in sediment components, and associated with them in different ways including adsorption, precipitation, and sedimentation processes (Dawson & Macklin, 1998; Deepulal et al., 2012). Metals tend to be accumulated in, or trapped immediately by bottom sediments (Dauvalter, 1998) because of their strong affinity for particulate matter and organic matter (Luoma, 1990 and Campbell & Tessier, 1996). Estuarine sediments provide a long-term record of the accumulation of trace metal inputs from riverine, atmospheric and anthropogenic sources (Kennish, 1992 and Windom, 1992). Chemical processes at the sediment/water interface are complex and are governed by physicochemical characteristics such as grain sizes and organic matter.

1.7.3. *Water and Sediment Quality Guidelines*

According to DWAF (1996) the term water quality describes the physical, chemical and biological properties of water that determine its fitness for a variety of applications and for protecting the health, integrity of aquatic ecosystems, and guidelines for the protection of the marine environment.

No sediment quality guidelines (SQGs) exist for fresh water in South Africa. The current South African Water Quality guidelines are focused on the effects of dissolved chemicals in the water column while ignoring both chemicals associated with settled sediment and the sediments themselves (erosion and sedimentation) (Gordon & Muller, 2010). For this reason, the study used international sediment quality guidelines such as CCME (1995), ANZECC (2000), Ontario (1993) and CMSQG (2000a) for compare the obtained results.

The Canadian Council of Ministers of the Environment (CCME) has developed sediment quality guidelines for the protection of aquatic life to assist in evaluating sediment quality. Screening levels have been established, based on toxicology data, to determine the potential effect of chemicals in sediment on aquatic organisms (CCME, 1999). Canadian sediment guidelines give two values, namely the interim sediment quality guidelines (ISQGs) and probable effect levels (PELs). For trace metals, SQG can be used to evaluating the degree to which adverse biological effects are likely to occur, as a result of exposure to metals in sediments.

Many factors, affect water and sediment quality in river systems: environmental characteristics of river basins such as climate, topography, geology, and vegetation and the activities that occur with them, shape the physicochemical features of the river. The links between characteristics of the drainage basin and water and sediment quality in the river are climate and river flow, winter conditions (flooding), soil erosion (sedimentation), pollution (point and nonpoint sources), river obstruction (dams) and wetlands (CCME, 2008). International guidelines for pollution classification of sediments are based on the determination of total trace metal concentrations (Perdomo et al., 1998).

1.7.4 Physical and chemical properties of sediment

Many physical and chemical factors affect sediment's ability to collect and concentrate heavy metals. The physical factors include grain size, surface area, composition and so forth. However, chemical factors (surface charge and cation exchange capacity) are equally important, especially for differentiating between samples having similar bulk chemistries and for inferring or predicting environmental availability. Chemical factors entail phase associations (with such sedimentary components as interstitial water, sulfides, carbonates and organic matter) and ways in which the metals are entrained by the sediments (such as adsorption, complexation and within mineral lattices).

1.7.4.1 The Grain Size Effect

Grain size is one of the main factors controlling both suspended- and bottom-sediment capacity for retaining trace metals (Hirst, 1962; Jenne, 1968; Gibbs, 1977; Jones and Bowser, 1978; Filpek & Owen, 1979; Jenne et al., 1980; Thorne and Nickless, 1981). In lakes, rivers, estuaries, and oceans and in sediment chemistry in general most sediment tends to be composed of materials smaller than 2 μm (very coarse sand). There is very strong positive correlation between decreasing grain size and increasing trace metal concentrations; this correlation results from numerous factors that are both physical and mineralogical (compositional). Clay-sized sediments (less than 2 to 4μm) have surface areas measured in square meters per gram, as opposed to, for example, sand-sized particles with surface areas usually measured in tens of square decimetres per gram (Grim, 1968; Jones & Bowser, 1978). Surface chemical reactions are critical to aquatic heavy metal sediment interactions; thus, fine-grained sediments, because of their large surface areas, are the main sites for the collection and transport of inorganic constituents (Jones & Bowser, 1978; Jenne et al., 1980). However, Jenne (1976) indicates that the clay-sized particles may be viewed only as mechanical substrates upon which trace metals can concentrate (without chemical interaction). Metal concentrations can and do accumulate on many substrates, including sand, pebbles, cobbles, and boulders (Filipek et al., 1981; Robinson, 1982); nevertheless, high concentrations are more commonly associated with fine-grained material.

The characteristics of iron and manganese oxides in the sediment are also important. These substances have long been known as excellent scavengers of trace metals from solution. The most spectacular demonstration of this effect is the manganese nodules located at the sediment-water interface on deep ocean floors or in river beds (Mero, 1962 and Moore et al., 1973). The separation and identification of manganese micronodules in core and grab samples indicate that they are ubiquitous and play a significant role throughout the sediment column as metal collectors in aquatic environments (Horowitz & Cronan, 1976; Jones & Bowser, 1978; Forstner, 1982a, b).

In soils, suspended sediment, bottom sediment, iron and manganese oxides also usually occur as coatings on various minerals and finely dispersed particles (Forstner and Wittmann, 1979). Those forms that are most capable of concentrating metals range from amorphous to microcrystalline to crystalline and have large surface areas on the order of 200 - 300 m^2/g (Buser and Graf, 1955). Regardless of the form, whether micronodules or coatings, hydrous iron and manganese oxides are significant concentrators for trace metals in aquatic systems.

1.7.4.2 Organic matter effect

Particulate organic matter (OM) enters rivers and estuaries through many processes: erosion of soils and sediments, organic productivity in the water column and disposal of wastes (sanitary, agricultural, and industrial). Because the organic solids are of low density, they are transported in and through sedimentary environments with the fine-grained (silt and clay) fraction of inorganic particles. Deposition of this material from quiescent waters produces organic-rich mud accumulations. This mud supports intense bio-geochemical activity which exerts a profound influence on the chemistry of both the sediments and, through nutrient regeneration and oxygen consumption, the overlying water. Organic matter is an essential component of the bio-geochemical cycles in these systems providing substrate for the detritus-based food webs that characterize many estuaries (Raymond and Bauer, 2000). Therefore, the bio-geochemical interactions in riverine and estuarine sediments are essential to the understanding of future changes in water quality.

In a riverine and coastal mud both the concentration of organic matter and the rates of processes of microbial degradation of organic matter decrease with increasing depth in the sediment column. At depths of more than a few tens of centimetres, the concentration of organic matter levels off at a finite value, and the rate of further degradation are too slow to be readily detectable (Berner, 1971; 1974; 1980).

The characteristics of aquatic and sediment organic matter are important, and the ability of organic matter to concentrate trace metals in and on soils as well as suspended and bottom sediments is well recognized (Singer, 1977; Nriagu & Coker, 1980; Forstner, 1982a, b). Aquatic organic matter, termed humic substances has been subdivided by Jonasson (1977) into four categories: humin, humic acids, fulvic acids, and yellow organic acids.

The ability of organic matter to concentrate metals varies with the constituent and the type of organic matter (Swanson et al., 1966; Saxby, 1969; Bunzl et al., 1976; Jonasson, 1977). Organic matter can concentrate between 1% and 10% dry weight of Co, Cu, Fe, Pb, Mn, Ni, and Zn (Swanson et al., 1966). The ability to concentrate different trace metals appears to be related to a number of factors, including large surface area, high cation exchange capacity, high negative surface charge, and material trapping. It is also related to the stability of the organic-metal constituent complex (Overnell, 2002).

1.8 Overview of related literature

The knowledge of related literature of the previous studies is essential for any research for the formulation of sound methodology that acts as a guiding force of research. Much analytical work has been done on both freshwater and marine sediments throughout the globe and as such a voluminous literature is available on the subject. Literature on total and chemical speciation of heavy metals in estuarine and river sediments and their adsorption on to sediment are available.

A review of the literature related to chemical speciation, mobility, bioavailability and total content of heavy metals in sediment using sequential chemical extraction is organized and presented as follows; Chukwujindu (2011) studied chemical partitioning of metals in the sediment of the Orogodo River (Southern Nigeria). Elisangela et al. (2010) performed partitioning of the heavy metals in sediments for samples collected from eight locations in the Poxim River estuary (Brazil), while Fatima et al. (2001) determined the chemical speciation of heavy metals (Zn, Cr, Mn and Fe) in estuarine sediment (Northeast of Brazil). Carlos et al. (2010) also studied heavy metal concentration and their partitioning in sediments of the Estrela River (Brazil). Morillo et al. (2002) analyzed seventeen sediment samples in the Tinto River and its main tributaries (Spain) while Morillo et al. (2004) determined the distribution of heavy metals with major sedimentary phases in samples from the south coast of Spain. Similarly, Morillo et al. (2002) also examined the distribution of heavy metals in core sediment samples from the Odiel River and its estuary and tributaries (Spain).

Studies have been done on cadmium in estuaries throughout the world (Edmond, 1985; Elbaz-Poulichet et al., 1987; Boutier et al., 1993 and Kraepiel et al., 1997). They showed unambiguously that this metal, bound to suspended matter, is mobilized when river water mixes with salt water.

In South Africa, water quality surveys have been conducted, mainly focusing on physico-chemical parameters of the Berg River such as pH, salinity, dissolved oxygen and nutrients (Fourie & Gorgens, 1977; Quibell, 1993; Gorgens & De Clercq, 2005; De Villiers, 2007; Schumann, 2009; Eric et al., 2012). Although a number of authors have studied the physical and chemical properties of some rivers in South Africa, information on the physic-chemical parameters of sediment from Berg River is limited.

Studies have been done by many authors in different areas in South Africa as follows; Greenfield et al. (2006) analyzed eight heavy metals in the Nyl River system, Limpopo Province. Similarly, Coetzee (1993) studied the speciation of ten heavy metals in the Hartbeespoort Dam (South Africa) sediments.

Other research also carried out on metal accumulation in fresh water sediment (South Africa) showed an increase in metal levels with addition of the industrial effluents and agricultural wastes; Songca et al. (2013) analyzed sediment and water samples collected from the Umzimvubu River Estuary, while Jackson et al. (2009) determined the concentration of heavy metals in water and sediment samples from the Plankenburg and Diep Rivers. Similarly, Jackson et al. (2007) determined the trace metals in collected sediment, biofilm and water samples from three sites along the Berg River to examine the level of metal pollution. Awofolu et al. (2005) also assessed the levels of trace metals in water, sediment and vegetables from the Tyume River. A survey of heavy metals was carried out in the sediments of the Swartkops River Estuary (South Africa) by Binning and

Baird (2001). Another study on South African estuaries those of the Bushmans, Kariege, Kowie and Great Fish Rivers were made by Watling and Watling (1983).

Studies have been conducted on total heavy metal concentrations in different areas around the World; (Maxfield et al., 1974, in a study of the delta of the Coeur d'Alene River (USA). Similarly Pilotte et al. (1978) analysed estuarine sediments in Florida for heavy metal deposits. Wingor & Andreasen (1985) analysed heavy metal residues in the sediments of lakes in the Atchafalaya River Basin (Louisiana). Moriarty & Hanson (1988) analysed heavy metal accumulation in sediments of the Ecclebourne River, Derbyshire (UK), while Marcus et al. (1988) analysed heavy metal concentrations in sediments of coastal South Carolina. Lietz and Galling (1989) examined sediments of the Oker River in the Federal Republic of Germany for contamination with Cd, Zn and Pb while Pardo et al. (1990) recorded contents of Zn, Cd, Pb, Cu, Ni, and Co in sediments of the Pisuerga River (Spain). Gibbs (1994) examined the distribution of metals in bottom and suspended sediments of the Hudson River Estuary. Ganasan et al. (1991) also analysed heavy metal concentration in sediments of the Khan and Kshipra Rivers (India) and identified pure textile dyes to be the primary source of all metals. Singh et al. (2002 and 2003) analysed heavy metals freshly deposited in stream sediments of rivers associated with urbanization of the Ganga plain. Impact of industrial and municipal waste on heavy metal levels has also been examined by Singh et al. (2005) and Jain et al. (2008) in bed sediments of the Gomti and Narmada Rivers (India) respectively. Alessandro et al. (2006) determined concentrations of heavy metals in surface sediment samples collected in the Taranto Gulf (lonian Sea, South Italy). A study has also been conducted on the areas around the Port River estuary and northern Spencer Gulf (Australia) over the past few years to examine of the fish and sediment quality by EPA.SA (2000).

In terms, spatial and vertical distribution of heavy metals in core sediments and its characteristics, a number of studies have used spatial and vertical distribution to determine the heavy metal pollution and contamination history at different environment conditions; Agnes et al. (2013) studied the spatial and vertical distribution of heavy metals in sediment and sediment texture of the Msimbazi River mangrove forest (Tanzania), while Mariam et al. (2012) examined the depth profile of some heavy metals in core sediment collected from the Seine River estuary (France). Adi Slamet et al. (2011) also examined the spatial and temporal variations of heavy metals contamination in the Jakarta Bay (Indonesia), whereas Liu et al. (2011) analyzed core sediment samples collected from the Pearl River Estuary (China).Usha and Ranga (2010) studied the vertical profile of heavy metals concentration in core sediments of the Buckingham canal, Ennore (India). Li et al. (2007) studied the distribution of heavy metals in sediment collected from Ell-Ren River (Taiwan). Harry (2006) investigated physical and chemical characteristics of water and sediment in four major river systems (Eastern South Africa).

Monteiro and Roychoudhury (2005) analysed core sediment samples collected from 37 sites throughout the St. Helena bay and the mouth of the Berg River using a multicorer. Spencer and Macleod (2002) determined the total metal concentrations and historical contaminated sediments in sediment cores collected from three estuaries (South-east England). Caeiro et al. (2005) studied the contamination of heavy metal in the Sado estuary sediment (Portugal) using an index analysis approach.

Finally, a few studies have focused on the adsorption of heavy metals on river and estuary sediment. There is not much literature associated with it. Most of these literatures contained results of batch experiments for the contact time, pH and metal concentration. However, there is much work available on the metal removal from wastewater using different materials.

A study has been carried out on competitive adsorption of heavy metals (Pb, Cu, Cd, Ni and Cr) on natural bed sediments of the Jajrood River (Iran) by Saeedi & Hosseinzadeh (2011). Wang & Li (2011) have measured of Cu and Zn adsorption on to surficial sediment components from the Songhua River (China). Rose (1989) found that the valence of heavy metal would affect the adsorbabilities of sediment to metals; the higher the valence of the metal, the higher the adsorbability of the sediment. Palheiros et al. (1989) have studied the adsorption of cadmium onto bed sediment of the Ganga River (India) and reported that pH is the most important parameter in the control of such adsorption. Fu and Allen (1992) also studied the adsorption of cadmium by oxic sediments using a multi-site binding model.

Studies indicated that levels of metals were higher in sediment than in water; Krauskopf (1955) suggested that the heavy metal concentration increases in the sediment due to the adsorption of cations by organic matter present in the sediment layers. Similarly Curits (1966) and Singer (1977) proposed that metals interact with organic matter in an aqueous phase and settle down resulting in high concentrations, in sediments. Gibbs (1973) indicated the importance of organic molecules in controlling trace metal concentrations on and in suspended and bottom sediments, and in sediment-water interactions. While Saxby (1969) showed that the relative attraction between metals with colloidal, suspended, and bottom sediment-associated organic matter can range from weak and readily replaceable (adsorption) to strong (chemically bonded).

1.9 Hypothesis for the present study:

The total concentrations of heavy metals in the Berg River may be affected by pollution. Sedimental accumulation of these metals may give a history of any such pollution. Also the distribution of heavy metals in sediments is affected by pH, adsorption, and sediment characteristics.

1.10 Objectives of the present study

In order to test the research hypothesis, the main purposes of the study are:

- To measure the total concentrations of heavy metals in Berg River sediment;
- To identify possible sources of contamination should it exist;
- To determine the anthropogenic impact on metal concentrations;
- To investigate the ability of Berg estuary sediment to adsorb heavy metals;

In order to achieve these broad objectives, many detail objectives are required:

- To study the mobility and bioavailability of metals in Berg River sediments and its estuary
- To determine vertical and spatial distribution of heavy metals in sediment
- To determine the adsorption isotherm models for Pb, Cr, Cu, Ni and Zn onto bed sediment of the estuary
- To examine the relationship between metal concentration and core composition;
- To compare metal concentrations in the river and its estuary with national standards for sediment quality and levels recorded in other estuaries around the world;

2.1 Introduction

This chapter outlines the research methodology involved in field tests as well as laboratory analysis and experimental methods. The analyzed parameters include total concentrations and speciation of heavy metals, as well as organic matter content and sediment characteristics. The sediment coring approach is used to determine the amounts of sediment laid down within the catchment from certain contributing landscape and land use areas. The study of the core sample gives a historical record of concentration of heavy metals in bottom and surface sediments representative of pre-industrial and recent times respectively. The study of sediment cores has also proved to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments (Singh and Nayak, 2009). Part of this study is also to ascertain if there is any correlation between the heavy metal levels and particle size of the sample taken. Particle sizes ranging from 0.01 to 2000 µm fractions have been analysed to determine fluvial transport conditions prior to deposition. The adsorption experiments were performed at room temperature and pH 6.0 to be representative of environmentally relevant conditions. Clean and unclean sediments were used for adsorption experiments.The sampling was conducted three times at nine different sites along the Berg River over a period from November 2011 to February 2013. Finally, the methods of sampling, processing, storage, preparation and analysis of sediment are discussed in this chapter.

2.2 Description of the study area

The Berg River is located in the Western Cape Province of South Africa. It rises in the Drakenstein mountains and flows northwards past Paarl and Wellington. The Berg River then flows westwards past Porterville, Piketberg, Hopefield and Velddrif to discharge into the ocean in an estuary at Laaiplek (DWAF, 1993). The river drains an area of approximately 8980 km^2 and has a total length of about 285 km (DWAF, 2007). It consists of nine major and seven minor tributaries, six of which are naturally perennial, such as the Franschhoek, Wemmershoek, Dwars, Klein Berg, Vier-en-Twintig and Matjies rivers. The Berg River drains the western slopes of the Olifants River Mountains, the Winterhoek Mountains and the Drakenstein Mountains as well as the Swartland. The map of the Berg River catchment is shown in figure 2.2.1.

Topographically, the Berg River catchment covers an area of almost 9000 km^2, and is subdivided into 12 quaternary catchments ranging in size from 125 km^2 near the headwaters to 2000 km^2 in the drier western parts of the catchments (Shillington 1998). Much of the catchment area is flat, with an average topographical gradient of 0.001between Paarl and the river mouth at Laaiplek (DWAF, 2007).

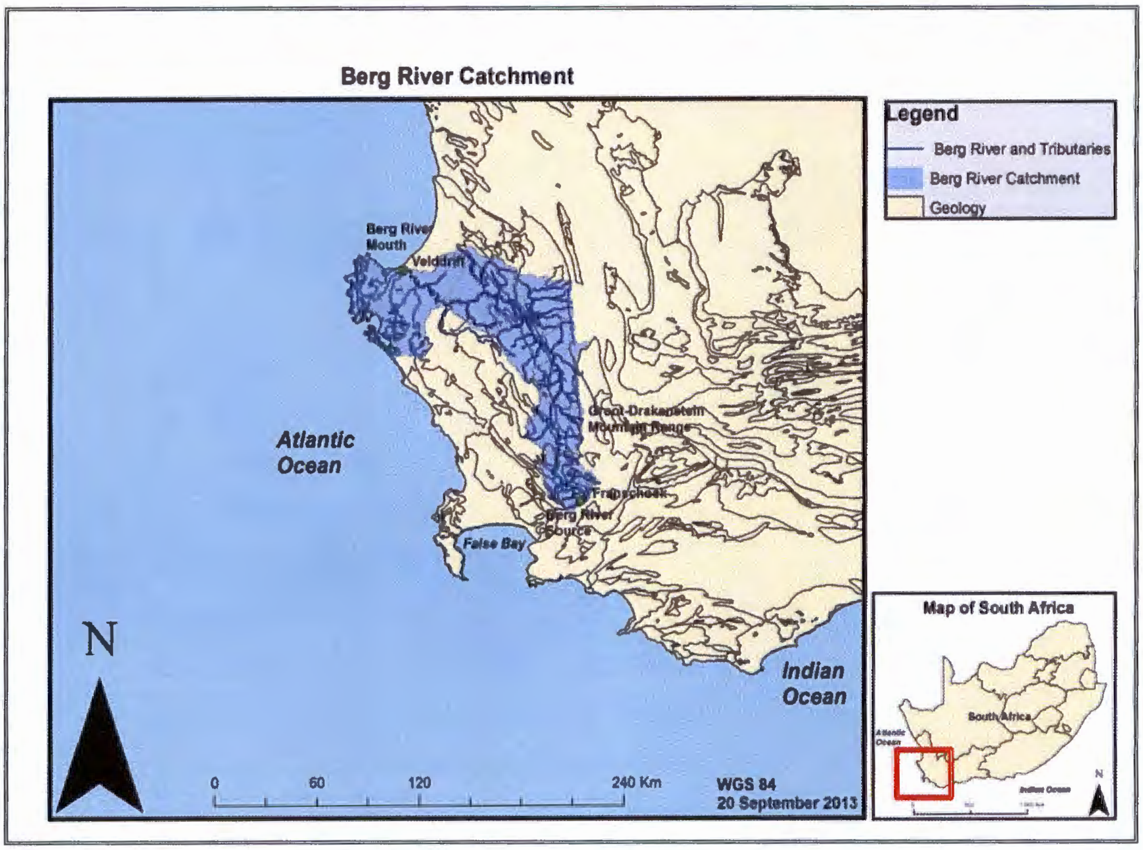

Figure 2.2.1 Map showing spatial representation of Berg River Catchment in respect to South Africa (source: Geographical Information System software, GIS 10.1)

In 1995, the number of the population living within the Berg River was 369 280, about 79% of them living in the urban areas. The main activities within the area are agricultures, commercial industries and residential development. About 15% of the catchment area is under alien vegetation. Historically, many economic activities (commercial fishing, fish processing factories and boat repair facilities) have been associated with the estuary, including tourism and recreation in the last years. In addition, small commercial salt works generate further income in the area (River Health Programme, 2004).

The Berg River estuary is located approximately 130 km north of Cape Town on the western coast of South Africa. The estuary extends about 69 km from the mouth, based on the extent of tidal influence (Slinger & Taljaard 1994), although sea water does not penetrate this far (Schumann 2007). Tidal range at the mouth is 0.5 – 1.5 m: in the middle of the estuary at the railway bridge it is 0.2 – 0.8 m, and in the upper estuary (Jantjiesfontein), it is less than 0.2 m. Tidal flows in the lower estuary (at the R27 bridge) are 50-100 $m^3.s^{-1}$ and 200-300 $m^3.s^{-1}$ during neap and spring tides, respectively (Beck & Basson 2007). Tidal action attenuates rapidly upstream, and inter-tidal areas occur mainly downstream of the railway bridge. Upstream of the railway bridge, the estuary is flanked by a seasonally-inundated flood plain that varies in width from 1.5 to 4 km. The estuary, including flood plain, is expected to cover an area of 61 km^2. The estuary's shallow gradient and extensive flood plain make it typical in relation to most South African estuaries (Schuman, 2007), which are short, in particular because of rapidly ascending coastal topography (Schumann, 2009). The main channel at Velddrif is about 100-200 m wide, becoming progressively narrower and shallower upstream. The depth is about 3-5 m on average, up to 9 m in places. The total volume of the estuary is estimated to be about $12x10^6$ m^3 (Beck and Basson, 2007).

In 1966, a new estuary mouth was cut through the sand dunes and stabilised between concrete walls (Slinger and Taljaard 1994). The original mouth has silted up and the former channel currently forms a blind arm or lagoon running parallel to the coast. The lower 4 km of the estuary is also dredged to a depth of at least 4 m to allow for boat navigation. However, these developments are not considered to have had a significant effect on the hydraulics and sediment transport in the estuary, except at the mouth (CAPE, 2008). Bridges lead to some local scouring of banks. Much of the lower estuary flood plain has been reclaimed for salt production.The Berg River catchment comprises sequences of rocks of the Malmesbury Group, the Cape Granite Suite, the Klipheuwel Group, the Table Mountain Group and younger cenozoic sediments in the western part of the catchment. The Malmesbury Group and Klipheuwel Group comprise soft, erodible rocks that form flat plains in low lying areas. In general, these areas have moderate to high agricultural potential. The Malmesbury Group is steeply folded along a North West axis (Visser 1989).

2.3 Sampling collection and Storage

The objective of any sampling programme is to deliver samples to the laboratory that are representative of the original material (IAEA, 2003). Collection and storage of sediment samples for heavy metals analysis require special handling in order to avoid contamination, especially if the variables to be measured occur in very low concentrations. The representative sampling sites for the assessment of heavy metals in sediments were chosen based on characteristics of the Berg River and its estuary, and the possible sources (point and non-point sources) of contamination. A total of nine sites were selected for the collection of core samples. Russian and Vibracorer methods were used to collect the sediments. The location of the selected sites along the river is shown in Figure 2.3.1.

For the investigation of metals speciation, six sediment cores, of 50 cm length, were obtained using a Russian Peat Corer from three sampling sites 3, 8, and 9 along the Berg River. Two of cores in the upper reach of the river (Site 3) while the other four cores were extracted from the estuary (Site 8) and coast (Site 9).

Russian Peat Corer is a hand-operated, mechanical sampling device that utilizes a side-filling mechanism to obtain uncompressed samples from wetlands and estuaries. One of the main advantages of using a smaller design is that it is manually controlled. Sites 3, 8 and 9 were selected for the collection of core samples. A single sediment core is a half-cylindrical sample with a five centimetre diameter and a fifty centimetre length. The corer was deployed (in the closed position) to the desired depth with hand pressure and most often using a hammer to penetrate compact sands and loose stone. The corer was rotated clockwise 180° so that the sharpened edge of the chamber cut a sediment core which was contained by the cover plate. The corer was turned to hold the captured semi-cylindrical shaped sediment sample in place before being extracted from the ground. The sediment core was exposed by a counter clockwise movement of the cover plate until the entire core was exposed onto the plate. The semi-cylindrical sediment core was then placed in a half-round 50 mm plastic pipe (figure 2.3.2). Duplicate, 5 cm samples were taken every 20 cm to investigate the speciation, mobility and bioavailability of heavy metals. In totally, 36 samples were selected from these 6 short cores.

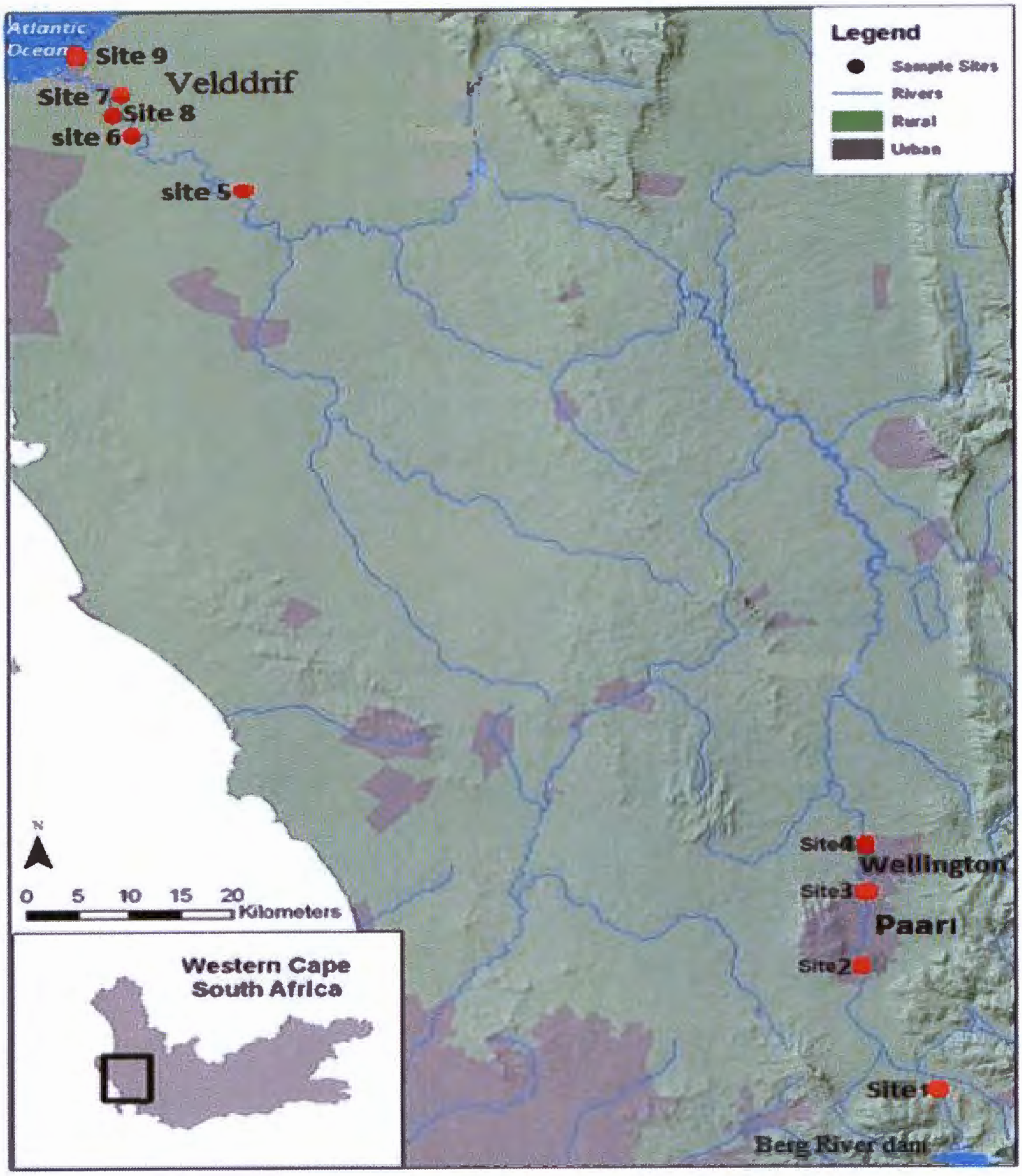

Figure 2.3.1: Map of study area, and core sampling sites in the Berg River and its estuary (Source Google Earth).

Figure 2.3.2 Inserting the short corer on the left and Storage of sub- samples on the right

The remaining three sediment cores (1, 2 and 3) were collected using a mechanical vibrating corer according to the US.EPA (2001) protocol. The advantage of the vibracorer is its success in recovering cores of significant length that cannot be sampled by other methods. The vibra coring system is manufactured by Fulton Milwaukee, USA. Four sediment cores each of 240 cm in length, and two cores of 160 cm length were collected from water depth varying between 0.5 to 1 m from the Berg River estuary using the vibracorer (figure 2.3.3). Sites 5, 6, and 7 were selected for the collection of these core samples.

The vibracorer was mounted on a safe, stable platform for the collection of cores. An aluminium tube of 5 cm diameter was pushed and vibrated into the muddy sediment to a depth of up 250 cm below the sediment/water interface. A new core tube was used at each site. Once the core had been extracted, each core was split longitudinally to expose the core sediments, which were photographed and logged prior to sampling.

In order to study the vertical distribution of heavy metals within each sediment profile, duplicate samples were taken at 20 cm intervals from the cores. Totally, 78 samples were selected from these 6 vibracores. The samples were immediately frozen with dry ice to avoid any changes in metal distribution among different phases. After being transported to the laboratory, the samples were stored in polyethylene bags under a nitrogen atmosphere in a freezer to avoid sample oxidation according to the US-EPA (1997) protocol.

Figure 2.3.3 Vibracores collection on the left and selected subsamples on the right.

All glassware and plastic containers used in the collection and storage of the sediment samples were cleaned in a detergent solution to avoid contamination. They were also rinsed with ultrapure water Milli-Q water and soaked in a nitric acid bath (20%, v/v) overnight. This was followed by: thoroughly rinsing with ultra-pure water and dried before use.

The coordinates, depths, and visual descriptions of the sediments for the core sampling sites are presented in Table 2.3.

Table 2.3 Berg River and its estuary core sampling sites (* Field Duplicate Sample)

Site	Kind of Corer	Date	Core Length (cm)	Latitude	Longitude	Description of the sediment core
1	Russian corer	26/09/12	50	19°.03'.1057"E	33°.53'.5923"S	Brown organic silts Sandy and clay
2	Russian corer	26/09/12	50	19°.02'.0440"E	33°.52'.3994"S	Sand and clay
3	Russian corer	26/09/12	50	18°.58'.5297"E	33°.40'.0216"S	Brown/yellow silts sand
4	Russian corer	26/09/12	50	18°.58'.3451"E	33°.37'.4456"S	Black organic/gray sills sand
5	Vibracorer	15/02/13	240	18°.19'.735"E	32°.54'.222"S	Brown organic silts Sandy and clay
6	Vibracorer	15/02/13	240	18°.19'.733"E	32°.47'.287"S	Black organic silts Sandy and clay
7	Vibracorer	15/02/13	160	18°.19'.733"E	32°.54'.432"S	Black organic silts Sandy and grey clay
8	Russian corer	18/11/11	50	18°.10'10.33"E	32°.47'.2958"S	Black organic silts Sandy and grey clay
9	Russian corer	18/11/11	50	18°.08'4944"E	32°.46'.0920"S	Sandy

2.4 Apparatus

A measurement of Varian 730-ES model inductively coupled plasma with optical emission spectroscopy (ICP-OES, Germany) was used for the of heavy metal concentrations in the sediment samples, Microwave plasma atomic emission spectrometer (MP-AES, model 4100) was used for adsorption experiments. Sediment extractions were conducted using a Balmar mechanical shaker (Model GFL 3005, USA). A centrifuge

(KUBOTA 5100, Japan) was used to obtain the supernatant extracts at 3000 rpm for 20 min. A Hotplate (CEM MARSX, USA) was used for the total digestion of sediment samples. A sieve set of 0.63 μm and 200 μm mesh size (GEO supplies Ltd, UK) was used to obtain fine sediment for metal speciation analysis. Stainless steel sieves of 63, 150, and 250 μm mesh sizes (ENDECOTTS Ltd, ENGLAND) were also used to obtain fine sediment for both metal speciation and total metal content. Malvern Mastersizer 2000 laser instrument was used for sediment characteristics. All plastic containers were made of polypropylene (PP) except the digestion vessels which were made of polytetrafluoroethylene (PTFE), in order to minimize contamination. pH meter (micropH 2000, Spain) was used to measure pH value for extraction and adsorption experiments.

2.5 Chemicals

All chemicals were pure analytical grade reagents and solutions were prepared in Millipore deionized water (16.2-18.2 MΩ). Concentrated nitric acid (Kimix), acetic acid (Kimix), hydrofluoric acid (Sigma-Aldrich), hydrogen peroxide (Merck), ammonium acetate (Kimix) and hydroxylamine hydrochloride (Sigma-Aldrich) were used as the sequential extraction reagent. All reagents used were checked and excluded for possible heavy metal contamination. Certified aqueous reference material, Multi-Element Standard (ULTRASPEC) was used for adsorption experiments.

2.6 Samples preparation and methodology

2.6.1 Metal speciation experiment

Hoenig (2001) states that the preparation of samples is one of the most crucial steps in trace element analysis and frequently controls the quality of the final results obtained. The primary goal of the sample preparation is to prepare a sample in such a way that the original elemental distribution at the time of sampling is preserved and that the introduction of foreign elements is prevented (IAEA, 2003). In order to minimize contamination, all laboratory glassware and plastic ware for samples preparation were first cleaned with deionized water, then with nitric acid 2% and rinsed again with deionized water.

In the laboratory, the samples that were previously deep frozen, in order to limit biological and chemical activities, were removed from the freezer, thawed and placed in polypropylene beakers then were defrosted and air-dried at 30 °C for 24 hours. The dried samples were homogenized and ground with a pestle and mortar, then sieved through a clean nylon sieve of < 200 µm mesh size to remove any large organic matter such as reeds and grass. The remaining material was sieved through a nylon sieve of < 63 µm mesh size to obtain the fine particle-size fraction. In this study, the < 63 µm fraction was used for metal speciation analyses due to a strong association of metals with fine-grained sediments (Che et al., 2003). The sieved material was then placed in polypropylene tubes and labelled for storage in a cool, dry place until analysis and processing.

In this study, the samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) in order to determine heavy metals in the sequential extracts. The instrument parameters for metal analysis were as recommended in the literature (Grasshoff et al., 1998). The main analytical advantages of ICP over other excitation sources originate from its capability for efficient and reproducible vaporization, atomization, excitation, and ionization for a wide range of elements in various sample matrices. This is mainly due to the high temperature, 6000 – 7000 K, excellent accuracy and precision, excellent detection (0.1-100 ng/mL^{-1}) low background emission and relatively low chemical interference.

2.6.1.1 Sequential extraction

The determination of heavy metal speciation in environmental media using sequential extraction techniques offers a more realistic estimate of actual environmental impact. The principle of this method is based on the selective extraction of trace metals in different physic-chemical fractions of material using specific solvents. These procedures have been widely used for determining specific chemical forms of trace metals in a range of environmental media. Additionally, sequential extraction schemes are increasingly considered useful tools for assessing potential metal mobility, bioavailability and toxicity in contaminated sediments and soils (Davidson *et al.*, 1998).

2.6.1.2 Extraction procedure

The metal speciation (fractionation) was determined by means of the sequential extraction scheme using a three-step modified BCR (European Community Bureau of Reference) according to Cuong and Obbard (2006). This scheme consists of three successive extractions steps that allow the determination of the metal concentrations at four phases: acid soluble, reducible, oxidizable and residual (Table 2.6.1.2).

A detailed description of this procedure is provided below;

Step 1: Acid soluble fraction – bound to carbonates

This fraction consists of weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes and metals that can be co-precipitated with carbonates present in many types of sediment. Changes in the ionic composition, influence adsorption–desorption reactions, as does lowering of pH. Exchangeable metal ions are measures of those trace metals which are released most readily into the environment (Ahnstrom and Parker, 1999; Narwal et al., 1999). The acid-soluble fraction is sensitive to pH changes, and metal release is achieved through dissolution of a fraction of the solid material at pH close to 5.0 (Accomasso et al., 1993).

Procedure

About 0.5g of the ground sediment was accurately weighed on a digital analytical balance (Sartorius; BP2110; D = 0.01 mg). 20 mL of 0.11 mol/L acetic acid was added to 0.5 g of air-dried sediment in a 50mL, polypropylene centrifuge tube. The tube was shaken for16 h at room temperature and with speed of 30±10 rpm. No delay occurred between the addition of the extracting solution and the beginning of the shaking.

The extract was separated from the solid phase using centrifugation at 3000 rpm for 20 minutes. The supernatant liquid was decanted into a 50 mL polypropylene centrifuge tube and stored in a freezer prior to analysis. The residue was washed with 15 mL of deionized water and shaken again for 15 min and then centrifuged for 20 min. The liquid phase was decanted and removed carefully to avoid loss of the solid phase.

Table 2.6.1.2: Extractants used in each step and the phases of sediments in the sequential extraction procedure

Extraction step	Reagent, concentration and time	Sediment fraction
1	Acetic acid (CH_3COOH)-0.11 mol.L^{-1} for 16h	Acid-soluble (exchangeable ions, carbonates)
2	Hydroxylamine hydrochloride (NH_2OHHCl)–0.5 mol.L^{-1} (pH 2 with HNO_3) for 16 h	Reducible (iron/manganese oxides)
3	Hydrogen peroxide H_2O_2–8.8 for 1h At room temperature at 85 °C Ammonium acetate ($CH_3COO\ NH_4$)–1.0 mol.L^{-1} (pH 2 with HNO_3) for16 h	Oxidizable (organic substances and sulfides)
4	Mixed acid (3:1) HNO_3: HF for 16 h	Residual (Insoluble components of metals in the steps before)

Digestion of the residual material is not a step of the BCR protocol.

Step 2: Reducible fraction (bound to Fe and Mn oxide)

This fraction is referred to as sinks in the surface environment for heavy metals. Scavenging by these secondary oxides, present as coatings on mineral surfaces or as fine discrete particles, can occur by any or a combination of the following mechanisms: co-precipitation, adsorption, surface complex formation, and ion exchange (Hall et al., 1996). Fe and Mn oxides are in the largest proportion in soil and sediments.

In general, this fraction can be divided into three sub-fractions: easily reducible fraction, moderately reducible fraction, and poorly reducible fraction. Each scheme allows differentiating between metals associated with moderately or easily reducible Fe–Mn oxides. In order to simplify the extraction of metals, most sequential extraction scheme (SES) proposed in the last years only includes a reducible fraction. Hydroxylamine hydrochloride in nitric acid medium is the most widely used reagent for leaching out the easily reducible fraction (Ure et al., 1995).

Procedure

20 mL of freshly prepared (0.5M) hydroxylamine hydrochloride (adjusted to pH 1.5 with nitric acid) was added to each residue from step one in the centrifuge tube. The tubes were shaken for16 h at 22±5 °C at a speed of 30±10 rpm and centrifuged at 3000 rpm. The extracted fraction was separated from the solid phase by centrifugation and decantation as described for Step 1 and stored in a freezer. The solid residue was washed as in Step one before proceeding to Step 3.

Step 3: Oxidizable fraction (bound to organic matter and sulfides)

The trace metals may be associated through a complexation process with various forms of organic material such as living organisms, detritus or coatings on mineral particles. Organic substances exhibit a high degree of selectivity for divalent ions compared to monovalent ions and in aquatic systems, the probable order of binding strength for metal ions on to organic matter is Hg > Cu > Pb > Zn > Ni > Co (Filgueiras et al., 2002). This fraction is most important, especially in polluted sediments and sewage sludge (Ridgway and Priece, 1987).

Procedure

5 ml of 8.8 mol.L^{-1} hydrogen peroxide (30%) was added carefully to the residue from step two in the centrifuge tube. The tube was covered with a watch glass and heated at room temperature for 1 h in a water bath, with occasional shaking. The tube was then continuously digested for 1 h at 85±2 °C in a water bath with occasional shaking for 30 min, and then the volume was reduced to around 2-3 mL by further heating of the uncovered tube. 5mL of 8.8 mol.L^{-1} hydrogen peroxide (pH 2-3) was added again. The covered tube was heated again to 85±2°C and digested for 1 h before the volume in the uncovered tube was reduced to a small volume (2 mL). After cooling 25mL of 1.0 mol.L^{-1} ammonium acetate (pH 2) was added to the cold, moist residue and shaken for16 h at room temperature. The extraction procedure was repeated with separation as described in step two.

Step 4: Residual fraction (inert fraction and strongly associated to the crystalline structures of the minerals)

The metal content of the residue from Step 3 was determined using a hotplate digestion method instead of a microwave-assisted acid digestion method. Two replicates of the residue from Step 3 were transferred to a Teflon digestion's vessel, and a mixture of acid (9 mL concentrated HNO3 and 3ml concentrated HF) was added carefully to the residue from Step 3. The digestion's vessels were then sealed and heated on a hot plate at 110 ±5 °C for 16 h. The vessels were opened and heated again until dryness. The dry residue was then mixed with 2 mol.L^{-1} nitric acid and the suspension was diluted to 25 ml. Finally, the suspension was centrifuged at 3000 rpm for 10 min to remove the supernatant and stored at 4 °C.

The total metal concentration digested as residue from Step three was digested in a mixture (3:1) of concentrated HNO_3 and HF. A detailed description of this procedure is given in the next section (Section 2.6.2).

2.6.2 Total metal concentration

For analysis of arsenic, cadmium, lead, mercury, chromium, copper, iron, manganese, nickel, and zinc, sediment samples were digested according to the US.EPA (2002) protocol. In order to quantify the total metal contents in sediment, the samples were immediately digested using the hotplate digestion procedure as follows:

The oven dried sediment samples were ground manually to a fine powder in an agate mortar and sieved through a clean metal sieve of 250 µm mesh size to remove any large organic matter and this was followed by sieving through a clean metal sieve of 150 µm mesh size.

For total metal analysis approximately, 0.5g of sediment was weighed directly into Teflon vessels. Each sample was thoroughly digested with 9 ml of 3:1 mixture of concentrated nitric acid and hydrofluoric acid. The vessels (30 mL) were then closed tightly (closed vessel digestion) and were heated on a hot plate at 110 ±5 °C for 16 h until dryness as described in step four. The contents were transferred into 50 mL centrifuge tubes and brought up to 50 mL with 2 mol.L^{-1} nitric acid after cooling. Samples were centrifuged for 5 minutes at 3000 rpm before analysis. The total concentration of metals was determined by ICP-OES (Chemical Engineering Services Laboratory).

2.6.3 Quality control for heavy metal analysis

The best method of checking the experimental extraction procedure is to use a sediment standard reference material. Unfortunately this was not available and so the extracted metal concentration was checked against the total metal concentration in the sediment. The samples were analysed using ICP-OES in the ppm and ppb range with confidence limits from 80 to 120%. Check samples were analysed according to the % recovery obtained, and a confidence limit was assigned to the calibration curve. Analytical blanks were prepared using the same procedures and reagents. Blanks determinations for total and metals speciation were carried out in the same conditions as the samples using the same acid concentrations and extraction. All the dilutions were done in 25 mL volumetric polypropylene flasks and the solutions were transferred immediately to 50 ml polypropylene tubes to avoid adsorption of trace metals on the walls of the flasks. All the analysis readings were performed in triplicate, and the samples were prepared in duplicate. The concentrations were expressed in mg/kg dry weight. Sediment data in this study are reported on a dry weight basis. Pearson's correlation analysis was performed in order to obtain information about the relation and behaviour of the metals in sediment.

2.6.4 Organic matter content

A common way to generate a rough sediment geochemistry profile is to use the loss-on-ignition (LOI) method. Numerous authors from Dean (1974) onwards have noted that this process can be considered to be a good tool for determining the organic matter of sediments, even if several uncertainties limit the absolute precision of the process (Dean, 1974; Bengtsson and Enell, 1986; Heiri et al., 2001). The relative changes of loss-on-ignition parameters throughout the analysed core sections were regarded as very useful in interpreting the impact of changing climatic conditions on different biogeochemical processes throughout the sediment sequence, and often are sufficient for correlation between overlapping cores. Loss-on-ignition analyses were carried out at 565 °C in a Naber-therm muffle furnace with digital temperature display and thermostatic temperature control (Nabertherm, Germany).

The sediments were dried, finely ground and homogenised by hand stirring and shaking in a closed container. Care was taken that no humidity remained in samples before weighing. Therefore, empty crucibles were dried at 105 °C overnight, and all samples were cooled to room temperature in desiccators before any measurements were made. Crucibles were put into the furnace only after a constant temperature was reached to avoid overheating. For a longer time, series crucibles were heated and cooled to room temperature, weighed, and the same sediment was then again exposed to the respective temperature.

After oven-drying of the sediment to constant weight (16 h at 105 °C), 5 g of dry sediment was combusted in a furnace to ash and carbon dioxide at a temperature of 565 °C (overnight). The LOI is then calculated using the following equation:

$$LOI_{565} = ((DW_{105} - DW_{565})/DW_{105}) * 100$$

Where LOI_{565} represents LOI at 565 °C (as a percentage), DW_{105} represents the dry weight of the sample before combustion and $DW_{565}$the dry weight of the sample after heating to 565 °C (both in grams).

2.6.5 Grain size analysis

The objective of grain size analysis is to determine the grain size characters of sediment samples and subsequently classify samples based upon their constituent parts, also to provide textual information that could be correlated with other types of data analysis (heavy metal concentration in core sediment and organic matter). Over 100 samples, each weighing approximately 5 g were prepared by drying at 30 °C for three days. Organic matter was removed from the sample as described in Sections 2.6.6.

Particle size analysis was conducted using a Malvern Mastersizer 2000 laser diffractometer with Hydro 2000MU dispersion unit. The measurement range of the apparatus was 0.02-2000 µm. About 0.5 g of the sediment sample was mixed in 20 ml of deionized water. The containers were shaken for 1 h using a horizontal mechanical shaker. The samples were run at 900 rpm and 2000 rpm on the sample stirrer and cell pump respectively. Background signals were automatically measured by the instrument prior to each test run and were close to the baseline. These, together with two minute sampling times, meant that air bubbles were unlikely to have had a significant effect on the analysis. The quality of the grain size results was evaluated through the measurement of two replicates. Precision was determined by the calculation of average of the repeated analysis.

2.6.6 Assessment of heavy metals contamination

As discussed in Section 2.1, the Berg estuary is known to receive a variety of anthropogenic pollutants through a number of sources. In order to identify possible sources of the heavy metals contamination and to evaluate the data in detail, the anthropogenic factor (AF) of the metals in the cores was calculated. AF is calculated from the metal surface and the concentration at depth according to the equation below. From this one can distinguish between geogenic and anthropogenic factors.

$$AF = C_s/C_d$$

Where, C_s and C_d refer to the concentrations of metals in the surface and at depth in the sediment column. According to Ruiz-fernandez et al. (2001), if $AF > 1$, it means contamination exists for that particular metal; otherwise, if $AF \leq 1$, there is no metal enrichment of anthropogenic origin.

The enrichment factor (EF) was also calculated because the AF value is not sufficient to assess the level of metal pollution. EF is a good tool to distinguish the metal source between anthropogenic and naturally occurring sources (Quevauviller et al., 1989). The EF gives similar information as an index of geoaccumulation (Igeo). In this technique metal concentrations are normalized to the textural characteristic of the sediments (grain size). The test element is standardized against a reference element. The best reference elements are ones characterized by low occurrence variability and mobility. The common reference elements are Sc, Mn, Ti, Al and Fe.

Normalization to Fe has been used previously as a grain size proxy by a number of researchers in marine and estuarine sediments (Ackerman et al., 1980; Lee et al., 1998). Iron geochemistry is similar to that of many trace metals both in oxic and anoxic environments. Fe has higher potential mobility than Mn. The difficulty with using Fe in this case is that the Berg river estuary is presumably contaminated with this element. For these reasons, in the present study, Mn was used as the reference metal to which all the other metal concentrations in sediments were normalized.

Enrichment Factors (EF) were computed utilizing the metal content in sediment and continental shale (Turekian and Wedepohl, 1961) as a reference (background). The following equation was used for calculating the enrichment factors:

$$EF = (Me/Mn)_{sample} / (Me/Mn)_{reference}$$

Where $(Me/Mn)_{sample}$ is the ratio of the metal (Me) to Mn in the samples of interest and $(Me/Mn)_{reference}$ is the natural reference value of the metal to Mn ratio. EF values were interpreted as suggested by Birch (2003) for metals studied with respect to natural background concentration. Many authors prefer to express the metal contamination with respect to average shale to quantify the extent and degree of metal pollution (Muller, 1969). In this study, the background metal concentrations were taken from Raju et al. (2012) and Thevenot et al. (2002). The EF values revealed enrichments for most metals by depth. Significant enrichment was found for Cd, Pb, As, Ni, Cr, Cu, Pb, Zn, and Ni in deposited sediments collected from the estuary. Brich (2003) divided contamination into different categories based on EF values. The main advantage of considering EF classes is that they reflect natural variability of sediments in the study area when compared with elemental concentrations of average shale. The enrichment categories are outlined in Table 2.6.6.

Table 2.6.6 Enrichment categories

EF class	Extent of Enrichment
< 1	Indicates no enrichment
1-3	Deficiency to minimal enrichment
3-5	Moderate enrichment
5-10	Moderately severe enrichment
10-25	Severe enrichment
25-50	Very severe enrichment
> 50	Extremely severe enrichment

2.6.7 Adsorption experiments

Pb, Cu, Ni, Cr and Zn are the main pollutants in the Berg Estuary which were investigated in the research as the adsorbates in the adsorption experiments. The adsorption studies were conducted in batch experiments as a function of adsorbent dosage (range of 0.1 to 0.7 g) and contact time (range of 30 to 180 min). The adsorption experiments were also conducted under conditions of both constant pH (pH = 6) at different metal ion concentrations, from which the adsorption isotherms were obtained, and an array of pH at fixed metal concentrations from which the effect of pH on adsorption of metal ions on bed sediment curves were obtained. Part of the sediment samples collected from the Berg Estuary at Site 6 was used to examine the adsorbability of metals mentioned above. The surface sediment was cleaned before an experiment to remove part of the adsorbed metals on the binding sites of surface sediment. The experiments were carried out in a series of polypropylene conical flasks of 150 ml capacity with ground-polypropylene stoppers. Adsorption capacity was calculated using the equation:

$$q = \frac{V(Ci - Ce)}{W}$$

Where q is the adsorption capacity (mg/g), Ci and Ce are the initial and equilibrium concentration of metal ions (mg/L) in the solution respectively. *V* is the volume of metal ion solution (L). W is the amount of the adsorbent on the dry basis (g).

2.6.7.1 Cleaning of sediment surface

Because of the sediment can act as a reservoir or long-term sink for heavy metals, sediment was cleaned to increase active sites on the surface sediment and to make easier penetration of the metal ions to the adsorption sites. 25 g of the sediment sample was placed in a 150 mL polypropylene conical flask. 100 mL of 0.11 mol.L^{-1} acetic acid was added to the flask that was then shaken for 16 h at room temperature. The sediment was separated from the liquid phase by centrifugation for 20 minutes at 3000 rpm. The residue was washed with 100 mL of de-ionized water and shaken again for 8 h and then centrifuged for 20 min at 3000 rpm. The liquid phase was decanted and removal carefully to avoid loss of fine sediment. The sediment was air-dried and stored prior to adsorption analysis.

2.6.7.2 Sediment (adsorbent) dose

In order to find the optimum sediment weight for maximum adsorption, the sediment dose experiment was carried out by using 50 ml of Pb, Cu, Ni, Cr and Zn solutions of initial concentration of 4 mg/l. The solutions were prepared by serial dilution of stock solutions (1000 mg/l). The pH was adjusted in 6 using 0.2 M of both HNO_3 and

NaOH. The solutions were transferred to polypropylene conical flasks of 150 ml containing 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 g of sediment (adsorbent). The contents of the conical flasks were shaken by using a mechanical shaker at about 50 rpm for three hours at room temperature till equilibrium is reached. The contents of conical flask were filtered through double filter paper (MN 615, Ø 70 mm) prior to analysis.

2.6.7.3 Effect of initial metal ion concentration

A batch mode experiment was performed with an optimum amount of sediment (absorbent) dose at different initial concentrations of 2, 4, 6, 8, 10 and 12 mg/L to study the effect of initial metal concentration. The solutions of different initial metal concentration were added to polypropylene conical flasks containing 0.2 g of sediment for Pb, Ni and Zn and 0.4 g for Cr and Cu. The contents of conical flask were also shaken by using a mechanical shaker at 50 rpm for three hours at room temperature till equilibrium is reached. The contents of the conical flasks were filtered through double filter paper (MN 615, Ø70 mm) prior to analysis.

2.6.7.4 Effect of pH

About 0.25 g of the sediment sample was added to the polypropylene conical flasks containing 4 mg/l of stock metal solution. One of the flasks as blank was treated like others without adding dissolved metals. The pH was adjusted in the range from 2 to 12 using 0.2 M of both HNO_3 and NaOH. The pH was measured before and after the solution had been contacted with the sediment, and the difference between the two values was less than 1 pH unit. The solutions were shaken for 3 hours, and then it was left aside for 30 min to settle out the particles. Aart of the supernatant was used for pH measurement and another one was filtered through double filter paper (MN 615, Ø70 mm). The filters were soaked in dilute (1% v/v) HNO_3 for 1 h, and thoroughly rinsed with Millipore deionized water prior to use. The metal concentrations were determined in the aqueous phase.

2.6.7.5 Effect of contact time

In order to study the ability of the sediment to remove the metal ion from the solution, about 0.2g of the sediment sample for Pb, Ni and Zn and 0.4 g for Cr and Cu were added to the flasks containing 4 mg/l of stock metal solution. One of the flasks as blank was also treated like the others without adding dissolved metals. The pH was adjusted to 6.0 using a 0.2 $mol.L^{-1}$ of both HNO_3 and NaOH to avoid metal precipitation at higher pH solutions. The flasks were shaken by using a mechanical shaker at about 50 rpm for 30, 60, 90, 120, 150 and 180 minutes. Shaking was stopped at different selected times and solutions were filtered through double filter paper (MN 615. Ø 70 mm). The metal concentrations were determined in the aqueous phase.

2.6.7.6 Quality control for adsorption experiments

For quality control purposes, in each batch adsorption experiment, control sediment samples, blank metal solutions and laboratory reagent blanks were analysed at the same conditions. All experiments were carried out in duplicate. The average value was used for further calculation. The samples bottles were washed thoroughly with deionized water to ensure that no residues remain that may have an effect on the result for the next experiment. The concentration of metal ions after pH adjustment and adsorption was determined using Microwave Plasma Atomic Emission spectroscopy (MP-AES). Relative standard deviations for three replicates ranged from 0.02 to 2.37 % and detection limits for each metal were 0.6, 4.4, 0.5, 1.3 and 2.8 $mg.L^{-1}$ for Cu, Pb, Cr, Ni and Zn respectively. Quantification of the metals was based upon calibration curves of standard solution of metal ions. These calibration curves were determined several times during the period of experiments. The quantity of metals adsorbed on the sediment was calculated by difference from the amount of metal added and the final solution concentration. The possible error sources in the adsorption experiments involve metals being adsorbed by the flask wall and metal retained by the filters.

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In this chapter, the results that were obtained from the experiments are presented in the form of tables with some explanations. Confidence interval was used to evaluate the standard error of adsorption data according to William (1997). AF values for cores collected from the Berg River estuary are tabulated in the corresponding appendix (A1-A7).

3.1 Chemical speciation of heavy metals in sediment of the Berg River and its estuary.

Three sampling sites along the Berg River (3, 8 and 9) were chosen for determination of heavy metal speciation in the sediments. The extractable contents of As, Cd, Pb, Cr, Cu, Zn, Co, Mn, Ni and Fe, and the extracted percentages of these metals with respect to the sums of four fractions in the river sediments from each extraction step are shown in Tables (3.1.1- 3.1.3).

In the absence of a suitable reference material, an internal check was performed on the results of the sequential extraction by comparing the total amount of metals from the extraction procedure with results of total digestion. The results showed that the sums of the four fractions are in good agreement with the total digestion results with the satisfactory recoveries (62.81-110.53%). Cd and Zn are the most mobile heavy metals in Sites 8 and 3, as they reach the highest percentage in the acid-soluble fraction and the lowest in the residual fraction. The residual of Pb, As, Cr, Fe and Co concentration in three sites appears to be higher than those in other fractions. The pH values of water samples measured in three sites were observed to be the range of 7.73-8.09 while the water temperature for these three sites was in the range from 17.25-25 °C.

Table 3.1.1: Mean and standard deviations for n=3 measurements of heavy metals concentrations (mg/kg, dry weight) in Berg Estuary sediments (Site 8).

Metal & percent	Fraction 1	Fraction 2	Fraction 3	Residual fraction	Sum	Total	Recovery (%)
As	0.69±0.16	0.30±0.25	0.23±0.21	8.75±2.08	9.96	13.90±9.08	64.16
%	6.88	3.01	2.30	87.97			
Cd	0.48±0.09	0.36±0.07	0.11±0.05	0.16±0.02	1.12	1.21±0.16	91.73
%	42.85	32.14	9.82	14.29			
Pb	2.35±0.35	1.73±0.47	50.91±0.52	515.87±22.46	570.86	674.94±5.89	90.31
%	0.41	0.29	8.92	90.37			
Cr	3.82±1.44	12.88±1.44	22.41±3.28	96.80±12.93	135.91	135.54±1.27	110.53
%	2.81	9.47	16.49	71.22			
Cu	0.51±0.33	0.84±0.31	0.99±0.30	3.99±0.11	6.33	5.36±0.9	76.71
%	8.00	10.69	15.63	63.03			
Zn	4.10±1.89	2.33±0.61	3.00±2.64	8.96±7.77	18.39	16.78±2. 31	62.81
%	22.29	12.66	16.31	48.72			
Co	0.20±0.11	0.13±0.03	0.29±0.15	1.64±0.34	2.26	2.34±0.61	70.81
%	8.84	5.75	12.83	72.56			
Mn	6.78±2.46	2.91±0.70	5.79±2.34	149.60±7.54	165.08	168.33±4.09	104.35
%	4.10	1.76	3.50	90.62			
Ni	2.04±0.59	6.04±0.70	10.09±1.65	16.34±6.72	34.52	33.35±1.70	67.18
%	5.90	10.34	29.23	47.33			
Fe	239.60±14.45	433.86±27.09	857.00±41.06	7100.70±42.83	8631.16	8815.00±16.68	97.78
%	2.77	5.02	9.93	82.26			

Table 3.1.2: Mean and standard deviations for n=3 measurements of heavy metals concentrations (mg/kg, dry weight) in coastal marine sediments (Site 9).

Metal & percent	Fraction 1	Fraction 2	Fraction 3	Residual fraction	Sum	Total	Recovery (%)
As	0.13±0.11	0.11±0.01	1.08±0.03	5.19±1.23	6.51	6.86±1.75	97.67
%	1.99	1.68	16.58	79.72			
Cd	1.00±0.02	0.60±0.03	0.01±0.02	0.15±0.08	1.76	2.01±0.08	115.67
%	56.68	19.36	1.10	8.52			
Pb	65.12±0.32	77.22±0.12	58.00±0.32	275.36±22.35	475.7	466.50±4.85	99.67
%	10.9	16.23	12.19	57.88			
Cr	3.56±0.01	5.24±0.01	17.10±0.03	60.90±0.10	86.8	78.50±0.13	114.33
%	4.10	6.02	19.7	70.16			
Cu	0.29±0.03	1.08±0.12	1.45±0.20	2.95±0.13	5.77	5.24±1.32	98.33
%	3.52	18.71	25.12	51.12			
Zn	1.35±1.03	2.06±0.87	1.85±1.44	7.46±0.73	12.71	13.96±5.33	92.67
%	10.62	16.21	14.56	58.69			
Co	0.04±0.72	0.02±0.01	0.03±1.07	0.40±0.19	0.49	0.46±0.12	106.67
%	8.16	4.08	6.12	81.63			
Mn	0.61±0.01	0.94±0.49	1.44±0.09	14.25±1.29	17.24	17.73±0.59	100
%	3.53	5.45	8.35	82.65			
Ni	1.61±0.47	2.58±1.34	8.63±0.73	22.02±9.59	34.84	29.94±2.38	121.67
%	4.62	7.40	24.77	63.2			
Fe	25.01±9.60	119.00±37.19	74.80±6.30	821.10±189.65	1039.91	1237.80±6.17	84
%	2.41	11.44	6.12	78.95			

Table 3.1.3: Mean and standard deviations for n=3 measurements of heavy metals concentrations (mg/kg, dry weight) in Berg River sediment (Site3).

Metal & percent	Fraction 1	Fraction 2	Fraction 3	Residual fraction	Sum	Total	Recovery (%)
As	3.17±0.91	2.13±0.95	0.26±0.03	31.80±2.70	37.36	39.71±0.56	100
%	8.49	5.70	0.69	82.96			
Cd	0.24±0.11	0.14±0.02	0.34±0.01	0.84±0.031	1.56	1.7±0.16	173
%	15.38	8.97	21.79	53.84			
Pb	13.12±1.44	12.6±2.31	8.76±1.75	310.45±22.23	344.93	348.9±6.30	100
%	3.80	3.65	2.54	90.00			
Cr	7.5±2.50	15±2.44	25.2±1.44	123±5.26	170.7	234±4.23	73
%	0.77	8.79	14.76	72.05			
Cu	2.1±1.22	3.66±1.02	4.44±0.41	6.24±1.23	16.44	13.08±0.07	125
%	12.77	22.26	27.00	37.95			
Zn	36.5±1.75	7.98±2.31	5.94±0.09	10.74±1.10	61.2	49.32±1.56	124
%	59.70	13.04	9.70	17.55			
Co	1.02±0.22	0.42±0.04	0.48±0.03	4.26±0.05	6.18	5.76±0.05	107
%	16.5	6.79	7.77	68.93			
Mn	41.94±5.56	5.82±1.53	3.36±0.03	22.8±3.12	73.92	69.66±1.15	106
%	56.73	7.87	4.55	30.84			
Ni	3.00±1.25	12.9±3.55	8.1±1.02	37.56±5.56	61.56	51.24±0.25	120
%	4.87	20.96	13.16	61.01			
Fe	103.2±52.25	124.2±15.22	171±34.2	772.2±19.12	1170.6	1060.2±21.20	110
%	8.81	10.60	14.60	65.60			

3.2 Distribution of heavy metals in core sediments and assessment of metals contamination.

3.2.1 Vertical distribution of heavy metals in core sediments

The concentrations of heavy metals (Cd, Pb, As, Cr, Cu, Fe, Ni, Mn and Zn) in core sediments as a function of depth are given in Tables 3.2.1.1 to 3.2.1.3.

Table 3.2.1.1 Concentration of heavy metals (mg/kg) and their standard deviation for Site 6, Core1

Depth (cm)	As	Cd	Pb	Cr	Co	Mn	Cu	Ni	Zn	Fe
Surface	23.22±0.08	1.29±0.01	373.96±0.08	90.69±6.29	9.87±0.21	158.81±5.17	6.67±0.01	39.62±2.64	19.17±0.25	8833.77±0.13
20	38.77±0.02	1.35±0.07	421.52±0.02	87.44±0.42	10.47±0.46	149.55±0.33	6.99±0.54	37.03±0.11	19.84±1.73	8881.79±0.62
40	32.69±0.06	1.32±0.11	379.13±0.06	89.90±2.12	10.51±1.01	143.91±14.19	6.86±0.02	38.17±1.51	19.48±0.26	8596.42±0.04
60	16.74±0.17	1.71±0.05	252.40±0.17	98.71±0.63	11.87±0.81	129.10±4.29	11.01±0.49	42.77±0.46	30.07±0.02	13008.35±0.34
80	24.00±0.27	1.42±0.08	308.11±0.27	94.57±3.64	10.35±0.17	133.52±5.49	8.77±0.96	41.08±1.31	24.68±1.05	12059.19±1.00
100	28.30±0.12	1.77±0.11	334.12±0.12	101.73±4.67	11.88±0.76	131.22±9.75	12.21±0.69	45.59±0.25	34.52±1.77	13552.85±0.56
120	27.01±0.11	1.43±0.02	277.12±0.11	96.09±0.65	11.08±0.69	115.21±10.07	9.53±0.25	43.02±0.85	27.08±0.26	12108.69±0.19
140	35.45±0.08	1.74±0.12	166.92±0.08	98.79±2.02	11.52±0.43	138.39±6.72	11.28±0.66	43.60±2.38	30.12±1.47	13320.95±0.33
160	30.47±0.07	1.34±0.04	208.79±0.07	98.51±0.05	11.00±0.52	135.36±12.77	8.41±0.18	44.48±0.66	23.92±0.36	11421.14±0.82

Table 3.2.1.2 Concentration of heavy metals (mg/kg) and their standard deviation for Site 7, Core 2

Depth (cm)	As	Cd	Pb	Cr	Co
Surface	22.35±0.02	0.98±0.01	140.57±0.2	87.71±2.35	7.64±0.16
20	27.25±0.03	4.51±0.11	122.90±0.03	120.10±0.78	13.51±0.10
40	14.25±0.08	1.79±0.03	392.86±0.08	108.35±2.00	11.36±0.31
60	20.83±0.06	2.07±0.07	209.91±0.06	95.29±0.72	9.54±0.05
80	17.88±0.20	1.72±0.34	500.32±0.20	100.93±5.60	9.92±0.16
100	38.59±0.07	1.64±0.13	253.77±0.07	96.73±5.08	11.69±0.43
120	12.93±0.03	1.38±0.06	504.11±0.03	96.12±2.86	9.15±0.12
140	20.33±0.17	1.74±0.22	354.09±0.17	101.27±3.95	10.23±0.06
160	15.85±0.07	1.40±0.22	169.50±0.07	100.83±4.05	9.47±0.93
180	44.12±0.01	1.43±0.06	166.16±0.01	92.55±3.79	8.89±1.37
200	32.13±0.18	1.46±0.04	316.37±0.018	97.78±2.07	8.30±0.01
220	17.36±0.16	1.30±0.13	390.72±0.016	94.02±0.15	9.14±0.13
240	12.04±0.41	1.34±0.07	370.90±0.21	95.90±3.68	8.03±0.04

Depth (cm)	Mn	Cu	Ni	Zn	Fe
Surface	148.03±16.91	6.64±0.30	40.06±0.81	20.64±0.49	9309.71±0.31
20	171.98±1.63	13.85±0.06	53.02±1.54	42.54±1.44	21455.28±0.22
40	145.86±4.21	8.44±0.17	48.12±0.49	25.68±0.41	12309.41±0.17
60	146.86±7.54	5.22±0.05	39.41±0.70	19.21±0.04	8356.59±0.15
80	139.89±27.39	4.94±0.71	41.54±2.25	18.78±3.19	8094.74±1.37
100	169.63±5.49	16.25±0.91	38.92±2.15	19.50±0.09	8549.39±0.16
120	150.34±4.07	4.84±0.03	40.25±0.62	16.06±0.04	7558.90±0.33
140	158.88±0.64	5.44±0.59	41.12±0.89	20.02±0.99	8690.72±0.20
160	155.62±6.74	4.91±0.25	40.59±2.85	17.06±1.67	7695.02±0.05
180	138.73±35.40	5.36±0.58	38.95±0.34	18.58±0.18	7584.39±1.16
200	129.26±3.10	7.59±0.57	40.64±1.70	17.95±0.21	7378.47±0.07
220	158.59±6.01	4.89±0.15	38.60±0.86	14.99±0.82	6976.04±0.39
240	126.02±7.28	4.41±0.08	40.72±2.32	15.59±1.01	6842.39±0.14

Table 3.2.1.3 Concentration of heavy metals (mg/kg) and their standard deviation for Site 5, Core 3

Depth (cm)	As	Cd	Pb	Cr	Co
Surface	15.31±0.04	3.24±0.28	434.10±0.02	99.36±7.74	11.70±0.90
20	24.17±0.16	2.87±0.14	232.31±0.16	80.68±3.78	10.30±0.48
40	39.30±0.09	3.14±0.31	152.36±0.09	85.45±6.85	14.76±2.10
60	30.67±0.07	8.38±0.07	120.27±0.07	77.95±4.75	9.94±0.11
80	40.51±0.03	2.93±0.11	124.15±0.03	80.36±8.68	16.06±0.65
100	41.72±0.01	2.93±0.30	138.58±0.01	82.59±8.33	8.31±0.53
120	45.57±0.08	2.07±0.11	133.33±0.08	77.39±7.95	4.36±0.13
140	43.30±0.06	6.39±1.0	131.66±0.06	86.17±5.53	7.22±0.94
160	61.26±0.01	0.71±0.0	157.10±0.01	79.82±2.77	5.71±0.11
180	23.96±01	1.08±0.60	191.90±0.1	114.14±37.97	7.57±3.26
200	24.33±0.27	0.64±0.01	273.62±0.27	70.94±0.80	4.57±0.14
220	15.87±0.02	1.25±0.14	159.93±0.04	91.83±2.45	5.51±0.83

Depth (cm)	Mn	Cu	Ni	Zn	Fe
Surface	67.74±3.76	9.19±0.08	58.42±1.06	30.37±1.29	10058.40±0.41
20	59.33±1.83	7.20±1.28	52.96±2.19	17.25±0.61	7926.93±0.68
40	65.25±9.86	7.07±1.71	63.21±5.94	29.23±3.42	8575.13±0.98
60	45.05±0.43	5.33±0.24	48.23±2.53	27.44±0.73	5994.20±0.17
80	42.92±4.92	11.11±1.42	52.86±5.39	54.53±1.43	6469.16±0.45
100	59.01±3.03	6.75±0.14	44.50±4.30	20.58±0.81	8100.92±0.45
120	63.41±2.22	6.38±2.20	39.82±4.38	11.48±0.66	7556.18±0.21
140	38.73±2.78	8.34±0.15	39.64±3.74	11.57±1.49	4752.32±0.37
160	28.11±1.72	5.28±0.66	39.25±1.12	8.77±0.06	3428.20±0.03
180	36.67±13.79	7.31±0.15	54.69±17.03	12.45±4.95	2824.15±0.63
200	19.02±1.34	3.02±0.06	37.27±0.33	10.96±2.90	5634.34±0.11
220	55.60±9.23	3.85±0.65	43.45±6.97	10.90±0.98	4487.67±0.34

3.2.2 Particle size distribution, moisture content and organic matter in core sediments by depth

Based on the results of particle size analysis using a Mastersizer 2000, sediment samples were generally classified into five groups as follows: clay (<2 µm); silt (2–20 µm); fine sand (20–200 µm); medium sand (200–500 µm) and coarse sand (500-2000 µm). Generally, sediment characteristics of all cores are presented in Tables 3.2.2.1 to 3.2.2.3. The Berg River estuary is dominated by three sediment types, fine sand and silt for Core 1, fine sand for Core 2 and fine and coarse sand for Core 3.

Table 3.2.2.1: Sediment characteristics for Site 6, Core 1

Depth (cm)	Moisture content (%)	% O.M	% Clay	% Silt	% FS	% MS	% CS	Surface area (m^2/g)
Surface	18.33	1.87	0.45	10.26	63.68	0.44	0.00	0.44
20	19.39	1.91	0.49	11.58	65.90	0.64	0.00	0.50
40	18.20	1.70	0.52	10.46	68.22	0.50	0.00	0.50
60	20.90	3.19	1.14	22.5	50.51	4.82	0.57	0.94
80	18.28	9.94	0.64	14.43	61.81	4.36	0.54	0.71
100	22.11	3.31	0.79	17.09	54.72	5.26	0.54	0.50
120	18.99	2.64	0.80	16.7	59.81	8.86	0.55	0.71
140	19.25	3.28	0.80	17.51	58.25	12.72	0.61	0.71
160	14.28	2.13	0.65	13.79	67.47	16.96	0.82	0.61

Table 3.2.2.2: Sediment characteristics for Site 7, Core 2

Depth (cm)	Moisture content (%)	% O.M	% Clay	% Silt	% FS	% MS	% CS	Surface area (m^2/g)
Surface	16.77	4.36	0.40	9.70	67.86	11.29	0.33	0.39
20	28.23	6.15	0.95	22.67	32.19	1.68	0.77	0.90
40	36.21	5.28	0.91	22.74	38.92	0.26	0.00	0.88
60	19.70	11.12	0.45	10.12	51.92	0.18	0.00	0.45
80	22.44	5.28	0.50	11.96	52.54	0.14	0.00	0.50
100	22.37	7.78	0.35	8.34	60.02	0.23	0.00	0.36
120	20.29	9.65	0.34	8.43	61.56	0.33	0.00	0.36
140	22.77	9.45	0.44	10.44	58.12	0.33	0.00	0.44
160	22.10	9.33	0.35	8.43	60.91	0.27	0.00	0.36
180	21.48	7.97	0.15	5.30	64.17	0.38	0.00	0.23
200	17.77	13.01	0.11	4.12	66.25	0.33	0.00	0.19
220	21.31	6.23	0.14	4.31	68.36	0.11	0.00	0.20
240	20.00	6.31	0.16	5.13	68.39	0.25	0.00	0.22

Table 3.2.2.3: Sediment characteristics for Site 5, Core 3

Depth (cm)	Moisture content (%)	% O.M	% clay	% Silt	% FS	% MS	% CS	Surface area (m^2/g)
Surface	20.18	6.96	0.27	9.73	69.31	28.59	1.81	0.34
20	22.17	2.55	0.13	5.94	81.31	41.28	3.19	0.21
40	21.35	4.42	0.08	4.60	83.07	38.74	2.48	0.16
60	18.12	9.53	0.04	3.24	87.35	38.05	2.13	0.12
80	17.85	3.89	0.05	3.79	85.35	37.54	2.17	0.14
100	19.23	2.68	0.17	7.24	74.81	32.31	1.85	0.26
120	20.29	9.23	0.04	3.50	86.64	34.06	1.18	0.12
140	22.77	14.75	0.17	7.61	75.29	27.52	1.06	0.26
160	18.35	0.68	0.14	6.49	80.28	42.97	3.00	0.22
180	17.22	0.76	0.18	7.57	78.70	47.19	4.00	0.26
200	15.33	0.43	0.10	4.21	86.07	53.16	4.98	0.16
220	14.25	2.86	0.84	23.44	40.51	12.04	0.89	0.87

3.3 Spatial variation of heavy metals concentrations, particle size and organic matter in surface sediments from the Berg River.

3.3.1 Sediment metal contents

Average concentration of heavy metals in surface sediment of the Berg River is summarized in Table 3.3.1. The total concentrations vary depending on the sampling site within the river and its estuary. The metal content of the sediment ranged from 6.82 to 46.47 mg/kg for arsenic (As), 1.07 to 2.97 mg/kg for cadmium (Cd), 187.94 to 674.94 for lead (Pb), 69.80 to 135.5 mg/kg for chromium (Cr), 4.43 to 12.57 mg/kg for cobalt (Co), 13.96 to 149.20 mg/kg for manganese (Mn), 0.45 to 16.13 mg/kg for copper (Cu), 17.73 to168.33 mg/kg for nickel (Ni), 9.35 to 47.76 mg/kg for zinc (Zn) and 1237.80 to 22690.76 mg/kg for iron (Fe). The range of concentrations of Co, Mn, Cu, Ni, Zn and Fe in the sediment were lower than average shale concentration, while those of As, Cd and Pb were higher than average shale concentration.

Table 3.3.1 Average concentrations of heavy metals in surface sediment (mg/kg) and its standard deviation

Site	As	Cd	Pb	Cr	Co
1	34.00±3.03	1.07±0.09	312.57±21.37	73.82±7.04	5.64±0.84
2	33.92±4.18	1.14±0.08	350.05±6.79	69.80±2.75	4.43±1.15
3	46.47±1.52	1.77±0.73	445.40±10.44	104.11±15.84	8.43±1.70
4	34.92±1.27	1.80±1.13	323.99±11.76	99.65±31.96	12.57±1.76
5	33.83±1.37	2.97±2.31	187.44±9.05	85.56±11.59	9.33±3.76
6	28.52±6.75	1.48±0.2	302.45±8.40	95.16±4.86	10.95±0.71
7	22.76±10.04	1.75±0.87	300.92±3.29	99.04±8.05	9.76±1.63
8	13.9±3.08	1.21±0.16	674.94±7.58	135.54±1.27	5.36±0.98
9	6.86±1.75	2.01±0.08	466.5±2.85	78.5±0.13	5.24±1.32
Site	**Mn**	**Cu**	**Ni**	**Zn**	**Fe**
1	27.67±6.56	6.03±0.72	36.64±1.32	9.35±1.19	3302.4±9.48
2	27.12±8.28	5.72±0.74	36.28±1.18	11.9±2.64	2908.2±9.13
3	65.9±18.41	16.13±1.71	52.6±4.66	47.76±12.54	22691±16.03
4	101.88±10.22	6.85±5.03	45.92±11.37	34.75±2.39	20611±21.04
5	48.4±1.71	7.3±2.30	47.86±8.50	22.54±1.59	6317.3±22.02
6	137.23±2.59	9.08±2.07	41.71±2.92	25.43±1.45	11309±11.75
7	149.21±3.87	7.14±3.74	41.69±4.16	20.51±1.16	9292.4±9.13
8	16.78±2.31	2.34±0.61	168.33±7.09	33.35±1.70	8815±2.56
9	13.96±0.33	0.46±0.04	17.73±8.59	29.94±8.23	1237.8±6.11

3.3.2 Heavy metals enrichment factors

The extent to which sediments are impacted by anthropogenic sources was estimated, by calculating an enrichment factor (EF) for each metal with respect to average concentration of manganese in shale as discussed in section 2.7. In general, calculated sediment metal enrichment factors were highest for As, Cd, Pb, Cr and Ni while they were similar to average shale (crustal abundances) in the case of Fe, Cu and Zn.

3.3.3. Sediment type and organic matter

Briefly, the Berg River is dominated by two sediment types, fine sand and clay (Table 3.3.3). Sediment types within the river range from fine-grained silt to larger-grained sand (coarse sand) and are affected by its geographic site within the river. The organic matter content ranged from a minimum of 0.39% at site 9 to 6.07% at site 1.

Table 3.3.3: Sediment characteristics and organic matter of the Berg River

Site	% OM	% silt	% clay	% FS	% MS	% CS
1	6.07	0.76	18.05	46.30	6.88	0.06
2	1.69	0.43	11.45	63.65	17.01	0.56
3	3.42	0.88	22.37	40.94	4.03	0.01
4	2.88	0.42	11.93	60.03	19.44	0.93
5	4.64	0.16	6.76	77.89	36.20	2.49
6	1.83	0.49	10.77	65.93	0.53	0.00
7	1.60	0.78	16.25	50.26	3.77	0.11
8	5.26	0.75	18.37	46.32	4.41	0.37
9	0.39	0.15	3.56	88.23	50.69	3.03

3.4 Adsorption of Cu, Pb, Cr, Ni and Zn on to bed sediment (Site 6 at 20 cm depth) of the Berg Estuary

The results obtained from the adsorption experiments are summarized in Tables 3.4.1 to 3.4.7.

Table 3.4.1 Effect of adsorbent dose on adsorption of Cu, Pb and Cr on bed sediment (Site 6 at 20 cm depth) at pH = 6; adsorbate concentration = 3 mg/L (± confidence interval)

Adsorbent Dose (g)	Ci (mg/L)	Ce (mg/L)	Ci-Ce (mg/L)	Metal adsorbed (mg/g)
Cu				
0.10	2.99±0.16	2.55±0.17	0.44±0.03	0.22
0.20	2.99±0.16	2.26±0.17	0.73±0.03	0.18
0.30	2.99±0.16	2.25±0.17	0.74±0.03	0.12
0.40	2.99±0.16	1.11±0.21	1.88±0.04	0.24
0.50	2.99±0.16	1.82±0.18	1.17±0.03	0.12
0.60	2.99±0.16	1.48±0.20	1.51±0.03	0.13
0.70	2.99±0.16	1.62±0.19	1.37±0.03	0.10
Pb				
0.10	3.00±0.12	2.12±0.12	0.88±0.01	0.44
0.20	3.00±0.12	0.87±0.15	2.13±0.02	0.53
0.30	3.00±0.12	1.70±0.13	1.3±0.02	0.22
0.40	3.00±0.12	0.75±0.13	2.25±0.02	0.28
0.50	3.00±0.12	1.06±0.14	1.94±0.02	0.19
0.60	3.00±0.12	0.66±0.15	2.34±0.02	0.20
0.70	3.00±0.12	0.80±0.15	2.20±0.02	0.16
Cr				
0.10	2.99±0.11	2.45±0.12	0.54±0.01	0.27
0.20	2.99±0.11	2.23±0.12	0.76±0.01	0.19
0.30	2.99±0.11	2.19±0.12	0.80±0.01	0.13
0.40	2.99±0.11	0.05±0.18	2.94±0.02	0.37
0.50	2.99±0.11	1.64±0.13	1.57±0.01	0.16
0.60	2.99±0.11	1.10±0.15	1.89±0.02	0.16
0.70	2.99±0.11	1.27±0.14	1.72±0.02	0.12

Table 3.4.2 Effect of adsorbent dose on adsorption of Ni and Zn on bed sediment (Site 6 at 20 cm depth) at pH = 6; adsorbate concentration = 3 mg/L (± confidence interval)

Adsorbent dose (g)	Ci (mg/L)	Ce (mg/L)	Ci-Ce (mg/L)	Metal adsorbed (mg/g)
Ni				
0.10	2.89±0.10	2.65±0.10	0.24±0.01	0.12
0.20	2.89±0.10	2.35±0.10	0.54±0.01	0.14
0.30	2.89±0.10	2.53±0.10	0.36±0.01	0.06
0.40	2.89±0.10	2.04±0.10	0.85±0.01	0.11
0.50	2.89±0.10	2.32±0.10	0.57±0.01	0.06
0.60	2.89±0.10	2.18±0.10	0.71±0.01	0.06
0.70	2.89±0.10	2.20±0.10	0.69±0.01	0.05
Zn				
0.10	3.03±0.28	2.81±0.28	0.22±0.08	0.11
0.20	3.03±0.28	2.41±0.28	0.62±0.08	0.16
0.30	3.03±0.28	2.58±0.28	0.45±0.08	0.08
0.40	3.03±0.28	2.04±0.31	0.99±0.09	0.12
0.50	3.03±0.28	2.34±0.29	0.69±0.08	0.07
0.60	3.03±0.28	2.2±0.30	0.83±0.08	0.07
0.70	3.03±0.28	2.22±0.30	0.81±0.08	0.06

Table 3.4.3: Effect of pH on the adsorption of metal ion on bed sediment (Site 6 at 20 cm depth) (± confidence interval)

pH before adsorption	pH after adsorption	*Ci* (mg/L)	*Ce* (mg/L)	*Ci*-*Ce* (mg/L)	Metal adsorbed (mg/g)
Cu					
2.00	2.22	4.17±0.17	3.61±0.18	0.56±0.03	0.07
3.99	5.07	4.17±0.17	0.04±0.26	4.14±0.05	0.52
6.00	6.46	4.17±0.17	0.00±0.26	4.17±0.05	0.52
8.00	7.66	4.17±0.17	0.01±0.26	4.17±0.05	0.52
10.2	10.18	4.17±0.17	0.02±0.25	4.16±0.05	0.52
11.9	11.96	4.17±0.17	0.08±0.25	4.09±0.05	0.51
Pb					
2.00	2.09	2.79±0.11	2.15±0.08	0.64±0.01	0.16
4.00	4.5	2.79±0.11	1.24±0.10	1.55±0.01	0.39
6.00	6.46	2.79±0.11	0.08±0.12	2.71±0.01	0.68
8.00	7.63	2.79±0.11	0.13±0.10	2.66±0.01	0.67
10.00	9.6	2.79±0.11	0.09±0.13	2.7±0.01	0.68
12.00	11.65	2.79±0.11	0.10±0.13	2.69±0.01	0.67
Cr					
2.00	2.22	4.09±0.14	3.99±0.13	0.11±0.02	0.01
3.99	5.07	4.09±0.14	0.05±0.20	4.05±0.03	0.51
6.00	6.46	4.09±0.14	0.03±0.20	4.06±0.03	0.51
8.00	7.66	4.09±0.14	0.03±0.20	4.06±0.03	0.51
10.20	10.18	4.09±0.14	0.05±0.20	4.04±0.03	0.51
11.90	11.96	4.09±0.14	0.25±0.16	3.84±0.02	0.48
Ni					
2.00	2.22	4.04±0.06	3.70±0.06	0.34±0.00	0.04
3.99	5.07	4.04±0.06	1.31±0.08	2.74±0.01	0.34
6.00	6.46	4.04±0.06	0.22±0.06	3.83±0.00	0.48
8.00	7.66	4.04±0.06	0.02±0.09	4.03±0.01	0.50
10.20	10.18	4.04±0.06	0.05±0.09	3.99±0.01	0.50
11.90	11.96	4.04±0.06	0.06±0.09	3.98±0.01	0.50
Zn					
2.00	2.22	4.10±0.27	3.62±0.25	0.48±0.07	0.02
3.99	5.07	4.10±0.27	0.55±0.37	3.56±0.10	0.18
6.00	6.46	4.10±0.27	0.05±0.41	4.05±0.12	0.20
8.00	7.66	4.10±0.27	0.13±0.41	3.98±0.12	0.20
10.2	10.18	4.10±0.27	0.14±0.41	3.96±0.12	0.20
11.9	11.96	4.10±0.27	0.13±0.41	3.98±0.12	0.20

Table 3.4.4: Effect of contact time on the adsorption of Cu, Pb and Cr onto bed sediment (Site 6 at 20 cm depth) (± confidence interval)

Time (min)	Ci (mg/L)	Ce (mg/L)	Ci-Ce (mg/L)	Metal adsorbed (mg/g)
Cu				
0	3.33±0.34	3.33±0.34	0.00±0.12	0.00
30	3.33±0.34	2.58±0.21	0.75±0.08	0.09
60	3.33±0.34	2.63±0.24	0.70±0.09	0.09
90	3.33±0.34	2.68±0.23	0.65±0.08	0.08
120	3.33±0.34	2.71±0.21	0.62±0.08	0.08
150	3.33±0.34	2.72±0.23	0.61±0.08	0.08
180	3.33±0.34	2.01±0.24	0.89±0.09	0.11
Pb				
0	4.04±0.08	4.04±0.08	0.00±0.01	0.00
30	4.04±0.08	0.09±0.02	3.96±0.00	0.50
60	4.04±0.08	0.18±0.05	3.86±0.00	0.48
90	4.04±0.08	0.25±0.06	3.79±0.01	0.47
120	4.04±0.08	0.18±0.05	3.86±0.00	0.48
150	4.04±0.08	0.29±0.02	3.75±0.00	0.47
180	4.04±0.08	0.35±0.08	3.69±0.01	0.46
Cr				
0	3.35±0.22	3.32±0.22	0.00±0.05	0.00
30	3.35±0.22	2.85±0.20	0.47±0.05	0.47
60	3.35±0.22	2.89±0.20	0.43±0.04	0.43
90	3.35±0.22	2.93±0.20	0.39±0.04	0.39
120	3.35±0.22	2.88±0.21	0.44±0.04	0.42
150	3.35±0.22	2.98±0.21	0.34±0.05	0.39
180	3.35±0.22	2.30±0.20	1.02±0.05	0.40

Table 3.4.5: Effect of contact time on the adsorption of Ni and Zn onto bed sediment (Site 6 at 20 cm depth) (± confidence interval)

Time (min)	Co (mg/L)	Ce (mg/L)	Co-Ce (mg/L)	Metal adsorbed (mg/g)
Ni				
0	2.84±0.27	2.84±0.27	0.00±0.07	0.00
30	2.84±0.27	2.41±0.26	0.43±0.07	0.11
60	2.84±0.27	2.57±0.25	0.27±0.07	0.07
90	2.84±0.27	2.71±0.26	0.13±0.07	0.03
120	2.84±0.27	2.77±0.26	0.07±0.07	0.02
150	2.84±0.27	2.77±0.26	0.07±0.07	0.02
180	2.84±0.27	2.68±0.25	0.16±0.07	0.04
Zn				
0	3.34±0.21	3.34±0.21	0.00±0.04	0.00
30	3.34±0.21	2.83±0.19	0.52±0.04	0.13
60	3.34±0.21	2.95±0.19	0.39±0.04	0.10
90	3.34±0.21	2.95±2.19	0.39±0.04	0.10
120	3.34±0.21	2.93±0.19	0.41±0.04	0.10
150	3.34±0.21	2.96±0.19	0.38±0.04	0.10
180	3.34±0.21	2.86±0.19	0.48±0.04	0.12

Table 3.4.6: Effect of initial concentration on the adsorption of metal ion on clean sediment of the Berg Estuary (Site 6 at 20 cm depth) (± confidence interval)

pH value	Ci (mg/L)	Ce (mg/L)	Ci-Ce (mg/L)	Metal adsorbed (mg/g)
Cu				
6	2.19±0.43	1.55±0.45	0.64±0.20	0.08
6	3.94±0.36	3.19±0.39	0.75±0.14	0.09
6	5.83±0.33	4.99±0.33	0.84±0.11	0.11
6	7.53±0.35	6.60±0.33	0.93±0.11	0.12
6	9.37±0.41	8.32±0.41	1.05±0.15	0.13
6	14.16±0.68	13.02±0.61	1.14±0.42	0.14
Pb				
6	2.88±0.26	1.38±0.30	1.50±0.08	0.26
6	4.58±0.24	2.91±0.26	1.67±0.06	0.42
6	6.81±0.24	4.99±0.24	1.83±0.06	0.46
6	9.10±0.26	6.95±0.26	2.15±0.07	0.54
6	11.69±0.32	9.10±0.31	2.59±0.10	0.65
6	14.67±0.32	12.22±0.24	2.45±0.08	0.62
Cr				
6	2.21±0.23	0.77±0.27	1.44±0.06	0.18
6	3.77±0.20	1.77±0.24	2.00±0.05	0.25
6	5.41±0.18	2.93±0.21	2.48±0.04	0.31
6	7.41±0.19	4.23±0.19	3.18±0.04	0.40
6	9.41±0.23	6.00±0.18	3.41±0.04	0.43
6	15.51±0.42	10.99±0.27	4.52±0.12	0.57
Ni				
6	2.06±0.26	1.70±0.27	0.36±0.07	0.09
6	3.87±0.21	3.49±0.22	0.38±0.05	0.10
6	5.55±0.19	5.16±0.19	0.39±0.04	0.10
6	7.41±0.20	6.99±0.20	0.42±0.04	0.11
6	9.24±0.24	8.85±0.23	0.39±0.06	0.10
6	14.41±0.41	13.85±0.39	0.56±0.16	0.14
Zn				
6	2.07±0.51	1.75±0.52	0.32±0.25	0.08
6	4.18±0.40	3.85±0.42	0.33±0.17	0.08
6	6.16±0.37	5.80±0.37	0.36±0.14	0.09
6	7.79±0.40	7.35±0.41	0.44±0.16	0.11
6	9.42±0.48	8.88±0.47	0.54±0.25	0.14
6	12.91±0.71	12.47±0.70	0.44±0.50	0.11

Table 3.4.7: Effect of initial concentration on the adsorption of metal ion on unclean sediment of the Berg Estuary (Site 6 at 20 cm depth) (± confidence interval)

pH value	Ci (mg/L)	Ce (mg/L)	Ci-Ce (mg/l)	Metal adsorbed (mg/g)
Cu				
6	2.16±0.11	1.09±0.18	1.07±0.02	0.13
6	3.26±0.11	1.03±0.14	2.23±0.02	0.28
6	4.27±0.12	3.81±0.11	0.46±0.01	0.06
6	5.13±0.15	4.78±0.11	0.35±0.02	0.04
6	5.98±0.18	4.97±0.14	1.01±0.03	0.13
6	7.15±0.23	6.31±0.19	0.84±0.04	0.11
Pb				
6	2.34±0.24	1.85±0.31	0.49±0.08	0.12
6	3.30±0.23	2.56±0.29	0.74±0.07	0.19
6	4.39±0.26	3.18±0.31	1.21±0.08	0.30
6	5.60±0.30	4.05±0.29	1.55±0.09	0.39
6	6.34±0.35	4.44±0.30	1.90±0.10	0.47
6	7.80±0.39	5.80±0.38	2.00±0.10	0.50
Cr				
6	2.11±0.21	0.10±0.31	2.01±0.07	0.25
6	3.08±0.19	2.05±0.27	1.03±0.05	0.13
6	3.98±0.21	2.70±0.25	1.28±0.05	0.16
6	4.97±0.26	3.95±0.26	1.02±0.07	0.13
6	5.94±0.32	4.6±0.31	1.34±0.08	0.17
6	7.35±0.31	6.00±0.33	1.35±0.08	0.17
Ni				
6	2.13±0.14	1.46±0.16	0.67±0.02	0.08
6	3.12±0.13	1.81±0.15	1.31±0.02	0.16
6	4.04±0.14	3.5±0.14	0.54±0.02	0.07
6	5.07±0.18	4.51±0.17	0.56±0.03	0.07
6	5.96±0.22	5.41±0.19	0.55±0.04	0.07
6	7.12±0.28	6.57±0.25	0.55±0.07	0.07
Zn				
6	2.17±0.18	1.33±0.22	0.84±0.04	0.11
6	3.18±0.17	1.67±0.22	1.51±0.04	0.19
6	4.04±0.19	3.81±0.20	0.23±0.04	0.03
6	5.07±0.23	4.76±0.18	0.31±0.04	0.04
6	5.83±0.28	5.05±0.22	0.78±0.06	0.10
6	6.83±0.34	6.09±0.23	0.74±0.08	0.09

4.1 Introduction

The most important findings of this study are discussed in this chapter. The study of chemical speciation of 10 heavy metals (As, Cd, Pb, Cr, Cu, Zn, Co, Mn, Ni and Fe) in sediment was undertaken to understand the relationship between the distributions of metals in different fractions and their mobility and bioavailability. The distribution of the heavy metals in four sediment fractions obtained using the optimized BCR protocol reflects the mechanisms by which the metals are associated with the sediments. The metals extracted in the first fraction correspond to those that are weakly adsorbed or associated with carbonates. In the second fraction, are those associated with Fe and Mn oxides, and in the third fraction are those associated with sulphides and organic matter. The residual fraction contains the primary and secondary minerals derived from natural geological formations, which can contain trace metals within their crystalline structures (Singh et al., 2005). The acid-soluble fraction represents the mobile and bioavailable heavy metal fraction. In this fraction, the metals are easily released into the environment. The presence of heavy metals in this fraction where they can be taken up by organisms from the sediments is the most hazardous to the ecosystem. However, metals in the residual fraction are a measure of the level of environmental pollution. The higher the proportion of metals presents in this fraction, the lower the level of pollution because these metals are of geological origin rather than anthropogenic origin (Howari and Banat, 2001).

In addition, the discussion of the results obtained from the vertical distribution of metals in sediment serves to clarify the relationship between the concentrations of metals and sediment components and see how they relate each other. In order to interpret data in more detail and to explain the anthropogenic impact on vertical and spatial distribution of heavy metals in sediment, anthropogenic and enrichment factors were estimated to determine if the levels of metals in sediments of the estuary and its surrounding environment were of anthropogenic origins.

The spatial profile of metals in sediment will also be discussed to discover the extent of the impact of the geographical location of the river and its estuary on the concentrations of metals in sediments.

Finally, adsorption of Pb, Cr, Cu, Ni and Zn on to bed sediment of the estuary will be discussed to describe the interactions between adsorbents and adsorbates. The adsorption studies were performed by conducting batch mode experiments, varying the parameters initial metal concentration, pH, adsorbent dose and contact time. The pH effect and contact time were varied to know their effect on the amount of metal ion that is adsorbed on sediment under different conditions. The adsorption data were analysed by both Langmuir and Freundlich isotherm models to study the type and the strength of metal ion adsorption on to the surface of the sediments.

4.2 Chemical speciation, potential mobility and bioavailability of heavy metals in sediment

The Berg River and its estuary have received a large load of contaminants; the heavy metals will be adsorbed onto suspended particulate sediment. Different size particles are then transported through the river channel by water. The partitioning of heavy metals between water and three binding fractions in sediments particles will be affected by change of conditions such as salinity and pH when the water flows down the river channel to, in the estuary. If the increase in salinity and pH can induce the remobilization of heavy metals in the acid-soluble fraction, the metal toxicology in the aquatic environment will increase (Rainbow, P.S., 1997a).

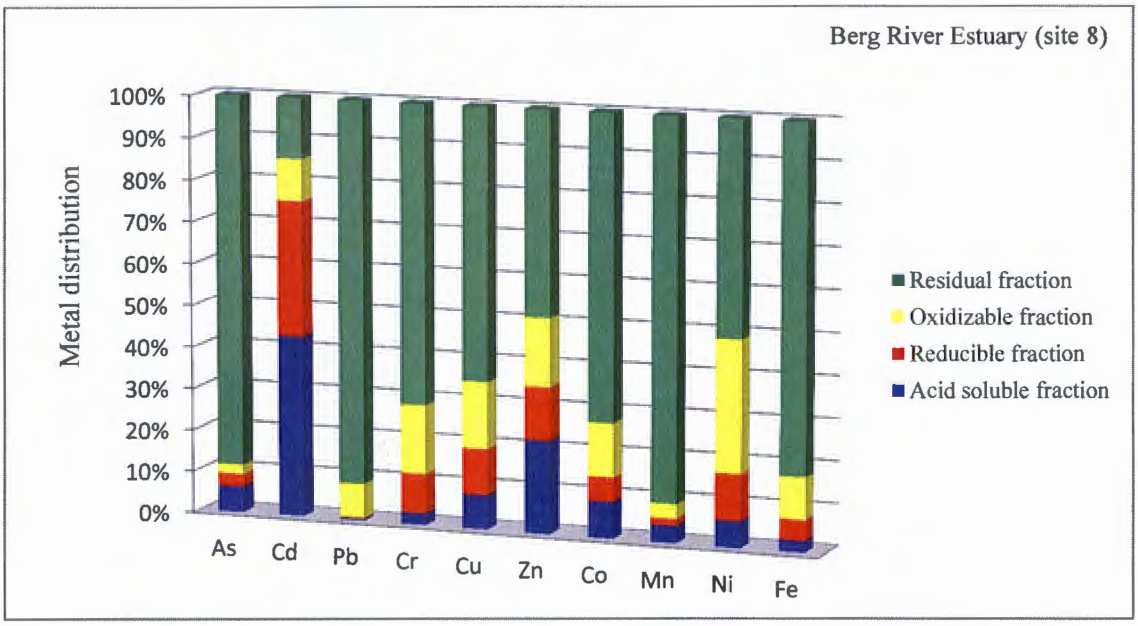

Figure 4.2.1 Distribution of heavy metals in sediments between different fractions for Site 8

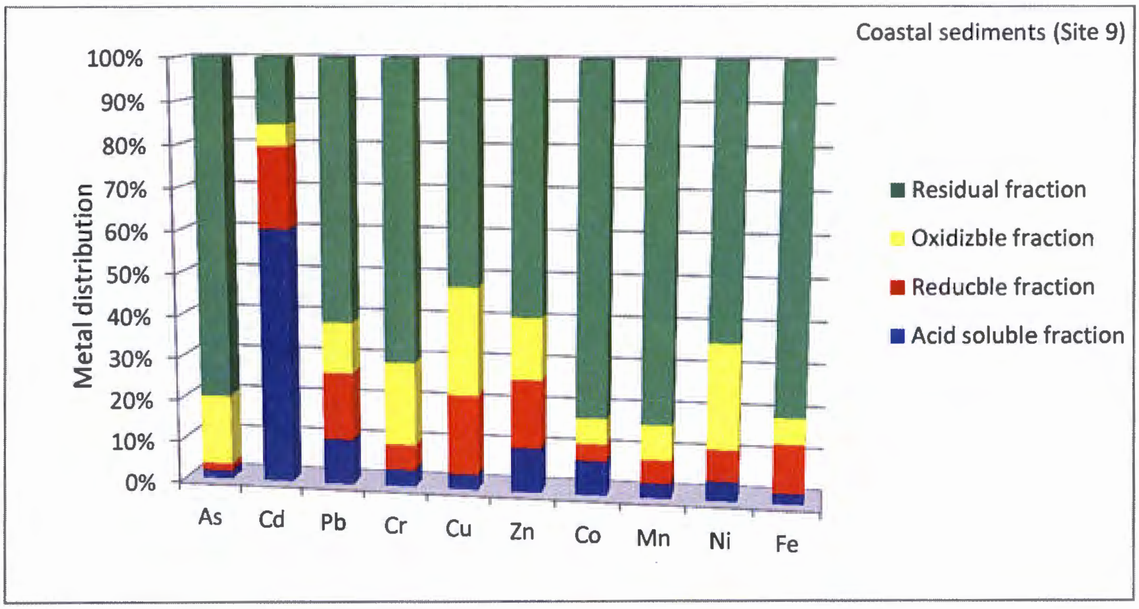

Figure 4.2.2 Distribution of heavy metals in sediment between different fractions for Site 9.

The results of the distribution of Fe and Mn in the Berg estuary and coastal marine sediments (see Figs. 4.2.1 and 4.2.2) show low percentages in the acid-soluble fraction compared to the total concentration. The dominant proportions were in the residual fraction and of geological origin. This result was similar to the data reported by Usero et al. (1998) who found that more than 89% of total Fe was in the residual fraction. These results are not surprising as the solubility of Fe and Mn at pH~6 is extremely low. Cd and Zn, which show comparable environmental behaviour, are the most mobile heavy metals given that they present the greatest percentages in the first two fractions (Sing et al., 1998). Based on the results in figure 4.2.4, Cd was the most mobile heavy metal, as it reaches the highest percentage in the acid-soluble fraction (42.85% for Site 8 and 60.68% for Site 9) and the lowest in the reducible fraction (32.14% and 19.63% for those same sites). Zn was distributed between all fractions with 51% of the total content found in the non-residual fractions at Site 8, while most of Zn was found in the residual fraction (58.63%) for sediments from the coast (Site 9), indicating that under changing environmental conditions Zn in sediments from the Berg estuary is possibly more available from the coast (estuary mouth). Zn mobility increases considerably in the estuary. Its percentage in the first fraction drops considerably, and increases in the reducible and oxidizable fractions, probably due to the incorporation into these phases of the Zn that precipitate when the river water mixes with ocean water.

Higher percentages of Cd and Zn were found to be associated with more labile fractions by numerous researche (Surija & Branica, 1995; Licheng & Guijiu, 1996; Lopez-Sanchezet al., 1996; Morillo et al., 2004). The metals in this fraction include metals weakly adsorbed on sediments or their essential components namely clays, Fe and Mn hydrated oxides, and humic acids, that can be released by ion-exchange processes and metals that can be co-precipitated with carbonates present in many types of sediment (Marin et al., 1997 and Tokhalioglu et al., 2000). Changes in ionic composition, influencing adsorption-desorption reactions, or lowering of pH could cause remobilization of metals from the acid-soluble fraction. In addition, this might also be related to the sediment containing a high concentration of carbonate, which came from different areas in the Berg River and formed $CdCl_3$ in the natural pH condition. The percentage of Cd in the acid-soluble fraction might be increased with the dissolution of $CdCl_3$ in the sediments at lower pH due to the acetic acid added in the first step of the extraction procedure. Cadmium and its compounds are compared to other metals, relatively soluble. They are, therefore also more mobile in sediment, more bioavailable and tend to bioaccumulate (Ole et al., 2002). This tendency was especially pronounced in the estuary and coastal sediments in which more than 42% of two elements extracted were distributed between the first two fractions. The mobility of these metals facilitates their uptake by benthic invertebrates living in sediments. Benthic invertebrates represent an important link in the transfer of metals to higher trophic levels because of their close association with sediment and their ability to accumulate metals (Galay Burgos and Rainbow, 2001). Furthermore, they are often a major component in the diet of many fish (Summers, 1980).

In the Berg estuary, Cu was mainly extracted from the residual fraction (63.03%) and to a lesser degree, the oxidizable and reducible fractions (10.69%) and was 8% in the acid-soluble fraction. However, in the coastal sediments, Cu was also found mainly in the residual fraction (51.12%). Copper was also bound to organic matter and sulphide, in both estuary and coastal sediments (15.63 and 25.12% respectively). Copper can easily bind and complex with organic matters resulting in a stable complex formation between Cu and organic matter (Morillo et al., 2004 and Conesa et al., 2006). Heavy metals with high abundance in the phase bound to organics are more available than metals in the residual fraction. It has been shown in other studies that, under oxidizing conditions, the solubility of Cu is increased as it is a chalcophile element that is mainly bound to sulphides in nature (Weisz et al., 2000: Tuzen, 2003). Cu can precipitate as a hydroxide, oxide, or hydroxycarbonate. Because of its tendency to associate with sulfides in reducing environments Cu is immobile, but this occurs only under pH conditions greater than 6, (Klassen, 1996; EPA, 2009). The results concur with the results of other studies (Tokhalioglu et al., 2000 and Morillo et al., 2004), who also found that a proportion of Cu in sediments is associated with an organic fraction.

Chromium was the least mobile in sediments from two sites (estuary and coast) with the highest percentage in the residual fraction (71.22% for the estuary and 70.16% for the coast respectively). These results are in agreement with the findings from Barcelona, Spain (Guevara-Riba et al., 2004). Other studies carried out in Spain, Singapore and China (Martin et al., 1998; Usero et al., 1998; Morillo et al., 2004; Yuan et al., 2004; Cuong & Obbard, 2006) also shows that Cr was found mainly in the residual fraction in all samples. These results show that Cr has the strongest association to the crystalline structures of sediments.

In general, estuaries seem to remain highly affected by lead, because the transport of this particle-reactive element is a very slow process in such systems (Steding et al., 2000). Pb was among the metals that show least mobility and was present mainly in the residual fraction in amounts over 90% in most of the samples. The highest percentage was found in this fraction in both estuary (90.73% for Site 8) and non-estuarial parts of the river (90% for Site 3). This indicates that it is unlikely that this metal will enter the water column, even under changing environmental conditions. This finding was of high interest since the sediment shows high Pb concentrations and, furthermore, it is a highly toxic element for organisms and fish (Routh and Ikramuddin, 1996). Many studies have focused on Pb in estuaries. They have showed that in the freshwater-seawater mixing zone, Pb behaviour varied from one estuary to the other and sometimes from season to the other (Elbaz-Poulichet et al., 1996 and Baeyens et al., 1998). Lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. At a total of 61.88% lead was also found in the residual fraction of coastal marine sediment (Site 9). Yuan et al. (2004) reported that Pb was dominant in the residual fraction of marine sediments from East China. Indeed, most of the Pb was contained in the residual fraction, followed by the reducible fraction (bound to Fe and Mn oxides) at 16.23%. It has been reported that Pb can form a stable complex with Fe hydroxide and Mn dioxide (Ramos, 1994), which has been proved to be sensitive to anthropogenic inputs (Modak et al., 1992).This concurs with results reported in Morillo et al. (2004) which showed that Fe and Mn hydrous oxides are important scavengers of Pb in sediments. Lead was also bound to organic matter in both estuary (8.92%) and coastal marine sediments (12.19%), and may thus accumulate for several years. Anthropogenic input of lead to the environment is thought to outweigh all other sources. It reaches the aquatic systems through rainfall, fallout of lead dust, gasoline emission, street runoff, and wastewater and discharges.

Arsenic is one of the major toxic metals with multiple side-effects and can form many different compounds. Arsenate sorbs to Fe and Al oxides, amorphous aluminosilicates, and layer silicate clays. Arsenic sorbs more efficiently at lower pH levels, which gives it low mobility at lower pH levels. The graphs 4.2.1, 4.2.2 and 4.2.3 show that most of the arsenic in three sites was present in the residual fraction. This effect also concurs with the result reported by Greenfield (2007).

In the river Site 3, Cd was distributed between the four fractions (Fig. 4.2.3), of which 54% of the total Cd was found in the residual fraction and 15.38% in the acid-soluble fraction, indicating that the mobility of Cd in this site was low. The percentage of Cd associated with different fractions was in the following order: residual > oxidizable > acid soluble > reducible.

Zn has the greatest mobility, since it presents the greatest content in fraction one (the most labile). Abundance of Zn in other fractions was low. This is particularly marked in Site 3 where the Zn associated with the acid-soluble fraction reaches levels of more than 59% of the total. The percentage of Zn in the residual fraction was 17.55%, which indicates that Zn mobility in this environment was higher than that of the metals that were mostly abundant in the residual fraction. This concurs with Zerbe et al. (1999). Zn is mostly abundant as carbonate with potential mobility 82.44%.

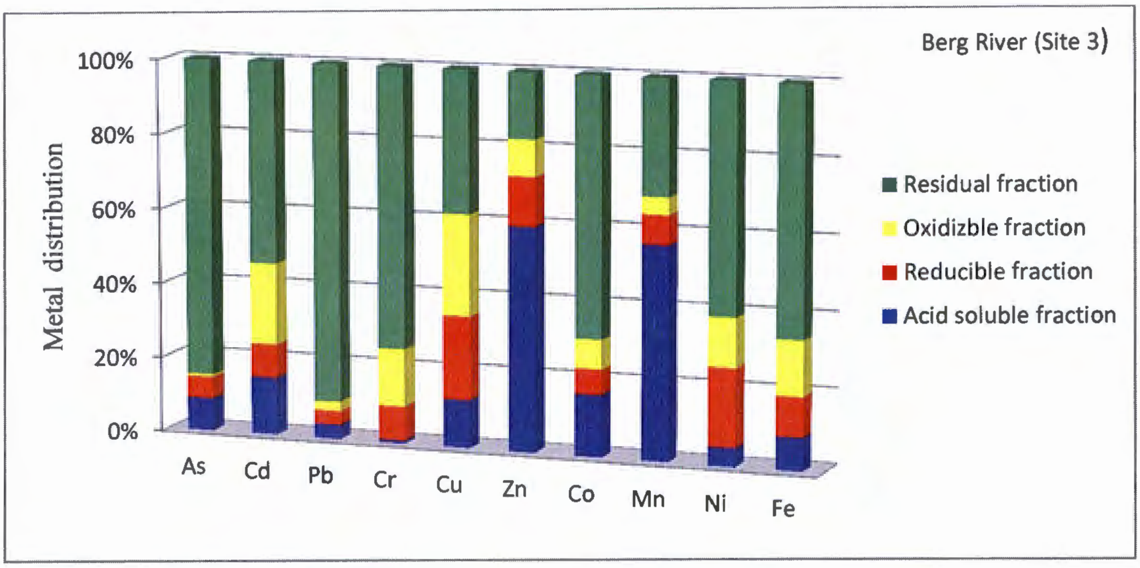

Figure 4.2.3 Distribution of heavy metals in sediment between different fractions for Site 3.

Fe and Mn were significantly distributed among the four fractions (Fig. 4.2.3). Compared to the estuary and coastal sediments much more Fe and Mn were in the acid-soluble, reducible, and oxidizable fractions. This means that these metals are more mobile and possibly more bio-available in the river as opposed to the estuary. It also points to possible pollution of the river. Chemical partitioning of Cu in the river sediments was different from those in the estuary and the coast (Fig.4.2.4). High percentage (37.95%) was associated with the residual fraction, and the rest was divided, for the most part, between the reducible fraction (22.26%) and the acid-soluble (12.77%). High copper content in the residual fraction of river sediment was also found by Budimir and Marko (1995). The high percentage of Cu in this fraction is likely because Cu is chemisorbed on or incorporated in clay minerals (Pickering, 1986) although 27% of Cu was found in the oxidizable fraction (bound to organic matter and sulphide). This percentage of Cu in the oxidizable fraction of the river sediments may be due to sewage and industrial discharge from the urban areas of Paarl, which carries organic matter that favours the entry of Cu into the oxidizable fraction through the formation of organic complexes of this element (Baruah et al., 1996). Therefore, the mobility of Cu in the river is less than that of Zn and Mn, since the organic fraction released in the oxidizable stage is not considered mobile or available because it is thought to be associated with stable high-molecular-weight humic substances that release a small amount of metals slowly (Sing et al., 1998).

Among the metals studied in the river sediments, Ni, Co and Cr showed similar behaviour (Fig. 4.2.3). They were found mainly in the residual fraction (61.01%, 68.93% and 72.05% respectively). These results concurred with other sediment studies (Lopez-Sanchez et al., 1996; Jones & Turki, 1997; Karbassi, 1998) in which large amounts of Ni, Co and Cr were found in the residual fraction. Thus, given that these elements have low mobility and are found in small concentrations, it is unlikely that the sediments of this river are an important source of Ni, Co and Cr for its water. Smith and Carson (1981) reported that the adsorption of cobalt by oxide minerals increased with increasing pH. Cobalt preferentially associates with Fe and Mn oxides if the sediments are under strongly oxidizing conditions. At higher pH, the solubility of Co decreases as it forms complexes with organic matter and there is precipitation of hydroxides. Cobalt sulfides can form in reducing conditions (Klassen, 1996 and EPA, 2009). The presence of organic matter in water also increases desorption of cobalt from inorganic fractions of sediments or suspended material. A large part of all nickel compounds that are released to the environment adsorb to sediment or soil particles and become immobile. At low pH (acidic ground), nickel becomes more mobile and will often rinse out to the water.

The potential mobility of metals in sediment from the coast, Berg Estuary and the river was in the following order:

Cd > Cu > Zn > Pb > Ni > Cr > As > Fe > Co > Mn (Site 9)

Cd > Zn > Ni > Cu > Cr > Co > Fe > As > Mn > Pb (Site 8)

Zn > Mn > Cu > Cd > Ni > Fe > Co > Cr > As > Pb (Site 3)

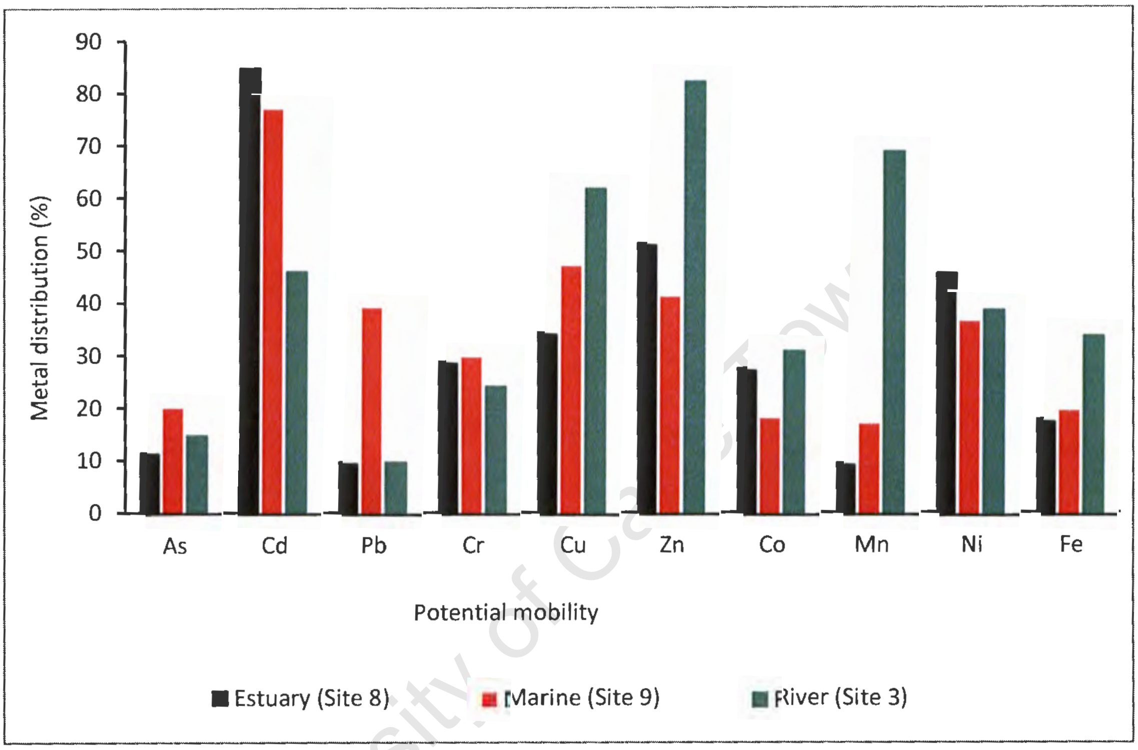

Figure 4.2.4 Potential mobility of heavy metals in sediment for three Sites (3, 8, and 9)

4.3 Vertical profiles of heavy metals, particle size, moisture and organic matter content in core sediments of the Berg River estuary.

4.3.1 Vertical distribution of heavy metals

In the last few decades, inputs of contaminants to the Berg River estuary have increased due to the direct or indirect discharges of sewage and wastewater (treated or untreated). These discharges contain heavy metals among a host of other pollutants. Most heavy metals contaminants associate with particles as they settle through the water column and are finally incorporated into the sediments (Simon et al., 1992). Metals accumulated in this way may be subsequently released to the overlying water column as a result of either physical disturbance or diagenesis. Moreover, diagenetic processes are important near the sediment-water interface, responding to redox changes and affecting metal concentrations in vertical sediment profiles (Santschi et al., 1990).

In order to evaluate the possible current and historic pollution of the river vertical sample cores were collected from Sites 5, in the river, Site 6 at the start of the estuary and Site 7 in the estuary. The metal profiles results are shown in Figures 4.3.1.1 to 4.3.1.5.

Cadmium (Cd) is a non-essential trace element that can be toxic to aquatic biota at elevated concentrations. Cd accumulates mostly in the kidneys of fish and mammals while plants can take it up from the soil and sediment (Australian Environment Council, 1982b). The Cd content of Site 7 was essentially constant at 1 mg/kg, which while still higher than natural levels of 0.3-0.38 mg/kg (Bervoets & Blust., 2003), can be considered unpolluted. Similarly Site 6 Cd levels were relatively low, with the exception of the sample at 20 cm depth. This indicates that perhaps there was an incident of Cd discharge into the river in the recent past. Without knowledge of the rate of sediment formation it is not possible to say when this incident occurred. The Cd content of Site 5 is much higher than the other two cores. At a depth of 60 and 140 cm the Cd levels are particularly high at ~8 mg/kg. Note however that after 160 cm the Cd levels return to background levels. This is another clear indication that the Cd levels are due to anthropogenic causes and that particular events occurred in the past. It is well recognized that Cd is sensitive to redox changes, where it is known to be soluble under oxygenated conditions and to precipitate immediately where post-oxic conditions are encountered (Thomson et al., 2001). Unfortunately, redox potentials were not measured in this study although the river is known to be well oxygenated (Day, 2007). In comparison with previous studies around the world, the Cd ranges were higher than those of the Seine Estuary, France (Mariam et al., 2012) and lower than those in the Kortalliyar River, India (Usha and Ranga., 2010).

High Cd values observed in most samples suggest an anthropogenic contribution to Cd mean concentrations. The AF value of Site 5 is 2.60 (Table A5), which suggested that Cd concentrations were anthropogenic. With the exception of 20 cm depth at Site 6, the AF is ~1 indicating no anthropogenic input. The vertical profile of Cd in three sites also showed extremely high enrichment (EF > 100) relative to Mn. Similar results were also obtained by Singh et al. (1997) for the Gomati River, India. Anthropogenic sources of cadmium could be Ni- Cd batteries (constitute 70% of cadmium), sewage and industrial discharges (Thevenot et al., 2002). It is well recognized that Cd is sensitive to redox changes, where it is known to be soluble under oxygenated conditions and to precipitate immediately where post-oxic conditions are encountered (Thomson et al., 2001). Unfortunately, redox potentials were not measured in this study. In comparison with previous studies around the world, the cadmium ranges were higher than those of the Seine Estuary, France (Mariam et al., 2012) and lower than those in the Kortalliyar River, India (Usha and Ranga., 2010).

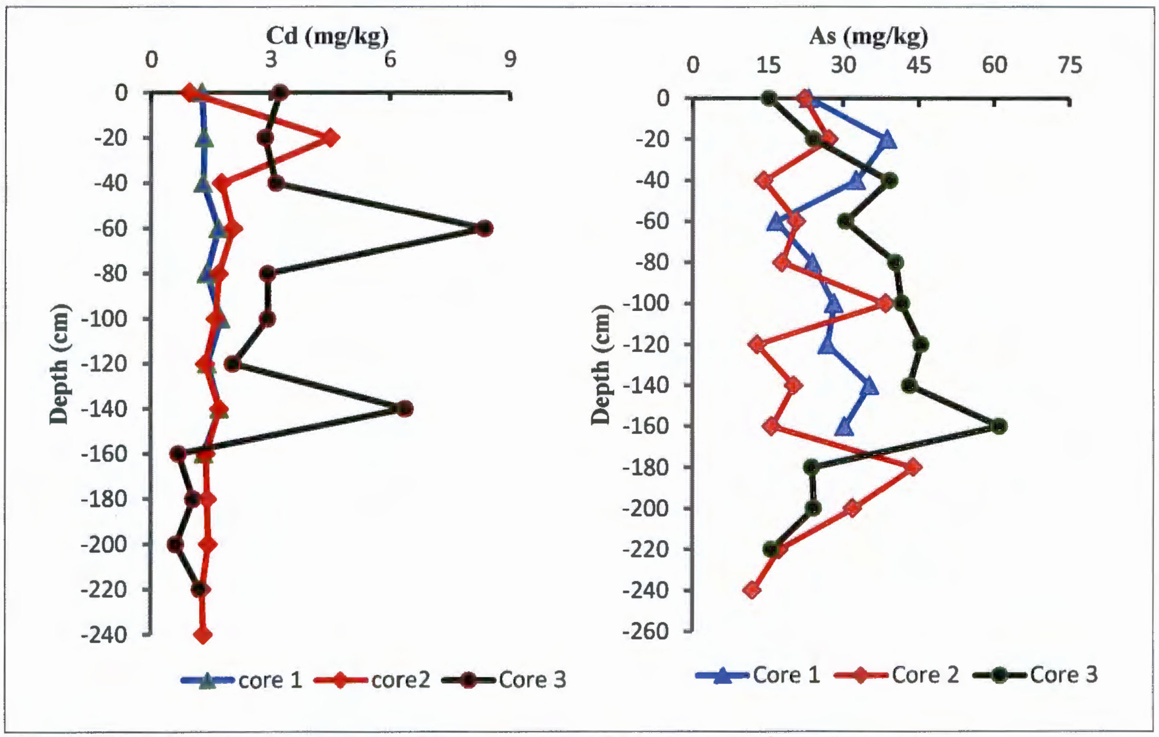

Figure 4.3.1.1 Vertical variations of heavy metals (Cd and As) in the sediment cores

Arsenic is fairly widespread in the environment, the average concentration in the earth's crust being approximately 2.2 mg/kg. It ranks 20th in abundance in relation to the other elements (NAS, 1977). Arsenic concentrations in sediment cores varied from 15.26 to 61.26 mg/kg with an average of 28.19±0.80 mg/kg. The highest concentration was observed in Site 5 at a depth of 160 cm, whereas the lowest value was found in the same core at a depth of 240 cm from the sediment-water interfaces. EF values for Arsenic were found to be greater than 50 (Table A6) in Site 5 (especially at 160 cm depth), suggesting that this site should be classified as having moderate to extremely severe enrichment of arsenic. Site 5 is close to farming activity, which indicates that the source of arsenic could be from agricultural discharge (pesticides use).

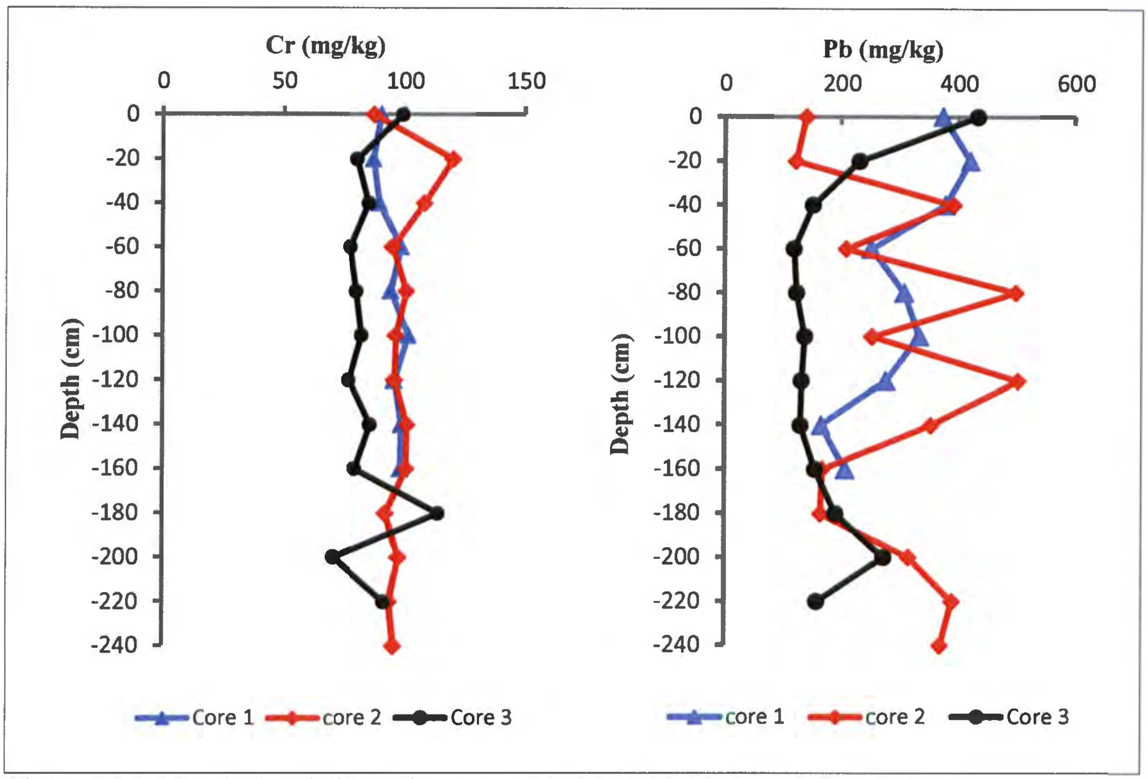

Figure 4.3.1.2 Vertical variations of heavy metals (Cr and Pb) in the sediment Cores

Pb concentrations in the sediment cores generally showed higher values than the other metals. It varied over a wide range from 120.27 to 504.11 mg/kg with an average of 261.27±8.04 mg/kg (Fig 4.3.1.2). The highest Pb levels were observed in Site 7 at a depth of 140 cm while the lowest level was in Site 5 at a depth of 80 cm. High enrichment factor values (EF>50) for Pb in the estuary cores suggest a strong anthropogenic source. High Pb concentration observed in these cores that are sampled close to residential areas indicate that the source of lead could be the urban and rural discharges, and may also be due to gasoline emissions and diesel operated motor boats used for recreational purposes. This is also well supported by the high average concentration of Pb at Site 5, 6 and 7 (261.27±118.04 mg/kg). Pb concentrations are significantly elevated from those reported in contaminated rivers such as the Seine River estuary, France (Mariam et al., 2012). It is tempting to speculate that the level of Pb at Site 5 reflects the increased use of motor cars with urbanisation. Unleaded petrol was only made mandatory in South Africa in 2006.

Chromium enters aquatic systems such as rivers and estuaries through aerial deposition or surface runoff, and subsequently, its association with particle matter results in its deposition in bed sediments. Because a variety of organisms live in bed sediments, sediments are an important route of exposure for aquatic life to Cr (CCME, 1995).

The vertical distribution of Cr ranged from 70.94 to 120.10 mg/kg with an average of 93.26±1.48 mg/kg (Fig.4.3.1.2). The levels are fairly consistent with depth and the same at all 3 sites. The highest Cr concentration was found in Site 7 at a depth of 20 cm but this was not significantly higher. While the concentrations of Cr are consistent, their levels do indicate a high amount of enrichment. Severe to extremely severe enrichment (EF>50) was observed. However, the AF values were ~ 1 suggesting that the enrichment is not of anthropogenic origin.

The Mn concentration in the Site 5 (Figure 4.3.1.3) was interesting and unusual. At all 3 sites there was no real change with depth but interestingly the level at Site 5, in the river was much lower than the other 2 cores. Although these values are higher, however, their absolute concentration is low and below natural values.

Cobalt is a relatively rare element of the earth's crust with an average concentration approximately 25 µg/g (Hamilton, 1994). The vertical profiles of cobalt ranged between 4.36 and 16.06 mg/kg with an average value of 9.92±0.50 mg/kg. Vertical profiles of Site 5 showed enrichment in the upper layers (0-100 cm) for Co (11.70-16.06 mg/kg) due to early diagenetic process.

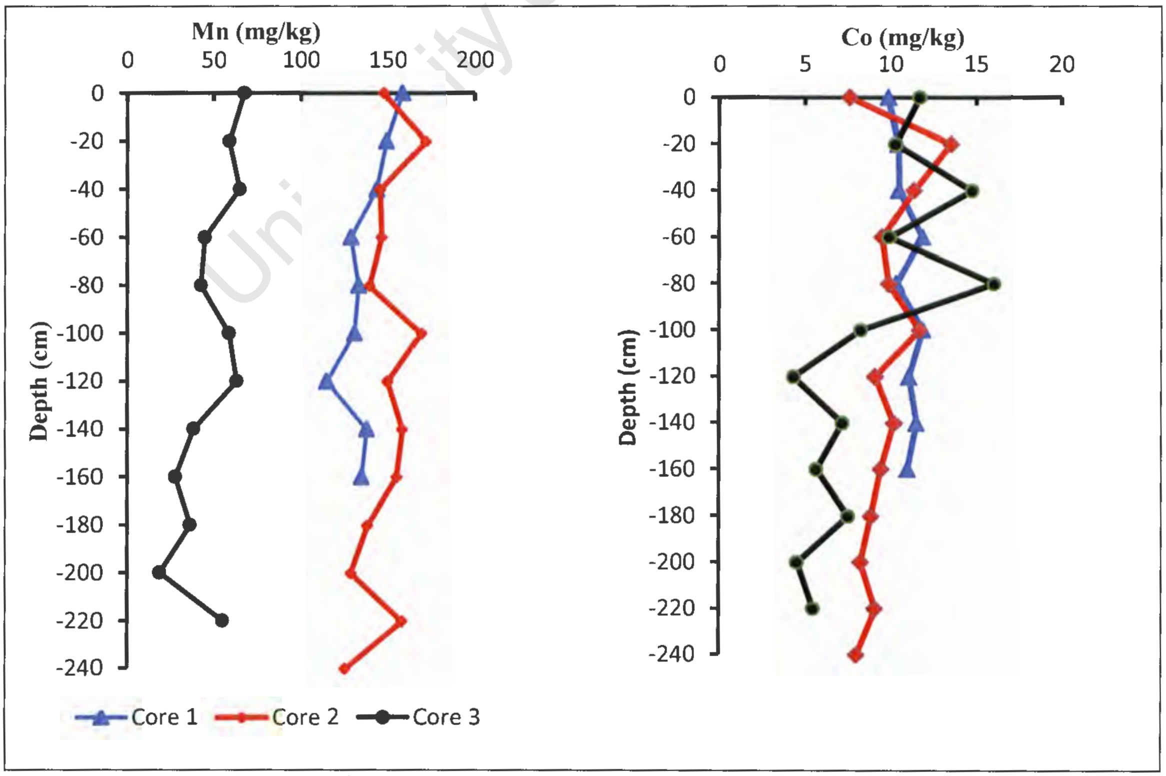

Figure 4.3.1.3 Vertical variations of heavy metals (Mn and Co) in the core sediments

Ni showed small variation with depths (38.60 to 63.21 mg/kg) in sediment cores of the Berg estuary with an average of 43.87±6.43 mg/kg (Figure 4.3.1.4). At a depth of 100 cm, the concentration of Ni, at Site 5, drops to the background level According to Zwolsman et al. (1996) the increase of Ni content at subsurface layers is due to Ni adsorption on to manganese oxyhydroxide. The redox status of the sediments determines the extent to which mobilization of Mn and associated Ni will occur. In addition, it is well known that Ni is insoluble at the pH values of marine and estuarine environment (pH>6.7) and exists predominantly as nickel hydroxide (Sunderman & Oskarsson, 1991), which in turn is quickly incorporated into sediments. EF values for nickel were greater than 50 (Tables A2, A4 and A6), suggesting that the three sites should be classified having extremely severe enrichment for Ni according to Brich (2003).

The vertical distribution pattern of Cu along the studied sites showed fluctuations, with concentrations ranging between 3.02 and 16.25 mg/kg with an average of 7.71±0.93 mg/kg. The highest Cu content was detected in Site 7 at depth of 100 cm, whereas the lowest Cu level was observed in Site 5 at 200 cm depth. In general, the high level of Cu in sediment cores may be due to wastewater discharge point and nonpoint sources suggesting an anthropogenic contribution to total Cu concentration in Berg River sediment. The enrichment factor (EF) value in the three sites was more than 5, suggesting that the estuary is classified as having moderate enrichment for Cu.

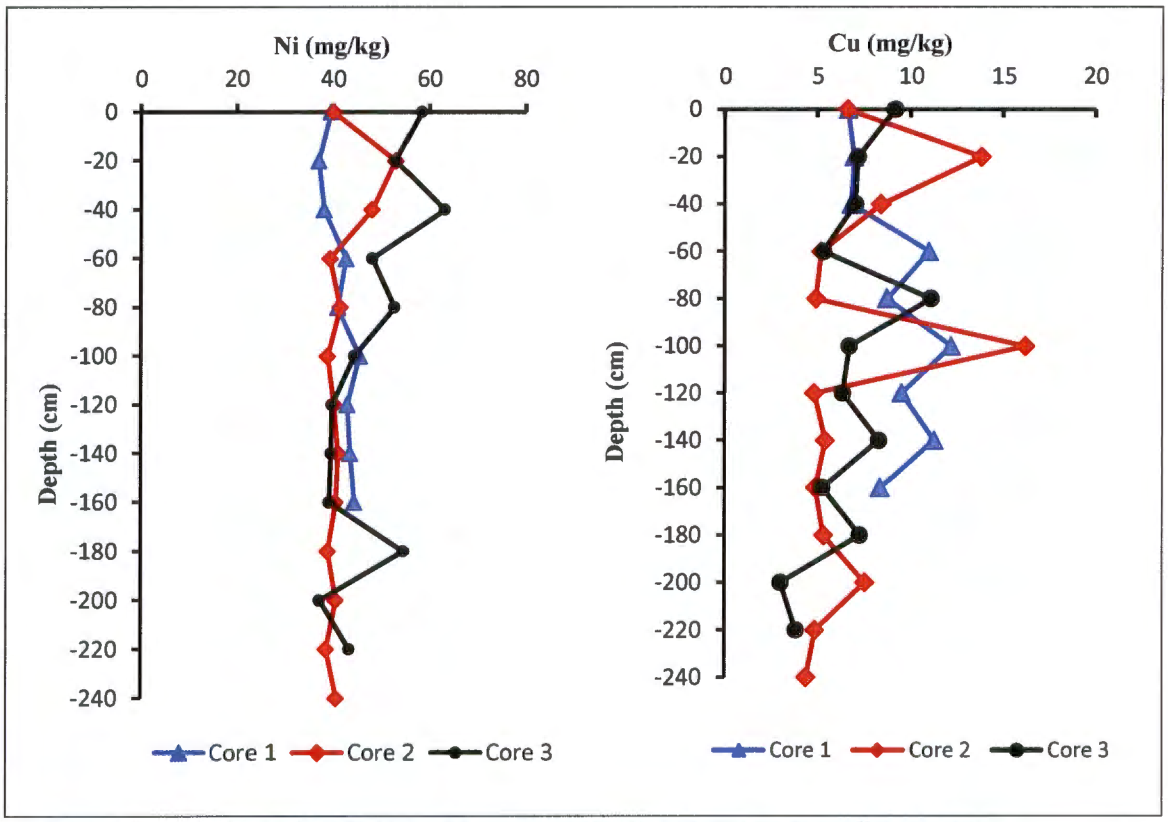

Figure 4.3.1.4 Vertical variations of heavy metals (Ni and Cu) in the sediment cores

Copper enters aquatic systems such as rivers and estuaries through aerial deposition or surface runoff. Bed sediments are a critical estuarine reservoir for particulate contaminants, where their overall residence time is regulated by periodic and intermittent shear stresses on the sediment-water interface. Cu tends to accumulate in bed sediments because of its affinity for particulate matter, mainly fractions of iron-manganese oxides and organic matter (Campbell & Tessier., 1996). Therefore, sediments act as an important route of exposure to aquatic life because a variety of organisms live in, are is in contact with, bed sediment (CCME, 1995).

Zinc concentration in the sediment cores of the Berg estuary ranged from 8.77 to 54.53 mg/kg with an average of 22.53±1.56 mg/kg. The highest concentration of zinc was observed in Site 3 at depth of 80 cm whereas the lowest was in the same site at depth of 160 cm. Zn in Site 6 has no anthropogenic origin (AF<1) while Site 7 and Site 5 showed anthropogenic input were ~1 (Tables A1 and A3). Zinc can enter the aquatic environment from a number of sources including industrial discharges, sewage effluent and runoff (Boxall et al., 2000). Zinc may also increase with decreasing pH of waters. It is known to bioaccumulate in some aquatic organisms (WHO, 2000b). A wide variety of organisms lives in or on sediments of aquatic systems. Some fish can accumulate zinc in their bodies; when zinc enters the bodies of these fish it is able to bio-magnify up the food chain (CCME, 1999). Zn in Sites 5 and 7 showed moderate enrichment (EF<5) throughout the vertical profile (Tables A4 and A6), whereas Site 6 which showed moderately severe enrichment was ~5 (Table A2).

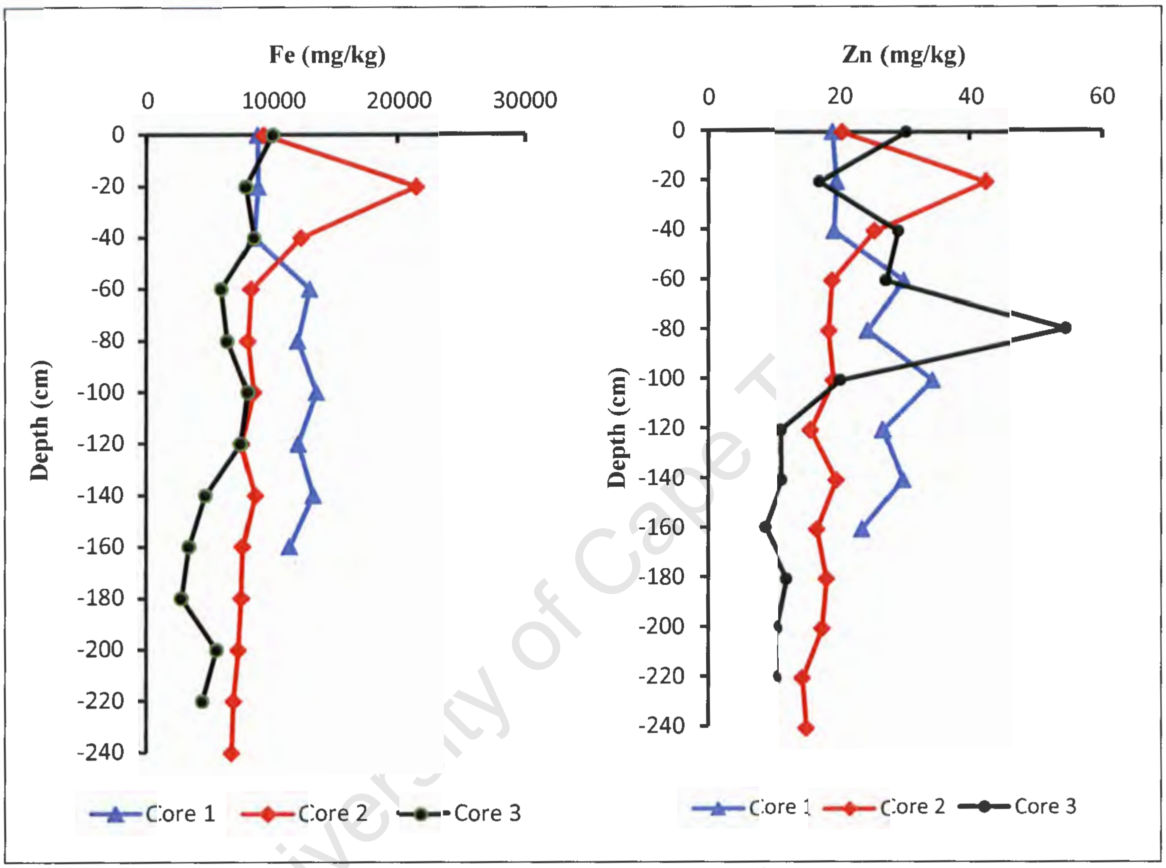

Figure 4.3.1.5 Vertical changes of trace metals (Fe and Zn) in sediment cores

During the study period, Fe was the major element in all sediment core samples, ranging from 2829.15 to 21455.28 mg/kg with an average of 8776.32±34.47 mg/kg. There is an increase in the concentration from bottom to the top of 20 cm of core sediment of Site 6 and low values at greater depth (especially in Sites 5 and 7), which confirmed the increased anthropogenic activities with time. Anthropogenic factor (AF) for Fe was ~1 in Sites 5 and 7 suggest input from anthropogenic sources while no anthropogenic input (AF<1) in Site 6. Moderately severe enrichment (EF= 5-10) was observed for Cr in the cores collected from the estuary. Elevated Fe concentrations could also be due to the effect of mixing of open ocean waters with the estuary waters, because the oceanic waters is very rich with iron.

It was noted previously that the highest levels of As, Cd, and Cr were observed in most of the sediment cores collected from Berg estuary. In contrast, the concentrations of the same metals were lower in the middle 100-160 cm than the top layers of all three sites. Levels then decrease dramatically as depth increased; indicating the source of contaminants is relatively recent. Little change was noted in the bottom cores layer as all metals remained in elevated concentrations in all the three sediment cores of the estuary which were high or comparable to levels detected in sediments classified as contaminated from other rivers of the world.

4.3.2 Vertical variation of particle size, moisture content and organic matter in core sediments

In general, the concentration of heavy metal in sediment increased with decreasing grain size, because of the affinity of metals to bind with finer particles (O'Reilly Weise et al., 1995). Grain size analysis showed that the sediment samples have clay, silt and sand textures. Particle size distribution is one of the most important factors affecting the capacity of sediment to accumulate heavy metals. The core sediments of the Berg River estuary are dominated by sand particles (>74 µm) with high percentages (46.45-84.18%). The particle size distribution was specific to the respective sediment.

Based on the results shown in figures below, the percentage of sand fractions in sediment Site 6, Core 1 ranged from 69.41 to 76.47% with an average of 70.83% while silt fraction ranged from 10.26 to 22.5% with an average of 14.92% and the percentage fraction of clay ranged from 0.45-1.14% with an average of 0.70%. The percentage of organic matter in core sediment ranged from 1.87 to 9.94% with an average of 3.33%. The percentage of moisture content in tested sediment samples ranged from 14.28 to 22.11% with an average of 18.86%. Site 6, Core 1 (Fig. 4.3.2.1) dominated be very fine sand and displayed the lowest content of OM, clay and coarse sand fractions.

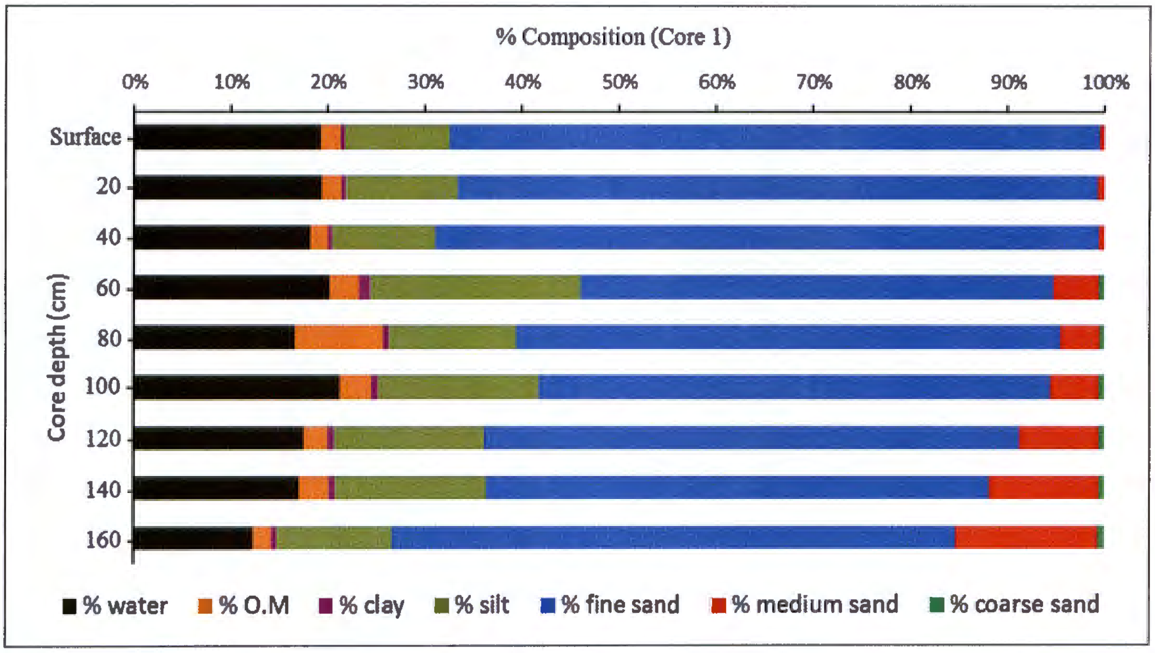

Figure 4.3.2.1 Sediment characteristics of Site 6, Core 1

In Site 7, Core 2 (Fig. 4.3.2.2), the percentage of sand fraction ranged from 62.93 to 84.18% with an average of 72.02% while silt fraction ranged from 4.12 to 22.74% with an average of 10.13% and the percentage fraction of clay ranged from 0.11 to 0.95% with an average of 0.40%. The organic matter percentage in core sediment ranged from 4.36 to 13.01% with an average of 7.84%. The moisture content in sediment samples ranged from 16.77 to 36.21% with an average of 22.42%.

In general, Site 7, Core 2 was also dominated by very fine sand with some contribution of OM and water content and displayed the lowest percentages of clay, medium and coarse sand fractions.

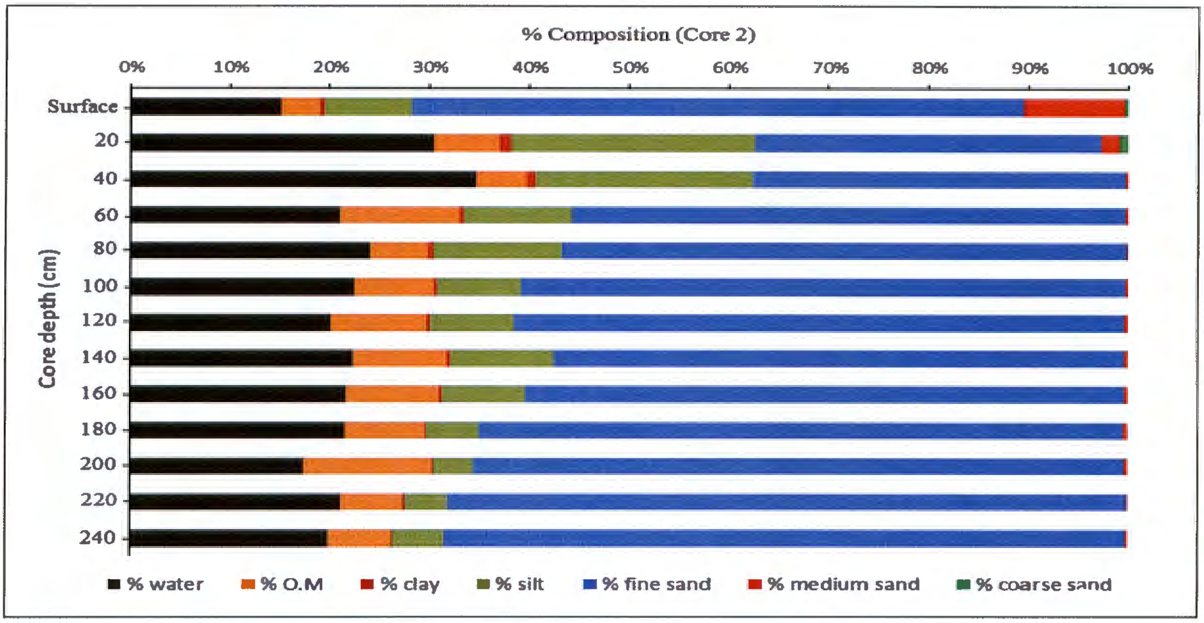

Figure 4.3.2.2 Sediment characteristics of Site 7, Core 2

In Site 5, Core 3 (Fig. 4.3.2.3), the percentage of sand fraction ranged from 46.45 to 77.85% with an average of 54.50% while silt fraction ranged from 3.24 to 23.44% with an average of 7.28% and the percentage fraction of clay ranged from 0.10 to 0.84% with an average of 0.19%. Organic matter content about of 0.43-14.75% was observed in core 3 with higher levels at depth of 140 cm and lower concentrations at the bottom. The moisture content ranged from 14.25 to 22.77% with an average of 18.93%. Core 3 was dominated by fine and coarse sand fractions. It also displayed the lowest percentages of clay and coarse sand fractions.

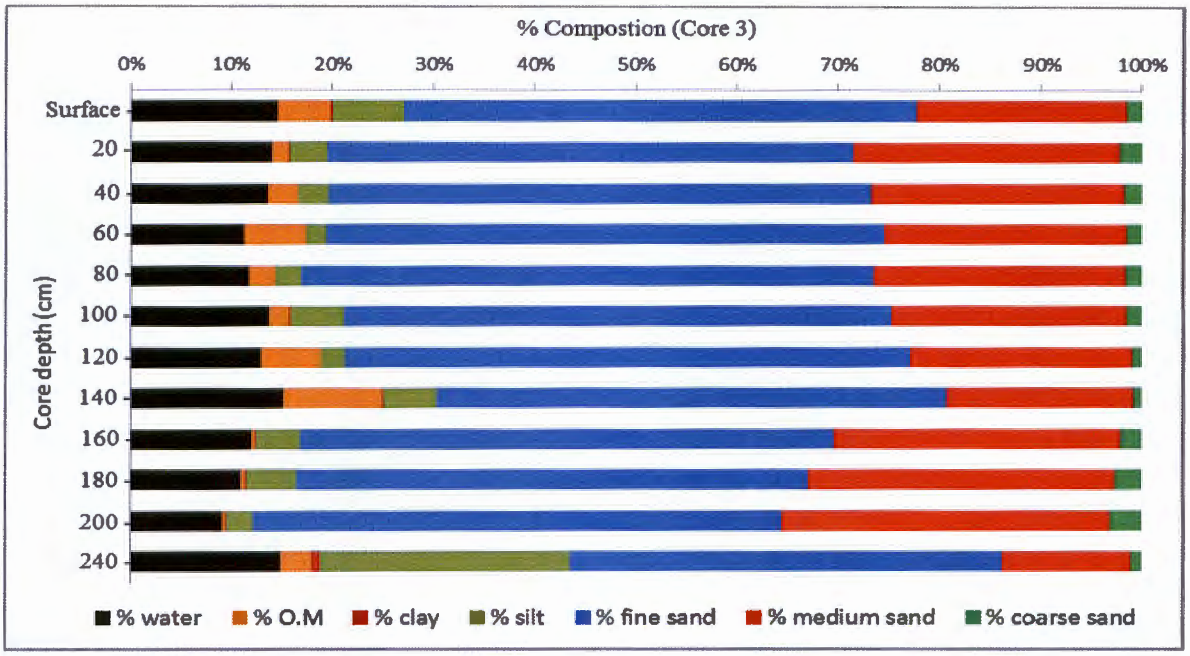

Figure 4.3.2.3 Sediment characteristics of Core 3 Site 5

4.3.3 Interrelationship between heavy metals, sediment textures and organic matter in core sediments

The data were analysed using Pearson's correlation matrix among the levels of water, organic matter, sands, silt, clay, with reference to As, Cd, Pb, Cr, Cu, Zn, Co, Mn, Ni and Fe in core sediments. The variability of metal concentration in the core sediment was found more identical when compared with vertical distribution of organic matter and sediment texture by depth. Considering this fact the Pearson's correlation analysis at a significance level of $p< 0.05$ was employed to establish the interrelationship among metals, texture and organic matter. Weak to strong positive and negative linear correlations between variables were clearly observed. The strong positive linear correlations among some metals indicate that these metals were associated with each other. The strong positive correlations between metal concentrations indicate similar origins of these elements, and there is some common factor controlling their variability. Singh et al. (2005) showed that textural concentration of river sediment plays an important role in the study of bioavailability of metals and toxicity of sediments.

Based on the correlation matrix obtained for core sediments, in Site 6, Core 1 (Table 4.3.3.1), strong to very strong positive correlations ($r = 0.66$-0.95) were observed between Cd and all variables at 0.05 level except Pb and Mn. Cu with Ni, Zn, Fe, % water, % organic matter, clay and silt showed moderate to strong positive correlations ($r = 0.56$-

0.99), while with fine sand (FS) it showed very strong negative correlation (r = - 0.85). There was weak positive correlation between arsenic (As) and organic matter (r = 0.28) but weak to moderate negative correlations (r = -0.48 to -0.52) with clay, silt and coarse sand (CS). Weak to strong positive correlations (r = 0.1-0.51) were found between Pb and Mn, organic matter, water, and fine sand while with other variables weak to strong negative correlations (r = - 0.1 to -0.75) were observed.

Table: 4.3.3.1 Pearson's correlation matrix of sediment characteristics and heavy metals for Site 6, Core 1.

	As	Cd	Pb	Cr	Co	Mn	Cu	Ni	Zn	Fe	% water	% O.M	% clay	% silt	% FS	% MS	% CS
As	1.00																
Cd	-0.18	1.00															
Pb	0.14	-0.50	1.00														
Cr	-0.33	0.77	-0.75	1.00													
Co	-0.15	0.89	-0.58	0.84	1.00												
Mn	0.28	-0.43	0.51	-0.64	-0.64	1.00											
Cu	-0.24	0.95	-0.60	0.90	0.92	-0.63	1.00										
Ni	-0.29	0.66	-0.74	0.98	0.75	-0.64	0.83	1.00									
Zn	-0.26	0.93	-0.56	0.91	0.91	-0.66	0.99	0.85	1.00								
Fe	-0.31	0.85	-0.73	0.93	0.83	-0.72	0.95	0.88	0.95	1.00							
% water	-0.20	0.68	0.24	0.20	0.48	-0.17	0.56	0.09	0.56	0.36	1.00						
% O.M	-0.32	0.12	0.13	0.17	-0.09	-0.26	0.19	0.11	0.19	0.37	0.05	1.00					
% clay	-0.52	0.79	-0.61	0.74	0.86	-0.70	0.82	0.63	0.80	0.81	0.45	0.10	1.00				
% silt	-0.48	0.83	-0.63	0.77	0.87	-0.70	0.87	0.67	0.85	0.87	0.48	0.18	0.99	1.00			
% FS	0.57	-0.87	0.36	-0.67	-0.76	0.50	-0.85	-0.57	-0.84	-0.78	-0.75	-0.18	-0.88	-0.90	1.00		
% MS	0.12	0.26	-0.88	0.67	0.46	-0.48	0.43	0.74	0.42	0.58	-0.47	-0.01	0.34	0.37	-0.06	1.00	
% CS	-0.25	0.51	-0.86	0.88	0.65	-0.72	0.70	0.88	0.70	0.85	-0.16	0.32	0.65	0.68	-0.43	0.86	1.00

0.8-1.0 = very strong correlation, 0.6-0.79 strong correlation, 0.40-0.59 moderate correlation, 0.2-0.39 weak correlation and 0.00-0.19 very weak correlation.

In Site 7, Core 2 (Table 4.3.3.2), Cd expressed moderate to strong positive correlations (r = 0.46-0.92) with Cr, Cu, Zn, Co, Mn, Ni, Fe clay, silt, and coarse sand, while with Pb, organic matter, fine sand and medium sand there were weak to strong negative correlations (r = -0.09 to -0.82). The value of arsenic concentration has weak to moderate positive correlation with Cu and organic matter (r = 0.21- 0.51). It has also weak to moderate negative correlations (r = -0.53) with Pb. Chromium correlated significantly with most variables ($p < 0.05$) except organic matter with which it has moderate to strong positive correlations (r = 0.41-0.92). Cu also showed strong positive correlations with Zn and Fe, indicating that the metal has general sources, and moderate positive correlations with clay, silt, medium sand and fine sand.

Table: 4.3.3.2 Pearson's correlation matrix of sediment characteristics and heavy metals for Site 7, Core 2

	As	Cd	Pb	Cr	Co	Mn	Cu	Ni	Zn	Fe	% water	% O.M	% clay	% silt	% FS	% MS	% CS
As	1.00																
Cd	0.13	1.00															
Pb	**-0.53**	-0.33	1.00														
Cr	-0.10	0.86	-0.07	1.00													
Co	0.16	0.81	-0.15	0.84	1.00												
Mn	0.13	0.50	-0.32	0.41	0.72	1.00											
Cu	**0.51**	0.55	-0.36	0.47	0.74	0.61	1.00										
Ni	-0.12	0.83	-0.16	**0.92**	0.73	0.31	0.46	1.00									
Zn	0.16	0.92	-0.42	0.84	0.78	0.49	**0.62**	0.92	1.00								
Fe	0.08	**0.92**	-0.39	0.85	0.79	0.52	**0.60**	0.93	0.99	1.00							
% water	-0.16	0.46	0.10	0.74	0.72	0.30	0.35	0.75	0.57	0.59	1.00						
% O.M	**0.21**	-0.09	0.44	-0.12	-0.18	-0.16	0.13	-0.32	-0.28	-0.31	-0.37	1.00					
% clay	-0.21	0.70	-0.12	0.80	0.78	0.45	0.44	0.87	0.82	0.83	0.80	-0.39	1.00				
% silt	-0.18	0.70	-0.11	0.82	0.77	0.41	0.44	0.90	0.83	**0.84**	0.84	-0.41	0.99	1.00			
% FS	0.07	-0.82	0.12	-0.88	-0.85	-0.41	-0.46	-0.88	-0.84	-0.84	-0.80	0.21	-0.95	-0.95	1.00		
% MS	0.01	-0.15	-0.42	-0.32	-0.31	0.03	0.03	-0.01	0.13	0.12	-0.30	-0.42	0.07	0.06	0.18	1.00	
% CS	0.12	0.79	-0.53	0.57	0.50	0.46	0.50	0.73	0.88	0.89	0.19	-0.35	0.58	0.58	-0.54	0.45	1.00

0.8-1.0 = very strong correlation, 0.6-0.79 strong correlation, 0.40-0.59 moderate correlation, 0.2-0.39 weak correlation and 0.00-0.19 very weak correlation.

In Site 5, Core 3 (Table 4.3.3.3), cadmium showed weak to strong positive correlation with all variables except with Pb, Cr, clay, silt, medium sand and coarse sand where there were weak to moderate negative correlation. Weak to moderate positive correlations were observed between arsenic and organic matter and fine sand. Lead and copper showed medium to very strong positive correlations with clay, silt and organic matter indicating that these metals have a strong association with fine-grain fractions. Strong positive correlation also observed between Mn and Fe.

Table 4.3.2.3 Pearson's correlation matrix of sediment characterize and heavy metals for Site 5, Core 3

	As	Cd	Pb	Cr	Co	Mn	Cu	Ni	Zn	Fe	% water	% O.M	% clay	% silt	% FS	% MS	% CS
As	1																
Cd	0.03	1.00															
Pb	**-0.59**	-0.47	1.00														
Cr	-0.43	-0.15	0.12	1.00													
Co	-0.25	0.22	0.00	0.17	1.00												
Mn	-0.22	0.17	-0.07	0.18	0.45	1.00											
Cu	-0.24	0.05	0.17	0.43	0.69	0.45	1.00										
Ni	-0.35	0.11	-0.19	**0.49**	0.76	0.54	0.39	1.00									
Zn	-0.25	0.16	0.07	0.04	0.89	0.33	0.72	0.49	1.00								
Fe	-0.19	0.19	-0.27	-0.20	0.38	**0.76**	0.12	0.47	0.30	1.00							
% water	0.33	0.44	-0.62	-0.06	0.08	0.44	0.04	0.29	-0.21	0.48	1.00						
% O.M	0.14	**0.78**	0.42	-0.10	-0.02	0.25	0.18	-0.11	-0.02	0.19	0.55	1.00					
% clay	-0.50	-0.27	**0.84**	0.36	0.15	0.18	**0.50**	-0.10	0.23	-0.21	-0.49	-0.16	1.00				
% silt	-0.47	-0.26	0.81	0.40	0.15	0.19	**0.53**	-0.08	0.21	-0.22	-0.44	-0.14	1.00	1.00			
% FS	**0.45**	0.22	-0.75	-0.40	-0.18	-0.25	-0.56	0.06	-0.24	0.15	0.38	0.09	-0.99	-0.99	1.00		
% MS	0.20	-0.20	-0.35	-0.19	-0.31	-0.54	-0.70	0.04	-0.39	-0.14	0.01	-0.41	-0.74	-0.76	0.81	1.00	
% CS	-0.13	-0.41	0.07	-0.02	-0.26	-0.61	-0.61	0.05	-0.34	-0.25	-0.28	-0.66	-0.37	-0.39	0.45	0.89	1.00

0.8-1.0 = very strong correlation, 0.6-0.79 strong correlation, 0.40-0.59 moderate correlation, 0.2-0.39 weak correlation and 0.00-0.19 very weak correlation.

4.4 Spatial distribution of heavy metals concentrations in surface sediments of the Berg River and its estuary.

The spatial distributions of metals as a function of the site are plotted in Figures 4.3.1.1-4.3.1.10. The sediments in the river constitute a fundamental step in the pathway of contaminants to the ocean, as estuaries filter the fluvial fluxes metals derived from both natural and anthropogenic sources (Larrose et al., 2010). The impact of anthropogenic perturbation is most strongly observed in estuarine and coastal environments adjacent to urban areas. Heavy metals from incoming tidal water and fresh water sources are rapidly removed from the water body and deposited into the sediments (Dwivedi and Padmakumar, 1983).

4.4.1 Heavy metals concentration and comparison with Sediment Quality guideline and average shale.

Without defensible sediment quality guidelines, it would be difficult to evaluate the extent of sediment contamination (Jones-Lee and Lee, 2005). Numerical sediment quality guidelines (SOGs) have been used to identify contaminants of concern in an aquatic ecosystem (Ontario, 1993; CCME, 1995; ANZECC, 2000; CMSQG, 2000a). The international sediment quality guidelines (SQGs) for aquatic life were used for comparison. Two values are present in the international guidelines: lower and higher levels. In this study, the lower level was used as a guideline value (Table 4.4.1). Since there are no specific guidelines for classifying freshwater and estuarine sediments in South Africa, the spatial profile should be used in future research to assess the quality of the sediment of the Berg River and its estuary.

Table 4.4.1: International sediment quality guidelines of heavy metals (mg/kg, dw) for aquatic systems and average shale values

Guidelines	ANZECC, 2000 (Estuarine)		CCME (1995) for aquatic life				Ontario (1993)	CMSQG (2000a) freshwater	Average shale*
			freshwater		Marine and estuarine				
Metals	Low	High	ISQG	PEL	ISQG	PEL			
As	20	70	5.9	17	7.24	41.6	-	-	
Cd	1.5	10	0.6	3.5	0.7	4.2	-	-	0.3
Cr	80	370	37	90	52.3	160	-	-	90
Pb	50	220	35	91.3	30.2	112	-	-	20
Ni	21	52	-	-	-	-	-	23	68
Mn									850
Cu	65	270	35.7	197	18.7	108	-	-	11.2
Zn	200	410	123	315	124	271	-	-	95
Fe	-	-	-	-	-	-	20.000	-	46700

Turekian and Wedepohl, 1961*

Cadmium is a very rare element in the natural environment; the average concentration in the earth's crust is 0.2 mg/kg. Cadmium concentration varied between

1.07 and 2.97 mg/kg with a mean value of 1.69±0.58 mg/kg. The highest Cd concentration was recorded at Site 5, while the lowest was observed at Site 1. It was higher than the average shale concentration as a geochemical background level (Fig.4.4.1.1). In comparison with local and world previous studies, it was lower than that reported by Awofolu et al. (2005) and Songca et al. (2013). The maximum value of Cd concentration was similar to that assessed by Morello et al. (2002), Morello et al. (2004) and Greenfield et al. (2007). The levels of Cd concentrations obtained from samples from the river and its estuary were higher than the CCME sediment quality guidelines for freshwater, estuarine and marine sediments. The highest level of Cd might be attributed to anthropogenic inputs such as sewage sludge and agricultural activities where pesticides and fertilizers are used (DWAF, 1996). The EF values for Cd in sediment varied between 33.06 mg/kg and 121.94 mg/kg, but were greater than 50 in most of the sampling sites, suggesting that these sites are classified as extremely severe enrichment, except for Site 3 which is classified as severe enrichment for Cd. Cadmium can enter the environment through discharge of wastewater from industries as well as through air emissions. In sediment, it enters aquatic system through aerial deposition or surface runoff, and accumulates in bed sediments by association with particulate matter such as organic matter, iron-manganese hydroxides, or by precipitating out of solution with carbonates or sulphide (Landrum and Robbins., 1990).

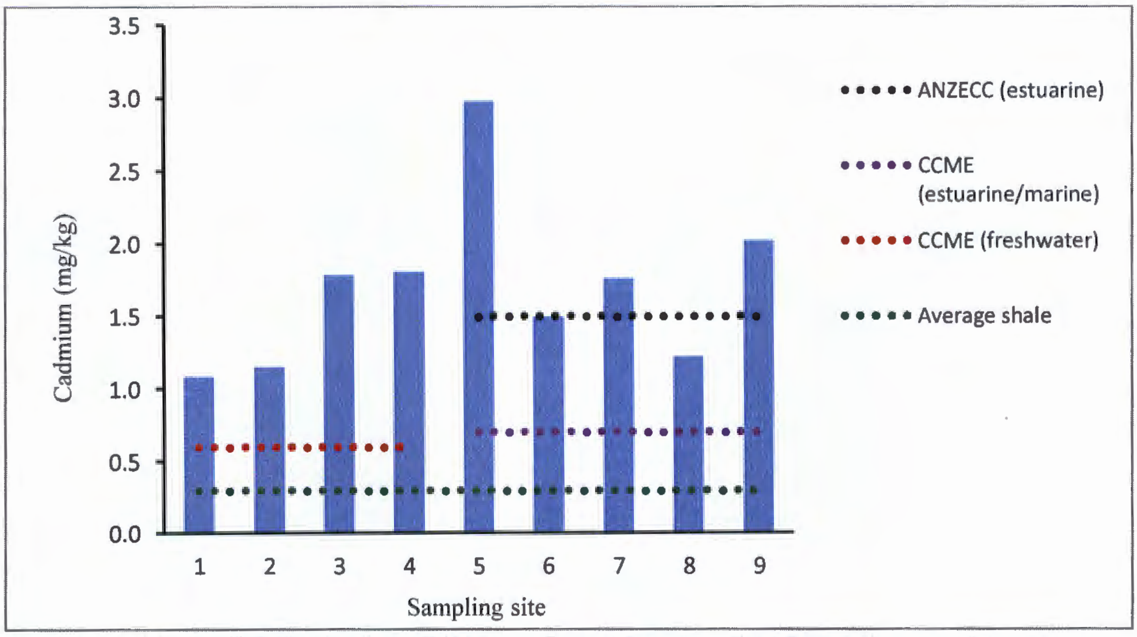

Figure 4.4.1.1: Spatial distribution of Cd in surface sediments of the Berg River and its estuary. Horizontal dash lines represent CCME-SQGs, ANZECC-SQGs and average shale of Cd

Arsenic (As) is fairly widespread in the environment, the average concentration in the earth's crust being approximately 2 mg/kg, ranks 20th in abundance in relation to the other elements (NAS, 1977). Spatial patterns for arsenic showed a minimum and maximum concentration of 6.83 mg/kg and 46.47 mg/kg with a mean value of 28.35±12.07 mg/kg (Fig.4.4.1.2). The maximum arsenic concentration was recorded at Site 3, whereas the minimum was recorded at Site 9. The highest arsenic concentration was significantly higher than the recommended environmental quality guidelines of 0.6 mg/kg in freshwater sediment as stipulated by the CCME (1995) and 20 mg/kg as stipulated by ANZEEC (2000). It was also higher than average concentration of arsenic (0.3mg/kg) in sediment of World Rivers (Martin and Meybeck, 1979). The higher level of arsenic obtained in sediment samples at Site 3 might be due to contribution from sources such as agricultural runoff where pesticides are used.

Arsenic enters the aquatic environment from natural and anthropogenic sources through aerial deposition or runoff. The strong affinity of arsenic for aquatic particles, particularly iron and manganese oxide, results in its deposition in bed sediment (CCME, 1995). The EF values of arsenic varied from 20.96 to 288.94 and were found to be greater than 50 in most sampling sites, suggesting that these sites are classified as having extremely severe enrichment for arsenic. At Sites 8 and 9, EF values were lower than 50, suggesting that these sites are classified as having severe enrichment.

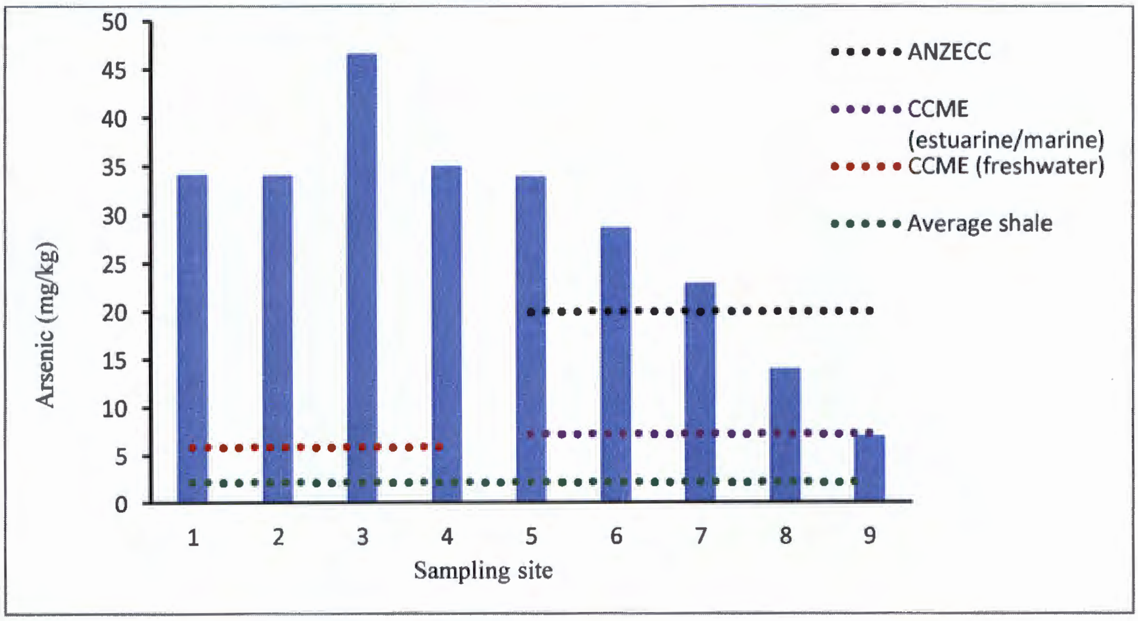

Figure 4.4.1.2: Spatial distribution of arsenic (As) in surface sediments of the river and its estuary. Horizontal dash lines represent CCME-SQGs, ANZECC-SQGs and average shale of Arsenic

In general, Pb concentrations in sediments were high during the study period. Pb concentration varied between 187.94 and 674.94 mg/kg with a mean value of 373.82±139.87 mg/kg. The highest Pb concentration in the Berg River was recorded at Site 8 while the lowest was recorded at Site 5. It was more than the African Rivers average (Jerome, 2009) and the shale concentration as a background level (Fig.4.4.1.3). This result was also higher than that reported by some South African authors (Jackson et al, 2009; Awofolu et al, 2005; Karen & Dan, 2001) and agrees with the results reported by Songca et al. (2013). In comparison with sediment quality guidelines, the highest Pb level exceeded the Australian and New Zealand quality guideline of 50 mg/kg (ANZECC, 2000) and was also higher than the SQG of 35 mg/kg. In aquatic system, lead binds strongly to particles, such as soil, sediment and sewage sludge. Pb tends to precipitate out of complex solutions because of the solubility of most of its salts, (Notter, 1993). Average Pb concentrations in different media worldwide tend to be much higher in sediments, and sediments now constitute the largest global reservoir of lead (Eisler 1988b). The EF values for Pb in the river sediments ranged from 184.26 to 480.43. The EF values of Pb were found to be greater than 50 for all sampling sites, suggesting that these sites are classified as extremely severe enrichment for Pb.

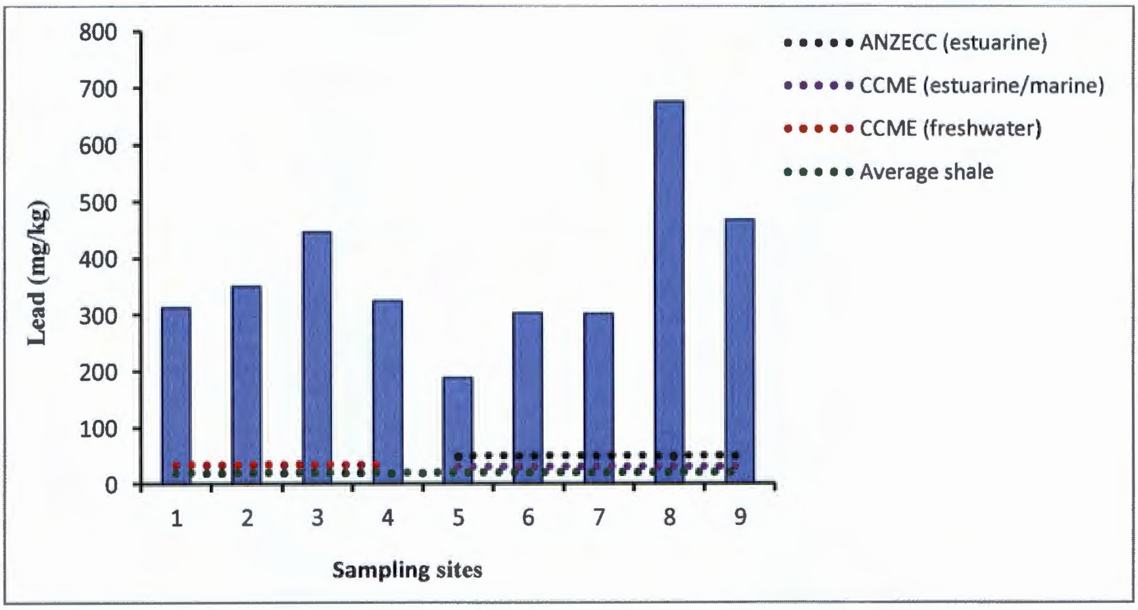

Figure 4.4.1.3: Spatial distribution of Pb in surface sediments of the river and its estuary. Horizontal dash lines represent CCME-SQGs, ANZECC-SQGs and average shale of Pb

Cr concentrations varied between 69.80 and 135.5 mg/kg with an average of 93.24±19.96 mg/kg. The highest Cr level was observed at Site 8 while the lowest level was observed at Site 2 (Fig.4.4.1.4). It concurs with average shale concentration as background level except at Site 8, which has high Cr concentration, in comparison with international SQGs was found that the Cr value exceeded Canadian sediment guidelines (CCME, 1995) in both freshwater and estuarine sources. The concentrations of Cr measured in the river and its estuary during this study was, by comparison, generally higher than those of other highly urbanized and industrialized South African estuaries. In aquatic systems such as rivers and estuaries, chromium enters through aerial deposition or surface runoff and, subsequently, its association with particle matter results in its deposition in bed sediments. Sediments are an important route for exposure of aquatic organisms to Cr because a variety of organisms live in bed sediments. The EF values for Cr in sediments from the Berg River and its estuary ranged from 21.80 to 78.96.

All sampling sites had EF more than 20, and Site 8 had a value more than 50, suggesting that the river and its estuary are classified as having severe to extremely severe enrichment for Cr (Brich, 2003). When compared with the reported Cr levels in the Berg River sediments, the concentration of Cr in the sediments of the river and its estuary were higher than those from the Tinto River (Spain) (Morillo et al., 2002).

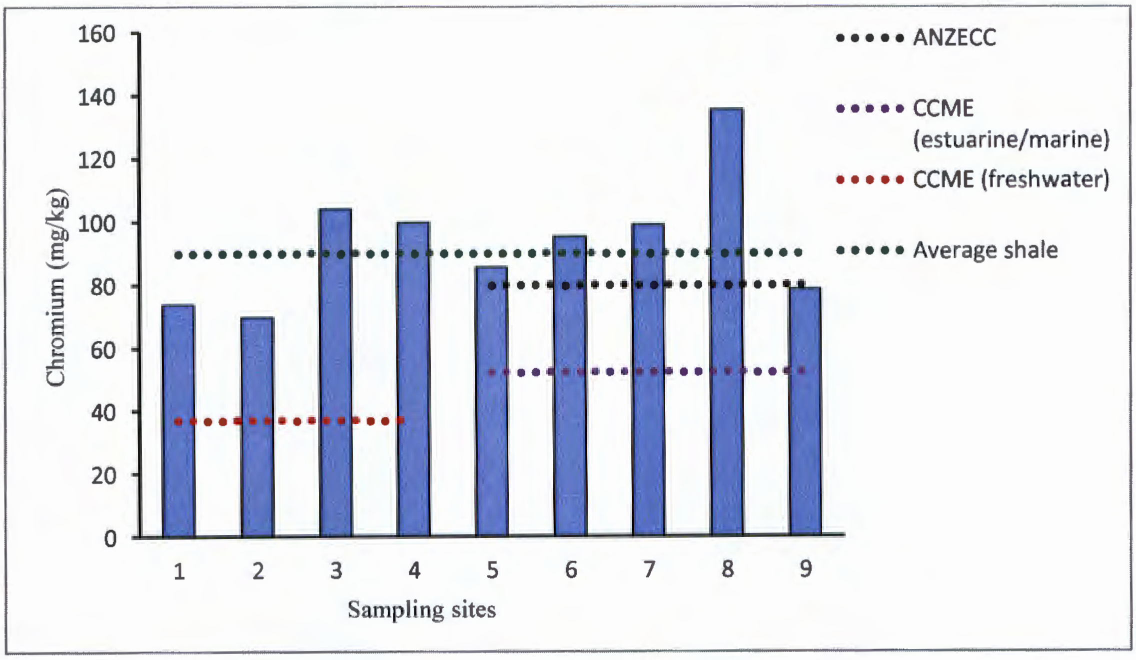

Figure 4.4.1.4: Spatial distribution of Cr in surface sediments of the river and its estuary. Horizontal dash lines represent CCME-SQGs, ANZECC-SQGs and average shale of Cr

The spatial variation of Co is given in Figure 4.4.1.5: the maximum level was 12.57 mg/kg at Site 4 while the minimum level was 4.43 mg/kg at Site 2 with an average of 7.97±2.91 mg/kg. The mean value of Co concentration was higher than the average of the African Rivers (Jerome, 2009) and lower than the average shale concentration. There is no recommended sediment quality guideline for Co, which may be due to its low hazardous level for the environment. In aquatic systems such as rivers and estuaries, cobalt is generally found in the Co (II) state as carbonate, hydroxide, sulfate, and adsorbed forms, as well as in the form of oxide coatings and crystalline sediments (Smith & Carson., 1981; Hamilton., 1994). In comparison with concentration in other locations locally and the world, it was lower than that reported for the Tinto River (Morillo et al., 2002). The EF values indicated that the Co has no enrichment factor (EF<1).

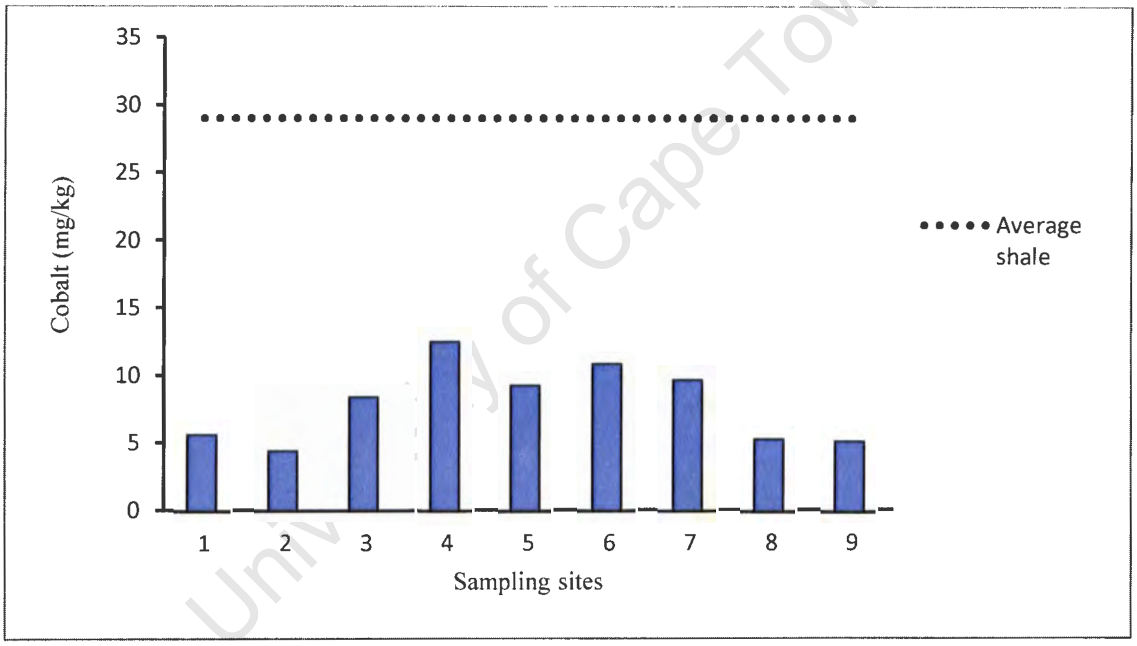

Figure 4.4.1.5: Spatial distribution of Co in surface sediments of the river and its estuary. Horizontal dash line represents the average shale of Co.

Levels of Mn in sediments of the river and its estuary ranged between 13.96 and 149.20 mg/kg with a mean value of 65.35±52.08mg/kg. The maximum Mn concentration was observed at site 7 while the minimum concentration was recorded at site 9 (Fig.4.4.1.6). No recommended sediment quality guidelines for Mn were available from CCME (1995) and ANZECC (2000), and the only guideline was available from Ontario (1993) and average shale concentration. Mn concentration was less than that reported in previous studies of the world and local sites (Jackson et al., 2009; Salah et al., 2012) and higher than that reported by Jackson et al. (2007) in the Berg River. In this study, the concentration of Mn indicated no enrichment factor because it had been used as a reference for assessment of pollution in the Berg River and its estuary (Turekian, 1961).

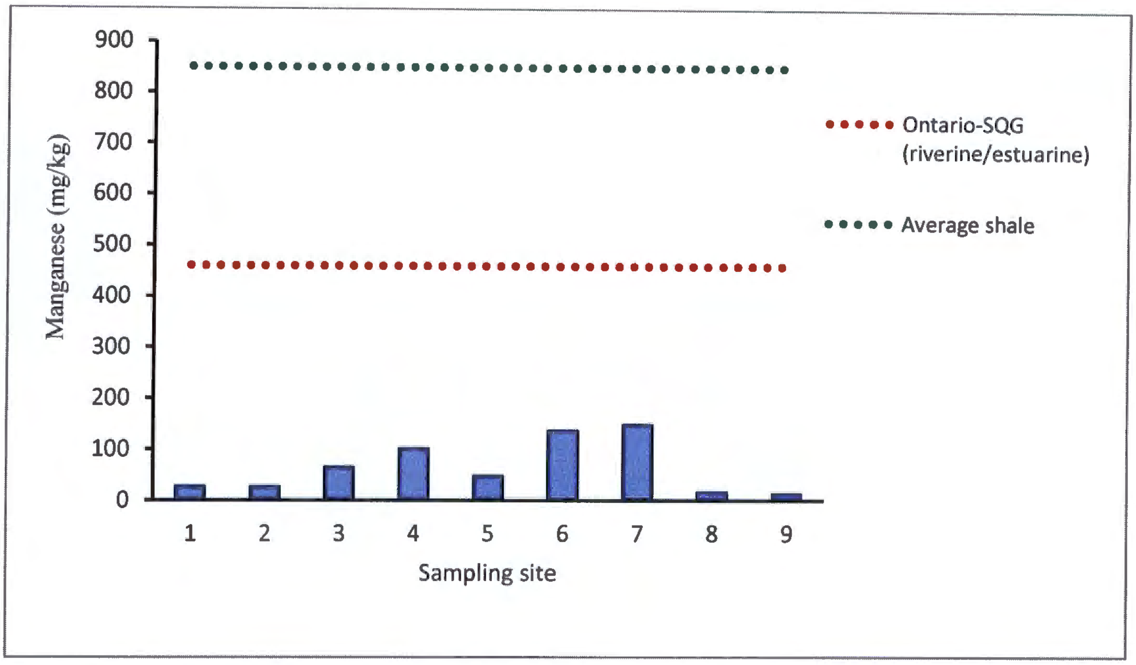

Figure 4.4.1.6: Spatial distribution of Mn in surface sediments of the river and its estuary. Horizontal dash lines represent the Ontario Sediment Quality Guideline and average shale of Mn.

Cu concentration varied from 0.45 to 16.13 mg/kg with a mean value of 6.78±4.39 mg/kg. The mean value was less than average shale concentration as geochemical background level (Fig.4.4.1.7). In comparison with sediment quality guidelines, the highest mean value for Cu was lower than the recommended environmental quality guidelines in marine /estuarine (18.7 mg/kg) and freshwater sediment (35.7 mg/kg) as specified by the CCME (1995). According to the guidelines mentioned above, the Berg River and its estuary were only slightly polluted by Cu (especially at Site 3). Mean Cu concentrations for a number of sites from the Berg River as reported by Jackson et al. (2007) were similar to those recorded in this study. The enrichment factor (EF) values for Cu in the Berg River and it estuary varied from 0.45 at site 9 to 4.90 at site 3. All sampling site except site 3 had EF values lower than 5, suggesting that sediments from the river and its estuary are classified as no enrichment to deficiency to minimal enrichment for Cu (Brich, 2003).

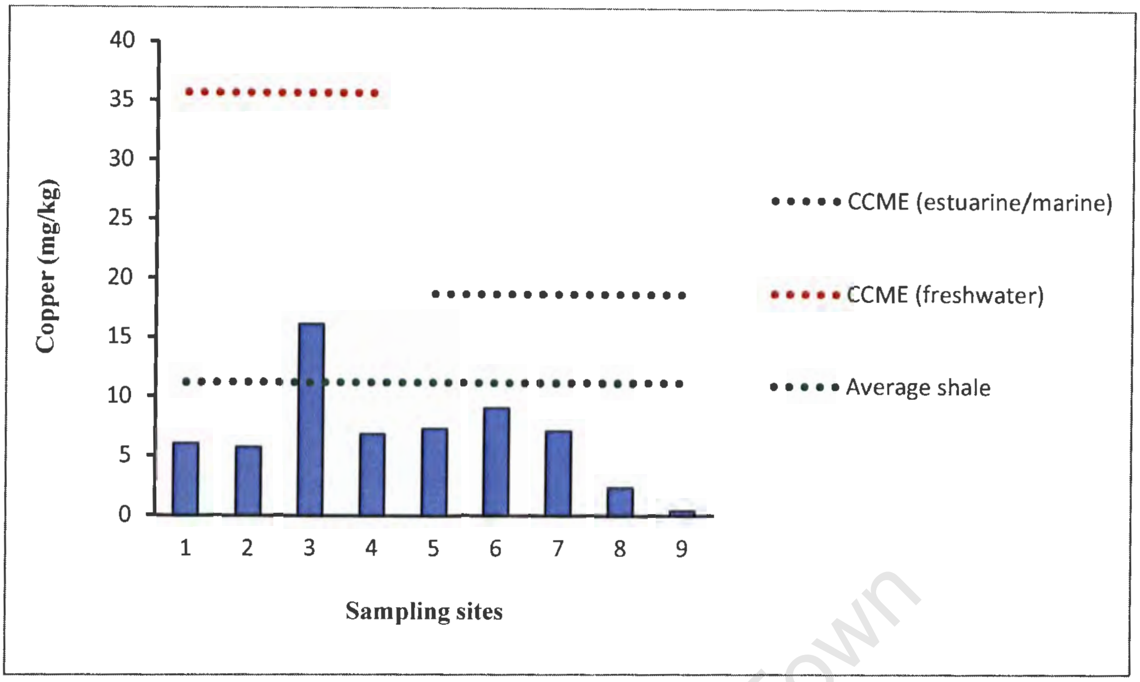

Figure 4.4.1.7: Spatial distribution of Cu in surface sediments of the river and its estuary. Horizontal dash lines represent the Sediment Quality Guidelines (CCME, 1995) and average shale of Cu.

Nickel is a trace metal that occurs in the environment only at very low levels and is an essential element in small concentrations, but it can be dangerous when the maximum tolerable amounts are exceeded (ANZECC 2000). Nickel concentration ranged between 17.73 and 168.33 mg/kg with a mean value of 54.31±43.88 mg/kg. The maximum Ni concentration was observed at site 8 while the minimum was recorded at Site 9 (Fig.4.4.1.8). In comparison to sediment quality guidelines, the mean Ni value was higher than the recommended guideline of 21mg/kg in fresh water systems as stipulated by CCME. (1995). It also was higher than the recommended SQGs of 23 mg/kg in estuarine systems as applied by CMSQG (2000a). The highest Ni concentration was recorded at site 8, higher than the average of the African River (Jerome, 2009) and shale concentrations (Raju et al., 2012). The highest EF value (95.99) was observed at Site 8, suggesting that this site is classified as having extremely severe enrichment for Ni according to Brich (2003).

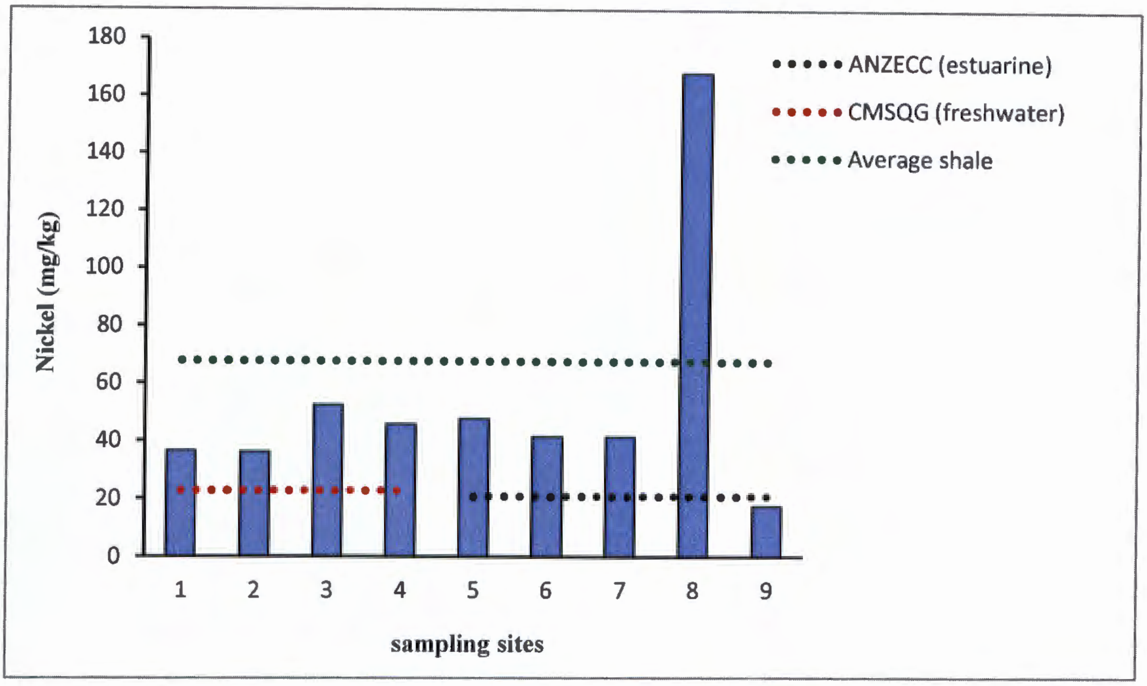

Figure 4.4.1.8: Spatial distribution of Ni in surface sediments of the river and its estuary. Horizontal dash lines represent the Sediment Quality Guidelines (CCME, 1995; CMSQG, 2000a) and average shale of Ni.

Iron was found in the maximum abundance of the metals during the study period, its concentration varying from 1237.80 to 22690.76 mg/kg with a mean value of 9609.32±7594.25 mg/kg. The maximum value was detected at Site 3 while the minimum value was detected at Site 9 (Fig.4.4.1.9). Elevated Fe concentrations may be related to iron-calcareous–rich sediments. However, contamination of anthropogenic origin can also be included, although the Fe content in the Berg River was lower than the values reported in contaminated rivers such as Tinto River, Spain (Morillo et al., 2002) and the Capibaribe River, Brazil (Fatima et al., 2001). The EF values for Fe in the Berg River and its estuary ranged from 0.8 to 11.43, suggesting that these sites are classified as having deficiency minimal to moderately severe enrichment.

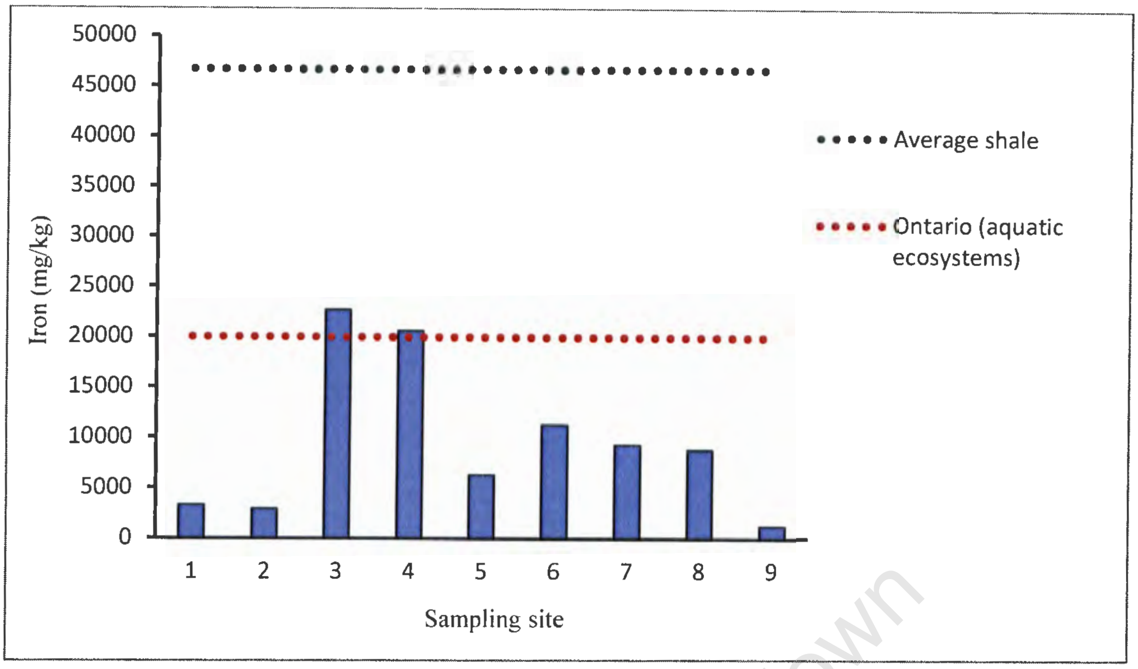

Figure 4.4.1.9: Spatial distribution of Fe in surface sediments of the river and its estuary. Horizontal dash lines represent the Sediment Quality Guidelines (Ontario, 1993) and average shale of Fe.

Zinc is an essential trace element that can be toxic to aquatic life at elevated concentrations. It is a very common substance that occurs naturally in air, sediment and soil, but zinc concentrations are rising unnaturally, due to the addition of zinc through human activities (Peterson & Batley., 1992). Zn concentration ranged between 9.35 and 47.76 mg/kg with a mean value of 26.17±11.92 mg/kg. The highest Zn concentration was detected at Site 3, whereas the lowest concentration was detected at Site 1 (Fig.4.4.1.10). In comparison with previous studies local and worldwide, it was found that the Zn concentration recorded in this study was lower than average of shale concentration (Raju et al., 2012). It was also lower than that recorded in contaminated rivers (Fatima et al., 2001; Morillo et al., 2002, 2004; Songca et al., 2013). The concentration of Zn fell within the recommended sediment quality guidelines range for all of the sampling sites. It was slightly below the lower level of CCME guidelines (1995) for freshwater and estuarine/marine environments. According to sediment quality guidelines and EF values, the Berg River and its estuary sediments were unpolluted by Zn.

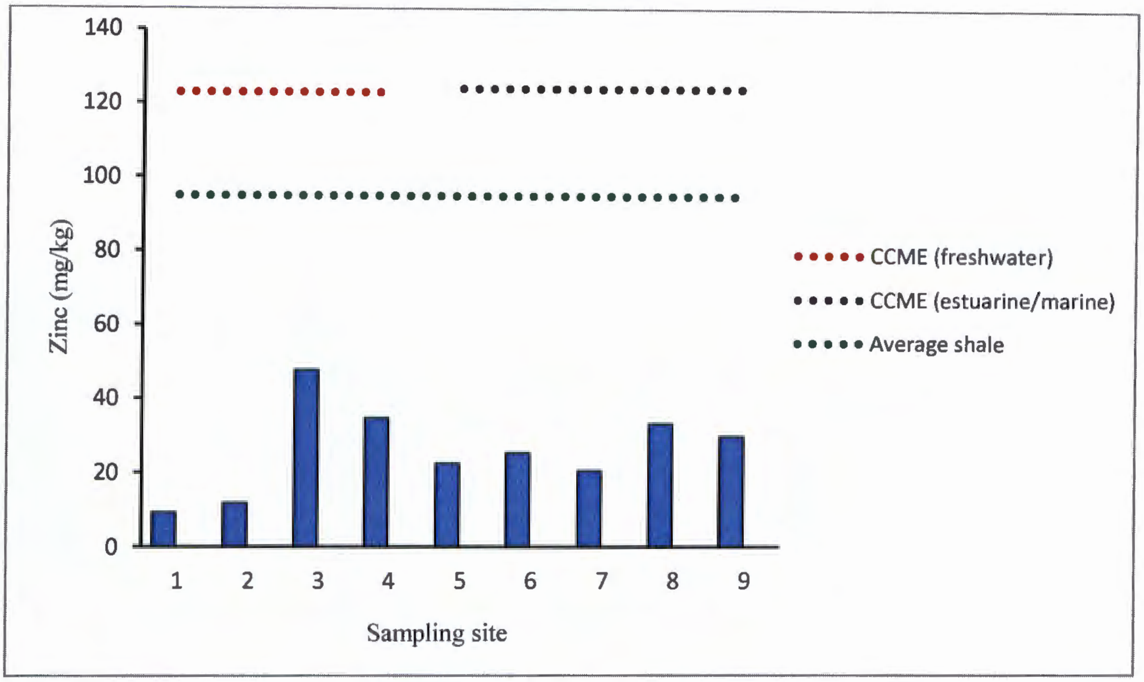

Figure 4.4.1.10: Spatial distribution of Zn in surface sediments of the river and its estuary. Horizontal dash lines represent the Sediment Quality Guidelines (CCME, 1995) and average shale of Zn.

4.4.2 Particle size and organic matter in sediment as a function of site

The characterization of the physical properties of the sediment within the Berg River shows different results in the sediment types based on the geographic sites within the catchment. For example, the portion of the catchment extending from Site 1 to Site 4 is characterized by clay and fine sand with medium organic matter content. In contrast, the coastal marine Site 9 where the river flows into the ocean is characterized by medium and fine sand with low organic matter content. The difference in sites and sediment properties allows sediment to be characterized and helps in comparison and discussion.

Based on the results shown in figure 4.4.2, the most important parameters in the river sediments were particle size distribution and organic matter. The most widespread grain size in the sediment of the river was fine sand and this was followed by clay, medium sand, silt and coarse sand. Site 6 presented the highest percentage of fine sand which is more than six times higher than the lowest clay. The percentage for coarse sand and silt was about 2% of the total. The results for organic matter showed that the percentages varied throughout the river and were medium in both downstream and upstream sites. OM detected in these sites is lower than that in the Klang River in Malaysia (no study was found involving OM from the Berg River) at 13.34%.

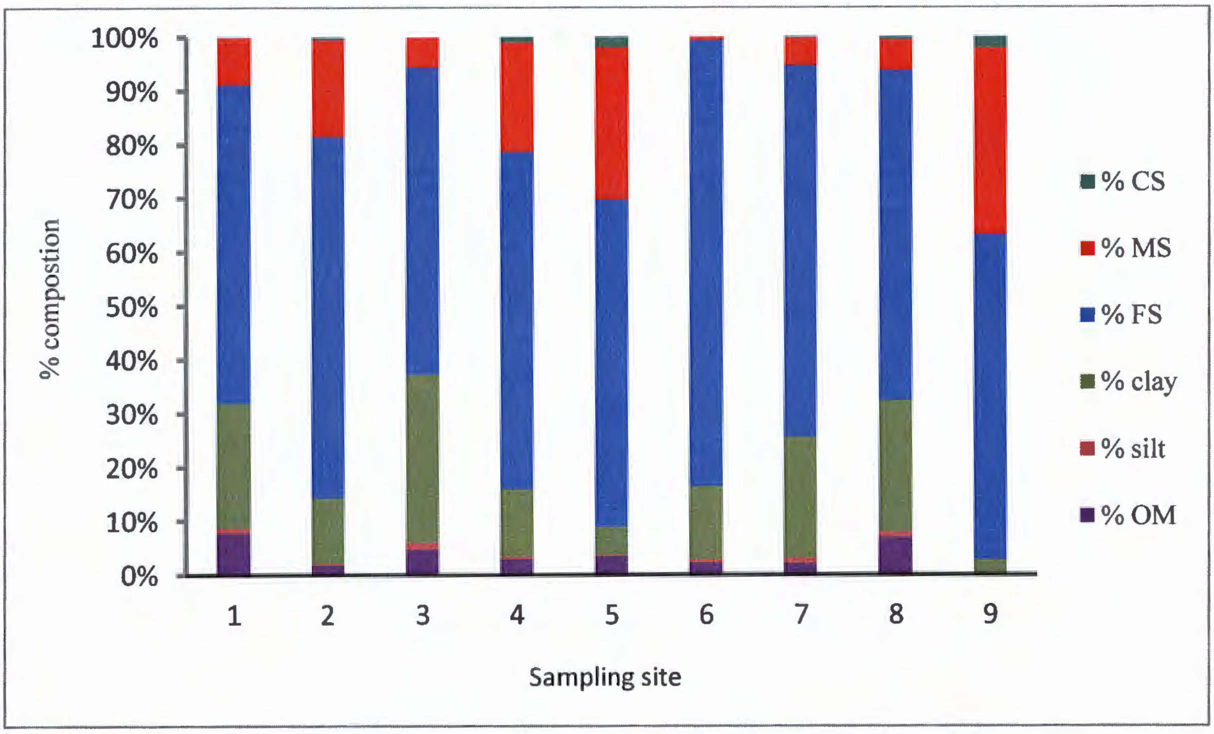

Figure 4.4.2 Sediment characteristics of the Berg River and its estuary

4.4.3 Relationship between metal concentrations and sediment characteristics

To assess which of the common variables controls the concentration of metals in the river, Pearson's correlation coefficients between metal concentrations; sediment particle size and organic matter were calculated for nine sites of the Berg River. The result of the correlation matrix for each site is presented in Table 4.4.3.

Moderate to strong positive correlation of most metals with silt and clay indicates that they are concentrated in fine-grained particles and hosted by clay phases. However, strong positive correlations between Cd and sand fractions were observed during the present study, which indicates that Cd was associated with larger grain particle, and it is thus more mobile.

Table 4.4.3 Pearson's correlation matrix of heavy metals, particle size and organic matter in sediment for nine sites within the Berg River

	As	Cd	Pb	Cr	Co	Mn	Cu	Ni	Zn	Fe	% OM	% silt	% clay	% FS	% MS	% CS
As	1															
Cd	-0.46	1.00														
Pb	0.13	-0.67	1.00													
Cr	0.22	-0.57	0.51	1.00												
Co	-0.44	0.83	-0.63	-0.71	1.00											
Mn	0.27	0.10	-0.46	0.19	-0.08	1.00										
Cu	0.74	0.11	-0.27	0.02	0.07	0.44	1.00									
Ni	-0.20	-0.26	0.43	0.64	-0.06	-0.24	-0.19	1.00								
Zn	0.15	0.25	0.06	0.51	-0.10	0.10	0.40	0.29	1.00							
Fe	0.61	0.08	-0.14	0.45	-0.13	0.48	0.72	0.13	0.76	1.00						
% OM	**0.09**	-0.09	-0.16	0.01	0.30	-0.35	**0.11**	0.51	-0.09	0.06	1.00					
% silt	**0.58**	-0.59	**0.24**	**0.65**	-0.51	**0.21**	**0.46**	**0.39**	**0.17**	**0.40**	**0.38**	**1.00**				
% clay	**0.65**	-0.52	**0.24**	**0.59**	-0.40	**0.11**	**0.54**	**0.43**	**0.24**	**0.49**	**0.50**	**0.97**	1.00			
% FS	-0.65	**0.56**	-0.22	-0.60	0.42	-0.17	-0.49	-0.44	-0.16	-0.48	-0.51	-0.97	-0.99	1.00		
% MS	-0.62	**0.62**	-0.15	-0.58	0.43	-0.46	-0.50	-0.37	-0.02	-0.42	-0.32	-0.86	-0.83	0.86	1.00	
% CS	-0.72	**0.71**	-0.23	-0.56	0.53	-0.41	-0.50	-0.26	0.03	-0.40	-0.26	-0.87	-0.83	0.87	0.98	1

0.8-1.0 = very strong correlation, 0.6-0.79 strong correlation, 0.40-0.59 moderate correlation, 0.2-0.39 weak correlation and 0.00-0.19 very weak correlation

4.5 Adsorption of Pb, Cr, Cu, Ni, and Zn on to bed sediment of the Berg River estuary

Heavy metals in the aquatic environment are generally concentrated on solid geochemical phases which, after transport through river systems, become incorporated into estuarine and marine sediments. The mechanism of heavy metal concentration is believed to be adsorption with various geochemical phases such as hydrous metal oxides, clays, and organic matter. In this section, results of adsorption data for both clean and unclean sediments are presented in the form of figures, with amount adsorbed (q_e) in mg/g. Adsorption values with duplicate reading of initial and final concentrations, are reported in tables in chapter 3.

4.5.1 Effect of adsorbent dose

The effect of adsorbent dose on the adsorption properties of bed sediments of the Berg River estuary was studied at natural pH value with different adsorbent doses ranging from 0.1 to 0.7g and at a fixed initial concentration of 3 mg/L (Fig 4.5.1). The adsorption values of metal ions were plotted against adsorbent dose. The maximum adsorption was 0.53 mg/g for Pb, 0.12 mg/g for Zn and 0.11mg/g for Ni with corresponding absorbent dosage of 0.2 g, while the value was 0.53 mg/g for Pb and 0.37 mg/g for Cr at absorbent dose of 0.4 g. It is clearly evident from figure 4.5.1that the adsorption of metals increases with adsorbent dosage until it reaches the maximum values then decreases with increasing adsorbent load. Obviously, higher dose of adsorbent results in higher surface area providing a greater number of binding sites for the metal ion. It is also observed that after dosage of 0.5g of sediment, there was no significant change in adsorption of metals. This may be due to the overlapping of active sites at higher dosage. However, the adsorption of Pb decreases from 0.53 to 0.16 mg/g under these conditions. Therefore, 0.4g of sediment for Cr and Cu, and 0.2g for Pb, Ni and Zn were considered as optimum dose and was used for further experiments.

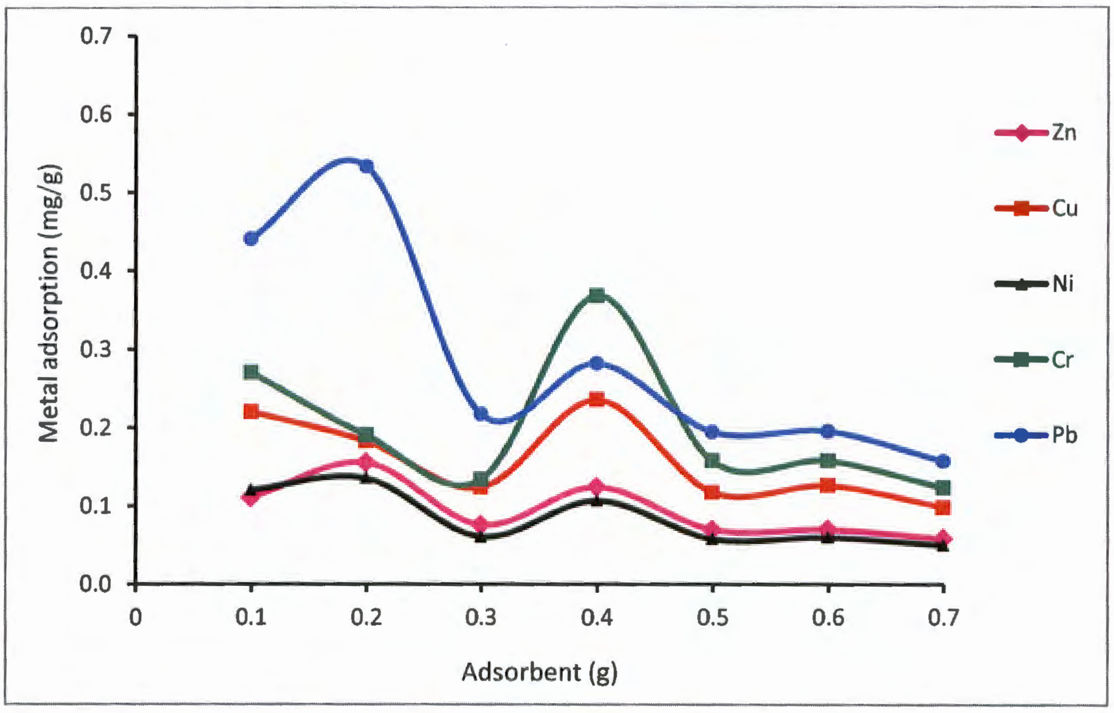

Figure 4.5.1 Effect of adsorbent dose on the adsorption of metal ion

4.5.2 Effect of pH

Many studies (Adediran, 1983; Saeedi et al., 2004) indicate that pH is one of the important factors controlling adsorption processes. Change in pH of solution influences metal speciation leading to the formation of complex inorganic species in solution. The effect of pH on the adsorption of metal ion is shown in Fig. 4.5.2. The adsorption of five metal ions on the bed sediment of the Berg Estuary was studied over the pH range 2 to 12 for a fixed initial concentration 4 mg/l and adsorbent dose of 0.2 g for Pb, Ni and Zn and 0.40 for Cr and Cu. A general increase in adsorption of metals with increasing pH of solution was observed up to the pH of 5.0, and then the adsorption becomes a stable, which may be due to low solubility of metal ions at higher pH.

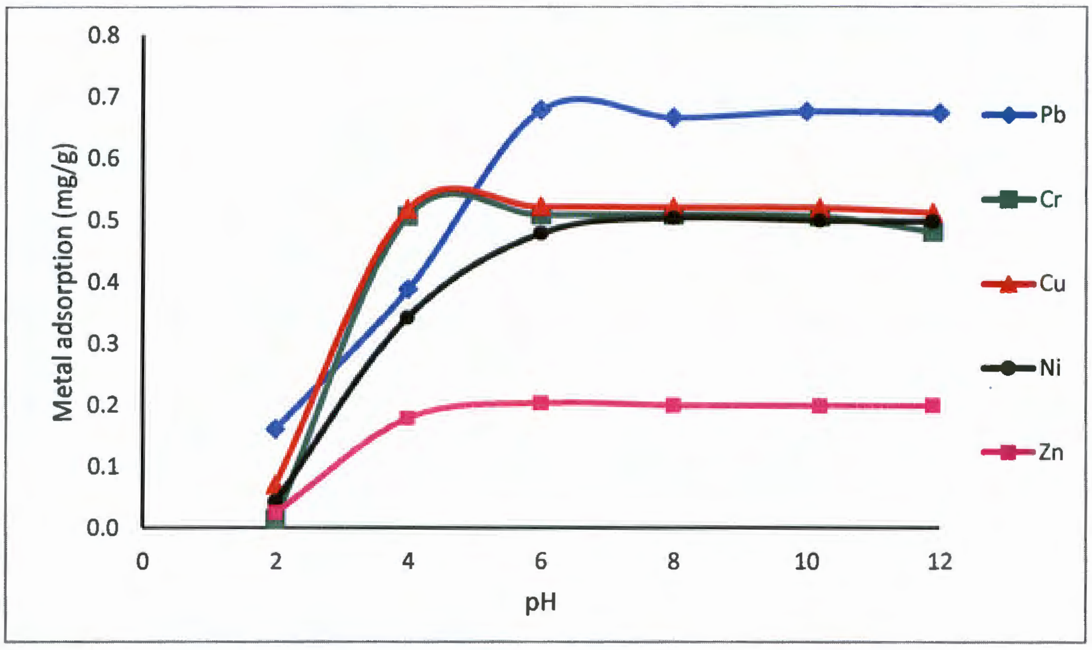

Figure 4.5.2 Effect of pH on adsorption of metal ion

Similar behaviour has been reported be many authors (Parker and Rae, 1998; Jain and Daya, 1997) for the uptake of metal ions on various adsorbents. From the results, it is evident that the pH for maximum adsorption of Pb ion (0.678 mg/g) is 6.0. At this pH, the concentration of Pb ion in solution is quite low (reduced to 2.79 mg/L from 6.46 mg/L due to pH adjustment). This behaviour applies also to the other metals tested.

4.5.3 Effect of contact time

Removal of heavy metals from solution also depends on its contact time with the adsorbents. Adsorption of Pb, Cu, Cr, Ni and Zn at various contact times was investigated to find the time for maximum adsorption. Batch adsorption experiments were conducted with sediment samples by varying the time from 30 to 180 minutes (30, 60, 90, 90, 120, 150 and 180 min) with fixed initial metal ion concentration of 4 mg/L. Based on the results shown in figure 4.5.3, the maximum adsorption value was observed at the first 30 min for Pb, Ni and Zn and at 60 min for Cu and Cr. The change in the rate of metal adsorption might be due to the fact that initially all adsorbent sites were vacant and metal ion concentration gradient was high. Therefore the adsorption of Pb, Ni and Zn was also high. Later, the rate of uptake of these metals by adsorbent (sediment) was decreased significantly, due to the decrease in number of adsorption sites as well as metal concentration. As time passes, the number of sites on the adsorbent filled up by adsorbate (metal) also increases. At equilibrium, when all sites are filled, the rate of adsorption is equal to the rate of desorption. Therefore, after equilibrium, it is found that there is no further increase in adsorption value with increase in contact time.

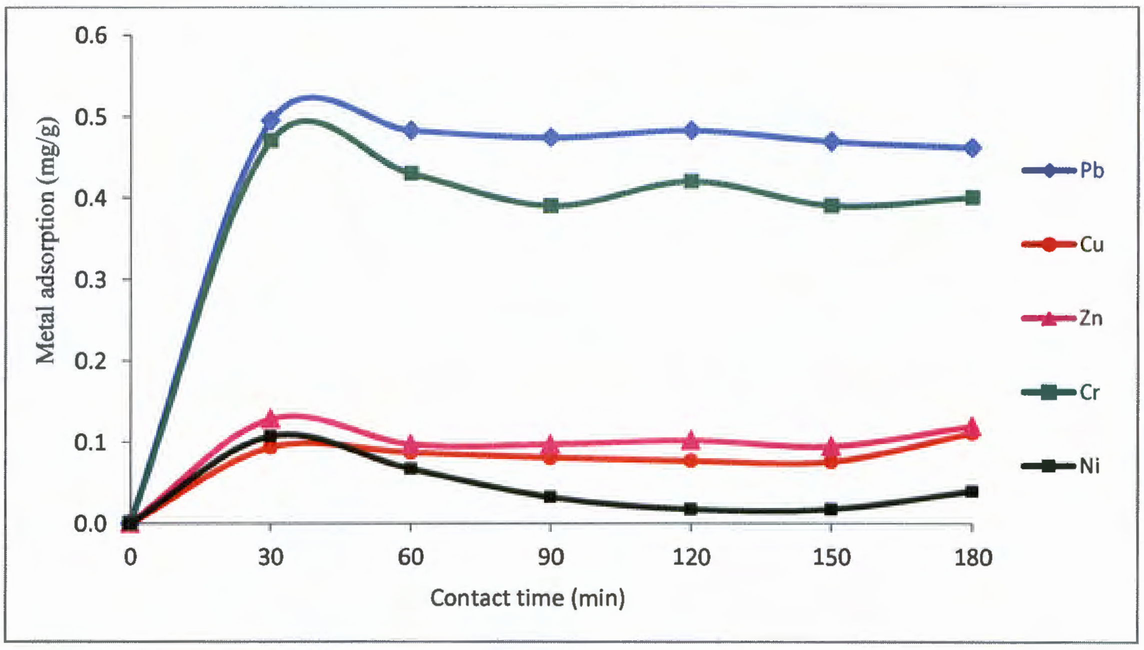

Figure 4.5.3 Effect of contact time on adsorption of metal ion

4.5.4 Effect of initial metal ion concentration (C_0)

In batch adsorption processes, the initial metal concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between solution and solid phase (sediment). In order to study the effect of initial concentration on the adsorption process, the initial concentrations were ranged from 2 to 12 mg/L and batch mode experiments were performed with optimum adsorbent dose of 0.2 g for Pb, Ni and Zn and 0.4 g for Cr and Cu. Based on the adsorption data, metal adsorption percent was plotted against initial metal ion concentration (Fig. 4.5.4). In general, an increase in the adsorbent concentration leads to a decrease in the final concentration. Strong correlation between adsorption of Pb, Cr and Cu and their initial and final concentrations was observed. It is evident from the graph that for an increase in initial metal concentration from 2 to 12 mg/L, the adsorption of Pb and Cr ions increases with increase of metal concentration. However it is clear that, for Cu, Ni and Zn, there was no appreciable increase in the adsorption values corresponding to an increase in initial metal concentration, which may be attributed to the fact that, for a fixed adsorbent dose, there are no available sites on the surface sediment for metal adsorption.

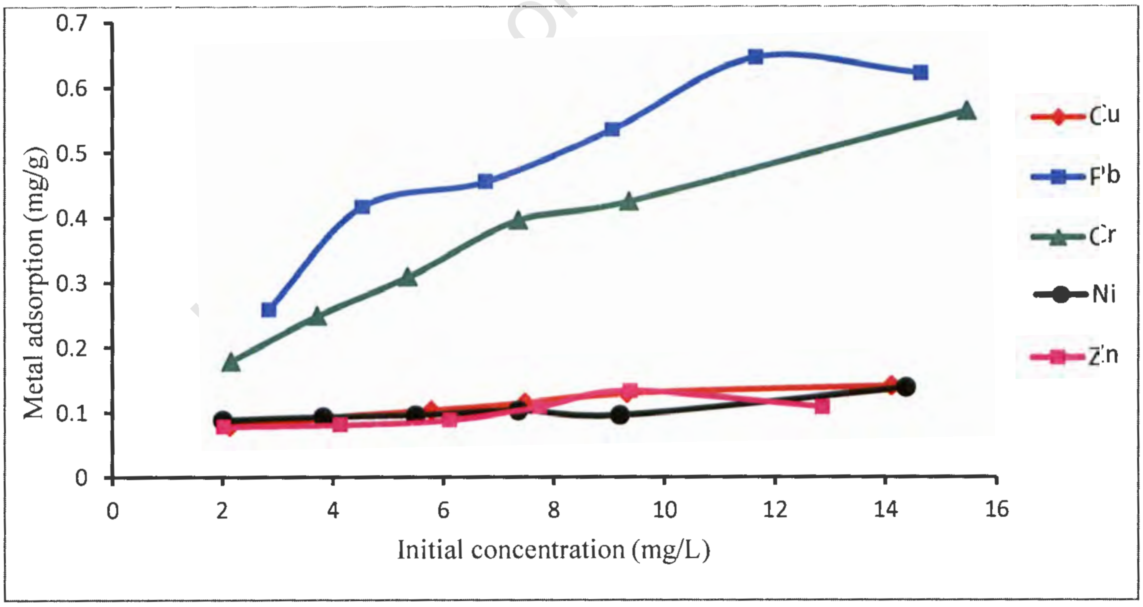

Figure 4.5.4 Effect of initial metal concentration on the adsorption.

4.5.5 Adsorption isotherm models

In general, the adsorption isotherm is an invaluable curve describing the phenomenon governing the mobility of substance from the aqueous porous media (aquatic environment) to the solid phase (sediment) at a constant temperature and pH (Limousin et al., 2007). Adsorption data for a wide range of adsorbate concentrations is most conveniently described by adsorption models such as the Langmuir and Freundlich isotherms. There are other isotherm models, but those of Langmuir and Freundlich are considered the most commonly used ones due to their widespread application in adsorption especially for monolayer adsorption processes.

In this study, the adsorption data for selected metal ions (for both clean and unclean sediments of the Berg estuary) were analysed by both Langmuir and Freundlich models to investigate the ability of sediment to adsorb heavy metals, and to allow quantification and further interpretation of data.

The Langmuir and Freundlich equations can be easily linearized and used to fit the experimental data through linear regression or correlation coefficient. If the correlation coefficient, R^2, is close to 1, the points on the figure lie more accurately on linearized isotherm line. However, if the R^2 value is not close to 1, it does not mean that the experiments are unreliable; rather, it refers to the inability of the points to be linearized using the isotherm models.

4.5.5.1 ***Langmuir model***

Langmuir's isotherm model, developed by Irving Langmuir in 1916, has been used by many authors for the study of the adsorption of heavy metals on river sediment (Jain & Daya., 1996; Jain et al., 2004). The model has been empirically most often used eventually since it contains the useful and easily imaginable parameters q_{max} and b. It quantitatively describes the build-up of layers of molecules on an adsorbent surface as a function of the concentration of the adsorbed materials in the liquid phase in which it is in contact. It suggests that the uptake occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules. The model assumes that there is no physical or chemical interaction between adsorbed molecules (no further adsorption takes place). Physical adsorption takes place through van der Waals interactions, whereas chemical adsorption occurs through formation of a covalent bond. Based upon these assumptions, the linear form of the Langmuir equation is as follows;

$$1/q_e = 1/Q^0 + 1/bQ^0Ce$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate ions, and Q^0 and b are Langmuir constants related to maximum adsorption capacity and the energy of adsorption respectively. In this study, $1/q_e$ was plotted against 1/Ce, and a straight line with slope $1/bQ^0$ and intercept $1/Q^0$ was obtained (Fig. 4.4.6.1). The K value was calculated from the relationship between b and the affinity constant K as follows;

$b = 1/K$, then $K = 1/b$

where K is the affinity between the adsorbent and adsorbate

The higher b value and the smaller K, the higher is the affinity of the adsorbent (e.g. sediment) for the adsorbate (e.g. metal ion).

Based on the constants and correlation coefficient obtained from figures 4.5.5.1.1 to 4.5.5.1.5, the isotherm model showed that the clean sediment of the Berg estuary adsorbed the highest Pb and Cr from water. However, low adsorption on unclean sediment was observed for all metals. As shown in the figures, high values of the correlation coefficient (R^2 = 0.902-0.980) for Pb, Cr and Cu were also observed while low values of R^2 were 0.444-0.581 for clean sediment. The highest values of R^2 indicate a good agreement between parameters and confirm the monolayer adsorption of Pb, Cr and Cu ions on to surface sediment. Therefore, the adsorption of these metals fitted to the Langmuir isotherm model. However, the adsorption of the same metals on unclean sediment did not fit the model, which may be due to the lack of available sites on the surface of the sediment for the occurrence high adsorption. The Langmuir adsorption model data for selected metals on clean sediment are presented in the Table 4.5.5.1.

Table 4.5.5.1: Langmuir isotherm model constants and correlation coefficients for the adsorption of metal ions on clean sediment of the Berg River estuary

Adsorption isotherm model	Isotherm constants	Metal ions				
		Pb	Cr	Cu	Ni	Zn
Langmuir	q_{max} (mg/g)	0.764	0.528	0.143	0.116	0.049
	K (mg/L)	0.376	0.632	1.318	1.748	1.087
	b (L/mg)	2.661	1.582	0.759	0.572	0.919
	R^2	0.980	0.948	0.902	0.444	0.581

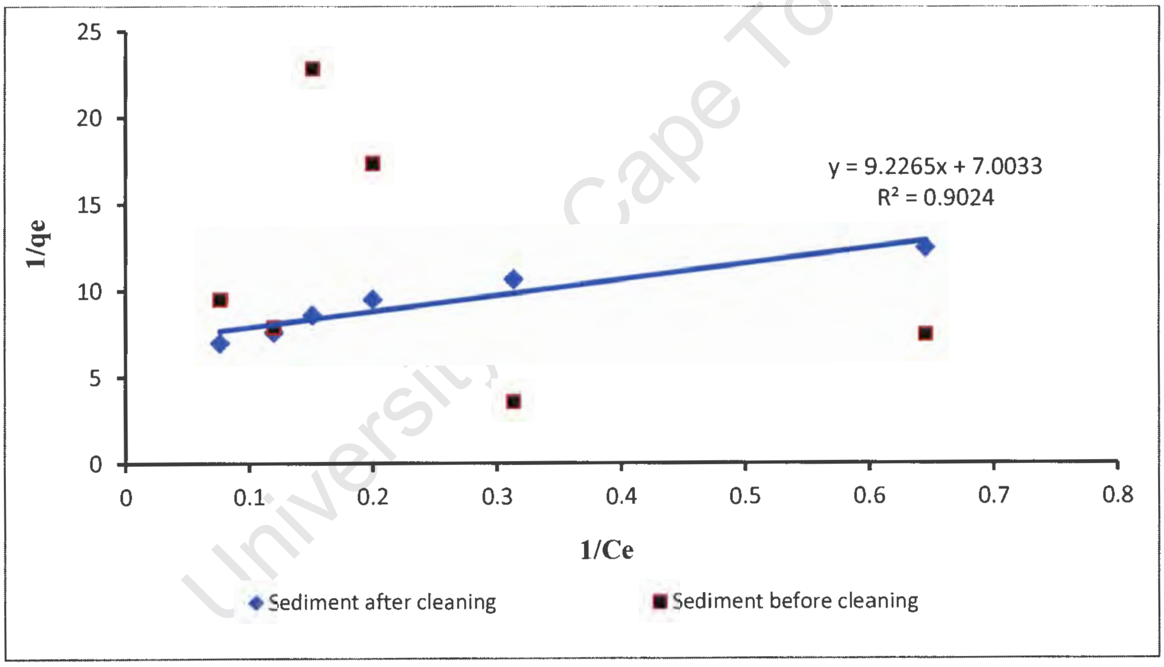

Figure 4.5.5.1.1 Langmuir isotherm for adsorption of Cu on the sediment of Berg estuary

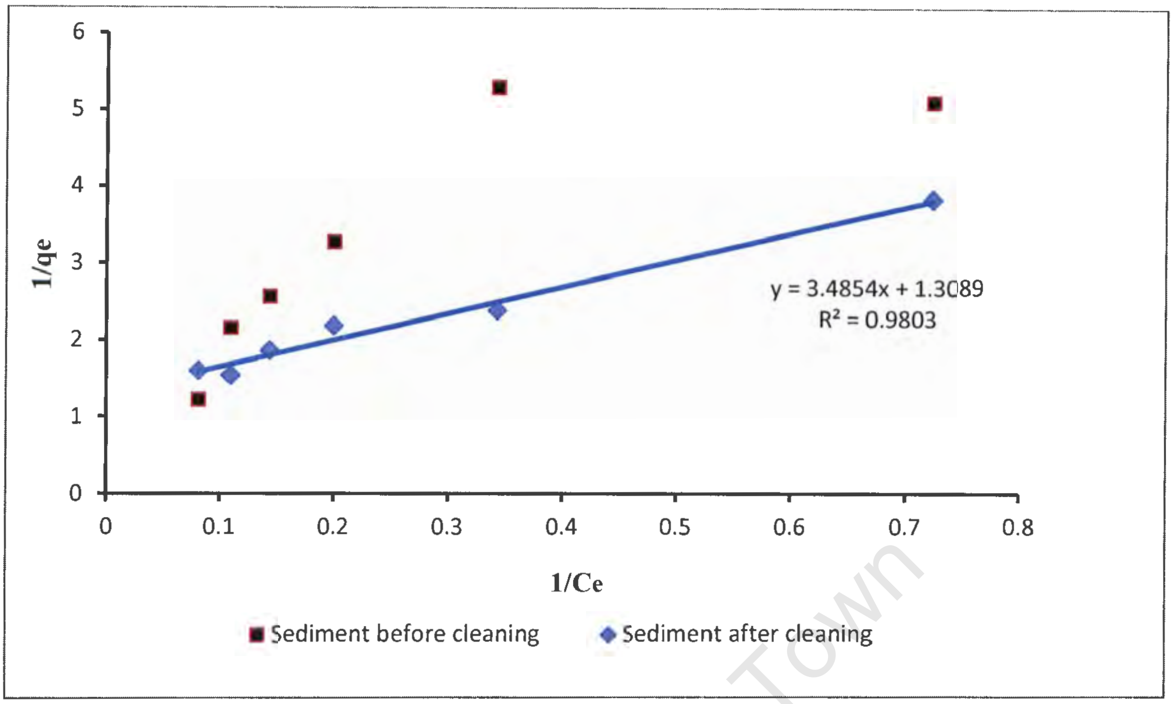

Figure 5.5.5.1.2 Langmuir isotherm for adsorption of Pb on the sediment of Berg River estuary

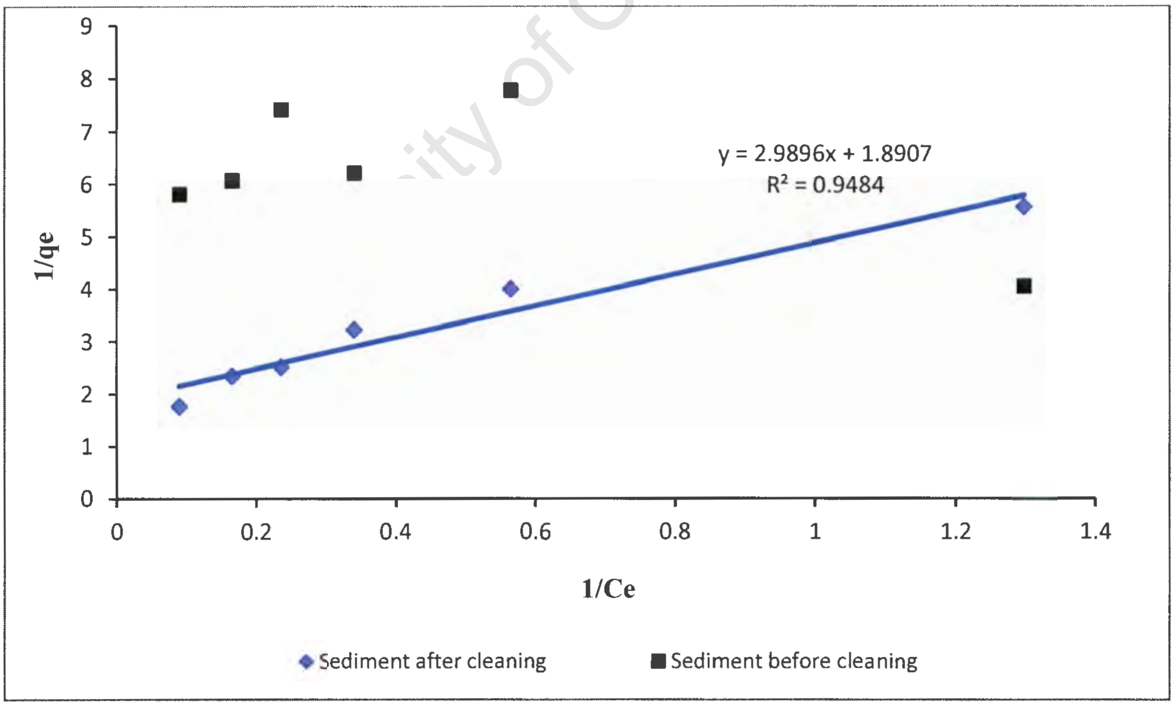

Figure 4.5.5.1.3 Langmuir isotherm for adsorption of Cr on the sediment of Berg River estuary

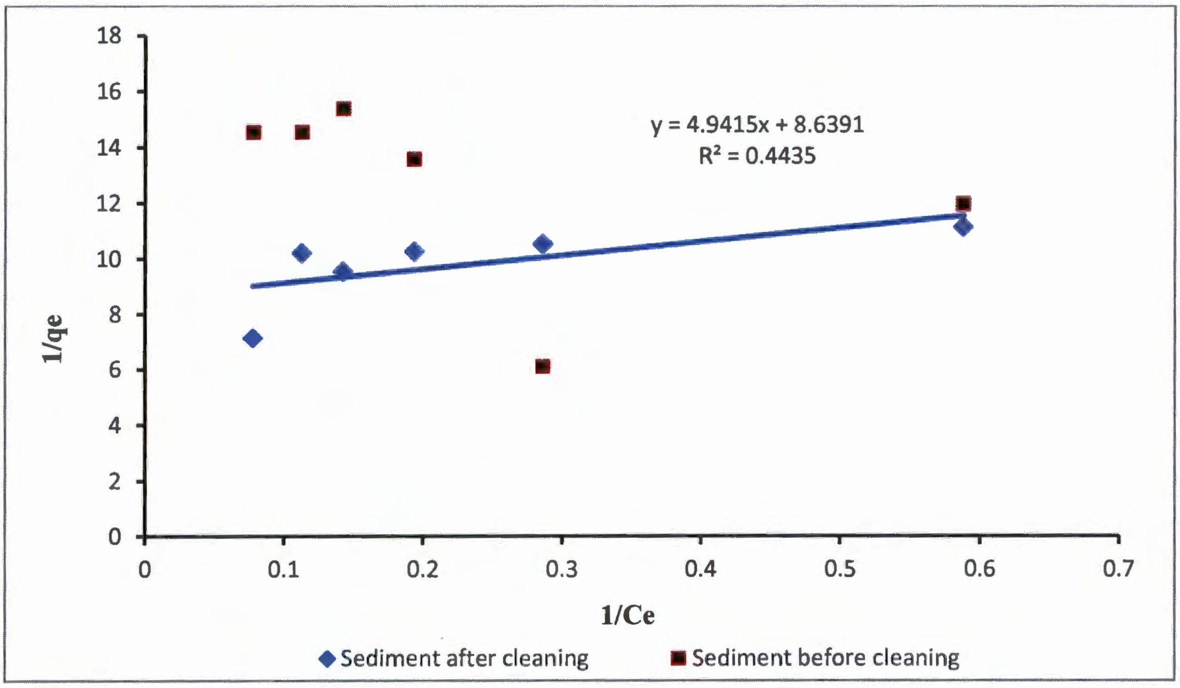

Figure 4.5.5.1.4 Langmuir isotherm for adsorption of Ni on the sediment of Berg River estuary

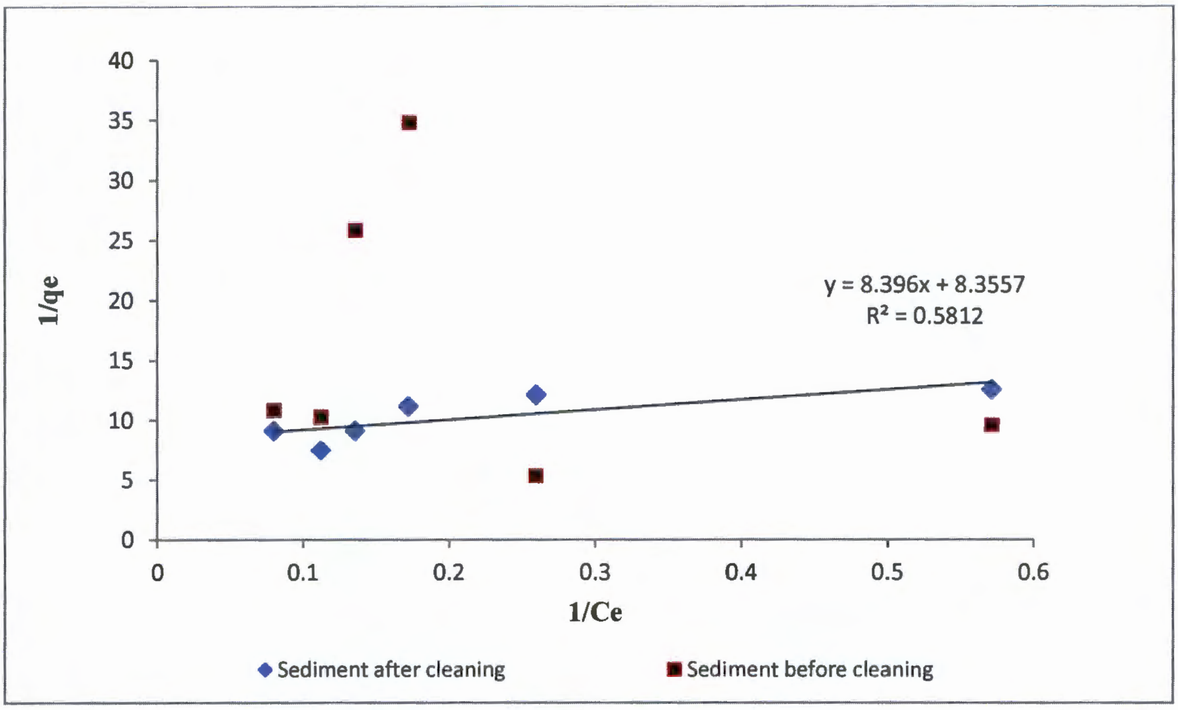

Figure 4.5.5.1.5 Langmuir isotherm for adsorption of Zn on the sediment of Berg River estuary

4.5.5.2 ***Freundlich model***

The model has been commonly used to describe the adsorption characteristics for heterogeneous surfaces (Hutson & Yang, 2000). It assumes that the sorbent has a heterogeneous valence distribution (surface energies) and therefore has a different affinity for adsorption. The adsorption of Pb, Cu, Cr, Ni and Zn ions was also analysed using the linear form of the logarithmic Freundlich isotherm model as shown by the following equation:

$$\log q_e = \log k_F + 1/\text{n} \log Ce$$

where q_e is the amount adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate ions (mg/l), and k_F and n represent Freundlich constants related to adsorption capacity and adsorption intensity respectively. Freundlich equilibrium constants were determined from the plot of log q_e against log Ce, a straight line with slope 1/n and intercept log k_F was obtained in each case (Figs. 4.5.5.2.1 - 4.5.5.2.5).

The value of k_f indicates affinity of metal species for the adsorbent (Rao and Bhole, 2001) and reflects the numbers of adsorptive sites (Singh et al., 2006). The model was applied to both clean and unclean sediment. For clean sediment, the graphs showed that the model fitted the experimental data of Pb, Cr and Cu ($R^2 > 0.947$) while Ni and Zn were not fitted to the model since the R^2 is lower. This may be due to their different adsorption abilities. However, in the case of unclean sediment, there is a good correlation between the experimental data for Pb and Cr, which also fitted to the Freundlich model as shown in Figs 4.5.5.2.2 and 4.5.5.2.3.

The constant n in Freundlich adsorption isotherm is actually a correlation factor for the mutual interaction among the adsorbed species, it is indicated the degree of nonlinearity between solution concentration and adsorption as follows: if n =1, then adsorption is linear; if the forces within the surface layers are repulsion then n <1 and the adsorption is a chemical process; if the forces are attraction then n >1 and the adsorption is a physical process (Jaya et al., 2001a). This reflects the fit of the Freundlich isotherm model for the adsorption of metal ions. The experiment values of n with clean sediment are greater than 1.0 for selected metals. These suggest the attraction forces between different adsorbed species as shown in Table 4.5.5.2).

The highest values of R^2 indicate a good agreement between parameters and confirm the multilayer adsorption of Pb, Cr and Cu ions on to surface sediment. As observed for adsorption of Zn and Ni, the correlation coefficients values are significantly lower (< 0.890). Although the values of the Freundlich affinity, n, are significantly greater than 1, multilayer adsorption cannot be said to be significant in the adsorption of Ni and Zn on the sediment, for this reason. It is evident from these data that the sediments of the Berg Estuary are made up of small heterogeneous surfaces.

Table 4.5.5.2: Freundlich isotherm model constants and correlation coefficients for the adsorption of metal ions on clean sediment of the Berg River estuary

Adsorption isotherm model	Isotherm constants	Metal ions				
		Pb	Cr	Cu	Ni	Zn
Freundlich	K_f (mg/g)	0.244	0.199	0.069	0.077	0.066
	n	2.457	2.295	3.536	5.886	4.259
	R^2	0.947	0.993	0.981	0.599	0.648

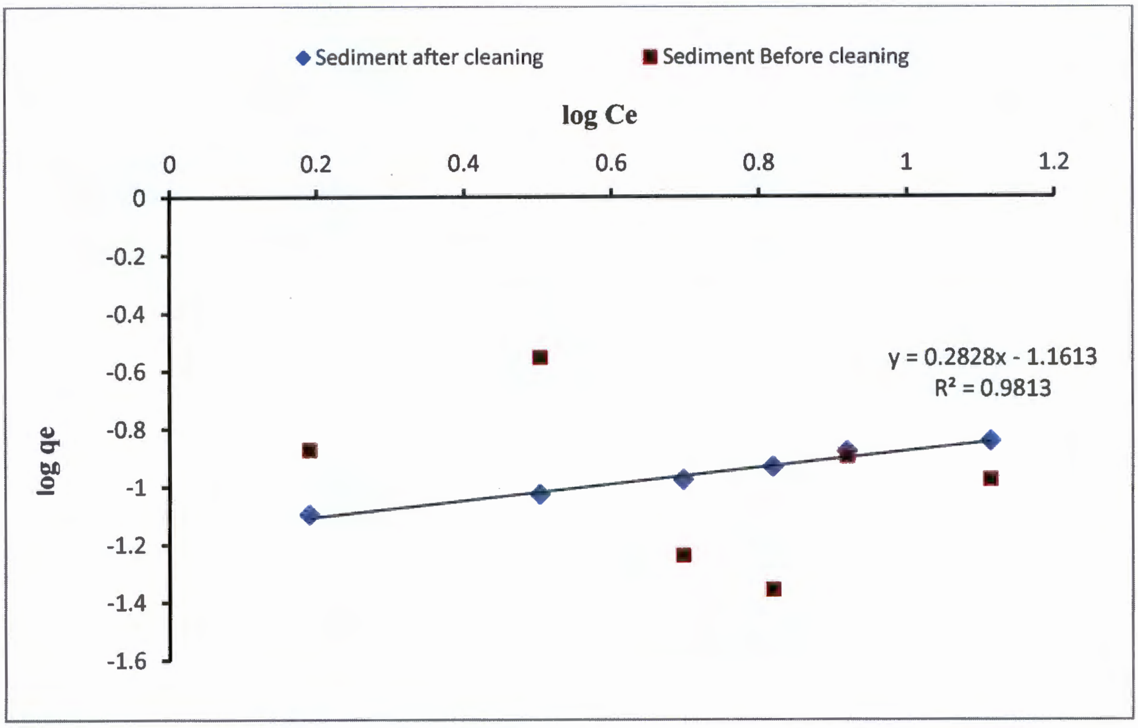

Figure 4.5.5.2.1 Freundlich isotherm model for adsorption of Cu on sediment of the Berg River estuary

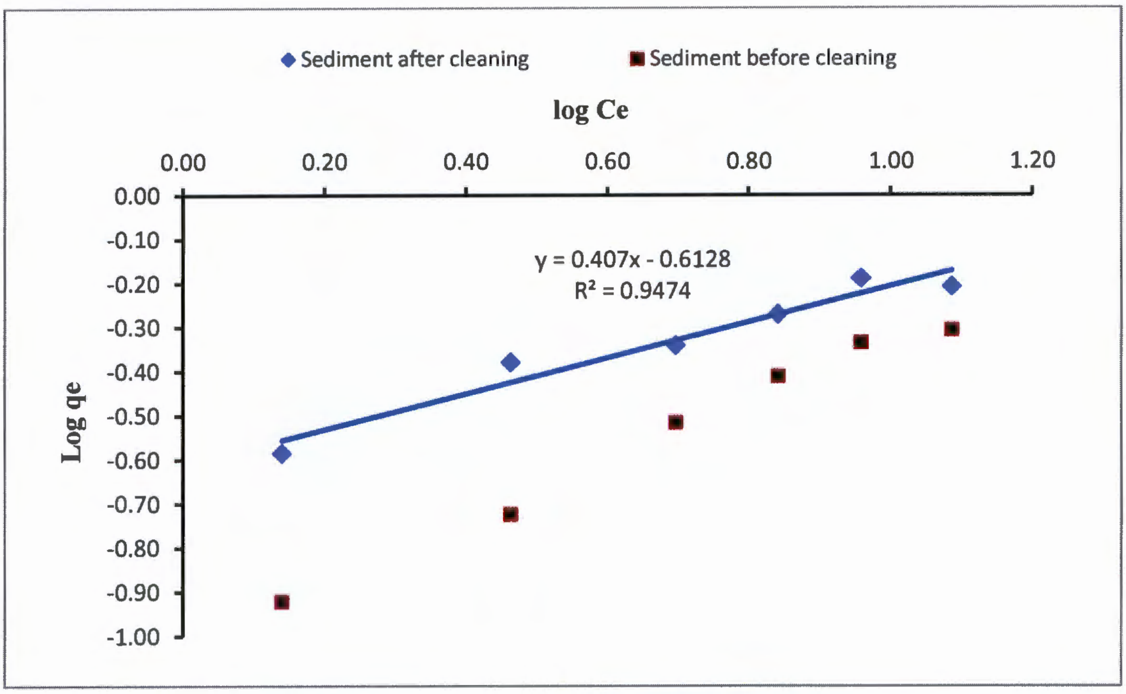

Figure 4.5.5.2.2 Freundlich isotherm model for adsorption of Pb on sediment of the Berg River estuary

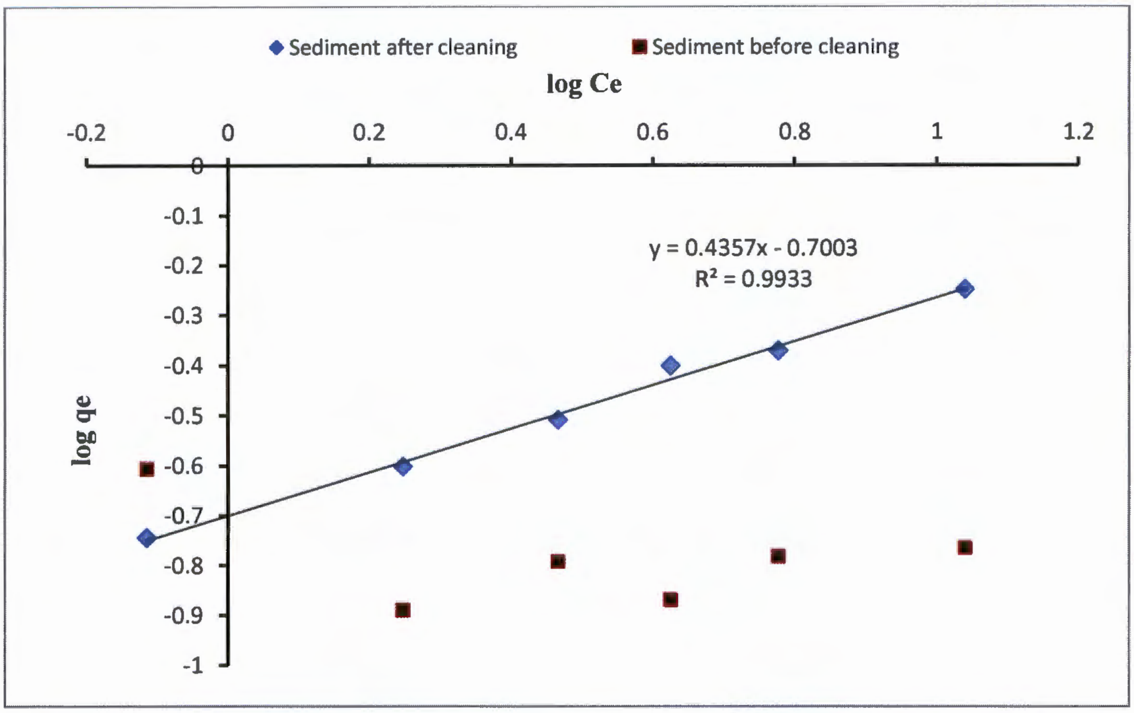

Figure 4.5.5.2.3 Freundlich isotherm model for adsorption of Cr on sediment of the Berg River estuary

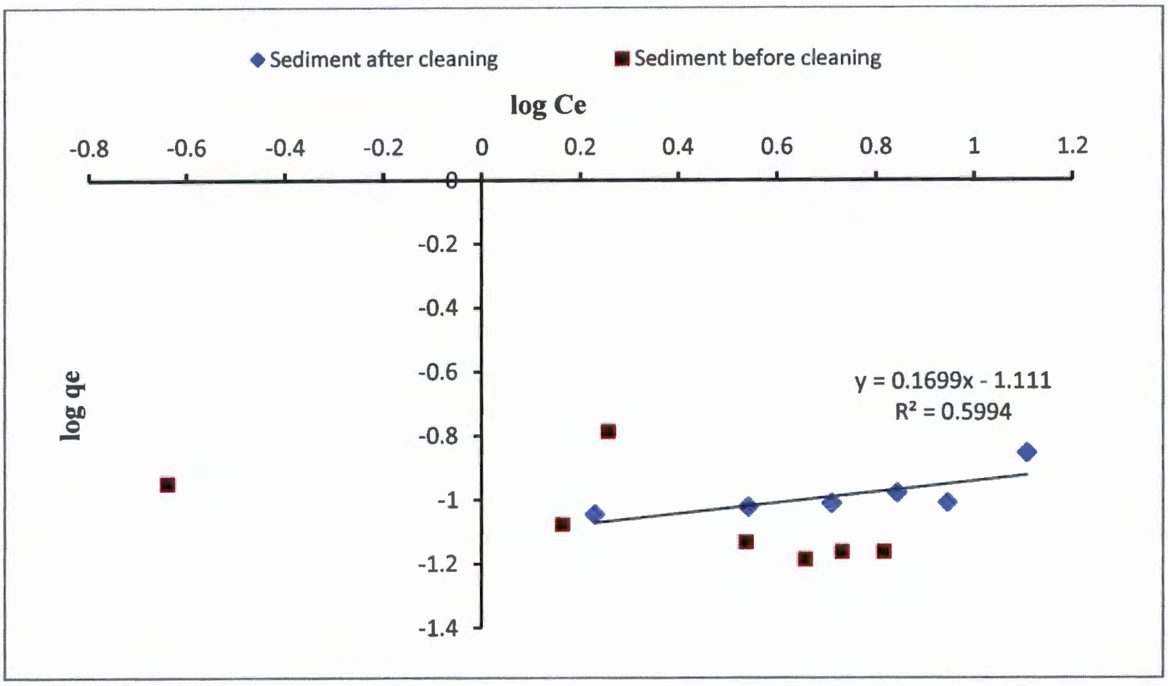

Figure 4.5.5.2.4 Freundlich isotherm model for adsorption of Ni on sediment of the Berg River estuary

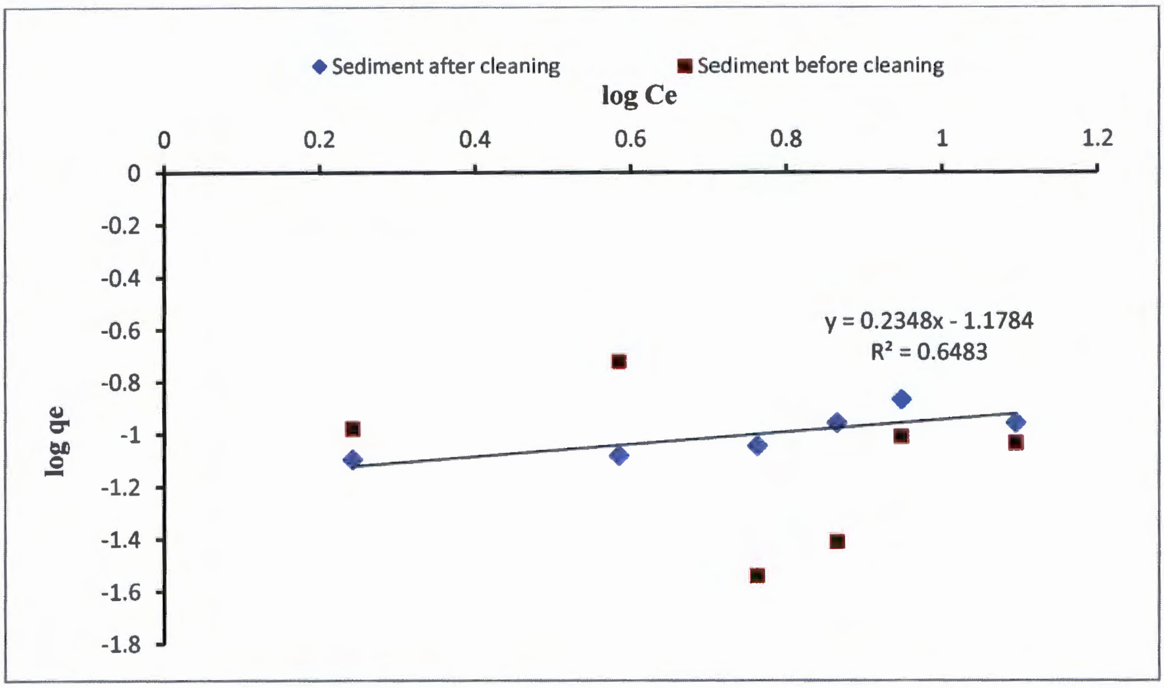

Figure 4.5.5.2.5 Freundlich isotherm model for adsorption of Zn on sediment of the Berg River estuary

The modified BCR sequential extraction procedure has been applied for three sites form the Berg River to evaluate the potential mobility, availability and the possible transfer of heavy metals from sediments to the surrounding environment. Moreover, in order to identify the storage of heavy metals in river sediments, total metal contents have been obtained. This study is the first report metal speciation data, spatial and vertical profiles of heavy metals in core sediments of the Berg River and its estuary. Adsorption of heavy metals on sediments also represents a significant dependence on their speciation and hence on the mobility and bioavailability in the aquatic environment. The present study has shown the potentiality of freshly deposited sediment to adsorb heavy metals that may enter the estuary system through the rivers contaminated sediments. The adsorption experiments have also provided an in-depth understanding of how heavy metals are attached to sediment particles. This understanding of adsorption processes has led to identifying the mobility of heavy metals in the sediments deposited in the estuary. Adsorption increases with increasing metal concentration and can be modeled with either the Langmuir or the non-linear Freundlich isotherms.

Based on the results of this study, the following conclusions can be drawn:

- The distribution of metals in sediment samples from the Berg River and its estuary showed that Cd and Zn were preferentially found in the acid-soluble fraction while most of the metals considered had the highest abundance in the residual fraction. Cu, Cr, Ni and Pb were present in the oxidizable fraction, due to their strong associated with organic matter. In the estuary, the reducible fraction increases and the residual fraction decreases, mainly as a result of the precipitation of metal association with hydrous Fe oxide that occurs when the river and ocean waters mix.

- Based on the distribution of these metals among fractions, it can also be concluded that Cd, Zn and Mn are more mobile and bioavailable than the other metals. In the river sediment, Zn was more mobile than Cd and Mn. However, with a change in the environmental conditions (pH and redox potential) of the Berg estuary, Cd had the highest mobility. The metals with the least mobility were Pb and Mn. It is unlikely that a large amount of these metals would be freed into the water. Despite the high concentrations of Pb (a highly toxic metal) in sediment, it is not likely that this metal is a significant hazard for the aquatic environment since it is found mainly in the residual fraction. The results of the speciation research have given the present status of metal pollution and the potential pollutants in the Berg River and its estuary.

- The metals studied can be ordered according to the mobility and bioavailability as following.
  Zn > Mn > Cu > Cd > Ni > Fe > Co > Cr > As > Pb (Berg River)
  Cd > Cu > Zn > Pb > Ni > Cr > As > Fe > Co > Mn (coastal sediments)
  Cd > Zn > Ni > Cu > Cr > Co > Fe > As > Mn > Pb (Berg estuary)

- The applications of sequential extraction methods to environmental samples provide relevant information about possible toxicity when they are discharged into the environment. Understanding of the mobility of potential toxic elements and how they might transfer under human induced conditions are essential for developing the future remediation plans and pollution control in surface sediments, in particular from the considered Berg River and its estuary that have been the subject of this research.

- According to the pH range obtained and in accordance with the research hypothesis, it can also be concluded the effect of pH on metal speciation in three sites of the Berg River and its estuary indicated the lower release rate of metal under the alkaline conditions found, since pH of the water was greater than 7.

- The variation of distribution with depth in cores showed that the metal concentration was higher in the top and meddles of cores than that in the deeper positions for most of the metals. Pb was found to be the highest occurring heavy metal and Co was the least occurring metal. The distribution patterns of Cd, As, Cr, Cu, Pb and Zn were controlled by the distribution of the fine-grain size and organic matter fraction in the sediments. Fine sand domination is observed in all cores. Core 3 showed the highest percentages of organic matter while core 1 showed the lowest.

- The correlation analysis of data showed medium and strong positive correlations among metal, organic matter and sediment characteristics. Statistical analysis helps to understand the geochemical processes governing the level of metal concentration in sediments and to partition the sources of metals (anthropogenic and natural). The increasing man-made impact, by uncontrolled industrial and sewage wastes, is reflected in the enrichment of metals in the estuary core sediments.

- Regarding the two sediment pollution indices (AF and EF), it can be concluded that Pb is the highest pollutant in the estuary. The EF values indicate that the studied sediments are highly polluted with Cd, Pb and As, and significantly polluted with Zn and Cu. The AF and EF values suggest anthropogenic input of pollutant load along the river and then to the estuary. In comparison with many polluted estuaries from all around the world, the collected sediments seems to be significantly polluted with Pb, As and Cd. AF and EF results could be used as baseline data for future research on anthropogenic impacts in the estuary. The results can also help to develop management strategies for pollution control, mainly in the areas surrounding the Berg estuary, which have high contamination.

- Based on the enrichment factor values of sediments, the spatial trends of metals enrichment of the river sediment reflected the sources/activities of the corresponding catchments. The Sites 3 (Paarl) and site 4 (Wellington) of the downstream receive mixed domestic and industrial waste water along with agricultural wastes from adjacent farms. The results showed that the lowest EF value was below one for Co while those for the other metals were higher than 1.

- From the adsorption data it can be conclude that the pH of the water estuary is the most important parameter in the control of the adsorption metal ions on to the bed sediments. The study has showed the ability of sediment to adsorb metal ions in different conditions of pH (acidic and alkaline condition). Adsorption of selected metals was found to increase with increasing pH. It can also be concluded that the sediments of the Berg estuary have lower potential for adsorb of Zn and Ni due to the high potential for mobility and bioavailability in these sediments. The adsorption of selected metal on to sediment of the Berg estuary increases in the efficiency order of Pb > Cr > Cu > Ni > Zn.

- Langmuir and Freundlich isotherm models were used to linearize the data of the final concentration effect on the adsorption process. Generally, the equilibrium data describe both isotherm models satisfactorily. It was shown that in most cases these models were capable of linearizing the data (Pb, Cr and Cu), however, proved unsuccessful in other cases (Ni and Zn). It is suggested that other isotherm models should be used.

- Based on the Langmuir isotherm model, it can be concluded that the highest values of R^2 indicate a good agreement between parameters and confirm the monolayer adsorption of Pb, Cr and Cu ions on to surface sediment.

- From Freunlich isotherm model data, it can be concluded that the low values of 1/n points out an adsorption mechanism of weak bond formation between adsorbate and adsorbent. Therefore, it may be inferred that strong bond between adsorbate and adsorbent is formed in case of Pb and Cr and it's confirm multilayer. The 1/n values of adsorbed metals were in order Ni< Zn< Cu< Pb<Cr.

Recommendations

Based on the findings of the present study, the following suggestions may be made for the future scope of studies.

- Radio-dating analysis should be conducted on sediment core to provide valuable information related to depositional history.

- One of the major unanswered questions arising from the results of this study is the extent to which the organisms living in the sediment or water (e.g. fish) accumulate metals from the contaminated sediment of the Berg River estuary. Chemical speciation of heavy metal in tissues of fish should be studied.

- Sediment quality guidelines for rivers and estuaries should be stipulated since there are no SQGs for South African freshwater. The need for chemical guidelines that could be used to predict adverse biological effect in contaminated sediments lead to the development of SQGs.

- It is clear in the case of the Berg River and its estuary that the water and sediment are highly affected by anthropogenic activities, these impacts should be studied.

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Appendix

Anthropogenic and enrichment values for three cores and at nine of the Berg River and its estuary are present in Tables (A1- A7)

Table A1: Anthropogenic factor (AF) values of heavy metals in sediment for Site 6

Depth	As	Cd	Pb	Cr	Co
Surface	1.00	1.00	1.00	1.00	1.00
20	0.60	0.96	0.89	1.04	0.94
40	0.71	0.97	0.99	1.01	0.94
60	1.39	0.75	1.48	0.92	0.83
80	0.97	0.91	1.21	0.96	0.95
100	0.82	0.73	1.12	0.89	0.83
120	0.86	0.90	1.35	0.94	0.89
140	0.65	0.74	2.24	0.92	0.86
160	0.76	0.96	1.79	0.92	0.90
Depth	Mn	Cu	Ni	Zn	Fe
Surface	1	1	1	1	1
20	1.06	0.95	1.07	0.97	0.99
40	1.10	0.97	1.04	0.98	1.03
60	1.23	0.61	0.93	0.64	0.68
80	1.19	0.76	1.02	0.78	0.73
100	1.21	0.55	0.87	0.56	0.65
120	1.38	0.70	0.92	0.71	0.73
140	1.15	0.59	0.91	0.64	0.66
160	1.17	0.79	0.89	0.80	0.77

Table A2: Enrichment Factor (EFs) of heavy metals in sediment for Site 6

Depth	As	Cd	Pb	Cr	Co
Surface	59.81	57.88	424.74	47.31	0.05
20	106.06	57.14	512.21	44.07	0.06
40	92.94	57.74	446.98	46.15	0.06
60	53.04	45.48	265.57	32.83	0.04
80	73.52	48.05	337.48	38.32	0.04
100	88.22	43.87	329.78	29.47	0.04
120	95.92	45.74	289.90	35.48	0.04
140	104.80	46.18	172.30	32.80	0.04
160	92.09	47.01	211.21	41.19	0.05

Depth	Mn	Cu	Ni	Zn	Fe
Surface	1.00	0.84	78.61	4.58	8.88
20	1.00	0.94	70.07	5.08	8.63
40	1.00	0.95	73.69	4.84	8.50
60	1.00	1.71	51.42	6.66	8.34
80	1.00	1.31	62.02	5.69	9.42
100	1.00	1.86	49.42	7.17	7.57
120	1.00	1.65	59.75	5.96	8.62
140	1.00	1.63	51.14	6.55	8.52
160	1.00	1.24	70.01	5.09	9.20

Table A3: Anthropogenic factors (AF) of heavy metals in sediment for Site 7

Depth (cm)	**As**	**Cd**	**Pb**	**Cr**	**Co**
Surface	1.00	1.00	1.00	1.00	1.00
20	0.82	0.22	1.14	0.73	0.57
40	1.57	0.55	0.36	0.81	0.67
60	1.07	0.47	0.67	0.92	0.80
80	1.25	0.57	0.28	0.87	0.77
100	0.58	0.59	0.55	0.91	0.65
120	1.73	0.71	0.28	0.91	0.83
140	1.10	0.56	0.40	0.87	0.75
160	1.41	0.70	0.83	0.87	0.81
180	0.51	0.68	0.85	0.95	0.86
200	0.70	0.67	0.44	0.90	0.92
220	1.29	0.75	0.36	0.93	0.84
240	1.86	0.73	0.26	0.91	0.95

Depth (cm)	Mn	Cu	Ni	Zn	Fe
Surface	1.00	1.00	1.00	1.00	1.00
20	0.86	0.48	0.76	0.49	0.43
40	1.01	0.79	0.83	0.80	0.76
60	1.01	1.27	1.02	1.07	1.11
80	1.06	1.34	0.96	1.10	1.15
100	0.87	0.41	1.03	1.06	1.09
120	0.98	1.37	1.00	1.29	1.23
140	0.93	1.22	0.97	1.03	1.07
160	0.95	1.35	0.99	1.21	1.21
180	1.07	1.24	1.03	1.11	1.23
200	1.15	0.87	0.99	1.15	1.26
220	0.93	1.36	1.04	1.38	1.33
240	1.17	1.51	0.98	1.32	1.36

Table A4: Enrichment factors (EF) of heavy metals in sediment for Site 7

Depth (cm)	As	Cd	Pb	Cr	Co
Surface	61.77	441.64	157.89	42.49	0.04
20	64.82	976.24	104.3	28.23	0.03
40	39.96	635.36	367.38	42.19	0.04
60	58.03	119.12	239.68	49.59	0.05
80	52.28	104.05	542.03	53.74	0.06
100	93.07	303.32	293.42	49.61	0.06
120	35.19	85.79	563.54	59.86	0.06
140	52.34	95.07	387.47	50.58	0.06
160	41.65	85.11	187.89	59.09	0.06
180	130.1	80.66	191.98	49.81	0.06
200	101.67	57.06	350.3	54.47	0.05
220	44.78	79.58	455.56	62.74	0.06
240	39.09	90.19	411.73	61.52	0.06
Depth (cm)	Mn	Cu	Ni	Zn	Fe
Surface	1.00	0.90	79.87	4.88	8.69
20	1.00	1.61	50.67	7.60	9.72
40	1.00	1.16	75.42	5.06	9.24
60	1.00	0.71	99.93	4.62	8.38
80	1.00	0.71	111.36	4.28	8.31
100	1.00	1.92	31.7	4.75	8.45
120	1.00	0.64	110.03	3.78	9.07
140	1.00	0.69	100.00	4.61	8.37
160	1.00	0.63	109.36	3.98	8.69
180	1.00	0.77	96.24	4.52	7.87
200	1.00	1.17	70.89	4.18	7.92
220	1.00	0.62	104.37	3.68	8.97
240	1.00	0.7	122.34	3.63	8.46

Table A5: Anthropogenic factor (AF) values of heavy metals for Site 5

Depth	As	Cd	Pb	Cr	Co
Surface	1.00	1 .00	1.00	1.00	1.00
20	0.63	1.13	0.69	1.23	1.14
40	0.39	1.03	1.05	1.16	0.79
60	0.50	0.39	1.33	1.27	1.18
80	0.38	1.10	1.29	1.24	0.73
100	0.37	1.10	1.15	1.20	1.41
120	0.34	1.56	1.20	1.28	2.68
140	0.35	0.51	1.21	1.15	1.62
160	0.25	4.59	1.02	1.24	2.05
180	0.64	3.00	0.83	0.87	1.55
200	0.63	5.04	0.58	1.40	2.56
220	0.96	2.60	0.37	1.08	1.02
Depth	**Mn**	**Cu**	**Ni**	**Zn**	**Fe**
Surface	1.00	1.00	1.00	1.00	1.00
20	1.14	1.28	1.10	1.76	1.27
40	1.04	1.30	0.92	1.04	1.17
60	1.50	1.72	1.21	1.11	1.68
80	1.58	0.83	1.11	0.56	1.55
100	1.15	1.36	1.31	1.48	1.24
120	1.07	1.44	1.47	2.65	1.33
140	1.75	1.10	1.47	2.63	2.12
160	2.41	1.74	1.49	3.46	2.93
180	1.85	1.26	1.07	2.44	3.56
200	3.56	3.04	1.57	2.77	1.79
220	1.22	0.86	1.34	0.85	2.24

Table A6: Enrichment factor (EFs) of heavy metals in sediment for Site 5

Depth (cm)	As	Cd	Pb	Cr	Co
Surface	5.04	105.56	4.58	76.53	70.64
20	14.01	119.72	1.39	68.55	71.03
40	13.45	133.10	0.84	60.83	92.53
60	11.18	471.59	0.95	72.73	90.22
80	7.43	72.15	0.91	68.41	153.08
100	20.27	130.07	0.81	83.52	57.58
120	39.71	97.33	0.84	87.45	28.14
140	37.43	229.09	1.31	97.83	76.31
160	69.85	40.79	2.17	91.51	83.10
180	19.24	44.16	3.22	93.93	84.39
200	22.19	63.27	2.30	85.64	98.26
220	4.42	35.42	0.75	95.11	84.69
Depth (cm)	Mn	Cu	Ni	Zn	Fe
Surface	1.00	2.71	84.17	4.92	6.38
20	1.00	2.43	97.34	3.09	8.85
40	1.00	2.17	118.32	4.38	5.65
60	1.00	2.37	119.66	5.39	4.21
80	1.00	5.18	62.96	9.77	2.29
100	1.00	2.29	87.30	4.38	7.59
120	1.00	2.01	82.57	2.73	12.69
140	1.00	4.30	62.93	2.76	7.92
160	1.00	3.76	98.40	2.12	7.53
180	1.00	3.99	98.99	2.16	4.37
200	1.00	3.18	163.21	2.79	9.90
220	1.00	3.84	53.91	7.83	2.41

Table A7: Enrichment factor (EF) of heavy metals in sediment at nine sites of the Berg River and its estuary

Sites	As	Cd	Pb	Cr	Co	Mn	Cu	Ni	Zn	Fe
1	50.59	53.53	383.89	45.66	0.08	1.00	4.36	80.38	2.42	6.81
2	51.52	59.13	395.56	40.64	0.07	1.00	4.22	84.00	3.11	4.71
3	288.51	33.06	381.06	21.80	0.02	1.00	4.90	43.15	8.60	9.16
4	140.20	78.32	317.47	28.68	0.03	1.00	1.34	88.73	7.17	11.43
5	85.91	121.94	176.24	37.95	0.07	1.00	3.02	86.72	4.46	5.40
6	85.01	49.53	326.33	37.42	0.05	1.00	1.32	60.79	5.78	8.57
7	62.41	73.83	324.82	40.29	0.05	1.00	0.96	77.31	4.66	8.73
8	33.88	55.74	480.43	78.96	0.03	1.00	2.79	95.99	1.88	5.09
9	20.96	59.50	184.26	26.22	0.20	1.00	0.67	50.19	1.25	0.80