SPATIAL AND TEMPORAL VARIATIONS IN METALS IN THE SEDIMENT AND WATER OF SELECTED EASTERN CAPE ESTUARIES, SOUTH AFRICA

A thesis submitted in fulfillment of the requirements for the degree of

MASTER OF SCIENCE (MARINE BIOLOGY)

Of

RHODES UNIVERSITY

By

Kyla Kathleen Orr

November 2007

ABSTRACT

The spatio-temporal patterns in concentrations of selected metals within the sediment (Cd, Co, Cu, Fe, Pb, Ni and Zn) and water (Cd and Pb) of three permanently open estuaries (Kariega, Kowie, Great Fish) and six temporary open-closed estuaries (Mpekweni, East Kleinemonde, West Kleinemonde, Riet, Kasouga, Boknes) were investigated. The concentrations of metals were influenced by size composition and total organic content of the sediments. Enrichment factors (EFs), using Fe as a reference element, and baseline linear regression models for metals *vs*. Fe were calculated to assess the extent of metal enrichment in the sediments.

The mean concentrations of metals in the sediments ($mg \cdot kg^{-1}$) showed ranges of 0.28 – 2.31 for Cd, 1.26 – 6.24 Co, 0.69 – 6.93 for Cu, 2119 – 14912 for Fe, 2.29 –14.01 for Ni, 4.81 – 22.20 for Pb and 5.77 – 21.75 for Zn. Mean normalized enrichment factors ranged between 0.75 – 6.19 for Cd, 0.53 – 2.71 for Co, 0.22 – 0.84 for Cu, 0.30 – 1.87 for Ni, 0.99 – 3.17 for Pb and 0.14 – 0.98 for Zn. All nine estuaries had average enrichment factors of greater than 1 for Cd. In general there was no enrichment of Cu and Zn in the sediments of any of the estuaries included in this study ($EFs < 1$). The Kariega, East Kleinemonde, West Kleinemonde, Riet and Great Fish Estuaries showed some degree of enrichment for Co ($1 < EF < 4$), Ni ($1 < EF < 2$) and Pb ($1 < EF < 4$), while the Mpekweni, Kasouga, Boknes and Kowie Estuaries were unenriched with these metals ($EF < 1$). Enrichment factors for Cd, Co and Pb typically followed the development gradient along the estuaries, suggesting anthropogenic enrichment.

The concentrations of Cd and Pb in the water of the nine estuaries were also determined. The average concentrations of Cd and Pb in the water ($\mu g \cdot \ell^{-1}$) ranged between 0.05 – 3.32 and 0.75 – 34.13 respectively. On average the concentrations of Cd and Pb in the

water of all the estuaries were below the South African recommended water quality guidelines for coastal marine waters.

Variations in metal concentrations associated with changes in hydrology (wet *vs*. dry season) were determined in the water and sediment of the Kariega, East Kleinemonde and Riet Estuaries. Cobalt, Pb and Ni enrichment in the Kariega Estuary sediment was significantly higher during the dry season, and the mean concentrations of Pb and Cd in the water column were 19-fold and 66-fold higher in the dry season. The elevated concentration of metals during the dry season could be related to accumulation of diffuse pollution from human activities within the catchment area. Conversely, inflow of fresh water into the estuary had the net effect of reducing the concentration and enrichment of these metals within the Kariega Estuary due to scouring and outflow of estuarine water and sediment into the marine environment. The temporal variations in metal concentrations and enrichment factors were less pronounced in the temporary open-closed estuaries than the permanently open Kariega Estuary. The observed trend can probably be related to the low anthropogenic impact within the catchment areas of these systems, and the relatively smaller size of the catchments. Significant spatial variations existed in metal enrichment in the sediment of both the East Kleinemonde and Riet estuaries, with the highest degrees of enrichment occurring in the sediments from the marine environment and lower reaches.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PREFACE

This study has been divided into two sections:

1. Metal concentrations in the sediment and water of selected temporary open-closed and permanently open estuaries.
2. The effects of increased freshwater inflow on metal enrichment in selected Eastern Cape estuaries, South Africa.

A summary of the work from the first section has bee submitted to the journal *Water SA:*

Orr K.K., Burgess J.E., and Froneman P.W. (2007). Metal concentrations and enrichment in the sediment and water of selected permanently open and temporary open-closed Eastern Cape estuaries, South Africa. *Water SA*. (Submitted 9th November 2007).

The work from the second section of this thesis has been accepted for publication in the journal *Water SA*:

Orr K.K., Burgess J.E., and Froneman P.W. (2007). The effects of increased freshwater inflow on metal enrichment in selected Eastern Cape estuaries, South Africa. *Water SA. In Press.* (Accepted 5th November 2007)

The work from the second section of this thesis has also been presented at the following national and international conferences:

Orr K.K., Burgess J., Froneman P.W. (2007). The effects of mouth phase and rainfall on the concentrations of heavy metals in the sediment and water of select Eastern Cape estuaries, South Africa. In: T*he 5th International Conference on Marine*

Pollution and Ecotoxicology. City University of Hong Kong, Hong Kong, China, June 3rd – 6th 2007.

Orr K.K., Burgess J.E., Froneman, P.W. (2007). The effects of increased freshwater inflow on the concentrations of metals in the sediment and water of the Kariega estuary. In: *The 33rd Meeting of the Zoological Society of Sothern Africa*. North-West University, Potchefstroom, South Africa, July 8th – 11th 2007.

ACKNOWLEDGEMENTS

Many thanks go to Prof. Will Froneman for his trust and confidence in my abilities, and for agreeing to be my supervisor at the eleventh hour. To Dr. Jo Burgess, my co-supervisor, who played a fundamental role in assisting with the analysis of metals and kindly allowed me to be part of her laboratory (129 C). I would thus also like to thank all the members of Lab 129 C for their assistance, humor, and patience, especially Cherie-Lynn, who helped me countless times with operating the FAAS. I would like to thank the students and staff of the Zoology and Entomology Department for their company at long awaited tea breaks, assistance with collecting samples, tolerance for the large volumes of dust and mess I generated, and general friendly support and encouragement.

This project has been truly multidisciplinary in nature as I have needed to use the equipment and facilities of the Geography, Chemistry, Zoology and Biotechnology Departments, so many thanks to all of these departments for allowing me to do so. Dr. Edith Antunes, Department of Chemistry, spent a considerable amount of her time training me to use the ICP-OES, and I am very grateful for this. Thanks also go to Mr. Johan Fourrie and Mr. Soneman for their technical assistance on the ICP.

Thanks to the National Research Foundation (NRF), Deutscher Akademischer Austausch Dienst (DAAD), Rhodes University and the Ernst and Ethel Eriksen Trust for financial support. Thank-you to Prof. Froneman and the JRC for providing additional funding for attending the conference in Hong Kong.

Thanks to my parents for always encouraging me to do what I love, and for providing all the emotional support needed during the past two years. And finally, to Cam, for being all that you are to me.

DECLARATION

The following thesis has not been submitted to any university other than Rhodes University, Grahamstown, South Africa. The work presented here is that of the author.

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Metal contamination within rivers and estuaries has been a subject of increasing attention over the last twenty years, largely due to the persistent and toxic nature of many metals. Some metals are essential for metabolism (Co, Cu, Fe, Zn and Mg) but become toxic at elevated concentrations, while others such as Cd, Pb, Hg, and Sn are not required for metabolism and are toxic to organisms at low concentrations (Biney *et al.*, 1994; Kennish, 1997). The existence of metals at toxic concentrations in water and sediment may threaten the health of the estuarine environment via bioaccumulation and biomagnification up the food chain (Fatoki and Mathabatha, 2001). It is thus necessary to monitor the extent of contamination within estuaries and compare metal concentrations to national sediment and water quality guidelines (Hennig, 1985).

Metals in the context of this project are commonly described in biological, botanical and chemical literature as “heavy metals”. However, the term “heavy metal” began to recur in formal texts without ever receiving an authoritative description (Nieboer and Richardson, 1980). The expression “heavy metal” is commonly used by authors when there is a connotation to toxicity, and the term “trace metals” is often used as a less evocative replacement for “heavy metals” (Nieboer and Richardson, 1980). Both these terms have been used by authors to encompass a wide variety of elements with heterogeneous chemical properties such as; Titanium (Ti), Vanadium (V), Chromium (Cr), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Niobium (Nb), Silver (Ag), Cadmium (Cd), Tin (Sn), Mercury (Hg), Lead (Pb), Calcium (Ca), Magnesium (Mg), Sodium (Na), Manganese (Mn) and Cobalt (Co) (Nieboer and Richardson, 1980).

Lepedes (1974) formally described "heavy metals" as being those metals whose specific gravity is greater than or equal to 5. Lesaca (1977) designated "heavy metals" to be those elements that fell into a rectangular block of the Periodic Table that is flanked by Titanium (Ti), Hafnium (Hf), Arsenic (As) and Bismuth (Bi). Selenium (Se) and Tellurium (Te) were also included to this definition. Another publication (Venugopal and Luckey, 1975) reported any elements beyond Ca in the Periodic Table to be "heavy metals". Since there is no general agreement on the definition of "heavy metals" the term has been avoided in this text. The elements that form part of this study are Cd, Co, Cu Fe, Ni, Pb and Zn and they have simply been referred to as "metals" in this thesis.

TABLE 1.1
Industrial and agricultural sources for heavy metals in the environment

Use	Metal
Batteries and other electricals	Cd, Hg, Zn, Mn, Ni
Pigments and paints	Ti, Cd, Hg, Pb, Zn, Mn, Sn, Cr, Al, As, Cu, Fe
Alloys and solders	Cd, As, Pb, Zn, Mn, Sn, Ni, Cu
Biocides (pesticides, herbicides, preservations)	As, Hg, Pb, Cu, Sn, Zn, Mn
Catalysts	Ni, Hg, Pb, Cu, Sn
Glass	As, Sn, Mn
Fertilizers	Cd, Hg, Pb, Al, As, Cr, Cu, Mn, Ni, Zn
Plastics	Cd, Sn, Pb
Textiles	Cr, Fe, Al
Refineries	Ni, V, Pb, Fe, Mn, Zn
Fuel	Ni, Hg, Cu, Fe, Pb, Cd

Source: Committee for Inland Fisheries of Africa (1991)

Metals are natural constituents of the environment, but their concentrations may become elevated as a result of human activities (Kennish, 1997; Clark 1989). Natural processes that contribute to the input of metals into water systems include; weathering of rocks, windblown dust from nearby shales, volcanic and hydrothermal vent activity, forest fires and the deposition of organic matter (Kennish, 1997; Clark, 1989). The concentration of metals in sediments thus often reflects the natural abundance of metals in that area, and this forms the base of geological prospecting (Clark, 1989). However, anthropogenic sources of metals are abundant (Table 1.1) and may equal or exceed the natural input of metals into the atmosphere, rivers and estuaries (Table 1.2) (De Groot *et al.*, 1976;

Nriagu, 1979). There has been a sharp increase in the anthropogenic release of trace metals since 1901, and the bulk of the anthropogenic emissions have occurred in the northern-hemisphere (Nriagu, 1979). In 1979, it was estimated that the quantities of metals that had been dispersed into the world ecosystems through anthropogenic emissions into the atmosphere were 0.32×10^6 kg for Cd, 2.2×10^9 kg for Cu, 20×10^9 kg for Pb, 1.0×10^9 kg for Ni and 14×10^9 kg for Zn (Nriagu, 1979). Human activities have thus led to the redistribution of large amounts of metals at the Earth's surface, which has resulted in a considerable alteration of the global cycle of metals in the last centaury (Nriagu, 1979). Metals that are enriched above background concentrations in the sediment and water column of estuaries are thus commonly used as indicators of pollution (Biney *et al*., 1994; Binning and Baird, 2001).

TABLE 1.2
Worldwide emissions of metals to the atmosphere ($\times 10^6$ kg.yr^{-1})

Metal	Natural Sources	Anthropogenic Sources
Cd	0.83	7.3
Cu	18.5	56
Ni	26.0	47
Pb	24.5	449
Zn	43.5	314

Source: Nriagu (1979)

Metals enter the aquatic environment via multiple anthropogenic non-point and point sources. Non-point sources of pollution are diffuse and enter water systems indirectly (US-EPA, 1993; Buntsma and Casey-Lafkowitz, 1999). Examples of non-point sources of metals include storm-water run-off from roads, parking lots and residential areas; leaching of metals from dumping sites, fertilizers and pesticides; and atmospheric deposition of metals from combusted fuels. Water that flows through or over land may accumulate pollutants and carry them into rivers and estuaries. The net load of pollutants entering aquatic systems may thus increase during periods of heavy rainfall (US-EPA, 1993; Buntsma and Casey-Lafkowitz, 1999). Identifying the sources of non-point pollutants and contaminants is problematic, and thus it is difficult to prevent their input. Non-point sources of pollution have therefore been identified as the greatest threat to the health of the environment (US-EPA, 1993; Buntsma and Casey-Lafkowitz, 1999).

Point source emissions occur where a pollutant or contaminant originates from a single identifiable source or location (Harrison and Laxen, 1981; US-EPA, 1993). The highest concentration of the pollutant is usually found near the source, examples of which include the discharge of industrial or municipal waste through an outlet pipe into a water system. The most common anthropogenic wastes that enter the estuarine and coastal environment are dredged spoils and sewage, industrial and municipal discharges (Kennish, 1997). The possible sources of metals in domestic water are listed in Table 1.3.

TABLE 1.3
Possible sources of metals in domestic waste water

	Cd	**Cu**	**Ni**	**Pb**	**Zn**	**Co**	**Fe**
Automotive Products				X	X	X	X
Caulking compounds				X	X	X	X
Cleaners		X			X		X
Cosmetics	X	X	X	X	X	X	X
Fillers					X		
Fire Extinguishers					X		X
Fuels		X		X			
Pesticides	X	X		X	X		X
Inks		X			X		
Lubricants				X	X		
Medicine		X			X	X	X
Oils		X		X	X		
Ointments		X			X	X	
Paints				X	X	X	X
Photography				X			X
Pigments	X	X	X	X	X	X	X
Polish		X			X		
Powders					X		X
Preservatives				X	X		X
Water treatment		X			X		X

Source: Stephenson (1987)
Note: X denotes presence of metal in source.

The words “contaminant” and “pollutant” are often used interchangeably with little understanding for their actual meaning. It is thus necessary to define them to abate any further confusion. Contamination is the presence of elevated concentrations of a substance above that of its background concentration in the environment or biota concerned (Clark, 1989). Pollution is the indirect or direct introduction of a substance

into the environment by man. A pollutant is harmful to the living resources, hazardous to human health and may hinder marine activities and degrade the quality of the water (Clark, 1989). A contaminant may become a pollutant if **1)** it is introduced by man, and **2)** has some damaging effect on the environment (Clark, 1989). It is important to note that although a contaminant may show toxic effects to organisms or plants in laboratory toxicity test, this does not necessarily prove that the contaminant is harmful in the natural environment. Elevated levels of contaminants should serve as a warning signal, yet the effects of the contaminant may be seen as insignificant unless the contaminant results in the change of a biological population as a whole (Clark, 1989).

1.2 AN INTRODUCTION TO ESTUARIES

Estuaries constitute the region where fresh water from terrestrial drainage meets and mixes with sea water (Allanson and Baird, 1999; Kennish, 2002), and are well known to be one of the most biologically productive ecosystems on Earth (Kennish, 2002). Estuaries are highly variable in terms of geology, hydrography, salinity and sedimentation and they may show considerable spatial and temporal variations in their physico-chemical parameters (Allanson and Baird, 1999; and Kennish, 2002).

Many scientists have attempted to define estuaries, and as many as 40 different definitions exist (Dyer, 1997). The most commonly used definition is that of Prichard (1976), which states that “an estuary is a semi-enclosed coastal body of water with a free connection to the open sea and within which seawater is measurably diluted with fresh water derived from land drainage”. This definition does not consider temporarily closed estuaries or those estuaries that receive very little or sporadic freshwater inflow and do not demonstrate a horizontal gradient in salinity. Thus, Day (1980) generated a more appropriate definition which states that an estuary is a “partially enclosed, coastal body of water which is either permanently or periodically open to the sea and within which, there is measurable variation of salinity due to the mixture of sea water with fresh water derived from land drainage”.

In South Africa, only 37 of the 289 river mouths (12.8%) that maintain permanently open connections with the sea can be considered as "true" estuaries (Reddering and Rust, 1990), and many of these estuaries have variable characteristics reflecting the different physical environments in which they are situated. Whitfield (1992) devised a classification system for South African estuaries, whereby they can be grouped in terms of their mouth phase and tidal influence. Five types of estuaries were identified using the Whitfield classification, namely; estuarine bays, river mouths, permanently open estuaries, estuarine lakes and temporarily open-closed estuaries. Permanently open estuaries experience a combination of tidal and riverine mixing and have an average salinity of 10 – 35 practical salinity units (psu). Temporary open-closed estuaries experience wind driven mixing and average salinities range from 1 – 35 psu.

The mouths of South African estuaries are subject to change according to wave action, wind, currents and sediment influx (Allanson and Baird, 1999). When an estuary is flooding, millions of cubic meters of sand can be displaced in a few hours, which may lead to breaching of temporarily closed estuaries. South African estuaries characteristically have relatively limited flow in comparison to other estuaries in the world, and in many cases the average flow is less than 1 $m^3 \cdot s^{-1}$ (Allanson and Baird, 1999). Approximately 70 % of South African estuaries are classified as closed systems, and yet the majority of estuarine research to date has been conducted on permanently open estuaries. This is mostly due to the fact that the permanently open systems are located close to coastal towns and cities and thus there is a greater need to monitor human impact (Vorwerk, 2000).

Estuaries typically receive sediment from three main sources, namely; from the sea, inflowing rivers and from material generated within the estuary itself. Most estuaries contain sediment of a marine rather than terrestrial origin, although in the case of deltas there is greater terrestrial input of sediment (Dyer, 1997). Once the sediments have been deposited they may be dispersed by tidal currents, inter-tidal waves or flooding episodes within the estuary, which will in turn result in the transport and deposition of metals and other pollutants (Dyer, 1997). Near the head of a well mixed estuary there is usually a

zone of high suspended sediments, which is known as the turbidity maximum zone, and this is commonly the area in which the highest concentrations of metals can be found in the water and sediment column (Dyer, 1997). As a very crude generalization, fine grained sediments will settle in the river-dominated upper reaches of the estuary and coarse sediments will be found in the lower, marine-dominated reaches. Sedimentation patterns are however controlled by the specific flow patterns and channel shape and structure of a particular estuary (Dyer 1997).

1.3 METALS IN THE ESTUARINE ENVIRONMENT

Estuaries may be the repositories of contaminants generated by human activities (Kennish, 1997). Metals typically bind to fine grained sediments, such as mud and organic matter. As a consequence of the sheltered nature of estuaries, these materials tend to settle out in estuaries, and thereby increase the propensity for contamination and accumulation in these environments (De Groot *et al.*, 1976). Metals, however, are not indefinitely bound to sediments and may be re-mobilized and returned to solution via physical, chemical and biological processes (De Groot *et al.*, 1976). Metals may thus occur in various chemical forms whilst being transported to the sea, such as ions in solution, organic or inorganic complexes in solution, adsorbed onto the surface of suspended mater or sediment particles, bound to sulfides, incorporated into solid organic particles, precipitated in their "pure" form which may then associate with detritus and co-precipitated with Fe and Mn-oxides, which may then coat detritus particles (Tessier and Campbell, 1978)

Concentrations of metals in the sediment are typically several orders of magnitude higher than those in the water column (Bryan and Langston, 1992), and thus the levels of metals within the water column may meet water quality guidelines for water use and ecological health but the sediment may not (Binning and Baird, 2001). The concentrations of metals in the water column are also subject to greater temporal and spatial variability than in the sediment, which make it difficult to obtain water samples that are representative of the contaminant status of the waterbody. Sediments, on the other hand, are long-term integrators of metals and provide a more accurate reflection of the extent of metal

contamination within a particular system (Binning and Baird, 2001). High total concentrations of metals in sediment, however, do not necessarily indicate input of metals from human activities, as elevated levels of metals may be a result of variations in sediment characteristics as well as naturally high background concentrations (Schropp *et al.*, 1990; Liu *et al.*, 2003).

Many factors affect the concentrations of metals in sediment, such as grain size, total organic carbon content and mineralogy (Schropp *et al*., 1990; Summers *et al*., 1996). In uncontaminated sediments, metal concentrations tend to increase as grain size decreases due to the fact that the surface area of sediments is grain size dependant, and thus smaller particles provide a larger surface area for the adsorption of metals (Schropp *et al*., 1990; Summers *et al*., 1996). Organic carbon acts as a matrix to which metals can complex, and several studies have shown strong linear relationships between total organic carbon and metal concentrations (Tam an Yao, 1998; Dasalakis and O'Connor, 1995).

Since the concentrations of metals in the sediment and water of estuaries are subject to considerable variations depending on their physico-chemical environment, it is not advisable to use absolute concentrations as conclusive indicators for the anthropogenic input of metals in a specific area (Schropp *et al*., 1990). Conclusions should rather be drawn on the overall spatial and temporal trends in metal concentrations, the inter-element correlations between metals, and metal enrichment factors calculated from uncontaminated sediments (Schropp *et al*., 1990; Summers *et al*., 1996). Sediment metal concentrations also need to be normalized to a grain size parameter before spatial and temporal variations can be analyzed. This will be discussed further in Chapter 3.

1.4 INTERNATIONAL METAL RESEARCH

Metals are some of the most commonly studied contaminants of estuarine and coastal environments and thus metal research has been conducted on thousands of estuaries, rivers, harbors and embayments worldwide (Kennish, 1997). The majority of these studies have been carried out by research bodies at universities or as part of national or

international monitoring programs. The Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) was established in 1969 and is an international advisory body that provides periodic reports on the health of the marine environment and plays a leading role in assessing global marine pollution problems (Kennish, 1997). The GESAMP has thus reported the sources and concentrations of many metals in the marine environment (Table 1.4).

TABLE 1.4
Natural and anthropogenic concentrations of some metals from various sources

	Unit	Pb	Cd	Cu	Zn
Earth crust concentration	$mg \cdot kg^{-1}$	15	0.2	45	40
Seawater concentration	$\mu g \cdot \ell^{-1}$	0.002	0.1	2	3
Total amount in world oceans	10^6 t	2.8	140	2800	4200
Input by erosion	$10^3 t \cdot y^{-1}$	150	0.5	325	720
Input by burning of fossil fuel and cement fabrication	$10^3 t \cdot y^{-1}$	34	0.2	2.1	37
Mine production	$10^3 t \cdot y^{-1}$	3500	15	7500	5000
Annual mine production in percent of total amount in the world oceans	%	125	0.01	0.3	0.1

Source: GESAMP (1976)

Other bodies under which large-scale metal research has been conducted include the Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA), both of which are based in the United States of America. Historically, the majority of metal research has been conducted in the northern hemisphere, and only recently has work been published on the estuaries and coastal systems of the developing countries in the southern hemisphere (Biney *et al*., 1994). The concentrations of metals in both contaminated and uncontaminated estuarine sediments from England, Scotland and California are presented in Table 1.5.

TABLE 1.5
Metal concentrations ($mg \cdot kg^{-1}$) in contaminated and uncontaminated sediments

Sediment	Cd	Co	Cu	Fe	Ni	Pb	Zn
Firth of Clyde, Scotland							
Control area (mean)	3.4	34	37	5.3×10^4	50	86	160
Sewage sludge deposite (max)	7	40	210	6.1×10^4	70	320	830
California Coast							
Control area (median)	0.33	-	8.3	-	9.7	6.1	43
Los Angales wastewater outfall (max)	66	-	940	-	130	580	2900
Southwestern England estuaries							
Control (Avon) (typical)	0.3	10	19	1.9×10^4	28	39	98
Restronguet Creek acid mine waste (max)	1.2	22	2500	5.8×10^4	32	290	3500
Source: Bryan *et al.* (1986)							

Africa is experiencing rapid urban and industrial development, particularly in coastal areas, and thus a need has arisen to monitor the concentrations of contaminants and pollutants in the receiving aquatic environments. According to a review compiled fourteen years ago by Biney *et al.* (1994), the concentrations of metals in most African coastal environments were low, with a few exceptions in developed areas. Metal concentrations in sediments taken from the east and west coasts of central and northern Africa in the early 1980s and 1990s can be seen in Table 1.6.

TABLE 1.6
Mean metal concentrations in African marine sediments

	Cd	Pb	Cu	Zn	Fe ($\times 10^3$)	References
Mediterranean						
Abu-Kir Bay Egypt	2.02	-	12	102	4.5	Saad *et al.*, 1981
Port Said, Egypt	3.2	-	14	50	2.5	Saad *et al.*, 1981
Eastern Harbour, Alexandria	2.89		14	51	1.1	Saad *et al.*, 1981
El Mex, Egypt	2.18		24.1	35.4	1.47	Saad *et al.*, 1981
Gulf of Guinea						
Ebrié Lagoon, Côte d'Ivoire		57.6	37.0	187	52.4	Kouadio and Trefry, 1987
Lagos Lagoon, Nigeria	4.1	178.9	15	147	36.38	Okoye *et al.*, 1991
Atlantic Coast, Nigeria	2.3	67.5		72.5		Ndiokwere, 1984
Source: Biney *et al.* (1994)						

Numerous marine pollution monitoring programs have been initiated in Africa in order to asses the level of metal contamination and pollution in aquatic environments. The three

most prevalent programs are; 1) The Mediterranean Pollution Monitoring Program (MED-POL), which covers Tunisia, Algeria and Morocco, 2) The West and Central African Pollution and Research Program (WACAF 2), and 3) The Eastern African Marine Pollution and Research Program (EAF 6) (Committee for Inland Fisheries of Africa, 1987).

1.5 SOUTH AFRICAN WATER AND SEDIMENT QUALITY GUIDELINES

South African water quality guidelines (WQGs) have been published by the Department of Water Affairs and Forestry (DWAF) for both freshwater and coastal marine environments (Table 1.7), but no specific guidelines are available for South African estuaries or river mouths (DWAF, 1995). The existing WQGs play an important role in the management of the quality of South African water systems to ensure that they are fit for use by man and the environment. There is, however, a need to expand the WQGs to include estuarine systems. The South African WQGs for Coastal Marine Waters focus on the area inshore of the continental shelf, unless the continental shelf is wider that 200 km, after which international conventions and agreements apply to all users of the ocean (DWAF, 1995).

TABLE 1.7
South African water quality guidelines for coastal marine waters: metals

Metal	Target value for South African coastal waters ($\mu g \cdot \ell^{-1}$)
Cd	4
Cu	5
Pb	12
Ni	25
Co	No target value has been determined for the SA coastal zone
Zn	25

Source: (DWAF, 1995)

There are currently no published sediment quality guidelines that have been specifically adapted for South African coastal marine or estuarine sediments (BCLME, 2006), and

thus it is necessary to use international sediment quality guidelines such as those supplied by the National Oceanic and Atmospheric Administration, USA (NOAA) (Buchman, 1999). This is not ideal as each country and more specifically each estuary has a unique set of physical, biological and chemical variables that influence the toxicity of certain metals. An organism's ability to tolerate elevated concentrations of metals may thus vary from region to region (BCLME, 2006).

Australia and New Zealand have adapted the NOAA sediment quality guidelines (SQGs) to suit local baseline concentrations and available toxicity data in order to fabricate more localized SQGs (ANZECC, 2000; BCLME, 2006). Similarly, The Benguela Current Large Marine Ecosystem (BCLME) has reviewed international SQGs in order to develop a common set of SQGs for the coastal zone of the BCLME (Angola, Namibia and west coast of South Africa) (Table 1.8). The BCLME guidelines, however, cover a broad concentration range and need to be refined to meet the specific requirements of each country within the region (BCLME, 2006). The sediment quality guidelines proposed for the west coast thus still need to be subjected to site-specific field measurements and modeling outputs. Thus, no official South African sediment quality guidelines have been published as yet, but theoretical concentrations have been proposed.

TABLE 1.8
Summary of national and international sediment quality guidelines

Metal ($mg \cdot kg^{-1}$ dry wt.)	**South Africa[1]**		**NOAA[2]**		**State of Florida[3] (NOAA)**	
	Special care	**Prohibited**	**ERL**	**ERM**	**TEL**	**PEL**
Cd	1.5 – 10	> 10	1.2	9.6	0.68	4.21
Cu	50 – 500	> 500	34	270	18.7	108
Pb	100 – 500	> 500	46.7	218	30.2	112
Ni	50 – 500	> 500	20.9	51.6	15.9	42.8
Zn	150 – 750	> 750	150	410	124	271

[1](BCLME, 2006 unpublished), [2] (Long *et al*., 1995; Buchman, 1999), [3](Mac Donald, 1996; Buchman, 1999)

Multiple sediment screening values, which cover a spectrum of concentrations from non-toxic to toxic levels, appear in Table 1.8. The Threshold Effects Level (TEL) represents

the concentration below which adverse effects will be observed only rarely. It is calculated as the geometric mean of the 15th percentile concentration of toxic effects data. The Effects Range Low (ERL) represents the concentration at which toxicity may begin to be observed in sensitive species. The ERL is calculated as the lower 10th percentile of sediment concentrations reported in literature that co-occur with any biological effect. The Probable Effects Level (PEL) is the concentration above which toxic effects are frequently observed. More than 50% of adverse effects occur above the PEL (CCME, 1995). The Effects Range Median (ERM) is the median concentration of available toxicity data. It is calculated as the lower 50th percentile of sediment concentrations reported in literature that co-occur with any biological effect (Buchman, 1999). The SQGs may thus be listed in the increasing toxicity gradient; TEL<ERL<PEL<ERM. (Buchman, 1999).

1.6 METAL CONCENTRATIONS IN COASTAL WATERS AND SEDIMENTS OF THE EASTERN CAPE, SOUTH AFRICA

Over the last three decades there has been an increase in urban, agricultural and rural development along the banks of Eastern Cape estuaries and within their catchment areas. As a result, many Eastern Cape estuaries are increasingly becoming the repositories of human, domestic, agricultural and industrial waste (Binning and Baird, 2001; Scharler and Baird, 2003). Despite these developments, very few studies have been conducted on metal enrichment and contamination within Eastern Cape estuaries.

In the late 1970s and early 1980s several papers were published on metal concentrations in South African estuaries (Watling and Watling, 1976 to 1983; Watling, 1988). These studies formed part of the National Marine Pollution Monitoring and Survey Programmes (Cloete and Oliff, 1976; Watling and Cloete, 1981; Hennig, 1985). The results for the Eastern Cape Marine Pollution Monitoring and Survey Program are shown in Tables 1.9 and 1.10. The overall conclusion from these surveys was that South and Eastern Cape estuaries were relatively uncontaminated with metals, with a few exceptions in the more industrialized and urban areas such as Port Elizabeth and East London (Watling and

Watling, 1976 to 1983; Talbot *et al.*, 1985). Metal concentrations within the sediment column thus reflected the extent of anthropogenic development of the area (Watling, 1988).

Two more recent studies have been completed on the Swartkops Estuary (Binning and Baird, 2001), and the East London and Port Elizabeth Harbours (Fatoki and Mathabatha, 2001), both of which revealed a marked increase in metal concentrations over time. These few publications are the sum total of metal research within Eastern Cape estuaries over the last three decades, and thus there is a great need to determine the current state of metal contamination within Eastern Cape estuaries.

The early studies provided good baseline data for surface waters and sediment within the Eastern Cape and their results will present interesting comparisons for future research. However, none of the above mentioned studies included any of the smaller temporary open-closed estuaries within the Eastern Cape. It is thus important to conduct baseline studies on those estuaries that have not yet been surveyed, as well as to determine the increase in metal concentrations in the permanently open Eastern Cape estuaries since they were first surveyed more than 20 years ago.

TABLE 1.9
Mean metal concentrations in surface sediments ($mg \cdot kg^{-1}$) of Eastern Cape estuaries

Estuary	Zn	Cd	Cu	Pb	Fe	Mn	Ni	Co	Cr	Hg
Kromme	12.0	0.3	3.0	8.4	7350	112	3.7	2.1	64.9	0.018
Gamtoos	22.1	0.28	7.4	8.6	11530	141	9.1	4.7	19.1	0.010
Papenkuils	230.0	0.40	33.7	92.6	18770	151	8.1	2.1	52.0	0.21
Swartkops	35.5	0.22	10.6	16.7	13020	177	7.5	1.1	3.5	0.018
Sundays	47.4	0.06	12.4	15.0	19600	360	18.3	9.4	38.4	0.024
Bushmans	12.3	0.05	2.8	5.4	7330	49	5.1	2.2	21.8	0.031
Kariega	27.1	0.05	7.5	10.7	16050	131	9.9	5.4	26.5	0.045
Kowie	96.0	0.06	16.5	29.8	32300	531	24.4	17.9	55.2	0.150
Great Fish	26.5	0.30	5.0	7.6	8712	85	7.5	3.1	10.8	0.010
Buffalo	196.2	0.10	186	19.5	36000	353	27.3	12.5	40.2	0.289
Nahoon	51.8	0.08	17.0	3.3	14210	184	18.9	7.1	32.0	0.081
Mossel Bay	4.1	0.02	1.9	4.3	2578	24	0.9	0.4	2.7	0.001
St Francis Bay	3.5	0.07	2.4	2.8	1450	31	0.6	0.4	32.7	0.003
Algoa Bay	5.6	0.33	1.8	2.6	2580	113	0.9	0.2	3.7	0.061

Source: Watling (1988).

TABLE 1.10
Metal concentrations in surface waters ($\mu g \cdot \ell^{-1}$) of Eastern Cape estuaries

Estuary	Zn	Cd	Cu	Pb	Fe	Mn	Ni	Co
Kromme	0.4	0.08	0.9	0.13	132	8	0.05	0.05
Gamtoos	1.6	<0.1	0.8	0.7	550	39	0.5	0.2
Papenkuils	154	0.1	8.3	21.0	3100	279	21.5	1.1
Swartkops	2.7	0.2	2.7	1.4	150	28	1.3	0.1
Sundays	2.9	0.04	4.0	1.0	378	20	1.1	0.2
Bushmans	0.5	0.13	1.8	0.2	302	10	0.23	0.2
Kariega	0.5	0.07	1.5	0.2	170	10	0.13	0.11
Kowie	0.6	0.05	1.7	0.2	214	12	0.54	0.16
Great Fish	3.0	0.07	2.2	1.1	1446	48	0.47	0.78
Buffalo	12.0	0.2	5.0	41.6	166	179	32.6	1.3
Nahoon	4.6	0.06	0.3	97.6	91	18	17.7	0.3
Mossel Bay	1.8	0.8	1.8	0.3	45	2	0.2	0.04
St Francis Bay	1.4	0.3	1.3	0.3	275	4	0.2	0.3
Algoa Bay	2.2	0.2	2.2	0.9	101	6	0.6	0.2

Source: Watling (1988).

The aims of this study were to determine the current state of metal enrichment and contamination in the sediment and water of selected Eastern Cape estuaries. The objectives of this study were to:

1) To conduct a baseline study of selected Eastern Cape estuaries to assess spatial patterns in metal concentrations in the surface water and sediments.
2) To investigate the influence of hydrology on the spatial and temporal patterns in metal concentrations within the surface water and sediments of selected permanently open and temporary open-closed Eastern Cape estuaries.

CHAPTER 2

STUDY AREA

2.1 INTRODUCTION

The estuaries sampled during this study are situated in the Eastern Cape Province, South Africa, and lie within a 70 km stretch of coast that runs from Boknes (33° 43′ 35″ S; 26° 35′ 9″ E) in the south east to Mpekweni Resort (33° 26′ 14″ S; 27° 13′ 52″ E) in the north west (Fig. 2.1). Nine estuaries were investigated, six of which are temporary open-closed estuaries and three which are permanently open systems. The temporary open-closed estuaries sampled were the Mpekweni, the East Kleinemonde, the West Kleinemonde, the Riet, the Kasouga and the Boknes Estuaries. The permanently open estuaries investigated were the Great Fish, the Kariega and the Kowie estuaries. The estuaries surveyed in this study are described in this chapter.

Estuaries selected for this study display a wide range of land-use patterns and population densities within their prospective catchments. They were also chosen due to paucity of data on metal concentrations and metal enrichment within the sediment and water of Eastern Cape estuaries. Not one of the temporary open-closed estuaries has been the subject of metal studies before, and the permanently open estuaries were briefly surveyed for metal concentrations in the early 1980s (Watling and Watling, 1983a). The Riet, East Kleinemonde and Kariega estuaries were sampled during both a dry season and wet season. All other estuaries were only sampled once. Sampling dates can be seen in Table 3.1 (Chapter 3).

The ecological health of the estuaries studied has been classified as “moderate” to “good”, and the water quality, which is based on the suitability for aquatic life, has been classified as “fair” to “good” (Harrison *et al.,* 2000). The type and size of developments associated

with each estuary vary, with some of the small temporary open-closed estuaries having minor developments within their catchment, whereas the permanently open Kowie and Kariega Estuaries are the sites of ever growing coastal developments. The banks of the Kowie Estuary are the most developed of all nine estuaries. All these estuaries (except the Boknes Estuary) are traversed by a coastal road, the R 72, which runs between East London and Port Elizabeth. Some of the estuaries have small to large housing developments situated on the banks of the lower reaches, and the Kowie and Kariega are surrounded by the coastal resort towns of Port Alfred and Kenton-on-sea, respectively. Land uses within the catchments of these estuaries comprise mainly pineapple farming, livestock rearing, and conservation / game farming (Vorwerk, 2000).

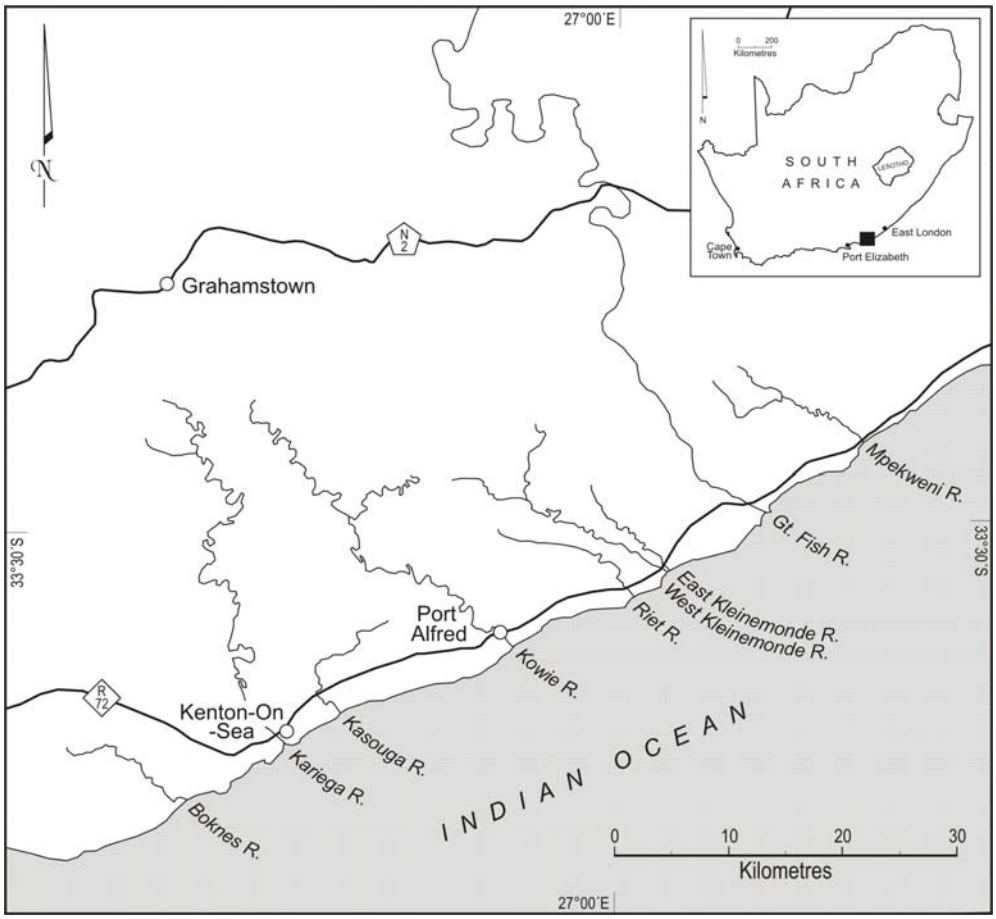

Figure 2.1: Map showing study area and the location of each estuary along the Eastern Cape coast (adapted from Walton, 1984).

2.1.1 COASTAL HYDROGRAPHY

The Eastern Cape coast is bordered by the Indian Ocean, with the tropical Agulhas Current flowing alongside the continental shelf in a south westerly direction. The Agulhas Current forms part of the South Indian Ocean gyre, and its warm waters originate from both the Equatorial Current flowing through the Mocambique Channel and the water flowing down the east coast of Madagascar (Ross, 1998). The Agulhas Current is fast flowing, reaching an average velocity of 1 $m \cdot sec^{-1}$, and it is approximately 100 m wide (Ross, 1998). The Agulhas Current diverges from the coast between East London and Port Elizabeth and this is due to a widening of the continental shelf (Lutjeharms *et al.,* 2000).

Intermittent upwelling events occur 40 % of the time on the landward side of the Agulhas Current between East London and Port Alfred (Lutjeharms *et al.,* 2000). These upwelling events are typical of a western boundary current that diverges from the coast due to a widening in the continental shelf (Lutjeharms *et al.,* 2000). The centre of this upwelling cell is located adjacent to Port Alfred, and it has a lateral range along the Agulhas Current of 85 to 300 km (Lutjeharms *et al*., 2000). The water that feeds these upwelling events is derived from the middle levels of the South Indian Central Water. Wind-driven upwelling events, which occur during periods of strong and persistent easterly winds, are also known to occur along this coastline and they usually bring cold water that is already on the shelf up from below the thermocline (Lutjeharms *et al*., 2000). These upwelling events contribute substantially to the nutrient loads observed along this section of the coast line (Lutjeharms *et al*., 2000).

2.1.2 CLIMATIC CONDITIONS

The section of Eastern Cape coast that stretches from East London to Port Elizabeth has a predominantly warm-temperate climate (Allanson and Baird, 1999), with average monthly temperatures ranging between 7.5 ^{o}C and 25.4 ^{o}C (Stone, 1998). The Eastern Cape is essentially a transition zone between climate types, and seasonal patterns in

rainfall are less pronounced than in other parts of the country (Stone, 1998). The Eastern Cape can however, be divided into climatic areas according to the seasonal distribution of rainfall. The belt of coast that was surveyed in this study experiences a bimodal rainfall pattern, with a maximum rainfall peak occurring in spring and a lesser peak occurring in autumn (Allanson and Baird, 1999). During the time of sampling the greatest amount of rainfall occurred in May and Aug, 2006, and March 2007. March and July were the driest months in 2006 and February was the driest month in 2007 (Fig. 2.2).

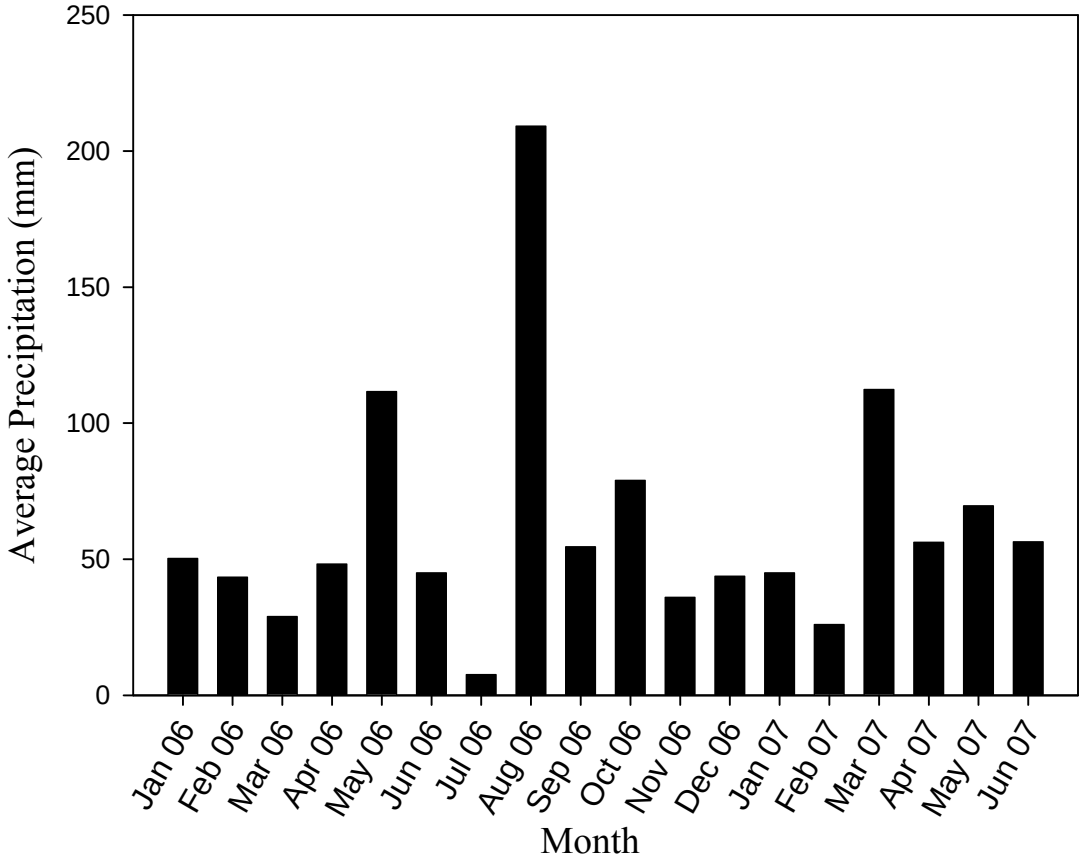

Figure 2.2: The mean monthly rainfall for Port Alfred between January 2006 and June 2007 (South African Weather Bureau).

Consistent eastward inshore currents, which are largely driven by persistent westerly to south-westerly winds, run along the Eastern Cape coast (Ross, 1998). These easterly nearshore currents run parallel to the Agulhas Current and transport aeolian sand in an

easterly direction (Ross, 1998). This transport of sediments is largely responsible for the closing of the mouths of temporary open-closed estuaries (Vorwerk, 2000).

2.2 MPEKWENI ESTUARY

The Mpekweni is a medium sized temporary open-closed estuary (Fig. 2.3) that is ~ 3 km long, has a catchment size of ~ 65 km^2, a surface area of 63 ha and a mean annual runoff (MAR) of 3.45 × 10^6 $m^3 \cdot yr^{-1}$ (Vorwerk, 2000). The mouth is positioned at 33º 26′ 13″ S and 27º 13′ 57″ E, which is ~ 15 km northeast of the Great Fish Estuary. The national road between East London and Port Elizabeth traverses the estuary 300 m from the mouth of the estuary. The Mpekweni Sun resort is situated on the northeast bank of the estuary, and a few holiday houses are built on the southwest bank of the lower reaches.

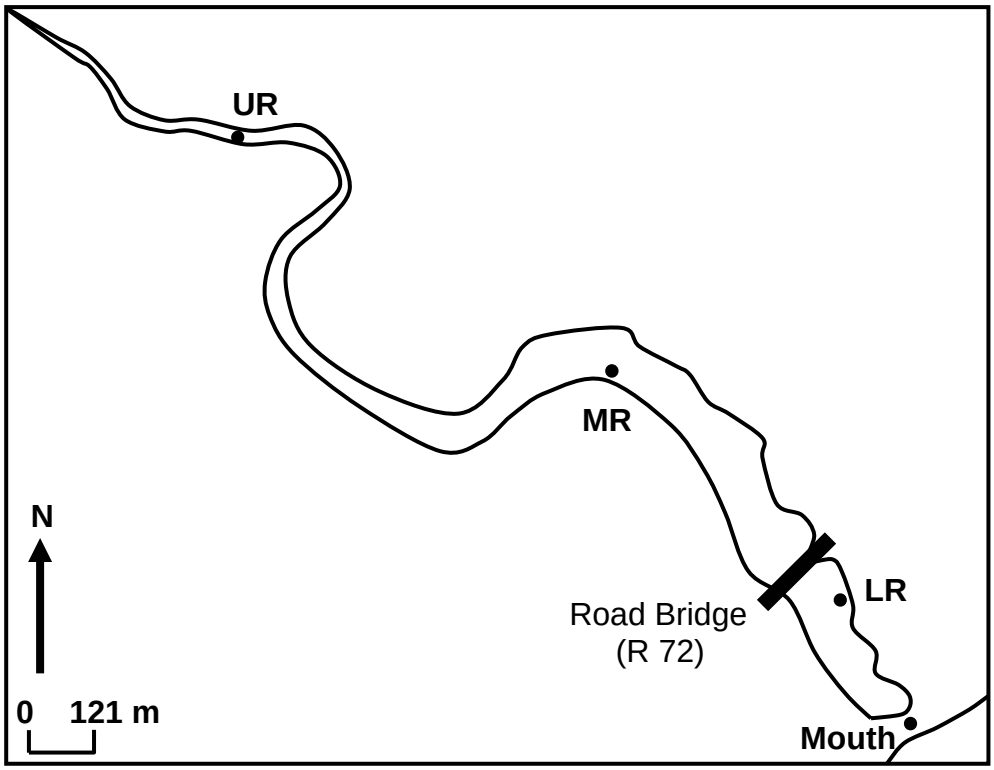

Figure 2.3: The Mpekweni Estuary, showing size and shape of the system and location of sampling sites. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

The mouth, lower and middle reaches are the widest part of the estuary (110 – 140 m), and the estuary narrows considerable in the upper reaches (40 m). The estuary is also shallowest at the mouth, having an average depth of less than one meter. The depth of the estuary will vary according to mouth phase, but when the mouth is closed the maximum depth is 2.6 m (Vorwerk, 2000). The estuary can thus be navigated by boat when the mouth is closed, although boating activity is minimal. The Mpekweni Estuary was sampled once (13th June 2006), during a dry period when the estuary mouth was closed.

2.3 EAST KLEINEMONDE ESTUARY

The East Kleinemonde is a medium sized temporary open-closed estuary (Fig. 2.4) that is situated ~ 20 km northeast of Port Alfred. The mouth of the estuary is situated at the coordinates 33º 32′ 21″ S and 27º 02′ 55″ E. The R 72 national road crosses the estuary ~ 500 m from the mouth. The northeast bank of the lower reaches of the estuary are surrounded by residential and holiday houses. A small township, Seafield, surrounds most of the southwestern bank of lower reaches of this estuary, as well as the neighboring West Kleinemonde Estuary. There is little development in the upper reaches of the East Kleinemonde Estuary. According to Harrison *et al.* (2000), the East Kleinemonde Estuary is in a "good" condition ecologically and the water quality is "good".

The estuary is 2.5 km long, has a catchment size of 46.3 km^2 and mean annual runoff of 2×10^6 m^3·yr^{-1} (Badenhorst, 1998). The width of the estuary is approximately 100 m at the mouth and narrows to 25 m in the upper reaches (Vorwerk, 2000). The main channel of the estuary is approximately 2.5 m deep, with most of the estuary being less than 1 m deep. The mouth remains predominately closed during the year, although mouth dynamics are highly variable. Data presented by Bell *et al.* (2001) show that the mouth of the estuary was only open 2.5 % of the time, and over-washing of marine water occurred 16.4 % of the time. The East Kleinemonde Estuary was sampled once during a dry season (24th June 2006) when the mouth of the estuary was closed, and once during the wet season (5th September 2006) when the estuary breached.

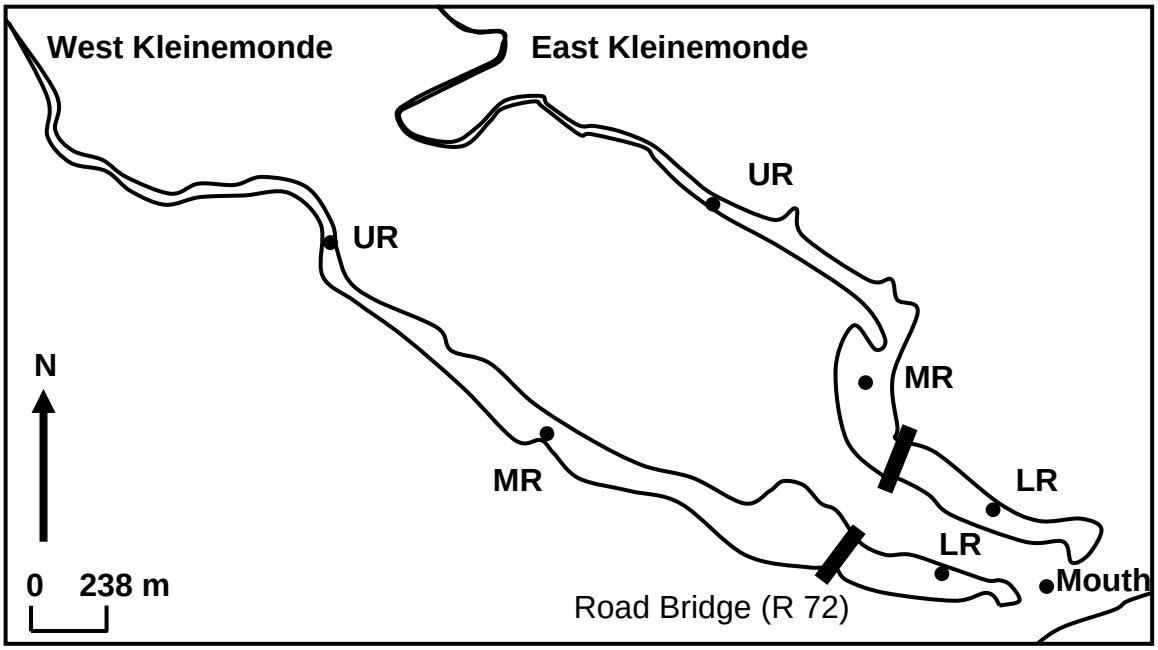

Figure 2.4: The East Kleinemonde and West Kleinemonde Estuaries, showing size and shape of the systems and location of sampling sites. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

2.4 WEST KLEINEMONDE ESTUARY

The West Kleinemonde Estuary is situated on the southwestern side of the East Kleinemonde Estuary (Fig. 2.4). It is ~ 7.8 km in length and is traversed by the R 72 coastal road 600 m from the mouth. The mouth of the estuary meets the sea 33° 32′ 27″ S and 27° 2′ 46″ E. The West Kleinemonde Estuary is larger than the East Kleinemonde, and has a catchment size of approximately 94 km^2, a MAR of 4×10^6 $m^3 \cdot yr^{-1}$ and a surface area of 19 ha (Whitfield and Bate, 2007). The West Kleinemonde Estuary was sampled once (24th June 2006), during a dry period when the mouth of the estuary was closed.

2.5 RIET ESTUARY

The Riet Estuary (33º 33′ 40″ S; 27º 00′ 53″ E) is a small temporary open-closed system (Fig. 2.5) situated ~ 10 km northeast of the coastal town of Port Alfred. The only developments along the banks of the estuary are residential and holiday cottages, which occupy a small area of the surroundings. The coastal road (R 72) between East London and Port Elizabeth crosses the estuary ~ 1.2 km from the mouth. The Riet Estuary has a catchment size of approximately 48 km^2, a MAR or 2 × 10^6 $m^3 \cdot yr^{-1}$ and a surface area of ~ 36 ha (Whitfield and Bate, 2007). The Riet Estuary was sampled once during a dry period (19th June 2006), during which time the mouth was closed, and it was sampled again during a wet period when the mouth opened to the sea (19th October 2006).

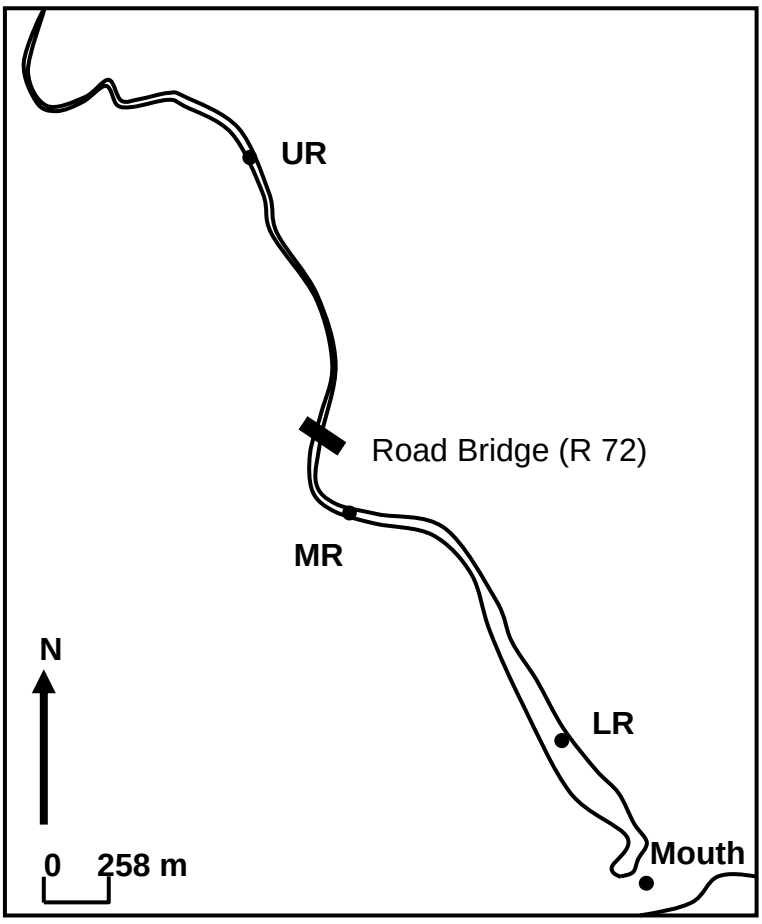

Figure 2.5: The Riet Estuary, showing size and shape of the system and location of sampling sites. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

2.6 KASOUGA ESTUARY

The Kasouga Estuary (Fig. 2.6) is a medium sized temporary open closed estuary with a surface area of ~ 15 ha (Whitfield and Bate, 2007). It is situated roughly mid way between the coastal towns of Port Alfred and Kenton-on-Sea. The mouth is located at 33° 39′ 10″ S and 26° 44′ 14″ E and the estuary is crossed by the R 72 national road ~ 2.34 km from the mouth. The catchment size of the Kasouga Estuary is ~ 142 km^2 and the MAR is ~ 6×10^6 $m^3 \cdot yr^{-1}$ (Whitfield and Bate, 2007). Land use within the catchment includes various forms of agriculture (pineapple, chicory) and cattle farming. The Kasouga Estuary was sampled once (2nd March 2007), during which time the mouth of the estuary was closed.

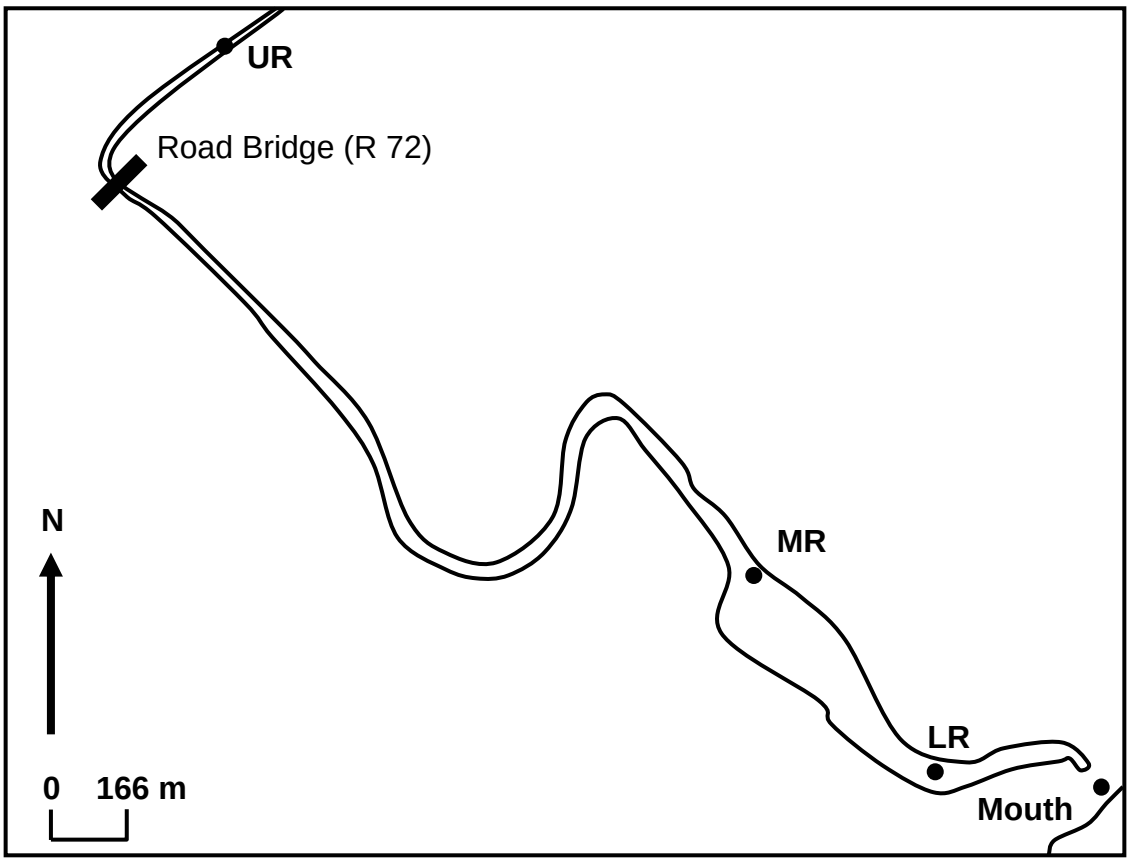

Figure 2.6: The Kasouga Estuary, showing size and shape of the system and location of sampling sites. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

2.7 BOKNES ESTUARY

The Boknes Estuary is a small temporary open-closed estuary (Fig. 2.7) that is situated ~ 10 km southeast of Kenton-on-Sea. The mouth of the estuary is situated at 33° 43′ 35″ and 26° 35′ 9″ E. The south eastern banks of lower and middle reaches of the estuary are surrounded by the seaside town of Boknes, which has grown considerably in recent years (Coetzee, 1998). The estuary has a catchment size of 200 km^2, a MAR of 10×10^6 $m^3 \cdot yr^{-1}$ and a surface area of ~ 7 ha (Whitfield and Bate, 2007). The estuary is utilized mostly during the holiday seasons as a fishing, canoeing and bathing site, but is too small for power boats and yachts. The catchment area of the estuary is used extensively by dairy farmers. At the time of sampling (21st January 2007) the mouth of the estuary was closed and large sections of the surface waters were covered by thick algal mats.

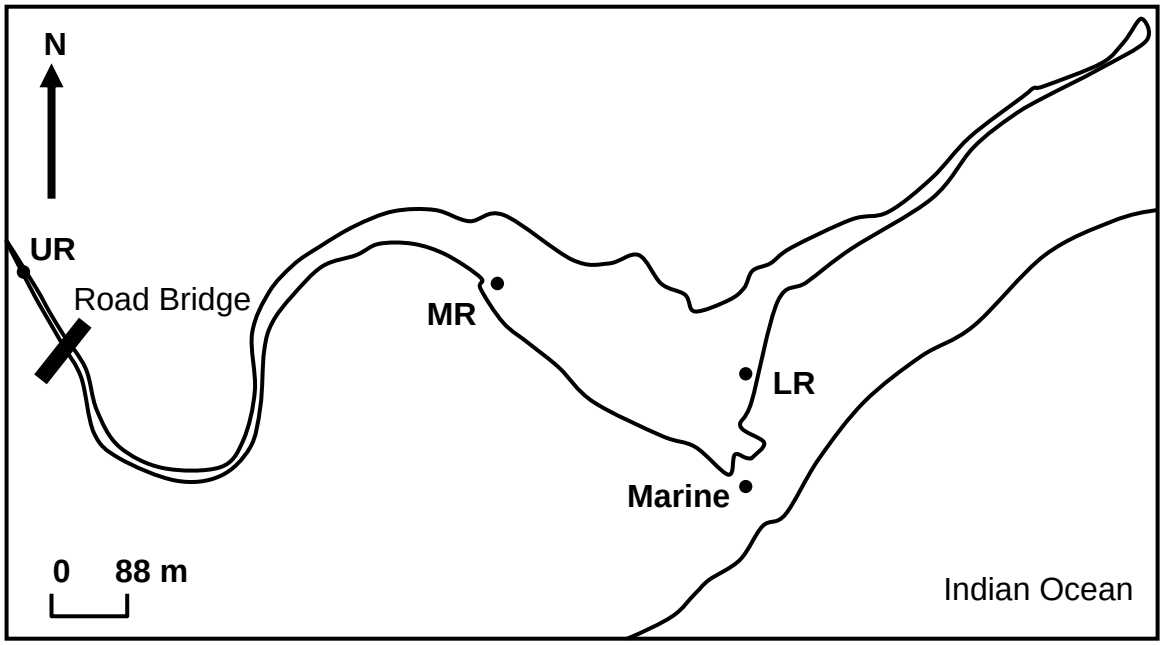

Figure 2.7: The Boknes Estuary, showing size and shape of the system and location of sampling sites. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

2.8 KARIEGA ESTUARY

The Kariega Estuary (33º 40′ 42″ S; 26º 40′ 51″ E) is a permanently open system (Fig. 2.8) with a small and highly regulated catchment, and as a result receives limited freshwater input (Allanson and Read, 1987). The catchment area of the Kariega is ~ 686 km^2 and the length of the estuary is ~ 18 km. Flow of freshwater into the estuary is regulated by three dams, namely Settlers, Howiesons Poort and Moss', and thus the estuary receives a negligible annual inflow of fresh water (~ 15×10^6 m^3) (Allanson and Read, 1987). It is situated approximately mid-way between the coastal cities of Port Elizabeth and East London, and connects to the sea on the north-eastern side of the coastal resort town, Kenton-on-Sea.

The road running between East London and Port Elizabeth (R 72) crosses the estuary ~ 1 km from the mouth, and residential and holiday developments are located along the banks of the lower reaches and at the mouth. There is no industrialization along the Kariega, but several storm water drains discharge into the estuary, the largest of which is located near the mouth (Jennings, 2005).

The Kariega is typically described as being a marine-dominated system that is homogenous with respect to its salinity (Allanson and Read, 1989; Grange and Allanson, 1995). During periods of drought the reservoirs within the catchment empty quickly due to the freshwater requirements of Grahamstown and riparian farmers, which in the past has resulted in zero river flow below the dams for up to three years at a time (Allanson and Read, 1987). During dry periods the upper reaches of the estuary are thus often hypersaline reaching salinities of up to 40 psu, and only during periods of sustained heavy rainfall has a decreasing salinity gradient been observed from the mouth to the upper reaches. The Kariega Estuary was sampled once during a dry period (15th July 2006) when it was in a marine-dominated phase, and once during wet period (9th November 2006) when it received a sustained supply of freshwater for almost a month.

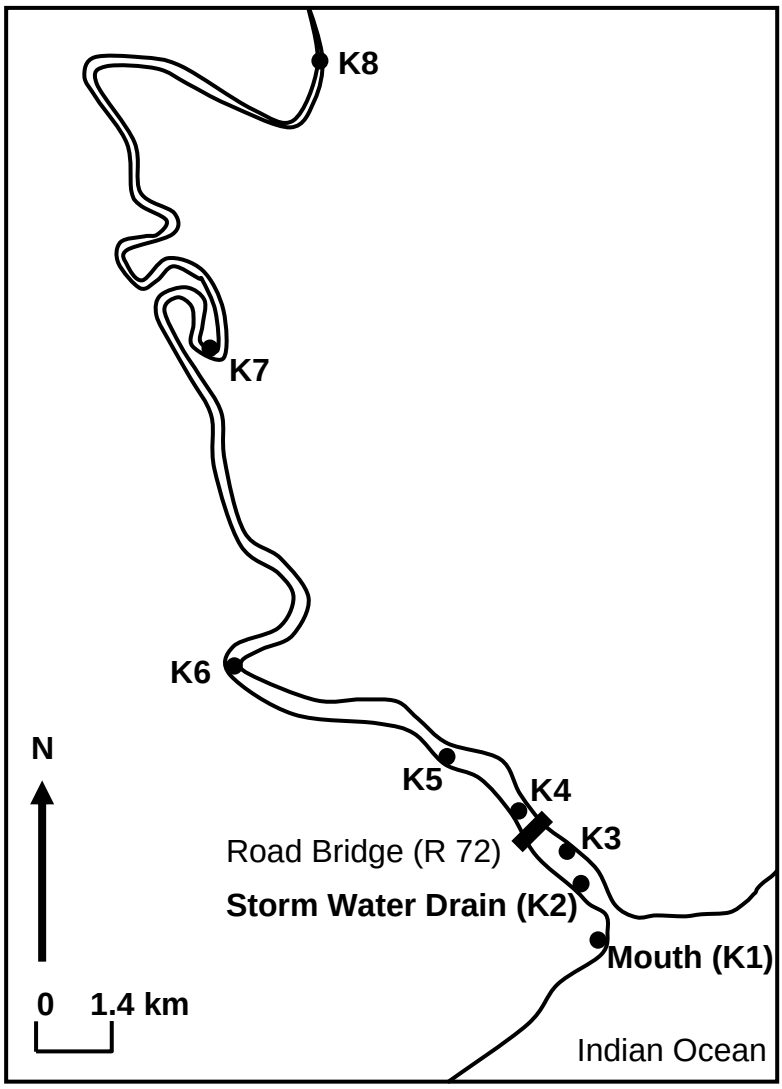

Figure 2.8: The Kariega Estuary, showing size and shape of the system and location of the eight sampling sites (K1 to K8).

2.9 GREAT FISH ESTUARY

The Great Fish system is a large permanently open estuary (Fig. 2.9) that connects to the sea at 33º 29′ 28″ S and 27º 08′ 06″ E. It has a longitudinal length of ~ 15 km and a catchment area of ~ 30427 km^2 (Allanson and Read, 1987). The R 72 coastal road crosses the estuary ~ 400 m from the mouth, and a small caravan park and coastal resort occupy the lower reaches of the estuary. The Great Fish Estuary was sampled on the 17th May 2007.

Copious amounts of turbid fresh water are translocated from the Orange River into the upper reaches of the Great Fish, and thus the Great Fish receives a sustained supply of fresh water year round (Allanson and Read, 1987). Marked sediment deposition has occurred in the Great Fish Estuary due to this continuous inflow of freshwater rich in suspended solids, which has contributed to a reduction in estuary depth.

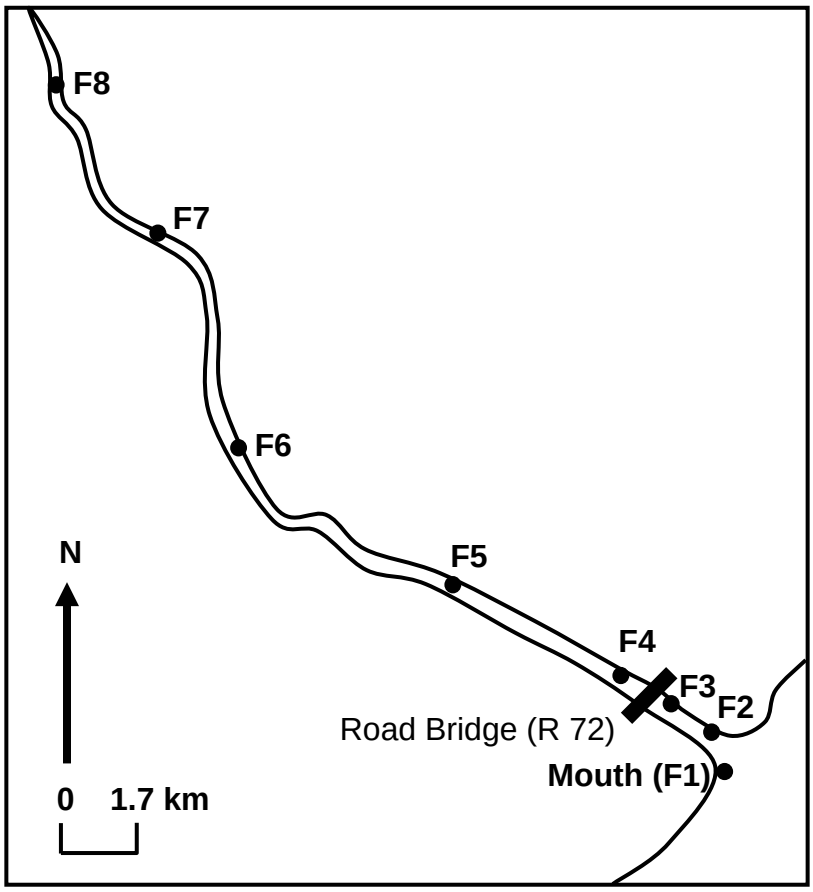

Figure 2.9: The Great Fish River Estuary, showing size and shape of the system and location of the eight sampling sites (F1 to F8).

2.10 KOWIE ESTUARY

The Kowie Estuary is a large sized permanently open system (Fig. 2.10) that connects to the sea at 33° 36′ 9″ S and 26° 54′ 2″ E. The Kowie estuary has a catchment size of

~ 800 km^2 and a MAR of 26 × 10^6 m·yr^{-1}. The Kowie River is ~ 70 km long and the estuarine conditions extend up to 21 km from the mouth (Whitfield and Bate, 2007). The Kowie Estuary was sampled once during autumn (2nd March 2007), which was a wet month, experiencing an average monthly rainfall of 112.4 mm.

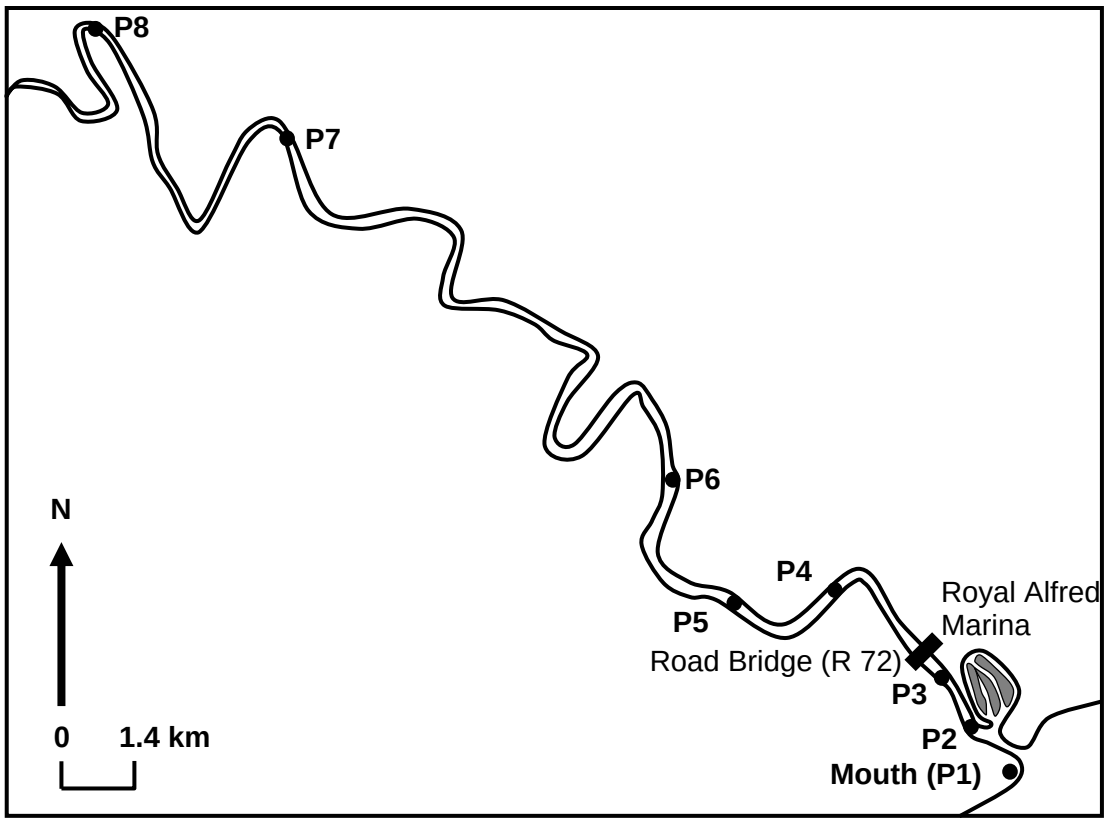

Figure 2.10: The Kowie Estuary, showing size and shape of the system and location of the eight sampling sites (P1 to P8).

The Kowie Estuary has been subject to considerable degradation and its ecological condition has been described as "fair" by Harrison *et al.* (2000). The upper reaches of the estuary flow through privately owned land and the densely wooded valleys of the Waters Meeting Nature Reserve. The middle and lower reaches of the estuary are surrounded by the coastal town of Port Alfred. The lower reaches have been artificially modified to form the Royal Alfred Marina, which is made up of a system of man-made canals. The R 72 national road crosses the estuary ~ 1.4 km from the mouth. The underlying rocks are

mainly composed of shale and sandstone and thus the estuary has a relatively low silt load and high alkalinity (Heydorn and Grindley, 1982).

CHAPTER 3

MATERIALS AND METHODS

3.1 SAMPLING

Three permanently open (PO) estuaries and six temporary open-closed (TOC) estuaries were surveyed during this study. Eight sites were sampled along the length of each permanently open estuary and four sites along each temporarily open-closed estuary. Sampling sites were chosen to cover the mouth and lower, middle and upper reaches of each estuary. Sediment and water samples were collected in triplicate at each site and each sample was analyzed separately. Sampling dates for each estuary are shown in Table 3.1.

TABLE 3.1
Dates at which estuaries were sampled, Whitfield classification of estuaries and mouth/flow status of estuaries

Estuary	Classification	Date sampled	Mouth / flow status
East Kleinemonde	TOC	24th June 2006	Mouth closed
		5th September 2006	Mouth open
West Kleinemonde	TOC	24th June 2006	Mouth closed
Riet River	TOC	19th June 2006	Mouth closed
		19th October 2006	Mouth open
Kasouga	TOC	2nd March 2007	Mouth closed
Boknes	TOC	21 January 2007	Mouth closed
Kariega	PO	15th July 2006	Marine dominated
		9th November 2006	Longitudinal salinity gradient
Great Fish	PO	17th May 2007	Longitudinal salinity gradient
Kowie	PO	2nd March 2007	Longitudinal salinity gradient

In order to study the effect of mouth phase on the concentration of metals in the sediment and water of temporary open-closed estuaries, samples were collected from the East Kleinemonde and Riet Estuaries during open and closed mouth phases (dry season and wet season). In order to study the effect of rainfall on the concentration of metals in the Kariega Estuary, samples were collected during a dry period and a high rainfall period.

All other estuaries were only sampled once and formed part of the broad survey of metal concentrations in the sediment and water of Eastern Cape estuaries.

3.2 DETERMINATION OF TRACE METALS IN ESTUARINE WATER AFTER MATRIX SEPARATION AND PRECONCENTRATION

3.2.1 INTRODUCTION

The analysis of trace metals in seawater is one of the most challenging of environmental analytical procedures (Rodushkin and Ruth, 1997; Sekhar *et al*., 2003), and a wide array of methods and techniques have been published on the subject. The techniques most commonly used are flame atomic absorption spectrometry (FAAS) (Brooks *et al*., 1967; Doner and Ege, 2005), graphite furnace atomic absorption (GFAA) (Subramanian, 1988), inductively coupled plasma atomic / optical emission spectrometry (ICP-AES, ICP-OES) (Akagi *et al*., 1985; Ramesh *et al*., 2002) and inductively coupled plasma mass spectrometry (ICP-MS) (Batterham *et al*., 1997; Rosland and Lund, 1998; Sekhar *et al*., 2003). Anodic stripping voltammetry (ASV) may also be used (Brügmann *et al*., 1983).

Trace metals usually occur in sea and estuarine water in the lower $\mu g \cdot \ell^{-1}$ concentration range and are incorporated in a complicated saline matrix (Sekhar *et al*., 2003). The presence of high concentrations of salt (NaCl) and alkaline (K) and alkaline earth metals (Mg and Ca) in seawater result in spectral and non-spectral interferences when seawater is analyzed directly by ICP or AAS, and thus the trace metals must be separated from this matrix before they can be analyzed. Recent advancements in ICP-MS have, however, allowed for the direct determination of trace metals in seawater using second generation high resolution instruments (Rodushkin and Ruth, 1997) and desolvating micronebulization (Field *et al*., 1999).

As trace metals are present in seawater and estuarine water at concentrations below the detection limits of most modern instruments, it is necessary to perform a preconcentration step prior to analysis (Doner and Ege, 2005). Various preconcentration methods have been developed such a liquid-liquid (solvent) extraction, the use of ion exchange and

chelating resins, solid phase extraction and adsorption and coprecipitation (Doner and Ege, 2005). Each of these methods results in different concentration factors, for example, with solid phase extraction / sorption one is able to concentrate metals more efficiently (up to 10^4 times) whereas with solvent extraction one may only achieve concentration factors of 10-100 times (Zolotov *et al*., 1987). These preconcentration procedures will also serve as matrix separators since the trace metals of interest are removed from the seawater whilst the interfering ions (Na^+, Cl^-, K^+, Mg^{2+} and Ca^{2+}) are left behind.

One of the first methods explored and successfully used for matrix separation and preconcentration was liquid-liquid extraction using ammonium pyrrolidine dithiocarbamate (APDC) and methyl isobulyl ketone (MIBK). Upon addition to the aqueous sample, APDC forms complexes simultaneously with transition elements and metals such as Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. These APDC-metal chelates are more miscible in organic than aqueous solutions and can be extracted into a small volume of organic solvent such as MIBK (Subramanian and Meranger, 1979). The organic solvent is then separated from the seawater and the metals of interest can be selectively analyzed using FAAS or GFAA. This technique is used for the routine analysis of metals in drinking water (Subramanian and Meranger, 1979), waste water (APHA *et al*., 1998) and seawater (Brooks *et al*., 1967).

The APDC-MIBK method, although apparently simple, has several disadvantages. Firstly, the APDC-metal complexes are unstable in the presence of hydrogen ions and will decompose rapidly if left in contact with the aqueous phase (Subramanian and Meranger, 1979). It is thus necessary to separate the organic phase from the aqueous phase as soon as possible to minimize transferal of metals back into the aqueous phase. However, it has been found that even after the aqueous and organic phases have been separated the metal-chelates still decompose and the metals adsorb onto the walls of the test tube or centrifuge tube (Subramanian and Meranger, 1979). Tessier *et al.* (1979) found that APDC-MIBK extracts could remain stable for up to 10 days if the extracts were stored in the dark at 4 ^oC, and thus their results suggest that it is possible to accumulate metals extracts from a large number of water samples before undertaking the metal analysis.

Metal-chelate stability is also pH dependant and the chelates are prone to decompose more rapidly outside an optimum pH range, which varies for each metal, and thus it is evident that errors can occur if samples are not analyzed within the time interval of stability and at the correct pH (Subramanian and Meranger, 1979). The pH of the seawater prior to the addition of APDC and MIBK is also very important for the quantitative extraction of metals, and the optimum pH range appears to differ slightly from one author to the next. Some authors suggest low pH values around 2.8 while others advise higher values of between 3 and 8 (Tessier *et al*., 1979). Brooks *et al*. (1967) advises a pH range of between 4 and 5.

Further problems may arise due to the differing solubility of MIBK in solutions of varying salinity. The salinity of estuarine water samples may range from 0 – 35 psu from the head to the mouth of the estuary and the solubility of MIBK is greatly dependant on the total salt content in the aqueous solution (Dornemann and Kleist, 1979) (Table 3.2).

TABLE 3.2
Solubility of MIBK in aqueous phase as a function of its salinity

Salinity (psu)	Percentage solubility of MIBK
0 (DDI)	0.024
< 3.6	0.024
8.3	0.019
16.6	0.018
25.3	0.016
33.4	0.015

DDI = distilled deionized water. Source: Kanai *et al*. (1979)

Methyl isobutyl ketone (MIBK) becomes less soluble in water as the salt content increases, and thus the concentration factor of metals in the MIBK will decrease as salinity increases. As MIBK is also highly soluble in water (~ 2 % V / V at room temperature), it is necessary to use very large seawater / solvent ratios in order to achieve the desired concentration factor without completely losing the MIBK in the aqueous phase (Brooks *et al*., 1967). For example, when 500 ml of seawater is shaken with 10 ml of MIBK, almost all the organic phase dissolves in the aqueous phase (Dornemann and

Kleist, 1979). Brooks *et al*. (1967) employed a seawater / solvent ratio of 750:20 by the addition of 35 ml MIBK to 750 ml seawater, and thus managed to concentrate metals into a 20 ml layer of MIBK for analysis of six trace metals by FAAS.

A second method that has gained popularity in the last two decades is the use of ion-exchange resins. Cations that are present in a large volume of solution (typically 1 liter) may be absorbed onto a relatively small amount of ion-exchanger (0.5 – 1 g for batch preconcentration), after which they can be eluted with a small volume of acid (Marr and Creser, 1983). Concentration factors of 20 to 100 fold may be achieved depending on the volume of sample and acid used.

Chelex-100 (Bio-Rad Laboratories), which is a polystyrene structured resin with iminodiacetic acid (IDA) functional groups (Pai *et al*., 1988), is one of the most widely used ion-exchange resins for the analysis of trace metals. The IDA functional groups form strong coordination bonds with multivalent metals and remove them from solution through the process of cation exchange (Lin and Juang, 2007). The cations in solution absorb onto the resin by the process of ion-exchange, whereby the resin will exchange a cation (typically H^+ or Na^+) with a cation in solution. Chelex-100 is thus a highly selective chelator towards metal ions (Leinonen and Jukka, 2000) and has been used successfully in both column preconcentration and batch preconcentration of trace metals in seawater, as well as the removal of metals from industrial waste water (Lin and Juang, 2007). Column preconcentration has several drawbacks, such as the long processing time, the high volumes of acid needed for elution of the metals and the relatively large amount of resin needed to pack the column (Cheng *et al.*, 1987). Batch methods are, however, rapid, efficient and require relatively small quantities of resin and acid.

During the first half of this study (2006) the APDC-MIBK method coupled with FAAS was used to analyze metals in seawater. This method proved to be laborious, prone to contamination and the continuous use of MIBK was hazardous to the health of all scientists working in the laboratory. During the second year of this study (2007) the

Chelex-100 batch method coupled with ICP-OES was employed as an alternative. Both methods are reported in this chapter.

3.2.2 COLLECTION AND STORAGE OF WATER SAMPLES

Prior to the collection of water samples, glass sampling bottles were pre-cleaned by soaking them in 5-10 % HNO_3 (55 %, chemically pure, Merck Chemicals ((Pty) Ltd., Johannesburg) for 24 hours and then rinsed thoroughly with deionized water. Approximately 1 liter of estuarine / marine surface water was collected and the samples were preserved by lowering their pH below 2 with concentrated HNO_3.The samples were transported to the laboratory and stored at 2 ºC prior to extraction and analysis. Water samples were collected in triplicate at each site and each sample was analyzed individually. All glassware and apparatus used in the following extraction procedures was pre-cleaned in 5-10 % HNO_3 for 24 hours and then rinsed thoroughly with deionized water.

3.2.3 MIBK-APDC EXTRACTION AND PRECONCENTRATION FOLLOWED BY ANALYSIS WITH FAAS

The following method was employed for the extraction of Cd and Pb from seawater samples. Exactly 750 ml of water sample was adjusted to a pH of 3 to 4 by the addition of 4 M NaOH (pellets, 98 % Merck Chemicals ((Pty) Ltd., Johannesburg) and / or 4 M HNO_3 (55 %, chemically pure, Merck Chemicals ((Pty) Ltd., Johannesburg) and was placed in 1 L glass volumetric flasks. A 1 % solution (w / v) of APDC (> 98.0 %, purum p.a., Sigma-Aldrich Ltd, Cape Town) was freshly prepared daily and was purified by shaking with 50 ml MIBK (> 99 %, spectrophotometric grade, Sigma-Aldrich Ltd, Cape Town). A 7 ml aliquot of a 1 % solution of APDC was added to each sample and briefly shaken, after which 35 ml of MIBK was added and the samples were shaken for 10 minutes at 150 rpm on a mechanical shaker (Brooks *et al.*, 1967). The phases were allowed to fully separate. Deionized water was carefully added to the aqueous layer using a funnel so that the organic layer was raised

into the neck of the volumetric flask (APHA *et al*., 1998). The organic layer was removed and stored in glass test tubes, in the dark, at 2 ºC until analysis.

Laboratory blanks were prepared from deionized water and extracted in the same manner as samples (APHA *et al*., 1998). Calibration standards were prepared by adding incremental volumes of 50 $mg \cdot \ell^{-1}$ solution of Cd and Pb to 750 ml deionized water to make 12-15 multi-element standards that covered the concentration range of 1-25 $\mu g \cdot \ell^{-1}$. The standards were extracted in the same manner as the samples. Calibration standards, blanks and samples were aspirated into a fuel-lean air-acetylene flame of the atomic absorption spectrophotometer (GBC 909 AA, Avanta, Australia). The atomizer was rinsed between samples with water-saturated MIBK. The wavelengths used to determine the concentrations of Cd and Pb were 228.8 and 283.3 nm, respectively. The concentrations of metals in the water column were compared to the target values for South African coastal waters as published in the South African Water Quality Guidelines for Coastal Marine Waters (DWAF, 1995).

As previously mentioned, the solubility of MIBK in aqueous solutions decreases as the salinity increases. Kanai *et al*. (1979) found that MIBK has a solubility of approximately 0.024 % in distilled deionized water, and a solubility of 0.015 % in seawater (salinity = 33.4 psu). The seawater extracts would thus appear to have a lower concentration of metals because the final volume of MIBK analyzed is greater than that of the standards, which were prepared from deionized water. It is therefore necessary to calculate a correction or multiplication factor that can be used to adjust the concentrations of metals in samples of different salinities to correct for the different volumes of MIBK obtained when metals were extracted from samples of different salinities. The concentrations obtained by FAAS were thus multiplied by specific correction factors (Table 3.3). The correction factors were calculated from MIBK solubility data presented by Kanai *et al.* (1979). An example of the calculation used to determine the correction factors can be found in Appendix 1: 1A.

To asses the extraction efficiency of this method seawater samples were spiked with Pb and Cd to give concentrations of 5 $\mu g \cdot \ell^{-1}$ and 10 $\mu g \cdot \ell^{-1}$, respectively. The spiked samples

were subjected to the same extraction procedure as that adopted for the analysis of metals in seawater. The spiking of seawater samples was repeated six times at each concentration, and the average percentage recoveries were determined for each concentration (Appendix 1: 1B). The limit of detection was calculated as three times the standard deviation of the blank (Marr and Cresser, 1983). Ten replicate readings were taken of the sample blank in order to determine the limit of detection. The limits of detection for Cd and Pb were 0.081µg·ℓ^{-1} and 1.032 µg·ℓ^{-1}, respectively.

TABLE 3.3
Correction factors used to adjust the concentrations of metals in estuarine and seawater samples of varying salinities

Salinity (psu)	Correction factor
0	1.00
< 3.6	1.00
8.3	1.22
16.6	1.26
25.3	1.35
33.4	1.40

3.2.4 CHELEX-100 EXTRACTION AND PRECONCENTRATION FOLLOWED BY ANALYSIS WITH ICP-OES

The following method of batch preconcentration of Cd and Pb from seawater / estuarine water using Chelex-100 was adapted from the method described by Cheng *et al.* (1987). Acidified water samples were filtered through 0.45 µm nylon membranes (Whatman International Inc., England) to remove particulates. Ten ml of 1 M ammonium acetate (min 98.0 %, Merck Chemicals (Pty) Ltd., Johannesburg) buffer solution was added to exactly one liter of water sample. The pH was adjusted to 6 with 1 M ammonia, prepared from ammonium hydroxide sol. (> 25.0 % in water, Trace Select, Sigma-Aldrich, USA) and 1M nitric acid (> 69.0 %, Trace Select, Sigma-Aldrich, France). Once the pH had been adjusted 0.5 g of Chelex-100 resin (Na^+ form, 200-400 mesh, Sigma-Aldrich, USA) was added to the solution. The sample was mixed on a mechanical shaker for 2 hours after which it was filtered through glass microfiber filter paper (GF / C, Whatman International Inc., England). The resin remaining on the filter paper was washed with 30

ml of 1 M ammonium acetate buffer and 15 ml water in order to remove the matrix salts Ca, Mg, Na and K. The metals adsorbed onto the resin were then eluted with 10 ml of 2 M nitric acid and the solution was made up to 25 ml with deionized water. Laboratory blanks were prepared from deionized water in the same manner as the samples. Composite calibration standards were made from 1000 $\mu g \cdot \ell^{-1}$ standard solutions (EC Labs, South Africa). The calibration standards, laboratory blanks and sample eluent were then analyzed by ICP-OES (iCAP 6000 Series, Thermo Fisher Scientific Inc.) under the conditions specified in Table 3.4. The wavelengths used for analysis were 228.8 nm for Cd and 220.3 nm for Pb. The concentrations of metals in the estuarine water were then compared to the target values for South African coastal waters as published in the South African Water Quality Guidelines for Coastal Marine Waters (DWAF, 1995).

TABLE 3.4
Instrumental operating parameters for the ICP-OES

	Analysis preferences	
Sample options:	# repeats:	3
	Sample flush time (sec):	30
Source:	Light Source:	ICAP
	Plasma View:	Axial
	WL Range:	Low
	Source settings	
Nebulizer Pump:	Flush pump rate (rpm):	100
	Analysis pump rate (rpm):	50
	Pump relaxation time (sec):	5
RF Power:	1150 W	
Auxiliary gas:	0.5 L / min	

The percentage recovery of Cd and Pb from seawater samples was determined by the spiking seawater samples with known concentrations of the analytes (EURACHEM, 1998). Seawater samples were spiked with 1000 $\mu g \cdot \ell^{-1}$ Pb and Cd to give concentrations of 5 $\mu g \cdot \ell^{-1}$ and 10 $\mu g \cdot \ell^{-1}$. The spiked samples were subjected to the same extraction procedure as that adopted for the analysis of metals in seawater. The spiking of seawater samples was repeated six times at each of the two concentrations, and the average percentage recoveries were determined for each concentration. The equation used to calculate the percentage recovery of metals from spiked seawater samples can be seen in Appendix 1B. The limit of detection was calculated as three times the standard

deviation of the blank (Marr and Cresser, 1983). Ten replicate readings were taken of the sample blank in order to determine the limit of detection. The limits of detection for Cd and Pb were 0.0635 $\mu g \cdot \ell^{-1}$ and 0.1515 $\mu g \cdot \ell^{-1}$, respectively.

The average percentage recoveries of Pb and Cd from seawater using the two methods described are shown in Table 3.5. There was no significant difference in percentage recoveries of Cd from seawater using the two methods ($p > 0.05$). There was an over-extraction of Pb from seawater using the Chelex-100 method. The sample concentrations of Pb obtained from the Chelex-100 method were thus adjusted to correct for the excess recovery. The equation used to adjust sample Pb concentrations can be seen in Appendix 1C.

TABLE 3.5
Average (± SD) percentage recoveries of metals from spiked seawater samples using extraction and preconcentration with MIBK-APDC and Chelex-100

		Method	
Metal	**Spiked concentration ($\mu g \cdot \ell^{-1}$)**	**MIBK-APDC**	**Chelex-100**
Cd	5	93.4 ± 31.2	70.2 ± 9.9
	10	87.8 ± 30.4	80.5 ± 3.2
Pb	5	79.8 ± 15.8	150.9 ± 7.3
	10	80.1 ± 6.6	159.9 ± 4.2

3.3 ANALYSIS OF METALS IN ESTUARINE SEDIMENTS USING FAAS AND ICP-OES

3.3.1 INTRODUCTION

The following section describes the digestion and subsequent analysis of metals in the estuarine sediments. During the first year of this study the concentrations of metals in sediments were determined by flame atomic absorption spectrometry (FAAS). At the end of 2006 the Rhodes University Chemistry Department acquired an inductively coupled plasma – optical emission spectrometer (ICP-OES), and thus all samples colleted in 2007 were analyzed using the ICP-OES. This change of method was due to the multi-element determination capability, high sensitivity and low detection limits of the ICP-OES.

3.3.2 COLLECTION AND STORAGE OF SEDIMENT SAMPLES

Surface sediment samples were collected from the shore edge of the estuary with a plastic scoop and were placed in clean, airtight, plastic Ziploc bags and transported to the laboratory and stored at 2 ºC until further processing. Sediment samples were collected in triplicate at each site and each sample was analyzed separately.

3.3.3 ACID DIGESTION AND ANALYSIS OF SEDIMENT SAMPLES

Sediment samples for the analysis of Cd, Cu, Pb, Zn, Ni, Co and Fe were acid digested according to US-EPA method 3050B. Although this is a very strong acid digestion technique, it does not result in a total digestion of sediments, and thus metals bound to silicates would not be dissolved (US-EPA, 1996). Approximately 1 g of dry, homogenized sediment was refluxed at 90 ± 10 ºC for approximately 3 hours with a HNO_3-HCl-H_2O_2 acid-peroxide mixture (reagents supplied by Merck Chemicals; HNO_3: 55 %, HCl: 32 %, H_2O_2: 30 %) to release the metals into solution (US-EPA, 1996). The digestate was diluted to 50 ml with deionized water and was centrifuged at 2500 rpm (Heraeus, Sepatech, Labofuge Ae, Germany) for 10 minutes to remove particulates, after which it was analyzed for metals using FAAS (GBC 909 AA, Avanta, Australia) by direct aspiration into an air-acetylene flame, or by ICP-OES (iCAP 6000 Series, Thermo Fisher Scientific Inc). Calibration standards were prepared from 1000 $mg \cdot \ell^{-1}$ standard solutions of Cd, Co, Cu, Fe, Ni, Pb and Zn (EC Labs, South Africa). Method blanks were prepared from the same acids and subjected to the same digestion procedure as the samples. Wavelengths used for analysis are shown in Table 3.6.

The percentage recovery of metals from the sediment was determined by digesting National Institute of Standards and Technology (NIST) certified reference estuarine sediment no. 1646a. The percentage recoveries for both FAAS and ICP-OES can be seen in Table 3.6. The percentage recoveries of metals from sediments using ICP-OES were in good agreement with those obtained using FAAS. Percentage recoveries for Cd exceeded 100% for both instruments, and thus sample Cd concentrations were adjusted to correct

for excess recovery (Appendix 1D). The limit of detection was calculated as three times the standard deviation of the blank (Marr and Cresser, 1983). Ten replicate readings were taken of the sample blank in order to determine the limit of detection. The limits of detection for each instrument are shown in Table 3.6.

TABLE 3.6
Wavelengths of analysis, limits of detection (LoD) and percentage recoveries of metals from sediments using two different instruments

	FAAS			ICP-OES		
Metal	**Wavelength (nm)**	**Recovery (%)**	**LoD ($mg \cdot \ell^{-1}$)**	**Wavelength (nm)**	**Recovery (%)**	**LoD ($mg \cdot \ell^{-1}$)**
Cd	228.8	120.5 (± 63.6)	0.032	226.5	132.5 (± 24.5)	0.006
Co	240.7	80.3 (± 19.9)	0.021	228.6	96.7 (± 6.0)	0.006
Cu	324.7	61.57 (± 1.1)	0.024	324.7	76.2 (± 2.5)	0.005
Fe	386.0	83.31 (± 4.5)	0.593	259.9	75.21 (± 4.2)	0.154
Ni	232.0	72.7 (± 4.6)	0.243	231.6	71.2 (± 3.9)	0.009
Pb	217.0	79.1 (± 29.5)	0.219	220.3	71.2 (± 2.3)	0.017
Zn	213.9	73.5 (± 5.6)	0.020	202.5	75.3 (± 5.1)	0.013

In the absence of sediment quality guidelines (SQGs) for South African estuarine and coastal sediments (Newman and Watling, 2007), it was decided that there are no suitable SQGs that could be used to screen sediment concentrations in this study.

3.3.4 GEOCHEMICAL NORMALIZATION AND ENRICHMENT FACTORS

As has already been mentioned in the Chapter 1, the concentrations of metals in sediments are affected by grain size, total organic content and mineralogy. Since these factors vary along the length of an estuary, one cannot simply use high absolute concentrations of metals as an indicator for anthropogenic metal contamination. Metal concentrations are thus commonly normalized to a grain-size parameter or a suitable substitute for grain size, and only then can the correct interpretation of sediment metal concentrations be made (Summers *et al*. 1996). Various constituents of the sediment may be used to normalize metal concentrations, and these include Al, Fe and total organic carbon. Iron is commonly used as a normalizer for grain size for the following reasons: it ubiquitously coats all sediments and is thus proportional the surface area of the sediment

(Gibbs, 1994), it is abundant in the earth crust and is not likely to have a significant anthropogenic source (Gibbs, 1994; Summers *et al.*, 1996), and ratios of metal concentrations to Fe concentrations are relatively constant in the earths crust (Summers *et al.*, 1996). Normalized metal / Fe ratios can thus be used to estimate the extent of metal contamination within an estuary, and to assess whether there has been enrichment of metals from anthropogenic activities.

In uncontaminated sediments strong linear relationships typically exist between Fe and metal concentrations (Schropp *et al.*, 1990; Summers *et al.*, 1996). Simple linear regression models can therefore be developed to explain background metal-Fe relationships, and these can then be used to assess enrichment of metals in sediment relative to natural concentrations. These models should be developed from a large regional database of uncontaminated sediments, and would thus be applicable to a variety of sediments (Summers *et al*., 1996). Ideally the sediments used in the baseline model should also cover a full grain-size distribution and thus yield a wide range of Fe concentrations (Summers *et al,* 1996). Data points may then be superimposed on the baseline regression models, and if the points fall within the 95 % prediction limits of the model, the sediments are considered to be uncontaminated (Schropp *et al.*, 1990; Summers *et al.*, 1996; Tam and Yao, 1998). Data points that fall above the upper 95 % prediction limit are identified as sediments that contain metals from both a natural and an anthropogenic source (Liu *et al.*, 2003). However, caution should be exercised when using this method, as a finding of enrichment is not always an indication of anthropogenic contamination (Schropp *et al*., 1990). Metals may exceed the upper 95 % prediction limit due to procedural errors (such as contamination during sampling) or due to the probability that a few samples from uncontaminated areas exceed the 95 % prediction limit (Schropp *et al.*, 1990).

In this study Fe has been used as a reference element for normalizing metal concentrations. Baseline regression models have been developed from regional metal concentrations reported during 1983 (Watling and Watling, 1983a).

3.3.5 DEVELOPMENT OF BASELINE LINEAR REGRESSION MODELS

Simple linear regression models were developed by plotting baseline concentrations of Cd, Co, Cu, Ni, Pb and Zn against baseline Fe concentrations. The baseline concentrations used were those published by Watling and Watling (1983) for surface and core sediments from the Bushmans, Kariega, Kowie and Great Fish Rivers. Any samples that were anthropogenically enriched with metals should be removed from the baseline data set (Schropp *et al*., 1990; Summers *et al*., 1996). The baseline data were thus examined for statistical outliers and influential cases using residual plots and Cook's distance test (Summers *et al*., 1996). Data points with a standard residual greater than 2*standard deviation were removed prior to performing the final regression analysis. Simple linear regression plots of each metal *vs*. Fe were constructed using the resulting data set (Summers *et al*., 1996). The concentrations of metals in sediments from this study were then superimposed onto the baseline regression plots, and data points that fell above the upper 95% prediction limit of the baseline models were identified as being enriched (Schropp *et al*., 1990).

Linear regression analysis of baseline data published by Watling and Watling (1983a) revealed that all metals, except Cd, exhibit significant linear relationships with Fe ($R^2 > 0.80$, $p < 0.05$). Results of the regression analyses are shown in Fig. 3.1. Once data were superimposed onto metal *vs*. Fe regression analyses it was possible to determine at which site metal concentrations were elevated above background concentrations.

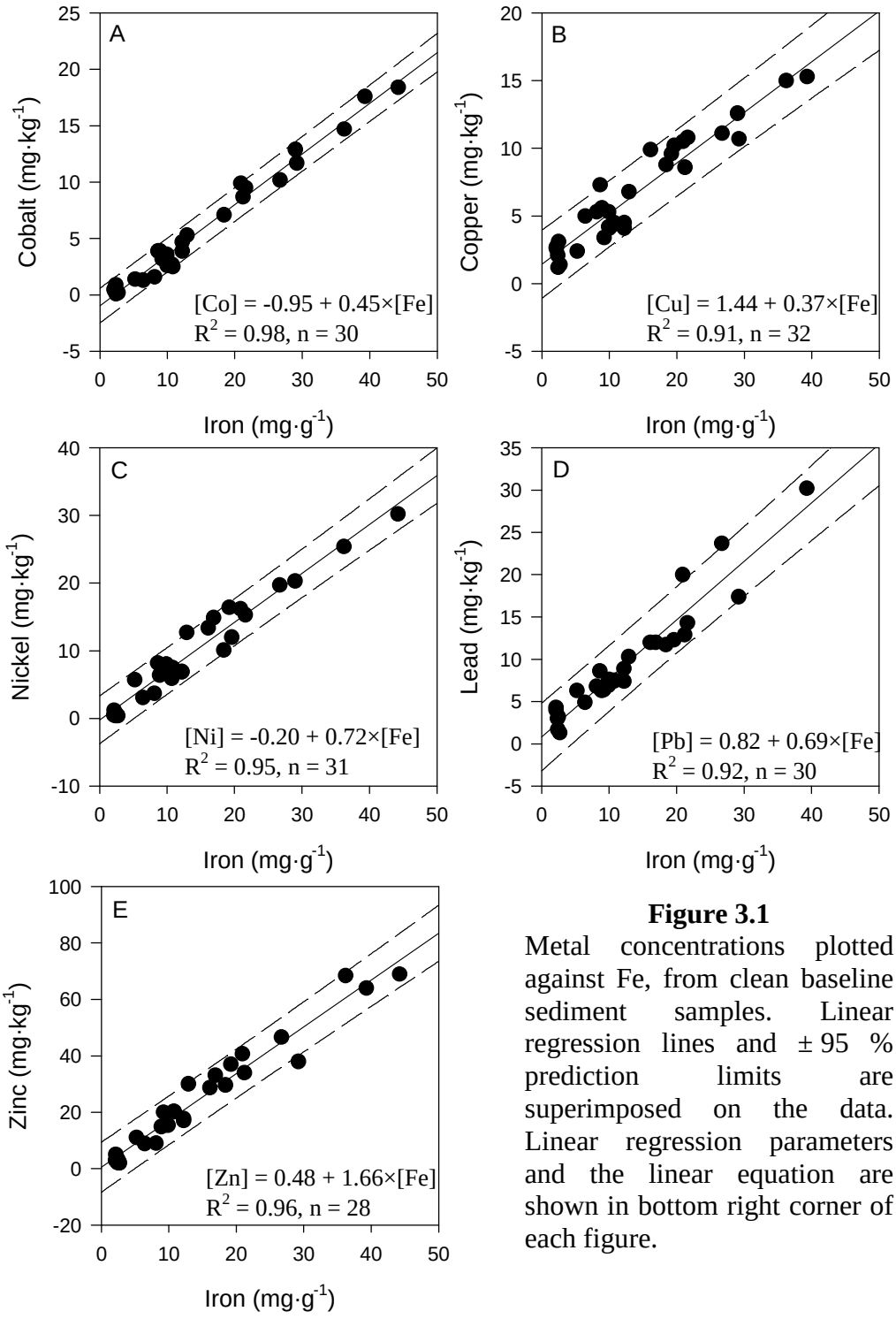

Figure 3.1

Metal concentrations plotted against Fe, from clean baseline sediment samples. Linear regression lines and ± 95 % prediction limits are superimposed on the data. Linear regression parameters and the linear equation are shown in bottom right corner of each figure.

3.3.6 ENRICHMENT FACTORS

Regression models were used to predict what metal concentrations would be obtained at the upper 95 % prediction limit for given (sample) Fe concentrations. Metal enrichment within surface sediments was then quantified by dividing the measured concentration by the baseline concentration predicted by the regression model. Thus, enrichment factor (EF) = $M_{observed} \div M_{predicted,}$ where M = metal concentration (Roach, 2005). All metals, except Cd, exhibit significant linear relationships with Fe ($p < 0.05$), thus for Cd, the EF was calculated by dividing the measured concentration by the highest regional baseline concentration above which enrichment can be inferred (Roach, 2005). This concentration was calculated to be 0.360 $\mu g \cdot g^{-1}$ Cd by Newman and Watling (2007). Enrichment factors were plotted against sampling site to asses the normalized distribution of metals along each estuary. Since Cd enrichment factors were not normalized for grain size, Cd / Fe ratios were calculated for samples in order to asses the normalized distribution of Cd along the estuaries.

3.4 PHYSICO-CHEMICAL PARAMETERS

3.4.1 GRAIN SIZE, TOTAL ORGANIC CARBON, SALINITY AND TOTAL SUSPENDED SOLIDS.

Total organic content (TOC) of the sediments was determined by the loss-on-ignition method (Schumacher, 2002). Sediment samples were pre-dried at 60 ^{o}C for a minimum of 8 hours or until constant mass. Sediment samples were then heated at 400 – 450 ^{o}C for 24 hours in ceramic crucibles and the percentage of TOC was determined as the mass of weight lost over the initial weight of the dry sediment multiplied by 100 %. The grain size distribution of sediments was estimated by a combination of wet and dry sieve methods. The percentage clay and silt content was determined by soaking a known weight of dry sediment in 250 ml water and 10 ml Sodium hexametaphosphate (6.2 $g \cdot \ell^{-1}$, practical grade, Sigma-Aldrich Ltd., Cape Town) for at least 2 hours, after which the

slurry was passed through a 63 µm sieve. The sand fraction remaining in the sieve was dried at 60 ºC for 24 hours and weighed. The mud fraction was determined by the difference in weights before and after wet sieving. The size distribution of the remaining sand fraction was determined by dry sieving the sand through a nest of sieves that was mechanically shaken for 10 minutes. The grain size of particles were classified according to the Udden-Wentworth scale. The mesh sizes of the sieves used for grain size analysis are shown in Table A1 (Appendix 2). The percentage of coarse sand, medium sand, fine sand, very fine sand and mud were thus determined for each sediment sample.

Salinity (psu) was determined at each sampling site at the time of sampling using a Reichert optical salinometer. Water samples were collected at each site for the laboratory analysis of total suspended solids (TSS), which was analyzed as follows; Whatman number 1 glass-fiber filter disks were dried at 103 – 105 ^{o}C overnight, cooled in a dessicator and weighed. A well mixed sample of water was vacuum-filtered through the weighed filter paper and the filter was then removed and dried at 103 – 105 ^{o}C overnight, after which it was cooled in a dessicator and weighed. Total suspended solids analysis was performed in triplicate. The TSS ($mg \cdot ml^{-1}$) was calculated as the weight of the filter paper after filtration minus the weight of the filter paper before filtration, divided by the sample volume.

3.5 STATISTICAL ANALYSIS

The software of Statistica 7 was used for all the following statistical analyses. Data were analyzed for temporal variations in metal concentrations using a t-test for independent samples. Data that were not normally distributed were analyzed using the Mann-Whitney U Test. Data were examined for spatial variations using one-way ANOVA. Spearman's Rank Order Correlation was used to measure the relationship between sediment characteristics and metal concentrations (Chen *et al.,* 2007).

Principal component analysis (PCA) was applied to sediment data (metals concentrations, TOC and grain size) in order to reduce the dimensionality of data set and understand the

underlying variability in the data (Meglen, 1992). It is assumed that the principals and theory behind PCA is understood by the readers and thus a detailed explanation behind this analysis will not be provided. Principal component analysis has been widely used for the analysis of environmental data as it can 'unmask' significant relationships between variables and relationships between samples (clustering of similar groups) (Meglen, 1992). Principal component analysis has also been used as a tool to characterize the anthropogenic and geogenic loads of metals by the extraction of 'latent' variables (principal components) that explain the underlying variability in the data set (Simeonov *et al.*, 2000; Wenchuan *et al*., 2001, Boruvka *et al*., 2005).

Each principal component (PC) extracted represents a separate source of variance in the system and PCs are commonly termed the 'latent' variables. The variable loadings provide information about the contribution of each individual variable to the new latent variable. If several variables have high loadings for one component they are identified as being associated, and the nature of their association may be either chemical or physical (Meglen, 1992). Loadings between ± 0.7 and ± 1.0 indicate substantially high relationships between the variable and principal component and loadings between ± 0.5 and ± 0.7 indicate moderate relationships (Meglen, 1992). The sign of the loading indicates whether the variable has a direct or inverse relationship with the principal component. Only principal components with eigenvalues > 1 were considered (Wenchuan *et al.*, 2001).

CHAPTER 4

METALS CONCENTRATIONS IN THE SEDIMENT AND WATER OF SELECTED TEMPORARY OPEN-CLOSED AND PERMANENTLY OPEN ESTUARIES

4.1 INTRODUCTION

To date very limited research has been conducted on the concentrations of metals in the sediment and water of Eastern Cape estuaries. Previous studies have largely concentrated on the larger, permanently open estuaries and pollution 'hot spots' such as harbors and heavily industrialized estuaries (Watling and Watling, 1983; Watling 1988; Binning and Baird, 2001; Fatoki and Mathabatha, 2001). Gaps thus exist in the monitoring of coastal areas and the smaller estuarine systems. There is currently limited literature on metal concentrations in temporary open-closed estuaries in the Eastern Cape (Orr *et al.*, 2007, In Press), despite the fact that they are numerically the dominant type of system within the region and are becoming the foci of booming coastal developments. There is therefore a need to conduct studies on metals within these smaller systems.

It is well documented that development within the catchment and in the vicinity of estuaries has been associated with an increase in metal concentrations within estuarine environments (Biney *et al*., 1994; Kennish 2002). The early surveys conducted on metal concentrations within Eastern Cape estuaries indicated that metal concentrations were elevated in the sediments of urbanized estuaries (Port Elizabeth and East London), and thus reflected the extent of development (Watling, 1988). The developments associated with the lower reaches these temporary open-closed estuaries are mainly residential / holiday houses and coastal resorts. There is currently no industrial development within the catchment areas of the temporary open-closed estuaries included

in this study, and thus the anthropogenic sources of metals are likely to be of a non-point nature.

This chapter presents the results of a baseline survey conducted in four temporary open-closed (the Mpekweni, the West Kleinemonde, the Kasouga and the Boknes Estuaries) and in two permanently open estuaries (the Kowie and the Great Fish Estuaries) along an approximately 200 km stretch of coastline. The permanently open estuaries were previously surveyed for metal concentrations in 1983 (Watling and Watling, 1983a), and thus provide a reference point to asses if there has been a significant change in metal concentrations within these systems over the last two decades. Furthermore, this chapter also assess if there is a significant difference in the concentrations and enrichment of metals in temporary open-closed and permanently open estuaries. The methods used to conduct this study are summarized in Chapter 3.

4.2 TEMPORARY OPEN-CLOSED ESTUARIES

4.2.1 MPEKWENI ESTUARY

Sediment Characteristics

The sediment at the mouth and lower reaches of the Mpekweni comprised mainly medium and fine sands whereas the middle and upper reaches comprised mainly fine sands and mud. The percentage of very coarse sands and gravel increase from the middle to upper reaches of the estuary (Fig 4.1). The organic content of the sediments increases consistently from the mouth of the estuary to the upper reaches (Fig. 4.1).

Metals in sediment

Metal concentrations in the sediment of the Mpekweni Estuary are shown in Table 4.1. The concentrations of all metals (except Cd) increase from the marine environment to the middle reaches of the estuary, and then decrease towards the upper reaches. This increasing trend in metal concentrations corresponds to the significant increase in total organic content (TOC) of the sediments, as well as an increase in fine grained particles.

All metals (except Cd) were thus positively correlated ($R > 0.50$, $p < 0.05$) to the organic content and percentage mud in the sediments (Table A2, Appendix 2). Cadmium was the only metal that was uncorrelated ($R < 0.50$) to TOC, mud and other metals. Cadmium, unlike the other metals, exhibited a decreasing concentration gradient from the marine environment to the middle and upper reaches of the estuary.

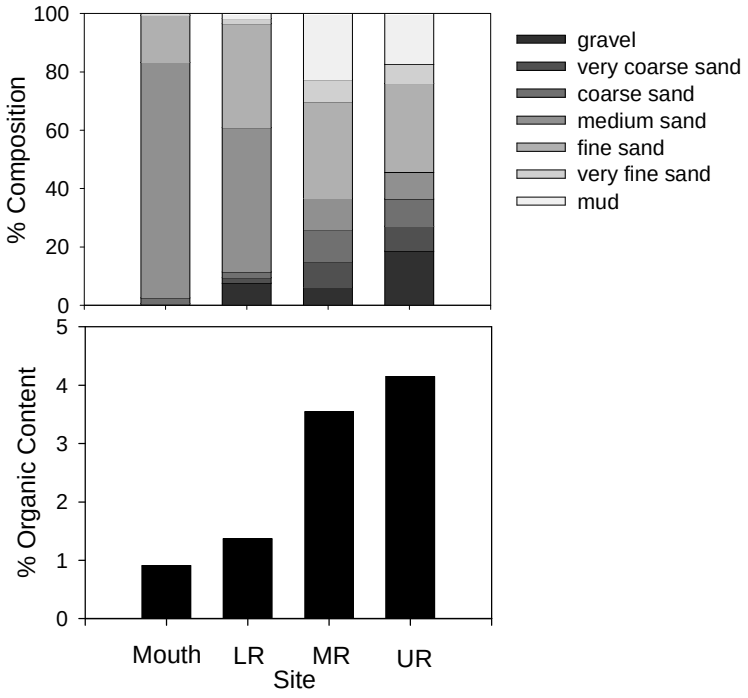

Figure 4.1: Grain size composition and organic content of the sediments at four sites along Mpekweni Estuary. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

TABLE 4.1
Mean (± SD) concentrations of metals (mg·kg^{-1}, dry wt.) in the sediments along the Mpekweni Estuary

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
Marine	0.97^{a} (± 0.06)	3.67^{a} (± 0.06)	3.97^{a} (± 0.21)	2790^{a} (± 90.79)	7.19^{a} (± 0.21)	10.72^{ab} (± 0.57)	4.52^{a} (± 3.25)
LR	0.53^{b} (± 0.28)	1.63^{a} (± 1.40)	3.68^{a} (± 2.10)	2475^{a} (± 656)	5.00^{a} (± 1.87)	6.74^{a} (± 3.82)	7.71^{a} (± 7.32)
MR	0.63^{ab} (± 0.03)	8.86^{a} (± 6.56)	10.81^{b} (± 2.99)	28998^{a} (± 21693)	13.35^{b} (± 4.16)	16.89^{b} (± 5.01)	33.29^{b} (± 14.01)
UR	0.44^{b} (± 0.12)	6.85^{a} (± 1.52)	9.26^{b} (± 0.75)	25385^{a} (± 8708)	10.07^{ab} (± 0.87)	13.09^{ab} (± 1.38)	19.55^{ab} (± 4.02)
Mean	0.64 (± 0.25)	5.25 (± 4.14)	6.93 (± 3.66)	14912 (± 16300)	3.41 (± 3.38)	11.86 (± 4.73)	16.27 (± 13.78)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$). n = 12

Principal component analysis was used to reduce the dimensionality of the data and to try and identify the 'latent' factors that may be influencing metal concentrations in the sediments. Principal component analysis was applied to 13 variables (7 metals, TOC and 5 grain size fractions) and three principal components were identified, explaining more than 94 % of the cumulative variance. The table of loadings (Table 4.2) reveals that component 1 (PC 1) was dominated by Co, Cu, Fe, Ni, Pb, Zn, coarse sand and mud. These variables were negatively correlated to the medium sand fraction. Principal component 2 (PC 2) had a high loading for sand, and PC 3 had a high loading for Cd. The first PC thus reflects the complexion nature of TOC and the increased 'adsorptive' capacity of fine grained sediments. Since PC 3 only has a significant loading for Cd it is evident that Cd concentrations represent a unique source of variance in the system. The Cd may thus be from an alternative natural source to all the other metals (such coastal upwelling, see Chapter 6)) or from a diffuse anthropogenic source. A scatterplot of the loading scores for PC 1 and PC 2 (Fig. 4.2) gives a clearer representation of the grouping between variables.

TABLE 4.2
Principal component loadings for metals and sediment characteristics in the Mpekweni Estuary

	Component 1 (62.76 %)*	**Component 2 (22.35 %)***	**Component 3 (9.83 %)***
Cd	0.29	-0.36	**0.88**
Co	**-0.85**	-0.51	0.03
Cu	**-0.98**	-0.09	0.09
Fe	**-0.92**	-0.34	-0.20
Ni	**-0.93**	-0.26	0.20
Pb	**-0.86**	-0.36	0.35
Zn	**-0.92**	-0.04	-0.03
TOC (%)	**-0.86**	0.46	0.11
Coarse sand	**-0.78**	-0.50	-0.35
Medium sand	**0.84**	-0.41	0.27
Fine sand	-0.08	**0.89**	0.14
Very fine sand	-0.67	0.67	0.13
Mud	**-0.76**	0.57	0.22

Note: Loadings greater than ± 0.7 are in bold and indicate substantially high relationships between the variable and principal component.
*Percentage total variance.

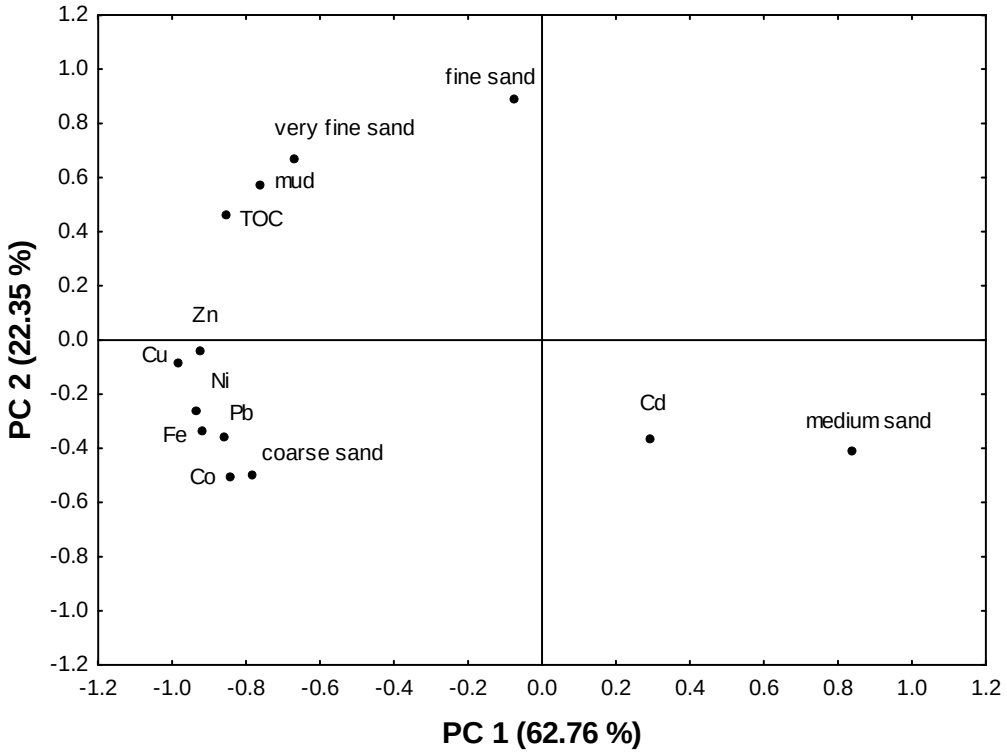

Figure 4.2: Principal component loading scatter plot (PC 1 *vs.* PC 2) for variables measured in Mpekweni Estuary sediments.

Metal concentrations were superimposed onto metal *vs.* Fe baseline linear regression plots, and the samples that fell above the 95 % prediction limit were considered to be enriched. One can clearly see from Fig. 4.3 that the majority of samples were un-enriched with metals in the sediment of the Mpekweni Estuary. The few samples that were enriched with Co, Cu, Ni, Pb and Zn were collected from the mouth of the estuary.

In order to get a clear representation of the distribution of the metals along the estuary geochemical data were normalized for grain size using Fe as a reference element and enrichment factors (EFs) were calculated. The enrichment factors were plotted against site (Fig. 4.4). The enrichment factors of all metals (except Zn and Cu) decreased significantly from the marine environment to the upper reaches of the Mpekweni Estuary ($p < 0.05$). The average EFs of all metals (except Cd) were below 1 in the middle and upper reaches indicating that there was no enrichment of metals at these sites.

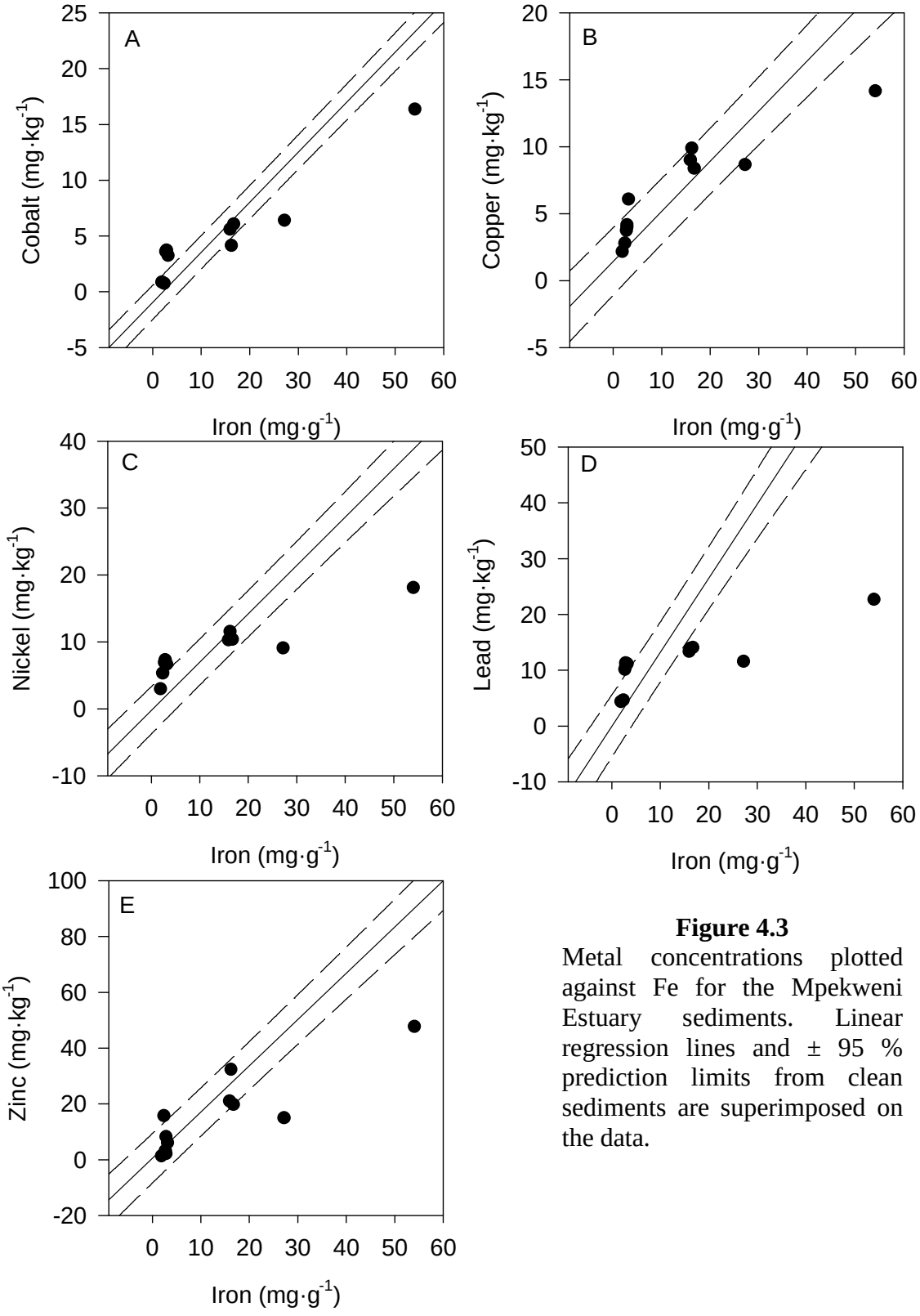

Figure 4.3
Metal concentrations plotted against Fe for the Mpekweni Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

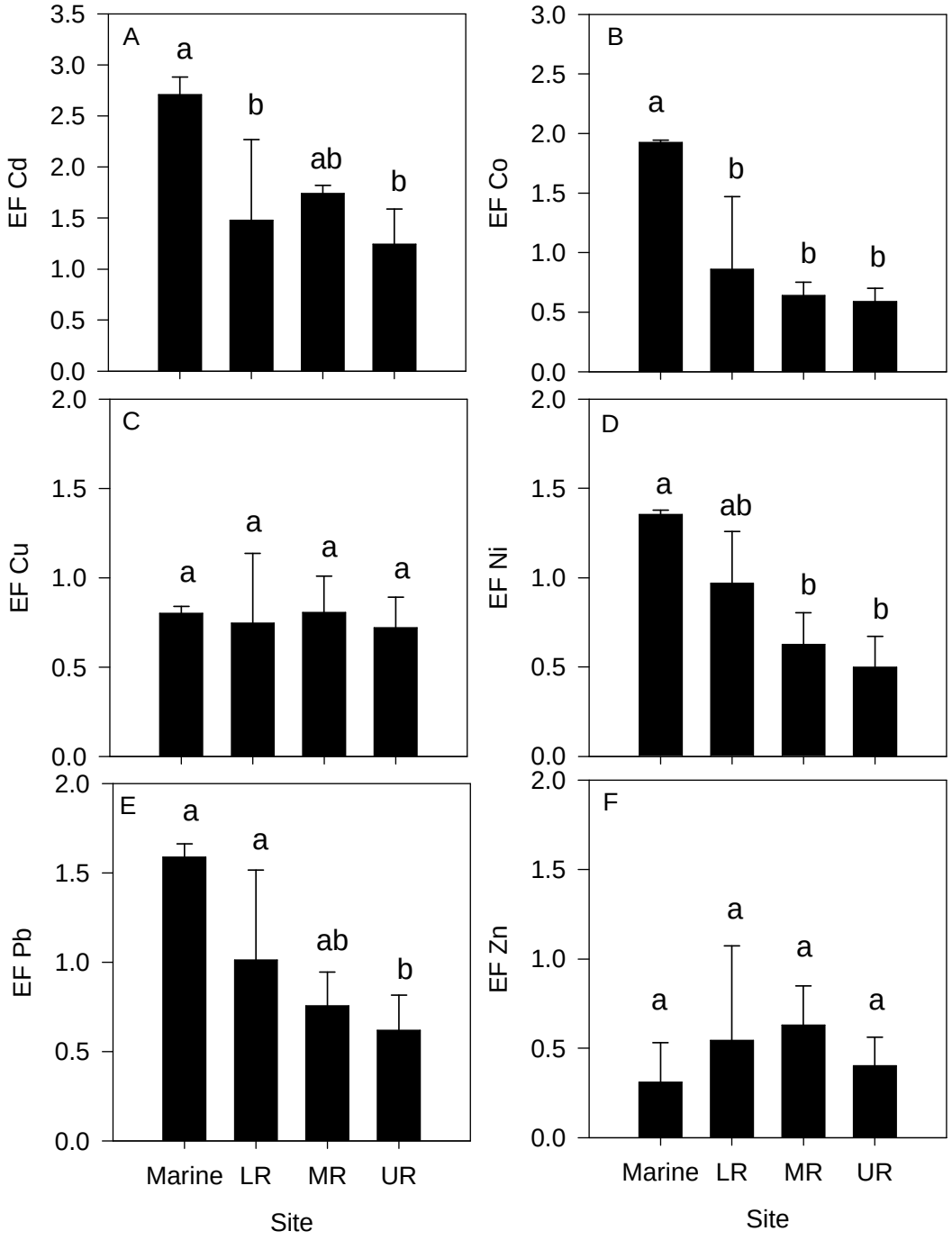

Figure 4.4: Spatial variation in mean (± SD) enrichment factors (EFs) for Mpekweni Estuary sediments. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

Please note that Cd enrichment was not normalized for grain size due to the fact that baseline linear regression plots could not be constructed for Cd *vs.* Fe (see Chapter 3). Fig. 4.4 A thus does not show the normalized Cd distribution. However, Cd / Fe ratios

decreased significantly ($p < 0.05$) in a landward direction suggesting accumulation of Cd in the marine environment and lower reach of the estuary (not shown). The average (± SD) enrichment factor for metals were: Cd 1.79 (± 0.69), Co 1.00 (± 0.63), Cu 0.77 (± 0.20), Ni 0.86 (± 0.38), Pb 0.99 (± 0.46) and Zn 0.47 (± 0.29). The Mpekweni Estuary sediments thus showed little to no enrichment for all metals except Cd. Since Cd was uncorrelated to any other metals, grain size and TOC it is possible that Cd originated from an alternative source (possibly anthropogenic) to all other metals.

Water

There was no significant spatial variation in the concentrations of Cd and Pb in the water of the Mpekweni Estuary ($p > 0.05$) (Fig. 4.5). Samples from the upper reaches were suspected to be contaminated with metals from unclean glassware during laboratory analysis and thus they were not included in these results. The average (± SD) concentrations of Cd and Pb were 0.40 (± 0.12) $\mu g \cdot \ell^{-1}$ and 3.51 (± 1.38) $\mu g \cdot \ell^{-1}$, respectively. These averages fell well below the South African water quality guidelines for coastal waters (DWAF, 1995) and thus the water of the Mpekweni Estuary was uncontaminated with Cd and Pb at the time of sampling.

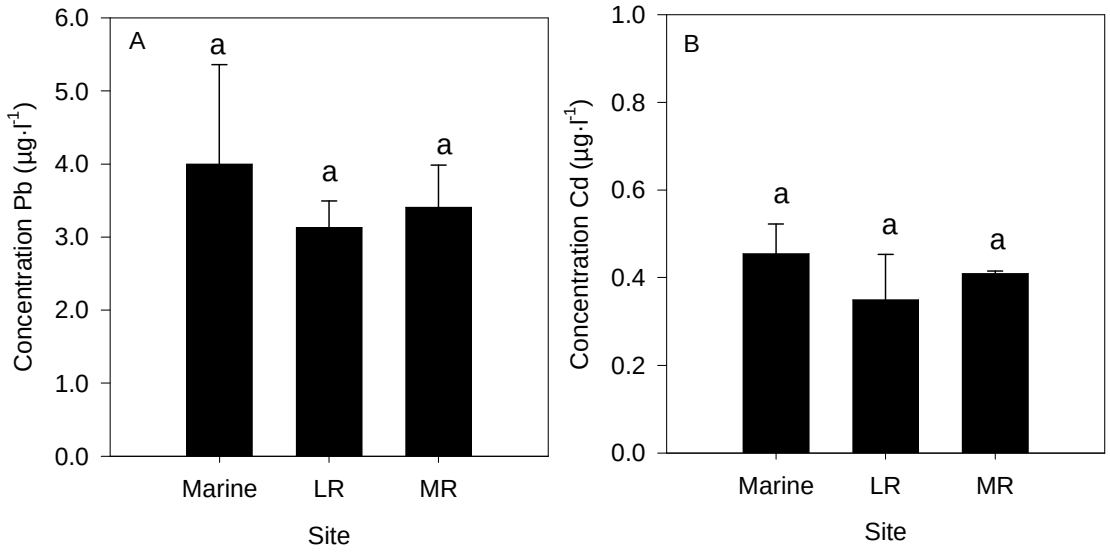

Figure 4.5: Spatial variation in the mean (± SD) concentrations of Pb and Cd in the water of the Mpekweni estuary. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

4.2.2 WEST KLEINEMONDE ESTUARY

Sediment Characteristics

At the time of sampling, the sediments of the mouth and lower reaches of the West Kleinemonde Estuary comprised mainly of medium sand. In the middle reaches of the estuary the sediments comprised mainly fine sand, while the sediments of the upper reaches were mostly composed of mud (Fig. 4.6). The percentage TOC increases from 0.78 % at the mouth to 9.16 % in the upper reaches of the system (Fig. 4.6).

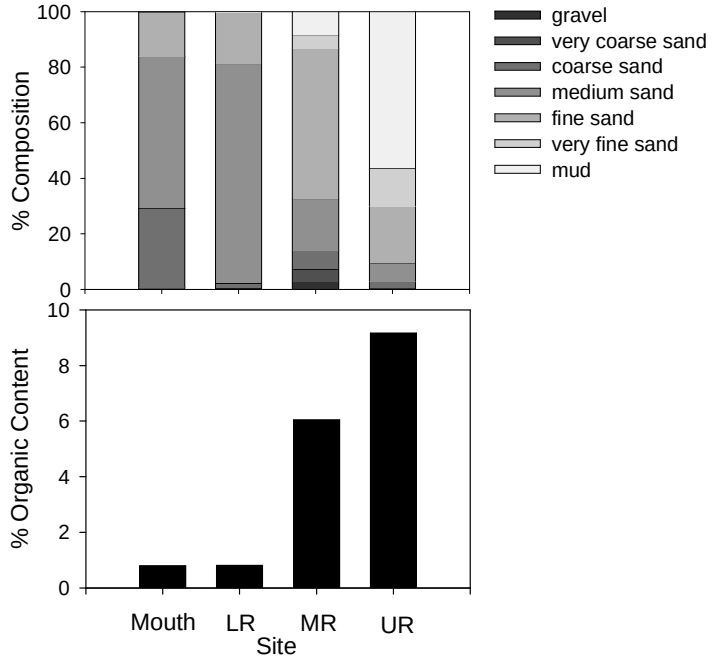

Figure 4.6: Grain size composition and organic content of the sediments at four sites along the West Kleinemonde Estuary. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

Metals in Sediment

The absolute concentrations of metals in the sediments of the West Kleinemonde Estuary can be seen in Table 4.3. There was no significant spatial variation in the concentrations of Cd, Co, Cu, Fe, Ni and Pb in the sediments of the West Kleinemonde Estuary ($p > 0.05$). The concentrations of Co, Cu, Ni and Fe increase from the marine environment to the middle reaches of the estuary. The concentrations of Pb and Cd on the other hand decreased from the marine environment to the upper reaches of the estuary.

TABLE 4.3
Mean (± SD) concentrations of metals (mg·kg^{-1}, dry wt.) in the sediments along the West Kleinemonde Estuary

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
Marine	1.18^{a} (± 0.41)	5.59^{a} (± 0.69)	2.29^{a} (± 0.33)	2066^{a} (± 105)	16.12^{a} (± 1.77)	26.05^{a} (± 1.65)	4.38^{a} (± 0.30)
LR	0.75^{a} (± 0.07)	4.81^{a} (± 0.48)	5.21^{a} (± 2.78)	2137^{a} (± 147)	13.31^{a} (± 1.11)	26.57^{a} (± 1.58)	24.29^{a} (± 6.28)
MR	0.74^{a} (± 0.38)	9.13^{a} (± 4.93)	7.18^{a} (± 4.15)	9168^{a} (± 7256)	12.17^{a} (± 6.79)	21.66^{a} (± 11.52)	43.66^{b} (± 21.30)
UR	0.74^{a} (± 0.38)	5.42^{a} (± 5.23)	3.54^{a} (± 3.81)	13134^{a} (± 5853)	5.74^{a} (± 4.44)	13.34^{a} (± 8.34)	14.66^{a} (± 14.86)
Mean	0.81 (± 0.34)	6.24 (± 3.23)	4.55 (± 3.29)	5435 (± 5474)	11.83 (± 5.34)	21.91 (± 8.27)	21.75 (± 18.93)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$). n = 12

Principal component analysis (PCA) was used to reduce the dimensionality of the data set and to extract the 'latent' variables that explained some of the variance in the data (Meglen, 1992). Thirteen variables were subjected to PCA (concentrations of 7 metals, TOC, and 5 grain size fractions). Three principal components accounted for 82.74 % of the cumulative variance. The relationships between variables and the principal components can be seen in the loadings table (Table 4.4). The first principal component has moderate to good positive relationships with Cd, Ni, Pb and coarse sand, and an inverse relationship to Fe, TOC, mud, and very fine sand. Evaluation of enrichment factors indicated that Cd, Ni and Pb may be of anthropogenic origin (EF > 1). The second principal component includes the positive contribution of Co, Cu and Zn. Component 3 has a positive loading for the fine sand fraction, which is uncorrelated to any of the metals. The loadings scatterplot (Fig. 4.7) gives a clearer depiction of the relationship between variables and their contribution to the principal components. It is however, unusual that all metals (except Fe) showed no correlation with the fine grained sediments and TOC. The distribution of these metals may thus be controlled by a variable not considered in thus study.

TABLE 4.4
Principal component loadings for metals and sediment characteristics in the West Kleinemonde Estuary

	Component 1 (45.68 %)*	Component 2 (27.75 %)*	Component 3 (9.31 %)*
Cd	0.53	-0.54	-0.11
Co	0.13	**0.89**	-0.32
Cu	0.08	**0.94**	-0.08
Fe	**-0.80**	-0.04	0.07
Ni	**0.84**	0.43	-0.22
Pb	**0.78**	0.52	-0.23
Zn	-0.06	**0.86**	0.10
TOC (%)	**-0.95**	0.17	-0.02
Coarse sand	0.66	-0.39	-0.23
Medium sand	**0.84**	-0.19	0.11
Fine sand	-0.23	0.47	**0.72**
Very fine sand	**-0.95**	0.00	-0.30
Mud	**-0.82**	-0.05	-0.55

Note: Loadings greater than ± 0.7 are in bold and indicate substantially high relationships between the variable and principal component.
*Percentage total variance.

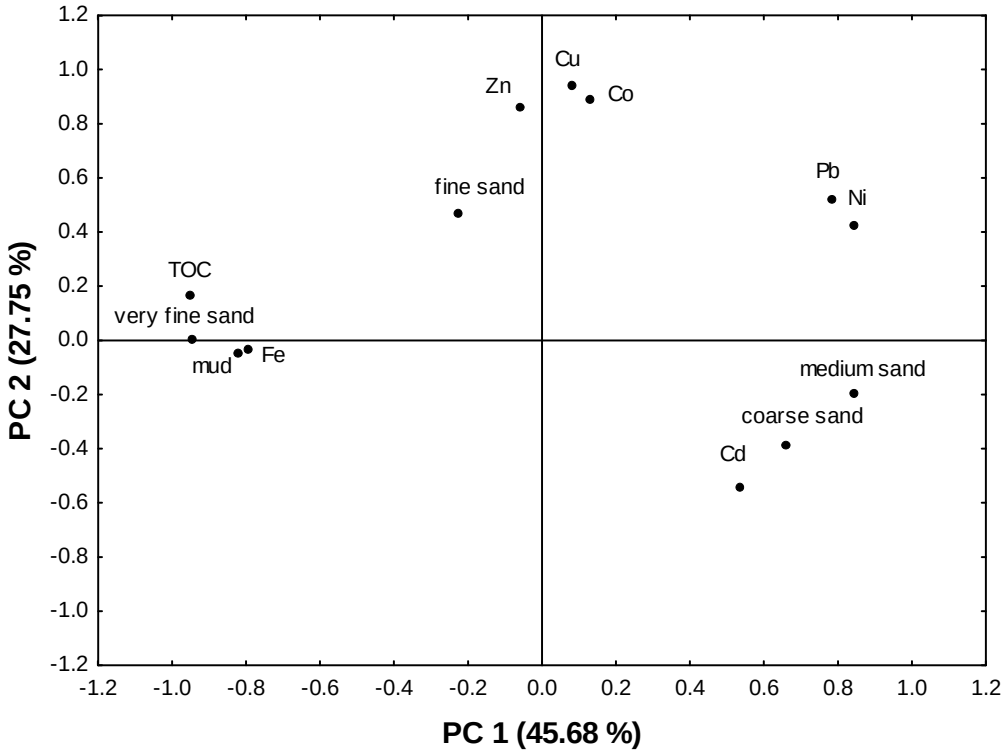

Figure 4.7: Principal component loading scatter plot (PC 1 *vs.* PC 2) for variables measured in West Kleinemonde Estuary sediments.

Metal concentrations were plotted against Fe for the West Kleinemonde Estuary sediments. Baseline Linear regression models for metals *vs.* Fe were superimposed onto the data and the samples that fell above the 95 % prediction limits were considered to be enriched. Figs. 4.8 A, 4.8 C and 4.8 D show that the majority of samples were enriched with Co, Ni and Pb, indicating enrichment of these metals above baseline concentrations, while few samples were enriched with Cu and Zn (Figs. 4.8 B and 4.8 E).

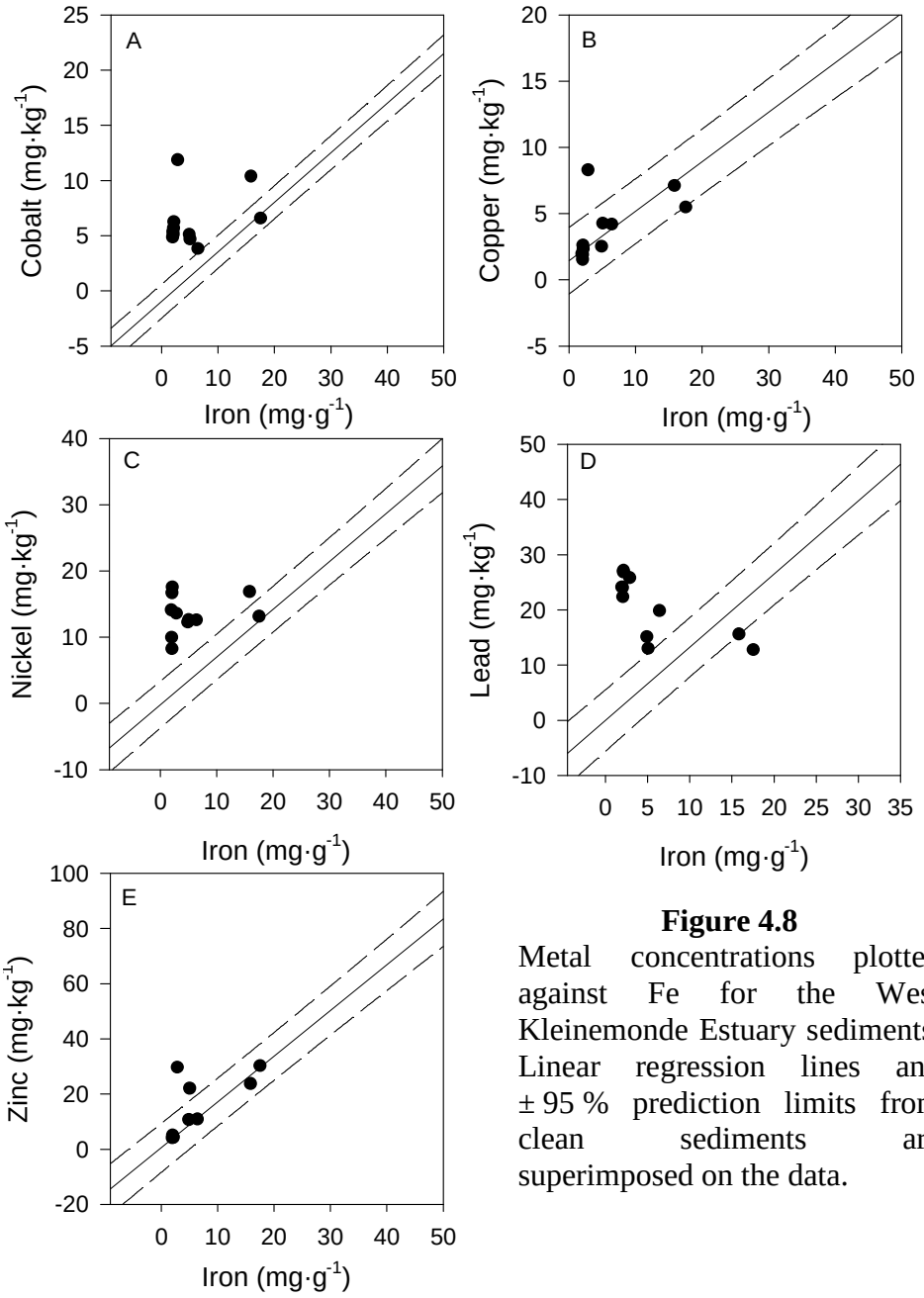

Figure 4.8
Metal concentrations plotted against Fe for the West Kleinemonde Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

In order to asses the spatial variation in metal enrichment, enrichment factors were plotted against sampling sites (Fig. 4.9). Enrichment of Co, Ni and Pb decreased significantly from the marine environment to the upper reaches of the estuary ($p < 0.05$). There was little spatial variation in the enrichment of Cd, Cu and Zn along the estuary (Figs. 4.9 A, 4.9 C and 4.9 F). The Cd enrichment factors were not normalized for grain size (see Chapter 3), and thus Cd / Fe ratios were calculated to asses the normalized distribution of Cd. There was no significant spatial vitiation in Cd / Fe ratios along the estuary ($p > 0.05$). Average (± SD) enrichment factors for metals were; Cd 2.27 (± 0.95), Co 2.42 (± 1.17), Cu 0.56 (± 0.15), Ni 1.83 (± 1.09), Pb 2.77 (± 1.41) and Zn 0.55 (± 0.27). Moderate enrichment was thus observed for Cd, Co, Ni and Pb ($1 < EF < 3$) and the sediments were not enriched with Cu and Zn ($EF < 1$). The elevated enrichment of metals at the mouth and lower reaches may be associated development in that area, or the input of metals from the marine environment.

Water

The surface salinity dropped from 36 psu in the marine environment to a constant 17 psu in the lower, middle and upper reaches of the West Kleinemonde Estuary. The concentration of total suspended solids (TSS) was greatest in the marine environment and upper reaches of the estuary (range: 30 – 31 $mg \cdot \ell^{-1}$) and was lowest in the lower and middle reaches (range: 15.4 – 15.5 $mg \cdot \ell^{-1}$).

The average concentrations of Pb (2.67 ± 1.45 $\mu g \cdot \ell^{-1}$) and Cd (0.43 ± 0.51 $\mu g \cdot \ell^{-1}$) in the water of the West Kleinemonde Estuary were well below the DWAF recommended guidelines of 12 and 4 $\mu g \cdot \ell^{-1}$, respectively. There was no significant spatial variation in the concentrations of Pb along the estuary (Fig. 4.10) ($p > 0.05$). The concentrations of Cd were significantly greater in the lower and upper reaches of the estuary ($p < 0.05$). Overall, the water of the West Kleinemonde was uncontaminated with Cd and Pb at the time of sampling.

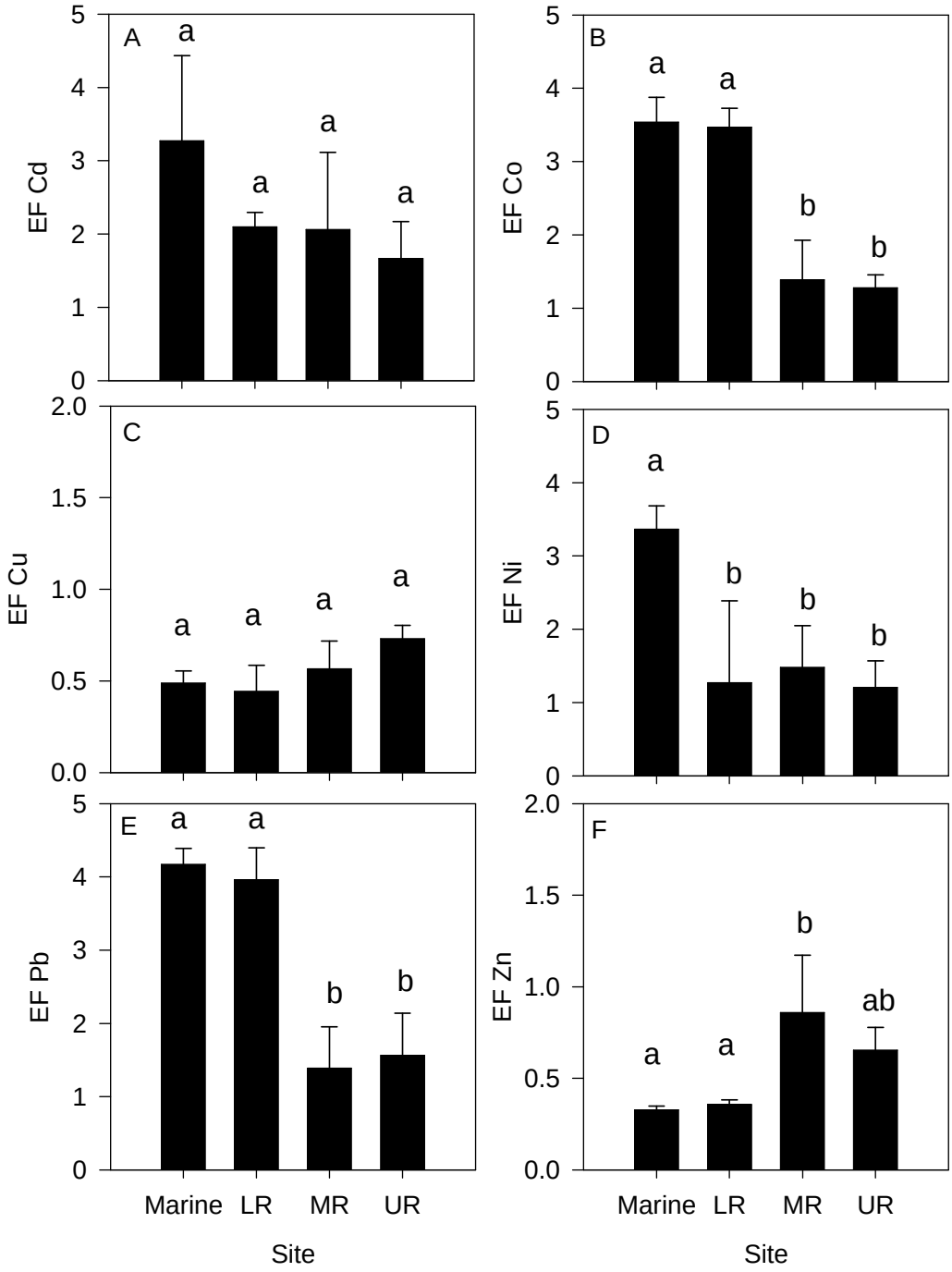

Figure 4.9: Spatial variation in the mean (± SD) enrichment factors for metals in the West Kleinemonde Estuary sediments. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

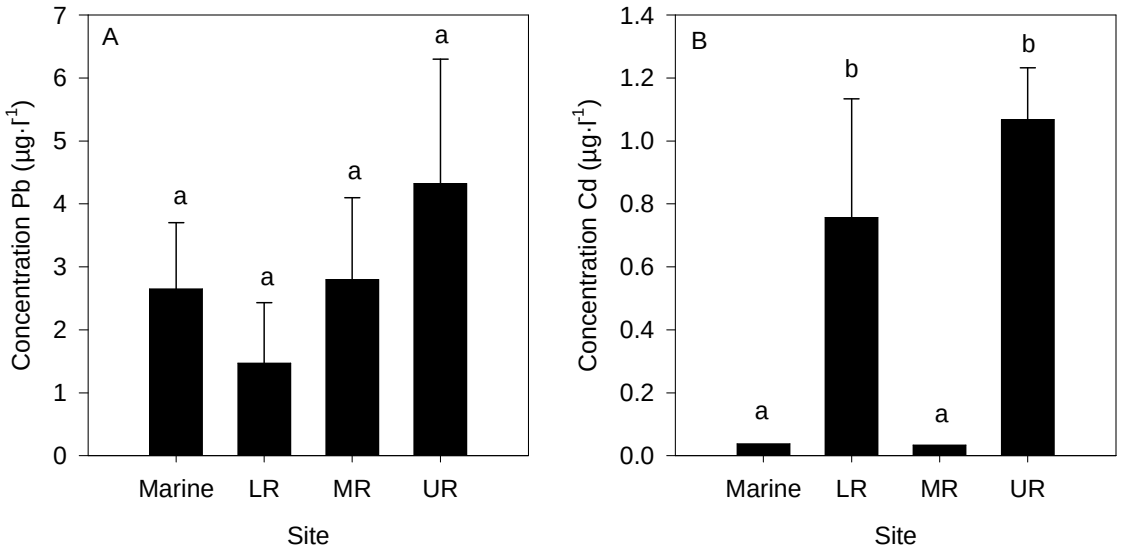

Figure 4.10: Spatial variations in the concentrations (mean ± SD) of Cd and Pb in the water of the West Kleinemonde Estuary. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

4.2.3 KASOUGA ESTUARY

Sediment Characteristics

The percentage organic content of the sediments of the Kasouga Estuary increased steadily from 0.88 % at the mouth to 7.47 % at the upper reaches of the estuary. Similarly, there was a steady decrease in large grained sediments from the mouth of the estuary to the upper reaches and a concurrent increase in fine grained sediments (Fig. 4.11).

Metals in Sediment

Metal concentrations in the sediments of the Kasouga Estuary increased significantly ($p < 0.05$) from the marine environment to the upper reaches of the system (Table 4.5). This increasing trend in metal concentrations can be attributed to the increase in fine grained particles and organic content of the sediments in a landward direction. All metals exhibited highly significant correlations with TOC, mud and Fe ($p < 0.01$), Table A4, Appendix 2, indicating that metal distribution along the estuary may have been controlled by grain size, organic content and formation of Fe-oxides.

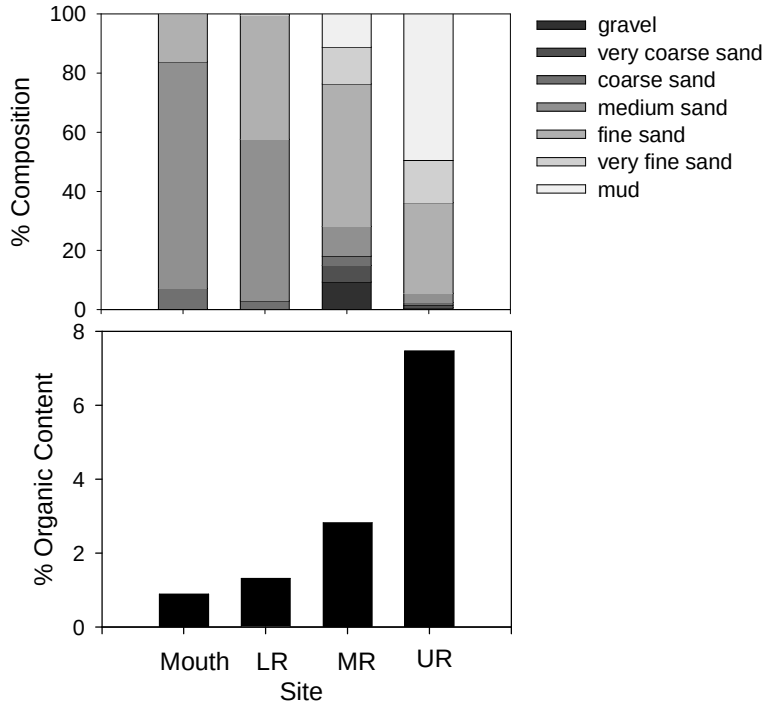

Figure 4.11: Grain size composition and organic content of the sediments at four sites along the Kasouga Estuary. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

TABLE 4.5
Mean (± SD) concentrations of metals (mg·kg^{-1}, dry wt.) in the sediments along the Kasouga Estuary

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
Marine	0.26^{a} (± 0.61)	0.45^{a} (± 0.03)	0.47^{a} (± 0.27)	1313^{a} (± 33)	<DL	3.55^{a} (± 0.25)	<DL
LR	0.16^{a} (± 0.01)	0.50^{a} (± 0.09)	<DL^{a}	1325^{a} (± 66)	0.07^{a} (± 0.10)	2.90^{a} (± 0.04)	<DL
MR	0.66^{a} (± 0.14)	3.72^{b} (± 0.66)	0.27^{a} (± 0.25)	5726^{b} (± 1207)	3.94^{b} (± 1.13)	6.58^{b} (± 0.52)	4.65^{a} (± 4.04)
UR	1.57^{b} (± 0.33)	7.76^{c} (± 1.40)	5.24^{b} (± 0.39)	12292^{c} (± 1882)	8.52^{c} (± 1.85)	11.47^{c} (± 1.56)	8.67^{a} (± 6.06)
Mean	0.71 (± 0.61)	3.34 (± 3.23)	1.63 (± 2.33)	5513 (± 4858)	3.41 (± 3.38)	6.42 (± 3.62)	3.63 (± 5.01)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$). n = 12

Principal component analysis was applied to 14 variables (7 metals, TOC and 5 grain size fractions) and 11 samples from the Kasouga Estuary. Two principal components were identified that explained 92.95 % of the cumulative variance (Table 4.6). A plot of variable loadings for component 1 and component 2 clearly shows the strong association between metals, TOC and mud content of the sediments (Fig. 4.12). The first principal component accounts for 80.19 % of the variance and has substantially high positive loadings for all 7 metals, TOC, very fine sand and mud. Principal component 2 (19.28 % of total variance) has a high loading for the fine sand fraction and does not appear to influence the concentration of metals. Principal component analysis thus reveals that the concentrations of metals in the Kasouga Estuary had a strong relationship to grain size and organic content of the sediments.

TABLE 4.6
Principal component loadings for metal concentrations and sediment characteristics in the Kasouga Estuary

	Component 1 (80.19 %)*	**Component 2 (19.28 %)***
Cd	**0.98**	-0.17
Co	**0.99**	-0.08
Cu	**0.89**	-0.37
Fe	**0.99**	-0.07
Ni	**0.99**	-0.07
Pb	**0.99**	-0.10
Zn	**0.85**	-0.06
TOC (%)	**0.98**	-0.16
Coarse sand	**-0.78**	-0.39
Medium sand	**-0.87**	-0.46
Fine sand	0.20	**0.97**
Very fine sand	**0.86**	0.34
Mud	**0.95**	-0.18

Note: Loadings greater than ± 0.7 are in bold and indicate substantially high relationships between the variable and principal component.
*Percentage total variance.

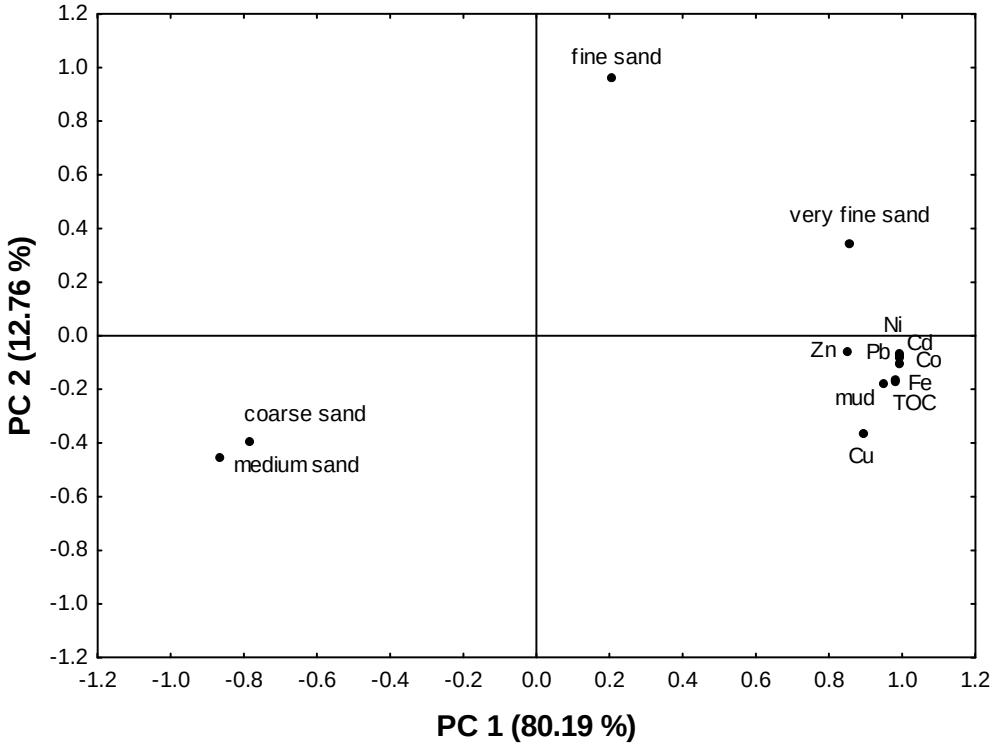

Figure 4.12: Principal component loading scatter plot (PC 1 *vs.* PC 2) for variables measured in Kasouga Estuary sediments.

Enrichment of metals within the Kasouga Estuary sediments was assessed by superimposing metals concentrations onto metal *vs.* Fe linear regression plots for baseline data (Fig. 4.13). Again, samples that fell above the 95 % prediction limits of the models were considered to be enriched with metals relative to baseline studies. The only metal that showed any degree of enrichment was Co (Fig. 4.13 A). The concentrations of all other metals fell within the 95 % prediction limits of the models (Figs. 4.13 B to 4.13 E).

Spatial variation in enrichment factors was investigated by plotting enrichment factors (EFs) against sampling sites Fig. 4.14. The Cd, Co, Ni and Pb plots display similar spatial trends, with enrichment increasing significantly from the marine environment to the upper reaches of the estuary ($p < 0.05$). The Kasouga Estuary was moderately enriched with Cd (EF > 1), with the average (± SD) enrichment factors for Cd being 2.02 (± 1.64). Average (± SD) enrichment factors for all other metals were: Co 0.73 (± 0.54), Cu 0.22 (± 0.27), Ni 0.38 (± 0.29), Pb 0.65 (± 0.19) and Zn (0.14 ± 0.17). The average

EFs for Co, Cu, Ni, Pb and Zn were thus below 1, indicating little or no enrichment. Since sediments were mostly enriched with Cd it is possible that a fraction of Cd originated from an anthropogenic source such as road runoff or degradation of phosphate fertilizers. It is important to note that Cd enrichment factors were not normalized for grain size due to the fact that Cd *vs.* Fe linear regression models could not be constructed (Chapter 3). Calculation of Cd / Fe ratios revealed that normalized Cd distribution actually decreased significantly in a landward direction ($p < 0.05$), possibly indicating input of Cd from a marine source.

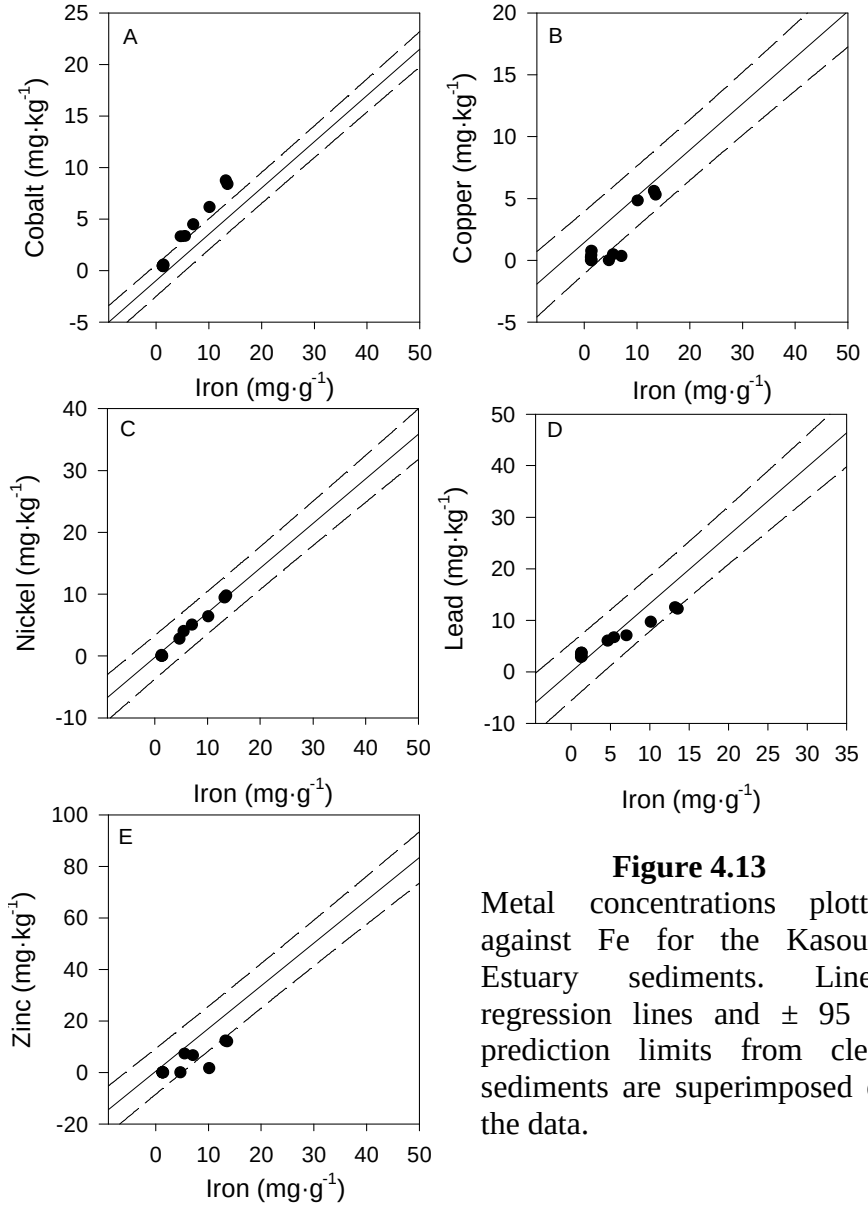

Figure 4.13
Metal concentrations plotted against Fe for the Kasouga Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

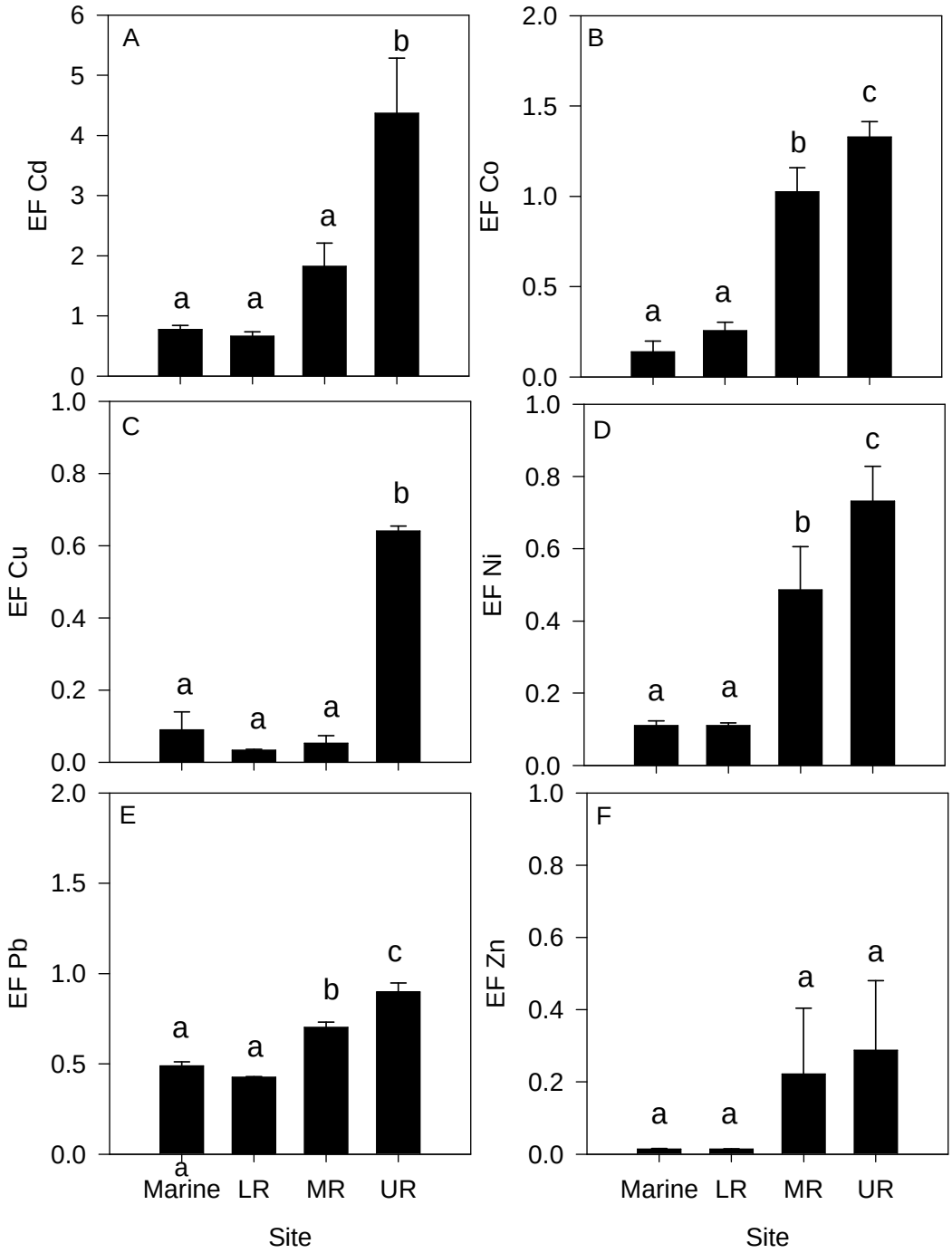

Figure 4.14: Spatial variation in the mean (± SD) enrichment factors for metals in the Kasouga Estuary sediments. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

Water

The salinity of the Kasouga Estuary decreased steadily from approximately 36 psu at the mouth to approximately 25 psu in the upper reaches. The spatial distribution in the concentrations of Cd and Pb in the water of the Kasouga Estuary can be seen in Fig. 4.15. The concentrations of Cd and Pb were homogenous from the mouth to the upper reaches of the estuary, with no significant differences in concentrations being observed between sites ($p < 0.05$). The mean concentrations of both Cd (0.07 ± 0.03 µg·ℓ$^{-1}$) and Pb (0.75 ± 0.27 µg·ℓ$^{-1}$) were below the DWAF recommended guidelines for coastal and marine waters and the Kasouga Estuary was therefore uncontaminated with these metals.

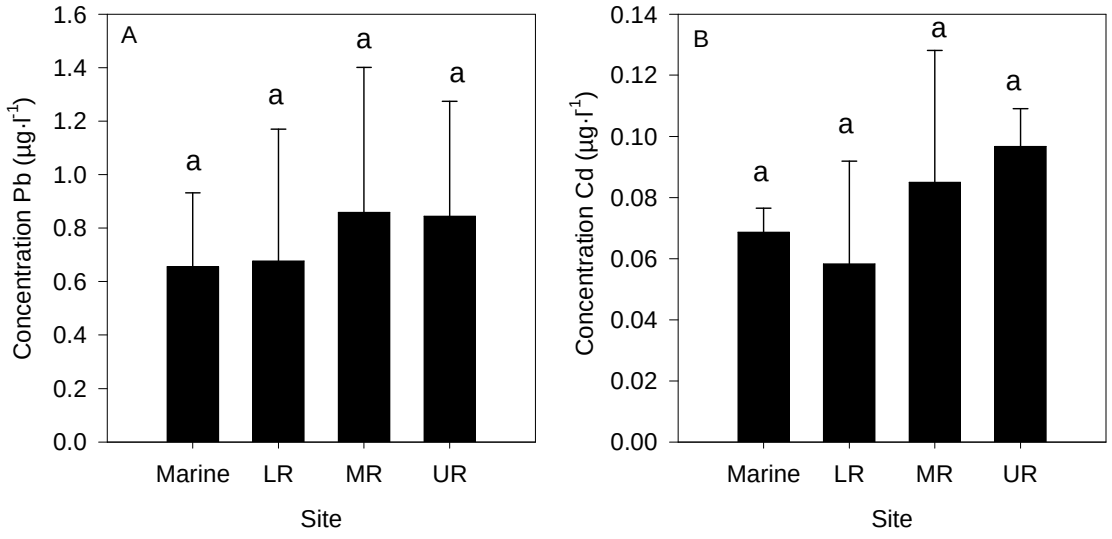

Figure 4.15: variations in the concentrations (mean ± SD) of Cd and Pb in the water of the Kasouga Estuary. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

4.2.4 BOKNES ESTUARY

Sediment Characteristics

The sediment at the mouth and lower reaches of the Boknes Estuary were dominated by medium sands, while the sediments of the middle and upper reaches were composed mainly of fine grained sands (Fig. 4.16). There was very little difference in particle size distribution between the middle and upper reaches of the estuary. No mud (< 63 µm grain

size) was present in the sediment at the sites located at the mouth and lower reaches of the estuary. The percentage of organic matter in the sediments increased from the mouth of the estuary to the upper reaches, although all sites had relatively low organic content (range: 0.7 % – 4.2 %).

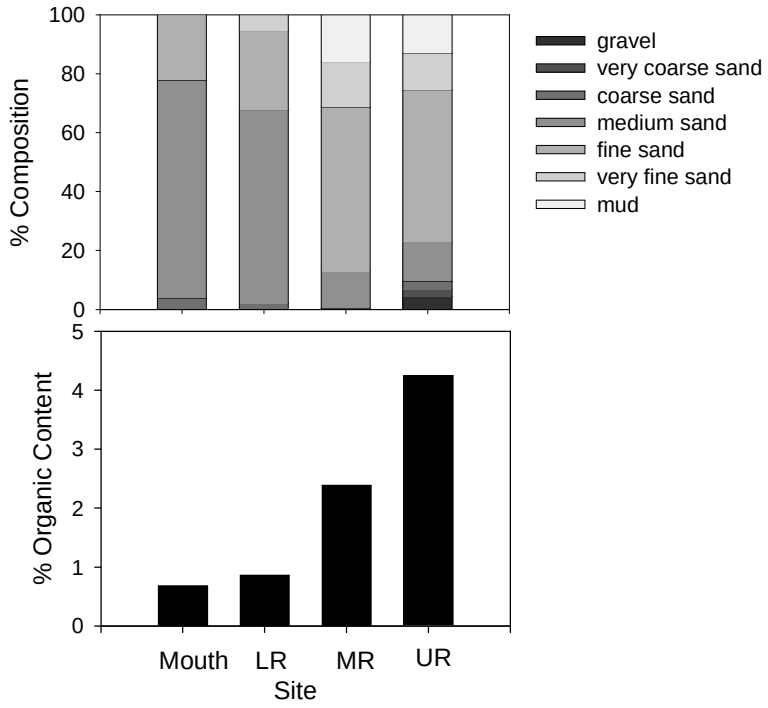

Figure 4.16: Grain size composition and organic content of the sediments from the Boknes Estuary during open and closed mouth phases. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

Metals in Sediment

The absolute concentration of metals in the sediments along the length of the Boknes Estuary can be seen in Table 4.7. The concentrations of all metals (except Zn) were significantly higher in the upper reaches than at the other sampling sites ($p < 0.05$). There were no spatial variations in metal concentrations between the marine, lower and middle reaches of the estuary. The significant increase in metals in the upper reaches reflects the increase in organic content of the sediment, as well as the increase in fine grained particles.

TABLE 4.7
Mean (± SD) concentrations of metals (mg·kg^{-1}, dry wt.) in the sediments along the Boknes Estuary

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
Marine	0.26^{a} (± 0.02)	0.00^{a} (± 0.00)	0.78^{a} (± 1.02)	1350^{a} (± 47)	<DL	3.82^{a} (± 0.56)	<DL
LR	0.21^{a} (± 0.02)	0.03^{a} (± 0.03)	0.58^{a} (± 0.20)	1482^{a} (± 67)	0.38^{a} (± 0.65)	4.01^{ab} (± 0.58)	<DL
MR	0.36^{a} (± 0.28)	1.16^{a} (± 1.20)	1.73^{a} (± 1.51)	2737^{a} (± 1844)	2.24^{a} (± 1.70)	4.06^{ab} (± 2.13)	27.4^{a} (± 32.8)
UR	0.89^{b} (± 0.11)	3.83^{b} (± 0.57)	6.52^{b} (± 1.80)	6835^{b} (± 880)	6.56^{b} (± 0.76)	7.36^{b} (± 1.44)	26.0^{a} (± 25.0)
Mean	0.43 (± 0.31)	1.26 (± 1.72)	2.40 (± 2.75)	3101 (± 2480)	2.30 (± 2.85)	4.81 (± 1.92)	13.3 (± 22.5)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$). n = 12

Principal component analysis was applied to the matrix of 14 features (7 metals, TOC and 5 grain size fractions) and 12 samples of the Boknes Estuary sediments to assess the relationship between variables. Three components were extracted that described 91.12 % of the variance in the data (Table 4.8). Loadings of between ± 0.7 and ± 1.0 indicated substantially high relationships. The first principal component (accounting for 62.2 % of the variance) had a good positive relationship with Cd, Co, Cu, Fe, Ni, Pb, TOC and mud and had a high negative loading for the medium-sized sand fraction. The interrelations among elements and sediment properties are clearly depicted in projections of components 1 and 2 (Fig. 4.17). It is thus evident that there was a strong positive relationship between metals, fine grained sediments and TOC in the Boknes Estuary. The loadings for grain size and PC 1 become progressively larger as grain size decreased, indicating the increased adsorptive capacity of smaller particles.

Component 2 (19.2 % total variance) had a large positive loading for the coarse sand fraction and accounted for very little of the variation in metal concentrations. Principal component 3 (9.63 % of total variance) exhibited a substantially high positive relationship with Zn and a positive moderate relationship with mud. The contribution of Zn to two different features (principal components) indicated that Zn had two sources of variation. Since the Zn is uncorrelated to any other metals on PC 3 it is possible that some of the Zn in the Boknes Estuary is from anthropogenic sources. It is also probable that PC 3 accounts for an artifact of measurement such as contamination of Zn within samples.

TABLE 4.8
Principal component loadings for metals and sediment characteristics in the Boknes Estuary

	Component 1 (62.21 %)*	Component 2 (19.28 %)*	Component 3 (9.63 %)*
Cd	**0.94**	0.28	-0.08
Co	**0.97**	0.15	-0.15
Cu	**0.88**	0.23	-0.24
Fe	**0.95**	0.21	-0.13
Ni	**0.86**	0.40	-0.17
Pb	**0.85**	0.33	0.15
Zn	0.57	-0.20	**0.72**
TOC (%)	**0.96**	0.03	0.02
Coarse sand	-0.09	**0.93**	0.05
Medium sand	**-0.82**	0.53	0.15
Fine sand	0.39	-0.67	-0.54
Very fine sand	0.67	-0.59	0.14
Mud	**0.78**	-0.22	0.50

Note: Loadings greater than ± 0.7 are in bold and indicate substantially high relationships between the variable and principal component.
*Percentage total variance.

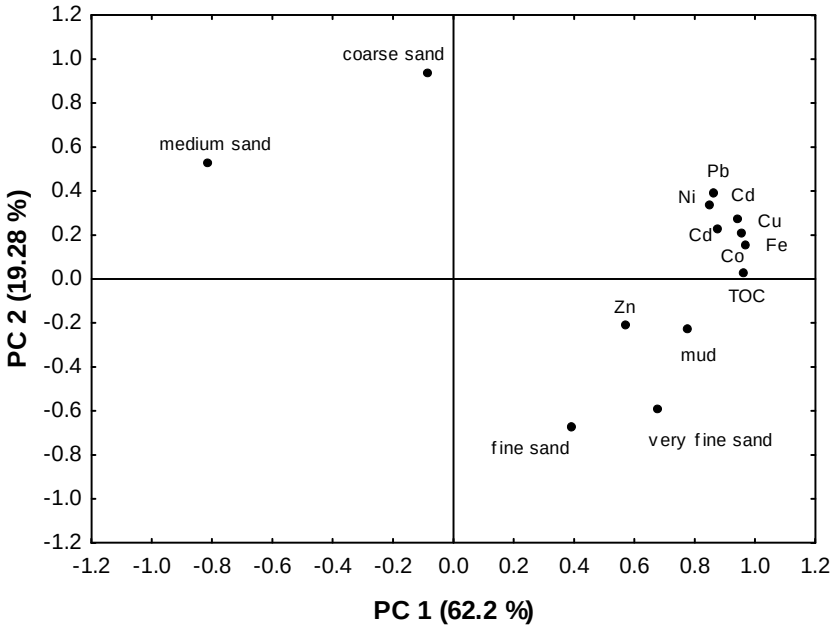

Figure 4.17: Principal component loading scatter plots (PC 1 *vs.* PC 2) for variables measured in Boknes Estuary sediments.

Enrichment of metals within sediment samples was assessed by superimposing metal concentrations on the metal *vs.* Fe regression plots for regional baseline concentrations. The samples that fell above the 95 % prediction limit for the model were considered to be enriched with metals. Figs. 4.18 A, 4.18 C and 4.18 D show that all samples fell within the 95 % prediction limits for Co, Ni and Pb, indicating no enrichment of these metals within the Boknes Estuary sediments. Several samples were enriched with Cu and Zn (Figs. 4.18 B and 4.18 E) in the upper reaches of the Boknes Estuary, which may suggest anthropogenic input of these metals.

The distribution of metals in the sediments of the estuary was assessed by calculating enrichment factors (EFs) for each metal at each site. This removed any interference that may occur in the interpretation of metal distribution due to variations in grain size. Please note that Cd enrichment was not normalized for grain size (see Chapter 3). The EFs for each site can be seen in Figs. 4.19 A to 4.19 F. There was no significant variation ($p > 0.05$) in the distribution of Ni, Pb and Zn along the length of the Boknes Estuary (Figs. 4.19 D, 4.19 E and 4.19 F). The enrichment factors for Cd, Co and Cu (Figs. 4.19 A, 4.19 B and 4.19 C) were significantly higher in the upper reaches of the estuary ($p < 0.05$), likely due to the high organic content of the sediments at this site which may have led to the accumulation of these metals. Cadmium concentrations were normalized for grain size by calculating Cd / Fe ratios. Although not shown, there was no significant spatial variation in normalized Cd concentrations along the Boknes Estuary ($p > 0.05$).

The mean (± SD) EFs for each metal were; Cd 1.19 (± 0.86), Co 0.53 (± 0.34), Cu 0.42 (± 0.41), Ni 0.29 (± 0.16), Pb 0.68 (± 0.16) and Zn 0.78 (± 1.20). On average, the Boknes Estuary sediments were un-enriched with all metals except Cd, which exhibited minor enrichment, and Cu and Zn which exhibited minor enrichment in the upper reaches of the estuary.

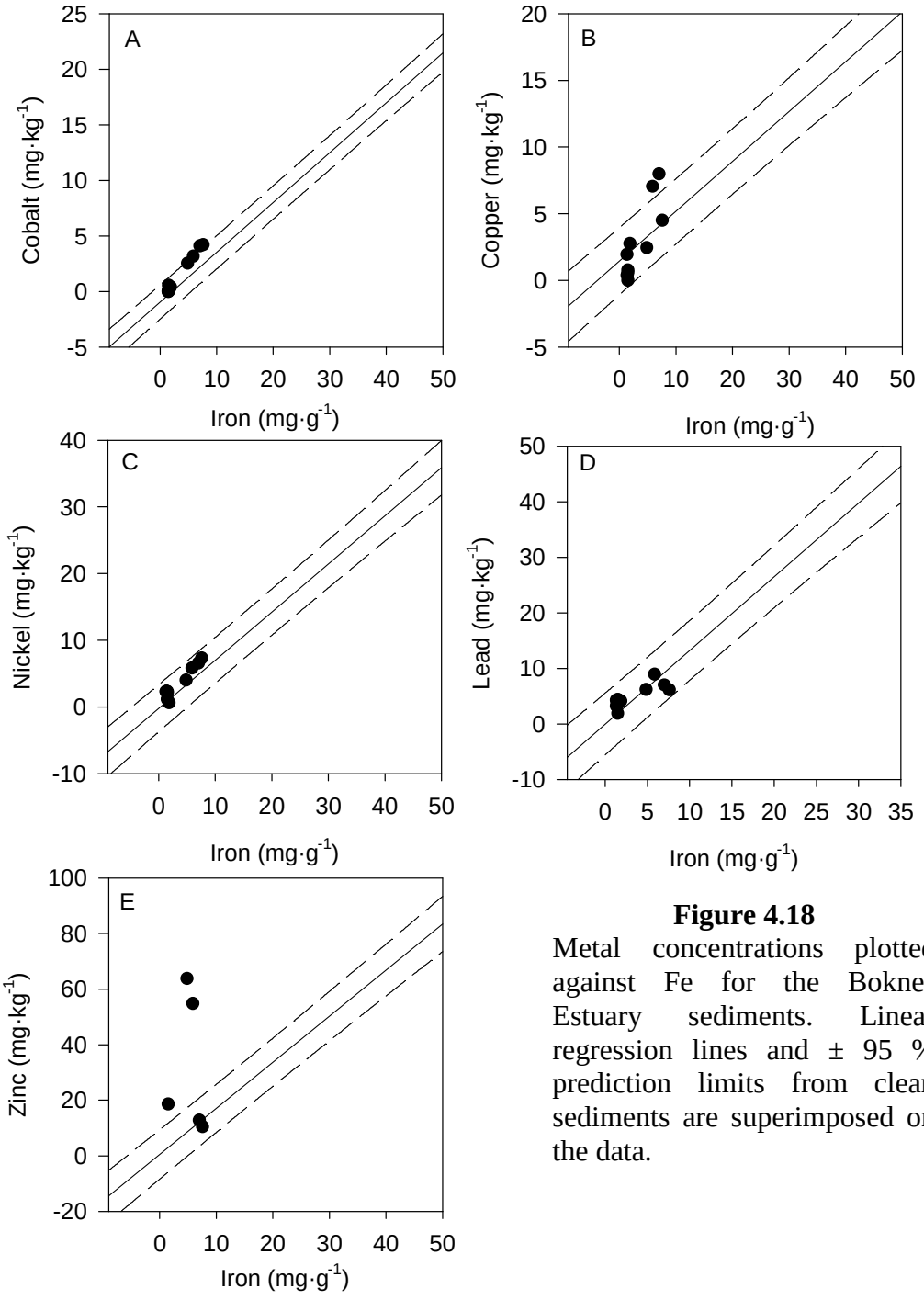

Figure 4.18
Metal concentrations plotted against Fe for the Boknes Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

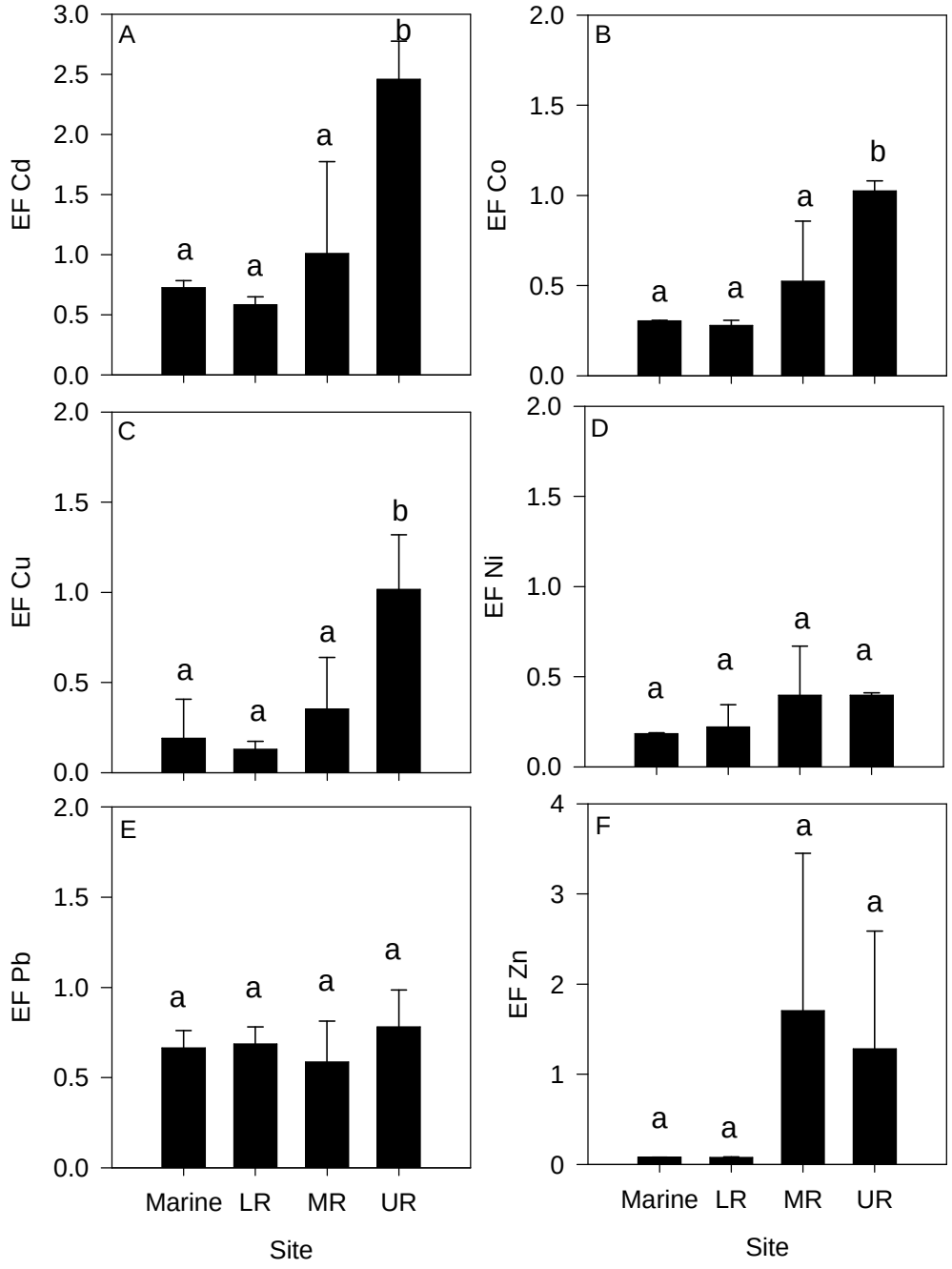

Figure 4.19: Spatial variation in the mean (± SD) enrichment factors for metals in the Boknes Estuary sediments. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

Water

The average (± SD) concentrations Pb and Cd in the water of the Boknes Estuary were 0.76 ± 0.51 µg·ℓ$^{-1}$ and 0.09 ± 0.05 µg·ℓ$^{-1}$, respectively. These values fall well below the DWAF recommended guidelines for coastal and marine waters and thus the water of the Boknes Estuary was uncontaminated at the time of sampling. The spatial distribution of Pb and Cd in the Boknes Estuary is represented in Fig. 4.20. There was no significant variation in the concentrations of Pb and Cd in the water along the Boknes Estuary ($p > 0.05$), probably due to the fact that the estuary is small and well mixed.

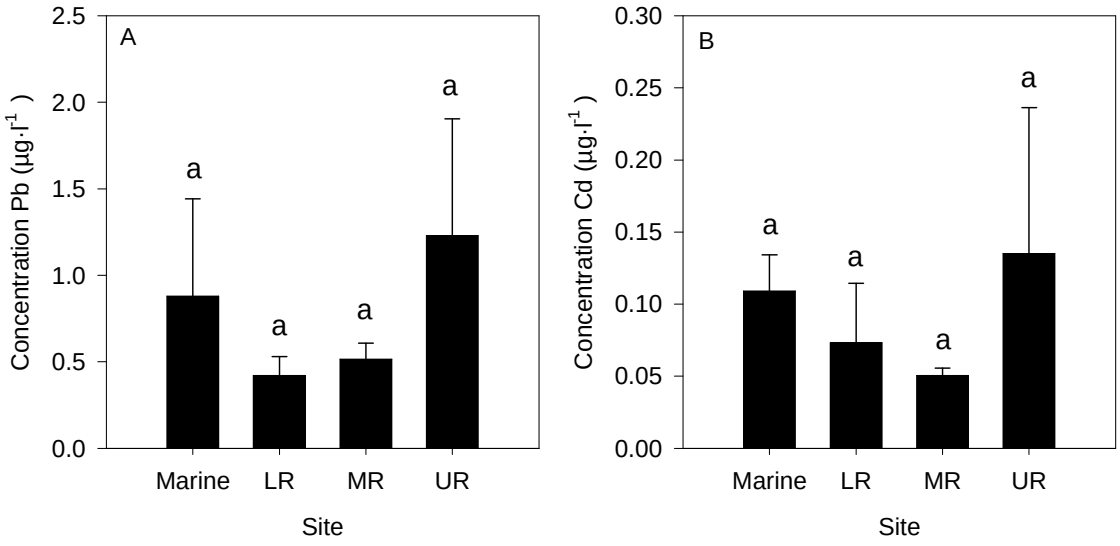

Figure 4.20: Variations in the concentrations (mean ± SD) of Cd and Pb in the water of the Boknes Estuary. Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches).

4.3 PERMANENTLY OPEN ESTUARIES

4.3.1 GREAT FISH ESTUARY

Sediment Characteristics

The sediments from Great Fish Estuary comprised mainly very fine grained sands and mud (Fig. 4.21). The percentage of fine grained sediments increased from the mouth (site

F1) of the estuary to the upper reaches (site F6). The sediments from sites F4 to F6 were comprised mainly of mud. The percentage organic content in the sediments reflected the distribution of mud, with the greatest percentage of organic content being located at site F6 (Fig. 4.21).

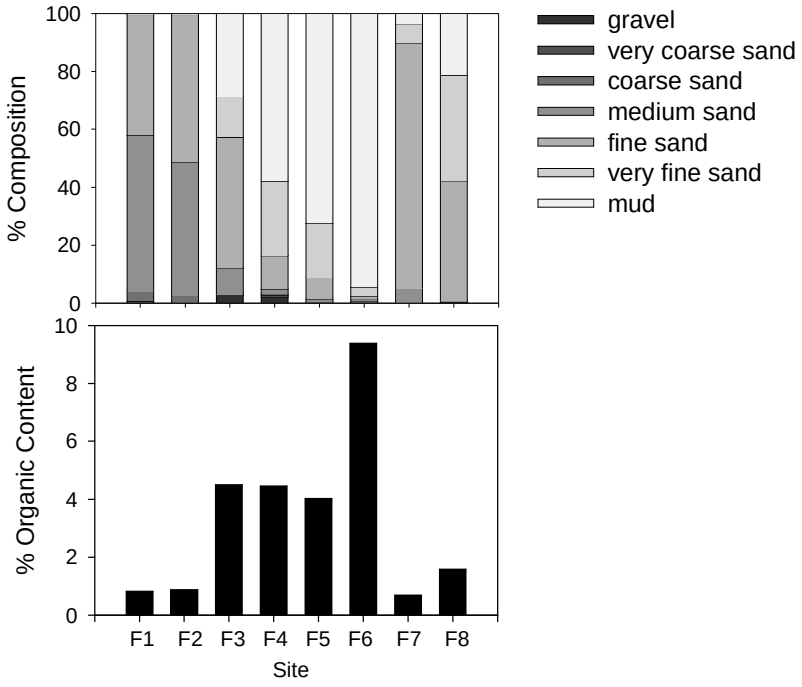

Figure 4.21: Grain size composition and organic content of the sediments at eight sites (F1 to F8) along the Great Fish Estuary.

Metals in Sediments

The absolute concentrations of metals in the Great Fish Estuary sediments are shown in Table 4.9. Significant spatial variation was observed in the concentrations of all metals ($p < 0.05$). Two overriding trends were observed in the concentrations of metals along the estuary. The first was the landward increase in Co, Cu, Fe, Ni and Zn. These metals were significantly correlated to TOC and mud (Table A6, Appendix 2) indicating that the elevated concentrations corresponded to an increase in fine grained particles (mud) and organic content of the sediments. The second trend was the seaward increase in the concentrations of Cd and Pb. Both Cd and Pb were uncorrelated to the fine grained particles and organic content of the sediments, but were significantly correlated to each other ($R = 0.71$, $p < 0.01$). This may suggest that Cd and Pb were from a common source.

TABLE 4.9
Mean (± SD) concentrations of metals (mg·kg^{-1}, dry wt.) in the sediments along the Great Fish Estuary

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
F 1 (marine)	1.20^{a} (± 0.10)	1.11^{a} (± 0.43)	0.78^{a} (± 0.40)	1036^{ad} (± 116)	6.82^{ab} (± 0.71)	19.13^{a} (± 2.35)	5.33^{a} (± 1.19)
F 2	0.50^{bc} (± 0.26)	2.48^{ac} (± 2.11)	0.48^{a} (± 0.22)	700^{a} (± 304)	4.37^{a} (± 0.89)	8.18^{b} (± 4.81)	5.10^{a} (± 1.46)
F 3	0.98^{ab} (± 0.06)	4.75^{ac} (± 1.13)	4.52^{b} (± 2.18)	2730^{ad} (± 578)	9.32^{b} (± 3.16)	7.63^{bc} (± 1.64)	13.79^{a} (± 0.19)
F 4	0.57^{bc} (± 0.01)	5.44^{bc} (± 1.31)	8.31^{c} (± 1.07)	9717^{b} (± 3942)	11.01^{bc} (± 1.33)	4.24^{bc} (± 1.42)	17.76^{a} (± 0.92)
F 5	0.67^{abc} (± 0.17)	6.02^{bc} (± 2.06)	8.27^{c} (± 0.82)	8123^{bd} (± 468)	13.79^{c} (± 1.87)	5.03^{bc} (± 0.38)	48.26^{b} (± 10.34)
F 6	0.83^{ab} (± 0.34)	8.77^{b} (± 0.84)	15.78^{d} (± 0.57)	14106^{c} (± 1432)	19.78^{d} (± 0.74)	10.19^{b} (± 1.93)	49.48^{b} (± 4.93)
F 7	0.25^{c} (± 0.12)	3.67^{ac} (± 0.98)	3.01^{ab} (± 1.12)	4781^{ad} (± 549)	8.01^{abc} (± 1.96)	1.38^{c} (± 1.55)	16.98^{a} (± 7.27)
F 8 (upper)	0.31^{c} (± 0.06)	5.10^{bc} (± 1.08)	5.32^{ab} (± 0.43)	5212^{d} (± 347)	8.28^{abc} (± 1.56)	3.54^{bc} (± 1.44)	14.52^{a} (± 2.21)
Mean	0.65 (± 0.32)	4.67 (± 2.49)	5.81 (± 4.85)	5801 (± 4592)	10.38 (± 4.77)	7.41 (± 5.60)	21.41 (± 17.33)
Great Fish 1988*	0.30 (± 0.36)	3.1 (± 1.9)	5.0 (± 2.0)	8712 (± 3994)	7.5 (± 4.1)	7.6 (± 2.3)	26.5 (± 12.3)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$). n = 24. * Watling (1988)

Principal component analysis (PCA) was used to reduce the dimensionality of the data and to identify 'latent' variables (Meglen, 1992). Principal component analysis was applied to the raw metal concentrations, grain size data and organic content of the sediments (13 variables in total). Two principal components were extracted that account for 79.33 % of the variance in the data. The composition of the principal components, referred to as 'loadings' is reported in Table 4.10 and is plotted in Fig. 4.22. The first principal component includes positive contributions of Co, Cu, Fe, Ni, Zn, TOC and mud, and thus PC 1 is likely to represent the natural variation in metal concentrations. The second principal component is made up of positive contributions from both Cd and Pb and the large grained sands, and Pb and Cd were thus associating with the sediments found predominantly at the mouth of the estuary. Component 2 is thus likely to represent an alternative source of metals (possibly anthropogenic).

TABLE 4.10
Principal component loadings for metal concentrations and sediment characteristics in the Great Fish Estuary

	Component 1 (56.92 %)*	Component 2 (22.41 %)*
Cd	0.01	**0.82**
Co	**0.88**	-0.07
Cu	**0.96**	0.16
Fe	**0.93**	0.06
Ni	**0.91**	0.24
Pb	-0.31	**0.86**
Zn	**0.86**	0.14
TOC (%)	**0.78**	0.35
Coarse sand	-0.66	0.63
Medium sand	**-0.75**	0.52
Fine sand	**-0.72**	-0.44
Very fine sand	0.36	-0.60
Mud	**0.96**	0.22

Note: Loadings greater than ± 0.7 are in bold and indicate substantially high relationships between the variable and principal component.
*Percentage total variance.

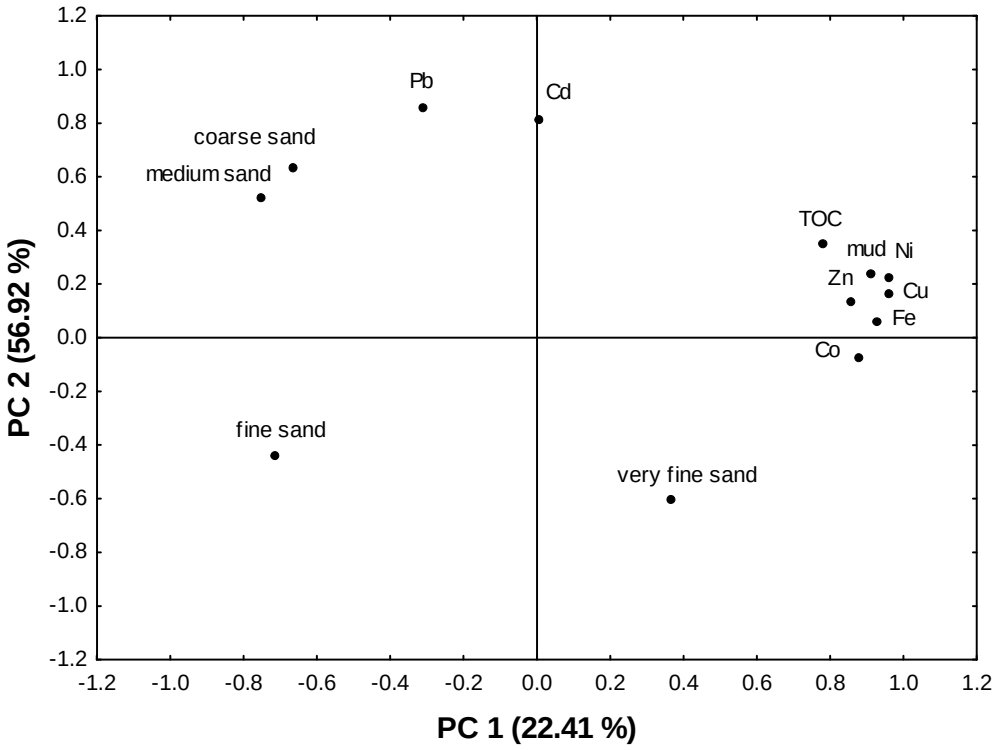

Figure 4.22: Principal component loading scatter plot (PC 1 *vs.* PC 2) for variables (metals, TOC, grain size) measured in Great Fish Estuary sediments.

Metal concentrations were plotted against Fe for the Great Fish Estuary sediments, on top of which baseline metal *vs.* Fe regression plots were superimposed (Fig. 4.23). All samples that fell above the 95 % prediction limits for the models were considered to be enriched with metals relative to baseline concentrations. One can clearly see that the sediments were extensively enriched with Co and Ni (Figs. 4.23 A and 4.23 C), while fewer samples were enriched with Cu, Pb and Zn (Figs. 4.23 B, 4.23 D and 4.23 E). Although not shown in Fig. 4.23., the samples that were enriched with Zn and Cu were collected at sites F5 and F6. The sediments from these sites also had the highest mud and organic matter content of all sites, which may have led to the accumulation of Cu and Zn.

Enrichment factors were calculated in order to quantify the degree of metals enrichment since baseline studies were conducted in 1983 (Watling and Watling, 1983a). The mean (± SD) enrichment factors for metals in the Great Fish Estuary sediments were; Cd 1.81 (± 0.90), Co 1.87 (± 2.03), Cu 0.84 (± 0.54), Ni 1.41 (± 0.32), Pb 1.03 (± 1.07) and Zn 0.98 (± 0.56). Thus, on average the Great Fish Estuary sediments were unenriched with Cu, Pb and Zn ($EF \leq 1$), and they were moderately enriched with Cd, Co and Ni ($1 < EF < 2$).

The spatial variation in enrichment factors is shown in Fig. 4.24. One can clearly see from Fig. 4.24B and 4.24E that Co and Pb enrichment was significantly higher in the marine sediments (sites F1 to F3) than the middle and upper reaches of the estuary ($P < 0.05$). The significantly higher enrichment of Co, and Pb in the marine environment and lower reaches of the Great Fish could be linked to runoff from the national road that crosses the estuary in the lower reaches, as well a the atmospheric deposition of the metals from combusted fuels. Cadmium enrichment also decreased significantly ($P < 0.05$) from the mouth to the upper reaches of the estuary, but the enrichment gradient was less clearly defined than for Co and Pb. It is important to note that Cd enrichment was calculated without normalizing for grain size (see Chapter 3), and thus Fig. 4.24 A does not show the normalized Cd distribution. Calculation of the Cd / Fe ratios revealed that normalized Cd concentrations were significantly higher at the mouth as compared to the rest of the estuary ($p < 0.05$). This may suggest input of Cd from the marine

environment or from road-runoff from the R 72 motorway. Copper and Zn showed significant spatial variation in metal enrichment along the estuary, with enrichment increasing significantly ($p < 0.05$) from the mouth to sites F5 and F6, and then decreasing again in a landward direction. The peak in Cu and Zn enrichment at sites F5 and F6 is likely to correspond to the increase in organic matter at these sites, since organic matter is well known to act as a binding substrate for these metals (Li *et al*., 2001).

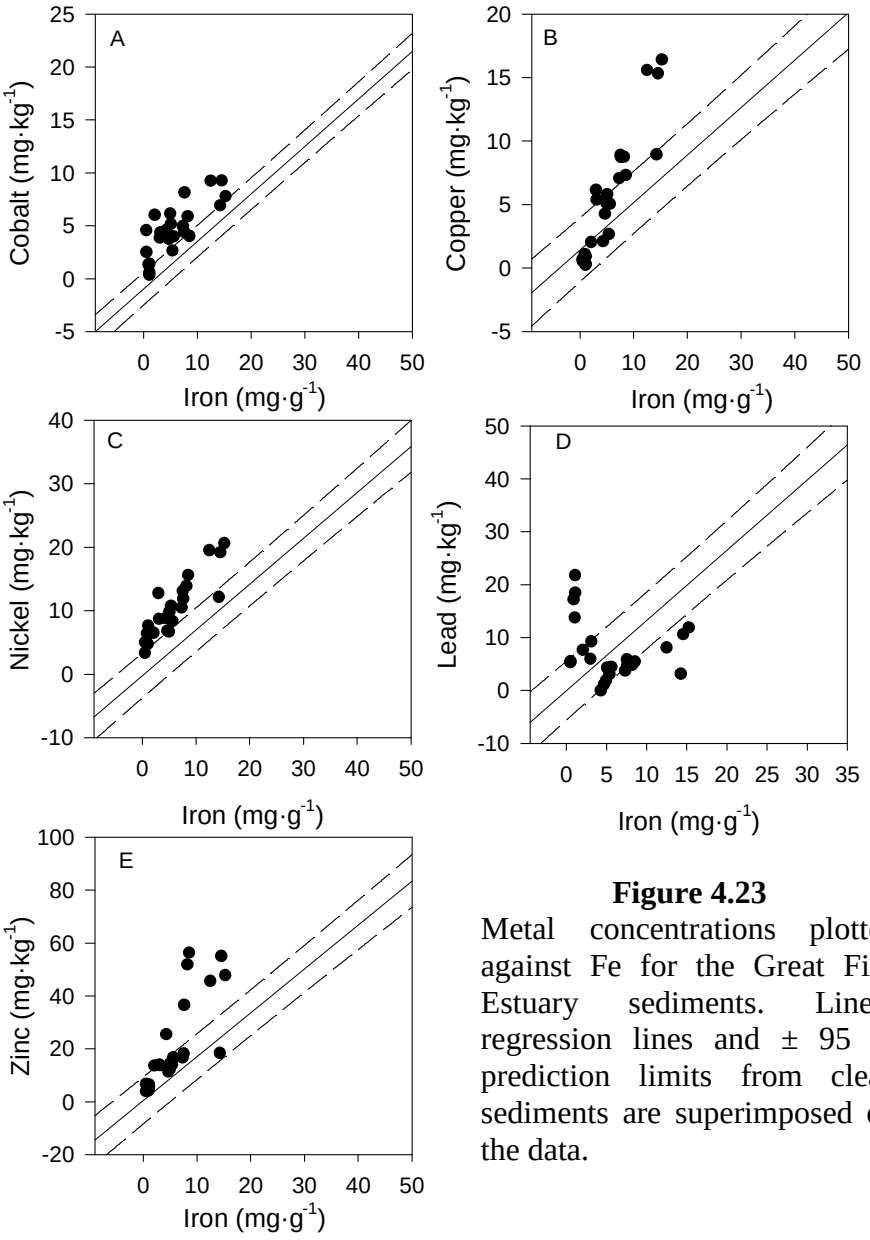

Figure 4.23
Metal concentrations plotted against Fe for the Great Fish Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

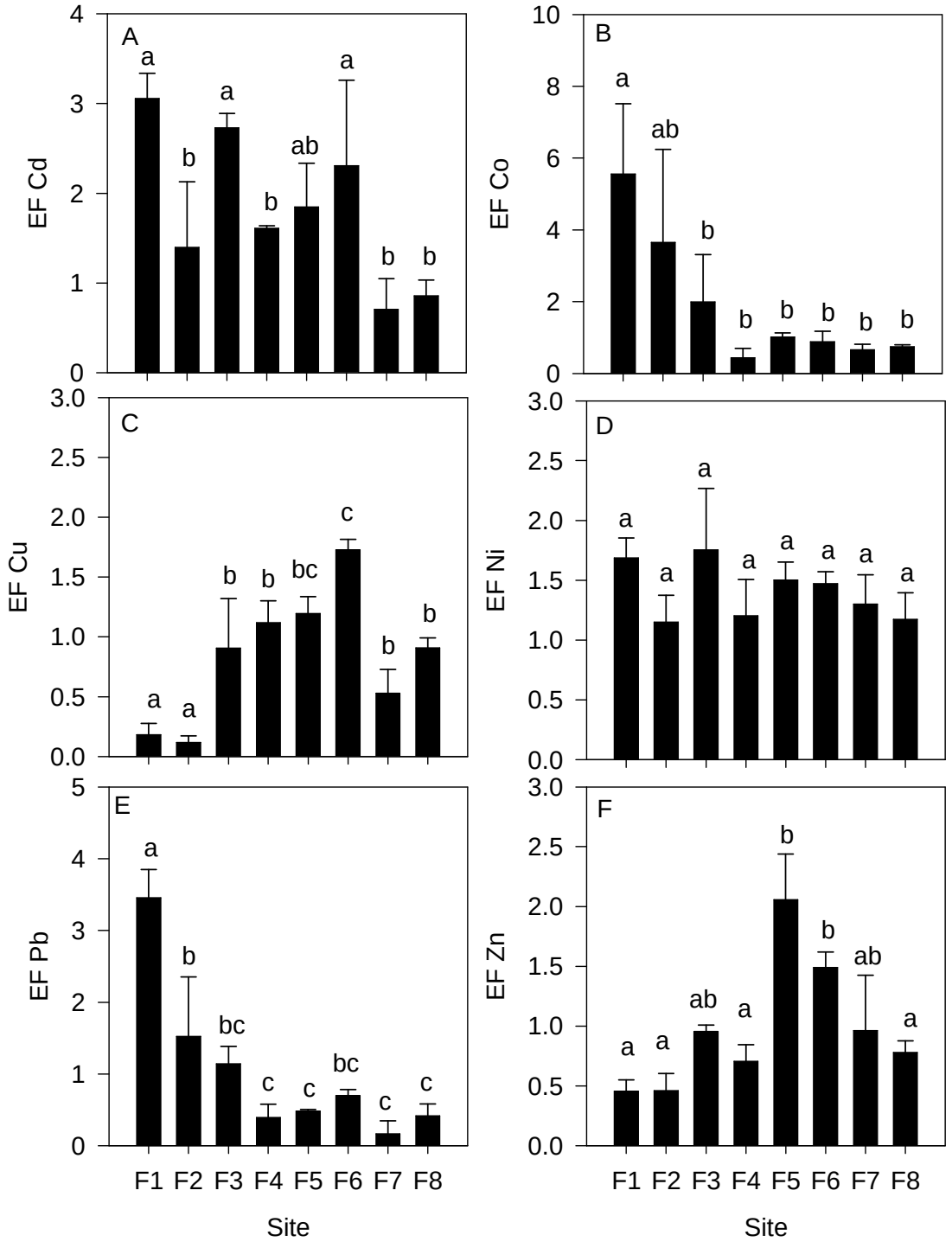

Figure 4.24: Spatial variation in the mean (± SD) enrichment factors of metals in the Great Fish Estuary sediments. Different superscript letters denote significant differences within columns ($p < 0.05$).

Water

At the time of sampling the concentration of total suspended solids (TSS) was greatest in the middle and upper reaches of the estuary (sites F4 and F6). The TSS maximum shifts depending on the rate of freshwater inflow. In this study the TSS maximum was located at site F6 (478 $mg \cdot \ell^{-1}$ suspended solids). The salinity decreased steadily from 35 psu at the mouth of the estuary to 0.5 psu at the head, with oligohaline conditions being observed approximately 7 km from the mouth.

The average (± SD) concentrations of Cd and Pb in the water of the Great Fish Estuary were 0.13 (± 0.09) $\mu g \cdot \ell^{-1}$ and 2.81 (± 1.74) $\mu g \cdot \ell^{-1}$, respectively. These concentrations were below the South African recommended water quality guidelines for coastal and marine waters and thus the water of the Great Fish Estuary was uncontaminated with Cd and Pb. The concentration of Pb varied significantly along the length of the estuary ($p < 0.05$), exhibiting a general landward increase that corresponded to an increase in the concentration of total suspended solids (TSS) in the water (Fig. 4.25 A). A significant positive correlation thus existed between Pb and TSS ($R = 0.89$; $p < 0.01$). There was no significant spatial variation in the concentration of Cd along the Great Fish Estuary ($p > 0.05$), as can be seen in Fig. 4.25B.

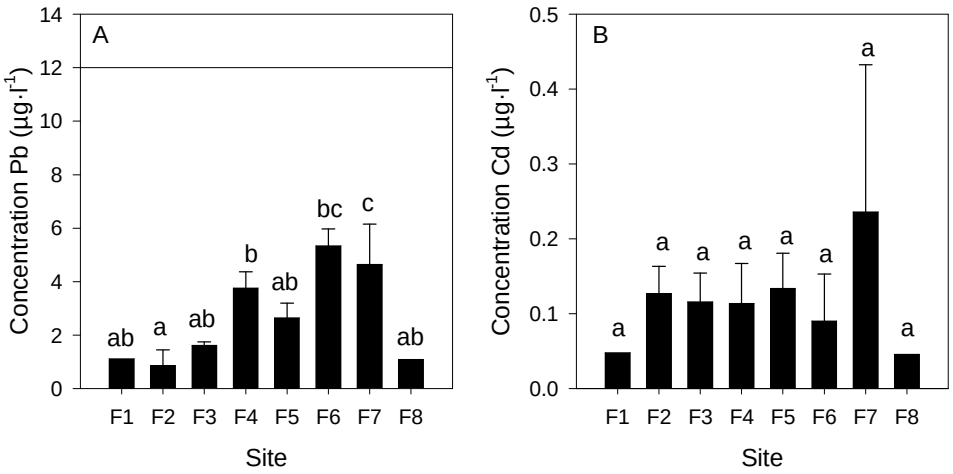

Figure 4.25: Spatial variations in the mean (± SD) concentrations of Pb and Cd in the water of the Great Fish Estuary. *Note:* horizontal bar denotes South African water quality guideline value for Pb. Different superscript letters denote significant differences within columns ($p < 0.05$).

4.3.2 KOWIE ESTUARY

Sediment Characteristics

At the time of sampling, the sediments of the Kowie Estuary were mainly composed of fine and medium grained sands and there was little variation in grain size along the length of the estuary (Fig. 4.26). The percentage organic content was generally highest in the middle and upper reaches of the estuary (sites P4 to P7), but remained fairly low throughout the estuary (range: 1 – 7 %).

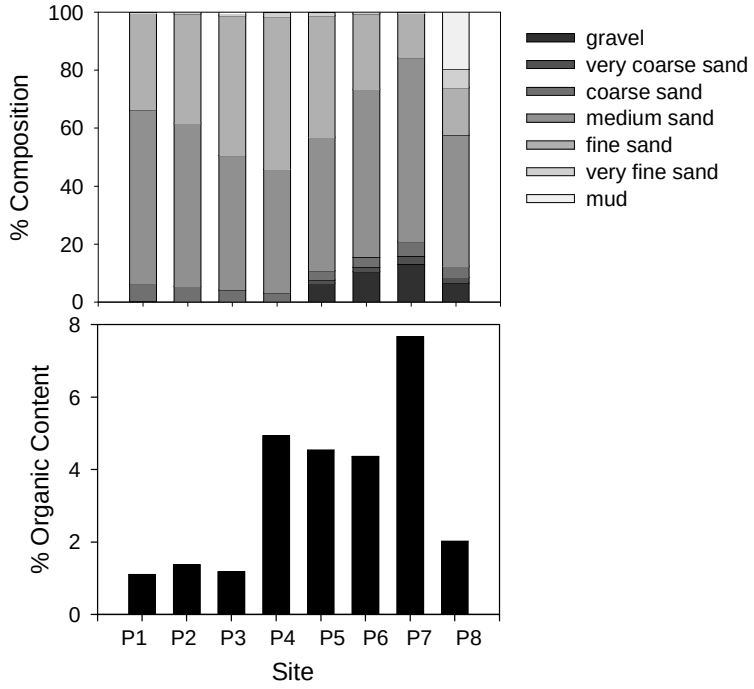

Figure 4.26: Grain size composition and organic content of the sediments at eight sites (P1 to P8) along the Kowie Estuary.

Metals in Sediment

The average concentrations of metals at sites along the Kowie Estuary can be seen in Table 4.11. The concentrations of all metals increased significantly from the marine environment (site P1) to the upper reaches (site P7) of the estuary ($p < 0.05$). Significant positive correlations existed between all metals, TOC and mud (Table A7, Appendix 2). The concentrations of all metals (except Cd) were noticeable lower than those reported by Watling in 1988 (Table 4.11). The average concentration of Cd in this study was

approximately 36-fold higher than the average reported for the Kowie sediments in 1988 (Watling, 1988).

TABLE 4.11
Mean (± SD) concentrations of metals (mg·kg^{-1}, dry wt.) in the sediments along the Kowie Estuary

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
P 1 (marine)	0.59^{a} (± 0.02)	0.52^{a} (± 0.02)	0.20^{a} (± 0.01)	1302^{a} (± 16)	0.66^{a} (± 0.03)	2.51^{a} (± 0.47)	1.03^{a} (± 0.02)
P 2	0.66^{a} (± 0.05)	0.53^{a} (± 0.04)	1.78^{ab} (± 2.73)	1527^{a} (± 7.7)	0.68^{ab} (± 0.05)	3.71^{ab} (± 0.50)	2.46^{a} (± 2.49)
P 3	1.51^{b} (± 0.26)	0.66^{a} (± 0.02)	3.00^{ab} (± 1.68)	3921^{b} (± 644)	2.52^{b} (± 0.99)	5.05^{bc} (± 0.99)	14.98^{ab} (± 9.92)
P 4	3.08^{c} (± 0.43)	2.93^{b} (± 2.78)	7.98^{b} (± 3.19)	7781^{c} (± 953)	5.95^{bc} (± 0.89)	5.02^{bc} (± 0.27)	16.73^{ab} (± 5.36
P 5	2.60^{c} (± 0.45)	2.79^{b} (± 0.49)	6.05^{ab} (± 2.31)	6810^{c} (± 1142)	4.93^{c} (± 0.86)	5.45^{c} (± 0.46)	7.17^{ab} (± 4.34)
P 6	2.59^{c} (± 0.22)	2.88^{b} (± 0.29)	6.06^{ab} (± 3.08)	6992^{c} (± 572)	5.30^{c} (± 0.78)	4.91^{bc} (± 0.63)	8.83^{ab} (± 6.06)
P 7	4.20^{d} (± 0.35)	4.81^{c} (± 0.35)	7.74^{b} (± 2.42)	10386^{d} (± 527)	7.85^{d} (± 0.56)	8.32^{d} (± 0.32)	21.57^{b} (± 5.27)
P 8 (upper)	2.56^{c} (± 0.34)	3.60^{b} (± 0.56)	2.56^{ab} (± 1.14)	7259^{c} (± 767)	5.78^{c} (± 0.61)	4.50^{bc} (± 0.26)	12.63^{ab} (± 7.36)
Mean	2.18 (± 1.21)	2.31 (± 1.58)	4.27 (± 3.30)	5659 (± 3140)	4.13 (± 2.60)	4.93 (± 1.68)	10.67 (± 8.35)
Kowie 1988*	0.06 (± 0.02)	17.9 (± 7.6)	16.5 (± 7.6)	32300 (± 9740)	24.4 (± 6.2)	29.8 (± 5.5)	96.0 (± 60.5)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$). n = 24.
* Watling (1988).

Principal component analysis was used to clarify the relationships between metals and sediment characteristics. Thirteen variables were subjected to PCA (7metals, grain size and TOC content) and two new 'latent' variables were extracted that explained 99.47 % of the variance in the data. The contribution of the original variables to the 'latent' variables is depicted by their loadings, as shown in Table 4.12. Principal component 1 had high positive loadings (> 0.70) for Cd, Co, Cu, Fe, Ni, Pb, TOC, very fine sand and mud. The organic content of the sediments and the particles smaller than 0.125 mm were possibly acting as binding substrates for the metals and were thus controlling their distribution. Component 2 has a high loading for the coarse sand fraction (0.50 to 1.00 mm), which showed no correlation to any of the metals and thus did not

play a role in their distribution. The strong correlations between metals and fine grained sediments is typically characteristic of uncontaminated sediments.

TABLE 4.12
Principal component loadings for metal concentrations and sediment characteristics in the Kowie Estuary

	Component 1 (80.19 %)*	Component 2 (19.28 %)*
Cd	**0.97**	0.19
Co	**0.91**	0.25
Cu	**0.86**	-0.13
Fe	**0.96**	0.23
Ni	**0.95**	0.26
Pb	**0.84**	0.11
Zn	0.66	0.40
TOC (%)	**0.95**	-0.19
Coarse sand	-0.29	**0.84**
Medium sand	**-0.86**	0.34
Fine sand	-0.31	**-0.78**
Very fine sand	**0.83**	-0.43
Mud	**0.92**	-0.30

Note: Loadings greater than ± 0.7 are in bold and indicate substantially high relationships between the variable and principal component.
*Percentage total variance.

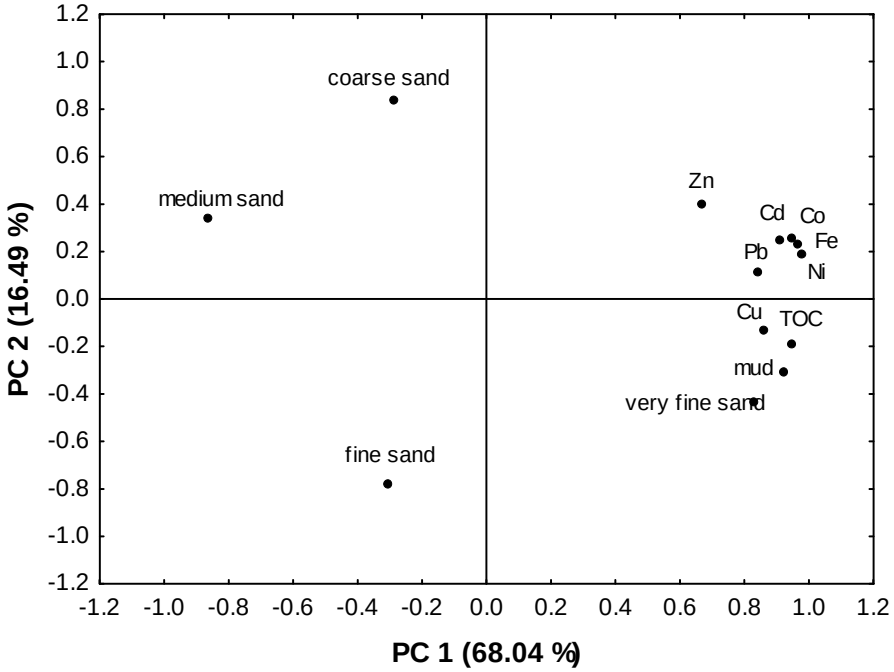

Figure 4.27: Principal component loading scatter plot (PC 1 *vs.* PC 2) for variables (metals, TOC, grain size) measured in Kowie Estuary sediments.

Metal concentrations were plotted against Fe, and baseline metal *vs.* Fe regression models were superimposed onto the plots (Fig. 4.28). As before, samples were considered to be enriched with a metal if the sample fell above the 95 % prediction limit for the model. Figs. 4.28 A, 4.28 C and 4.28 D show that the concentrations of Co, Ni and Pb from all samples fell well within the prediction limits of the models, and this indicates that the sediments were un-enriched with these metals at the time of sampling. Several samples were enriched with Cu, and Zn (Figs. 4.28 B and 4.28 E).

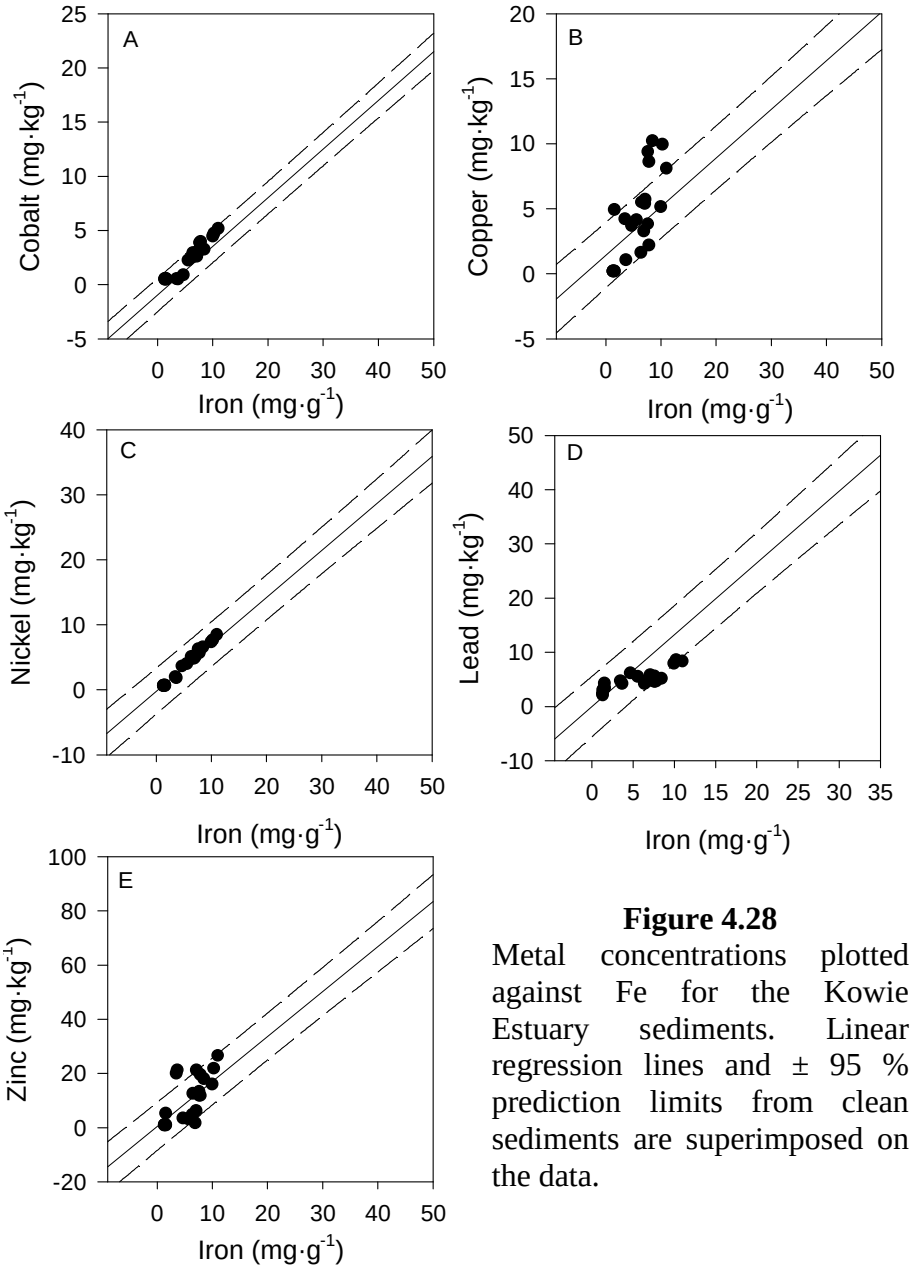

Figure 4.28
Metal concentrations plotted against Fe for the Kowie Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

Enrichment of metals within the Kowie Estuary sediments was quantified by calculating enrichment factors (EFs) for metals at each site. The spatial variation in metal enrichment is shown in Fig. 4.29. One can clearly see from Fig. 4.29 A that Cd had the highest EFs ($1 < EF < 15$), while EFs for all other metal were below 2. Cadmium, Co, Cu and Ni enrichment increased from the mouth of the estuary in a landward direction (Fig. 4.29 A to 5.29 D), while Pb and Zn did not show any obvious gradient in metal enrichment along the estuary (Fig. 4.29 E and 4.29 F). Fig. 4.29 A shows Cd enrichment values that have not been normalized for grain sized (see Chapter 3). Calculation of Cd / Fe values (Fe used as a normalizer for grain size) revealed that Cd distribution decreased significantly in a landward direction ($p < 0.05$). The average (± SD) enrichment factors for metals in the Kowie Estuary sediments were; Cd 6.20 (± 3.35), Co 0.64 (± 0.23), Cu 0.65 (± 0.23), Ni 0.50 (± 0.23), Pb 0.60 (± 0.11) and Zn 0.50 (± 0.38). Enrichment factors of less than one indicate no enrichment. The sediments of the Kowie Estuary were thus un-enriched with all metals except Cd, which exhibited moderate enrichment relative to baseline concentrations.

Water

A decreasing salinity gradient was observed along the length of Kowie Estuary from the euhaline mouth to the oligohaline upper reaches. The concentration of total suspended solids increased steadily from the mouth of the estuary up to site P4, and then decreased towards the upper reaches. The turbidity maximum zone was thus located approximately 3 km from the mouth (site P4) at the time of sampling.

The average (± SD) concentrations of Cd and Pb in the water of the Kowie Estuary were 0.18 (± 0.10) $\mu g \cdot \ell^{-1}$ and 1.65 (± 0.44) $\mu g \cdot \ell^{-1}$, respectively. These concentrations fell well below the DWAF recommended guidelines for Cd (4 $\mu g \cdot \ell^{-1}$) and Pb (12 $\mu g \cdot \ell^{-1}$), and thus the water of the Kowie Estuary was uncontaminated with these metals at the time of sampling. The spatial distribution of Cd and Pb in the water of the Kowie is depicted in Fig. 4.30. The metals exhibited similar concentration gradients and were significantly correlated at $p < 0.05$ ($R = 0.61$), indicating that they may be from the same source. Lead concentrations varied significantly along the estuary and Pb was significantly correlated

to TSS ($p < 0.05$, $R = 0.54$) suggesting that Pb was being adsorbed by the particulate matter in the water column.

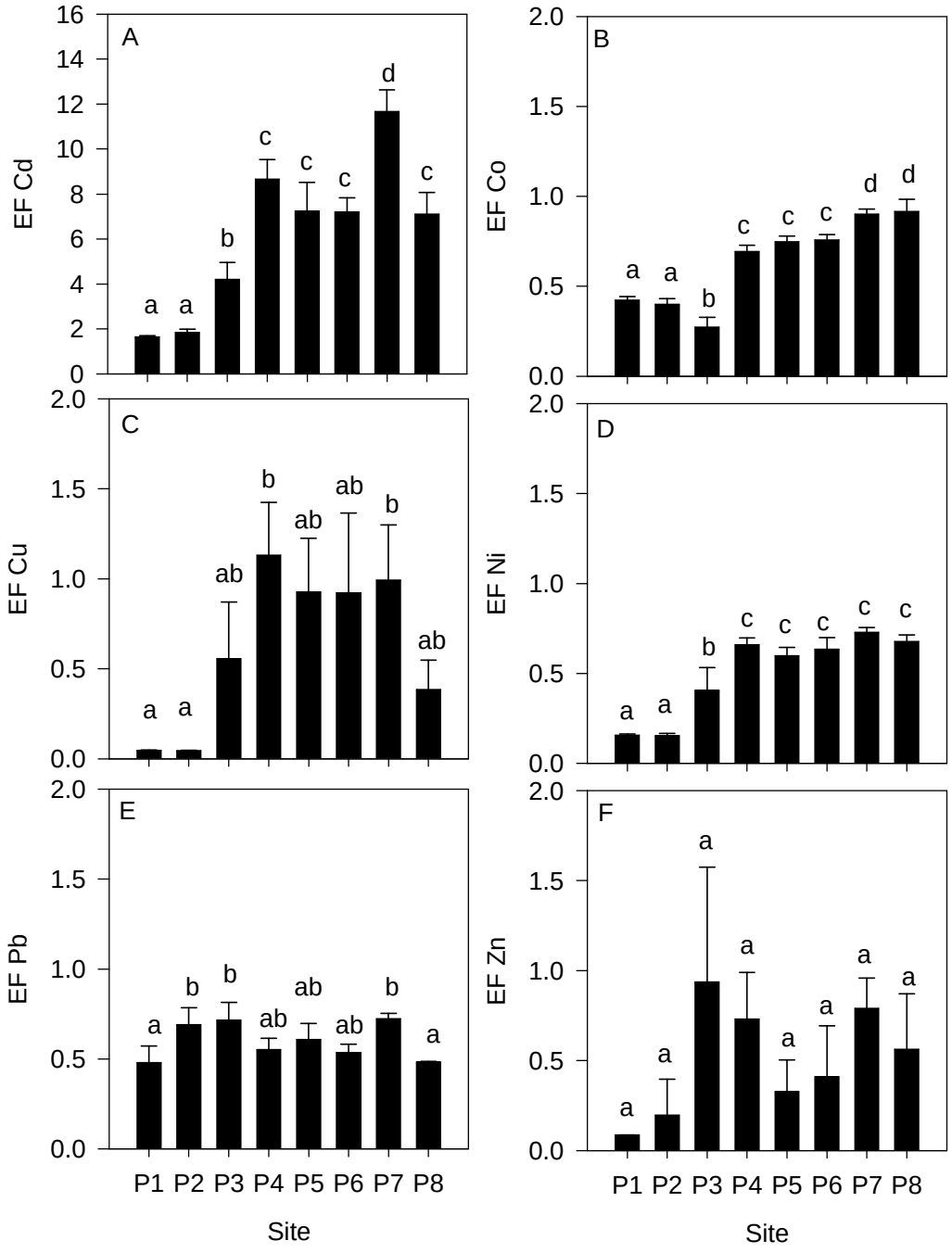

Figure 4.29: Spatial variations in the mean (± SD) enrichment factors for metals from the Kowie Estuary sediments. Different superscript letters denote significant differences within columns ($p < 0.05$).

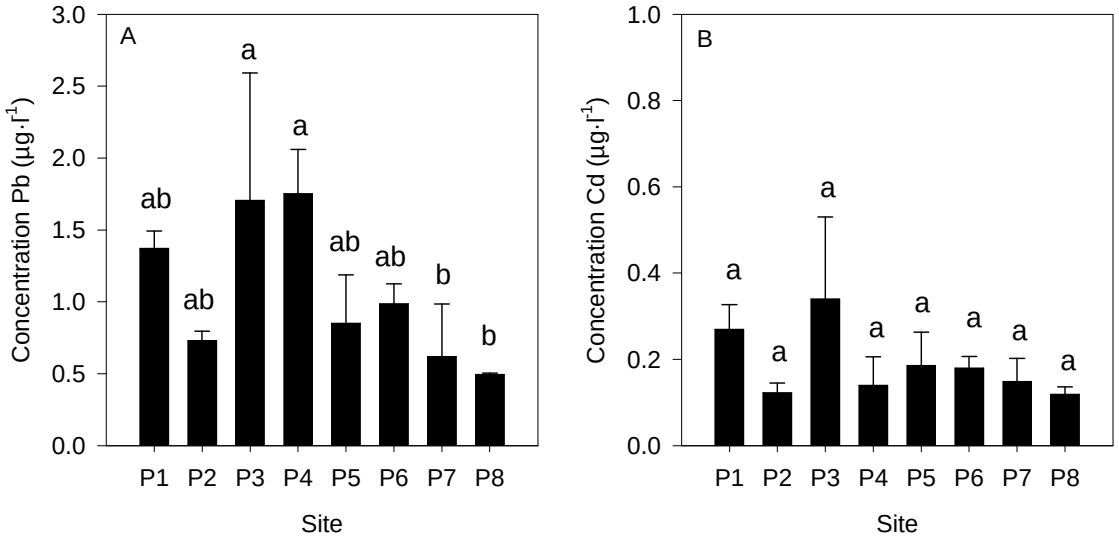

Figure 4.30: Spatial variations in the mean (± SD) concentrations of Pb and Cd in the water of the Kowie. Different superscript letters denote significant differences within columns ($p < 0.05$).

4.3 DISCUSSION AND CONCLUSIONS

The concentrations and enrichment of metals in the sediment and water of the Mpekweni, West Kleinemonde, Kasouga, Boknes, Great Fish and Kowie Estuaries were determined. The following section provides a brief summary of the metal concentrations and enrichment in these estuaries. Table 4.13 gives the average concentrations of metals in the sediments of the above estuaries. No single estuary included in this study appeared to have exclusively high concentrations of all metals. Variations of metal concentrations within estuaries may largely be due to variations in the underlying geology and mineralogy rather than variations in anthropogenic inputs of metals. Changes in metal concentrations were also linked to sediment size composition and organic content of sediment, and this has been well documented by other authors (De Groot *et al*., 1976; Tessier *et al*., 1979; Dasalakis and O'Conner, 1995; Tam and Yao, 1998). The geology of the Eastern Cape coastline is comprised mainly of sandstone deposits, shale deposits and a mixture of the two. Shale generally contains higher concentrations of metals than sandstone (Turekian and Wedepohl, 1961) and thus the estuaries that flow over large

shale deposits are likely to have higher concentrations of metals than those with catchment areas containing more sandstone. It is thus not advisable to deduce that one estuary is more contaminated with metals than another purely by comparison of sediment metal concentrations.

TABLE 4.13
Mean (± SD) absolute concentrations ($mg \cdot kg^{-1}$, dry wt) of metals in sediments from the Mpekweni, West Kleinemonde, Kasouga, Boknes, Great Fish and Kowie Estuaries

Estuary	Mouth Phase	Cd	Co	Cu	Fe	Ni	Pb	Zn
Mpekweni	Mouth closed	0.64 (± 0.25)	5.25 (± 4.14)	6.93 (± 3.66)	14912 (± 16300)	3.41 (± 3.38)	11.86 (± 4.73)	16.27 (± 13.78)
West Kleinemonde	Closed Mouth	0.81 (± 0.34)	6.24 (± 3.23)	4.55 (± 3.29)	5435 (± 5474)	11.83 (± 5.34)	21.91 (± 8.27)	21.75 (± 18.93)
Kasouga	Closed Mouth	0.71 (± 0.61)	3.34 (± 3.23)	1.63 (± 2.33)	5513 (± 4858)	3.41 (± 3.38)	6.42 (± 3.62)	3.63 (± 5.01)
Boknes	Closed Mouth	0.43 (± 0.31)	1.26 (± 1.72)	2.40 (± 2.75)	3101 (± 2480)	2.30 (± 2.85)	4.81 (± 1.92)	13.3 (± 22.5)
Great Fish	-	0.65 (± 0.32)	4.67 (± 2.49)	5.81 (± 4.85)	5801 (± 4592)	10.38 (± 4.77)	7.41 (± 5.60)	21.41 (± 17.33)
Kowie	-	2.18 (± 1.21)	2.31 (± 1.58)	4.27 (± 3.30)	5659 (± 3140)	4.13 (± 2.60)	4.93 (± 1.68)	10.67 (± 8.35)

Enrichment factors were calculated for each estuary in order to remove some of the variation caused by differences in mineralogy and grain size. The average enrichment factors (EFs) for the Mpekweni, West Kleinemonde, Boknes, Kasouga, Great Fish and Kowie Estuaries are shown in Table 4.14. All estuaries exhibited Cd enrichment (average EF > 1), with the Kowie Estuary having the highest average enrichment factor for Cd (average EF = 6.19). With a few exceptions, average EFs were below 1 for all other metals. The Kasouga, Boknes and Mpekweni estuaries had the lowest average enrichment factors of all six estuaries included in this chapter, and thus they can be considered to be relatively pristine.

The enrichment factors (and Cd / Fe values) of several metals (Cd, Co, Pb and Ni) increased in a seaward direction along the Mpekweni, West Kleinemonde, Kowie and Great Fish Estuaries. The elevated enrichment levels of metals at the mouth and lower

reaches of the above estuaries may be due to non-point inputs such as runoff from the national road that crosses the lower reaches of all these estuaries (Gobel *et al*., 2007). They may also be due to input of metals from boating activities, or runoff from dumping sites and parking lots. The higher enrichment of metals in the sediments at the mouth may also suggest that the metals were from a marine source, such as coastal upwelling. It is also possible that Fe was not the best normalizer for all the metals in each estuary and it would be interesting to determine if enrichment factors showed the same distribution along the estuaries if Al, Mn or TOC were used as the normalizer. Manganese in particular may have been a much more appropriate normalizer for Cd concentrations in the sediment since Cd is well known to adsorb onto particulates coated with manganese oxides (Simpson, 1981).

TABLE 4.14
Mean (± SD) enrichment factors (EFs) of metals in sediments from the Mpekweni, West Kleinemonde, Kasouga, Boknes, Great Fish and Kowie Estuaries

Estuary	Mouth Phase	Cd	Co	Cu	Ni	Pb	Zn
Mpekweni	Mouth closed	1.79 (± 0.69)	1.00 (± 0.63)	0.77 (± 0.20)	0.86 (± 0.38)	0.99 (± 0.46)	0.47 (± 0.30)
West Kleinemonde	Closed Mouth	2.27 (± 0.95)	2.42 (± 1.17)	0.56 (± 0.15)	1.83 (± 1.09)	2.77 (± 1.41)	0.55 (± 0.27)
Kasouga	Closed Mouth	2.02 (± 1.64)	0.73 (± 0.54)	0.22 (± 0.27)	0.38 (± 0.29)	0.65 (± 0.19)	0.14 (± 0.17)
Boknes	Closed Mouth	1.19 (± 0.86)	0.53 (± 0.34)	0.42 (± 0.42)	0.30 (± 0.16)	0.68 (± 0.16)	0.79 (± 1.20)
Great Fish	-	1.81 (± 0.90)	1.86 (± 2.03)	0.84 (± 0.54)	1.41 (± 1.10)	1.03 (± 1.10)	0.98 (± 0.56)
Kowie	-	6.19 (± 3.35)	0.63 (± 0.23)	0.65 (± 0.46)	0.50 (± 0.23)	0.59 (± 0.11)	0.50 (± 0.38)

CHAPTER 5

THE EFFECTS OF INCREASED FRESHWATER INFLOW ON METAL ENRICHMENT IN SELECTED EASTERN CAPE ESTUARIES, SOUTH AFRICA

5.1 INTRODUCTION

Numerous studies have demonstrated that the concentrations of metals in the sediments and water of estuaries are influence by the hydrodynamics of the system (Geesey *et al*., 1984; Ruiz and Saiz-Salinas, 2000; Jain and Sharma, 2001). Metal concentrations in river and estuarine water are often negatively correlated to flow rate largely due to the dilution effect caused by increased rainfall (Jain and Sharma, 2001). The concentrations of metals in the sediment are also known to decrease significantly after heavy rainfall due to the remobilization of metals and the erosion and scouring of the riverbed (Geesey *et al.,* 1984; Jain and Sharma, 2001).

Reduced freshwater inflow into estuaries may contribute to the accumulation of metals within an estuary, whereas increases in river-inflow may in turn dilute contaminants and / or flush them from the system (Ruiz and Saiz-Salinas, 2000). Temporal variations in metal concentrations are theoretically related to river flow processes, but practical evidence for such effects is scarce (Ruiz and Saiz-Salinas, 2000). It is thus important to conduct flow-related studies on metal contamination, especially in flow-restricted estuaries. The aims of the following study were to investigate the effects of rainfall on the concentrations and enrichment of metals in the surface water and sediment of three different estuaries, namely; the Kariega, the Riet and the East Kleinemonde Estuaries.

The Kariega Estuary was sampled during a dry season (July 2006) and a wet season (November 2006), the East Kleinemonde Estuary was sampled during open and closed

mouth phases (May 2006 and September 2006) as was the Riet Estuary (June 2006 and October 2006). Heavy rainfall within the catchment contributed to the formation of an axial salinity gradient in the Kariega Estuary for the first time in ten years (Vorwerk *et al*., 2007). Similarly, the high rainfall also resulted in the breaching of the East Kleinemonde and Riet Estuaries. The methods used to undertake this study are summarized in Chapter 3.

5.2 KARIEGA ESTUARY

Sediment Characteristics

No major changes were observed in the grain size composition of sediments along the Kariega Estuary between dry and wet seasons (Fig. 5.1). The sediments from the mouth, lower and middle reaches of the Kariega Estuary comprised mainly medium and fine sands. The percentage of medium sands decreased and the percentage of mud increased in a landward direction. During both the dry season and wet season, the percentage organic content of sediments steadily increased from the mouth to the upper reaches of the estuary (Fig. 5.1). There was a reduction in the average percentage organic content from ± 2.95 % during the dry season to ± 1.83 % during the wet season, although the difference between the two seasons was not significant ($p > 0.05$).

Metals in Sediments

The concentrations of metals in the sediment of the Kariega Estuary, sampled during the dry season, are shown in Table 5.1 A. A significant land-to-sea increase was observed in Cd and Pb concentrations ($p < 0.05$), and Pb and Cd were thus positively ($R = 0.50$, $p < 0.05$). Cobalt and Ni showed homogenous distribution at all sites along the estuary. The concentration of Fe increased significantly in the upper reaches of the estuary, which correlated with an increase in mud ($R = 0.92$, $p < 0.01$) and organic content of the sediments ($R = 0.91$, $p < 0.01$). The Spearman Rank correlations between all other metals and sediment characteristics are shown in Table A8 (i) (Appendix 2).

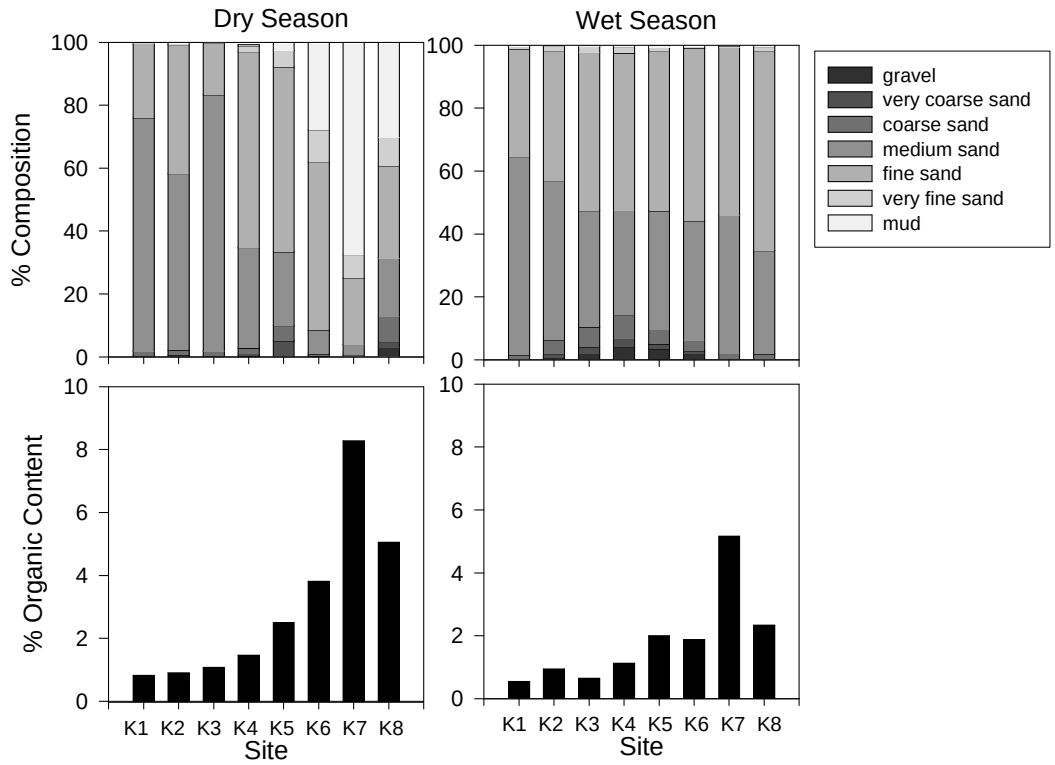

Figure 5.1: Grain size composition and organic content of the sediments at eight sites (K1 to K8) along the Kariega Estuary during the dry season and a wet season.

The absolute concentrations of metals obtained from the Kariega sediments during the wet season are shown in Table 5.1 B. There was no significant spatial variation in the concentrations of Cd, Co, Cu, Ni and Zn along the length of the estuary. The average Pb concentration was significantly higher in the sediment at site K2 ($p < 0.05$), which was situated directly below the storm water drain. The concentration of Fe increased significantly in the upper reaches, which corresponded to an increase in fine grained particles. The correlations between metals and sediment characteristics are shown in Table A8 (ii) (Appendix 2).

TABLE 5.1 A
Mean (± SD) concentrations of all metals (mg·kg^{-1}, dry wt.) in the sediments along the Kariega Estuary during the dry season (July)

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
K1 (marine)	0.40^{ab} (± 0.05)	4.87^{a} (± 0.11)	2.45^{ab} (± 2.77)	1369^{a} (± 50)	7.91^{a} (± 7.12)	22.83^{ab} (± 1.32)	0.41^{a} (± 0.44)
K2 (storm water)	0.45^{ab} (± 0.02)	4.95^{a} (± 0.43)	0.92^{ab} (± 0.06)	1558^{a} (± 20)	5.75^{a} (± 1.48)	22.50^{ab} (± 0.29)	5.61^{a} (± 4.56)
K3	0.33^{a} (± 0.05)	5.02^{a} (± 0.19)	1.20^{ab} (± 0.39)	1374^{a} (± 16)	8.45^{a} (± 6.94)	26.10^{a} (± 0.85)	0.43^{a} (± 0.47)
K4	0.38^{ab} (± 0.21)	5.16^{a} (± 0.51)	1.15^{ab} (± 0.43)	1858^{a} (± 218)	8.78^{a} (± 3.98)	25.41^{a} (± 0.23)	0.54^{a} (± 0.66)
K5	0.65^{b} (± 0.25)	5.04^{a} (± 0.49)	3.25^{ab} (± 3.07)	2878^{a} (± 93)	22.56^{a} (± 1.83)	22.43^{a} (± 0.65)	51.75^{b} (± 39.54)
K6	<DL^{c}	3.45^{a} (± 0.53)	1.56^{a} (± 0.99)	3474^{a} (± 1385)	8.52^{a} (± 6.89)	17.35^{b} (± 0.75)	7.12^{a} (± 3.17)
K7	<DL^{c}	7.42^{a} (± 0.88)	7.56^{ab} (± 0.79)	11170^{b} (± 4459)	11.30^{a} (± 3.02)	22.82^{ab} (± 2.01)	18.75^{a} (± 2.95)
K8 (upper)	<DL^{c}	7.81^{a} (± 4.56)	10.35^{b} (± 6.45)	15196^{b} (± 9042)	15.37^{a} (± 5.61)	18.21^{b} (± 4.64)	31.81^{ab} (± 13.13)
Mean July	0.27 (± 0.23)	5.48 (± 2.01)	3.57 (± 4.10)	5659 (± 3140)	10.58 (± 6.39)	22.20 (± 3.41)	12.93 (± 18.87)

TABLE 5.1 B
Mean (± SD) concentrations of all metals (mg·kg^{-1}, dry wt.) in the sediments along the Kariega Estuary during the wet season (November)

K1 (marine)	0.59^{a} (± 0.11)	3.66^{a} (± 0.58)	2.72^{a} (± 1.04)	1443^{a} (± 116)	5.30^{a} (± 2.72)	11.75^{a} (± 0.35)	5.65^{a} (± 2.92)
K2 (storm water)	0.11^{a} (± 0.08)	3.17^{a} (± 0.19)	3.31^{a} (± 0.64)	3301^{ab} (± 1118)	1.86^{a} (± 1.78)	30.91^{b} (± 6.42)	13.19^{a} (± 2.92)
K3	0.85^{a} (± 0.51)	3.71^{a} (± 0.11)	1.84^{a} (± 1.12)	1401^{a} (± 47)	2.39^{a} (± 1.86)	11.53^{a} (± 0.37)	3.74^{a} (± 5.10)
K4	0.49^{a} (± 0.12)	3.99^{a} (± 0.55)	2.26^{a} (± 0.23)	1965^{a} (± 313)	3.34^{a} (± 1.78)	14.82^{a} (± 3.09)	6.93^{a} (± 5.66)
K5	0.56^{a} (± 0.46)	3.82^{a} (± 0.76)	1.98^{a} (± 1.69)	2823^{ab} (± 1021)	3.61^{a} (± 6.23)	10.79^{a} (± 1.11)	6.72^{a} (± 11.51)
K6	2.78^{a} (± 2.46)	3.09^{a} (± 6.66)	2.18^{a} (± 1.45)	2334^{ab} (± 145)	24.16^{a} (± 26.68)	8.81^{a} (± 6.07)	29.60^{a} (± 27.18)
K7	1.23^{a} (± 1.84)	6.66^{a} (± 1.02)	5.63^{a} (± 2.27)	9665^{b} (± 3627)	13.24^{a} (± 5.83)	11.89^{a} (± 2.35)	13.85^{a} (± 12.36)
K8 (upper)	<DL	5.69^{a} (± 3.65)	6.23^{a} (± 4.45)	13113^{b} (± 8597)	3.68^{a} (± 5.19)	10.37^{a} (± 4.66)	20.81^{a} (± 17.06)
Mean November	0.88 (± 1.28)	4.16 (± 1.59)	3.14 (± 2.11)	4129 (± 4439)	7.35 (± 11.43)	14.01 (± 7.59)	12.21 (± 13.61)
Kariega 1988*	0.05 (± 0.01)	5.4 (± 4.7)	7.5 (± 3.6)	16050 (± 9740)	9.9 (± 8.6)	10.7 (± 5.2)	27.1 (± 20.1)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$) for each season. n = 24.
* Watling (1988)

Principal component analysis was used to explore the correlations between metal concentrations and sediment characteristics during the dry season, as well as to identify new "latent" variables that account for the variability in the data (Meglen, 1992). Three principal components were extracted that account for approximately 80 % of the cumulative variance in the data. The principal component loadings for each variable are shown in Table 5.2. The first component, describing ~ 45 % of the common variance, is highly loaded with Co, Cu, Fe, Cd, TOC and mud content. The negative loading for Cd in component 1 suggests antagonistic effects with respect to Co, Cu, Fe, TOC and mud. The second component describing 18.59 % of the common variance in the data set is highly loaded for Co and Pb, and Component 3 (16.67 % of common variance) has substantial positive loadings for Zn and Ni. A plot of loadings for PC 1 *vs.* PC 2 gives a clearer depiction of the association between variables (Fig. 5.2). There is an obvious separation of Cd and Pb from the other metals, suggesting that Cd and Pb are from an alternative, possibly anthropogenic source. A second group is formed by Co, Cu, Fe, Ni, Zn, TOC and mud. The distributions of these metals are thus partly controlled by fine grained particles (mud) and the organic content of the sediments, and this group is thus likely to represent the geogenic metals.

TABLE 5.2
Principal component loadings for metal concentrations and sediment characteristics in the Kariega Estuary, sampled during the dry season (July)

	Component 1 (45.23 %)	**Component 2 (18.59 %)**	**Component 3 (16.67 %)**
Cd	**-0.62**	-0.42	0.49
Co	**0.73**	**-0.61**	-0.13
Cu	**0.84**	-0.31	0.02
Fe	**0.94**	-0.23	-0.16
Ni	0.48	-0.26	**0.67**
Pb	-0.38	**-0.68**	0.02
Zn	0.48	-0.18	0.63
TOC (%)	**0.89**	0.07	-0.21
Coarse sand	0.53	-0.45	0.44
Medium sand	-0.72	-0.51	-0.28
Fine sand	-0.26	0.50	**0.69**
Very fine sand	**0.67**	**0.63**	0.27
Mud	**0.82**	0.17	-0.41

Note: Loadings greater than ± 0.6 are in bold and indicate moderate relationships between the variable and principal component. *Percentage total variance.

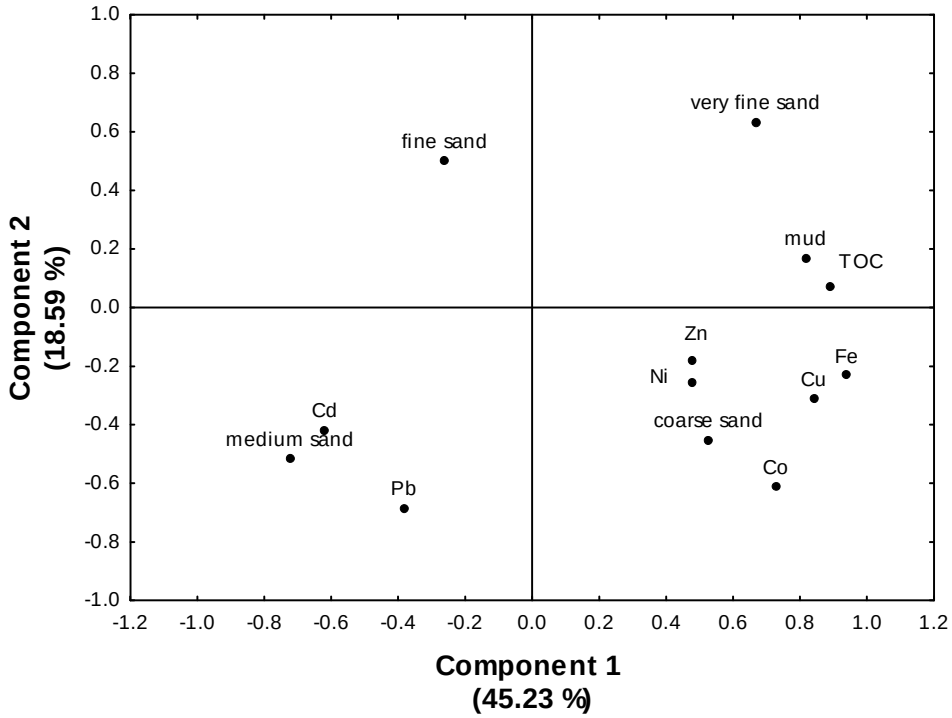

Figure 5.2: Principal component loadings plot (PC 1 *vs.* PC 2) for metals concentrations and sediment characteristics of the Kariega Estuary sediments during the dry season (July).

The associations between all metals and sediment characteristics during the wet season were difficult to asses simply from the Spearman Rank correlation matrix, and thus the data was subjected to principal component analysis. Three components were extracted that described approximately 77 % of the common variance. Table 5.3 shows the variable loadings for the three principal components. Component 1 has high loadings for Co, Cu, Fe, TOC and mud, as in the dry season. Component 2 has high loadings for Cd and Ni, and component 3 has high loadings for Pb and Zn. The PCA loadings scatterplot (Fig. 5.3) was used to view the relation between the variables. It is evident that Pb is separated from all the other metals and that it is associated with the coarse sands which dominated the mouth and lower reaches of the estuary. There is a second cluster of Cd, Ni and Zn which are associated with the fine sands, and a third cluster of Cu, Co, and Fe which are correlated to TOC and mud. The Pb is likely to be of anthropogenic origin given that it is uncorrelated to any of the other metals and that the highest Pb concentrations were found below the storm water drain.

TABLE 5.3
Principal component loadings for metal concentrations and sediment characteristics in the Kariega Estuary, sampled during the wet season (November)

	Component 1 (40.62 %)	Component 2 (21.04 %)	Component 3 (15.26 %)
Cd	0.20	**0.80**	0.43
Co	**0.74**	-0.22	-0.04
Cu	**0.81**	-0.43	0.25
Fe	**0.86**	-0.40	-0.04
Ni	0.42	**0.66**	0.55
Pb	-0.21	-0.51	**0.68**
Zn	0.56	0.36	**0.68**
TOC (%)	**0.86**	-0.07	-0.05
Coarse sand	-0.29	-0.58	0.56
Medium sand	**-0.62**	-0.32	0.23
Fine sand	**-0.60**	0.48	-0.03
Very fine sand	0.55	0.41	-0.32
Mud	**0.94**	-0.15	-0.20

Note: Loadings greater than ± 0.6 are in bold and indicate moderate relationships between the variable and principal component. *Percentage total variance.

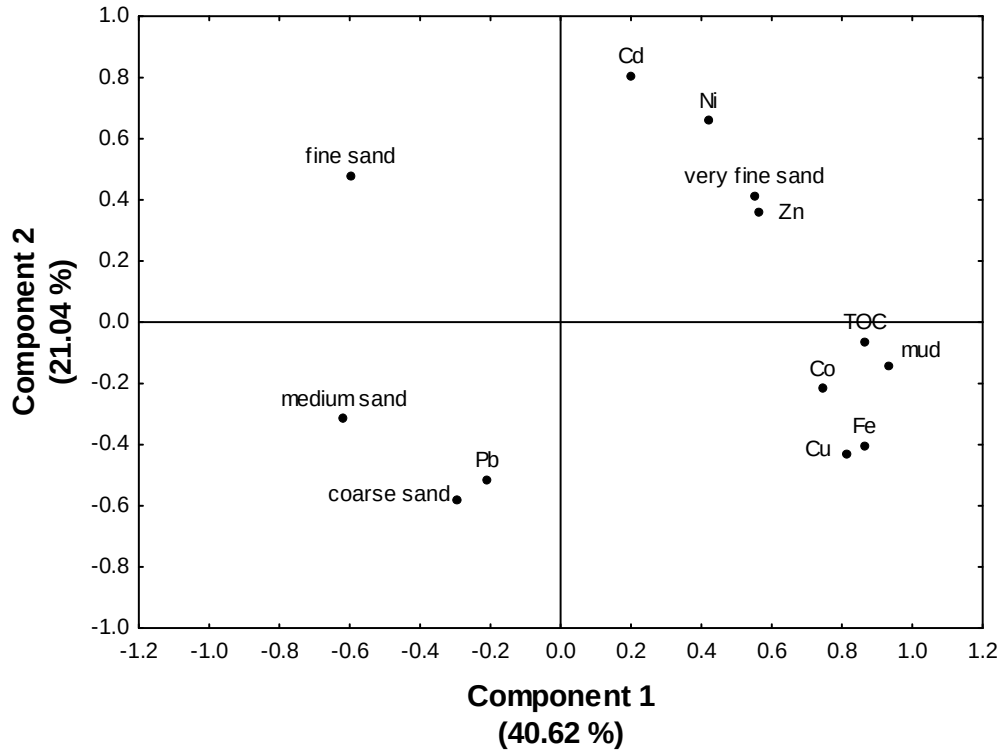

Figure 5.3: Principal component loadings plot (PC 1 *vs.* PC 2) for metals concentrations and sediment characteristics of the Kariega Estuary sediments during the wet season (November).

The average sediment concentrations of Co and Pb were significantly lower during the wet season ($p < 0.05$), and the average sediment concentration of Cd were significantly higher ($p < 0.05$). During the wet season the mean Cd concentration was above the regional baseline concentration of 0.360 $\mu g \cdot g^{-1}$ above which enrichment can be suspected. These variations in absolute concentrations may have been due to variations in grain size between seasons, and thus enrichment factors were calculated that normalized metal concentrations for grain size.

Enrichment of metals within sediment samples was assessed by superimposing metal concentrations onto baseline metal *vs.* Fe regression plots (Fig. 5.4). The points that fell above the 95 % prediction limits for the models were considered to be enriched. During both dry and wet periods, the metals that showed the most extensive enrichment were Co, Ni and Pb (Figs. 5.4 A, 5.4 C and 5.4 D). During the dry season samples from all sites within the Kariega Estuary fell above the upper 95% prediction limit of the regression model for Co (Fig. 5.4 A), while during the wet season fewer samples fell above this 95 % prediction limit. Five samples were enriched with Cu during the dry season, and no Cu enrichment was evident in the sediment of the Kariega Estuary during the wet season (Fig. 5.4 B). Sediment samples were enriched with Ni during both dry and wet seasons, but the enrichment was more evident during the dry season with the majority of samples falling above the upper 95 % prediction limit. The bulk of sediment samples were enriched with Pb during the dry season and fewer samples were enriched with Pb during the wet season (Fig. 5.4 D). There were very few samples that fell above the 95 % prediction limit for Zn during both seasons. There thus appeared to be more extensive enrichment of Pb, Cu, Co and Ni relative to background concentrations during July (dry season) as compared to November (wet season) within the Kariega Estuary.

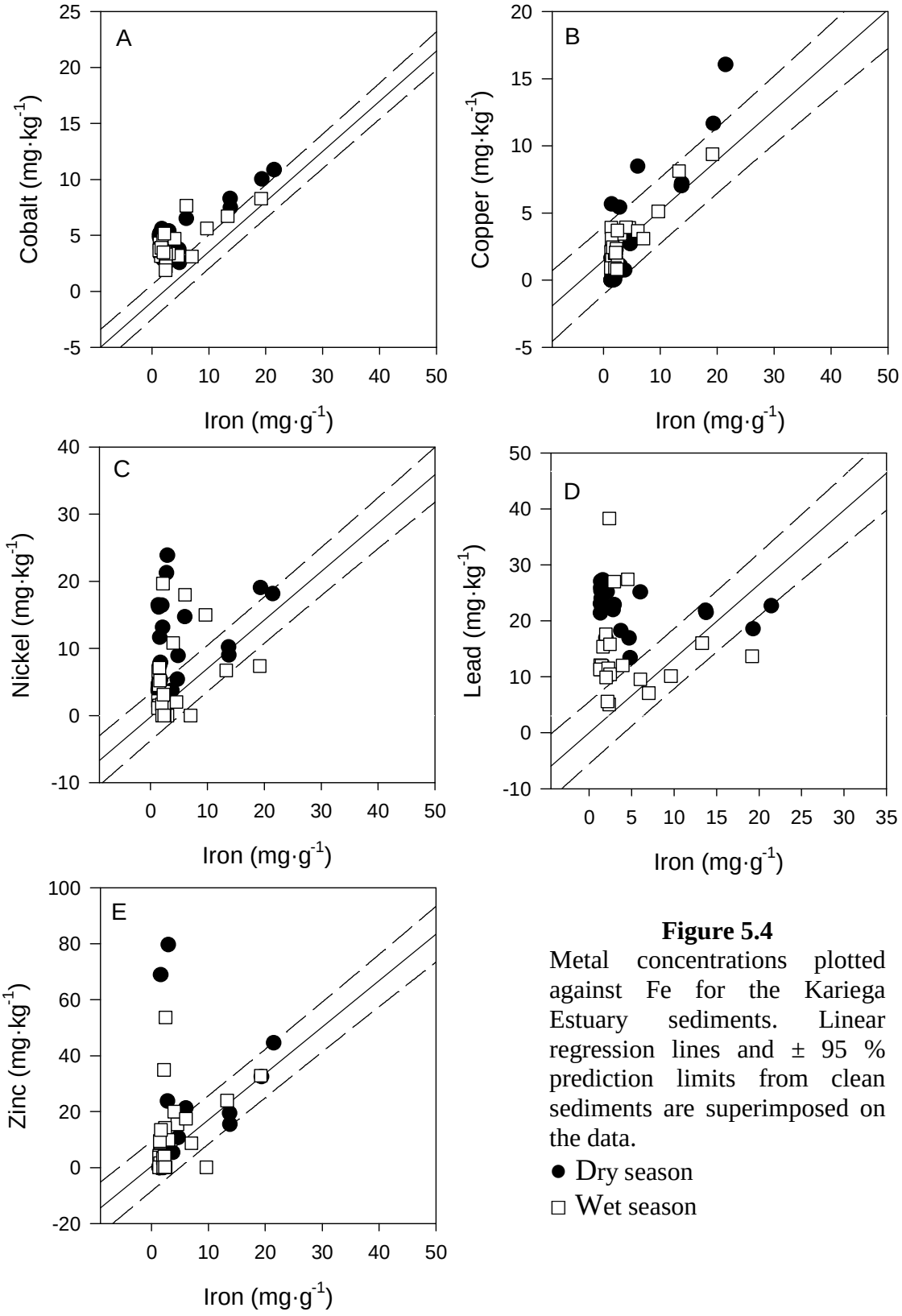

Figure 5.4

Metal concentrations plotted against Fe for the Kariega Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

● Dry season

□ Wet season

Fig. 5.5 shows the spatial variation in enrichment factors (EFs) for metals in the Kariega Estuary sediments during the dry and wet season. Cobalt and Pb enrichment increased significantly ($P < 0.05$) in a seaward direction during both seasons (Figs. 5.5 B and 5.5 E). In the wet season, Pb enrichment was significantly higher at site K2 ($p < 0.05$), which was situated directly below the storm water drain. There was no significant spatial variation in Cu and Ni enrichment during both the dry and wet seasons (Figs. 5.5 C and 5.5 D) ($p > 0.05$). There was no significant variation in Zn enrichment along the Kariega Estuary during the dry season (Fig. 5.5 F). Seven out of the eight sites along the Kariega Estuary showed no significant spatial variation in Zn during the wet season, however, site K5 was significantly more enriched ($p < 0.05$) with Zn than all other sites (Fig. 5.5 F). Cadmium enrichment was significantly higher in the mouth to middle reaches of the estuary during the dry season (sites K1 to K5) and showed no significant spatial variation during the wet season (Fig. 5.5 A). Please note that Cd enrichment factors were not normalized for grain size, and this is due to the fact that suitable Cd *vs.* Fe baseline regression plots could not be constructed (see Chapter 3). Thus Cd / Fe ratios were calculated to asses the normalized distribution of Cd. Using this method, Cd / Fe ratios were significantly higher in the mouth to middle reaches of the estuary (sites K1 to K5) during the dry season and showed no significant spatial variation during the wet season. It is interesting to note that the enrichment factors for Co, Ni and Pb were generally higher during the dry season at sites K1-K5 than during the wet season. This may suggests that these metals were scoured from the surface sediments of the estuary during the period of heavy rainfall via the process of erosion.

Enrichment factors for Co, Ni and Pb were significantly higher in July (dry season) than in November (wet season) ($p < 0.05$). There was no significant difference in enrichment factors for Cd, Cu and Zn between the two seasons ($p > 0.05$); however there was a noticeable increase in the average Cd enrichment during the wet season. Enrichment factors for Pb, Co and Ni were greater than 1 during the dry season indicating enrichment relative to baseline concentrations. Samples obtained during the wet season had EFs > 1 for Pb, Co, Ni and Cd (Table 5.11, pg 127).

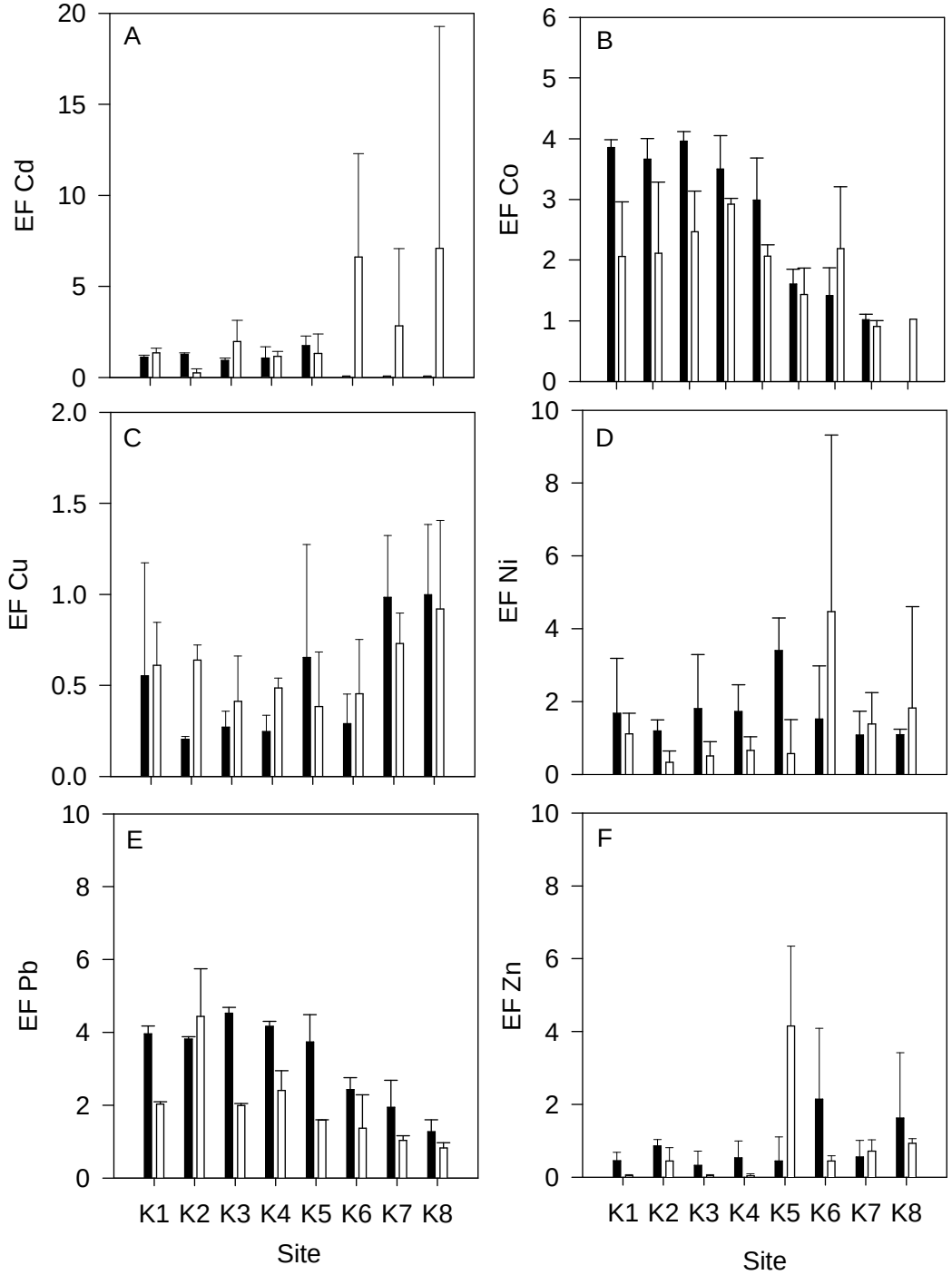

Figure 5.5: Spatial variation in mean (± SD) enrichment factors (EF) for sediments taken from the Kariega Estuary during a dry season and a wet season.
■ Dry season, □ Wet season.

Water

The lack of freshwater input to the Kariega Estuary during the dry season resulted in a homogenous salinity profile along the length of the Kariega Estuary, with the salinities ranging between 32 psu and 39 psu. Heavy rainfall within the catchment of the Kariega Estuary during November contributed to the formation of a longitudinal gradient in salinity within the estuary for the first time in ten years (Vorwerk *et al*., 2007). The average concentration of suspended solids in the water column increased during the wet season, and the turbidity maximum zone was located at site K4, which is approximately 1.3 km from the mouth. During the dry season there was little variation in the concentration of total suspended solids along the length of the estuary.

There was a significant reduction in the net concentrations of Cd and Pb in the water of the Kariega Estuary during the wet season ($p < 0.05$). The mean (± SD) concentration of Cd decreased from 3.32 (± 4.09) $\mu g \cdot \ell^{-1}$ in the dry season to 0.05 (± 0.99) $\mu g \cdot \ell^{-1}$ in the wet season (Fig. 5.6 B). The mean concentration of Pb decreased from 34.13 (± 42.56) $\mu g \cdot \ell^{-1}$ in the dry season to 1.75 (± 1.01) $\mu g \cdot \ell^{-1}$ in the wet season (Fig. 5.6 A).

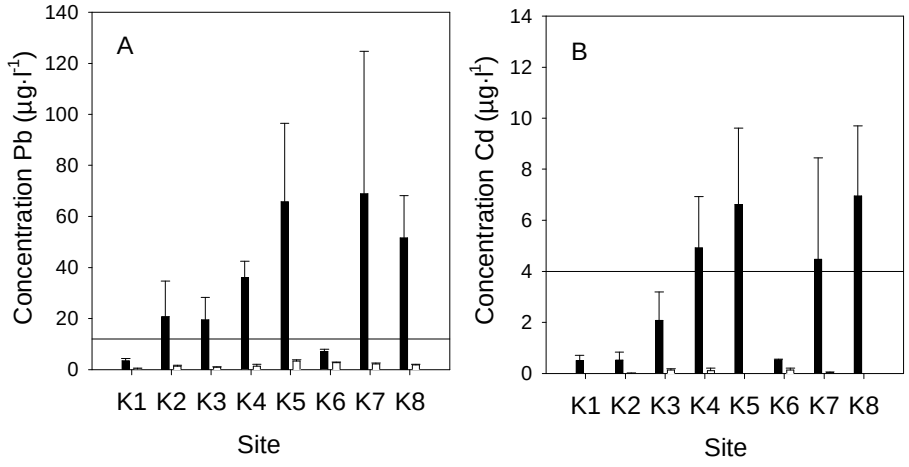

Figure 5.6: Spatial and temporal variations in the mean concentrations (± SD) of Pb and Cd in water collected from the Kariega Estuary during a dry season (July) and a wet season (November.) *Note:* Horizontal bar represents South African water quality guidelines for coastal marine waters. ■ Dry season, □ Wet season.

Both the mean concentrations of Cd and Pb during the dry season were above the target values (4 $\mu g \cdot \ell^{-1}$ and 12 $\mu g \cdot \ell^{-1}$, respectively) recommended for South African coastal waters (DWAF, 1995). These results suggest that the inflow of freshwater into the Kariega Estuary had the net effect of reducing the concentrations of Pb and Cd in the surface water by flushing estuarine water into the marine environment, or via dilution with large volumes of freshwater.

5.3 EAST KLEINEMONDE ESTUARY

Sediment Characteristics

The mouth and lower reaches within the East Kleinemonde Estuary comprised mainly medium and fine sands when the mouth was both closed and open, however the percentage of fine sands increased when the estuary breached. When the mouth of the estuary was closed the sediments of the middle and upper reaches comprised mainly very fine sands and mud (Fig. 5.7).

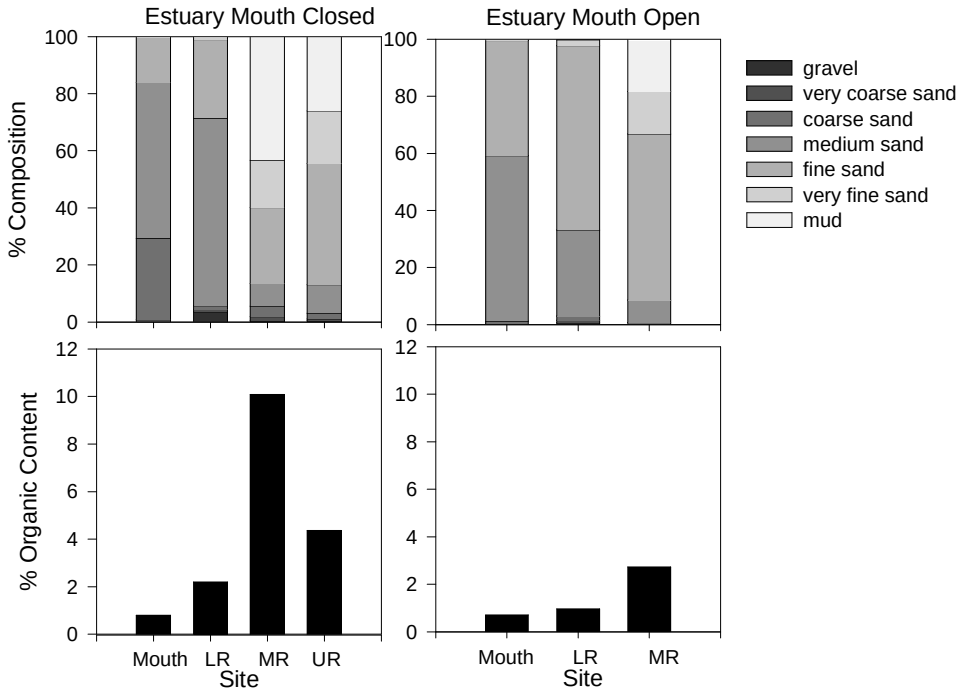

Figure 5.7: Grain size composition and organic content of the sediments from the East Kleinemonde Estuary during open and closed mouth phases. *Note*: The upper reaches were not sampled during the wet season due to access problems. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

There was a noticeable reduction in the percentage of mud in the middle reaches of the estuary when the estuary breached (Fig 5.7). The percent organic content of the sediments showed an increasing trend from the mouth to the middle reaches during both dry and wet seasons. When the mouth was closed, the percent organic content was greatest in the middle reaches. The average percentage organic content decreased from 4.36 % to 1.46 % when to estuary breached (Fig. 5.7).

Metals in Sediments

Mean (± SD) absolute concentrations of metals in the East Kleinemonde sediments during both the dry and wet seasons can be seen in Table 5.4 A and 5.4 B. Zinc and Fe were the only metals that showed a significant change in concentration between the two seasons, with the mean concentration of both Zn and Fe decreasing significantly ($p < 0.05$) during the wet season.

TABLE 5.4A
Mean (± SD) concentrations of all metals (mg·kg^{-1}, dry wt.) in the sediments of the East Kleinemonde Estuary during a dry season

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
Marine	1.18^{ab} (± 0.41)	5.59^{a} (± 0.69)	2.29^{a} (± 0.32)	2066^{a} (± 105)	16.12^{a} (± 1.77)	26.06^{a} (± 1.65)	4.38^{a} (± 0.30)
LR	1.93^{a} (± 0.68)	4.81^{a} (± 0.48)	5.21^{a} (± 2.78)	2433^{a} (± 417)	13.31^{a} (± 1.11)	26.57^{a} (± 1.58)	24.29^{ab} (± 6.28)
MR	1.14^{ab} (± 0.59)	9.14^{a} (± 4.93)	7.18^{a} (± 4.15)	21289^{a} (± 14013)	12.17^{a} (± 6.79)	21.66^{a} (± 11.52)	43.66^{b} (± 21.30)
UR	0.47^{b} (± 0.13)	5.41^{a} (± 5.52)	3.54^{a} (± 3.81)	8426^{a} (± 7077)	5.74^{a} (± 4.44)	13.34^{a} (± 8.34)	14.66^{ab} (± 14.86)
Mean (dry season)	1.18 (± 0.69)	6.23 (± 3.64)	4.55 (± 3.29)	8554 (± 10525)	11.83 (± 5.34)	21.91 (± 8.27)	21.75 (± 18.93)

TABLE 5.4B
Mean (± SD) concentrations of all metals (mg·kg^{-1}, dry wt.) in the sediments of the East Kleinemonde Estuary during a wet season

Marine	1.22^{a} (± 0.64)	5.45^{a} (± 0.41)	0.91^{a} (± 0.08)	1269^{a} (± 36)	8.22^{a} (± 2.51)	28.78^{a} (± 1.99)	2.49^{a} (± 2.16)
LR	0.78^{a} (± 0.64)	5.27^{a} (± 0.15)	0.80^{a} (± 0.10)	1557^{a} (± 13)	5.29^{a} (± 1.64)	23.88^{a} (± 2.28)	0.69^{a} (± 0.29)
MR	0.01^{a} (± 0.00)	4.76^{a} (± 1.02)	0.93^{a} (± 0.02)	3897^{ab} (± 206)	8.12^{a} (± 1.72)	12.51^{b} (± 2.34)	3.21^{a} (± 2.38)
Mean (wet season)	0.60 (± 0.67)	5.12 (± 0.65)	0.88 (± 0.08)	2362 (± 1281)	7.08 (± 2.17)	20.84 (± 7.44)	2.08 (± 1.93)

Note: Different superscript letters denote significant differences within columns ($p < 0.05$). (LR = lower reaches, MR = middle reaches, UR = upper reaches)
The upper reaches were not sampled during the wet season due to access problems.

Principal component analysis was used to reduce the dimensionality of the data and assess relationships between variables (Meglen, 1992). Principal component analysis was applied to dry season and wet season data separately. Three principal components were extracted for the dry season data that accounted for approximately 88 % of the cumulative variance. Principal component loadings for variables measured during the dry season are shown in Table 5.5 A plot of these loadings (Fig. 5.8) shows a clear grouping of variables. Cobalt, Cu, Zn, Fe and TOC all have high loadings for component 1 and form a distinct group to the top-right of the plot. Organic matter and Fe were most likely controlling the distribution of Co, Cu and Zn through the formation of Fe-oxides and organic complexes. Lead, Cd and Ni formed a second cluster on the left of the plot. These metals were uncorrelated with organic matter, fine grained particles or Fe. Cadmium and Pb had the highest enrichment factors of all metals ($1 < EF < 3$) suggesting that these metals were possibly of anthropogenic origin.

TABLE 5.5
Principal component loadings for metal concentrations and sediment characteristics in the East Kleinemonde Estuary, sampled during the dry season (mouth closed)

	Component 1 (43.59 %)*	**Component 2 (33.94 %)***	**Component 3 (10.48 %)***
Cd	-0.21	**0.73**	0.46
Co	0.57	**0.71**	-0.23
Cu	**0.64**	**0.71**	0.25
Fe	**0.85**	0.45	-0.23
Ni	-0.24	**0.93**	-0.21
Pb	-0.21	**0.96**	-0.04
Zn	**0.73**	0.49	0.10
TOC (%)	**0.83**	0.28	-0.13
Coarse sand	**-0.62**	0.20	**-0.64**
Medium sand	**-0.85**	0.39	0.20
Fine sand	0.56	-0.20	**0.61**
Very fine sand	**0.87**	-0.44	-0.12
Mud	**0.82**	-0.35	-0.27

Note: Loadings greater than ± 0.6 are in bold and indicate moderate relationships between the variable and principal component. *Percentage total variance.

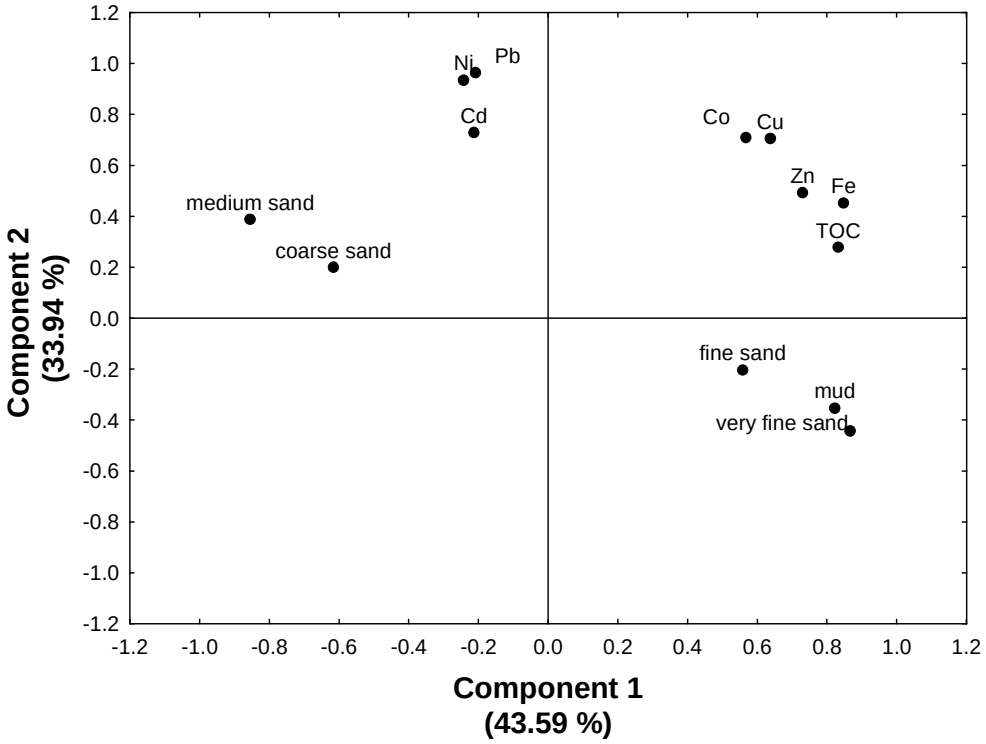

Figure 5.8: Principal component loadings plot (PC 1 *vs.* PC 2) for metals concentrations and sediment characteristics of the East Kleinemonde Estuary sediments during the dry season (mouth closed).

Principal component analysis of the wet season data revealed a change in the associations between variables. Two principal components were extracted that accounted for approximately 80 % of the variance in the data. The variable loadings for each component are shown in Table 5.6. The plot of variable loadings for component 1 and component 2 (Fig. 5.9) shows that Cd, Pb and Co were highly correlated to the medium and coarse grained particles found in the marine environment and lower reaches of the estuary. Not surprisingly, organic content and Fe were highly correlated with the fine grained particles. Copper and Ni introduced a new source of variance into the system as each of these metals had high loadings for component 2.

TABLE 5.6
Principal component loadings for metal concentrations and sediment characteristics in the East Kleinemonde Estuary, sampled during the wet season (mouth open)

	Component 1 (59.64 %)*	Component 2 (20.23 %)*
Cd	**0.89**	0.14
Co	**0.68**	0.34
Cu	0.49	**0.75**
Fe	**-0.94**	0.24
Ni	0.45	**0.82**
Pb	**0.94**	-0.08
Zn	-0.42	0.37
TOC (%)	**-0.89**	0.30
Coarse sand	**0.70**	-0.45
Medium sand	**0.94**	0.22
Fine sand	-0.53	**-0.72**
Very fine sand	**-0.90**	0.31
Mud	**-0.93**	0.32

Note: Loadings greater than ± 0.6 are in bold and indicate moderate relationships between the variable and principal component. *Percentage total variance.

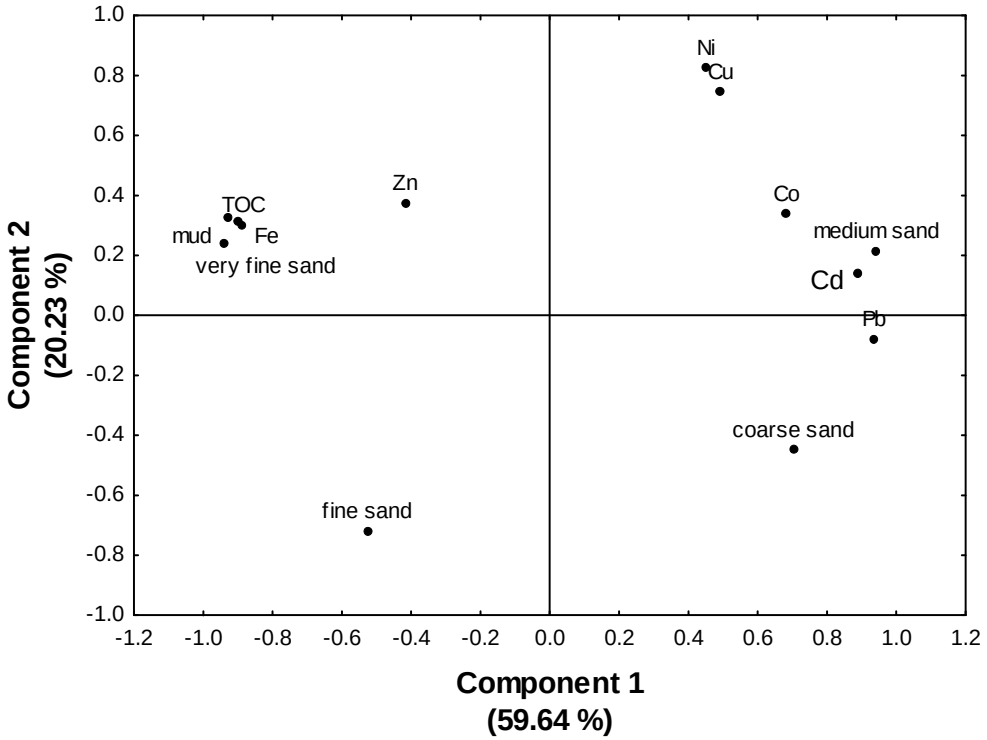

Figure 5.9: Principal component loadings plot (PC 1 *vs.* PC 2) for metals concentrations and sediment characteristics of the East Kleinemonde Estuary sediments during the wet season (mouth open).

The geochemistry of the East Kleinemonde is thus complex and it is beyond the scope of this project to decipher the exact physico-chemical interactions taking place in the sediments. The variability in metal interactions may be due to variations in the underlying bedrock, as well as variations in anthropogenic inputs of the metals. Cadmium and Pb were, however, associated during both seasons, and this may indicate a common (anthropogenic) source. The concentrations of Pb and Cd were elevated in the marine environment and lower reaches of the estuary. Most of the residential development is restricted to the lower reaches of the estuary and thus Pb and Cd may have been entering the system from non-point sources such as road runoff, boating activity and combustion of fuel.

The concentrations of metals from dry and wet seasons were superimposed onto baseline linear regression plots for metals *vs.* Fe. Samples that fell above the 95 %prediction limits for the models were enriched with metals relative to baseline concentrations. Copper and Zn showed almost no enrichment in the East Kleinemonde Estuary sediments, with only a few samples from the dry season falling above the 95 % prediction limits of the regression models (Figs. 5.10 B and 5.10 E). Cobalt, Ni and Pb enrichment was more extensive when the estuary breached as opposed to when the mouth was closed. This can be seen in Figs. 5.10 A, 5.10 C and 5.10 D in which more samples from the wet season fall above the 95 % prediction limits of the corresponding regression models as compared to the dry season. This may suggest that there was an increase of metals flowing into the system during the wet season.

The mean enrichment factors (EFs) for metals from the East Kleinemonde Estuary are shown in Table 5.11 (pg 127). Cobalt and Pb enrichment increased during the wet season, while Cd, Cu, Ni and Zn enrichment decreased. Sediments were not enriched with Cu and Zn during both seasons since EFs < 1. Cadmium, Co, Ni and Pb were moderately enriched (1 < EF < 3.5) within sediments during both seasons. These metals may have been elevated above background values due to both natural and anthropogenic inputs.

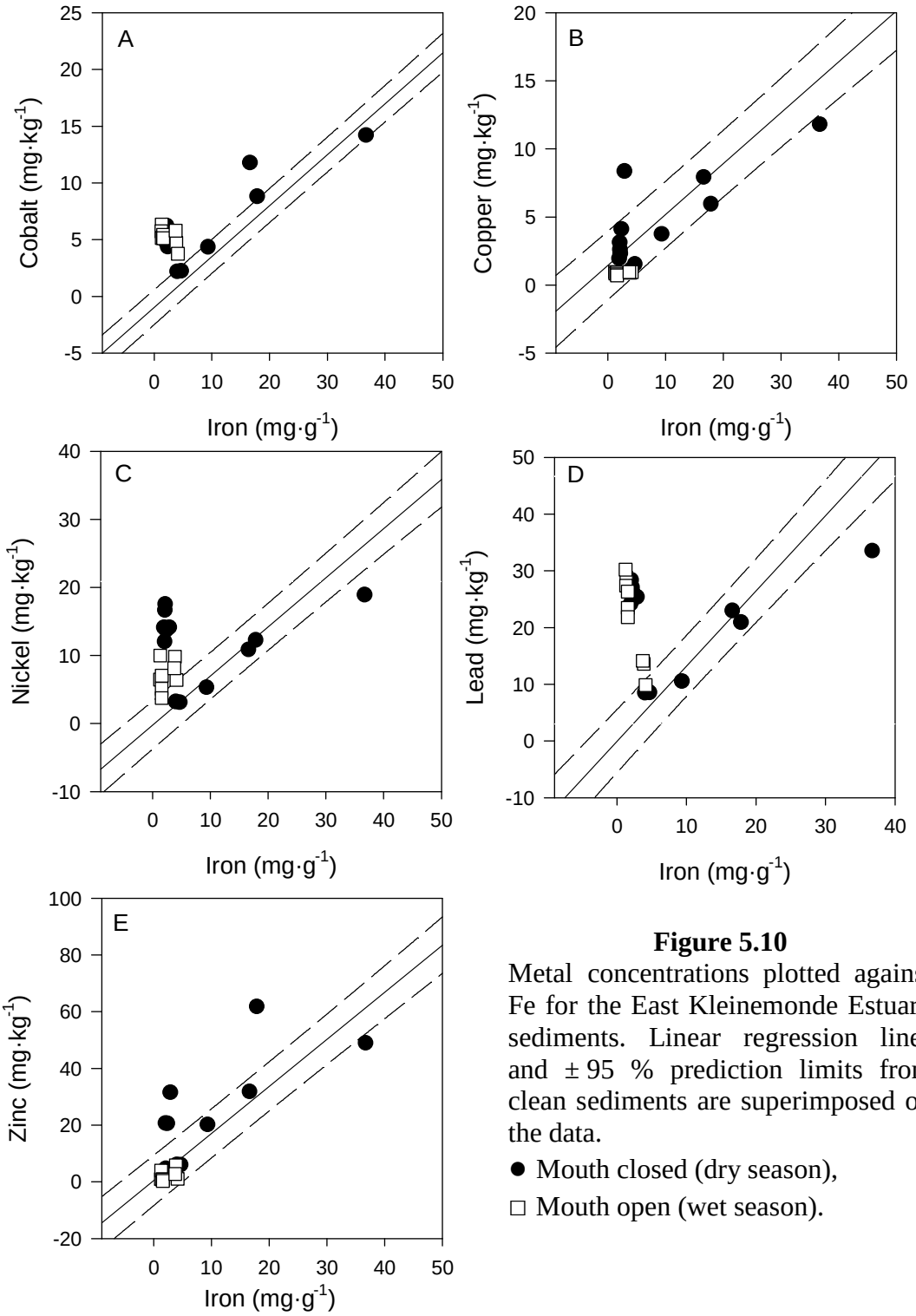

Figure 5.10

Metal concentrations plotted against Fe for the East Kleinemonde Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.

● Mouth closed (dry season),

□ Mouth open (wet season).

Significant spatial variations existed for all metals in the sediment during the dry and wet periods, with the highest levels of enrichment occurring at the mouth and in the lower reaches of the estuary (Fig. 5.11). When the mouth was closed, enrichment factors for all metals decreased significantly in a landward direction ($p < 0.05$), with Cd, Co and Pb maintaining this gradient during the wet season. This spatial distribution of metals thus appeared to reflect the land-use gradient along the East Kleinemonde Estuary during both seasons, since the majority of developments are situated along the beach-front and the banks of the lower reaches.

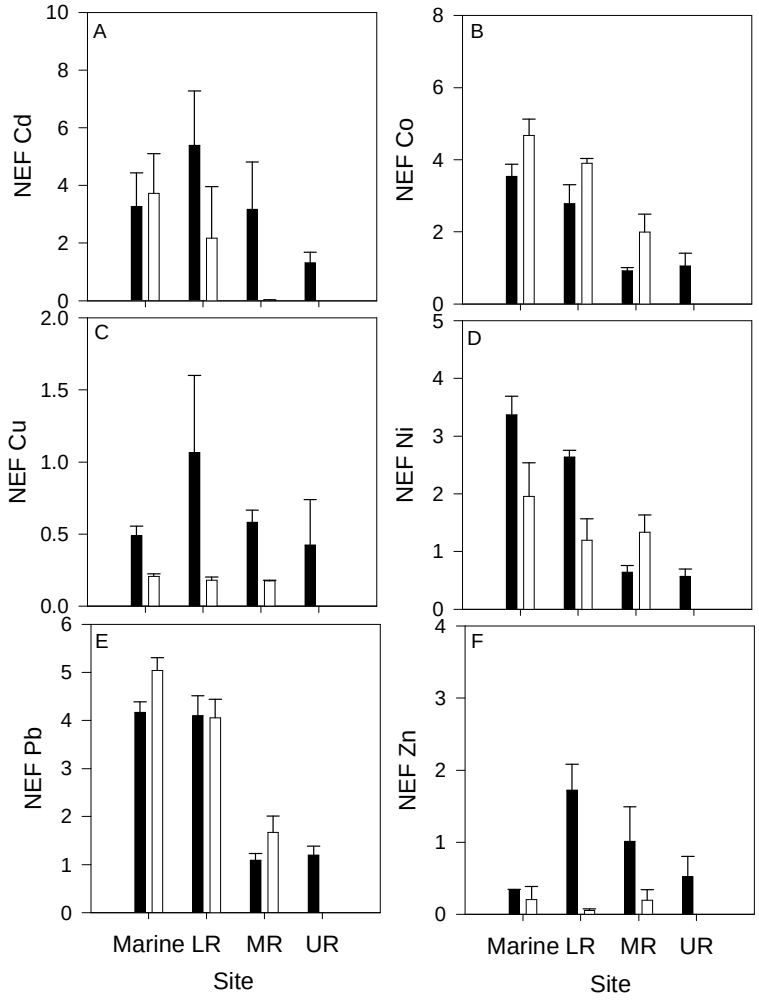

Figure 5.11: Spatial variation in mean (± SD) enrichment factors (EF) for sediments taken from the East Kleinemonde Estuary during open and closed mouth phases. *Note:* The upper reaches were not sampled during the wet season due to access problems. (LR = lower reaches, MR = middle reaches, UR = upper reaches).
■ Mouth closed (dry season), □ Mouth open (wet season).

Water

Salinities recorded during this study reflect the elevated input of freshwater during the wet season. The average salinity dropped from 23.3 psu during the dry season to 9.8 psu during the wet season, with all sites having lower salinities when the mouth was open. More suspended matter was present in the water column of the East Kleinemonde Estuary during the wet season, which can be attributed to the increased turbulence caused by rapid freshwater inflow as well as the reduction in depth due to breaching of the estuary.

The mean (± SD) concentration of Pb in the water of the East Kleinemonde Estuary during the closed and open mouth phases were 2.46 (± 1.41) $\mu g \cdot \ell^{-1}$ and 3.71 (± 2.41) $\mu g \cdot \ell^{-1}$, respectively. The mean (± SD) concentration of Cd in the water of the East Kleinemonde Estuary during the closed and open mouth phases were 0.110 (± 0.21) $\mu g \cdot \ell^{-1}$ and 0.386 (± 0.62) $\mu g \cdot \ell^{-1}$, respectively. Following freshwater inflow, the concentrations of Pb and Cd in the water were higher in the middle reaches, suggesting fluvial or terrestrial input (Fig. 5.12). During both seasons, the mean concentrations of Pb and Cd both fell well below the South African recommended water quality guidelines for coastal marine waters (DWAF, 1995), indicating that the water of the East Kleinemonde Estuary was uncontaminated with these metals at the time of sampling.

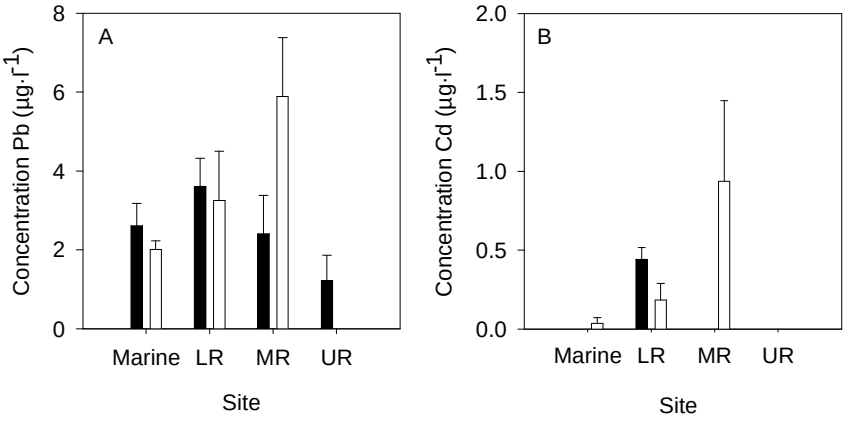

Figure 5.12: Spatial and temporal variations in the mean (± SD) concentrations of Pb and Cd in water collected from the East Kleinemonde Estuary when the mouth was closed and open *Note*: The upper reaches were not sampled during the wet season due to access problems. (LR = lower reaches, MR = middle reaches, UR = upper reaches).
■ Mouth closed (dry season), □ Mouth open (wet season).

5.4 RIET ESTUARY

Sediment Characteristics

The spatial patterns in the grain size composition for the Riet Estuary can be seen in Fig. 5.13. A distinct temporal pattern was evident with a marked increase in fine grained sands and mud at all sites when the estuary breached. During both seasons the fraction of medium sands decreased in a landward direction, and the percentage of fine grained sands and mud increased.

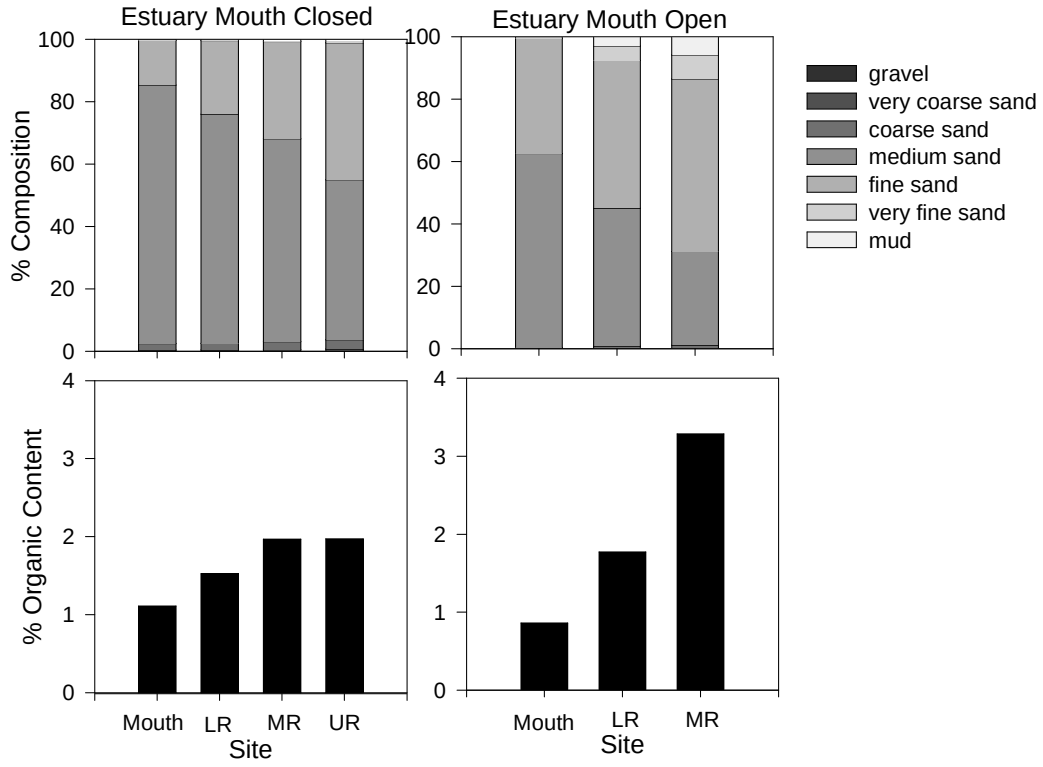

Figure 5.13: Grain size composition and organic content of the sediments from the Riet Estuary during open and closed mouth phases. *Note*: The upper reaches were not sampled during the wet season due to access problems. (LR = lower reaches, MR = middle reaches, UR = upper reaches).

There was an increasing trend in percentage organic content from the mouth of the estuary to the upper reaches, although all sites had a relatively low organic content (Fig. 5.13). There was a slight increase in the average organic content from the dry season (1.53 %) to the wet season (2.11 %), although the increase was not significant ($p > 0.05$).

Metals in Sediment

The concentrations of metals in the sediment of the Riet Estuary during both the dry season and wet seasons are shown in Table 5.7 A and 4.7 B. The average concentrations of Cd, Co, Cu, Ni and Pb decreased significantly in a landward direction during the dry season (Table 5.7 A). These metals were thus uncorrelated to the organic content and mud content of the sediments, which increased in a landward direction (Table A 10, Appendix 2). Iron and Zn concentrations showed no significant spatial variation along the estuary during the dry season (Table 5.7 A).

TABLE 5.7 A
Mean (± SD) concentrations of all metals (mg·kg^{-1}, dry wt.) in the sediments along the Riet Estuary during a dry season

Site	Cd	Co	Cu	Fe	Ni	Pb	Zn
Marine	1.33^{a} (± 0.09)	5.06^{a} (± 0.17)	5.52^{a} (± 1.67)	1589^{a} (± 49)	9.38^{a} (± 1.16)	17.97^{a} (± 0.56)	1.48^{a} (± 0.77)
LR	1.17^{a} (± 0.18)	4.86^{a} (± 0.44)	5.03^{a} (± 1.32)	1996^{a} (± 240)	9.82^{a} (± 2.41)	17.03^{a} (± 0.87)	4.55^{a} (± 3.63)
MR	0.40^{b} (± 0.12)	1.80^{b} (± 0.98)	2.04^{ab} (± 1.02)	2333^{a} (± 731)	3.60^{b} (± 1.69)	7.25^{b} (± 1.26)	4.18^{a} (± 5.33)
UR	0.36^{b} (± 0.07)	1.45^{b} (± 1.60)	1.20^{b} (± 1.35)	2560^{a} (± 2108)	2.44^{b} (± 2.43)	5.61^{b} (± 2.28)	2.42^{a} (± 2.73)
Mean (dry season)	0.81 (± 0.47)	3.29 (± 1.93)	3.44 (± 2.26)	2119 (± 1030)	6.31 (± 3.82)	11.96 (± 5.94)	6.26 (± 10.71)

TABLE 5.7 B
Mean (± SD) concentrations of all metals (mg·kg^{-1}, dry wt.) in the sediments along the Riet Estuary during a wet season

Marine	1.40^{a} (± 0.44)	4.39^{a} (± 0.21)	0.95^{a} (± 0.37)	1350^{a} (± 74)	11.8^{a} (± 1.44)	12.3^{a} (± 10.7)	4.3^{a} (± 3.97)
LR	0.51^{a} (± 0.14)	2.96^{a} (± 0.88)	0.87^{a} (± 1.06)	2389^{a} (± 155)	6.6^{a} (± 1.96)	9.8^{a} (± 0.1)	3.1^{a} (± 2.43)
MR	0.55^{a} (± 0.09)	2.83^{a} (± 1.98)	3.49^{b} (± 0.94)	8232^{b} (± 1936)	9.3^{a} (± 1.76)	8.3^{a} (± 1.0)	11.5^{a} (± 1.18)
Mean (wet season)	0.90 (± 0.53)	3.53 (± 1.20)	1.65 (± 1.40)	3613 (± 3287)	9.6 (± 2.70)	10.5 (± 6.5)	6.01 (± 4.56)

Note: Different superscript letters denote significant differences within columns, ($p < 0.05$).

There was no significant spatial variation in Cd, Co, Ni, Pb and Zn concentrations during the wet season ($p > 0.05$). The estuary thus appeared to be more homogenous with respect to sediment metal concentrations during the wet season and this may be due to increased mixing and scouring of the sediments. There were no significant differences in

average metal concentrations in the sediment of the Riet Estuary between dry and wet seasons ($p > 0.05$), with the exception of Ni, which increased significantly during the wet season.

Principal component analysis was used to identify similarities between variables during the dry season. Three principal components were extracted that explained approximately 87 % of the cumulative variance in the data. Variable loadings for each principal component are given in Table 5.8. The principal components loadings plot (component 1 *vs.* component 2) clearly shows that Cd and Pb were highly correlated, as were Co, Cu and Ni (Fig. 5.14). These metals were also associated with the medium sized sand fraction, which was found predominantly in the marine environment and lower reaches of the estuary. Sediment organic content (TOC), mud and Fe were highly correlated, which was expected since both Fe and organic matter are known to associate with fine grained particles. Zinc introduced a unique source of variance into the system and was uncorrelated to the other variables.

Principal component analysis was also applied to wet season data. Three new "latent variables" were extracted that accounted for approximately 87 % of the cumulative variance in the data. The principal component loadings for each variable are given in Table 5.9. A plot of the loadings for PC 1*vs.* PC 2 indicates two distinct clusters of variables (Fig. 5.15). The cluster on the far right comprises Cd, Pb, Co and Ni. These metals were associated with the medium sands of the marine environment. The second cluster on the far left is made up of very fine sand, mud, TOC, Fe, Cu and Zn. The distribution of Cu and Zn during the wet season was thus probably being controlled by binding to organic matter, adsorption to the surfaces of fine grained sediments and formation of Fe-oxides.

TABLE 5.8
Principal component loadings for metal concentrations and sediment characteristics in the Riet Estuary, sampled during the dry season (mouth closed)

	Component 1 (53.72 %)*	Component 2 (25.25 %)*	Component 3 (8.30 %)*
Cd	**0.96**	0.13	0.08
Co	**0.87**	0.44	-0.09
Cu	**0.85**	0.39	0.09
Fe	-0.41	**0.86**	-0.19
Ni	**0.87**	0.42	0.14
Pb	**0.95**	0.22	-0.02
Zn	-0.05	0.48	**0.76**
TOC (%)	-0.43	**0.86**	-0.08
Coarse sand	-0.43	-0.48	-0.07
Medium sand	**0.91**	-0.21	-0.24
Fine sand	**-0.81**	0.06	0.47
Very fine sand	**-0.82**	0.32	-0.18
Mud	-0.49	**0.77**	-0.31

Note: Loadings greater than ± 0.6 are in bold and indicate moderate relationships between the variable and principal component. *Percentage total variance.

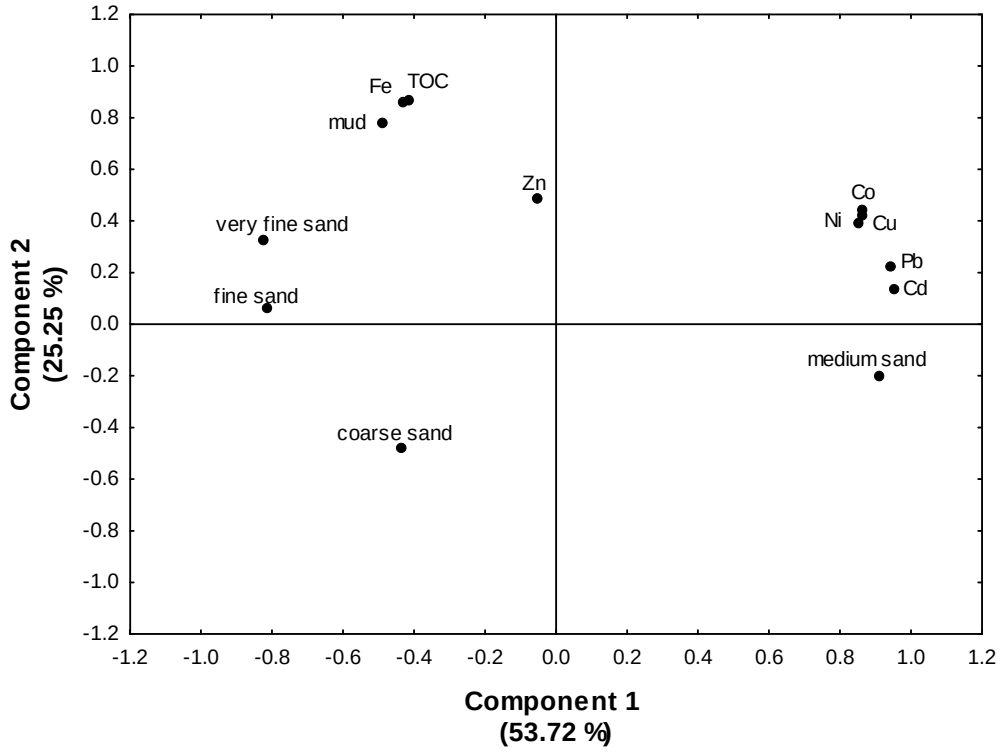

Figure 5.14: Principal component loadings plot (PC 1 *vs.* PC 2) for metals concentrations and sediment characteristics of the Riet Estuary sediments during the dry season (mouth closed).

TABLE 5.9
Principal component loadings for metal concentrations and sediment characteristics in the Riet Estuary, sampled during the wet season (mouth open)

	Component 1 (56.59 %)*	Component 2 (17.02 %)*	Component 3 (13.11 %)*
Cd	0.31	-0.29	**0.87**
Co	0.58	-0.41	0.10
Cu	**-0.64**	-0.44	0.56
Fe	**-0.91**	-0.36	-0.10
Ni	0.49	**-0.65**	0.26
Pb	**0.78**	-0.25	-0.14
Zn	**-0.63**	-0.56	0.01
TOC (%)	**-0.94**	-0.23	0.02
Coarse sand	**-0.96**	0.23	0.05
Medium sand	**0.86**	-0.39	-0.31
Fine sand	-0.01	**0.75**	**0.64**
Very fine sand	**-0.98**	-0.02	-0.06
Mud	**-0.97**	-0.13	-0.12

Note: Loadings greater than ± 0.6 are in bold and indicate moderate relationships between the variable and principal component. *Percentage total variance.

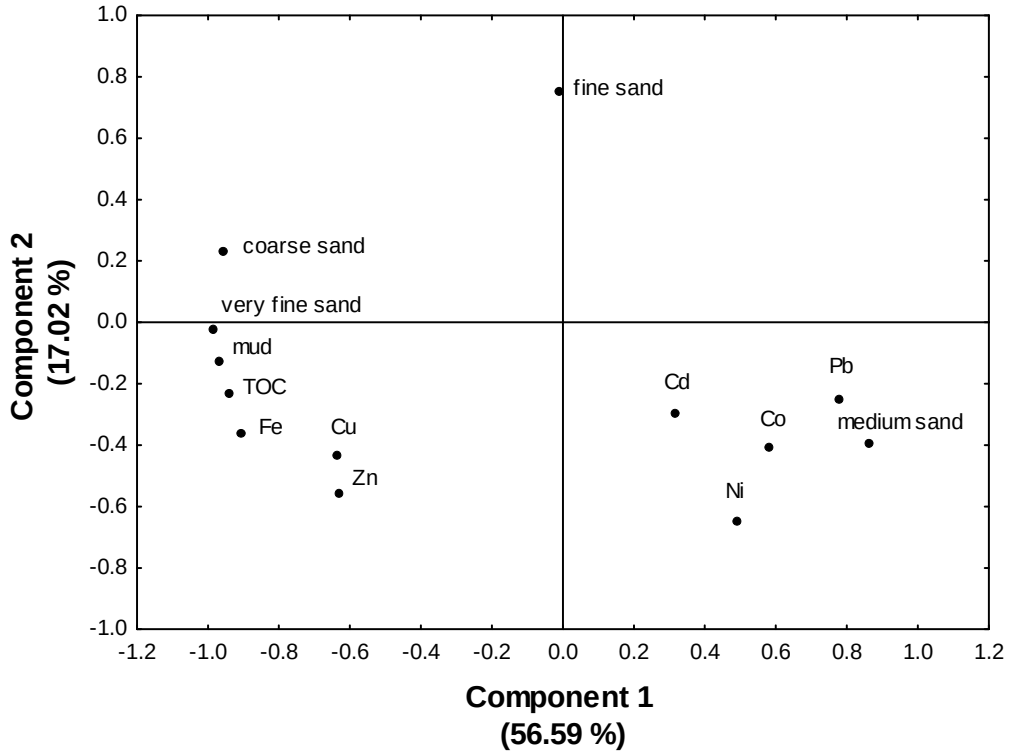

Figure 5.15: Principal component loadings plot (PC 1 *vs.* PC 2) for metals concentrations and sediment characteristics of the Riet Estuary sediments during the wet season (mouth open).

Evidence for enrichment of metals was obtained by superimposing metal concentrations for the Riet Estuary on baseline metal *vs.* Fe linear regression models (Fig. 5.16) Cobalt, Ni and Pb were enriched in several sediment samples during both the dry and wet seasons (Figs. 5.16 A, 5.16 C and 5.16 D), while sediments were only enriched with Cu during the dry season. Sediments were evidently more enriched with Ni during the wet season, with the majority of samples falling above the 95 % prediction limit (Fig. 5.16 C). Zinc concentrations fell within the predicted baseline concentration range during both seasons.

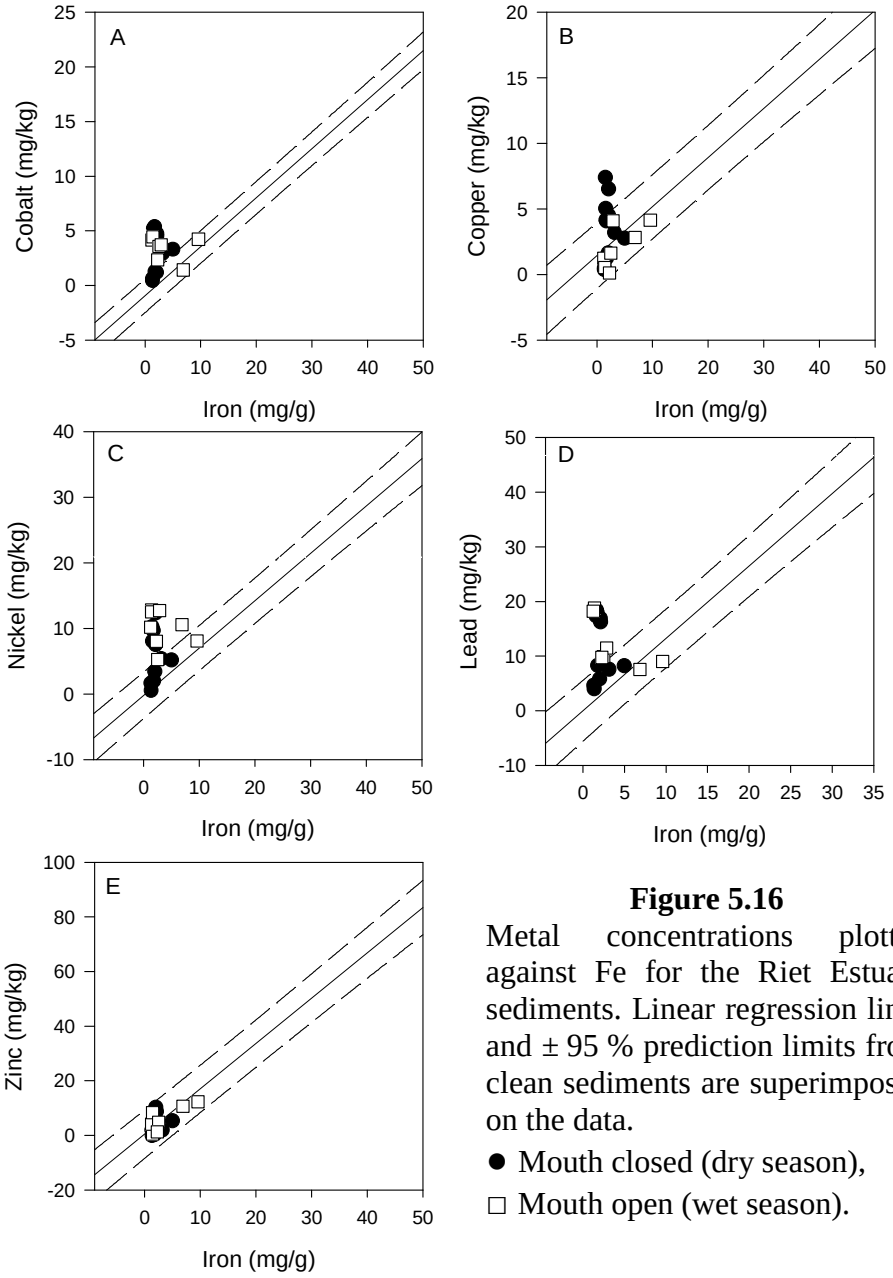

Figure 5.16
Metal concentrations plotted against Fe for the Riet Estuary sediments. Linear regression lines and ± 95 % prediction limits from clean sediments are superimposed on the data.
● Mouth closed (dry season),
□ Mouth open (wet season).

There were no significant temporal changes in the average enrichment factors for all metals (except Ni) within the Riet Estuary sediment (Table 5.11, pg 127), and this may be due to the small size of the catchment and the limited development around the estuary. Calculation of enrichment factors revealed that on average sediments were not enriched with Cu and Zn during both seasons (EF < 1). The Riet Estuary sediments were not enriched with Ni during the dry season but were enriched during the wet season (1 < EF < 2). Cadmium, Co and Pb exhibited moderate enrichment during both seasons (1 < EF < 4), with Cd having the highest enrichment factors.

The Riet Estuary displayed similar spatial variations in metals as the East Kleinemonde Estuary, with the highest levels of enrichment occurring in the marine environment and lower reaches of the system (Figs. 5.17 A to 5.17 F). During the dry season, all metals except Zn were significantly more enriched ($p < 0.05$) in the marine environment and lower reaches as compared to the middle and upper reaches. During the wet season, the only metals that showed significant spatial variation ($p < 0.05$) were Co, Ni and Pb, which decreased significantly in a landward direction. There was thus less spatial variation in metal enrichment during the wet season, and this is probably due to the mixing and scouring of sediments caused by the increased freshwater inflow. Please note that Cd enrichment was not normalized for grain size, and thus Cd / Fe ratios were calculated in order to asses the normalized distribution of Cd. Although not shown, Cd / Fe values increased significantly in a seaward direction indicating an accumulation of Cd at the mouth and lower reaches of the estuary. This normalized Cd distribution was observed in both seasons.

Water

The increased freshwater input into the Riet Estuary during spring (October) resulted in a reduction in salinity in the lower and middle reaches of the system. The average salinity within the Riet Estuary dropped from 23.25 psu in the dry season to 18.33 psu during the wet season. The freshwater influx concurrently resulted in an increase in suspended solids from 31.25 $mg \cdot \ell^{-1}$ during the dry season to 49.06 $mg \cdot \ell^{-1}$ during the wet season, although the difference between seasons was not significant ($p > 0.05$).

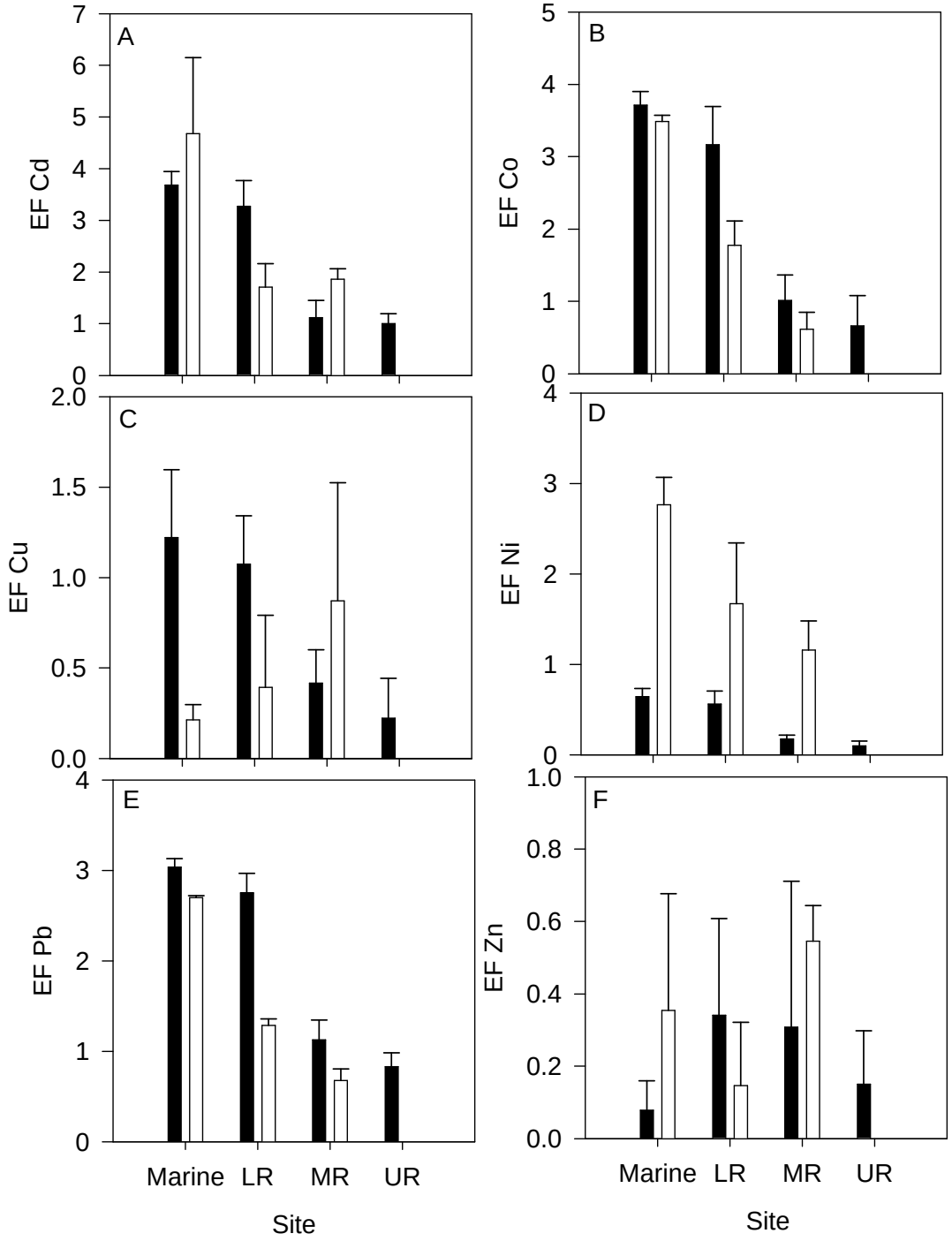

Figure 5.17: Spatial variation in mean (± SD) enrichment factors (EF) for sediments taken from the Riet Estuary during open and closed mouth *Note:* The upper reaches were not sampled during the wet season due to access problems (LR = lower reaches, MR = middle reaches, UR = upper reaches).
■ Mouth closed (dry season), □ Mouth open (wet season).

There was no significant spatial variation in the concentrations of Cd and Pb in the water along the Riet Estuary (Fig. 5.18 A and 5.18 B). There was a slight reduction in the mean concentrations of Pb and Cd in the water collected from the Riet Estuary when the mouth of the estuary was open (Figs. 5.18 A and 5.18 B), but the difference was not significant ($p > 0.05$). The mean (± SD) concentrations of Pb and Cd in the water when the mouth was closed were 2.747 (± 1.751) $\mu g \cdot \ell^{-1}$ and 0.475 (± 0.191) $\mu g \cdot \ell^{-1}$, respectively. The mean concentrations when the estuary breached were 1.107 (± 2.480) $\mu g \cdot \ell^{-1}$ and 0.362 (± 0.430) $\mu g \cdot \ell^{-1}$, respectively. The mean concentrations of Cd and Pb at all sites were well below the DWAF recommended guidelines for those metals.

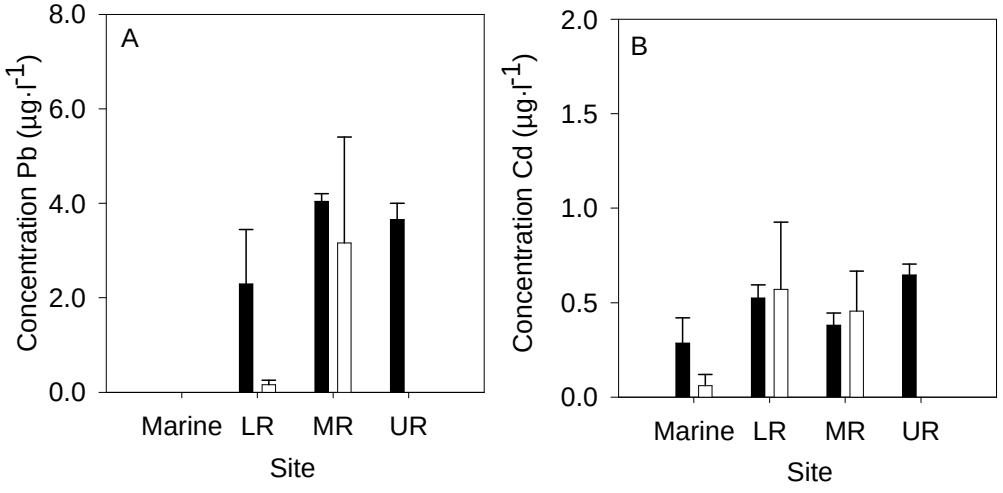

Figure 5.18: Spatial and temporal variations in the mean (± SD) concentrations of Pb and Cd in water collected from the Riet Estuary when the mouth was closed and open. *Note*: The upper reaches were not sampled during the wet season due to access problems. (LR = lower reaches, MR = middle reaches, UR = upper reaches).
■ Mouth closed (dry season), □ Mouth open (wet season).

5.5 DISCUSSION

A summary of the absolute concentrations and enrichment factors of metals in the sediments of the three estuaries studied are shown in Tables 5.10 (pg. 126) and 5.11 (pg. 127). The temporal variations in metal concentrations and enrichment within sediments differed for each estuary and each metal, and this may be due to differences in the extent and type of development surrounding the estuaries, the magnitude and

frequency of freshwater inflow, the biological uptake and cycling of metals within the estuary, the physico-chemical interactions between metals and sediment characteristics and differences in the underlying geology. Each estuary thus needs to be considered independently when trying to develop management strategies to prevent metal enrichment and contamination.

Cadmium and Pb, elements of great environmental concern, displayed average enrichment factors of $0.75 < EF < 4.07$ for Cd and $1.55 < EF < 3.17$ for Pb within the sediments of the three estuaries studied. These enrichment factors suggest minor to moderate enrichment of Cd and Pb. Elevated rainfall resulted in an overall reduction in Pb concentrations and enrichment within the sediment and water of the Kariega and Riet Estuaries, whereas it resulted in an increase in Pb concentrations and enrichment within the water and sediment of the East Kleinemonde Estuary. Conversely, Cd enrichment increased in the sediments of the Kariega and Riet Estuaries during heavy rainfall, but decreased in the East Kleinemonde Estuary. Cadmium is a common constituent of phosphate fertilizers, which are widely used in the Eastern Cape (Loewe, 2007) and it has been found that Cd may enter aquatic systems via the degradation these fertilizers (Bettet-Chambers, 1999). The elevated levels of Cd within these estuaries may thus be linked to the use of phosphate fertilizers within their catchments. It is possible that anthropogenic enrichment of Cd during the wet season is also coupled with geological enrichment, which would increase with higher levels of rainfall and runoff. The significant reduction in Cd concentrations in the water column of the Kariega Estuary during the wet season is likely to be as a result of the diluting effect of the increased flow of freshwater into the estuary. It may also be due to up-take of Cd from the water column by phytoplankton or suspended sediments.

The elevated enrichment of metals at the mouth and lower reaches of the estuaries studied is an interesting phenomenon, and at first sight appears to reflect the land-use gradient along the estuaries. It is however difficult to conclude that metals were elevated at these sites due to anthropogenic enrichment given the limitations of the current data set. It is possible that metal enrichment increased in a seaward direction as a result of natural

processes that were not accounted for in data analysis. Phytoplankton blooms and upwelling events have been found to play an important role in the bio-geochemical cycling of metals, especially Cd, in the world's oceans and estuaries (Bruland *et al.*, 1978; Takesue and van Geen, 2002). Biological uptake of metals from surface waters by phytoplankton and microplankton would lower concentrations of metals in the surface waters, and the organic detritus would return the Cd to the sediment. Cd is thus cycled in much the same way as PO_4 and NO_3, and in coastal waters where upwelling occurs, Cd will be carried to surface waters together with plant nutrients that stimulate plant growth (Bruland *et al.*, 1978). Seasonal changes in phytoplankton density may thus be responsible for some of the variation seen in metal concentrations in the water column and sediment. Upwelling events are known to occur on the landward side of the Agulhas Current between East London and Port Elizabeth. The centre of this upwelling cell is adjacent to Port Alfred (a coastal town ~ 40 km south west of the Kariega Estuary), and has a lateral range along the Agulhas Current of 85 to 300 km (Lutjeharms *et al.*, 2000). This upwelling event, which occurs 40 % of the time, contributes substantially to the high nutrient loads observed for this section of the coast (Lutjeharms *et al.*, 2000). These continual upwelling events may have thus contributed to the enrichment of metals in the marine and estuarine sediments of the Kariega, East Kleinemonde and Riet Estuaries, although further research needs to be conducted to substantiate this hypothesis.

Cobalt enrichment was evident in the sediments of all three estuaries studied ($1.9 < EF < 3.4$), with the majority of samples falling above the 95 % prediction limit for the Co *vs.* Fe linear regression model. Cobalt enrichment also consistently increased in a seaward direction for all the three estuaries during both seasons. This may suggest that Co is entering the estuaries from a marine source. Cobalt is an essential micronutrient for the growth of marine phytoplankton (Tovar-Sanchez *et al.*, 2004), and thus, like Cd, it may be enriched in the marine sediments due to biological cycling.

5.6 CONCLUSIONS

The effects of rainfall on metal concentrations and enrichment within estuarine sediment and water in the Kariega, Riet and East Kleinemonde Estuaries during both dry and wet seasons was investigated. The increased freshwater inflow led to a reduction in Co, Ni and Pb enrichment in the sediments of the Kariega Estuary. The average concentrations of Cd and Pb in the water of the Kariega Estuary were higher than the South African water quality guidelines for coastal marine waters during the dry season, and decreased significantly during the wet season. Increased freshwater inflow appears to have played an important role in flushing metals from the sediment and water column during the wet season, and should be considered as a management strategy for preventing excessive accumulation of metals in the estuary. Temporal variations existed in metal concentrations and enrichment within the Riet and East Kleinemonde Estuaries, but the variations were less pronounced than in the Kariega Estuary.

Despite the minor to moderate enrichment of metals in the sediments of these estuaries since the study by Watling and Watling (1983a), the absolute concentrations of metals are still relatively low. Metal contamination may not yet pose a threat to these estuarine environments. However, Eastern Cape rainfall is limited and impoundments together with poor catchment management may lead to the accumulation of metals in estuaries, particularly those in which coastal development occurs. It is thus important to consider the natural flow of an estuary when trying to limit contamination.

TABLE 5.10
Mean (± SD) absolute concentrations (mg·kg^{-1}, dry wt) of metals in sediments from the Kariega, East Kleinemonde and Riet estuaries, sampled during dry and wet seasons

Estuary	season	Cd	Co	Cu	Fe	Ni	Pb	Zn
Kariega	Dry	0.27* (± 0.23)	5.48* (± 2.01)	3.57 (± 4.10)	5659 (± 3140)	10.58 (± 6.39)	22.20* (± 3.41)	12.93 (± 18.87)
	Wet	0.88* (± 1.28)	4.16* (± 1.59)	3.14 (± 2.11)	4129 (± 4439)	7.35 (± 11.43)	14.01* (± 7.59)	12.21 (± 13.61)
East Kleinemonde	Closed mouth (dry)	1.18 (± 0.69)	6.23 (± 3.64)	4.55 (± 3.29)	8554** (± 10525)	11.83 (± 5.34)	21.91 (± 8.27)	21.75** (± 18.93)
	Open mouth (wet)	0.60 (± 0.67)	5.12 (± 0.65)	0.88 (± 0.08)	2362** (± 1281)	7.08 (± 2.17)	20.84 (± 7.44)	2.08** (± 1.93)
Riet	Closed Mouth (dry)	0.81 (± 0.47)	3.29 (± 1.93)	3.44 (± 2.26)	2119 (± 1030)	6.31• (± 3.82)	11.96 (± 5.94)	6.26 (± 10.71)
	Open Mouth (wet)	0.90 (± 0.53)	3.53 (± 1.20)	1.65 (± 1.40)	3613 (± 3287)	9.6• (± 2.70)	10.5 (± 6.5)	6.01 (± 4.56)
[1]Kariega 1983		0.05	5.4	7.5	16050	9.9	10.7	27.1

*Significant difference between metal concentration in Kariega Estuary sediments during dry and wet seasons ($p < 0.05$).
** Significant difference between metal concentrations in East Kleinemonde Estuary sediments during closed and open mouth phases. ($p < 0.05$).
• Significant difference between metal concentrations in Riet Estuary sediments during closed and open mouth phases. ($p < 0.05$).
[1]Watling and Watling (1983a)

TABLE 5.11
Mean (± SD) enrichment factors (EFs) for sediments from the Kariega, East Kleinemonde and Riet Estuaries, sampled during dry and wet seasons

Estuary	season	Cd	Co	Cu	Ni	Pb	Zn
Kariega	Dry	0.75 (± 0.65)	2.71* (± 1.21)	0.52 (± 0.43)	1.66* (± 1.13)	3.17* (± 1.17)	0.65 (± 1.12)
	Wet	2.82 (± 4.86)	2.02* (± 0.83)	0.58 (± 0.28)	1.36* (± 2.14)	1.96* (± 1.19)	0.87 (± 1.05)
East Kleinemonde	Closed mouth (dry)	3.28 (± 1.92)	2.07** (± 1.21)	0.64** (± 0.38)	1.81 (± 1.29)	2.64 (± 1.58)	0.90** (± 0.63)
	Open mouth (wet)	1.67 (± 1.87)	3.33** (± 1.17)	0.18** (± 0.02)	1.44 (± 0.47)	3.41 (± 1.53)	0.15** (± 0.13)
Riet	Closed Mouth (dry)	2.27 (± 1.31)	2.14 (± 1.42)	0.73 (± 0.50)	0.37• (± 0.26)	1.94 (± 1.02)	0.22 (± 0.25)
	Open Mouth (wet)	4.07 (± 3.93)	1.96 (± 1.27)	0.49 (± 0.48)	1.87• (± 0.82)	1.55 (± 0.90)	0.35 (± 0.26)

*Significant difference between EF for Kariega Estuary sediments during dry and wet seasons ($p < 0.05$).
** Significant difference between EF for East Kleinemonde Estuary sediments during closed and open mouth phases. ($p < 0.05$).
• Significant difference between EF Riet Estuary sediments during closed and open mouth phases. ($p < 0.05$).

CHAPTER 6

FINAL DISCUSSION AND CONCLUSIONS

6.1 DISCUSSION AND CONCLUSIONS

The spatial variation of metals in the sediment and water of nine Eastern Cape estuaries was investigated during this study. Three of the estuaries were permanently open systems (Kariega, Great Fish and Kowie Estuaries) and six were temporary open-closed systems (Riet River, East Kleinemonde, West Kleinemonde, Mpekweni, Kasouga and Boknes Estuaries). A baseline survey was conducted on the concentrations of metals in the Kariega, Great Fish and Kowie estuaries in 1983 (Watling and Watling, 1983a), which provided valuable data necessary to calculate regional metal *vs.* Fe linear regression models and enrichment factors of metals in the sediments collected in this study. No prior assessments have been performed on metal concentrations in the temporary open-closed estuaries of the Eastern Cape. The concentrations of metals obtained for the temporary open-closed estuaries in this study will thus provide important reference points for future research.

The effects of rainfall on metal concentrations were assessed by sampling the Kariega, Riet and East Kleinemonde Estuaries during both dry and wet seasons. Unfortunately time did not allow for all estuaries included in this study to be assessed for seasonal variations. Increased rainfall is known to reduce the concentrations of metals in the sediment and water of estuaries through the processes of dilution, erosion and scouring (Geesey *et al*., 1984; Jain and Sharma, 2001). Seasonal variations in metals are usually less pronounced in sediment than in the water column, due to the fact that metals are largely immobilized by physical and chemical binding and adsorption to the sediments (De Groot *et al.*, 1976). The Seasonal variations in metal concentrations were most

pronounced in the water of the Kariega Estuary, with average Cd and Pb concentrations decreasing 66-fold and 19-fold respectively during the wet season. The concentrations of Cd and Pb were higher than the South African water quality guidelines for coastal marine waters during the dry season, indicating that the Kariega Estuary was contaminated with these metals at the time of sampling (July 2006). Variations in metal concentrations in the sediment were less extreme, with a maximum of a 2-fold increase / reduction in concentrations being observed. The influx of freshwater to the Kariega Estuary led to a significant reduction in the enrichment of Co, Ni and Pb in the sediment, and a significant increase in Cu enrichment. The continual input of metals from non-point sources together with the lack of freshwater inflow may thus have led to the accumulation of metals in the Kariega Estuary during the dry season.

Temporal variations existed in metal concentrations within the Riet River and East Kleinemonde estuaries, but the variations were less pronounced than in the Kariega Estuary. This may be attributed to the fact that they have smaller catchments associated with less development. It is important to note that the temporal variations differed for each estuary and each metal. These variations may be due to a variety of geological, physical and chemical factors not accounted for in this study. More detailed studies are thus needed to identify the factors that influence temporal variations in metal concentrations in individual systems.

On average, the concentrations of metals in the sediment of the nine estuaries studied were within the regional baseline concentration ranges for those metals (Table 6.1). The sediments of the Kowie had the highest sediment Cd concentrations and enrichment factors. The Kowie Estuary is surrounded by the greatest degree development as compared to the other estuaries studied, and it also has a large catchment area that is dominated by shale (Retief, 1995). These features combined may have contributed to the elevated Cd concentrations within the sediments this system. The concentrations of Cd and Pb in the water column of the nine estuaries were below South African Water quality guidelines, except for the Kariega Estuary which exhibited elevated levels of these metals during the dry season (Table 6.2).

Enrichment factors were calculated in order to asses the extent of metal enrichment within the sediments since baseline data was collected in 1983 (Watling and Watling, 1983a). The average enrichment factors for all estuaries are shown in Table 6.3. On average, the sediments of all estuaries showed no enrichment of Cu and Zn (EFs < 1). Average enrichment factors of greater that 1 were observed for Cd, Co, Ni and Pb in the Kariega, East Kleinemonde, Riet, West Kleinemonde and Great Fish Estuaries. The sediments of the Boknes, Kasouga, Mpekweni and Kowie Estuaries were unenriched with all metal except Cd. In general, the normalized concentrations of Cd and Pb decreased in a landward direction, following the development gradient along the estuaries. This distribution was also mimicked by Ni and Co in select estuaries. Enrichment of metals in the marine environment and lower reaches of the estuaries could suggest anthropogenic input. Given that there is no industrial development within the catchments of the estuaries studies, the most likely anthropogenic sources for these metals are non-point sources such as storm water runoff and atmospheric deposition of combusted fuels.

Lead, Cd, Ni, Cu and Zn are common constituents of runoff and they are known to contribute to the degradation of water quality (Gobel *et al*., 2007). Roads, sidewalks, commercial and residential structures collect metals from both dry and wet atmospheric deposition. Metals are removed from these surfaces during precipitation and are channeled into water ways (Gobel *et al*., 2007). Roofing materials also release metals such Cu, Zn, Al and Pb during the process of corrosion, and they typically contribute to a large fraction of the metals entering storm water runoff (Gobel *et al*., 2007).

The largest source of anthropogenic Pb entering the environment results from the combustion of leaded petrol (Duzgoren-Aydin *et al*. 2004). Lead is typically deposited onto surrounding surfaces from which it eventually enters storm water runoff (Gobel *et al.,* 2007). Leaded petrol has recently been phased out of use in South Africa and thus it is likely that lead concentrations within the estuaries studied will decrease over time. Road traffic is another major source of metals in runoff, and metal sources from traffic include; road surface abrasion, tyre abrasion (Zn, Pb, Cd, Cr, Ni, Pb), brake pad abrasion (Ni, Cr, Cu, Pb) drip loss (fuel, oil, grease) and corrosion products (Gobel *et al*., 2007).

The average concentrations of Cd, Pb and Ni in surface runoff originating from motorways is greater that that of main roads, service roads, car parks and pedestrian paths (Gobel *et al*., 2007). All the estuaries surveyed (except the Boknes) were traversed by a two-laned highway (the R72), which may be contributing substantially to the total load of metals entering the lower reaches of the estuaries.

Cadmium enrichment was observed in all estuaries studied ($0 < EF < 7$). Cadmium was also predominately associated with the coarse and medium grained sand fractions found in the marine environment and lower reaches of the estuaries. This may suggest that the source of Cd enrichment is from the marine environment. Biological activity has been identified as the most important factor in controlling the distribution and transport of Cd (Boyle *et al.*, 1976; Simpson, 1981). Cadmium is removed from surface waters by phytoplankton, and zooplankton grazing subsequently returns Cd to the sediment as fecal pellets (Boyle *et al.*, 1976; Simpson, 1981). Upwelling events bring dissolved Cd back to the surface waters where some accumulates in the sediment. Maximum Cd concentrations are thus usually associated with areas of high biological activity such as upwelling zones (Simpson, 1981). An upwelling cell is located adjacent to Port Alfred and it has a lateral range of 85 – 300 km (Lutjeharms *et al*., 2000) and contributes to the elevated nutrient loads observed along this stretch of coastline (Lutjeharms *et al*., 2000). It is thus possible that the elevated concentrations of Cd in the sediments of the marine environment are due to upwelling associated enrichment.

Cadmium enters the oceans via both natural and anthropogenic sources and approximately 50 % of Cd entering the oceans is from anthropogenic input (Simpson, 1981). It was estimated that by Simpson (1981) that by the year 2000, human activities would have introduced more than 250, 000 tones of Cd into the oceans. The atmospheric deposition of Cd into the ocean is thus thought to be an equally important source of Cd as riverine input, and up to 80 % of the atmospheric Cd entering the oceans results from man's activities (Simpson, 1981). Cadmium is regarded as a chalcophile element and has a similar ionic radius as Ca (Garrett, 2000). Cadmium is thus present in calcium phosphate and is incorporated into various sedimentary rock-phosphates that are used as

agricultural fertilizers (Garrett, 2000). Most of the Cd remains in the fertilizer during production, and hence Cd is added to agricultural lands that use such fertilizers (Garrett, 2000). Phosphate fertilizers are extensively used by pineapple farmers in the Eastern Cape, and it is possible that Cd is also entering the estuaries via degradation of these fertilizers. The average concentrations of Cd within the sediment of the Eastern Cape estuaries studied did however fall into the worldwide 'normal range' of 0.1 – 2.0 $mg \cdot kg^{-1}$ reported for estuaries and closed bays (Simpson, 1981), and thus the Eastern Cape estuaries are generally uncontaminated with Cd with respects to international standards.

6.2 RECOMMENDATIONS FOR FUTURE RESEARCH

This project has served as an introduction to metals research in the Eastern Cape, and will hopefully provide a platform from which future research can be conducted. The most logical progression from this project would be to conduct a study on the extent of bioaccumulation of metals in estuarine biota, particularly filter feeding and burrowing organisms. It is also important to asses the bioavailability of metals within the sediments of Eastern Cape estuaries, as bioavailability of metals is inseparably linked with metal uptake in many benthic organisms (Bryan and Langston, 1992). The Kowie, Kariega and East and West Kleinemonde Estuaries would be interesting systems on which to conduct such studies as they exhibited notably higher Cd (Kowie) and Pb (Kariega and East and West Kleinemonde) enrichment within the sediments.

Most countries have well established chemical monitoring programs, and it is imperative that such long term monitoring programs are initiated on the South African coastline. Chemical monitoring alone can not, however, be used to asses the environmental risks imposed by chemical contamination (Wu, 2007). Ecotoxicology and use of bioindicators and biomarkers has emerged as a powerful means of assessing the effects of contaminants on living organisms and ecosystem health, and a combination of chemical and biological monitoring allows scientists to better assess environmental risk (Wu, 2007). It is advised that future research focuses on identifying the most suitable bioindicators within Eastern Cape estuaries that can be used alongside chemical monitoring to assess ecosystem health.

Future surveys of metal concentrations within sediment should also include analysis of acid volatile sulfides, Al, Mn, Ca, Eh and pH as these variables are known to influence metal distribution and bioavailability. Analysis of Al and Ca would provide valuable information on the associations of metals with the terrigenous and marine sediments, and would have aided in understanding the distribution of metals within this study.

It has been identified that river flow influences the concentrations of metals in the sediment and water of permanently open and temporary open-closed estuaries. The effects of freshwater inflow, however, varied between estuaries, and thus more detailed studies need to be conducted on seasonal variations of metal concentrations within Eastern Cape estuaries. The Kariega Estuary had significantly higher concentrations of Pb in the water and sediment during the dry season, and it would be interesting to model the input of Pb into the Kariega Estuary over time. It would also be of interest to conduct stable Pb isotope studies to yield information on the geological and anthropogenic origin of Pb (Farmer and Eades, 1996).

It was found that the concentrations and enrichment of several metals in the sediments increased significantly in a seaward direction, possibly suggesting input from the marine environment. It was hypothesized that this pattern of enrichment may be due to upwelling events that take place on the shore edge of the Agulhas Current. It would thus be interesting to conduct spatial and temporal studies on metal concentrations in the offshore environment of the Eastern Cape to identify if upwelling is an influencing factor. Such studies should be coupled with nutrient and phytoplankton analysis (Bruland *et al.*, 1978; Tekesue and van Geen, 2002).

TABLE 6.1
Mean (± SD) absolute concentrations ($mg \cdot kg^{-1}$, dry wt) of metals in sediments of nine Eastern Cape estuaries

Estuary	Season	Cd	Co	Cu	Fe	Ni	Pb	Zn
Kariega	Dry	0.27 (± 0.23)	5.48 (± 2.01)	3.57 (± 4.10)	5659 (± 3140)	10.58 (± 6.39)	22.20 (± 3.41)	12.93 (± 18.87)
	Wet	0.88 (± 1.28)	4.16 (± 1.59)	3.14 (± 2.11)	4129 (± 4439)	7.35 (± 11.43)	14.0 (± 7.59)	12.21 (± 13.61)
East Kleinemonde	Closed mouth (dry)	1.18 (± 0.69)	6.23 (± 3.64)	4.55 (± 3.29)	8554 (± 10525)	11.83 (± 5.34)	21.91 (± 8.27)	21.75 (± 18.93)
	Open mouth (wet)	0.60 (± 0.67)	5.12 (± 0.65)	0.88 (± 0.08)	2362 (± 1281)	7.08 (± 2.17)	20.84 (± 7.44)	2.08 (± 1.93)
Riet River	Closed Mouth (dry)	0.81 (± 0.47)	3.29 (± 1.93)	3.44 (± 2.26)	2119 (± 1030)	6.31 (± 3.82)	11.96 (± 5.94)	6.26 (± 10.71)
	Open Mouth (wet)	0.90 (± 0.53)	3.53 (± 1.20)	1.65 (± 1.40)	3613 (± 3287)	9.6 (± 2.70)	10.5 (± 6.5)	6.01 (± 4.56)
Mpekweni	-	0.64 (± 0.25)	5.25 (± 4.14)	6.93 (± 3.66)	14912 (± 16300)	3.41 (± 3.38)	11.86 (± 4.73)	16.27 (± 13.78)
West Kleinemonde	-	0.81 (± 0.34)	6.24 (± 3.23)	4.55 (± 3.29)	5435 (± 5474)	11.83 (± 5.34)	21.91 (± 8.27)	21.75 (± 18.93)
Kasouga	-	0.71 (± 0.61)	3.34 (± 3.23)	1.63 (± 2.33)	5513 (± 4858)	3.41 (± 3.38)	6.42 (± 3.62)	3.63 (± 5.01)
Boknes	-	0.43 (± 0.31)	1.26 (± 1.72)	2.40 (± 2.75)	3101 (± 2480)	2.30 (± 2.85)	4.81 (± 1.92)	13.3 (± 22.5)
Great Fish	-	0.65 (± 0.32)	4.67 (± 2.49)	5.81 (± 4.85)	5801 (± 4592)	10.38 (± 4.77)	7.41 (± 5.60)	21.41 (± 17.33)
Kowie	-	2.18 (± 1.21)	2.31 (± 1.58)	4.27 (± 3.30)	5659 (± 3140)	4.13 (± 2.60)	4.93 (± 1.68)	10.67 (± 8.35)

TABLE 6.2
Mean (± SD) concentrations (µg·ℓ$^{-1}$) of Cd and Pb in the water of nine Eastern Cape estuaries

Estuary	Season	Cd	Pb
Kariega	Dry	3.32 (± 4.09)	34.13 (± 42.56)
	Wet	0.05 (± 0.99)	1.75 (± 1.09)
East Kleinemonde	Closed mouth (dry)	0.11 (± 0.21)	2.46 (± 1.41)
	Open mouth (wet)	0.38 (± 0.61)	3.71 (± 2.41)
Riet River	Closed Mouth (dry)	0.48 (± 0.19)	2.74 (± 1.75)
	Open Mouth (wet)	0.36 (± 0.43)	1.11 (± 2.48)
Mpekweni	-	0.40 (± 0.12)	3.51 (± 1.37)
West Kleinemonde	-	0.43 (± 0.51)	2.67 (± 1.45)
Kasouga	-	0.07 (± 0.03)	0.75 (± 0.27)
Boknes	-	0.09 (± 0.05)	0.76 (± 0.51)
Great Fish	-	0.13 (± 0.09)	2.81 (± 1.75)
Kowie	-	0.18 (± 0.08)	1.65 (± 0.44)

TABLE 6.3
Mean (± SD) enrichment factors (EFs) for sediments of nine Eastern Cape estuaries

Estuary	Season	Cd	Co	Cu	Ni	Pb	Zn
Kariega	Dry	0.75 (± 0.65)	2.71 (± 1.21)	0.52 (± 0.43)	1.66 (± 1.13)	3.17 (± 1.17)	0.65 (± 1.12)
	Wet	2.82 (± 4.86)	2.02 (± 0.83)	0.58 (± 0.28)	1.36 (± 2.14)	1.96 (± 1.19)	0.87 (± 1.05)
East Kleinemonde	Closed mouth (dry)	3.28 (± 1.92)	2.07 (± 1.21)	0.64 (± 0.38)	1.81 (± 1.29)	2.64 (± 1.58)	0.90 (± 0.63)
	Open mouth (wet)	1.67 (± 1.87)	3.33 (± 1.17)	0.18 (± 0.02)	1.44 (± 0.47)	3.41 (± 1.53)	0.15 (± 0.13)
Riet	Closed Mouth (dry)	2.27 (± 1.31)	2.14 (± 1.42)	0.73 (± 0.50)	0.37 (± 0.26)	1.94 (± 1.02)	0.22 (± 0.25)
	Open Mouth (wet)	4.07 (± 3.93)	1.96 (± 1.27)	0.49 (± 0.48)	1.87 (± 0.82)	1.55 (± 0.90)	0.35 (± 0.26)
Mpekweni	-	1.79 (± 0.69)	1.00 (± 0.63)	0.77 (± 0.20)	0.86 (± 0.38)	0.99 (± 0.46)	0.47 (± 0.30)
West Kleinemonde	-	2.27 (± 0.95)	2.42 (± 1.17)	0.56 (± 0.15)	1.83 (± 1.09)	2.77 (± 1.41)	0.55 (± 0.27)
Kasouga	-	2.02 (± 1.64)	0.73 (± 0.54)	0.22 (± 0.27)	0.38 (± 0.29)	0.65 (± 0.19)	0.14 (± 0.17)
Boknes	-	1.19 (± 0.86)	0.53 (± 0.34)	0.42 (± 0.42)	0.30 (± 0.16)	0.68 (± 0.16)	0.79 (± 1.20)
Great Fish	-	1.81 (± 0.90)	1.86 (± 2.03)	0.84 (± 0.54)	1.41 (± 1.10)	1.03 (± 1.10)	0.98 (± 0.56)
Kowie	-	6.19 (± 3.35)	0.63 (± 0.23)	0.65 (± 0.46)	0.50 (± 0.23)	0.59 (± 0.11)	0.50 (± 0.38)

REFERENCES

Akagi T., Fuwa K., and Haraguchi H. (1985). Simultaneous multi-element determination of trace metals in sea water by inductively-coupled plasma atomic emission spectrometry after coprecipitation with gallium. *Analitica Chimica Acta* **177**, 139-151.

Allanson B. and Baird D. (1999). Estuaries of South Africa. Cambridge University Press: Cambridge.

Allanson B.R. and Read G.H.L. (1987). The response of estuaries along the South Eastern Coast of Southern Africa to marked variation in freshwater inflow. Rhodes University, Institute for Freshwater Studies, Grahamstown.

ANZEC. (2000). Australian and New Zealand guidelines for fresh and marine water quality. Canberra, Australia, Australia and New Zealand Environment and Conservation Council. National water quality management strategy No. 4.

APHA (1998). Standard Methods for the Examination of Water and Wastewater. APHA, AWWA, and WEF (Eds). American Public Health Association: Washington.

Badenhorst P. (1988). Report on the dynamics of the Kleinemonde West and East estuaries. South Africa. CSIR Report EMA/T. 8805, 1-14.

Batterham G.J., Munksgaard N.C., and Parry D. (1997). Determination of trace metals in sea-water by inductively coupled plasma mass spectrometry after off-line dithiocarbamate solvent extraction. *Journal of Analytical Atomic Spectrometry* **12**, 1277-1280.

BCLME. (2006). The development of a common set of water and sediment quality guidelines for the coastal zone of BCLME, South Africa. CSIR/NRE/ECO/2006/0011/C. CSIR. CSIR Report.

Bell K.N., Cowley P.D., and Whitfield A.K. (2001). Seasonality in frequency of marine access to an intermittently open estuary: implications for recruitment strategies. *Estuarine, Coastal and Shelf Science* **52**(3), 327-337.

Bettet-Chambers M., Davies P., and Knott B. (1999). Cadmium in aquatic ecosystems in Western Australia: a legacy of nutrient-deficient soil. *Journal Environmental Management* **57**, 283-295.

Biney C.H., Amuzu A.T., Calamari D., Kaba N., Mbome I.L., Naeve H., Ochumba P.B.O., Radegonde V., and Saad M.A.H. (1994). Review of heavy metals in the African aquatic environment. *Ecotoxicology and Environmental Safety* **28**, 134-159.

Binning K. and Baird D. (2001). Survey of heavy metals in the sediments of the Swartkops River estuary, Port Elizabeth South Africa. *Water SA* **27**(4), 461-466.

Boruvka L., Vaceck O., and Jehlicha J. (2005). Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils. *Geoderma* **128**, 289-300.

Boyle A.E., Sclater F., and Edmond J.M. (1976). On the marine geochemistry of cadmium. *Nature* **263**, 42-44.

Brooks R.R., Presley B.J., and Kaplan I.R. (1967). APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic-absorption spectrophotometry. *Talanta* **14**, 809-816.

Brugmann L., Danielsson L-G., Magnusson B., and Westerlund S. (1983). Intercomparison of different methods for the determination of trace metals in seawater. *Marine Chemistry* **13**(327), 339.

Bruland K.W., Knauer G.A., and Martin J.H. (1978). Cadmium in Northeast Pacific waters. *Limnology and Oceanography* **23**(4), 618-625.

Bryan G.W. (1986). Wastes in the ocean: nearshore waste disposal. Duedall I.W., Ketchum B.H., Kester D.R., Capuzzo J.M., Burt V.W., and Park P.K. (Eds). John Wiley & Sons: New York.

Bryan G.W. and Langston W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution* **76**, 89-131.

Buchman M.F. (1999). NOAA screening quick reference tables. Seattle WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration. NOAA HAZMAT Report.

Buntsma J. and Casey-Lefkowitz S. (1999). Summary workshop: nonpoint source water pollution compliance. International Network for Environmental Compliance and Enforcement. Fifth International Conference on Environmental Compliance and Enforcement. 6-7-1999, 41, 383-386.

CCME. (1995). Protocol for the derivation of Canadian Sediment Quality Guidelines for the protection of Aquatic life. Canadian Council of Ministers of the Environment, Winnipeg, Canada.

Chen C.W., Kao C.M., Chen C.H., and Dong C.D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbour, Taiwan. *Chemosphere* **66**(8), 1431-1440.

Cheng C.J., Akagi T., and Haraguchi H. (1987). Simultaneous multi-element analysis for trace metals in sea water by inductively-coupled plasma/atomic emission spectrometry after batch preconcentration on a chelating resin. *Analitica Chimica Acta* **198**, 173-181.

Clark R.B. (1989). Marine pollution. Claredon Press: Oxford.

Cloete C.E. and Oliff W.D. (1976). South African marine pollution survey report, 1974-1975: a report of the Committee for Marine Pollution National Programme for Environmental Sciences. Pretoria, CSIR. South African national scientific programmes report. 8, 1-59.

Coetzee P.W. (1988). A guide to resorts and recreation. In: 'A field guide to the Eastern Cape coast'. Lubke R.A., Gess F.W., and Bruton M.N. (Eds). The Grahamstown centre of the Wildlife Society of Southern Africa: Grahamstown. pp. 409-427.

Committee for Inland Fisheries of Africa. (1987). Report of the first session of the working party on pollution and fisheries. Accra. FAO Fisheries Report. 369, 23.

Committee for Inland Fisheries of Africa. (1991). Report of the third session of the Working Party on Pollution and Fisheries: review of heavy metals in the African aquatic environment. Rome, FOA. FAO Fisheries Report. 471, 1-43.

Dasalakis K.D. and O'Connor T.P. (1995). Normalization and elemental sediment contamination in the coastal United States. *Environmental Science and Technology* **29**(470), 477.

Day J.H. (1980). What is an estuary? *South African Journal of Science,* 76-198.

De Groot A.J., Salmons W., and Allersma E. (1976). Processes affecting heavy metals in estuarine sediments. In: 'Estuarine Chemistry'. Burton L.J.W and Liss P.S. (Eds). Academic Press: London. pp. 131-153.

Doner G. and Ege A. (2005). Determination of copper, cadmium and lead in seawater and mineral water by flame atomic absorption spectrometry after coprecipitation with aluminum hydroxide. *Analitica Chimica Acta* **547**, 14-17.

Dornemann A. and Kleist H. (1979). Extraction of nanogram amounts of cadmium and other metals from aqueous solution using hexamethyleneammonium hexamethylenedithiocarbamate as the chelating agent. *Analyst* **104**, 1030-1036.

Duzgoren-Aydin N.S., Li, X. D., and Wong S.C. (2004). Lead contamination and isotope signatures in the urban environment of Hong Kong. *Environmental International* **30**, 209-217.

DWAF. (1995). South African Water Quality Guidelines for Coastal Marine Waters. 1. Pretoria, Republic of South Africa Department of Water Affairs and Forestry. Natural Environment.

Dyer K.R. (1997). Estuaries, a physical introduction. John Wiley & Sons: England.

EURACHEM (1998). The fitness for purpose of analytical methods, a laboratory guide to method validation and related topics. EURACHEM: Teddington.

Farmer J.G. and Eades L.J. (1996). Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D. *Environmental Science and Technology* **30**(10), 3080-3083.

Fatoki O.S. and Mathabatha S. (2001). An assessment of heavy metal pollution in the East London and Port Elizabeth Harbours. *Water SA* **27**(2), 233-240.

Field P.M., Cullen J.T., and Sherrell R.M. (1999). Direct determination of 10 trace metals in 50 µL samples of coastal seawater using desolvating micronebulization sector field ICP-MS. *Journal of Analytical Atomic Spectrometry* **14**, 1425-1431.

Garrett R.G. (2007). Natural sources of metals in the environment. *Human and Ecological Risk Assessment* **6**(6), 945-963.

Geesey G.G., Borstad L., and Chapman P.M. (1984). Influence of flow-related events on concentration and phase distribution of metals in the Lower Fraser River and a small tributary in British Columbia, Canada. *Water Research* **18**(2), 233-238.

GESAMP. (1976). Principals for developing coastal water criteria. Rome, The United Nations Group of Experts on the Scientific Aspects of Marine Pollution.

Gibbs R.J. (1994). Metals in sediments along the Hudson River Estuary. *Environmental International* **20**(4), 507-516.

Gobel P., Dierkes C., and Coldewey W.G. (2007). Storm water runoff concentration matrix for urban areas. *Journal of Contaminant Hydrology* **91**, 26-42.

Grange N. and Allanson B.R. (1995). Influence of freshwater inflow on the nature, amount and distribution of seston in estuaries of the Eastern Cape, South Africa. *Estuarine and Coastal Shelf Science* **40**, 403-420.

Harrison R.M. and Laxen S.P.H. (1981). Lead pollution causes and control. Chapman and Hall: New York.

Harrison T.D., Cooper J.A.G., and Ramm A.E.L. (2000). State of South African estuaries; geomorphology, ichthyofauna, water quality and aesthetics. 2. Pretoria, Department of Environmental Affairs and Tourism. State of the Environment Series.

Hennig H.F.-K.O. (1985). A review of metal concentrations in Southern African coastal waters, sediments and organisms. South African National Scientific Programmes Report. 108, 1-140.

Heydorn A.E.F. and Grindley J.R. (1982). Estuaries of the Cape. Part 2: synopsis of available information on individual systems. Report No 10, Kowie. Research Report 409. South Africa, CSIR.

Jain C.K. and Sharma M.K. (2001). Distribution of trace metals in the Hindon River. *Journal of Hydrology* **243**(1-4), 81-90.

Jennings M.E. (2005). Nutrient dynamics in and offshore of two permanently open South African estuaries with contrasting fresh water inflow. Rhodes University MSc Thesis, Grahamstown.

Kanai H., Inouye V., Goo R., and Wakatsuki H. (1979). Solubility of 4-methyl-2-pentanone in aqueous phase of various salt concentrations. *Analytical Chemistry* **51**, 1019-1021.

Kennish M.J. (1997). Practical handbook of estuarine and marine pollution. CRC Press: New York.

Kennish M.J. (2002). Environmental threats and environmental future of estuaries. *Environmental Conservation* **29**(1), 78-107.

Kouadio I. and Trefry J.H. (1987). Sediment trace metals contamination in Ivory Coast, West Africa. *Water Air Soil Pollution* **32**, 145-154.

Leinonen H. and Jukka L. (2000). Ion-exchange of nickel by iminodiacetic acid chelating resin Chelex 100. *Reactive and Functional Polymers* **43**(1-2), 1-6.

Lepedes D.N. (1974). Dictionary of scientific and technical terms. McGraw & Hill: New York.

Lesaca R.M. (1977). Monitoring metals in the Philippine rivers, bay waters and lakes. Toronto. Symposium proceedings of the first international conference on heavy metals in the environment. 2(1), 285-307.

Li X., Shen Z., Wai O.W.H., and LI Y.S. (2001). Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. *Marine Pollution Bulletin* **42**(3), 215-223.

Lin L-C. and Juang R-S. (2007). Ion-exchange kinetics of Cu(II) and Zn(II) from aqueous solutions with two chelating resins. *Chemical Engineering Journal* **132**(1-3), 205-213.

Liu W.X., Li X.D., Shen Z.G., Wang D.C., Wai O.W.H., and Li Y.S. (2003). Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environmental Pollution* **121**, 377-388.

Loewe M. (13-7-2007). Fertilizer saga: supplier to face R70m lawsuit. The Herald . Port Elizabeth.

Long E.R., MacDonald D.D., Smith S.L., and Calder F.D. (1995). Incidence of adverse biological effects within ranges of concentrations in marine and estuarine sediments. *Environmental Management* **19**(1), 81-97.

Lutjeharms J.R.E, Cooper J., and Roberts M. (2000). Upwelling at the inshore edge of the Agulhas Current. *Continental Shelf Research* **20**, 737-761.

MacDonald D.D., Carr R.S., Calder F.D., Longer E.R., and Ingersoll C.G. (1996). Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* **5**, 253-278.

Marr I.L. and Cresser M.S. (1983). Performance and structure of analytical methods. In: 'Environmental chemical analysis'. International Textbook Company: New York. p. 44.

Meglen R.R. (1992). Examining large databases: a chemometric approach using principal component analysis. *Marine Chemistry* **39**, 217-237.

Ndiokwere C.L. (1984). An investigation of heavy metal content of sediments and algae from River Niger and Nigerian Atlantic coastal water. *Environmental Pollution* **7**(B), 247-254.

Newman B.K. and Watling R.J. (2007). Definition of baseline metal concentrations for assessing metal enrichment of sediment from the south eastern Cape coastline of South Africa. *Water SA* **33**(5), 675-681.

Nieboer E. and Richardson D.H.S. (1980). The replacement of the nondescript term 'heavy metals' by a biologically and chemically significant classification of metal ions. *Environmental Pollution* **1**(B), 3-26.

Nriagu J. (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* **279**, 409-411.

Okoye B.C.O., Afolabi O.A., and Ajao E.A. (1991). Heavy metals in the Lagos Lagoon sediments. *International Journal of Environmental Studies* **37**, 35-41.

Pai S-C., Whung P-Y., and Lai R-L. (1988). Pre-Concentration efficiency of Chelex-100 resin for heavy metals in sea water. *Analitica Chimica Acta* **211**, 257-270.

Prichard D.W. (1976). What is an estuary: physical standpoint. In: 'Estuaries'. (Ed). Lauff G.H. American Association for the Advancement of Science: Washington DC. pp. 3-5.

Ramesh A., Mohan K.R., and Seshaiah K. (2002). Preconcentration of trace metals on Amberlite XAD-4 resin coated with dithiocarbamates and determination by inductively coupled plasma-atomic emission spectrometry in saline marices. *Talanta* **57**, 243-252.

Reddering J.S.V and Rust I.C. (1990). Historical changes and sedimentary characteristics of Southern African estuaries. *South African Journal of Science* **86**, 425-428.

Retief P.F. (1995). 1: 250 000 geological series, 3326 Grahamstown. Council for Geoscience. Chief Director of Surveys and Land Information, Mowbray, South Africa.

Roach A.C. (2005). Assessment of metals in sediments from Lake Macquarie, New South Wales, Australia, using normalization models and sediment quality guidelines. *Marine environmental Research* **59**, 453-472.

Rodushkin I. and Ruth T. (1997). Determination of trace metals in estuarine and sea-water reference materials by high resolution inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry* **12**, 1181-1185.

Rosland E. and Lund W. (1998). Direct determination of trace metals in sea-water by inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry* **13**, 1239-1244.

Ross G.J.B. (1988). Coastal Hydrography. In: 'A field guide to the Eastern Cape coast'. Lubke R.A., Gess F.W., and Bruton M.N. (Eds). The Grahamstown centre of the Wildlife Society of Southern Africa: Grahamstown. pp. 31-32.

Ruiz J.M. and Saiz-Salinas J.I. (2000). extreme variation in the concentration of trace metals in sedimnets and bivalves from the Bilbao estuary (Spain) caused by the 1989-1990 drought. *Marine environmental Research* **49**(4), 307-317.

Saad, M. A. H., El Rayis, O. A., and El Nady, F. E. (1980). Occurrence of some trace metals in bottom deposits from Abu Kir Bay, Egypt. *V es Journees Etud.Pollut., Cagliari*, CIESM, 555-560.

Scharler U.M. and Baird D. (2003). The influence of catchment management and phytoplankton biomass of Eastern Cape estuaries, South Africa. *Estuarine and Coastal Shelf Science* **56**(3), 735-748.

Schropp S.J., Lewis G., Windom H.L., Ryan J.D., Calder F.D., and Burney L.C. (1990). Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. *Estuaries* **13**(3), 227-235.

Schumacher B.A. (2002). Methods for the determination of total organic carbon (TOC) in soils and sediments. Las Vegas, United States Environmental Protection Agency.

Sekhar C.K., Chary S.N., Tirumala K.C., and Aparna V. (2003). Determination of trace metals in sea water by ICP-MS after matrix separation. *Acta Chimica Slovenica.* **50**, 409-418.

Simeonov V., Massart D.L., Andreev G., and Tsakovski S. (2000). Assessment of metal pollution based on multivariate statistical modeling of 'hot spot' sediments from the Black Sea. *Chemosphere* **41**, 1411-1417.

Simpson W.R. (1981). A critical review of cadmium in the marine environment. *Progress in Oceanography* **10**(1), 70.

Stephenson T. (1987). Heavy metals in wastewater and sludge treatment processes, Vol.1, sources, analysis and lesilation. (Ed). Lester J.N. CRC Press: Boca Raton.

Stone A.W. (1988). Climate and weather. In: 'A field guide to the Eastern Cape coast'. Lubke R.A., Gess F.W., and Bruton M.N. (Eds). The Grahamstown centre of the Wildlife Society of Southern Africa, Grahamstown: Grahamstown. pp. 19-30.

Subramanian K.S. and Meranger J.C. (1979). Ammonium pyrrolidinedithiocarbamate-methyl isobutyl ketone – graphite furnace atomic absorption system for some trace metals in drinking water. *International Journal of Environmental Analytical Chemistry* **7**, 25-40.

Summers J.K., Wade T.L., Engle V.W., and Malaeb Z.A. (1996). Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries* **19**(3), 581-594.

Takesue R.K. and van Geen A. (2002). Nearshore circulation during upwelling inferred from the distribution of dissolved cadmium off the Oregon coast. *Limnology and Oceanography* **47**(1), 176-185.

Talbot M.M.J.F., Branch E., Marsland S., and Watling R.J. (1985). Metals in South African estuaries. X. Blind, Ihlanza, Nahoon and Quinera Rivers. *Water SA* **11**, 65-68.

Tam N.F.Y. and Yao M.W.Y. (1998). Normalization of heavy metal contamination in mangrove sediments. *Science of the Total Environment* **216**, 33-39.

Tessier A. and Campbell P.G.C (1978). Partitioning of trace metals in sediments: relationships with bioavailability. *Hydrobiologia* **149**, 43-52.

Tessier A., Campbell P.G.C., and Bison M. (1979). Evaluation of the APDC-MIBK extraction method for the analysis of trace metals in river water. *International Journal of Environmental Analytical Chemistry* **7**, 41-54.

Tovar-Sanchez A., Sanudo-Wilhelmy S.A., and Flegal A.R. (2004). Temporal and spatial variations in the biogeochemical cycling of cobalt in two urban estuaries: Hudson River Estuary and San Francisco Bay. *Estuarine and Coastal Shelf Science* **60**(4), 717-728.

Turekian K.K. and Wadepohl K.H. (1961). Distribution of the elements in some major units of the earths crust. *Geological Society of America Bulletin* **72**, 175-192.

US-EPA. (1993). Guidance specifying management measures for sources of nonpoint pollution in coastal waters. EPA 840-B-92-002. United States Environmental Protection Agency. Polluted runoff (nonpoint source pollution).

US-EPA. (1996). Method 3050B, Acid digestion of sediment sludges and soils. Revision 2, 1-12. United States Environmental Protection Agency.

Venugopal B. and Luckey T.P. (1975). Toxicology of non-radioactive metals and their salts. In: 'Metal toxicity, safety and hormology'. Luckey T.P., Venugopal B., and Hutcheson D. (Eds). George Thieme: Stuttergart. pp. 4-73.

Vorwerk P.D. (2000). Ichthyofaunal community structures in different types of Eastern Cape estuaries. Rhodes University MSc Thesis, Grahamstown.

Vorwerk P.D., Froneman P.W., and Paterson A.W. (2007). Recovery of the critically endangered river pipefish, *Syngnathus watermeyeri*, in the Kariega Estuary, Eastern Cape Province. *South African Journal of Science* **103**, 199-201.

Walton C. (1984). Reader's digest atlas of Southern Africa. Reader's Digest Association South Africa: Cape Town.

Watling H.R. and Watling R.J. (1976). Trace metals in oysters from Knysna Estuary. *Marine Pollution Bulletin* **7**(3), 45-48.

Watling R.J. (1988). Metal studies in the coastal environment of the Eastern Cape: a review. In: 'Towards an environmental plan for the Eastern Cape'. Grocott and Sherry: Grahamstown, South Africa. pp. 367-377.

Watling R.J. and Cloete C.E. (1981). South African marine pollution monitoring programme, 1979-1982. Watling R.J. and Cloete C.E. 51, 1-52. Pretoria, CSIR. South African national scientific programmes report.

Watling R.J. and Watling H.R. (1981). A preliminary pollution survey of the Papenkuils River, Port Elizabeth. *Water SA* **7**(4), 211-215.

Watling R.J. and Watling H.R. (1982a). Metal surveys in South African estuaries I. Swartkops River. *Water SA* **8**(1), 27-35.

Watling R.J. and Watling H.R. (1982b). Metal surveys in South African estuaries II. Knysna River. *Water SA* **8**(1), 37-44.

Watling R.J. and Watling H.R. (1982c). Metal surveys in South African estuaries III. Hartenbos, Little Brak and Great Brak Rivers (Mossel Bay). *Water SA* **8**(2), 109-113.

Watling R.J. and Watling H.R. (1982d). Metal surveys in South African estuaries IV. Keurbooms and Bietou Rivers (Plettenberg Lagoon). *Water SA* **8**(2), 115-119.

Watling R.J. and Watling H.R. (1982e). Metal surveys in South African estuaries VI. Sundays River. *Water SA* **8**(4), 193-195.

Watling R.J. and Watling H.R. (1983a). Metal surveys in South African estuaries VII. Bushmans, Kariega, Kowie and Great Fish. *Water SA* **9**(2), 67-70.

Watling R.J. and Watling H.R. (1983b). Trace metal surveys in Mossel Bay, St Francis Bay and Algoa Bay South Africa. *Water SA* **9**(2), 57-65.

Wenchuan Qu., Dickman M., and Sumin W. (2001). Multivariate analysis of heavy metals and nutrient concentrations in sediments of Taihu Lake, China. *Hydrobiologia* **450**, 83-89.

Whitfield A.K. (1992). A characterization of Southern African estuarine systems. *South African Journal of Science* **18**(1-2), 89-103.

Whitfield A.K. and Bate G.C. (2007). A review of information on temporarily open-closed estuaries in the warm and cool temperate biogeographic regions of South Africa, with particular emphasis on the influence of river flow on these systems. 1581/1/07, 214. Water Research Commission (WRC), South Africa.

Wu R. (2007). 5th International conference on marine pollution and ecotoxicology. Hong Kong, City University of Hong Kong. 3-6-2007, 1-3.

Zolotov Yu.A., Malofeeva O.M., Petrukhin O.M., and Timberbaev A.R. (1987). New methods for preconcentration and determination of heavy metals in natural water. *Pure and Applied Chemistry* **59**, 497-504.

APPENDICES

APPENDIX 1: EQUATIONS

1A. Example of calculation used to determine correction factor:

1. First calculate the volume of MIBK remaining for analysis after extraction of metals from seawater.

Salinity = 33.4 psu
% solubility MIBK in 33.4 psu seawater = 0.015
Volume seawater used for extraction = 750 ml
Volume MIBK added to seawater = 35 ml

Volume of MIBK that dissolves in 750 ml seawater of salinity 33.4 psu
= 0.015 × 750 ml
= 11.25 ml

Volume of MIBK remaining for analysis after extraction
= 35 ml – 11.25 ml
= 23.75 ml

2. Second calculate the volume of MIBK remaining for analysis after extraction of metals from standards made with deionized water.

Salinity = 0 psu
% solubility MIBK in deionized water = 0.024
Volume seawater used for extraction = 750 ml
Volume MIBK added to seawater = 35 ml

Volume of MIBK that dissolves in 750 ml deionized water
= 0.024 × 750 ml
= 18 ml

Volume of MIBK remaining for analysis after extraction
= 35ml – 18 ml
= 17 ml

3. Determine a correction factor needed to equilibrate the volumes of MIBK that remained after extraction with seawater and Deionized Water

Volume MIBK after deionized extraction = 17 ml
Volume MIBK after seawater extraction = 23. 75 ml

Correction factor = 23.75 ÷ 17 = 1.4

i.e. The concentrations of metals in seawater of salinity 33.4 psu need to be multiplied by 1.4 to correct for the reduced solubility of MIBK in saline waters as compared to the deionized water that was used to make the standards.

1B. Equation used to calculate the percentage recovery of metals from spiked seawater samples (EURACHEM, 1998):

% recovery = ((C1-C2) ÷ C3) × 100

Where: C1 = Concentration determined in fortified sample
C2 = Concentration determined in unfortified sample
C3 = Concentration of fortification

1C. Equation used to adjust for excess percentage recovery of Pb from seawater using Chelex-100 method:

Concentration of Pb in seawater = (A × 100 %) ÷ B

Where: A = initial Pb concentration obtained from ICP-OES

B = average percentage recovery of Pb obtained for the two spiked concentrations. i.e ((150.0 % + 159.9 %) ÷ 2) = 155.4 %

Thus, Concentration of Pb in seawater = (A × 100 %) ÷ 155.4 %

1D. Equation used to adjust for excess percentage recovery of Cd from sediment using FAAS (a) analysis and ICP-OES analysis (b):

(a) Concentration of Cd in sediment = (A × 100 %) ÷ B

Where: A = initial Cd concentration obtained from FAAS

B = average percentage recovery of Cd obtained from NIST reference sediment (120.5%)

Thus, Concentration of Cd in sediment = (A × 100 %) ÷ 120.5 %

(b) Concentration of Cd in sediment = (A × 100 %) ÷ B

Where: A = initial Cd concentration obtained from ICP-OES

B = average percentage recovery of Cd obtained from NIST reference sediment (132.5%)

Thus, Concentration of Cd in sediment = (A × 100 %) ÷ 132.5 %

APPENDIX 2: TABLES

TABLE A1
Mesh sizes of sieves used to determine grain size distribution of sediments according to the Udden-Wentworth sedimentary grain-size scale

Sieve mesh size (mm)	Particle size retained on sieve (mm)	Grade
0.500	> 0.05	Coarse sand
0.250	0.250 - 0.50	Medium sand
0.125	0.125 - 0.250	Fine sand
0.063	0.063 - 0.125	Very fine sand
*	Smaller than 0.063 mm	Mud (silt + clay)
*All particles that passed through 0.063 mm sieve were classed as mud		

TABLE A2

Spearman rank order correlations for metals concentrations and sediment properties for the Mpekweni Estuary sediments

	Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**TOC**	**Coarse sand**	**Medium sand**	**Fine sand**	**Very fine sand**	**mud**
Cd	1.00												
Co	-0.05	1.00											
Cu	-0.01	**0.85***	1.00										
Fe	-0.06	**0.92***	**0.93***	1.00									
Ni	0.11	**0.91***	**0.91***	**0.87***	1.00								
Pb	0.05	**0.88***	**0.94***	**0.94***	**0.95***	1.00							
Zn	-0.20	**0.63**	**0.83***	**0.74***	**0.79***	**0.83***	1.00						
TOC	-0.45	0.56	**0.73**	**0.67**	**0.63**	**0.72**	**0.79***	1.00					
Coarse sand	-0.45	**0.85***	**0.68**	**0.75***	**0.73**	**0.68**	0.53	**0.67**	1.00				
Medium sand	0.58	**-0.67**	**-0.75***	**-0.76***	**-0.64**	**-0.65**	**-0.74***	**-0.79***	**-0.81***	1.00			
Fine sand	-0.16	-0.33	-0.09	-0.24	-0.11	-0.12	0.19	0.39	-0.17	-0.12	1.00		
Very fine sand	-0.50	0.55	**0.65**	**0.62**	**0.61**	**0.64**	**0.65**	**0.92***	**0.75***	**-0.81***	0.35	1.00	
Mud	-0.41	0.56	**0.75***	**0.70**	**0.66**	**0.75***	**0.77***	**0.95***	**0.66**	**-0.78***	0.30	**0.95***	1.00

Note: correlations in bold are significant at $p < 0.05$.

*Correlations significant at $p < 0.01$.

TABLE A3
Spearman rank order correlations for metals concentrations and sediment properties for the West Kleinemonde Estuary sediments

	Cd	Co	Cu	Fe	Ni	Pb	Zn	TOC	Coarse sand	Medium sand	Fine sand	Very fine sand	mud
Cd	1.00												
Co	-0.13	1.00											
Cu	-0.15	0.60	1.00										
Fe	-0.24	-0.02	0.03	1.00									
Ni	0.24	**0.62**	0.41	-0.48	1.00								
Pb	-0.03	**0.62**	0.41	-0.57	**0.81***	1.00							
Zn	-0.34	0.44	**0.82**	0.41	-0.01	0.10	1.00						
TOC	-0.53	-0.17	-0.13	**0.84***	**-0.65**	-0.51	0.26	1.00					
Coarse sand	**0.61**	0.42	-0.03	-0.19	0.59	0.25	-0.35	-0.45	1.00				
Medium sand	0.35	0.04	0.15	**-0.78***	0.55	0.60	-0.18	**-0.90***	0.15	1.00			
Fine sand	-0.27	0.08	0.16	0.14	0.06	0.15	0.16	0.18	-0.02	0.03	1.00		
Very fine sand	-0.55	-0.19	-0.19	**0.68***	**-0.73**	-0.63	0.26	**0.93***	-0.42	**-0.90***	0.05	1.00	
Mud	-0.39	-0.09	-0.05	**0.79***	**-0.70**	-0.60	0.40	**0.92***	-0.42	**-0.91***	-0.04	**0.93***	1.00

Note: correlations in bold are significant at $p < 0.05$.
*Correlations significant at $p < 0.01$. $n = 12$.

TABLE A4
Spearman rank order correlations for metals concentrations and sediment properties for the Kasouga Estuary sediments

	Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**TOC**	**Coarse sand**	**Medium sand**	**Fine sand**	**Very fine sand**	**mud**
Cd	1.00												
Co	**0.92***	1.00											
Cu	**0.75***	0.60	1.00										
Fe	**0.92***	**0.94***	**0.70**	1.00									
Ni	**0.88***	**0.90***	**0.62**	**0.88***	1.00								
Pb	**0.98***	**0.91***	**0.80***	**0.93***	**0.87***	1.00							
Zn	**0.87***	**0.88***	**0.75***	**0.87***	**0.89***	**0.88***	1.00						
TOC	**0.95***	**0.85***	**0.80***	**0.92***	**0.86***	**0.95***	**0.83***	1.00					
Coarse sand	-0.47	**-0.68**	-0.31	-0.61	**-0.74***	-0.48	-0.55	-0.47	1.00				
Medium sand	**-0.76***	**-0.86***	-0.51	**-0.87***	**-0.88***	**-0.79***	**-0.72**	**-0.82***	**0.81***	1.00			
Fine sand	0.07	0.29	-0.37	0.26	0.30	0.11	0.18	0.10	-0.28	-0.44	1.00		
Very fine sand	**0.68**	**0.81***	0.46	**0.79***	**0.80***	**0.74***	**0.76***	**0.76***	**-0.67**	**-0.92***	0.57	1.00	
Mud	**0.92***	**0.90***	**0.66**	**0.92***	**0.94***	**0.90***	**0.83***	**0.94***	**-0.66**	**-0.92***	0.23	**0.83***	1.00

Note: correlations in bold are significant at $p < 0.05$.
*Correlations significant at $p < 0.01$. $n = 12$.

TABLE A5
Spearman rank order correlations for metals concentrations and sediment properties for the Boknes Estuary sediments

	Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**TOC**	**Coarse sand**	**Medium sand**	**Fine sand**	**Very fine sand**	**mud**
Cd	1.00												
Co	0.48	1.00											
Cu	**0.76***	**0.66**	1.00										
Fe	0.53	**0.92***	**0.78***	1.00									
Ni	**0.64**	**0.87***	**0.70**	**0.87***	1.00								
Pb	**0.76***	**0.59**	**0.89***	**0.76***	**0.67**	1.00							
Zn	0.49	**0.77***	0.43	**0.62**	**0.79***	0.51	1.00						
TOC	0.48	**0.86***	**0.71**	**0.88***	**0.89***	**0.67**	**0.79***	1.00					
Coarse sand	0.34	-0.34	0.00	-0.37	-0.34	0.04	-0.29	-0.50	1.00				
Medium sand	-0.28	**-0.76***	-0.48	**-0.69**	**-0.82***	-0.47	**-0.87***	**-0.83***	**0.59**	1.00			
Fine sand	0.10	0.69	0.46	**0.61**	**0.62**	0.27	0.56	**0.66**	**-0.59**	**-0.85***	1.00		
Very fine sand	0.12	0.55	0.34	**0.62**	**0.72***	0.43	**0.65**	**0.72***	**-0.73***	**-0.81***	0.55	1.00	
Mud	**0.60**	**0.87***	**0.66**	**0.79***	**0.87***	**0.62**	**0.92***	**0.92***	-0.36	**-0.84***	**0.64**	**0.63**	1.00

Note: correlations in bold are significant at $p < 0.05$.
*Correlations significant at $p < 0.01$. $n = 12$.

TABLE A6
Spearman rank order correlations for metals concentrations and sediment properties for the Great Fish Estuary sediments

	Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**TOC**	**Coarse sand**	**Medium sand**	**Fine sand**	**Very fine sand**	**mud**
Cd	1.00												
Co	-0.03	1.00											
Cu	-0.02	**0.77***	1.00										
Fe	-0.13	**0.72***	**0.92***	1.00									
Ni	0.05	**0.60***	**0.93***	**0.89***	1.00								
Pb	**0.71***	-0.26	-0.14	-0.23	-0.07	1.00							
Zn	-0.07	**0.72***	**0.86***	**0.91***	**0.90***	-0.24	1.00						
TOC	0.32	**0.68***	**0.74***	**0.65***	**0.64***	0.20	**0.60***	1.00					
Coarse sand	**0.48**	-0.24	-0.25	-0.33	-0.30*	**0.69***	**-0.43**	0.04	1.00				
Medium sand	0.36	**-0.60***	**-0.69***	**-0.81***	**-0.69***	0.35	**-0.75***	-0.40	**0.54***	1.00			
Fine sand	-0.26	**-0.62***	**-0.74***	**-0.67***	**-0.64***	-0.19	**-0.63***	**-0.77***	-0.23	0.39	1.00		
Very fine sand	-0.37	**0.45**	**0.51**	**0.54***	**0.42**	**-0.53***	**0.52***	0.38	**-0.56***	**-0.70***	-0.23	1.00	
Mud	0.06	**0.79***	**0.92***	**0.89***	**0.89***	-0.04	**0.88***	**0.83***	-0.25	**-0.68***	**-0.72***	**0.52***	1.00

Note: correlations in bold are significant at $p < 0.05$.
*Correlations significant at $p < 0.01$. $n = 24$.

TABLE A7
Spearman rank order correlations for metals concentrations and sediment properties for the Kowie Estuary sediments

	Cd	**Co**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**	**TOC**	**Coarse sand**	**Medium sand**	**Fine sand**	**Very fine sand**	**mud**
Cd	1.00												
Co	**0.90***	1.00											
Cu	**0.83***	**0.68***	1.00										
Fe	**0.99***	**0.93***	**0.78***	1.00									
Ni	**0.96***	**0.97***	**0.77***	**0.97***	1.00								
Pb	**0.83***	**0.71***	**0.79***	**0.82***	**0.78***	1.00							
Zn	**0.71***	**0.62***	**0.60***	**0.72***	**0.73***	**0.55***	1.00						
TOC	**0.93***	**0.83***	**0.82***	**0.92***	**0.86***	**0.80***	**0.53***	1.00					
Coarse sand	**-0.43**	-0.22	**-0.62***	-0.36	-0.27	**-0.46**	-0.15	**-0.62***	1.00				
Medium sand	**-0.75***	**-0.63***	**-0.73***	**-0.71***	**-0.67***	**-0.51**	-0.39	**-0.86***	**0.77***	1.00			
Fine sand	-0.35	-0.37	-0.18	-0.37	**-0.44**	-0.26	**-0.51**	-0.05	**-0.43**	-0.15	1.00		
Very fine sand	**0.72***	**0.61***	**0.72***	**0.68***	**0.64***	**0.55***	0.30	**0.85***	**-0.73***	**-0.93***	0.11	1.00	
Mud	**0.90***	**0.76***	**0.83***	**0.86***	**0.81***	**0.73***	**0.55***	**0.94***	**-0.64***	**-0.87***	-0.14	**0.89***	1.00

Note: correlations in bold are significant at $p < 0.05$.
*Correlations significant at $p < 0.01$. $n = 24$.

TABLE A8

(i) Spearman rank order correlations for metals concentrations and sediment properties for the Kariega Estuary sediments (dry season)

	Cd	Co	Cu	Fe	Ni	Pb	Zn	TOC	Coarse sand	Medium sand	Fine sand	Very fine sand	mud
Cd	1.00												
Co	-0.11	1.00											
Cu	-0.41	0.38	1.00										
Fe	**-0.53***	0.32	**0.75***	1.00									
Ni	0.07	0.30	**0.69***	**0.50**	1.00								
Pb	**0.50***	0.31	-0.20	**-0.48**	0.03	1.00							
Zn	-0.12	0.33	**0.68***	**0.72***	**0.58***	-0.30	1.00						
TOC	-0.56	0.41	**0.72***	**0.91***	**0.48**	-0.35	**0.62***	1.00					
Coarse sand	0.41	0.05	0.06	0.01	0.30	0.00	0.25	-0.06	1.00				
Medium sand	0.48	-0.20	**-0.50**	**-0.85***	-0.38	**0.52***	**-0.61***	**-0.90***	0.30	1.00			
Fine sand	0.28	-0.27	-0.18	0.13	0.15	-0.00	0.19	0.07	-0.06	-0.32	1.00		
Very fine sand	**-0.47**	-0.02	**0.51**	**0.85***	**0.41**	**-0.59***	**0.66***	**0.79***	-0.08	**-0.87***	**0.46**	1.00	
Mud	**-0.54***	0.28	**0.58***	**0.92***	0.38	**-0.58***	**0.67***	**0.90***	-0.07	**-0.92***	0.11	**0.85***	1.00

(ii) Spearman rank order correlations for metals concentrations and sediment properties for the Kariega Estuary sediments (wet season)

Cd	1.00												
Co	0.18	1.00											
Cu	-0.17	0.37	1.00										
Fe	**-0.48**	0.17	**0.62***	1.00									
Ni	**0.47**	**0.49**	**0.60***	0.21	1.00								
Pb	-0.20	-0.03	0.36	0.08	0.06	1.00							
Zn	0.15	0.21	**0.62***	0.41	**0.66***	0.38	1.00						
TOC	-0.03	0.38	**0.48**	**0.78***	**0.43**	-0.12	0.39	1.00					
Coarse sand	-0.33	-0.07	0.19	-0.06	-0.18	0.38	0.09	**-0.43**	1.00				
Medium sand	0.16	-0.24	-0.20	**-0.68***	-0.14	0.23	-0.13	**-0.84***	**0.62***	1.00			
Fine sand	0.37	-0.12	**-0.57***	-0.41	-0.20	-0.08	-0.19	-0.11	-0.21	-0.11	1.00		
Very fine sand	-0.22	-0.00	0.18	**0.71***	0.17	**-0.42**	0.13	**0.73***	**-0.43**	**-0.78***	-0.03	1.00	
Mud	-0.29	0.32	**0.43**	**0.85***	0.28	-0.21	0.28	**0.89***	-0.39	**-0.89***	-0.19	**0.87***	1.00

Note: correlations in bold are significant at $p < 0.05$.

*Correlations significant at $p < 0.01$. $n = 24$.

TABLE A9

(i) Spearman rank order correlations (R) for variables measured in the East Kleinemonde Estuary sediments (dry season)

	Cd	Co	Cu	Fe	Ni	Pb	Zn	TOC	Coarse sand	Medium sand	Fine sand	Very fine sand	mud
Cd	1.00												
Co	0.36	1.00											
Cu	**0.61**	**0.60**	1.00										
Fe	-0.16	0.26	0.52	1.00									
Ni	**0.72***	**0.62**	0.41	-0.19	1.00								
Pb	**0.80***	**0.62**	0.41	-0.29	**0.81***	1.00							
Zn	0.30	0.44	**0.82***	**0.71**	-0.01	0.10	1.00						
TOC	-0.13	-0.01	0.33	**0.89***	-0.29	-0.34	**0.65**	1.00					
Coarse sand	0.12	0.27	-0.26	-0.28	0.57	0.34	-0.48	-0.38	1.00				
Medium sand	0.38	0.13	-0.06	**-0.79***	0.37	**0.62**	-0.29	**-0.77***	0.03	1.00			
Fine sand	-0.31	-0.10	0.33	**0.70**	-0.44	-0.48	0.49	**0.67**	**-0.69**	-0.54	1.00		
Very fine sand	-0.41	-0.29	0.05	**0.76***	-0.57	**-0.60**	0.45	**0.90***	-0.43	**-0.77***	**0.75***	1.00	
Mud	-0.23	-0.10	0.31	**0.86***	-0.48	-0.53	**0.62**	**0.85***	-0.31	**-0.87***	**0.59**	**0.83***	1.00

(ii) Spearman rank order correlations (R) for variables measured in the East Kleinemonde Estuary sediments (wet season)

Cd	1.00												
Co	0.45	1.00											
Cu	0.15	0.57	1.00										
Fe	**-0.83***	-0.58	-0.17	1.00									
Ni	0.27	0.20	0.28	-0.15	1.00								
Pb	**0.88***	0.65	0.32	**-0.97***	0.18	1.00							
Zn	-0.40	-0.17	0.36	0.26	**0.71**	-0.24	1.00						
TOC	**-0.77**	-0.50	-0.27	**0.87***	-0.22	**-0.90***	0.26	1.00					
Coarse sand	**0.70**	0.50	-0.17	**-0.70**	-0.30	**0.67**	**-0.71**	-0.52	1.00				
Medium sand	**0.90***	0.60	0.23	**-0.88***	0.30	**0.90***	-0.40	**-0.90***	**0.68**	1.00			
Fine sand	**-0.70**	-0.33	-0.37	0.53	**-0.77**	-0.55	-0.26	0.50	-0.18	**-0.70**	1.00		
Very fine sand	**-0.77**	-0.28	-0.10	**0.90***	-0.13	**-0.88***	0.21	**0.93***	-0.50	**-0.82***	0.47	1.00	
Mud	**-0.88***	-0.62	-0.35	**0.88***	-0.27	**-0.95***	0.33	**0.95***	-0.58	**-0.95***	0.60	**0.87***	1.00

Note: correlations in bold are significant at $p < 0.05$.

*Correlations significant at $p < 0.01$. n = 12 dry season, n = 9 wet season.

TABLE A10

(i) Spearman rank order correlations (R) for metals concentrations and sediment properties for the Riet Estuary sediments (dry season)

	Cd	Co	Cu	Fe	Ni	Pb	Zn	TOC	Coarse sand	Medium sand	Fine sand	Very fine sand	mud
Cd	1.00												
Co	**0.91***	1.00											
Cu	**0.81***	**0.85***	1.00										
Fe	-0.15	0.06	0.16	1.00									
Ni	**0.84***	**0.90***	**0.97***	0.15	1.00								
Pb	**0.87***	**0.93***	**0.81***	-0.01	**0.83***	1.00							
Zn	0.47	0.34	0.46	0.55	0.48	0.17	1.00						
TOC	-0.13	0.02	0.13	**0.95***	0.13	-0.06	**0.63**	1.00					
Coarse sand	-0.50	-0.54	-0.28	-0.20	-0.34	-0.48	-0.37	-0.23	1.00				
Medium sand	**0.58**	**0.61**	**0.64**	-0.37	**0.65**	**0.70**	-0.22	-0.43	-0.07	1.00			
Fine sand	-0.52	**-0.59**	**-0.59**	0.37	**-0.59**	**-0.64**	0.27	0.43	0.06	**-0.92***	1.00		
Very fine sand	**-0.75***	**-0.73***	**-0.68**	0.36	**-0.69**	**-0.83***	0.09	0.42	0.24	**-0.94***	**0.80***	1.00	
Mud	**-0.76***	**-0.74***	**-0.69**	0.36	**-0.70**	**-0.84***	0.09	0.41	0.22	**-0.94***	**0.81***	**0.99***	1.00

(ii) Spearman rank order correlations (R) for metals concentrations and sediment properties for the Riet Estuary sediments (wet season)

Cd	1.00												
Co	0.38	1.00											
Cu	0.07	-0.12	1.00										
Fe	-0.33	-0.43	**0.74**	1.00									
Ni	**0.74**	0.52	0.00	-0.24	1.00								
Pb	0.61	0.64	-0.43	**-0.79**	0.43	1.0							
Zn	-0.07	-0.21	0.71	0.75	-0.14	**-0.77**	1.00						
TOC	-0.32	-0.47	**0.75**	**0.99**	-0.29	**-0.81**	**0.79**	1.00					
Coarse sand	-0.67	-0.64	0.52	**0.83**	-0.62	**-0.96**	0.68	**0.86**	1.00				
Medium sand	0.62	**0.71**	-0.60	**-0.81**	0.55	**0.96**	-0.57	**-0.83**	**-0.93**	1.00			
Fine sand	0.00	-0.31	0.12	-0.02	-0.24	0.43	-0.54	-0.01	0.00	-0.07	1.00		
Very fine sand	-0.67	**-0.74**	0.50	0.79	-0.52	-1.00	0.50	**0.80**	**0.95**	**-0.98**	0.05	1.0	
Mud	-0.69	-0.67	0.48	0.81	-0.43	**-0.96**	0.43	**0.80**	**0.90**	**-0.95**	0.02	1.0	1.00

Note: correlations in bold are significant at $p < 0.05$.

*Correlations significant at $p < 0.01$. n = 12 dry season, n = 9 wet season.