Spatio-temporal variations of the sedimentology and geochemistry of six estuaries within the eThekwini Municipality, KwaZulu-Natal, South Africa.

By

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Preface

The experimental work described and presented in this dissertation was carried out in the School of Agricultural, Earth and Environmental Sciences, University of KwaZulu-Natal, Durban, from February 2011 to November 2013 under the supervision of Dr. Srinivasan Pillay.

This study represents the original work by the author, Keshia Pather, and has not been submitted in any form for any degree, diploma or award at this or any other tertiary institution. Except for those acknowledged as such, all figures, sketches and maps were drawn by the author. The use of information sources and work of others has been duly acknowledged as such in the text.

Acknowledgments

- I would firstly like to thank God for giving me the strength to pursue and complete this dissertation. Thank you for the everlasting guidance.
- To my supervisor, Dr Pillay, you deserve such a big thank you for all of your time, effort, guidance, and constructive criticism on my dissertation. Your expertise and assistance throughout the years were greatly appreciated.
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- Many thanks go to the NRF for funding this project.
- Finally, I would like to thank anyone else who has assisted me in some way with this dissertation.

Declaration- Plagiarism

I, Keshia Pather, declare that:

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

2. This thesis has not been submitted for any degree or examination at any other university.

3. This thesis does not contain other persons' data, pictures, graphs of other information unless specifically acknowledged as being sourced from other persons'.

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Declaration – Publications

The author of this dissertation will be working towards the production of individual research papers from this dissertation, as well as the submission of these papers to the relevant journals for publication.

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Keshia Pather

Abstract

Estuaries are dynamic features of a coastline whose sediments are influenced by riverine and marine processes. Periodic events such as floods, as well as variations in mouth status, greatly affect the energy levels within an estuary and subsequently the amount of sediment erosion and deposition that takes place. Concurrently, pollutants are transported and deposited into estuaries and can reside in the sediments for many years. The estuaries of the eThekwini Municipality in KwaZulu-Natal, South Africa, are exposed to a variety of pollutants; however with the expanding industrial sector within this region, metal contamination is of concern.

This study investigates the sedimentology and geochemical variations of six estuaries within the municipality namely, the uTongati, uMdloti, uMgeni, Isipingo and uMbokodweni estuaries as well as the Durban Harbour. To determine the spatial variations in estuarine sedimentology, sediment cores were collected longitudinal to the estuary axis. The core samples were analysed for sediment colour, texture and organic matter content. To assess the geochemical variations, core samples were analysed for Zn, Cu, Cr, Ni, Pb, As, Fe, Al, Ca, S, P, Mg, Mn, Cd and V concentrations. Some samples were also carbon dated to provide a temporal aspect to the sediment and geochemical variations. Descriptive and graphic techniques were used to examine the sedimentology within the estuaries; and the geochemical data was analysed with the use of multivariate statistics. Additionally, pollution indices and sediment quality guidelines were utilized to assess the pollution levels within the sediments.

The results indicated that lower energy environments caused by protracted mouth closures in the uMdloti and Isipingo estuaries accounted for large amassing of fines. In contrast, the accumulation of mixed coarse and fine sediments in the uTongati and uMgeni estuaries was an indication of high fluvial flows and open mouth conditions. All carbon dated ages for all estuaries were greater than 700 years which may be attributed to a combination of scouring effects from past and recent flood events and also possibly due to the deposition of re-worked older sediments from upstream. Low metal concentrations were found within the sediments of all estuaries, and the presence of fines and organic matter governed their concentration variations with depth. The uMgeni and uMbokodweni estuaries which are located immediately downstream of industrial and urban areas, were found to contain relatively higher concentrations of elements Pb, Cu, As and Ni. These metals showed high enrichment within the sediments; however actual concentrations were below sediment quality guideline levels. General pollution levels within all estuaries were very low, and can be attributed to the

climatic influences within this region which has a ‘cleansing’ effect on the estuarine environments in removing contaminants.

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List of Abbreviations

Al	Aluminium
AMS	Accelerator Mass Spectrometry
ANZECC	Australian and New Zealand Environment and Conservation Council
As	Arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
BCLME	Benguela Current Large Marine Ecosystem Programme
Be	Beryllium
BP	Before Present
Ca	Calcium
CA	Cluster Analysis
Cd	Cadmium
CF	Contamination Factor
Cr	Chromium
Cu	Copper
DEAT	Department of Environmental Affairs and Tourism
DWAF	Department of Water Affairs and Forestry
EF	Enrichment Factor
ENSO	El Niño- Southern Oscillation
ERM	Environmental Resources Management
Fe	Iron
Hg	Mercury
I.D.	Insufficient Data
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectroscopy
I_{geo}	Geo-accumulation Factor
MER	Marine Estuarine Research

Mg	Magnesium
Mn	Manganese
N.D.	No Data
NDMC	National Disaster Management Centre
Ni	Nickel
NOAA	National Ocean and Atmospheric Administration
NSDP	National Spatial Development Plan
OM	Organic matter
P	Phosphorous
Pb	Lead
PC1	Principal Component 1
PC2	Principal Component 2
PCA	Principal Component Analysis
PLI	Pollution Load Index
PVC	Polyvinylchloride
S	Sulphur
SAHO	South African History Online
SASRI	South African Sugarcane Research Institute
SSI	Stewart Scott International
V	Vanadium
Zn	Zinc

Chapter 1

INTRODUCTION

Estuaries are the interface environment where rivers meet the sea, and are diverse and productive ecosystems, essential for the health and well-being of the coastal and marine environments (Abed, 2009). They also contain high economic, aesthetic and recreational value. As a result of this value, estuarine areas are favoured for many residential, industrial and recreational developments, which create added pressure on these systems. These developments together with activities such as harbour developments, sand mining, and freshwater abstraction from catchments all negatively impact the natural status and functioning of the estuaries (Tinmouth, 2009).

Estuaries are important zones of sediment transfer between fluvial and marine systems, forming sinks for sediments moving downstream, alongshore, or landwards (Ridgway and Shimmield, 2002). Within the estuary, mixing of the water and sediments is caused by higher energy occurrences such as strong wave and tidal action. Alternatively during calm conditions, when water velocities are lowered, sediments are deposited within the estuary. The deposition of sediments over long periods of time provides a measure of the types of conditions that have prevailed within the estuary through the history of the sediment record. With this knowledge, chronological records can be established and this information can be used for determining sedimentological changes over time (Callow, 1994).

Originally, estuaries were a product of the inundation of river valleys during the Holocene sea-level rise following the end of the last major glaciation. Sea-level rise and morphological changes in estuaries were most rapid between 10000 and 5000 years ago (Ridgway and Shimmield, 2002). Following this period, estuaries maintained a more or less constant morphology. Their erosive and depositional sediment processes (with the exception of extreme events such as floods and storms) have remained steady over time thus allowing for the natural accumulation of sediment layers within the estuary. Subsequently, estuarine sediments are considered repositories of important historical information such as contaminant accumulation (Achyuthan and Richardmohan, 2002).

Contaminants from various upstream sources such as industry, agriculture and urban areas, as well as activities offshore, are transported into estuaries and are eventually deposited in the sediments (Du Laing *et al*., 2009). These contaminants may be harmful to organisms dwelling within the estuarine sediments, especially when absorbed directly through the skin.

Upon consumption of the contaminated organisms by predators, the contaminants can be passed along the food chain through fish, birds, mammals and eventually humans (Fergusson, 1990). Therefore the distribution of contaminants in sediments is important throughout the estuarine ecosystem. Estuarine sediments act as a store for buried contaminants however, they can be remobilised through extreme events such as floods and storms, dredging or changes in currents brought about by construction (Whitfield and Bate, 2007). Metals are one of the most persistent and harmful contaminants to enter the estuarine environment (Martin *et al*., 2012).

Metal contamination within estuaries has been an important topic with increasing attention in the last twenty years, largely due to the persistent and toxic nature of many metals (Orr, 2007). Since the industrial revolution approximately 100 years ago, there has been a sharp increase in the anthropogenic release of metals into the environment. The release and subsequent accumulation of metals within the sediments of aquatic environments, such as estuaries, is harmful to the flora and fauna within the area (Nadal *et al*., 2004).

Estuaries receive large amounts of fine sediments from catchments which provide greater sites for metals adsorption (Wang *et al*., 2000). This contributes to the accumulation of metals in estuaries resulting in a sink of contaminants. The accumulation of metals within the estuarine sediments allows for the determination of contaminant accumulation over time, in relation to the development of the catchment and surrounding coastal area (Wang *et al*., 2000). However given the dynamic nature of estuaries, inclusive of tides, waves and floods, estuarine sediments may become disturbed. Estuarine sediments are moved on a daily basis by tides and waves, and substantially disturbed by storm and flood events which can cause irregularities within the sediment record (Ridgway and Shimmield, 2002). This can prevent the stable accumulation of sediments over time and may remove layers of sediment, along with its contaminants, in one single flood event (Whitfield and Bate, 2007). Therefore an undisturbed estuary can provide a useful historical contamination record, however a disturbed estuary can allow for a natural cleansing of its own sediments from harmful contaminants (Ridgway and Shimmield, 2002).

1.1. Contextualization of the study and motivation

South Africa has some 250 estuaries along its approximately 3000 km coastline (Abed, 2009) and the province of KwaZulu-Natal contains 74 of that total (Chili, 2008). The city of Durban is situated along the central coastline of the eThekwini Municipality in KwaZulu-Natal, and is the third largest city in the country. The founding of the Durban Bay, now called Durban Harbour, sparked the development of the city of Durban and its neighbouring towns. Urban development introduces anthropogenic pressures to the river catchments for the provision of water, as well as the surrounding estuaries which are affected by the urban settlements and industrial developments (Alexander *et al*., 1997).

Developments introduce contaminants such as heavy metals into the estuarine water and sediments over time. Estuarine sediments can hold these contaminants for long periods of time, given there are no disturbances. From an undisturbed estuarine environment, a contaminant accumulation record can be determined. This record is useful and important in discovering the developmental effects from a city such as Durban on the natural status of its estuarine sediments (Lopez-Gonzalez *et al*., 2006).

The power of a single flood, like those that occurred in 1984 and 1987 within this region, can remove years of sediment accumulation, along with its contaminants (Whitfield and Bate, 2007). Contaminants such as metals are of concern given the recent urbanization and industrialisation increase within this region (Hai *et al*., 2006). Therefore it would be useful to determine the concentrations of metals within the sediments over time, to assess the influence of natural flood events on the 'cleansing' of estuarine sediments.

The majority of the estuaries in this province are temporarily open to the sea due to the high wave energy along the coast (Perissinotto *et al*., 2010). They have limited opportunities for efficient exchange of water and sediments due to mouth closures. This coastline is also subjected to extreme events such as periodic floods (usually caused by cut-off lows) which have a recurrence period of approximately 50 years (Perissinotto *et al*., 2010). During these flood events, if runoff is sufficient, it will cause the breaching of the closed mouths. Therefore the relationship between mouth conditions and flood events is important. Sedimentological analyses of deep sediments allows for the determination of estimated mouth and energy conditions that occurred over time (Hai *et al*., 2006).

Relatively few studies have been conducted on the nature, dynamics and chemical character of sediments within the estuaries found along the coast of KwaZulu-Natal. Even fewer

studies (e.g. Leuci, 1998; Shozi, 2011; Pillay *et al*., 2013) have focused on estuaries of the eThekwini Municipality coastline, where the greatest concentration of development has occurred over the past century, particularly with regard to their relative contaminant status with respect to heavy metals emanating from the recent rapid surge in urbanization and industrialization. A detailed study of these sedimentological characteristics may reveal trends in pollution episodes that occurred in the recent past or an understanding of the dynamical cleansing potential that allows for the removal of accumulated contaminated sediment and the maintenance of estuarine health. Updated concentrations of elements such as metals are also always useful in monitoring estuarine health. This ensures that pollution has not occurred within the estuarine environment or provides the basis for identifying potentially harmful contamination episodes. Acceptable standards of element concentrations are given by sediment quality guidelines and through regular monitoring of element concentrations, these standards can be upheld. Therefore it is important to provide an updated set of data for estuarine monitoring and management purposes. As far as the eThekwini Municipality coastal strip is concerned, the tracking of sedimentation characteristics and potential metal contamination over time has not been conducted before, and thus can be useful for assessing current trends and for future comparative research.

1.2. Aim and objectives

Aim:

This research aims to spatially and temporally assess the sedimentology of six estuaries within the eThekwini Municipality, as well as to determine the metal concentrations within these sediments and examine the general estuarine contamination status

Objectives:

The objectives of the study, which set out to achieve the aim of the study, are as follows:

1. To sample the six main estuaries along the eThekwini Municipality coastline along their longitudinal axes (near mouth, mid-estuary and upper estuary) for core sediment samples of up to 2 m length.
2. To use the cores to describe and assess the variations in sedimentology within each estuary in relation to sediment age, sediment texture, mouth conditions, and possible flood events.

3. To determine the metal concentrations of the core sediments and to assess the pollution status of each estuary by using pollution indices and sediment quality guidelines.
4. To compare the overall metal contamination within the sediments of these estuaries in the municipality, and relate these to natural or anthropogenic sources.

1.3. Structure of thesis

Chapter 2 focuses on the study area and describes the physical characteristics of each estuary including geology, climate and topography of the municipality, as well as the land use within each catchment. This chapter also provides a brief section on flooding which describes the main flood events that have occurred within this municipality, as well as a brief historical background of the region.

Chapter 3 includes the main theoretical concepts used in this study. It provides a review of the main topics such as estuary types, sedimentological processes that occur within estuaries, mouth dynamics, radiometric dating and a detailed section on heavy metals.

Chapter 4 outlines the methods used in the study. It describes methods used in the field for collecting sediment cores, sample preparation, as well as all laboratory methods conducted. These laboratory methods include determining the age of sediments, organic matter, metal concentrations and texture of sediments. It also briefly describes the statistical analyses applied to the data as well as pollution indices used.

Chapter 5 presents the results of the study. This chapter includes sections divided into sedimentology, geochemistry, statistical analyses and pollution indices per estuary. The results are presented in the form of core profiles, schematic stratigraphic cross-sections, graphs and tables. The results are averaged for all estuaries in the last section which focuses on the eThekwini Municipality as a whole.

Chapter 6 discusses the results of the study. This chapter identifies the main similarities that have occurred within all estuaries in terms of the sedimentological and geochemical results. It also contains common statistical interpretations from the results. Lastly, the overall pollution level within the estuarine sediments of the eThekwini Municipality is discussed.

Chapter 7 is the final chapter which concludes this study. It outlines the main findings and conclusions of the study. It also includes recommendations for future research.

Chapter 2

BACKGROUND

2.1. Introduction

This chapter describes the general physiographic characteristics of the study area, inclusive of locality and size. It provides information that contextualizes the natural and anthropogenic aspects of the study area. This includes an outline of the catchment and estuarine physical characteristics, mouth behaviour, geology, soils, land use, topography, and climate. This chapter also presents a review of the flood history within the municipality and a brief historical background to this region.

2.2. Location and physical characteristics

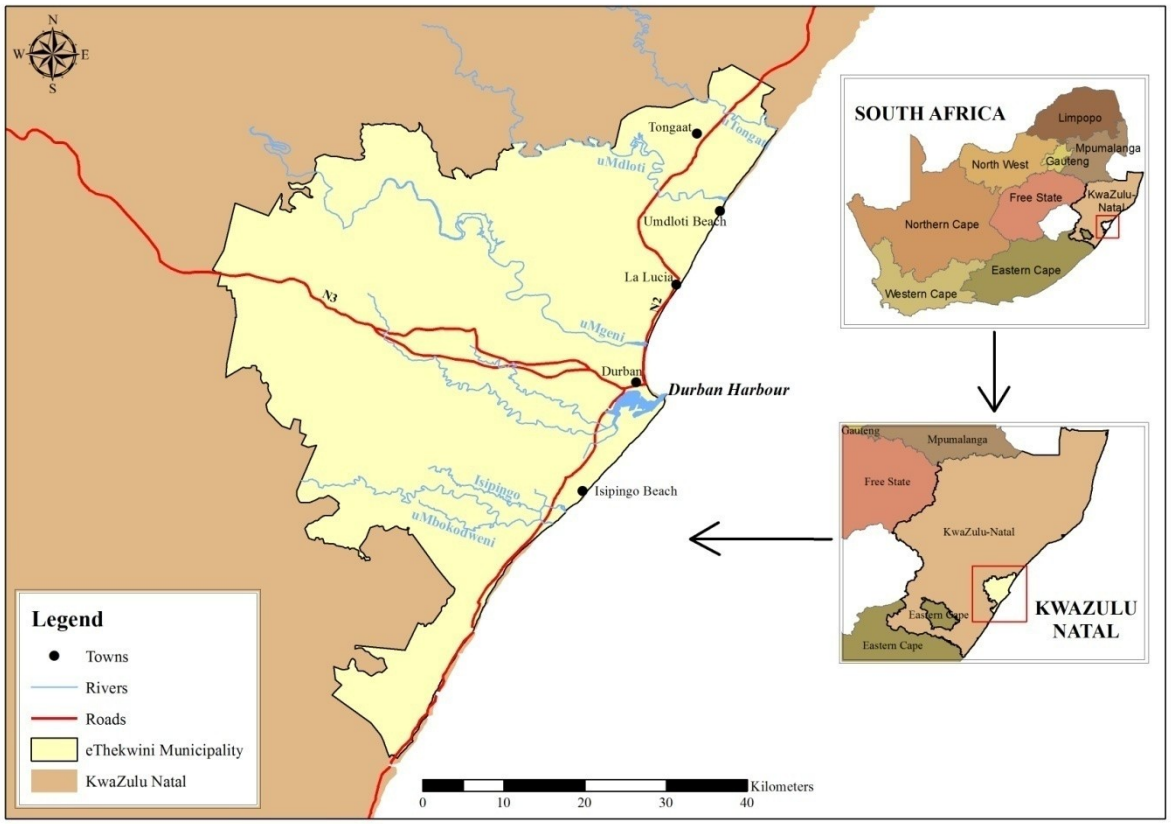

Figure 1: The location of the eThekwini Municipality within KwaZulu-Natal and South Africa.

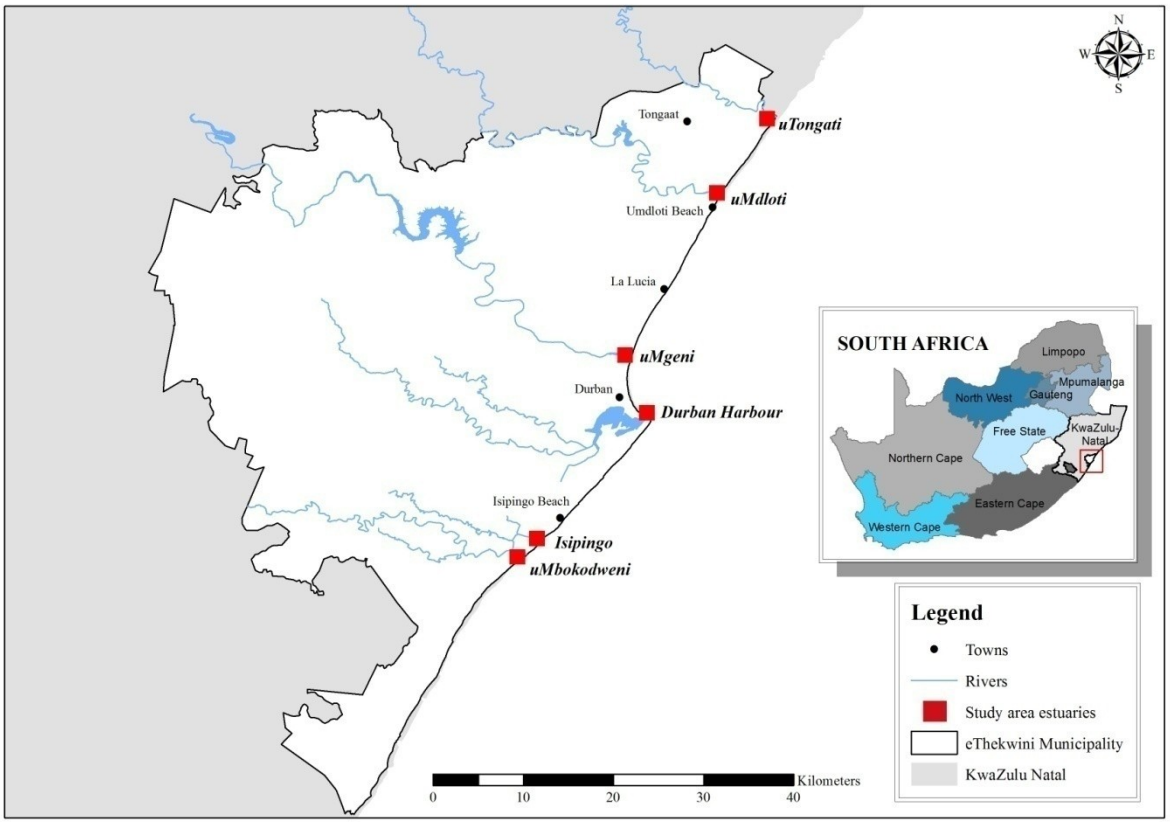

Figure 2: The location of the six estuaries selected for this study within the eThekwini Municipality.

The eThekwini Municipality is located along the coastline of the province of KwaZulu-Natal on the eastern seaboard of South Africa (Figure 1). This municipality is the largest economic hub of the province and it contains the city of Durban, the third largest city in the country. This municipality covers an area of 2291 km^2. The estuarine study areas located within this municipality are shown in Figure 2. The six estuaries, focussed on in this study, located from north to south are uTongati, uMdloti, uMgeni, Durban Harbour, Isipingo and uMbokodweni.

Table 1: Physical characteristics/features of the estuaries in this study.

Physical characteristics /features	Estuary					
	uTongati	**uMdloti**	**uMgeni**	**Durban Harbour**	**Isipingo**	**uMbokodweni**
Location (co-ordinates)	29º 33'S 31º 11'E	29º 38'S 31º08'E	29º48'S 30º02'E	29º 52' S 31º 04' E	30º 00'S 30º 57' E	30º 01' S 30º 56' E
Catchment area (km^2)	422	596	4439	272*	39	235
River length (km)	59	88	230	89*	29	59
Mean annual runoff (m^3) (Forbes and Demetriades, 2008)	66.05 x 10^6	84 x 10^6	707 x 10^6	N.D.	3.34 x 10^6	9.5 x 10^6
Dams	Dudley Pringle, Siphon	Hazelmere	Henly, Nagle, Midmar, Albert falls, Inanda	None	None	None
Estuary area (ha)	3.3	22	46	816	6.4	6.3
Estuary length (km)	1	2	2.3	5.7	1.2	1.2
Bridges over estuary	M4, N2	M4, N2	M4, Athlone, Connaught	None	Road bridge	Two foot bridges

* This is a combined calculation of the Umbilo and Umhlatuzana Rivers and Amanzimyana canal
N.D. – no data

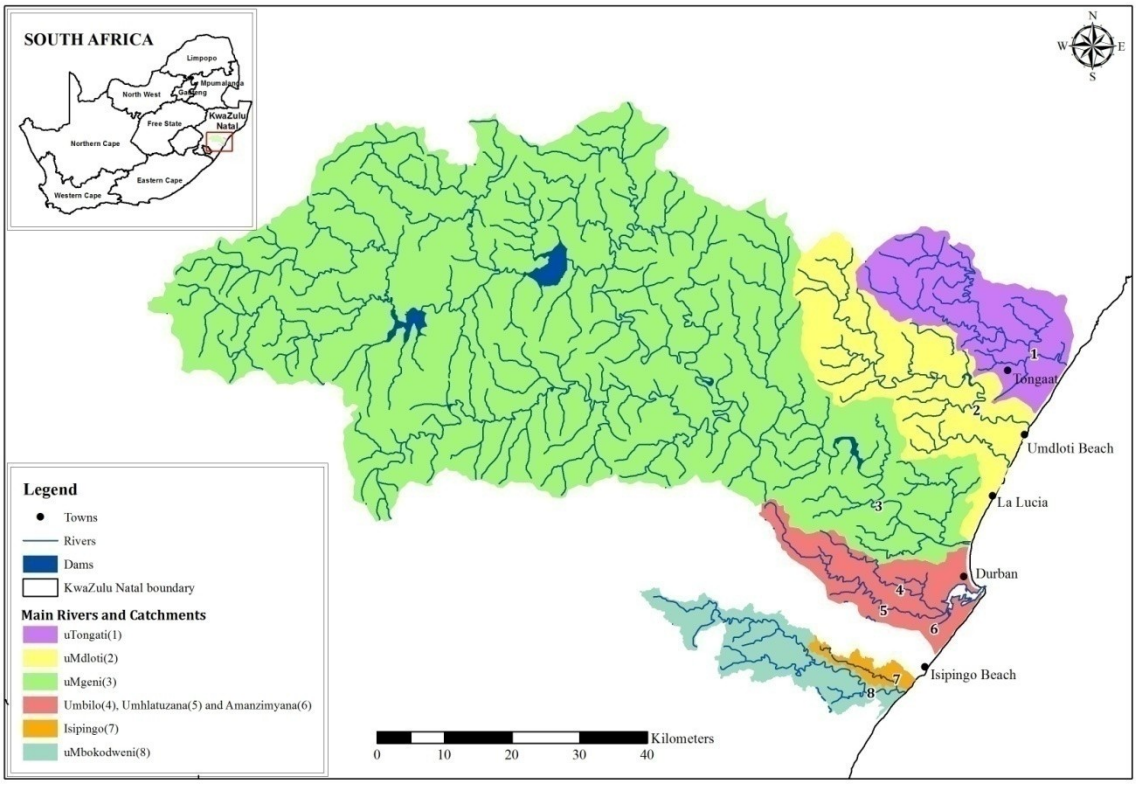

Figure 3: Map of the main rivers, dams and catchments of the six selected estuaries.

Figure 3 displays the catchments, rivers and dams of the six estuaries in proximity to the towns such as Durban. It can be seen that the uMgeni catchment is the largest in size and contains five dams. The uMgeni, Durban Harbour and Isipingo estuaries have had substantial development occur within their catchments and around their estuaries.

A significant amount of development has occurred over the last 100 years in the Durban area adjacent to the uMgeni River. The development around the estuary has resulted in infilling particularly in the upper reaches, and in 1980 this had led to about 187 ha of its floodplain being destroyed (Forbes and Demetriades, 2008). The originally meandering upper course was reduced to a concrete lined canal surrounded by the Springfield industrial estate. Prior to any development, the uMgeni River flowed directly into the Durban bay (now known as Durban Harbour) (Appendix A-Figure A4), especially during times of flooding (Barnes, 1984). This historic river link between this estuary and the Durban Harbour has also been lost due to the large urban and industrial development that has taken place to the south of the lower reaches. An artificial groyne (refer to Figure 7) was built in the early 1900's on the

southern bank of the mouth to allow for a permanently open mouth to reduce flooding (Forbes and Demetriades, 2008).

The city of Durban has developed around the Durban bay (now Durban Harbour) from the 1800's (Begg, 1978). There has been major removal of natural vegetation to allow space for industrial development. A major loss of a variety of habitats has occurred due to the reclamation of land and dredging (MER/ERM, 2011). The bulk of the mangrove environment as well as the last traces of sea grasses were removed in the mid 1960's. The wetlands present behind the mangroves in the southern areas have been filled or drained (refer to Figure 8). All incoming streams and rivers in the area have also been canalised (MER/ERM, 2011). There are also a number of storm water drains which empty into the harbour carrying large amounts of pollutants from the urban and industrial areas, flowing through the informal settlements in the area (MER/ERM, 2011).

Figure 4: The original condition of the Isipingo and uMlazi Rivers (A), and diversion of the uMlazi River for the development of the airport (B) (Adapted from SSI/MER, 2011).

The Isipingo estuary is the most altered estuary in this study area. The uMlazi River initially flowed into the Isipingo estuary (pre-1952) and entered the estuary on the northern side (Figure 4A) (SSI/MER, 2011). Between 1953 and 1959 the development of an airport near the uMlazi and Isipingo River floodplain caused the diversion of the uMlazi River into the sea directly north of the Isipingo estuary (Figure 4B) via a canalised section. This diversion

caused a substantial reduction in flow to the estuary and resulted in the eventual closure of the Isipingo estuary mouth. A double-piped outlet was built in 1961 which has kept the connection between the estuary and sea open (refer to Figure 9). A further decrease in flow occurred through the construction of a flood diversion system installed in 1969 to divert high flow levels from the Isipingo to the uMbokodweni River system (SSI/MER, 2011).

2.3. Estuarine characteristics

Table 2: Type of estuary, sand bar/spit measurements, and depth of each estuary.

Feature	Estuary					
	uTongati	**uMdloti**	**uMgeni**	**Durban Harbour**	**Isipingo**	**uMbokodweni**
Type of estuary	Perched and barred open	Perched closed*	River dominated and barred open* (open permanently through groyne)	Estuarine bay	Barred open (through piped inlet)	Barred open
Sand bar/spit present	Yes	Yes	Yes	No	Yes	Yes
Length of sand bar/spit (m)	175	700	447	-	213	80
Width of sand bar/spit (m)	60	80	156	-	82	85
Approximate Depth (m) (Forbes and Demetriades, 2008)	2 (near mouth)	2-3 (near mouth)	3.2 (near Connaught bridge)	13.7	1.33	2.2 (under lower foot bridge)

*Cooper (2001)

Table 2 provides estuarine features such as sand bar/spit measurements. The presence of the sand bar/spit across the mouth of these estuaries is a common feature along this coastline due to the high energy wave conditions. Further information regarding the historical changes of the mouth and sedimentary behaviour of each estuary follows.

2.3.1. uTongati estuary

Figure 5: Aerial photograph of the uTongati estuary illustrating its mouth, sandbar and surrounding area (Photo sourced from www.google.com/earth date accessed: 25-02-13).

Figure 5 illustrates the open mouth conditions which are prevalent in the uTongati estuary. The mouth of the estuary is usually open for long periods of time. It does close on occasion (e.g. in 1981 and 1983) and seldom requires breaching, as natural processes such as increased amounts of runoff, can breach the mouth (Cooper, 2001). Increased siltation within the lagoon has occurred in recent years due to increased cultivation and sugarcane farming within its catchment. This increased sedimentation has resulted in a shallow estuary, when compared to a previous depth of 3.1 m measured by Begg (1978).

2.3.2. uMdloti estuary

Figure 6: Aerial photograph of the uMdloti estuary illustrating its closed mouth, sandbar and surrounding area (Photo sourced from www.google.com/earth date accessed: 25-02-13).

The uMdloti estuary is typically closed for majority of the year. This creates a large expanse of open water in the estuary (Figure 6). When the mouth is open, most of the water is drained to reveal extensive mud and sand banks. The bar is frequently breached artificially at various times of the year by sugarcane farmers to prevent flooding of upstream cane fields and access roads (Forbes and Demetriades, 2008). When the lagoon is drained, a strong odour is produced from decomposing anoxic mud beds (Jorgensen *et al*., 1990). The sand bar is usually overtopped during high tides. During the equinox tides of March 1980, rough seas breached the central portion of the bar, and deposited the sandbar sediments into the estuary (Forbes and Demetriades, 2008).

2.3.3. uMgeni estuary

Figure 7: Aerial photograph of the uMgeni estuary illustrating its mouth, sandbar, mangroves and surrounding area (Photo sourced from www.google.com/earth date accessed: 25-02-13).

The uMgeni estuary mouth is characterised by the formation of tidal deltas, bars and sandbanks and currently has a south extending spit (Figure 7). In 1987, high floods resulted in the total removal of the sandbar; however it re-formed within months (Badenhorst *et al.*, 1989). During spring tides, the width of the estuary mouth can reach up to 600 m, and the channel entrance to the Beachwood Mangroves can reach 20 m in width (Forbes and Demetriades, 2008).

2.3.4. Durban Harbour

Figure 8: Aerial photograph of the Durban Harbour illustrating its entrance, mangroves and surrounding areas (Photo sourced from www.google.com/earth date accessed: 25-02-13).

The Durban Harbour is usually kept open by dredging. There is no real evidence that the bay was ever closed off from the sea however a shifting sandbar existed in the past (Begg, 1978). This sandbar lay across the entrance of the harbour over which the water was seldom deeper than 2 m. In 1854, the construction of the north pier began and was accompanied by the formation of a channel through the sandbar. Presently dredging of the harbour occurs to prevent the sandbar from reforming as well as to facilitate the movement of progressively larger vessels through the harbour (MER/ERM, 2011).

Prior to the mid-1800s, the bay consisted of naturally supportive estuarine features. Tidally exposed sandbanks, deeper channels and two vegetated islands were present in the central bay area (MER/ERM, 2011). Extensive mangrove habitats and swamp areas were once a large part of the bay (Appendix A – Figures A2 and A3), however due to the expansive development around the bay, these habitats have diminished. The current mangrove habitat is

currently 15 ha (previously 440 ha) in size (Figure 8) and is now protected by port authorities (Forbes and Demetriades, 2008).

2.3.5. Isipingo estuary

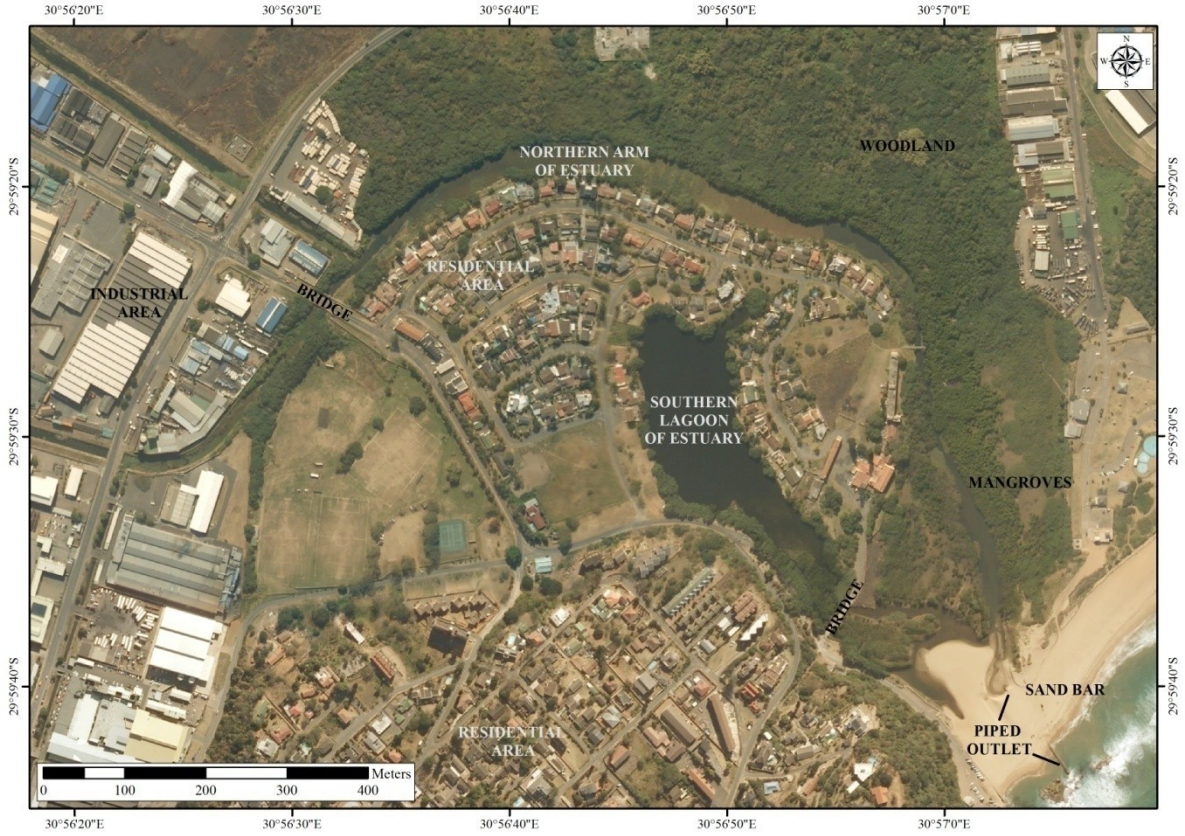

Figure 9: Aerial photograph of the Isipingo estuary illustrating its piped outlet, sandbar, mangroves and surrounding area (Photo sourced from www.google.com/earth date accessed: 25-02-13).

Figure 9 illustrates the current status of the Isipingo estuary. The piped outlet can be seen passing through the sandbar at the mouth. The estuarine morphology is described as, and inclusive of, a northern 'arm' and a southern 'blind' lagoon. Before the diversion of the uMlazi River, this estuary used to be open temporarily during the year and its mouth was located towards the south of the pipes. These pipes are permanently open and allows for tidal exchange, which is evident even in the upper reaches during spring tides (SSI/MER, 2011).

2.3.6. uMbokodweni estuary

Figure 10: Aerial photograph of the uMbokodweni estuary illustrating its mouth, sandbar, and surrounding area (Photo sourced from www.google.com/earth date accessed: 25-02-13).

Figure 10 illustrates the present status of the uMbokodweni estuary. Prior to the 1980's (and any modification), the position of the mouth was located behind a 400 m south extending spit. Due to the diversion of the Isipingo River into the uMbokodweni River, it led to the necessary creation of a new mouth (SSI/MER, 2011). The new mouth was created to reduce flood levels, but it caused accelerated water velocities which began eroding the golf course which occupied the flood plain on both sides of the estuary (Forbes and Demetriades, 2008). The mouth of the estuary now diverted to the north created a body of water called the 'southern arm', which became a stagnant pool over time. Physical breaching was required for the new mouth as well as the 'southern arm' as they both tended to close. This physical breaching has lessened over time and the mouth of the estuary is usually open for the majority of the year (SSI/MER, 2011). Presently, the 'southern arm' has completely dried up and is an area consisting of mainly grass and reeds.

2.4. Geology and soils

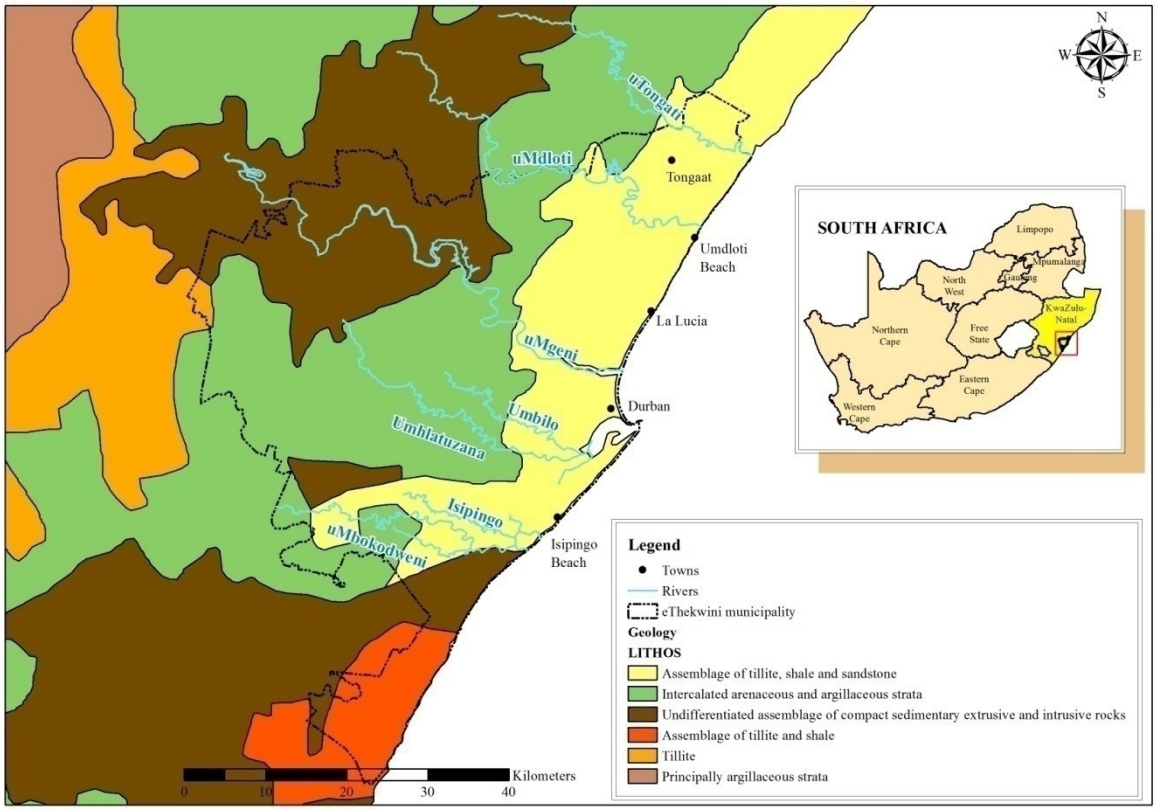

Figure 11: The geology of the study area within the municipality along the KwaZulu-Natal coastline (map created with data sourced from www.durban.gov.za date accessed: 23-02-13).

The KwaZulu-Natal coastal belt has a variety of geological formations. Sedimentary rocks such as the Natal Group Sandstone, Ecca Shale and Dwyka Tillite beds with intrusions of basic igneous rock (Dolerite), together with igneous outcrops of Granite constitute the dominant geology of this belt (Marshall, 2005). Figure 11 illustrates the geological outcrops across the eThekwini Municipality within KwaZulu-Natal. Each catchment therefore consists of an assortment of sedimentary rock strata, some igneous rocks and surficial deposits. The weathered product of these rocks eventually reaches the estuaries as a mix of sediments through erosion and deposition processes.

2.4.1. uTongati

In the uTongati River catchment, Natal Group Sandstone, Granite, Dwyka conglomerates and Ecca shale occur (Begg, 1978). In the estuary itself, below the lagoon, bedrock of shale,

sandstone and dolerite are present, sloping down to a maximum of 30 m below mean sea level (Begg, 1978). In 1978, the nature of the bottom materials in the estuary consisted of a homogenous mixture of fluvial muds and marine sands, becoming less muddy and sandier towards the north. Recently, it was found by Forbes and Demetriades (2008) that the estuarine sediment was well sorted with medium to coarse sand in the middle and upper reaches, and medium to fine sand at the mouth. This could be due to the flood events which occurred in 1984 and 1987 which deposited large amounts of fluvial sands within the estuary.

2.4.2. uMdloti

The uMdloti River transverses Archaean Granite, Natal Group Sandstone, Dwyka Tillites, Ecca Shale and recent deposits found in its drainage basin (Begg, 1978). Borehole data reveals bedrock at 31 m to be Ecca Shale. In 1978, the first 2 m of the uMdloti lagoon deposits consisted of fine sand, coarse fluvial sand and lenses of mud and clay (Begg, 1978). In 1981, 80% or more of the estuary was found to have fine to medium sediments. In 2002/2003, sediments ranged from medium sand at the mouth to coarse sand in the middle and upper reaches (Forbes and Demetriades, 2008). In 2007, sediments throughout the estuary consisted of coarse and medium sands, with the middle and upper reaches having greater proportions of the coarser sediments than the mouth (Forbes and Demetriades, 2008).

2.4.3. uMgeni

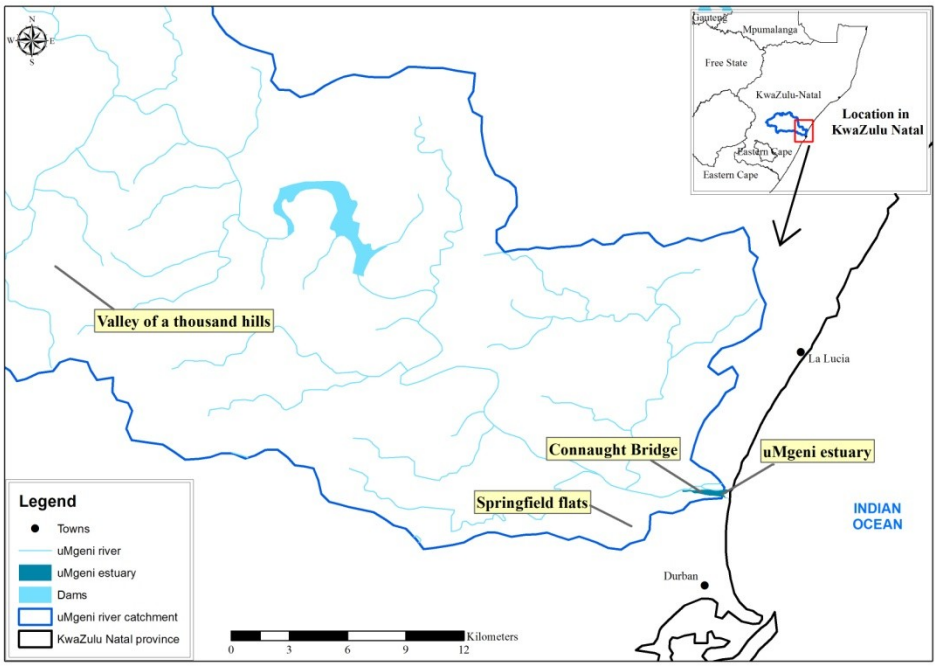

Figure 12: Map of the lower uMgeni River catchment.

The uMgeni catchment is the largest catchment in this study and consists of a wide variety of rock types. The upper catchment contains Ecca Shale and Beaufort sedimentary rocks which consist of fine-grained lacustrine and fluvial sedimentary rock, with late Jurassic Karoo Dolerite intrusions that overlie Dwyka Tillite (Abed, 2009). Archaean Granite is found in the middle section of the catchment in the Valley of a Thousand Hills (Figure 12). This rock type is said to be the source of most of the sands generated in the catchment as well as the pink sands found in the estuary (Begg, 1978). Near the Springfield flats region (Figure 12) which is located further downstream, Ecca Shale is found, with rocky outcrops of Dwyka Tillite located near the Connaught Bridge (Abed, 2009). Alluvium is found in the Springfield flats and the lower valley with exposed Tertiary and Pleistocene coastal deposits on the sides of the valley and the coast.

The bedrock underlying the uMgeni estuary is described by Begg (1978) as shale which is fractured and weathered towards the surface and contains some Dolerite intrusions. In 1972 the nature of bottom materials in the estuary were described as fine sands near the head of the estuary, sandy to gravelly substrates in the middle reaches, black anaerobic silt beneath deposits of sand or silt near the lower reaches, sand of uniform composition in the Beachwood Mangroves, and sand at the mouth of the estuary (Begg, 1978). Sediment

analyses conducted in 2007/2008 by Forbes and Demetriades (2008) indicated mainly fine to medium sand near the mouth, uniform medium sands in the middle and upper reaches, and very fine sands in the upper reaches.

2.4.4. Durban Harbour

The geology of the Durban Harbour catchment inclusive of the Umbilo and Umhlatuzana Rivers include a variety of rock types. Granites and Gneisses of the basement complex, Natal Group Sandstone, glacial Tillite and Shales of the Dwyka and Ecca groups, and minor Karoo Dolerite intrusions all occur within this catchment (MER/ERM, 2011). Beneath the Durban Harbour, the bedrock is composed of strongly dipping and faulted Karoo sediments of the Dwyka and Ecca groups. These sediments are overlain by a shallow crust of Cretaceous rocks which thicken eastwards beneath the Bluff (Begg, 1978). Calcareous sandstones make up the Bluff Ridge (refer to Figure 8) while the hills west of the bay are composed of Berea Red Sands. The Cretaceous rocks are overlain by approximately 30 m of unconsolidated sands, silt, clay and shell material known as the 'Harbour Beds' (MER/ERM, 2011).

Begg (1978) stated that there are two major types of substrates found in the bay namely hard substrata, which are composed of rocky embankments, quays, walls, piers etc. and soft substrata which make up the sands and mud. It is said that the bay was originally composed of muddy, estuarine silty clays known as 'hippo muds' while still in its lagoon state (Forbes and Demetriades, 2008) however sediments in this bay have changed over the last 30 years to predominantly coarser sandy sediments in the shallows of the central areas of the bay. This change was enhanced by the burrowing activities of the sand prawn *Callianassa krausi* as well as increased tidal exchange caused by dredging of the mouth (MER/ERM, 2011). Dredging also produced deep channels which tended to fill with soft silt. Black, hydrogen-sulphide laden sludge deposits developed in the silt canals, at the points of entry to the drainage canals (Begg, 1978). This description of sediments was confirmed 30 years later in 2008 which indicated sustained environmental degradation in the area (MER/ERM, 2011).

2.4.5. Isipingo

The sediments of the Isipingo estuary are described by Begg (1978) as a deposition of various proportions of sands, silts and clays. Marine sand does however wash into the mouth of the system at high spring tide (Begg, 1978). In 1982, the sediments in the northern arm of the

estuary were so badly polluted that the bottom materials comprised of a foul smelling, anaerobic black sludge (SSI/MER, 2011). The southern lagoon mostly comprised of silt with some sludge occurring in the deepest area. In 2007/2008, sediment analysis conducted by Forbes and Demetriades (2008) indicated that the sediments in the mouth and the lagoon area consisted of mainly medium to coarse sand. It was also found that there were localised areas, especially in the middle and upper reaches, that were composed of large amounts of clays and silts, which indicated long periods of deposition and absence of any water movement (Forbes and Demetriades, 2008). This amount of fines could be attributed to the re-routing of the Isipingo and uMlazi Rivers, which removed any scouring effect on the estuary and resulted in the accumulation of very fine, soft material (SSI/MER, 2011).

2.4.6. uMbokodweni

The geology of the uMbokodweni River catchment includes Natal Group Sandstone and Dywka Tillite. In addition to these, rocks of the basement complex also occur (Begg, 1978). Bedrock occurring beneath the N2 Bridge (comprising of Natal Group Sandstone) lies at depths of 22 to 42 m (refer to Figure 10). This is overlain by sand, boulders and pebbles and 15 m of very soft black mud. The bedrock present at the mouth of the estuary is Bluff Sandstone overlain by a cap of beach sand and ilmenite (Begg, 1978). The bed level in the estuary grades very rapidly to above mean sea level which results in steep hydraulic gradients. These gradients combined with highly erodible materials on the adjacent floodplain have consequently lead to unstable banks (Begg, 1978). In 2007/2008, sediment analyses undertaken by Forbes and Demetriades (2008) found medium to coarse sands throughout the estuary.

2.5. Land use

Land use is defined as the human modification of the natural environment into another dominant activity, occurring on an area of land (SSI/MER, 2011). Figure 13 below illustrates the variety of land use in the municipality. The majority of land towards the west is undeveloped or natural land. The urban environment, inclusive of all anthropogenic development, is mostly concentrated around the cities and major towns. Agriculture forms a large part of the municipality, with sugarcane occupying most of the northern sector; and other farming occurring in the western and southern parts of the municipality (DEAT, 2006).

The general land use of each estuarine catchment in the eThekwini Municipality is described below.

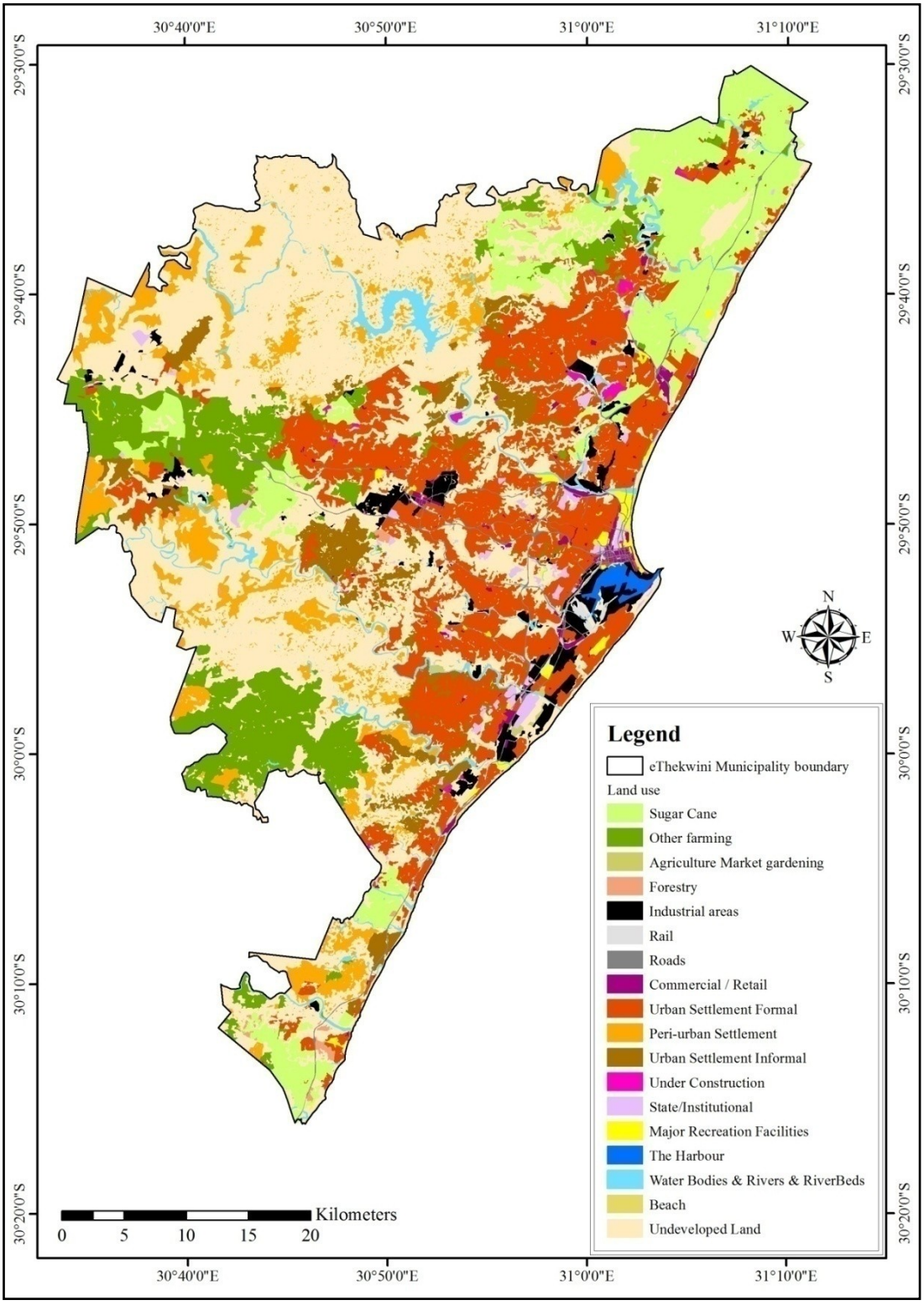

Figure 13: Land use of the eThekwini Municipality (map created with data sourced from www.durban.gov.za date accessed: 23-02-13).

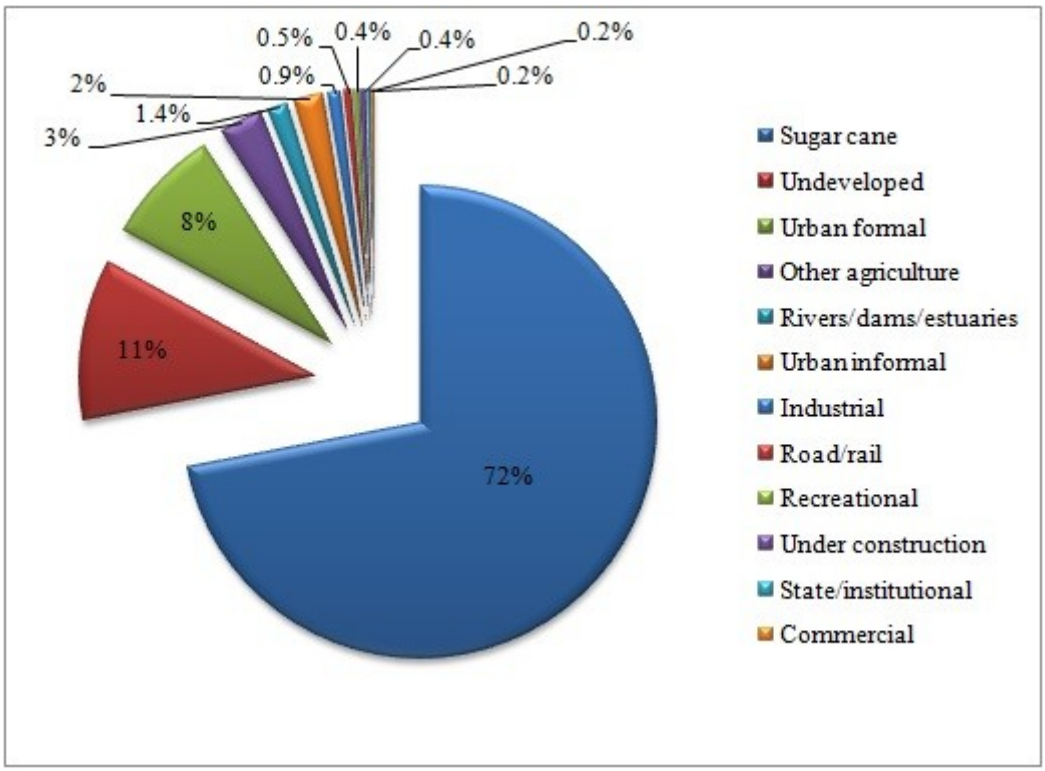

Figure 14: Land use of the uTongati River catchment (data sourced from Diederichs *et al.*, 2002).

The uTongati River catchment consists of a variety of land use which mainly consists of agriculture, formal urban development and undeveloped land. Figure 14 above illustrates the land use percentages in this catchment. The primary land use is agriculture with sugarcane farming at 72%, followed by undeveloped land at 11%, and urban formal at 8%. There are also industrial activities (0.9%) taking place in this catchment inclusive of sugar mills and textile factories in the Tongaat industrial zone (Begg, 1978). There is also a small percentage (2%) which makes up urban informal sector represented by informal settlements in the Tongaat area (Diederichs *et al.*, 2002). The coastal zone of the uTongati estuary is surrounded by sugarcane farms, with coastal forest south of the lagoon (Begg, 1978).

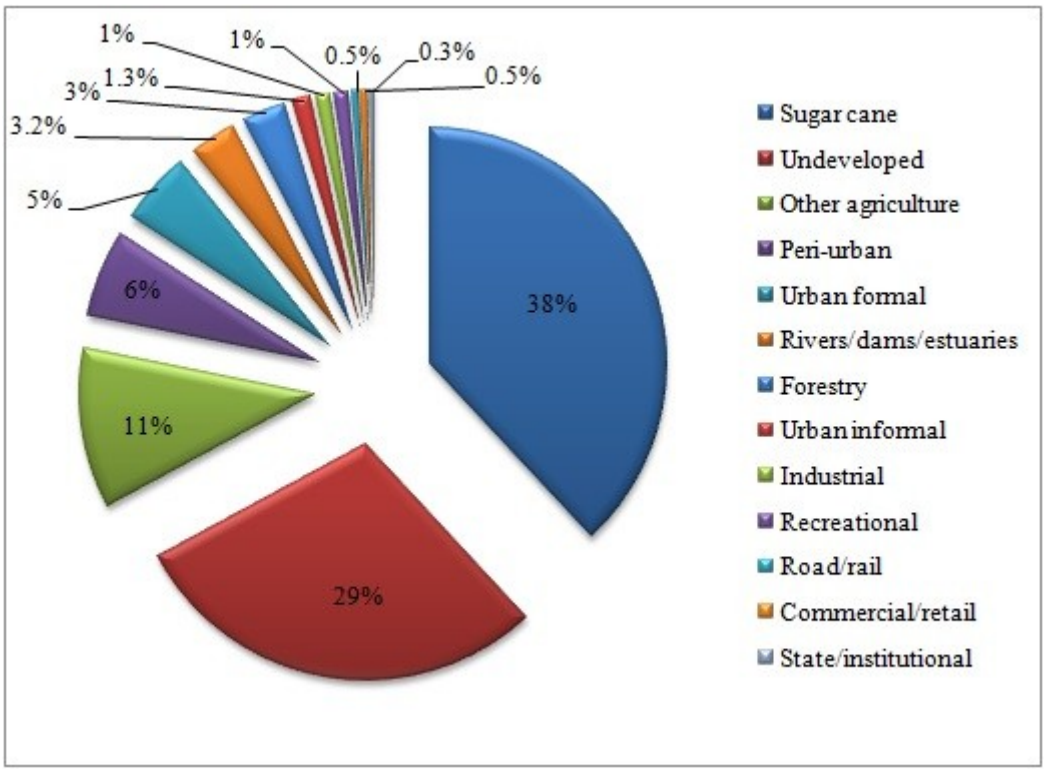

Figure 15: Land use of the uMdloti River catchment (data sourced from Diederichs *et al*., 2002).

The dominant land uses in the uMdloti River catchment is semi-commercial/subsistence cultivation, degraded grasslands and commercial sugarcane (Hodgson and Simpson, 2002). There are also a number of large urban centres containing industrial activities. Figure 15 represents the percentages of the land use activities in this catchment. Sugarcane farming is the largest constituent, making up 38% of the total land use (Diederichs *et al*., 2002). There is also forestry and other crop farming such as subsistence farming, market gardeners and small scale vegetable farming that take place (NSDP, 2009). There is also a large quantity (29%) of land that is undeveloped. Industrial activities make up 1% of the entire catchment, and include sugar mills, and manufacturing factories. Urban formal and peri-urban combined form 11% of the urban development, with 1.3% representing the informal sector. This catchment, although not indicated by Figure 15, consists of large areas of thicket, bushveld extending to the northwest and west of the region ans is used for grazing by animals (Read, 2002). The land around the uMdloti lagoon is mainly residential and commercial, with the towns of La Mercy to the north, and uMdloti to the south (Begg, 1978).

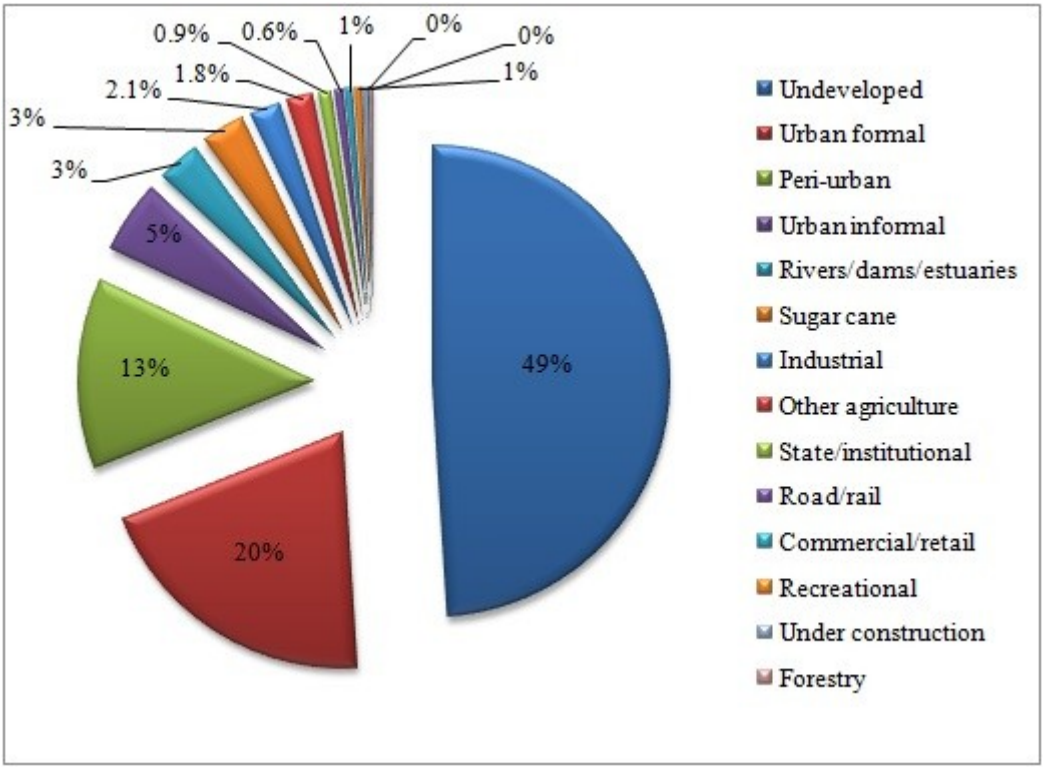

Figure 16: Land use of the uMgeni River catchment (data sourced from Diederichs *et al*., 2002).

The uMgeni River catchment, being the largest catchment in this study, contains a wide variety of land uses. Abed (2009) explains that the main land use in this catchment is intensive farming of tropical fruits, sugar, crops, as well as beef and dairy cattle. As seen in Figure 16, the majority of the land (49%) is undeveloped, with the next highest being urban formal (20%). This 20% represents residential areas within the catchment. Following this, the peri-urban and urban informal sectors are 13% and 5% respectively (Diederichs *et al*., 2002). 2.1% of the catchment is industrial, which is inclusive of the Springfield flats industrial area upstream of the estuary (Begg, 1978). At the uMgeni estuary further developments have taken place. On the southern bank of the estuary is a golf course, yacht club, and other recreational facilities and restaurants; with residential and commercial development taking place on the northern bank (Begg, 1978).

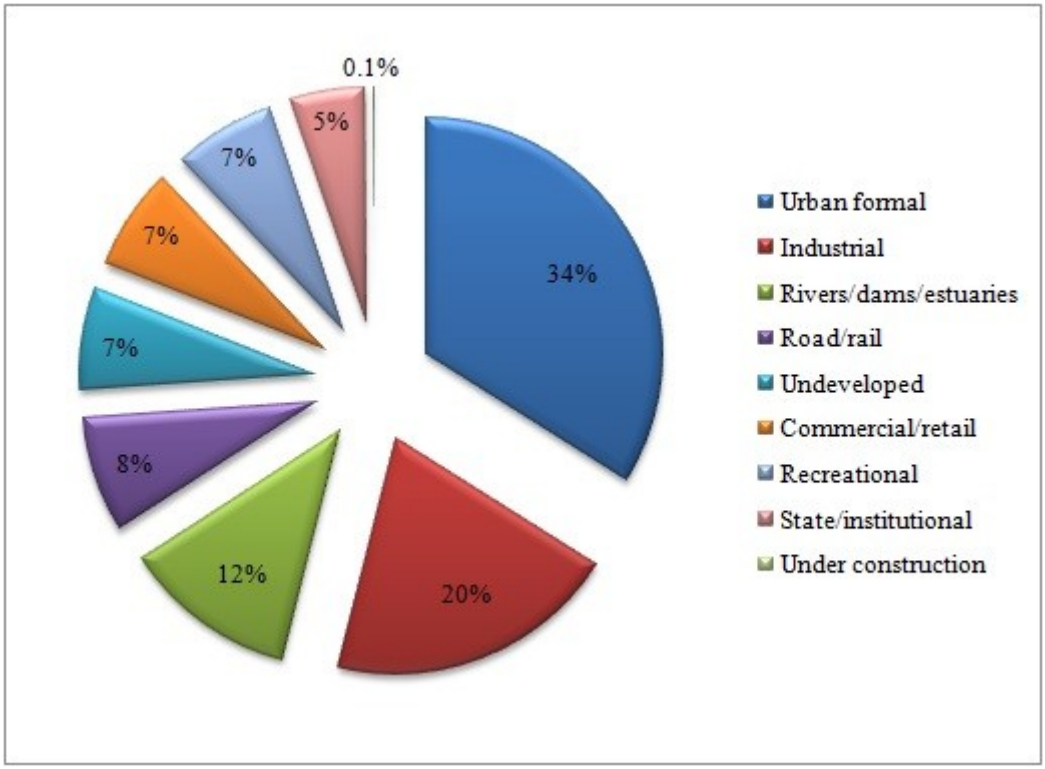

Figure 17: Land use surrounding the Durban Harbour (data sourced from Diederichs *et al*., 2002).

As mentioned earlier, the Durban Harbour drains two river catchments namely the Umbilo and the Umhlatuzana Rivers. According to a study by MER/ERM (2011), these two catchments were described as having a high proportion of urban land cover with extensive residential and industrial development, and very little open space. It was also noted that the rivers were extensively canalised. Other land uses in these catchments include subsistence farming, commercial sugarcane, commercial forestry and modified grasslands and bushlands (MER/ERM, 2011). Figure 17 represents the land use around the bay itself which is highly urbanised as well. The highest occuring activities are urban formal and industrial activities forming 34% and 20% of the total area respectively. The industries located at the harbour include oil refineries, sugar terminals, chemical, textile, food processing, tyre manufacturing, bulk printing, paper and board mills, along with various other industrial activities (MER/ERM, 2011). The Bayhead mangroves is the only small piece of natural vegetation remaining at the bay, which is now a protected area (MER/ERM, 2011).

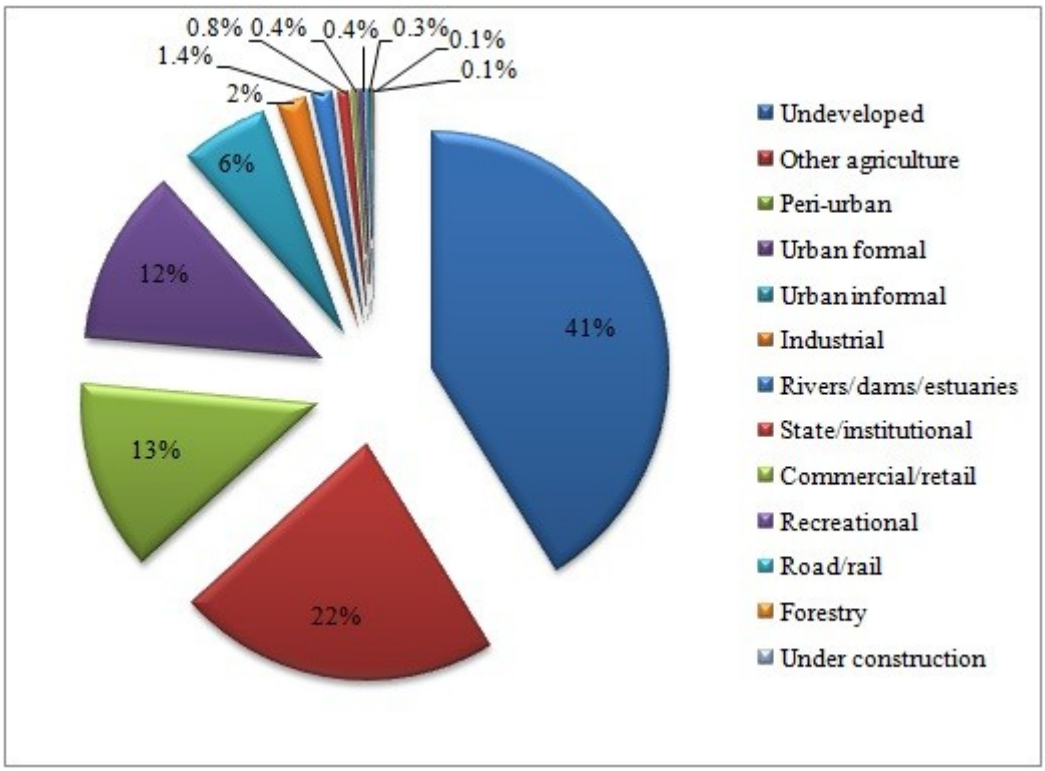

Figure 18: Land use of the Isipingo and uMbokodweni River catchments (data sourced from Diederichs *et al*., 2002).

Due to their relatively close proximity and size of the Isipingo and the uMbokodweni rivers and estuaries, the land use for these catchments have been graphed together in Figure 18. These catchments contain a variety of land uses and settlement densities. Figure 18 illustrates the majority of the land use within the catchments as undeveloped land at 41%, and the second highest as other agriculture at 22%. The urban sector (peri-urban, urban formal and urban informal) is representative of a combined total of 31% which is largely in the lower reaches of the catchments (Diederichs *et al*., 2002).

Focussing on the Isipingo catchment, it must be noted that industrial activities form a significantly large portion of the overall land use (SSI/MER, 2011) with the Prospection industrial area surrounding the upper reaches of the estuary. The residential area of Isipingo to the south of the estuary is the only residential zone, with commercial activities located predominantly north west of the estuary. There is also agricultural land use such as commercial sugarcane and vegetable farms, commercial timber and market gardeners within the catchment (Merryweather, 2008).

The uMbokodweni catchment is host to a variety of land uses. The major land use in this catchment is the formal residential and peri urban settlement areas. Towards the upper reaches of the river, small-scale farming occurs with most of the surrounding area undeveloped. The Umlazi residential area, as well as large informal settlements are located in the middle reaches, with sugarcane farming near the coast. The estuary itself is surrounded by the Amanzimtoti Golf course. Towards the north of the estuary lies the industrial Prospection area and towards the south is the town of Umbogintwini (Forbes and Demetraides, 2008).

2.6. Topography

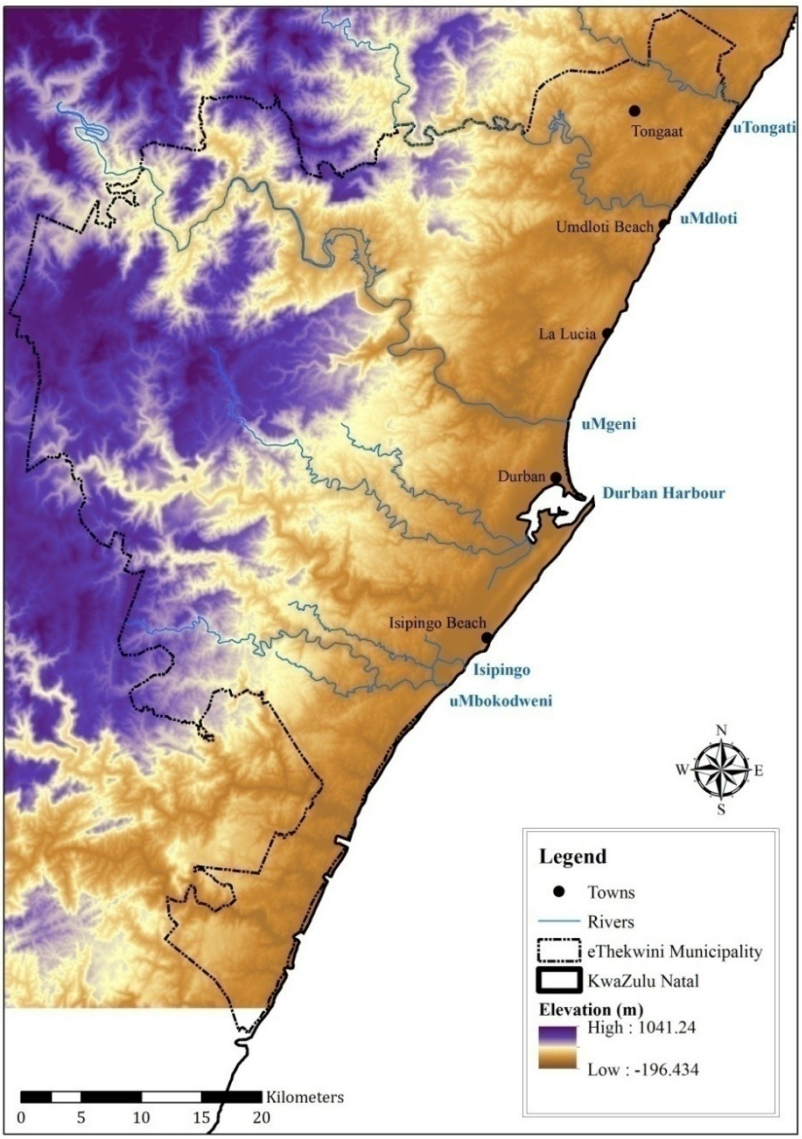

Figure 19: Digital Elevation Model of the eThekwini Municipality within KwaZulu-Natal.

The topography of the KwaZulu-Natal province is described by Cooper (1993) as an area that is characterized by steep hinterland and a lack of coastal plains in the southern parts of the province. Coastal plains dominate the northern areas of the province near Zululand and beyond the border towards Mozambique. The digital elevation model (Figure 19) illustrates the general topography of the KwaZulu-Natal coast, contrasting the flat coastal area with the steep inland. The Drakensberg mountain range, which lies about 250 km from the coastline, forms a large watershed which is drained by approximately 74 rivers. This total consists of 9 major perennial, 55 minor perennial and 10 secondary rivers (Abed, 2009), all draining into the Indian Ocean. The discharge of the rivers is perennial, with some seasonal variations (Cooper, 1993).

These rivers, along with the majority of rivers in South Africa, flow through incised valleys which yield high sediment loads at the coast (Ngetar, 2002; Sukdeo, 2010). Due to the high fluvial sediment yield, the KwaZulu-Natal coastline is dominated by sandy beaches and barrier environments which develop across the mouths of the estuaries (Abed, 2009).

2.7. Climate

The study area located on the east coast of South Africa experiences a subtropical climate with warm and wet summers, and cool and dry winters (Ngetar, 2002). These seasonal weather patterns are mainly influenced by the presence of the South Indian Anticyclone and an easterly tropical flow (Abed, 2009). The warm Agulhas ocean current's close proximity to the east coast contributes to the average annual temperatures which are warm to hot in summer and mild in winter (Glennie, 2001).

The rainfall patterns associated with KwaZulu-Natal are largely seasonal. Around 80% of the annual rainfall is received in the summer months, which is between 900-1000 mm (Cooper, 1993). The high rise in altitude inland produces orographic rainfall as well. Winter rainfall in this region is mostly associated with northward moving coastal low pressure systems which adds to the annual rainfall total (Cooper, 1993; Sukdeo, 2010).

Periodically, intense rainfall events occur which gives rise to widespread flooding throughout the province (Cooper, 1993). These fairly frequent floods scour the river channels and alter sediment patterns, eroding and transporting high sediment loads to and even out of the estuaries (Ngetar, 2002). An example of this would be the floods of September, 1987, due to the formation of a cut-off low (Abed, 2009).). Cut-off lows are unstable baroclinic systems

which slope to the west with increasing height, and are associated with strong convergence. These systems are responsible for many flood-producing rains over South Africa (Badenhorst *et al*., 1989).

2.8. Flood history

Flooding in KwaZulu-Natal is a periodic phenomenon due to climatic conditions. Severe floods occur several times per century and their effects are usually devastating, especially to the estuarine environment (Badenhorst *et al*., 1989). Coning *et al.* (1996) explains that extreme rainfall events develop in southern Africa when weather systems originating in the tropical easterlies migrate south and interact with systems in the mid-latitude westerly circulation during the summer months. Barnes (1984) explains that winter storms, such as sea-gale storms, are usually associated with the occurrence of the southerly shift of the south-east trade wind belt in conjunction with the passage of a cold front from the south-west. This combination results in destructive winter storms along the KwaZulu-Natal coast.

Rainfall data has been acquired from the South African Sugar Research Institute weather station in Mount Edgecombe (20 km north of Durban) to allow comparison between the regional rainfall of the affected flood area and localised rainfall near the Durban area. The storms in April 1856 and September 1987 produced the most damaging floods to date (Badenhorst *et al*., 1989). Each of these flood events will be briefly discussed below, using the uMgeni estuary as the representative site for the region.

Table 3: Major flooding events that affected the KwaZulu-Natal coast over the past 156 years.

Date	Type of storm	Rainfall (mm)	Rainfall period recorded	Flood area*	Source	Rainfall data (mm) from South Africa Sugarcane Research Institute (SASRI) (5 day period)
April 1856	Cold front system	706.9	5 days	KwaZulu-Natal coastline	Barnes, 1984	No data
May-June 1905	Sea-gale storm	448.3	1 day	South coast to Piet Retief	Barnes, 1984; Maki, 2007	No data
October 1917	Sea-gale storm	428.5	3 days	Between Empangeni and Umzumbe	Barnes, 1984; Maki, 2007	No data
May 1959	Cold Front system	>300	1 day	Southern KwaZulu-Natal	Adamson, 1981	70.5
February 1977	Cut-off low	158	2 hours	KwaZulu-Natal and Mpumalanga	Adamson, 1981	215.3
January 1984	Tropical Cyclone Domoina	400-600	2-3 days	Southern Mozambique, Mpumalanga low veld, Swaziland and Northern KwaZulu-Natal	Mason et al., 1998	218.6
September 1987	Cut-off low	>800	5 days	KwaZulu-Natal and Free state	Badenhorst *et al*., 1989; Cooper, 1993	436.6
February 1996	Tropical-temperate trough	150	3 days	From Umzinto in KwaZulu-Natal to Mpumalanga.	Coning et al., 1996	165.9
March 2007	Cut-off low	57	5 days	KwaZulu-Natal coastline	SASRI, 2007	57
March 2012	Tropical Cyclone Irina	140.8	1 day	Mozambique, Mpumalanga and KwaZulu-Natal coasts	Spies, 2012	152.6

* Flood affected areas information taken from National Disaster Management Centre www.ndmc.gov.za Date accessed: 25-01-2013.

2.8.1. The Great Flood of 1856

The flood event of 1856 was caused by a mixture of a cold front system and gale force winds. This storm made landfall in Durban on 13 April 1856 and lasted for a period of five days. Within these five days, 706.9 mm of rainfall was experienced in the greater Durban area (Barnes, 1984). Over a period of 66 hours, 691 mm of rain fell, and was mostly concentrated within the uMgeni catchment (Barnes, 1984).

During this flood event, the uMgeni River rose by 8.5 m and flowed directly over the adjacent sand flats and into the Durban bay (now Durban Harbour). This had also occurred previously in 1848 during a similar flood event (Spencer, 2008). Following the storm event, the uMgeni estuary's banks were removed on both sides, resulting in a widening of the channel width to 215 m. The original bottom materials were scoured away and replaced by large boulders mixed with clumps of clay. The outlet remained open for less than three years until siltation had begun again (Spencer, 2008).

Other areas of KwaZulu-Natal were affected by this flood event as well. The uTongati River had risen by 9 m above its normal level, and this flooded the neighbouring sugarcane farms. The uMvoti River rose by 5 m which caused a widening of its channel four times its usual width (Barnes, 1984). It also transported a 1 m thick layer of sand which was spread over nearby pastures. To the south of this, the uMdloti River rose to a height of 9 m and covered the bordering land with 1.5 m of sand. The southern coast of KwaZulu-Natal was also affected, as well as the inland areas which encountered 40% of Durban's total rainfall (Spencer, 2008).

2.8.2. The cut-off low flood of 1987

On the 26th of September 1987, a cut-off low formed along the east coast of South Africa and produced more than 800 mm of rain over a five day period (Badenhorst *et al*., 1989). Most of the rainfall was concentrated over the central KwaZulu-Natal region. During these floods the water level in the uMgeni estuary rose by 5 m above its normal high tide. A 2 km plume of turbid freshwater entered the Indian Ocean, and the peak discharge calculated during this period was 10 000 m^3s^{-1}, which is almost double the previous peak discharge of 5700 m^3s^{-1} in the flood of 1917 (Cooper, 1993).

During the flood of 1987, the uMgeni estuary was altered to a large extent (Appendix A-Figure A1). The mouth of the estuary was widened substantially by the complete erosion of

the spit, which was 150 m in length at the time, and a portion of the mangrove trees on the north bank was removed (Forbes and Demetriades, 2008). Large amounts of sediment were scoured from the estuarine channel and bed. This included the vegetated island in the midstream which was completely removed, and sections of the southern bank were eroded as well. In total $1.8x10^6$ m^3 of sediment was removed from the estuary (Badenhorst *et al*., 1989).

Sediments present before and after the flood were analysed by Badenhorst *et al*. (1989) and Cooper (1993) and is discussed below. The estuary is situated on unconsolidated sediments which accumulated during and since the Flandrian Transgression. Pre-flood sediments in the uMgeni estuary consisted of mainly fluvial derived gravel and mud with marine sand deposited in the lower 200 m of the estuary by flood-tidal transport through the mouth and overwash across the spit (Badenhorst *et al*. 1989). Post-flood sediments in the estuary consisted primarily of coarse sand and gravel. All the mud was eroded from the estuary. The carbonate and organic content of the sediment was reduced to zero and this indicated the removal of the marine sand, fine sediment and organic detritus (Cooper, 1993).

Deposition during the falling flood stage produced overbank deposits in the estuary. This consisted of well sorted, fine-grained sand on the south bank and a 1 m layer of mud was deposited from suspension in sections (intertidal and supratidal) in the Beachwood mangrove swamps to the north (Badenhorst *et al*., 1989).

Following the floods, in approximately 8 months, the estuary bed had undergone accretion due to the deposition of fine-grained fluvial sand. Also the sand spit was reconstructed due to the rapid reworking of coarse sediment by wave action (Badenhorst *et al*., 1989). The speedy accumulation of sediments in the estuary indicated a high sediment accumulation rate.

2.9. Historical origins of Durban

Current archaeological evidence indicates that the coastal region of Natal was first inhabited by humans some 1.6 million years ago (Glennie, 2001). Closer to 100 000 years ago, dated rock paintings and artefacts revealed that ancestors of the San people were widely distributed in southern Africa (Muller, 1981). Tools dating back to 70 000 years ago were found in the Sibudu caves near Durban and included compound tools, such as hafted harpoons and compound glues for hafting spear points (Mitchell, 2002).

The Iron Age, roughly from 200 B.C., incorporated the use of metal tools and more intensive farming methods. These people cultivated sorghum and millets, herded cattle, sheep and

goats and manufactured iron tools and copper ornaments (SAHO, 2000). The climate during this period was much warmer and wetter than today and promoted such activities. Archaeological evidence placed Iron Age farmers at the coastal region of Natal at approximately 250 A.D. (Glennie, 2001). During this time, they settled near the dense forests edge where soils were rich and marine resources could be obtained. Between about 700-900 A.D., the climate was colder and drier than at present, but became favourable again for farming activities during 900-1300 A.D. (late Iron Age) (Mitchell, 2002).

During the last 2500 years, El Niño-Southern Oscillation (ENSO) activity was frequent and produced severe droughts that lasted long periods of time, as well as regular floods which also impacted on the farming activities of the residents (Mitchell, 2002; Glennie, 2001). This subtropical climate together with the advancement in technology aided by fire, metal axes etc. facilitated an environmental change along the Natal coast, where dense forests, marshes and natural grasslands were replaced by crop fields (Glennie, 2001).

The first European discovery of the KwaZulu-Natal province was made by Vasco Da Gama, a Portuguese traveller, in 1497, when his ship entered the bay to seek refuge from a heavy storm. Over the next 200-300 years or so, a number of shipwrecks occurred at the Durban bay which marooned many European travellers. Approximately 1000 survivors were left stranded at the coast of Natal and settled near the bay (SAHO, 2000). Following this, small settlements started to emerge around the Durban Bay. In 1824, a small group of British traders arrived in Natal and a settlement named Port Natal was established. Over the next century, the Durban bay developed into the Durban Harbour, along with the city of Durban which surrounds the bay.

2.10. Conclusion

Different components of the study area inclusive of the physical and estuarine properties of each estuary in this study were provided in this chapter. Other aspects such as geology, soils, land use, topography and climate were also described. A brief flood history containing descriptions of two major flood events that occurred in this municipality were discussed. Finally the historical origins of the province of Natal and the city of Durban were also briefly described. Following this chapter is a detailed account of the literature pertaining to the concepts discussed in this study.

Chapter 3

LITERATURE REVIEW

3.1. Introduction

Relevant theoretical concepts on which this research is based, is explained in this chapter. A short definition of estuaries and their origins are provided, followed by a classification of estuaries relevant to the different types of estuaries in this study. Thereafter, sedimentological processes within estuaries relating to the transport and deposition of fluvial and marine derived sediments are described. Mouth sediment dynamics will also be examined briefly. Radiometric dating processes are outlined thereafter. Following this is a section focussed on heavy metals, which includes details of the sources of metals, factors affecting sediment-metal relationships and the toxicity of the metals focussed on in this study. Lastly information on background heavy metal concentrations is described.

3.2. Estuary definition and origin

The most commonly used definition for an estuary is given by Pritchard (1952, pg 3) who states that an estuary is "*a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage*." However the type of estuary is not included in this definition, which is a crucial part of the sedimentary mechanisms within an estuary. Perillo (1995, pg 20) mentions 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 a measurable variation of salinity due to the mixture of sea water with fresh water derived from land drainage*."

The above definitions do cover the main typological aspects pertaining to estuaries, however the definition from Dyer (1997, pg 5) does incorporate the sections within each estuary i.e. "*An estuary is an inlet of the sea, reaching into the river valley as far as the upper limit of the tidal rise, usually being divisible into three sectors: a) a marine or lower estuary, in free connection with the open sea; b) a middle estuary, subject to strong salt and freshwater mixing; and c) an upper or fluvial estuary, characterised by fresh water but subject to daily tidal action*." Along with this definition which focuses on zonal classification within estuaries, sedimentary movement and facies differentiation within estuaries are other concepts which should be included in the definition. Dyer (1997, pg 5) proposes this

definition as related to sedimentary facies within estuaries: "*The seaward portion of a drowned valley system which receives sediment from both fluvial and marine sources and which contains facies influenced by tide, wave and fluvial process. The estuary is considered to extend from the landward limit of tidal facies at its head to the seaward limit of coastal facies at its mouth*."

The origins of estuaries are linked to the changes in sea level. Since estuaries are shallow and the sea level has undergone drastic changes on the geological time scale, estuarine sediments may not be very widely preserved in the geological column and may be fairly thin in vertical extent (Pye, 1994). Estuaries are ephemeral features, being quickly altered, thus having an average life of only thousands of years. During the Pleistocene epoch, a period of lowered sea levels, rivers incised their valleys to a base level approximately 100 m below present sea level. Subsequently, sea levels rose about 130 m during the Flandrian transgression, approximately 13 000 years ago, resulting in the inundation of these incised river valleys and thus forming the estuaries present today. The present sea levels along the coasts were reached between 5000 and 6000 years ago (Pye, 1994; Baird, 2006).

3.3. Estuarine classification

The variations between estuary types are great, as not all were formed the same way. They are classified by a number of factors which control their development and form. Factors that contribute to variability along the South African coastline include catchment size, gradient, sediment supply, marine sediment availability, climate and fluvial discharge (Cooper, 2001). The estuarine variations along the subtropical region of KwaZulu-Natal are mainly due to the very steep hinterland which has resulted in laterally confined estuaries along the coast (Cooper, 2001). Only areas of northern KwaZulu-Natal, which are less steep, contain examples of estuaries which have not been confined by their bedrock valley. Further variation between estuaries in South Africa is based on its connection with the sea by a surface channel (Cooper, 2001). KwaZulu-Natal has the most frequent observations of mouth openings, where estuaries are divided into those that are open more than 70% of the time, and those that are open less than 30% of the time (Cooper, 2001). A South African based classification system has been proposed by Cooper (2001) and is explained further below.

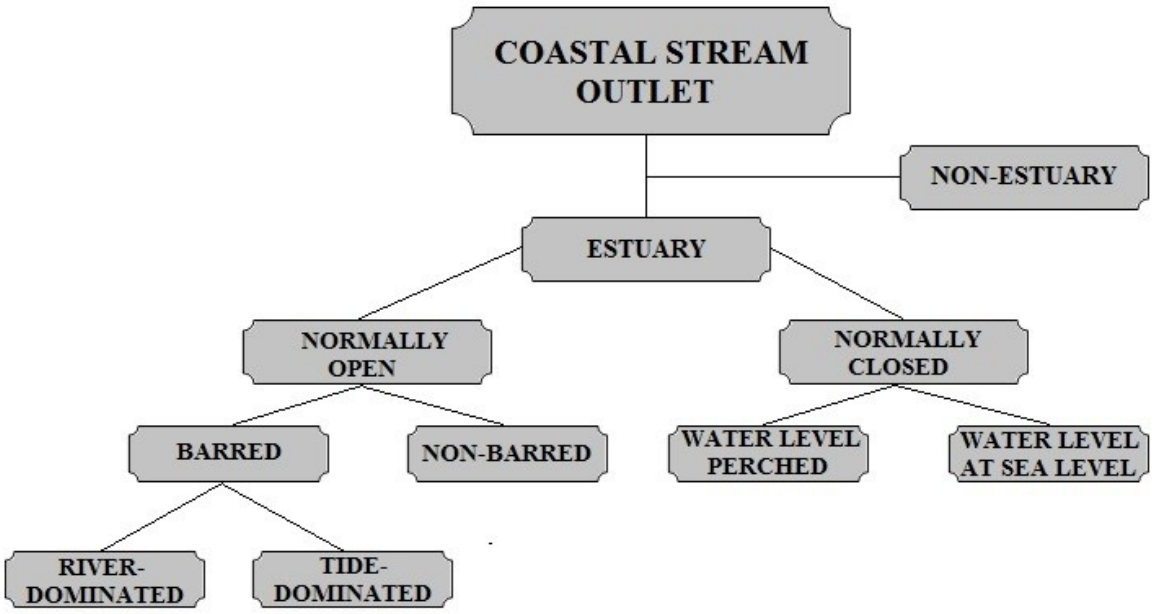

Figure 20: Conceptual morphodynamic classification of microtidal estuaries (after Cooper, 2001).

Figure 20 is an adaptation of the classification system created by Cooper (2001) to identify South African estuaries. It mainly focuses on the geomorphic variations between estuaries. Two types of estuaries are proposed i.e. normally open and normally closed, and this is then further subdivided to include other morphodynamic variables such as sand bars present at the mouth. The uMgeni, Isipingo (through concrete pipes) and uMbokodweni estuaries fall into these specific groups i.e. normally open, barred open and river dominated. The uTongati and uMdloti estuaries represent perched estuaries, however the uTongati is normally open and the uMdloti is closed for the majority of the year. The Durban Harbour represents an estuarine bay (which is not included in Cooper (2001) classification). These categories are discussed below.

3.3.1. Normally open estuaries

Normally open estuaries are defined as having a connection to the open sea via a surface channel (Cooper, 2001). They lack sand accumulation at the mouth which allows the free connection to the sea. This contrasts to closed estuaries which are blocked by a sand bar or barrier and has no connection to the sea (Sukdeo, 2010). The high energy coastline of South

Africa typically results in the closure of estuarine mouths due to strong wave action at the shore; therefore it is rare to have a permanently open estuary without at least a sand barrier present at the mouth (Abed, 2009). Normally open estuaries vary in mouth dynamics and size and can be further subdivided into two categories i.e. barred and non-barred estuaries.

3.3.2. Barred open estuaries

A barred open estuary is one that consists of a supratidal sand barrier at the mouth with a surface channel allowing some drainage and exchange within the estuary. Cooper (2001) stated that these systems may range in fluvial discharge from small, localised stream catchments to large systems that can drain large areas of the subcontinent. Smaller systems' outlets are usually kept open by river discharge as it is difficult to maintain large tidal prisms (Cooper, 2001). However frequent over-washing and occasional surges can increase tidal penetration into the estuary which imparts on estuarine characteristics. The sand barriers at the mouth also tend to be short and this reduces the volume of discharge by seepage through the barrier (Sukdeo, 2010). The barred open estuaries that are usually larger in size can be subdivided into two more categories of river- and tide-dominated estuaries.

3.3.3. River-dominated estuaries

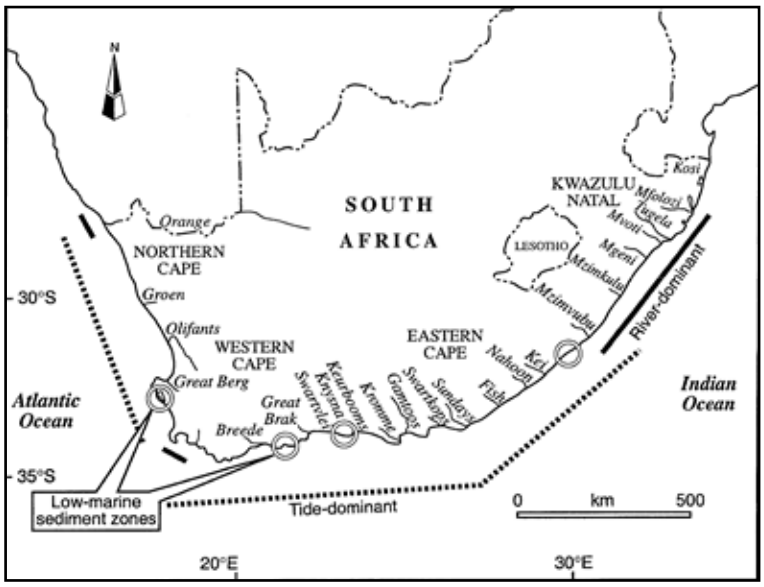

Figure 21: The distribution of river- and tide- dominated estuaries along the South African coastline (Cooper, 2001).

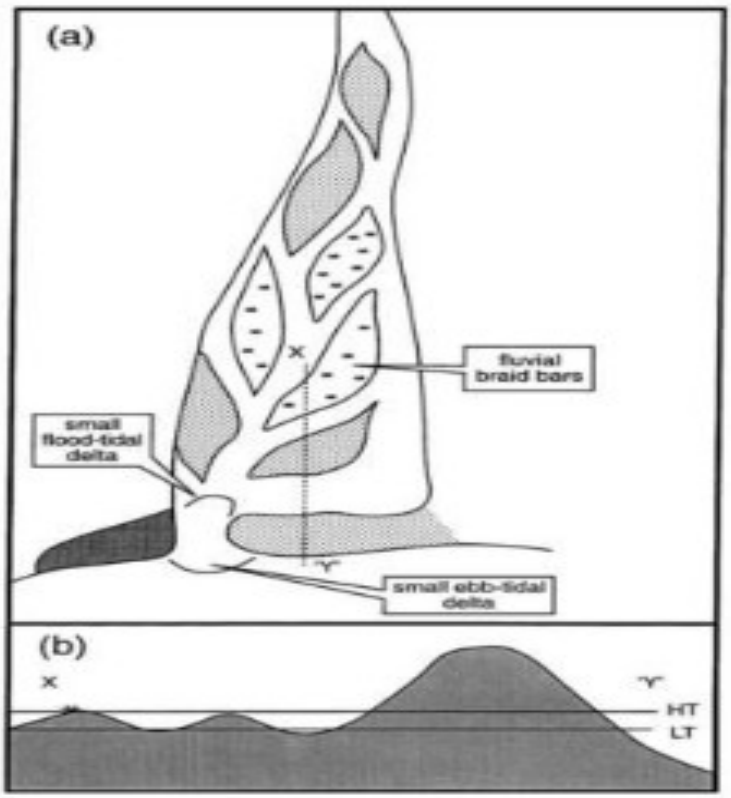

Figure 22: The generalised morphology of a river-dominated estuary in plan (a) and cross section (b) (Cooper, 2001).

River-dominated estuaries are defined as those in which an inlet is maintained by fluvial discharge and where the tidal prism is too small to generate currents that can work against wave-induced sediment transport in the nearshore, which acts to close the barrier inlet (Cooper, 2001). The KwaZulu-Natal coastline is dominated by these types of estuaries as they form due to steep gradients, high sediment supplies during transgression and narrow bedrock valleys (Figure 21) (Cooper, 2001). These systems are dominated by river flow and have limited tidal penetration due to the steep hinterland (Sukdeo, 2010). The sediments are therefore mainly fluvial, and fluvial facies dominate the estuary, extending as far as the barrier. This accumulation of fluvial sediments as well as increased bed levels, tend to create a shallow back-barrier region (Abed, 2009). Strong wave energy results in small or absent ebb-tidal deltas along with poorly developed flood-tidal deltas due to weak tidal currents and lack of space in the sediment-filled channel (Figure 22) (Cooper, 2001).

According to Cooper (2001), seasonal river floods play a vital role in eroding accumulated sediments and deepening the channel temporarily. Erosion during river floods is distributed

throughout the channel and may even erode cohesive sediments. The uMgeni estuary can be used as an example, where in 1987 an entire vegetated island was removed from the lower reaches as a result of a riverine flood. Contrasting this are drought conditions which may cause the closure of the mouth for long periods of time (Abed, 2009). Dam construction within the catchment may also compound on this mouth closure effect, as a lack of fluvial discharge may discourage the open state of the mouth (Cooper, 2001; Abed, 2009).

3.3.4. Perched closed estuaries

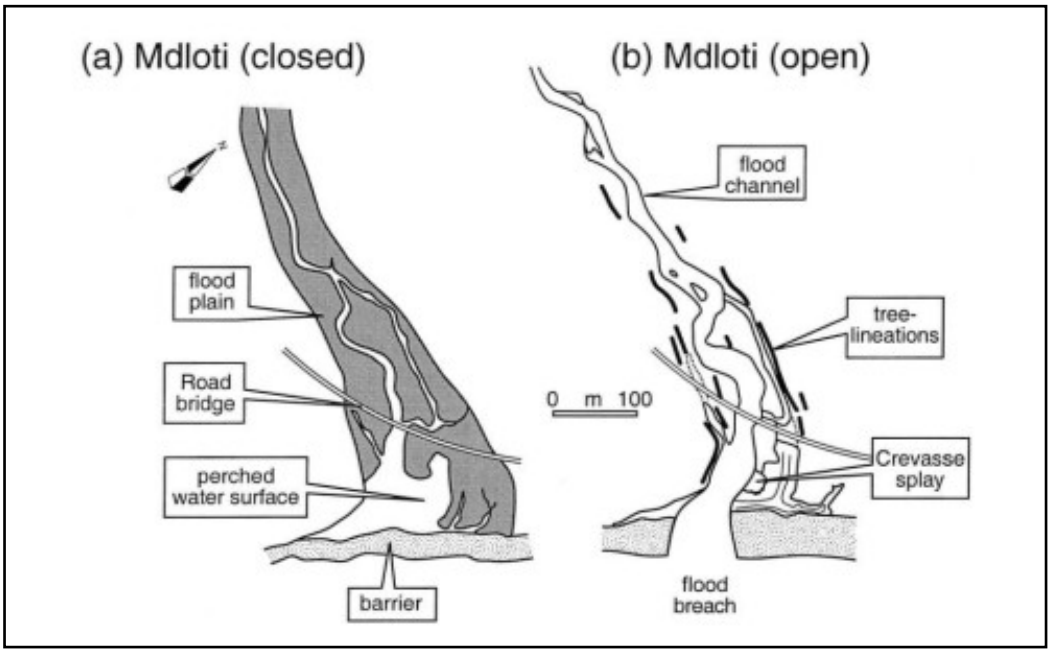

Figure 23: The uMdloti estuary during normal closed conditions (a) and after flood-induced breaching (b) (Cooper, 2001).

The normally closed estuaries of South Africa are split into two categories i.e. perched, where the water levels behind their berms are at elevations above the levels of most high tides; and non-perched, where the water level within the estuary is at or close to high tide levels (Cooper, 2001). The perched estuaries have high berms which are a result of coarse grained barrier sediment and relatively low wave energy. Their inputs from fluvial, rainfall and barrier overwash are equal to their outputs which include evaporation and seepage through the barrier (Abed, 2009). Quiet water conditions prevail in these estuaries which promote the settling of suspended material and mud deposition (Cooper, 2001).

Breaching occurs when the inputs (freshwater discharge and overwash) exceed the outputs (evaporation and barrier seepage) of the estuary and a surface channel is cut to permit discharge into the ocean (Cooper, 2001). This can result in the drainage of the entire lagoon as the elevated bed levels contribute to the quick release of discharge through the berm. This exposes previously submerged areas of the bed sub-aerially. If the freshwater discharge is prolonged, the sediments present on the bed can be scoured as the base level of the system has decreased (Cooper, 2001). River floods can also cause breaching, and causes the production of large bedforms on the lagoon bed which is generated by strong seaward flowing currents. It can also produce significant modification to the estuarine bed through removal of sediments. When the estuary re-seals, through onshore input, these bedforms are preserved and fine-grained deposition is re-instated (Cooper, 2001). Figure 23 illustrates the conditions within the uMdloti estuary during closed periods and after breaching of the berm.

3.3.5. Estuarine bays

An estuarine bay, which is usually permanently linked to the sea, can either be natural or partly artificial due to anthropogenic activities near the mouth or harbour region (Whitfield, 1992). These types of estuaries have large tidal prisms, thus mixing of marine and freshwater are common. The replacement of estuarine water in the lower and sometimes middle reaches of the estuary also takes place. Wetland/mangrove swamps commonly occur with these types of estuaries, and are inhabited by many estuarine and marine organisms (Forbes and Demetriades, 2008).

3.4. Sediment processes in estuaries

Sediment may be defined as fragmental material that originates from the disintegration of rocks. It is transported by, suspended in or deposited by water or air, or is accumulated in beds by other natural agencies (Colby, 1963). Sediments form a crucial link in estuarine processes. Estuaries are the route by which sediments are transported from the interior of land masses to the coastal areas and eventually the open ocean (Pye, 1994). Sediments entering estuaries are either catchment or marine derived. The processes involved with the transport and deposition of fluvial and marine sediments into the estuary are explained in this section. Mouth sediment dynamics in temporarily open-closed estuaries, are described as well.

3.4.1. Sediment texture

Sediment texture refers to the collective characteristics of grain size, sphericity and roundness of grains, as well as the packaging and orientation of grains. For this study, only grain size was considered. This is due to the significant influence grain size has on the contaminant concentration present within the sediment (Sukdeo, 2010). Sediment can be classified into several textural groups, of which the three most important are: sand, silt and clay (Wild, 1993). Based on the Wentworth scale classification of sediments, sand grains are between 63 μm – 2 mm. Following this are silts and clays which are known as fines, as they consist of the smallest grain size (Townsend, 1973).

Silt ranges between 2 μm – 63 μm in size, and consists of particles intermediate between very fine sand and clay (McNally and Mehta, 2004). They resemble sand particles, but since they are smaller, and have a larger surface area per unit mass, and are often coated with clay, they may exhibit some physiochemical properties of clay. Clay minerals are less than 2 μm and make up part of the finest fraction of sediments along with the colloidal fraction. Clay particles are plate-like and belong to the alumina-silicate group of minerals (Townsend, 1973). These particles have the largest surface area per unit mass, and thus have a great influence on soil behaviour. Clay particles adsorb water and hydrate. They also typically carry negative charges and when hydrated form electrostatic double layers with exchangeable ions in the surrounding solution (Hillel, 1980). Silts and clays combined are typically called mud and tend to dominate the bed and banks of most estuaries (McNally and Mehta, 2004).

3.4.2. Transport and deposition of fluvial sediments

The method of transporting fluvial sediments from the catchment into an estuarine environment is mainly governed by the grain size of the sediments. Upon entering the saline estuarine environment, cohesive sediment transport processes dominate for finer particles (Villars and Delvigne, 2001).

Transport of fluvial sediments into estuaries

Grain size plays an important role in the transportation of sediments within the water column. Coarse sediments such as sand grains, gravels, or larger particles are transported via bedload within a river (Dyer, 1986). The amount of bedload transported by a river also determines its

channel geometry and its ability to recover from natural or anthropogenic disturbances such as floods and upstream impoundments (McNally and Mehta, 2004).

Finer sediments, such as silts and clays, which are less dense and easily suspended within the water column, are transported as such (Villars and Delvigne, 2001). Suspended load is important for natural floodplain deposition processes and maintenance of deltaic and estuarine wetland environments as it carries the necessary sediments used for the development of these environments. Fine sediment particles that are transported through suspension within the catchment eventually encounter the saline estuarine environment, near the head of the estuary, and this immediately introduces cohesive sediment processes (Gibbs, 1987).

Cohesive sediments, or mud, are a mixture of clay, silt, fine sand, organic materials and colloidal particles. Due to mainly the size and shape of the particles as well as the electrical charge distribution, the clay minerals are largely responsible for cohesion (Guillou *et al*., n.d.). As these sediments reach the first traces of saline water in an estuary, the double layer around each particle is compressed by ions in the saline water. This destabilizes the particles and creates a condition conducive to coagulation. Once this occurs, the collision between two particles produces an aggregate of two, and this process continues until equilibrium is reached (Mehta, 1987). This results in an aggregate which can consist of hundreds of original particles. This process is also known as flocculation and occurs when clay particles reach saline waters. All suspended clay particles become cohesive when the salinity exceeds 2-3 ppt, although further increases in salinity, up to 10 ppt, increases inter-particle cohesion and can influence aggregate structure (Mehta, 1987). Flocculation greatly influences the settling velocity of suspended particles and subsequently the deposition rate within an estuary (Villars and Delvigne, 2001).

Deposition of fluvial sediments in estuaries

Deposition of fluvial sediments occurs when gradients decrease as it reaches the coastline, and flow velocities diminish to allow for increased settling velocities of sediments (Pye, 1994). Settling velocity is defined as the settling rate in quiescent fluid (Pye, 1994). Sediment particles tend to settle with respect to the water. Particles settle at rates that depend on the differences in density between the particles and the water, on the viscosity of the water, and on the size, shape and flocculation of the particles (Dyer, 1986). The fall velocities of the

particles are also influenced by the viscosity of the fluid-sediment mixture and this is dependent on the water temperature and the presence of interfering sediment particles (Colby, 1963).

In water that is quiescent, and contains concentrations of sediments which are low enough to prevent significant interference amongst other particles, each particle settles at its own characteristic fall velocity in a particular fluid of given density (Villars and Delvigne, 2001). Mud flats usually occurs as areas of deposition in estuaries where settling velocities are higher, given that there are longer periods of time with high water levels and low energy (Mcnally and Mehta, 2004).

Flocculation of fine sediment also changes the fall velocities of the affected particles. A cohesive sediment bed is formed by the combined action of hindered settling and consolidation (Gibbs, 1987). Aggregated particles (formed through flocculation) settle at the bottom of the estuary and create a consolidated layer of mud. The stress brought about by further falling aggregates expulses pore water from this consolidated sediment and eventually a solid structure begins to form. This leads to the slow compaction or densification of the bed (Mehta, 1987).

Areas of deposition in an estuary differ greatly to sediment that deposit into a lake or reservoir. The chemical composition of the ocean water entering the estuary and mixing with the fresh water from the river creates a brackish environment which affects the deposition of sediment particles (Guillou *et al*, n.d.). The place of first deposition may occur near the head of the estuary where the saline waters are first introduced and flocculation occurs. Muds are usually deposited on the fringes of the central basin by river processes, tides and internally generated waves (Mcnally and Mehta, 2004). Deposition in these environments is also aided by vegetation such as mangroves (Villars and Delvigne, 2001). Significant reworking of near surface sediments is caused by biological activities such as bioturbation. Two types of organisms exist that mix the sediment: organisms that mix the sediment vertically (e.g. by burrowing) and those that mix the sediment horizontally. Pollutant transport from the sediment beds to the overlying water column depends on bioturbation processes. This takes place in particular areas where contaminated sediments occurs in stable sediments that is not subjected to significant erosion (Villars and Delvigne, 2001).

High or low tides can affect the flow of the incoming waters from the catchment which will determine the sites of deposition (Dyer, 1986). Sediments that are deposited at high tide can

become eroded from the bed at low tides. Low tides may also allow for slower deposition of particles further downstream, and may deposit more quickly at high tides. However, the site of deposition will vary with the discharge of the river. Usually during low stream flow, fine sediments can become entrained and carried back upstream while the tide is rising and can be deposited before downstream flow begins again (Dyer, 1986). Furthermore, fine sediments can be easily transported directly out to sea by the current during high flow events such as fluvial floods (Dyer, 1986).

Coarser fluvial sediments which do not flocculate will move as bed load material downstream to the tip of the saline intrusion (Pye, 1994). At this tip, as the maximum currents are equal on ebb and flood at the bottom, the material will become deposited. Closer to the sea, the maximum flood current will transport the bed material into a position where the velocities do not exceed the threshold for that grain size (Pye, 1994). Subsequently, there should be a decrease in grain size inland. However, tidal currents are not so simply distributed and will result in local constrictions that will create coarse patches and widening the deposition of mud (Mehta, 1987). Lateral variations in velocity can be large in the lower parts of the estuary. This can lead to sediment being transported and deposited differently on one side of the channel compared to the other side (McNally and Mehta, 2004).

Periods of low water velocity may be followed by high velocity periods which can produce the consequential erosion of the estuarine bed. During turbulent flows, when water flows over unconsolidated sediments, some sediment particles can be removed from the bed, but some may be carried upward and added to the particles in suspension once again (Colby, 1963). Floc erosion occurs when the flocs or part of the flocs from the bed are individually disrupted or broken up. This can take place under peaks of shear stresses. Finally, mass erosion occurs when lumps of sediment are removed during flood events (Guillou *et al*., n.d.).

In terms of floods, periods of high river-discharge are extremely important and will tend to flush the sediment out of estuaries. Sediments accumulated over decades can be scoured out during one single, large-scale flood event (Dyer, 1986; Whitfield and Bate, 2007; Beck, 2005). This also allows for the estuary to remove any pollutants trapped within its sediment. Despite this, floods also carry with it large amounts of sediment from the catchment. If flood levels are very high, sediments can be deposited directly into the ocean, creating extensive sediment plumes at the mouth depending on the volume of discharge. Only at the falling stages of the flood, will sediments be deposited into the estuary (Dyer, 1986).

3.4.3. Transport and deposition of marine sediments

Sediments that are located near the inshore environment, especially sediments associated with estuary mouths along the coast, are usually derived from fluvial sources and the disintegration of rocks and shells on the seashore (Whitfield and Bate, 2007). The major sources of marine sediments are mostly from the erosion of beach or dune sediment, possible offshore sources and larger rivers in the region. Large river systems are responsible for depositing varying amounts of sediment in the inshore area during periodic flood events. This sediment is continuously moved and reworked by wind, wave and current action. During storms, large quantities of sands are moved by wave action. Along the South African eastern seaboard, wave directions can become more easterly and flood-derived sediments are likely to be moved south westward along the coastline to estuaries located further south (Whitfield and Bate, 2007). The transport of marine sediments into the estuary occurs at the mouth of the estuary or inlet. Three processes enable the movement of sediments into the estuary namely: tidal inflow, barrier overwash, and wind action.

Tidal sediment transport is a result of both currents and wave action, and is most important in the mouth region (Perissinotto *et al*., 2010). During neap tides, the maximum water velocities within the estuary are low and involve little sediment transport. During spring tides, the opposite occurs and velocities and transport of sediments increase into the estuary (Whitfield and Bate, 2007). It is understood that greater amounts of sediment transport occurs during spring tides. This is because suspended sediment concentrations are higher resulting from strong currents which erode large amounts of sediments from the bed and maintain it in suspension (Abed, 2009). Therefore, given the lower velocities and tidal amplitudes at neap tides, deposition of sediments is more likely to occur, along with lowered suspended sediment concentrations (Abed, 2009). In some estuaries, a net upstream movement of sediments can occur over the neap to spring tide periods. If a long-term net input of marine sediments occurs, then a possible solution for re-establishment of equilibrium is if large river floods, on occasion, flush out this accumulated sediment (Whitfield and Bate, 2007).

As mentioned previously, temporarily open-closed estuaries consist of a feature known as a sand bar which extends partially across the mouth of the estuary. These sand bars or barriers constrict tidal exchange with the estuarine environment (Beck, 2005). However during storms or spring high tides, large waves transport sediment over the barrier and form washover fans that extend into the central basin. This process of marine sediment transport and deposition into the estuarine environment is known as barrier overwash (Whitfield and Bate, 2007).

Wind action or aeolian transport of sediments is another process that can inject marine sediments into the estuary (NOAA, 2005). This occurs when strong coastal winds pick up marine sands present along the coastal zone i.e. beaches, dunes etc. and deposition occurs within the estuary. This type of transport occurs in areas with high prevailing onshore winds which can carry sediment particles from the shoreline to the estuary with deposition occurring within the estuarine environment (Whitfield and Bate, 2007).

In addition to these methods of marine sediment transport into estuaries, are nearshore processes that are categorized as longshore (parallel to the coastline) and cross-shore (perpendicular to the coastline) sediment transport. Longshore transport or longshore drift is the transport or movement of sediment along the coastline (Abed, 2009). This movement is influenced by the surf zone currents created by waves and the predominant wave direction (Beck, 2005). Under these conditions, waves break at an angle to the shoreline and the sediment is moved along the beach in the surf zone (Abed, 2009). Along the South African coastline, longshore sediment transport is estimated at 400 000 – 1 200 000 m^3 per annum, whilst potentially this could be much higher due to wave energy (Whitfield and Bate, 2007). Sea storms which occur over two to three days can cause extreme cross-shore transport rates of sediments as high as 150 000 m^3 on a shoreline length of 500 m (Whitfield and Bate, 2007). Typically South African sea storms have durations of a few hours to a few days, so the amount of sediment transported into estuaries via these means can vary substantially (Whitfield and Bate, 2007).

3.4.4. Mouth sediment dynamics

In temporarily open-closed estuaries, the dynamics of the mouth play a vital role in sedimentation. The inlet opening is dependent on factors such as the size of the system and the tidal prism. Usually systems which are large in size and have high tidal prisms, create larger inlet openings (Beck, 2005). This is because greater tidal prisms will be accommodated in larger inlet channels and if this opening is too small, scouring would occur to increase the cross-sectional area of the inlet. Increased sedimentation in the estuary may cause the tidal prism to decrease (Whitfield and Bate, 2007). Reduced tidal currents would not be able to remove the accumulated sediment from the mouth area, and the inlet would decrease in size. Therefore increased sedimentation in estuaries with small tidal prisms may eventually cause mouth closure (Beck, 2005).

Whitfield and Bate (2007) have stated that mouth closure often occurs during sea storms. The entrainment of high sediment loads by turbulent storm wave action can occur and these loads can be transported into the estuary and mouth area and deposited in lower energy environments. Net-sediment accretion occurs when the deposition rate exceeds the erosion potential of tidal flow. If this situation continues for an extended period of time, allowing sufficient deposition volume, the mouth will close.

The closed mouth condition has implications for the estuary itself. When the mouth of a temporarily open-closed estuary closes, the exchange with the ocean ceases (apart from occasional overtopping events) (Defra, 2005). The water level within the estuary and subsequently the depth increases significantly from the open mouth state. During this time, changes to the physio-chemical environment occur (Perissinotto *et al*., 2010). Water velocities decrease which allow for the settling of fine particles on the estuarine bed. This accumulation can continue for a period of time until breaching occurs. Breaching of the sand bar can occur when the river flow is sufficient to exceed losses from the system due to seepage and evaporation. This allows for the water level to rise and lead to the breaching of the sand bar and the restoration of the connection to the sea. Following breaching, sudden changes in water levels can lead to the flushing of stored water from the system. Also significant scouring of sediment can accompany such events (Defra, 2005).

Estuaries along the eastern seaboard of South Africa are mainly temporarily open-closed systems. Given the strong wave energy and river dominated estuaries, the temporary closure of most of the systems is inevitable. The distribution of KwaZulu-Natal estuaries proposed by Cooper (2001), are grouped based on whether they are open more than 70% of the time or less than 30% of the time (mentioned in section 3.3). This distribution seems to indicate that some systems only open during episodic extreme events such as river floods, while others only close due to extreme events such as droughts or high waves associated with storms (Perissinotto *et al*., 2010). This could be the case along this particular coastline, given the historical periodic extreme events such as the floods of 1984 and 1987 which have resulted in the breaching of estuary mouths (Beck, 2005). Furthermore, the recent pressure on scarce water resources has generally reduced the amount of river flow into estuaries, thereby increasing the amount of time that temporarily open-closed estuaries are closed (Perissinotto *et al*., 2010).

3.5. Radiometric dating of sediments

Radiometric dating is used to date many materials, for example fossils, rocks or sediments. This is usually based on a comparison between the observed abundance of a naturally occurring radioactive isotope and its decay products, using known decay rates (Geyh and Schleicher, 1990). This method provides the absolute age of rocks and other geological features, including the age of the earth itself, as well as natural and man-made materials. Techniques include radiocarbon dating, potassium-argon dating and uranium-lead dating. Dating of sediments are useful in pollution studies as the concentrations of pollutants can be assessed over time in relation to the urban and industrial development of a region (Vaalgamaa and Korhola, 2004).

The basic process of radioactive decay needs to be known in order to understand the dating methods. Elements in the environment exist as different isotopes. A particular isotope of a specific element is called a nuclide, and some of these nuclides are inherently unstable (MacRae, 1998). This is due to the fact that at some point in time, an atom of such a nuclide will spontaneously transform into a different nuclide. This can occur through a number of processes including radioactive decay, spontaneous fission, and electron capture (Hamilton and Farquar, 1968).

With dating techniques, a parameter known as 'half-life' is given as the rate at which a collection of atoms of a radioactive nuclide decays exponentially (Vaalgamaa and Korhola, 2004). This is usually given in units as a number of years. In general, the half-life of a nuclide is solely dependent on its nuclear properties, and not affected by external factors such as temperature, pressure or the chemical environment (Vaalgamaa and Korhola, 2004). The decay product or 'daughter' nuclide is produced when one half-life has elapsed and one half of the atoms in question would have decayed, resulting in the 'daughter' nuclide. In most cases, the daughter nuclide itself is radioactive, resulting in a decay chain, eventually ending with the formation of a stable daughter nuclide. Each step in this chain is thus characterised by a distinct half-life (MacRae, 1998). Determination of the relative proportions of nuclides and daughter nuclides are used in quantifying the age of the material in question.

3.6. Heavy metals

Heavy metals are chemical elements which are naturally found in the earth's crust. They are termed heavy metals due to their atomic weight which is greater than a hundred and their

density which is higher than five (Lenntech, 2009). Over fifty elements are classified as heavy metals; seventeen of which are very toxic. Existing in water, sediment, plants, animals and humans, they are found in nearly all parts of the living and non-living environment (Delfosse *et al*., 2003). Trace metals are those metals that are naturally found in low concentrations in mass fractions of parts per million or less, in a specified source such as rocks, plants or sediments (Rybicka *et al*., 2005). These are levels which occur naturally and do not pose a threat to the environment (Cheung *et al*., 2003). Some examples of heavy metals are cadmium (Cd), mercury (Hg), beryllium (Be), lead (Pb), vanadium (V) and iron (Fe).

Heavy metals are metallic in nature, and they often exist in a positively-charged form and can bind onto negatively-charged organic molecules to form complexes (Petrucci *et al*., 1997). These complexes can form as chelates, where the metal is bound to an organic molecule at two or more points, which creates a stronger bond (Pickering, 1995). These complexes also have relatively low toxicity (Petrucci *et al*., 1997).

3.6.1. Sources of metals

Natural sources

Heavy or trace metals are found both naturally as well as injected into the environment from anthropogenic sources. Metals exist naturally within certain rocks present within the earth's crust (Rubin, 1974). Rising magma cools to form a wide variety of crystalline rocks (Delfosse *et al*., 2003). The metals originally distributed in trace amounts in magma or surrounding solid rocks become concentrated by circulating hot fluids and can be re-deposited, under favourable temperature and pressure conditions, to form rich mineral veins (Marshak, 2005).

Igneous and metamorphic rocks are the most important in terms of their metal content. Weathering of these rocks at the surface can introduce metals into the environment naturally (Delfosse *et al*., 2003).

Anthropogenic sources

The most common anthropogenic sources of heavy metals include industry, agriculture, mining, urban areas, households, atmospheric pollution and oil and chemical spills (Nadal *et al*., 2004). They can directly affect the quality of river water through harmful effluents that

are disposed into rivers, or indirectly through runoff transporting the metals in solution to the rivers and eventually estuaries (Assah and Abimbola, 2005).

Industrial activities are a major source of heavy metals (Chen *et al*., 2005). Petrochemical plants, steel and iron mills, paint production, smelting, sheet metal production, combustion emissions, and industrial sewage are just a few industrial activities that either use or produce metals (Nadal *et al*., 2004). The metal containing effluents of these activities which are passed into rivers can negatively affect the aquatic life in rivers and eventually estuaries (Fergusson, 1990). For example, with the machinery and equipment used in the production of sheet metal, fine dust particles of metals would be discarded in production and would then become part of the effluents through cleaning processes. Metals are mostly used in industry and would result in the highest levels of metals released from areas concentrated with high levels of industrial activity (Nadal *et al*., 2004).

Urban areas are also a major anthropogenic source of metals (Chen *et al*., 2005). Congested highways and high traffic areas provide supplies of lead from leaded petrol from cars and buses and other modes of transportation. Factories and industrial plants produce atmospheric pollution from different industrial activities, such as oil combustion which produces vanadium and nickel (Novotny, 1995). The tarred surfaces increase road runoff which carries different pollutants, including metals into storm water drains which eventually end up in rivers if not filtered (Pereira *et al*., 2007). Municipal and urban sewage from industrial activities also contain high amounts of metals (Chen *et al*., 2005).

3.6.2. Factors affecting sediment-metal concentrations

Sediments have a strong affinity for metals, and within the natural environment, sediments usually carry the bulk of metals through adsorption. Metals tend to adsorb onto sediment particles more so than water, and become temporarily trapped (Dube *et al*., 2001). Metals may be bound or adsorbed by particular natural substances, such as organic materials, which may increase or decrease their mobility. Desorption or dissolution of metals is the release of metals from its binding site. The binding capacity of the sediment particles to metals are dependent on a number of factors, such as grain size, organic matter content and cation exchange capacity (Bufflap and Allen. 1994).

Grain size

Metals are specifically attracted to fine grained sediment particles such as silts and clays, as they are negatively charged (Wang *et al*., 2000). Coarser grained sediments do not possess the charges and would inhibit the adsorption of metals onto their surface (Martin, 2004). Therefore finer grained sediments act as sinks to metals and keep them temporarily trapped, but they can still be potentially mobile. An environmental change, such as a flood, or changing physic-chemical properties may cause the release of the metals in the sediment (Sakai *et al*., 1986).

Estuaries are usually sinks for fine-grained sediments. The fine-grained sediments, as mentioned above, attract metals due to their negative charges, therefore the level of metal contamination within estuarine sediments are generally quite high (Abed, 2009). According to Sukdeo (2010), the greatest concentrations of metals occur within the first 10 cm of undisturbed sediments. Sources of pollution as well as the ability for an estuary to flush out and disperse pollutants, affects the distribution of these contaminants within the estuary and its sediments. Partially enclosed estuaries have a lower ability to flush out sediments than permanently open estuaries, and therefore are more susceptible to contamination by pollutants (Abed, 2009). However periodic flood events have the ability to flush out the estuarine sediments along with its pollutants (Dyer, 1986).

Organic matter

Organic matter is an important constituent of the sediment (Zhou and Wong, 2003). In estuarine systems, it is a key component of the biogeochemical cycles and provides substrate for the detritus-based food webs that characterise most estuaries (Goni *et al*., 2003). Estuaries receive inputs of organic matter from a variety of sources, including terrigenous materials exported from the land by the river and groundwater, marine materials which is carried in through tidal action, as well as autochthonous production of algae and intertidal vegetation. Mangrove environments also supply organic matter to the estuary from their decomposition of leaf litter and other plant material (Goni *et al*., 2003).

Like clay, organic particles are negatively charged and act as a giant composite anion, which adsorbs numerous cations such as metals (Hillel, 1980; Ashworth and Alloway, 2008). The positively charged metals are attracted to the negatively charged organic matter, and the mobility of the metals becomes impeded (Zhou and Wong, 2003).

Cation exchange capacity

The cation exchange capacity of sediments can also affect the mobility of metals within the sediment (Selim and Amacher, 2001). The cation exchange capacity of sediments is its ability to hold and exchange ions. Clays are effective ion exchangers. The large surface area of clays provides a good ion-exchanger capacity for metals (Wang *et al*., 2000). Increasing the ionic strength in the sediment generally decreases the sorption of cations such as metals, assuming that the surfaces are negatively charged. This increase will restrict the mobility of metals in the sediment and result in their subsequent trapping within the sediment (Fergusson, 1990). However, the cation exchange capacity depends not only on the clay content, but also on the clay type, i.e. on specific surface and charge density (Hillel, 1980).

3.6.3. Toxicity of metals

The dangerous characteristics of heavy metals include their ability to accumulate and magnify in organisms. Processes known as *bioaccumulation* and *biomagnification* are responsible for the accumulation of metals within an organism (Kar *et al*., 2008). *Bioaccumulation* refers to an increase in the concentration of an element in a biological organism over time, compared to the element's concentration in the environment. This process can occur through the intake of food and absorbed through the gut wall, or through absorption from the environment through the skin (Oliver, 1973).

Biomagnification occurs across the trophic levels (Fergusson, 1990). As the organism (prey) containing the accumulated metals is consumed, the predator will experience the negative impacts of the metals (He *et al*., 2010). This is because the metals consumed by the predator become a part of its body. Through cell and tissue repair, the metals become a part of the predator's tissues and organs etc., and depending on the amount consumed; the organism will experience the dangerous impacts of the metals within its body (Cheung *et al*., 2003). Thus the concentration of pollutants in the predator is a large multiple of that measured in the prey.

Metals are known to be naturally occurring in the environment, however an excess of metals due to anthropogenic activities can have severe effects on the environment and on the organisms present (Cheung *et al*., 2003). The severity of metals is only experienced when they exceed their natural limit in the environment. Metals are non-degradable elements, and persist in the environment and are transported through different mediums (Kramer and Allen,

1988). The sources of the elements studied and their related health problems resulting from their elevated concentrations are described below.

Aluminium (Al)

Aluminium is an abundant element present within the earth's crust. Anthropogenic releases of this element are in the form of air emissions, waste water effluents, and solid waste primarily associated with industrial processes, such as aluminium production. It can have toxic effects on the biotic communities in the environment when natural levels are exceeded (Delhaize and Ryan, 1995). It may accumulate in plants and cause health problems for animals that consume these plants. High aluminium concentrations do not only cause effects upon fish in water systems, but also upon birds and other animals that consume contaminated fish (DWAF, 1996). The health problems for birds include eggshell thinning and chicks with low birth-weights. Another negative effect of aluminium is its ionic reaction with phosphates, which reduces the phosphate availability to water dwelling organisms. Root damage to trees can also occur if high levels of aluminium are present in ground water (Delhaize and Ryan, 1995).

Arsenic (As)

Arsenic is a natural element that is present on earth in both an organic and inorganic form. The inorganic form is considered to be more toxic (Hardy *et al*., 2008). Living organisms, both on land and in water, react in a variety of ways to the toxicity of arsenic. The effects depend on the chemical form of the element, the nature of the surrounding environment and their own biological sensitivity (DWAF, 1996). Adverse effects include death, poor growth, and failure to reproduce. Species reduction can also occur in areas where arsenic contamination is high (Lenntech, 2009).

Calcium (Ca)

Calcium is essential for the life of plants and animals (Townsend, 1973). It is vital for growth in plants. In animals it is contained in the soft tissue and fluids within the tissue, as well as forms part of the structure of every animal's skeleton. Vertebrates' bones contain calcium in

the form of calcium fluoride, calcium carbonate and calcium phosphate. Calcium phosphide is a very toxic form and is harmful to aquatic organisms (Lenntech, 2009).

Cadmium (Cd)

Cadmium is a very lustrous, silver-white metal that is present in the earth's crust. It mostly occurs in the environment in combination with zinc (Lenntech, 2009). This element is found in manures and pesticides and therefore can enter the environment through the ground and surface runoff from farmlands. Through the weathering of rocks, cadmium is released into rivers and eventually estuaries. Industrial wastes are anthropogenic sources of cadmium (Lenntech, 2009). This metal strongly adsorbs onto organic matter in soils and acidic soils enhance the uptake of cadmium by plants (DWAF, 1996). Cadmium can accumulate in the bodies of animals which consume these plants and cause cadmium poisoning. In aquatic ecosystems, *bioaccumulation* of this metal can occur in mussels, oysters, shrimps, lobsters and fish. Despite this accumulation, organisms inhabiting saline environments are more resistant to cadmium poisoning than freshwater organisms (Lenntech, 2009).

Chromium (Cr)

The toxicity of this element is related to the specific forms of the metal. Chromium is a relatively scarce metal and has a variety of forms (DWAF, 1996). It is an essential metal for our bodies; however in other forms it can be quite toxic. Chromic acid is toxic to aquatic organisms and can be absorbed through the skin to cause liver and kidney damage (Lenntech, 2009). Fish are most resistant; however a temporarily reduced growth phase has been reported for young fish (Lenntech, 2009). Invertebrates and green algae are the most sensitive to chromium concentrations (Hardy *et al*., 2008).

Copper (Cu)

Copper is a natural trace element that is essential to life and is necessary for the well-being of all living organisms (Callow, 1994). It occurs in a variety of different forms and concentrations. It can be toxic at low concentrations and can also cause brain damage in mammals. The toxicity of Cu in aquatic organisms is related to the duration of exposure to the metal as well as the life stage of the organism (DWAF, 1996). The early life stages of an

organism are more sensitive to copper pollution than the adult stages. As the copper levels increase, changes are exhibited in the species richness and composition of invertebrate communities (DWAF, 1996).

Iron (Fe)

Iron is another abundant element on earth, making up 5.63% of the earth's crustal mass (Lenntech, 2009). Iron is essential to almost all living things, from micro-organisms to humans. The toxicity of iron varies with its different forms. Iron arsenitepentahydrate may be hazardous to the environment, where special attention should be given to plants, where growth is affected (DWAF, 1996). Iron does accumulate in aquatic organisms and high levels have shown to affect the development, physiology and histology of the organisms (Bryan, 1971).

Lead (Pb)

Lead occurs naturally in the earth's crust usually as lead sulphide. Increases of lead in the environment due to anthropogenic activities, have negatively affected aquatic organisms (Agius, 2006). Accumulation of Pb often occurs in organisms, and affects haemoglobin synthesis as it interacts with iron metabolically. It also affects membrane permeability and the inhibition of enzyme activity in energy metabolism. Low concentrations of lead affect fish by causing the formation of a film of coagulated mucous over the gills and subsequently over the entire body (DWAF, 1996). This has been attributed to a reaction between lead and an organic constituent of the mucous. Due to the suffocation brought about by the mucous layer, fish mortality increases. Lead also bioaccumulates in benthic bacteria, freshwater plants, invertebrates and fish (Hardy *et al*., 2008).

Magnesium (Mg)

Magnesium is another abundant element in the earth's crust. It is a dietary mineral for all organisms with the exception of insects. It is a central atom of the chlorophyll molecule, and is therefore a requirement for plant photosynthesis (Lenntech, 2009). Magnesium sulphide is very toxic to aquatic organisms, and includes changes in behaviour, an increase in mortality, and causes intoxication for annelids (Kegley *et al*., 2010).

Manganese (Mn)

Manganese is found naturally in most ores. Soils, metamorphic and sedimentary rocks are also significant sources of manganese (DWAF, 1996). Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leaves and brown spots on leaves. For animals, manganese is an essential component of over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism. Some manganese substances can cause lung, liver and vascular disturbances, declines in blood pressure, failure in development of animal foetuses and brain damage (Lenntech, 2009).

Nickel (Ni)

This element is mostly present in the earth's iron-nickel molten core, where it constitutes 10% of nickel (Lenntech, 2009). It is a compound that occurs in the environment at very low levels, but humans do use nickel for many applications. At high levels the toxicity of this metal can have adverse effects on organisms. In sandy soils, woody plants are inhibited due to high levels of nickel. It can also diminish the growth rates of algae in surface waters (Hardy *et al*., 2008). Micro-organisms can also suffer from a growth decline due to the presence of this element, however with time they do develop a resistance towards it. For animals, it is an essential element in small amounts. When this metal exceeds normal amounts, it can cause various kinds of cancer on different sites within the bodies of animals (Lenntech, 2009).

Phosphorus (P)

Phosphorus is a multivalent non-metal of the nitrogen group (Lenntech, 2009). In the environment, phosphorus is present as organic and inorganic forms of phosphate. Naturally, phosphorus is derived from the weathering of phosphorus-bearing rocks and decomposition of organic matter (Sukdeo, 2010). Phosphorus can also enter the environment via industrial, domestic and agricultural inputs. In soil, phosphorus can persist for many years, and in deep sediments of river and lakes, it can remain for even a thousand years. It is also a macronutrient which is needed for plant growth in aquatic systems. However, excessive inputs of phosphorus can lead to large amounts of algal growth, eventually leading to eutrophication (DWAF, 1996).

Sulphur (S)

Sulphur is a non-metal which occurs in nature as a pure element, sulphide or sulphate materials (Lenntech, 2009). Some sulphide minerals are known such as pyrite, marcaiste and iron sulphide. Sulphur is used in the manufacturing of many products such as detergents, fertilisers, gun powder, matches etc. Many industries emit sulphur to the air, as well as dispose of forms of sulphur in wastewaters which enter the natural environment through rivers (DWAF, 1996). When present in the air, sulphur can cause irritation to the eyes and throats of animals when inhaled. Furthermore, sulphur can cause brain damage and nervous system damage to organisms (Lenntech, 2009).

Vanadium (V)

Vanadium is a metal that is never found unbound in nature. Vanadium occurs in about 65 different minerals (Lenntech, 2009). Streams and rivers distribute vanadium in the environment as their forms are generally very soluble. Vanadium is an essential component of some enzymes. It is abundant in most soils in variable amounts, which can be taken up by plants (Hardy *et al*., 2008). It can also be found in algae, invertebrates, fishes and many other species. The toxicity of this element is exhibited in high amounts and can cause the inhibition of certain enzymes in animals, which leads to several neurological effects (Lenntech, 2009). It can also cause breathing disorders, paralysis and negative effects on the liver and kidneys and can cause harm to the reproductive system of male animals, and accumulates in the female placenta (ATSDR, 1995).

Zinc (Zn)

Zinc is a very common element that occurs naturally on earth. Zinc occurs naturally in air, water and soil (Hardy *et al*., 2008). It is a trace element that is essential to human health; however it does have toxic effects at high concentrations. This element can accumulate in bodies of fish, and can biomagnify up the food chain. It produces lethal effects in fish from the formation of insoluble compounds in the mucus covering the gills (DWAF, 1996). Sub-lethal concentrations at which toxic effects are evident include symptoms like depressed white blood cell-thrombocyte counts. Although invertebrate responses to zinc toxicity vary, it was found that molluscs are generally more resilient than other organisms. Sub-lethal effects

include reduced rates of shell growth, oxygen uptake and larval development. Algal photosynthesis can be inhibited by zinc as well (DWAF, 1996).

3.7. Background values

Background values or natural values of sediments are the values that are present naturally in the sediment before any anthropogenic input. For a specific region of geology type, background values may differ (Woitke *et al*., 2003). Background values are mainly used to determine whether the presence of a certain element, and its corresponding concentration, is due to natural or anthropogenic sources. This will provide a measure of the level of pollution within that area in terms of metal concentrations in the absence of sediment quality guidelines (Martinez *et al*., 2007).

South Africa has not devised its own set of sediment quality guidelines as yet, therefore in this study, Clarke values were used instead. Clarke values can serve as background values for the earth's crust (Olivares- Rieumont *et al*., 2005). Clarke values were calculated based on geochemical backgrounds, which refers to the typical abundance of the element in a specific rock or geology type or for a particular region (Sukdeo, 2010). The term 'Clarke values' was advocated by A.E. Fersman in 1923 who introduced it in honour of the one of the founders of geochemistry, F.W. Clarke (Woitke *et al*., 2003). Reliable Clarke values are needed for determining whether the concentration of elements present within the sediment are normal or deviate from the typical geological pattern. The values are also very useful in determining the pollution levels within sediments (Sukdeo, 2010). Clarke values for sedimentary rocks were used in this study, as the geology for all the estuaries within the study area are predominantly sedimentary.

Enrichment factor is an index which uses background values in determining the status of metal enrichment within the sediment. The term 'enrichment' implies that the natural levels of metals in the soil are exceeded. The enrichment of sediments can occur from natural or anthropogenic sources but is generally attributed to anthropogenic inputs (Olivares-Rieumont *et al*., 2005). When metals are lacking in sediment, it is known as depleted. Depletion can occur from the weathering and erosion of the sediment that can become entrained and carried by streams and rivers (Manjunatha *et al*., 1996). In this study, the contamination factor, geo-accumulation index and pollution load index were also used to

determine the pollution status of the sediments, all of which also required the use of background values.

3.8. Conclusion

Relevant theories pertaining to this study were discussed in this chapter. Estuaries are present along every coastline around the world, however based on specific regional characteristics; each estuary is placed into its respective classification. Sediments play an important role in this classification, as well as the general functioning of the estuary. The transport and deposition of sediments within an estuary allows for the development of sedimentary facies and features. Sediment dynamics at the mouth controls the sediment environment within an estuary, and this is dominant along the KwaZulu-Natal coastline, where estuaries open and close temporarily. Major constituents of estuarine sediments are metals, received from both natural and anthropogenic inputs. Their presence within sediments is controlled by chemical interactions as well as factors such as grain size and organic matter content. However elevated concentrations within the sediments can have adverse effects on the flora and fauna within the estuary, so regular monitoring of these levels are important. Following this chapter is a detailed account of the methods used in this study pertaining to the data collection and data analysis.

Chapter 4

METHODS

4.1. Introduction

This chapter presents a description of the general methods conducted in this study. The reasons for sample site selection are explained as well as the sampling methods used in the field for the collection of sediment samples. Thereafter, sample preparation is discussed, which comprises of methods used for sample determination within each core. The laboratory analysis of the variables including texture of sediment, organic matter, elemental analysis and carbon dating of sediment are described. Following this, the methods used for data analysis are discussed, which includes the statistical techniques and the geochemical indices used to facilitate pollution assessment of the sediment.

4.2. Site selection

The eThekwini Municipality is regarded as one of the highly developed regions in the country. River catchments within this region were selected for study based on the level of development within each. Therefore the anthropogenic developmental impacts on the estuarine systems could be assessed. Accordingly six river catchments, uTongati, uMdloti, uMgeni, Durban Harbour, Isipingo and uMbokodweni, which comprise of 71% of the total land area of the eThekwini Municipality, were selected. Sediment samples were taken at the estuaries of each of these river systems.

In each estuary, a site was selected near the mouth, in the approximate middle reaches, and towards the upper reaches of the estuary. This sampling strategy was used to ensure that the marine, estuarine, and riverine influences were taken into account, as well as the variations in geomorphology. Only one site was selected for the Durban Harbour, near the Bayhead Canal as all other areas are restricted; and an extra Mangroves site was selected for the uMgeni estuary. Table 4 below indicates the site names for each of the estuaries, and Figures 24-29 below illustrate the sample sites per estuary.

Table 4: Site names for each estuary.

Estuary	Site names			
uTongati	T1	T2	T3	-
uMdloti	D1	D2	D3	-
uMgeni	G1	G2	G3	G4 (Mangroves)
Durban Harbour	H	-	-	-
Isipingo	S1	S2	S3	-
uMbokodweni	B1	B2	B3	-

Note: Site names are divided into two units: letters that represent the estuary i.e. T, D, G, H, S and B which are uTongati, uMdloti, uMgeni, Durban Harbour, Isipingo and uMbokodweni estuaries respectively; and numbers which represent the location of the site within the estuary i.e. 1 - near the mouth, 2 - approximate middle reaches, and 3 - approximate upper reaches of the estuary.

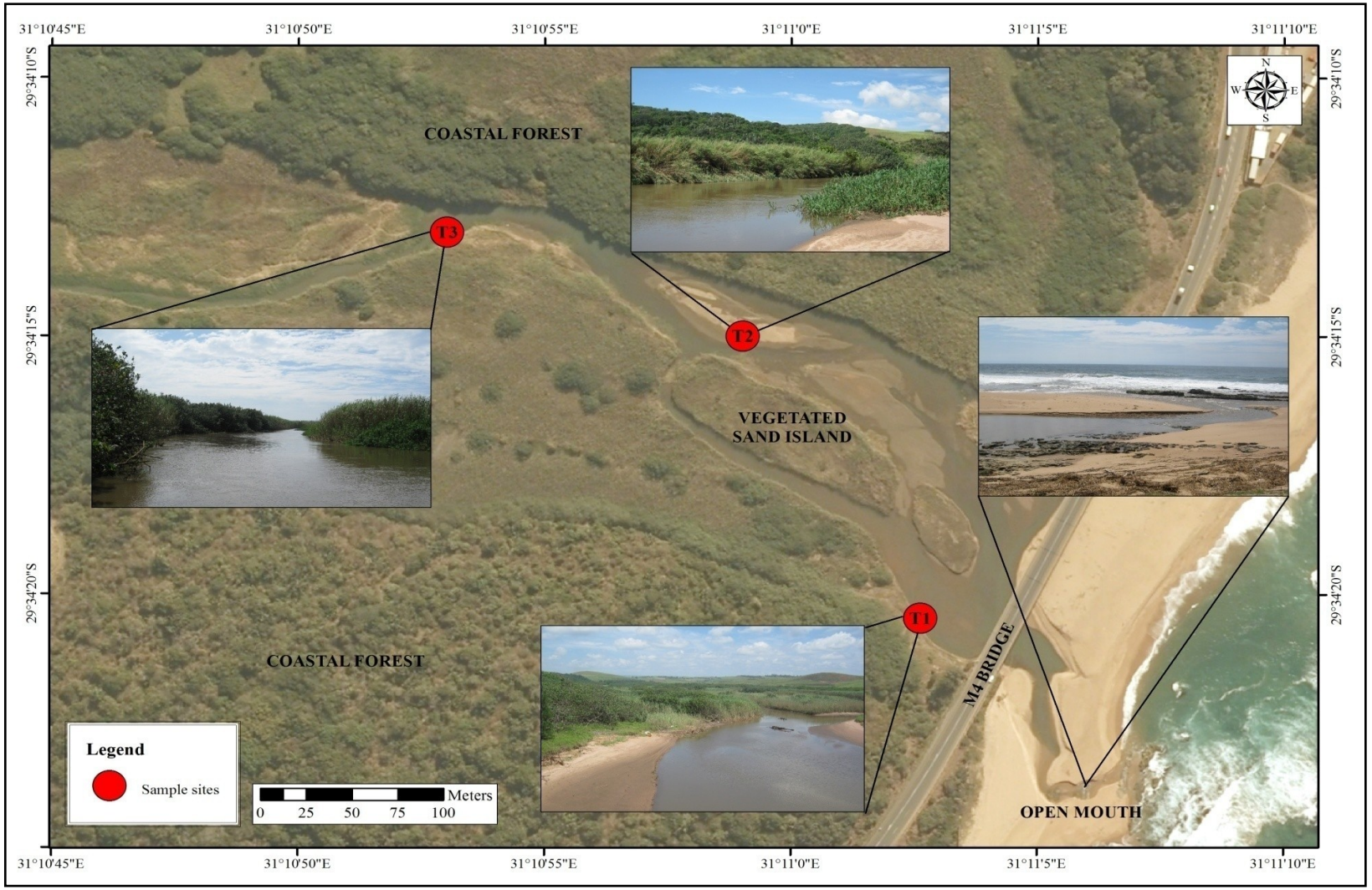

Figure 24: Sample sites in the uTongati estuary.

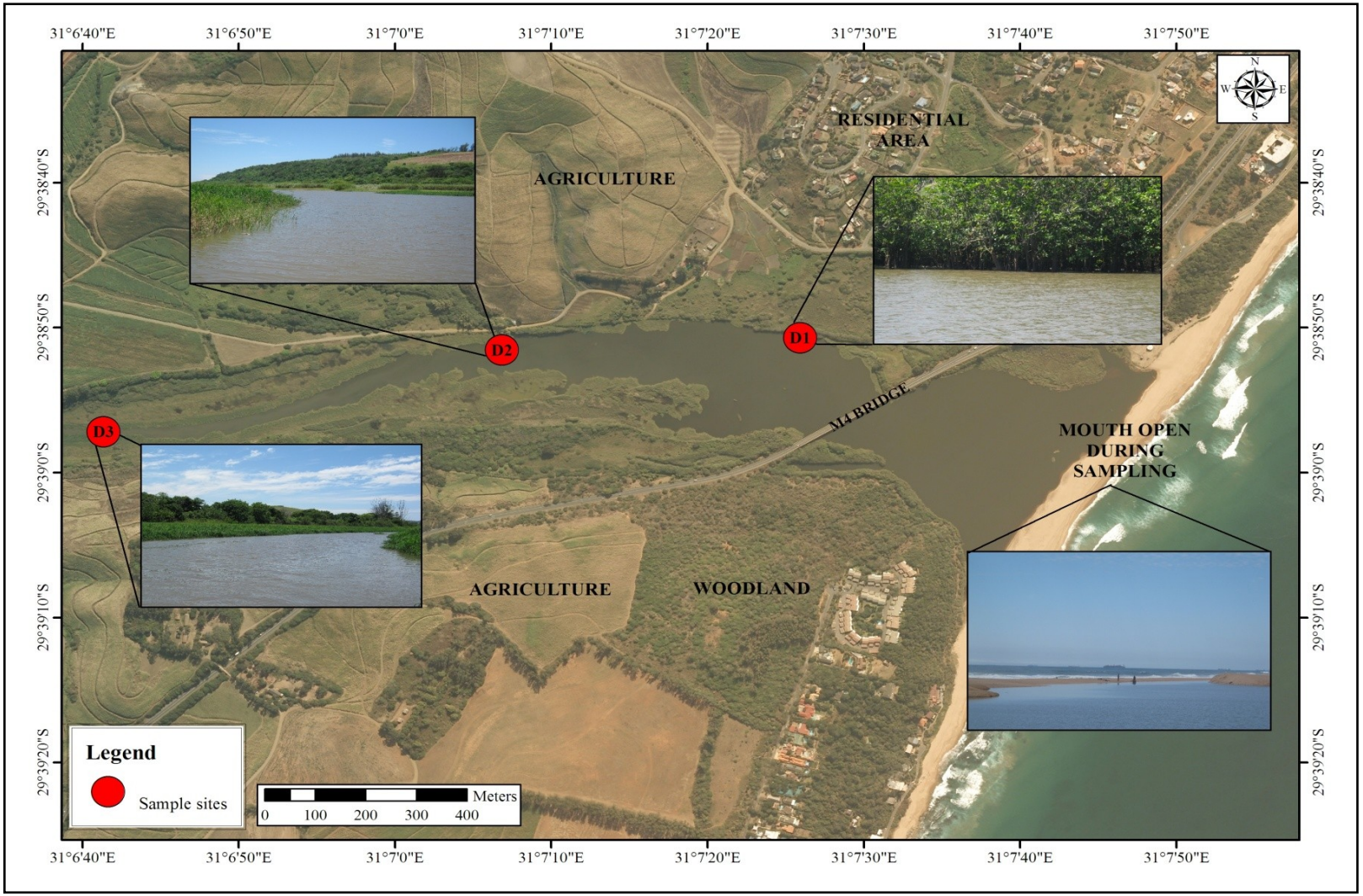

Figure 25: Sample sites in the uMdloti estuary.

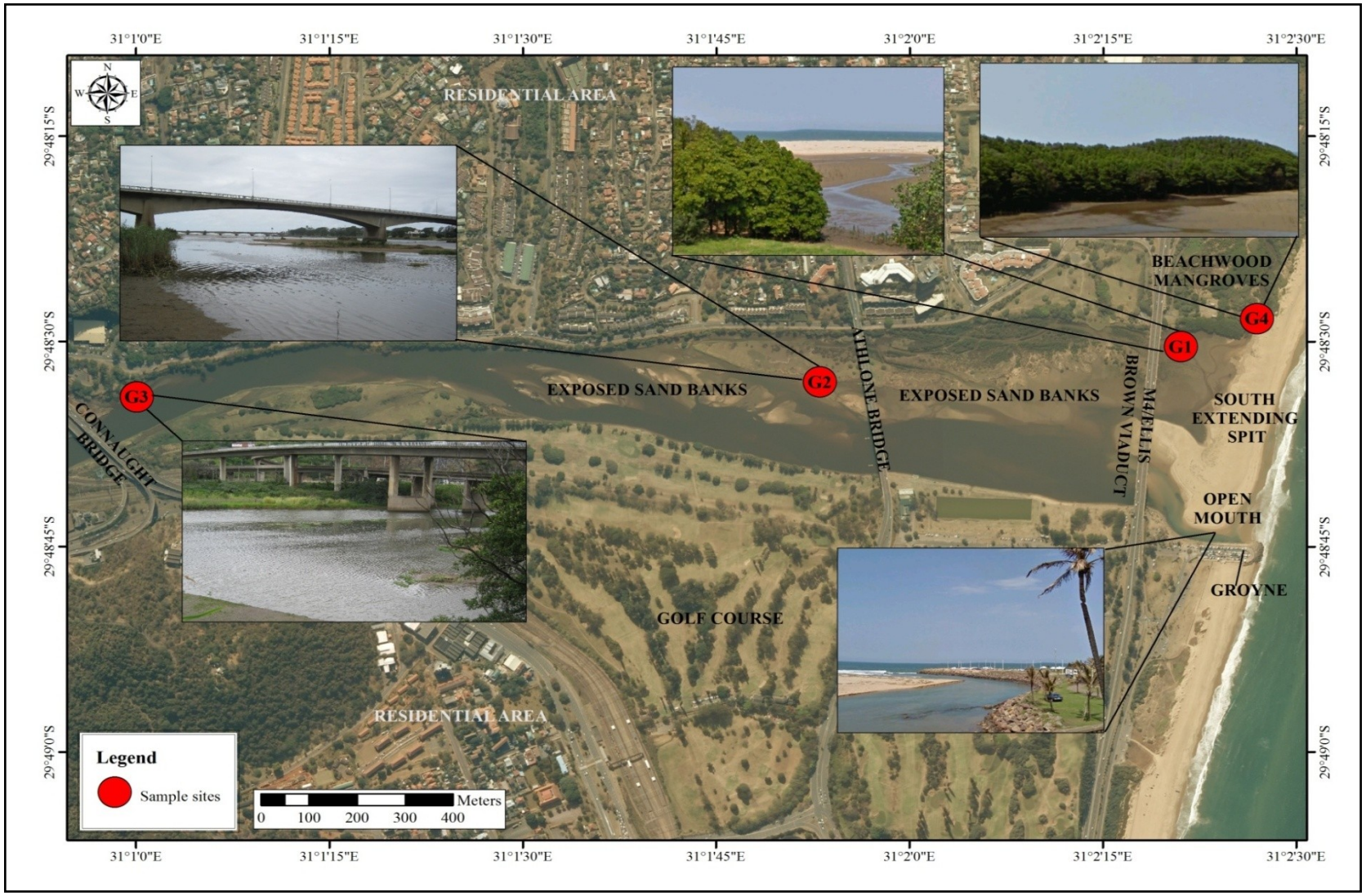

Figure 26: Sample sites in the uMgeni estuary.

Figure 27: Sample site in the Durban Harbour.

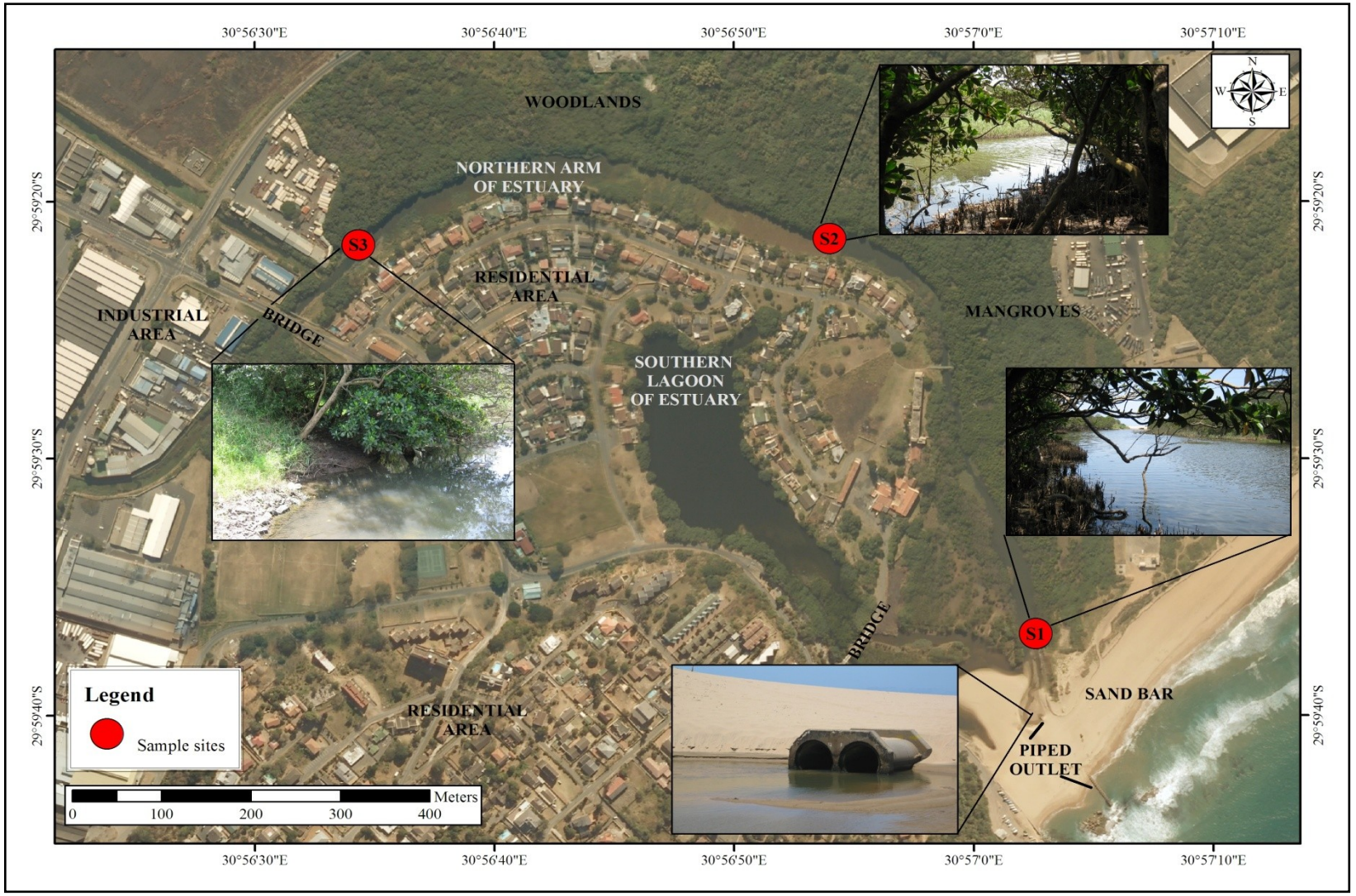

Figure 28: Sample sites in the Isipingo estuary.

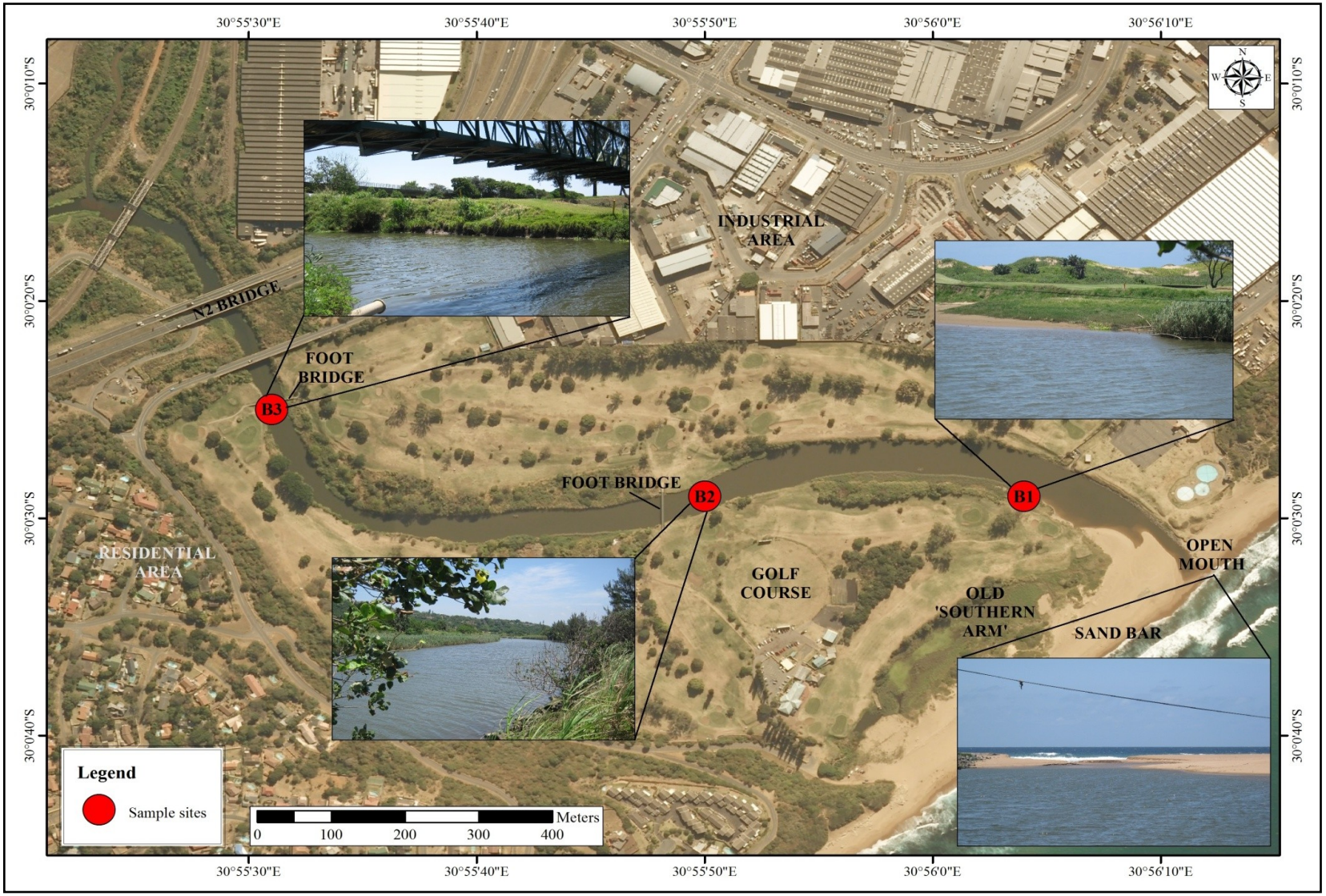

Figure 29: Sample sites in the uMbokodweni estuary.

4.3. Field sampling

Figure 30: The placement of the 2 m PVC pipe into the estuarine sediments with the custom made cap sealed at the top to create suction within the pipe.

Field work for this study was carried out between September and December 2011. In each estuary, one sediment core sample was taken at each site. Sediment samples were collected using a 2 m polyvinylchloride (PVC) pipe with a 5 cm diameter. These samples were collected once per site. Sediment cores of up to 1.8 m were extracted after inserting the PVC pipes into the soft estuarine sediments. Where more resistant sediments were encountered a 10 kg weight was used as a ram to force the pipe into the sediment to the required depth. The open end of the pipe was then covered with a custom made cap and sealed with duct tape to prevent the entry of air, thus creating the necessary suction required within the pipe to keep the sediment core in place as the pipe was carefully pulled out of the ground (Figure 30). Sediment samples were collected as core samples to determine the age of the sediment and the temporal metal concentration in the estuary.

4.4. Sample preparation

Figure 31: Careful splitting of the sediment core using an electric saw in the mechanical engineering workshop.

Following collection of the sediment core samples, the pipes were kept on ice during transportation to the mechanical engineering workshop at the University of KwaZulu-Natal (Westville campus). Here the pipes were carefully sliced longitudinally using an electric saw (Figure 31). Once sliced, the split cores were transferred to the soils laboratory for further analysis.

Figure 32: Green strips to mark the sediment layers/units of the core sample, based on texture and colour.

Further analysis of the cores included logging the core samples. This process was based on physical properties of sediment colour, composition and texture which were aspects used to divide each sediment layer/unit within the core. Notes on mottling and presence of plant material, roots and shells within each unit were also recorded. Each core was photographed in its original state to allow for visual representation of the sediment units. Figure 32 represents an example of a logged core based on the variations of colour and texture. Green strips marked with depth indicate the boundaries between each sediment unit. In each core, three or four samples were taken from grouped sediment units. These grouped units were based on the similarity of texture and colour with depth, and were used as representative samples per core.

The samples were oven-dried at 100 ºC overnight or until completely dried. Once fully dried, the samples were disaggregated with a pestle and mortar, and split into three labelled polyethylene zip-lock bags for analysis. A sub-sample was used for chemical analysis at the analytical chemistry laboratory at the University of KwaZulu-Natal (Westville campus) of elements namely Aluminium (Al), Arsenic (As), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Nickel (Ni), Phosphorus (P), Sulphur (S), Vanadium (V) and Zinc (Zn). A second sub-sample was utilized for analysis of organic matter and texture of the sediment at the South African Sugarcane Research Institute soil laboratory. The third sub-sample was dispatched to BETA Analytic Inc. in the United States of America for carbon dating. Only 10 samples were chosen for carbon dating due to budget constraints.

4.5. Laboratory analysis of variables

4.5.1. Sediment textural analysis

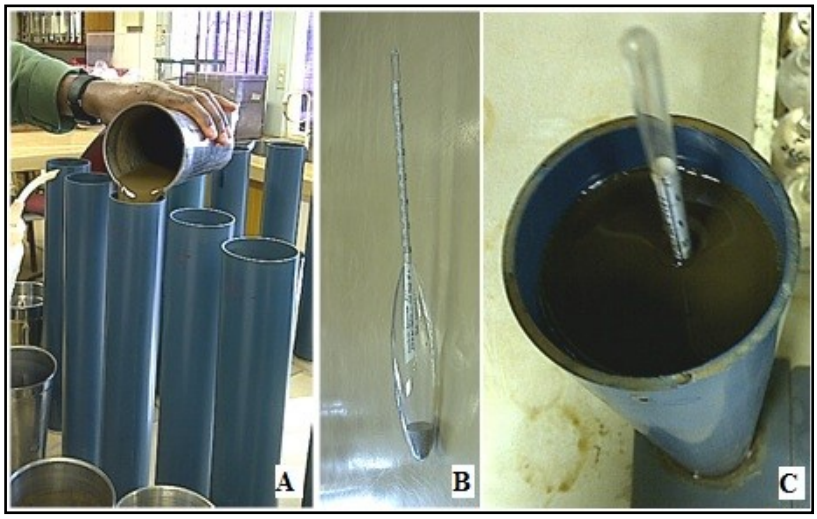

Figure 33: The Bouyoucos hydrometer method used for determining sediment texture.

The Bouyoucos hydrometer method was used to determine the sand, silt and clay percentages (texture) in the sediment samples. This method is considered most accurate as it allows for non-destructive sampling of suspensions undergoing settling (Loveland and Whalley, 2001). It also provides detailed particle size distributions obtained from minimal effort (Gee and Bauder, 1986; Loveland and Whalley, 2001).

A weighed soil sample of 48 g was used in this method to determine the different percentages of sand, silt and clay. The sample was first pre-treated using a dispersing agent of sodium hexametaphosphate which created a sediment solution. The solution was shaken using an electric mixer for 50 minutes. Thereafter the solution was transferred to a 1 litre clay cylinder and brought to the mark with distilled water (Figure 33A). The top of the cylinder was then sealed using a stopper and the solution was shaken for another 30 seconds by hand. Following this, the hydrometer (Figure 33B) was placed into the cylinder (Figure 33C) and readings were taken for silt after 4 minutes and for clay after 2 hours. The percentage of clay was determined after the 2 hour reading. The silt percentage was determined by the difference between the 4 minute and 2 hour reading. Finally, the sand percentage was calculated by a subtraction of the total clay and silt percentages from a hundred percent (SASRI, 2012).

4.5.2. Organic matter determination

Organic matter content was determined using the 'colorimetric determination of soil organic matter' which is a method that determines the total amount of carbon and organic matter content in the sediment (Sims and Haby, 1970).

This method required a measured sediment sample of 0.5 g which was mixed with 10 ml of potassium dichromate and 20 ml of sulphuric acid and was left to stand for 30 minutes. 200 ml of water, 10 ml of phosphoric acid and 0.2 g of sodium fluoride were then added to the solution. A diphenylamine indicator was added to produce a reactive colour during titration. A solution of iron sulphate was then titrated into the solution until a green endpoint colour was reached. Once the endpoint was reached, the difference between the total volume and titrant volume, multiplied by the constant 0.60 determined the carbon percentage. The organic matter percentage was then calculated by multiplying the carbon percentage by the constant 1.72 (SASRI, 2012).

4.5.3. Element analysis

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the element concentrations present within the sediment samples. This included Aluminium (Al), Arsenic (As), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Nickel (Ni), Phosphorus (P), Sulphur (S), Vanadium (V) and Zinc (Zn).

ICP-OES is very useful as it allows the simultaneous determination of several different element concentrations. Its advantages include low detection limits and a large analytical range (Sukdeo, 2010). Standard solutions per element were determined prior to the sample solutions being analysed. This also involved the production of calibration graphs (each graph represents a single metal) from measured intensity readings of standard metal concentrations from ICP-OES analysis.

For the analysis of sediments, 0.5 g of each dried sediment sample was added to 15 ml of *aqua regia* (which consists of one part nitric acid and three parts hydrochloric acid). This mixture was then boiled for thirty minutes, allowed to cool, and filtered under gravity into a 100 ml volumetric flask and made to the mark using de-ionised water. This solution was then injected into the Optical Emission Spectrometer which produced intensity readings in the form of electromagnetic radiation, at wavelengths characteristic to each element. These

readings were then used to calculate the actual concentration of each metal by using its representative calibration graph i.e. by substituting the metal intensity reading into its graph equation, the actual concentration of each metal could be determined (pers.comm., Chetty, 2010).

4.5.4. Carbon dating methods used by BETA Analytic Inc. (to date sediment cores of study)

Accelerator Mass Spectrometry (AMS) was used to determine the amount of carbon isotopes present in the sediment samples. This enables the calculation of an approximate age of the sample. There are three principal isotopes of carbon that naturally occur namely ^{12}C, ^{13}C (both stable) and ^{14}C (unstable or radioactive). This method is based on the rate of decay of the radioactive or unstable carbon isotope (^{14}C), which is formed in the upper atmosphere (BETA Analytic, 2012).

Carbon was first isolated by pre-treating the sediment sample. The carbon was then chemically separated from the original sample and converted to graphite. Thereafter, the carbon was used in an accelerator to determine the ^{14}C ions through AMS counting. Within the accelerator, the atoms present within the sample were converted into a beam of rapidly moving ions (BETA Analytic, 2012). Magnetic and electric fields separated the ions based on their mass, and were measured by nuclear particle detection techniques. The ^{12}C, ^{13}C and ^{14}C ions were measured and counted. A ratio of $^{14}C/^{13}C$ was calculated and compared to measurements conducted on standard samples with known ratios. The age of the sample was calculated through the measurement of the residual activity (per gram carbon) remaining in the sample and the activity present in the background samples (BETA Analytic, 2012).

4.6. Data Analysis

The data from this study was analysed in a number of ways. To gain more insight into the data, three statistical techniques were employed to interpret the relationships and variances within the data sets. To assess the pollution status of the estuaries, four pollution indices were used, and a comparison of the metal concentrations to sediment guidelines were utilized. The display of data was presented using various tables and graphs, inclusive of diagrams pertaining to the estuarine sedimentology. The diagrams, namely core profiles and estuarine stratigraphic cross-sections, were created using CorelDraw12®.

4.6.1. Statistical analysis

Statistics is a tool that allows the researcher to organise, interpret and display data in a scientific manner. Descriptive and inferential statistics and, exploratory data analysis were used in this study. Inferential statistics use patterns in the data to draw inferences about the sample represented, accounting for randomness (Van Elst, 2012). Pearson correlation was used in this study to find associations within the data. Cluster analysis (CA) and Principal Component Analysis (PCA) are exploratory data analysis techniques (Mertler and Vannatta, 2002). The former was used to determine similarities between groups of variables within each estuary; and the latter to determine the variables within the data which accounted for the greatest variance across all estuaries. GenStat 14th edition was the statistical software package used to analyze the data.

4.6.2. Pollution assessment indices

Various environmental indices are used to determine the pollution, contamination or ecological risk of sediments. They are powerful tools for processing, analyzing and conveying raw environmental information in a useful way (Caeiro *et al*., 2005). Contamination factor (CF), Enrichment Factor (EF), Pollution load index (PLI) and Geo-accumulation Index (I_{geo}) are all examples of environmental indices that give an indication of the level of pollution in a system (Praveena *et al*., 2007), and were used in this study.

Contamination factor (CF)

The contamination factor is used to determine the contamination of the sediment by a specific element, using the concentration of the element with background values for that particular element (Saha and Hossain, 2011). This index is calculated using the following equation:

$$\boldsymbol{CF = \frac{[Concentration\ of\ element]}{[Background\ value\ of\ element]}}$$

Where CF < 1 refers to low contamination, 1 ≥ CF ≥ 3 indicates moderate contamination, 3 ≥ CF ≥ 6 indicated considerable contamination, and CF > 6 indicates very high contamination (Harikumar and Jisha, 2010).

Enrichment factor (EF)

The enrichment factor is an index used to evaluate the relative abundance of an element in the sediment compared to the background values of the bedrock (Praveena et al., 2007). It uses the value of a reference element and the background value of that same element in the earth's crust. This is a useful index as it provides the magnitude of contamination in the environment (Harikumar and Jisha, 2010), as well as allowing for differentiation between natural and anthropogenic sources of the elements (Praveena *et al*., 2007). Iron was used as the reference element as it is a naturally abundant element in the earth's crust (Harikumar and Jisha, 2010). This index is calculated using the following equation:

$$\boldsymbol{EF} = \frac{[\boldsymbol{Concentration\ of\ element}]/[\boldsymbol{Concentration\ of\ reference\ element}]}{[\boldsymbol{Background\ of\ element}]/[\boldsymbol{Background\ of\ reference\ element}]}$$

Where < 2 suggests deficiency to minimal enrichment, 2-5 represents moderate enrichment, 5-20 indicates significant enrichment, 20-40 suggests very high enrichment, and > 40 indicates extremely high enrichment, most likely from anthropogenic sources (Kumar and Edward, 2009).

Pollution load index (PLI)

The pollution load index provides a comparative means of assessing the pollution for a particular site or estuarine quality (Praveena *et al*., 2007). It uses the contamination factor calculated for each element per site with the number of elements found at that site. This index is calculated using the following equation:

$$\boldsymbol{PLI} = \boldsymbol{n}\sqrt{(\boldsymbol{CF1\ x\ CF2\ x\ CF3\ x} \ldots\ldots\ldots \boldsymbol{x\ CFn})}$$

Where CF is the contamination factor for each site and n refers to the number of elements (Harikumar and Jisha, 2010). The scale of pollution varies from PLI = 0 which indicates unpolluted to PLI = 10 which indicates highly polluted.

Geo-accumulation index (I_{geo})

The Geo-accumulation index is used to assess the metal pollution in the sediments. It is similar to enrichment factor; however this index includes various degrees of enrichment above the background value ranging from unpolluted to very highly polluted sediment quality (Praveena *et al*., 2007). This index is calculated using the following equation:

$$I_{geo} = log_2 \frac{C_n}{1.5\ x\ B_n}$$

Where C_n is the measured concentration of the element, B_n is the background value of the element, and 1.5 is the factor used because of possible variations of the background data to lithogenic effects (Ruiz, 2001). The pollution intensities for the various degrees of pollution are as follows: $I_{geo} < 1$ is unpolluted, $1 < I_{geo} < 2$ is very low polluted, $2 < I_{geo} < 3$ is low polluted, $3 < I_{geo} < 4$ is moderately polluted, $4 < I_{geo} < 5$ is highly polluted, and $I_{geo} > 5$ is very highly polluted (Ruiz, 2001).

4.7. Conclusion

The methods described in this chapter have included a variety of techniques. The selection of sites was based on the development that occurred within the selected river catchments. Sampling within the estuary included the collection of 2 m sediment cores at three sites. The preparation of these samples involved the detailed logging of the cores based on sediment composition, colour and texture. The variables analysed included sediment texture, organic matter content, element concentrations and dating of the sediment. Statistical interpretations of the data acquired included the methods of Pearson correlation, Cluster Analysis and Principal Component analysis. Pollution indices were also adopted to estimate the level of pollution within each estuary. Following this chapter are the results of the study, which consists of tables, graphs and diagrams of the data.

Chapter 5

RESULTS

5.1. Introduction

The results of this study are described in this chapter. The results are presented in an array of forms: tables, graphs, drawings, cross-sections and figures with the intention of conveying information in the most representative way and to enable the extrapolation and interpretation of results as incisively as possible. The results are grouped and described per estuary according to sedimentology, geochemistry, statistical analyses and pollution indices. The structure of this chapter consists of eight main sections. The first six sections contain results per estuary, namely uTongati, uMdloti, uMgeni, Durban Harbour, Isipingo and uMbokodweni estuaries, which contain different sub-sections of results. Following this are sediment quality guidelines, and finally a comparison of all estuaries studied.

5.2. uTongati estuary

Estuary: uTongati
Site: T1

Recovered core length: 123cm
Date sampled: 11/12/2011

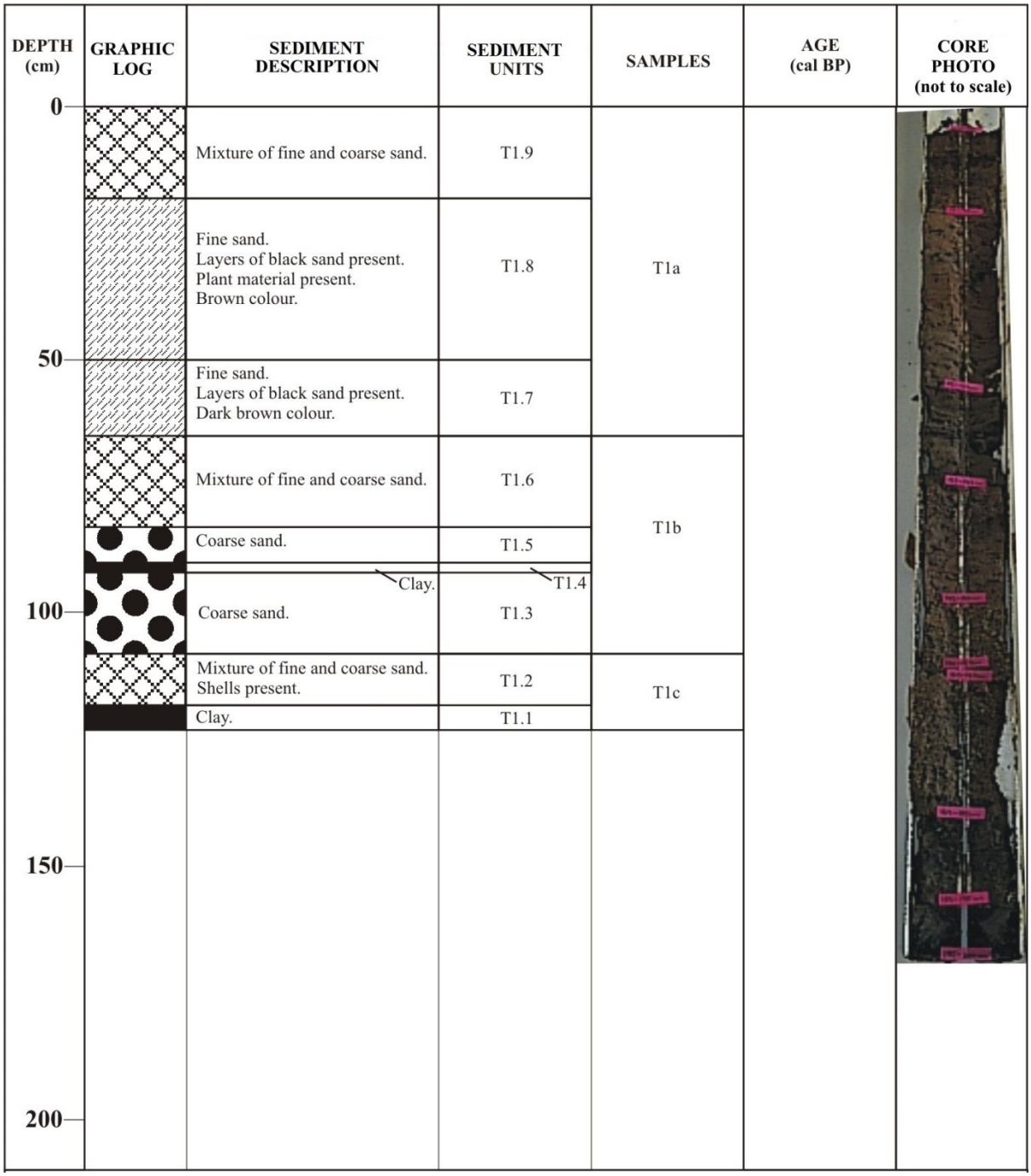

Figure 34: A graphic profile of the core retrieved at site T1 in the uTongati estuary.

Estuary: uTongati
Site: T2

Recovered core length: 146cm
Date sampled: 11/12/2011

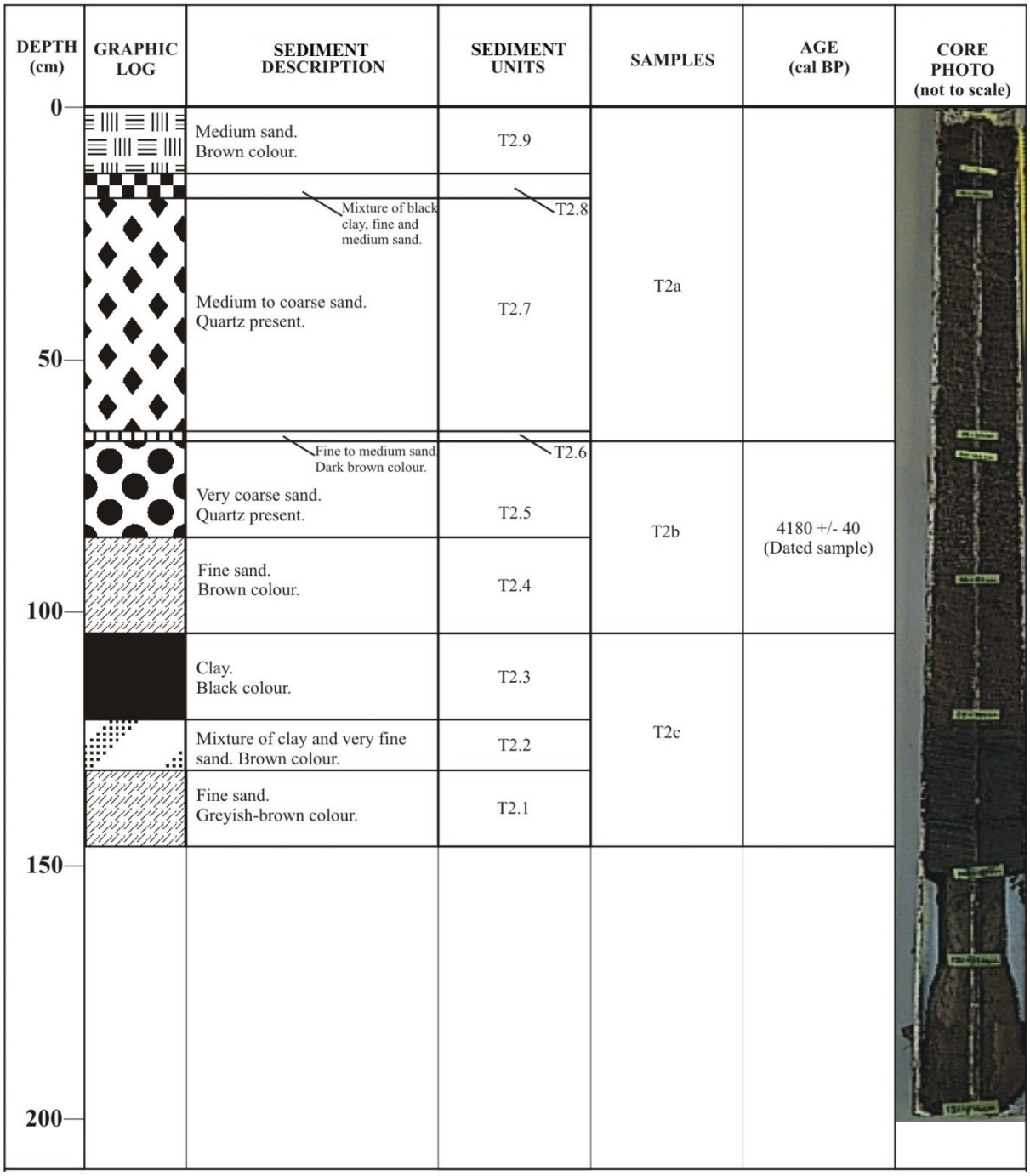

Figure 35: A graphic profile of the core retrieved at site T2 in the uTongati estuary.

Estuary: uTongati
Site: T3

Recovered core length: 95cm
Date sampled: 11/12/2011

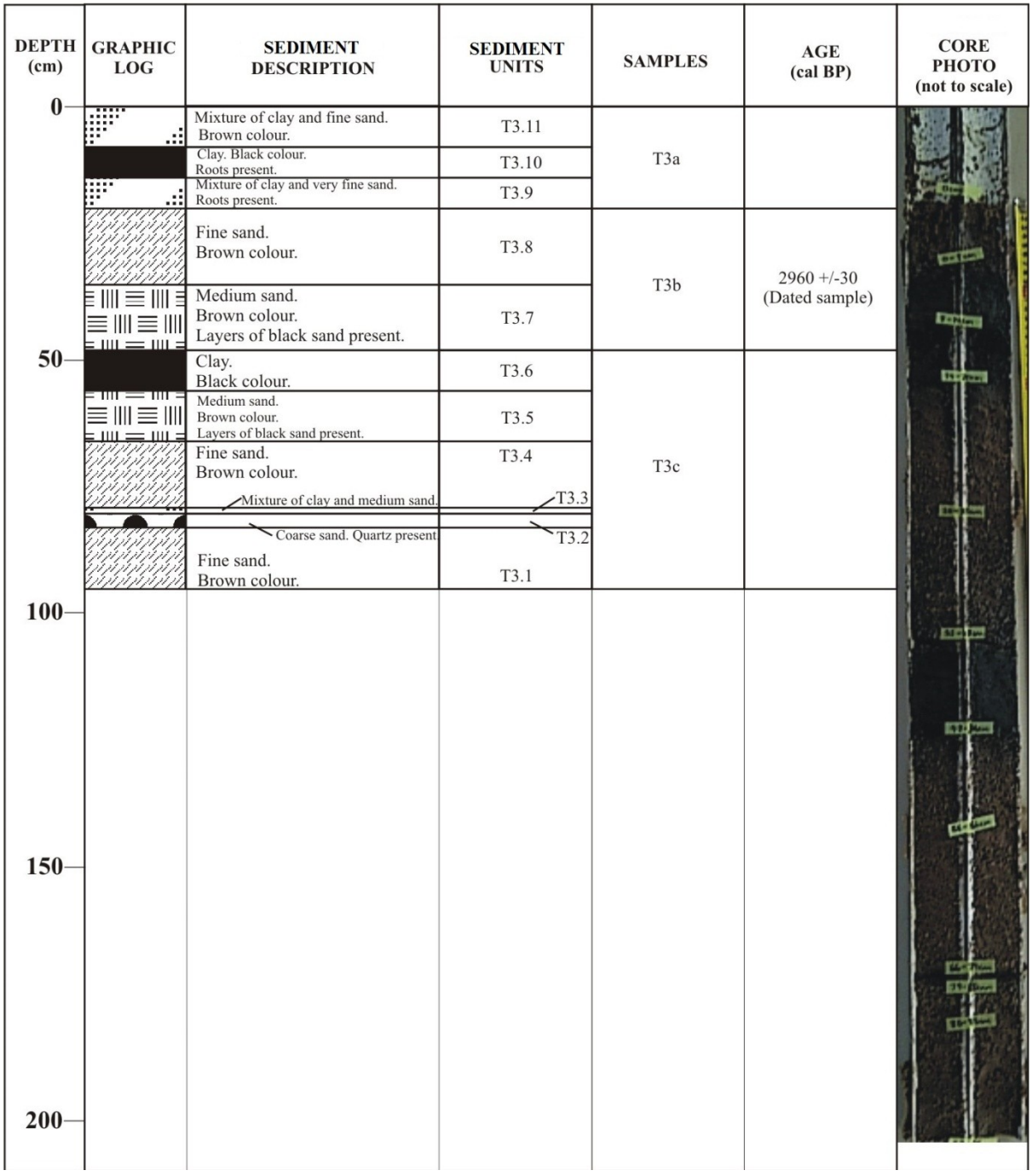

Figure 36: A graphic profile of the core retrieved at site T3 in the uTongati estuary.

5.2.1. Core profiles

Three cores sampled from the uTongati estuary are depicted above (Figures 34, 35 and 36). Sedimentological analysis permitted the delimitation of the nine sediment units in the core sampled at site T1 (Figure 34). The sediment units present within the core lie over a layer of clay which constitutes the lower 9 cm of the core (unit T1.1). The overlying 10 cm is made up of a mixture of fine and coarse sand which is dark brown in colour (unit T1.2), followed by 25 cm of coarse sand and a thin layer of clay wedged in between (units T1.3- T1.5). The remaining 83 cm of the core consists of fine sand and mixtures of fine and coarse sand (units T1.6 - T1.9) with some plant material (leaves and twigs) present in unit T1.8. Sediment colour gradually lightens towards the surface from dark brown to brown.

At site T2 (Figure 35), nine sediment units are present in the core. The sediments are composed of mainly sand with a gradual fining of sediments with depth. The lowest 15 cm unit of the core consisted of greyish-brown, fine sand (unit T2.1) overlain by 27 cm of very fine sand and black clay (units T2.2 - T2.3). The remaining 104 cm of the core constitutes the main sandy portion of the core (units T2.4 – T2.9) with fine, medium and coarse grained sand, and thin layers of fine - medium grained sand and clay in between (units T2.6 and T2.8). The colour of the sediment is mainly brown (sand) and black (clay).

The core sampled at site T3 (Figure 36) consists of eleven sediment units with variations of sediment texture and colour throughout the core. The 12 cm base of fine, brown sand (unit T3.1) is overlain with 4 cm of clay and coarse marine sand (units T3.2 – T3.3). This is followed by another 13 cm of fine sand (unit T3.4). Following this, 8 cm of clay (unit T3.6) is sandwiched between 10 cm (unit T3.5) and 13 cm (unit T3.7) of medium grained sand. The remaining 35 cm of the core consists of finer sands with very fine, brown sand and black clay located at the surface (units T3.8 – T3.11).

5.2.2. Stratigraphic cross-section

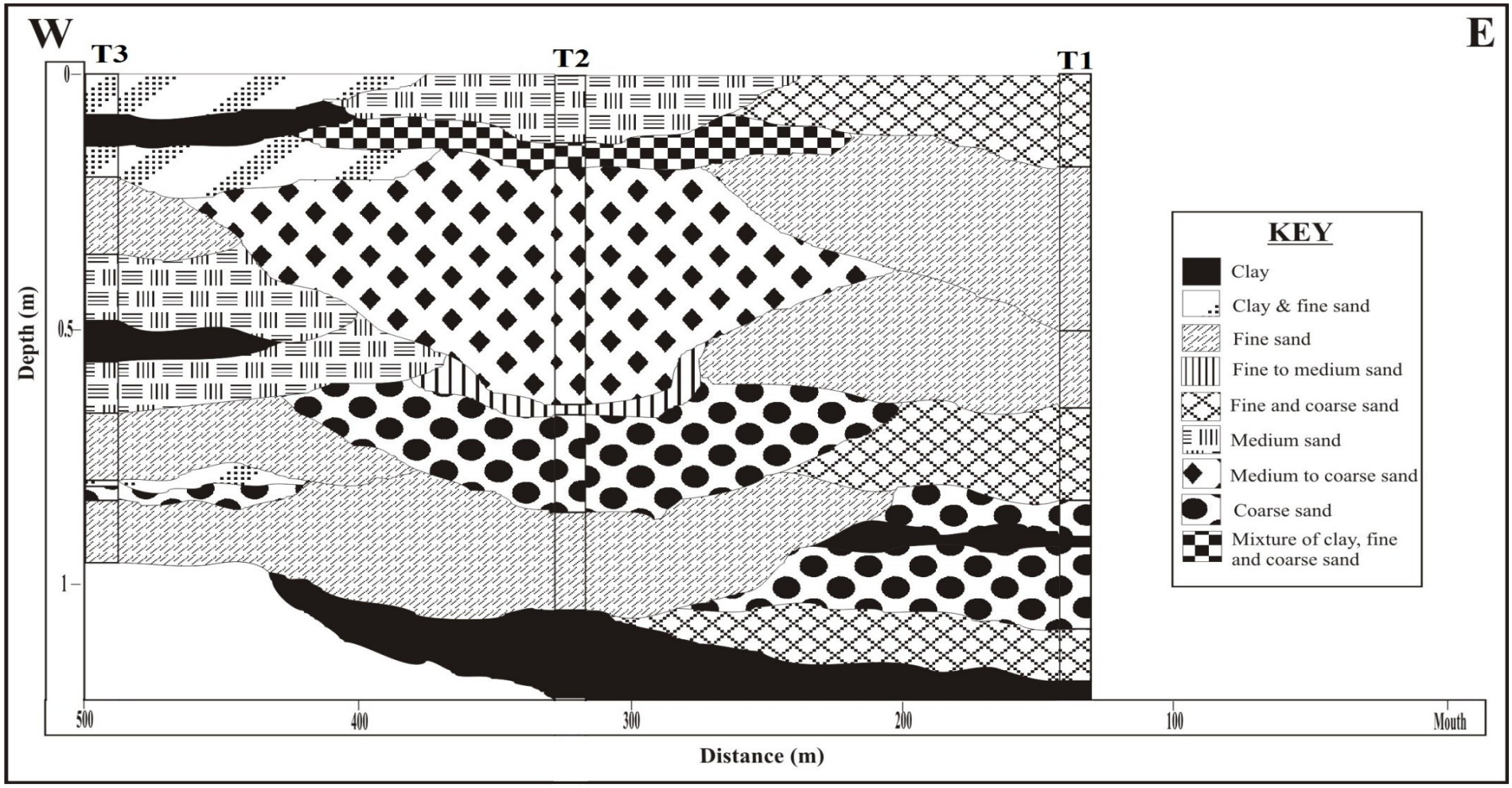

Figure 37: Schematic stratigraphic cross-sectional representation, longitudinal to the estuary axis based on and showing the three core sites from the head (left side of the diagram) to the mouth (right of the diagram) of the uTongati estuary.

For each estuary sampled, an estimated representation of the sediment layers in the form of a stratigraphic cross-section was drawn longitudinal to the estuary axis from west to east. The recent sediment stratigraphic sequences were interpolated on the basis of the location of the cores and similar depths of specific sediment units, and provide a visual representation of the estuarine sediment layers from the head to the mouth of the estuary.

Figure 37 displays the stratigraphic cross-section of the top 1.2 m of sediments in the uTongati estuary, including the locations of cores sampled at sites T1, T2 and T3. Due to the variation of recovered core depths with sites, the sediment units T2.1 and T2.2 at site T2 were omitted. The top 1.2 m of sediments sampled within the estuary are composed of mainly sand with layers of clay dispersed (at greater depths) throughout the head, middle reaches and near the mouth of the estuary. The sandy surface sediments (approximately 0 - 0.3 m depth) display increased coarsening towards the mouth of the estuary. However a fining of sediments occurs downstream from 0.3 - 0.85 m in the middle reaches of the estuary. Below the latter depth, a coarsening of sediments occurs up to 1.18 m, from the upper reaches to near the mouth. Clay is found beneath this in the middle reaches, and near the mouth of the estuary (Refer to Appendix C for texture results of all estuaries).

5.2.3. Organic matter and texture

Table 5: Organic matter content within each core sample for sites T1, T2 and T3.

Core sample sites	Samples	Organic matter (%)
T1	**T1a**	1.340
	T1b	0.400
	T1c	1.480
	Mean	**1.073**
T2	**T2a**	0.140
	T2b	0.140
	T2c	1.880
	Mean	**0.720**
T3	**T3a**	1.620
	T3b	0.950
	T3c	0.950
	Mean	**1.173**

Organic matter content varies at each site with the highest mean value at 1.173% at site T3 and the lowest mean value of 0.720% at site T2 (Table 5). The highest percentage occurs at site T2 in sample T2c at 1.880%. Organic matter increases with depth at site T2 with the opposite occurring at site T3.

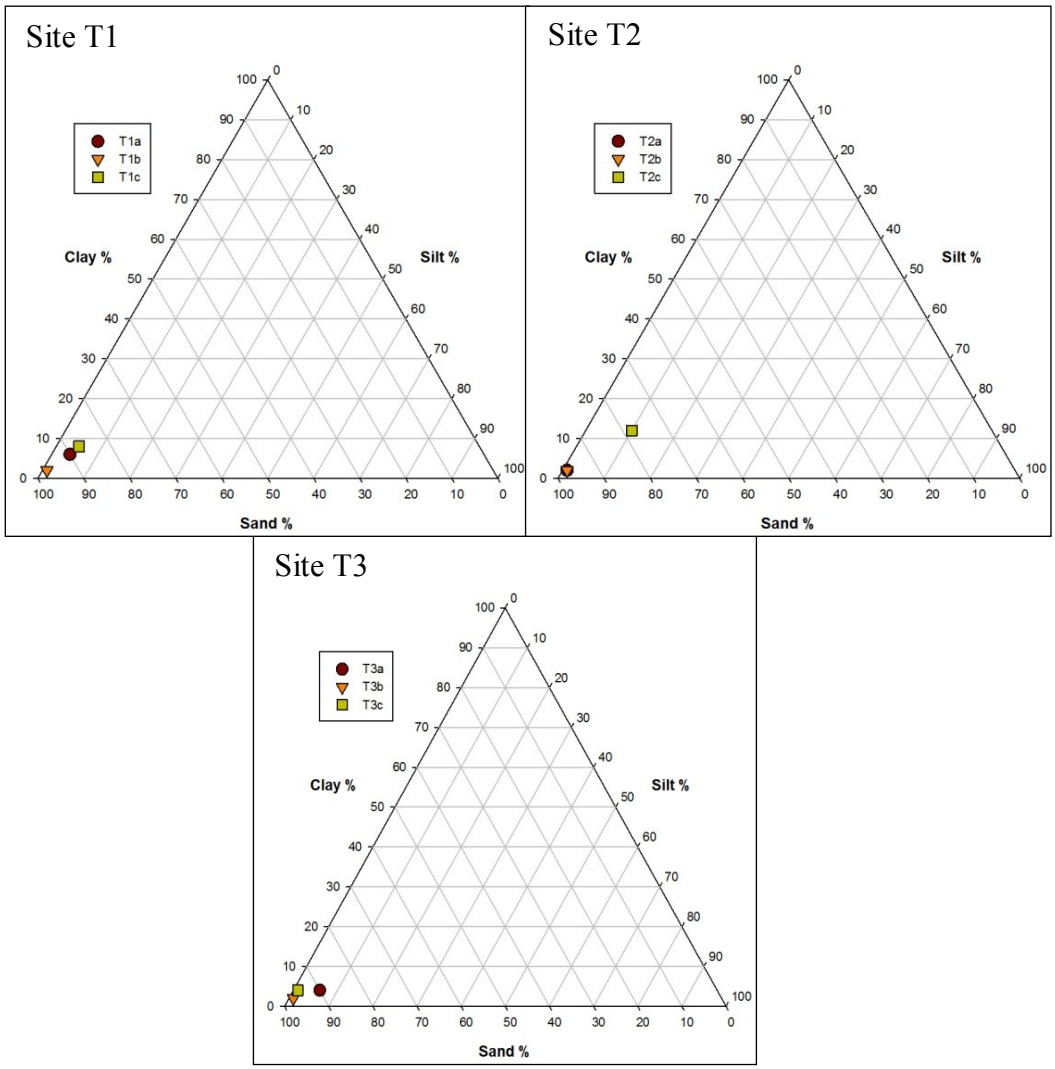

Figure 38: Ternary plots of sand, silt and clay (texture) percentages for each core sample at sites T1, T2 and T3.

Texture percentages in each sample are shown in Figure 38. It can be seen that the main textural component of these cores is sand with all samples consisting of over 90% sand with the exception of samples T1c and T2c which contain 87% and 78% sand respectively. The highest combined clay and silt percentage occurs at site T2, in sample T2c at 22%.

5.2.4. Geochemistry

Table 6: Element concentrations with means per core at each core site in the uTongati estuary.

Core sites	Samples	Core depth (cm)	Element concentrations (ppm)									
			Cu	Ni	Fe	Al	V	P	Ca	Mg	Mn	S
T1	T1a	0-65	0.000	0.000	2.721	2.010	0.025	0.134	0.204	0.341	0.000	0.256
	T1b	65-108	0.000	0.000	0.774	0.450	0.000	0.028	0.685	0.112	0.000	0.163
	T1c	108-123	0.000	0.023	3.609	2.635	0.000	0.150	7.085	0.577	0.000	1.559
Mean			**0.000**	**0.008**	**2.368**	**1.698**	**0.008**	**0.104**	**2.658**	**0.343**	**0.000**	**0.660**
T2	T2a	0-66	0.008	0.020	0.826	0.500	0.003	0.053	0.791	0.056	0.000	0.034
	T2b	66-104	0.000	0.026	1.072	0.693	0.000	0.051	7.811	0.277	0.000	0.172
	T2c	104-146	0.000	0.000	1.948	2.773	0.000	0.551	6.802	7.422	0.225	0.270
Mean			**0.003**	**0.015**	**1.282**	**1.322**	**0.001**	**0.218**	**5.135**	**2.585**	**0.075**	**0.159**
T3	T3a	0-20	0.000	0.000	0.660	0.450	0.000	0.026	0.234	0.077	0.000	0.000
	T3b	20-48	0.000	0.000	2.498	2.897	0.000	0.984	1.901	1.955	0.175	0.090
	T3c	48-95	0.000	0.000	0.833	0.550	0.000	0.024	0.161	0.089	0.000	0.000
Mean			**0.000**	**0.000**	**1.330**	**1.299**	**0.000**	**0.345**	**0.765**	**0.707**	**0.058**	**0.030**

Element concentrations of all core samples from the uTongati estuary are shown in Table 6. The hierarchy of mean metal concentrations per site are as follows:

T1: Ca>Fe>Al>S>Mg>P>V>Ni>Cu>Mn;

T2: Ca>Mg>Al>Fe>P>S>Mn>Ni>Cu>V and,

T3: Fe>Al>Ca>Mg>P>Mn>S>Cu, Ni, V.

Maximum mean concentrations of metals such as Fe, Al, V, and S i.e. 2.368 ppm, 1.698 ppm, 0.008 ppm and 0.660 ppm respectively were observed at site T1 located near the mouth of the estuary. These elements gradually decreased towards the head of the estuary except for Fe

which increased in concentration at site T3. Cu, Ni, Ca, Mg and Mn concentrations i.e. 0.003 ppm, 0.015 ppm, 5.135 ppm, 2.585 ppm and 0.075 ppm respectively were highest at site T2 with levels decreasing towards sites T1 and T3. P exhibited its highest concentration at site T3 with 0.345 ppm and decreased steadily towards the mouth of the estuary.

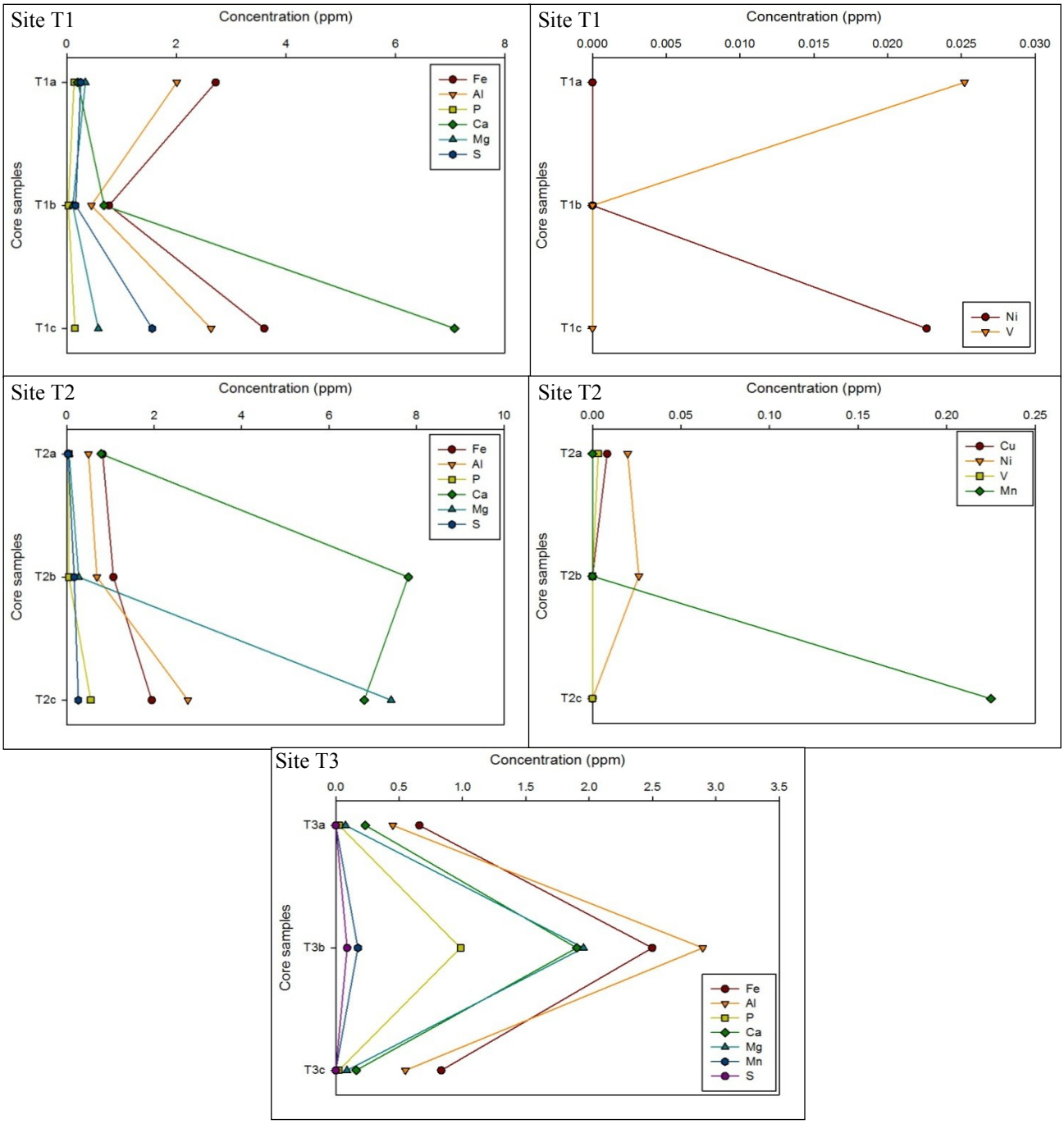

Figure 39: Vertical profiles of element concentrations at core sites in the uTongati estuary.

Each sediment core in this study was divided based on methods described in section 4.4 and samples were assigned letters a, b and c to denote the changes in depth i.e. ‘a’ represents the surface sample within the core, ‘b’ is the middle sample and ‘c’ (and‘d’ for uMgeni and Isipingo estuaries) represents the sample towards the bottom of the core. The corresponding depth ranges (cm) are presented in Table 6 for this estuary.

Figure 39 displays the trends in down core variation in metal concentrations at each core site. At site T1, all element concentrations, with the exception of Ca, Ni and V, decreased from surface sample T1a to sample T1b. This was followed by a rise in concentration by the same elements in sample T1c. Ca concentrations increased with depth, rising steeply in sample T1c.

At site T2, concentrations of Fe, Al, P, Mg, S and Mn increased with depth. Cu and V concentrations were present within surface sample T2a only and thereafter were not detected. From samples T2a to T2b, Ni concentration increased but was absent in sample T2c. The Ca concentration increased sharply from samples T2a to T2b and decreased slightly in sample T2c.

At site T3, low concentrations of all elements were found at the surface (T3a), with the exceptions of Cu, Ni and V which were undetectable at this site. This was followed by a sharp rise in concentrations of all elements in sample T3b which then decreased in sample T3c. Mn and S were only present in sample T3b at this site.

5.2.5. Statistical analyses

Table 7: Pearson correlation matrix of elements, organic matter (OM) and texture within all core samples in the uTongati estuary.

Al	1.000													
Ca	0.432	1.000												
Clay	0.619	0.472	1.000											
Cu	-0.318	-0.232	-0.289	1.000										
Fe	0.878**	0.396	0.510	-0.291	1.000									
Mg	0.614	0.461	0.755*	-0.180	0.233	1.000								
Mn	0.702*	0.304	0.480	-0.187	0.276	0.892**	1.000							
Ni	-0.109	0.599	-0.148	0.397	0.122	-0.278	-0.371	1.000						
OM	0.582	0.114	0.806**	-0.492	0.483	0.533	0.420	-0.468	1.000					
P	0.770*	0.166	0.186	-0.192	0.448	0.589	0.879**	-0.311	0.283	1.000				
S	0.501	0.561	0.464	-0.191	0.759*	0.016	-0.105	0.465	0.324	-0.036	1.000			
Sand	-0.565	-0.433	-0.977**	0.288	-0.425	-0.763*	-0.492	0.195	-0.851**	-0.182	-0.384	1.000		
Silt	0.477	0.368	0.902**	-0.273	0.312	0.732*	0.479	-0.236	0.857**	0.168	0.279	-0.973**	1.000	
V	0.153	-0.330	0.108	0.004	0.335	-0.160	-0.213	-0.198	0.141	-0.126	-0.046	-0.079	0.043	1.000
	Al	**Ca**	**Clay**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**OM**	**P**	**S**	**Sand**	**Silt**	**V**

* Correlation is significant at the 0.05 level ($p < 0.05$).
** Correlation is significant at the 0.01 level ($p < 0.01$).

The correlation of elements, organic matter content, and texture in the sediment samples from the uTongati estuary are given in Table 7 above. Correlation analysis revealed close relationships between individual elements with strong, significant positive correlation: Al and Fe (r = 0.878), Al and Mn (r = 0.702), Al and P (r = 0.770), Fe and S (r = 0.759), Mg and Mn (r = 0.892) and Mn and P (r = 0.879). Textural correlation within the matrix includes similar, significant positive correlation with both clay and silt with Mg i.e. clay and Mg (r = 0.755) and silt and Mg (r = 0.732). There are significant negative correlations related to sand: sand and clay (r = -0.977), sand and Mg (r = -0.763) and sand and silt (r = -0.973). Organic matter displays strong relationships with silt (r = 0.857) and clay (r = 0.806).

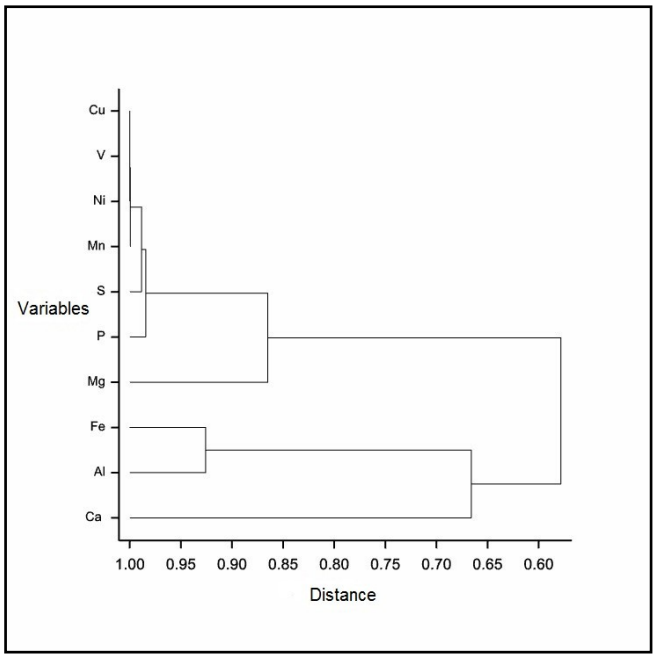

Figure 40: Dendogram obtained by hierarchical cluster analysis of element concentrations in all core samples from the uTongati estuary.

Hierarchical cluster analyses were performed using average link method with Euclidean distance. Distance on the horizontal axis represents the level of association between groups of variables. Distance values closer to 1 indicate greatest similarity between variables (Milhomens *et al*., 2010). The dendogram in Figure 40 represents groupings of elements in all core samples in the uTongati estuary. The variables fall into two main clusters. The first cluster is inclusive of elements Cu, Ni, V, Mn, S, P and Mg. Within this group, a subgroup consisting of Cu, Ni, V and Mn formed, which shows very high similarity as they share distance values of 1. S and P are also closely linked to this subgroup. Mg is also linked to this group except has less similarity as its distance is lower. The second cluster consists of Fe, Al and Ca. Fe and Al are similar. Ca is linked to Fe and Al, but has a lower distance which indicates less similarity between itself and Fe and Al.

5.2.6. Pollution indices

Table 8: Enrichment Factors of elements present within the sediments of the core samples in the uTongati estuary.

Elements	Clarke value	Core samples								
		T1a	T1b	T1c	T2a	T2b	T2c	T3a	T3b	T3c
Cu	70	0.000	0.000	0.000	7.191**	0.000	0.000	0.000	0.000	0.000
Ni	80	0.000	0.000	3.922*	15.062**	15.302**	0.000	0.000	0.000	0.000
Fe	50000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Al	81300	0.454	0.357	0.449	0.373	0.397	0.876	0.419	0.713	0.406
V	150	3.088*	0.000	0.000	1.316	0.000	0.000	0.000	0.000	0.000
P	1180	2.089*	1.552	1.756	2.731*	2.010*	11.990**	1.694	16.698**	1.237
Ca	36300	0.103	1.218	2.704*	1.319	10.036**	4.811*	0.488	1.048	0.266
Mg	20900	0.300	0.345	0.383	0.161	0.619	9.117**	0.279	1.873	0.254
Mn	1000	0.000	0.000	0.000	0.000	0.000	5.774**	0.000	3.495*	0.000
S	2400	1.959	4.397*	9.001**	0.857	3.346*	2.884*	0.000	0.751	0.000

Clarke values after: Martinez *et al*. (2007)
*Moderate enrichment (EF class: 2-5)
** Significant enrichment (EF class: 5-20)

Four pollution indices were used to assess the nature of metal pollution in the sediments of the uTongati estuary, namely Enrichment factor, geo-accumulation index, contamination factor and pollution load index. Enrichment factors of elements within core samples are shown in Table 8 above. Most of the metals in the sediments display minimal to moderate enrichment. S is significantly enriched in sample T1c (EF = 9.001), and P is significantly enriched in sample T3b (EF = 16.698). Six elements at site T2 are significantly enriched (Cu, Ni, P, Ca, Mg and Mn). Cu, Ni and Ca are enriched in the samples T2a and T2b and P, Mg and Mn are enriched in sample T2c. The hierarchy at site T2 for enriched metals are as follows: Ni>P>Ca>Mg>Cu>Mn.

The geo-accumulation index was calculated per sample and the results are shown in Table B7 in Appendix B. All resulting values from this index were less than one. Contamination factors for each element were calculated per core along with the pollution load index and the results are shown in Table B1 in Appendix B. All elements presented a contamination factor of less than one. The calculated pollution load index resulted in values less than one for all three cores and is presented in Table B1 in Appendix B.

5.3. uMdloti estuary

Estuary: uMdloti
Site: D1

Recovered core length: 88cm
Date sampled: 11/12/2011

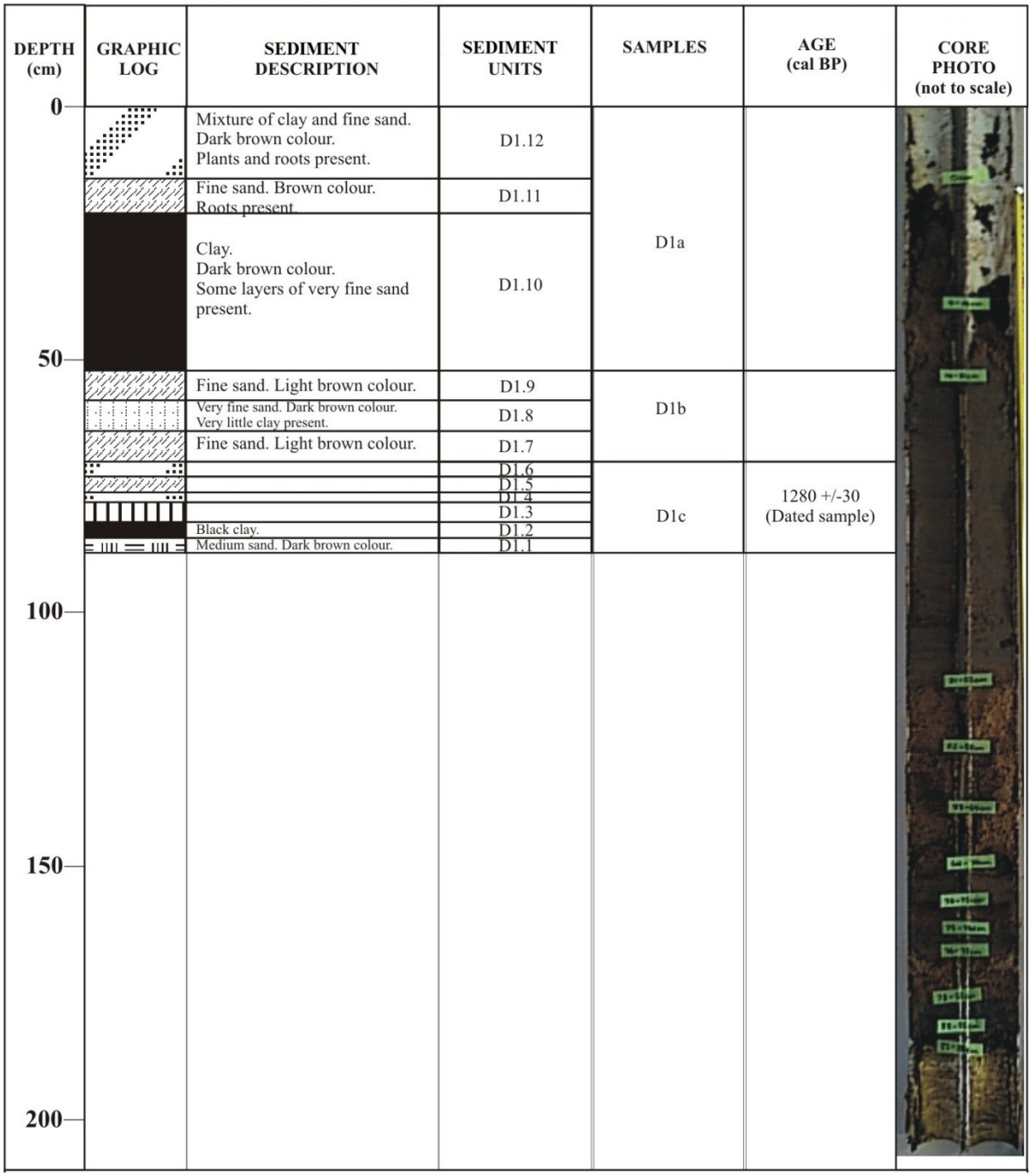

Figure 41: A graphic profile of the core retrieved at site D1 in the uMdloti estuary.

Estuary: uMdloti
Site: D2

Recovered core length: 100cm
Date sampled: 11/12/2011

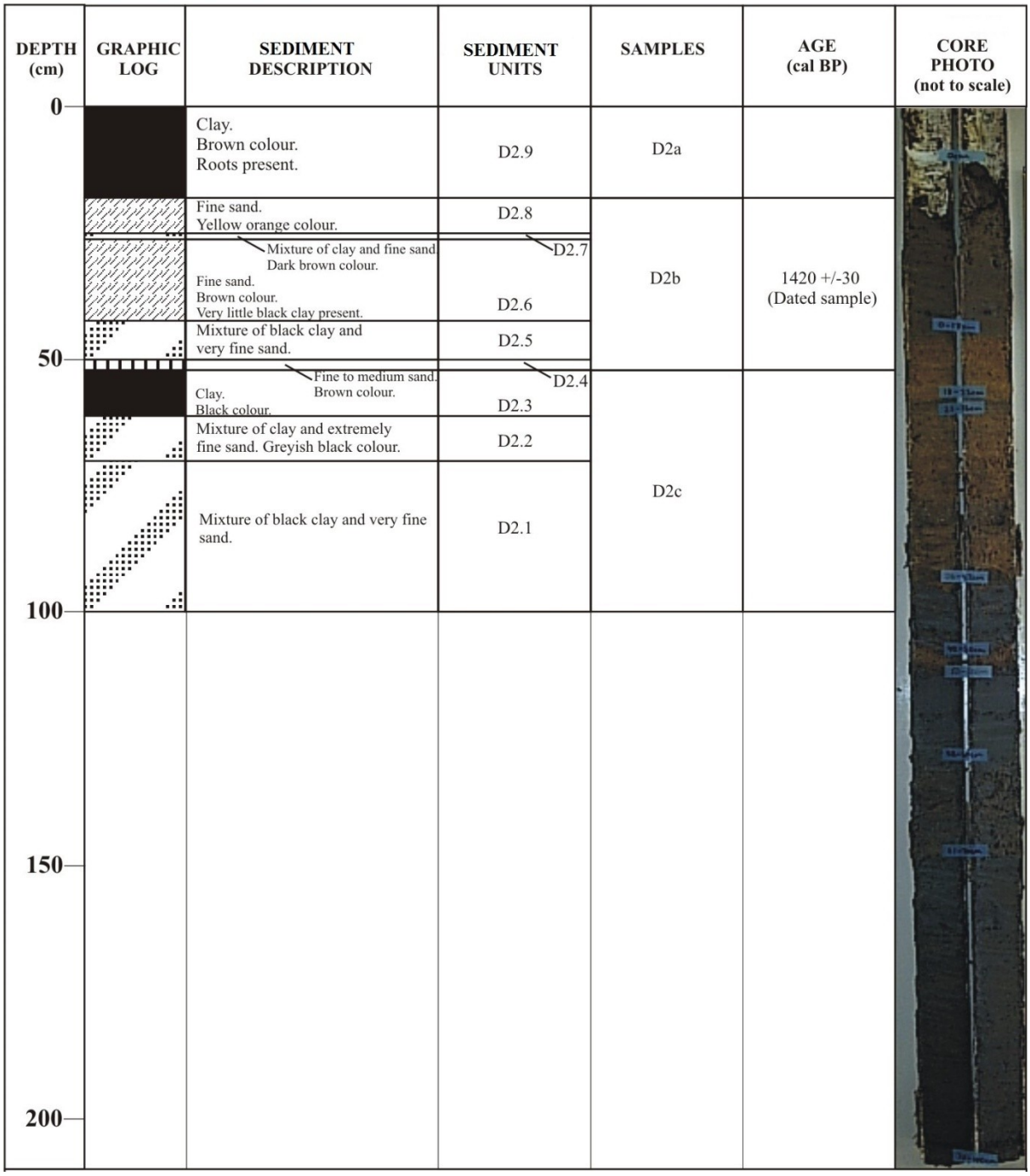

Figure 42: A graphic profile of the core retrieved at site D2 in the uMdloti estuary.

Estuary: uMdloti
Site: D3

Recovered core length: 130cm
Date sampled: 11/12/2011

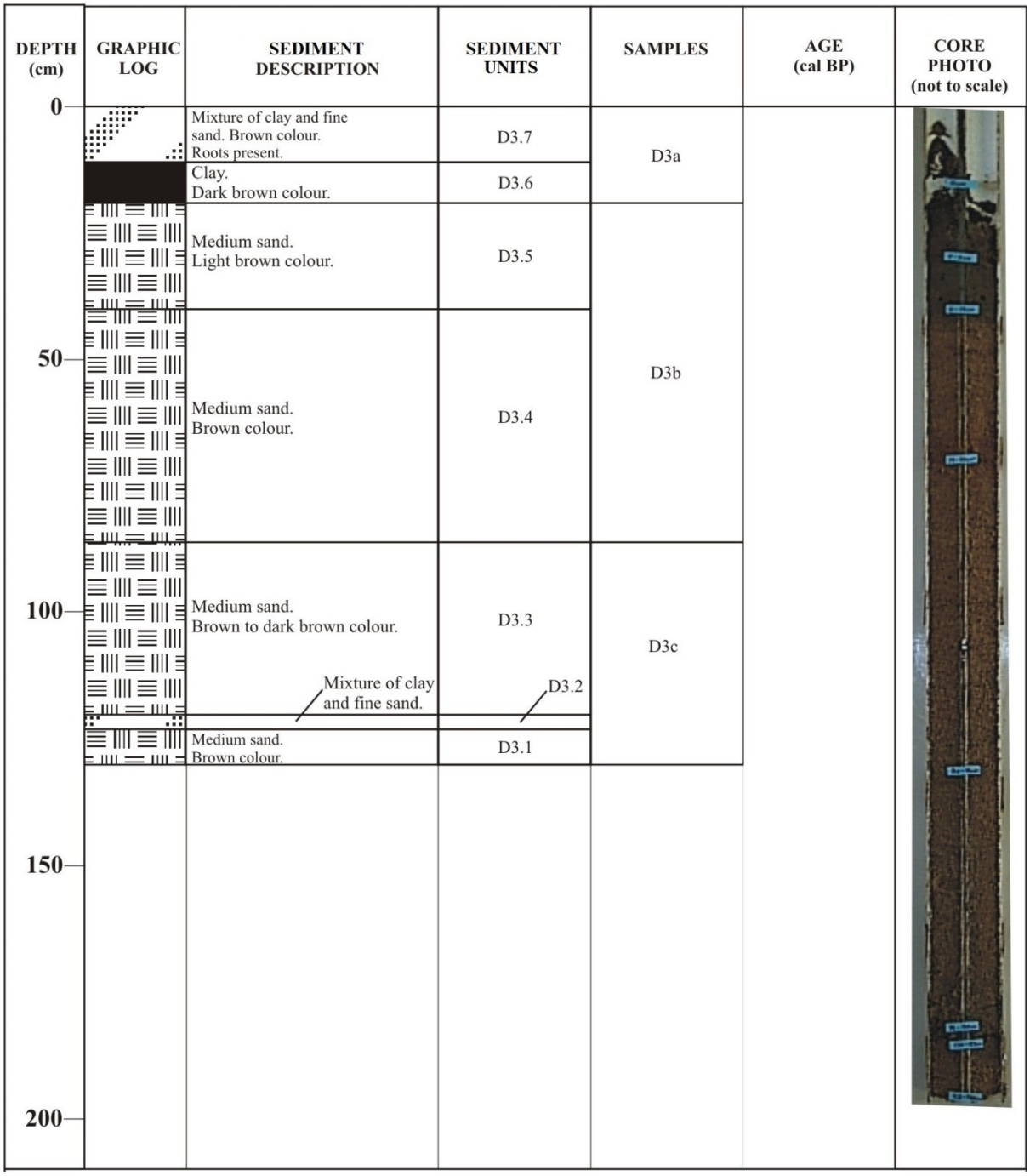

Figure 43: A graphic profile of the core retrieved at site D3 in the uMdloti estuary.

5.3.1. Core profiles

Graphic core profiles of the cores sampled in the uMdloti estuary are presented by Figures 41, 42 and 43. The core sampled at site D1 (Figure 41) was located in a mangrove environment on the northern bank of the estuary. The core consists of twelve sediment units, constituting mainly fine sand and clay, with a general upward fining of sediment. The lowest unit (unit D1.1) is made up of 3 cm of medium grained sand which is overlain by alternating layers of fine sand and clay (units D1.2 – D2.6). The next 18 cm is made up of fine sand (units D1.7 – D1.9) with 21 cm of clay above that (unit D1.10). The last 21 cm of sediments on the surface of the core consists of brown, very fine sand and clay with roots, dried leaves and twigs (D1.11 – D1.12).

At site D2, the core sampled and analysed, permitted the delimitation of nine sediment units (Figure 42). The core sediments mostly consists of dark brown to black clay and very fine sand, with some light brown, fine sand present in the middle section of the core. Eight sediment units rest upon a thick 30 cm layer of black clay and very fine sand (unit D2.1). The overlying 18 cm is made up of more clay and fine sand with a change in colour from greyish-black to black upward (units D2.2 – D2.3). The next 34 cm (D2.4 – D2.8) of sediments consists of fine sand, with 8 cm (unit D2.5) of fine sand and clay in between. An interesting colour change from dark brown to yellow-orange (unit D2.8) occurs upward near the surface of the core. Lastly, the core is capped by 18 cm of brownish clay (unit D2.9), with roots present.

Seven sediment units were determined in the core sampled at site D3 which comprises of mainly medium grained sand, and a layer of clay and very fine sand at the surface (Figure 43). The base unit (unit D3.1) consists of 7 cm of medium grained sand with 3 cm of clay and fine sand above this. The next 101 cm (units D3.3 – D3.5) of sediment is medium grained sand with a gradual upward change in colour from dark brown to light brown. The last 19 cm of the core (units D3. 6 – D3.7) consists of finer materials such as clay and fine grained sand.

5.3.2. Stratigraphic cross-section

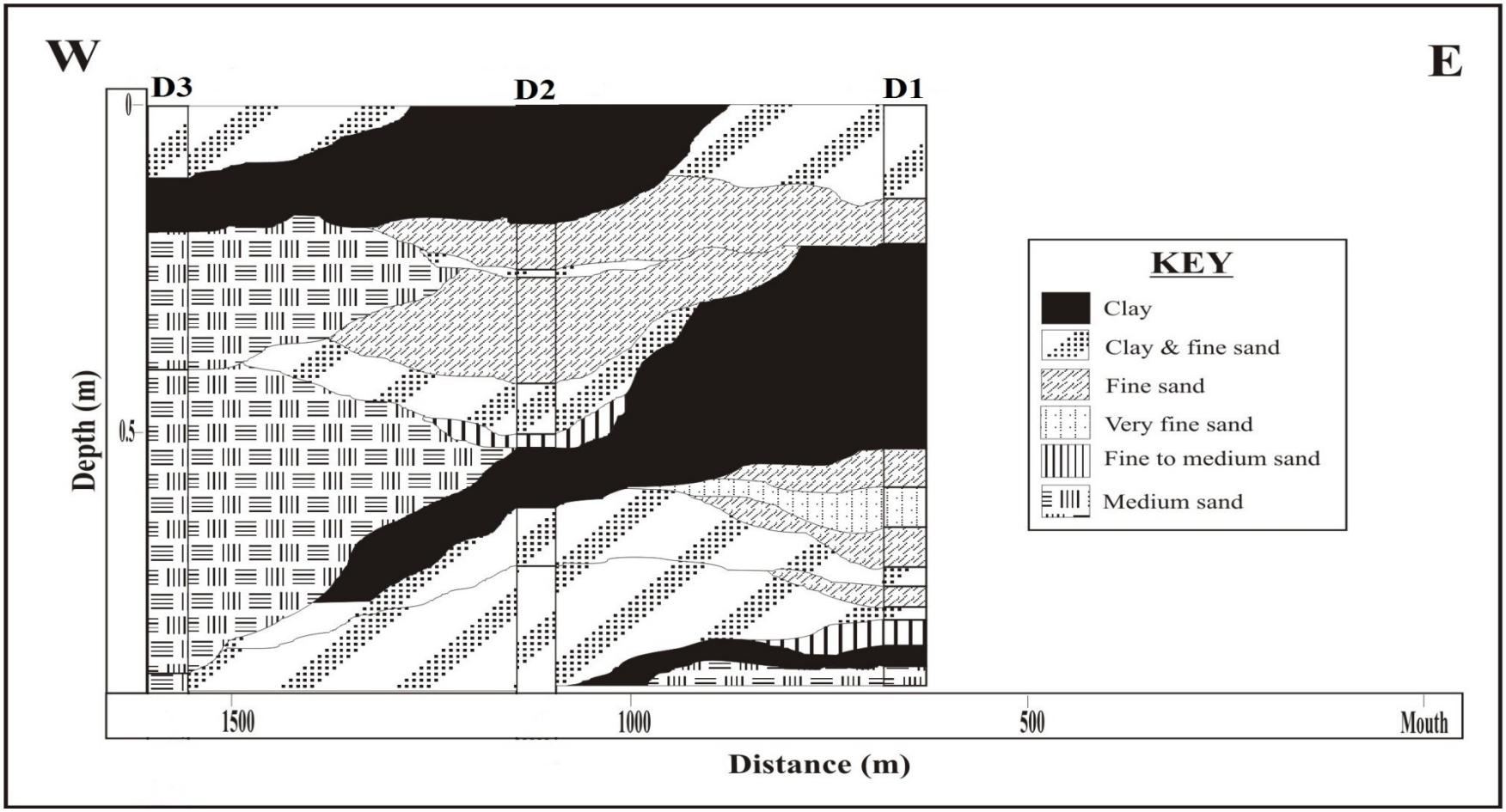

Figure 44: Schematic stratigraphic cross-sectional representation, longitudinal to the estuary axis based on and showing the three core sites from the head (left side of the diagram) to the mouth (right of the diagram) of the uMdloti estuary.

Figure 44 represents a stratigraphic cross-section of the top 1 m of sediments in the uMdloti estuary, including the locations of the cores sampled at sites D1, D2 and D3. Due to the variation of recovered core depths with sites, sediment units D3.1 – D3.3 at site D3 were omitted from the diagram. The general sediment composition is inclusive of mainly finer sediments such as clay, and mixtures of very fine sand and clay near the surface down to approximately 0.2 m in depth. Below this, near the head and middle sections of the estuary (to approximately 0.5 m in depth), there is a coarsening of sediments which includes fine to medium grained sand. Closer to the mouth of the estuary, at similar depths (0.5 m), finer sediments such as clay and fine grained sands exist. This indicates a fining of sediments occurring downstream at approximately 0.5 - 1 m depths.

5.3.3. Organic matter and texture

Table 9: Organic matter content within each core sample for sites D1, D2 and D3.

Core sample sites	Samples	Organic matter (%)
D1	**D1a**	1.880
	D1b	0.670
	D1c	2.550
	Mean	**1.700**
D2	**D2a**	2.410
	D2b	0.810
	D2c	3.350
	Mean	**2.190**
D3	**D3a**	1.070
	D3b	0.280
	D3c	0.400
	Mean	**0.583**

Organic matter content in the uMdloti estuary varies from site to site. The highest mean organic matter content occurs at site D2 with 2.190% whereas the lowest mean is 0.583% at site D3 near the head of the estuary (Table 9). Sample D2c has the highest organic matter percentage at 3.350% and sample D3b contains the lowest with 0.280%. The trend exhibited in all cores showed organic matter decreasing with depth and then increasing again in the bottom sample.

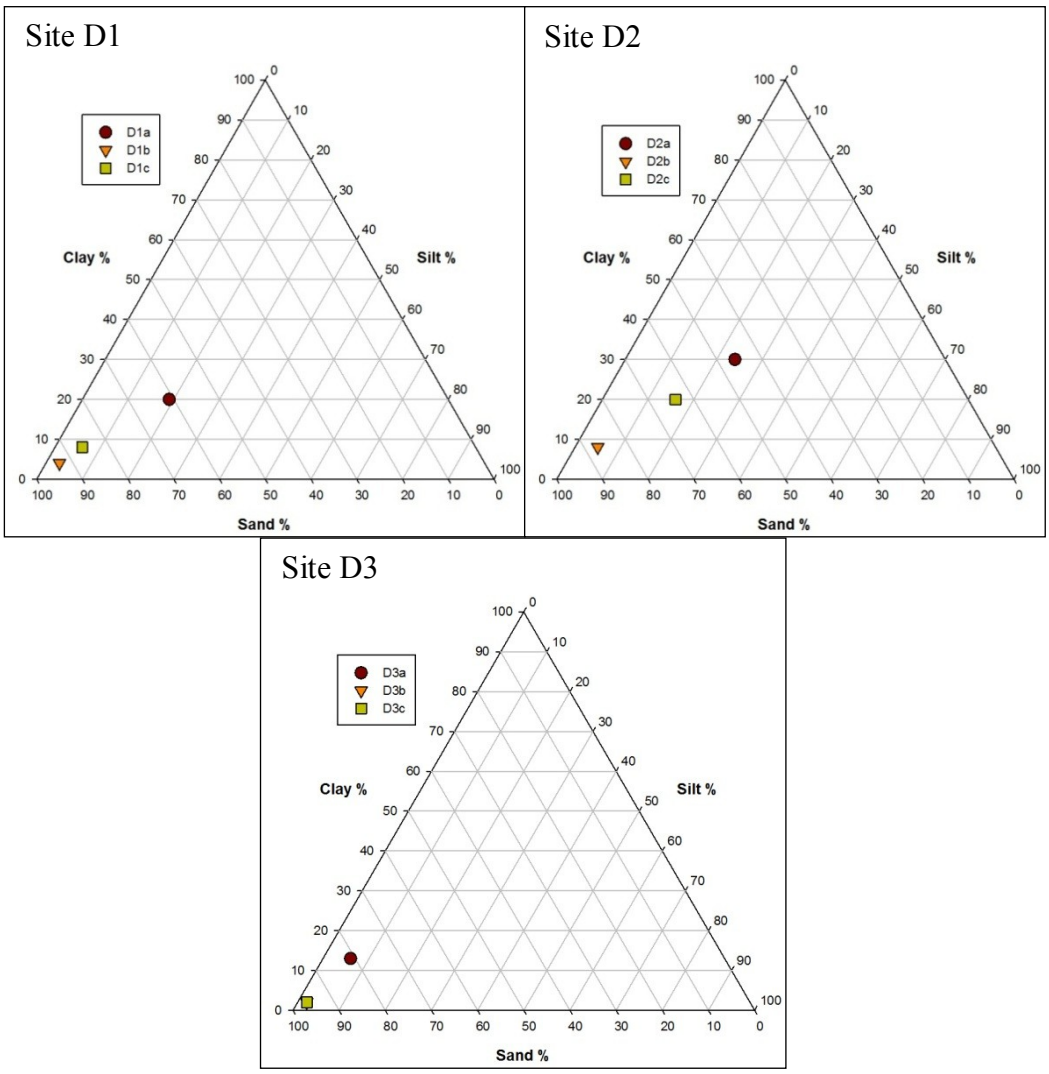

Figure 45: Ternary plots of sand, silt and clay (texture) percentages for each core sample at sites D1, D2 and D3.

Textural analysis of the core sediments at uMdloti estuary reveal higher sand content at sites D1 and D3, with higher clay and silt content at site D2 (Figure 45). All core samples at sites D1 and D3 consist of more than 80% sand. Samples D2a and D2c contain 54% and 36% clay and silt respectively. The top samples of all cores (D1a, D2a and D3a) contain more clay and silt in relation to the lower depth samples, indicating high clay content at the surface of the estuary.

5.3.4. Geochemistry

Table 10: Element concentrations with means per core at each core site in the uMdloti estuary.

Core sites	Samples	Core depth (cm)	Element concentrations (ppm)												
			Cu	**Cd**	**Pb**	**Cr**	**As**	**Fe**	**Al**	**V**	**P**	**Ca**	**Mg**	**Mn**	**S**
D1	**D1a**	**0-52**	0.009	0.020	0.000	0.000	0.000	13.558	4.549	0.000	0.170	13.677	1.825	0.000	0.000
	D1b	**52-70**	0.026	0.000	0.011	0.000	0.000	1.828	1.448	0.025	0.063	0.350	0.392	0.062	0.000
	D1c	**70-88**	0.055	0.000	0.019	0.000	0.027	7.214	5.899	0.049	0.124	1.697	1.484	0.064	0.000
Mean			**0.030**	**0.007**	**0.010**	**0.000**	**0.009**	**7.534**	**3.965**	**0.025**	**0.119**	**5.241**	**1.234**	**0.042**	**0.000**
D2	**D2a**	**0-18**	0.051	0.000	0.006	0.000	0.000	4.998	2.769	0.035	0.071	0.619	0.773	0.062	0.087
	D2b	**18-52**	0.050	0.000	0.012	0.000	0.000	4.005	1.931	0.033	0.064	0.476	0.546	0.008	0.033
	D2c	**52-100**	0.094	0.000	0.044	0.001	0.017	6.302	5.024	0.078	0.151	1.267	1.682	0.084	1.847
Mean			**0.065**	**0.000**	**0.021**	**0.000**	**0.006**	**5.102**	**3.241**	**0.049**	**0.095**	**0.787**	**1.000**	**0.051**	**0.656**
D3	**D3a**	**0-19**	0.081	0.000	0.207	0.000	0.013	3.997	3.231	0.066	0.219	0.658	0.673	0.031	0.213
	D3b	**19-86**	0.076	0.000	0.034	0.000	0.014	1.127	0.760	0.053	0.095	0.357	0.182	0.006	0.153
	D3c	**86-130**	0.075	0.000	0.032	0.000	0.014	0.816	0.633	0.054	0.089	0.166	0.151	0.004	0.169
Mean			**0.077**	**0.000**	**0.091**	**0.000**	**0.014**	**1.980**	**1.541**	**0.058**	**0.135**	**0.394**	**0.335**	**0.014**	**0.178**

Element concentrations of all core samples from the uMdloti estuary are shown in Table 10. The hierarchy of mean metal concentrations per site are as follows:

D1: Fe>Ca>Al>Mg>P>Mn>Cu>V>Pb>As> Cd> Cr, S;

D2: Fe>Al>Mg>Ca>S>P>Cu>Mn>V>Pb>As>Cr>Cd and,

D3: Fe>Al>Ca>Mg>S>P>Pb>Cu>V>Mn>As>Cr>Cd.

Maximum mean concentrations of elements such as Fe (7.534 ppm), Al (3.965 ppm), Ca (5.241 ppm) and Mg (1.234 ppm) were present at site D1 and decreased towards the head of the estuary. In contrast, Cu (0.077 ppm), Pb (0.091 ppm), As (0.014 ppm) and V (0.058 ppm)

concentrations were highest at the head of the estuary and gradually decreased towards the mouth. The remaining elements present in the uMdloti estuary sediments, Cd, Cr, P, Mn and S, were either detected at one site only (Cd and Cr) or varied in concentration throughout the estuary.

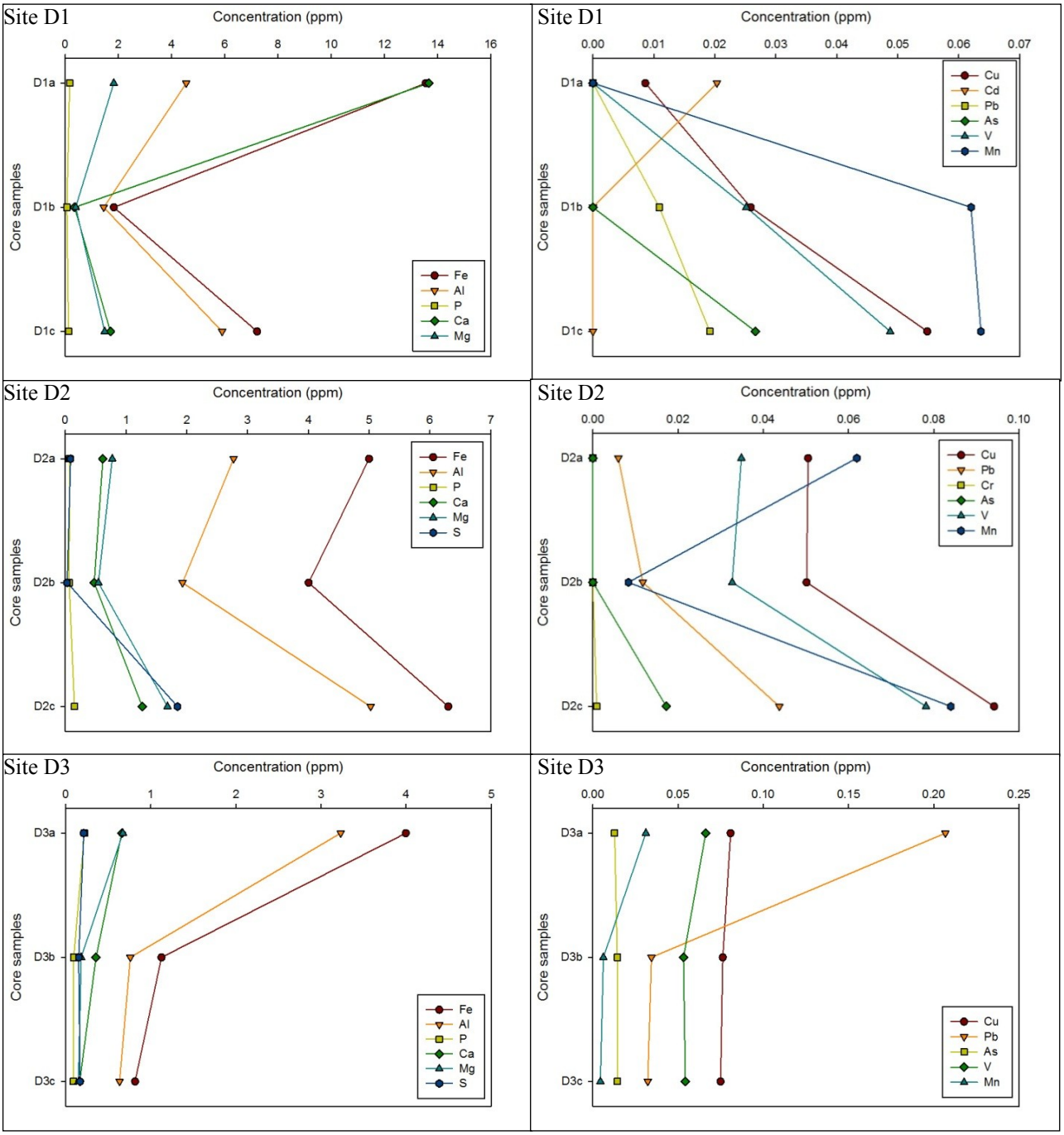

Figure 46: Vertical profiles of element concentrations at core sites in the uMdloti estuary.

Figure 46 displays the trends in down core variation in metal concentrations in the uMdloti estuary. At site D1, Fe, Al, P, Ca and Mg concentrations are highest at the surface in sample D1a and decreased with depth to sample D1b. Thereafter the concentrations rose again in sample D1c. Cu, Pb, V and Mn concentrations increased with depth from the surface sample (D1a). Cd and As were only detected in the samples D1a and D1c respectively.

At site D2, all element concentrations with the exception of Cd, Cr, Pb and As decreased with depth from sample D2a to D2b. This was followed by a rise in concentrations from sample D2b to D2c. Cd was not detected at this site. Cr and As were only found in sample D2c, and Pb increased continuously with depth.

At site D3, As, V and S shared similar concentration variation with depth. These elements decreased with depth from sample D3a, only to slightly increase at the base of the core (sample D3c). For the remaining elements present in this core, a large concentration drop occurred from sample D3a to D3b and continued to decrease gradually from sample D3b to D3c.

5.3.5. Statistical analyses

Table 11: Pearson correlation matrix of elements, organic matter (OM) and texture within all core samples in the uMdloti estuary.

Al	1.000																
As	0.372	1.000															
Ca	0.422	-0.292	1.000														
Cd	0.321	-0.362	0.994**	1.000													
Clay	0.513	-0.308	0.347	0.314	1.000												
Cr	0.414	0.295	-0.075	-0.125	0.314	1.000											
Cu	-0.069	0.645	-0.645	-0.665	-0.127	0.502	1.000										
Fe	0.774*	-0.118	0.879**	0.827**	0.586	0.136	-0.506	1.000									
Mg	0.936**	0.172	0.647	0.564	0.580	0.481	-0.215	0.900**	1.000								
Mn	0.495	0.250	-0.343	-0.414	0.385	0.559	0.200	0.012	0.358	1.000							
OM	0.865**	0.252	0.224	0.134	0.735*	0.638	0.080	0.611	0.845**	0.701*	1.000						
P	0.557	0.338	0.407	0.368	0.256	0.243	0.217	0.486	0.518	-0.010	0.304	1.000					
Pb	0.039	0.279	-0.236	-0.238	-0.035	0.019	0.509	-0.186	-0.136	-0.013	-0.132	0.717*	1.000				
S	0.353	0.331	-0.132	-0.176	0.293	0.991**	0.597	0.063	0.407	0.518	0.584	0.284	0.115	1.000			
Sand	-0.511	0.324	-0.408	-0.377	-0.994**	-0.314	0.180	-0.623	-0.606	-0.357	-0.738*	-0.221	0.122	-0.286	1.000		
Silt	0.500	-0.338	0.474	0.446	0.972**	0.309	-0.239	0.658	0.627	0.320	0.731*	0.176	-0.224	0.272	-0.992**	1.000	
V	0.051	0.710*	-0.666	-0.701*	-0.132	0.553	0.973**	-0.477	-0.132	0.369	0.169	0.269	0.547	0.635	0.191	-0.257	1.000
	Al	**As**	**Ca**	**Cd**	**Clay**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**OM**	**P**	**Pb**	**S**	**Sand**	**Silt**	**V**

* Correlation is significant at the 0.05 level ($p < 0.05$).
** Correlation is significant at the 0.01 level ($p < 0.01$).

The correlation of elements, organic matter content, and texture in the sediment samples from the uMdloti estuary are given in Table 11 above. Significant positive correlation between elements includes Al and Fe (r = 0.774), Al and Mg (r = 0.936), As and V (r = 0.710), Ca and Cd (r = 0.994), Ca and Fe (r = 0.879), Cd and Fe (r = 0.827), Cr and S (r = 0.991), Fe and Mg (r = 0.900) and P and Pb (r = 0.717). Significant negative correlation of elements includes only Cd and V (r = -0.701). In terms of organic matter, the correlation matrix revealed strong, significant, positive correlations with elements Al, Mg and Mn (r = 0.865 r = 0.845 and r = 0.701 respectively) and textural properties clay

and silt (r = 0.735 and r = 0.731 respectively). Clay and silt were significantly correlated with each other (r = 0.972) however, showed a significant negative correlation with sand (r = -0.994 and r = -0.992 respectively).

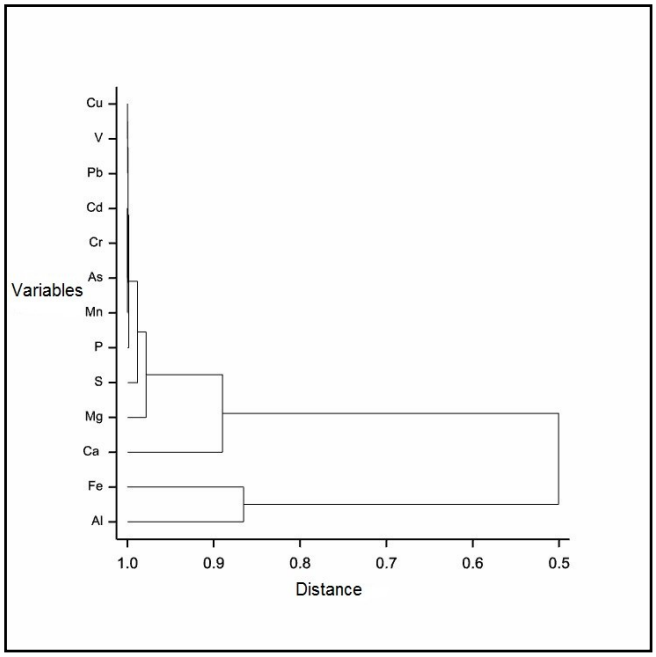

Figure 47: Dendogram obtained by hierarchical cluster analysis of element concentrations in all core samples from the uMdloti estuary.

The dendogram in Figure 47 represents groupings of elements in all core samples in the uMdloti estuary. This dendogram consists of two main clusters. The first cluster consists of elements Cu, V, Pb, Cd, Cr, As, Mn, P, S, Mg and Ca. It can be seen that the elements Cu, V, Pb, Cd, Cr, As and Mn are highly similar as they have a distance of 1. P, S and Mg are linked closely to these elements, which indicate high similarity between these groups of elements. Ca is linked to all of these elements; however it is grouped at a lower distance which indicates less similarity. The second cluster is inclusive of Fe and Al which indicate these two elements share a high degree of similarity.

5.3.6. Pollution indices

Table 12: Enrichment Factors of elements present within the sediments of the core samples in the uMdloti estuary.

Elements	Clarke value	Core samples								
		D1a	D1b	D1c	D2a	D2b	D2c	D3a	D3b	D3c
Cu	70	0.453	10.117**	5.430**	7.220**	8.947**	10.676**	14.452**	**48.348**	**65.661**
Cd	0.15	**499.884**	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pb	16	0.000	18.639**	8.307**	3.757*	9.163**	**21.699**	**161.736**	**95.515**	**123.657**
Cr	200	0.000	0.000	0.000	0.000	0.000	0.036	0.000	0.000	0.000
As	5	0.000	0.000	**36.948**	0.000	0.000	**27.386**	**32.033**	**127.651**	**177.745**
Fe	50000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Al	81300	0.206	0.487	0.503	0.341	0.296	0.490	0.497	0.415	0.477
V	150	0.000	4.589*	2.253*	2.326*	2.722*	4.136*	5.527**	15.751**	**22.175**
P	1180	0.530	1.462	0.731	0.601	0.676	1.018	2.324*	3.590*	4.633*
Ca	36300	1.389	0.263	0.324	0.171	0.164	0.277	0.227	0.436	0.280
Mg	20900	0.322	0.512	0.492	0.370	0.326	0.639	0.403	0.387	0.442
Mn	1000	0.000	1.696	0.441	0.620	0.104	0.667	0.389	0.275	0.274
S	2400	0.000	0.000	0.000	0.362	0.170	6.106**	1.110	2.833*	4.323*

Clarke values after: Martinez *et al.* (2007)
*Moderate enrichment (EF class: 2-5)
**Significant enrichment (EF class: 5-20)
Bold values indicate very high enrichment (EF class: 20-40)
Red bold values indicate extremely high enrichment (EF class: > 40)

Enrichment factors of elements within core samples in the uMdloti estuary are shown in Table 12 above. The elements in the sediments of this estuary are varied in terms of enrichment levels. In samples D1b and D1c, V is moderately enriched along with Cu and Pb which are significantly enriched. V enrichment in the sediment increased towards the head of the estuary reaching very high enrichment (EF = 22.175) in sample D3c. Cu and Pb followed the same pattern, but reached extremely high enrichment values at site D3, especially Pb, with an EF value of 161.736 in surface sample D3a. As exhibited very high enrichment near the mouth of the estuary in sample D1c with EF = 36.948. At site D3, As enrichment increased with depth from very high to extremely high enrichment, with its highest value of EF = 177.745 in sample D3c. Site D3 is also moderately enriched by P and S.

The geo-accumulation index was calculated per sample and the results are shown in Table B8 in Appendix B. All resulting values from this index were less than one. Contamination factors for each element were calculated per core along with the pollution load index and the results are shown in Table B2 in Appendix B. All elements presented a contamination factor of less than one. The calculated pollution load index resulted in values less than one for all three cores and is presented in Table B2 in Appendix B.

5.4. uMgeni estuary

Estuary: uMgeni
Site: G1

Recovered core length: 146cm
Date sampled: 28/09/2011

DEPTH (cm)	GRAPHIC LOG	SEDIMENT DESCRIPTION	SEDIMENT UNITS	SAMPLES	AGE (cal BP)	CORE PHOTO (not to scale)
0		Mixture of clay and fine sand. Roots present. Layers of black sand present.	G1.11	G1a		
50		Fine sand. Grey brown colour.	G1.10	G1b		
		Black clay.	G1.9			
		Mixture of clay, fine and coarse sand.	G1.8			
100		Very coarse sand and gravel.	G1.7	G1c	700 +/- 30 (Dated sample)	
		Black clay. Roots present.	G1.6			
		Mixture of clay and fine sand. Roots present.	G1.5			
		Mixture of fine and coarse sand.	G1.4	G1d		
		Mixture of clay, fine and coarse sand.	G1.3			
		Mixture of fine and coarse sand.	G1.2			
		Very coarse sand and gravel.	G1.1			
150						
200						

Figure 48: A graphic profile of the core retrieved at site G1 in the uMgeni estuary.

Estuary: uMgeni
Site: G2

Recovered core length: 112cm
Date sampled: 28/09/2011

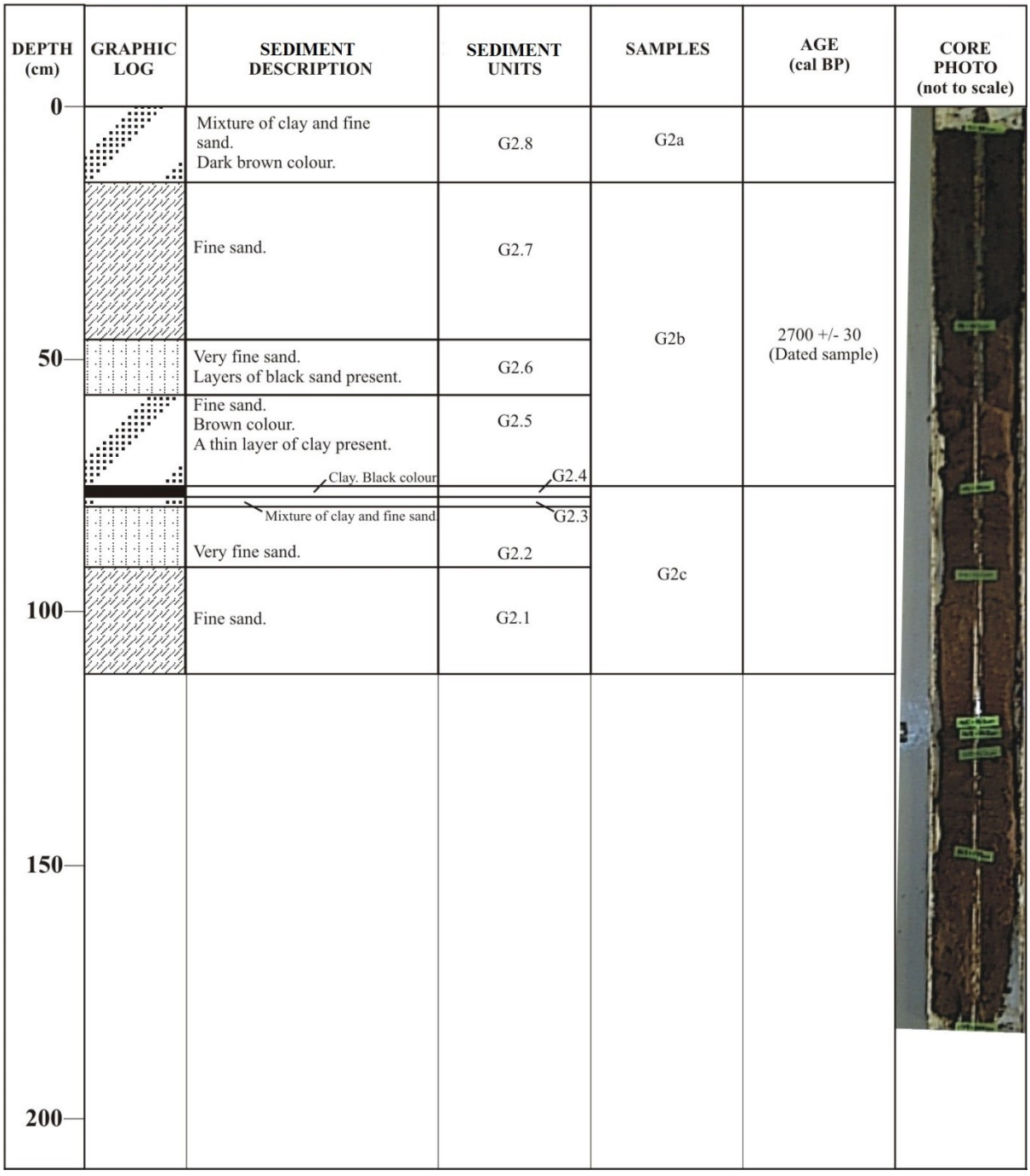

Figure 49: A graphic profile of the core retrieved at site G2 in the uMgeni estuary.

Estuary: uMgeni
Site: G3

Recovered core length: 92cm
Date sampled: 28/09/2011

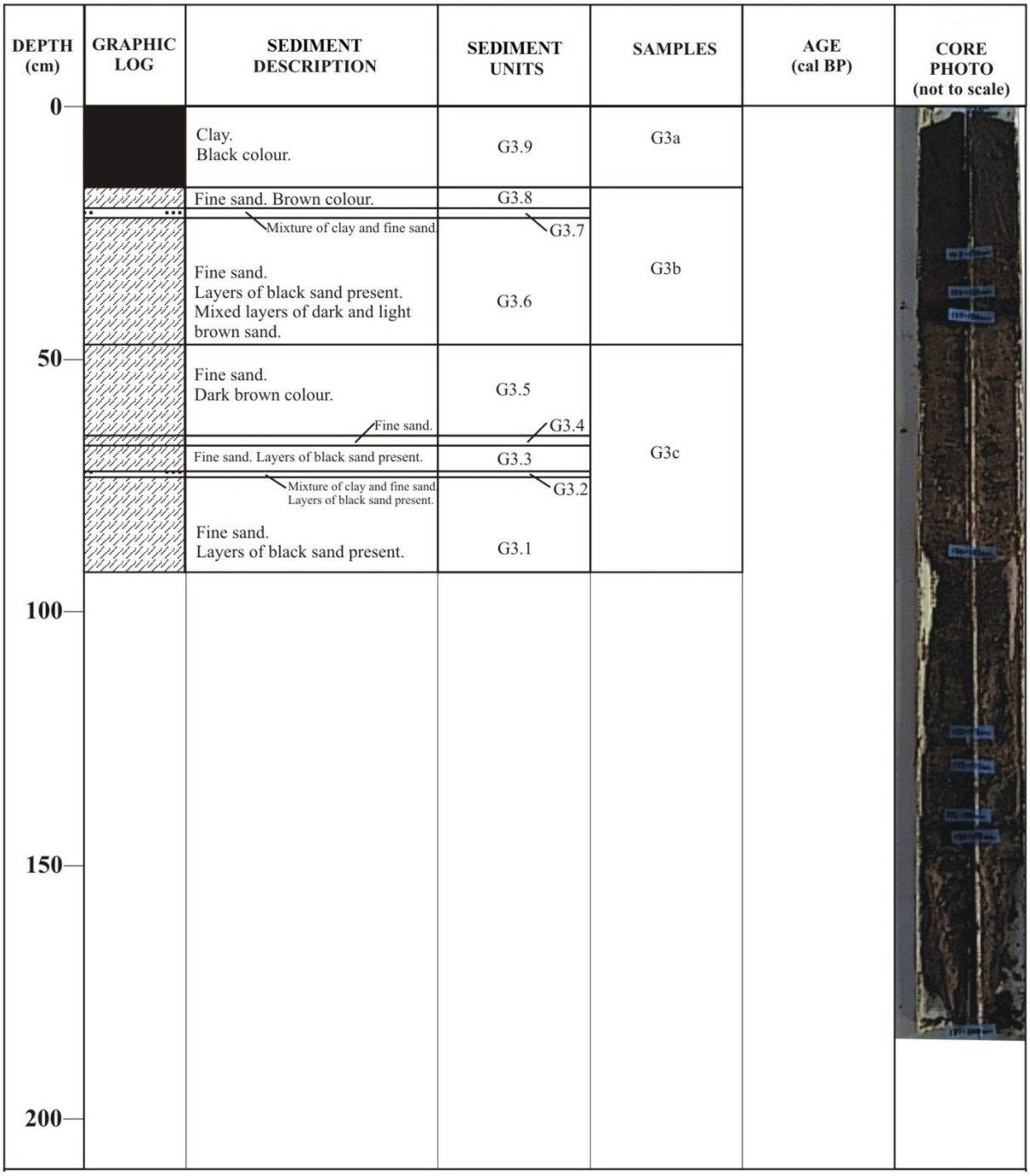

Figure 50: A graphic profile of the core retrieved at site G3 in the uMgeni estuary.

Estuary: uMgeni
Site: G4

Recovered core length: 104cm
Date sampled: 28/09/2011

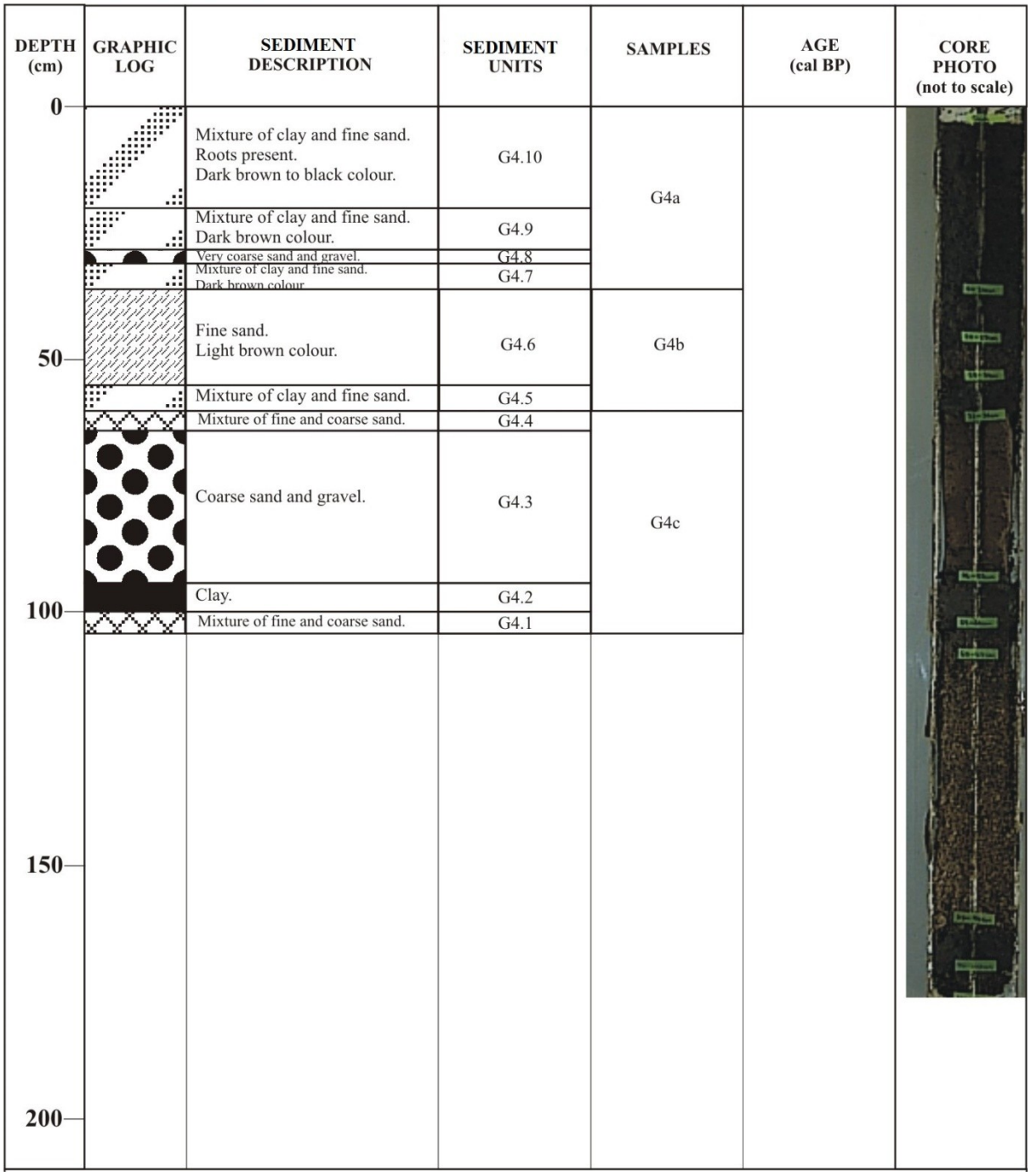

Figure 51: A graphic profile of the core retrieved at site G4 in the uMgeni estuary.

5.4.1. Core profiles

Graphic core profiles of the cores sampled in the uMgeni estuary are presented by Figures 48, 49, 50 and 51. Sedimentological analysis allowed for the determination of eleven sediment units in the core sampled at site G1 (Figure 48). At the base of the core, a 9 cm layer of coarse marine sand and gravel is present (unit G1.1). The overlying 31 cm (units G1.2 – G1.5) of sediments are split into mixed layers of fine sand combined with either clay or coarse sand. The next 15 cm (units G1.6 – G1.8) are separated into 5 cm units of clay, very coarse marine sand and gravel, and a mixture of fine sand, clay and coarse sand. These units are covered by 8 cm of clay (unit G1.9) which is overlain by a thick 36 cm of grey-brown fine sand (unit G1.10). The 47 cm surface layer (unit G1.11) composes of a mixture of very fine sand and clay with roots present.

The core sampled at site G2 (Figure 49) is composed of eight sediment units, whose base consists of 21 cm of brown, fine sand (unit G1.1). The overlying layers (76 cm) contain fine to very fine sand units interrupted by thin 2 cm layers of clay and mixtures of clay and very fine sand (units G1.2 –GI.7) as well as black striations within unit G1.6. This core is capped by 15 cm of clay mixed with very fine sand, and is dark brown in colour (unit G1.8).

Site G3 core (Figure 50) sampled near the head of the estuary, consists of nine sediment units which are mainly sandy sediments capped by a layer of clay. The base of the core (unit G3.1) contains 19 cm of fine sand with black striations, overlain by 1 cm of clay and very fine sand (unit G3.2). The next 50 cm of the core (units G3.3 – G3.6) consists of fine sand with units G3.3 and G3.6 containing black striations, and this is covered by a thin 2 cm layer (unit G3.7) mixture of clay and fine sand. The next 4 cm (unit G3.8) is brown, fine sand, and is capped by 16 cm of clay at the surface (unit G3.9).

Delimitation of the core sampled in the mangrove area of the uMgeni estuary i.e. site G4 (Figure 51), allowed for identification of ten sediment units. This core shows a general trend of coarsening with depth. The base of the core contains a 4 cm mixture of fine and coarse sand (unit G4.1) overlain by 6 cm of clay (unit G4.2). A thick 30 cm layer (unit G4.3) of coarse sand and gravel follows, covered by a 4 cm mixture of fine and coarse sand (unit G4.4). Gradual fining of sediment begins with the next three units (G4.5- G4.7) comprising of 29 cm of fine sand (unit G4.6) and mixtures of clay and fine sand (units G4.5 and G5.7). This is disturbed by a 3 cm layer of very coarse sand and gravel (unit G4.8). This is overlain by a dark brown 8 cm (unit G4.9) and a 20 cm (unit G4.10) mixture of fine sand and clay with roots present at the surface.

5.4.2. Stratigraphic cross-section

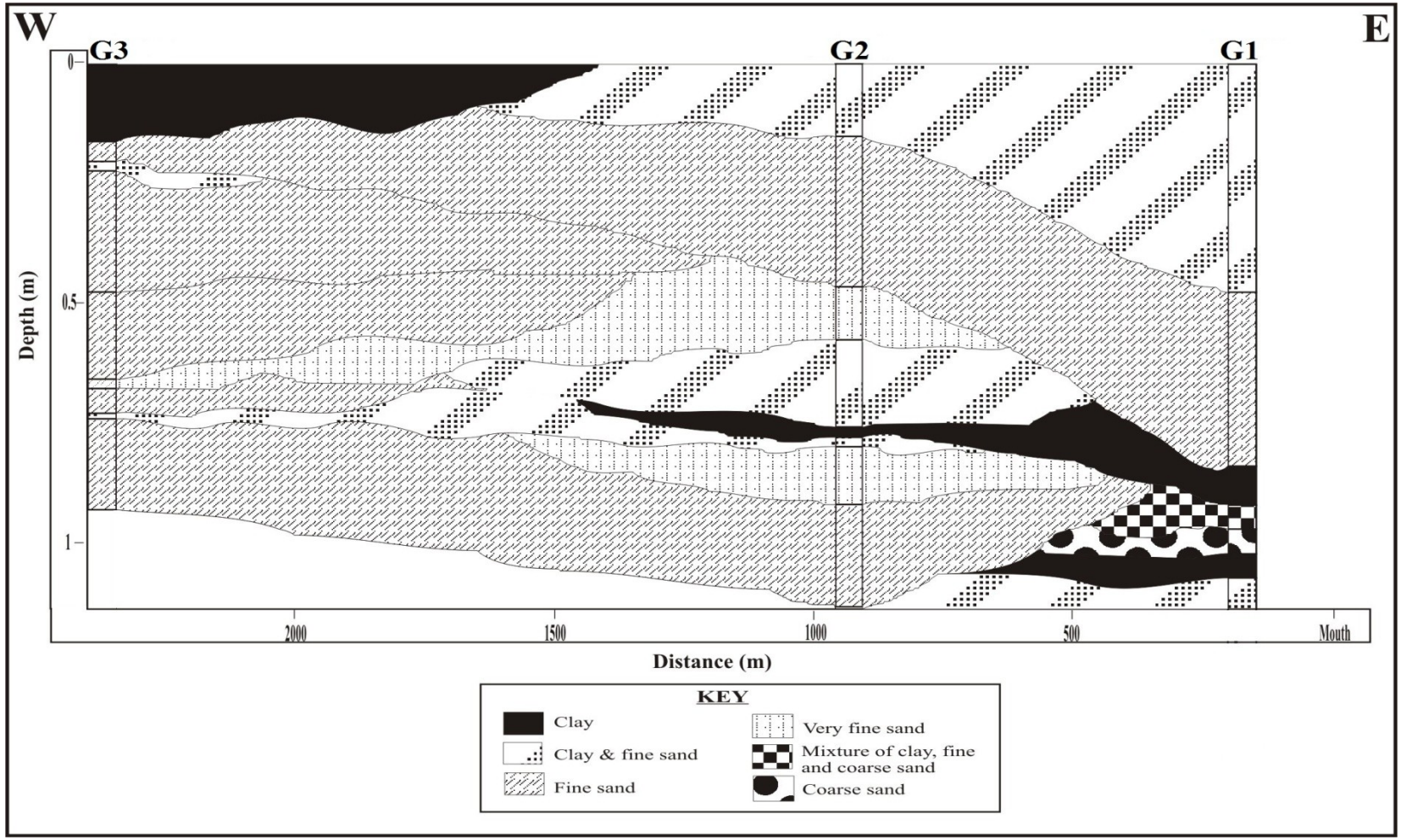

Figure 52: Schematic stratigraphic cross-sectional representation, longitudinal to the estuary axis based on and showing the three core sites from the head (left side of the diagram) to the mouth (right of the diagram) of the uMgeni estuary.

Figure 52 above represents a stratigraphic cross-section of the top 1.1 m of the uMgeni estuary, including the locations of the cores sampled at sites G1, G2 and G3. Due to the variation of recovered core depths with sites, units G1.1- G1.4 at site G1 were omitted to allow for the accurate interpolation of the sediment layers. The main composition of sediments includes mainly fine to very fine sand, with a fining of sediments at the surface (0.15 – 0.2 m), and the coarsening of sediments near the mouth of the estuary at depths of 0.95 m and below. The head of the estuary consists of mainly sandy sediments with clay at the surface and a fining of sediments downstream at depths of 0.45 – 0.8 cm towards the middle sections of the estuary.

5.4.3. Organic matter and texture

Table 13: Organic matter content within each core sample for sites G1, G2, G3 and G4.

Core sample sites	Samples	Organic matter (%)
G1	**G1a**	1.200
	G1b	0.400
	G1c	2.150
	G1d	0.810
	Mean	**1.140**
G2	**G2a**	2.150
	G2b	1.570
	G2c	3.220
	Mean	**2.313**
G3	**G3a**	6.040
	G3b	1.880
	G3c	0.400
	Mean	**2.773**
G4	**G4a**	1.880
	G4b	0.530
	G4c	0.020
	Mean	**0.810**

Organic matter content in the uMgeni estuary is displayed in Table 13 above. A general trend of decreasing organic matter content downstream is observed. The highest mean organic matter percentage is at the head of the estuary at site G3, with 2.773%. The lowest mean content occurs at the mangroves habitat with 0.810%. Sample G3a contains the highest percentage at 6.040% and the lowest is found in sample G4c with 0.020%. There is a similar trend in cores sampled at site G1 and G2, with the initial decrease of organic matter percentage with depth from the surface, followed by an increase. Upstream at site G3, the

organic matter content decreases with depth, and this pattern is mirrored by the mangrove site core, G4.

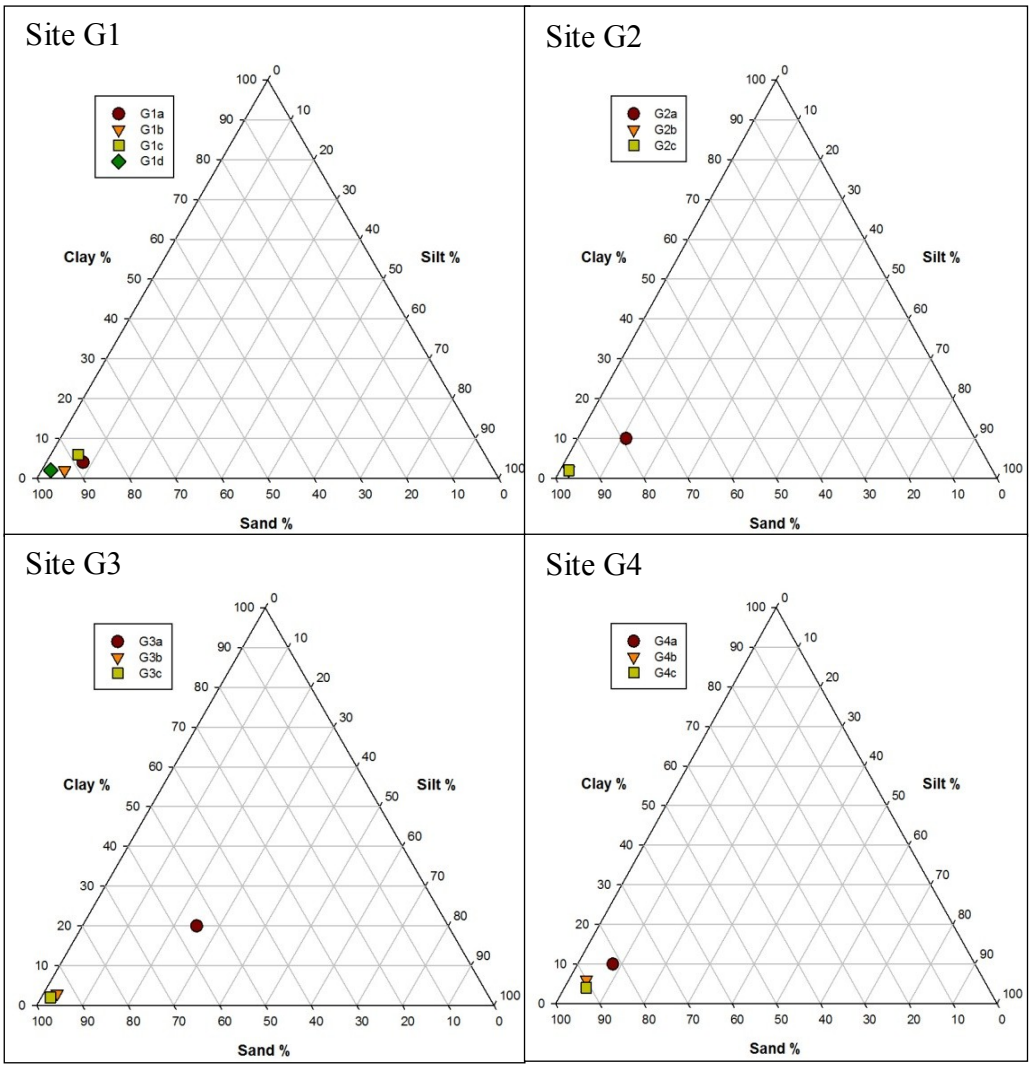

Figure 53: Ternary plots of sand, silt and clay (texture) percentages for each core sample at sites G1, G2, G3 and G4.

Texture percentages for each core sample are represented in Figure 53 above. The majority of the samples consist of greater than 80% sand. All 'b' samples contain greater than 90% sand content. Samples G2a and G3a have the highest content of clay and silt with 21% and 45% respectively. The patterns per core show a coarsening of sediments with depth especially in sites G2, G3 and G4.

5.4.4. Geochemistry

Table 14: Element concentrations with means per core at each core site in the uMgeni estuary.

Core sites	Samples	Core depth (cm)	Element concentrations (ppm)												
			Zn	Cu	Ni	Pb	As	Fe	Al	V	P	Ca	Mg	Mn	S
G1	G1a	0-47	0.000	0.071	0.000	0.056	0.008	7.374	4.202	0.065	0.484	2.966	1.827	0.072	0.892
	G1b	47-96	0.000	0.075	0.000	0.030	0.001	3.637	2.336	0.048	0.232	2.189	0.872	0.076	0.059
	G1c	96-115	0.000	0.053	0.000	0.027	0.000	2.851	1.920	0.042	0.102	1.668	0.593	0.042	1.107
	G1d	115-146	0.000	0.053	0.000	0.027	0.003	2.597	1.574	0.042	0.113	1.020	0.548	0.057	0.804
Mean			**0.000**	**0.063**	**0.000**	**0.035**	**0.003**	**4.115**	**2.508**	**0.049**	**0.233**	**1.961**	**0.960**	**0.062**	**0.715**
G2	G2a	0-15	0.020	0.048	0.000	0.026	0.538	2.854	1.282	0.068	0.452	0.627	0.546	0.078	0.000
	G2b	15-75	0.000	0.048	0.124	0.022	0.000	0.000	0.101	0.028	0.026	0.000	0.001	0.000	0.119
	G2c	75-112	0.000	0.002	0.000	0.000	0.000	3.146	1.544	0.000	0.160	0.596	0.635	0.000	0.043
Mean			**0.007**	**0.033**	**0.041**	**0.016**	**0.179**	**2.000**	**0.975**	**0.032**	**0.213**	**0.408**	**0.394**	**0.026**	**0.054**
G3	G3a	0-16	0.096	0.019	0.000	0.011	0.000	7.398	3.915	0.002	0.542	0.973	1.096	2.188	1.502
	G3b	16-47	0.000	0.000	0.000	0.000	0.000	2.813	1.201	0.000	0.166	0.752	0.382	0.000	0.242
	G3c	47-92	0.000	0.001	0.000	0.000	0.000	2.988	1.291	0.000	0.147	0.551	0.425	0.000	0.170
Mean			**0.032**	**0.007**	**0.000**	**0.004**	**0.000**	**4.399**	**2.136**	**0.001**	**0.285**	**0.759**	**0.634**	**0.729**	**0.638**
G4	G4a	0-36	0.000	0.080	0.120	0.049	0.015	5.443	3.607	0.068	0.370	1.523	1.346	0.038	1.789
	G4b	36-60	0.000	0.075	0.084	0.143	0.013	2.367	1.612	0.058	0.122	0.448	0.496	0.030	0.697
	G4c	60-104	0.000	0.039	0.118	0.035	0.016	3.991	2.851	0.062	0.163	2.612	0.723	0.031	1.187
Mean			**0.000**	**0.065**	**0.108**	**0.076**	**0.015**	**3.934**	**2.690**	**0.063**	**0.218**	**1.528**	**0.855**	**0.033**	**1.224**

Element concentrations of all core samples from the uMgeni estuary are shown in Table 14. The hierarchy of mean metal concentrations per site are as follows:

G1: Fe>Al>Ca>Mg>S>P>Cu>Mn>V>Pb>As>Zn, Ni;

G2: Fe>Al>Ca>Mg>P>As>S>Ni>Cu>V>Mn>Pb>Zn and,

G3: Fe>Al>Ca>Mn>S>Mg>P>Zn>Cu>Pb>V>Ni, As.

Maximum mean concentrations of elements Cu (0.063 ppm), Pb (0.035 ppm), Al (2.508 ppm), V (0.049 ppm), Ca (1.961 ppm), Mg (0.960 ppm) and S (0.715 ppm) occurred at site G1 nearest to the mouth of the estuary. Concentrations of Cu, Pb and V decreased towards the head of the estuary. Al, Ca, Mg and S concentrations were lowest at site G2, and increased at site G3. In contrast, mean concentrations of Zn (0.032 ppm), Fe (4.399 ppm), P (0.285 ppm) and Mn (0.729 ppm) were highest at site G3 near the head of the estuary. Zn concentrations decreased towards the mouth, however Fe, P and Mn were high at both site G3 and G1. Mean concentrations of Ni and As were highest in the middle reaches of the estuary (site G2) with 0.041 ppm and 0.179 ppm respectively.

The core sampled at site G4 is located within the Beachwood mangrove area of the estuary and was sampled to examine the differences between mangrove and estuarine sediments. The hierarchy of mean metal concentrations at site G4 are as follows: Fe>Al>Ca>S>Mg>P>Ni>Pb>Cu>V>Mn>As>Zn. All elements except Zn were present in this core. Compared to the rest of the sites sampled, mean concentrations of Cu (0.065 ppm), Ni (0.108 ppm), Pb (0.076 ppm), Al (2.690 ppm), V (0.063 ppm) and S (1.224 ppm) were highest at site G4.

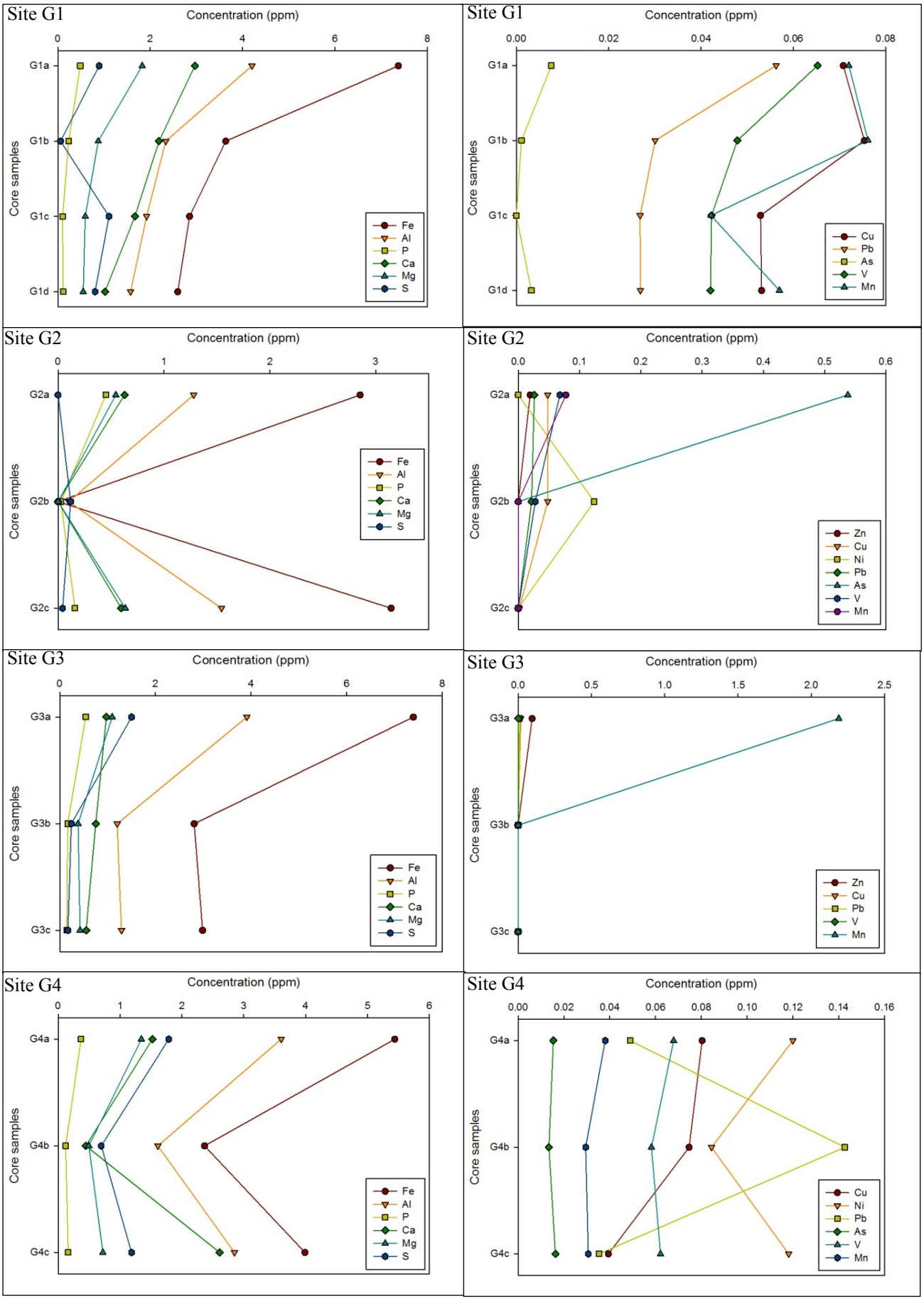

Figure 54: Vertical profiles of element concentrations at core sites in the uMgeni estuary.

Figure 54 displays the trends in down core variation in metal concentrations in the uMgeni estuary. At site G1, all elements with the exception of Cu, Mn and S gradually decreased with depth from the surface. S imitated this pattern however with a rise in concentration in sample G1c. In contrast, Cu and Mn concentrations increased with depth from the surface to sample G1b, and then decreased in concentration in sample G1c. Their highest concentrations occurred in samples G1b and G1d.

Concentrations of Fe, Al, P, Ca and Mg at site G2 followed the same pattern in the core, whereby their highest concentrations were recorded in sample G2b, and then decreased with depth thereafter. Zn, As, and Mn concentrations were observed only at the surface in sample G1a. Pb and V decreased with depth from the surface and were undetected in sample G2c. Maximum concentrations of Cu, Ni and S were recorded in sample G2b.

At site G3, Fe, Al and Mg concentrations decreased by a substantial amount from sample G3a to G3b, and increased slightly in sample G3c. Concentrations of Ca, P and S were highest at the surface and decreased with depth. Zn, Pb, V and Mn were only detected at the surface of the core in sample G3a. As and Ni were not detected in all samples.

In the mangrove area, site G4, concentrations of Fe, Al, P, Ca, Mg, S, Ni, V, As and Mn all decreased with depth from sample G4a to sample G4b, and increased in sample G4c at the base of the core. Variations in concentrations of P, V, As and Mn were minimal with depth. Cu and Pb were observed differently as Cu continually decreased with depth, whereas Pb concentrations increased from the surface, then decreased in sample G4c. Zn was not detected at this site.

5.4.5. Statistical analyses

Table 15: Pearson correlation matrix of elements, organic matter (OM) and texture within all core samples in the uMgeni estuary.

Al	1.000																
As	-0.187	1.000															
Ca	0.730**	-0.181	1.000														
Clay	0.528	0.258	-0.044	1.000													
Cu	0.314	0.071	0.423	0.030	1.000												
Fe	0.959**	-0.107	0.610	0.585	0.112	1.000											
Mg	0.938**	-0.102	0.732**	0.356	0.397	0.916**	1.000										
Mn	0.469	-0.071	-0.056	0.843**	-0.219	0.570	0.261	1.000									
Ni	-0.031	-0.161	-0.030	-0.024	0.374	-0.229	-0.121	-0.202	1.000								
OM	0.278	0.066	-0.260	0.764**	-0.365	0.419	0.174	0.813**	-0.287	1.000							
P	0.738**	0.393	0.339	0.727**	0.141	0.837**	0.753**	0.576	-0.263	0.520	1.000						
Pb	0.161	-0.024	0.101	0.052	0.688	0.018	0.177	-0.161	0.416	-0.343	-0.017	1.000					
S	0.741**	-0.305	0.424	0.578	0.335	0.616	0.570	0.423	0.335	0.265	0.361	0.253	1.000				
Sand	-0.582	-0.240	-0.044	-0.985**	-0.014	-0.653	-0.416	-0.889**	0.108	-0.777**	-0.782**	0.007	-0.540	1.000			
Silt	0.613	0.220	0.116	0.951**	0.000	0.694	0.457	0.907**	-0.175	0.771**	0.810**	-0.056	0.497	-0.990**	1.000		
V	0.311	0.361	0.513	0.018	0.872**	0.122	0.385	-0.343	0.398	-0.457	0.215	0.618	0.312	0.005	-0.023	1.000	
Zn	0.405	0.110	-0.124	0.881**	-0.242	0.526	0.210	0.983**	-0.227	0.833**	0.626	-0.184	0.348	-0.922**	0.934**	-0.310	1.000
	Al	**As**	**Ca**	**Clay**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**OM**	**P**	**Pb**	**S**	**Sand**	**Silt**	**V**	**Zn**

* Correlation is significant at the 0.05 level ($p < 0.05$).
** Correlation is significant at the 0.01 level ($p < 0.01$).

The correlation of elements, organic matter content, and texture in the sediment samples from the uMgeni estuary are given in Table 15 above. The correlation matrix revealed significant relationships between certain elements: Al and Ca, Fe, Mg, P and S ($r = 0.730$, $r = 0.959$, $r = 0.938$, $r = 0.738$ and $r = 0.741$ respectively), Ca and Mg ($r = 0.732$), Cu and V ($r = 0.872$), Fe and Mg ($r = 0.916$), Fe and P ($r = 0.837$), Mg and P ($r = 0.753$), and Mn and Zn ($r = 0.983$). OM correlated significantly with clay, silt, Mn and Zn ($r = 0.764$, $r = 0.771$, $r = 0.813$ and $r = 0.833$ respectively).

Relationships with texture include significant correlation with clay and elements Mn, P, and Zn (r = 0.843, r = 0.727 and r = 0.881 respectively). Silt was significantly correlated to the same elements Mn, P and Zn (r = 0.907, r = 0.810 and r = 0.934 respectively). Sand exhibited only significant negative correlation with the Mn, P, Zn, OM, clay and silt (r = -0.889, r = -0.782, r = -0.922, r = -0.777, r = -0.985 and r = -0.990 respectively).

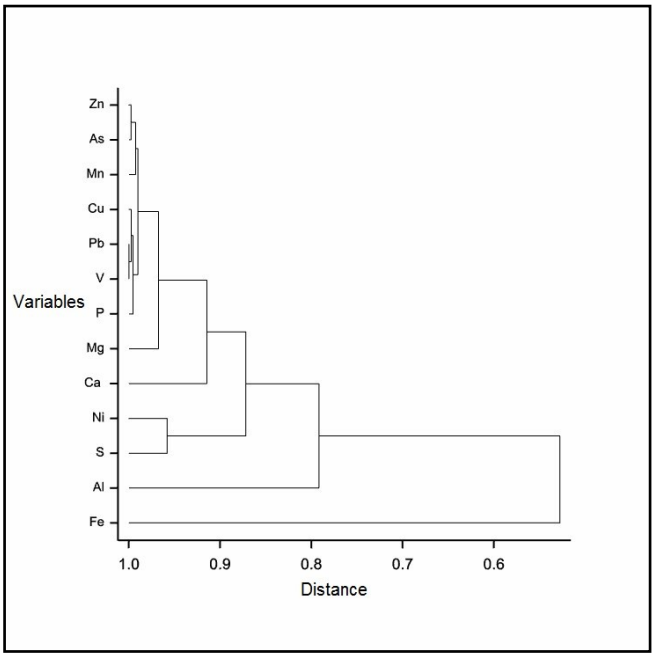

Figure 55: Dendogram obtained by hierarchical cluster analysis of element concentrations in all core samples from the uMgeni estuary.

The dendogram in Figure 55 represents groupings of elements in all core samples in the uMgeni estuary. There are two clusters and two outliers in this dendogram. The first cluster consists of Zn, As, Mn, Cu, Pb, V, Mg and Ca. High similarities exist between subgroups Zn and As, and Pb and V. Zn and As are closely linked to Mn; and Pb and V have high similarities with Cu and P. These two groups are closely linked as their distance is close to 1. Mg and Ca are linked to this group but at lower distances. The second cluster includes Ni and S. This pair shares high similarities and are also linked to the first cluster. Al is linked to the first two clusters but with less similarity. Fe is grouped on its own in this dendogram and displays the highest dissimilarity to the rest of the elements.

5.4.6. Pollution indices

Table 16: Enrichment Factors of elements present within the sediments of the core samples in the uMgeni estuary.

Elements	Clarke value	Core samples												
		G1a	G1b	G1c	G1d	G2a	G2b[1]	G2c	G3a	G3b	G3c	G4a	G4b	G4c
Zn	132	0.000	0.000	0.000	0.000	2.588*	0.000	0.000	4.918*	0.000	0.000	0.000	0.000	0.000
Cu	70	6.859**	14.804**	13.248**	14.612**	12.040**	0.000	0.404	1.808	0.000	0.270	10.548**	**22.532**	7.061**
Ni	80	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	13.775**	**22.295**	18.503**
Pb	16	**23.837**	**25.825**	**29.375**	**32.328**	**28.767**	0.000	0.000	4.657*	0.000	0.000	**28.067**	**188.225**	**27.688**
As	5	10.279**	3.070*	0.000	12.480**	**1884.681**	0.000	0.000	0.000	0.000	0.000	**28.325**	**56.991**	**40.831**
Fe	50000	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Al	81300	0.351	0.395	0.414	0.373	0.276	0.000	0.302	0.325	0.263	0.266	0.408	0.419	0.439
V	150	2.948*	4.387*	4.943*	5.397**	7.937**	0.000	0.000	0.088	0.000	0.000	4.160*	8.197**	5.196**
P	1180	2.784*	2.705*	1.515	1.838	6.706**	0.000	2.152*	3.107*	2.505*	2.084*	2.878*	2.182*	1.729
Ca	36300	0.554	0.829	0.806	0.541	0.303	0.000	0.261	0.181	0.368	0.254	0.386	0.261	0.902
Mg	20900	0.593	0.574	0.498	0.505	0.457	0.000	0.483	0.354	0.325	0.340	0.591	0.502	0.434
Mn	1000	0.488	1.047	0.739	1.097	1.363	0.000	0.000	14.786**	0.000	0.000	0.349	0.623	0.384
S	2400	2.521*	0.338	8.089**	6.447**	0.000	0.000	0.285	4.229*	1.793	1.186	6.848**	6.136**	6.195**

Clarke values after: Martinez *et al*. (2007)
[1]Fe concentration not detected in sample
*Moderate enrichment (EF class: 2-5)
**Significant enrichment (EF class: 5-20)
Bold values indicate very high enrichment (EF class: 20-40)
Red bold values indicate extremely high enrichment (EF class: > 40)

Enrichment factors of elements within core samples in the uMgeni estuary are shown in Table 16 above. From Table 16 it can be seen that overall the sediments in sites G1 and G4 display greater metal enrichment than the other two sites. Cu, Pb, As, V, P and S are all enriched at site G1. Cu, As, V and S are significantly enriched at lower depths i.e. sample G1d. Pb shows very high enrichment in all samples. At site G2, Cu, Pb, As, V and P are enriched. This is mostly concentrated in the surface sample G2a. Cu, V and P are moderately enriched. Pb has very high enrichment (EF = 28.767) and As exhibits extremely high enrichment (EF = 1884.681) at the surface. Site G3 is moderately enriched with Zn, Pb, P, Mn and S, however Mn is significantly enriched in sample G3a (EF = 14.786).

The Beachwood mangroves (site G4) contain a mixed variation of enrichment classes. Cu, Ni, Pb, As, V, P and S are all enriched at this site. Sample G4a is moderately enriched by V and P, significantly enriched by Cu, Ni and S, and is very highly enriched by Pb and As. P is moderately enriched, and V and S are significantly enriched in sample G4b. Very high enrichment of Cu and Ni exists in sample G4b, and Pb and As indicate extremely high EF values in the same sample. In sample G4c, Cu, Ni, V and S are significantly enriched. Pb shows very high enrichment (EF = 27.688) and As displays extremely high enrichment values (EF = 40.831).

The geo-accumulation index was calculated per sample and the results are shown in Table B9 in Appendix B. All resulting values from this index were less than one. Contamination factors for each element were calculated per core along with the pollution load index and the results are shown in Table B3 in Appendix B. All elements presented a contamination factor of less than one. The calculated pollution load index resulted in values less than one for all three cores and is presented in Table B3 in Appendix B.

5.5. Durban Harbour

Estuary: Durban Harbour
Site: H

Recovered core length: 118cm
Date sampled: 9/11/2011

DEPTH (cm)	GRAPHIC LOG	SEDIMENT DESCRIPTION	SEDIMENT UNITS	SAMPLES	AGE (cal BP)	CORE PHOTO (not to scale)
0		Mixture of clay and very fine sand. Dark grey colour. Layers of black sand present. Shells, roots and glass present.	H7	Ha		
		Very fine sand. Dark brown colour. Some black sand present near the top of this layer. Shells and roots present.	H6			
50		Very fine sand. Dark brown colour. Layers of black sand present. Shells and roots present.	H5			
		Fine sand. Shells present.	H4	Hb		
		Mixture of clay and fine sand. Dark brown to black colour. Large shells and roots present.	H3			
		Very fine sand. Grey-brown colour. Tiny shells present.	H2	Hc		
100		Fine to medium sand. Brown colour. Shells present.	H1			
150						
200						

Figure 56: A graphic profile of the core retrieved at site H in the Durban Harbour.

5.5.1. Core profile

A graphic core profile of the sediment sampled in Durban Harbour is presented in Figure 56. This core was sampled on the banks of the Mangrove habitat in the harbour. Analysis of the core allowed for the demarcation of seven sediment units, which are mostly composed of fine sand or mixtures of fine sand and clay, with the inclusion of numerous shell fragments. The 13 cm base consists of fine to medium grained sand (unit H1) overlain by very fine, grey-brown sand (unit H2). The next unit (unit H3) is composed of a 14 cm mixture of dark brown, fine sand and clay, and is followed by a thin, 4 cm layer of fine sand (unit H4). Units H5 and H6 (25 cm) consists of very fine sand that contain black striations. The 42 cm surface layer (unit H7) is made up of a mixture of very fine sand and clay, and includes a high accumulation of shells, roots and pieces of broken glass. Black striations are also visible in this unit.

5.5.2. Organic matter and texture

Table 17: Organic matter content within each core sample for site H.

Core sample site	Samples	Organic matter (%)
H	**Ha**	1.070
	Hb	0.950
	Hc	0.140
	Mean	**0.720**

Organic matter content from the core sampled at site H is presented in Table 17 above. Mean organic matter content is 0.720% for this site. The highest percentage is present in the surface sample Ha with 1.070% and the lowest is in the bottom sample Hc, indicating a decreasing organic matter pattern with depth.

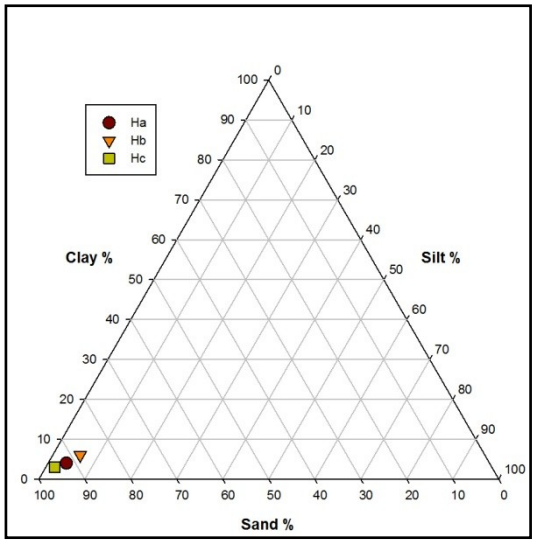

Figure 57: Ternary plot of sand, silt and clay (texture) percentages for each core sample at site H.

Texture results for the core sampled at site H in the Durban Harbour are presented in Figure 57 above. From the graph, it can be seen that the major component of each sample is sand with all samples in the core consisting of over 85% sand. The highest amount of clay and silt is present in sample Hb with 12%, followed by site Ha at 8%, and site Hc at 5%.

5.5.3. Geochemistry

Table 18: Element concentrations with mean at the Durban Harbour core site.

Core sites	Samples	Core depth (cm)	Element concentrations (ppm)											
			Cu	**Ni**	**Pb**	**As**	**Fe**	**Al**	**V**	**P**	**Ca**	**Mg**	**Mn**	**S**
H	**Ha**	**0-67**	0.080	0.118	0.037	0.022	1.643	1.178	0.056	0.196	54.240	1.038	0.017	1.594
	Hb	**67-85**	0.070	0.111	0.038	0.027	2.528	2.020	0.061	0.260	128.524	1.291	0.017	1.717
	Hc	**85-115**	0.038	0.117	0.031	0.021	0.676	0.673	0.054	1.855	37.456	1.196	0.010	0.780
Mean			**0.063**	**0.116**	**0.035**	**0.023**	**1.616**	**1.290**	**0.057**	**0.770**	**73.406**	**1.175**	**0.015**	**1.364**

Element concentrations of core samples from the Durban Harbour are shown in Table 18. The hierarchy of mean metal concentrations for this site are as follows:

H: Ca>Fe>S>Al>Mg>P>Ni>Cu>V>Pb>As>Mn.

Ca occurred at very high concentrations compared to the rest of the elements at this site. Its highest concentration was 128.524 ppm in sample Hb. The other elements were all recorded at mean concentrations less than 2 ppm.

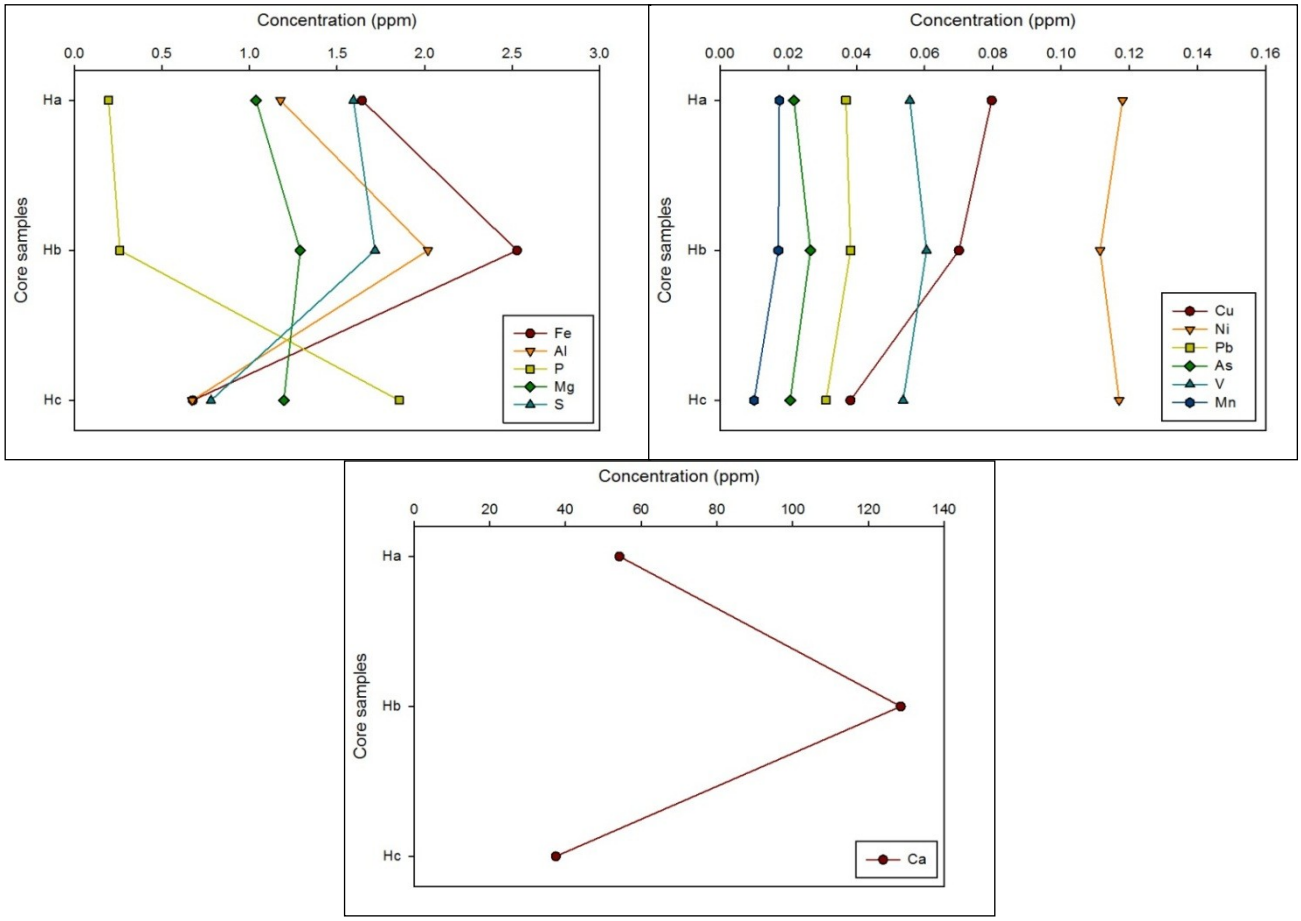

Figure 58: Vertical profiles of element concentrations at the core site in the Durban Harbour.

Figure 58 displays the trends in down core variation of metal concentrations for the Durban Harbour sediment core. Ca was graphed separately due to the large concentration difference to the rest of the elements. At this site, all elements except P, Cu and Ni, increased in concentration from the surface to the lower depths in sample Hb. In sample Hc, their concentrations decreased. Ni displayed different variations with depth as it decreased in concentration from sample Ha to Hb, and then increased in sample Hc. P and Cu concentrations contrasted each other as P increased with depth and Cu decreased with depth.

5.5.4. Statistical analyses

Table 19: Pearson correlation matrix of elements, organic matter (OM) and texture within all core samples in the Durban Harbour.

Al	1.000															
As	0.981	1.000														
Ca	0.979	1.000**	1.000													
Clay	0.999*	0.989	0.987	1.000												
Cu	0.629	0.465	0.457	0.592	1.000											
Fe	0.986	0.934	0.930	0.977	0.751	1.000										
Mg	0.499	0.659	0.666	0.539	-0.359	0.346	1.000									
Mn	0.762	0.621	0.614	0.732	0.983	0.860	-0.180	1.000								
Ni	-0.868	-0.948	-0.951	-0.890	-0.161	-0.772	-0.863	-0.341	1.000							
OM	0.707	0.555	0.547	0.673	0.995	0.816	-0.260	0.997	-0.263	1.000						
P	-0.764	-0.623	-0.616	-0.733	-0.982	-0.862	0.177	-1.000**	0.343	-0.996	1.000					
Pb	0.886	0.778	0.772	0.863	0.918	0.951	0.040	0.976	-0.539	0.954	-0.976	1.000				
S	0.855	0.737	0.730	0.829	0.941	0.930	-0.023	0.988	-0.484	0.971	-0.988	0.998*	1.000			
Sand	-0.998*	-0.967	-0.964	-0.994	-0.676	-0.994	-0.445	-0.801	0.836	-0.749	0.802	-0.912	-0.885	1.000		
Silt	0.990	0.943	0.940	0.982	0.734	1.000*	0.370	0.847	-0.788	0.801	-0.848	0.943	0.920	-0.997	1.000	
V	0.995	0.995	0.994	0.999*	0.551	0.965	0.581	0.696	-0.912	0.634	-0.698	0.836	0.800	-0.987	0.971	1.000
	Al	**As**	**Ca**	**Clay**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**OM**	**P**	**Pb**	**S**	**Sand**	**Silt**	**V**

***** Correlation is significant at the 0.05 level ($p < 0.05$).
****** Correlation is significant at the 0.01 level ($p < 0.01$).

Correlation was the only statistical analysis performed for this estuary as only one core was sampled. The correlation of elements, organic matter content, and texture in the sediment samples from the Durban Harbour are given in Table 19 above. Significant positive correlations between elements were As and Ca (r = 1.000) and Pb and S (r = 0.998). Mn and P displayed significant negative correlation at this site (r = -1.000). The correlation matrix also revealed significant correlations between textural properties and elements: clay and Al (r = 0.999), clay and V (r = 0.999) and silt and Fe (r = 1.000). Sand showed significant negative correlation with Al (r = -0.998).

5.5.5. Pollution indices

Table 20: Enrichment Factors of elements present within the sediments of the core samples in the Durban Harbour.

Elements	Clarke value	Core samples		
		Ha	Hb	Hc
Cu	70	**34.636**	19.802**	**40.395**
Ni	80	**44.894**	**27.556**	**108.145**
Pb	16	**70.192**	**47.351**	**143.723**
As	5	**132.195**	**104.872**	**304.120**
Fe	50000	1.000	1.000	1.000
Al	81300	0.441	0.491	0.612
V	150	11.291**	7.987**	**26.450**
P	1180	5.059**	4.363*	**116.207**
Ca	36300	**45.472**	**70.032**	**76.276**
Mg	20900	1.511	1.221	4.230*
Mn	1000	0.530	0.338	0.742
S	2400	**20.211**	14.150**	**24.036**

Clarke values after: Martinez *et al.* (2007)
*Moderate enrichment (EF class: 2-5)
**Significant enrichment (EF class: 5-20)
Bold values indicate very high enrichment (EF class: 20-40)
Red bold values indicate extremely high enrichment (EF class: > 40)

Enrichment factors of elements within core samples in the Durban Harbour are shown in Table 20 above. It can be seen that the sediment samples are highly enriched with most of the elements. Al and Mn are the only two elements that are not enriched at this site. Pb, As and Ca exhibit extremely high enrichment in all three samples in this core with a hierarchy of As>Pb>Ca. The maximum EF value is retained by As with 304.120 in sample Hc. Cu, Ni, V, P and S have significant to extremely high enrichment values, with their highest EF values occurring in sample Hc. Generally, the hierarchy of enrichment factor values per sample are Hc>Ha>Hb.

The geo-accumulation index was calculated per sample and the results are shown in Table B10 in Appendix B. All resulting values from this index were less than one. Contamination factors for each element were calculated per core along with the pollution load index and the results are shown in Table B4 in Appendix B. All elements presented a contamination factor of less than one. The calculated pollution load index resulted in values less than one for all three cores and is presented in Table B4 in Appendix B.

5.6. Isipingo estuary

Estuary: Isipingo
Site: S1

Recovered core length: 116cm
Date sampled: 9/11/2011

DEPTH (cm)	GRAPHIC LOG	SEDIMENT DESCRIPTION	SEDIMENT UNITS	SAMPLES	AGE (cal BP)	CORE PHOTO (not to scale)
0		Mixture of clay and fine sand. Dark brown colour. Roots present.	S1.9	S1a		
		Clay. Brown colour.	S1.8			
		Mixture of clay and fine sand.	S1.7			
50		Clay. Dark brown colour. Roots present.	S1.6	S1b		
		Mixture of clay and fine sand. Brown colour.	S1.5			
		Very fine sand.	S1.4	S1c		
		Fine sand.	S1.3			
		Mixture of clay and fine sand.	S1.2			
100		Fine sand. Light brown colour. Some thin layers of black sand present.	S1.1			
150						
200						

Figure 59: A graphic profile of the core retrieved at site S1 in the Isipingo estuary.

Estuary: Isipingo
Site: S2

Recovered core length: 100cm
Date sampled: 9/11/2011

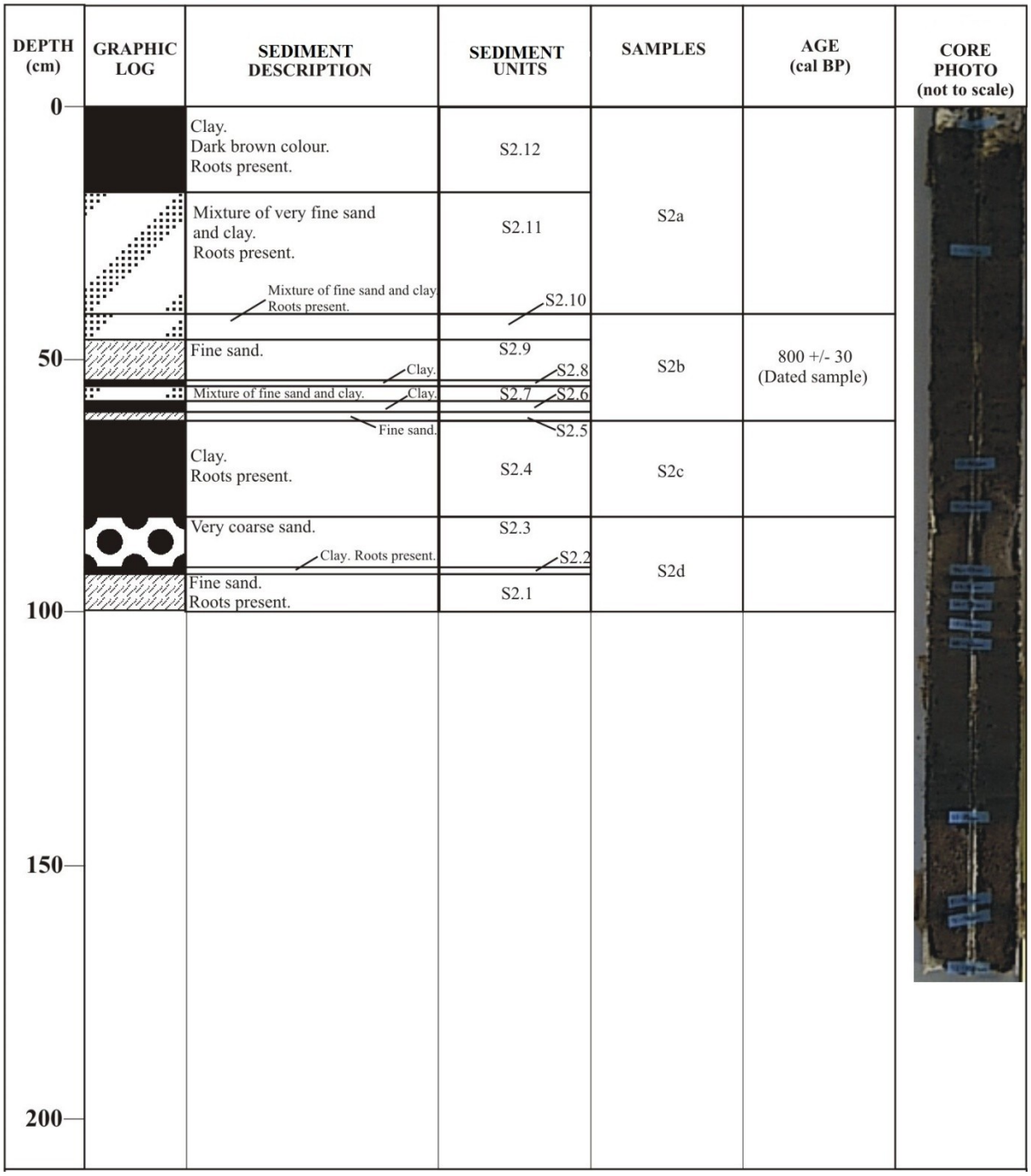

Figure 60: A graphic profile of the core retrieved at site S2 in the Isipingo estuary.

Estuary: Isipingo
Site: S3

Recovered core length: 142cm
Date sampled: 9/11/2011

DEPTH (cm)	GRAPHIC LOG	SEDIMENT DESCRIPTION	SEDIMENT UNITS	SAMPLES	AGE (cal BP)	CORE PHOTO (not to scale)
0		Mixture of very fine sand and clay. Brown colour. Roots present.	S3.8	S3a		
		Mixture of very fine sand and clay. Dark brown colour. Roots present.	S3.7			
50		Clay. Dark brown colour. Roots present.	S3.6			
		Mixture of very fine sand and clay. Dark brown colour. Roots present.	S3.5	S3b		
		Fine sand. Dark brown colour. Roots present.	S3.4			
		Mixture of very fine sand and clay.	S3.3			
		Fine sand. Brown colour.	S3.2			
100		Clay. Dark brown colour. Roots present.	S3.1	S3c	830 +/-30 (Dated sample)	
150						
200						

Figure 61: A graphic profile of the core retrieved at site S3 in the Isipingo estuary.

5.6.1. Core profiles

Graphic core profiles of the cores sampled in the Isipingo estuary are presented by Figures 59, 60 and 61. Cores S1 and S2 were sampled along the banks of the mangrove habitat in the Isipingo estuary. The core sampled at site S1 presented nine sediment units after analysis (Figure 59). Eight sediment units rest upon 21 cm of brown, fine sand (unit S1.1) which is followed by a thin 4 cm layer of clay and fine sand (unit S1.2). The next three overlying layers (units S1.3 – S1.5) represent a gradual fining of sediments from fine sand to a mixture of clay and fine sand. The next four layers (unit S1.6- S1.9) reaching the surface contains alternating layers of clay and mixtures of clay and fine sand. The surface layer consists of a dark brown mixture of clay and sand, with roots present (unit S1.9).

Sedimentological analysis of the core sampled at site S2 permitted the delimitation of twelve sediment units whose base consists of 8 cm of fine sand (unit S2.1) (Figure 60). The overlying unit consists of a thin 1 cm layer of clay (unit S2.2), followed by 10 cm of very coarse sand (unit S2.3). The next overlying layer (unit S2.4) is clay with numerous roots present. The next four layers (units S2.5 – S2.8) are made up of thin 1-3 cm layers of clay, mixtures of fine sand and clay, and fine sand. Unit S2.9 consists of fine sand, followed by unit S2.10 containing a mixture of fine sand and clay. A 24 cm thick layer (unit S2.11) follows this, comprising of a mixture of very fine sand and clay. Finally the core is capped by 17 cm of dark brown clay (unit S2.12) containing roots.

Eight sediment units were demarcated in the core sampled at site S3, and are mainly composed of clay, mixtures of clay and fine sand and fine sand (Figure 61). The first unit (S3.1) at the base of the core is made up of 46 cm of black clay with numerous roots present. The next four overlying layers (units S3.2 - S3.5) make up the sandy portion of the core consisting of 31 cm of alternating layers of fine sand and mixtures of fine sand and clay. Another 47 cm of black clay follows this (unit S3.6) and is overlain by an 11 cm mixture of very fine sand and clay, which is dark brown in colour (unit S3.7). The surface layer is a 7 cm mixture of brown, very fine sand and clay with roots present (unit S3.8).

5.6.2. Stratigraphic cross-section

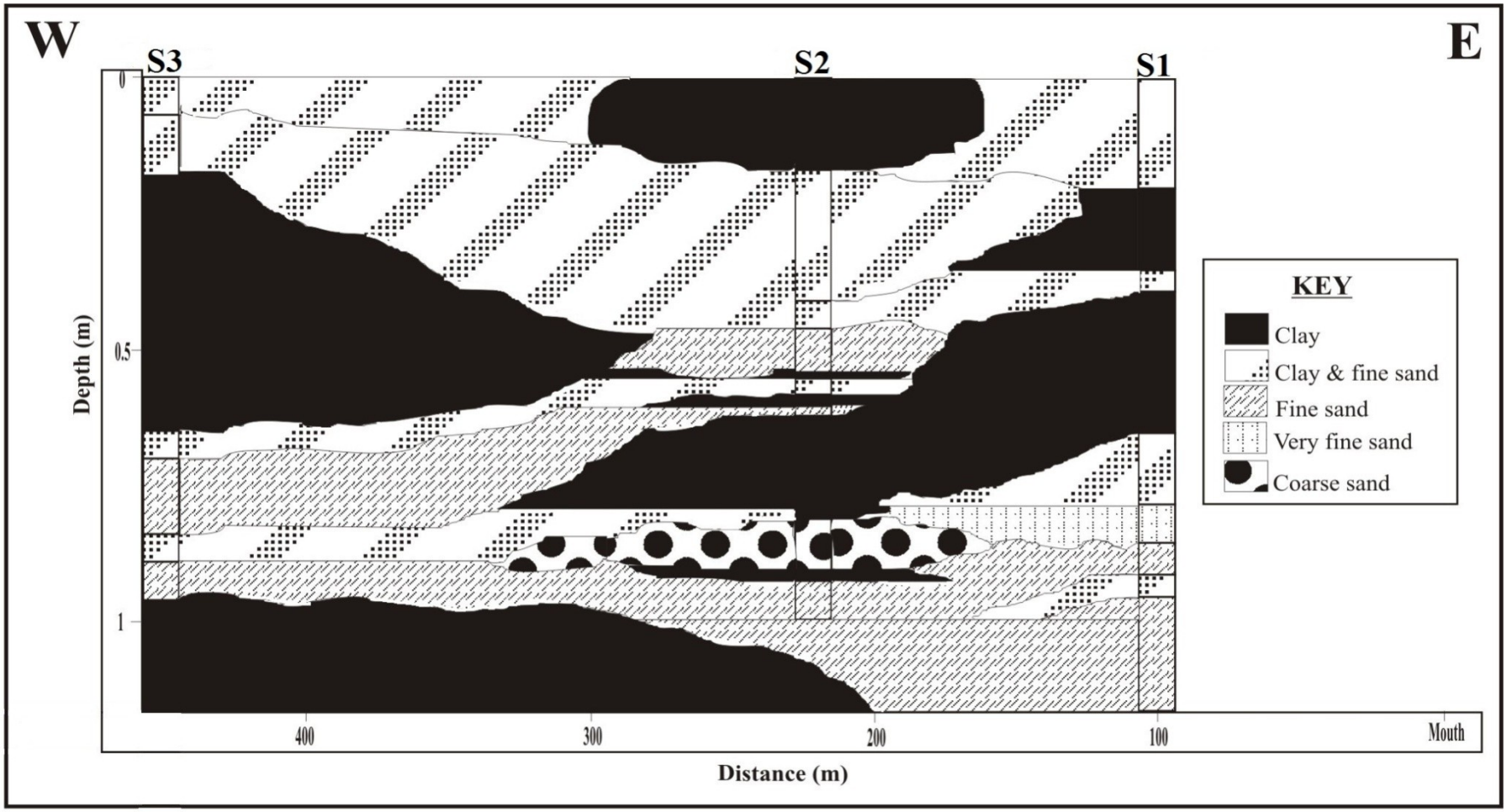

Figure 62: Schematic stratigraphic cross-sectional representation, longitudinal to the estuary axis based on and showing the three core sites from the head (left side of the diagram) to the mouth (right of the diagram) of the Isipingo estuary.

Figure 62 above presents a stratigraphic cross-section of the top 1.15 m of the Isipingo estuary, including the locations of the cores sampled at sites S1, S2 and S3. Due to the variation of recovered core depths with sites, the last 0.27 m of unit S3.1 at site S3 has been omitted from the diagram. From the cross-section, it can be seen that the majority of the sediments are clay and mixtures of fine sand and clay, especially at the surface of the estuary down to approximately 0.45 m depth. Below this there is an accumulation of fine sand at the head of the estuary to approximately 0.95 cm and this continues to the mouth of the estuary, with an interruption of clay in the middle section of the estuary at approximately 0.6 m. The sediments (depth of 1.15 m) in this estuary are generally fine however there is a presence of coarse sand in the middle section of the estuary at 0.8 m, which is distinct and different to the rest of the sediment body, and indicates a coarsening of sediments with depth downstream towards the mouth.

5.6.3. Organic matter and texture

Table 21: Organic matter content within each core sample for sites S1, S2 and S3.

Core sample sites	Samples	Organic matter (%)
S1	**S1a**	3.630
	S1b	2.410
	S1c	1.070
	Mean	**2.370**
S2	**S2a**	3.080
	S2b	0.530
	S2c	5.370
	S2d	0.280
	Mean	**2.315**
S3	**S3a**	3.220
	S3b	0.950
	S3c	5.090
	Mean	**3.087**

Organic matter content in the Isipingo estuary is given in Table 21 above. Mean organic matter content is highest at site S3 with 3.087% and the lowest occurring at site S2 with 2.315%. Organic matter percentages are highest for sample S2c at 5.370%, followed closely by sample S3c at 5.090%. The lowest percentage is found within sample S2d containing 0.280%. The patterns exhibited by the cores indicate a decrease of organic matter with depth at site S1 near the mouth; and a decrease and then increase with depth at sites S2 and S3.

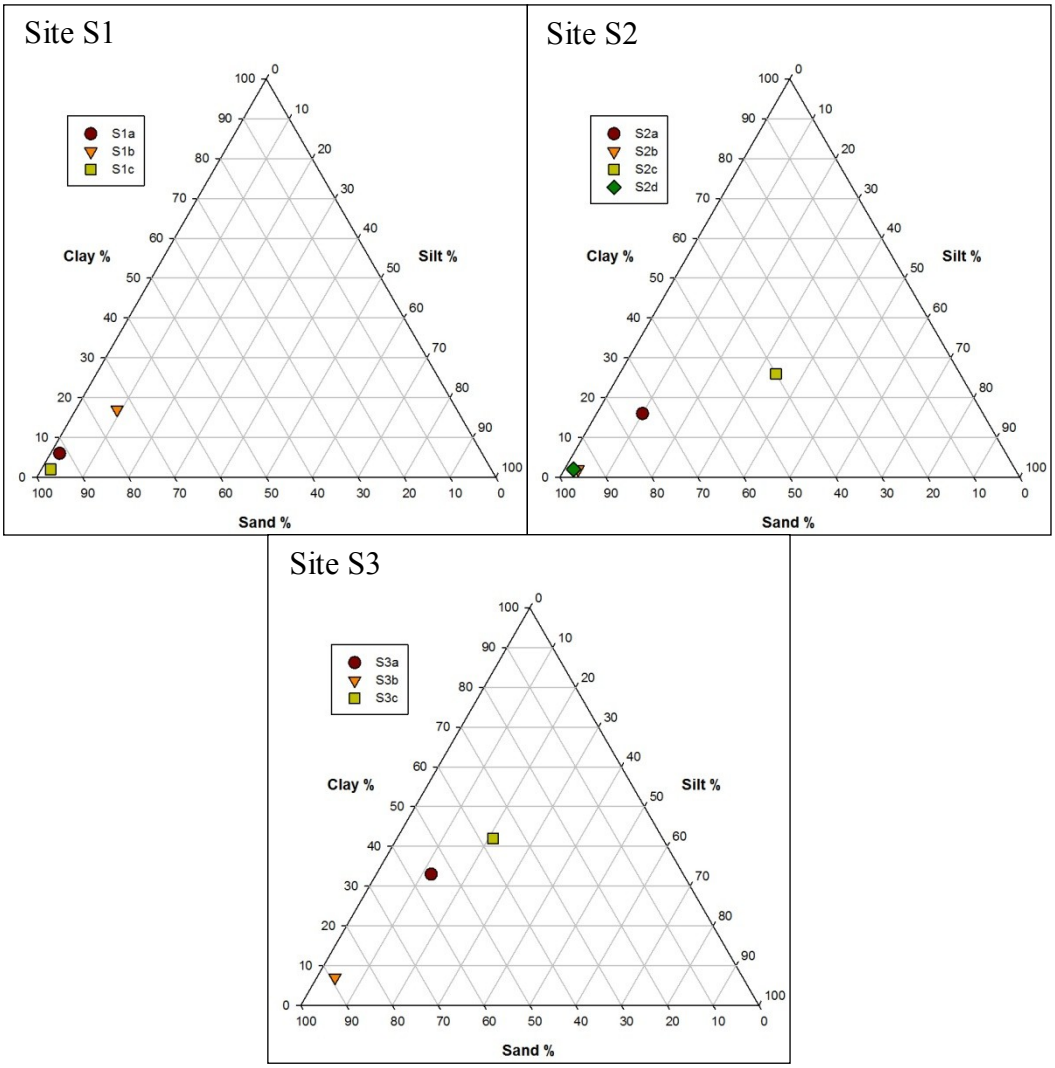

Figure 63: Ternary plots of sand, silt and clay (texture) percentages for each core sample at sites S1, S2 and S3.

Texture results for cores sampled in the Isipingo estuary are shown above (Figure 63). The major composition of the sediments includes clays and silts especially at sites S2 and S3. The highest percentage of clay and silt is found at site S3. Site S1 has the lowest percentages of clay and silt with the majority of that core composed of sand. Sample S3c contains the highest amount of clay and silt with 63%, followed closely by sample S2c with 60%. At sites S2 and S3 it can be seen that the amount of fine material (clay and silt) decreases with depth and then increases again.

5.6.4. Geochemistry

Table 22: Element concentrations with means per core at each core site in the Isipingo estuary.

Core sites	Samples	Core depth (cm)	Element concentrations (ppm)									
			Zn	Cu	Ni	Fe	Al	P	Ca	Mg	Mn	S
S1	S1a	0-39	0.115	0.014	0.093	7.626	2.839	0.178	14.911	1.153	0.000	2.670
	S1b	39-78	0.000	0.010	0.092	14.924	5.927	0.346	27.318	2.248	0.051	5.600
	S1c	78-116	0.000	0.003	0.088	4.167	1.557	0.193	34.804	1.050	0.000	1.211
Mean			**0.038**	**0.009**	**0.091**	**8.905**	**3.441**	**0.239**	**25.678**	**1.484**	**0.017**	**3.160**
S2	S2a	0-41	0.043	0.017	0.059	14.902	6.320	0.292	11.992	1.703	0.006	8.300
	S2b	41-62	0.000	0.006	0.095	4.538	1.770	0.070	20.814	0.666	0.000	1.247
	S2c	62-81	0.000	0.007	0.096	14.102	5.447	0.110	3.989	1.194	0.179	6.551
	S2d	81-100	0.000	0.004	0.062	4.156	2.024	1.243	3.780	0.426	0.000	0.882
Mean			**0.011**	**0.008**	**0.078**	**9.425**	**3.890**	**0.429**	**10.144**	**0.997**	**0.046**	**4.245**
S3	S3a	0-65	0.000	0.024	0.102	12.098	16.282	5.940	6.597	5.970	1.070	3.752
	S3b	65-96	0.000	0.005	0.094	6.359	2.377	0.070	4.432	0.686	0.000	1.449
	S3c	96-142	0.000	0.011	0.049	16.757	5.987	0.242	20.666	2.484	0.144	6.640
Mean			**0.000**	**0.013**	**0.081**	**11.738**	**8.215**	**2.084**	**10.565**	**3.047**	**0.405**	**3.947**

Element concentrations of all core samples from the Isipingo estuary are shown in Table 22. The hierarchy of mean metal concentrations per site are as follows:

S1: Ca>Fe>Al>S>Mg>P>Ni>Zn>Mn>Cu;

S2: Ca>Fe>S>Al>Mg>P>Ni>Mn>Zn>Cu and,

S3: Fe>Ca>Al>S>Mg>P>Mn>Ni>Cu>Zn.

Maximum mean concentrations of elements Cu (0.013 ppm), Fe (11.738 ppm), Al (8.215 ppm), P (2.084 ppm), Mg (3.047 ppm) and Mn (0.405 ppm) occurred at site S3. Mean concentrations of Fe, Al, P and Mn decreased towards the mouth of the estuary. Mean concentrations of Zn (0.038 ppm) and Ca (25.678 ppm) were highest at site S1 near the mouth of the estuary and decreased towards the head of the estuary (site S3). S was the only element (4.245 ppm) whose highest mean concentration occurred at site S2.

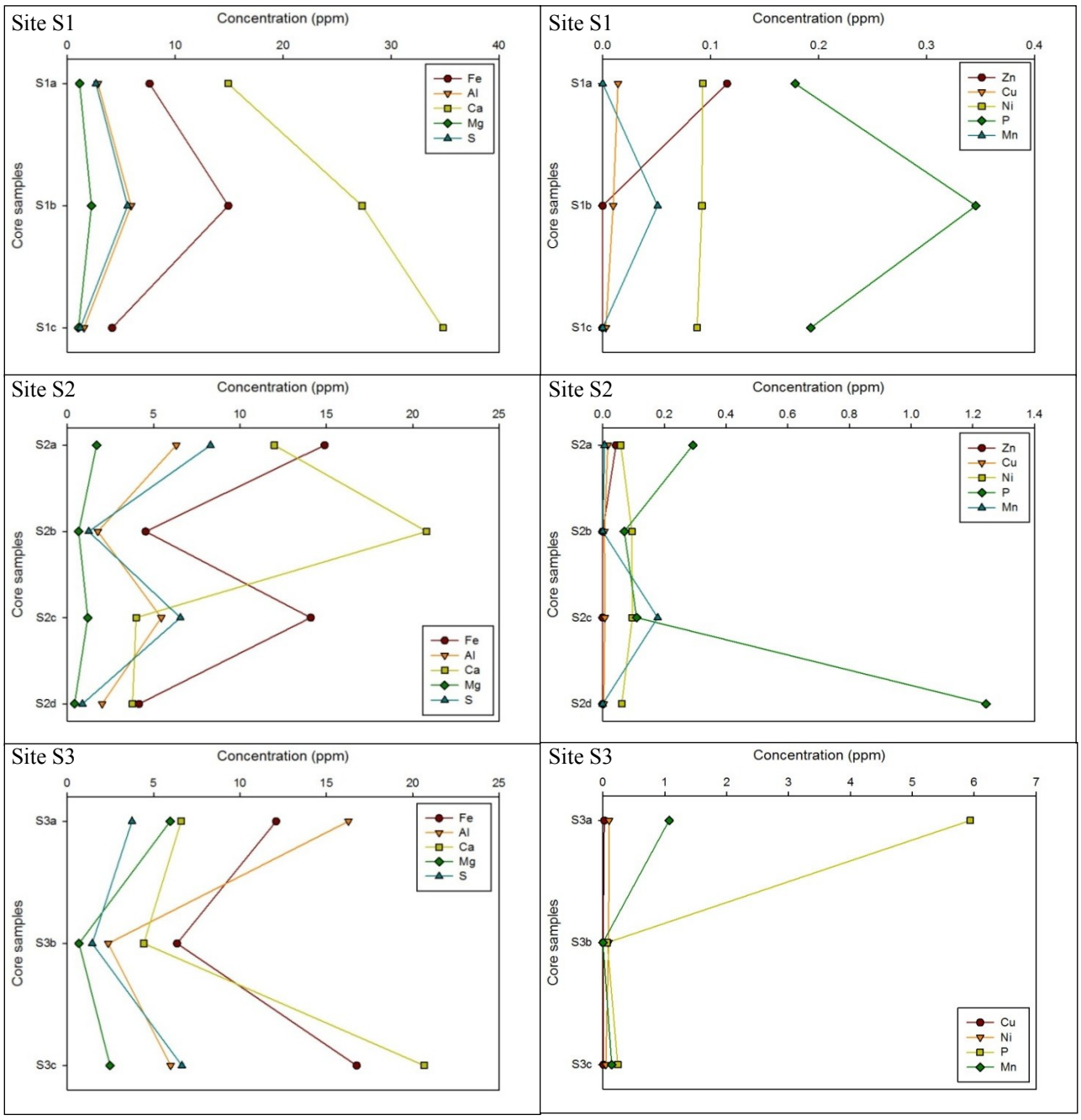

Figure 64: Vertical profiles of element concentrations at core sites in the Isipingo estuary.

Figure 64 displays the trends in down core variation in metal concentrations in the Isipingo estuary. The core sampled at site S1, which is located near the mouth of the estuary, exhibited down core variation with all metals. Zn, Cu and Ni concentrations decreased continually with depth. Other elements present in the samples, Fe, Al, P, Mg, Mn and S, displayed a different pattern with depth. These elements increased from sample S1a to S1b, and then decreased in concentrations in sample S1c. Ca concentrations increased continually with depth.

Site S2 displayed similar concentration variation with depth with certain elements. Surface concentrations of Cu, Fe, Al, Mg, Mn and S were high and decreased with depth; however it spiked in concentration in sample S2c. Zn was only detected in surface sample S2a. Ni concentrations increased from the surface to sample S2c and decreased in sample S2d. P generally increased with depth, but dropped in concentration in sample S2b. Ca decreased with depth overall, however a sharp increase in concentration in sample S2b was detected.

Similar variations in concentrations occurred with depth at site S3. All elements present within the samples (Cu, Fe, Al, P, Ca, Mg, Mn and S) with the exception of Ni, exhibited the same trend with depth. These elements exhibited high concentrations in surface sample S3a, and was followed by a drop in concentration in sample S3b. Thereafter increased concentrations at the base of the core (sample S3c) existed. Concentrations of Ni continually decreased with depth. Zn was not present at this site.

5.6.5. Statistical analyses

Table 23: Pearson correlation matrix of elements, organic matter (OM) and texture within all core samples in the Isipingo estuary.

Al	1.000													
Ca	-0.263	1.000												
Clay	0.716*	-0.144	1.000											
Cu	0.857**	-0.217	0.556	1.000										
Fe	0.563	-0.044	0.849**	0.539	1.000									
Mg	0.970**	-0.082	0.694	0.832**	0.495	1.000								
Mn	0.936**	-0.293	0.582	0.730*	0.283	0.934**	1.000							
Ni	0.160	-0.019	-0.236	0.065	-0.284	0.169	0.320	1.000						
OM	0.443	-0.137	0.807**	0.481	0.814**	0.384	0.285	-0.133	1.000					
P	0.869**	-0.319	0.392	0.691	0.103	0.875**	0.955**	0.260	0.058	1.000				
S	0.420	-0.051	0.704*	0.476	0.947**	0.315	0.113	-0.369	0.778**	-0.051	1.000			
Sand	-0.605	0.206	-0.956**	-0.417	-0.848**	-0.539	-0.476	0.180	-0.869**	-0.253	-0.751*	1.000		
Silt	0.364	-0.273	0.758*	0.161	0.723*	0.246	0.260	-0.073	0.826**	0.023	0.701*	-0.916**	1.000	
Zn	-0.135	-0.035	-0.217	0.351	-0.033	-0.132	-0.203	0.019	0.235	-0.171	0.064	0.246	-0.258	1.000
	Al	**Ca**	**Clay**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**OM**	**P**	**S**	**Sand**	**Silt**	**Zn**

* Correlation is significant at the 0.05 level ($p < 0.05$).
** Correlation is significant at the 0.01 level ($p < 0.01$).

The correlation of elements, organic matter content, and texture in the sediment samples from the Isipingo estuary are given in Table 23 above. The correlation matrix revealed significant relationships between elements: Al and Cu, Mg, Mn and P ($r = 0.857$, $r = 0.970$, $r = 0.936$ and $r = 0.869$ respectively), Cu and Mg ($r = 0.832$) and Cu and Mn ($r = 0.730$), Fe and S ($r = 0.947$), Mg and Mn ($r = 0.934$) and Mg and P ($r = 0.875$) and Mn and P ($r = 0.955$). Organic matter was significantly correlated with Fe ($r = 0.814$) and S ($r = 0.778$) as well as clay and silt ($r = 0.807$ and $r = 0.826$ respectively). Textural properties, clay, silt and sand were also significantly correlated with elements: clay and Al, Fe and S ($r = 0.716$, $r = 0.849$ and $r = 0.704$ respectively); silt and Fe ($r = 0.723$) and silt and S ($r = 0.701$); sand displayed a significant negative correlation

with Fe and S (r = -0.848 and r = -0.751 respectively). Clay and silt also showed a significant negative correlation with sand (r = -0.956 and r = -0.916 respectively).

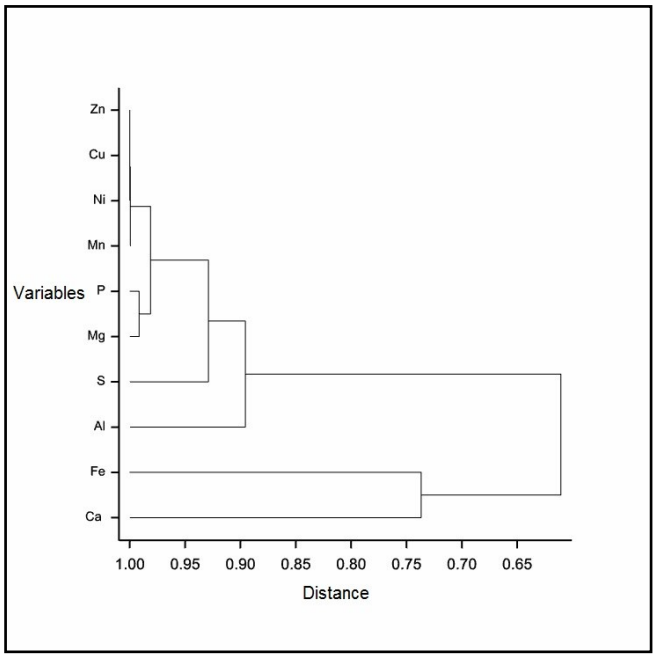

Figure 65: Dendogram obtained by hierarchical cluster analysis of element concentrations in all core samples from the Isipingo estuary.

The dendogram in Figure 65 represents groupings of elements in all core samples in the Isipingo estuary. There are two clusters that are evident in the dendogram. The first cluster consists of Zn, Cu, Ni, Mn, P, Mg, S and Al. This cluster contains two subgroups. The first subgroup includes Zn, Cu, Ni, Mn which have distances of 1 indicating very high similarities. P and Mg have formed another subgroup with high similarities. S and Al are related to these groups but with lower distances indicating decreasing similarities. The second cluster consists of Fe and Ca, which are similar and are also linked to the first cluster.

5.6.6. Pollution indices

Table 24: Enrichment Factors of elements present within the sediments of the core samples in the Isipingo estuary.

Elements	Clarke value	Core samples									
		S1a	**S1b**	**S1c**	**S2a**	**S2b**	**S2c**	**S2d**	**S3a**	**S3b**	**S3c**
Zn	132	5.723**	0.000	0.000	1.096	0.000	0.000	0.000	0.000	0.000	0.000
Cu	70	1.328	0.466	0.500	0.793	0.918	0.359	0.616	1.398	0.528	0.453
Ni	80	7.605**	3.851*	13.132**	2.476*	13.064**	4.262*	9.328**	5.253**	9.209**	1.813
Fe	50000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Al	81300	0.229	0.244	0.230	0.261	0.240	0.238	0.299	0.828	0.230	0.220
P	1180	0.991	0.982	1.959	0.830	0.655	0.331	12.674**	**20.806**	0.467	0.612
Ca	36300	2.693*	2.521*	11.504**	1.108	6.318	0.390	1.253	0.751	0.960	1.699
Mg	20900	0.362	0.360	0.603	0.273	0.351	0.203	0.245	1.181	0.258	0.355
Mn	1000	0.000	0.171	0.000	0.021	0.000	0.633	0.000	4.424*	0.000	0.429
S	2400	7.295**	7.817**	6.055**	11.603**	5.724**	9.678**	4.421*	6.461**	4.747*	8.255**

Clarke values after: Martinez *et al*. (2007)
*Moderate enrichment (EF class: 2-5)
**Significant enrichment (EF class: 5-20)
Bold values indicate very high enrichment (EF class: 20-40)

Enrichment factors of elements within core samples in the Isipingo estuary are shown in Table 24 above. Elements enriched in this estuary include Zn, Ni, P, Ca, Mn and S. Zn displayed significant enrichment in sample S1a, at the surface of site S1, near the mouth of the estuary. Ni and S were moderately to significantly enriched throughout all samples, except in sample S3c for Ni where there was no enrichment. P was moderately enriched in sample S2d, but displayed very high enrichment in surface sample S3a (EF = 20.806), near the head of the estuary. Ca was enriched only at site S1, where the soils were moderately to significantly enriched. Mn was only enriched in sample S3a, and this value (EF = 4.424) fell within the moderate enrichment class.

The geo-accumulation index was calculated per sample and the results are shown in Table B11 in Appendix B. All resulting values from this index were less than one. Contamination factors for each element were calculated per core along with the pollution load index and the results are shown in Table B5 in Appendix B. All elements presented a contamination factor of less than one. The calculated pollution load index resulted in values less than one for all three cores and is presented in Table B5 in Appendix B.

5.7. uMbokodweni estuary

Estuary: uMbokodweni
Site: B1

Recovered core length: 116cm
Date sampled: 9/11/2011

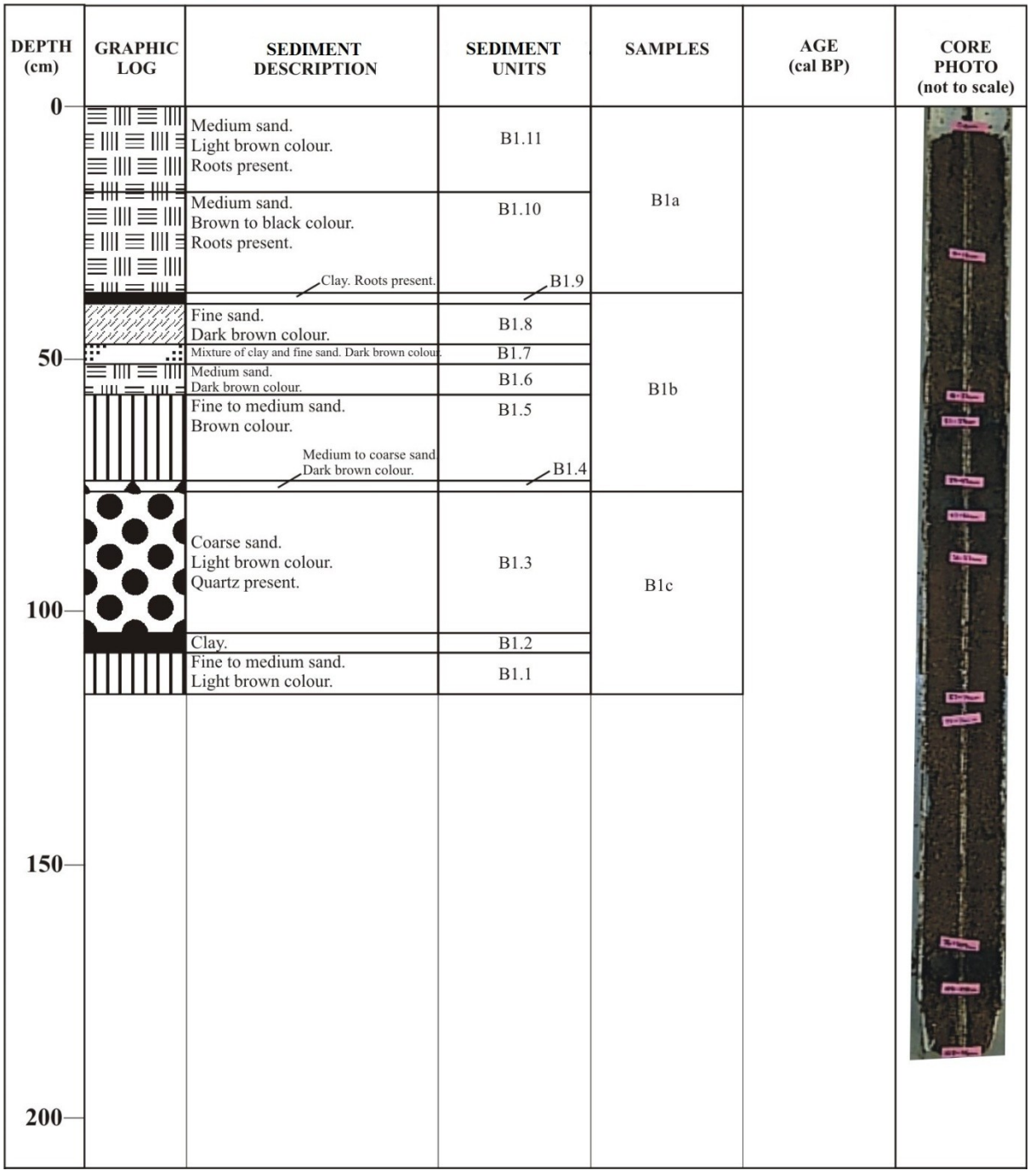

Figure 66: A graphic profile of the core retrieved at site B1 in the uMbokodweni estuary.

Estuary: uMbokodweni
Site: B2

Recovered core length: 90cm
Date sampled: 9/11/2011

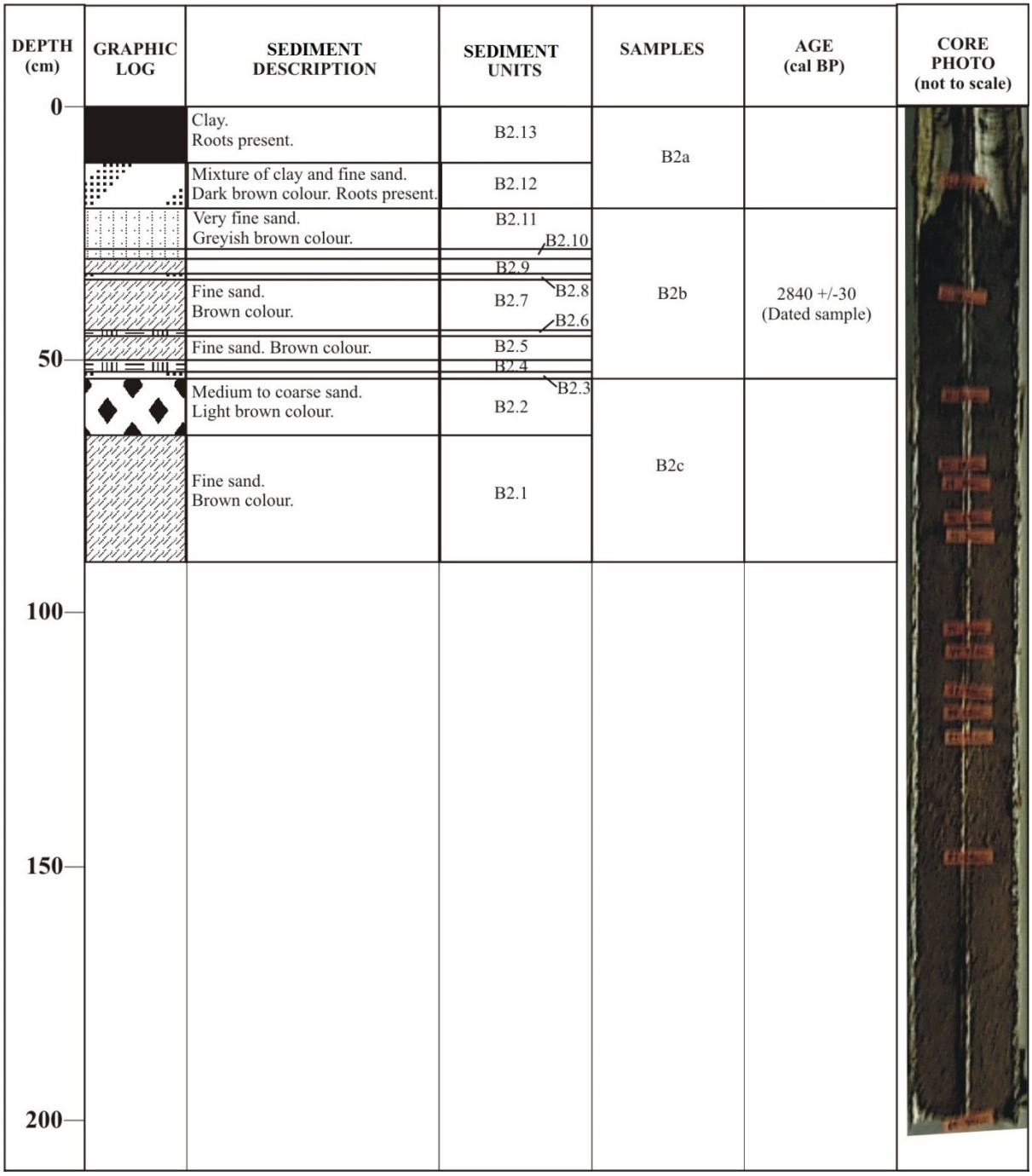

Figure 67: A graphic profile of the core retrieved at site B2 in the uMbokodweni estuary.

Estuary: uMbokodweni
Site: B3

Recovered core length: 80cm
Date sampled: 9/11/2011

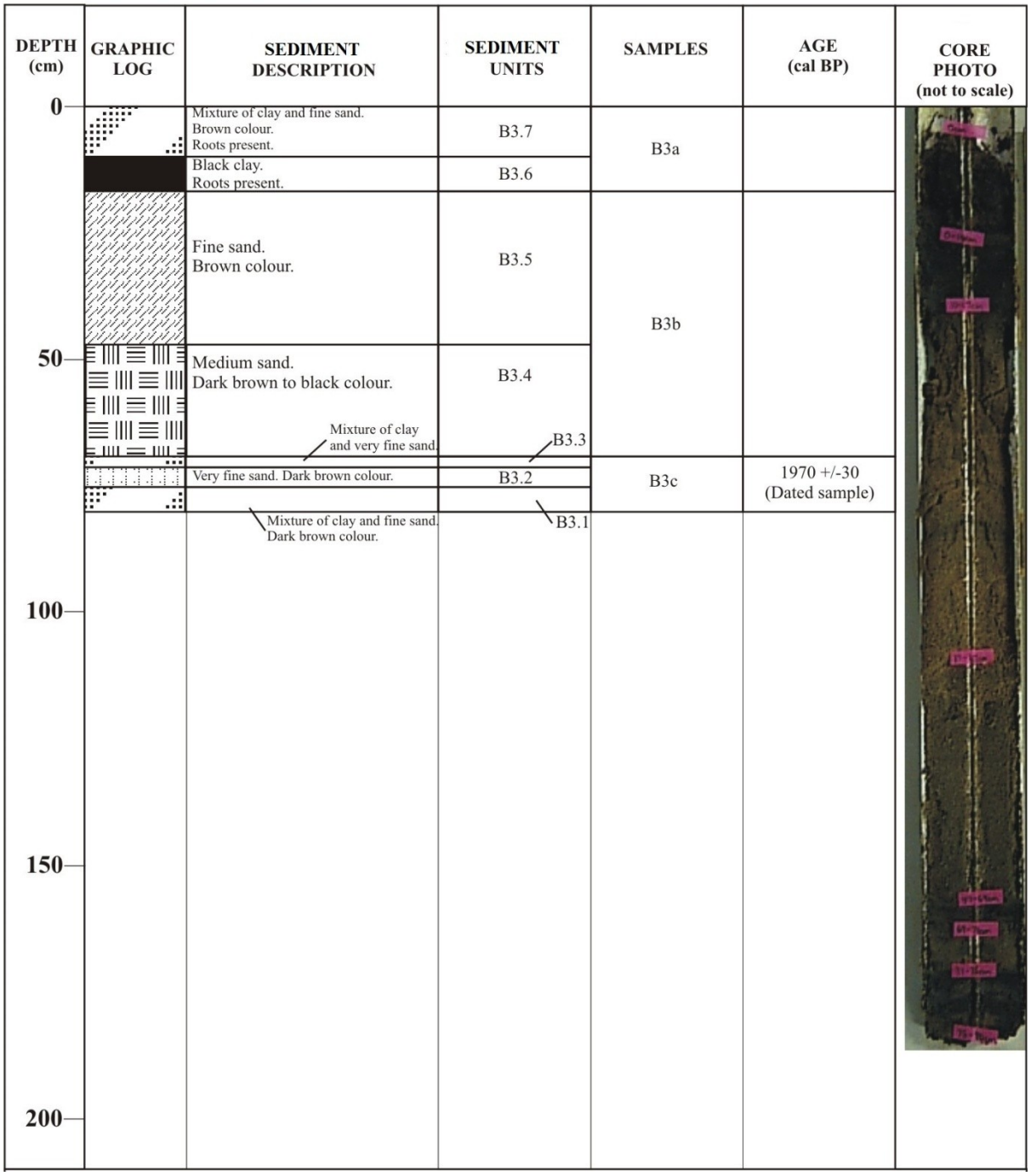

Figure 68: A graphic profile of the core retrieved at site B3 in the uMbokodweni estuary.

5.7.1. Core profiles

Graphic core profiles of the cores sampled in the uMbokodweni estuary are presented by Figures 66, 67 and 68. Analysis of the core at site B1 allowed for the determination of eleven sediment units (Figure 66). The bottom layer is composed of 8 cm of fine to medium grained sand (unit B1.1) and is overlain by 4cm of clay (unit B1.2). The next layer is 28 cm thick, and composes of coarse sand that is light brown in colour (unit B1.3). Following this unit are three units (units B1.4 – B1.6) composed of sand that varies in grain size from medium-coarse, fine to medium, and medium grained sand. Overlying these layers is a thin 4 cm layer of clay and fine sand (unit B1.7) covered by an 8 cm layer of dark brown, fine sand (unit B1.8). The next unit (unit B1.9) is a 2 cm layer of clay, and this is followed by a 19 cm layer (unit B1.10) of medium grained sand that is brown in colour and contains roots. The surface layer is a light brown, 18 cm unit, which composes of medium sand and roots (B1.11).

At site B2, thirteen sediment units were delimited based on sedimentological analysis (Figure 67). The base of the core consists of 25 cm of brown, fine sand (unit B2.1). This is overlain by 12 cm of light brown, medium to coarse sand (unit B2.2). Unit B2.3 and B2.4 contain a mixture of clay and fine sand, and medium sand respectively. The next units (units B2.5 – B2.9) are composed of alternating layers of fine sand (units B2.5, B2.7 and B2.9) and medium sand (unit B2.6) and a mixture of clay and fine sand (unit B2.8). The next sediment units are composed of very fine sand which varies in colour from dark brown (unit B2.10) and greyish-brown (unit B2.11). This is overlain by a mixture of very fine sand and clay which is dark brown in colour (unit B2.12), and is followed by an 11 cm surface layer (B2.13) composing of clay with black striations. Numerous roots are also present in the surface unit.

The core sampled at site B3 contains seven sediment units (Figure 68) which has a 5 cm base composed of a mixture of laminated clay and dark brown sand (unit B3.1). The layer above this consists of 4 cm of dark brown, very fine sand (unit B3.2) which is overlain by 2 cm of very fine sand and clay (unit B3.3). The next unit (unit B3.4) is a 22 cm layer of medium grained sand, which is covered by another thick 30 cm layer of light brown, fine sand with three black striations (unit B3.5). Finer sediment is located near the surface with the next unit containing 7 cm of clay (unit B3.6), followed by 10 cm of brown clay and fine sand at the surface (unit B3.7). Roots are also present in units B3.6 and B3.7.

5.7.2. Stratigraphic cross-section

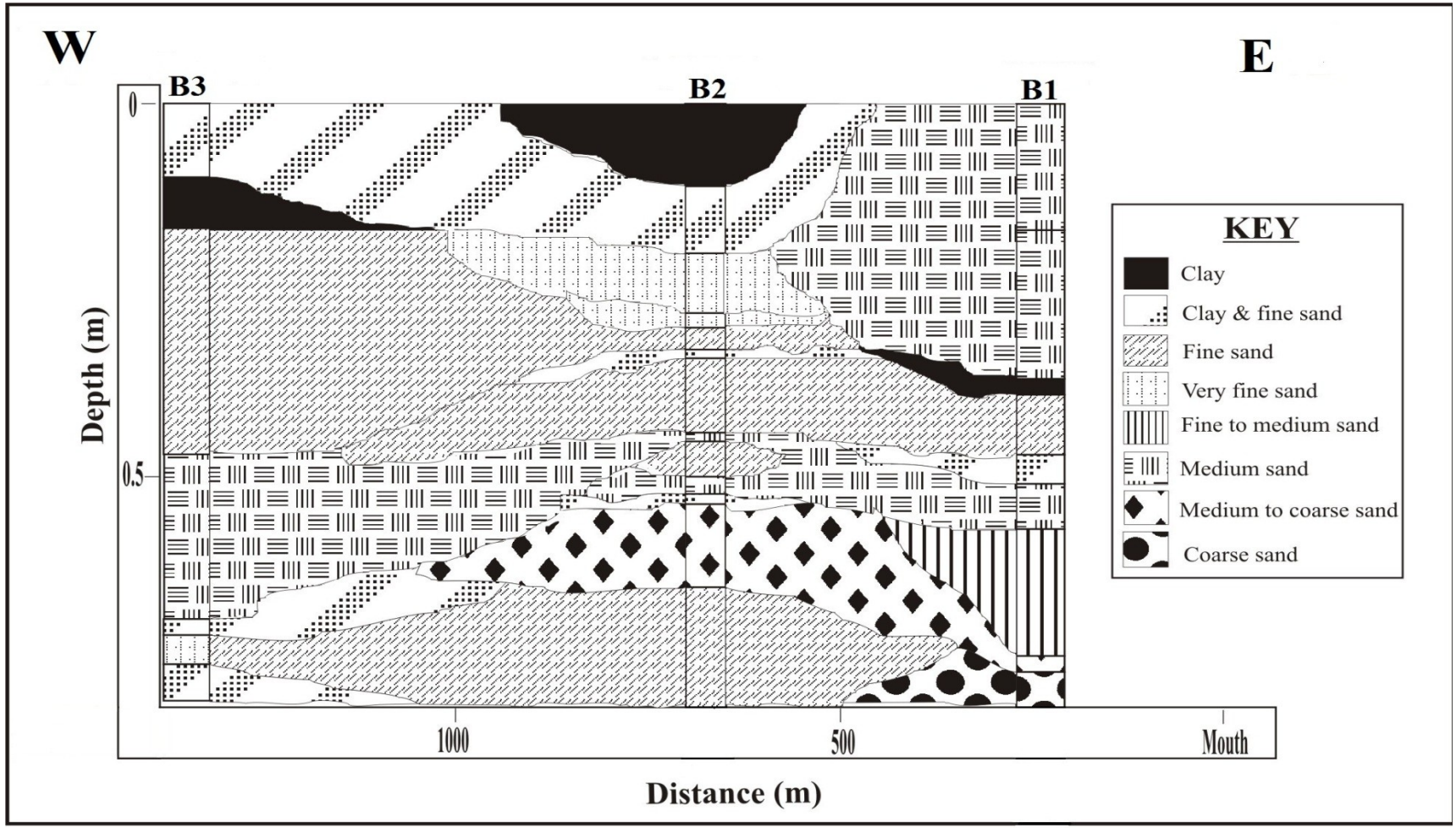

Figure 69: Schematic stratigraphic cross-sectional representation, longitudinal to the estuary axis based on and showing the three core sites from the head (left side of the diagram) to the mouth (right of the diagram) of the uMbokodweni estuary.

Figure 69 above presents a stratigraphic cross-section of the top 0.8 m of the uMbokodweni estuary, including the locations of the cores sampled at sites B1, B2 and B3. Due to the variation of recovered core depths with sites, units B1.1 and B1.2 at site B1 were omitted for accurate interpolation of the sediment layers. From the cross-section, it can be seen that the main sediment contained within the estuary is sand. At the surface, near the head of the estuary, composition is largely clay and fine sediments, to depths of 0.2 m which coarsens towards the mouth of the estuary. Below these sediments, fine and medium grained sands dominate to depths of approximately 0.5 - 0.6 m throughout the estuary. This is followed by medium to coarse and coarse grained sands near the mouth of the estuary at depths of 0.6 m and below. Fine sediments still exist at these depths (> 0.6 m) at the head and middle sections of the estuary.

5.7.3. Organic matter and texture

Table 25: Organic matter content within each core sample for sites B1, B2 and B3.

Core sample sites	Samples	Organic matter (%)
B1	**B1a**	0.400
	B1b	1.070
	B1c	0.950
	Mean	**0.807**
B2	**B2a**	3.350
	B2b	0.530
	B2c	0.670
	Mean	**1.517**
B3	**B3a**	2.010
	B3b	0.670
	B3c	1.340
	Mean	**1.340**

Organic matter content in the uMbokodweni estuary is shown in Table 25 above. The site containing the highest mean organic matter content is site B2 with 1.517%. The lowest mean content is nearest the mouth at site B1 with 0.807%. Sample B2a contains the highest organic matter percentage with 3.350% whereas sample B1a has the least with 0.400%. Sites B2 and B3 share similar trends as the organic matter content first decreases and then increases with depth.

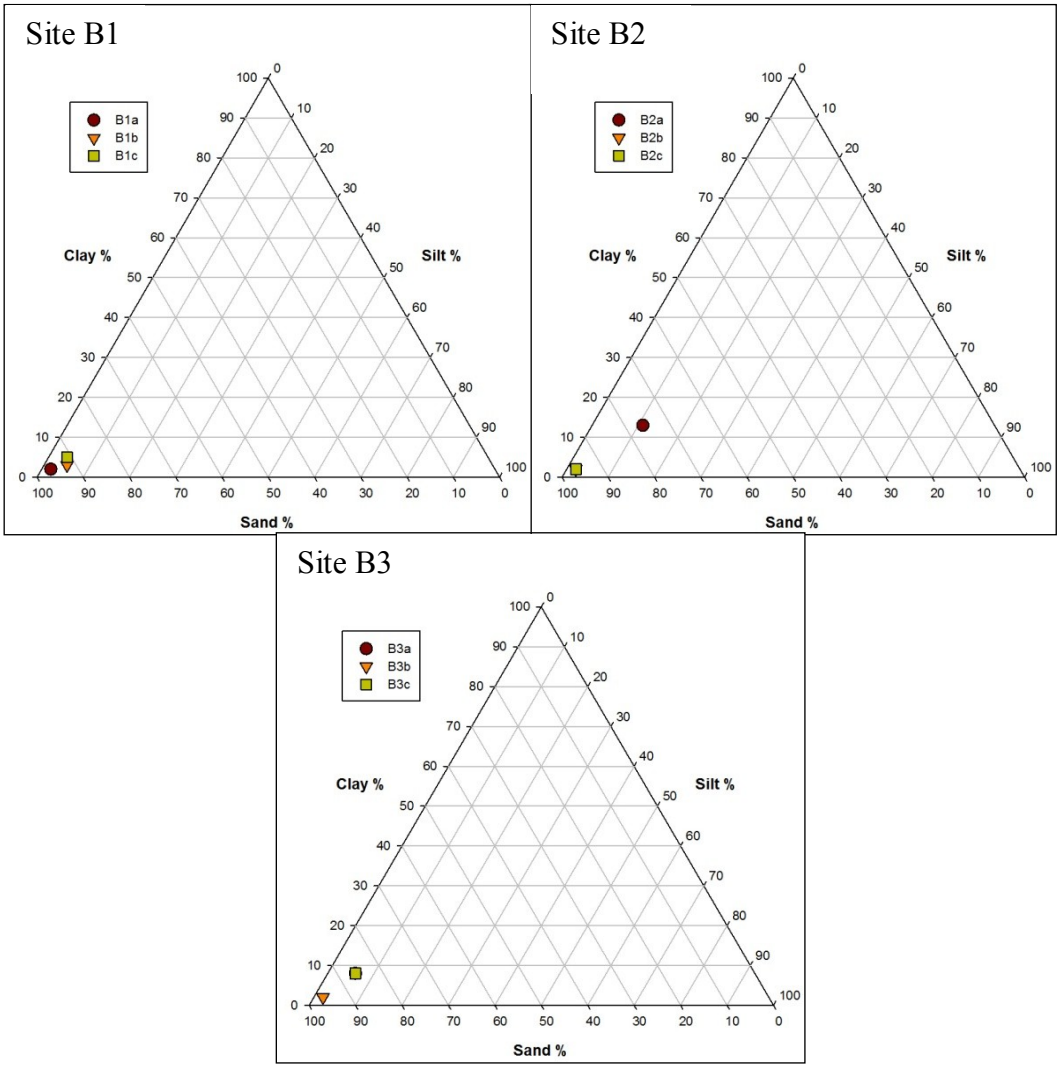

Figure 70: Ternary plots of sand, silt and clay (texture) percentages for each core sample at sites B1, B2 and B3.

Texture results from the core sampled at uMbokodweni estuary are presented in Figure 70 above. The major composition of all samples in this estuary is sand with all samples consisting over 75% of sand. Site B1 contains the highest amount of sand with all samples consisting of over 90% sand. In terms of clay and silt, site B2 has the highest amount with 24% in sample B2a. Samples B3a and B3c had the second highest amounts of clay and silt with 14% each. The core sampled at site B1 shows clay and silt percentages increasing with depth, whereas the opposite occurs at site B2.

5.7.4. Geochemistry

Table 26: Element concentrations with means per core at each core site in the uMbokodweni estuary.

Core sites	Samples	Core depth (cm)	Element concentrations (ppm)											
			Cu	Ni	Pb	As	Fe	Al	V	P	Ca	Mg	Mn	S
B1	B1a	0-37	0.038	0.121	0.049	0.018	1.690	1.025	0.056	0.262	10.918	0.688	0.021	0.266
	B1b	37-76	0.076	0.124	0.038	0.015	2.196	1.613	0.057	0.246	2.170	0.515	0.021	0.642
	B1c	76-116	0.075	0.117	0.034	0.016	1.628	0.865	0.054	0.110	0.818	0.363	0.015	0.197
Mean			**0.063**	**0.121**	**0.040**	**0.016**	**1.838**	**1.168**	**0.055**	**0.206**	**4.635**	**0.522**	**0.019**	**0.368**
B2	B2a	0-20	0.078	0.140	0.052	0.033	0.000	0.032	0.055	0.065	0.000	0.006	0.003	0.011
	B2b	20-53	0.049	0.115	0.021	0.000	0.000	0.044	0.018	0.012	0.000	0.000	0.000	0.000
	B2c	53-90	0.078	0.139	0.052	0.020	0.000	0.075	0.054	0.063	0.000	0.006	0.003	0.045
Mean			**0.068**	**0.132**	**0.042**	**0.018**	**0.000**	**0.050**	**0.042**	**0.047**	**0.000**	**0.004**	**0.002**	**0.019**
B3	B3a	0-17	0.051	0.139	0.052	0.033	0.000	0.075	0.054	0.062	0.000	0.006	0.003	0.045
	B3b	17-69	0.051	0.139	0.052	0.018	0.000	0.075	0.054	0.060	0.000	0.006	0.003	0.043
	B3c	69-80	0.049	0.116	0.021	0.000	0.000	0.079	0.018	0.015	0.000	0.000	0.000	0.000
Mean			**0.050**	**0.131**	**0.042**	**0.017**	**0.000**	**0.076**	**0.042**	**0.046**	**0.000**	**0.004**	**0.002**	**0.029**

Element concentrations of all core samples from the uMbokodweni estuary are shown in Table 26. The hierarchy of mean metal concentrations per site are as follows:

B1: Ca>Fe>Al>Mg>S>P>Ni>Cu>V>Pb>Mn>As;

B2: Ni>Cu>Al>P>V>Pb>S>As>Mg>Mn>Fe, Ca and,

B3: Ni>Al>Cu>P>V>Pb>S>As>Mg>Mn>Fe, Ca.

Maximum mean concentrations of Fe (1.838 ppm), Al (1.168 ppm), V (0.055 ppm), P (0.206 ppm), Ca (4.635 ppm), Mg (0.522 ppm), Mn (0.019 ppm) and S (0.368 ppm) were observed at site B1 near the mouth of the estuary. Mean concentrations of Fe, V, P and Mn decreased

towards the head of the estuary; however Fe and Ca were only present at site B1. Al, Mg and S had similar concentrations at sites B2 and B3. Mean concentrations of Cu (0.068 ppm), Ni (0.132 ppm), Pb (0.042 ppm) and As (0.018 ppm) were highest at site B2 and had similar concentrations at sites B1 and B3.

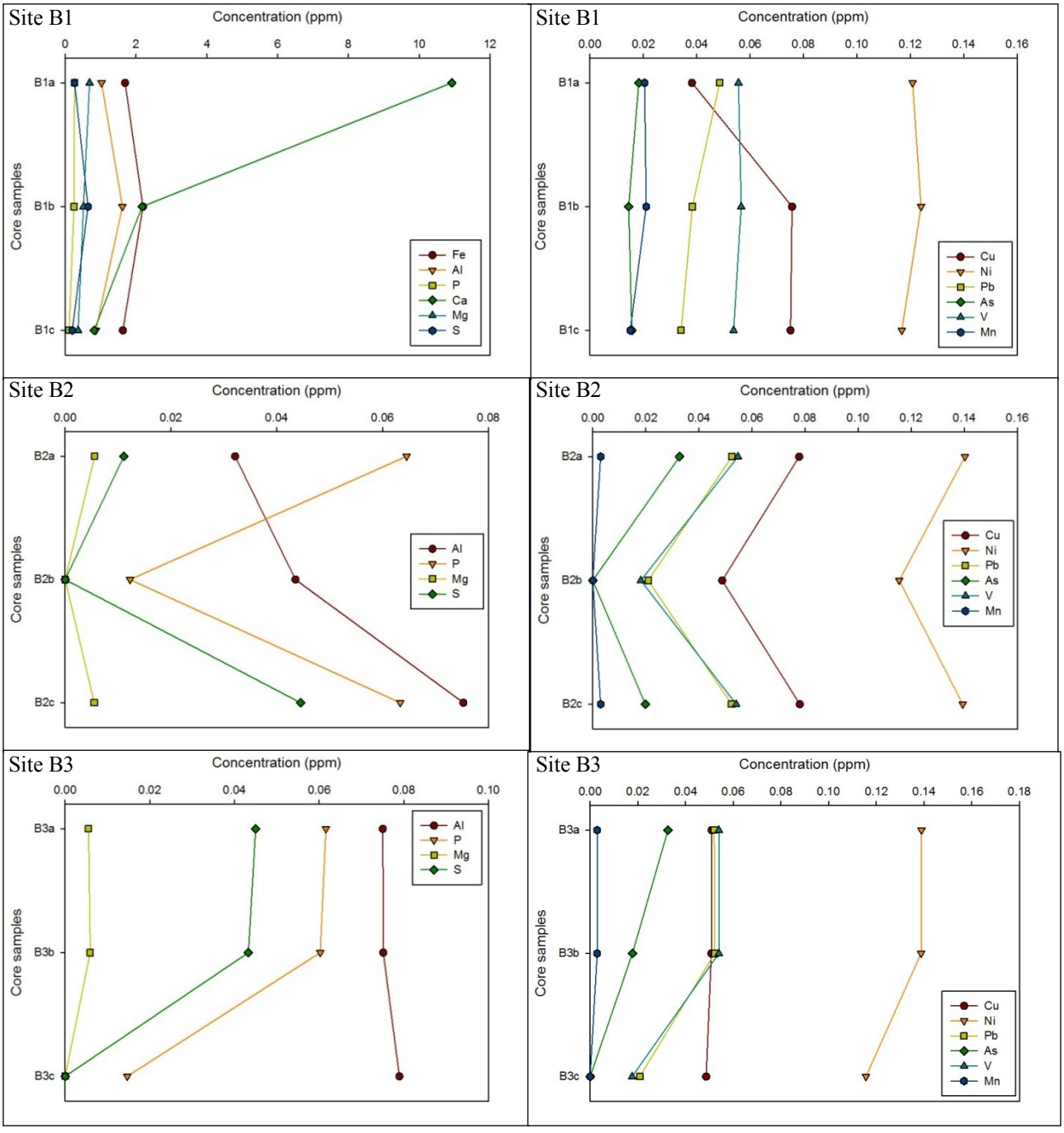

Figure 71: Vertical profiles of element concentrations at core sites in the uMbokodweni estuary.

Figure 71 displays the trends in down core variation in metal concentrations in the uMbokodweni estuary. At site B1, which is located nearest to the mouth, the element concentration variations with depth is relatively constant with the exception of Ca and Cu. Ca concentrations were highest at the surface and declined with depth. Pb, P and Mg also decreased in concentration with depth. Cu increased in concentration with depth. The concentrations of elements Ni, Fe, Al, V, Mn and S also increased with depth but by very small amounts and then decreased in sample B1c slightly. As was the only element whose concentration decreased from sample B1a to B1b, and increased in sample B1c.

The down core variations at site B2 were the same for all elements except Al. All element concentrations decreased from the surface sample (B2a) to sample B2b and increased in sample B2c. Al concentrations increased with depth continuously. Fe and Ca were not present at this site.

At site B3, similar concentration variations with depth were observed. All element concentrations, with the exception of Pb, Al and Mg, decreased continually with depth. Pb and Mg increased very slightly from sample B3a to B3b and decreased in sample B3c. Al increased continuously with depth. Fe and Ca were not present at this site as well.

5.7.5. Statistical analyses

Table 27: Pearson correlation matrix of elements, organic matter (OM) and texture within all core samples in the uMbokodweni estuary.

Al	1.000															
As	-0.058	1.000														
Ca	0.558	0.031	1.000													
Clay	-0.359	0.449	-0.323	1.000												
Cu	0.183	0.325	-0.434	0.216	1.000											
Fe	0.984**	-0.050	0.599	-0.358	0.169	1.000										
Mg	0.915**	-0.014	0.830**	-0.382	-0.058	0.944**	1.000									
Mn	0.962**	0.088	0.704*	-0.353	0.124	0.979**	0.973**	1.000								
Ni	-0.402	0.800**	-0.287	0.298	0.301	-0.451	-0.427	-0.319	1.000							
OM	-0.295	0.609	-0.354	0.959**	0.367	-0.309	-0.359	-0.286	0.463	1.000						
P	0.905**	0.174	0.792*	-0.328	0.026	0.891**	0.948**	0.955**	-0.168	-0.247	1.000					
Pb	-0.050	0.885**	0.176	0.110	0.205	-0.058	0.040	0.118	0.866**	0.280	0.261	1.000				
S	0.962**	-0.012	0.418	-0.330	0.260	0.902**	0.799**	0.879**	-0.253	-0.227	0.862**	0.009	1.000			
Sand	0.255	-0.459	0.320	-0.991**	-0.309	0.257	0.310	0.261	-0.274	-0.969**	0.254	-0.104	0.224	1.000		
Silt	-0.143	0.463	-0.300	0.960**	0.383	-0.162	-0.236	-0.169	0.276	0.968**	-0.155	0.117	-0.090	-0.987**	1.000	
V	0.400	0.807**	0.273	-0.026	0.419	0.409	0.406	0.533	0.595	0.167	0.569	0.858**	0.419	-0.031	0.085	1.000
	Al	**As**	**Ca**	**Clay**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**OM**	**P**	**Pb**	**S**	**Sand**	**Silt**	**V**

***** Correlation is significant at the 0.05 level ($p < 0.05$).
****** Correlation is significant at the 0.01 level ($p < 0.01$).

The correlation of elements, organic matter content, and texture in the sediment samples from the uMbokodweni estuary are given in Table 27 above. Significant correlations between elements were revealed in the correlation matrix: Al and Fe, Mg, Mn, P and S (r = 0.984, r = 0.915, r = 0.962, r = 0.905 and r = 0.962 respectively), As and Ni, Pb and V (r = 0.800, r = 0.885 and r = 0.807 respectively), Ca and Mg, Mn and P (r = 0.830, r = 0.704 and r = 0.792 respectively), Fe and Mg, Mn, P and S (r = 0.944, r = 0.979, r = 0.891 and r = 0.902 respectively), Mg and Mn, P and S (r = 0.973, r = 0.948 and r = 0.799 respectively), Mn and P (r = 0.955), Mn and S (r = 0.879), Ni and Pb (r = 0.866), P and S (r = 0.862)

and lastly Pb and V (r = 0.858). Organic matter was only significantly correlated with textural properties clay and silt (r = 0.959 and r = 0.968 respectively), and negatively correlated with sand (r = -0.969). Clay and silt were significantly correlated with each other (r = 0.960) and negatively correlated with sand (r = -0.991 and r = -0.987 respectively).

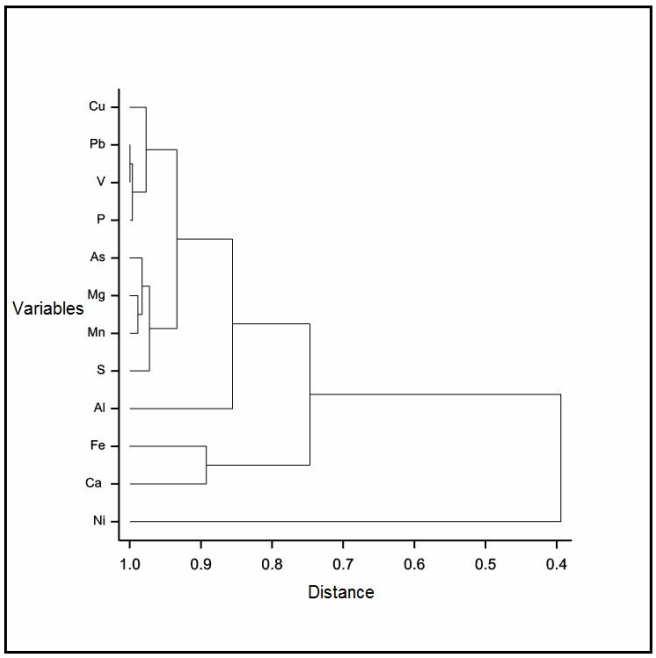

Figure 72: Dendogram obtained by hierarchical cluster analysis of element concentrations in all core samples from the uMbokodweni estuary.

The dendogram in Figure 72 represents groupings of elements in all core samples in the uMbokodweni estuary. There are two clusters and an outlier within this dendogram. The first cluster contains elements Cu, Pb, V, P, As, Mg, Mn, S and Al. There are subgroups within this cluster. The first subgroup includes Pb and V, which are closely linked to P and Cu and display a high degree of similarity. The second subgroup includes As, Mg, Mn and S. Mg and Mn share a high degree of similarity and are closely linked to As and S. Al is related to these two subgroups however it lies on its own which indicates lower similarity. The second cluster contains Fe and Ca. These two elements share a similarity given their high distance value. Ni has been grouped on its own as an outlier as it displays a very low degree of similarity to the rest of the elements.

5.7.6. Pollution indices

Table 28: Enrichment Factors of elements present within the sediments of the core samples in the uMbokodweni estuary.

Elements	Clarke value	Core samples								
		B1a	B1b	B1c	B2a[1]	B2b[1]	B2c[1]	B3a[1]	B3b[1]	B3c[1]
Cu	70	16.168**	**24.635**	**32.972**	0.000	0.000	0.000	0.000	0.000	0.000
Ni	80	**44.693**	**35.298**	**44.833**	0.000	0.000	0.000	0.000	0.000	0.000
Pb	16	**89.949**	**54.607**	**65.628**	0.000	0.000	0.000	0.000	0.000	0.000
As	5	**108.484**	**66.251**	**96.627**	0.000	0.000	0.000	0.000	0.000	0.000
Fe	50000	1.000	1.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000
Al	81300	0.373	0.452	0.327	0.000	0.000	0.000	0.000	0.000	0.000
V	150	10.978**	8.605**	11.024**	0.000	0.000	0.000	0.000	0.000	0.000
P	1180	6.568**	4.745*	2.864*	0.000	0.000	0.000	0.000	0.000	0.000
Ca	36300	8.899**	1.361	0.692	0.000	0.000	0.000	0.000	0.000	0.000
Mg	20900	0.974	0.561	0.534	0.000	0.000	0.000	0.000	0.000	0.000
Mn	1000	0.607	0.481	0.465	0.000	0.000	0.000	0.000	0.000	0.000
S	2400	3.281*	6.090**	2.526*	0.000	0.000	0.000	0.000	0.000	0.000

Clarke values after: Martinez *et al*. (2007)
[1] Fe concentration not detected
*Moderate enrichment (EF class: 2-5)
**Significant enrichment (EF class: 5-20)
Bold values indicate very high enrichment (EF class: 20-40)
Red bold values indicate extremely high enrichment (EF class: > 40)

Enrichment factors of elements within core samples in the uMbokodweni estuary are shown in Table 28 above. Fe was not present at sites B2 and B3 and thus EF = 0. Site B1 was enriched with all elements except for Al, Mg and Mn. Pb and As showed extremely high enrichment in all samples. As exhibited the highest EF in the estuary in sample B1a (EF = 108.484). Ni had extremely high enrichment in samples B1a and B1c, and very high enrichment in sample B1b (EF = 35.298). Cu increased from significant to very high enrichment with depth at this site. All samples were significantly enriched by V. P and S were moderately to significantly enriched is some samples, whereas Ca was only significantly enriched in surface sample B1a (EF = 8.899).

The geo-accumulation index was calculated per sample and the results are shown in Table B12 in Appendix B. All resulting values from this index were less than one. Contamination factors for each element were calculated per core along with the pollution load index and the results are shown in Table B6 in Appendix B. All elements presented a contamination factor of less than one. The calculated pollution load index resulted in values less than one for all three cores and is presented in Table B6 in Appendix B.

5.8. Sediment quality guidelines

Table 29: Sediment quality guidelines for metals in national and international coastal environments (mg/kg).

Metals	National	International		
	South Africa[1] (BCLME)	Australia/ New Zealand[2]	Netherlands[3]	Hong Kong[4]
Zn	124	200	140	200
Cu	18.7	65	36	65
Ni	15.9	21	ID	40
Cd	0.68	1.5	0.8	1.5
Pb	30.2	50	85	75
Cr	52.3	80	ID	80
As	7.24	20	2.9	8.2

[1]Taljaard, 2006
[2]ANZECC, 2000
[3&4]Burton, 2002
ID – insufficient data

National and international sediment quality guidelines for coastal environments are given in Table 29 above. To date, no official guidelines for South African coastal sediments have been developed, but theoretical concentrations have been proposed (Taljaard, 2006). Therefore international guidelines for Australia/New Zealand, Netherlands and Hong Kong have been included for comparative purposes. The Benguela Current Large Marine Ecosystem Programme (BCLME) guidelines have critically reviewed international water and sediment quality guidelines and international best practice in terms of the implementation of quality guidelines in the management of coastal areas (Taljaard, 2006). It has developed interim sediment quality guidelines for this specific coastal zone (including Angola, Namibia and the west coast of South Africa). These guidelines however cover a broad range of concentrations and need to be refined specifically for each country.

The element concentrations observed in all estuarine sediments in this study (Tables 6, 10, 14, 18, 22 and 26 in sections 5.2.4, 5.3.4, 5.4.4, 5.5.3, 5.6.4 and 5.7.4 respectively), fall well below the standards presented by the national and international guidelines. Therefore these elements pose no threat to aquatic organisms present in the sediments.

5.9. eThekwini Municipality

This section focuses on the comparison of all estuaries investigated in the eThekwini Municipality in this study. Mean values of each of the estuaries are used in this section for comparative purposes.

5.9.1. Organic matter and texture

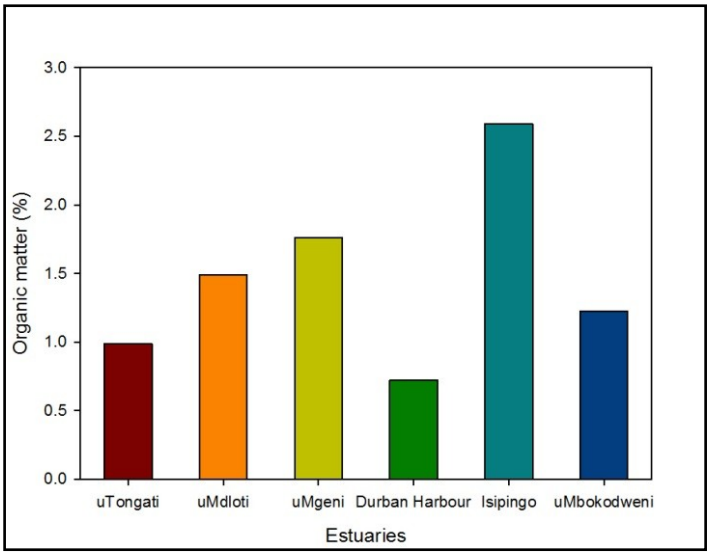

Figure 73: Bar graph displaying the mean organic matter (OM) content within each estuary.

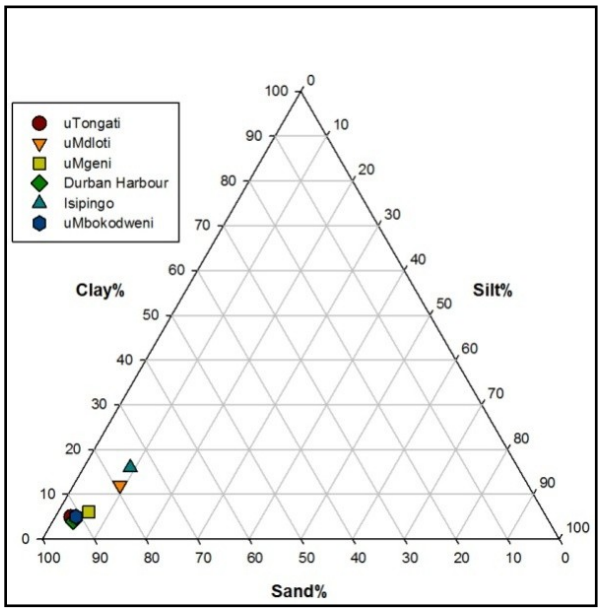

Figure 74: Ternary plot of mean sand, silt and clay percentages within each estuary.

The mean organic matter content for all estuaries is displayed in Figure 73. Isipingo estuary contains the highest amount of OM content at 2.591%, and the Durban Harbour consists of the least amount at 0.720%.

The mean sand, silt and clay percentages for each estuary are given in Figure 74. From this ternary plot it can be seen that Isipingo estuary contains the largest amount of clay at an overall 16%, followed closely by uMdloti estuary at 12%. The other estuaries are grouped together indicating high sand content. The highest sand percentage is found in uTongati estuary and the Durban Harbour at 92% for both.

5.9.2. Geochemistry

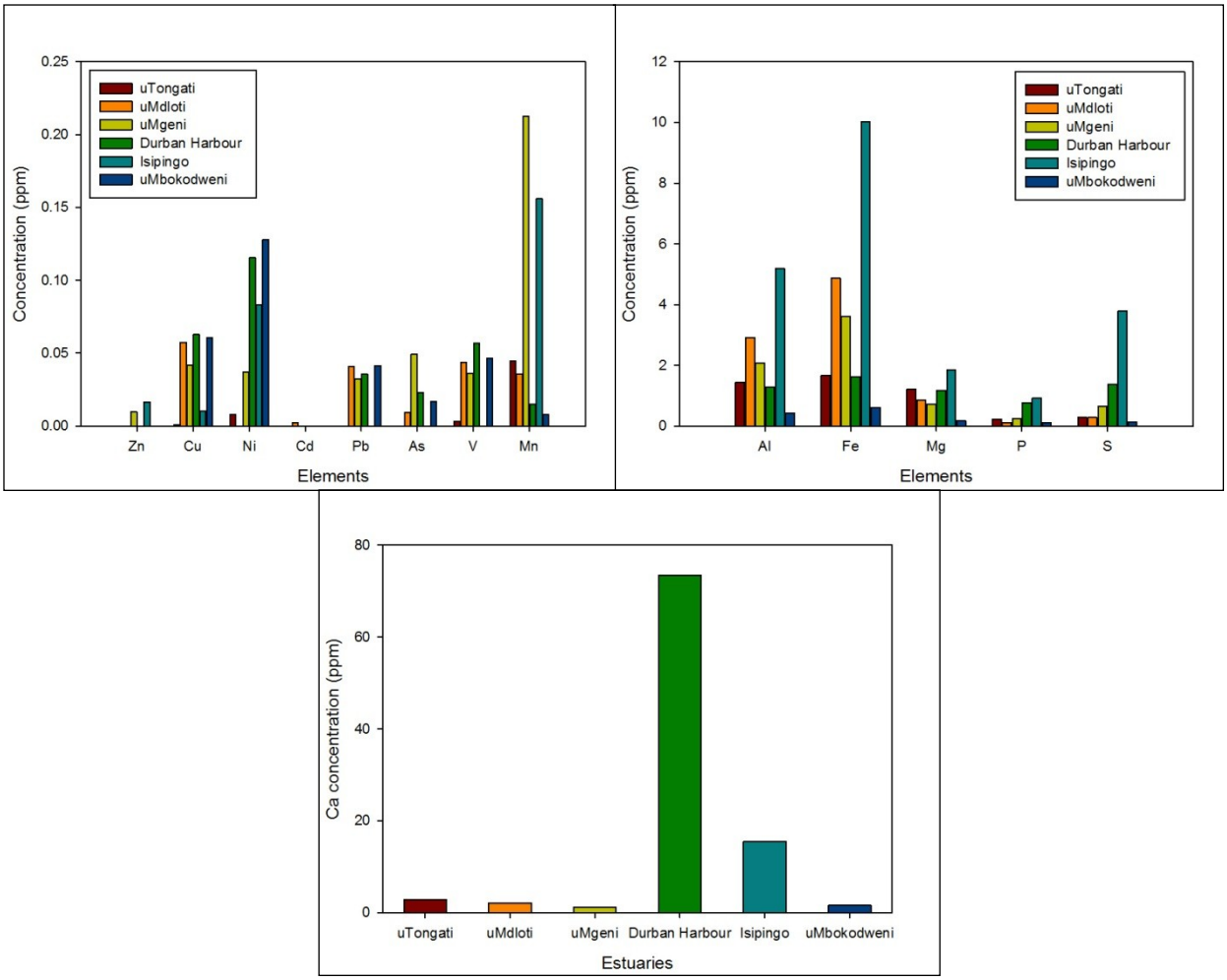

Figure 75: Grouped bar graphs indicating the mean concentration of elements per estuary.

Mean concentrations of elements per estuary are displayed in Figure 75. Elements were grouped according to similar mean concentrations. Ca recorded the highest mean concentration in the Durban Harbour at 73.406 ppm. This was followed by Isipingo estuary at 15.462 ppm. The rest of the estuaries all had mean Ca concentrations below 3 ppm.

The Isipingo estuary contained the highest mean concentrations of elements Fe = 10.023 ppm, Al = 5.182 ppm, Mg = 1.843 ppm, P = 0.917 ppm and S = 3.784 ppm except. The Durban Harbour had the highest mean Cu concentrations at 0.063 ppm, and the uMgeni estuary contained the highest mean Mn concentrations at 0.212 ppm. Zn was only detected in the uMgeni and Isipingo estuaries at low concentrations. The Isipingo estuary had the highest Zn mean concentration at 0.016 ppm. Cd was only detected in very low mean concentrations in the uMdloti estuary (0.002 ppm).

The remaining elements (Ni, Pb, As and V) examined in this study were detected in some of the estuaries. Ni was present in all estuaries except the uMdloti estuary. Its highest mean concentration occurred in the uMbokodweni estuary at 0.128 ppm, followed closely by the Durban Harbour at 0.116 ppm. Pb was detected in all estuaries except for the uTongati and Isipingo estuaries. It highest mean concentration was recorded in the uMbokodweni estuary at 0.041 ppm. As was not present in the uTongati estuary and the Isipingo estuary. Its highest mean concentration occurred in the uMgeni estuary at 0.049 ppm. V was present in all estuaries except for the Isipingo estuary. Its highest mean concentration was 0.057 ppm recorded in the Durban Harbour. Cr was omitted from the above graphs as its mean concentration calculation resulted in a mean value of 0. It was present in one sample only (D2c) in the uMdloti estuary at 0.001 ppm.

5.9.3. Statistical analyses

Table 30: Pearson correlation matrix of mean concentrations of elements, organic matter (OM) and texture within all core samples in all estuaries.

Al	1.000																		
As	-0.081	1.000																	
Ca	0.050	-0.019	1.000																
Cd	0.118	-0.032	0.037	1.000															
Clay	0.706**	0.011	0.021	0.187	1.000														
Cr	0.143	0.000	-0.050	-0.019	0.187	1.000													
Cu	-0.115	0.145	0.061	-0.125	-0.065	0.262	1.000												
Fe	0.779**	-0.080	0.102	0.309	0.748**	0.073	-0.256	1.000											
Mg	0.699	-0.064	0.151	0.092	0.503	0.077	-0.181	0.467	1.000										
Mn	0.448	-0.026	-0.058	-0.039	0.403	-0.004	-0.102	0.262	0.337	1.000									
Ni	-0.062	-0.072	0.280	-0.135	-0.044	-0.135	0.265	-0.073	-0.082	-0.105	1.000								
OM	0.511	0.043	-0.042	0.031	0.749**	0.182	-0.134	0.634	0.327	0.539	-0.047	1.000							
P	0.726**	0.009	0.061	-0.028	0.353	-0.031	-0.094	0.265	0.596	0.444	0.122	0.139	1.000						
Pb	-0.122	0.080	-0.029	-0.092	-0.079	0.076	0.672	-0.223	-0.165	-0.092	0.168	-0.185	-0.097	1.000					
S	0.611	-0.107	0.235	-0.082	0.615	0.058	-0.200	0.824**	0.361	0.162	0.194	0.580	0.214	-0.197	1.000				
Sand	-0.634	-0.041	-0.008	-0.224	-0.970**	-0.196	0.042	-0.732**	-0.442	-0.444	0.063	-0.794**	-0.251	0.087	-0.587	1.000			
Silt	0.489	0.076	-0.009	0.252	0.849**	0.192	-0.015	0.650	0.327	0.459	-0.084	0.783**	0.098	-0.091	0.502	-0.951**	1.000		
V	-0.195	0.306	0.074	-0.145	-0.163	0.257	0.908**	-0.332	-0.214	-0.186	0.227	-0.234	-0.129	0.683	-0.284	0.131	-0.084	1.000	
Zn	0.123	0.072	0.002	-0.034	0.129	-0.034	-0.142	0.248	0.041	0.513	-0.024	0.492	0.001	-0.125	0.254	-0.164	0.195	-0.207	1.000
	Al	**As**	**Ca**	**Cd**	**Clay**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**OM**	**P**	**Pb**	**S**	**Sand**	**Silt**	**V**	**Zn**

* Correlation is significant at the 0.05 level ($p < 0.05$).
** Correlation is significant at the 0.01 level ($p < 0.01$).

The correlation of the mean concentrations of elements, mean organic matter content, and mean texture percentages in the sediment samples from all estuaries are given in Table 30 above. Significant correlations between elements were revealed in the correlation matrix: Al and Fe (r = 0.779), Al and P (r = 0.726), Cu and V (r = 0.908) and Fe and S (r = 0.824). Organic matter was significantly correlated with clay and silt (r = 0.749 and r = 0.783 respectively) and showed a significant negative correlation with sand (r = -0.794). Textural properties displayed significant correlations with elements: clay and Al (r = 0.706), clay and Fe (r = 0.748) and significant negative correlation with sand and Fe (r = -0.732). Sand also showed significant negative correlations with clay and silt (r = -0.970 and r = -0.951 respectively). Lastly clay and silt were significantly correlated to each other (r = 0.849).

Table 31: Component loadings of principal components 1 and 2 for all elements, and the percentage variance for each principal component.

Variables	PC1	PC2
Al	-0.007	0.410*
As	0.000	-0.001
Ca	1.000*	0.011
Cd	0.000	0.000
Cu	0.000	-0.003
Fe	-0.016	0.848*
Mg	0.006	0.109
Mn	-0.001	0.012
Ni	0.001	-0.001
P	0.008	0.060
Pb	0.000	-0.002
S	0.014	0.311
V	0.000	-0.003
Zn	0.000	0.001
% variation	98.02	1.94
* High loadings within component.		

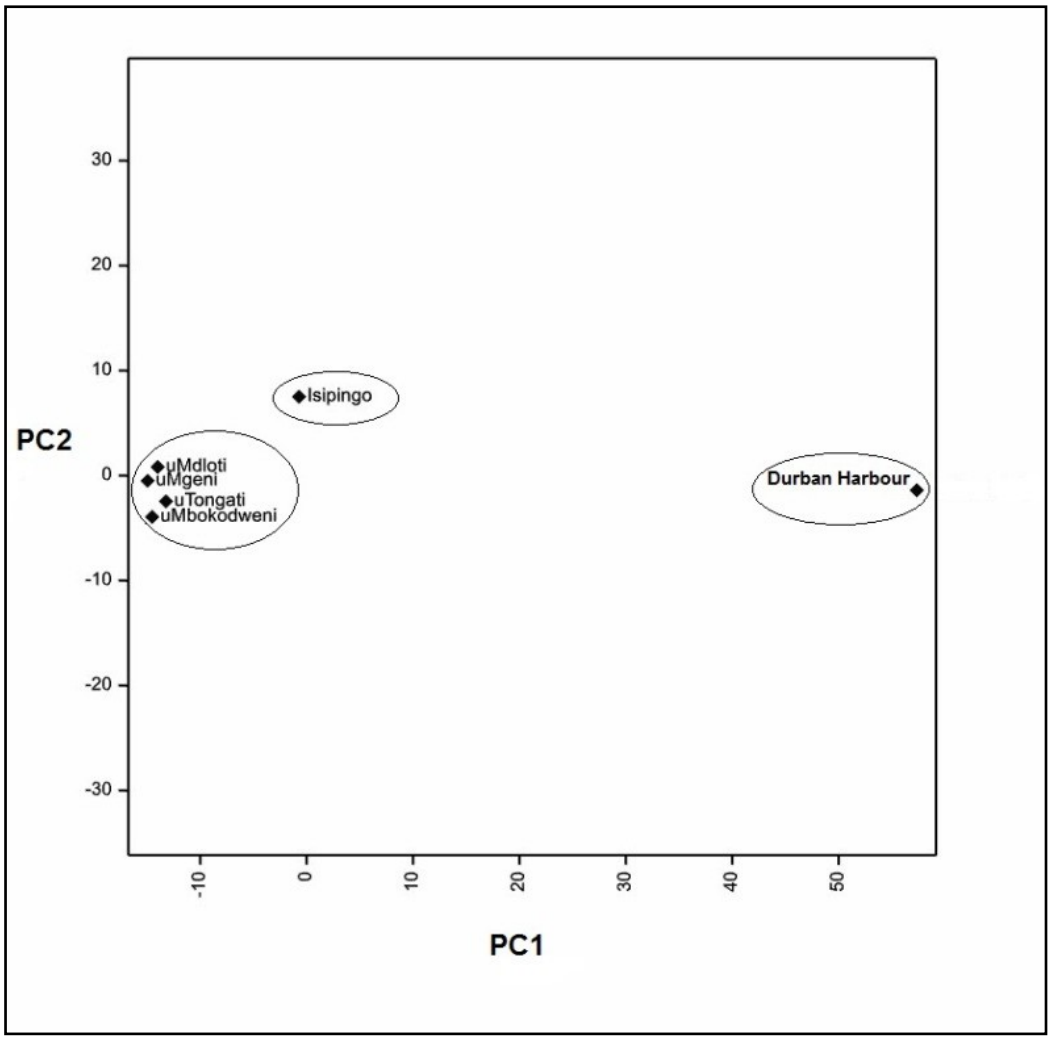

Figure 76: Loading plot of principal component analysis of all estuaries examined in this study.

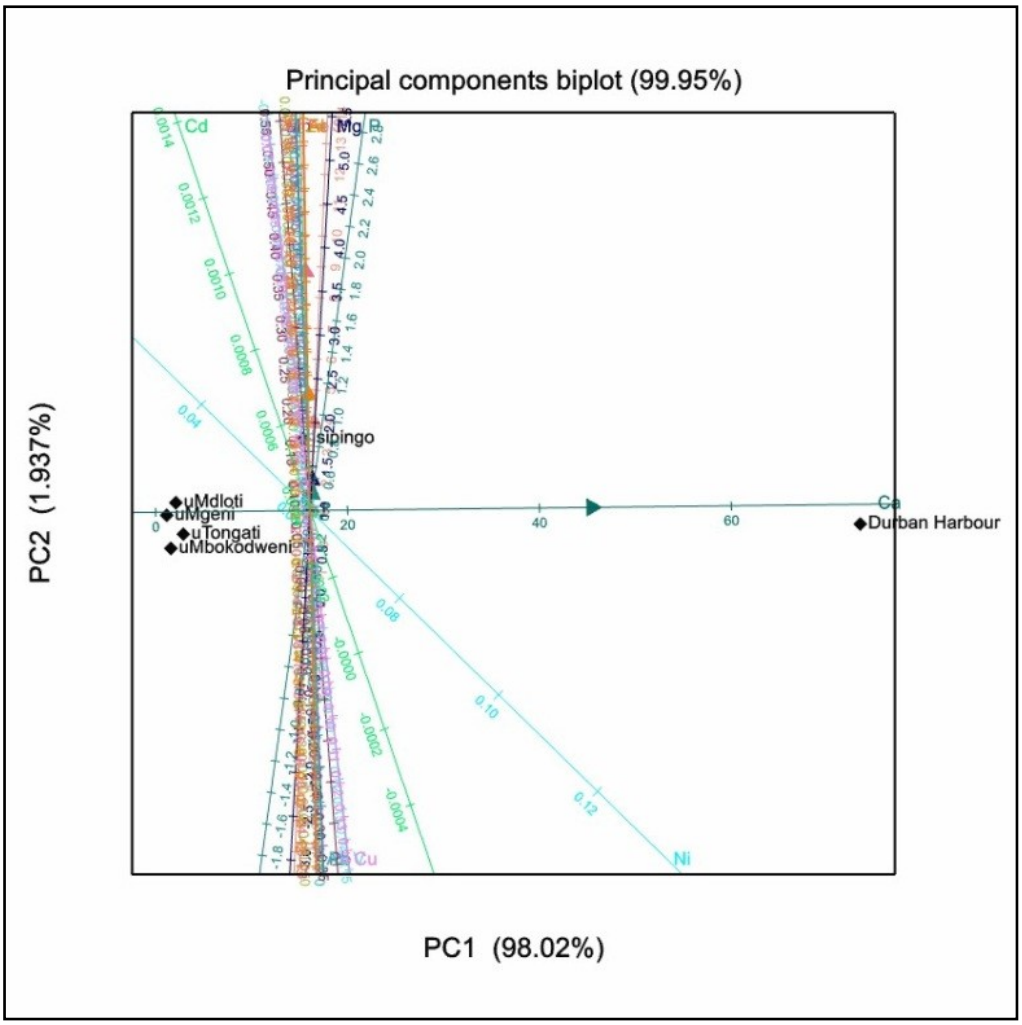

Figure 77: Biplot of principal component analysis of all estuaries examined in this study with mean concentrations of elements per estuary.

Results of principal component analysis (PCA) for all estuaries are shown in Table 31 as well as Figures 76 and 77. Mean concentrations of all elements were used as variables to determine the variance among all estuaries studied. Cr was omitted as the mean concentration value was zero. In Table 31, principal component 1 (PC1) can explain 98.02% of the total variance, however principal component 2 (PC2) can only explain 1.94% of total variance. Component 1 may indicate marine influence within the estuaries. Ca has the highest loading value of PC1 at 1.000. Al, Cd, Fe, Mn and Zn all have negative loadings for PC1, where Fe exhibited the highest loading at -0.016. Contrasting this are the high positive loadings in PC2 for Fe and Al (0.848 and 0.410 respectively). As, Cu, Ni, Pb and V have negative loadings for PC2 where V had the highest negative loading of -0.003.

The loading plot (Figure 76) shows that uMdloti, uMgeni, uTongati and uMbokodweni estuaries are clustered together. These estuaries have high negative loading values (> -10) for component 1. The Isipingo estuary is closer to this cluster; however has a positive loading (> 0) with component 1. Durban Harbour is mainly influenced by PC1 as it has very high loadings (> 50) and is distinctly separate from the cluster of estuaries. Component 2 has barely affected the location of clusters in the loading plot as all estuaries are near the central axis of PC2 (< 10 and > -10). This second component may represent the geological or lithogenic sources of elements within each estuary.

Figure 77 displays the location of the estuaries within the biplot based on the mean concentration of the elements within each estuary. It can be seen that Ca concentrations have the greatest influence on the location of the estuaries in the biplot, separating Durban Harbour from the rest of the estuaries. The remaining elements' concentrations have a strong influence on the location of the estuaries in the biplot, and are strongly correlated as their lines lie very close together. Cd and Ni show less correlation with the rest of the elements as they lie further away. This biplot is supported by significant correlations of elements (Appendix B-Table B13) which include Cu, Pb and V ($r > 0.95$). Other elements that are significantly correlated with each other include Al, Fe and S ($r > 0.80$). Zn has shown significant correlation with Fe, Mn and S ($r > 0.80$). This large association between these elements may indicate a similar source or a similar distribution pattern within the sediments of the estuaries.

5.9.4. Pollution indices

Table 32: Enrichment factors of mean concentrations of elements present within the sediments of all estuaries.

Elements	Clarke values	uTongati	uMdloti	uMgeni	Durban Harbour	Isipingo	uMbokodweni
Zn	132	0.000	0.000	1.010	0.000	0.620	0.000
Cu	70	0.397	8.412**	8.265**	**27.704**	0.718	**70.490**
Ni	80	2.878*	0.000	6.438**	**44.679**	5.199**	**130.365**
Cd	0.15	0.000	**154.577**	0.000	0.000	0.000	0.000
Pb	16	0.000	**26.027**	**28.185**	**68.541**	0.000	**210.815**
As	5	0.000	19.523**	**136.589**	**141.937**	0.000	**274.838**
Fe	50000	1.000	1.000	1.000	1.000	1.000	1.000
Al	81300	0.533	0.368	0.354	0.491	0.318	0.433
V	150	0.635	2.991*	3.339*	11.683**	0.000	**25.311**
P	1180	5.679**	1.012	2.783*	**20.206**	3.878*	6.875**
Ca	36300	2.367*	0.605	0.444	**62.578**	2.125*	3.474*
Mg	20900	1.746	0.421	0.471	1.739	0.440	0.689
Mn	1000	1.337	0.367	2.941*	0.460	0.778	0.623
S	2400	3.548*	1.189	3.795*	17.584**	7.866**	4.720*

Clarke values after: Martinez *et al*. (2007)
*Moderate enrichment (EF class: 2-5)
**Significant enrichment (EF class: 5-20)
Bold values indicate very high enrichment (EF class: 20-40)
Red bold values indicate extremely high enrichment (EF class: > 40)

Enrichment factors of mean concentrations of elements within all core samples in all estuaries are shown in Table 32 above. From the table, it can be seen that Durban Harbour and the uMbokodweni estuary contain four red bold values each, which indicates extremely high enrichment of those metals within the sediments. Durban Harbour contains the highest EF values for P (EF = 20.206) which indicates very high enrichment, Ca (EF = 62.578) indicates extremely high enrichment, and S (EF = 17.584) which falls within the significant enrichment class. Maximum EF values for Cu (EF = 70.490), Ni (EF = 130.365), Pb (EF = 210.815), As (EF = 274.838) which indicate extremely high enrichment, and V (EF = 25.311) which indicates very high enrichment, are found in the uMbokodweni estuary. Cd shows the highest enrichment in the uMdloti estuary at EF = 154.577 which falls in the extremely high enrichment class. Mn is only moderately enriched in the uMgeni estuary at EF = 2.941. Zn, Al and Mg were not enriched in all estuaries.

5.10. Conclusion

This chapter has presented the individual results per estuary, sediment quality guidelines, as well as a comparative overview of all the estuaries studied. Each estuarine section included subsections which consisted of sediment descriptions of data such as core drawings and schematic stratigraphic cross-sections. Organic matter results were presented in tables and textural results in the form of ternary plots. This was followed by geochemical results of elements per core represented by tables and graphs. Elements present in each core sample were analysed statistically using Pearson correlation and Cluster Analysis. The pollution levels in each estuary were evaluated by various pollution indices.

Following these individual estuarine sections, an overall view of all the estuaries was presented. Graphs were used to represent mean organic matter and the mean elemental concentrations per estuary. Mean texture per estuary was illustrated by a ternary plot. Pearson correlation and PCA statistical methods were utilised to analyse patterns and trends within the data. Enrichment factor was used to provide an overview of the pollution in each estuary. A discussion interpreting the findings within this chapter will follow.

Chapter 6

DISCUSSION

6.1. Introduction

This chapter interprets the findings of this study. The general sedimentology and geochemical aspects are discussed, as well as a brief discussion on all estuaries combined in the eThekwini Municipality. To facilitate such a presentation, the chapter is divided into the following sections: sedimentology, age of sediments, geochemistry and eThekwini Municipality. The eThekwini municipality section discussion focuses on the overall organic matter and textural variations, geochemistry and the state of pollution for all estuaries.

6.2. Sedimentology

The sedimentological aspects that are discussed in this section consist of colour and textural variations, and include the movement of sediments i.e. fine and coarse sediments in relation to energy conditions within the estuary, and mouth status. Each estuary exhibits individual sedimentological characteristics however similar aspects are noted amongst all estuaries.

A variety of sediment colours characterized each of the sediment cores collected. Light to dark brown sediments, indicative of organic matter presence (Ujevic *et al*., 2000), were observed for all estuarine sediments at various depths, but mostly at the surface. The highest organic matter content amongst all estuaries occurred at the surface of site G3 in the uMgeni estuary, at 6.04% (Table 13). This high percentage is possibly due to a high density of leaf litter around this site. Light brown sediments were present at lower depths within most cores and signify a drop in organic matter content with depth (Mikkelsen *et al*., 2009). This can be seen in uMdloti at site D3 (Figure 43), uMgeni at sites G1, G3 and G4 (Figures 48, 50 and 51), Durban Harbour (Figure 56), Isipingo at site S1 (Figure 59), and uMbokodweni at site B2 (Figure 67).

The greyish-brown and greyish-black sediments which are present in the uTongati and uMdloti estuaries (Figures 35 and 42) may signify alumina-silicates content that possibly originate from geological sources (Schropp, 1988) or perhaps through the weathering of rock such as Ecca Shale which is present in both catchments that is transported and deposited into the estuaries (Beater, 1957). Fe undergoes different oxidation states within sediment and is indicated by different shades of red or orange (Lynn and Pearson, 2000) such as the yellow-

orange sediments at site D2 in the uMdloti estuary (Figure 42). Black clays or mixtures of black clay and fine sand were present in all estuaries except the uMbokodweni estuary, and were most abundant in the Isipingo estuary. This colour which was present at the base of cores T1, T2, D2, and S3, is indicative of anaerobic conditions (Burke *et al*., 1989) and also contained corresponding high levels of organic matter (Tables 5, 9 and 21).

Organic matter together with silts and clays, possess electrical charges that facilitate adsorption (Goni *et al*., 2003). For all estuaries, with the exception of Durban Harbour, there was a significant positive correlation associated with organic matter and clay and silt (Tables 7, 11, 15, 23 and 27). This is supported by the presence of high percentages of organic matter in sediment units containing high levels of clay and silt in all estuaries. Furthermore, in the mangrove environments of the uMdloti (site D1), uMgeni (site G4) and Isipingo (site S1 and S2) estuaries, the surface samples contained high percentages of organic matter, confirmed by the data in Tables 9, 13 and 21 respectively, and possibly derived from abundant mangrove leaf litter. These high percentages of organic matter were associated with high levels of clays and silts in the surface samples at these sites (Figures 45, 53, 63).

Clays and finer particles like silt can be deposited in very low energy environments, such as closed mouth and lagoonal type conditions which facilitate the settling of fine particles and are indicated by accumulations of clay on the bed (Ladachart *et al*., 2011). In the uMdloti estuary, the dominant southward longshore drift current tends to rapidly close up the mouth and so create these calm lagoonal conditions within the estuary which are ideal for deposition of fines (Bell *et al*., 2000). The accumulations of clay can be identified at sites D1 and D2 (Figures 41 and 42). The Isipingo estuary experiences different conditions as the only link it shares with the sea is via two concrete pipes which extend through the high berm at the mouth. The thickness of the clay units at sites S1and S2 and especially at site S3 (Figures 59, 60 and 61) indicate low energy conditions which existed for a protracted period of time. This is associated with decreased riverine flow (a consequence of the diversion of the uMlazi River and the canalisation of the Isipingo River) and the restricted connection to the sea which has led to calm conditions throughout the estuary. The uMgeni estuary on the other hand, is largely open to the sea; however the configuration of this estuary, along with the well developed barrier and the presence of the large stand of mangroves of Beachwood, creates tranquil conditions in the estuary allowing for considerable deposition and accumulation of fines. This is evident by the fines and clay accumulation even at the mouth of the estuary as well as the other two sites (G2 and G3) (Figure 52).

Layers of clay are also deposited following increased flocculation which occurs within the mid-estuary, caused by the mixing of fresh and saline waters (NOAA, 2005). This is shown at sites T2 in the uTongati estuary, G2 in the uMgeni estuary, and B2 in the uMbokodweni estuary, which are sites located at the approximate middle reaches of the estuary. The energy conditions of these estuaries are sufficient to enable the mixing of fresh and saline waters through wave action from the open mouth and riverine flow from the landward side.

Heavier particles like sand are not transported as easily as fines and the distance to which a river can transport heavier sediments downstream is limited to the energy is possesses (Lessa *et al*., 1998). The change in flow conditions such as the decrease in slope towards the mouth and a subsequent decrease in flow velocity deters the movement of coarser sediments further downstream (Lessa *et al*., 1998). Large amounts of coarse sediments present at the head of the uMdloti estuary at site D3 signify this (Figure 43). However, if conditions within the estuary are turbulent, heavier particles can be transported further downstream towards the mouth.

Periods of high energy are associated with turbulent conditions within the estuary brought on by strong wave action or periods of high riverine flow into the estuary such as with floods, seasonal or high rainfall events (Cooper, 2001). Seasonal rainfall or short periods of rainfall transport riverine sediment downstream and deposition is evident as thin layers of sand on the estuarine bed (Wright and Mason, 1999). This is evident in the uMdloti estuary at site D1 (Figure 44), Isipingo estuary at site S2 (Figure 62) and in the uMbokodweni estuary at site B2 (Figure 69). Evidence of fluvial flood conditions following heavy rains in the uTongati catchment hinterland is present at all three sites in the estuary (T1, T2 and T3) by an accumulation of coarse sediments at similar depths (Figure 37). Mixtures of coarse sands and fine materials with pebbles are also indicators of floods (NOAA, 2005). This is shown in the uTongati estuary at site T2 (Figure 35) and in the uMgeni estuary at site G1 (Figures 48).

An important component of an estuary is its link to the ocean and the transport of marine sediments into the estuary. The transport of marine sediments into an estuary can occur via wave action or during closed mouth conditions via overwash (Whitfield and Bate, 2007). During closed mouth conditions following spring tides, washover fans can occur within the estuary near the mouth. These very coarse washover sand deposits are present in the cores of the uTongati estuary in sample T1b (Figure 34), the uMgeni estuary in samples G1c, G1d and G4c (Figure 48), and the uMbokodweni estuary in sample B1c (Figure 66).

The Durban Harbour is an ideal example of marine transport of sediments into the estuary as every sediment unit within the core sampled contained shells, which signifies a marine dominated harbour (Figure 56). Since the canalisation of the Umbilo and Umhlatuzana rivers entering the harbour, it is likely that the freshwater input into the harbour has decreased, which has subsequently lowered flood effects, and allowed for greater settling of fines (Van Rooyen, 2001). Therefore it is possible that riverine influence on the harbour has diminished to a large extent as less sediment enters the harbour through these canals, resulting in a dominant marine environment (DEAT, 2006).

The mouth conditions of the estuaries studied are unique. The uTongati and uMbokodweni estuary share a similarity in that they are temporarily closed during the year, and remain open naturally for longer periods of time. The uMdloti estuary stays closed for most of the year, and at times breaches naturally during fluvial floods or spring high tides or is anthropogenically breached to prevent flooding of the sugarcane fields and roads (Forbes and Demetriades, 2008). The uMgeni estuary is permanently kept open by a groyne and is similar to the Isipingo estuary, in that the latter is also kept open by physical structures i.e. two concrete pipes establishing its link to the sea. The Durban harbour is also permanently open but requires a regular dredging programme to prevent silting up at the mouth. The common aspect and most continuous feature amongst all of these estuaries (except the Durban Harbour) is the presence of a sand bar at the mouth. The development of a sand bar in a southerly direction at the mouth is due to the strong onshore transport of sediments driven by the dominant southward longshore drift currents (Abed, 2009). These currents carry marine sediments near the mouth area and also allows for sediment transport into the estuary through the inlet (Whitefield and Bate, 2007).

Historically, these estuaries experienced various sedimentary changes within the estuary based on mouth and climate conditions (Cooper, 2001). Mouth conditions, whether open or closed influenced the transport of sediments within the estuary, and over time this can be seen through the accumulation of different types of sediment layers within the estuary. Climate conditions related to rainfall events and floods create great variation within the sediment layers as mixing of sediments from high flow velocities disturb the sedimentary environment (Ridgway and Shimmield, 2002). Although the deposition of some mixed sediments remain after floods, most surface layers may be removed during the flood, thus disrupting the historical layered sediment pattern created over time (Ridgway and Shimmield, 2002).

6.3. Age of sediments

Dated sediment samples from all collected cores revealed Holocene period sediments. The Holocene period dates from approximately 11 400 years ago to present times (Roberts, 1989). The oldest sediments were located in the uTongati estuary at site T2 which was dated at 4180 +/- 30 years and was situated at 60-104 cm below the surface. The youngest sediments were located in the uMgeni estuary at site G1 which was dated at 700 +/- 30 years and was situated at 96-115 cm below the surface.

The ages of the sediment in the estuaries are older than would be expected of general surface sediments. In the last century, high magnitude floods such as the 1856, 1984 and 1987 floods caused scouring of the bed and banks within the estuaries (Barnes, 1984; Badenhorst *et al*., 1989; Cooper, 2002). The younger estuarine sediments would have been removed from the bed and banks and the scoured sediments would have been washed out to sea and deposited offshore (Swales *et al*., 2003). The transport of riverine sediments offshore was evident in the flood of 1987 at the uMgeni estuary when organic-rich mud was found off the KwaZulu-Natal coast several months after the flood (Badenhorst *et al*., 1989). Furthermore, during floods the high energies of the flood waters also allow for the erosion and reworking of older sediments present within the catchment, and can be transported with the flood sediment load to the estuary. Post flood sediment deposition occurs during the falling stages of the flood (Badenhorst *et al*., 1989). The older, re-worked sediments can be deposited onto the estuarine bed at this time, which may also be distributed unevenly throughout the estuary depending on the post flood energy within the estuary (Cooper, 1993). These deposits usually consist of mixed sediments such as fine and coarse material. These deposits are evident in the uTongati estuary at site T2 (Figure 37) and the uMgeni estuary at site G1 (Figure 48).

The sequential deposition of the dated sediment layers is not uniform for all estuaries. The uTongati and the Isipingo estuaries confirm that the sediment layers beneath the surface are uniform and continuous as the younger sediments rest upon the sequentially older sediments within the estuary. However in the uMdloti, uMgeni and uMbokodweni estuaries, the older sediments are located closer to the surface than the younger sediments. This may be caused by the re-worked sediments which have been re-deposited downstream over the younger sediments in the vicinity of the core site (Cooper, 1993).

6.4. Geochemistry

The geochemical analyses for each estuary were based on metal concentrations detected in each estuary. Various concentrations of elements were recorded at each site; however similar patterns were detected among some estuaries. From a statistical point of view, certain variables were correlated in all estuaries. In terms of enrichment, similarities amongst certain elements were also detected across estuaries. Interpretations to these patterns and similarities are discussed below.

Metal concentrations detected at all sites were relatively low. The age of the sediments described in section 6.3 could explain the low concentrations of metals. Ca was the only metal which displayed relatively higher concentrations, especially in the Durban Harbour (Table 18). Ca concentrations in estuaries such as the uTongati (sites T1 and T2) (Table 6), Isipingo (sites S1 and S2) (Table 22) and uMbokodweni (site B1) (Table 26) were also dominant. This is to be expected as calcium carbonates dominate the estuarine environment due to the marine influence (Wiley, 1977). Shells and marine organisms which contain high levels of calcium carbonates, enter the estuary through tidal cycles and waves and are deposited with estuarine sediments (Du Laing *et al*., 2009).

Fe concentrations were relatively high in estuaries such as the uTongati (site T3), uMdloti, uMgeni and Isipingo (site S3) estuaries. A geological source for the high Fe is likely as Ecca Shale and Dwyka Tillite, prevalent in much of the region, and contains high amounts of iron which, upon weathering, is transported to the estuary (Drennan, 1965). The bedrock beneath the uMdloti estuary is Ecca Shale which could also be contributing to the high levels of iron (Drennan, 1965). The geology present beneath the uMgeni estuary as well as soils derived from its catchment are rich in iron (Beater and Frankel, 1965). The abundant dolerite present in the catchment and estuary contribute to the high iron levels which are released as iron oxides into the derived soils within the catchment and estuary (Beater and Frankel, 1965). Late Jurassic Karoo Dolerite intrusions that overlie Dwyka Tillite are present within the catchment and within the upper catchment. Located further downstream, Ecca rocks are found, with rocky outcrops of Dwyka Tillite located near the Connaught Bridge (Abed, 2009). The bedrock underlying the uMgeni estuary is shale which is fractured and weathered towards the surface with some Dolerite intrusions. The Fe concentrations detected in the approximate upper reaches of the uTongati (site T3) and Isipingo (site S3) estuaries were consistent throughout the core which suggests a natural source. The uTongati catchment contains Dwyka conglomerates and Ecca shale as well as bedrock of shale and dolerite which

are present beneath the estuary (Begg, 1978). Dwyka Tillite is present in the Isipingo catchment (Begg, 1978) which may be contributing to the levels of iron at this site.

Al concentrations were relatively high in estuaries such as the uMdloti at sites D2 and D3 and most likely emanate from geological alumina-silicate rich sources of the catchment (Olubunmi and Olorunsola, 2010). Significant correlations with Al and other metals which occurred in the uTongati (Fe, Mg and P), uMdloti (Fe and Mg), uMgeni (Ca, Fe, Mg, P and S) Isipingo (Cu, Mg, Mn and P) and uMbokodweni (Fe, Mg, Mn, P and S) estuaries may indicate a bonding of these metals to the clay particles which are transported into the estuaries (Schropp, 1988). Al and Mg are significantly correlated in all estuaries which may indicate a geological source which is present in all catchments, such a Dwyka Tillite which is rich in Al and Mg (Beater and Frankel, 1965). In the uTongati and uMdloti estuaries, Fe and Al share a high degree of similarity in the dendograms (Figures 40 and 47 respectively). These adjacent catchments contain the same geology i.e. Ecca Shale and Dwyka Tillite which are rich in iron and aluminium (Moor *et al*., 2001). The principal mineral hosts for iron are the authigenic minerals, chamosite and siderite which make up a large percentage of Ecca Shale (Drennan, 1965). According to a study conducted by Beater and Frankel (1965), the progressive weathering of Dwyka Tillite in KwaZulu-Natal introduces increased alumina content into the soils.

Anthropogenic influences for the element concentrations are improbable given the age of the sediments. However with the probable integration of re-worked older sediments with recent metal concentrations upstream, following the recent flood events, the presence of anthropogenically sourced elements would be possible, although detected in very low concentrations. Concentrations of Cu, Pb and V were highest at the surface at site D3 in the uMdloti estuary (Figure 46) along with As concentrations at site G2 and Pb concentrations at site G3 in the uMgeni estuary (Table 14) which may indicate an anthropogenic source which is supported by a high enrichment factor (Tables 12 and 16).

Similarities among elements in the dendograms may also suggest an anthropogenic influence. High similarities between elements in the dendograms occurred in the uTongati estuary between Cu, V, Ni and Mn (Figure 40); the uMdloti estuary between Cu, V, Pb, Cd, Cr, As and Mn (Figure 47); the uMgeni estuary between Zn, As and Mn in one sub-cluster and between Cu, Pb and V in another sub-cluster (Figure 55); the Isipingo estuary between Zn, Cu, Ni and Mn (Figure 65); and lastly the uMbokodweni estuary between Cu, Pb and V (Figure 72). Pb, As and Ni are also significantly correlated in the uMbokodweni estuary

(Table 27). The enrichment factor supports the similarities in the uTongati (Table 8) and uMbokodweni (Table 28) estuaries. In the uMdloti estuary, Cr and Mn are not enriched and could explain their similarity to the other elements in the dendogram through similar concentration variation throughout the estuary (Table 12). The similarity between the uMgeni estuary elements in the dendogram may be due to concentration variations per site and are also related to the enrichment of these elements. The enrichment of elements Zn, As and Mn occurs mainly at sites G2 and G3 whereas the enrichment of elements Cu, Pb and V occurs mostly at sites G1 and G4 (Table 16). This element enrichment distribution may suggest that Zn, As and Mn are sourced from anthropogenic sources upstream. Zn, Ni and Mn are enriched in the Isipingo estuary (Table 24); however Cu, which is not enriched, may share similarity with the other elements in the dendogram due to similar concentration variations.

Sulphur concentrations within the estuaries were relatively higher towards the base of cores, where oxygen levels were depleted. Sulphate is the dominant electron acceptor for oxidation of organic carbon via dissimilatory sulphate reduction in oxygen depleted marine environments (Panutrakul *et al*., 2001). It has been reported that 65% to 85% of organic carbon in coastal marine sediments is decomposed by sulphate reduction (Jorgensen *et al*., 1990). Anaerobic conditions at the base of cores at sites D2, G4, S1, S2 and S3, have provided the environment conducive for sulphate respiring bacteria thus resulting in the increased concentrations of sulphur at these sites.

Maximum concentrations of elements (Cu, Ni, Pb, Al, V and S) within the mangrove environment such as the uMgeni Beachwood mangroves (site G4), suggests that the sediments within these environments are metal traps within estuaries (Table 14). The high levels of clays present at the surface do act as a sink for metals thus contributing to the high levels present there (Tam and Wang, 2000; Leuci, 2000). However intrinsic characteristics of mangrove sediments may assist in this accumulation. The sediments present in mangrove environments are poorly drained, saline and anaerobic. These soils tend to remain waterlogged even at low tide due to the very fine sediments and clays it contains (Steinke, 1995). Consequently, mangrove sediments are typically anaerobic with only a thin oxygenated layer of soil at the surface. Due to these low oxygen conditions, iron sulphides form within the sediment and they provide high adsorption sites for other metals. Metal sulphides are produced thus trapping them in anoxic sediments (Wilkin, n.d).

Significant correlations between Fe and S within the uTongati (Table 7) and Isipingo (Table 23) estuaries may indicate the formation of iron sulphides within the estuarine sediments. The

possible bonding of sulphates with metals within the estuarine sediments may include Ni at site G4 where Ni and S concentrations follow the same concentration pattern with depth. A significant correlation between Pb and S in the Durban Harbour may also be due to possible bonding as both elements' concentrations increased in sample Hb (Table 19).

Fe-Mn oxides which are present within the sediment provide high adsorption sites for other metals (Ruiz-Fernandez *et al*., 2001). The significant correlation between Fe and P and Fe and Mg, as well as Mn with Zn in the uMgeni estuary (Table 15), as well as the similarity in the dendogram between Mn and Zn, Cu and Ni in the Isipingo estuary (Figure 65) may be due to the bonding of Fe-Mn oxides to metals.

Phosphorus was detected at high values in the Isipingo estuary at site S3 and is possibly from catchment sources. Phosphatic sedimentary rocks which are rich in phosphates are usually inter-bedded with shales and sandstones, which are abundant in this catchment and could be the source of the phosphorous present in the sediments (Annan, 2002). Phosphates immobilise metals in soils and therefore can also be known as a metal trapping agent (Cao *et al*., 2003). P is significantly correlated with Fe and Mg in the uMgeni estuary as well as grouped in the same sub-cluster as elements Cu, Pb and V, and linked to the sub-cluster containing elements Zn, As and Mn in the dendogram (Figure 55). In the uMdloti estuary, P is closely linked to V and Pb in the dendogram (Figure 47). These links to other metals in the dendograms may suggest the trapping of metals by phosphates in the sediment within these two estuaries.

As previously mentioned clays and silts act as adsorption sites for metals (Inel *et al*., 1998). The variation of metal concentration with depth was largely dependent on the clay and silt concentrations present within the samples. At sites where there was an abundance of clay and fines at the base of the cores i.e. sites T1, T2, D1, D2, G4 and Hb, and an abundance of clays at the surface of the cores i.e. sites G1, G3, B2 and B3, the concentrations of metals were higher. In the Isipingo estuary which contained the greatest amounts of clays, the variation of metal concentrations with depth followed the same pattern. Significant correlations between metals and clays and silts included Mg in the uTongati estuary (Table 7), Zn, P and Mn with clay and Mn and P with silt in the uMgeni estuary (Table 15), V with clay and Fe with silt in the Durban Harbour (Table 19), and Al, Fe and S which was correlated to both clays and silt in the Isipingo estuary (Table 23). These correlations may indicate an adsorption of these elements to clay and silt.

Significant negative correlations occurred between sand, clays and silts in the uTongati, uMdloti, uMgeni, Isipingo and uMbokodweni estuaries. During turbulent conditions within the estuary, large amounts of sand accumulate onto the estuary floor and the clay is re-suspended into the water column, thus lowering the amount of clay present in the sediments (NOAA, 2005). Significant negative correlations also occurred between sand and metals. This is due to the preference of metals to finer particles like clays and silts (as mentioned above) (Stathi *et al*., 2010). Elements such as Mg in the uTongati estuary (Table 7), Mn, P and Zn in the uMgeni estuary (Table 15), Al in the Durban Harbour (Table 19), and Fe and S in the Isipingo estuary (Table 23) were significantly negatively correlated to sand.

Organic matter also provides adsorptive sites as does clays and silts, allowing for adsorption (Dias Filno and do Carmo, 2006). Al, Mg and Mn in the uMdloti estuary (Table 11), Zn in the uMgeni estuary (Table 15), and S and Fe in the Isipingo estuary (Table 23) were significantly correlated with organic matter.

Comparing the results from contamination factor (CF), pollution load index (PLI) and geological accumulation index (I_{geo}) (Appendix B), enrichment factor (EF) showed enrichment of elements in the sediments whereas the others indicated no contamination by any element. The quantitative analysis basis of each of the indices varies i.e. for each, the mathematical structure varies, and thus they each express the level of contamination in different ways. Hence, some of them may show contamination and others may not depending on the emphasis of each index. Thus the results have to be viewed in the context of each index. Based on actual concentrations, each estuary contains very low concentrations of elements which can be linked to its ability to naturally recover from pollution episodes from flood events. Furthermore, the combination of re-worked older sediments and recent metal concentrations from upstream may have been deposited into the estuaries following flood events, and may explain the detection of certain low metal concentrations in the sediment samples such as Cu, Ni, Pb, As, and V.

Cu, Ni, As and Pb displayed similar high enrichment in the uMgeni estuary at sites G1 and G4 (Table 16), the Durban Harbour (Table 20) and the uMbokodweni estuary at all sites (Table 28), and showed a general down core decrease in concentration in these estuaries (Tables 14, 18 and 26 respectively). The enrichment of these elements also increased towards the head of the uMdloti estuary (Table 12). These four elements which have similar high enrichment in these estuaries are indicative of an anthropogenic source, possibly from upstream industrial areas, such as the Springfield or Pinetown Industrial area in the uMgeni

catchment, the industrial area surrounding the Durban harbour, and the Prospecton Industrial area upstream of the uMbokodweni estuary. The Isipingo estuary displayed different enrichment with metals S and Ni which were enriched in all samples except S2d and S3b for S and S3c for Ni (Table 24). The anoxic environment of the Isipingo estuary has encouraged the accumulation of sulphur within the estuarine sediments explained above.

6.5. eThekwini Municipality

Focusing on the eThekwini municipality as a whole, mean values from the estuaries were used to determine the overall status of the estuaries in terms of metals. The organic matter content, textural properties and the geochemical aspects are discussed here together with the statistical interpretations from Pearson correlation and Principal Component Analysis and the pollution status based on the enrichment factor.

In ascending order, Isipingo, uMgeni and uMdloti estuaries accounted for the highest mean organic matter content within the study area (Figure 73). Some of the sites sampled in the Isipingo and uMdloti estuaries were in mangrove habitats (sites S1 and S2 in Isipingo; and D1 in uMdloti). This may have contributed to greater leaf litter deposited at the surface of the sites which attributed to the high organic matter content (Goni *et al*., 2003). These estuaries may also receive large amounts of organic wastes from their catchments, especially the uMgeni which has the largest catchment size, is mainly urbanised, and receives greater urban runoff (Diederichs *et al*., 2002).

As mentioned previously, the types of estuarine sediments may also play a role in the amount of organic matter present. Organic matter is positively correlated to clays and silts, and negatively correlated with sand (Table 30). This suggests that the organic matter increases as fines increase (Burke *et al*., 1989).

The other estuaries (uTongati, Durban Harbour and uMbokodweni) contain lower values of organic matter and are mainly dominated by sandy sediments. This is due to longer periods of open mouth conditions creating greater marine and fluvial exchange of water and sediments and higher energy environments.

The texture results revealed that Isipingo, uMdloti and uMgeni estuaries contained the greatest amounts of clays and silts (Figure 74). The very low energy environments in the uMdloti and Isipingo estuaries have resulted in high accumulations of clay within the estuary (Ladachart *et al*., 2011). The uMdloti estuary is usually in a closed mouth state for 70% of the

year, which allows for the settling of fine particles such as clays and fines. The Isipingo River is canalised which lowers riverine input, and has two concrete pipes at the mouth of its estuary which limits marine input, thus accretion of fines occurs throughout the estuary (Ladachart *et al*., 2011). The uMgeni estuary contains greater amounts of clay in the sheltered mangrove habitat and near the mouth, behind the sand bar where clays have accumulated in an area protected from strong wave action.

All estuaries yielded low mean concentrations for all elements. A high abundance of shells in the sediments collected at the Durban Harbour site accounted for the highest mean Ca concentration among all estuaries (Figure 75) (Achyuthan and Richardmohan, 2002). Cu and V mean concentrations were also highest in this estuary. Maximum mean concentrations of Ni and Pb were exhibited by the uMbokodweni estuary, while the uMgeni estuary contained the highest mean concentrations of Mn and As. The remainder of the elements, Zn, Fe, Al, Mg, P and S exhibited their highest mean concentrations in the Isipingo estuary which may be due to the high clay content in the sediment (Dube *et al*., 2001).

It can be seen that the Isipingo, uMbokodweni, and uMgeni estuaries and the Durban Harbour contain the greatest concentrations of elements (Figure 75). Their catchments contain greater amounts of urban and industrial development, which may be impacting on the presence of these elements in the estuarine sediments (Diederichs *et al*., 2002). The uTongati and uMdloti catchments are mainly covered by natural bush or sugarcane farms. The limited or lack of industrial development in these catchments is reflected in the relatively lower concentrations of elements present within the estuarine sediments.

Pearson correlation was used to determine the relationships amongst all mean element concentrations, organic matter and texture percentages that were present in all estuaries (Table 30). Significant correlations between Al, Fe and P were displayed in all estuaries, reflecting alumina-silicate sources (Schropp, 1988). Fe and S were significantly correlated as well, which may be due to their combination in anoxic sediments to form iron sulphide or pyrite (Chandran *et al*., 2012). Fe is again seen to have a significant correlation with clays reflecting the strong affinity of this element to charged clay surfaces. In all estuaries, clays and silts were significantly negatively correlated to sand demonstrating the redistribution of lighter, fine particles during high energy conditions to another part of the estuary, while heavier sand particles remain behind (NOAA, 2005).

Principal component analysis was also performed on the mean concentrations of elements from all estuaries to determine the possible influencing factors that determine the greatest variance amongst the variables. The first principal component (PC1) displays 98.02% variance and dominates the variance within this data. Ca exhibited the highest positive loading at 1.000 (Table 31- indicated by *). This component may indicate the marine input on the estuary as Ca has the highest positive loading. All the estuaries in this study have a marine influence as they are temporarily open/closed estuaries and are not permanently closed throughout the year (Whitfield and Bate, 2007). The negative loadings within this first component include Al, Cd, Fe, Mn and Zn. This may suggest that these elements are sourced from their respective catchments from geological sources.

Principal component 2 (PC2) has high positive loadings of Al and Fe (Table 31- indicated by *) which may be interpreted as a lithogenic or geological component. Al and Fe are the two most abundant elements within the earth's crust and therefore would be present in estuaries originating from sediment erosion from the catchment or perhaps from bedrock present beneath the estuary (Moor *et al*., 2001). The negative loadings of As, Cu, Ni, Pb and V in PC2 may indicate a different source of origin for these elements. Usually these elements are considered anthropogenic as most of these elements are used or released from industrial processing and manufacturing (Vaalgamaa and Conley, 2008). The negative loadings could also indicate a different distribution pattern of these elements within the estuaries i.e. some of these elements are found only at certain sites depending of the deposition of sediments, unlike Fe and Al which are present at every site.

The PCA loading plot (Figure 76) exhibits a grouping of the uMdloti, uMgeni, uTongati and uMbokodweni estuaries, with the Isipingo estuary and Durban Harbour lying separately to this group. PC1 mainly influences the distance between these groups whereas PC2 affects the location of the Isipingo estuary in the biplot. As seen in the PCA biplot (Figure 77), Ca concentrations have the greatest influence as the concentrations present within the Durban Harbour separate it from the rest of the group. The permanently open mouth of the harbour allows for greatest exchange of marine waters and sediments even in the upper reaches (Dyer, 1986). The grouping of the first four estuaries (uMdloti, uMgeni, uTongati and uMbokodweni) may indicate that these estuaries share similar catchment/geological input of elements, contrasting the dominantly marine input from the Durban Harbour.

The Isipingo estuary lies slightly further away from the group of estuaries (uMdloti, uMgeni, uTongati and uMbokodweni) in the PCA biplot, and is mainly influenced by PC2. This could

mean that this estuary is not that greatly affected by the marine environment (given its limited connection), but more associated with its lithogenic or geological component as Fe and Al have the highest positive loadings in the component loadings table (Table 31). Fe has also influenced the position of the Isipingo estuary in the PCA biplot (Figure 77 – orange line). Despite this estuary's limited catchment input due to the diversion of the uMlazi River (SSI/MER, 2011), it still recorded the highest mean concentration of Fe across all estuaries (Figure 75) which indicates a strong geological input, thus influencing its location in the loading plot.

The enrichment factor values for each estuary are shown in Table 32. Cu, Ni, Pb, As and V exhibit very high enrichment values in the uMbokdweni estuary whereas Ca, P and S enrichment values are highest in the Durban harbour. These enrichment values are exceptionally high when taking into account the mean concentrations per estuary. Despite these high enrichment values, the individual concentrations per site for each element are below sediment quality guideline levels (Table 29). Also the calculations of other pollution indices, as mentioned above for each estuary, yielded results which indicate no contamination. Therefore the metals currently present within the sediments of each estuary pose no threat to the aquatic biota.

Overall, the estuaries studied within the eThekwini Municipality have exhibited low concentrations of elements within their sediments which indicate that they are in a fairly good environmental condition in terms of heavy metal loading. Previous research conducted on the sediment quality of these estuaries has stated that the surface sediments within some of the estuaries are poor due to high contamination of metals (Chili, 2008; Tinmouth, 2010; Shozi, 2011). Monitoring studies conducted to monitor the level of pollution in rivers and estuaries are usually related to isolated anthropogenic pollution episodes which calls for research to be pursued within that polluted area. However with the current samples taken in this study to depths up to 2 m, it can be seen that even at the general surface of the estuaries, the sediments are not contaminated or polluted. It is perhaps due to the major flood events that have occurred over time that has allowed the flushing of the polluted sediments from the estuary into the sea (Cooper, 2002). Floods, therefore, provide a necessary mechanism to 'flush out' the estuaries of its accumulated pollutants. Studies conducted before and after major floods have noted significant textural changes in the estuarine sediments (Badenhorst et al., 1989; Cooper, 1993; Cooper, 2002). This could be related to the sediments which are flushed out and likely replaced by re-worked older sediments from upstream, which may explain the age

of the sediments at the general surface. It is also probable that along with the re-worked sediments, recent concentrations of metals are transported as well which may explain the presence of metals such as Pb, Ni, Cu, As and V which are commonly used in industry, in aged sediments. Despite the transport of these metals, the concentrations of these elements within the sediments are still very low and do not pollute the environment. This is indicative by the abundance of flora and fauna present within these estuaries, which would be absent if conditions were truly degraded. Therefore it may be possible that the estuaries along this coastline have the ability to recover after pollution events and re-establish as dynamic features of the coastline.

6.6. Conclusion

This chapter has discussed the findings of this study. It has interpreted the sedimentology, age of sediments and the geochemistry. The sedimentology section has discussed colour and textural changes, organic matter, sediment movements based on energy conditions within the estuaries, and mouth conditions. Reasons for the variations of metal concentrations among the estuaries were discussed in the geochemistry section, along with statistical evidence to support certain interpretations. The enrichment factor pollution index was also discussed in relation to the other indices applied. All estuaries were summed together in the final eThekwini Municipality section which highlighted organic matter and texture variations. Geochemical interpretations of mean metal concentrations as well as statistical analyses from Pearson correlation and Principal Component Analysis were also discussed. The enrichment factor was discussed and highlighted elements which displayed high levels of enrichment. A conclusion and recommendations chapter follows this which provides concluding remarks and some recommendations for further research.

Chapter 7

CONCLUSION AND RECOMMENDATIONS

7.1. Conclusions and key findings of this study

This research aims to spatially and temporally assess the sedimentology of six estuaries within the eThekwini Municipality, as well as to determine the metal concentrations within these sediments and examine the general estuarine contamination status. The results of the research indicate that:

- A considerable amount of organic matter was found to be present in the sediments of all estuaries lending a brown to dark colour to the cores, especially at the surface. Organic matter content was found to typically increase towards the head of the estuary or in mangrove environments given the greater leaf litter at the surface. Black sediments characterised the Isipingo estuary where anaerobic conditions prevailed.

- The texture of the sediments varied per estuary. The uTongati, uMgeni, uMbokodweni estuaries and the Durban Harbour contained greater sand percentages; and the uMdloti and Isipingo estuaries contained greater amounts of clays and fines. Low energy environments, caused by closed mouth conditions in the uMdloti and Isipingo estuaries or sheltered environments like the Beachwood mangroves in the uMgeni estuary allowed for the accumulation of fines.

- The development of sand bars is a common feature along the mouths of the estuaries studied. The sand bar forms in a southerly direction in each estuary, which coincides with the dominant southerly longshore drift current that also aids in the onshore transport of marine sediment into the estuaries.

- The estuaries studied within the municipality are all temporarily open/closed estuaries that are also subjected to high energy events such as floods. The coarse and fine sediment strata down core indicate periods of open and closed mouth conditions through time. Accumulations of mixtures of coarse and fine sands in dated samples provided evidence of high fluvial flow occurrences in the past.

- The dated ages of the sediments within all estuaries were between approximately 700 years and 4180 years BP. The combination of scoured recent surface sediments across all estuaries by flood events as well as the deposition of re-worked older sediments from upstream, accounts for the old age of sediments near the surface.

- Metal concentrations within all estuaries were very low. Ca concentrations were dominant, especially at the mouths of the estuaries, and result from a strong marine influence in estuaries such as the uTongati, Isipingo and uMbokodweni as well as the Durban Harbour. Geological or natural sources of elements were prevalent in estuaries like the uMdloti and the uMgeni where Fe concentrations were dominant throughout.

- Metal concentration variations with depth were mainly governed by the presence of fines. The strong adsorptive properties of fines influenced the accumulation of elements throughout the core samples. Large amounts of clays present at lower depths also allowed for dominant anoxic conditions and the increase of sulphur concentrations as was found in the Isipingo estuary sediments.

- Estuaries such as the uMgeni and uMbokodweni which are located immediately downstream of industrial and urban areas were found to contain relatively higher concentrations of elements Pb, Cu, As and Ni. During high fluvial flow events, re-worked upstream sediments along with these anthropogenically sourced elements were transported to the estuaries and deposited onto the estuarine beds.

- Relatively high enrichment level of metals Pb, Cu, As and Ni were obtained for the uMgeni and uMbokodweni estuaries and for the Durban Harbour sediments. However, considering that the actual concentrations of these metals within the estuarine sediments are all below sediment quality guideline levels, it is clear that their concentrations pose no threat to the aquatic biota within the estuaries.

Overall, the general pollution level of the estuarine sediments within the eThekwini Municipality is very low. The metal concentrations in all samples were lower than the stipulated sediment quality guideline levels and the presence of abundant flora and fauna within the estuarine environments studied provided visual evidence of their relatively good

health status. The removal of sediments by flood events within this region may be considered a useful tool to help eradicate the possible accumulations of metals and other harmful pollutants. Therefore it may be said that the climatic influence on estuaries within this region has a 'cleansing' effect on the estuarine environments in removing contaminants.

7.2. Recommendations

The aims and objectives of this study have been addressed, however further recommendations include:

- A greater amount of core sites should be taken in future studies to allow for a more detailed representation of the estuarine sediments, especially for the creation of cross-sections across the estuary. It would also account for sediment variations occurring in close proximity.
- Despite the low concentrations of metals in the sediments found in this study, other studies have stated that surface sediments (1-5 cm) may be contaminated. Therefore ongoing monitoring of sediment contamination, especially surface sediments, should be conducted.
- Special attention should be given to testing the levels of Pb, Cu, As and Ni in the estuarine sediments, as most of the estuaries within this municipality have very urban and industrial catchments, and these metals can be very harmful to aquatic biota if levels should accumulate to above sediment quality guideline levels.
- Future research examining the health of the flora and fauna in these estuarine environments should be pursued as it may be useful to determine whether any bioaccumulation of metals has taken place during that time.
- There is also a lack of information on the current health status of the mangrove environments of the uMdloti, uMgeni and Isipingo estuaries and the Durban Harbour. Future research should focus on these areas within the estuaries as they tend to become sinks for metals and are not flushed as easily compared to the other areas of an estuary.

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Appendices

Appendix A:

Historical Images

Figure A1: The complete removal of the sand bar across the uMgeni estuary mouth during the 1987 floods (www.stad.com date accessed 30-01-2013).

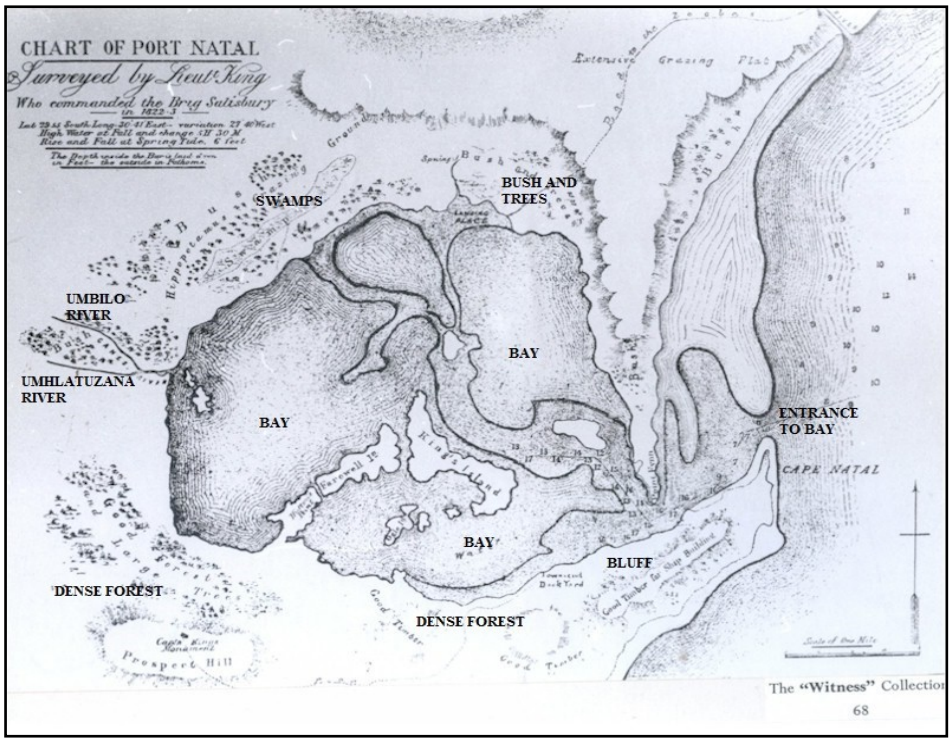

Figure A2: The Durban Harbour (previously known as the Durban Bay) surveyed by Lieutenant King in 1822 in its original state, surrounded by dense forests and swamps (www.umgenisteamrailway.co.za date accessed: 16-03-13).

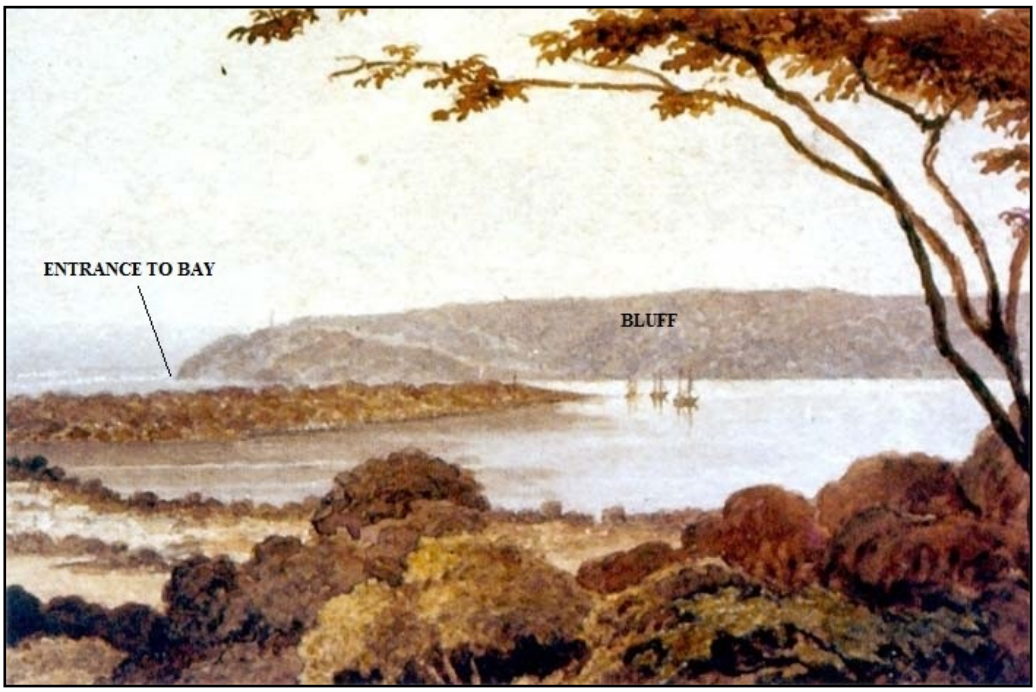

Figure A3: A painting of the Durban Harbour in 1859 (www.umgenisteamrailway.co.za date accessed: 16-03-13).

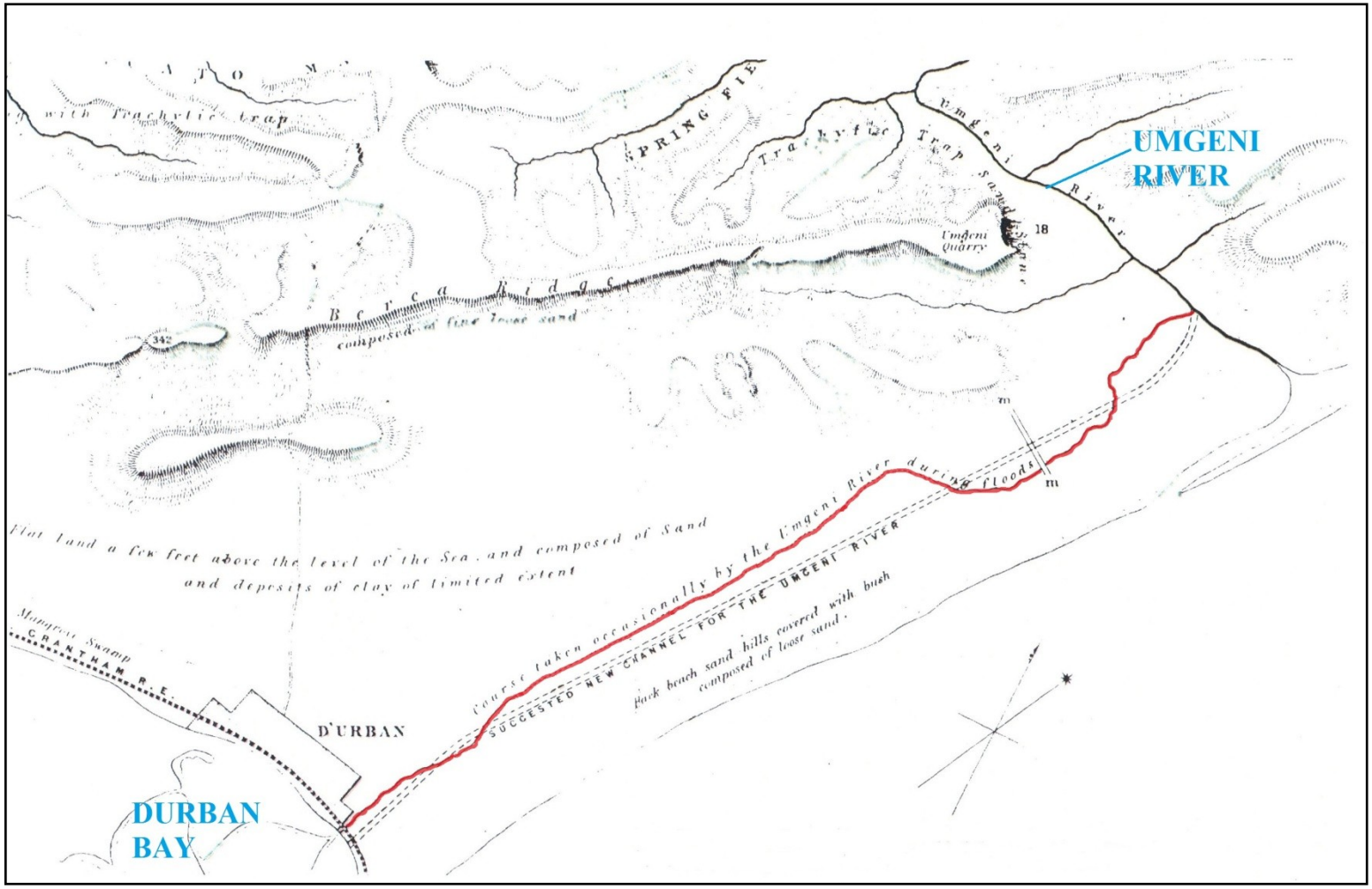

Figure A4: An illustration of the route taken by the uMgeni River (indicated in red) into the Durban Bay during the flood of 1856 (Barnes, 1984).

Appendix B:

Indices (CF, PLI and I_{geo}) and correlation results

Contamination Factor and Pollution Load Index results per estuary

Table B1: Contamination Factors of elements present within the sediments of the core sites, and Pollution Load Index per core site in the uTongati estuary.

Element	Clarke Value	Core sites		
		T1	T2	T3
Cu	70	0.000	0.000	0.000
Ni	80	0.000	0.000	0.000
Fe	50000	0.000	0.000	0.000
Al	81300	0.000	0.000	0.000
V	150	0.000	0.000	0.000
P	1180	0.000	0.000	0.000
Ca	36300	0.000	0.000	0.000
Mg	20900	0.000	0.000	0.000
Mn	1000	0.000	0.000	0.000
S	2400	0.000	0.000	0.000
PLI		0.000	0.000	0.000

Clarke values after Martinez *et al.*, 2007

Table B2: Contamination Factors of elements present within the sediments of the core sites, and Pollution Load Index per core site in the uMdloti estuary.

Element	Clarke Value	Core sites		
		D1	D2	D3
Cu	70	0.000	0.001	0.001
Cd	0.15	0.045	0.000	0.000
Pb	16	0.001	0.001	0.006
Cr	200	0.000	0.000	0.000
As	5	0.002	0.001	0.003
Fe	50000	0.000	0.000	0.000
Al	81300	0.000	0.000	0.000
V	150	0.000	0.000	0.000
P	1180	0.000	0.000	0.000
Ca	36300	0.000	0.000	0.000
Mg	20900	0.000	0.000	0.000
Mn	1000	0.000	0.000	0.000
S	2400	0.000	0.000	0.000
PLI		0.000	0.000	0.000

Clarke values after Martinez *et al.*, 2007

Table B3: Contamination Factors of elements present within the sediments of the core sites, and Pollution Load Index per core site in the uMgeni estuary.

Element	Clarke Value	Core sites			
		G1	G2	G3	G4
Zn	132	0.000	0.000	0.000	0.000
Cu	70	0.001	0.000	0.000	0.001
Ni	80	0.000	0.001	0.000	0.001
Pb	16	0.002	0.001	0.000	0.005
As	5	0.001	0.036	0.000	0.003
Fe	50000	0.000	0.000	0.000	0.000
Al	81300	0.000	0.000	0.000	0.000
V	150	0.000	0.000	0.000	0.000
P	1180	0.000	0.000	0.000	0.000
Ca	36300	0.000	0.000	0.000	0.000
Mg	20900	0.000	0.000	0.000	0.000
Mn	1000	0.000	0.000	0.001	0.000
S	2400	0.000	0.000	0.000	0.001
PLI		0.000	0.000	0.000	0.000

Clarke values after Martinez *et al.*, 2007

Table B4: Contamination Factors of elements present within the sediments of the core site, and Pollution Load Index of the core site in the Durban Harbour.

Element	Clarke Value	Core site
		H
Cu	70	0.001
Ni	80	0.001
Pb	16	0.002
As	5	0.005
Fe	50000	0.000
Al	81300	0.000
V	150	0.000
P	1180	0.001
Ca	36300	0.002
Mg	20900	0.000
Mn	1000	0.000
S	2400	0.001
PLI		0.000

Clarke values after Martinez *et al.*, 2007

Table B5: Contamination Factors of elements present within the sediments of the core sites, and Pollution Load Index per core site in the Isipingo estuary.

Element	Clarke Value	Core sites		
		S1	S2	S3
Zn	132	0.000	0.000	0.000
Cu	70	0.000	0.000	0.000
Ni	80	0.001	0.001	0.001
Fe	50000	0.000	0.000	0.000
Al	81300	0.000	0.000	0.000
P	1180	0.000	0.000	0.002
Ca	36300	0.001	0.000	0.000
Mg	20900	0.000	0.000	0.000
Mn	1000	0.000	0.000	0.000
S	2400	0.001	0.002	0.002
PLI		0.000	0.000	0.000

Clarke values after Martinez *et al*., 2007

Table B6: Contamination Factors of elements present within the sediments of the core sites, and Pollution Load Index per core site in the uMbokodweni estuary.

Element	Clarke Value	Core sites		
		B1	B2	B3
Cu	70	0.001	0.001	0.001
Ni	80	0.002	0.002	0.002
Pb	16	0.003	0.003	0.003
As	5	0.003	0.004	0.003
Fe	50000	0.000	0.000	0.000
Al	81300	0.000	0.000	0.000
V	150	0.000	0.000	0.000
P	1180	0.000	0.000	0.000
Ca	36300	0.000	0.000	0.000
Mg	20900	0.000	0.000	0.000
Mn	1000	0.000	0.000	0.000
S	2400	0.000	0.000	0.000
PLI		0.000	0.000	0.000

Clarke values after Martinez *et al*., 2007

Geo-accumulation Index results per estuary

Table B7: Geo-accumulation index values of elements present within the sediments of the core samples in the uTongati estuary.

Elements	Clarke value	Core samples								
		T1a	**T1b**	**T1c**	**T2a**	**T2b**	**T2c**	**T3a**	**T3b**	**T3c**
Cu	70	0.000	0.000	0.000	-13.624	0.000	0.000	0.000	0.000	0.000
Ni	80	0.000	0.000	-12.371	-12.558	-12.159	0.000	0.000	0.000	0.000
Fe	50000	-14.751	-16.564	-14.343	-16.471	-16.094	-15.233	-16.793	-14.874	-16.458
Al	81300	-15.888	-18.049	-15.498	-17.895	-17.425	-15.424	-18.047	-15.361	-17.759
V	150	-13.124	0.000	0.000	-16.075	0.000	0.000	0.000	0.000	0.000
P	1180	-13.688	-15.929	-13.531	-15.021	-15.087	-11.649	-16.033	-10.812	-16.151
Ca	36300	-18.025	-16.279	-12.908	-16.071	-12.767	-12.967	-17.829	-14.806	-18.371
Mg	20900	-16.490	-18.101	-15.728	-19.103	-16.787	-12.044	-18.634	-13.969	-18.434
Mn	1000	0.000	0.000	0.000	0.000	0.000	-12.703	0.000	-13.069	0.000
S	2400	-13.780	-14.427	-11.173	-16.693	-14.352	-13.705	0.000	-15.287	0.000

Clarke values after Martinez *et al*., 2007

Table B8: Geo-accumulation index values of elements present within the sediments of the core samples in the uMdloti estuary.

Elements	Clarke value	Core samples								
		D1a	**D1b**	**D1c**	**D2a**	**D2b**	**D2c**	**D3a**	**D3b**	**D3c**
Cu	70	-13.576	-11.986	-10.903	-11.021	-11.031	-10.122	-10.342	-10.427	-10.452
Cd	0.15	-3.468	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pb	16	0.000	-11.104	-10.289	-11.964	-10.997	-9.099	-6.858	-9.445	-9.538
Cr	200	0.000	0.000	0.000	0.000	0.000	-18.320	0.000	0.000	0.000
As	5	0.000	0.000	-8.136	0.000	0.000	-8.763	-9.194	-9.027	-9.015
Fe	50000	-12.434	-15.324	-13.344	-13.873	-14.193	-13.539	-14.196	-16.023	-16.489
Al	81300	-14.710	-16.362	-14.335	-15.426	-15.947	-14.567	-15.204	-17.292	-17.556
V	150	0.000	-13.126	-12.172	-12.656	-12.748	-11.490	-11.729	-12.045	-12.018
P	1180	-13.350	-14.777	-13.796	-14.607	-14.757	-13.512	-12.979	-14.179	-14.276
Ca	36300	-11.959	-17.249	-14.969	-16.424	-16.804	-15.391	-16.336	-17.221	-18.324
Mg	20900	-14.068	-16.289	-14.367	-15.307	-15.810	-14.186	-15.508	-17.393	-17.666
Mn	1000	0.000	-14.562	-14.525	-14.563	-17.454	-14.124	-15.556	-17.883	-18.359
S	2400	0.000	0.000	0.000	-15.339	-16.746	-10.928	-14.046	-14.520	-14.377

Clarke values after Martinez *et al*., 2007

Table B9: Geo-accumulation index values of elements present within the sediments of the core samples in the uMgeni estuary.

Elements	Clarke value	Core samples												
		G1a	G1b	G1c	G1d	G2a	G2b	G2c	G3a	G3b	G3c	G4a	G4b	G4c
Zn	132	0.000	0.000	0.000	0.000	-13.310	0.000	0.000	-11.010	0.000	0.000	0.000	0.000	0.000
Cu	70	-10.534	-10.444	-10.955	-10.949	-11.092	-11.092	-15.847	-12.453	0.000	-16.506	-10.351	-10.457	-11.378
Ni	80	0.000	0.000	0.000	0.000	0.000	-9.919	0.000	0.000	0.000	0.000	-9.966	-10.473	-9.988
Pb	16	-8.737	-9.641	-9.806	-9.803	-9.835	-10.104	0.000	-11.088	0.000	0.000	-8.939	-7.395	-9.407
As	5	-9.951	-12.714	0.000	-11.176	-3.802	0.000	0.000	0.000	0.000	0.000	-8.926	-9.119	-8.846
Fe	50000	-13.312	-14.332	-14.683	-14.818	-14.682	0.000	-14.541	-13.308	-14.703	-14.616	-13.750	-14.951	-14.198
Al	81300	-14.825	-15.672	-15.955	-16.241	-16.538	-20.202	-16.270	-14.927	-16.632	-16.528	-15.045	-16.207	-15.385
V	150	-11.752	-12.199	-12.378	-12.386	-11.693	-12.977	0.000	-16.806	0.000	0.000	-11.694	-11.916	-11.821
P	1180	-11.835	-12.896	-14.084	-13.940	-11.936	-16.030	-13.435	-11.672	-13.378	-13.557	-12.225	-13.826	-13.408
Ca	36300	-14.164	-14.602	-14.994	-15.704	-16.405	0.000	-16.479	-15.772	-16.144	-16.592	-15.125	-16.890	-14.347
Mg	20900	-14.067	-15.134	-15.690	-15.803	-15.810	-24.651	-15.590	-14.804	-16.326	-16.171	-14.508	-15.946	-15.404
Mn	1000	-14.347	-14.265	-15.119	-14.685	-14.235	0.000	0.000	-9.421	0.000	0.000	-15.268	-15.633	-15.577
S	2400	-11.978	-15.896	-11.667	-12.129	0.000	-14.889	-16.352	-11.227	-13.860	-14.370	-10.975	-12.334	-11.567

Clarke values after Martinez *et al.*, 2007

Table B10: Geo-accumulation index values of elements present within the sediments of the core samples in the Durban Harbour.

Elements	Clarke value	Core samples		
		Ha	Hb	Hc
Cu	70	-10.364	-10.549	-11.423
Ni	80	-9.990	-10.072	-10.002
Pb	16	-9.345	-9.291	-9.592
As	5	-8.432	-8.144	-8.510
Fe	50000	-15.478	-14.857	-16.759
Al	81300	-16.660	-15.882	-17.468
V	150	-11.981	-11.859	-12.033
P	1180	-13.139	-12.731	-9.898
Ca	36300	-9.971	-8.727	-10.506
Mg	20900	-14.883	-14.568	-14.678
Mn	1000	-16.394	-16.420	-17.190
S	2400	-11.141	-11.034	-12.172

Clarke values after Martinez *et al*., 2007

Table B11: Geo-accumulation index values of elements present within the sediments of the core samples in the Isipingo estuary.

Elements	Clarke value	Core samples									
		S1a	S1b	S1c	S2a	S2b	S2c	S2d	S3a	S3b	S3c
Zn	132	-10.747	0.000	0.000	-12.165	0.000	0.000	0.000	0.000	0.000	0.000
Cu	70	-12.854	-13.395	-15.135	-12.631	-14.135	-13.853	-14.837	-12.115	-14.448	-13.270
Ni	80	-10.337	-10.350	-10.421	-10.989	-10.305	-10.285	-10.918	-10.205	-10.323	-11.270
Fe	50000	-13.264	-12.295	-14.136	-12.297	-14.013	-12.377	-14.139	-12.598	-13.526	-12.128
Al	81300	-15.391	-14.329	-16.258	-14.236	-16.072	-14.450	-15.879	-12.871	-15.647	-14.314
P	1180	-13.277	-12.322	-13.165	-12.565	-14.623	-13.973	-10.475	-8.219	-14.625	-12.836
Ca	36300	-11.834	-10.961	-10.611	-12.149	-11.353	-13.737	-13.814	-13.011	-13.585	-11.363
Mg	20900	-14.731	-13.767	-14.866	-14.168	-15.522	-14.681	-16.167	-12.359	-15.479	-13.623
Mn	1000	0.000	-14.847	0.000	-17.861	0.000	-13.036	0.000	-10.453	0.000	-13.350
S	2400	-10.397	-9.328	-11.537	-8.761	-11.495	-9.102	-11.995	-9.906	-11.279	-9.083

Clarke values after Martinez *et al*., 2007

Table B12: Geo-accumulation index values of elements present within the sediments of the core samples in the uMbokodweni estuary.

Elements	Clarke value	Core samples								
		B1a	**B1b**	**B1c**	**B2a**	**B2b**	**B2c**	**B3a**	**B3b**	**B3c**
Cu	70	-11.423	-10.437	-10.448	-10.399	-11.072	-10.395	-11.009	-11.011	-11.075
Ni	80	-9.956	-9.918	-10.005	-9.741	-10.021	-9.749	-9.754	-9.756	-10.019
Pb	16	-8.947	-9.289	-9.455	-8.839	-10.165	-8.841	-8.850	-8.843	-10.169
As	5	-8.676	-9.010	-8.897	-7.840	0.000	-8.563	-7.845	-8.723	0.000
Fe	50000	-15.438	-15.060	-15.491	0.000	0.000	0.000	0.000	0.000	0.000
Al	81300	-16.860	-16.206	-17.105	-21.856	-21.418	-20.628	-20.632	-20.630	-20.558
V	150	-11.981	-11.955	-12.029	-12.005	-13.600	-12.023	-12.025	-12.025	-13.641
P	1180	-12.722	-12.814	-13.973	-14.743	-17.137	-14.770	-14.810	-14.842	-16.879
Ca	36300	-12.284	-14.615	-16.022	0.000	0.000	0.000	0.000	0.000	0.000
Mg	20900	-15.475	-15.894	-16.397	-22.420	0.000	-22.441	-22.427	-22.327	0.000
Mn	1000	-16.158	-16.116	-16.597	-18.935	0.000	-18.939	-18.942	-18.941	0.000
S	2400	-13.724	-12.453	-14.154	-18.306	0.000	-16.304	-16.288	-16.343	0.000

Clarke values after Martinez *et al*., 2007

Pearson correlation of mean elemental concentrations from all estuaries

Table B13: Pearson correlation of mean elemental concentrations from all estuaries.

Al	1.000													
As	-0.337	1.000												
Ca	-0.111	0.076	1.000											
Cd	0.203	-0.183	-0.239	1.000										
Cu	-0.461	0.491	0.328	0.335	1.000									
Fe	0.994**	-0.302	-0.135	0.162	-0.428	1.000								
Mg	0.766	-0.483	0.312	-0.122	-0.653	0.718	1.000							
Mn	0.555	0.452	-0.298	-0.247	-0.382	0.581	0.306	1.000						
Ni	-0.221	0.104	0.516	-0.553	0.394	-0.147	-0.145	-0.225	1.000					
P	0.568	-0.203	0.668	-0.382	-0.240	0.566	0.801	0.226	0.434	1.000				
Pb	-0.511	0.571	0.134	0.389	0.973**	-0.478	-0.772	-0.307	0.242	-0.435	1.000			
S	0.820**	-0.296	0.282	-0.283	-0.410	0.837*	0.812*	0.444	0.299	0.896*	-0.553	1.000		
V	-0.572	0.556	0.405	0.262	0.979**	-0.552	-0.656	-0.400	0.357	-0.253	0.956**	-0.491	1.000	
Zn	0.800	0.072	-0.153	-0.301	-0.466	0.839*	0.565	0.855*	0.059	0.564	-0.486	0.816*	-0.548	1.000
	Al	**As**	**Ca**	**Cd**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**P**	**Pb**	**S**	**V**	**Zn**

***** Correlation is significant at the 0.05 level ($p < 0.05$).
****** Correlation is significant at the 0.01 level ($p < 0.01$).

Appendix C

All results for all samples per estuary

Table C1: All results including carbon age, organic matter, texture and element concentrations for each sample per core per estuary.

Core sample	Carbon age (BP)	OM (%)	Texture (%)			Element concentrations (ppm)														
			Clay	Silt	Sand	Zn	Cu	Ni	Cd	Pb	Cr	As	Fe	Al	V	P	Ca	Mg	Mn	S
uTongati																				
T1a		1.340	6	4	90	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.721	2.010	0.025	0.134	0.204	0.341	0.000	0.256
T1b		0.400	2	1	97	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.774	0.450	0.000	0.028	0.685	0.112	0.000	0.163
T1c		1.480	8	5	87	0.000	0.000	0.023	0.000	0.000	0.000	0.000	3.609	2.635	0.000	0.150	7.085	0.577	0.000	1.559
T2a		0.140	2	1	97	0.000	0.008	0.020	0.000	0.000	0.000	0.000	0.826	0.500	0.003	0.053	0.791	0.056	0.000	0.034
T2b	4180 +/- 40	0.140	2	1	97	0.000	0.000	0.026	0.000	0.000	0.000	0.000	1.072	0.693	0.000	0.051	7.811	0.277	0.000	0.172
T2c		1.880	12	10	78	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.948	2.773	0.000	0.551	6.802	7.422	0.225	0.270
T3a		1.620	4	6	90	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.660	0.450	0.000	0.026	0.234	0.077	0.000	0.000
T3b	2960 +/- 30	0.950	2	1	97	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.498	2.897	0.000	0.984	1.901	1.955	0.175	0.090
T3c		0.950	4	1	95	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.833	0.550	0.000	0.024	0.161	0.089	0.000	0.000
uMdloti																				
D1a		1.880	20	19	61	0.000	0.009	0.000	0.020	0.000	0.000	0.000	13.558	4.549	0.000	0.170	13.677	1.825	0.000	0.000
D1b		0.670	4	3	93	0.000	0.026	0.000	0.000	0.011	0.000	0.000	1.828	1.448	0.025	0.063	0.350	0.392	0.062	0.000
D1c	1280 +/- 30	2.550	8	6	86	0.000	0.055	0.000	0.000	0.019	0.000	0.027	7.214	5.899	0.049	0.124	1.697	1.484	0.064	0.000
D2a		2.410	30	24	46	0.000	0.051	0.000	0.000	0.006	0.000	0.000	4.998	2.769	0.035	0.071	0.619	0.773	0.062	0.087
D2b	1420 +/- 30	0.810	8	5	87	0.000	0.050	0.000	0.000	0.012	0.000	0.000	4.005	1.931	0.033	0.064	0.476	0.546	0.008	0.033
D2c		3.350	20	16	64	0.000	0.094	0.000	0.000	0.044	0.001	0.017	6.302	5.024	0.078	0.151	1.267	1.682	0.084	1.847
D3a		1.070	13	6	81	0.000	0.081	0.000	0.000	0.207	0.000	0.013	3.997	3.231	0.066	0.219	0.658	0.673	0.031	0.213
D3b		0.280	2	2	96	0.000	0.076	0.000	0.000	0.034	0.000	0.014	1.127	0.760	0.053	0.095	0.357	0.182	0.006	0.153
D3c		0.400	2	2	96	0.000	0.075	0.000	0.000	0.032	0.000	0.014	0.816	0.633	0.054	0.089	0.166	0.151	0.004	0.169
uMgeni																				
G1a		1.200	4	8	88	0.000	0.071	0.000	0.000	0.056	0.000	0.008	7.374	4.202	0.065	0.484	2.966	1.827	0.072	0.892

G1b		0.400	2	5	93	0.000	0.075	0.000	0.000	0.030	0.000	0.001	3.637	2.336	0.048	0.232	2.189	0.872	0.076	0.059
G1c	700 +/- 30	2.150	6	6	88	0.000	0.053	0.000	0.000	0.027	0.000	0.000	2.851	1.920	0.042	0.102	1.668	0.593	0.042	1.107
G1d		0.810	2	2	96	0.000	0.053	0.000	0.000	0.027	0.000	0.003	2.597	1.574	0.042	0.113	1.020	0.548	0.057	0.804
G2a		2.150	10	11	79	0.020	0.048	0.000	0.000	0.026	0.000	0.538	2.854	1.282	0.068	0.452	0.627	0.546	0.078	0.000
G2b	2700 +/- 30	1.570	2	2	96	0.000	0.048	0.124	0.000	0.022	0.000	0.000	0.000	0.101	0.028	0.026	0.000	0.001	0.000	0.119
G2c		3.220	2	2	96	0.000	0.002	0.000	0.000	0.000	0.000	0.000	3.146	1.544	0.000	0.160	0.596	0.635	0.000	0.043
G3a		6.040	20	25	55	0.096	0.019	0.000	0.000	0.011	0.000	0.000	7.398	3.915	0.002	0.542	0.973	1.096	2.188	1.502
G3b		1.880	3	3	94	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.813	1.201	0.000	0.166	0.752	0.382	0.000	0.242
G3c		0.400	2	2	96	0.000	0.001	0.000	0.000	0.000	0.000	0.000	2.988	1.291	0.000	0.147	0.551	0.425	0.000	0.170
G4a		1.880	10	8	82	0.000	0.080	0.120	0.000	0.049	0.000	0.015	5.443	3.607	0.068	0.370	1.523	1.346	0.038	1.789
G4b		0.530	6	4	90	0.000	0.075	0.084	0.000	0.143	0.000	0.013	2.367	1.612	0.058	0.122	0.448	0.496	0.030	0.697
G4c		0.020	4	5	91	0.000	0.039	0.118	0.000	0.035	0.000	0.016	3.991	2.851	0.062	0.163	2.612	0.723	0.031	1.187
Durban Harbour																				
Ha		1.070	4	4	92	0.000	0.080	0.118	0.000	0.037	0.000	0.022	1.643	1.178	0.056	0.196	54.240	1.038	0.017	1.594
Hb		0.950	6	6	88	0.000	0.070	0.111	0.000	0.038	0.000	0.027	2.528	2.020	0.061	0.260	128.524	1.291	0.017	1.717
Hc		0.140	3	2	95	0.000	0.038	0.117	0.000	0.031	0.000	0.021	0.676	0.673	0.054	1.855	37.456	1.196	0.010	0.780
Isipingo																				
S1a		3.630	6	2	92	0.115	0.014	0.093	0.000	0.000	0.000	0.000	7.626	2.839	0.000	0.178	14.911	1.153	0.000	2.670
S1b		2.410	17	9	74	0.000	0.010	0.092	0.000	0.000	0.000	0.000	14.924	5.927	0.000	0.346	27.318	2.248	0.051	5.600
S1c		1.070	2	2	96	0.000	0.003	0.088	0.000	0.000	0.000	0.000	4.167	1.557	0.000	0.193	34.804	1.050	0.000	1.211
S2a		3.080	16	10	74	0.043	0.017	0.059	0.000	0.000	0.000	0.000	14.902	6.320	0.000	0.292	11.992	1.703	0.006	8.300
S2b	800 +/- 30	0.530	2	3	95	0.000	0.006	0.095	0.000	0.000	0.000	0.000	4.538	1.770	0.000	0.070	20.814	0.666	0.000	1.247
S2c		5.370	26	34	40	0.000	0.007	0.096	0.000	0.000	0.000	0.000	14.102	5.447	0.000	0.110	3.989	1.194	0.179	6.551
S2d		0.280	2	2	96	0.000	0.004	0.062	0.000	0.000	0.000	0.000	4.156	2.024	0.000	1.243	3.780	0.426	0.000	0.882
S3a		3.220	33	12	55	0.000	0.024	0.102	0.000	0.000	0.000	0.000	12.098	16.282	0.000	5.940	6.597	5.970	1.070	3.752
S3b		0.950	7	4	90	0.000	0.005	0.094	0.000	0.000	0.000	0.000	6.359	2.377	0.000	0.070	4.432	0.686	0.000	1.449
S3c	830 +/- 30	5.090	42	21	37	0.000	0.011	0.049	0.000	0.000	0.000	0.000	16.757	5.987	0.000	0.242	20.666	2.484	0.144	6.640
uMbokodweni																				
B1a		0.400	2	2	96	0.000	0.038	0.121	0.000	0.049	0.000	0.018	1.690	1.025	0.056	0.262	10.918	0.688	0.021	0.266
B1b		1.070	3	5	92	0.000	0.076	0.124	0.000	0.038	0.000	0.015	2.196	1.613	0.057	0.246	2.170	0.515	0.021	0.642

B1c		0.950	4	4	91	0.000	0.075	0.117	0.000	0.034	0.000	0.016	1.628	0.865	0.054	0.110	0.818	0.363	0.015	0.197
B2a		3.350	13	11	76	0.000	0.078	0.140	0.000	0.052	0.000	0.033	0.000	0.032	0.055	0.065	0.000	0.006	0.003	0.011
B2b	2840 +/- 30	0.530	2	2	96	0.000	0.049	0.115	0.000	0.021	0.000	0.000	0.000	0.044	0.018	0.012	0.000	0.000	0.000	0.000
B2c		0.670	2	2	96	0.000	0.078	0.139	0.000	0.052	0.000	0.020	0.000	0.075	0.054	0.063	0.000	0.006	0.003	0.045
B3a		2.010	8	6	86	0.000	0.051	0.139	0.000	0.052	0.000	0.033	0.000	0.075	0.054	0.062	0.000	0.006	0.003	0.045
B3b		0.670	2	2	96	0.000	0.051	0.139	0.000	0.052	0.000	0.018	0.000	0.075	0.054	0.060	0.000	0.006	0.003	0.043
B3c	1970 +/- 30	1.340	8	6	86	0.000	0.049	0.116	0.000	0.021	0.000	0.000	0.000	0.079	0.018	0.015	0.000	0.000	0.000	0.000