

**AN INTERGRATED STUDY OF THE EZIMBOKODWENI
ESTUARY: WATER AND SEDIMENT QUALITY, AND ESTUARY-
NEARSHORE MATERIAL FLUXES**

by

ADIKA RAMBALLY

208512041

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Supervised by: Dr. Srinivasan Pillay

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PREFACE

The experimental work described in this dissertation was carried out in the School of Agricultural, Earth and Environmental Science at the University of KwaZulu-Natal, Durban, South Africa, from February 2012 to November 2013, under the supervision of Dr. Srinivasan Pillay.

This dissertation represents original work by the author, Adika Rambally, and has not otherwise been submitted in any form for any degree or diploma to any other tertiary institution. Where use has been made of the work of others it is duly acknowledged in text.

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It is anticipated that at least two research publications will be developed from this dissertation.

ABSTRACT

This study represents an integrated and holistic assessment of the eziMbokodweni Estuary's water and sediment quality. The estuary was once relatively un-impacted but now flows through a highly anthropogenically-modified catchment, comprising industrial and residential developments (formal and informal), and the eziMbokodweni Wastewater Treatment Works, furthermore the floodplain has been completely transformed to accommodate the Amanzimtoti golf course. Flow from the highly degraded Isipingo River and Estuary is occasionally diverted into the eziMbokodweni and the Southern Sewage Works Outfall, one of the largest deep sea sewage outfalls in the eThekweni Municipality, is located at sea, approximately 1.5 km south of the estuary mouth.

Estuarine health can be studied on various fronts, in this study, the following variables were monitored in the water and sediment columns, seasonally for spring and neap tides: heavy metals, nutrients, bacteria and selected physico-chemical parameters. The results demonstrated that the eziMbokodweni catchment was a major contributor of heavy metals and nutrients to the estuarine system. The quantity of the majority of heavy metals and nutrients transported by the river at the upper estuary exceeded the amount exported to sea at the estuary mouth-nearshore interface, resulting in the estuary accruing large quantities of material seasonally. It was noted that the nearshore waters are enriched, as a variety of heavy metals and nutrients entered the estuary mouth during flood tide episodes.

A range of heavy metals were detected within the sediment profiles obtained from the estuary, with fine to medium grained sediment exhibiting greater heavy metal content, in some cases, multi-fold higher than that detected in medium to coarse grained sediment. Geochemical indices were employed to ascertain the extent to which these metals constituted a pollution threat to the environment. The contamination factor calculated for all sediment layers and sampling sites implied low contamination. The enrichment factor calculated for the majority of heavy metals alluded to natural causes while some heavy metals exhibited significant to extremely high levels of enrichment thus implicating anthropogenic causes as likely sources of these heavy metals. The degree of contamination of the estuary was classified as low. Overall, the heavy metal and nutrient content detected in the sediments were low as compared to the large quantities detected from the budget. This indicates that natural mechanisms exist which facilitate the utilization or removal of these heavy metals and nutrients from the estuary. It is proposed that the most

significant manner by which these heavy metals and nutrients are eliminated from the estuary is through episodic flood events that scour and strip fine grained sediment from the estuary bed.

The pH assessment of the estuary revealed that this environment was slightly basic through most of the year with mildly acidic conditions noted during winter. The average Dissolved Oxygen levels were within acceptable levels, with the exception of winter when levels were very close to hypoxic conditions. The average Total Dissolved Solid content indicated that the estuary was compliant with the target water quality range for domestic use on selected seasonal-tidal cycles, and the average Electrical Conductivity levels were compliant with the ideal target water quality range for aquatic ecosystems and domestic use as per the South African water quality guidelines (DWAF, 1996a-e). A salinity gradient was evident in the estuary, as salinity levels decreased with distance from the estuary mouth. The saline nature of the lower estuary provided for the flocculation of material, which was alarming as large quantities of heavy metals and nutrients were detected in the estuary. The lower estuary is therefore susceptible to contamination due to the salinity regime and the dominance of fine grained sediment. The demand for oxygen in the estuary was high during summer, autumn and spring, and within acceptable levels for natural waters during winter. Extremely high levels of Chemical Oxygen Demand were recorded in the estuary which provides prime growth and survival opportunities for bacteria. This correlated with the results from microbiological investigations as high levels of bacteria were noted within the estuary, in both the sediment and water columns. The detected quantities of Total Coliforms, Faecal Coliforms and *Escherichia* Coliforms exceeded the target water quality thresholds for domestic and full contact recreational use. While at selected sites, the recorded Faecal Coliforms and *Escherichia* Coliforms levels were deemed compliant for intermediate contact recreational use. However, these sites were not compliant throughout the sampling period. Overall, the upper and mid-estuary exhibited greater counts of bacteria, in both the sediment and water column, than the estuary mouth and was attributed to factors such as flushing, sediment particle size, salinity and the '*dilution effect*'. Furthermore, the sediment of the eziMbokodweni Estuary is serving as a reservoir for bacteria.

A number of options have been proposed to improve the degraded state of the eziMbokodweni Estuary and are ultimately aimed at curbing the anthropogenic input of these contaminants. The insight gained from this study provides the database from which more integrated and holistic estuarine management strategies can stem, that are applicable not just to the eziMbokodweni Estuary but estuaries in general.

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LIST OF ABBREVIATIONS

A	Area
ANOVA	Analysis of Variance
BOD	Biological Oxygen Demand
C	Concentration
C _d	Contamination Degree
CF	Contamination Factor
cfu	Colony forming units
COD	Chemical Oxygen Demand
CSIR	Council for Scientific and Industrial Research
DEAT	Department of Environmental Affairs and Tourism
DO	Dissolved Oxygen
DWAF	Department of Water Affairs and Forestry
EC	<i>Escherichia</i> coliforms
EC	Electrical Conductivity
ECA	Environmental Conservation Act
EF	Enrichment Factor
EIA	Environmental Impact Assessment
EMP	Environmental Management Plan
F	Transport
FC	Faecal coliforms
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy

ICRU	Intermediate contact recreational use
MFT	Membrane Filtration Technique
MLRA	Marine Living Resources Act
NEMA	National Environmental Management Act
NWA	National Water Act
PIA	Prospection Industrial Area
PVC	Polyvinyl chloride
Q	Discharge
SAWQG	South African Water Quality Guidelines
TC	Total coliforms
TDS	Total Dissolved Solids
TWQR	Target Water Quality Range
US-EPA	United States – Environmental Protection Agency
V	Velocity
WHO	World Health Organisation
WWTWs	Wastewater Treatment Works

CHAPTER ONE

Introduction and Literature Review

1.1 Contextualisation of the Problem and Rationale for the Study

The South African coastline spans for nearly 3000 km (Morant and Quinn, 1999; Schumann, 2003) from the Gariep River at the Namibian border in the west to Kosi Bay near the Mozambique border in the east (DEAT, 2001). Approximately two hundred and fifty estuaries comprising a total area of 70 000 ha (Turpie *et al.*, 2002; Scharler and Baird, 2005), occur along the coastline (Whitfield, 2000; Chili, 2008). According to DEAT (2001), in South Africa estuaries can range from small water bodies that are occasionally connected to the sea, to large permanently open estuaries and estuarine lakes, connected to the sea *via* a narrow channel.

Estuaries serve as the link between the marine and freshwater environments and as such are some of the most variable ecosystems on earth (Falco *et al.*, 2010). These ecosystems are characterised by high productivity and play an important role as habitats and nurseries for numerous plant and animal species (Breen and McKenzie, 2001; Hosking *et al.*, 2004; Scharler and Baird, 2005). In addition, estuaries provide environmental benefits such as water purification, biogeochemical cycling, flood attenuation (Dent and Breen, 2001) and regulate the flux of material between land and sea (Crossland *et al.*, 2005). According to Schumann (2003) and Pillay (2013a), estuaries are also popular sites for recreational activities (e.g. fishing, swimming, boating) and eco-tourism.

Turpie *et al.* (2002), state that estuaries are classified as one of the most vulnerable ecosystems in South Africa. Their unique position at the foot of watersheds, results in estuaries being the receiving bodies for wastes derived from catchment activities such as agriculture and industry (Neilson and Cronin, 1981; McLusky, 1989; Jennings, 2005; Sukdeo, 2010). According to Walmsley (2000) and Dallas and Day (2004), the enrichment of estuaries with contaminants, such as heavy metals and nutrients, has numerous adverse effects on estuarine processes, biota and human-users of estuaries. Studies conducted on estuaries within the eThekweni Municipality (Brijlal, 2005; Chili, 2008; McLean, 2008; Govender, 2009; Sukdeo, 2010; Fernandes, 2011; Pillay, 2013a) have documented the declining health of these systems which has been largely attributable to anthropogenic activities in the catchment. However, due to economic drivers the scale and intensity of anthropogenic activities is steadily increasing, resulting in increasing

quantities of these contaminants in estuarine systems (CENR, 2000; NRC, 2000; Brijlal, 2005; Abed, 2009; Kandasamy, 2008). The adverse impacts of these contaminants and the dynamic nature of estuarine systems create the need for an integrated and holistic approach when investigating an estuaries health status, this includes an assessment of catchment landuse and activities, riverine and estuarine processes (such as hydrodynamics, biogeochemical and geochemical processes, morphology) as well as interchange with the nearshore environment.

According to Pillay (2013a), such integrated and holistic studies are limited in South Africa, particularly in terms of the fate and interchange of material (heavy metals, nutrients and micro-organisms) between the estuary and nearshore environment. This has led to the presumption that the heavy metal and nutrient concentrations measured within estuaries also reflect the amounts exchanged with the nearshore environment (Fernandes and Pillay, 2012). However, estuaries are dynamic zones of interaction making such exchanges much more complex to quantify. Ekholm *et al.* (1997), state that the exchanges require the calculation of a budget which represents all of the material already present in an estuary, plus inputs, less outputs and what remains is equal to the internal load. Determining the budget of an estuary provides valuable information on the estuary's health status, such as the influence of tidal dynamics on contaminant loads, and can therefore inform estuarine rehabilitation and management.

According to Sukdeo (2010) and Pather (2013), within estuaries physico-chemical conditions can induce a number of interactions that may concentrate heavy metals in sediment. Furthermore, heavy metals have a greater affinity for fine grained sediment and are absorbed more often than they remain in solution (Villars and Delvigne, 2001; Chatterjee *et al.*, 2006; Lin *et al.*, 2007; Ram *et al.*, 2009; Sukdeo, 2010). Sediment analysis is therefore an integral part to investigating heavy metal content in estuaries and the overall health status of the system.

In addition to heavy metal and nutrient content, bacteria such as Total coliforms, Faecal coliforms and *Escherichia* coliforms, are commonly used as estuarine health indicators due to their strong association with faecal pollution (The Australian Government, 2003; Pachepsky and Shelton, 2011). Csuros and Csuros (1999), state that monitoring bacterial levels provides a reliable indication of the pollution status of estuaries and the use of bacteria as a health indicator is a cost efficient and less time-consuming alternative to monitoring pathogens directly (Sigeo, 2005; Pachepsky and Shelton, 2011).

The eziMbokodweni Estuary, which is the focus of this research, is one of the smaller systems in the eThekweni Municipality. According to Pillay (2013a), estuarine research has generally focused on the larger systems; hence this study will represent the first attempt at an integrated and holistic assessment of the eziMbokodweni Estuary's health status. The estuary was once relatively un-impacted but now flows through a highly anthropogenically-modified catchment. The insight gained from this study will provide the database from which more holistic estuarine management strategies can stem, that are applicable not just to the eziMbokodweni Estuary but estuaries in general.

1.2 Aim and Objectives

The aim of this study is to holistically evaluate the water and sediment quality along the eziMbokodweni Estuary, and to quantify the net heavy metal and nutrient exchange between the estuarine and marine environments.

The objectives of the study are:

- To quantify and assess the physico-chemical water quality at selected sites along the eziMbokodweni Estuary;
- To determine the quantity of heavy metals and nutrients that are imported or exported through tidal interchange between the estuarine and marine environments;
- To quantify and assess heavy metal concentrations in sediment at selected sites along the eziMbokodweni Estuary;
- To quantify and assess the microbiological water and sediment quality at selected sites along the eziMbokodweni Estuary; and
- To develop recommendations for heavy metal, nutrient and bacterial control as warranted by the research findings.

1.3 Chapter Sequence

Following on from this introductory chapter (Chapter One) are four further chapters. Chapter Two, details a description of the eziMbokodweni Estuary, its regional location and catchment characteristics; the physical and biotic characteristics of the estuary are also discussed and include a review of past research conducted on the system. The sampling regime, analytical procedures and, data analysis and interpretation techniques employed are detailed in Chapter Three. Due to the considerable amount of water and sediment quality parameters analysed and the amount of data generated, the results and discussions are presented under specific subheadings in Chapter Four. These include an assessment of the content of selected physico-chemical parameters in water samples, the transport of heavy metals and nutrients seasonally, for spring and neap tides and the net budget of the estuary, a geochemical assessment of heavy metals in sediments and, bacterial content in water and sediment samples. The thesis concludes with Chapter Five which summarises the main discursive points developed during the study and presents recommendations for the rehabilitation of the estuary and future research.

1.4 Introduction to Literature Review

The remainder of this chapter presents a review of the literature and theoretical concepts upon which this research is based. The concepts include a discussion of estuarine types, the goods and services derived from estuaries, estuarine flora and fauna, tidal dynamics and legislation pertaining to estuaries in South Africa. The issue of estuarine health, particularly the effects of heavy metals, nutrients, bacteria and selected physico-chemical parameters is also detailed.

1.5 Estuaries

Estuaries form at the interface of marine and freshwater environments, and as such are amongst the most dynamic and productive ecosystems on earth (Falco *et al.*, 2010; Fernandes, 2011). Their location makes estuaries susceptible to both marine and terrestrial influences (Cooper, 2001; Jennings, 2005) and shapes estuarine soil, micro-organisms and, plant and animal communities in unique ways. In South Africa, estuaries span 600 km² of the coastline and have become the focus of anthropogenic activities (Baird, 2002).

According to Whitfield (1992), the high degree of variability in terms of climate, topography and catchment geology has resulted in five types of estuaries in South Africa. The five types identified by Whitfield (1992) are: permanently open estuaries, river mouths, estuarine bays, estuarine lakes and temporarily open/closed estuaries. The first three types of estuaries tend to remain open to the sea on a permanent basis; whereas several lakes and all temporarily open/closed estuaries close periodically, sometimes for a number of years (Breen and McKenzie, 2001; Hosking *et al.*, 2004; Pillay, 2013a).

Estuaries comprise of biotic and abiotic features which include soil, water, plants and animals. These features provide important ecosystem goods and services such as nutrient supply and cycling, and water purification (Dent and Breen, 2001; Breen and McKenzie, 2001; Brijlal, 2005). The ecosystem goods and services provisioned by estuaries in South Africa was estimated to be worth R 153 000 ha⁻¹ year⁻¹; specifically R 3500 ha⁻¹ in food production; R 2250 ha⁻¹ in recreation and R 141 000 ha⁻¹ in nutrient cycling (Lamberth and Turpie, 2003).

In addition to providing important ecosystem goods and services, estuaries support an array of plant and animal life forms that reside, feed or develop in estuaries. The plant life is inclusive of small algae, large algae, submerged large plants, salt marshes, reeds, sedges and mangroves (Breen and McKenzie, 2001; Hosking *et al.*, 2004). Hay (2007) and McLean (2008), state that estuaries provide habitats for numerous invertebrate, fish and bird species.

1.6 Estuarine Tidal Dynamics

Tides refer to the alternating rise and fall in sea level with respect to the land and are determined by the gravitational attraction of the moon and the sun, and the rotation of the earth (King, 1972; Komar, 1998; Masselink and Hughes, 2003; Davis and FitzGerald, 2004). These tidal oscillations are not distinct within the deep waters of the ocean but are extremely evident along shallow coastlines, estuaries and funnel-shaped embayments (Schumann *et al.*, 1999; Masselink and Hughes, 2003; Davis and FitzGerald, 2004). According to Masselink and Hughes (2003), tides contribute significantly to the morphology of estuaries, and determine the residence time and transport of material between the estuary and marine environment. Hence, Fernandes (2011) and Pillay (2013a), state that by understanding water movements one can quantify the transport of material within/from estuaries and hence the susceptibility of the system to experience water quality problems such as eutrophication.

Tides can be classified as either spring or neap tides. Spring tides occur when the sun, earth and moon are aligned, and the gravitational force of the sun amplifies that of the moon (Komar, 1998; Bird, 2000; Masselink and Hughes, 2003; Davis and FitzGerald, 2004). According to Masselink and Hughes (2003), spring tides are the largest tides, containing the highest high tides and lowest low tides, compared to lunar tides and occur when the moon is new or full. In comparison, neap tides are generated when the earth, sun and moon are orientated at a right angle, which results in tides that are out of phase and opposed, and an overall reduced tidal range (Komar, 1998; Bird, 2000; Masselink and Hughes, 2003; Davis and FitzGerald, 2004). Neap tides coincide with the moons first quarter and last quarter phase (Bird, 2000; Masselink and Hughes, 2003; Davis and FitzGerald, 2004).

According to Masselink and Hughes (2003), spring tides as opposed to neap tides, entail stronger and faster tidal currents due to higher volumes of water being transported. Consequently, during spring tides sediment transport and disturbance, as well as, estuarine ‘flushing’ is exacerbated (Dyer, 1995; Kitheka *et al.*, 2005; Theron, 2007). A study conducted by Pillay (2013a), demonstrated that the heavy metal concentrations detected over spring and neap tidal fluxes were significantly different in the Isipingo Estuary and was attributed to the greater tidal prism experienced during the spring tide resulting in a greater volume of material exchanged.

In addition to spring and neap tides, flood and ebb channels play an important role as tidal channels or water movements in estuaries. Ebb channels are outgoing currents which are seaward directed; these channels develop around the flood-tide sand bank and become broadened out and shallower towards the sea (Bird, 2000; van Niekerk, 2007). While, flood channels push seawater up into the estuary, introducing more saline water into the system and increase water levels (Brijlal, 2005). Flood channels become shallower towards the land (Bird, 2000) with flow velocity declining progressively as the channel cross-section increases (Dyer, 1994). According to Masselink and Hughes (2003), during a complete tidal cycle flood and ebb channels are experienced in equal periods referred to as tidal symmetry. While, tidal asymmetry occurs as a result of cyclic asymmetry in the ebb and flood channels (Beck *et al.*, 2004). Tidal symmetry and asymmetry are controlling factors in the transport, as well as, residence time of material within estuaries (Fernandes, 2011).

1.7 Estuarine Health

According to Davies and Day (1998), the nature of an estuary is directly related to its catchments' characteristics. This is particularly evident in South Africa where Kosi Bay in the north-east of the country retains an almost pristine character as its catchment is little affected by human activities (Fernandes and Pillay, 2012). However, estuaries with highly anthropogenically modified catchments such as those in the eThekweni Municipality - the largest urban developed area on the eastern seaboard of South Africa (Fernandes and Pillay, 2012) - have shown a steady decline in estuarine health. Forbes and Demetriades (2008), classified the estuaries in the eThekweni Municipality into five categories based on their health status. Table 1.1 below, outlines these categories.

Table 1.1 Estuarine classification based on health and functioning (Source: Forbes and Demetriades, 2008)

Status	Description
Excellent	Estuaries with a high level of habitat integrity, water quality, diversity and provision of goods and services.
Good	Estuaries with most of the core habitat and support habitats still present, good water quality, a diversity of habitats and, species and estuarine processes in place.
Fair	Estuaries with the core habitat intact, some support habitats, impacted water quality, some loss of diversity and key estuarine processes still in place.
Poor	Estuaries with an impacted core estuarine habitat, substantially reduced or no estuarine support habitats, polluted water, a substantial loss of diversity and/or abundance and key estuarine processes impaired.
Highly degraded	Estuaries inflicted by major impacts on the core habitat through infilling, canalisation and pollution, substantially reduced or no support habitats and major loss of key estuarine processes.

Of the estuaries in the eThekweni Municipality none could be considered in 'excellent' condition, only three estuaries were assigned to the 'good' category, a further four systems were

categorized as 'fair', two systems were categorized as being in 'poor' condition and the remaining five were considered as 'highly degraded' (Forbes and Demetriades, 2008). The eziMbokodweni Estuary, which is the focus of this research was one of the five estuaries considered as 'highly degraded'.

1.7.1 Processes Influencing Estuarine Health (Water and Sediment Quality)

1.7.1.1 Natural Processes

Natural variations in water and sediment quality can be attributed to seasonal changes, climatic changes and the geology of the landscape (DWAF, 2000; Pillay, 2013a). High temperatures result in increased evaporation rates coupled with low rainfall, and results in decreased water levels and flow rates. Under these conditions the ability of a river system or estuary to dilute contaminants diminishes (Dallas and Day, 1993). Conversely, low temperatures and high rainfall events result in increased discharge which flushes estuaries of substances such as contaminants (Brijlal, 2005). Sukdeo (2010) noted lower nutrient levels in the Mvoti Estuary following summer rainfall and was attributed to increased flows flushing the system.

According to Davies and Day (1998), climate affects the reaction rates of selected chemicals in water. Furthermore, changes in physico-chemical parameters can result in a change in chemical species through oxidation or reduction reactions (Horne and Goldman, 1994; Walmsley, 2000; Dallas and Day, 2004). For example the presence of oxidisable organic matter and Fe (II) salts encourage the conversion of Cr (VI) to the less toxic oxidation states, and Al occurs as soluble and toxic hexahydrate species ($Al^{6+} \cdot H_2O$) under acidic conditions (Dallas and Day, 2004).

Sigee (2005) and Bucus (2006), state that the chemical weathering of bedrock is an important natural process influencing estuarine health as it influences the chemistry of water particularly in un-impacted systems. The impacts associated with weathering is determined by the geological characteristics of the bedrock such as composition and texture, the purity and size of minerals, porosity and exposure time (Bucus, 2006).

Using Carbon dating techniques Pather (2013), dated the uppermost sediment layers of six estuaries in the eThekweni Municipality. The results indicated that the sediment were more than 700 years old. According to Pather (2013), sediment is flushed out of these estuaries during

periods of high discharge such as episodic flood events. Fine grained sediment have a greater affinity for heavy metals due to their charged and large surfaces (Villars and Delvigne, 2001; Chatterjee *et al.*, 2006; Lin *et al.*, 2007; Ram *et al.*, 2009; Sukdeo, 2010) these sediments however, are easily scoured and stripped from the estuary bed during such events resulting in a net loss of large quantities of contaminants from the estuary. However, the inefficient removal of contaminated sediments from estuaries result in the formation of a contaminant ‘sinks’ in the system (Arakel, 1995; Kennish, 1997; Sukdeo, 2010). Upon disturbance of the ‘sink’ contaminants are released back into the water column increasing the systems susceptibility to water quality problems such as algal blooms.

The ebb and flow channels and factors such as tidal prism, direction and duration also have a bearing on the transport and residence time of contaminants in estuaries. The majority of estuaries in South Africa are flood-dominated, thus the volume of material transported into estuaries exceed those removed by ebb tides (Pillay, 2013a). This is alarming for estuaries were the nearshore waters are enriched. The status of the estuary mouth also impacts the health status of the system. During mouth narrowing or closer the estuary functions as a lagoon, with a drop in salinity levels and contaminants being trapped in the system. Breaching will give rise to strong ebb channels with a high scour potential, which can constitute a rapid release of contaminants from the system (Pillay, 2013b). During open mouth conditions estuarine waters tend to be fresher, the system is subject to tidal dynamics, and either material import or export depending on tide direction and duration (Brijlal, 2005). Salinity levels are subject to factors such as the duration of floods and the efficiency of ebbing in preventing the entry of marine waters. Under saline conditions ionic charges are introduced onto sediment affording it a greater capacity to absorb heavy metals (Sukdeo, 2010).

Estuarine biotas are also impacting on the contaminant status of these systems. Significant quantities of contaminants are cycled through the food web through the processes of bioaccumulation and biomagnification, and are eventually released from this component through the excretion of waste products or decomposition of organism (Dallas and Day, 2004; Sigeo 2005). Activities such as burrowing by benthic biota can disturb contaminant sinks in estuaries, making these contaminants water borne. The natural vegetative buffer zones along estuaries also serve as filters and assist in the purification of water and attenuate floods by dissipating the energy of flow, which in turn reduces erosion and subsequently reduces the sediment load to a water resource (Pillay, 2013a). Furthermore, vegetation can assimilate the contaminants and in

conjunction with the process of photosynthesis produce and accumulate organic matter in estuaries (Pillay, 2013a). Horne and Goldman (1994) and Sigeo (2005), state that the bacterial conversion of nitrate to gaseous nitrogen (denitrification) is another important process for N removal from estuaries.

1.7.1.2 Anthropogenic Processes

Anthropogenic activities such as agriculture, urbanisation and industrialisation are integral to development. However, Adebayo and Kehinde (2008), state that poor monitoring of these activities and enforcement of environmental legislation has resulted in the pollution and degradation of the environment. Water bodies such as estuaries serve as the primary disposal sites for anthropogenic pollution (Walmsley, 2000; Malan and Day, 2002; Adebayo and Kehinde, 2008). On entry, the pollutants alter the physical and chemical nature of the system, and threaten estuarine biota and processes (Dallas and Day, 2004; Sukdeo, 2010). According to Carpenter *et al.* (1998), landward drainage consisting primarily of agricultural, industrial and urban run-off is the largest sources of N to surface waters in the United States. A study by Tabayashi and Yamamuro (2009), established a positive correlation between the impact associated with urbanisation and deteriorating water quality. While, Caraco (1995), demonstrated that the transport of nutrients in rivers increased with population and the proportion of the catchment that was urbanised. Falco *et al.* (2010), also showed that leaching from fertilised fields and lawns contribute significantly to nutrient levels in water bodies. In a South African context, Sukdeo (2010), noted excessive levels of contaminants in the Mvoti Estuary which were consistent with the contaminants associated with agricultural run-off and industrial activities in the catchment. Furthermore, contaminant concentrations were higher at the sites located just below effluent disposal outlets (paper and sugar mills, sewage works). Hence, Sukdeo (2010), attributed these anthropogenic activities as responsible for the deterioration of water and sediment quality in the Mvoti Estuary.

According to Forbes and Demetriades (2008), the eThekweni Municipality has experienced an increase in development in estuarine catchments, and is earmarked for further economic growth (eThekweni Municipality, 2011). The manufacturing sector aims to grow fuel, petroleum, chemical and rubber industries by a total of 24.3% by 2014; while the agriculture, fishing and mining sector has a projected growth of 17.5% by 2014 and the construction and civil

engineering sector expects growth of up to 53.9% by 2014 (eThekweni Municipality, 2011). Coupled with such steady economic growth will be further escalations in the amount of contaminants draining into estuaries.

1.8 Indicators of Estuarine Health

In recent years numerous methods for assessing estuarine health have been developed and central to these methods are the use of estuarine indicators. According to Adams (2005) and Bortone (2005), estuarine indicators assist in one's understanding of the effects of stressors on estuaries and the underlying causes of these effects. In addition, estuarine indicators assess estuarine health objectively and have immense utility in the management of these systems (Bortone, 2005). Adams (2005) and Hubertz *et al.* (2005), state that estuarine health can be assessed through the study of abiotic and biotic indicators such as physico-chemical parameters (e.g. temperature and salinity) or species community features and their biological attributes. This research studied the content of nutrients, heavy metals, selected physico-chemical parameters, as well as, bacteria in the sediments and water column of the eziMbokodweni Estuary, to obtain an integrated and holistic assessment of the health status of the estuary. Each of these variables is discussed in greater detail below.

1.9 Nutrients

Nutrients are chemical substances used for maintenance and growth, and are critical for survival (US-EPA, 2006). The relationship between nutrient content and estuarine health was first noted in the early part of the nineteenth century however, it was only during the 1960s when considerable limnological research was directed at identifying the key nutrients impacting on estuarine health (Walmsley, 2000). They include Calcium (Ca), Potassium (K), Magnesium (Mg), Nitrogen (N), Phosphorus (P) and Sulphur (S). These examples are termed macro-nutrients, while micro-nutrients are required in smaller quantities (Dallas and Day, 2004).

1.9.1 Nitrogen (N)

According to Horne and Goldman (1994) and Walmsley (2000), N plays a significant role in estuarine health. Vollenweider (1970) and Dallas and Day (2004), state that N is either dissolved or particulate bound and can occur as inorganic or organic N (Table 1.2). Inorganic N comprises ammonia (NH₃), ammonium (NH₄⁺), nitrate (NO₃⁻) and nitrite (NO₂⁻). NH₃ and NH₄⁺ are the reduced forms of inorganic N and their proportions are determined by water temperature and pH, and both species can exist in the dissolved form or can be adsorbed onto sediment (DWAF, 1996a). NO₂⁻ is the inorganic intermediate and NO₃⁻ is the end product of the oxidation of organic N and NH₃ (Dallas and Day, 2004). Under aerobic conditions NO₂⁻ is oxidized to NO₃⁻ while under anaerobic conditions, the NO₃⁻ is reduced to NO₂⁻ (US-EPA, 2006).

Table 1.2 Nitrogen species present in water (Source: Vollenweider, 1970)

TOTAL NITROGEN				
Dissolved N		N in Suspension		Gaseous N
Inorganic compounds e.g. NH ₄ , NO ₃ , NO ₂	Organic compounds e.g. amino acids, polypeptides, peptides	Organisms	Organic detritus, inorganic and organic compounds adsorbed on particles	N ₂ , N ₂ O, NO
Total N content of unfiltered water				
Total N in filtrate				
Dissolved inorganic N				

N can enter an estuary from several natural or anthropogenic sources however, in most cases the majority of N found in estuaries are anthropogenically derived (Sigee, 2005; Bricker *et al.*, 2008; Kandasamy, 2008). Anthropogenic sources of N include: surface run-off from catchment areas and industrial or sewage discharge (DWAF, 1996a; Pillay, 2013a).

According to Dallas and Day (2004), N undergoes a complex sequence of transformations in estuarine water and sediment before it is eventually flushed out to sea or returned to the atmosphere (Figure 1.1). During this process estuarine plants and algae take up inorganic N and assimilate it into organic molecules (Horne and Goldman, 1994; Dallas and Day, 2004). Organic N is then cycled through the estuarine food web and is eventually released from this component through the excretion of metabolic waste products or the decomposition of organisms (Dallas and Day, 2004; Sigeo, 2005). According to Sigeo (2005), bacteria and fungi assist at this stage by decomposing the remaining detritus into NH_3 , and under aerobic conditions the NH_3 is converted into NO_3^- (Dallas and Day, 2004; Sigeo, 2005).

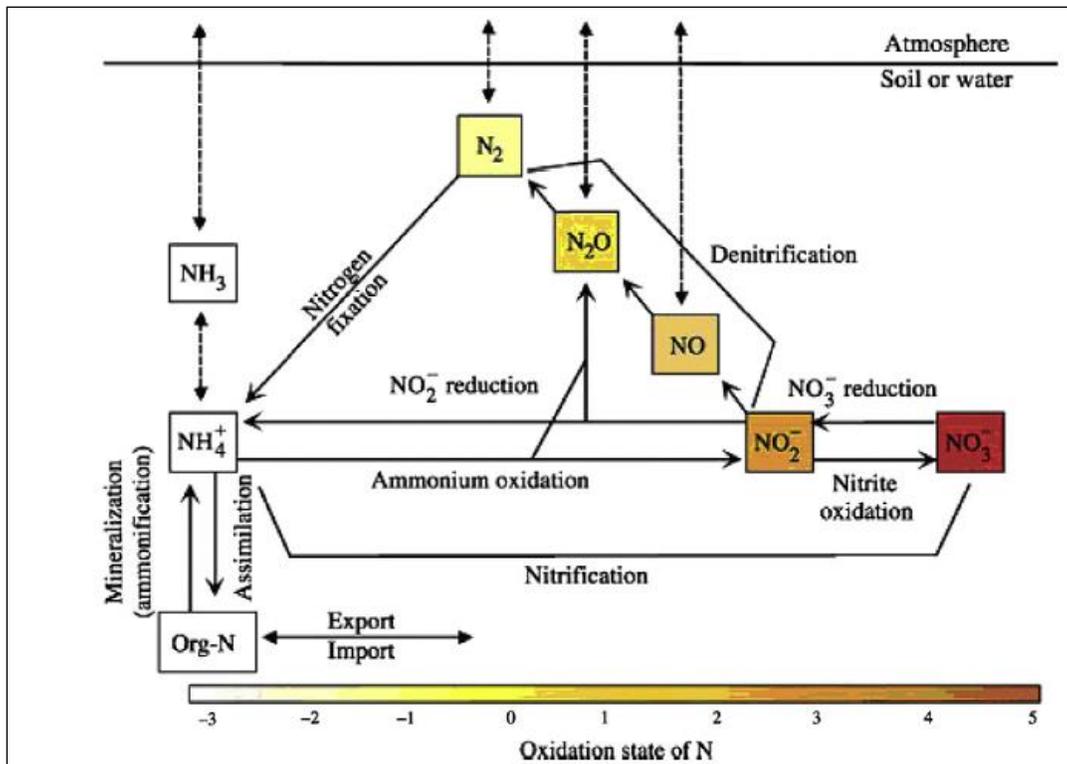


Figure 1.1 Schematic representation of the Nitrogen Cycle (Source: Statham, 2011; pg 07)

N is removed from estuaries by being flushed out to sea as a result of fluvial flows. Sukdeo (2010) noted lower nutrient levels in the Mvoti Estuary following summer rainfall and was attributed to increased flows flushing the system. Rambally (2011), also noted the export of large quantities of N being flushed out to sea from the eziMbokodweni Estuary due to the summer

rains. Dallas and Day (2004), state that the removal of organisms from estuaries can also constitute a N loss to the system due to processes such as bioaccumulation and biomagnification. Furthermore, the bacterial conversion of NO_3^- to gaseous N (denitrification) is another important process for N removal from estuaries (Horne and Goldman, 1994; Dallas and Day, 2004; Sigeo, 2005). Estuaries that are inefficient at N removal can experience a deposition of N onto sediments thus forming a N sink, on disturbance N is released from these sediments and back into the water column, increasing the risk of eutrophication and other water quality problems for the system (Horne and Goldman, 1994; Walmsley, 2000; Dallas and Day, 2004).

Inorganic N concentrations below 0.5 mg/L are generally low enough to inhibit eutrophication (DWAF, 1996a). Elevated levels (>0.5 mg/L) however, alter the trophic status of water bodies and are accompanied by algal and other aquatic plant growth (Walmsley, 2000). According to DWAF (1996a), eutrophic conditions are associated with inorganic N concentrations of 2.5-10 mg/L and above.

1.9.2 Phosphorus (P)

P is an essential element in all living organisms (Karl, 2000; Sigeo, 2005; Sukdeo, 2010). According to Dallas and Day (2004) and Statham (2011), P is a constituent of the structural and storage component in cells, and is involved in energy transformations. P can be either dissolved or particulate bound and occurs in water as: organic phosphates (PO_4^{3-}), orthophosphates (inorganic and dissolved P), total P (dissolved and particulate) and polyphosphates (Vollenweider, 1970; Walmsley, 2000; US-EPA, 2006) (Table 1.3). According to DWAF (1996a), inter-conversions between the different forms of P are part of the P cycle and are characterized by the exchange of P between the water column and sediment. Physical, chemical and biological factors such as pH levels, sorption processes and the activities of organisms control these inter-conversions (DWAF, 1996a).

Table 1.3 Phosphorus species present in water (Source: Vollenweider, 1970)

TOTAL PHOSPHORUS				
Dissolved P		P in Suspension		
Orthophosphate PO ₄	As organic colloids or combined with an adsorptive colloid	As mineral particles or adsorbed on inorganic complexes	Organisms	Adsorbed on detritus or present in organic compounds
 Total P content of unfiltered water				
 Total P in filtrate				
 Dissolved Inorganic P				

Naturally sourced P is derived mainly through the weathering of P bearing rocks and the decomposition of organic matter (DWAf, 1996a). According to Dallas and Day (2004) and Pillay (2013a), large quantities of anthropogenic P enter estuaries as discharge from sewage treatment works, as run-off from agricultural land, industrial effluent and domestic wastes, particularly those containing detergents. P is easily adsorbed to clay and silt particles or precipitated as the mineral P (Webster *et al.*, 2001; Dallas and Day, 2004). As a result, large quantities of P are locked in the bottom sediments and once disturbed the sediment serves as a significant source of P contamination in estuaries (Correll, 1998; Webster *et al.*, 2001). During flood events the scouring of these sediments constitute a loss of P from the system (Horne and Goldman, 1994).

According to Horne and Goldman (1994) and Dallas and Day (2004), changes in physico-chemical conditions such as dissolved oxygen, salinity or pH levels can also result in the release of P from sediment. The US-EPA (2006), noted that when estuarine bottom sediments exhibit anoxic conditions, the P bound to the sediments were released back into the water column, these releases can fuel phytoplankton blooms. pH is also influential on P content in estuaries, according to Dallas and Day (2004), under strongly alkali conditions dissolved P binds with Ca and settles out in sediments. The US-EPA (2006), also noted that under oxygenated conditions

several species of P can form chemical complexes with minerals such as Aluminum (Al), Iron (Fe) and Manganese (Mn), and fall to the bottom sediments.

Estuarine biota play an important role in P cycling in estuaries (Horne and Goldman, 1994); Dallas and Day, 2004; Sigeo, 2005). Estuarine biota obtain P compounds through the consumption of plants and other animals or detritus (Figure 1.2). Upon their death and decomposition organic PO_4^{3-} is broken down by micro-organisms and is made available once more in estuaries (Dallas and Day, 2004). P is therefore continuously cycled through both bioavailable and organic forms in estuaries. According to DWAF (1996a), inorganic P levels ranging from 25-250 μ/L in water are generally associated with eutrophic conditions.

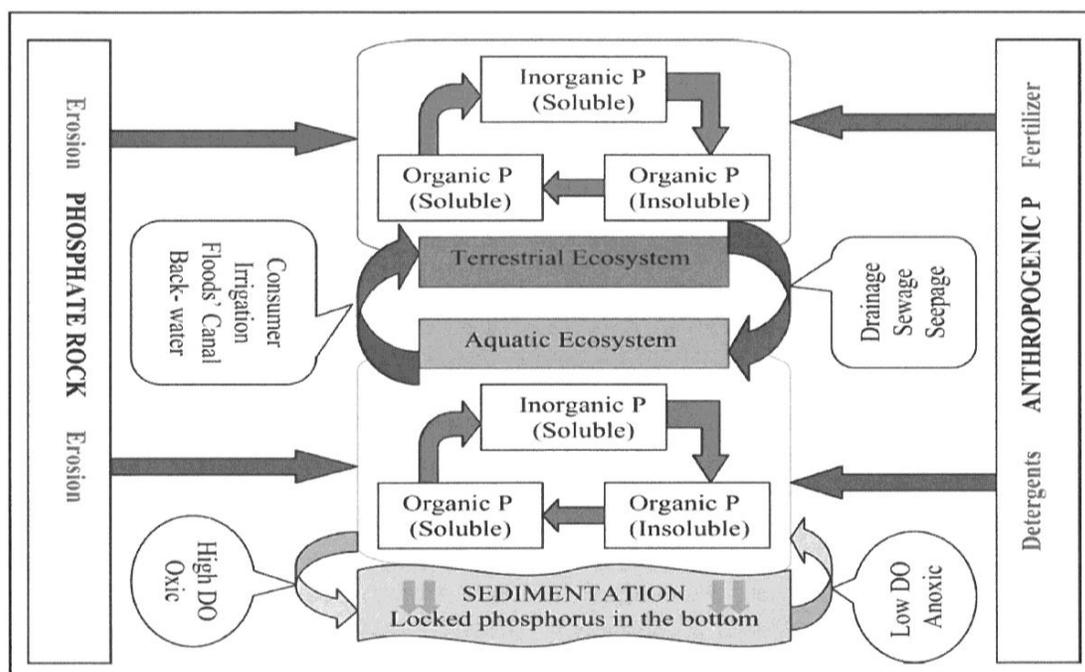


Figure 1.2 Schematic representation of the Phosphorus Cycle (Source: Khan and Ansari, 2005; pg 459)

1.9.3 Potassium (K)

K is an alkali metal that occurs in water in association with Bicarbonate (HCO_3^-), Chloride (Cl^-), Nitrate (NO_3^-) or Sulphate (SO_4^{2-}) (DWAF, 1996b). According to Dallas and Day (2004), K plays an important role in the transmission of nervous impulses, ionic balance and muscle

contraction in animals. It is also a limiting nutrient particularly in plant growth (Vollenweider, 1970; Walmsley, 2000; Dallas and Day, 2004). Horne and Goldman (1994), state that K enrichment in estuaries can occur as a result of run-off from agricultural land and fertilized lawns, as well as, industrial effluent. According to DWAF (1996b), urine has high concentrations of K and Na therefore K:Na ratios are used as an indicator of sewage pollution. K levels <50 mg/L pose no threat to humans however, beyond these levels there is an increasing risk of electrolyte imbalances and mucous membrane irritations, in infants and patients with kidney defects (DWAF, 1996b).

1.9.4 Calcium (Ca)

Ca is an essential constituent of bones, teeth, mollusk shells and crustacean exoskeletons (Dallas and Day, 2004) and plays an important role in muscle contraction, nervous activity and biochemical interactions in all living organisms (Horne and Goldman, 1994; Dallas and Day, 2004). As a result, waters with low Ca levels pose a developmental and physiological threat to estuarine biota (Sukdeo, 2010). According to Horne and Goldman (1994), Ca together with Mg are considered buffering nutrients due to their influence on estuarine pH levels. When Ca (>15 mg/L) and Mg (>70 mg/L) are coupled, they render water 'hard' (DWAF, 1996a). Hard water results in the formation of scum - a mixture of Ca, Mg and contaminants; which is unsightly, foul smelling and damage pipe infrastructure (Sukdeo, 2010). According to Pillay (2013a), industrial effluent and return flow from wastewater treatment processes can contribute to Ca enrichment in surface waters.

1.9.5 Magnesium (Mg)

According to Chapman (1992), Mg is an essential macro-nutrient for plants and animals, and is naturally derived through the weathering of rocks. Mg plays an important role in energy transfer and plants require the nutrient to form the active center of the major pigment, chlorophyll-a (Horne and Goldman, 1994). The general solubility of Mg in water is governed by pH (Pillay, 2013a). According to DWAF (1996b), Mg levels <70 mg/L pose no threat to estuarine and human health. Excessive levels however, can result in disturbances to metabolism (Horne and Goldman, 1994) and water becoming aesthetically unpleasing (DWAF, 1996b). Potential sources

of Mg to estuaries include run-off and leaching of fertilizers from agricultural fields and lawns, as well as, discharge from industries (DWAF, 1996b).

1.9.6 Sulphur (S)

In most natural waters S occurs in concentrations lower to those of Chloride (Cl^-) (Brijlal, 2005; Dallas and Day, 2004). However, due to the scale and intensity of anthropogenic activities S content is steadily increasing in estuaries (CENR, 2000; NRC 2000). Kellogg *et al.* (1972), state that the burning of fossil fuels is responsible for a large percentage of S in rivers. While, according to Horne and Goldman (1994), the breakdown of parent material in the drainage basin is a major source of S to rivers and estuaries. S concentrations <0.001 mg/L pose no threat to estuarine biota (DWAF, 1996d) however, at higher concentrations there is a greater likelihood for the formation of Sulphuric acid (H_2SO_4), a pH reducing acid, which has harmful effects on humans and estuarine biota (Brijlal, 2005).

1.10 Heavy Metals

According to Hardman *et al.* (1993) and Lenntech (2009), the term ‘heavy metal’ refers to metallic elements which are low in the periodic table and have atomic weights greater than one hundred or have a relative density greater than five. Naturally occurring heavy metals are found moving through the hydrological cycle and can be sourced from processes such as the weathering of igneous and metamorphic rock, and volcanic activity (Abed, 2009; Harikumar and Jisha, 2010). The main anthropogenic sources of heavy metals are domestic sewage, industrial effluent, oil and chemical spills, agricultural runoff and, mining and metallurgical activities (Dallas and Day, 2004). According to Abed (2009) and Kandasamy (2008), the present day rate of anthropogenic heavy metal input is exceeding natural inputs. This is problematic as many heavy metals has adverse environmental effects and are non-biodegradable (Sukdeo, 2010) hence, heavy metals tend to accumulate in the environment.

1.10.1 Heavy Metal Content in Sediment

Heavy metals are transformed through various media namely water, sediment and organisms (Horne and Goldman, 1994; Dallas and Day, 2004; Sukdeo, 2010). This research focused on investigating heavy metal content in sediments collected from the eziMbokodweni estuary. According to Bird (2000) and Schumann (2003), sediment is continually being transported into and out of estuaries from marine and fluvial sources. Fluvial sediments are of special concern as these sediments are subject to the type and extent of anthropogenic activity in the catchment (Horne and Goldman, 1994; Abed, 2009; Sukdeo, 2010). According to Chenhall *et al.* (2004), estuaries and open lagoonal systems have been regarded as avenues for waste disposal under the pretext that these discharged will be diluted and dispersed in adjacent open marine settings. However, estuarine sediments can serve as a potential 'sink' for these heavy metals (Arakel, 1995; Kennish, 1997; Sukdeo, 2010). According to Kennish (1997), in excess of 90% of the particulate matter (and its associated contaminants) arriving into estuaries and coastal lagoons settles out by flocculation with small amounts of this sediment actually reaching the open ocean. As a result, bottom sediments can function as a 'sink' for contaminants. These metals and pollutants can persist for many years and can become concentrated in bottom sediments resulting in adverse impacts on benthic organisms (Pillay, 2013a).

According to Jones *et al.* (2003) and Sukdeo (2010), under changing physical and physico-chemical conditions estuarine sediment function as a medium from which these contaminants are released back into the water column. Lewis and McConchie (1994), showed that oxidation and reduction reactions are amongst the most important processes influencing such releases. Examples of this, as suggested by Lewis and McConchie (1994), are Cadmium (Cd) where the heavy metal is more mobile under oxidizing conditions, and Iron (Fe) which is more mobile under reducing conditions. Physical interactions such as flooding are also influential on the heavy metal content of estuaries. Numerous authors have shown that scouring of the bed sediment upon flooding resulted in heavy metal deposits being released from sediments back into the water column (Sukdeo, 2010; Fernandes, 2011; Rambally, 2011; Pillay, 2013a).

Sediment particle size plays a significant role in determining the quantities of heavy metals absorbed by sediment. Fine grained sediment (<0.063 mm) such as silt, clay and organic matter have large surface areas and charged surfaces allowing the particles a greater capacity to absorb ions from solution (Villars and Delvigne, 2001; Chatterjee *et al.*, 2006; Lin *et al.*, 2007; Ram *et*

al., 2009; Sukdeo, 2010). These ions however, are not permanently fixed to the sediment particles and can become desorbed with a change in physico-chemical conditions, or may be exchanged with other ions in the surrounding solution (Lewis and McConchie, 1994). In comparison, larger grained sediments (>0.063 mm to <2 mm) have round surfaces, no charges and are non-cohesive, and hence are associated with minimal heavy metal content (Horne and Goldman, 1994; Webster *et al.*, 2001; Sukdeo, 2010).

1.10.2 Heavy Metals Affecting Estuaries

Aluminum (Al)

Al is a silvery-white heavy metal that is common in the earth's crust. According to DWAF (1996d), Al occurs in water in two main phases: as suspended Al minerals and as dissolved Al species. Al speciation is pH dependent, it is relatively insoluble at a neutral pH (6.5-7.5), at pH<4 Al occurs in the Al_3^+ form which is very soluble (DWAF, 1996a). Between pH 4.5-6.5 Al undergoes hydrolysis and decreases in solubility (DWAF, 1996a). At pH>8 Al is present as soluble but biologically unavailable hydroxide complexes or as colloids or flocculants (DWAF, 1996a). The toxicity of Al depends on the chemical species involved and pH levels. Al is more toxic between pH 4.4-5.4 with maximum toxicity occurring at pH 5.0-5.2 (DWAF, 1996a, 1996c). The primary anthropogenic sources of Al to rivers and estuaries are effluent from paper, leather and textile industries (DWAF, 1996a). Al is also used extensively in water treatment processes and as a result is present in large amounts in post-treatment water (DWAF, 1996b). The SAWQG target value for aquatic ecosystems is 0.005 mg/L, domestic use is 0.15 mg/l and the ecological environment is 0.02 mg/L (DWAF, 1996a).

Arsenic (As)

As is naturally present in both organic and inorganic forms of which the latter is considered more toxic (Hardy *et al.*, 2008). According to DWAF (1995), human activities have significantly increased As concentrations in the environment through the burning of fossil fuels and effluent derived from the manufacture of pesticides and pharmaceuticals. Physical parameters such as redox potentials and pH levels are a key determinant of As concentrations in the environment

(DWAF, 1995; 1996d). According to DWAF (1995) and Sukeo (2010), certain marine organisms can transform inorganic As into more complex organic compounds and upon death settle to the estuary floor where As is liberated and once again recycled within the system. Excessive levels of As can result in growth deficiencies and decreased reproduction in biota (Sukdeo, 2010) and is a known carcinogen (DWAF, 1996a). Cases of As bioaccumulation have resulted in human health complications such as hyper-pigmentation, hyper-keratosis and cancer (Ferguson, 1990; Harrison, 2007). The SAWQG target value for aquatic ecosystems is 0.01 mg/L, domestic use is 0.01 mg/L and the ecological environment is 0.02 mg/L (DWAF, 1996a).

Barium (Ba)

Ba is a silvery-white heavy metal that occurs combined with other elements such as Sulphur, Oxygen and Carbon (Sukdeo, 2010). Ba is used extensively in activities such as mining and, coal and oil combustion. According to Lenntech (2009), Ba is capable of reacting with almost all non-metallic elements, forming poisonous substances. The water soluble forms are harmful to health with effects such as paralysis and death in humans (Dallas and Day, 2004). At lower concentrations Ba can result in increased blood pressure, stomach irritations and swelling of internal organs (Dallas and Day, 2004). The World Health Organisation (WHO) drinking water limit for Ba is 0.7 mg/l (DWAF, 1996a). There are no ideal thresholds available in terms of the SAWQG for domestic use, the aquatic or ecological environment (DWAF, 1996a).

Boron (B)

B is a non-metallic element, it enters water bodies *via* weathering of parent rock and leaching, anthropogenic sources include industrial discharges and agricultural run-off containing pesticides (Chapman, 1992; Sukdeo, 2010). At elevated levels B results in organ infections in humans (Sukdeo, 2010). Lenntech (2009), has reported the bioaccumulation of B in aquatic organisms. Currently, there are no guideline values available in the SAWQG for domestic use, the aquatic or ecological environment (DWAF, 1996a).

Chromium (Cr)

Cr is a micro-nutrient of silver-grey color (DWAF, 1996d, Lenntech, 2009). According to DWAF (1996d), Cr enters the environment through natural weathering. Cr is a relatively scarce metal and should therefore be present at low concentrations in the natural environment (DWAF, 1996a). Elevated concentrations can be attributed to anthropogenic sources, such as, wastes from ferrochrome production, electro-plating, pigment production and tanning as well as burning of fossil fuels (DWAF, 1995; US-EPA, 2006; Lenntech, 2009). According to DWAF (1996d), Cr speciation is determined by the amount of organic matter and dissolved oxygen present in water and physico-chemical parameters such as pH and redox potentials. DWAF (1996d), also states that the presence of oxidisable organic matter and Fe (II) salts encourage the conversion of Cr (VI) to the less toxic oxidation states. Most species of Cr are very mobile and readily move through the soil profile resulting in the contamination of groundwater supplies (DWAF, 1996d). The SAWQG target value for aquatic ecosystems is 0.007 mg/l, domestic use is 0.05 mg/l and the ecological environment is 0.024 mg/l (DWAF, 1996a).

Cobalt (Co)

Co is an essential micro-nutrient and is toxic in fairly small quantities (Dallas and Day, 2004). According to Ackermann and Sommer (1988), Co is present in mineral waters and the primary anthropogenic source of Co results from mining effluent. According to DWAF (1996a) and Sukdeo (2010), Co is strongly adsorbed by sediment and is non-biodegradable. Co is reported to cause nausea, vision impairments, heart defects and thyroid damage in humans (Lenntech, 2009). Currently, there are no guideline values available for Co concentration in terms of the SAWQG for domestic use, the aquatic or ecological environment (DWAF, 1996a).

Copper (Cu)

Cu is a reddish micro-nutrient that is rapidly accumulated in plants and animals (DWAF, 1996d; US-EPA, 2006; Lenntech; 2009). According to DWAF (1996b), organic and inorganic substances form complexes with Cu^{2+} and the free ion is rarely found except in pure acidic soft water. Cu precipitates in waters with a high pH and at low pH it is soluble and more toxic

(Nussey, 1998). The speciation of Cu is dependent on numerous variables such as pH and the presence of ligands such as sulphate, chloride and nitrate in the water and is easily adsorbed and precipitated in sediments at alkaline pH. The main anthropogenic sources of Cu include effluent from paper mills and steel industries (DWAF, 1996d; US-EPA, 2006). High levels of Cu have adverse effects on estuarine biota and humans. These include brain damage, gastro-intestinal disturbances and blood cell damage (DWAF 1996a; 1996b; Abed, 2009). The SAWQG target value for aquatic ecosystems is 0.0003 mg/l, domestic use is 1 mg/l and the ecological environment is 0.0005 mg/l (DWAF, 1996a).

Iron (Fe)

Fe is an essential micro-nutrient required by all organisms (DWAF, 1996d). It is important for chlorophyll and protein synthesis, and respiration (DWAF 1996a). Fe is released naturally through the weathering of sulphide ores and igneous, sedimentary and metamorphic rocks (DWAF, 1996a). Anthropogenic sources include mining, sewage effluent, landfill leachates and some industrial effluents (DWAF, 1996a). According to DWAF (1996d), Fe speciation is related to the pH and redox potential of water. Concentrations in unpolluted surface waters range from 0.001-0.5 mg/L and seawater 0.002 mg/L (DWAF, 1996d). The human health and aesthetic target range of Fe is 0-1 mg/L and for optimum fish fitness <0.01 mg/L (DWAF, 1996d). Beyond these levels Fe can result in decreased fish fitness, and due to its ability to bioaccumulate, the consumption of contaminated fish can result in poisoning (DWAF, 1996d).

Lead (Pb)

Pb is a lustrous metal and shares a strong interdependence with alkalinity and water hardness (DWAF, 1996d). Pb has widespread industrial application and is used in the manufacture of paints, explosives, gasoline and batteries (DWAF, 1995; DWAF, 1996d; Abed, 2009; Lenntech, 2009). According to DWAF (1996d), the contamination of water and sediment with Pb is common especially in the vicinity of these industries and manufacturing plants. Furthermore, sediments serve as the primary 'sink' for Pb as the heavy metal is adsorbed readily by organic matter and clay particles (DWAF, 1995). According to DWAF (1996a), the SAWQG target

value for aquatic ecosystem is 0.0002 mg/l, domestic use is 0.01 mg/l and the ecological environment is 0.0005 mg/l.

Manganese (Mn)

Mn is a grey-white brittle chemically active heavy metal (DWAF, 1996d; Lenntech, 2009) and is an essential micro-nutrient for plants and animals (DWAF, 1996a). In the aquatic environment, Mn does not occur naturally as a metal but is found in various salts and minerals, and is frequently in association with Fe compounds (DWAF, 1996a). Concentration of dissolved Mn is influenced by redox potential, dissolved oxygen content, pH and organic matter. According to DWAF (1996d), Mn levels in freshwater is approximately 8 µg/L and 0.2 µg/L in seawater. DWAF (1996d), states that elevated concentrations of Mn are associated with effluent discharge from industries producing chemicals (paints, dyes, glass and ceramics), fertilizers and herbicides. Mn is threatening to the aesthetics of water bodies as it produces a green discoloration in water (DWAF, 1996d). At concentrations >0.05 mg/L Mn poses a serious health risk to humans resulting in liver, kidney, pancreas and glandular problems (DWAF, 1996d; Lenntech, 2009). The heavy metal also has the ability to bioaccumulate in diatoms, molluscs and sponges (Lenntech, 2009).

Molybdenum (Mo)

Mo is a rare element that is naturally present in estuarine systems in trace amounts (Savvin, 1988). According to Lenntech (2009), Mo is sensitive to drainage conditions and pH levels, with its solubility increasing from acidic to alkaline sediment. Elevated concentrations of Mo are usually a result of anthropogenic activities such as effluent derived from metallurgical, chemical, dye and varnish industries (Savvin, 1988). Mo does not accumulate in the tissues of organisms nor is it toxic, except at high concentrations (DWAF, 1996a). Currently, there are no guideline values available in the SAWQG for Mo in terms of domestic use, the aquatic or ecological environment (DWAF, 1996a).

Nickel (Ni)

DWAF (1995) and David (2006), state that naturally sourced Ni is derived from weathering and volcanism while, anthropogenic sources include mining activities, the burning of fossil fuels, sewage sludge, waste incineration and effluent from refineries. According to Dallas and Day (1993), Ni ions tend to be soluble at pH values <6.5 and form insoluble Ni hydroxides above pH of 6.7. Ni has been noted as readily adsorbed by organic matter and sediment however, when the adsorption processes are reversed Ni is released back into the water column (DWAF, 1995). Ni is toxic even in small amounts and is a carcinogenic in mammals (Dallas and Day, 1993). There are no ideal thresholds available in terms of the SAWQG for domestic use, the aquatic or ecological environment (DWAF, 1996a).

Selenium (Se)

Se is a rare heavy metal and is an essential nutritional micro-element at low concentrations (DWAF, 1996d). According to DWAF (1996d), pH and redox reactions control Se speciation. Significant sources of anthropogenic Se include industrial effluent from paint, plastic and rubber industries (DWAF, 1996d). According to DWAF (1996a; 1996d), Se can bioaccumulate in plants and benthic invertebrates. In aquatic birds, Se enrichment results in embryonic deformities and death (Harrison, 2007). The SAWQG target value for the aquatic ecosystem is 0.002 mg/l and domestic use is 0.02 mg/l (DWAF, 1996a). There are no values available for the ecological environment (DWAF, 1996a).

Silicon (Si)

Si is one of the most abundant heavy metals on earth (Rosler and Lange, 1972). DWAF (1995) and Statham (2011), state that Si is a biolimiting heavy metal and an essential constituent of the rigid parts of diatoms, fungi and siliceous sponges. The primary source of dissolved Si to riverine flows and estuaries is derived from weathering (Drever, 1997). According to Le Gall and Raillard (1988), diatoms excrete Si in the form of opal and upon death; siliceous organisms liberate Si into seawater. At abnormally high concentrations Si can limit algal growth (Sukdeo, 2010) and result in respiratory complications in humans (Lenntech, 2009). There are no ideal

thresholds available in terms of the SAWQG for domestic use, the aquatic or ecological environment (Sukdeo, 2010; Pillay, 2013a).

Sodium (Na)

According to DWAF (1996b), Na is essential for the maintenance of electrolyte balances and other physiological processes. Common anthropogenic sources of Na to water bodies include industrial effluent and agricultural run-off. The excessive intake of Na is harmful to humans, especially infants and those with pre-existing health conditions such as hypertension and cardiovascular diseases (DWAF, 1996b). According to DWAF (1996a), there are no guideline values available in the SAWQG for domestic use, the aquatic or ecological environment.

Strontium (Sr)

Sr is sourced naturally from various rocks and minerals in the earth's crust and occurs at low concentrations (Boyd, 2000; Lenntech, 2009). According to Lenntech (2009), Sr compounds in a water soluble form are widespread in the environment. Currently, there are no guideline values available in the SAWQG for domestic use, the aquatic or ecological environment (DWAF, 1996a).

Titanium (Ti)

Ti is an abundant element in the earth's crust and is found naturally bound to other elements (Lenntech, 2009). Ti poses no health risks in water unless present in a halogenated form which is toxic to aquatic organisms and capable of altering pH levels (Lenntech, 2009; Sukdeo, 2010). According to DWAF (1996a), there are no guideline values available in the SAWQG for domestic use, the aquatic or ecological environment.

Vanadium (V)

According to Lenntech (2009) and Sukdeo (2010), V is a metallic element and is extremely soluble and hence easily distributed in the environment *via* watercourses (Sukdeo, 2010). Certain species of V are soluble in water and are not strongly adsorbed onto soil particles (hence stays in solution) (DWAF, 1996a). High levels of V inhibit tissue oxidation and can also hamper the synthesis of cholesterol, lipids and amino acids (Dallas and Day, 1993). V compounds have various industrial applications and are used as catalysts in the chemical industry, in certain glassware and ceramic products, in the textile industry and in the manufacture of dyes. The SAWQG target value for domestic use is 0.1 mg/l (DWAF, 1996a). There are no values available for the aquatic ecosystem and the ecological environment (DWAF, 1996a).

Zinc (Zn)

Zn occurs abundantly in nature (DWAF, 1995; 1996d). According to DWAF (1996d), Zn is essential in plants and animals, and is used in nucleic acid synthesis and enzyme activity. Water with a low pH, low alkalinity or high ionic strength will have the highest concentration of dissolved Zn (DWAF, 1996a). Anthropogenic sources of Zn include effluent derived from the manufacture of paper and pulp, fertilizers, paint, dye and pharmaceuticals (DWAF, 1995; 1996d). Excessive concentrations of Zn can result in fish kills, growth deformities and decreased reproduction in other aquatic organisms (DWAF, 1996a), as well as, gastro-intestinal discomfort in humans (DWAF, 1996b). The SAWQG target value for the aquatic ecosystem is 0.002 mg/l and domestic use is 20 mg/l (DWAF, 1996a). There are no target values available for the ecological environment (DWAF, 1996a).

1.10.3 Budgets

A good understanding of the heavy metal and nutrient content of an estuary is essential to be able to protect it from the aforementioned problems. According to Ekholm *et al.* (1997), one of the most suitable approaches to attaining this is through quantifying a budget of the estuary. A budget represents all of the material already present in the estuary, plus inputs, less the outputs and what remains equals the internal load (Ekholm *et al.*, 1997). Few studies have been

conducted on material exchange between estuaries and the marine environment in South Africa and include the following. Baird *et al.* (1987), studied the flux of carbon, inorganic and organic particulate matter between the Swartskops Estuary (near Port Elizabeth) and the marine environment. It was concluded that the estuary was a net exporter of total suspended particulate matter. Fernandes (2011), studied the nitrate fluxes of the Isipingo, Umgeni and Tongati Estuary, located within the eThekweni Municipality. The findings demonstrated that the Isipingo Estuary was a net importer of nitrates on the spring tide for all seasons except winter while, the Umgeni system exported nitrates for all seasons except autumn, when nitrates were imported on both the spring and neap tide. The Tongati Estuary was a net exporter of nitrates throughout the year (Fernandes, 2011; Fernandes and Pillay, 2012).

1.11 Bacteria

Bacteria are a diverse assemblage of prokaryotic organisms that occur abundantly in water and sediment (DWAF, 1996d; Sigeo, 2005; US-EPA, 2006; Pachepsky and Shelton, 2011). According to numerous researchers bacteria are important indicators of estuarine health particularly when determining the pathogenic state of the system (Erkenbrecher, 1980; the Australian Government, 2003; Sigeo, 2005). The direct monitoring of pathogens is a very expensive and time-consuming process (US-EPA, 2006). These challenges are being addressed by monitoring indicator bacteria instead (DWAF, 1996b). The presence of indicator bacteria however, does not directly indicate the presence of pathogens but indicates fecal pollution and the microbiological impairment of water and sediment; which result in the presence of pathogens (DWAF, 1996b; Govender, 2009). Indicator bacteria are inclusive of Total coliforms (TC), Faecal coliforms (FC) and *Escherichia* coliforms (EC). According to Pillay (2013a), TC comprises of a composite of bacteria found in soil and water and includes FC. The presence of the latter in a sample (water or sediment) is indicative of faecal pollution. EC is a sub-group of FC and is more indicative of contamination by human and animal waste.

1.11.1 Total coliforms (TC)

TC bacteria are indicative of pathogens responsible for infectious diseases such as gastroenteritis, salmonellosis, dysentery, cholera and typhoid fever (DWAF, 1996b). According to DWAF (1996b) and, Csuros and Csuros (1999), TC content can be used to assess the sanitary

quality of water, to evaluate the efficiency of drinking water treatments' and the integrity of the distribution system. If TC is detectable in treated water supplies it would suggest inadequate water treatment (DWAF, 1996b). The monitoring of TC in water and sediment samples from the eziMbokodweni Estuary is imperative as the estuary receives return flow from the eziMbokodweni Waste Water Treatment Works (McLean, 2008) furthermore, the Southern Sewage Works Outfall - one of the largest deep sea sewage outfalls in the eThekweni Municipality - is located approximately 1.5 km from the eziMbokodweni Estuary (Bailey, 2000). It is likely that the nutrient enriched waters are transported to the near shore environment *via* longshore drift. The SAWQG for domestic use is 0-5 cfu/100 ml (DWAF, 1996b). No guidelines are available for aquatic ecosystems and recreational use.

1.11.2 Faecal coliforms (FC)

FC bacteria are a sub-group of TC bacteria (Pillay, 2013a). According to DWAF (1996b), FC are a more reliable indicator of faecal pollution than the broader TC group, as the sub-group is more closely associated with faecal pollution. FC are therefore used extensively to evaluate the quality of waste water effluent, river and sea water at bathing zones, raw water for drinking water supply and water used for irrigation, livestock watering and aquaculture (DWAF, 1996b). According to DWAF (1996c), FC indicates the presence of pathogens responsible for the transmission of diseases such as gastroenteritis, salmonellosis, dysentery, cholera and typhoid fever (DWAF, 1996b). The SAWQG for domestic use is 0 cfu/100 ml and recreational use (full-contact) 0-130 cfu/100 ml (DWAF, 1996b; 1996c). No guidelines are available for aquatic ecosystems.

1.11.3 *Escherichia coliforms* (EC)

EC bacteria are a normal inhabitant of the intestine of humans and other warm-blooded animals (DWAF 1996b; Pillay, 2013a). According to DWAF (1996b) and, Csuros and Csuros (1999), EC is the most specific indicator of faecal pollution. EC is also used as an indicator of microbial pathogens that cause external infections and respiratory illnesses (DWAF, 1996c). The SAWQG for recreational use (full-contact) is 0-130 cfu/100 ml (DWAF, 1996c). No guidelines are available for aquatic ecosystems or domestic use.

1.11.4 Factors Influencing Bacterial Content in Estuaries

Several physical, chemical and biological factors, such as, turbidity, nutrient content and fluctuations in temperature and pH can determine the survival or elimination of bacteria in aquatic systems (DWAF, 1996a). While, other natural processes such as sedimentation, adsorption and coagulation may remove bacteria from water with or without inactivation (CSIR, 2010). The key factors influencing bacterial content in the eziMbokodweni Estuary are sedimentation, salinity levels and disturbance; these factors are discussed in greater detail below.

1.11.4.1 Sedimentation

Matson *et al.* (1978; pg 18), states that '*observed or predicted reductions in waterborne indicators should not be the sole criterion for determining potential health hazard presence, since many viable organisms (coliforms and pathogens) are deposited in the sediments*'. This statement has become increasingly evident as numerous comparisons between bacterial content in estuarine sediment and the overlying subsurface waters have led to the conclusion that sediment is the dominant reservoir for bacteria, with their concentrations being multiple-fold higher in sediments (Van Donsel and Geldreich, 1971; Goyal *et al.*, 1977; Erkenbrecher, 1980; Doyle *et al.*, 1992).

Bacterial content is determined by sediment properties such as texture, type and depth of the sediment profile. Atwill *et al.* (2007), confirmed a directly proportional relationship between the percentage of clay and silt particles and, EC and FC concentrations in riverine and estuarine sediment samples collected in Northern California. This was also noted by Garzio (2009) in the sediment collected from a Maryland Creek as EC concentrations increased with silt content. Slower EC and FC die-off rates were noted by Pachepsky and Shelton (2011) in sediments as the percentage of clay and silt particles increased. The increased survival of bacteria in such sediments was attributed to the reduced pore spaces of clay and silt particles providing greater protection to bacteria from predation (Davies and Bavor, 2000; Decamp and Warren, 2000), and the effects of sunlight inactivation (Pachepsky and Shelton, 2011). Hendricks (1971) and Ferguson *et al.* (1996), also point out that increased bacterial survival rates in sediment is due to sediments having a greater affinity for organic matter than the water column. In terms of depth of the sediment profile Alm *et al.* (2003), noted a two-fold decline in EC concentrations in beach sand with 5 cm increments of depth within the first 15 cm. However, this may be further

attributed to organic matter content as Callow (1994), noted that heavy metal concentrations were highest in the initial 10 cm of undisturbed sediments.

1.11.4.2 Salinity

Salinity is a key determinant of bacterial concentration in water (Goyal *et al.*, 1977; Erkenbrecher, 1981; Lipp *et al.*, 2001; Sigee, 2005) with faster die-off rates associated with increasing salinity (Goyal *et al.*, 1977; Anderson *et al.*, 2005). Studies conducted by He *et al.* (2007), have shown that average EC concentrations in ponded water with conductivity levels greater than 5 mS/cm were significantly lower than that with conductivity levels lower than 5 mS/cm. Atwill *et al.* (2007), observed a similar pattern of declining EC concentrations with increasing salinity and depth. While, Erkenbrecher (1980), recorded declining FC counts in the Lynnhaven Estuary as the more saline waters of the inlet were approached. Erkenbrecher (1980), also noted that the highest FC counts in both aquatic and benthic samples were detected at the headwaters where freshwater input dominated and tidal flushing was poor.

1.11.4.3 Disturbance

According to Pachepsky and Shelton (2011), a number of publications have shown that the re-suspension of sediment can result in elevated bacterial concentrations in water. Numerous physical mechanisms can result in the re-suspension of bed sediment these include: tidal action, wind induced turbulence and storm activity, recreational activities such as boating and swimming and activities by bottom-feeding fish and invertebrates.

Buck (1973) and, Erkenbrecher and Stevenson (1975) both in Erkenbrecher (1980), demonstrated that the density of aquatic bacteria responded directly to fluxes in tidal flow, with the lowest bacterial counts recorded prior to or at high tide, while the highest bacterial counts were found to occur on the ebbing tide and were at a maximum just prior to low slack water. Disturbance can also influence bacterial residence time in estuaries as increased tidal action facilitates the transport of bacteria within the estuary, as well as, its export to the marine environment.

1.12 Physico-Chemical Parameters

The content of selected physico-chemical parameters were investigated in water samples collected from the eziMbokodweni Estuary as the parameters assist in interpreting estuarine health. These parameters include pH, Dissolved Oxygen (DO), Total Dissolved Solids (TDS), Electrical Conductivity (EC), salinity, Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

1.12.1 pH

According to DWAF (1996d) and Dallas and Day (2004), pH is a measure of the acidic or basic character of a solution, and is effectively the hydrogen ion activity in the solution. The pH levels of seawater range between 7.9 - 8.2 pH units (DWAF, 1995; 1996a). pH levels are determined by numerous natural and anthropogenic factors such as the physico-chemical properties of soil and rocks, and catchment run-off (Dallas and Day, 2004; Forbes and Demetriades, 2008). pH levels range between 6.5-9 pH units in un-impacted estuaries (Forbes and Demetriades, 2008). The solubility and biological availability of heavy metals and nutrients are dependent on pH levels thus deviations from optimal pH levels can have severe impacts on estuarine dynamics and biota (DWAF, 1996a). According to DWAF (1996a), most freshwater in South Africa is well buffered and more or less neutral with pH ranging from 6-8 pH units. The SAWQG for aquatic ecosystems is 6.5-8 pH units; domestic use 5-9.5 pH units and recreational use (full-contact) (DWAF, 1996a; 1996b; 1996c)

1.12.2 Dissolved Oxygen (DO)

DO is the relative measure of the amount of gaseous oxygen that is dissolved in an aqueous solution, and is one of the principle limiting factors in aquatic respiration and metabolic reactions (Brijlal, 2005). According to DWAF (1996a), DO levels fluctuate diurnally, depending on the rates of photosynthesis and respiration. Factors such as temperature, pressure, salinity and aeration also influence DO levels (DWAF, 1996a; Dallas and Day, 2004). The degradation of organic material through bacterial activity - a process which consumes available oxygen - is one of the main reasons for a decline in DO levels (Whitfield and Bate, 2007). According to the US-EPA (2006), an overload of nutrients adds to this problem.

Estuarine biota can grow and reproduce un-impaired at DO levels >5 mg/L (US-EPA, 2006). However, when these levels drop to 3-5 mg/L organisms become stressed resulting in a reduced appetite, poor growth and productivity, and an increased susceptibility to infectious diseases (US-EPA, 2006). Estuaries are also prone to eutrophication and bio-loading at these levels (DWAF, 1996d). According to the US-EPA (2006), when DO levels fall below 3 mg/L (hypoxic conditions) mobile species move elsewhere while immobile species die, and when DO levels fall below 0.5 mg/L (anoxic conditions) all species reliant on oxygen die and the affected estuary is unable to maintain the delivery of most estuarine goods and services (Boyd, 2000). The SAWQG for aquatic ecosystems is 6 mg/L (DWAF, 1996a).

1.12.3 Electrical Conductivity (EC), Total Dissolved Solids (TDS) and Salinity

One of the major descriptors of water quality is the total amount of material dissolved in it. According to Dallas and Day (2004), this property can be measured in one of three ways: as EC, TDS or salinity. TDS represents the total quantity of dissolved material, organic and inorganic, ionized and unionized in a water sample (DWAF, 1996d; Dallas and Day, 2004). EC refers to the number of charged particles in a water sample and is a measure of the ability of the sample to conduct an electrical current (Dallas and Day, 2004). EC is often used as a surrogate for TDS since the EC of water is a function of the number of charged particles (ions) in solution, which is also a measure of the TDS in a sample of water (Dallas and Day, 2004).

According to the US-EPA (2006) and DWAF (1996d), salinity is a measure of only the dissolved inorganic content of a solution. Salinity levels vary throughout the length of an estuary, as freshwater enters an estuary from tributaries and mixes with seawater moving in from the ocean (US-EPA, 2006). Salinity levels play a significant role in the distribution of biota in an estuary. According to the US-EPA (2006), freshwater biotas are restricted to the upper reaches of estuaries where there is fluvial inflow, while marine species inhabit the estuarine mouth region. Species that are tolerant to salinity at intermediate levels are found in the mid-reaches, while highly adaptive species that can acclimate to any salinity level occupy any region along the estuary (US-EPA, 2006).

According to Dallas and Day (2004) and the US-EPA (2006), salinity also controls the flocculation of particles in estuaries and, hence the turbidity of the system. Saline waters

introduce ionic charges onto fine sediments, affording it a greater capacity to adsorb heavy metals from solution and function as a heavy metal 'sink' (Sukdeo, 2010). In addition, as river flow decreases, the ability to maintain an open mouth status diminishes which can result in a semi-closed or permanently closed mouth state, the estuary then becomes more saline with evaporation or gradually fresher if river inflow exceeds the evaporation rate, and when natural breaching occurs (Pillay, 2013a).

1.12.4 Biological Oxygen Demand (BOD)

BOD measures the amount of oxygen that micro-organisms consume while decomposing organic matter, it also measures the extraction of oxygen from the water *via* chemical reactions (US-EPA, 2006; Govender, 2009). A number of factors influence the rate of oxygen consumption in an estuary including temperature, micro-organisms, and the type of organic and inorganic material in water (US-EPA, 2006). According to Govender (2009), BOD affects the amount of DO in estuaries, as the greater the BOD the more rapidly DO is depleted. Hence, less oxygen is available to aquatic organisms. The consequence of high BOD is the same as those for low DO (US-EPA, 2006). According to the US-EPA (2006), BOD levels of <5 mg/L are characteristic of unpolluted and natural waters.

1.12.5 Chemical Oxygen Demand (COD)

According to DWAF (1996d; pg 25), COD is defined as '*a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant*'. Govender (2009), states that COD gives an estimate of the organic matter present in a water body, and is therefore a useful measure for assessing the conformity of effluent discharge (wastewater and industrial) to water quality requirements (DWAF, 1996a). According to DWAF (1996e), excessive organic matter content results in undesirable tastes and odours, as well as, the formation of microbial slimes, which is a nutrient source and promote bacterial growth in estuaries. According to Govender (2009), COD levels <75 mg/L pose no adverse effects to estuarine biota or humans.

1.13 Legislation Pertaining to Estuaries in South Africa

In South Africa, there are a number of pieces legislation that afford protection to estuaries and regulate the sustainable use of water resources. A brief overview is given below:

1.13.1 The Environmental Conservation Act (73 of 1989)

The Environmental Conservation Act (73 of 1989) was introduced to govern a range of factors surrounding the protection of ecological processes, natural systems, as well as, the preservation of biotic diversity in the natural environment. A key feature of the Act is that provisions are made for environmental conservation policies and, the establishment and requirement of protected areas (ECA, 1989). The Act also prohibits any activity or development that may present detrimental effects to the environment and calls for the administering of penalties and fines to perpetrators (ECA, 1989).

1.13.2 The Water Services Act (108 of 1997)

The Water Services Act (108 of 1997) provides a regulatory framework for local authorities to supply water and sanitation in their respective areas; and is more specifically concerned with the abstraction, transfer, treatment and distribution of water and sanitation (Glazewski, 2000). The removal of wastewater and sewerage is also addressed under this Act (Glazewski, 2000).

1.13.3 The Marine Living Resources Act (MLRA) (18 of 1998)

The management and control of living resources in estuaries is primarily dealt with under the Marine Living Resources Act (18 of 1998). The purpose of the Act is to protect marine living resources through establishing sustainability limits for the utilisation of these resources, declaring fisheries management areas for the management of species, and controlling destructive fishing methods (Perissinotto *et al.*, 2010; Sukdeo, 2010). Under this Act marine protected areas should be established to offer protection to the living resources.

1.13.4 The National Water Act (36 of 1998)

The National Water Act (36 of 1998) governs the protection of estuaries to ensure the continued provision of goods and services (NWA, 1998; van Niekerk, 2007; Sukdeo, 2010). More specifically water management strategies, the classification and provision of water resources and water use licenses are dealt with under this Act (Glazewski, 2000). The Act also calls for the classification of estuaries according to their health status (Perissinotto *et al.*, 2010).

1.13.5 The National Environmental Management Act (NEMA) (107 of 1998)

The National Environmental Management Act (107 of 1998) is concerned with co-operative environment governance and addresses environmental decision-making (Perissinotto *et al.*, 2010; Sukdeo, 2010). The Act provides a number of mechanisms to achieve these ideals such as all proposed activities or developments that would impact on an estuary would require an environmental impact assessment (EIA) prior to it being undertaken (Perissinotto *et al.*, 2010). The EIA will ensure that all adverse environmental impacts are mitigated for (Perissinotto *et al.*, 2010).

1.13.6 The National Environmental Management: Integrated Coastal Management Act (24 of 2008)

The National Environmental Management: Integrated Coastal Management Act (24 of 2008) is an important step forward in the management and protection of estuaries. The Act aims to promote sustainable coastal development through the introduction of an integrated coastal management approach (Perissinotto *et al.*, 2010). The Act identifies the need for estuary management plans (EMPs) to co-ordinate estuary management at a local level (Perissinotto *et al.*, 2010). The EMP must outline the vision and objective for the estuary, state and guide the management of the estuary, define roles and responsibilities of organs of state and provide recommendations for community involvement (Perissinotto *et al.*, 2010).

1.14 Conclusion

Estuaries are highly dynamic and productive systems that provide important ecosystem goods and services (Falco *et al.*, 2010). According to Davies and Day (1998), estuarine health is related to catchment characteristics. This is evident in South Africa where estuaries with catchments that are little affected by human activities retain an almost pristine character (Fernandes and Pillay, 2012). Estuaries with catchments that have been anthropogenically modified for activities such as construction, forestry, mining and industry receive large quantities of contaminants as is the case for numerous estuaries in the eThekweni Municipality (Forbes and Demetriades, 2008). These contaminants particularly heavy metals, nutrients and bacteria threaten estuarine biota and processes. According to Ekholm *et al.* (1997), one needs a good understanding of the material content of an estuary to be able to protect it from these impacts and one of the most suitable approaches to attaining this is by developing a budget of the estuary. Studies have also shown that the rate of anthropogenic heavy metal addition into estuaries is steadily increasing (Abed, 2009, Kandasamy, 2008). This is alarming as according to Sukdeo (2010), heavy metals are non-biodegradable. Furthermore, according to Abed (2009) and Sukdeo (2010), fine grained sediment serve as heavy metal ‘accumulators’ or ‘sinks’, and on disturbance release heavy metal deposits back into the water column. Changes in physico-chemical conditions can also alter redox potentials in estuaries and with such changes heavy metals can be reduced or oxidized into toxic forms (Lewis and McConchie, 1994) endangering estuarine dynamics, biota and humans. According to the Australian Government (2003) and Sigeo (2005), in addition to the traditional methods of monitoring heavy metal and nutrient content in estuaries, bacteria are increasing being used as indicators of estuarine health. Bacteria assist in monitoring the pathogenic status of the system and are an economical and less time-consuming alternative to monitoring pathogens directly (Sigeo, 2005; Pachepsky and Shelton, 2011). Given the foregoing it is evident that estuarine health can be studied on various fronts. In this study the content of heavy metals, nutrients, selected physico-chemical parameters and bacterial content was studied in water and sediment samples collected seasonally, for spring and neap tides in the eziMbokodweni Estuary. The results obtained will provide the database from which more holistic and integrated mitigation and management strategies can stem.

CHAPTER TWO

Study Area

2.1 Introduction

This chapter details a description of the eziMbokodweni Estuary, its regional location and catchment characteristics. The physical and biotic characteristics of the estuary are also discussed and include a review of past research conducted on the system.

2.2 Description and Regional Location

The eziMbokodweni Estuary is located along the east coast of South Africa within the province of KwaZulu-Natal (Figure 2.1). The estuary is a temporarily open/closed system and maintained an open mouth status throughout this study. The eziMbokodweni river has a length of approximately 47 km with a catchment size of 240 km² (Perry, 1989 in Forbes and Demetriades, 2008).

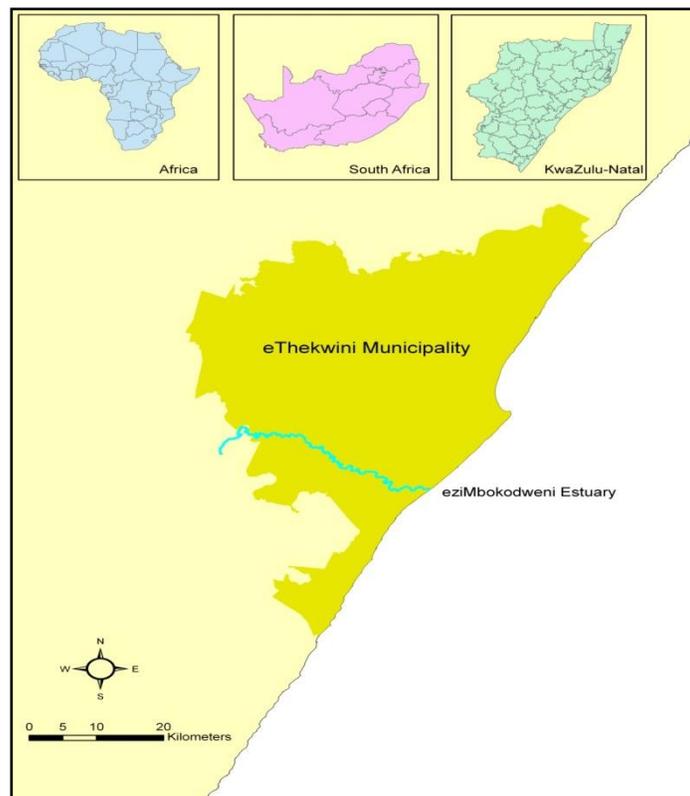


Figure 2.1 Location of the eziMbokodweni Estuary in relation to the KwaZulu-Natal coastline

2.3 General Climatology and Hydrodynamics

The climate of the region is classified as subtropical due to the northerly south Indian anticyclone and an easterly tropical flow (Allanson and Baird, 1999). Summers are warm and wet, and winters cool and dry (Cooper, 1990; Allanson and Baird, 1999; Tyson and Preston-Whyte, 2000; Green *et al.*, 2004). Maximum summer temperatures reach approximately 27°C, while minimum winter temperatures vary between 10.9°C and 16.7°C. Annual rainfall fluctuates between 900 mm to 1000 mm, of which 80 % falls during summer months (Preston-Whyte and Tyson, 2000).

The coastline is dominated by south westerly and north westerly winds (Cooper, 1986; Schumann *et al.*, 1999) and generally the winds are strongest during October and November, while the calmest period is experienced during June (Cooper, 1991; Schumann *et al.*, 1999). Tides along the coastline are semi-diurnal and the main wave approach is south-easterly which generates longshore drift currents responsible for northerly transport of sediment and material (Fernandes and Pillay, 2012). The mean spring and neap tidal ranges are approximately 1.72 m and 0.5 m, respectively with an average tidal range of about 2 m (Cooper, 1993).

2.4 Catchment Landuse

The eziMbokodweni Estuary is positioned at the foot of a highly anthropogenically-modified catchment. The surrounding landuse and associated activities that likely impact on the health status of the lower eziMbokodweni River and Estuary were identified using satellite images (Google Earth, 2009). These include:

- a. Industrialisation - The Prospection Industrial Area (PIA);
- b. Urbanisation - The Suburbs of Amanzimtoti, eziMbokodweni, Isipingo and Umlazi;
- c. The Southern Sewage Works Outfall;
- d. The eziMbokodweni Wastewater Treatment Works (WWTWs);
- e. The Amanzimtoti golf course; and
- f. Diversion of flow from the Isipingo Estuary into the eziMbokodweni River.



Figure 2.2 Satellite image showing the land uses and associated activities surrounding the lower eziMbokodweni River and Estuary (adapted from Google Earth, 2009).

2.4.1 Industrialisation - The Prospection Industrial Area (PIA)

The catchment of the lower eziMbokodweni River and Estuary is flanked by dense industrial development referred to as the PIA. The PIA was developed in the late 1960s and comprises a number of petroleum refineries, automotive and, light and heavy industries. Numerous authors have noted that water bodies serve as disposal sites for industrial effluent and wastes (Walmsley, 2000; Malan and Day, 2002; Adebayo and Kehinde, 2008). In the case of the eziMbokodweni Estuary, the PIA is a significant source of non-point pollution. The area is completely transformed, with impervious surfaces that restrict groundwater contributions to the estuary while increasing the volume and rate of surface run-off

(Anderson, 1970; Lazaro, 1990; Calder *et al.*, 1995; Moscrip and Montgomery, 1997; Sukdeo, 2010). Unregulated and non-compliant discharge from industries is also a likely source of contaminants to the eziMbokodweni Estuary.

2.4.2 Urbanisation - The Suburbs of Amanzimtoti, eziMbokodweni, Isipingo and Umlazi

A number of studies have highlighted the link between urbanisation and changes in water quality (Neilson and Cronin, 1981; Carpenter *et al.*, 1998; Tabayashi and Yamamuro, 2009; Statham, 2011). The catchment of the eziMbokodweni Estuary has been transformed to accommodate residential developments in Amanzimtoti, eziMbokodweni, Isipingo and Umlazi. Large portions of the catchment have as a result been replaced with impermeable surfaces. The resultant run-off from these residential nodes comprises nutrients, heavy metals, sediment, organic compounds and FC (DEAT, 2006). The suburbs consist of both formal and informal dwellings as a result inadequate sanitation facilities and the poor maintenance of sewage infrastructure is a likely occurrence. Bucus (2006), highlighted sewage effluent contamination, as a result of inadequate sanitation facilities and sewage infrastructure, as one of the major contributors of pollution to fluvial systems.

2.4.3 The Southern Sewage Works Outfall

The Southern Sewage Works Outfall, one of the largest deep sea sewage outfalls in the eThekweni Municipality, is located on the northern banks of the Umlaas Canal (Bailey, 2000) approximately 1.5 km from the eziMbokodweni Estuary. The outfall has a design capacity of 230 000 m³/day (Bailey, 2000). According to Fernandes (2011), effluent from the outfall contains high concentrations of nutrient-enriched compounds. It is likely that the nutrient-enriched waters are transported to the nearshore environment *via* longshore drift.

2.4.4 The eziMbokodweni Wastewater Treatment Works (WWTWs)

The eziMbokodweni River and Estuary also receives return flow from the eziMbokodweni WWTWs (McLean, 2008) situated upstream of the estuary. According to Fernandes (2011), return flow is defined as water that is used by WWTWs and returned to rivers; these discharges generally contain contaminants and high nitrate concentrations. Infrastructure failures, as well as, unregulated or non-

compliant discharges from the WWTWs are significant sources of enrichment to the eziMbokodweni Estuary.

2.4.5 The Amanzimtoti golf course

The Amanzimtoti golf course is located on the floodplain of the eziMbokodweni Estuary. The lawns of the golf course are regularly fertilised and chemically treated to maintain grasses conducive to the sport. As a result, run-off and seepage from the lawns is a significant contributor of nutrients to the estuary. Numerous researchers have found that leaching of fertilisers from lawns and agricultural land results in increased nutrient content in water bodies (Neilson and Cronin, 1981; Carpenter *et al.*, 1998; Falco *et al.*, 2010; Sukdeo, 2010). Furthermore, these researchers reported higher volumes of the nutrients in the water body following rainfall.

2.4.6 Diversion of flow from the Isipingo Estuary into the eziMbokodweni River

Flow from the Isipingo Estuary is periodically diverted into the eziMbokodweni Estuary to alleviate flooding, *via* the Diversion Works System and the Prospection Canal System. Fernandes (2011) and Pillay (2013a), have noted high levels of contaminants in the Isipingo Estuary and Forbes and Demetriades (2008) have classified the system as 'highly degraded'. These contaminants are therefore entering the eziMbokodweni Estuary through the diverted flows.

2.5 Physical and Biotic Characteristics of the Estuary (including a review of past research conducted on the system)

2.5.1 Engineering structures

The engineering structures along the eziMbokodweni Estuary include: two golf club foot bridges (Plate 2.1), three road bridges constructed in 1954, 1959 and 1970 (Plate 2.2) and a rail bridge constructed in 1932 (Begg; 1978; Begg, 1984) which crosses the river about 500 m upstream of the estuary. The northern bank of the estuary has been artificially stabilized with gabion baskets to protect the PIA from flooding (Begg, 1978; Forbes and Demetriades, 2008). The gabion baskets have since deteriorated and remnants occur as isolated rock piles along the banks of the lower estuary (Plate 2.3).



Plate 2.1 Golf club foot bridge across the estuary
(Author, 2012)



Plate 2.2 Road bridge across the lower river
(Author, 2012)



Plate 2.3 Remnants of the gabion baskets used to artificially stabilize the northern bank of the estuary
(Author, 2012)

2.5.2 Flow Characteristics

According to Begg (1978) and Forbes and Demetriades (2008), floods in the estuary occurred during 1953, 1957, 1961 and 1967; with a flood event in March 1968 resulting in discharge levels exceeding 300 m³/s. In present times discharge levels in the estuary are attenuated by anthropogenic activities such as water abstraction and the diversion of flow from the Isipingo River into the estuary (Forbes and Demetriades, 2008; Pillay, 2013a).

2.5.3 Mouth Behavior

Prior to any modification the mouth of the estuary was deflected southwards behind a 400 m long sandbar (Begg, 1978). The creation of a new mouth became necessary to deal with the additional flow added to the estuary through the diversion of the Isipingo River, thus a new mouth was blasted through rocks at the northern end (Figure 2.3) (Begg, 1978).

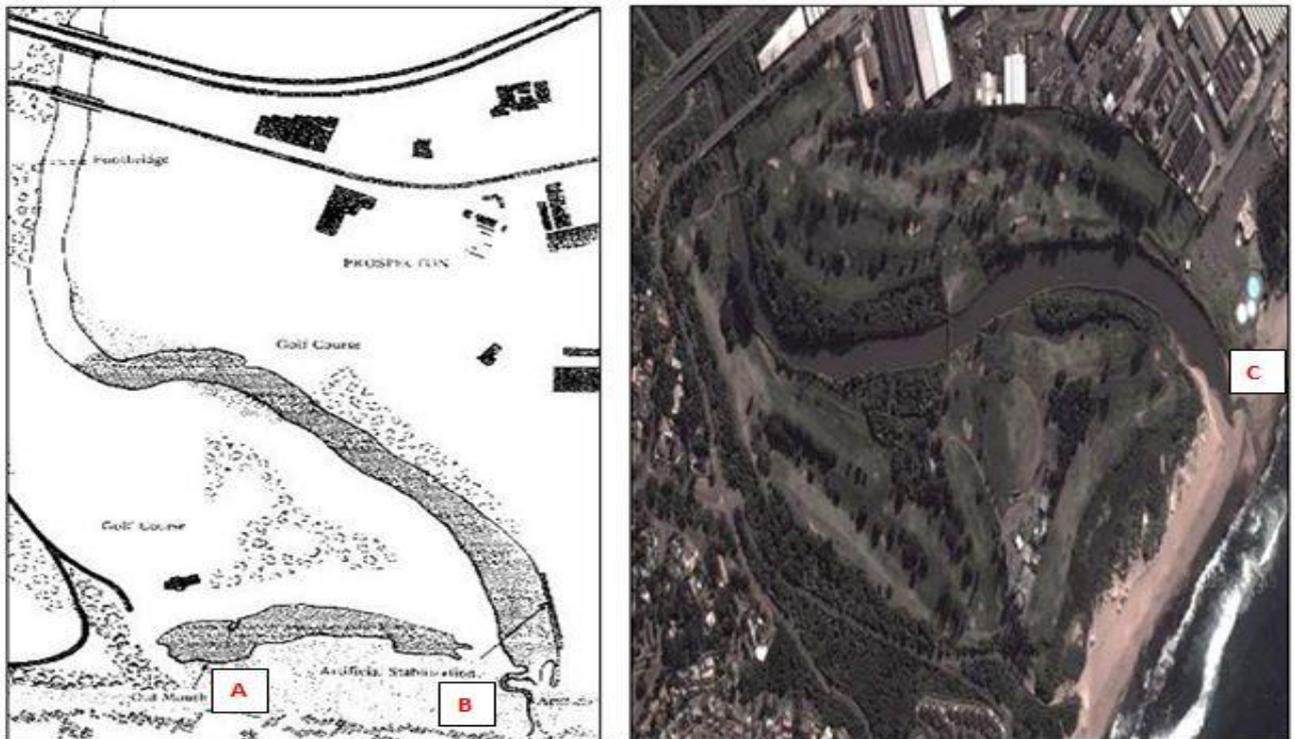


Figure 2.3 The positioning of the mouth of the eziMbokodweni Estuary prior to any modification (A), the ‘new mouth’ which was blasted through rocks at the northern end in the 1970s (B), the current position of the mouth (C) (Plate to the left Begg, 1978; Plate to the right adapted from Google Earth, 2009)

2.5.4 Water and Sediment Quality

During the summer and winter period of 1982 Begg (1984), recorded strong salinity layering in the estuary. McLean (2008), also observed a horizontal and vertical salinity gradient, and relatively high salinity throughout the system in 2006/2007 and 2007/2008 which was attributed to the prevalence of open mouth conditions.

According to Begg (1984), high levels of dissolved oxygen were noted in the estuary by day, ranging from 10.1 mg l^{-1} to 22.1 mg l^{-1} in the southern arm of the estuary. However, the northern arm of the estuary was characterized by deoxygenated water, ranging from 1.2 mg l^{-1} to 5.7 mg l^{-1} at the surface and 0.9 mg l^{-1} to 0.0 mg l^{-1} at the bottom. Samples collected during 2007/2008 indicated generally low dissolved oxygen levels with anoxic and hypoxic conditions persisting at several stations along the estuary (McLean, 2008).

The floor of the eziMbokodweni channel was characterized by '*black anoxic sludge deposits*' in the 1980s, which were attributed to sewage effluent (Begg, 1984; pg 142). Surveys conducted during 2007 indicated that nutrient concentrations were highest during winter when the system received a reduced fresh water supply and the dilution of treated waste water with rain water was low (Forbes and Demetriades, 2008). Begg (1978), also noted high bacterial levels in the estuary, with EC levels ranging from 9000 to 160 000 counts/100 ml during the 1970s. The samples collected during 2006/2007 and 2007/2008 reflected high bacterial levels, the maximum values recorded for TC, FC and EC were 37 000 counts/100 ml, 6000 counts/100 ml and 2400 counts/100 ml, respectively with notably higher levels during summer (McLean, 2008).

Sediment analysis conducted between 2006 and 2008 revealed a trend of decreasing sediment particle size away from the estuary mouth (McLean, 2008). Coarse and medium grained sediment dominated the upper and middle reaches of the estuary, respectively while medium grained sediment and mud were the major contributors to the sediments in the lower reaches (McLean, 2008). Sediment organic content was also highly variable in the estuary. In summer 2006/2007 and winter 2007 organic content was highest at the upper reaches, while in summer 2007/2008 there was an increase in the organic content at the lower reaches of the estuary (McLean, 2008). During the same period the organic content of sediments at the mouth and mid-reaches were low having a maximum of 1.45 % and 2.9 % respectively (Forbes and Demetriades, 2008). Sediment organic content in the upper reaches were all high in winter, approximately 3.3 %, but less than 1 % in summer which was attributed to greater flushing during the wetter summer months (Forbes and Demetriades, 2008).

2.5.5 Flora and Fauna

According to Forbes and Demetriades (2008), most of the riparian vegetation on the northern bank of the estuary was removed by 1937 due to farming activities and the floodplain on the southern bank appeared relatively un-impacted as the golf course was yet to be established. Currently, riparian vegetation along the eziMbokodweni Estuary comprises a narrow strip of natural vegetation (Figures 2.4 A-B), and the floodplain has been transformed into the Amanzimtoti golf course comprising lawns which are regularly fertilized and chemically treated.



Figure 2.4 A-B Riparian vegetation along the eziMbokodweni Estuary is confined to a narrow strip of natural vegetation (**A**) (Forbes and Demetriades, 2008). The floodplain has been transformed to accommodate the Amanzimtoti golf course comprising grasses with isolated trees (**B**) (Author, 2012)

Begg (1978), stated that in the late 1970s alien plant species such as water cabbage (*Pistia stratiotes*) were present in the estuary. During this study water hyacinth (*Eichhornia crassipes*) was noted on several occasions, occurring in isolated bands along the banks of the estuary. Forbes and Demetriades (2008), also noted a degraded benthic fauna community in the estuary dominated by oligochaete

worms, which are indicative of organic pollution, and a small variety and lower number of amphipod, isopod and tanaid crustaceans. In contrast, twenty seven fish species were recorded and attributed to the open mouth status of the estuary (Forbes and Demetriades, 2008).

2.6 Conclusion

This chapter described the regional location and catchment of the eziMbokodweni Estuary. The physical and biotic features of the system were also discussed and included historical changes and findings on the system. From these records, it is evident that the eziMbokodweni Estuary has been transformed from a relatively un-impacted system to one experiencing degraded conditions which have been attributed to the anthropogenic activities in the catchment.

CHAPTER THREE

Methodology

3.1 Introduction

Estuarine health can be assessed by using abiotic and biotic indicators such as physico-chemical parameters (e.g. pH and conductivity) or species community features and their biological attributes (Adams, 2005; Hubertz *et al.*, 2005). This research studied the content of heavy metals, nutrients, bacteria and selected physico-chemical parameters in sediments and the water column of the eziMbokodweni Estuary. The sampling regime, analytical procedures and, data analysis and interpretation techniques employed are detailed in this chapter.

3.2 Heavy Metal and Nutrient Content in the Water Column

3.2.1 Sampling Regime

The heavy metal and nutrient content of the water column was investigated by quantifying a budget for the system. According to Ekholm *et al.* (1997), a budget represents all of the material (e.g. heavy metals and nutrients) already present in an estuary, plus the inputs, less the outputs and what remains equals the internal load of the system. The heavy metal and nutrient transport and budget of the eziMbokodweni Estuary was quantified from water samples collected over spring and neap tides during summer (February 2012), autumn (March 2012), winter (June 2012) and spring (September 2012). The samples were collected at two sites in the estuary simultaneously, at hourly intervals spanning 12 hours (Figure 3.1). The sites were:

- a. E1: the upper estuary, where heavy metals and nutrients that enter the estuary from the catchment were quantified; and
- b. E3: the estuary mouth, where tidal interchange with the marine environment controlled the overall import or export of heavy metals and nutrients in this region.

0.5 L of water, per sample, was collected at mid-depth of the water column and stored in polyethylene bottles. Since the parameters measured for are dissolved constituents it was assumed that they would be homogeneously distributed across the channel. The samples were placed on ice and prepared for chemical analysis within 24 hours of collection. A total of 192 samples were collected.



Figure 3.1 Aerial view of the sampling sites in the eziMbokodweni Estuary (Satellite image adapted from Google Earth, 2009; Plates to the left sourced by Author)

3.2.2 Sample Analysis

The heavy metal and nutrient content of the water samples were analysed at the Analytical Chemistry Laboratory of the University of KwaZulu-Natal. The techniques and equipment used are detailed below.

3.2.2.1 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma - Atomic Emission Spectroscopy was used to determine the content of the following heavy metals in water samples: Aluminium (Al), Calcium (Ca), Chromium (Cr), Copper (Cu), Iron (Fe), Magnesium (Mg), Manganese (Mn), Mercury (Hg), Nickel (Ni), Phosphorus (P), Selenium (Se), Strontium (Sr), Vanadium (V), Zinc (Zn) and Zirconium (Zr). According to Skoog *et al.* (2004), ICP-AES is a type of emission spectroscopy that uses inductively coupled plasma to produce excited atoms and ions, that emit electromagnetic radiation at wavelengths and intensities that are unique to elements and indicative of their concentration within the sample.

According to Walsh (1997), the three main instruments used during the ICP-AES process are the source unit or the ICP torch, spectrometer and computer software. The source unit or the ICP torch is responsible for supplying the energy required to produce spectral lines (Walsh, 1997). The spectrometer separates and resolves the emission spectral lines and measures their strength, while the computer software enables the user to convert the signal into a numerical value representative of the concentration of the elements being analysed (Walsh, 1997; Skoog *et al.*, 2004).

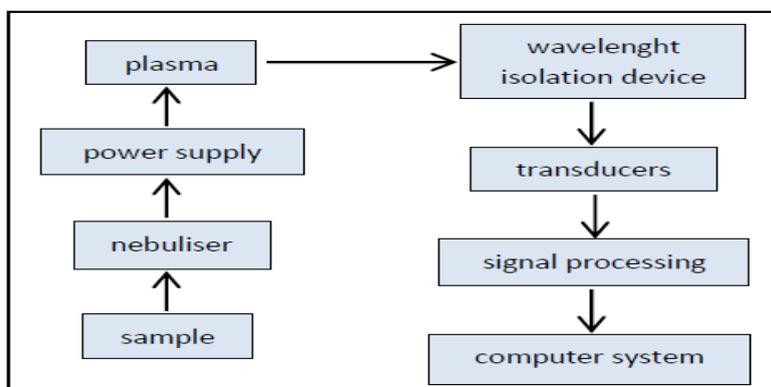


Figure 3.2 Apparatus used and processes followed during ICP-AES analysis (Adapted from: Skoog *et al.*, 2004)

The ICP-AES analysis was used in this study because it:

- is able to test samples in solution;
- has high sensitivity (can detect parts-per million to parts-per billion);
- can detect several elements simultaneously;
- is quick;
- produces reproducible results; and
- is easy to utilize (Walsh, 1997; Skoog *et al.*, 2004).

3.2.2.2 Flame Emission Spectrometry

Flame emission spectrometry was used to measure Potassium (K) and Sodium (Na) content in the water samples. According to Ngila (2008) and Sukdeo (2010), flame emission spectrometry involves aspirating metallic ions in solution into a low flame in aerosol form; which results in their electrons proceeding to higher energy states and becoming unstable before quickly returning to ground state. The loss in energy is then displayed as a discrete wavelength of visible light which is detected by a photo-detector and distinguished from other wavelengths with an optical filter (Ngila, 2008). Within the flame photometer the electrical signal from the photo-detector is amplified and presented as a digital readout (Sukdeo, 2010). According to Christian (2007) and Ngila (2008), flame emission spectrometry is a cost effective technique and is less susceptible to spectral interferences.

3.2.2.3 Ion Chromatography

Ion chromatography was used to determine the Ammonium (NH_4) and Sulphate (SO_4^{2-}) ions content in the water samples. According to Ngila (2008) and Sukdeo (2010), ion chromatography comprises numerous steps, first the aqueous sample is injected into a stream of carbonate/bicarbonate eluent, the eluent is then pumped through a resin-packed column ion-exchanger for which ions in the sample have different affinities hence the ions are separated. The original eluent and the separated ions then pass through the ion-exchanger, where the conductivity of the eluent is curbed to enhance the detection and conductivity of the ions, the ions are then transformed into highly conductive states (Ngila, 2008). Thereafter,

the ions are identified using respective retention times, and quantified *via* a comparison between the calibration standards and their peak areas (Ngila, 2008).

3.2.3 Data Analysis and Interpretation

3.2.3.1 Budget Calculation

As a precursor to determining the budget, the discharge (Q) from the estuary and transport (F) of heavy metals and nutrients were calculated. The discharge from the estuary was attained by taking the following measurements at both sites, simultaneously:

- the cross-sectional area (A) of the channel or mouth; and
- the velocity of flow (V)

The cross-sectional area of the channel/mouth was attained by measuring the width of the channel/mouth and multiplying it by the depth of the water level, and the velocity of flow was obtained by noting the time taken for a plume of dye to pass 10 m along the channel/mouth. The product of these values (AxV) was then calculated to obtain discharge at each site. This was repeated at hourly intervals spanning 12 hours.

The transport of heavy metals and nutrients was determined using the equation (Pillay, 1988; Frick *et al.*, 2007; Fan and Haijun, 2008):

$$F = QC \quad \text{where:} \quad (1)$$

F is the transport of the heavy metal or nutrient in kg/s;

Q is the discharge in m³/s; and

C is the heavy metal or nutrient concentration in mg/L.

Whilst material is continuously supplied to the estuary by the unidirectional riverine flow at the upper estuary (site E1) the situation is different at the estuary mouth (site E3). Here, seawater enters into the estuary on the flood flow and estuarine waters leave the estuary on the ebb flow (Brijlal, 2005; Hay, 2007). The transport of heavy metals and nutrients for the entire sampling period at the estuary mouth was thus calculated as the difference between the transport of heavy metals and nutrients entering during flood flows and leaving during ebb flows (Fernandes and Pillay, 2012; Pillay, 2013a). A positive transport value implied export

to the nearshore environment whilst a negative transport value implied import into the estuary.

The heavy metal and nutrient budget for the estuary was then calculated as the difference between the transport values of heavy metals and nutrients yielded for the entire sampling period entering the estuary from the landward side (site E1) and the net exchange between the estuary and the sea (site E3).

According to Gordon *et al.* (1996) and Falco *et al.* (2010), budgets are comprehensive and give an overall indication of the health status of the system very quickly. Furthermore, budgets can help to identify the major processes which determine the fluxes of heavy metals and nutrients and make the transition from a purely descriptive budget to a predictive process-based model (Wepener *et al.*, 2006). However, according to Fernandes and Pillay (2012), the data collection process is cumbersome as the flood and ebb flows at the estuary mouth are difficult to measure due to the continuous change in water levels with tides and the reversal in flow direction when flood changes to ebb.

3.2.3.2 Statistical Analysis

According to Naidoo (2005) and Pallant (2010), statistics allows for data to be objectively interpreted within a scientific context and helps to determine whether observed trends, relationships and differences are significant or stochastic. The statistical program SPSS (version 21 for Windows) was utilized for the statistical analyses. Based on the nature of the sampling protocol and the characteristics of the data collected, the technique Analysis of Variance (ANOVA) was conducted to assess whether the tidal and seasonal differences in heavy metal and nutrient content were statistically significant. The significant relationships in group means of the parameter groups were identified and the level of significance was assessed using the corresponding *p*-value.

3.3 Physico-Chemical Parameters in the Water Column

3.3.1 Sampling Regime

The water samples collected for the calculation of the heavy metal and nutrient budget (as outlined in section 3.2.1) were also subjected to physico-chemical analysis.

3.3.2 Sample Analysis

The physico-chemical parameters analysed for were pH, Dissolved Oxygen (DO), Total Dissolved Solids (TDS), Electrical Conductivity (EC), salinity, Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

3.3.2.1 pH

An electronic pH meter was used to measure pH. The meter comprises of a glass and reference electrode, potentiometer and a temperature-compensation device (Christian, 2007). Calibration of the meter was conducted using standard solutions. According to Christian (2007), the glass electrode converts H^+ ion concentration signal activity to an electric current which is read as the electrode potential or pH.

3.3.2.2 Dissolved Oxygen (DO)

The levels of DO in the samples were measured using a DO meter. The meter comprises a cathode, anode, electrolyte solution and gas permeable membrane. DO enters the electrolyte solution *via* the gas membrane; during this process voltage is generated between the anode and cathode, from the difference in voltage the DO meter then calculates the concentration of DO in the sample (Christian, 2007).

3.3.2.3 Total Dissolved Solids (TDS)

TDS content was measured using an electronic TDS meter. The meter was submerged into the sample upon calibration with standard solutions. According to Christian (2007), the movement of ions result in the generation of an electric current, the meter then records the amount of ions that pass between the electrodes.

3.3.2.4 Electrical Conductivity (EC)

EC was measured using a meter which measures the electrical resistance of a solution (Pillay, 2013a). The meter comprises a conductivity cell (two platinum plate electrodes) connected by

cables (Ngila, 2008). The electric current source in the meter applies a potential to the plates and the meter measures electrical resistance of the solution (Ngila, 2008).

3.3.2.5 Biological Oxygen Demand (BOD)

BOD was determined using the dilution method as follows: DO content of the sample was determined before and after incubation for 5 days at 20°C (Bartram and Ballance, 1996). The difference in these values yielded the BOD of the sample.

3.3.2.6 Chemical Oxygen Demand (COD)

COD was determined using the dichromate method. The sample was boiled under reflux with Potassium Dichromate ($K_2Cr_2O_7$) and Silver Sulphate (Ag_2SO_4) catalyst in strong Sulphuric acid (H_2SO_4). During this process particles of the dichromate is reduced by organic matter and the remainder is titrated with Ferrous Ammonium Sulphate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) to yield the COD content (Bartram and Ballance, 1996).

3.3.3 Data Analysis and Interpretation

3.3.3.1 South African Water Quality Guidelines (SAWQG)

The content of each physico-chemical parameter was calculated seasonally, for spring and neap tides. The results were compared to the Target Water Quality Range (TWQR) for ideal conditions for aquatic ecosystems, domestic use and recreation (full contact) use, as prescribed in the South African Water Quality Guidelines (SAWQG). According to DWAF (1996a) and Pillay (2013a), the ideal TWQR for a particular parameter is defined as the range of concentration/levels at which the parameter would have no adverse effects on the fitness of the water, biota and human-users of the estuary.

3.4 Bacterial Content in the Sediment and Water Column

3.4.1 Sampling Regime

The microbiological status of the estuary was determined through the assessment of indicator bacteria in water and sediment samples collected over spring and neap tides during summer (February 2012), autumn (March 2012), winter (June 2012) and spring (September 2012). The samples were collected at three sites in the estuary (Figure 3.1):

- a. E1: the upper estuary, where heavy metals and nutrients that enter the estuary from the catchment were quantified;
- b. E2: the mid-estuary; and
- c. E3: the estuary mouth, where tidal interchange with the marine environment controlled the overall import or export of heavy metals and nutrients in this region.

0.5 L of water and 500 g of sediment was collected at each site and stored in sterile glass bottles. The water samples were collected at mid-depth and the sediment samples were collected from the initial 10 cm of undisturbed bed sediment, as numerous authors have noted a decline in bacterial content with depth (Ferguson *et al.*, 1996; Alm *et al.*, 2003; Garzio, 2009). The samples were placed on ice and prepared for sediment particle size analysis and microbiological analysis within 24 hours of collection. A total of 24 water and 24 sediment samples were collected.

3.4.2 Sample Analysis

3.4.2.1 Sediment Particle Size Analysis

The sediment samples were split in half, one portion was reserved for microbiological analyses and the remaining portion was subjected to sediment particle size analysis using a standard dry sieving technique as outlined by Buller and McManus (1979), Dyer (1986) and Gordon *et al.* (1992) at the Soil Science Laboratory of the University of Kwa-Zulu Natal. The sediment was disaggregated using a pestle and mortar and passed through a set of sieves with aperture sizes 2 mm, 1 mm, 0.5 mm, 0.25 mm and 0.125 mm in an automated sieve shaker. After 10 minutes the sediment within each sieve size was weighted (recorded as mass retained) and classified according to the Udden-Wentworth sediment grade scale. The percentage of the total weight of sieved sediment was recorded and from this the percentage

finer than each specific grain size was calculated as suggested by Dyer (1986) and Gordon *et al.* (1992). According to Buller and McManus (1979) and Gordon *et al.* (1992), this technique is simple and commonly used.

3.4.2.2 Membrane Filtration Technique (MFT)

The remaining portion of the sediment samples and water samples were then analysed at the Microbiological Laboratory of the University of KwaZulu-Natal. Samples were analysed for the indicator bacteria: Total coliforms (TC), Faecal coliforms (FC) and *Escherichia* coliforms (EC) using the MFT. The MFT was introduced in the late 1950s for microbiological analysis of water and sediment samples, and has become one of the most frequently used for determining the presence of bacteria (US-EPA, 2006). It entails drawing water or sediment aquoits through a sterile filter with a 0.45 μm pore size; which retains bacteria (US-EPA, 2006; Environmental Microbial Biotechnology, 2012).

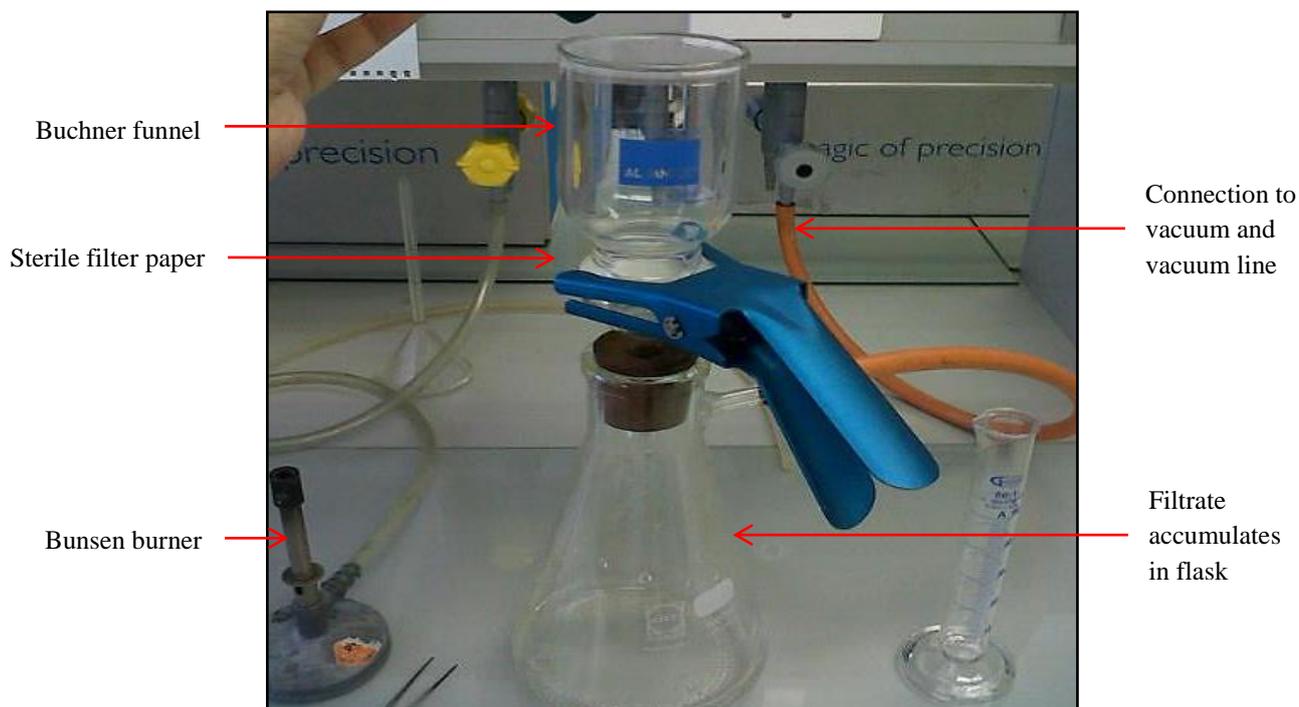


Plate 3.1 Apparatus utilised to undertake the Membrane Filtration Technique (Source: Author)

Since bacteria are too minute to count individually, the MFT relies on an incubation stage followed by a count of the resultant bacterial colonies (US-EPA, 2006). The filter is incubated at specific conditions and on a culture medium determined by the bacteria being investigated. For this study the presence of TC and EC was assessed using the culture medium chromocult, incubated at 35°C for 4 hours. TC and EC produce colonies that appear red and blue, respectively on the filter. To test for FC the enriched lactose medium (m-FC) was used and incubated at 44.5°C for 24 hours, and was indicated by blue colonies on the filter.



Plate 3.2 Filter papers post-incubation showing bacterial colonies (Source: Author)

According to the US-EPA (2006), each colony has grown from a single bacteria cell therefore by counting the colonies one can obtain a count of the bacteria present in the sample. The results are reported in terms of colony forming units (cfu) per 100 mL using the following equation (US-EPA, 2006):

$$\frac{\text{colonies counted} \times 100}{\text{mL sample filtered}} \quad (2)$$

The MFT involves less preparation than traditional methods, permits testing of large sample volumes and yields bacteria presence or absence information very quickly. The predominant concern however, is its inability to represent stressed or injured coliform bacterial content in samples, as damaged cells are unable to form colonies and are therefore not counted (US-EPA, 2006; Environmental Microbial Biotechnology, 2012).

3.4.3 Data Analysis and Interpretation

3.4.3.1 Statistical Analysis

The statistical program SPSS (version 21 for Windows) was used to undertake the statistical analyse. ANOVA was used to assess whether the differences in bacterial content in the estuary, within both sediment and water media were statistically significant. While, the Independent Samples t-Test was used to assess whether differences in bacterial content between the sediment and water columns were statistically significant. The significant relationships in group means of the parameter groups were identified and the level of significance was assessed using the corresponding *p*-value.

3.4.3.2 South African Water Quality Guidelines (SAWQG)

The quantities of TC, FC and EC detected at all three sampling sites were compared to the ideal TWQR for domestic use and recreational use (full contact and intermediate contact).

3.5 Heavy Metal Content in Sediment Profiles

3.5.1 Sampling Regime

The heavy metal content of the eziMbokodweni Estuary was assessed in sediment profiles collected at three sites in the estuary (Figure 3.1):

- a. E1: the upper estuary, where heavy metals and nutrients that enter the estuary from the catchment were quantified;
- b. E2: the mid-estuary; and
- c. E3: the estuary mouth, where tidal interchange with the marine environment controlled the overall import or export of heavy metals and nutrients in this region.

A polyvinyl chloride (PVC) pipe sediment extractor was inserted to a depth of 1.5 m at each site. A stopper was placed at the end of each pipe to create a suction force and the sediment core was extracted from the ground. The cores were transported immediately to the Soil

Science Laboratory of the University of KwaZulu-Natal for sediment particle size analysis and preparation for chemical analysis.

3.5.2 Sample Analysis

Each sediment core was cut horizontally and divided into sub-samples based on layering patterns. One half of each sub-sample was subjected to sediment particle size analyses and the remaining half was reserved for chemical analyses by the Analytical Chemistry Laboratory of the University of KwaZulu-Natal. The techniques and equipment used are described below.

3.5.2.1 Sediment Particle Size Analysis

According to Ram *et al.* (2009), sediment particle size has a significant bearing on the concentration of heavy metals. Fine grained sediment (<0.063 mm) such as silts, clays and organic matter have large surface areas and charged surfaces, allowing the particles a greater capacity to adsorb ions from solution. In comparison, coarse sediments have round surfaces, no charges and are non-cohesive. As a result, coarse sediments are associated with minimal heavy metal content. Sub-samples from each sediment core were subjected to sediment particle size analysis using the standard dry sieving technique as outlined by Buller and McManus (1979), Dyer (1986) and Gordon *et al.* (1992) as detailed in sub-section 3.4.2.1.

3.5.2.2 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

The remaining portion of each sediment sub-sample was sent to the Analytical Chemistry Laboratory of the University of KwaZulu-Natal for heavy metal content analyses using the ICP-AES technique as described in Section 3.2.2.1. The following heavy metals were analysed for: Aluminium (Al), Arsenic (As), Calcium (Ca), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Phosphorus (P), Sulphur (S), Vanadium (V) and Zinc (Zn).

3.5.3 Data Analysis and Interpretation

3.5.3.1 Background Values and Pollution Assessments

The heavy metal content values obtained from the chemical analyses of the sediment were then interpreted with the aid of Background Values and Pollution Assessments. According to Hawkes and Webb (1962), geochemical background has been defined as the normal abundance of an element in barren earth material. As a result, background values are being used to differentiate between natural element concentrations and anomalies (Chenhall *et al.*, 2004; Martinez *et al.*, 2007). Sukdeo (2010), states that background values are important guides for pollution remediation in sediment and are especially valuable for enrichment detection when sediment quality guidelines have not been established or are not available.

There are currently no sediment quality guidelines available for South African sediments (Orr, 2007) and no specific background concentrations for the eziMbokodweni catchment. As a result, for this study Clark Values were utilised. According to Rosler and Lange (1972) and Martinez *et al.* (2007), Clark Values serve as background values for the average elemental composition of the Earth's crust. The values are representative of the mean elemental composition of all rock groups (Sukdeo, 2010) and since the eziMbokodweni catchment is predominantly sedimentary rock Clark Values of these rocks were used in this study. Clark Values are also an essential component in the computation of the following geochemical indices: Contamination Factor (CF), Enrichment Factor (EF) and Contamination Degree (C_d). These indices were applied to the data to establish the geochemical character of the sediments and to determine whether the presence and corresponding concentrations fell within acceptable limits as per guideline standards.

3.5.3.1.1 Determination of Contamination Factor (CF)

According to Harikumar and Jisha (2010), the level of contamination in sediment can be expressed in terms of a contamination factor. For this study, the contamination factor for each metal noted was calculated using the equation (Harikumar and Jisha, 2010; Pillay, 2013a):

$$\text{Contamination Factor} = \frac{[\text{concentration metal}]}{[\text{Clark value of metal}]} \quad (3)$$

Where, [concentration metal] and [Clark value of metal] is reflected in parts per million (ppm; mg/kg). The level of contamination can be classified as follows:

- $CF < 1$ implies low contamination
- $1 \leq CF < 3$ implies moderate contamination
- $3 \leq CF < 6$ implies considerable contamination
- $CF \geq 6$ implies high contamination.

3.5.3.1.2 Determination of Enrichment Factor (EF)

The Enrichment Factor evaluates the degree of contamination by normalising the measured metal content with respect to a sample reference metal (Devesa - Rey *et al.*, 2010) and is used to differentiate heavy metals arising through natural or anthropogenic activities (Chakravarty and Patgiri, 2009). As the Enrichment Factor increases, the contribution of anthropogenic influence also increases. The Enrichment Factor was calculated for each metal detected in the samples using the following equation (Chester and Stoner, 1973 in Martinez *et al.*, 2007; Sukdeo, 2010).

$$\text{Enrichment Factor} = \frac{[\text{concentration metal}]/[\text{concentration Fe}]}{[\text{Clarke value of metal}]/[\text{Clark value of Fe}]} \quad (4)$$

Where, [concentration metal] is the concentration of the metal analysed (ppm), [concentration Fe] is the concentration of Fe in the sediment (ppm), [Clarke value of metal] is the Clark value of the metal (ppm) and [Clark value of Fe] is the Clark value of Fe (ppm).

According to Tippie (1984) in Harikumar and Jisha (2010), Fe is used as the element of normalisation because natural sources vastly dominate its input. Sutherland (2000), proposed a detailed categorisation based on Enrichment Factors. According to this categorisation:

- $EF < 1$ implies no enrichment
- $1 \leq EF < 2$ implies minimal enrichment
- $2 \leq EF < 5$ implies moderate enrichment
- $5 \leq EF < 20$ implies significant enrichment
- $20 \leq EF < 40$ implies very high enrichment
- $EF \geq 40$ implies extremely high enrichment

3.5.3.1.3 Determination of the Contamination Degree (C_d)

The Contamination Degree is defined as the sum of all contamination factors at a particular site (Hakanson, 1980). It provides an indication of the extent of pollution constituted by the range of metals in the assessment region (Hakanson, 1980). The degree of contamination was calculated using the following equation (Pillay, 2013a):

$$C_d = CF_1 + CF_2 + \dots + CF_n \quad (5)$$

Where, [CF] refers to the contamination factor for each heavy metal detected at a particular site. The degree of contamination can be classified as follows:

- $C_d < 6$ implies low contamination degree
- $6 \leq C_d < 12$ implies moderate contamination degree
- $12 \leq C_d < 24$ implies considerable contamination degree
- $C_d \geq 24$ implies very high contamination degree

3.6 Conclusion

The research methods adopted in this study resulted in an integrated and holistic assessment of the eziMbokodweni Estuary's health status. A variety of measurements were taken and samples (water and sediment) collected. The heavy metal and nutrient transport and budget of the estuary was quantified seasonally, for spring and neap tides and selected physico-chemical parameters were analysed in water samples. The microbiology of the estuary was determined through the assessment of indicator bacteria in the sediment and water columns using indicator bacteria. While, a geochemical assessment of the estuary was undertaken from sediment core profiles obtained along the estuary. The sampling regime, analytical procedures and, data analysis and interpretation techniques used were all detailed in this chapter.

CHAPTER FOUR

Results and Discussion

4.1 Introduction

Due to the considerable amount of water and sediment quality parameters analysed and the amount of data generated, the results and discussions are presented under the following subheadings: the content of selected physico-chemical parameters in water samples, the transport of heavy metals and nutrients seasonally, for spring and neap tides and the net budget of the estuary, a geochemical assessment of heavy metals in sediments and the bacterial content in water and sediment samples.

4.2.1 The Content of Selected Physico-Chemical Parameters in Water Samples

This sub-section presents an assessment of the seasonal and tidal changes in selected physico-chemical parameters that were studied in the water column of the eziMbokodweni Estuary. The parameters include: pH, Dissolved Oxygen (DO), Total Dissolved Solids (TDS), Electrical Conductivity (EC), salinity, Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). The average content of each parameter was compared to the target water quality range (TWQR) for ideal conditions as set out in the South African Water Quality Guidelines (SAWQG). The likely reasons for the levels of each physico-chemical parameter detected and their implications for aquatic ecosystems, domestic use, the ecological environment and recreational use are discussed. The concentrations detected for each physico-chemical parameter is presented in Appendix A.

4.2.1.1 pH

The average pH of the eziMbokodweni Estuary was relatively well buffered ranging from 6.74 – 7.01 pH units (Figure 4.1). The estuarine waters were basic (>7 pH units) during summer, autumn and spring. While during winter average pH levels of 6.74 – 6.96 units were detected, hence the waters were mildly acidic. According to Dallas and Day (2004), a decline in pH levels (acidification) can result from natural and anthropogenic processes, such as, changes in the physico-chemical properties of bedrock, effluent discharges from industry and

agricultural run-off. The latter are most likely a controlling factor of pH in the eziMbokodweni as the river flows through a highly anthropogenically-modified catchment.

Throughout the study average pH levels detected at the upper estuary and estuary mouth conformed to the ideal TWQR for aquatic ecosystems, domestic use and recreational use (full contact). However, despite pH levels being within the tolerance range for freshwater fish, fish were rarely sighted in the estuary. Therefore apart from pH, other factors are rendering the eziMbokodweni Estuary unfavourable for fish. According to DWAF (1996a), pH levels vary diurnally and seasonally. The pH levels detected in the eziMbokodweni Estuary exhibited slight variation among the summer, autumn and spring seasons; with greater variability noted when compared to winter (average minima: 6.74 pH units and average maxima: 6.90 pH units).

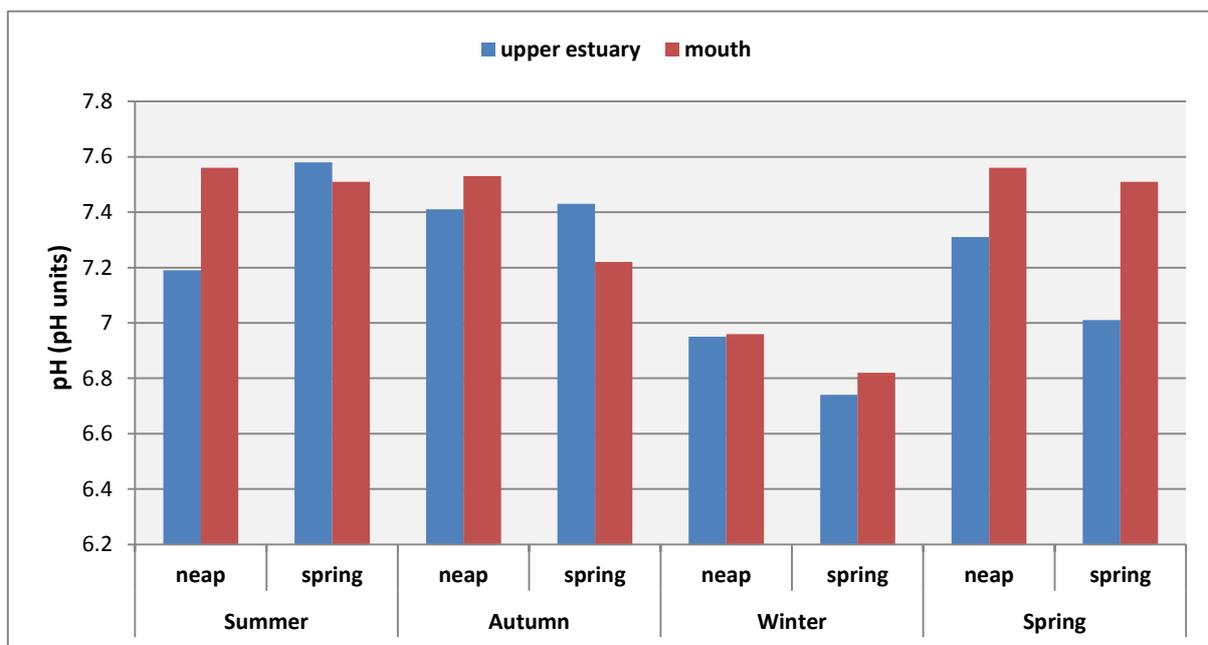


Figure 4.1 Average pH levels (pH units) seasonally, for spring and neap tides

4.2.1.2 Dissolved Oxygen (DO)

Average DO levels in the eziMbokodweni Estuary ranged from 5.96 – 8.41 mg/L during summer, autumn and spring (Figure 4.2). The SAWQGs prescribe an acceptable range of 80-120% DO saturation for aquatic organisms (DWAF, 1996c). According to Dallas and Day (1993), DO concentrations of >4 mg/L are acceptable and the US-EPA (2006) state that at DO

levels >5 mg/L estuarine biota can grow and reproduce unimpaired. Based on these guidelines as references DO levels in the estuary were compliant and within acceptable levels during summer, autumn and spring. However, during winter average DO levels were very close to hypoxic conditions ranging from 3.65 – 3.84 mg/L. At these levels aquatic biota experience reduced appetite and, poor growth and development (DWAF, 1996d). According to Dallas and Day (2004), a reduction in DO levels can be caused by several factors such as the: re-suspension of anoxic sediment, the turnover or release of anoxic bottom water and the presence of oxidisable organic matter.

Flushing can enhance the supply of oxygen in an estuary (DWAF, 1996d). However, despite the estuary mouth being subject to constant tidal action, DO levels varied slightly from the calmer upper estuary. DO levels also varied slightly among spring and neap tides, despite the turbulence of the former.

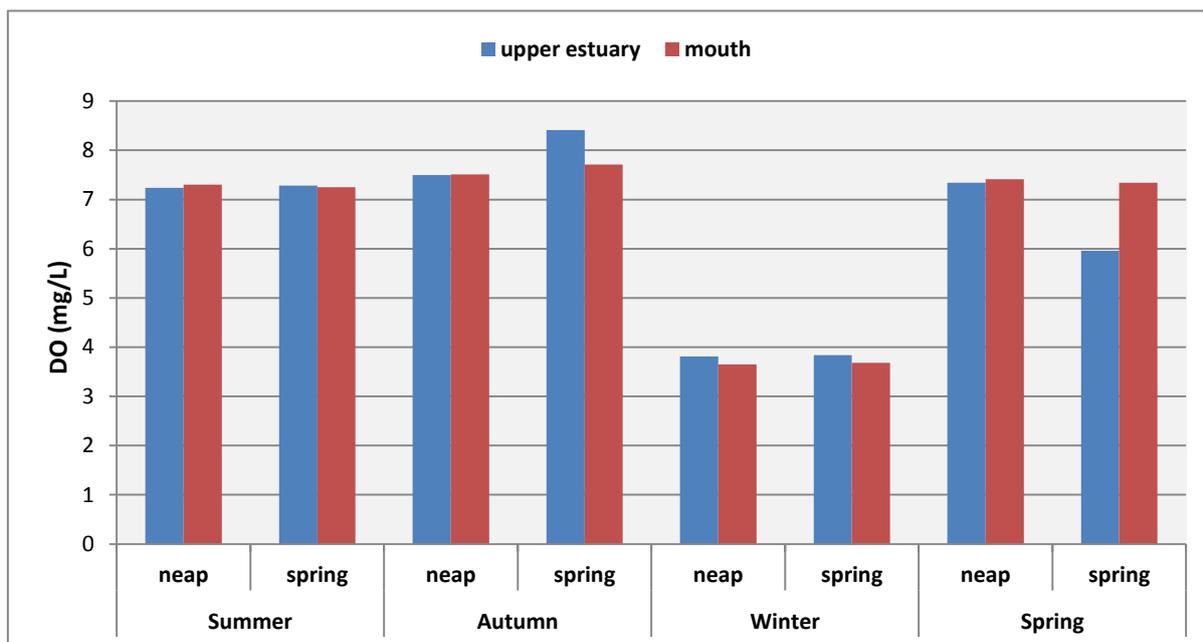


Figure 4.2 Average DO levels (mg/L) seasonally, for spring and neap tides

4.2.1.3 Total Dissolved Solids (TDS)

The average TDS levels indicated that the estuary was compliant with the TWQR for domestic use (0 - 450 mg/L) on selected occasions (Figure 4.3). Non-compliance was noted during the summer-spring tide (upper estuary and mouth), autumn-neap tide (estuary mouth),

winter-neap tide (estuary mouth), winter-spring tide (upper estuary and mouth), spring-neap (upper estuary and mouth) and spring-spring tide (upper estuary and mouth). During these periods average TDS levels ranged from 494.32 - 746.39 mg/L. The average TDS levels were also notable higher at the estuary mouth than upper estuary, suggesting that the nearshore waters were a major contributor of dissolved inorganic and organic compounds to the estuary.

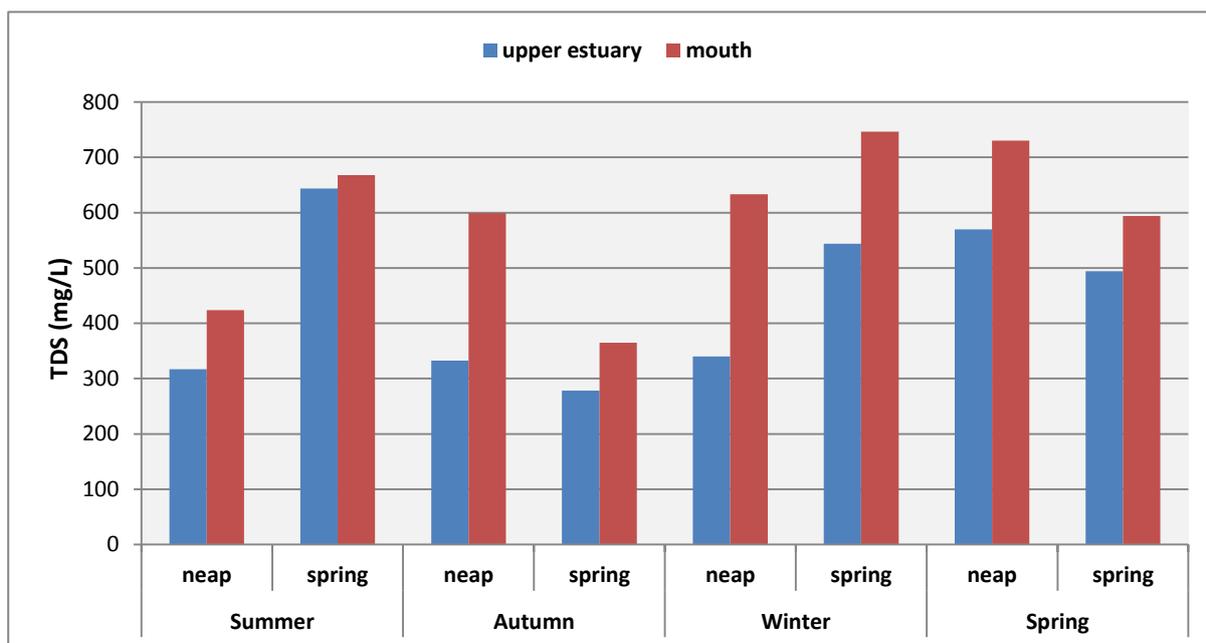


Figure 4.3 Average TDS levels (mg/L) seasonally, for spring and neap tides

4.2.1.4 Electrical Conductivity (EC)

The average EC levels were well below 30mS/cm therefore the estuary was compliant with the ideal TWQR for aquatic ecosystems and domestic use (Table 4.4). EC levels were notably higher at the estuary mouth and may be attributed to the metal ion enriched flood-flows accumulating in this region. The peaks in EC at the estuary mouth also show a degree of correspondence to the TDS concentrations.

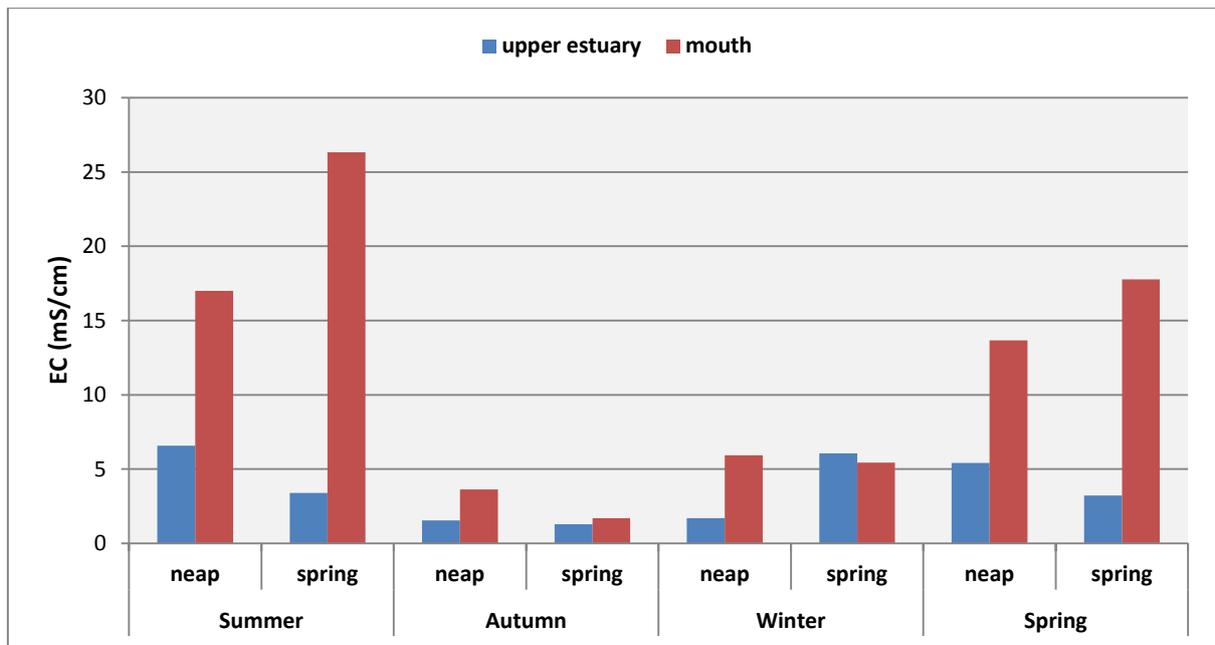


Figure 4.4 Average EC levels (mS/cm) seasonally, for spring and neap tides

4.2.1.5 Salinity

Salinity levels were inversely proportional with distance from the estuary mouth during all seasons and tides sampled (Figure 4.5). According to the US-EPA (2006), salinity gradients gradually change with length, as freshwater enter the estuary from tributaries and mix with seawater moving in from the ocean. Average salinity levels ranged from 0.41 – 3.59 ppt at the upper estuary and 0.69 – 16.14 ppt at the estuary mouth.

The saline nature of the lower estuary provides for the flocculation of material which is alarming as large quantities of heavy metals and nutrients were detected in the estuary. Hence, the lower estuary is very susceptible to sediment contamination. The US-EPA (2006), state that salinity levels are subject to seasonality, with higher levels noted during periods of reduced freshwater input (dry weather). The salinity levels detected in the eziMbokodweni Estuary however, were highly variable and can be attributed to non-seasonal rainfall and anthropogenic activities such as water abstraction and effluent discharge from industries affecting the dilution potential, flushing capabilities and discharge of the estuary.

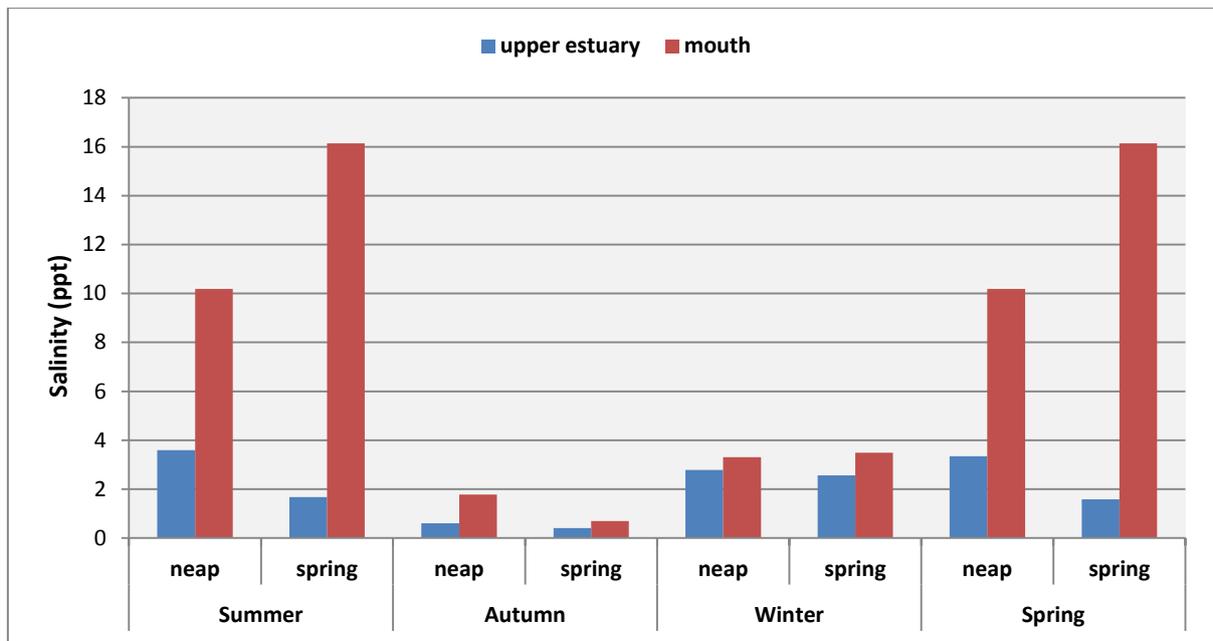


Figure 4.5 Average salinity levels (ppt) seasonally, for spring and neap tides

4.2.1.6 Biological Oxygen Demand (BOD)

The demand for oxygen in the eziMbokodweni Estuary was high during summer, autumn and spring as average BOD levels ranged from 14.55 – 32.07 mg/L. According to the US-EPA (2006), the demand for oxygen is proportional to bacterial and nutrient content in an estuary. The eziMbokodweni Estuary demonstrated high bacterial and nutrient levels in the study. Govender (2009), states that as BOD levels increase less oxygen becomes available in the estuary. Hence, high BOD levels have the same adverse effects as low DO levels on estuarine biota and processes. The BOD levels detected during winter ranged from 1.68 – 2.16 mg/L. According to the US-EPA (2006), the detected levels of BOD are acceptable for natural waters.

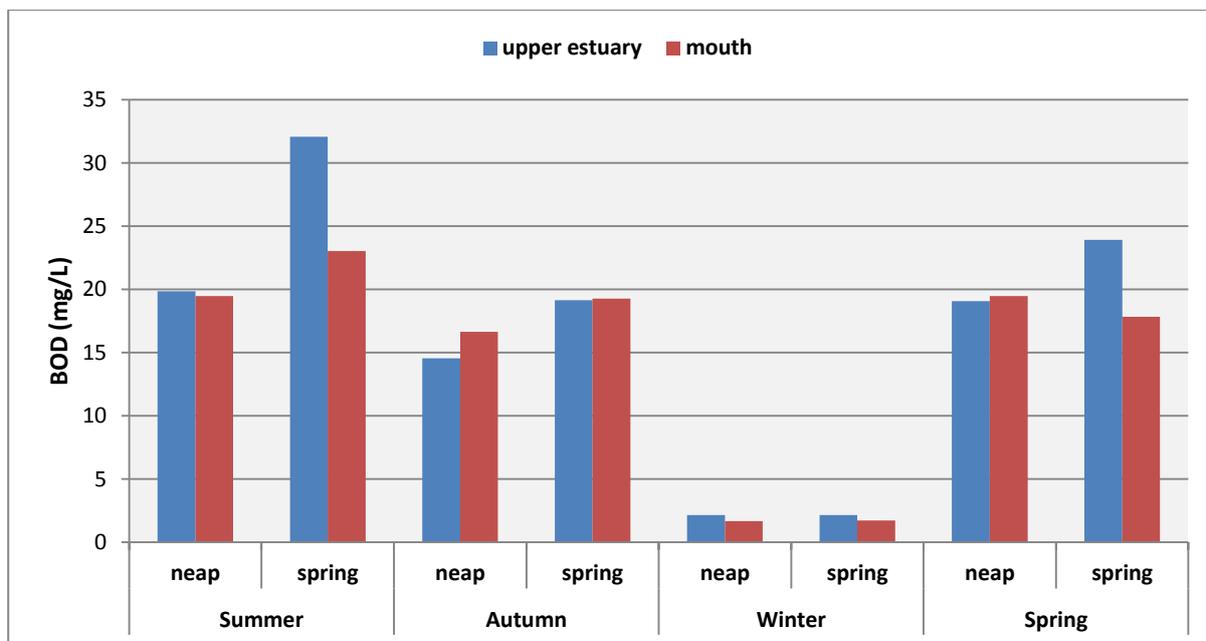


Figure 4.6 Average BOD levels (mg/L) seasonally, for spring and neap tides

4.2.1.7 Chemical Oxygen Demand (COD)

Average COD levels detected in the estuary varied from 470.23 – 959.33 mg/L (Figure 4.7). The TWQR for COD is 75 mg/L (Govender, 2009) hence extremely high levels were recorded in the estuary and the estuary was non-compliant throughout the study. According to DWAF (1996e), COD is a nutrient source for bacteria therefore at these levels COD provides prime growth and survival opportunities for bacteria in the eziMbokodweni Estuary.

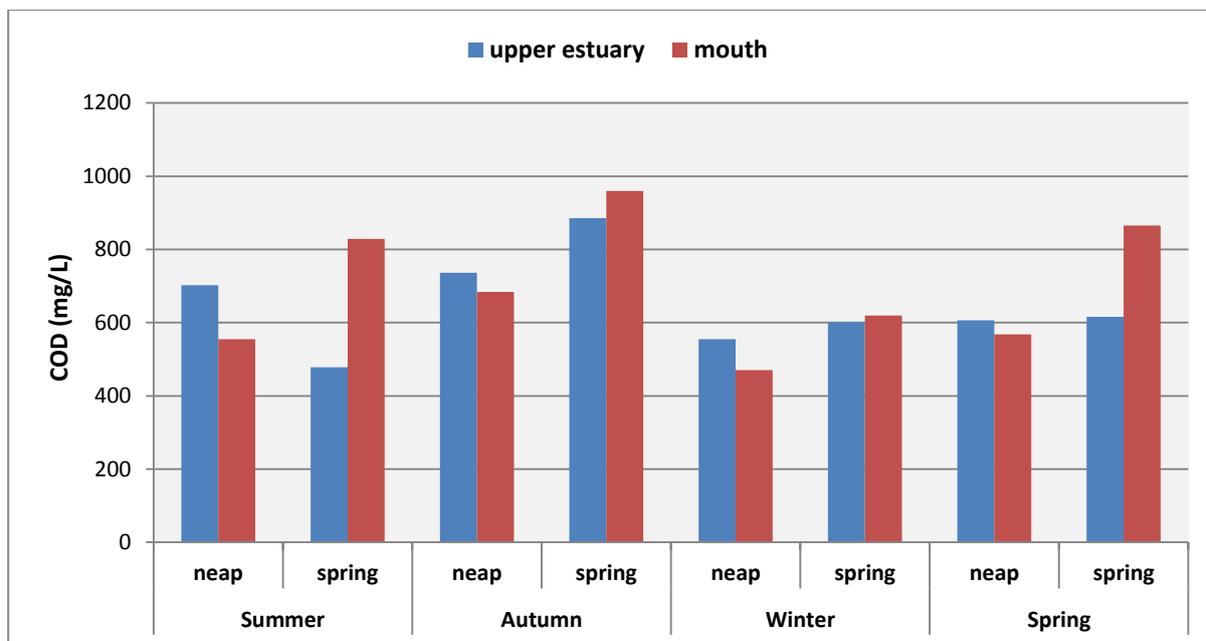


Figure 4.7 Average COD levels (mg/L) seasonally, for spring and neap tides

4.2.2 Conclusion

The eziMbokodweni River flows through a highly anthropogenically-modified catchment, which had a significant bearing on the pH of the estuary. The estuarine waters were basic during summer, autumn and spring and mildly acidic during winter. Throughout the study average pH levels detected at the upper estuary and estuary mouth conformed to the ideal TWQR for aquatic ecosystems, domestic use and recreational use (full contact). The average DO levels detected were also within acceptable levels, with the exception of winter when DO levels were very close to hypoxic conditions (3.65 - 3.84 mg/L). At these levels aquatic biota are susceptible to metabolic, growth and development impediments (DWAf, 1996d). Furthermore, despite constant tidal action at the estuary mouth the DO levels recorded varied only slightly from the calmer upper estuary. The average TDS levels indicated that the estuary was compliant with the TWQR for domestic use during summer-neap tide (upper estuary and mouth), autumn-neap tide (upper estuary), autumn-spring tide (upper estuary and mouth) and winter-neap tide (upper estuary). The average TDS levels were also notably higher at the estuary mouth than upper estuary, suggesting that the nearshore waters are a major contributor of dissolved inorganic and organic compounds to the estuary. The average EC levels were compliant with the ideal TWQR for aquatic ecosystems and domestic use. EC levels were notably higher at the estuary mouth and may be attributed to the metal ion enriched flood-flows accumulating in this region. EC levels also showed a degree of correspondence to the

TDS levels. A salinity gradient was evident in the estuary, as salinity levels decreased with increasing distance from the estuary mouth. The saline nature of the lower estuary provides for the flocculation of material, which is alarming as large quantities of heavy metals and nutrients were detected in the estuary. The lower estuary is therefore susceptible to sediment contamination. The salinity levels detected in the estuary were also highly variable and can be attributed to non-seasonal rainfall and anthropogenic activities, such as, water abstraction and effluent discharge from industries. The demand for oxygen in the estuary was high during summer, autumn and spring, during winter however, BOD levels were within acceptable limits for natural waters. Extremely high levels of COD were recorded in the estuary which provides prime growth and survival opportunities for bacteria within the estuary.

4.3.1 The Transport of Heavy Metals and Nutrients Seasonally, for Spring and Neap Tides and the Net Budget of the Estuary

This subsection presents results from the heavy metal and nutrient transport and budget of the eziMbokodweni Estuary. Heavy metal and nutrient transport was studied seasonally, for spring and neap tides at three sites along the estuary:

- a. the upper estuary, where heavy metals and nutrients that enter the estuary from the catchment were quantified;
- b. the mid-estuary; and
- c. the estuary mouth, where tidal interchange with the marine environment controlled the overall import or export of heavy metals and nutrients in this region.

The results were subsequently used to quantify the heavy metal and nutrient budget of the estuary and were extrapolated to yield the annual net budget. Analysis of Variance (ANOVA) was applied to determine whether tidal and seasonal variations in heavy metal and nutrient content were statistically significant.

4.3.1.1 Heavy Metal and Nutrient Transport and Budget

The interchange of heavy metals and nutrients at the estuary mouth, as well as, the net budget of the estuary seasonally, for spring and neap tides is discussed below.

4.3.1.1.1 Tidal Flow Characteristics

With reference to Table 4.1, tidal interchange at the estuary mouth had a substantial influence on the overall heavy metal and nutrient content of the estuary. Tidal measurements indicated that the estuary mouth was subject to tidal asymmetry, characterised by dominant and longer periods of flooding over spring tides (with the exception of the summer-spring tide). It was also noted that large quantities and a variety of heavy metals and nutrients entered the estuary mouth during flooding, thus the nearshore waters of the eziMbokodweni Estuary are enriched. Dominant flooding further impaired heavy metal and nutrient export at the estuary mouth. The majority of neap tides were characterised by protracted ebbing which facilitated the transport of heavy metals and nutrients from the estuary. However, the quantity of heavy metals and nutrients exported were tempered due to import on the subsequent flood tide,

which was the case for all seasons and tides. Tidal symmetry was evident over the summer-spring tide however, due to the large tidal prism associated with spring tides a larger volume of heavy metals and nutrients were exchanged at the estuary mouth with import values exceeding export values.

Table 4.1 Tide direction and measurements at the estuary mouth seasonally, for spring and neap tides

Season	Tide	Ebb (%)	Flood (%)
summer	neap	67	33
	spring	50	50
autumn	neap	67	33
	spring	17	83
winter	neap	33	67
	spring	33	67
spring	neap	67	33
	spring	17	83

4.3.1.1.2 Summer Transport

During the summer-neap tide the estuary mouth was characterised by tidal asymmetry: 8 hours of ebbing followed by 4 hours of flooding, and resulted in the export of Al, Ca, Mg, Na and NH₄ in this region (Table 4.1 and 4.2 together with Figures 4.8 a-b). Overall, a net accumulation of Ca, Hg, Mg, Na and NH₄, and a net loss of Al was noted in the system. In comparison, the spring tide was characterised by tidal symmetry (Table 4.1 and 4.2 together with Figures 4.9 a-b). The large tidal prism associated with spring tides allowed for the

exchange of a greater volume of heavy metals and nutrients at the estuary mouth with import exceeding export quantities for Ca, Mg, Na, NH₄ and Ni, and vice versa for Al and Hg. With the exception of Hg, heavy metals and nutrients were supplied from the catchment to the upper estuary in much higher quantities than were recorded over the neap tide. Overall, a net accumulation of Al, Ca, K, Mg, Na, NH₄ and Ni and a net loss of Hg was recorded for the system.

4.3.1.1.3 Autumn Transport

During the autumn-neap tide the estuary mouth was ebb dominant and resulted in the export of all detected heavy metals and nutrients, with the exception of Hg (Table 4.1 and 4.3 together with Figures 4.8 a-b). The system however, maintained a net accumulation of Al, Ca, Cu, Hg, NH₄, Ni and P with a net export of Mg and Na. During the spring tide the estuary mouth was characterised by a 2 hour ebb followed by 10 hours of flooding (Table 4.1 and 4.3 together with Figures 4.9 a-b). The protracted flood drew in nearshore waters enriched with heavy metals and nutrients resulting in the net import of all detected heavy metals and nutrients. Overall, the estuary experienced a net accumulation of Al, Ca, Mg, Na, NH₄ and P during the spring tide. The quantity of heavy metals and nutrients accumulated during the spring tide exceeded respective quantities over the neap tide and was due to a greater supply of heavy metals and nutrients from landward drainage and the import orientation of the estuary mouth over the spring tide (17% ebb; 83% flood).

4.3.1.1.4 Winter Transport

The estuary mouth was characterised by flood dominance during the winter-neap tide (Table 4.1) resulting in the net accumulation of K, Na and NH₄ in the estuary (Table 4.4 together with Figures 4.8 a-b). All other heavy metals and nutrients were either absent from the water column or present at low levels (below detection limit). During the spring tide the estuary mouth was also flood dominated resulting in the import and accumulation of Ca, Hg, Mg, Na, NH₄, P, S and V (Table 4.1 and 4.4 together with Figures 4.9 a-b). A greater quantity of Na and NH₄ were accrued during the neap tide in comparison to the spring tide, and was attributed to higher quantities derived from landward drainage than during the spring tide.

4.3.1.1.5 Spring Transport

During the spring-neap tide the estuary mouth was ebb orientated resulting in heavy metal and nutrient export however, a net accumulation of Cr, Cu, Fe, Mn, Ni, Se, Sr, Zn and Zr was noted in the estuary (Table 4.1 and 4.5 together with Figures 4.8 a-b). These heavy metals and nutrients were also detected and accumulated during the spring tide. However, the quantities accrued during the spring tide were greater due to a higher supply from landward drainage (Table 4.5 together with Figures 4.9 a-b). Furthermore, the estuary mouth was import orientated during the spring tide (2 hours of ebbing followed by 10 hours of flooding) which facilitated heavy metal and nutrient accumulation in the estuary.

Table 4.2 The transport of heavy metals and nutrients at the upper estuary and their flux upon tidal interchange at the estuary mouth in kilograms (kg), during the summer - spring and neap tides (showing only the detected heavy metals and nutrients)

SUMMER								
Nutrient/ Heavy metal	Neap tide				Spring tide			
	Location		Net accumulation (+)/loss (-) (kg)	Location		Net accumulation (+)/loss (-) (kg)		
	upper estuary	mouth		upper estuary	mouth			
Al	0.92	2.51	1.26	-0.34	6.87	1.92	0.86	6.01
		1.25				1.06		
Ca	708.37	1015.40	624.18	84.19	3908.17	267.00	-102.57	4010.74
		391.22				369.57		
Hg	0.20	0	0	0.20	0.16	2.30	1.64	-1.48
		0				0.66		
K	0	0	0	0	723.69	0	0	723.69
		0				0		
Mg	1288.98	2081.03	1272.82	16.16	7981.51	346.63	-191.77	8173.28
		808.21				538.40		
Na	11013.99	12370.45	7264.27	3749.72	44704.68	4041.15	-1787.93	46492.61
		5106.18				5829.08		
NH ₄	157.03	412.94	134.60	22.43	708.92	648.73	-84.10	793.02
		278.33				732.83		
Ni	0	0	0	0	9.62	16.74	-2.17	11.79
		0				18.91		

Zero indicates either the absence of the heavy metal/nutrient or concentration levels below the detection limit
Green indicates Ebb flow; Pink indicates Flood flow

Table 4.3 The transport of heavy metals and nutrients at the upper estuary and their flux upon tidal interchange at the estuary mouth in kilograms (kg), during the autumn - spring and neap tides (showing only the detected heavy metals and nutrients)

AUTUMN								
Nutrient/ Heavy metal	Neap tide				Spring tide			
	Location		Net accumulation (+)/loss (-) (kg)	Location		Net accumulation (+)/loss (-) (kg)		
	upper estuary	mouth		upper estuary	mouth			
Al	16.21	5.01	2.70	13.51	14.23	1.68	-8.35	22.58
		2.31				10.03		
Ca	313.62	250.08	157.91	155.71	421.06	46.71	-232.19	653.25
		92.16				278.90		
Cu	13.66	0.92	0.74	12.92	0	0	0	0
		0.19				0		
Hg	1.07	0.60	-0.43	1.50	0	0	0	0
		1.03				0		
Mg	197.76	349.44	240.72	-42.96	337.66	47.29	-234.27	571.93
		108.72				281.56		
Na	1727.76	3516.99	2250.22	-522.46	2333.24	450.34	-2182.16	4515.40
		1266.78				2632.50		
NH ₄	379.02	492.46	309.57	69.45	1035.74	154.47	-796.92	1832.66
		182.89				951.38		
Ni	40.08	3.49	2.60	37.48	0	0	0	0
		0.89				0		
P	13.89	0	0	13.89	47.48	4.21	-6.88	54.36
		0				11.09		

Zero indicates either the absence of the heavy metal/nutrient or concentration levels below the detection limit
Green indicates Ebb flow; Pink indicates Flood flow

Table 4.4 The transport of heavy metals and nutrients at the upper estuary and their flux upon tidal interchange at the estuary mouth in kilograms (kg), during the winter - spring and neap tides (showing only the detected heavy metals and nutrients)

WINTER								
Nutrient/ Heavy metal	Neap tide				Spring tide			
	Location		Net accumulation (+)/loss (-) (kg)	Location		Net accumulation (+)/loss (-) (kg)		
	upper estuary	mouth		upper estuary	mouth			
Ca	0	0	0	398.12	181.52	-63.25	461.37	
		0			244.77			
Hg	0	0	0	0	9.81	-49.90	49.90	
		0			59.71			
K	193.56	0	193.56	0	0	0	0	
		0			0			
Mg	0	0	0	803.41	196.41	-352.74	1156.15	
		0			549.15			
Na	9141.86	2064.13	-4117.88	13259.74	7210.45	-4685.68	11895.78	
		6182.01			8662.47			
NH₄	1022.50	7.90	-14.80	1037.30	199.44	-19.66	219.10	
		22.70			100.36			
P	0	0	0	304.43	37.77	-27.91	332.34	
		0			65.68			
S	0	0	0	610.68	370.63	-365.72	976.40	
		0			736.35			
V	0	0	0	0	1.09	-12.65	12.65	
		0			13.74			

Zero indicates either the absence of the heavy metal/nutrient or concentration levels below the detection limit
 Green indicates Ebb flow; Pink indicates Flood flow

Table 4.5 The transport of heavy metals and nutrients at the upper estuary and their flux upon tidal interchange at the estuary mouth in kilograms (kg), during the spring - spring and neap tides (showing only the detected heavy metals and nutrients)

SPRING								
Nutrient/ Heavy metal	Neap tide				Spring tide			
	Location			Net accumulation (+)/loss (-) (kg)	Location			Net accumulation (+)/loss (-) (kg)
	upper estuary	mouth			upper estuary	mouth		
Cr	0.12	0	0	0.12	0.51	0.06	-0.70	1.21
		0				0.76		
Cu	7.31	0.48	0.13	7.18	8.07	1.13	-3.19	11.26
		0.35				4.32		
Fe	1.85	1.99	1.57	0.28	4.04	0.17	-2.07	6.11
		0.42				2.25		
Mn	3.85	0.27	0.06	3.79	5.32	0.83	-1.93	6.93
		0.21				2.76		
Ni	0.90	0	0	0.90	1.25	0.19	-0.74	1.99
		0				0.93		
Se	10.96	6.05	2.05	8.91	13.23	2.18	-11.53	24.76
		4.00				13.71		
Sr	0.41	0	0	0.41	2.93	0	-0.69	3.62
		0				0.69		
Zn	6.89	2.10	0.89	5.91	16.55	1.43	-6.27	22.82
		1.12				7.70		
Zr	32.76	11.35	1.90	30.86	44.17	6.18	-26.22	70.39
		9.44				32.40		

Zero indicates either the absence of the heavy metal/nutrient or concentration levels below the detection limit
Green indicates Ebb flow; Pink indicates Flood flow

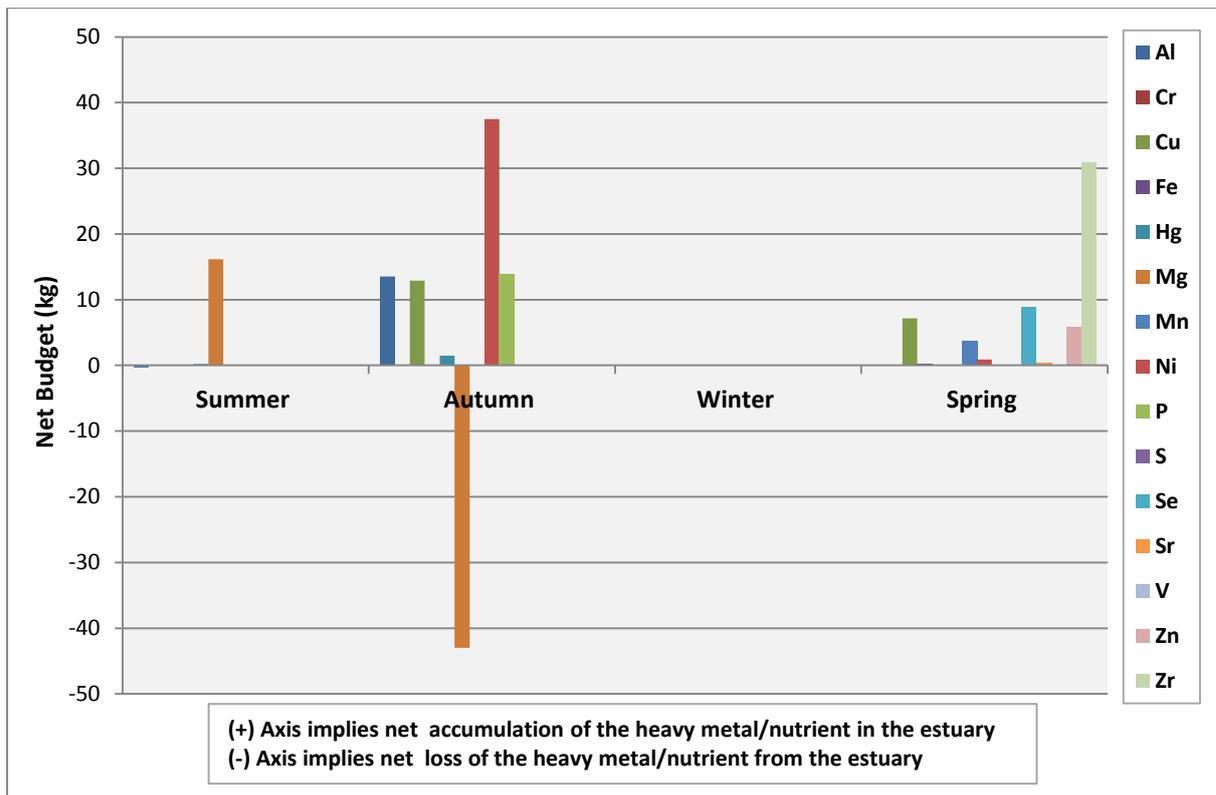


Figure 4.8 (a) Net budget (kg) of heavy metals and nutrients (seasonal – neap tidal cycle)

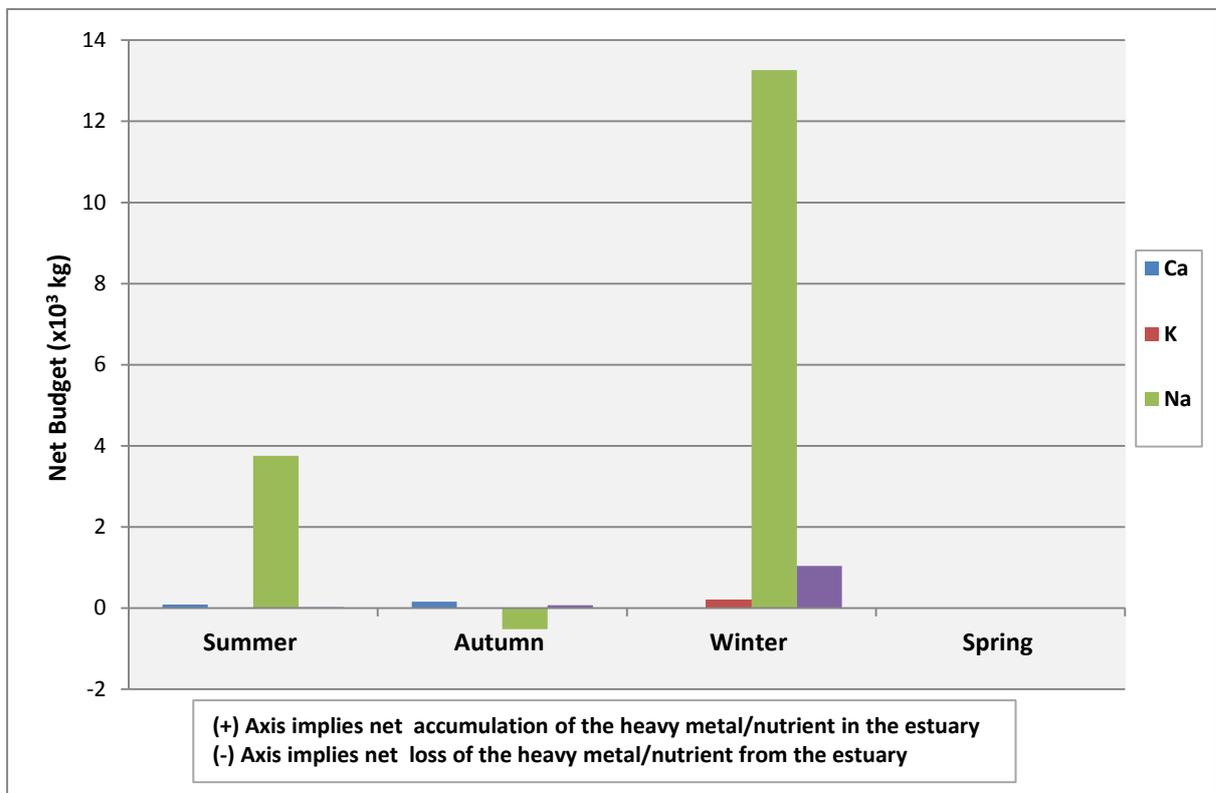


Figure 4.8 (b) Net budget ($\times 10^3$ kg) of heavy metals and nutrients (seasonal – neap tidal cycle)

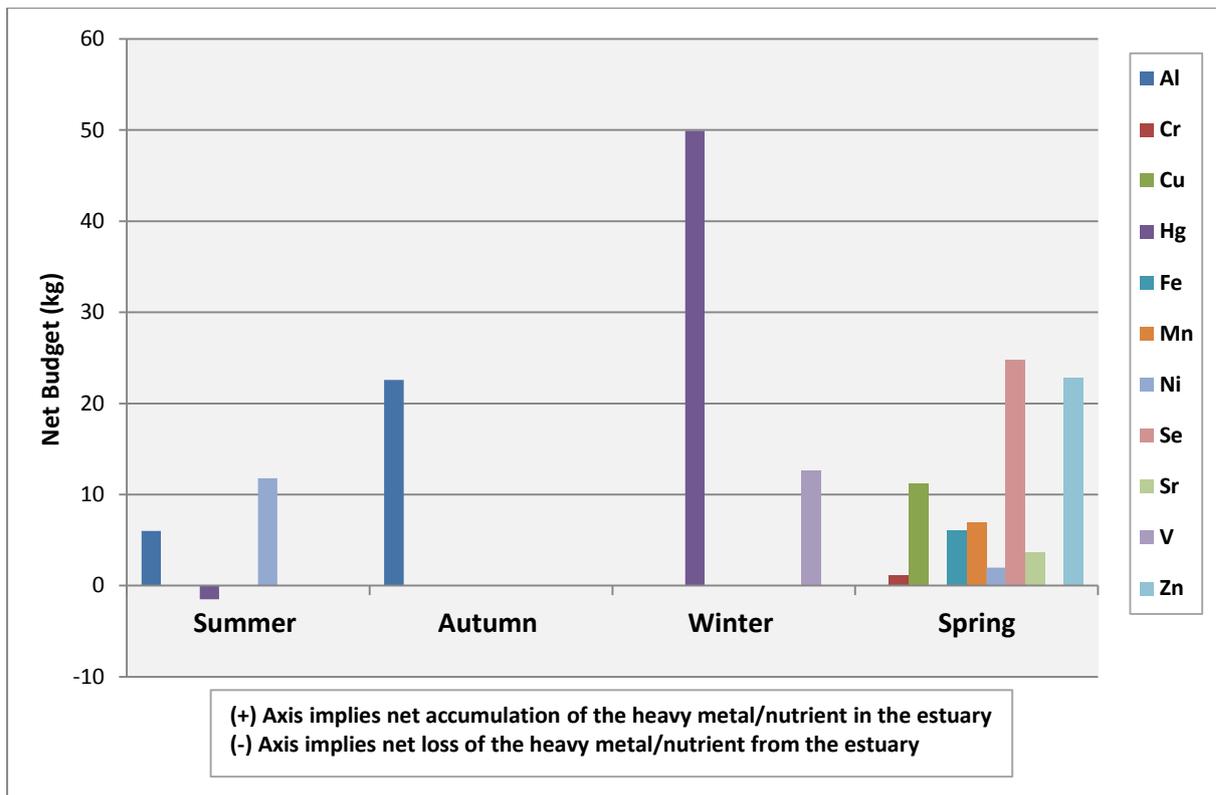


Figure 4.9 (a) Net budget (kg) of heavy metals and nutrients (seasonal – spring tidal cycle)

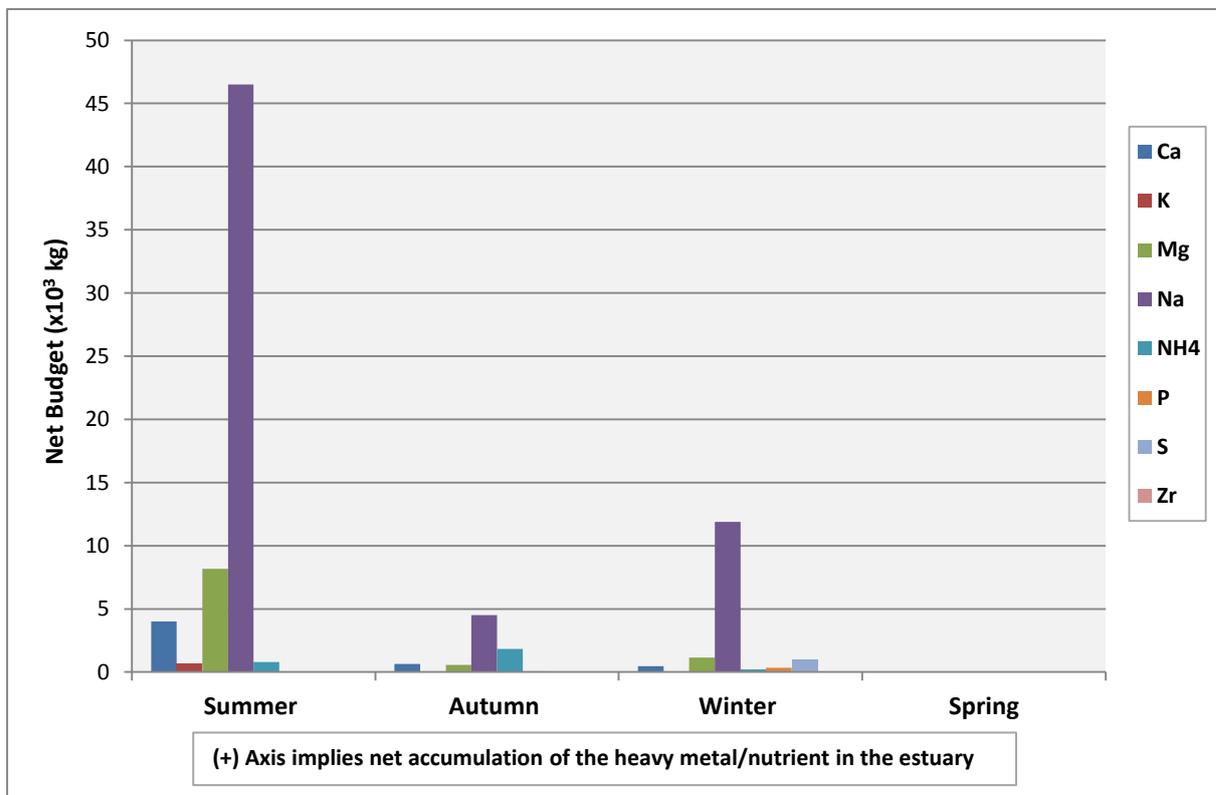


Figure 4.9 (b) Net budget ($\times 10^3$ kg) of heavy metals and nutrients (seasonal – spring tidal cycle)

4.3.1.2 Net Budget of Heavy Metals and Nutrients on an Annual Basis

On an annual basis (Table 4.6 together with Figures 4.10 a-b) there was a net accumulation of all detected heavy metals and nutrients in the estuary, with the exception of Hg during summer, which demonstrates the poor flushing capabilities of the estuary. At these concentrations the heavy metals and nutrients pose a significant threat to estuarine processes, biota and human-users of the estuary. However, it must be noted that whilst the annual budget (Table 4.6) is generated from data collected during this study, it makes the assumption that the tidal cycles measured have the same import and export ability throughout the year which may not be true. There may be cases which allow for the removal of heavy metals and nutrients from the estuary, such as, episodic flood events and is discussed in greater detail under section 4.3.8.

Table 4.6 Annual estimated net heavy metal and nutrient budget in metric tons (T) (data extrapolated from Tables 4.2 – 4.5)

Total Seasonal and Annual Net Budget (T)					
Nutrient/ Heavy metal	Summer	Autumn	Winter	Spring	Total per Annum
Al	0.52	3.29	0	0	3.81
Ca	373.66	73.82	42.10	0	489.58
Cr	0	0	0	0.12	0.12
Cu	0	1.18	0	1.68	2.86
Fe	0	0	0	0.58	0.58
Hg	-0.12	0.14	4.55	0	4.57
K	66.04	0	17.66	0	83.7
Mg	747.29	48.27	105.50	0	901.06
Mn	0	0	0	0.98	0.98
Na	4584.61	364.36	2295.44	0	7244.41
Ni	1.08	3.42	0	0.26	4.76
NH ₄	74.41	173.57	114.65	0	362.63
P	0	6.23	30.33	0	36.56
S	0	0	89.10	0	89.1
Se	0	0	0	3.1	3.1
Sr	0	0	0	0.37	0.37
V	0	0	1.15	0	1.15
Zr	0	0	0	9.24	9.24
Zn	0	0	0	2.62	2.62

Zero indicates either the absence of the heavy metal/nutrient or concentration levels below the detection limit
 (+) Implies net accumulation of the heavy metal/nutrient in the estuary
 (-) Implies net loss of the heavy metal/nutrient from the estuary

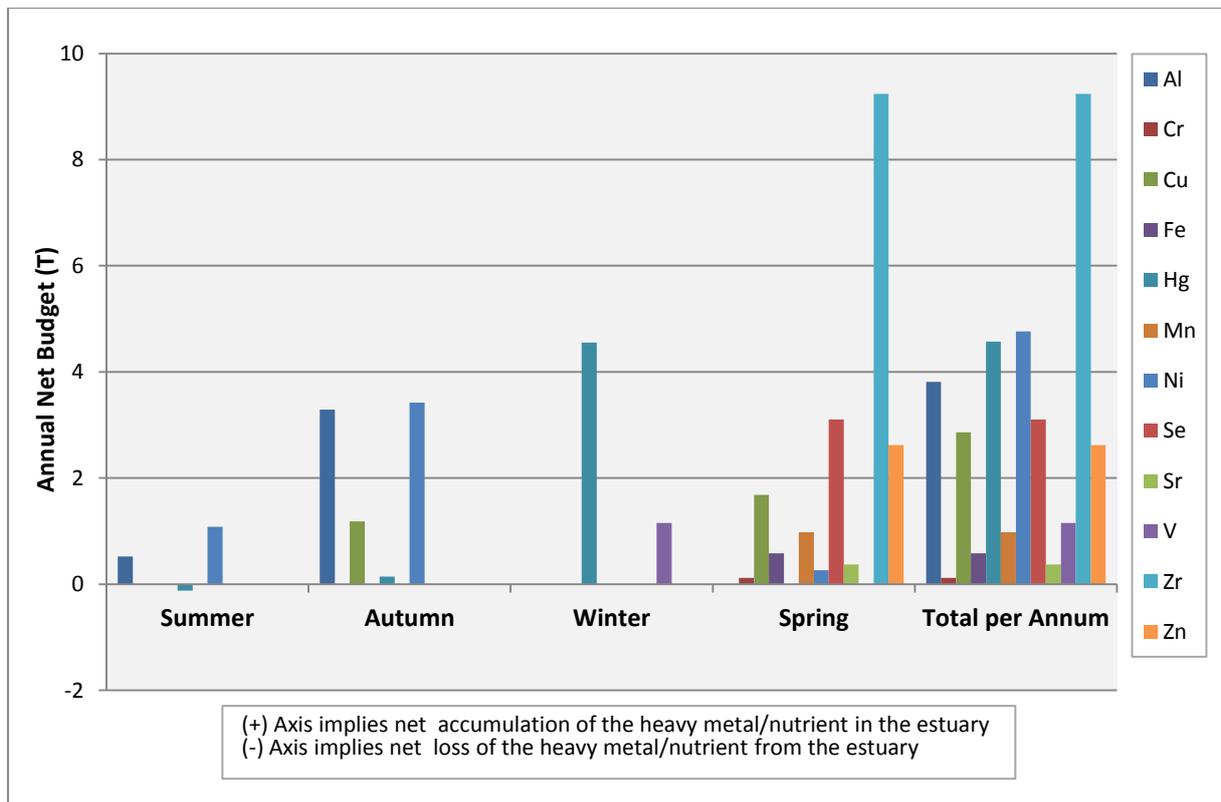


Figure 4.10 (a) Net heavy metal and nutrient budget (T) per season on an annual basis

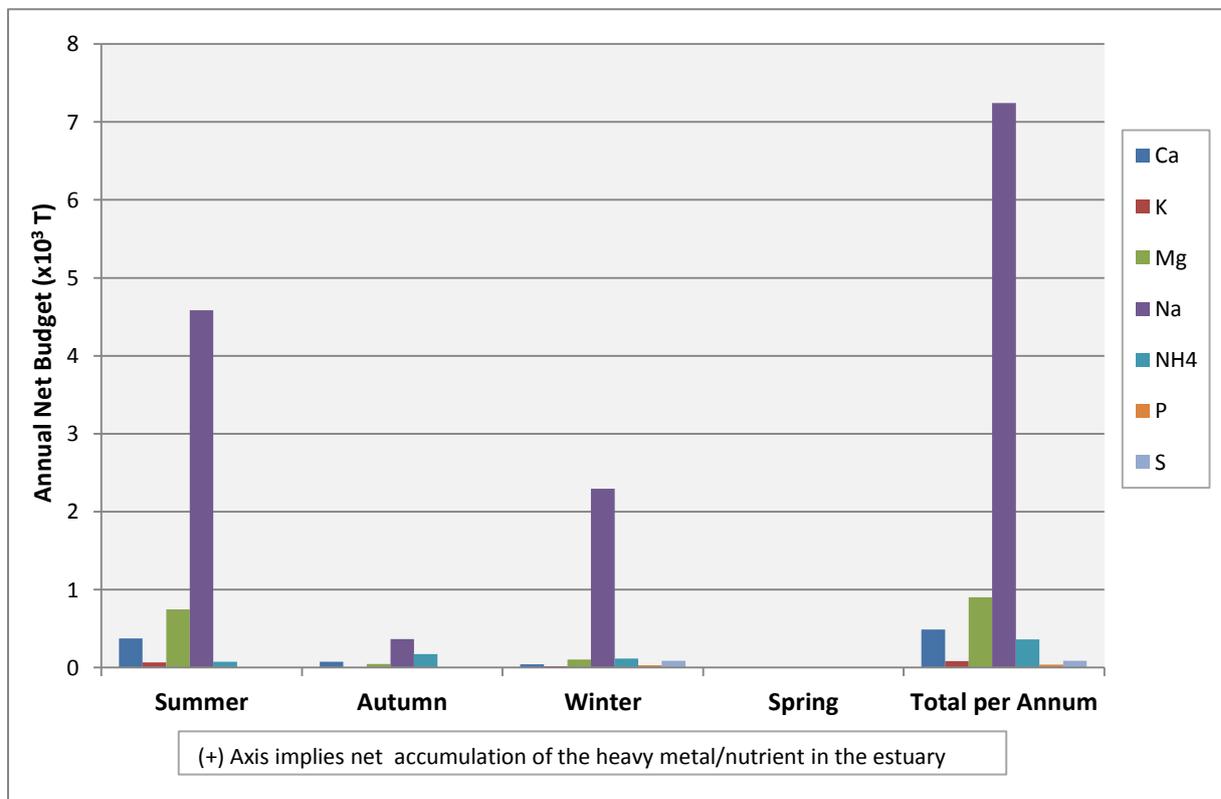


Figure 4.10 (b) Net heavy metal and nutrient budget ($\times 10^3 T$) per season on an annual basis

4.3.1.3 Discussion

Large quantities of heavy metals and nutrients were supplied from the catchment to the upper estuary, with the majority of detected heavy metals and nutrients being accrued in the estuary. Identifying the actual source of these heavy metals and nutrients did not form part of this study but it is noteworthy to mention that the eziMbokodweni catchment is highly anthropogenically modified. The likely sources of heavy metals and nutrients to the estuary include: surface run-off and discharge from the PIA, surface run-off from the suburbs of Amanzimtoti, eziMbokodweni, Isipingo and Umlazi, discharge from the Southern Sewage Works Outfall transported into the estuary *via* longshore drift on flood flows or spring tides, discharge from the eziMbokodweni WWTWs, run-off and leachate from the Amanzimtoti golf course situated on the floodplain of the estuary and enriched flows diverted from the Isipingo Estuary into the eziMbokodweni River. These landuses and activities are inferred as possible contaminant sources to the lower eziMbokodweni River and Estuary. The associated impacts of these land uses and activities may interact synergistically and often may have cumulative impacts on the health status of the estuary.

There were cases however, were detected heavy metal and nutrient quantities at the upper estuary exceeded the quantities noted and exported at the estuary mouth and in some cases vice versa. This may be an expression of a lag effect arising from heavy metals and nutrients which were trapped in sediment and expressed later in the water column following activities such as changes in the physico-chemical characteristics of the system or flushing. This also explains why some heavy metals and nutrients were detected sporadically during the sampling regime. A possibility also exists that selected heavy metals and nutrients were absent in the water column or present at low levels (below detection limits).

Heavy metal and nutrient content was also studied in the sediments of the estuary and revealed low concentrations, however considering the large quantities of heavy metals and nutrients that were detected in the estuary from the budgets, there are methods by which heavy metals and nutrients are being utilized or removed from the estuary. These may include that heavy metals and nutrients are: assimilated by plants (particularly alien invasive species, as noted in the estuary), cycled through the food web through bioaccumulation and biomagnification, or converted into gaseous forms as a result of anaerobic bacteria (the bacterial counts noted in the estuary were high). However, it is proposed that the most significant manner by which these high quantities of heavy metals and nutrients are eliminated from the estuary is through episodic flood events that scour and strip fine grained

sediment from the estuary bed. Fine grained sediment have a greater affinity to adsorb heavy metals and nutrients (Villars and Delvigne, 2001; Chatterjee *et al.*, 2006; Lin *et al.*, 2007; Ram *et al.*, 2009; Sukdeo, 2010) and are easily removed during periods of high discharge. Hence, what remains in the estuary is an aged sediment profile which is not reflective of the recent/current health status of the system. Pather (2013), dated the uppermost sediment layers of the eziMbokodweni Estuary using Carbon-dating techniques. The results indicated that the sediments were more than 700 years old. According to Pather (2013), sediment is flushed out of the estuary during periods of high discharge, such as, episodic flood events hence the accumulation of recent sediment only remains in the eziMbokodweni Estuary for a short period of time. This explains the likely fate of the high quantities of heavy metals and nutrients detected in the nutrient budget, and why it is not reflective in the sediment profiles obtained from the estuary. Furthermore, as a result of such high discharge events the likelihood that the excessive quantities of heavy metals and nutrients reflected as being accrued by the system annually (Table 4.6) is unlikely due to the flushing of the system (of water and sediment) sporadically throughout the year.

4.3.1.4 ANOVA of Heavy Metal and Nutrient Content, Seasonally and Tidally

An assessment of the tables and graphs contained in this sub-section indicate that heavy metal and nutrient content differed seasonally, as well as, tidally in the eziMbokodweni Estuary. ANOVA was conducted to determine whether these differences were statistically significant, the results are presented in Table 4.7 below.

Table 4.7 Results of the ANOVA of heavy metal and nutrient content, seasonally and tidally

	SS	df	MS	F	p-value	Conclusion
Tide	3.17E+08	7	4.53E+07	1.351	0.241	• The differences in heavy metal and nutrient content detected tidally were not statistically significant
Season	1.08E+06	3	3.61E+05	1.041	0.380	• The differences in heavy metal and nutrient content detected seasonally were not statistically significant
SS = Sum of Squares df = Degrees of Freedom MS = Mean of Squares Where $p > 0.05$ results are deemed not significant						

The differences in heavy metal and nutrient content, seasonally and tidally, were not statistically significant (both $p > 0.05$) and can be attributed to the non-seasonal and tidal character of discharge from the estuary. The estuary is located within a summer rainfall region, however both high and low rainfall events were noted sporadically throughout the study. The discharge of the estuary has also been modified by anthropogenic activities, such as, water abstraction and the diversion of flow from the Isipingo River into the estuary (Forbes and Demetriades, 2008; Pillay, 2013a). Furthermore, the heavy metal and nutrient quantities detected were subject to a lag effect, where heavy metals and nutrients trapped in sediment were introduced into the water column following changes in factors such as physico-chemical conditions or flushing.

4.3.2 Conclusion

This study demonstrated that the eziMbokodweni catchment was a major contributor of heavy metals and nutrients to the system. The quantity of the majority of heavy metals and nutrients transported by the river at the upper estuary exceeded those exported at the estuary mouth, resulting in the estuary accruing large quantities seasonally, for spring and neap tides. The quantities detected may also be an expression of a lag effect arising from the introduction of heavy metals and nutrients to the system which were trapped in sediment and expressed later in the water column. The estuary mouth was subject to dominant tidal asymmetry, characterised by dominant and longer periods of flooding over spring tides. It was also noted that large quantities and a variety of heavy metals and nutrients entered the estuary mouth during flooding, thus the nearshore waters of the estuary are enriched. In comparison, neap tides were characterised by protracted ebbing. The export of heavy metals and nutrients were however, tempered due to import on the subsequent flood tides which was the case for all seasons and tides. The heavy metal and nutrient content detected in the sediments were low as compared to the large quantities that were detected from the budget. Hence, there are methods by which heavy metals and nutrients are utilized or removed from the estuary. It is proposed that the most significant manner by which these heavy metals and nutrients are eliminated from the estuary is through episodic flood events that scour and strip fine grained sediment from the estuary bed. Thus, what remains in the estuary is an aged sediment profile which is not reflective of the recent/current health status of the system. ANOVA indicated that the differences in heavy metal and nutrient content seasonally and tidally were not statistically

significant (both $p > 0.05$) and can be attributed to the non-seasonal and tidal character of discharge from the estuary.

4.4.1 A Geochemical Assessment of Heavy Metals in Sediments

This subsection presents an assessment of the heavy metal content and distribution in sediment profiles obtained from the eziMbokodweni estuary, as well as, the results from geochemical indices (Contamination Factor, Enrichment Factor and Contamination Degree) that were applied to establish the geochemical characteristics of the sediments. The indices were also used to determine whether the presence and corresponding concentrations of these heavy metals fell within acceptable limits as per guideline standards and if they were attributable to natural or anthropogenic causes.

4.4.1.1 Heavy Metal Content of Estuarine Sediments

The sediment profile obtained from the upper estuary comprised 7 sediment layers (Table 4.8). With the exception of As, Cr and Zn, the detected heavy metals were present throughout the sediment profile. Heavy metal content was notably higher within layers 2, 4, 5 and 7. Based on textural analysis the sediment particle sizes within these layers were graded as follows: medium (layer 2), fine (layer 4), fine to medium (layer 5) and fine (layer 7). Numerous researchers have indicated that sediment particle size is a key determinant of heavy metal content as features such as the electrical charges and large surface area of fine grained sediment afford it greater capacity to adsorb ions from solution (Villars and Delvigne, 2001; Chatterjee *et al.*, 2006; Lin *et al.*, 2007; Ram *et al.*, 2009; Sukdeo, 2010). The fine to medium grained sediment within layers 2, 4, 5 and 7 ensured significant adsorption of heavy metals and were characterised by greater heavy metal content than the remaining medium to coarse grained layers. The heavy metal As was only detected within layer 2 and 7, with higher levels in the latter fine-grained layer. Cr and Zn were not detected in layer 1.

According to Binning and Baird (2001) and Landajo *et al.* (2004), sediment assimilates pollutants over time and is therefore used to determine the pollution history of a system. The most recent sediment layer (layer 1) of the upper estuary was characterised by fine grained sediment, however the lowest levels of Al, Cu, Fe, Mg, Mn, P, Pb and V were recorded in this layer; implying that the assimilation of these heavy metals has declined over time at the upper

estuary. The content of Ca and S were however, relatively higher in layer 1 as compared to the other layers. Thus, implying that the assimilation of these heavy metals have increased over time at the upper estuary. The heavy metals As, Cr and Zn were not detected in layer 1.

The sediment profile obtained from the mid-estuary comprised 7 sediment layers (Table 4.9). The upper estuary also comprised 7 layers however, the depth and composition of each layer differed between the two sites. With the exception of Cr all other detected heavy metals were present throughout the sediment profile. Cr was only detected from layer 3 to 7. The content of the majority of heavy metals increased progressively from layer 2 to 7 with the highest levels of Al, P, S and V detected within layer 6 and Ca, Cr, Fe, Mg, Pb and Zn within layer 7. Cu was an exception as the highest levels detected were within layer 3.

Fine grained sediment with high water content dominated the sediment profile from the mid-estuary. The estuary encounters gentle gradient in its mid-reaches resulting in a decrease in flow velocity and flushing, these conditions were conducive for the settlement of fine grained suspended particles. The estuary also meanders with a defined curvature along the mid-reaches which contributes further to decreased flow velocity and thus the dominance of fine grained sediment within this sediment profile. According to Pillay (2013b), the interaction of freshwater fluvial flows and marine waters in the relative calm of this region allowed for the saline waters to introduce ionic charges onto the abundant fine grained sediments thus affording it a greater capacity to adsorb heavy metals from solution. Consequently, heavy metal content was notably higher within this region.

The sediment profile collected from the estuary mouth comprised 3 sediment layers (Table 4.10). Zn was only detectable in layer 2 the remaining heavy metals were detected throughout the sediment profile. The highest levels of Ca were detected in layer 1, while the highest levels of Cu, P, Pb, V and Zn were detected within layer 2. Layer 3 demonstrated the highest levels for Al, Fe, Mg, Mn and S. The sediment profile was dominated by medium grained sediment and is attributable to the constant tidal action at the estuary mouth scouring and stripping fine grained sediment from the uppermost layers of the sediment profile. Sukdeo (2010), states that medium to large grained sediment have a reduced affinity as heavy metal 'accumulators' due to their surface characteristics and lack of electric charges. Tidal action at the estuary mouth also contributed to remobilising benthic heavy metals. In addition, the sediment obtained from the estuary mouth displayed high water content; water percolation is therefore a likely controlling factor of heavy metal distribution in the sediments at the estuary

mouth. Heavy metals are also likely being adsorbed and removed from the sediments in this region.

Table 4.8 Heavy metal concentration (ppm) within each layer of the sediment profile obtained at upper estuary

Layer	Sediment Profile (not to scale)	Al	As	Ca	Cu	Cr	Fe	Mg	Mn	P	Pb	S	V	Zn
		81300	5	36300	70	200	50000	20900	1000	1180	16	*260	150	132
1		0.4366	0.0000	0.2945	0.0025	0.0000	0.8852	0.2222	0.0130	0.0388	0.0021	0.0920	0.0028	0.0000
2		1.3045	0.0002	0.5188	0.0097	0.0040	2.5315	0.4874	0.0265	0.1924	0.0114	1.3446	0.0101	0.0479
3		0.6747	0.0000	0.3989	0.0046	0.0003	1.7599	0.3318	0.0170	0.1175	0.0043	0.0433	0.0078	0.0056
4		1.3037	0.0000	0.6610	0.0050	0.0046	2.3739	0.4466	0.0387	0.2956	0.0099	0.3047	0.0106	0.0243
5		1.4029	0.0000	0.6202	0.0037	0.0046	2.4973	0.5050	0.0593	0.3080	0.0096	0.1504	0.0107	0.0238
6		0.6782	0.0000	0.1982	0.0043	0.0005	1.6480	0.2224	0.0150	0.1125	0.0038	0.0111	0.0083	0.0020
7		1.7393	0.0019	0.3546	0.0044	0.0179	3.2220	0.3456	0.0876	0.2153	0.0092	0.0643	0.0239	0.0028

Clark values after: *Rosler and Lange (1972) and Martinez *et al.* (2007)
Zero indicates either the absence of the heavy metal or concentration levels below the detection limit

Table 4.9 Heavy metal concentration (ppm) within each layer of the sediment profile obtained at the mid-estuary

Layer	Sediment Profile (not to scale)	Al	As	Ca	Cu	Cr	Fe	Mg	Mn	P	Pb	S	V	Zn
		81300	5	36300	70	200	50000	20900	1000	1180	16	*260	150	132
1		0.8482	0.0000	0.2109	0.0044	0.0000	1.4114	0.2771	0.0075	0.0731	0.0087	0.1114	0.0071	0.0048
2		1.0962	0.0000	0.2285	0.0055	0.0000	1.3446	0.2786	0.0086	0.0950	0.0049	0.3568	0.0065	0.0071
3		1.6176	0.0000	0.2899	0.0179	0.0014	1.8776	0.4056	0.0162	0.1058	0.0114	0.3202	0.0096	0.0119
4		1.5422	0.0000	0.3363	0.0069	0.0018	2.2780	0.4879	0.0205	0.1401	0.0087	0.6907	0.0108	0.0213
5		1.7079	0.0000	0.3108	0.0047	0.0036	2.2982	0.524	0.0204	0.1069	0.0050	0.3595	0.0104	0.0153
6		2.5696	0.0000	0.8204	0.0093	0.0094	3.2371	0.8021	0.0512	0.4313	0.0170	1.6936	0.0129	0.0733
7		2.2693	0.0000	5.3363	0.0094	0.0617	3.6382	1.2341	0.2767	0.3577	0.0154	0.5473	0.0130	0.0914

Clark values after: *Rosler and Lange (1972) and Martinez *et al.* (2007)
Zero indicates either the absence of the heavy metal or concentration levels below the detection limit

Table 4.10 Heavy metal concentration (ppm) within each layer of the sediment profile obtained at the estuary mouth

Layer	Sediment Profile (not to scale)	Al	As	Ca	Cu	Cr	Fe	Mg	Mn	P	Pb	S	V	Zn
		81300	5	36300	70	200	50000	20900	1000	1180	16	*260	150	132
1		0.5856	0.0000	2.2077	0.0025	0.0000	1.0786	0.2157	0.0086	0.0568	0.0019	0.0699	0.0027	0.0000
2		0.7542	0.0000	0.2991	0.0034	0.0000	1.4850	0.2502	0.0135	0.1118	0.0074	0.0728	0.0050	0.0031
3		0.9969	0.0000	0.3638	0.0032	0.0000	1.7273	0.2865	0.0164	0.0639	0.0041	0.4858	0.0046	0.0000

Clark values after: *Rosler and Lange (1972) and Martinez *et al.* (2007)
Zero indicates either the absence of the heavy metal or concentration levels below the detection limit

4.4.1.2 Contamination Factors (CF)

The CF calculated for the heavy metals detected within each layer of the sediment profiles collected along the estuary is presented in Table 4.11. The data shows that the CF is well below 1 for all layers and sampling sites implying low contamination. The highest CFs, albeit below 1, were noted for Pb and S throughout the sediment profile at each sampling site. Regular monitoring of Pb and S content is therefore essential as these heavy metals are the most likely to reach levels of contamination within the estuary.

4.4.1.3 Enrichment Factors (EF)

The EF calculated for the heavy metals detected within each layer of the sediment profiles collected along the estuary is presented in Table 4.12. The upper estuary was minimally enriched with Al, Ca, Cr, Fe, Mg and Mn while, isolated cases of moderate to significant enrichment was noted for As, Cu and V. Pb maintained significant enrichment throughout the upper estuary. P and Zn showed greater enrichment variability ranging from minimal to significant enrichment. S also exhibited a range of enrichment from minimal to extremely high enrichment (EF of 102.14). At the mid-estuary Al, As, Fe, Mg, Mn and V alluded to minimal enrichment, while Ca and Cr exhibited moderate levels of enrichment on isolated cases in layer 7. Cu, P and Zn were minimally to significantly enriched and Pb maintained significantly enriched throughout the profile. S was significantly enriched in layer 1 and overall very to extremely highly enriched at the mid-estuary. Minimal enrichment was detected for Al, As, Cu, Fe, Mg, Mn, V and Zn at the estuary mouth. While, Ca and P showed signs of minimal to moderate enrichment and enrichment of Pb and S ranged from significantly to extremely highly enriched at the estuary mouth.

Overall, the minimal to moderate enrichment of Al, As, Ca, Cr, Fe, Mg, Mn and V alludes to enrichment by natural causes. For all other heavy metals particularly, Pb and S, enrichment was significant to extremely high which suggest anthropogenic causes responsible for the high levels of these heavy metals in the estuary. According to Pillay (2013b), industries located in the PIA utilise large quantities of S in their processing operations, with S being stored in open air within the industrial site. Industries are therefore a likely source of the considerable S enrichment noted in the estuarine sediments (Pillay, 2013b).

Table 4.11 Contamination factors ($\times 10^{-4}$) of heavy metals within each layer of the sediment profiles obtained along the estuary

Heavy Metal	Clark Value	Upper estuary							Mid-estuary							Estuary mouth		
		Layer							Layer							Layer		
		1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3
Al	81300	0.1	0.2	0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.1	0.1	0.1
As	5	0.0	0.3	0.0	0.0	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca	36300	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	1.5	0.6	0.1	0.1
Cu	70	0.4	1.4	0.7	0.7	0.5	0.6	0.6	0.6	0.8	2.6	1.0	0.7	1.3	1.3	0.4	0.5	0.5
Cr	200	0.0	0.2	0.0	0.2	0.2	0.0	0.9	0.0	0.0	0.1	0.1	0.2	0.5	3.1	0.0	0.0	0.0
Fe	50000	0.2	0.5	0.4	0.5	0.5	0.3	0.6	0.3	0.3	0.4	0.5	0.5	0.6	0.7	0.2	0.3	0.3
Mg	20900	0.1	0.2	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.3	0.4	0.6	0.1	0.1	0.1
Mn	1000	0.1	0.3	0.2	0.4	0.6	0.2	0.9	0.1	0.1	0.2	0.2	0.2	0.5	2.8	0.1	0.1	0.2
P	1180	0.3	1.6	1.0	2.5	2.6	1.0	1.8	0.6	0.8	0.9	1.2	0.9	3.7	3.0	0.5	0.9	0.5
Pb	16	1.3	0.71	2.7	6.2	6.0	2.4	5.7	5.4	3.1	7.1	5.4	3.1	10.6	9.6	1.2	4.6	2.6
S	*260	3.5	51.7	1.7	11.7	5.8	0.4	2.5	4.3	13.7	12.3	26.6	13.8	65.1	21.0	2.7	2.8	18.7
V	150	0.2	0.7	0.5	0.7	0.7	0.6	1.6	0.5	0.4	0.6	0.7	0.7	0.9	0.9	0.2	0.3	0.3
Zn	132	0.0	3.6	0.4	1.8	1.8	0.2	0.2	0.4	0.5	0.9	1.6	1.2	5.6	6.9	0.0	0.2	0.0

Clark values after: *Rosler and Lange (1972) and Martinez *et al.* (2007)
Zeros indicates either the absence of the heavy metal or concentration levels below the detection limit
CF<1 implies low contamination

Table 4.12 Enrichment factors of heavy metals within each layer of the sediment profiles obtained along the estuary

Heavy Metal	Clark value	Upper estuary							Mid-estuary							Estuary mouth		
		Layer							Layer							Layer		
		1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3
Al	81300	0.30	0.32	0.24	0.34	0.35	0.25	0.33	0.37	0.50	0.53	0.42	0.46	0.49	0.38	0.33	0.31	0.35
As	5	0.00	0.68	0.00	0.00	0.00	0.00	6.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	36300	0.46	0.28	0.31	0.38	0.34	0.17	0.15	0.21	0.23	0.21	0.20	0.19	0.35	2.02	2.82	0.28	0.29
Cu	70	1.99	2.73	1.85	1.50	1.07	1.87	0.99	2.23	2.90	6.80	2.16	1.46	2.06	1.85	1.64	1.64	1.33
Cr	200	0.00	0.40	0.04	0.49	0.46	0.07	1.39	0.00	0.00	0.18	0.20	0.39	0.72	4.24	0.00	0.00	0.00
Fe	50000	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Mg	20900	0.60	0.46	0.45	0.45	0.48	0.32	0.26	0.47	0.50	0.52	0.51	0.55	0.59	0.81	0.48	0.40	0.40
Mn	1000	0.74	0.52	0.48	0.82	1.19	0.46	1.36	0.26	0.32	0.43	0.45	0.44	0.79	3.80	0.40	0.46	0.48
P	1180	1.86	3.22	2.83	5.28	5.23	2.89	2.83	2.19	2.99	2.39	2.61	1.97	5.65	4.17	2.23	3.19	1.57
Pb	16	7.37	14.10	7.65	13.09	12.00	7.28	8.89	19.21	11.48	18.93	11.90	6.77	16.41	13.25	5.48	15.58	7.38
S	*260	19.98	102.14	4.74	24.69	11.58	1.29	3.84	15.18	51.03	32.80	58.31	30.08	100.61	28.93	12.45	9.42	54.08
V	150	1.07	1.32	1.47	1.49	1.43	1.68	2.47	1.67	1.62	1.71	1.58	1.51	1.33	1.19	0.84	1.13	0.89
Zn	132	0.00	7.17	1.21	3.88	3.61	0.46	0.33	1.29	2.00	2.41	3.55	2.52	8.58	9.51	0.00	0.79	0.00

■ minimal ■ moderate ■ significant ■ very high ■ extremely high

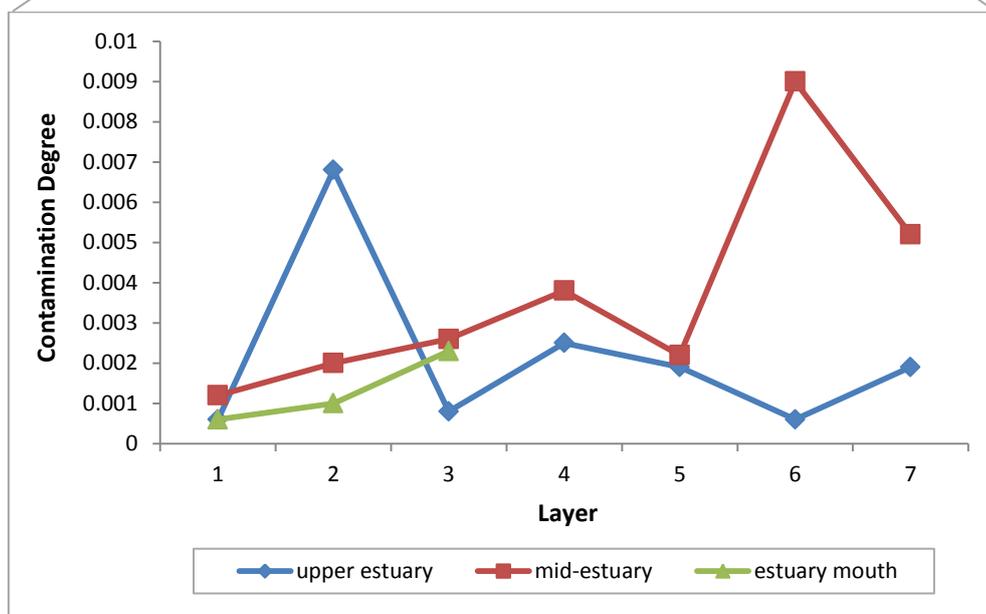
Clark values after: *Rosler and Lange (1972) and Martinez *et al.* (2007)
 Zeros indicates either the absence of the heavy metal or concentration levels below the detection limit

4.4.1.4 Contamination Degree (C_d)

The C_d for heavy metals detected within each layer of the sediment profiles collected at the upper estuary, mid-estuary and estuary mouth are presented in Table 4.13. The C_d ranged from 0.0006-0.0068 at the upper estuary, 0.0012-0.0090 at the mid-estuary and 0.0006-0.0023 at the estuary mouth. The C_d was well below 6 implying a low degree of contamination within each layer. The cumulative C_d calculated for each sediment profile was also below the threshold of 6 thus, the sediment of the eziMbokodweni Estuary is subject to a low degree of contamination.

Table 4.13 Contamination Degree within each layer of the sediment profiles obtained along the estuary and the total C_d at each sampling site

Location	Layer							Total C_d
	1	2	3	4	5	6	7	
upper estuary	0.0006	0.0068	0.0008	0.0025	0.0019	0.0006	0.0019	0.0152
mid-estuary	0.0012	0.0020	0.0026	0.0038	0.0022	0.0090	0.0052	0.0259
estuary mouth	0.0006	0.0010	0.0023					0.0040



4.4.2 Conclusion

Numerous heavy metals were detected within the sediment profiles obtained from the eziMbokodweni Estuary. Sediment grain size was a key determinant of heavy metal content and distribution as fine to medium grained sediment exhibited greater heavy metal content, in some cases, multi-fold higher than medium to coarse grained sediment. This was particularly evident in the mid-reaches of the estuary as gentle gradient and meandering of the estuary provided conditions which were conducive for the settlement of fine grained suspended particles. The relative calm of the mid-estuary also allowed saline waters to introduce ionic charges onto the abundant fine sediments; affording it a greater capacity to adsorb heavy metals from solution. Larger components of sediment exhibited a reduced affinity as heavy metal 'accumulators' due to their round surfaces and lack of electrical charges. The estuary mouth was dominated by medium grained sediment which was attributed to constant tidal action in the region scouring and stripping fine grained sediment from the uppermost layers of the sediment profile. The constant tidal action at the estuary mouth also resulted in increased waterborne heavy metal content by remobilising benthic heavy metals. High water content was also noted within sediment profiles obtained from the estuary mouth, it is therefore likely that heavy metals are being desorbed and removed from the sediments in this region. The CF calculated for each heavy metal, across all sediment layers and sampling sites were well below 1 implying low contamination. The EF calculated for the majority of heavy metals alluded to natural causes while some heavy metals exhibited significant to extremely high levels of enrichment thus implicating anthropogenic causes as likely sources of these heavy metals. A low C_d was calculated for all sampling sites and the cumulative C_d yielded a low degree of contamination for the eziMbokodweni Estuary.

4.5.1 Bacterial Content in Water and Sediment Samples

An assessment of the microbiological quality of sediment and water obtained from the eziMbokodweni Estuary is presented in this subsection. The assessment was based on the content of the following indicator bacteria in the estuary: Faecal coliforms (FC), Total coliforms (TC) and *Escherichia* coliforms (EC). The SAWQG were consulted to determine whether the detected quantities fell within the prescribed limits and, the ANOVA and Independent Samples t-Test were applied to determine whether spatial (upper estuary, mid-estuary and estuary mouth) differences in bacterial content, as well as, differences in bacterial content among the sediment and water columns were statistically significant.

4.5.1.1 Microbiological Quality of Sediment and Water

The bacterial counts noted were highly variable spatially, as well as, among the sediment and water columns, resulting in a wide range of counts (Table 4.4). The TC, FC and EC content failed to comply with the TWQR for domestic and full contact recreational use at the three sampling sites. Hence, the waters of the eziMbokodweni Estuary are unfit for drinking purposes and recreational uses such as swimming or bathing. TC content also failed to comply with the TWQR for intermediate contact recreational use (ICRU) at the three sites. At selected sites the FC and EC content were deemed compliant for ICRU however, these sites were not compliant throughout the sampling period (Table 4.14).

Table 4.14 A summary of the microbiological data collected seasonally, for spring and neap tides

Season	Tide	Location	Bacterial Group (cfu/100ml)x10 ⁴					
			T.coli		F.coli		E.coli	
			Sediment	Water	Sediment	Water	Sediment	Water
summer	neap	upper estuary	2.97	0.95	1.15	*0.07	1.55	0.40
		mid estuary	1.05	0.89	1.85	0.10	1.66	0.21
		mouth	0.93	0.63	0.56	*0.04	1.08	*0.03
	spring	upper estuary	3.38	2.44	0.20	0.13	2.56	1.35
		mid estuary	4.95	1.31	0.88	*0.07	3.56	0.24
		mouth	0.34	0.45	0.16	*0.10	0.05	*0.03
autumn	neap	upper estuary	3.25	1.69	1.28	0.67	3.25	1.89
		mid estuary	2.79	0.37	1.90	0.28	0.80	0.26
		mouth	0.25	0.20	0.74	0.20	0.40	*0.08
	spring	upper estuary	1.84	1.51	2.70	1.75	1.27	1.67
		mid estuary	3.44	2.31	3.56	1.20	3.21	2.95
		mouth	0.57	0.92	1.04	0.47	0.87	0.40
winter	neap	upper estuary	4.29	3.88	0.84	0.36	3.25	2.01
		mid estuary	1.16	0.60	2.01	0.13	4.29	1.28
		mouth	1.09	0.13	0.59	0.20	0.82	*0.09
	spring	upper estuary	4.46	3.28	1.63	0.94	2.17	0.78
		mid estuary	1.95	1.26	3.50	0.47	3.14	1.93
		mouth	0.99	0.51	1.26	*0.06	1.28	0.17
spring	neap	upper estuary	2.94	1.91	0.35	0.49	1.92	1.10
		mid estuary	3.37	0.85	2.70	1.29	2.78	0.36
		mouth	0.75	0.34	0.24	0.38	1.26	*0.08
	spring	upper estuary	4.91	3.61	0.46	0.28	2.50	1.26
		mid estuary	2.28	1.47	0.93	0.67	0.83	0.52
		mouth	0.98	0.80	0.38	*0.06	0.36	*0.06
Range (cfu/100ml)x10⁴		upper estuary	1.84-4.91	0.95-3.88	0.20-2.70	0.07-1.75	1.27-3.25	0.40-2.01
		mid estuary	1.05-4.95	0.37-2.32	0.88-3.56	0.08-1.29	0.81-4.29	0.21-2.95
		mouth	0.25-1.09	0.13-0.92	0.16-1.26	0.04-0.47	0.05-1.28	0.03-0.40
Average (cfu/100ml)x10⁴		upper estuary	3.31	2.68	1.08	0.58	2.31	1.31
		mid estuary	2.16	1.60	2.17	0.53	2.53	0.97
		mouth	0.63	1.01	0.62	0.19	0.76	0.12
*Compliant with the ICRU TWQR of 0-1000 cfu/100ml								

4.5.1.2 Distribution of Bacteria along the Estuary and among the Sediment and Water Columns

On average TC were the most abundant bacteria at the upper estuary in both the sediment and water columns. At the mid-estuary and estuary mouth EC had the highest average count in the sediment, while TC dominated the water column (Table 4.14 and Figure 4.11 - 4.14). According to Pillay (2013a), FC (a sub-group of TC) is a more reliable indicator of faecal pollution than the broader TC group, and EC (a sub-group of FC) is more indicative of contamination by human and animal wastes. Hence, the deterioration of sediment in the lower reaches of the eziMbokodweni and estuary mouth is attributed to contamination by human and animal wastes. High counts of the TC group were detected for all other sites, within both the sediment and water columns and is too broad to link to possible sources of contamination within eziMbokodweni catchment.

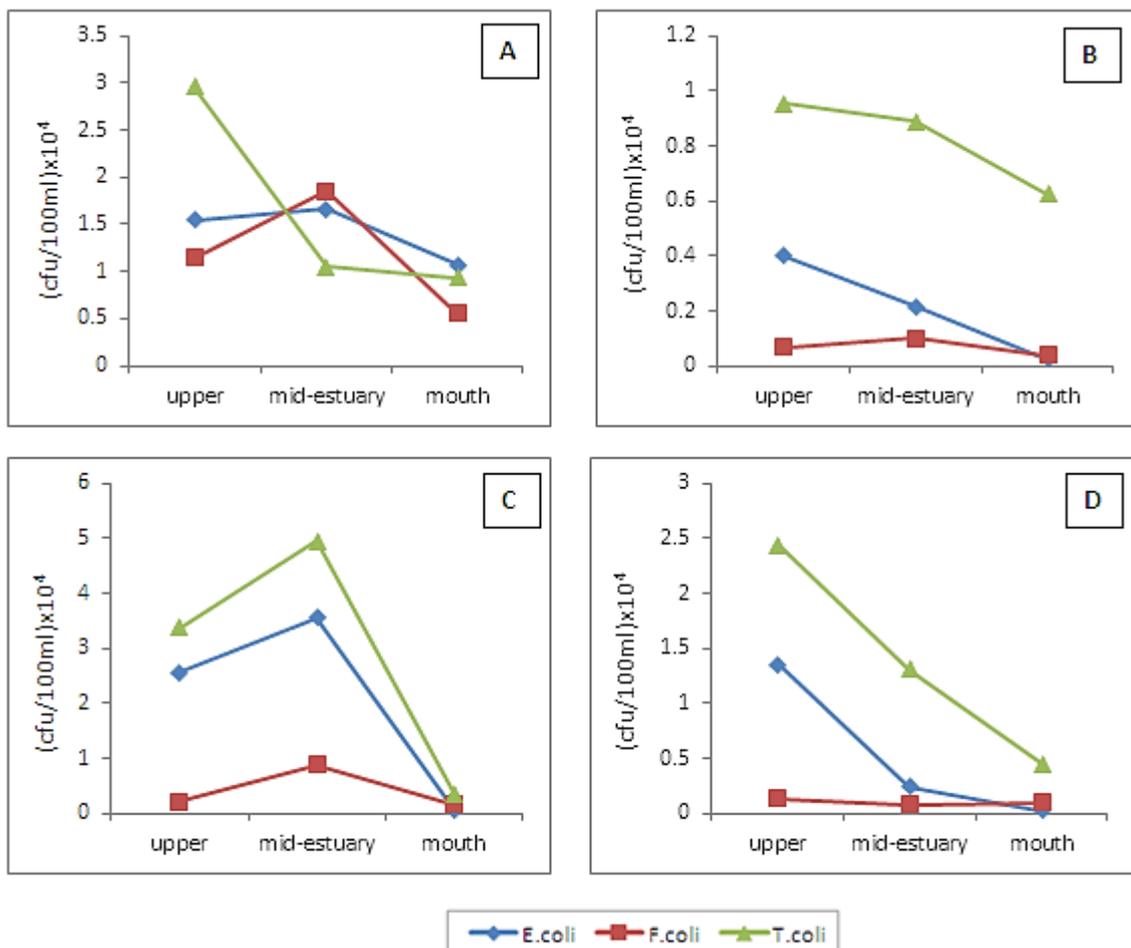


Figure 4.11 Content and distribution of each bacterial group detected at selected sites along the estuary, within the sediment and water columns: (A) summer-neap tide sediment column, (B) summer-neap tide water column, (C) summer-spring tide sediment column, (D) summer-spring tide water column

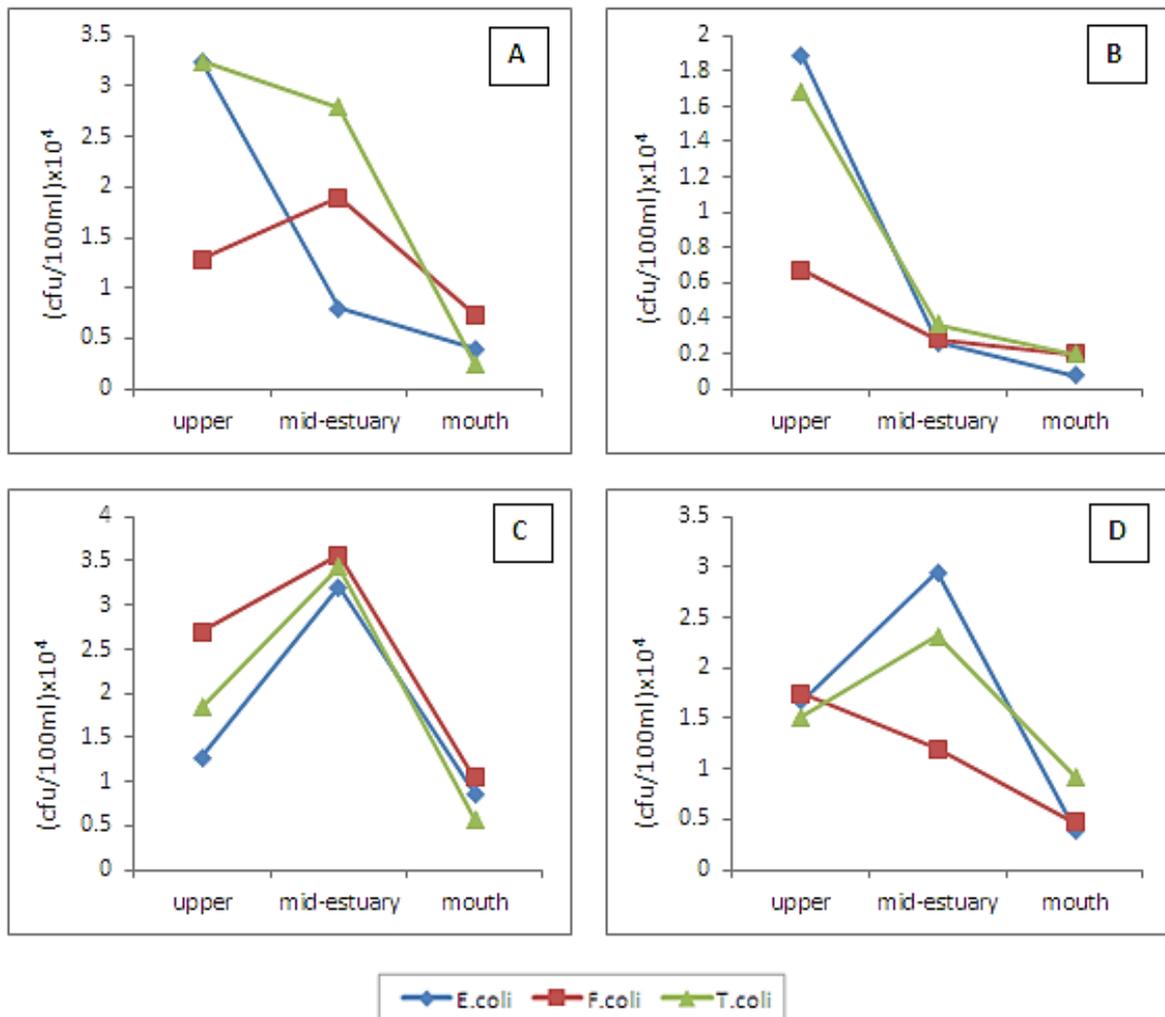


Figure 4.12 Content and distribution of each bacterial group detected at selected sites along the estuary, within the sediment and water columns: (A) autumn-neap tide sediment column, (B) autumn-neap tide water column, (C) autumn-spring tide sediment column, (D) autumn-spring tide water column

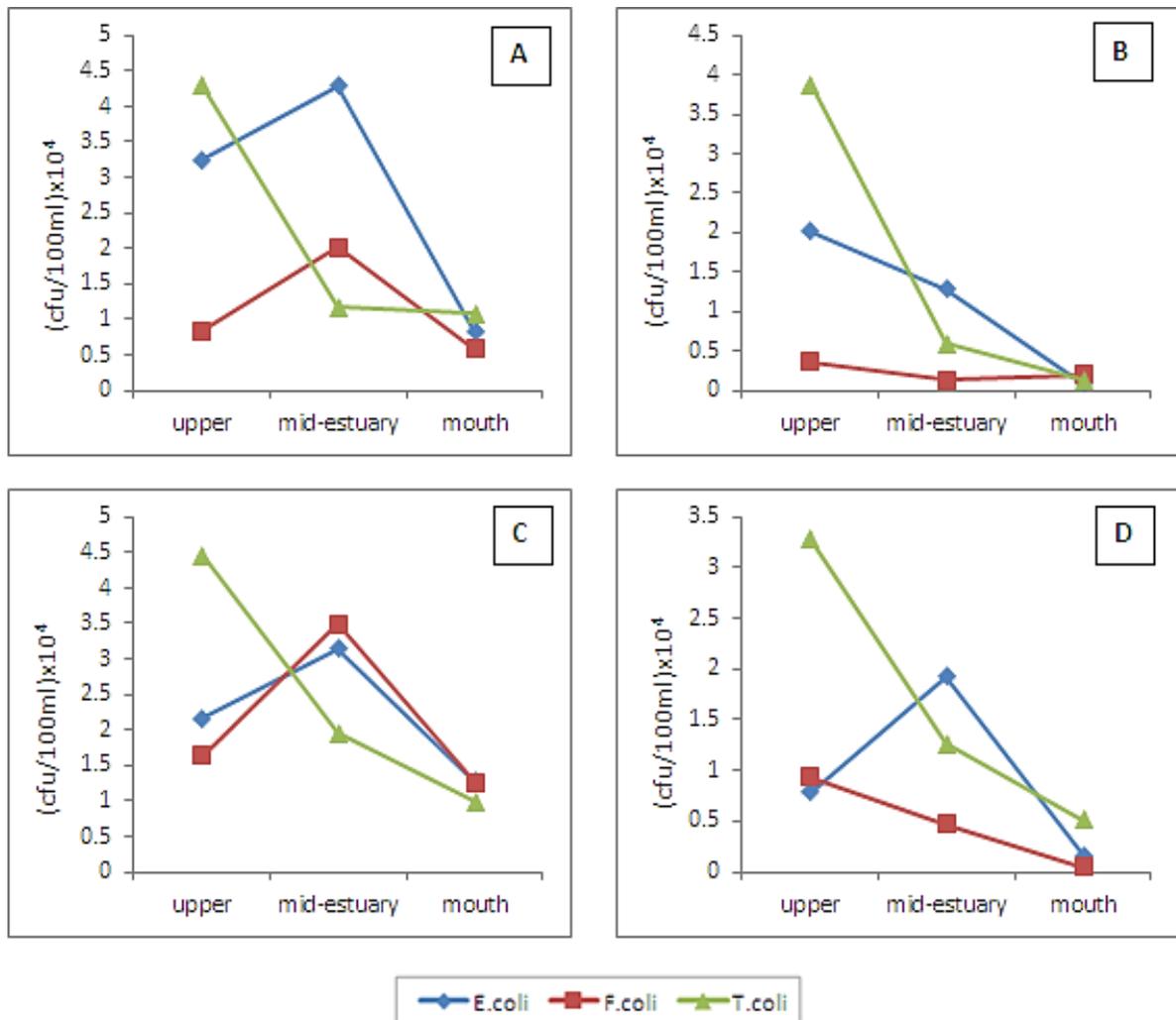


Figure 4.13 Content and distribution of each bacterial group detected at selected sites along the estuary, within the sediment and water columns: (A) winter-neap tide sediment column, (B) winter-neap tide water column, (C) winter-spring tide sediment column, (D) winter-spring tide water column

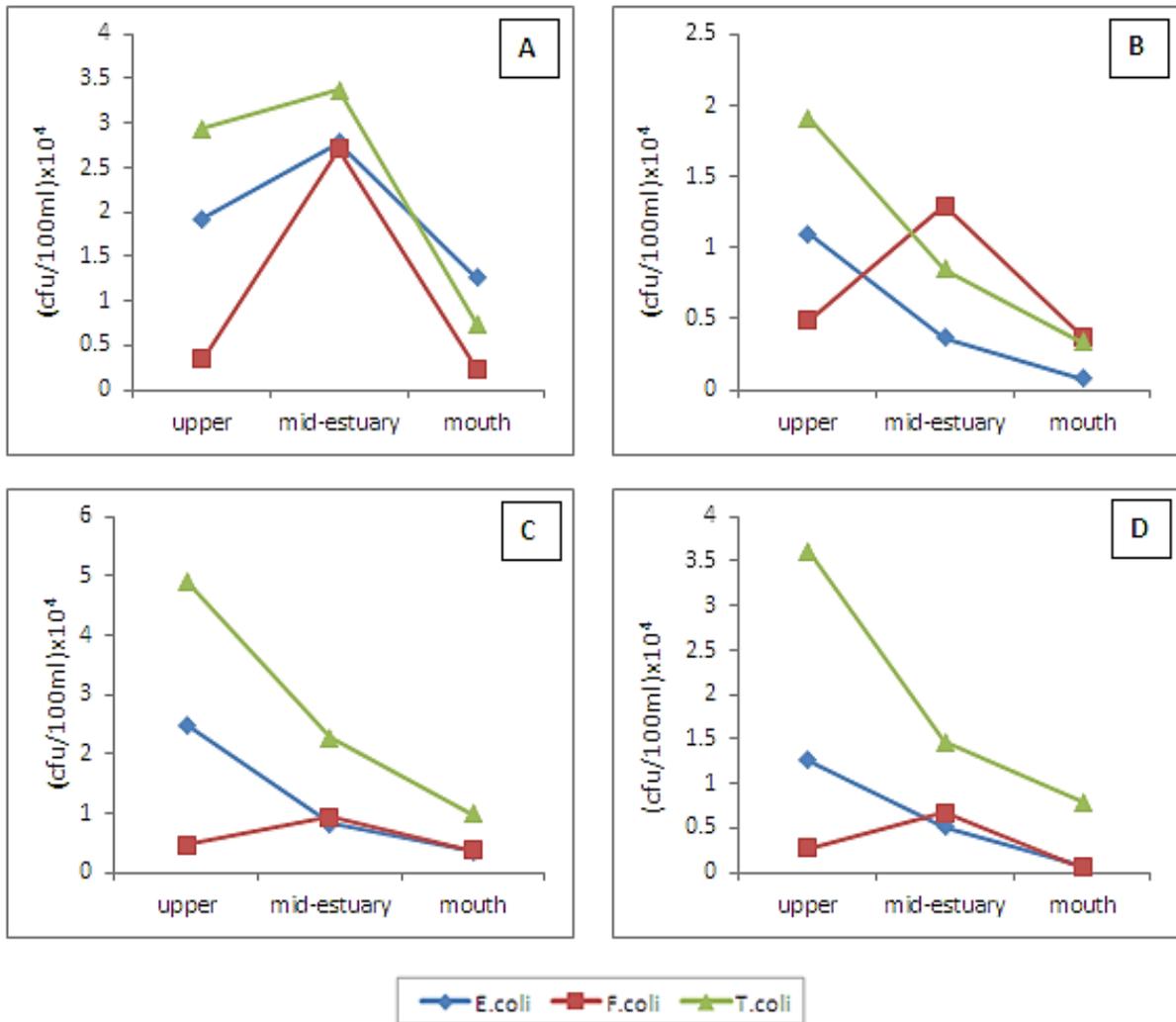


Figure 4.14 Content and distribution of each bacterial group detected at selected sites along the estuary, within the sediment and water columns: (A) spring-neap tide sediment column, (B) spring-neap tide water column, (C) spring-spring tide sediment column, (D) spring-spring tide water column

4.5.1.3 ANOVA of Bacterial Content Spatially, within the Sediment and Water Columns

An assessment of the Table 4.14 and Figures 4.11 – 4.14 indicate that bacterial content of each group differs spatially (upper estuary, mid-estuary and estuary mouth) along the eziMbokodweni Estuary, within both the sediment and water columns. ANOVA was

conducted to determine whether these differences were statistically significant, the results are presented in Table 4.15 below.

Table 4.15 Results of the ANOVA of bacterial content spatially, within the sediment and water columns

Bacterial Group		SS	df	MS	F	p-value	Conclusion
T.coli	sediment	3.20E+09	2	1.60E+09	17.18	0.000	<ul style="list-style-type: none"> • TC content at the upper estuary is greater than at the estuary mouth • TC content at the mid-estuary is greater than at the estuary mouth • The estuary mouth had the lowest detected TC content
	water	1.52E+09	2	7.59E+08	14.26	0.000	<ul style="list-style-type: none"> • TC content at the upper estuary is greater than at the estuary mouth • TC content at the upper estuary is greater than at the mid-estuary • The estuary mouth had the lowest detected TC content
F.coli	sediment	1.01E+09	2	5.04E+08	8.07	0.003	<ul style="list-style-type: none"> • FC content at the at the upper estuary is less than at the mid-estuary • FC content at the mid-estuary is greater than at the estuary mouth • The estuary mouth had the lowest detected FC content
	water	7.43E+07	2	3.72E+07	1.97	0.165	<ul style="list-style-type: none"> • The spatial differences in bacterial content were not statistically different • The estuary mouth had the lowest detected FC content
E.coli	sediment	1.48E+09	2	7.42E+08	9.28	0.001	<ul style="list-style-type: none"> • EC content at the upper estuary is greater than at the estuary mouth • EC content at the mid-estuary is greater than at the estuary mouth • The estuary mouth had the lowest detected EC content
	water	6.05E+08	2	3.02E+08	6.81	0.005	<ul style="list-style-type: none"> • EC content at the upper estuary is greater than at the estuary mouth • EC content at the mid-estuary is greater than at the estuary mouth • The estuary mouth had the lowest detected EC content
SS = Sum of Squares df = Degrees of Freedom MS = Mean of Squares Where p<0.05 results are deemed significant							

The spatial differences in bacterial content were statistically significant ($p < 0.05$) within both the sediment and water column, with the exception of FC in the water column ($p > 0.05$). The upper and mid-estuary exhibited greater counts of bacteria in both the sediment and water column than the estuary mouth. The controlling factors were flushing, sediment particle size, salinity and the ‘*dilution effect*’. The decreased tidal action at the upper and mid-estuary allowed for the sedimentation of bacteria and subsequent growth and multiplication in this region. The estuary mouth however, was subject to constant tidal action resulting in the scouring of benthic bacteria and its export to the marine environment. Furthermore, the sediment layers interacting at the sediment-water interface of the eziMbokodweni Estuary was heterogenic in terms of sediment grain size. The upper and mid-estuary was dominated by fine to medium grained sediment while the estuary mouth was characterized by medium to coarse grained sediment. Fine to medium grained sediment provide bacteria with prime survival and growth factors, such as, protection from predators and the effects of sunlight inactivation (Pachepsky and Shelton, 2011; Sukdeo, 2010) and greater organic content (Hendricks, 1971; Ferguson *et al.*, 1996). The lower bacterial counts detected at the estuary mouth may also be attributable to the constant flux of saline waters from the marine environment. Pillay (2013a), states that saline waters are not conducive to the survival of bacteria. Much faster die-off rates associated with increasing salinity have been noted by several authors (Goyal *et al.*, 1977; Anderson *et al.*, 2005; He *et al.*, 2007). Pillay (2013a), also states that as a result of the ‘*dilution effect*’ the lower extremity of estuaries tend to exhibit reduced bacterial levels in comparison to the upper reaches, which are the receiving waters for catchment drainage.

4.5.1.4 Independent Samples t-Test of Bacterial Content amongst the Sediment and Water Columns

Based on the data contained in the Table 4.14 and Figures 4.11 – 4.14 it is evident that bacterial content was greater in the sediment than water column. The Independent Samples T-test was applied to determine whether these differences were statistically significant. The results are presented in Table 4.16 below.

Table 4.16 Results of the Independent Samples T-test of bacterial content amongst the sediment and water columns

Bacterial Group	<i>t</i> -value	df	<i>p</i> -value
F.coli	3.804	31.954	0.001
T.coli	2.511	41.646	0.016
E.coli	3.672	41.074	0.001
df = Degrees of Freedom Where $p < 0.05$ results are deemed significant			

The difference in bacterial content among the sediment and water columns were statistically significant for each bacterial group ($p < 0.05$). Bacterial content within the sediment was overall greater than the water column and in some cases several orders of magnitude greater. This suggests that the sediment of the eziMbokodweni Estuary is serving as a reservoir for bacteria in densities exceeding the water column and sufficient to jeopardize the health status of the estuary and humans. Numerous studies have led to the conclusion that sediment is the dominant reservoir for bacteria and was attributed to favorable survival and growth opportunities provided by the larger pore spaces (Van Donsel and Geldreich, 1971; Goyal *et al.*, 1977; Erkenbrecher, 1980; Doyle *et al.*, 1992).

4.5.2 Conclusion

The study has highlighted the presence of high levels of bacteria within the eziMbokodweni Estuary, in both the sediment and water columns. The detected quantities of TC, FC and EC failed to comply with the TWQR for domestic and full contact recreational use. While, at selected sites the recorded FC and EC levels were deemed compliant for ICRU, however these sites were not compliant throughout the sampling period. Results from the ANOVA indicate that the spatial (upper estuary, mid-estuary and estuary mouth) differences in bacterial content were statistically significant ($p < 0.05$) with the exception of FC in the water column ($p > 0.05$). Overall, the upper and mid-estuary exhibited greater counts of bacteria in both the sediment and water column than the estuary mouth and was attributed to factors such as flushing, sediment particle size, salinity and the ‘*dilution effect*’. According to results from the Independent Samples t-Test, the difference in bacterial content among the sediment and

water columns were statistically significant ($p < 0.05$) for each bacterial group, thus the sediment of the eziMbokodweni Estuary is serving as a reservoir for bacteria.

CHAPTER FIVE

Conclusion and Recommendations

5.1 Key Findings

This study demonstrated that the eziMbokodweni catchment was a major contributor of heavy metals and nutrients to the system. The quantity of the majority of heavy metals and nutrients transported by the river at the upper estuary exceeded those exported at the estuary mouth, resulting in the estuary accruing large quantities seasonally, for spring and neap tides. It was noted that a variety of heavy metals and nutrients, in large quantities, entered the estuary mouth during flooding thus the nearshore waters are enriched.

Numerous heavy metals were detected within the sediment profiles obtained from the estuary, with fine to medium grained sediment exhibiting greater heavy metal content, in some cases, multi-fold higher than medium to coarse grained sediment. This was particularly evident in the mid-reaches of the estuary as gentle gradient and meandering of the estuary provided conditions which were conducive for the settlement of fine grained suspended particles. The relative calm of the mid-estuary also allowed saline waters to introduce ionic charges onto the abundant fine sediments, affording it a greater capacity to adsorb heavy metals from solution. The contamination factor calculated for all sediment layers and sampling sites implied low contamination. The enrichment factor calculated for the majority of heavy metals alluded to natural causes while some heavy metals exhibited significant to extremely high levels of enrichment thus implicating anthropogenic causes as likely sources of these heavy metals. The degree of contamination of the estuary was classified as low.

Overall, the heavy metal and nutrient content detected in the sediments were low as compared to the large quantities detected from the budget. Hence, there are methods by which heavy metals and nutrients are being utilized or removed from the estuary. It is proposed that the most significant manner by which these heavy metals and nutrients are eliminated from the estuary is through episodic flood events that scour and strip fine grained sediment from the estuary bed. Thus, what remains in the estuary is an aged sediment profile which is not reflective of the recent/current health status of the system.

During summer, autumn and spring the estuarine waters were basic; and mildly acidic during winter. The average DO levels detected were within acceptable levels, with the exception of winter when DO levels were very close to hypoxic conditions. The average TDS levels

indicated that the estuary was compliant with the TWQR for domestic use on selected seasonal-tidal cycles, and the average EC levels were compliant with the ideal TWQR for aquatic ecosystems and domestic use. The average EC and TDS levels were notable higher at the estuary mouth than upper estuary, suggesting that the nearshore waters are a major contributor of dissolved inorganic and organic compounds to the estuary. A salinity gradient was evident in the estuary, as salinity levels decreased with distance from the estuary mouth. The saline nature of the lower estuary provides for the flocculation of material, which is alarming as large quantities of heavy metals and nutrients were detected in the estuary. The lower estuary is therefore susceptible to sediment contamination. The demand for oxygen in the estuary was high during summer, autumn and spring, and within acceptable levels for natural waters during winter. Extremely high levels of COD were recorded in the estuary which provides prime growth and survival opportunities for bacteria within the estuary. This correlated with the results from microbiological investigations as high levels of bacteria were noted within the estuary, in both the sediment and water columns. The detected quantities of TC, FC and EC failed to comply with the TWQR for domestic and full contact recreational use. While, at selected sites the recorded FC and EC levels were deemed compliant for ICRU, however these sites were not compliant throughout the sampling period. Overall, the upper and mid-estuary exhibited greater counts of bacteria, in both the sediment and water column, than the estuary mouth and was attributed to factors such as flushing, sediment particle size, salinity and the '*dilution effect*'. Furthermore, the sediment of the eziMbokodweni Estuary is serving as a reservoir for bacteria.

5.2 Recommendations

A number of options can be considered to improve the degraded state of the eziMbokodweni Estuary these include:

- Regulating the diversion of flow from the Isipingo River into the eziMbokodweni River and Estuary, to ensure that such flows do not result in the degradation of the receiving waters.
- Regularly removing alien invasive vegetation from the river and estuary banks, and reinstating indigenous riparian vegetation.

- Monitoring and regulating catchment landuse and processes, and compiling an industry inventory to assist with compliance monitoring.
- Investigating opportunities to improve tidal exchange.

It is also recommended that in order to fully understand the fate of the accumulated material in the estuary, the biogeochemical cycles operating in the system must be studied, as well as, heavy metal and nutrient content of interstitial waters in bed sediment.

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APPENDIX

Appendix A. Average content of selected physico-chemical parameters seasonally, for spring and neap tides

Season	Tide	Location	pH	DO (mg/L)	TDS (mg/L)	EC (mS/cm)	Salinity (ppt)	BOD (mg/L)	COD (mg/L)
summer	neap	upper estuary	7.19	7.24	316.89	6.58	3.59	19.84	702.33
		mouth	7.56	7.3	423.9	16.99	10.19	19.47	554.75
	spring	upper estuary	7.58	7.28	643.5	3.4	1.68	32.07	478
		mouth	7.51	7.25	667.93	26.32	16.14	23.03	828.67
autumn	neap	upper estuary	7.41	7.5	332.56	1.54	0.61	14.55	736
		mouth	7.53	7.51	599.46	3.63	1.78	16.64	684.33
	spring	upper estuary	7.43	8.41	278.24	1.29	0.41	19.14	885.63
		mouth	7.22	7.71	364.76	1.69	0.69	19.27	959.33
winter	neap	upper estuary	6.95	3.81	340.09	1.7	2.78	2.15	554.67
		mouth	6.96	3.65	633.31	5.92	3.31	1.68	470.23
	spring	upper estuary	6.74	3.84	543.99	6.05	2.56	2.16	600.84
		mouth	6.82	3.68	746.39	5.44	3.49	1.72	619
spring	neap	upper estuary	7.31	7.34	569.81	5.41	3.35	19.06	606.67
		mouth	7.56	7.41	729.94	13.67	10.19	19.47	568.17
	spring	upper estuary	7.01	5.96	494.32	3.23	1.58	23.92	615.67
		mouth	7.51	7.34	593.82	17.78	16.14	17.82	865