AN INVESTIGATION INTO THE POLLUTION STATUS OF THE DURBAN HARBOUR RIVER CATCHMENTS, KWAZULU-NATAL, SOUTH AFRICA

By

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PREFACE

All of the work presented henceforth is ultimately based on the experimental work conducted in the School of Agricultural, Earth and Environmental Sciences, University of KwaZulu-Natal, Durban (South Africa) – from February 2011 to October 2013 under the supervision of Dr. Srinivasan Pillay.

This dissertation comprises the original intellectual product of the author, Kavandren Moodley, and has not been submitted in substance for any other degree or award at this or any other learning institution, nor is it being submitted concurrently for any other degree or award. Information sources and the work of others are duly acknowledged as such.

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9. To anybody I failed to recognize that helped in the compilation of this thesis. It is most appreciated.

DECLARATION - PLAGIARISM

I, Kavandren Moodley, declare that:

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This thesis has not been submitted for any degree or examination at any other university.
3. This thesis does not contain other persons' data, pictures, graphs of other information unless specifically acknowledged as being sourced from other persons'.
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Kavandren Moodley

As the candidate's supervisor I have/have not approved this dissertation/thesis for submission.

Signed: __________________ Name: __________________ Date: __________________

DECLARATION - PUBLICATIONS

The chapters of this thesis were synthesized as individual research papers which were submitted for publication in the journals listed hereunder:

Publication 1

Spatiotemporal characterization of water chemistry and pollution sources of the uMhlatuzana, uMbilo and aManzimnyama River catchments of Durban, KwaZulu-Natal, South Africa.

This article has been submitted to the *Environmental Earth Sciences Journal* and is under review.

Publication 2

Seasonal discharge and chemical flux variations of rivers flowing into the Bayhead Canal of Durban Harbour, South Africa.

This article has been submitted to the *International Journal of Environmental Research* and is under review.

Publication 3

Effects of land use on water quality and diatom communities in the fluvial catchments of Durban Harbour, KwaZulu-Natal, South Africa.

This article has been submitted to the *Journal of Geographical Sciences* and is under review.

Publication 4

Spatiotemporal evaluation of heavy metal contamination in river sediments of the Durban Harbour catchments, South Africa.

This article has been submitted to the journal *Frontiers of Earth Science* and is under review.

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Kavandren Moodley

ABSTRACT

River pollution as a consequence of urbanization and industrialization has tremendously increased over the past few decades with rapid population growth, and often with profound negative effects on ecosystem health and functioning. The river systems of the Durban Harbour catchments are no exception. The uMhlatuzana, uMbilo and aManzimnyama river catchments of KwaZulu-Natal, South Africa, comprise three freshwater systems which are predominantly urbanized and industrialized rivers ultimately flowing into the Bayhead Canal of the Durban Harbour as corresponding canals at the confluence.

This study explores the pollution status of these river catchments in relation to seasonality and surrounding land use in an attempt to identify principal contributors influencing pollution. To examine the impacts of land use on pollution levels, samples collected from predetermined locations were analyzed for several physico-chemical parameters in the water and sediment column. Additionally, benthic diatoms from these predetermined locations were studied in assessing diatom responses to physico-chemical water gradients and to establish overall aquatic habitat quality. This allowed for the appraisal of the suitability of diatoms as potential biological indicators of river health in the study area. The impacts of each river system on the Bayhead Canal of the Durban Harbour into which they flow were assessed following further sampling that was conducted in the Bayhead Canal and the data presented as interpolated images using ArcGIS 9®. All data was analyzed using relevant statistical analyses techniques.

Results indicated that an intensification of anthropogenic activities and processes operating in the catchments of the Durban Harbour, in particular industry, have caused general deteriorations in certain water and sediment parameters on the basis of variables that were analyzed. This has resulted in substantial spatio-temporal variability across all sample sites. This was further substantiated by low counts of diatom taxa found across all sites and seasons which represented deteriorations in water quality and necessitated the need for drastic remedial measures for restoration of the catchment river systems. The study was useful in identifying zones and contaminants of concern so as to enable water

managers and planners to correctly prioritize stressed zones for rehabilitation and for on-going monitoring in the attempt to restore the ecological state of the systems, whilst saving on monitoring time and costs.

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LIST OF ABBREVIATIONS AND UNITS

Abbreviations

Al	Aluminium
ANOVA	Analysis of Variance
As	Arsenic
AsO_4^{3-}	Arsenate
$BaSO_4$	Barium Sulphate
BCME	British Columbia Ministry of Environment
BOD	Biological Oxygen Demand
C	Concentration
CA	Cluster Analysis
Ca	Calcium
CCME	Canadian Council of Ministers of the Environment
CEQG	Canadian Environmental Quality Guidelines
CF	Contamination Factor
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
Cond.	Conductivity
Cr	Chromium
CSIR	Council for Scientific and Industrial Research
Cu	Copper
DDT	Dichlorodiphenyltrichloroethane
DEAT	Department of Environmental Affairs and Tourism
DO	Dissolved Oxygen
DWAF	Department of Water Affairs and Forestry
E.coli	*Escherichia coli*
EEC	European Economic Community
EF	Enrichment Factor
ERM	Environmental Resource Management
Fe	Iron
Fe^{2+}	Ferrous Iron

Fe^{3+}	Ferric Iron
GPS	Global Positioning System
H_2O	Water
HCl	Hydrochloric Acid
Hg	Mercury
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
K	Potassium
$KMnO_4$	Potassium Permanganate
MER	Marine Environmental Research
Mg	Magnesium
$MgSO_4$	Magnesium Sulphate
MLRA	Marine Living Resources Act (No. 18 of 1998)
Mn	Manganese
Mn^{2+}	Divalent Manganese ion
MUT	Mangosuthu University of Technology
Na	Sodium
NEMA	National Environmental Management Act (No. 107 of 1998)
NH_3	Un-ionized Ammonia
NH_4^+	Ammonium ion
Ni	Nickel
NWA	National Water Act (No. 36 of 1998)
NWRS	National Water Resource Strategy
O_2	Oxygen
OM	Organic matter
P	Phosphorous
Pb	Lead
PC	Principal Component
PCA	Principal Component Analysis
PEL	Probable Effect Level
pH	Potential of Hydrogen
ppm	Parts per million

PVC	Polyvinyl Chloride
Q	Flow discharge
r	Pearson Correlation Coefficient
RDM	Resource Directed Measures
rpm	Revolutions per minute
RQO	Resource Quality Objectives
S	Sulphur
SASRI	South African Sugarcane Research Institute
SDC	Source Directed Controls
Se	Selenium
SeO_3^{2+}	Selenium ion
SO_4^{2-}	Sulphate ions
SQG	Sediment Quality Guideline
TC	Total coliforms
TDS	Total Dissolved Solids
UKZN	University of KwaZulu-Natal
US-EPA	United States – Environmental Protection Agency
V	Vanadium
WHO	World Health Organization
WRC	Water Research Commission
WWTW	Waste Water Treatment Works
Zn	Zinc

Units

cm	Centimetre
g	Gram
g/s	Grams per second
km	Kilometre
km^2	Square kilometre
L	Litre
m	Metre

M	Mol
m^2	Square metres
m^3/s	Cubic metres per second
mg/kg	Milligrams per Kilogram
mg/L	Milligrams per litre
mL	Millilitre
%	Percentage
μS/cm	Microsiemens per centimetre
°C	Degrees centigrade
<	Less than
>	Greater than

CHAPTER ONE

A GENERAL INTRODUCTION

1.1 INTRODUCTION AND MOTIVATION FOR STUDY

Water constitutes a continuum ranging from freshwater river systems to marine salt waters which cover more than 71% of the Earth's surface and are interconnected and influence each other either directly or indirectly (Chapman, 1992). Water in rivers constitutes merely 0.0001% of the Earth's surface and is the single most important commodity that is required by man and yet it is the one most taken for granted (Gray, 1994). From a socio-economic perspective, freshwater serves to fulfil a diverse range of functions including its use by humans for drinking, bathing, cooking, recreational and agricultural activities (Tomar, 1999). In addition, water is considered to be the main limiting factor governing the propagation of aquatic and terrestrial plants and animals (Gutierrez and Whitford, 1987). Whilst water forms an essential component throughout the world, the growing economic demands and pressures placed on water as a resource could ultimately lead to devastating water crises and conflicts (Department of Water Affairs and Forestry (DWAF), 1997). In the South African context, this is exacerbated by a large number of rivers that are short in length or with flow mainly confined to the wet season, thereby rendering freshwater resources an extremely limited resource in the country (Van Stormbroek, 2007).

It is well known that river chemistry and water quality on the catchment scale is generally related to land use or land cover, such that a combination of natural and anthropogenic catchment activities is often reflected in river chemistry through various in-stream physical and chemical processes (Ahearn *et al*., 2005). In recent years there has been a decline in freshwater resources in terms of quantity and quality primarily due to unsustainable land use practices (Li *et al*., 2008). Most human activities on the catchment scale and the associated by products displays the potential to contaminate and pollute river systems, including industries, urban infrastructure, agriculture, transport, mine discharges and pollution incidents (Gower, 1980). The effects of anthropogenic land use on river chemistry and water quality has been demonstrated in several studies, often with devastating implications on aquatic quality and chemistry through the transport and delivery of sediment, pollutants and nutrients (Dauer *et al*., 2000; Farnsworth and Milliman, 2003; Bullard, 1966; Wilkinson and McElroy, 2007; Weijters *et al*., 2009). These alterations can have strong negative implications on the biodiversity of terrestrial, freshwater and marine ecosystems (Weijters *et al*., 2009).

By 2005, more than 95% of the South Africa's freshwater resources had already been allocated, the qualities of which had rapidly declined due to pollution generated through land use specifically associated with industry, urbanization, mining, agriculture and power generation (Council for Scientific and Industrial Research (CSIR), 2010). The transport and fate of contaminants generated through associated pollution processes causes much concern for human and ecosystem health, mainly due to health-threatening microorganisms, and persistent toxic chemical compounds in the environment which can cause irreversible pollution and damage to natural ecosystems (CSIR, 2010). Controlling point source pollution loading into rivers is not sufficient in meeting water quality objectives; instead a broader catchment based management approach is needed to help control non-point source pollution (Ly, 2010). This emphasizes the need for effective catchment management strategies which in turn requires a thorough understanding of the interactions between land use and river chemistry on the catchment scale (Ly, 2010).

Due to the negative environmental and socio-economic implications of poor water quality, water quality based monitoring studies is now the concern of experts in all countries of the world (Abdo and El-Nasharty, 2010). Whilst water quality monitoring studies were previously undertaken to verify the suitability of water for an intended use, it has since evolved to determine trends in water quality in the aquatic ecosystems and its subsequent effects on the environment (Osman and Kloas, 2010). Aquatic monitoring has also more recently evolved into river sediment and biological monitoring techniques as an indication of long term pollution trends and nutrient presence in water bodies, as in-stream sediment and biological organisms are known to capture and respond to pollutants entering a water resource over time (Jahnig and Qinghua, 2010; Osman and Kloas, 2010). Consequently, several studies have focused on sediment and biological monitoring in rivers as more accurate long term indicators of water quality (Kalyoncu *et al*., 2009; Osman and Kloas, 2010; Singh *et al*., 2010; Varol, 2011; Wang *et al*., 2012).

The uMhlatuzana, uMbilo and aManzimnyama river catchments of KwaZulu-Natal, South Africa, comprise three freshwater systems which are predominantly urbanized rivers flowing into the Bayhead Canal of the Durban Harbour as corresponding canals at the confluence. Aerial imagery and ground truthing *via* site visits shows that each of these catchment systems comprise a core of urbanization with dense industrial and residential development, laced with isolated land parcels of natural vegetation and undisturbed areas (www.googleearth.com, accessed June 2012). In recent years, the increase in anthropogenic land use in these catchments has led to an increasing demand for water and subsequent deteriorations in river health primarily as a consequence of land use contributions. This presents an ideal opportunity in investigating the impacts of various land use types on river chemistry at the catchment scale using water quality, sediment quality and biological indicators for comparative evaluation. Subsequently, this study utilizes several biological and chemical analytical techniques to accurately and effectively determine the impacts of anthropogenic and natural land use of these three highly urbanized catchments in KwaZulu-Natal, as well as assessing their chemical impacts on the Bayhead Canal of the Durban Harbour into which they flow.

1.2 AIM AND OBJECTIVES

It is expected that the continued increase in industrialization and urbanization within the Durban Harbour catchments may cause further deteriorations in the physico-chemical quality of the river systems and the Bayhead Canal of the Durban Harbour into which they flow. This may necessitate the need for proactive measures in an attempt to conserve the ecological state of the systems which first requires an understanding of the current pollution status of these systems. Therefore, the aim of this study is to provide a situational assessment of the pollution status of the uMhlatuzana, uMbilo and aManzimnyama river systems with the focus on water quality, sediment quality and material mass transport capacity using a range of chemical and biological monitoring techniques.

Following the aim of this study, the objectives are specifically set out to:

- Quantify and assess the present day physico-chemical water and sediment quality of three fluvial systems subjected to different levels of land use practice, which ultimately flows into the Bayhead Canal of the Durban Harbour;
- Draw up a comparative analysis between seasonal water quality, land use and material fluxes along each of the rivers;
- In the absence of appropriate South African sediment quality guidelines, compare measured sediment parameters against international target values;
- Utilize biomonitoring as a tool for pollution assessment by studying the influence of the measured physico-chemical findings on the community structure of diatoms within the fluvial systems, and to identify the responses of key diatom indicator species to changes in physico-chemical water quality; and
- Provide practical recommendations which can assist authorities in the on-going management of the catchment systems.

1.3 STRUCTURE OF THESIS

With the exception of the introductory, methods and conclusion chapters in this thesis, each chapter is synthesized as an individual paper that has been submitted for review to peer-reviewed journals.

Chapter one addresses the theoretical framework and key ideas forming part of this study. Emphasis is placed on the characteristics and significance of catchment river systems, followed by the catchment coast continuum concept and the ways in which river chemistry and water quality has been altered across these scales through a combination of natural and anthropogenic processes dominant within the catchment ecosystem. Further insight is provided on the physico-chemical characteristics of fluvial systems, together with stresses influencing these characteristics and the resulting ecological implications arising from pollution processes. This chapter also serves as an evaluation of the key monitoring and assessment techniques available for the evaluation of river chemistry and water quality on the catchment scale.

Chapter two serves to highlight the biophysical characteristics and geographic setting of the study area, together with the sampling and analytical methods employed in this study. This facilitates an understanding of the geographical context of the study area, as well as the ways in which samples were collected and analyzed, and the data presented.

Chapter three explores the impacts of catchment land use on the seasonal water quality of the receiving water bodies and ultimately the Bayhead Canal into which they flow. This is accomplished through several biological and chemical analytical techniques and is compared against prescribed South African water quality guidelines where available. In addition, the spatio-temporal characterization of sampling sites reflecting land use change was statistically examined through Principal Component Analysis (PCA).

Chapter four evaluates the implications of land use and seasonality on river flow velocity and discharge at the predetermined locations, enabling an estimation of the seasonal material mass transport capacity of the fluvial systems to the Bayhead Canal into which they flow, for selected chemical parameters.

Chapter five examines diatom community structures and abundances relative to land use change and seasonality in an attempt to relate these factors to environmental gradients, and to test the efficiencies of diatoms as indicators of aquatic health through their response to physico-chemical water quality gradients.

Chapter six adopts an indices-based and multivariate statistical approach in exploring the sediment geochemistry of the catchment river systems and Bayhead Canal into which they flow, with reference to land use change and seasonality.

Chapter seven provides a general synthesis of the overall study by drawing on insight into the main research findings obtained from the individual chapters as well as providing recommendations in an attempt to ecologically restore and better manage the fluvial systems on the catchment scale, thereby placing the context of the study into perspective.

1.4 INTRODUCTION TO LITERATURE REVIEW

The remaining sections of this chapter provide a conceptual framework of the background information and main ideas forming part of this study. These sections follow a logical sequence of topics to facilitate continuity and progression, such that each section provides insight to the processes and methods involved in a situational assessment of river chemistry and water quality at the catchment scale. This is attained by outlining the catchment coast continuum concept and the significance of catchment river systems, followed by the ways in which river chemistry and water quality have been altered by a combination of natural and anthropogenic processes operating within the catchment ecosystem. Further insight is provided into available monitoring and assessment techniques commonly utilized for situational assessments of catchment river systems.

1.5 CHARACTERISTICS AND SIGNIFICANCE OF CATCHMENT RIVER SYSTEMS

River catchments include all land from source to sea that is drained by a single river system (Sukdeo, 2010). As such, sediment and water in river systems provides an important link between fluvial, estuarine and marine environments (Owens, 2007). Sediment eroded within catchments is transported by a channel network into the sea, and this implies that a catchment river system is not closed in terms of water and sediment transport (Sekiguchi *et al*., 2005). Consequently, the quantity and quality of water and sediment moving between catchment and coast is important for several reasons including aquatic ecology and estuarine habitats (Owens, 2007). Owing to this dynamic catchment and coast continuum relationship, estuaries often serve as sinks for material derived from their respective inland catchments (Bird, 2000; Jennings, 2005). This is substantiated by studies which have shown that catchment land use patterns often influence the delivery of nutrients, sediments and contaminants into estuarine waters through surface and subsurface flow, as well as atmospheric fallout (Dauer *et al*., 2000).

The river systems of catchments are often characterized by their flow regime and discharge magnitude, in which discharge is the single most important measurement allowing for the estimation of water quantity and the calculation of water quality variable loads to the estuarine environment (Chapman, 1992). A rivers discharge is related to the nature of its associated catchment particularly geological, geographical and climatological influences, and is extremely important for the calculation and interpretation of water quality measurements, especially for those including suspended sediment, or intended to determine the flux of sediment or contaminants (Bartram and Ballance, 1996). The simplest form of a water quality model is the discharge-concentration relationship which provides a long-term time series estimate of water quality (Walton and Hunter, 2009). Discharge, in many cases, forms the basis of most multiple regression analyses when examining land use effects from river water quality data (Walton and Hunter, 2009). Fluctuations in river discharge are attributed mainly to climate and rainfall, surface and subsurface geology, as well as land cover exerting an influence through modification of infiltration rates (Chapman, 1992). Climate changes runoff over watersheds and river flow within rivers, thereby modifying the transformation and transportation of in-stream chemical constituents (Tu, 2009). Consequently, seasonal changes in water quality are an important aspect in establishing and quantifying river pollution due to natural or anthropogenic inputs, and form the basis of many studies (Crosa *et al*., 2006; Guo *et al*., 2008; Ouyang *et al*., 2006).

As a natural resource, rivers play an important role in the transport of dissolved nutrients from upstream to downstream regions which in turn influence biogeochemical processes operating in a river system (Ogura and Kanki, n.d.). Whilst these biogeochemical processes reflect a combination of physical and chemical factors including temperature, light, riverbed substrate, and dissolved substances in water, biogeochemical cycling ultimately influences the water quality of river systems and the subsequent suitability of rivers as habitats for algae, rooted-plants, benthic animals, fish and other wildlife (Ogura and Kanki, n.d.). As a socio-economic resource, Jordaan (n.d.) identifies some of the most relevant development activities and processes supported by catchment river systems including:

- Use in navigation;
- Hydro-electric power projects supported by rivers;
- Supporting fisheries;
- Source of fresh water supply;
- Use for recreational activities;
- Use as cooling water for industrial processes;

- Use for agriculture/irrigation purposes;
- Use in mining processes;
- Wastewater disposal medium; and
- Use as international borders.

1.6 CATCHMENT PROCESSES AFFECTING RIVER CHEMISTRY AND WATER QUALITY

An important area of scientific research is the increasing focus on understanding mechanisms of hydrological processes at ecosystem and catchment levels in an attempt to characterize changes in hydrological processes and river chemistry with landscape alteration, which often has a direct application to catchment management planning (Zhou *et al*., 2004). The processes contributing to river chemistry and water quality can be best understood in the context of the catchment ecosystem, which requires recognition of the catchment as an inter-related system containing complex biotic and abiotic components that interact through the flow of energy and nutrient cycles thereby influencing the physical, chemical and biological quality of in-stream water and sediment (Gower, 1980). River chemistry and water quality is a sensitive issue which is influenced by the dynamic and interactive relationship between anthropogenic sources (urban, industrial and agricultural activities) and natural processes (governed by hydrographic inputs facilitating weathering processes) (Simeonov *et al*., 2003). Gower (1980) further identifies a complex system of dynamic interactions, in which the quality of water and sediment associated with a river or channel is a product of a series of interactions between soil, rock and biotic components within the catchment, as well as their associated processes including weathering and mineralization of sediment, soil leaching and sorption processes. Catchments vary in characteristics such as landscape structures and processes including geographical location, geology, geomorphology, biogeochemical processes, and the extent of human activity such as resource exploitation, transportation and urbanization, all of which are ultimately reflected in the physico-chemical quality of catchment river systems (Gower, 1980).

1.6.1 Natural catchment processes

Although the deterioration of river chemistry and water quality is primarily attributed to human activities, certain natural phenomena can also exert substantial influence (Bartram and Ballance, 1996). Within a catchment system, there is a complex interplay between landscape ecology and hydrology at different spatial and temporal scales, all of which ultimately govern the quality of water and sediment in river systems through the processes, pathways, and the variation extent of controlling factors dominant in a given drainage basin (Perona *et al*., 1999; Schröder, 2006). This is facilitated by an intimate connectivity between the catchment landscape components and ecological processes in response to hydrological regime operating within a catchment, and has subsequently led to an interdisciplinary approach to catchment sciences involving hydrological and ecological considerations in watershed studies (Tetzlaff *et al*., 2007). These interdependencies and connections between catchment hydrology and ecology at different spatial and temporal scales form the basis of new hydrological theories in an attempt to gain understanding of process interactions and the subsequent effects on river chemistry and water quality (Hopp *et al*., 2009). It is therefore important to acknowledge that the physico-chemical composition of any hydrological system is highly variable over space and time, and approaches an equilibrium state in composition through various geological, hydrological and biological interactions (Bartram and Ballance, 1996). Rodriguez-Iturbe *et al*. (2001), illustrate the complexity and dynamic properties of water-controlled ecosystem characteristics which can be attributed to the interrelated links between climate, soil and vegetation (**Figure 1.1**). Whilst this list is not all inclusive in terms of catchment processes, it does represent some of the most dominant processes governing a catchment river systems quality which have been extensively reported on in international journals (Sidle *et al*., 2006).

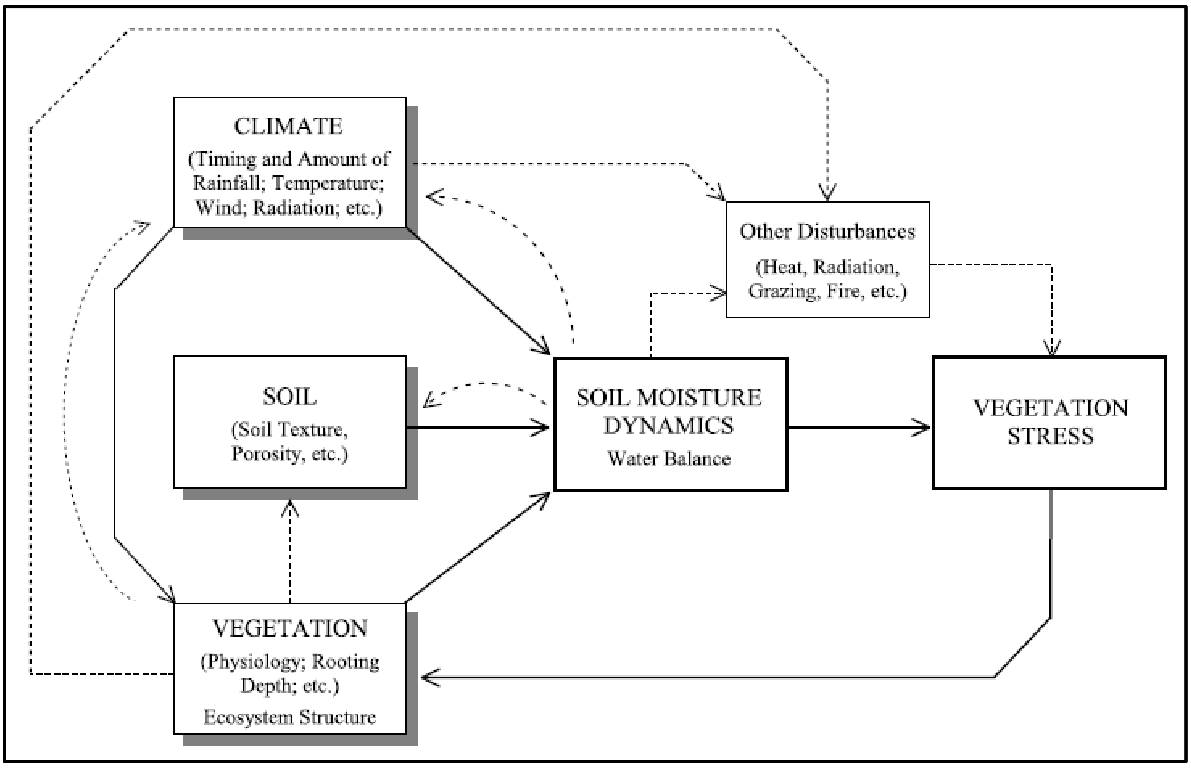

Figure 1.1: Conceptual model showing the interactions of natural catchment processes across different spatial and temporal scales (Source: Rodriguez-Iturbe *et al*., 2001).

1.6.1.1 Hydrological processes

On a broad scale, Gower (1980) identifies precipitation input resulting from climatic and landscape interactions, as the cause of the dynamic environment adapting to the disturbance regime which is ultimately reflected in the quality of receiving systems. Climatic changes affecting the intensity and duration of rainfall, are important in terms of catchment processes (hillslope runoff and erosion) and resulting channel processes (magnitude and frequency of flow events and sediment regime), all of which are reflected in channel morphology and chemistry (Dollar and Rowntree, 1995). In fact, hydrographic inputs as a result of seasonal variations on the catchment scale, have resulted in significant effects on dissolved nutrient concentrations and loadings relative to the river's discharge (Interlandi and Crockett, 2003; Sigleo and Frick, 2007; Zhu *et al*., 2005). Further local and international studies have shown the range of chemical parameters in river systems to be modified by the diluting and concentrating effects of tributary inflows which in turn may be directly related to precipitation input and subsequent surface runoff into receiving water bodies or lack thereof, or as a consequence of specific physico-chemical characteristics governing element persistence in the water column (De Villiers and Malan, 1985; Papafilippaki *et al*., 2008; Raj and Azeez, 2009).

Precipitation input resulting from large scale climatic variability is also intricately linked to a series of smaller and more complex sub-processes within the catchment ecosystem as a result of soil processes and catchment condition such as biological responses and geochemical cycles, and is facilitated by the hydrological response of the associated catchment by a number of catchment landscape characteristics including shape, size, land cover and drainage network geometry (Gironas *et al*., 2007). As such, precipitation input and seasonal changes in river dynamics are important in quantifying water quality facilitated by the transformation and transportation of in-stream constituents, and has formed the basis of many studies (Crosa *et al*., 2006; Guo *et al*., 2008; Perona *et al*., 1999; Simeonov *et al*., 2003; Solidoro *et al*., 2004). Although DeFries and Eshleman (2004) states that the present understanding of land use effects on hydrological processes can be obtained by controlled experimental observations on precipitation inputs and river discharge outputs, Moldan and Cerny (1994) states that the major limitation of such watershed studies is the lack of understanding and influence of principle biological and geochemical processes influencing the quality of in-stream water and sediment. It is therefore important to recognize that the hydrological processes operating on a catchment scale are tightly connected to other aspects of ecosystem function (Zhou *et al*., 2004).

1.6.1.2 Biological processes

On a less extensive scale, ecological patterns and processes may respond to hydrological patterns through biotic interactions such as competition and predation, which can ultimately govern the quantity and quality of water reaching surface water bodies (Schröder, 2006). This is often demonstrated by the composition and density of vegetation cover in response to hydrological input, which in turn directly influences the quality of receiving waters by direct interception of surface flow or lack thereof, thus affecting sediment delivery (Gurnell and Gregory, 1995). Organic matter, alive or dead, changes incoming precipitation with respect to both quantity and quality as a substantial part of deposited heavy metals accumulate in the catchment and is bound to organic matter, with runoff concentrations showing strong correlation to soil acidification and leaching of soluble humic substances (Moldan and Cerny, 1994). Vegetation cover has also been shown to indirectly influence the quality of receiving waters through the routing of water transmitted to rocks and a subsequent effect on the geochemistry of receiving waters which is further altered through in-stream processes (Gurnell and Gregory, 1995). It is clear that on the one hand vegetation dynamics may be controlled by climate and soil, whilst on the other hand vegetation exerts control on the water balance and governs feedbacks to the atmosphere (Rodriguez-Iturbe *et al.*, 2001). The hydro-chemical response of catchment ecosystems could serve as a clear reflection of these terrestrial biochemical processes facilitated by the drainage of soils from the land habitat (Sliva and Williams, 2001). Schröder (2006) uses the example of riparian vegetation adapting to environmental conditions which can ultimately affect the quality of water reaching a water body through alterations in surface runoff as a consequence of the impact of plant physiology on water uptake and storage. In fact riparian processes have shown to play a significant role in controlling general nutrient chemistry (Jarvie *et al.*, 2008; Lowrance *et al.*, 1984). However, Tran *et al*. (2010) states that although riparian habitat can effectively reduce non-point source pollution, it cannot eliminate all water quality issues resulting from land use management especially in cases when contaminants are piped directly into rivers.

On an even smaller and microscopic scale, Weiner and Matthews (2003) further identifies an interplay of ecological cycles driven by biodegradation as well as aerobic and anaerobic decomposition processes, all of which governs the quantity of nutrients occurring in natural waters. There are various processes of nutrient balance in a catchment ecosystem including decomposition, nitrogen transformations (nitrogen fixation, nitrification, ammonification, denitrification), mineralization of nutrients and the cycling of energy which are all directly or indirectly mediated by microbiological components of the ecosystem (Moldan and Cerny, 1994). Furthermore, the concentration of biologically active components within an aquatic ecosystem (Oxygen, Nitrogen, Sulphur and Iron) are predominantly controlled by microbial processes which in turn relate to redox conditions, which illustrates the intimate link between microbial composition and chemical conditions (Bougon *et al.*, 2009). This may be illustrated by the growth, death and decomposition of both terrestrial and aquatic vegetation which can further affect the concentrations of nitrogenous and phosphorous nutrients, pH, carbonates, dissolved oxygen and other chemicals sensitive to oxidation/reduction conditions, either directly through their biological life cycles within a hydrological system, or in conjunction with various slope processes (Bartram and Ballance, 1996).

1.6.1.3 Geochemical processes

Apart from biochemical processes involving the interactions between biota and the atmosphere or biota and soil, most important are the interactions between solution and soil (adsorption, chemical weathering, cation exchange), which are largely dependent on river chemistry and soil geochemical properties of the system, which in turn are influenced by various geological processes (Moldan and Cerny, 1994; Moog *et al*., n.d.). These geochemical processes can significantly affect the flux of nutrients and trace elements to adjacent marine environments (DeMaster *et al*., 1991). The bedrock geology and mineralogy of a catchment are important components of the hydrological processes operating within a catchment and are important factors governing the distribution of flow rates and river chemistry (Moldan and Cerny, 1994). Precipitation input may further interact with the surrounding landscape geology which results in physical and geochemical weathering and the subsequent transfer of soil particles and its associated constituents into receiving water bodies (Novotny, 2003). This is facilitated by the conversion of precipitation input into runoff which is then absorbed into the soil, such that the quality of water produced as river flow largely depends on its associated conversion and absorption processes, as well as the condition of land receiving the precipitation (Bullard, 1966). For example, the bioavailability and geochemical cycling of trace metals within a rivers water column, which has been shown to be highly variable and severely influenced by factors such as pH and ionic strength of the substrate, may in effect be strongly influenced by an influx of low pH waters from catchment runoff (Abraham *et al*., 2006; Kramer and Allen, 1988; Urban *et al*., 1990).

Bartram and Ballance (1996), further state that some chemical elements occurring within the water column in any given hydrological system, may be related to their affinity for fine particulate matter and, as a result of precipitation/dissolution and adsorption/desorption reactions, may occur in trace amounts in solution. During their transport within the water column, trace metals may undergo numerous changes in their speciation owing to chemical processes such as dissolution, precipitation input, and sorption processes; all of which affects their behaviour and bioavailability in the environment which in turn relates to the subsequent concentration or accumulation as well as biomagnifications across the trophic levels of the food chain (Fergusson, 1990; Papafilippaki *et al*., 2008). This situation is even more worrisome owing to rapid industrial development and the subsequent impact on the environment, such that concentrations of metals in soils are elevated far beyond the natural occurrence, or natural background values associated with the underlying geological substrate (Manjunatha *et al*., 1996). These background values or Clarke values form the basis of enrichment detection and are important in discriminating between natural and anthropogenic sources of sediment contaminants, and have become particularly useful in the absence of appropriate South African sediment quality guidelines (Sukdeo, 2010). Several studies have successfully applied geochemical background or Clarke values in universally accepted geochemical indices as a method of analyzing enrichment due to land use management, and this has allowed for the successful discrimination of natural and anthropogenic inputs of trace metals in the sediment column (Chakravarty and Patgiri, 2009; Kaushik *et al*., 2009; Liu *et al*., 2005; Manjunatha *et al*., 1996; Olivares-Rieumont *et al*., 2005; Sekabira *et al*., 2010; Varol, 2011; Wang *et al*., 2012). The importance of various soil types on river chemistry depends on the water pathways in the terrestrial system which may vary as a function of precipitation intensity and subsequent biochemical processes (Moldan and Cerny, 1994).

1.6.2 ANTHROPOGENIC CATCHMENT ACTIVITIES

Natural processes which operate within a catchment ecosystem are often affected by anthropogenic activities, with profound effects on the biogeochemical metabolism of catchment ecosystems and subsequent ecological stability of the surrounding landscape (**Figure 1.2**) (Moldan and Cerny, 1994; Finger, n.d.). This may be facilitated by changes in leaching of nutrients to water bodies, enhanced chemical weathering, and enhanced mobilization of heavy metals as a result of organic pollution for example (Herczeg *et al*., 2004; Moldan and Cerny, 1994). This is achieved either directly through structural interventions in the hydrological cycle such as canalization and damming of rivers, or indirectly through uncontrolled land use development including urbanization and agriculture (Chapman, 1992). Humans have proven to be the most effective geomorphic agent in altering the landscape and thus river dynamics and chemistry (Farnsworth and Milliman, 2003). Several studies have shown that rivers are generally stressed by nutrients from catchment associated activities (Mokaya *et al*., 2004; Ahearn *et al*., 2005; Masamba and Mazvimavi, 2008; Mendiguchia *et al*., 2007; Monaghan *et al*., 2007). The effects of anthropogenic influences on in-stream chemistry is often detrimental to the ecological patterns and processes of the natural aquatic environment, with possible long term effects on ground and surface water sources (Chapman, 1992).

Human-induced changes, in particular land use management, are strongly associated with degrading river chemistry and water quality and has shown to have significant impacts and relationships on the transport and delivery of sediment, pollutants and nutrients (Bullard, 1966; Dauer *et al*., 2000; Farnsworth and Milliman, 2003; Rhodes *et al*., 2001; Roselli *et al*., 2009; Wilkinson and McElroy, 2007; Weijters *et al*., 2009). Further studies show that human-induced catchment changes have profound effects on the integrity of aquatic ecosystems, including the functioning, abundance and biodiversity of aquatic organisms (Allan *et al*., 1997; Chapin *et al*., 1997; Harding and Winterbourn, 1995; Harding *et al*., 1998; Osmundson *et al*., 2002; Quinn *et al*., 1997; Richards *et al*., 1997; Wood and Armitage, 1997). In the South African context, several catchment studies have highlighted the negative impacts of anthropogenic land use on river water quantity and quality, and stress the need for rehabilitation and restoration efforts (Dabrowski and de Klerk, 2013; De Villiers, 1993; De Villiers and Malan, 1985; Du Preez and De Villiers, 1987; Naidoo, 2005; Pillay, 2002; Walsh and Wepener, 2009). Bayley (1995) attributes these relationships to the dynamic interaction between rivers and land which is considered to be the principal process in the formation of river-floodplains affecting the adaptation and evolution of biota. Physical alteration of the catchment such as urbanization, agriculture, deforestation, mining and transportation results in the alteration of hydrological systems thus affecting river chemistry based on the materials present in the water column (Gower, 1980). In general human activities have strongly influenced quality of river systems by upsetting the natural *status quo* (Boyd, 2000).

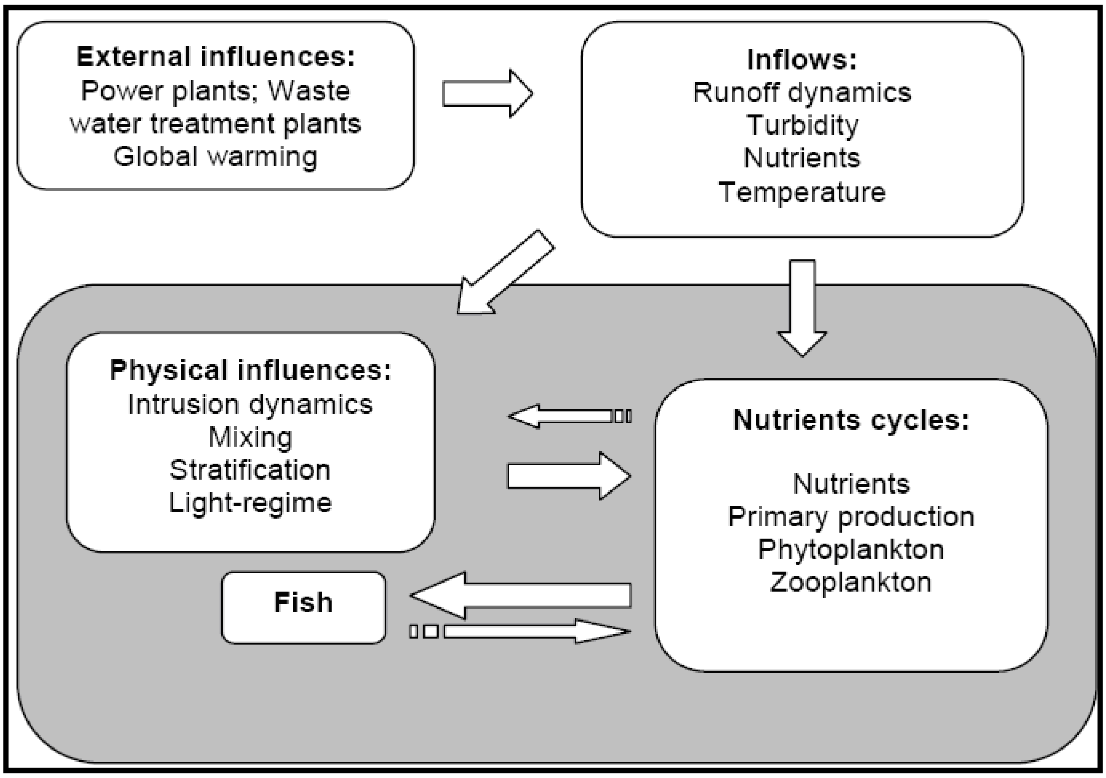

Figure 1.2: Conceptual model showing the influence of anthropogenic catchment processes across the dominant natural processes and cycles within the catchment (Source: Finger, n.d.).

1.6.2.1 Impacts of urbanization

The construction of urban areas and impervious artificial surfaces increases the volume of surface runoff in relation to infiltration, resulting in poor recharge of groundwater reserves and causing the transportation of excess pollutants and sediments from these surfaces into the river (Butler and Davies, 2000). This increases the potential to scour surfaces and to raise pollutant levels by both eroding surfaces and releasing material from temporary sinks, all of which ultimately governs the water and sediment quality of the river (Mitchell, 2005). Rapid urbanization and population growth have further led to increasing loads of faecal wastes and pollutants damaging natural water resources, such that the extent of pollution often has significant impacts on the use of water by humans for drinking, recreation and irrigation (Griesel and Jagals, 2002). Water resources in South Africa face a severe pollution threat due to rapid demographic changes coinciding with settlements that have a lack of proper water supply and sanitation (Fatoki *et al*., 2001). Several studies reveal that certain changes in river chemistry and water quality were attributed to the effects of urbanization (Atasoy *et al*., 2006; Chang, 2008; Masamba and Mazvimavi, 2008; Ometo *et al*., 2000; Ren *et al*., 2003; Tong and Chen, 2002). This is again verified in studies by Poor and McDonnell (2007), where high base flows were observed in the residential catchment. Additionally, Li *et al*. (2008) show a positive correlation was observed between dissolved phosphorous and percentage urban area within the Han River basin of China.

1.6.2.2 Impacts of agriculture

Modern intensive agriculture further affects river chemistry and water quality in catchment ecosystems primarily by increasing nutrient leakage and sediment loading into water sources through the extensive use of fertilizers and pesticides (Gower, 1980; Weiner and Matthews, 2003). In addition, feedlot drainage and aquaculture can significantly increase the amount of *faecal coliform* bacteria and nutrient loading into rivers through nearby surface runoff (Weiner and Matthews, 2003). Numerous studies have shown agriculture to play a significant role in governing the nutrient status and chemistry of river systems (Ahearn *et al*., 2005; Arbuckle and Downing, 2001; Collins and Jenkins, 1996; Fatoki *et al*., 2001; Poor and McDonnell, 2007; Monaghan *et al*., 2009; Monaghan *et al*., 2007; Tong and Chen, 2002). In addition, cultivated lands serve as a major source of erosion and are responsible for the transfer of sediment and its associated constituents into surface channels (Bullard, 1966). Ultimately, humans have simultaneously increased the sediment transport of global rivers yet reduced the flux of sediment and nutrients reaching the coastline as a consequence of being trapped by water impoundments, resulting in accelerated coastal erosion with negative implications on river chemistry (Ahearn *et al*., 2005; Syvitski *et al*., 2005).

1.6.2.3 Impacts of industry

The effect of humans' social and industrial activities can be seen in the extent to which river chemistry and water quality changes as a river flows from its source to the sea, during which, water is abstracted for potable and industrial use and then returned to the river as effluent

(Gower, 1980). Acids and bases associated with industrial and mining activities pose a severe threat to aquatic organisms and people dependant on rivers as a source of domestic water supply (Weiner and Matthews, 2003). Discharge of untreated waste and leaching of noxious liquids associated with industrial activity poses a similar threat to the aquatic environment (Chapman, 1992; Nedeau *et al*., 2003). In general, effluents are rarely the same quality as the raw water from which they are derived and are normally contaminated with some form of pollution posing a threat to water quality and aquatic communities (Gower, 1980). Other studies have shown that river chemistry and water quality associated with industrial activity is generally contaminated by high concentrations of heavy metals (Birch and Taylor, 1999; Mendiguchia *et al*., 2007; Rosales-Hoz *et al*., 2003).

1.7 MONITORING TECHNIQUES FOR RIVER CHEMISTRY AND WATER QUALITY

The process of monitoring involves the sampling, measurement and recording of data which is often measured against required objectives and targets (Bartram and Ballance, 1996). Traditionally, the monitoring of river chemistry and water quality focused on ascertaining whether observed findings rendered a water source suitable for intended uses, but has now evolved to determine water quality trends and causes in the environment, to determine ways in which it is affected by contaminant release, land use and other anthropogenic activities, and to enforce standards and water quality legislation (Antonopoulos *et al*., 2001; Peters *et al*., 1994). More recently, the analyses of sediments has been seen as a favourable method of heavy metal pollution detection in surface waters as heavy metals seldom remain in the water column and are often readily adsorbed to fine particulates and sediment in the aquatic environment (Charkhabi *et al*., 2008). In fact, several recent studies in South Africa have focussed on sediment analyses as a method of pollution detection in water bodies (Abed, 2006; Binning and Baird, 2001; David, 2006; Sukdeo, 2010). Watershed management and catchment monitoring studies focusing on in-stream water and sediment quality have become crucial in assessing the impact and extent of human development and subsequent effects on receiving waters (Sliva and Williams, 2001). Most river monitoring is mainly based on the analyses of chemical data, however biological data has become an increasingly important tool in assessing the long-term water quality status and disturbance regime of freshwater river systems (Jahnig and Qinghua, 2010). The subsections that follow further explore each of these analytical tools in assessing river quality and health.

1.7.1 ANALYTICAL ANALYSIS TECHNIQUES

Skoog *et al.* (2004) identifies and classifies the typical quantitative physico-chemical monitoring process into a number of analytical methods and techniques which, depending on the parameter of interest, requires the application of prescribed steps and procedures. The methods of sample analyses can be broadly classified to include gravimetric methods, volumetric methods, electro-analytical methods and spectroscopic methods (Skoog *et al.,* 2004).

Gravimetric analyses comprise a series of steps to obtain the final mass of an analyte or compound of interest by means of an analytical balance (Skoog *et al.,* 2004). The main use of gravimetric analyses is based on the determination of total solids by evaporation and suspended solids by filtration, with a sensitive analytical balance and drying apparatus being essential in this type of analytical analysis process (Tchobanoglous and Schroeder, 1985). An example of the application is in the measuring of suspended solids after solid-liquid separation and sulphate ions (SO_4^{2-}) which can be determined by barium sulphate ($BaSO_4$) precipitation (Naidoo, 2005). However, gravimetric procedures are avoided as much as possible owing to their time consuming processes (Sawyer *et al.,* 2003).

Volumetric analyses allow for the rapid and convenient determination of variables including alkalinity and chlorides, where the reagent volume of standard solutions completely reacts with an analyte and is measured, such that the final calculation is based on volume measurements (Skoog *et al.,* 2004). Reactions carried out as titrations with indicators, used to determine the end point of the reactions, are termed titrimetric analyses (Naidoo, 2005). Most elemental determinations can be easily and conveniently obtained through volumetric analysis techniques making it suitable for field applications if necessary (Tchobanoglous and Schroeder, 1985). Volumetric methods are more commonly used in relation to gravimetric methods owing to the time saving process, and is utilized for many determinations such as dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD) and chlorides (Sawyer *et al.,* 2003).

Electro-analytical methods involve a series of steps to measure the electrical properties of the analyte including potential, current, resistance and electrical charge (Skoog *et al.,* 2004). For many years pH, which is an indication of the acidity or alkalinity of a solution, was measured using a glass electrode sensitive to hydrogen ions in solution (Gray, 1994). More recently many electrodes have become available which are sensitive to specific ions in solution such as ammonium, nitrate, sodium and calcium, thus greatly enhancing the accuracy of the ion concentration determination (Tchobanoglous and Schroeder, 1985). In such a process the suitable electrodes are placed into a solution of interest and a voltage is applied, with the current flow dependent upon the solution composition thus enabling the derivation of analytical measurements (Sawyer *et al.,* 2003). Several other methods based on this principle allow for the modifications of different electrical methods of analyses suited for the parameter of interest (Sawyer *et al.,* 2003).

Spectroscopic methods involve the measurement of radiation by analytes or the interaction between electromagnetic radiations and the analyte atoms or molecules (Skoog *et al.,* 2004). All instruments designed to measure radiant energy comprise of three basic components as identified by Sawyer *et al*. (2003):

- An energy source to provide radiation at a given wavelength;
- An energy spreader permitting the separation of radiation of the desired wavelength from other radiation; and
- An energy detector which measures the proportion of radiation intensity that passes through the sample.

Bartram and Balance (1996) differentiate the use of quantitative physico-chemical monitoring activities into long-term, short term and continuous monitoring. According to these authors, long-term monitoring involves the prolonged period of measurement and observation of aquatic environments to observe trends and patterns in the data; short-term monitoring is finite and is generally used to assess the aquatic environment through measurements and observations, and to determine the water quality for an intended purpose; and continuous monitoring generally involves the continuous measurement and observations for water quality management purposes.

Although these quantitative techniques are based on evolving instrumental laboratory analyses and has been extensively utilized with high degrees of accuracy, it has more recently been described as falling short in water quality assessments of aquatic ecosystems in the sense that it merely provides snapshot information on a constantly changing and dynamic ecosystem (Schletterer *et al.*, 2011). These classic approaches to water quality assessments and monitoring are also costly and merely provide instantaneous measurements in a dynamic ecosystem, and as such there has more recently been a shift toward biological monitoring of aquatic ecosystems owing to a better evaluation of prevailing ecosystem conditions in terms of water quality (Du *et al.*, 2009; Taylor *et al.*, 2007a and b; Kalyoncu *et al.*, 2009; Wunsam *et al.*, 2002).

1.7.2 Biological monitoring techniques

Biological indicators are considered organisms which, by their own presence or absence, indicate the existence or abundance of a particular critical factor, thus exhibiting a defined tolerance to environmental stimuli (whether the latter is natural or anthropogenic by origin) (Phillips and Rainbow, 1993). Biological communities within aquatic ecosystems are useful in reflecting both the present and past water quality within the environment facilitated by the continuous integration and reflection of various physical and chemical stressors as depicted in **Figure 1.3** (de la Rey *et al.*, 2004; Taylor *et al.*, n.d.(b)). This period of integration and reflection may not necessarily be present at the time of sampling involved in analytical analysis procedures thereby making the use of biological assessments more appealing in terms of water quality assessments (Kalyoncu *et al.*, 2009). As such, biological monitoring techniques have been extensively utilized to assess freshwater organic pollution and the overall status of habitat conditions owing to their simple and reliable application and higher degrees of temporal stability thus providing a more long term and accurate picture of prevailing environmental conditions (Jahnig and Qinghua, 2010). For example, in mineral exploration, geologists may study the distribution of plant species to indicate the presence or absence of critical concentrations of minerals or trace metals in soils (Phillips and Rainbow, 1993).

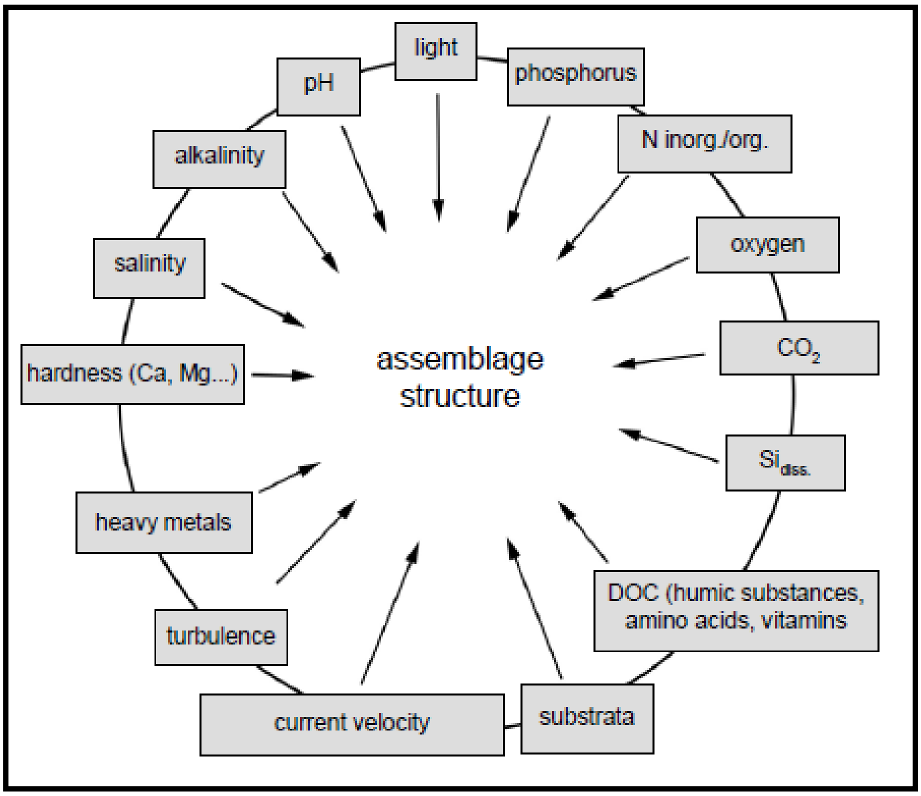

Figure 1.3: Influence of environmental factors on diatom assemblages (Source: Taylor *et al.*, n.d.(b)).

In aquatic environments, the degree of pollution in particular locations is commonly quantified through the analyses of benthic community structures, with alterations in biomass and structure of aquatic communities being widely documented as useful pollution indicators such as organic enrichment (Phillips and Rainbow, 1993). Whilst there are several approaches to biological monitoring, one of the most commonly used biological monitoring indicators utilized in river systems are diatoms, owing to their strong responses to environmental change, their availability throughout the year, and their short life cycles; allowing for the rapid identification of these changes (Schletterer *et al*., 2011). Diatoms are autotrophic unicellular organisms which form the base of aquatic food chains and comprise important components of algal assemblages in freshwater bodies (de la Rey *et al*., 2004). In terms of the South African context, Harding *et al*. (2005) states that diatoms provide a clear indication of specific changes in water quality and underlying substrate, and are useful as biological indicators of ecosystem changes for several reasons:

- Their occurrence in all types of aquatic habitats for most parts of the year and sensitivity to nutrient concentrations and environmental change (e.g. light intensity) therein. This is largely related to the fact that diatoms are primarily autotrophic forming the base of the food chain within aquatic ecosystems;
- Each taxon is defined by specific water chemistry requirements and an optimum tolerance range which can be used as indicators of ecosystem change reflected in the assemblage composition and structure of the taxon;
- As they possess the shortest life cycles of all biological indicators, they reflect these changes in the ecosystem to a measurable extent within two to three weeks;
- Owing to their diverse assemblage structure, diatoms serve as a source of significant ecological information pertaining to the surrounding aquatic habitat; and
- The taxonomy and environmental preferences of diatoms is comprehensively documented allowing the direct applicability of diatom bio-monitoring in most South African rivers.

Owing to their suitability for river pollution assessments, diatoms have been extensively utilized as bio-indicators in numerous countries across the world and this has led to the generation of several diatom-based pollution indices for routine use in environmental monitoring, with index scores often showing an accurate reflection of environmental conditions (Kalyoncu *et al*., 2009; Taylor *et al*., 2007a and 2007b; Walsh and Wepener, 2009). In fact, it has become internationally recognized with research showing that the use of diatoms as environmental indicators of organic pollution and morphological changes has shown to reveal important relationships between surrounding environmental parameters (including substrate sediment size and physico-chemical parameters) in aquatic ecosystems and the distribution, abundance and size of diatom species assemblages (Blackburn *et al*., 2009; McQuoid and Nordberg, 2003; Mendes *et al*., 2009; Singh *et al*., 2010; Uthicke and Nobes, 2008).

1.8 PHYSICO-CHEMICAL PARAMETERS IN THE ENVIRONMENT

Physico-chemical parameters can be classified in several ways but are commonly grouped in the physical, chemical and microbiological categories (Boyd, 2000). Analytical estimations of variables belonging to these categories provide important information on water and sediment quality, and require analysis of various characteristics including colour, dissolved and suspended solids, heavy metals and pathogenic microbes (Tomar, 1999). The selection of individual or combination of variables for an assessment or program is largely related to meeting the objectives of that program in the most accurate, efficient and cost effective way (Chapman, 1992). The sub divisions that follow, based on Tomar (1999), provide information pertaining to the origins, properties, behaviours and ecological effects of variables that were utilized to assess the water and sediment quality of the catchments in this study.

1.8.1 PHYSICAL CHARACTERISTICS

Physical characteristics reflect palatability and aesthetic acceptability in response to the senses of touch, sight, smell, or taste (Tomar, 1999). Physical characteristics of a water body collectively include turbidity, temperature, conductivity and total dissolved solids (Tchobanoglous and Schroeder, 1985).

1.8.1.1 Total dissolved solids (TDS)

TDS is a measure of the quantity of all compounds dissolved in the water column and is directly proportional to electrical conductivity, which can be used to estimate TDS concentration (DWAF, 1996a). Since most dissolved substances in water carry an electrical charge, the total dissolved salts concentration is used as an estimate of the TDS concentrations in water (DWAF, 1996a). Water bodies can contain varying amounts of TDS attributed to the dissolution of minerals of geological formations, and physical processes such as evaporation and rainfall (DWAF, 1996a). A high concentration of TDS is damaging to aquatic plants and organisms and poses a threat where water is used for irrigation. TDS is expressed in mg/L (Hounslow, 1995).

1.8.1.2 Conductivity

Conductivity or electrical conductivity is the ability of water to conduct an electrical current and is an indirect measure of ion concentration (Hounslow, 1995). Conductivity is a measure of ions, within the water body, that carry an electrical charge (DWAF, 1996a). The more ions present, the more electricity can be conducted by water. Conductivity is measured in microsiemens per centimetre (μS/cm) (Chapman, 1992). Most organic compounds dissolved in water do not dissociate into ions, and consequently do not affect the conductivity (DWAF, 1996a).

1.8.2 Chemical characteristics

The quantity and quality of chemical substances produced by human activities may be present in water and in-stream sediment in varying concentrations according to their abundance, solubility and other physico-chemical qualities (Tomar, 1999). Chemical parameters commonly include acidity and alkalinity (pH), nutrients and ions (Tchobanoglous and Schroeder, 1985).

1.8.2.1 pH

The pH parameter or the 'potential of hydrogen' measures the concentration of hydrogen ions present in a medium, providing an indication of the acidity or alkalinity therein (Weiner and Matthews, 2003). On a scale of 0 – 14, a reading of 7 is considered neutral, below 7 indicates acidity and above 7 indicates alkalinity (Chapman, 1992). Most naturally occurring freshwater bodies in South Africa range between pH 6 and 8 (DWAF, 1996a). The pH of water is important as it affects the solubility and availability of nutrients and how they are utilized by aquatic organisms, and also affects the toxicity of trace metals, ammonium and certain elements within a water and sediment column in a water body (DWAF, 1996a).

1.8.2.2 Ammonia (NH_4)

Ammonia can occur in an un-ionized form (NH_3) or in the ionized form as the ammonium ion (NH_4^+), of which its toxicity is a function of the concentration of the NH_3 form (DWAF, 1996a). Ammonia is an important component in the nitrogen cycle and is often oxidized in the environment by microorganisms, making it a large source of available nitrogen to the aquatic environment (Canadian Council of Ministers of the Environment (CCME), 2010). It can be produced naturally through degradation of nitrogenous matter or introduced as a pollutant from fertilizer runoff or sewage discharge (DWAF, 1996a). The toxicity of ammonia is a function of temperature and pH, such that an increase in either will result in an increase in toxicity with chronic and lethal effects on aquatic biota (DWAF, 1996a). Ammonia is highly soluble in water and its chemical speciation is largely affected by a range of chemical parameters including pH, temperature and ionic strength (CCME, 2010). The target water quality range of unionized ammonia in South African freshwater ecosystems is 0.007 mg/L (DWAF, 1996a). The South African water quality target range of ammonia in the coastal zone is 0.02 mg/L for the un-ionized form (as NH_3), and 0.6 mg/L for the ionized form (NH_4^+) (DWAF, 1995).

1.8.2.3 Phosphorous (P)

Phosphorous is an essential macronutrient controlling plant growth in aquatic systems and is seldom present in high concentrations (Boyd, 2000). It does not occur as elemental phosphorous in the environment but instead occurs in several organic and inorganic forms of phosphate (DWAF, 1996a). These can be subdivided into three main forms in aquatic ecosystems namely inorganic phosphorous, particulate organic phosphorous, and dissolved (soluble) organic phosphorous (CCME, 2004). The different forms of phosphorous in the aquatic environment are continuously changing through decomposition and synthesis processes between the organic and oxidized inorganic forms (DWAF, 1996a). Phosphorous occurs naturally in the aquatic environment by the weathering of phosphorous-bearing rocks and decomposition of organic matter, but can also have elevated levels attributed to domestic, industrial or agricultural effluent, all of which have the potential to cause eutrophic conditions (DWAF, 1996a). Phosphorous levels range from 0.005 to 0.020 mg/L in most natural surface waters (Chapman, 1992). Inorganic phosphorous concentrations in South African freshwater sources at concentrations < 0.005 mg/L indicates oligotrophic conditions characterized by moderate levels of species diversity, low productivity, rapid nutrient cycling and no nuisance growth of aquatic plants; concentrations ranging from

0.005 – 0.025 mg/L indicates mesotrophic conditions with high levels of species diversity, productive systems, nuisance growth of aquatic plants and algal blooms which are seldom toxic; concentrations ranging from 0.025 – 0.25 mg/L indicates eutrophic conditions with low levels of species diversity, highly productive systems with aquatic plants and algal blooms that are toxic to man and animals; and concentrations greater than 0.25 mg/L indicates toxic hypertrophic conditions with very low levels of species diversity, very highly productive systems and nuisance growth of aquatic plants and algae which are toxic to man and animals (DWAF, 1996a). The US-EPA international target value for total phosphorous in the marine/estuarine environment is 0.0001 mg/L (DWAF, 1995).

1.8.2.4 Dissolved oxygen (DO)

Dissolved oxygen is the amount of oxygen dissolved in water in mg/L and is critical to the survival of all aerobic aquatic life in rivers, including fish and most invertebrates (Weiner and Matthews, 2003). The ability of water to hold oxygen in solution is inversely proportional to the temperature of the water i.e. the lower the water temperature, the more dissolved oxygen it can hold (DWAF, 1996a). Concentrations of dissolved oxygen less than 100% saturation can reduce reproduction and growth in fish species, whilst super-saturation conditions can prevent photosynthesis as well as the survival of most aerobic aquatic species (DWAF, 1996a).

1.8.2.5 Biological Oxygen Demand (BOD)

Biological oxygen demand is a measure of the amount of oxygen required for the microbial decomposition of biodegradable organic matter present in a water sample (Tomar, 1999). It is defined as the amount of oxygen required for the aerobic micro-organisms to oxidize organic matter into a stable inorganic form within a sample (Chapman, 1992). Toxic substances within the sample affect microbiological activity thereby resulting in very low BOD concentrations (Chapman, 1992). Unpolluted waters generally have BOD values of less than 2 mg O_2/L with areas receiving wastewaters having values of up to 10 mg O_2/L or more (Chapman, 1992).

1.8.2.6 Chemical Oxygen Demand (COD)

Chemical oxygen demand is a measure of the oxygen required to oxidize the organic matter in a water sample to CO_2 and water (Tomar, 1999). Due to the fact that this process involves the oxidation of organic matter with strong oxidizing chemicals, COD values include the biodegradable and non-biodegradable oxygen demand, and consequently COD values are larger than BOD values especially in the presence of large amounts of biologically resistant organic matter (Tomar, 1999). COD concentrations in surface waters occur at values of 20 mg O_2/L or less in unpolluted waters, to values greater than 200 mg O_2/L in waters receiving effluents (Chapman, 1992).

1.8.2.7 Sulphur (S)

Sulphur occurs naturally in numerous minerals in the Earth's crust such as barite, epsomite, and gypsum (British Columbia Ministry of Environment (BCME), 2000). Sulphur often combines with oxygen to form the divalent sulphate ion (SO_4^{2-}), and the reversible reaction between sulphide and sulphate in the natural environment is often referred to as the sulphur cycle (BCME, 2000). Sulphide formation is principally through anaerobic, bacterial decay of organic substances in the bottom sediments of rivers (Chapman, 1992). Sulphate is the stable, oxidized form of sulphur which is readily soluble in water (Chapman, 1992). Common anthropogenic sources of sulphur into the aquatic environment include industries and atmospheric precipitation (Chapman, 1992). Sulphate concentrations in natural waters usually range between 2 – 80 mg/L, but can exceed concentrations of 1 000 mg/L through industrial input and in arid regions with sulphur containing minerals. Concentrations of sulphate above 400 mg/L give drinking water an unpleasant taste (Chapman, 1992).

1.8.2.8 Calcium (Ca)

Calcium occurs naturally in the Earth's crust with a single common oxidation state of +2 (vanLoon and Duffy, 2000). Calcium is an essential component of all organisms as it is incorporated in the shells of most invertebrates and the bones of all vertebrates (Chapman, 1992). It occurs in most suspended and sedimentary material and can dissociate from these solids and become mobile in the water column under acidic conditions, therefore any natural or anthropogenic process producing acidity results in an increase of calcium concentration in water (vanLoon and Duffy, 2000). In fact this is a common property of most heavy metals and is illustrated in many studies (Cheung *et al*., 2003; Papafilippaki *et al*., 2008; Yahaya *et al*., 2009). Another distinguishing property of calcium, together with other heavy metals, is the ability to transport and concentrate within the food chain thereby resulting in toxic effects at high levels of the food chain – a phenomenon commonly known as bioaccumulation of heavy metals at higher trophic levels (Oliver, 1973). Anthropogenic sources that increase the levels of naturally occurring calcium include industrial and wastewater treatment processes (Chapman, 1992). The typical concentration of calcium in freshwater is less than 15 mg/L (Chapman, 1992).

1.8.2.9 Magnesium (Mg)

Magnesium is an essential macronutrient for plants and animals and is naturally derived in water bodies through the weathering of rocks with ferromagnesian minerals as well as some carbonate rocks (Chapman, 1992). Together with calcium, it is responsible for the hardness of water (Sawyer *et al*., 2003). It is an essential element for living organisms with natural concentrations ranging from 1 to 100 mg/L (Chapman, 1992). Deficiency of magnesium has negative implications on plant photosynthesis and causes skeletal deformities and reduced reproductive capabilities in vertebrates (DWAF, 1996a). However, high concentrations are toxic and can cause disturbances to metabolism and the central nervous system of vertebrates (DWAF, 1996a). Toxic sources of magnesium include various steel, fertilizer and chemical industries (DWAF, 1996a).

1.8.2.10 Sodium (Na)

Sodium is the most nontoxic metal found in natural waters and is abundant in the Earth's crust (Tomar, 1999). Sodium salts are highly soluble in water and they are naturally occurring elements, with occurrences in larger concentrations in surface waters as they are commonly derived from industrial effluent and sewage (Chapman, 1992). High concentrations of sodium in water can be hazardous for people suffering from cardiac and kidney ailments and can deteriorate the physical condition of soil, thus reducing its permeability and affecting plant growth (Tomar, 1999).

1.8.2.11 Potassium (K)

Rocks which contain potassium are relatively resistant to weathering accounting for the low concentrations of potassium found in natural waters (Chapman, 1992). Potassium salts are highly soluble in water and is an essential nutritional element easily absorbed by aquatic biota (Chapman, 1992). Potassium salts are widely used in industry and agricultural fertilizers, and consequently enters a water body through industrial discharge or run-off from agricultural land (Chapman, 1992). They usually occur in concentrations of less than 10 mg/L in natural waters (Chapman, 1992).

1.8.2.12 Selenium (Se)

Selenium occurs in the Earth's crust as elemental selenium, ferric selenite and calcium selenite with the SeO_3^{2+} ion being the most stable form of selenium in water (Boyd, 2000). Increased concentrations of selenium in water bodies can be attributed to industrial activities utilizing or discharging selenium and selenium compounds, with its toxicity to fish species being directly related to water temperature (DWAF, 1996a). At low levels selenium is essential in the diet of humans and animals, but can be toxic at high concentrations (Sawyer *et al*., 2003). Selenium can occur in soils in trace amounts but can accumulate in certain plants in quantities that are harmful when ingested (Sawyer *et al*., 2003). Concentrations of selenium are usually below 0.001 mg/L in natural waters, but can range between 0.05 – 0.3 mg/L in areas with seleniferous soils (Boyd, 2000). High concentrations of selenium can be toxic to aquatic organisms resulting in immobilization, reduced survival, reduced reproduction and ultimately death (DWAF, 1996a). Another important effect of selenium on biological organisms is its ability to accumulate in the liver of mammals and fish as it is passed up the food chain, posing a threat to predators (DWAF, 1996a). The target water quality range for total selenium in freshwater sources is 0.002 mg/L (DWAF, 1996a). The US-EPA target water quality value of total selenium in the coastal zone is 0.41 mg/L (DWAF, 1995). The interim soil quality criteria of total selenium concentrations is 2.9 mg/kg in sediment associated with residential land use, and 10 mg/kg in sediment associated with industrial land use (CCME, 2009).

1.8.2.13 Arsenic (As)

Arsenic occurs in many minerals within the Earth's crust as arsenate (AsO_4^{3-}) and occurs naturally at low concentrations in the environment due to its poor solubility and absence in sediment at high concentrations (Boyd, 2000). Arsenic can further occur in several oxidation states depending on the pH and redox potential of the water, with most forms being highly toxic to aquatic organisms (DWAF, 1996a). Factors which control the fate of arsenic in the aquatic system and ultimately its bioavailability include pH and oxidation/reduction potential (CCME, 1999a). Addition of arsenic into the aquatic environment can be attributed through mining operations, arsenical insecticides and combustion of fossil fuels with fallout occurring in aquatic areas (Sawyer *et al*., 2003). Arsenic can be bio-concentrated in aquatic organisms owing to its affinity for organic substances, with exposure causing reduced growth and reproduction in fish and invertebrates, as well as behavioural changes such as reduced migration in fish (DWAF, 1996a). Humans are more sensitive to arsenic than aquatic organisms and therefore consumption of contaminated water poses a greater health risk to humans (DWAF, 1996a). Biological effects associated with elevated arsenic in sediments include decreased invertebrate abundance, increased mortality and behavioural changes (CCME, 1999a). The target water quality range of total arsenic in freshwater ecosystems in South Africa is 0.01 mg/L (DWAF, 1996a). The target marine water quality range for total arsenic in South African coasts is 0.012 mg/L (DWAF, 1995). The probable effect levels of arsenic in sediment associated with frequent adverse biological effects is 17 mg/kg in freshwater sediment and 41.6 mg/kg in marine sediment (CCME, 1999a).

1.8.2.14 Zinc (Zn)

Zinc is an essential micronutrient for all organisms and occurs in two oxidation states in the aquatic environment namely as the metal and as zinc (II), the latter being toxic to aquatic organisms at low concentrations (DWAF, 1996a). Zinc occurs naturally in small amounts in almost all igneous rock, with the natural content of zinc in soils ranging from 1 – 300 mg/kg

(WHO, 2003d). Industries comprise the most influential anthropogenic sources of zinc in the natural environment (DWAF, 1996a). Zinc is one of the more mobile metals in soil with solubility increasing especially at pH < 6 (Fellenberg, 2000). Consequently, soils with a pH > 6 and a high content of clay minerals are commonly characterized with high concentrations of zinc owing to the pH-dependant adsorption process (Fellenberg, 2000). In natural surface waters the concentration of zinc is usually 0.01 mg/L. The toxic effects of zinc in plants begin at 200 mg/kg. Since humans are relatively more resistant to zinc, danger to humans due to its presence is rare (Fellenberg, 2000). The target water quality range for dissolved zinc in freshwater sources is 0.002 mg/L (DWAF, 1996a). The target water quality value of total zinc in the South African coastal zone is 0.025 mg/L (DWAF, 1995). The probable effect levels of zinc concentrations in sediment associated with frequent adverse biological effects is 315 mg/kg in freshwater sediment and 271 mg/kg in marine/estuarine sediment (CCME, 1999g).

1.8.2.15 Copper (Cu)

Copper is an essential trace element which can be toxic to aquatic organisms at elevated concentrations (CCME, 1999b). Copper is a common constituent of surface waters commonly found as complexes or as particulate matter (WHO, 2004). Copper occurs in four oxidation states (0, I, II and III) and can be derived naturally into surface water bodies from weathering and the dissolution of copper minerals in the aquatic environment (DWAF, 1996a). Due to its affinity to particulate matter, iron, manganese and organic matter, copper tends to accumulate in sediment which serves as an important route of exposure to benthic organisms through ingestion (CCME, 1999b). The fate of elemental copper in water is complex and is often influenced by pH and dissolved oxygen (WHO, 2004). Copper is mobile in soil and its solubility in soil increases noticeably at pH < 5 (Fellenberg, 2000). Whilst copper constitutes an important trace element essential for life, it can be toxic to plants at concentrations of 20 mg/kg or more, and toxic to microorganisms at concentrations of about 0.1 mg/L (Fellenberg, 2000). The probable effect levels of copper in sediment associated with frequent adverse biological effects is 197 mg/kg in freshwater sediment and 108 mg/kg in marine sediment (CCME, 1999b). The target water quality range for dissolved copper in freshwater sources ranges from 0.0003 to 0.0014 mg/L as a function of the hardness of water (DWAF, 1996a). The target water quality value of total copper in the South African coastal zone is 0.005 mg/L (DWAF, 1995).

1.8.2.16 Aluminium (Al)

Aluminium is the most abundant metallic element and constitutes 8% of the Earth's crust (WHO, 2003a). Aluminium is released in the environment primarily through natural processes which also influence aluminium mobility and transport in the environment – including chemical speciation, hydrological flow paths, and soil-water interactions and underlying geological material (WHO, 2003a). The solubility of aluminium in surface waters is strongly dependant on pH, whereby elevated concentrations may be mobilized under acidic conditions (DWAF, 1996a). Common natural sources responsible for the mobilization of aluminium in surface waters from soils and sediments include weathering and accelerated acidification processes (DWAF, 1996a). Anthropogenic sources commonly include acid mine drainage or acid rain which have been shown to increase dissolved Al content of natural waters (WHO, 2003a). The concentration of aluminium in natural waters can vary significantly depending on physico-chemical and mineralogical factors (WHO, 2003a). Dissolved aluminium concentrations in waters near neutral pH values usually range from 0.001 to 0.05 mg/L but rise to 0.5 to 1 mg/L in acidic waters or waters rich in organic matter (WHO, 2003a). The South African freshwater quality target range for acid-soluble aluminium at pH < 6.5 is 0.005 mg/L, and 0.01 mg/L for pH > 6.5 (DWAF, 1996a).

1.8.2.17 Vanadium (V)

Vanadium is found throughout the Earth's crust, and the average concentration of vanadium in the Earth's crust is 150 mg/kg, with soil concentrations of up to 310 mg/kg (WHO, 2000). Vanadium occurs in several oxidations states in the environment with +5 being the principle oxidation state which is most soluble and mobile in the aquatic environment (CCME, 1999f). Vanadium has been recognized as an essential element for certain species of green algae, and the soluble form appears to be easily taken up by plants which show a great ability to accumulate this metal (CCME, 1999f). The concentration of vanadium in water is region specific and generally ranges from 0.0002 – 0.1 mg/L in freshwaters (WHO, 2000). For the most part, geography governs vanadium concentration in water, with a higher range in freshwater than in seawater (Ziemacki *et al*., 1989). Anthropogenic sources of vanadium in the natural environment include metallurgic works, and activities involving the processing of residual oil and coal (Ziemacki *et al*., 1989). The freshwater soil quality guideline for environmental health is 130 mg/kg (CCME, 1999f). The European Economic Community (EEC) international target value for vanadium in the coastal environment is 0.1 mg/L (DWAF, 1995).

1.8.2.18 Nickel (Ni)

Nickel occurs particularly in iron and magnesium ores in oxidation states of +1, +3 or +4, and is released into water and soil naturally through weathering and erosion processes, but is also derived from anthropogenic sources such as mining smelting and refining activities (CCME, 1999d; WHO, 2005b). Nickel concentrations in the Earth's crust range from 58 – 94 mg/kg, with much lower levels in natural water bodies (Ziemacki *et al*., 1989). Nickel has a high affinity for negatively charged particles which accounts for its rapid removal from solution (depending on pH and soil type) and its presence in surface soils and aquatic sediments which act as temporary sinks (CCME, 1999d). The target water quality value of nickel in the South African coastal zone is 0.025 mg/L (DWAF, 1995). The recommended freshwater soil quality guideline for environmental health is 50 mg/kg (CCME, 1999d). Although there are no available guidelines on specific concentrations of nickel that are considered safe for aquatic life, DWAF (1996b) suggests that concentrations exceeding 0.2 mg/L are unsuitable for irrigation.

1.8.2.19 Mercury (Hg)

Mercury occurs in three oxidation states in the natural aquatic environment namely as the metal, as mercury (I) and as mercury (II) (DWAF, 1996a). Naturally occurring mercury, due to geological occurrence, is rare and is mostly associated with processes such as volcanic activity but has significantly increased as a consequence of industrial activities since the industrial revolution in the 19th century (WHO, 2005a). Levels of mercury in rainwater are in the range of 5×10^{-6} – 0.0001 mg/L, and less than 0.0005 mg/L in surface and groundwater sources – depending largely on local mineral deposits (WHO, 2005a). Man-made sources of mercury are wide spread and are mainly attributed to the mining and manufacturing sectors (Ziemacki *et al*., 1989). Other natural sources of mercury include microorganisms (Ziemacki *et al*., 1989). It was discovered that mercury concentrated in algae within the food chain can be hydrated out of dead algae and made mobile again (Fellenberg, 2000). Consequently, eutrophic waters characterized by algal blooms pose an ecological threat for animals owing to the remobilization process (Ziemacki *et al*., 1989). Mercury and mercury-organic complexes in the aquatic environment pose a threat due to their extreme toxicity to aquatic organisms and their ability to bio-accumulate in the food chain (DWAF, 1996a). The effects of mercury on humans are toxic and can result in sickness, paralysis, and disturbances in sight and hearing (Fellenberg, 2000). The target water quality value of total mercury in the South African coastal zone is 0.0003 mg/L (DWAF, 1995). The South African target water quality range for total mercury in freshwater is 0.00004 mg/L (DWAF, 1996a). The probable effect levels of mercury in sediment associated with frequent adverse biological effects is 0.486 mg/kg in freshwater sediment and 0.7 mg/kg in marine sediment (CCME, 1999h).

1.8.2.20 Lead (Pb)

Lead typically takes the form of four naturally occurring isotopes in the environment depending on surrounding mineral sources (0, I, II and IV), and is mostly poorly soluble in water (Ziemacki *et al*., 1989). Consequently, lead exhibits a pronounced tendency for accumulation in soil as it is minimally mobile even at low pH values (Fellenberg, 2000). Common anthropogenic sources of lead in the natural environment include mining and refining activities, activities associated with refuse incineration and industries using coal (Ziemacki *et al*., 1989). Lead is defined as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms (DWAF, 1996a). The effects of lead are toxic if the daily dosage of lead reaches 50 mg/kg for grazing animals and 7.5 mg/kg for humans consuming leafy material (Fellenberg, 2000). The target water quality for dissolved lead in freshwater sources ranges from 0.0002 to 0.0012 mg/L as a function of the hardness of water (DWAF, 1996a). The target water quality value of total lead in the South African coastal zone is 0.012 mg/L (DWAF, 1995). The probable effect levels of lead in sediment associated with frequent adverse biological effects is 91.3 mg/kg in freshwater sediment and 112 mg/kg in marine sediment (CCME, 1999e).

1.8.2.21 Manganese (Mn)

Manganese is an essential micronutrient for plants and animals and the eighth most abundant metal in nature (DWAF, 1996a). Manganese is a naturally abundant element widely distributed in the Earth's crust (Ziemacki *et al*., 1989). It does not occur naturally in its pure form but is instead found in manganese-containing minerals such as oxides, silicates and carbonates, iron ores, coal and in lower concentrations in crude oil (Ziemacki *et al*., 1989). In surface waters manganese occurs both in dissolved and suspended forms depending on factors such as pH, anions present and oxidation-reduction potential (WHO, 2011). The divalent form of manganese (Mn^{2+}) dominates most water at pH 4 – 7, with highly oxidized forms that can occur at higher pH values or as a result of microbial oxidation (WHO, 2011). At concentrations greater than 0.1 mg/L manganese imparts an undesirable taste (WHO, 2011). Manganese can be adsorbed in soil with the extent of adsorption depending on organic content and cation exchange capacity (WHO, 2011). It can also bio-accumulate in lower organisms such as molluscs and fish, but not in higher organisms and therefore biomagnification in food chains is not usually significant (WHO, 2011). Anthropogenic sources of manganese include metallurgic processes, fertilizers, organic carbonyl compounds used in fuel-oil additives (Ziemacki *et al*., 1989). The target water quality range for dissolved manganese in South African freshwater ecosystems is 0.18 mg/L (DWAF, 1996a).

1.8.2.22 Iron (Fe)

Iron is the second most abundant metal in the Earth's crust and accounts for about 5% (WHO, 2003c). It is rarely found in nature in its elemental form as ions readily combine with oxygen and sulphur containing compounds to form oxides, hydroxides, carbonates and sulphides (WHO, 2003c). The two common states of iron in water are reduced Fe^{2+} (ferrous) and oxidized Fe^{3+} (ferric) states (DWAF, 1996a). Iron as Fe^{2+} at concentrations of 0.04 mg/L can be detected by taste in distilled water and its dissolution can occur due to oxidation and an increase in pH (WHO, 2003c). Iron is released naturally into the environment from the weathering of sulphide ores, igneous, sedimentary and metamorphic rocks (DWAF, 1996a). It is also released into the environment from human activities such as burning of coal, acid mine drainage, metal processing, sewage, landfill leachates and from the corrosion of iron and steel (DWAF, 1996a). The median iron concentration in river water is reported to be 0.7 mg/L and is usually less than 0.3 mg/L in drinking water (WHO, 2003c). The toxicity of iron depends on its oxidation state and if it is in suspension or solution – although its limited toxicity and bio-availability classifies iron as a non-critical element (DWAF, 1996a). The iron concentration in freshwater ecosystems should not be allowed to vary by more than 10% of the dissolved background iron concentration for a particular site at a specific time (DWAF, 1996a). The European Economic Community (EEC) international target value for iron in the coastal zone is 1 mg/L (DWAF, 1995).

1.8.2.23 Chromium (Cr)

Chromium is widely distributed in the Earth's crust and can occur in oxidation states +2 to +6 (WHO, 2003b). Chromium III and VI is more common in the environment with oxidation states depending on redox potential, pH and the presence of oxidizing and reducing compounds (WHO, 2003b). Soils and rocks may contain small amounts of chromium mainly in the trivalent state (WHO, 2003b). Chromium VI can be easily reduced to chromium III and its occurrence in soil is mainly due to human activities (WHO, 2003b). Chromium concentrations in soil vary considerably with an average ranging from 14 – 70 mg/kg (Ziemacki *et al.*, 1989). The average concentration of chromium in seawater is 0.00004 to 0.0005 mg/L, and 0.0005 to 0.002 mg/L in surface waters (WHO, 2003b). Benthic organisms are exposed to dissolved and particulate chromium in overlying waters and ingestion of sediment bound chromium (CCME, 1999c). In general chromium content of surface waters reflects the extent of industrial activities (WHO, 2003b). The chromium III to chromium VI ratio in surface waters varies widely as a result of chromium VI being more soluble than chromium III, thus making chromium VI relatively mobile (WHO, 2003b). The probable effect levels of chromium in sediment associated with adverse biological effects is 90 mg/kg in freshwater sediment and 160 mg/kg in marine sediment (CCME, 1999c). The water quality guidelines for chromium for the protection of aquatic life are 0.0089 mg/L and 0.056 mg/L for chromium III in freshwater and marine environments respectively; and 0.001 mg/L and 0.0015 mg/L for chromium VI in freshwater and marine environments respectively (CCME, 1999c).

1.8.3 Microbiological characteristics of water

Microbiological characteristics include the microbiological estimation of pathogenic and non-pathogenic microbes occurring in water, including various species of aerobic and anaerobic bacteria, fungi and viruses (Tomar, 1999). Coliform bacteria are an important human health concern, but most aquatic organisms are not harmed by the presence of coliforms (Weiner and Matthews, 2003). Pathogens could cause illness or even death to humans, the effects of which are related to the strain of the virus or bacteria in question (Tomar, 1999). In many parts of the world particularly in non-industrialized countries, the presence of pathogens in water supplies is still a critical public health problem that exacts a high toll on human life (Rubin, 2001). Several types of pathogens can be identified, two of which are explained below:

1.8.3.1 Total coliforms

This group includes four genera in the *Enterobacteriaceae* family including *Escherichia*, *Klesbisella*, *Citrobactor* and *Enterobactor* (Tomar, 1999). These organisms occur in the human intestine and other warm-blooded animals, of which *Escherichia* (*E.coli* species) is the most common indicator of faecal pollution, with the presence of the other indicators further confirming faecal pollution (Tomar, 1999).

1.8.3.2 *Esherichia coli (E.coli)*

E.coli constitutes a larger proportion of the species of coliform bacteria that forms the normal intestinal flora of humans and warm blooded animals as compared to any of the other organisms (Tomar, 1999). It is therefore an effective and confirmed indicator of faecal contamination or pollution (Tomar, 1999). Under warm nutrient rich conditions they are able to multiply in water (Gray, 1994). There are 14 distinct serotypes of *E.coli* that cause gastroenteritis in humans and animals, and are potentially serious in children under five years of age (Gray, 1994).

1.9 POLLUTION IN RIVER SYSTEMS

Whilst several definitions have been offered to define pollution, it can most simply be interpreted by measured parameters that exceed an accepted threshold, thus affecting the physical, chemical and biological integrity of a water body (Novotny, 2003). River pollutants are categorized as point or non-point source, the former incorporating pollutants entering water courses directly through pipes or channels, and the latter including storm drainage and surface runoff charged with pollutants of land based activities (Weiner and Matthews, 2003). Point sources such as sewage treatment discharge are relatively easy to detect, whilst non-point sources are somewhat more difficult to detect owing to complex biotic and abiotic interactions within the catchment ecosystem (Sliva and Williams, 2001). Rivers contaminated with pollution is one of the oldest environmental problems confronting people throughout the world (Rubin, 2001). In this section a brief review on the principle types of river contaminants and the reasons for concern are highlighted.

1.9.1 SOURCES AND TYPES OF POLLUTANTS

Whilst pollution refers to the state of a water body in terms of its integrity, a pollutant refers to a dredged spoil, solid waste, incineration residue, sewage, garbage, sludge or any biological, chemical or radioactive waste product discharged into a water body (Novotny, 2003). The range of pollutants is vast but is categorized below according to Weiner and Matthews (2003):

- Oxygen demanding substances discharged from industries including paper mills and breweries, as well as wastewater treatment plants;
- Sediments and suspended solids associated with cultivation, construction and mining operations;
- Nutrients including nitrogen and phosphorous common in urban and agricultural runoff and associated with plant debris, fertilizer, animal wastes and wastewater discharges;

- Heated effluents, petroleum compounds and synthetic organics associated primarily with industrial activity; and
- Pathogenic bacteria and viruses associated with urban and municipal discharge, as well as agricultural runoff from feedlots.

1.9.2 Ecological effects of pollution

The effects of pollutant in rivers largely depend on the type of pollutant, as certain types of pollutant can be harmful to selected individuals or communities (Weiner and Matthews, 2003). It is essential to understand aquatic ecosystem functioning in order to appreciate the ecological consequences of human impact on river systems (Gower, 1980). The impacts of pollutants on local ecology are identified below:

1.9.2.1 Nutrients

Eutrophication is a consequence of nutrient loading into rivers such that an increase in nutrients facilitates the flow of solar energy through the primary producers and as a result, biological production increases resulting in larger biotic compartments (Gower, 1980). Essentially, this explosion in nutrients supports a dense plant population in aquatic ecosystems, which ultimately kills off animal life by depriving it of oxygen and thereby affecting the abundance of higher trophic levels (Starr and Taggart, 2004). Nutrient enrichment also results in the depletion of dissolved oxygen as various decomposers feed on increased quantities of dead and decaying matter (Rubin, 2001).

1.9.2.2 Organic and oxygen demanding wastes

When high energy organic or oxygen demanding material is discharged into a river, oxygen is used at a greater rate when the components are oxidized, causing a distinct decrease in dissolved oxygen concentrations within a river faster than it can be replenished through natural processes (Weiner and Matthews, 2003). De-oxygenation associated with organic wastes limits respiratory functions of organisms thereby limiting aquatic communities to mainly anaerobic bacteria with negative implications on fish diversity and abundance (Gower, 1980).

1.9.2.3 Heavy metal discharges

The health effects of organisms requiring trace levels of heavy metals can be extremely toxic at high concentrations of accumulation (Rubin, 2001). The impacts of toxic metal discharge on the biotic community of the aquatic ecosystem reduces diversity due to the elimination of most species, causes an overall reduction in the number of individuals in the community and results in the survival of species tolerant to the contamination, all depending on the degree/level of toxicity of these heavy metal discharges (Gower, 1980). Furthermore, certain toxic metals such as mercury tends to bio-accumulate in the tissues of fish and other organisms high in the food chain, and can result in serious health implications when consumed by humans (Rubin, 2001).

1.9.2.4 Pesticides

Like heavy metals, pesticides are toxic and contaminate virtually every part of an aquatic ecosystem (Gower, 1980). If pesticides have a persistent chemical composition, such as DDT, they will inevitably find their way to freshwater sources at some stage, resulting in oxygen depletion and the poisoning of some aquatic organisms (Gower, 1980).

1.9.2.5 Heated effluent

Heated industrial effluent is considered a pollutant where an increase in river temperatures lower the solubility of oxygen in water, thereby reducing the amount of dissolved oxygen available to aerobic species (Weiner and Matthews, 2003). In addition, the metabolic rates of aquatic organisms are increased which further reduces the amount of available dissolved oxygen, ultimately altering the ecology of a river system (Weiner and Matthews, 2003).

1.9.2.6 Pathogenic bacteria and viruses

Coliform bacteria are an important human health concern, but most aquatic organisms are not harmed by the presence of coliforms (Weiner and Matthews, 2003). Pathogens could cause illness or even death to humans, the effects of which are related to the strain of the virus or bacteria in question (Tomar, 1999). In many parts of the world particularly in non-industrialized countries, the presence of pathogens in water supplies is still a critical public health problem that exacts a high toll on human life (Rubin, 2001).

1.9.2.7 Sediments and suspended solids

Excess fine sediments and suspended solids in water bodies prevents light penetration into the water affecting the photosynthetic capability in primary producers and interfering with fish spawning due to decreased visibility making food harder to find (Wood and Armitage, 1997). Sediments can also affect the gill structures of fish, cause damage to macrophyte leaves and stems through abrasion, prevent the attachment of algal cells to the substrate, affect filter feeders and have a smothering effect on benthic organisms (Wood and Armitage, 1997). In addition, organic sediments can deplete the oxygen in water causing anaerobic conditions, with negative implications on the abundance and biodiversity of aerobic organisms (Weiner and Matthews, 2003).

1.9.2.8 Complex pollutants

Unlike the above pollutants which cause specific changes in water quality, complex pollutants can contain an agglomeration of toxic components which can result in several conditions within a river system following their chemical transformation including, eutrophication, low oxygen waters and sedimentation (Gower, 1980). This results in an inhospitable environment with a larger reduction on aquatic diversity and abundance (Gower, 1980).

1.9.3 Pollution control

Recent years have shown an increasing awareness of and concern about water pollution around the world, resulting in new approaches to the sustainable exploitation of water resources internationally particularly through policy frameworks (Helmer and Hespanhol, 1997). Helmer and Hespanhol (1997), identify several core policy guiding principles that provide a suitable basis for the sound management of water pollution, some of which already inform South African water legislative frameworks:

- **Prevent pollution rather than treating the symptoms of it:** It has often been shown that remedial actions to treat polluted water sources are far more expensive than applying pollution prevention measures. This may include waste minimization, in-house refinement of raw materials and production processes, and waste minimization to mention a few. Non-point sources of pollution may be controlled to a significant degree by adopting the principle of best environmental practice which involves sharing of good codes of agricultural practice for example;
- **Use the precautionary principle:** The discharge of toxic substances into the aquatic environment may often be suspected of having detrimental effects and links without scientific research proving a causal link between the substance and the environment owing to a long period of time to scientifically establish the link. Consequently, by the time the relevant documentation is obtained to indicate the effects, the receiving environment is already contaminated. This shows the need for action to postpone substance usage until validated through science;
- **Apply the polluter-pays-principle:** This is a widely recognized but poorly implemented economic instrument which applies financial charges or special taxes that corresponds to the degree of pollution discharge by an industry into an aquatic ecosystem. The difficulty in implementing the principle in developing countries lies in the conflict of existing subsidized programs for the supply of water and removal of wastewater for social reasons. Nonetheless, it should be maintained as the ultimate goal by all countries;
- **Apply realistic standards and regulations:** This is an important element in water pollution control which must be both achievable and enforceable. Standards should be tailored to match the economic and administrative capacity of individual countries and tightened with progress, as failure to do so may result in the general indifference towards rules and regulations;
- **Establishment mechanisms for cross – sectorial integration:** This involves the establishment of co-ordination between different water-related sectors such as health and agriculture to enable co-operation and effective information exchange. This should further encompass all decision makers and interested and affected parties to comment on ideas and development plans between sectors and

ultimately facilitate in a transparent process in policy formulation and pollution control; and

- **Promote international co-operation on water pollution control:** This principle requires recognition of trans-boundary water pollution and requires international co-operation and co-ordination efforts such as the establishment of international regulations and bodies with knowledgeable representatives in an effort to strengthen international co-operation on the pollution control of shared resources.

Reform in South African water resource management has been a key focus for a number of years since the first democratic elections in 1994, and has resulted in a few highlights, amongst which were the formulation of several legal frameworks and regulations pertaining to the management, prevention and remediation of pollution in the water resources. These include legislation such as the National Water Act (NWA) (No. 36 of 1998), the Marine Living Resources Act (MLRA) (No. 18 of 1998) and the National Environmental Management Act (NEMA) (No. 107 of 1998) (Sukdeo, 2010). The objective underpinning these legislation types is the sustainable exploitation of water as a resource such that human basic needs and economic demands are met, whilst ensuring long term resource conservation and protection (MLRA, 1998; NEMA, 1998; NWA, 1998).

Of particular importance in the management of freshwater systems was the enactment of the National Water Act (NWA) (No 36 of 1998), which adopts an integrated approach to water policy, law and implementation through linking biophysical and socio-economic processes impacting on water resources at a national level (Palmer *et al.*, 2004). This incorporates the constitutional recognition of the right of usage and access to water and the right to an environment that ensures health and well-being, as well as the prevention of pollution and the sustainable use of natural water resources (White Paper on a National Water Policy for South Africa, 1997). The NWA adopts two approaches to ensure this balance between resource protection and water resource use (i.e. Integrated Water Resource Management), namely Resource Directed Measures (RDM) and Source Directed Controls (SDC) (Palmer *et al.*, 2004).

RDM focuses on the water quality of the resource itself including overall water quantity and quality, the condition of in-stream and riparian habitats and the condition and distribution of aquatic biota (NWRS, 2004). There exists four RDM to ensure protection of the water resource namely, a classification system for the water resource; the process of ecological classification of each major resource; setting the reserve; and determining the Resource Quality Objectives (RQO) (DWAF, n.d.). There are three management classes namely natural, moderately impacted and heavily impacted (NWRS, 2004). Upon classification of the major resource, the RQO and reserve is obtained as a combined exercise to determine the type of resource protection and usage (DWAF, n.d.). The RQO sets aside targets for each water resource in terms of desired protection levels which are based on what the quantity and quality of the water resource should be, and what the conditions of in-stream riparian vegetation, as well as aquatic fauna and flora should be (DWAF, n.d.). The reserve sets aside water requirements to provide for basic human needs and to protect and sustain healthy water ecosystems (DWAF, n.d.). These series of measures are intended to ensure the protection of all water resources in the country.

SDC are intended to control impacts on water resources by imposing limits through tools such as licences, registrations and authorisations (Palmer *et al*., 2004). SDC closely ties in with the RQO highlighted above and are intended to ensure that the impacts of water use in terms of quantity and quality do not exceed the limits prescribed to the class of the resource (NWRS, 2004). In the South African freshwater legislative framework, RDM and SDC serve as effective tools for the establishment of integrated water resource management, which in turn necessitates the need for on-going water quality monitoring and assessment programs at a national level to allow for information generation and an understanding of the long term management and utilization of the country's freshwater resources (Odume, 2011).

1.10 CONCLUSION

A study in river chemistry and water quality is fundamental as it gives insight into the benefits to be gained from catchment management and the consequences of its mismanagement. The environmental quality of surface water bodies is dictated by several interactions between biotic and abiotic components and is best understood in the context of the catchment ecosystem. Water forms a key ingredient in anthropogenic processes and activities, and this has consequently led to a strong influence of these activities on water quality and river chemistry. Observed aquatic communities have become a product of the interactions between these natural and anthropogenic processes, and this is reflected through their biodiversity, functioning and abundance which serve as a clear indicator on the quality of associated water bodies. The impact of humans emphasizes the need for careful management of available water sources within the entire catchment ecosystem. There are several methods of evaluating river chemistry and water quality including the analyses of in-stream water, sediment and biological indicators; all of which provides valuable information in understanding the water resource and is crucial in the control and management of the water resource.

<u>CHAPTER TWO</u>

STUDY AREA AND METHODOLOGY

2.1 INTRODUCTION

This section provides an account of the study area in terms of locality and biophysical catchment characteristics, thus enabling an understanding of the study area in a geographical context. In addition, all sampling and investigation techniques adopted in this study, as well as analytical procedures, are outlined to provide insight to the study and explain the way in which the data was generated. This elucidates the way in which the samples were collected, analyzed and the data presented.

2.2 REGIONAL DESCRIPTION

The uMhlatuzana, uMbilo and aManzimnyama Rivers and their associated catchments located on the eastern seaboard of KwaZulu-Natal, form the core of urbanization and industrialization in the region, and comprise three major river systems flowing into the Bayhead Canal of the Durban Harbour (**Figure 2.1**). All three river catchments fall entirely within the eThekwini Municipal boundary and have a combined total area of approximately 264 km^2, approximately 70% of which is described as land cover associated with extensive residential, industrial and commercial development (DEAT, 2001). The respective catchment areas and river lengths of the uMbilo, uMhlatuzana and aManzimnyama Rivers are 67 km^2 and 35 km; 113 km^2 and 50 km; and 15 km^2 and 5.5 km (Marine Environmental Research/Environmental Resource Management (MER/ERM), 2011). Each of these rivers supply freshwater to the Durban Harbour predominantly through rainfall runoff received from the variety of land use practices located along each of the river's courses including a combination of light and heavy industry, residential and informal sectors as well as isolated parcels of recreational parks and nature reserves (MER/ERM, 2011).

Figure 2.1: Geographical context of the study area.

2.2.1 GEOLOGY AND TOPOGRAPHY

The geology of the catchments predominantly comprise granites and gneisses of the Basement Complex, sandstones of the Natal Group, glacial tillite and shales of the Dwyka and Ecca Groups and minor Karoo dolerite intrusions (**Figure 2.2**) (MER/ERM, 2011). The geology of Durban Harbour comprises faulted Karoo sediments of the Dwyka and Ecca Groups, overlain by a shallow veneer of Cretaceous sediments that thicken eastward beneath the Bluff (MER/ERM, 2011).

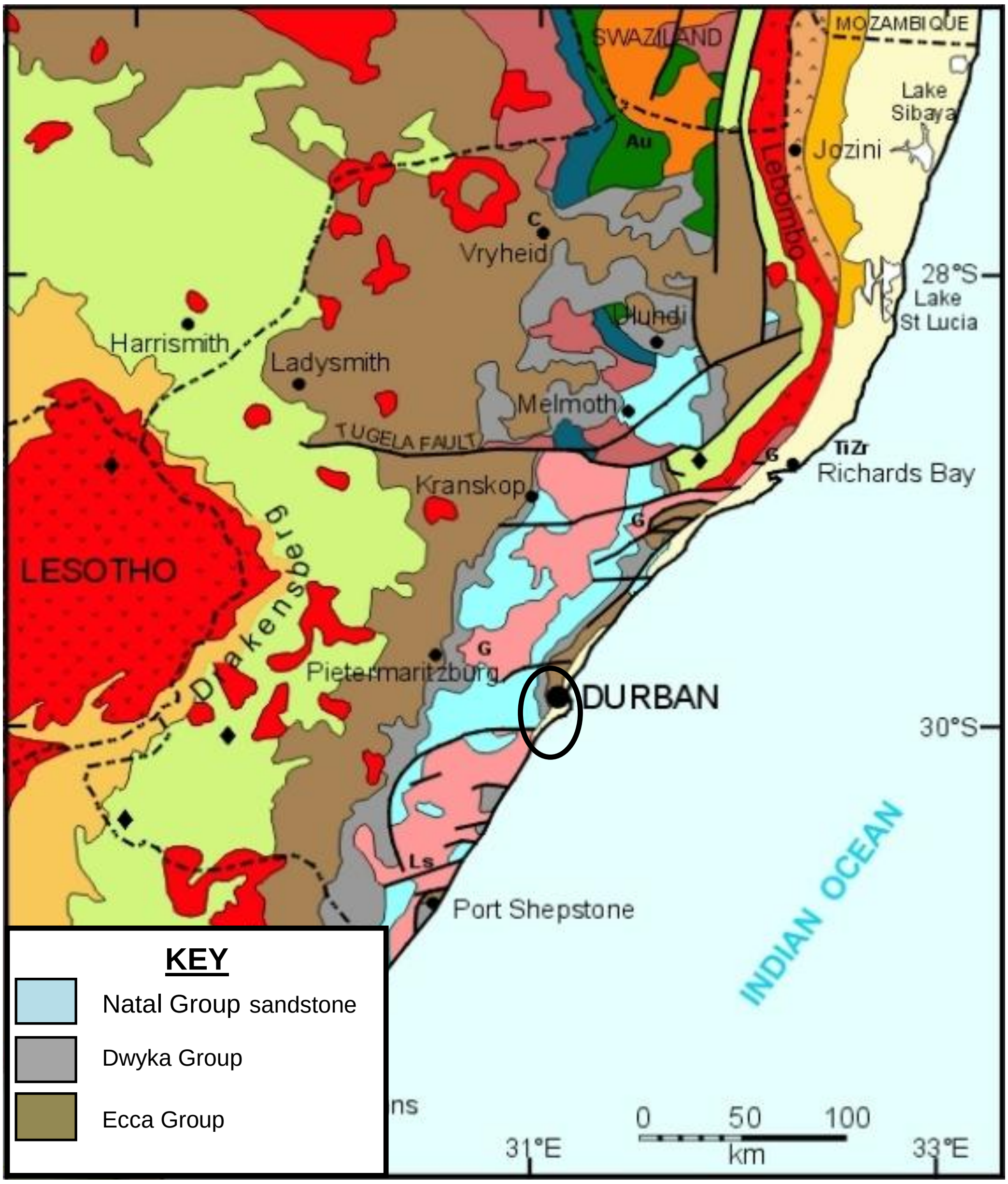

Figure 2.2: Geology map for KwaZulu-Natal with study area circled (Source: www.geology.ukzn.ac.za, June 2012).

A large portion of the uMbilo and uMhlatuzana River catchments are characterized by highly dissected undulating hills with Natal red-brown sandstone, granite and shale rock sequences/strata (Water Research Commission (WRC), 2002). A massive drop in sea level approximately 20 000 years ago caused a sudden increase in gradient, which in turn caused the rivers to incise the already existing channels, accounting for the present state where the river valleys which occupy deep and undulating gorges (Cottrell, 2003). On the other hand, much of the catchment of the aManzimnyama canal together with the lower reaches of the uMhlatuzana and uMbilo River valleys are predominantly characterized by relatively flat topography, and geological sequences/strata inclusive of mainly Berea red sands and beach sands (WRC, 2002).

2.2.2 LAND USE AND LAND COVER

The land cover of the catchments is dominated by built up residential and industrial areas accounting for more than 70% of urban development (**Figure 2.3**) (DEAT, 2001). Dominant natural vegetation types occurring within the catchments are composed of coastal forest, thornveld, bushland and grassland, which cumulatively account for 23% of the natural vegetation within the broader catchment and are mainly restricted to recreational parks and nature reserves (DEAT, 2001; WRC 2002). The remaining portion of the total catchment areas of the Durban Harbour comprises mostly subsistence agriculture with a small portion of degraded bushland (DEAT, 2001).

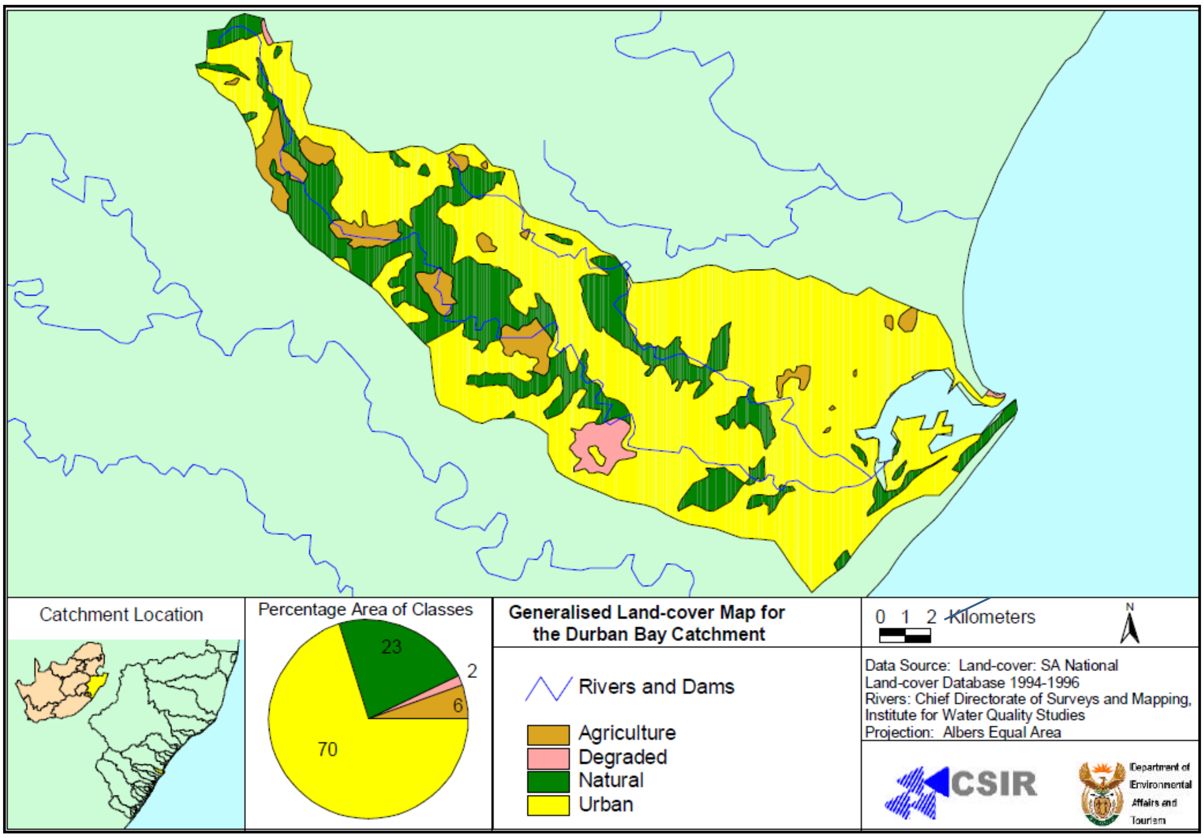

Figure 2.3: Generalized land cover map for the Durban Harbour Catchment area (Source: DEAT, 2001).

2.2.3 Weather and climate

The region is characterized by a typical warm sub-tropical climate of KwaZulu-Natal with an average winter temperature of 16°C between the months of May to July and an average summer temperature of 27°C between the much warmer months of January to March, coupled with an average annual rainfall of 1054 mm mainly during the summer months (**Figure 2.4**) (MER/ERM, 2011). Approximately 80% of the annual rainfall occurs in the warmer summer months which lead to regular flooding of the catchments and high river flow velocities in the steep hinterland (Tinmouth, 2009). The implications are increased freshwater inflows into the harbour during the warm summer months with associated implications on pollutant loads and the general water quality of the harbour (MER/ERM, 2011).

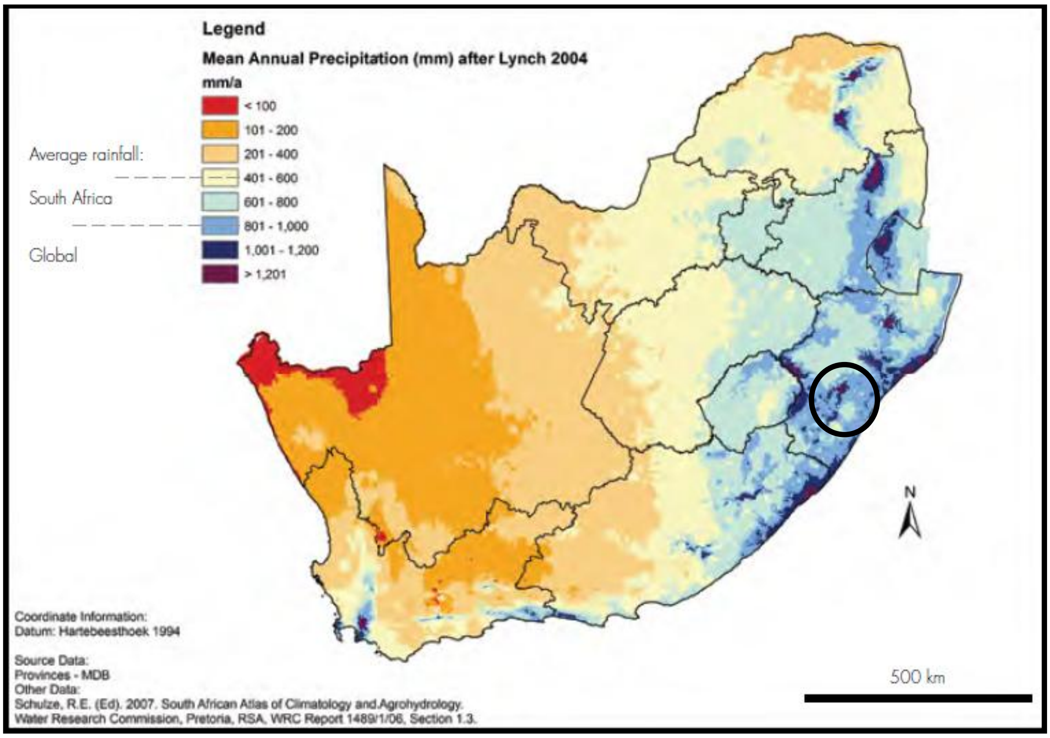

Figure 2.4: South Africa's average annual rainfall with study area encircled (Source: CSIR, 2010).

2.3 RESEARCH METHODOLOGY

The research methodology of this study incorporated the collection of water samples from predetermined sample locations, and their subsequent analytical analyses at independent laboratories. Data obtained from these analyses were then statistically examined to allow for seasonal comparison, as well as comparison with relevant water quality standards as prescribed by the South African Water Quality Guidelines for Aquatic Ecosystems (DWAF, 1996a), and Canadian soil quality guidelines for the protection of aquatic life as outlined in CCME (1999a to h) and CCME (2009).

2.3.1 SELECTION OF SAMPLING SITES

The locations of the sampling sites were methodically chosen along the uMhlatuzana, uMbilo and aManzimnyama Rivers, and are shown in **Figure 2.5**. The sampling sites were systematically chosen before and after each land use type in each of the river systems to reflect the influence on land use management on water quality. Land use identification and sampling site identification was effected with the use of topographic maps and aerial photographs, and was validated by ground truthing *via* site visits.

A total of 25 sample sites were established, 17 of which are representative of all three fluvial systems (8 sites along the uMhlatuzana River, 6 sites along the uMbilo river, 1 site after the confluence of the uMhlatuzana and uMbilo Rivers, 2 sites along the aMamzimnyama Canal, and the remaining 8 sites along the Bayhead Canal of the Durban Harbour – see overleaf). Sampling sites along each of the fluvial systems were representative of land use changes and were positioned at the interface of succeeding land use types. The 8 sample sites along the Bayhead Canal were strategically selected at regular intervals to assess the effects of the subsequent inflows emanating from each of the fluvial systems. The sample locations are described in **Table 2.1** and represented in **Figures 2.5** and **2.6** below:

Table 2.1: Description of sample locations and corresponding catchment land use types.

uMbilo River	
Site	**Land use description**
1	Source (Sparse residential area)
2	Interface of industrial and residential area (sited downstream of industrial area)
3	Interface of residential area and nature reserve (sited downstream of residential area)
4	Interface of nature reserve and residential area – also impacted on by the Waste Water Treatment Works (WWTW) (sited downstream of nature reserve)
5	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
6	Interface of industrial area and confluence with uMhlatuzana River (sited downstream of industrial area)
uMhlatuzana River	
Site	**Land use description**
7	Source (Sparse residential area)
8	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
9	Interface of industrial area and nature reserve (sited downstream of industrial area)
10	Interface of nature reserve and residential area – also impacted on by WWTW (sited downstream of nature reserve)
11	Interface of residential and industrial area (sited downstream of residential area)
12	Interface of industrial area and nature reserve (sited downstream of industrial area)
13	Interface of nature reserve and industrial area (sited downstream of nature reserve)
14	Interface of industrial area and confluence with uMbilo River (sited downstream of industrial area)

uMbilo/uMhlatuzana Canal confluence	
Site	**Land use description**
15	Sited at confluence
aManzimnyama Canal	
Site	**Land use description**
16	Source (Low density industrial area)
17	Interface of industrial area and confluence to Bayhead Canal (sited downstream of industrial area)
Bayhead Canal of Durban Harbour	
Sites	**18, 19, 20, 21, 22, 23, 24, 25** (equidistant)

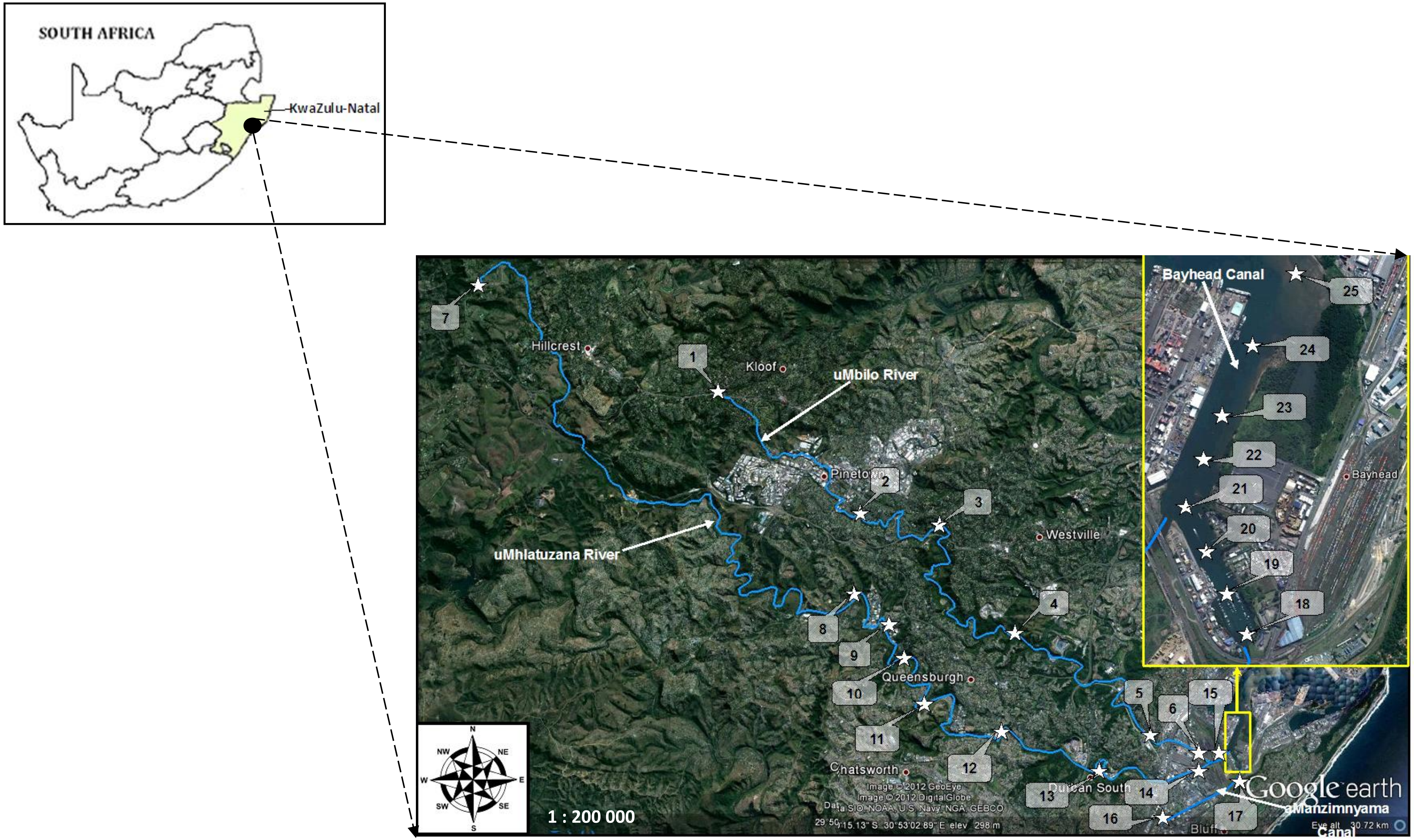

Figure 2.5: Location of study area with sampling points depicted (www.googleearth.com, accessed June 2012).

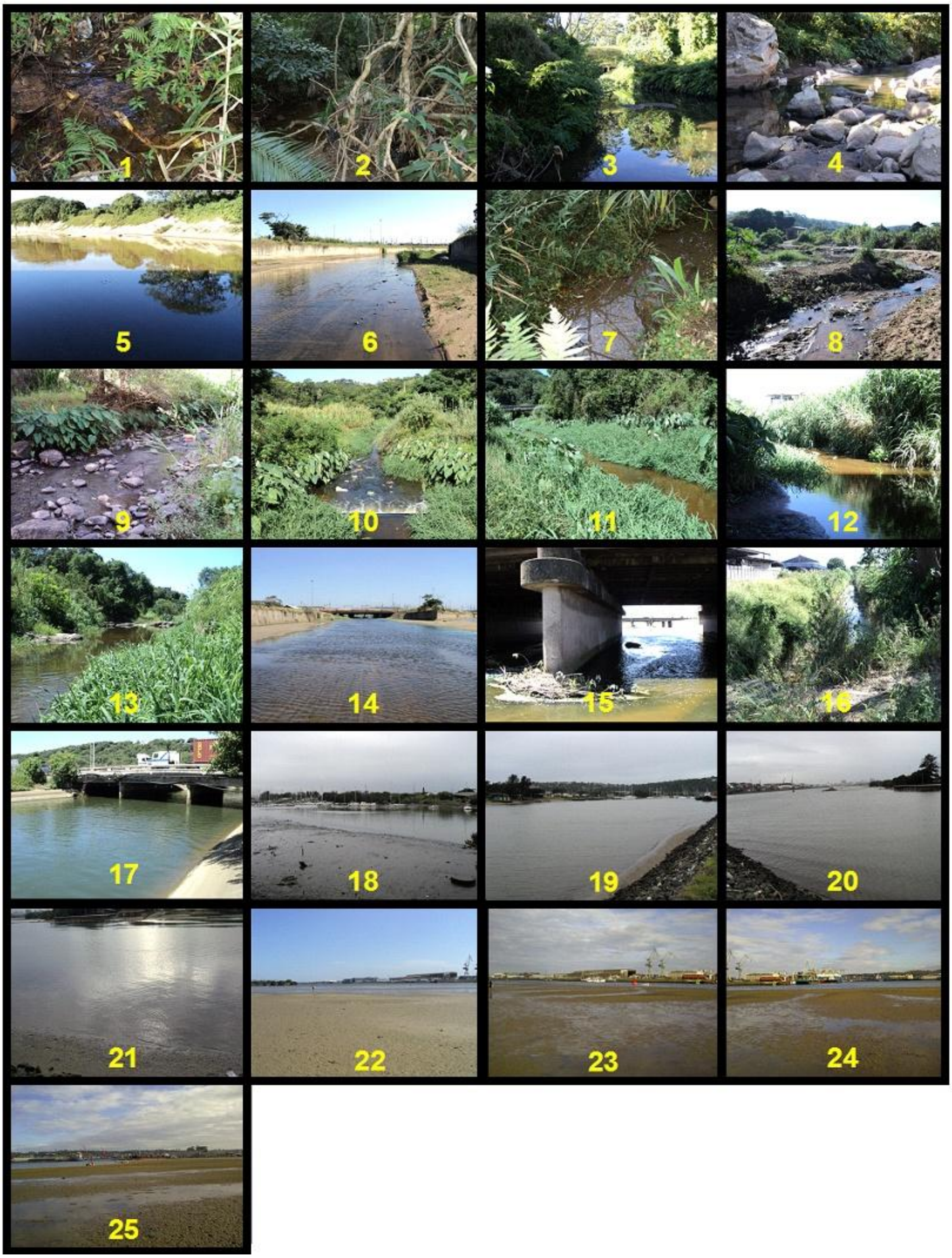

Figure 2.6: Photographic record of sample sites.

2.3.2 Sampling protocols

Field surveys involved the sampling of (i) surface water, (ii) surface sediment and (iii) diatoms in-stream. Four field surveys were conducted between December 2011 and December 2012 for water and diatom samples, and were representative of seasonal sampling – December 2011 (summer); March 2012 (autumn); June 2012 (winter); September 2012 (spring). Due to the fact that sediment tends to display long-term pollution trends in a water body as compared to water, two field surveys were conducted for sediment in December 2011 (summer) and June 2012 (winter), which were grouped into wet and dry season sampling respectively.

Water samples were collected at approximately mid-depth at each site in accordance with methods prescribed by Naidoo (2005). The samples were collected directly into the plastic sample bottles to prevent cross contamination by hand. Before collecting samples, the sampling bottles were cleaned thoroughly with de-ionized water. The bottles were then thoroughly rinsed with water on site before being completely filled. Surface grab sediment samples were also collected in-stream and placed into plastic bags as outlined by Sukdeo (2010). Once collected, the water and sediment samples were placed in cool boxes on ice bags to prevent possible physical, chemical or biological changes to the samples. The samples were then taken back to the laboratories for testing within a twenty four hour period.

Diatom sampling involved carefully removing the upper 1 cm of the river bed sediment (radius of approximately 3 cm) using a scraper as prescribed by Naicker (2006). Care was taken so as not to disturb/ break up the collected sediment. This was done in the slow flowing, shallow portions of the river with sufficient light penetration, and was replicated three times in close proximity to represent microhabitats. The samples were gently placed into sterilized petri dishes and covered with sample water on site. Diatom samples were then transported to the laboratories for sample preparations preceding the diatom enumeration and identification process.

In all cases, the sample labels comprised of: the Global Positioning System (GPS) sample reference point, time and date, depth, and sample number. On subsequent surveys the samples were taken as close as possible to the original GPS positions pertaining to each sample location. The sediment and water samples were allowed to adjust to room temperature prior to submission for testing. Physical and chemical components of the water and sediment samples were analyzed by the University of KwaZulu-Natal (UKZN) Westville Campus analytical chemistry laboratory, whilst microbiological analysis of the water samples was conducted by the Department of Water Affairs (DWA). Chemical components of sediment samples were also analyzed by the UKZN Westville Campus chemistry laboratory, whilst sediment organic matter content and textural analyses were undertaken by the South African Sugarcane Research Institute (SASRI). Diatom sample preparations were undertaken at the UKZN environmental sciences laboratory and the subsequent diatom identification and enumeration was undertaken by the Mangosuthu University of Technology (MUT).

In order to calculate the discharge and flux of material passing each sampling point, the channel cross sectional area was determined by measuring channel width and depth. Multiple depth measures were made along a transect using a measuring staff. Measurements of water levels are necessary for mass flow calculations within water bodies (Chapman, 1992).

In addition, the current velocity was measured by recording the time taken for biodegradable ink to travel a distance of ten metres along an undisturbed portion of the channel. Flow discharge was then calculated using the following equation as stated in Chapman (1992):

$$Q = V \times A \qquad (1)$$

Where Q is the flow discharge, V is the flow velocity and A is the cross sectional area.

Thereafter, the nutrient flux (Φ) or the amount of suspended and dissolved matter passing through the sample location was established as a product of discharge (Q) and nutrient concentration (C) as reflected below (Chapman, 1992):

$$\Phi = Q \times C \qquad (2)$$

2.3.3 LABORATORY ANALYSIS

Analytical analysis is crucial in obtaining knowledge of water constituents and its effects at varying concentrations (Naidoo, 2005). Whilst a wide variety of methods are available to measure pollutant concentrations, attention must be paid to the choice of analytical methods in order to obtain sound results (Chapman, 1992; Weiner and Matthews, 2003). For example, if standards require the absence of a pollutant in a water body, the analytical method must be accurate and sensitive enough to detect very low concentrations of that pollutant (Chapman, 1992). For the purposes of this investigation, water samples were analyzed for the following variables:

- Total Dissolved Solids (TDS);
- Electrical Conductivity;
- pH;
- Dissolved Oxygen;
- Biological Oxygen Demand;
- Chemical Oxygen Demand;
- Ammonia;
- Phosphorous;
- Sulphur;
- Calcium;
- Magnesium;
- Copper;
- Sodium;
- Potassium;
- Aluminium;
- Mercury;
- Vanadium;
- Lead;
- Nickel;

- Chromium;
- *Escherichia coli* (*E. coli*); and
- Total coliforms.

In addition sediment samples were oven dried at 100°C for 24 hours, and then analyzed for the following:

- Aluminium;
- Arsenic;
- Calcium;
- Copper;
- Chromium;
- Iron;
- Magnesium;
- Manganese;
- Nickel;
- Phosphorous;
- Lead;
- Sulphur;
- Selenium;
- Vanadium;
- Zinc;
- Percent organic matter content; and
- Percent fines (silt and clay) content.

Several specialized analysis techniques were employed in this study depending on the properties of the parameters, which include the use of electronic meters, ion-selective electrodes, flame photometer analysis, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis, as well as various incubation, titration, filtration and fermentation techniques, the procedures of which are discussed in greater detail in the paragraphs that follow. These procedures were adopted in the series of analyses conducted in this study. Instrument calibration was done prior to use of the instruments where necessary.

2.3.3.1 Total dissolved solids (TDS)

TDS in the water column was measured using an electronic TDS meter. TDS meters apply a voltage between two or more electrodes such that positively charged ions move towards the negatively charged electrode and negative ions move towards the positively charged electrode (Farley, 2008). The moving ions constitute an electric current and the meter records the amount of ions passing between the electrodes (Farley, 2008). TDS meters are disguised conductivity meters which output a reading in TDS units by converting the conductivity reading into parts per million (ppm) concentrations that give the same measured conductivity (Farley, 2008).

2.3.3.2 Conductivity

Conductivity in the water column was measured using an electronic conductivity meter. A conductivity meter comprises of a conductivity cell and meter (United Nations Environmental Programme (UNEP), n.d.). The conductivity cell comprises of two platinum plate electrodes connected by cables to the meter. The electric current source in the meter applies a potential to the plates and the meter measures electrical resistance of the solution. The resistance is read in the units of conductivity being microsiemens per centimeter (UNEP, n.d.).

2.3.3.3 pH

The pH of water samples was measured using an electronic pH meter. A typical pH meter comprises of a glass and reference electrode, potentiometer and a temperature-compensating device (Weiner and Matthews, 2003). The glass electrode converts the H^+ ion concentration signal activity to an electric current which is read as electrode potential or pH (Weiner and Matthews, 2003).

2.3.3.4 Ammonia (NH_4)

Ion-selective electrodes were used to analyze the ammonia concentration in water. The analysis was conducted as outlined by Ngila (2008). According to Ngila (2008), the ion-selective system has an electrode with a PVC membrane sensitive to ammonium ions in the sample, a reference electrode, as well as a readout meter. Following the addition of $MgSO_4$ to the standards and samples to attain a constant level in ionic strength, the potential is measured off the reference electrode and plotted against the concentration standards to form a calibration curve. Using this curve, the measured potential enables measurement of the ammonia concentration of the sample.

2.3.3.5 Sodium and potassium cations

Analysis of sodium and potassium cation concentrations in the water column was quantitatively determined by using a flame photometer as outlined by Ngila (2008). According to Ngila (2008), the metal ions in solution must be blended in a low temperature flame to produce electrons excited to high energy states. They are unstable and rapidly return to ground state whilst losing energy as a wavelength of visible light. The emission lines are isolated by an optical filter and the emitted light is detected by a photo-detector. Within the instrument, the electrical signal from the photo-detector is displayed as a digital readout. This is an effective analytical method in terms of cost and lack of spectral disturbances (Ngila, 2008).

2.3.3.6 Dissolved Oxygen (DO)

Concentrations of dissolved oxygen were determined using the Winkler method as outlined by Ngila (2008). This comprises a series of titrations to obtain the dissolved oxygen concentrations. The sample is treated with a combined solution of manganous sulphate, potassium hydroxide, sodium azide and potassium iodide, and is finally treated with sulphuric acid. An initial precipitate of manganese hydroxide combines with dissolved oxygen in the sample and forms a brown precipitate. When acidified, manganese sulphate is formed which releases iodine from the potassium iodide. The iodine is then titrated with sodium thiosulphate to provide the dissolved oxygen concentration. Indicators are used to determine the equivalence point of the reactions attained, where the final calculation is based on volume measurements.

2.3.3.7 Biological Oxygen Demand (BOD)

Determination of BOD concentrations were obtained by the aerobic decomposition of organic matter within a BOD incubator as outlined by Tomar (1999). According to Tomar (1999), portions of water samples are filled in two or more BOD bottles adjusted to approximately 20°C and without the entrapment of any air bubbles. Upon measuring the initial DO content, the bottles are incubated for five days in a BOD incubator at a constant temperature of approximately 20°C. It is in the duration of this incubation period that the bacteria complete the aerobic decomposition of organic matter using the available DO in the sample. After the incubation period, the remaining DO is measured, and the relationship between the sample volume and oxygen consumed is used to calculate BOD. Very high concentrations of organic material in the sample require dilution with distilled water before the incubation period such that the oxygen is not completely utilized (Tomar, 1999).

2.3.3.8 Chemical Oxygen Demand (COD)

COD concentrations were determined using a series of titrations as outlined by Tomar (1999). According to Tomar (1999), the COD of water measures the oxygen corresponding to the organic matter susceptible to oxidation by a mixture of strong oxidizing chemicals including chromic and sulphuric acid. The nascent oxygen produced in this reaction oxidizes the organic matter to CO_2 and H_2O, whilst the dichromate reduces to the Cr^{3+} state imparting a green colour to the solution. The excess dichromate is then titrated with ferrous ammonium sulphate using a feroin indicator. First a green colour appears owing to the reduction of the dichromate, but thereafter discharges with only the reddish-brown colour of the indicator remaining at the end point (Tomar, 1999).

2.3.3.9 Microbiological analysis

Microbiological analysis was measured using membrane filtration and fermentation techniques to indicate the number of microbiological organisms in a measured volume of sample (Naidoo, 2005). This is the most commonly used microbiological process in which the bacteria is recovered through selective sterilized membrane filters with appropriate diameters and porosities to retain the organisms of interest, and is thereafter incubated at specific temperatures and times depending on the organisms of interest, using agar plate and liquid media techniques (Köster *et al.*, n.d.). Thereafter, the colonies of microbes retained by the membrane are counted with the help of a colony counter with the results expressed as the number of colonies per 100 mL of the sample (Tomar, 1999).

2.3.3.10 Cation analysis

Analysis of the cations (magnesium, calcium, silicon, selenium, strontium, boron, arsenic and phosphorous) was attained through atomic adsorption Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis. ICP-OES is a simple application which permits the simultaneous determination of several elements in a sample and is based on the use of emitted, absorbed or scattered light to identify the concentration of an atomic or molecular species in a chemical system (Willard *et al.*, 1988). A calibration curve for each element was attained from the measured intensities of the standard metal concentrations from ICP-OES analysis. Using this curve, all measured intensities from ICP-OES gives rise to the metal ion concentrations of the sample through substitution into the representative curve equation (pers comm. Chetty, 2010).

In the case of sediment samples, 0.5 g of each oven dried sample was added to 15 mL of *aqua regia* (mixture comprising one part nitric acid and three parts hydrochloric acid), which was then boiled for thirty minutes. The resulting solution was then cooled and filtered under gravity before commencing with standard ICP-OES methods indicated above (pers comm. Chetty, 2010).

2.3.3.11 Percent organic matter content

The percent organic matter content of sediment was quantitatively determined through titrations with prepared ferrous sulphate solutions (SASRI, 2012). In this process, 0.5 g of the soil sample was added to 10 mL of potassium dichromate, 20 mL of concentrated sulphuric acid, and was allowed to stand for 30 minutes. Following this, 200 mL of water, 10 mL of phosphoric acid, and 0.2 g of sodium fluoride was added to the settled mixture. The resulting mixture was then titrated with ferrous sulphate using a few drops of diphenylamine indicator for the endpoint (green colour). Once the endpoint was reached, the percent carbon was calculated by the difference between the total volume and titrant volume, multiplied by the constant 0.60. Following this, the percent organic matter was determined by the percent carbon multiplied by the constant 1.72 (SASRI, 2012).

2.3.3.12 Percent fines (silt and clay) content

The percent fines in the sediment were determined using the Bouyoucos hydrometer method using sodium hexametaphosphate as dispersing agent (SASRI, 2012). In this process a calgon solution was prepared through weighing 400 g sodium hexametaphosphate and 160 g of sodium hydroxide pellets into a 5 L beaker. Water was then added to this mixture and stirred until dissolved. Following this, 48 g of soil sample was weighed into clay cups to which 150 mL of calgon solution and a drop of silicon antifoaming agent was added. The cups were sealed and then shaken in a flatbed shaker for 50 minutes at 250 rpm. The samples were then transferred into clay cylinders and rinsed out with water with water accumulating in the cylinder itself. The cylinder was then sealed and shaken for 30 seconds by hand. A 4 minute hydrometer reading was then taken from the resulting solution for the silt determination, and a 2 hour reading for the clay determination. The percent clay was then determined after the 2 hour reading. The percent silt was determined by the difference between the 4 minute and 2 hour readings, and the percent sand was determined by the difference between 100 percent and the sum of the clay and silt percentages (SASRI, 2012).

2.3.3.13 Diatom analysis

Diatom sample preparation and analysis was based on the methods highlighted by Naicker (2006). Sediment samples collected from the field for diatom analysis was allowed to settle overnight in the UKZN environmental science laboratory in the same petri dishes. The covers of the petri dishes were removed and allowed to stand under fluorescent lighting for 12 hours. The following morning, the supernatant within the petri dishes were drawn off and 4 – 5 cover slips were placed over the surface of the exposed wet sediment in each of the petri dishes (covering approximately 90% of the sediment surface). Two hours later the cover slips were removed with as little sediment as possible, to ensure that only living cells were attached to the cover slips.

The cover slips were then placed into a separate new petri dish, to which 2 mL of saturated $KMnO_4$ and 2 mL of HCl (10M) was added. The acid cleaned samples were then washed with distilled water using 5 consecutive spins at 2000 rpm for 10 minutes. This process was repeated for each sample. Microscope slides were then made using 2 drops of resulting diatom digest, placed onto acid washed; ethanol stored cover slips and was left overnight to air dry. When the cover slips were completely dry, a small amount of Di-n-butyl Phthalate Xylene (DPX) mounting medium was dotted onto a microscope slide, and the cover slip was gently placed over it. Once the DPX mountant was allowed to air dry (approximately 2 days), each slide was sealed around the edge of the cover slip with Bioseal in order to prevent biological degradation of diatom species therein.

Diatom species in the prepared slides were then identified and enumerated at the Mangosuthu University of Technology (MUT) using a Zeiss Primo Star microscope (Carl Zeiss Micromaging GmbH, Germany – Model 41550). Diatom valves were counted from each sample using 1000X magnification. Identifications were facilitated using various guidelines (Bate *et al*., 2004; Cholnoky, 1960; Round, 1991; Schoeman, 1979; Schoeman and Archibald, 1976).

2.3.4 Data analysis

Several statistical analysis techniques were employed in this study depending on the type of data being analyzed. This included Analysis of Variance (ANOVA), Pearsons Correlation Coefficient and Principal Component Analysis (PCA), all of which provide powerful comparative techniques. All statistical analyses were performed on the Microsoft Excel® Analysis ToolPak 2007 (for ANOVA and Pearson Correlation Coefficient) and Genstat® Statistical Package (for PCA). In addition, the kriging spatial interpolation function in ArcGIS® version 9 was used to derive predicted surfaces for measured sediment and water parameters in the Bayhead Canal of the Durban Harbour, which allowed for the determination of trends for measured parameters at unsampled locations. Sediment parameters were further explored using several geochemical indices depending on the area of applicability. These included the Enrichment Factor (EF) and Contamination Factor (CF) indices for analysis of soil geochemistry. Each of the above statistical methods and indices are described in greater detail in the subsections that follow.

2.3.4.1 Principal Component Analysis (PCA)

PCA is used as a data reduction tool which reduces data dimensionality by explaining the correlation of large sets of variables by a small number of Principal Components (PC's) (Vega *et al*., 1998). This is often achieved through the interpretation of complex multidimensional data through a reduced set of orthogonal (non-correlated) variables (principal components, PC's) arranged in a decreasing order of importance and accounting for 75% of the total variance with an eigenvalue greater than one (Wang *et al*., 2012). PCA has been widely used in water quality studies as an unbiased statistical measure which can effectively indicate relationships between samples and/or variables, where these associations are often linked to similar magnitudes or variations in physico-chemical parameters which allows for subsequent discrimination of seasonal or man-made influences (Vega *et al*., 1998).

2.3.4.2 Cluster Analysis (CA)

Cluster Analysis (CA) is a multivariate statistical technique which helps group observations into classes or clusters which are based on similarities within a class and dissimilarities between other classes (Panda *et al*., 2006). The class characteristics are not known in advance, but are determined from the data analysis itself (Zhao and Cui, 2009). This statistical method is effectively used to explain the data structure of observations through the arrangement of a tree diagram or dendogram, and has been successfully applied to several water and sediment quality studies for useful conclusions (Charkhabi *et al*., 2008; Diaz-de Alba *et al*., 2011; Grande *et al*., 2003; Harikumar and Jisha, 2010; Luo *et al*., 2007; Pejman *et al*., 2009; Praus, 2007).

2.3.4.3 Analysis of variance (ANOVA)

ANOVA allows for the examination of different sources of variation on data for two or more samples operating simultaneously on a response, in order to test which effects are statistically significant and to determine their contribution to the variability of the response (Vega *et al*., 1998). Different types of variance analysis tools are used depending on the number of factors and samples requiring testing, including ANOVA single factor, ANOVA two-factor with replication and ANOVA two-factor without replication. More often, one-way ANOVA is effectively used as a tool in water quality studies to determine whether the mean values of water quality parameters of different monitoring stations vary spatially and temporally (Gyawali *et al*., 2012).

2.3.4.4 Pearson's correlation coefficient

Correlation is a method which effectively measures how variables vary in relation to each other, whereby a coefficient is calculated which then describes the degree of association between different variables in a dataset (Roberts, 1996). The resulting coefficient ranges between +1 and -1, where +1 represents a perfect positive correlation, -1 represents a perfect negative correlation and 0 represents no correlation (Roberts, 1996). The use of correlations in hydrological studies is particularly useful when exploring inter-elemental relationships, and has widely been used in several studies (Bordalo *et al*., 2001; Chidya *et al*., 2011; Ouyang *et al*., 2006; Singh *et al*., 2010; Thareja and Trivedi, 2010).

2.3.4.5 Kriging

Kriging is a statistical technique which allows for the estimation of values at unsampled locations through spatial interpolations (Sahebjalal, 2012). This is achieved by calculating the value at a specific point using the weighted sum of known points, where the weights are derived through the calculation of the co-variance between the pair of known points and the co-variance of the point of interest in relation to those of the known points (Ranade and Katpatal, 2007). Evaluation of semi-variograms and their properties (sill, range and nugget) form the basis of modelling the spatial data through calculated co-variances, and allows for the selection of the most suitable model on the basis of the measure of precision (El-Ayouti and Abou-Ali, 2013). El-Ayouti and Abou-Ali (2013) further states that the use of the kriging as a measure of spatial interpolation has many advantages:

- It provides the best linear unbiased estimator;
- Spatial variability is used to enhance the effectiveness of prediction; and
- It provides a measure of precision.

It is for this reason that the application of geostatistical kriging as a technique of spatial interpolation is particularly useful in hydrological sciences and has been successfully applied in several international studies (Al-Mashagbah *et al*., 2012; El-Ayouti and Abou-Ali, 2013; Forsythe *et al*., 2004; Kambhammettu *et al*., 2011; Mehrjardi *et al*., 2008; Ranade and Katpatal, 2007; Yang and Jin, 2010).

2.3.4.6 Enrichment Factor index

The Enrichment factor Index evaluates the magnitude of metal enrichment of an element in the environment as a result of anthropogenic influence, and is useful in indicating the extent to which measured concentrations of elements exceed the natural background concentrations for a particular site (Varol, 2011). The Enrichment Factor index is computed by the following equation according to Varol (2011):

$$\textit{Enrichment Factor (EF)} = \frac{\textit{[Concentration of Metal] / [Concentration of Fe]}}{\textit{[Clarke value of Metal] / [Clarke value of Fe]}} \qquad \textit{(3)}$$

Fe is commonly used as the reference metal for the following reasons as identified by Varol (2011):

- Its natural abundance in fine solid substrates;
- Similar geochemical composition to most heavy metals; and
- Its homogeneous natural concentration with distribution patterns.

As EF values increase, so too does the levels of anthropogenic influence, with 0 < EF < 10 often indicating natural metal sources from initial soil or parent rock and EF > 10 often associated with anthropogenic sources of metals (Moore *et al*., 2009). However, Varol (2011) further distinguishes between 7 classes of Enrichment Factors:

- EF < 1, No enrichment;
- 1 < EF < 3, Minor enrichment;
- 3 < EF < 5, Moderate enrichment;
- 5 < EF < 10, Moderately severe enrichment;
- 10 < EF < 25, Severe enrichment;
- 25 < EF < 50, Very severe enrichment; and
- EF > 50, Extremely severe enrichment.

2.3.4.7 Contamination Factor index

The Contamination Factor (CF) Index is used to assess soil contamination through comparison metal concentrations in the soil surface layer in relation to geochemical background values in uncontaminated soil and is given by the following ratio after Varol (2011):

$$\textit{Contamination Factor (CF)} = (C_{\textit{heavy metal}}) / (C_{\textit{background}}) \qquad (4)$$

Where:

C is the metal concentration of a given element.

Varol (2011) further identifies the following classes of contamination for analytical interpretation:

- CF < 1, Low contamination;
- 1 < CF < 3, Moderate contamination;
- 3 < CF < 6, Considerable contamination; and
- CF > 6, Very contaminated.

2.3.5 WATER AND SEDIMENT QUALITY GUIDELINES

Water results obtained from this study were compared to the prescribed South African water quality guidelines as outlined in DWAF (1996a and b) for freshwater and DWAF (1995) for marine environments. These guidelines provide insight on the water quality requirements for consumption and the protection of aquatic ecosystems, with specific background information on physico-chemical parameters and their possible ecological effects. Furthermore, in the absence of appropriate South African sediment quality guidelines for aquatic systems, measured soil parameters were compared against Canadian soil quality guidelines for the protection of aquatic life as outlined in CCME (1999a to h) and CCME (2009).

2.4 CONCLUSION

The uMhlatuzana, uMbilo and aManzimnyama river catchments form the core of industrialization and urbanization, and have been subject to intense industrial and residential development over the past few decades. Successful management of the river catchments as a consequence of this development requires the quantification of water quality parameters to identify possible pollution sources. In this study, seasonal water and sediment samples were subjected to a range of rigorous laboratory analyses to determine physical, chemical and biological parameters. Data thus obtained was subjected to statistical analyses and pollution assessments to allow for objective interpretation.

CHAPTER THREE

SPATIOTEMPORAL CHARACTERIZATION OF WATER CHEMISTRY AND POLLUTION SOURCES OF THE UMHLATUZANA, UMBILO AND AMANZIMNYAMA RIVER CATCHMENTS OF DURBAN, KWAZULU-NATAL, SOUTH AFRICA

This chapter is developed as a research article and has been submitted for publication to the *Environmental Earth Sciences Journal*.

3.1 ABSTRACT

The physical, chemical and microbiological properties of three freshwater systems contributing inflows to the Bayhead Canal of the Durban Harbour: the uMhlatuzana and uMbilo Rivers, and the aManzimnyama Canal of KwaZulu-Natal, South Africa are presented. Parameters targeted for analysis collectively included pH, total dissolved solids, dissolved oxygen, biological oxygen demand, chemical oxygen demand, conductivity, ammonium ions, phosphorous, sodium ions, sulphur, copper, calcium, magnesium, chromium, aluminium, nickel, lead, vanadium, mercury, potassium ions, *E*. *coli* and total coliforms. These parameters were analyzed seasonally during the wet and dry seasons in relation to land use change for spatial characterization. Comparisons with relevant South African water quality guidelines for freshwater systems showed that pollution associated with catchment activities was the main factor governing water quality, with nutrient concentrations that frequently exceeded prescribed standards and often rendered the system hypertrophic. In addition, the sanitary state of the rivers across all land use types was shown to be contaminated and polluted. This study also attempted to determine spatiotemporal (dis)similarity in the water quality of sample sites through Principal Component Analysis. Results show that although these systems were separated on the basis of water quality (both spatially and temporally), no apparent trends in water quality based on specific land use patterns linked sites across different catchments. Finally, the study examined the impacts of the three freshwater systems on the water quality of the Bayhead Canal of the Durban Harbour, and identified the aManzimnyama Canal as the most influential on heavy metal and microbiological contamination near the confluence.

Key words

Water quality, land use, seasonality, Principal Component Analysis, Durban Harbour

3.2 INTRODUCTION

The concerns of water resource sustainability in the face of climate change and increasing demands have resulted in several process based studies in many countries which attempt to examine the influence of catchment activities on water quantity and quality (Zhou *et al*., 2004). This is due to the fact that addressing water quantity and quality issues requires knowledge on the ways in which water resources are affected by these changes (Guo *et al*., 2008; Jahnig and Qinghua, 2010).

On a catchment scale, river chemistry is controlled by both natural and anthropogenic factors through diffuse or point pollutants (Ahearn *et al*., 2005). Gower (1980) identifies a complex system of dynamic interactions, in which river water quality is a product of several interactions between soil, rock and biotic components facilitated by catchment characteristics including geographical location, geology, geomorphology, biogeochemical processes, and the extent of human activity.

However, in recent years, several studies show that human-induced changes, in particular land use management, are strongly associated with declining water quality and river chemistry (Bullard, 1966; Dauer *et al*., 2000; Farnsworth and Milliman, 2003; Rhodes *et al*., 2001; Roselli *et al*., 2009; Weijters *et al*., 2009; Wilkinson and McElroy, 2007). These have further been shown to have profound effects on the integrity of aquatic ecosystems, including the functioning, abundance and biodiversity of aquatic organisms (Allan *et al*., 1997; Chapin *et al*., 1997; Harding and Winterbourn, 1995; Harding *et al*., 1998; Osmundson *et al*., 2002; Quinn *et al*., 1997; Richards *et al*., 1997; Wood and Armitage, 1997). In the South African context, several studies over the last decade have highlighted the negative impacts of anthropogenic catchment land use on river water quantity and quality (Dabrowski and de Klerk, 2013; Naidoo, 2005; Pillay, 2002; Walsh and Wepener, 2009). However, published research on the Durban Harbour catchments forming part of this study is limited. In general, it can be stated that human activities have strongly influenced water quality by upsetting the natural *status quo* (Boyd, 2000).

The impact of human activities on the natural environment emphasizes the need for careful management of available water sources within the catchment ecosystem. Consequently, a comprehensive study of fluvial water quality is essential. This study attempted to account for seasonal pollutant loading in relation to natural causes and anthropogenic land use and activities of three major catchments contributing to freshwater inflows in the Bayhead Canal of the Durban Harbour – the uMhlatuzana, uMbilo and aManzimnyama river catchments. In addition, the direct influence of these river systems on the quality of water in the Bayhead Canal of Durban Harbour into which they flow was explored through examination of water quality variables upstream and downstream of the associated confluences. Whilst such characterization serves as a useful indicator for natural and anthropogenic influences on water quality, it may also contribute to water quality management for the broader catchment region on the basis of future land use planning.

3.3 STUDY AREA

The uMhlatuzana and uMbilo Rivers, and aManzimnyama Canal are located in the eThekwini municipal area of KwaZulu-Natal, South Africa, at the core of its urban and industrial zone and comprise the three major freshwater systems contributing to inflows of the Bayhead Canal, Durban Harbour through associated canals at the confluence (**Figure 3.1**). The catchments of these systems are cumulatively described as having land use associated with extensive residential, industrial and commercial development, with dispersed and isolated parcels of recreational parks and nature reserves (DEAT, 2001). The catchments are also characterized by the presence of four registered wastewater treatment works (WWTW) discharging effluents into the river systems of the uMbilo and uMhlatuzana catchments (MER/ERM, 2011). The broader catchment area is characterized by a typical warm sub-tropical climate and experiences an average annual rainfall of 1054 mm mainly between the summer months of December and February (MER/ERM, 2011).

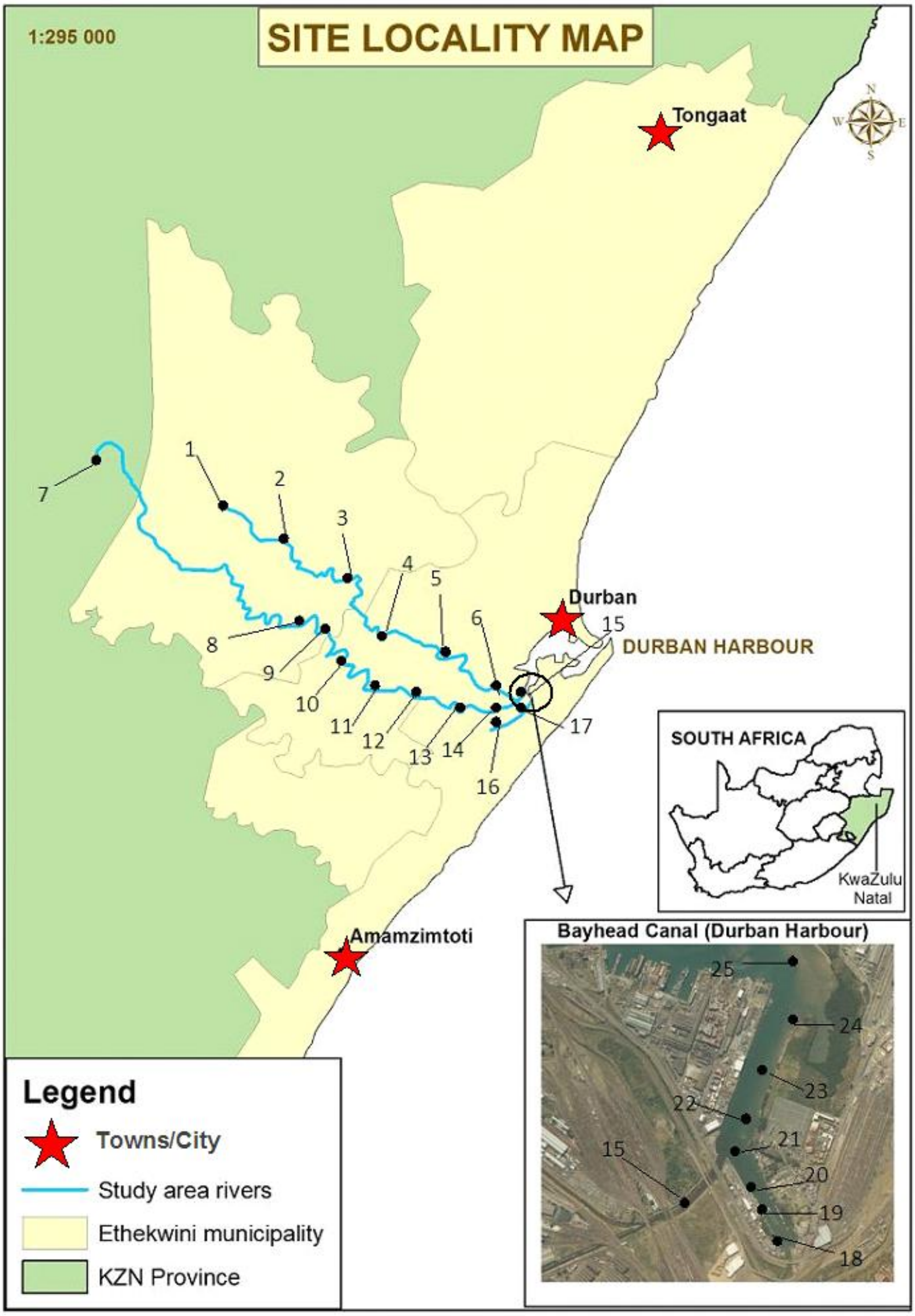

Figure 3.1: Study area with sample locations (Source: Moodley, 2013).

3.4 MATERIALS AND METHODS

The locations of the sampling sites were chosen along the uMhlatuzana, uMbilo and aManzimnyama river catchments in a manner to account for changes in land use practice, and are shown graphically in **Figure 3.1**. As such, sampling sites were systematically sited at the interface of each land use type along the river systems to reflect the potential influence of land use management on water quality. Land use identification and sampling site identification was achieved from the use of topographic maps and aerial photographs, and was validated by ground truthing *via* site visits. Further sampling was conducted along the Bayhead Canal at regular intervals to assess the effects of the subsequent inflows emanating from each of the fluvial systems. Sample locations appearing in **Figure 3.1** are described in **Table 3.1** below.

Table 3.1: Description of sample locations and corresponding catchment land use types (Source: Moodley, 2013).

uMbilo River	
Site	**Land use description**
1	Source (Sparse residential area)
2	Interface of industrial and residential area (sited downstream of industrial area)
3	Interface of residential area and nature reserve (sited downstream of residential area)
4	Interface of nature reserve and residential area – also impacted on by the Waste Water Treatment Works (WWTW) (sited downstream of nature reserve)
5	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
6	Interface of industrial area and confluence with uMhlatuzana River (sited downstream of industrial area)
uMhlatuzana River	
Site	**Land use description**
7	Source (Sparse residential area)
8	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
9	Interface of industrial area and nature reserve (sited downstream of industrial area)
10	Interface of nature reserve and residential area – also impacted on by WWTW (sited downstream of nature reserve)
11	Interface of residential and industrial area (sited downstream of residential area)
12	Interface of industrial area and nature reserve (sited downstream of industrial area)
13	Interface of nature reserve and industrial area (sited downstream of nature reserve)

14	Interface of industrial area and confluence with uMbilo River (sited downstream of industrial area)
uMbilo/uMhlatuzana Canal confluence	
Site	**Land use description**
15	Sited at confluence
aManzimnyama Canal	
Site	**Land use description**
16	Source (Low density industrial area)
17	Interface of industrial area and confluence to Bayhead Canal (sited downstream of industrial area)
Bayhead Canal of Durban Harbour	
Sites	**18, 19, 20, 21, 22, 23, 24, 25** (equidistant)

Four field surveys were conducted seasonally between December 2011 and September 2012, and were categorized into wet and dry season sampling. Following reconnaissance survey results which demonstrated near homogeneous mixing due to shallow depths (< 1 m) and high turbulence, water samples were collected at approximately mid-depth at each site and were analyzed for several physico-chemical parameters including pH, total dissolved solids (TDS), dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), conductivity (Cond.), ammonium ions (NH_4), phosphorous (P), sodium ions (Na), sulphur (S), copper (Cu), calcium (Ca), magnesium (Mg), chromium (Cr), aluminium (Al), nickel (Ni), lead (Pb), vanadium (V), mercury (Hg), potassium ions (K) and microbiological parameters *E*. *coli* (EC) and total coliforms (TC).

Analysis of metal ions (P, Cu, Ca, Mg, Cr, Al, Ni, Pb, V and Hg) was attained through atomic adsorption Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis.

An ion-selective electrode system comprising a polyvinylchloride (PVC) membrane sensitive to ammonium ions was used to analyze the concentration of ammonia in the sample (Ngila, 2008).

Analysis of sodium and potassium cation concentrations was quantitatively determined using a flame photometer. Concentrations of dissolved oxygen were determined using the Winkler method (Ngila, 2008).

Determination of BOD concentrations were obtained by the aerobic decomposition of organic matter within a BOD incubator as outlined by Tomar (1999).

The COD of the sample was measured by the oxygen corresponding to the organic matter susceptible to oxidation by chromic acid following Tomar (1999).

Microbiological analysis was measured using membrane filtration and fermentation techniques as detailed by Köster *et al*. (n.d.).

TDS was measured using an electronic TDS meter.

Water quality parameters were compared to the reference standards as outlined by the South African Department of Water Affairs and Forestry (DWAF, 1996a and b).

3.5 RESULTS AND DISCUSSION

The variations of parameters defining water quality measured during the dry and wet seasons are illustrated in **Table 3.2**.

Statistical analysis: Principal Component Analysis (PCA) was used to detect spatiotemporal site variations across river catchments using measured parameters of both seasons (**Figures 3.3a** to **c**).

Table 3.2: Variations in water quality parameters for the dry (*D*) and wet (*W*) seasons along the river catchments [highlights indicate exceedances of guideline values; N/A – guideline values not available; a – guideline values according to DWAF (1996a); b – guideline values according to DWAF (1996b)].

SEASONAL PARAMETERS		SITES																	DWA Guideline values
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
pH	*D*	7.56E+00	7.29E+00	7.17E+00	7.70E+00	7.58E+00	8.31E+00	6.96E+00	7.42E+00	6.92E+00	7.25E+00	7.17E+00	7.24E+00	7.54E+00	8.41E+00	8.62E+00	7.34E+00	7.40E+00	6 – 8a
	W	7.57E+00	7.67E+00	7.21E+00	7.33E+00	7.47E+00	7.89E+00	7.75E+00	7.58E+00	7.59E+00	7.54E+00	7.58E+00	7.52E+00	7.61E+00	8.20E+00	8.06E+00	7.34E+00	8.08E+00	
Cond.*	*D*	1.58E+02	1.95E+02	8.15E+02	3.61E+02	5.96E+02	5.96E+02	2.54E+02	2.79E+02	4.46E+02	2.94E+02	4.18E+02	4.40E+02	4.37E+02	4.66E+02	4.43E+02	6.97E+02	1.58E+04	N/A
	W	1.55E+02	2.05E+02	6.17E+02	3.11E+02	5.33E+02	5.01E+02	2.10E+02	2.58E+02	4.87E+02	2.96E+02	3.43E+02	3.70E+02	4.35E+02	4.64E+02	4.81E+02	1.35E+04	1.59E+04	
TDS**	*D*	6.80E+01	8.40E+01	3.50E+02	1.55E+02	2.56E+02	2.56E+02	1.09E+02	1.20E+02	1.91E+02	1.26E+02	1.80E+02	1.89E+02	1.88E+02	2.00E+02	1.92E+02	3.00E+02	1.01E+04	N/A
	W	6.65E+01	8.85E+01	2.65E+02	1.34E+02	2.29E+02	2.16E+02	9.03E+01	1.11E+02	2.09E+02	1.27E+02	1.48E+02	1.59E+02	1.87E+02	2.00E+02	2.07E+02	1.75E+03	1.10E+03	
DO**	*D*	8.62E+00	8.69E+00	8.48E+00	8.47E+00	8.69E+00	8.62E+00	8.42E+00	8.64E+00	8.56E+00	8.68E+00	8.63E+00	8.50E+00	8.67E+00	8.66E+00	8.71E+00	8.42E+00	8.74E+00	N/A
	W	7.05E+00	7.07E+00	7.07E+00	7.09E+00	7.07E+00	7.10E+00	7.20E+00	7.25E+00	7.02E+00	7.58E+00	7.13E+00	7.38E+00	7.57E+00	7.04E+00	7.09E+00	7.04E+00	7.19E+00	
BOD**	*D*	3.52E+00	3.53E+00	3.52E+00	3.56E+00	3.54E+00	3.48E+00	3.41E+00	3.39E+00	3.27E+00	3.38E+00	3.47E+00	3.47E+00	3.49E+00	3.50E+00	3.45E+00	3.50E+00	3.53E+00	N/A
	W	6.84E+00	5.82E+00	5.33E+00	5.14E+00	5.37E+00	5.08E+00	1.99E+00	1.60E+00	1.51E+00	1.51E+00	1.50E+00	5.23E+00	5.23E+00	1.51E+00	4.69E+00	5.81E+00	8.61E+00	
COD**	*D*	6.74E+00	7.22E+00	7.42E+00	6.06E+00	8.04E+00	6.38E+00	8.90E+00	7.44E+00	9.10E+00	9.00E+00	5.30E+00	8.10E+00	5.98E+00	7.92E+00	5.44E+00	2.70E+01	2.31E+01	N/A
	W	3.47E+00	6.64E+00	7.08E+00	4.67E+00	3.13E+00	7.01E+00	1.34E+01	1.22E+01	1.47E+01	7.41E+00	9.54E+00	8.93E+00	6.23E+00	2.90E+00	5.22E+00	4.18E+00	5.46E+00	
Na**	*D*	0.00E+00	0.00E+00	2.92E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.60E+02	100b
	W	0.00E+00	0.00E+00	6.05E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.61E+03	1.91E+03	
NH_4**	*D*	1.19E-02	1.47E-02	2.39E-02	1.87E-02	3.26E-02	2.04E-02	2.10E-02	1.70E-02	3.55E-02	2.27E-02	3.21E-02	4.33E-02	4.02E-02	3.82E-02	1.55E-02	4.18E-02	1.19E+00	0.007a
	W	6.49E+00	5.82E+00	8.51E+00	5.40E+00	4.58E+00	8.94E+00	7.52E+00	1.48E+01	1.22E+01	5.92E+00	3.66E+00	3.91E+00	3.23E+00	4.81E+00	4.16E+00	1.69E+01	1.41E+01	
Cu**	*D*	1.45E+00	1.45E+00	1.46E+00	1.45E+00	1.45E+00	1.44E+00	6.00E-02	6.00E-02	3.50E-02	3.50E-02	3.50E-02	4.50E-02	3.50E-02	3.50E-02	1.45E+00	1.49E+00	1.47E+00	0.0014a
	W	1.09E+00	1.03E+00	1.05E+00	1.03E+00	1.04E+00	1.04E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.04E+00	1.20E+00	1.11E+00	
Ca**	*D*	6.92E+00	9.97E+00	2.98E+01	2.80E+01	3.13E+01	2.75E+01	1.12E+01	2.04E+01	2.25E+01	1.33E+01	2.33E+01	2.58E+01	2.55E+01	3.48E+01	3.47E+01	6.18E+01	2.36E+02	N/A
	W	2.44E+00	7.73E+00	2.81E+01	2.47E+01	3.20E+01	2.82E+01	1.46E+01	1.41E+01	1.85E+01	1.35E+01	2.21E+01	1.93E+01	2.38E+01	3.13E+01	3.89E+01	1.83E+02	1.83E+02	
K**	*D*	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.62E+00	N/A
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.06E+01	1.21E+02	
Mg**	*D*	1.62E+00	3.92E+00	5.58E+00	8.16E+00	8.17E+00	8.29E+00	4.48E+00	5.19E+00	5.50E+00	5.56E+00	5.98E+00	3.34E+00	6.45E+00	9.07E+00	7.24E+00	1.38E+01	4.57E+02	N/A
	W	1.25E+00	3.43E+00	6.17E+00	5.88E+00	9.43E+00	8.83E+00	2.52E+00	4.21E+00	6.21E+00	5.19E+00	5.62E+00	5.76E+00	7.34E+00	1.08E+01	1.01E+01	3.18E+02	3.28E+02	
P**	*D*	0.00E+00	0.00E+00	9.10E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.11E+00	0.00E+00	1.27E+00	1.09E+00	7.55E-01	2.50E-01	0.00E+00	0.00E+00	0.00E+00	0.025a
	W	6.50E-02	5.50E-02	3.61E+00	1.70E-01	1.57E+00	1.67E+00	2.69E+00	2.36E+00	1.65E+01	3.98E+00	3.33E+00	3.66E+00	3.24E+00	3.18E+00	2.25E-01	1.37E+00	1.15E-01	
S**	*D*	5.75E-01	5.25E-01	1.83E+01	3.21E+00	1.03E+01	8.01E+00	0.00E+00	0.00E+00	1.34E+00	0.00E+00	7.40E-01	1.27E+00	1.11E+00	3.52E+00	8.20E+00	2.21E+01	2.94E+02	N/A
	W	3.29E+00	5.07E+00	1.56E+01	7.31E+00	1.46E+01	1.21E+01	4.14E+00	1.01E+00	6.18E+00	1.69E+00	2.62E+00	3.77E+00	2.42E+00	1.03E+01	1.92E+01	2.24E+02	2.49E+02	
Al**	*D*	1.97E+00	1.92E+00	1.91E+00	1.88E+00	1.89E+00	1.90E+00	1.13E+00	1.10E+00	1.96E+00	1.18E+00	1.33E+00	9.60E-01	1.27E+00	1.31E+00	1.89E+00	1.97E+00	1.94E+00	0.01a
	W	1.80E+00	1.72E+00	1.66E+00	1.64E+00	1.64E+00	1.65E+00	7.35E-01	7.60E-01	4.65E-01	4.65E-01	4.70E-01	5.10E-01	7.25E-01	4.80E-01	1.69E+00	1.91E+00	1.86E+00	
Hg**	*D*	5.10E-01	4.65E-01	4.40E-01	4.30E-01	4.15E-01	4.10E-01	0.00E+00	0.00E+00	5.45E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.05E-01	9.95E-01	6.55E-01	0.00004a
	W	0.00E+00	5.40E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	
V**	*D*	7.85E-01	7.85E-01	7.85E-01	7.85E-01	7.90E-01	7.90E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.90E-01	7.90E-01	7.70E-01	0.1b
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.02E+00	
Pb**	*D*	9.80E-01	9.65E-01	9.65E-01	9.50E-01	9.60E-01	9.60E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.60E-01	1.02E+00	9.70E-01	0.0012a
	W	6.85E-01	9.15E-01	1.85E-01	9.00E-02	3.65E-01	2.35E-01	5.55E-01	1.20E-01	2.50E-01	1.35E-01	1.50E-02	3.60E+00	2.85E-01	1.35E-01	1.05E-01	2.15E-01	1.65E-01	
Ni**	*D*	4.50E-01	4.50E-01	5.30E-01	4.45E-01	4.55E-01	4.65E-01	1.07E+00	1.37E+00	1.23E+00	1.12E+00	1.04E+00	1.05E+00	1.10E+00	9.25E-01	4.40E-01	4.60E-01	4.55E-01	0.2b
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	
Cr**	*D*	3.15E-01	1.85E-01	1.75E-01	1.75E-01	3.80E-01	1.75E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.75E-01	3.65E-01	3.85E-01	0.012a
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	
EC***	*D*	3.00E+02	3.00E+01	1.23E+02	2.70E+02	2.00E+01	1.50E+01	9.80E+01	1.05E+02	1.30E+02	6.50E+01	1.25E+03	6.75E+02	3.10E+02	1.60E+01	4.00E+00	2.10E+03	5.60E+03	0 b
	W	4.05E+02	7.50E+01	1.95E+02	1.00E+02	9.50E+01	1.90E+01	1.95E+02	4.45E+02	2.15E+02	1.65E+02	2.90E+02	4.85E+02	1.90E+02	5.90E+01	5.80E+01	4.50E+01	2.03E+02	
TC***	*D*	1.33E+03	3.60E+02	5.66E+02	4.35E+02	1.65E+02	1.50E+01	1.61E+03	1.46E+03	1.04E+03	3.80E+02	6.15E+03	2.73E+03	3.65E+02	2.20E+01	2.70E+01	1.01E+04	9.51E+04	0 – 5 b
	W	5.55E+02	4.30E+02	6.60E+02	1.59E+03	5.20E+02	6.90E+01	2.23E+03	2.61E+03	5.28E+03	5.51E+03	2.40E+04	4.14E+03	3.58E+03	4.79E+02	4.93E+02	1.95E+02	9.37E+02	

*Represented as µS/cm. **Represented as mg/L. ***Represented as colonies per 100mL.

3.5.1 Water quality of the river catchments

The measured water quality parameters at sample sites along the river catchments are depicted in **Table 3.2**. Analytical findings indicated that nutrient water quality determinants (for NH_4, P, Cu) generally fell outside the target freshwater quality range for aquatic ecosystems, rendering the systems as hypertrophic and toxic for human and animal consumption (DWAF, 1996a). Exceptions were noted for P at sites 1, 2, 4, 5, 6, 7, 8, 10, 15, 16 and 17 in the dry season; and Cu at sites 7 – 14 in the wet season. Decreases in P concentrations during the dry season has been shown to be a direct consequence of low surface runoff emanating from surrounding land use types and the subsequent reduction of nutrient loading into the systems (Shah *et al*., 2007). The reduction of Cu concentrations at sites 7 – 14 (uMhlatuzana River) in the wet season was indicative of low geochemical input of the system and in-stream diluting effects as a consequence of higher rainfall in the wet season. In the absence of relevant South African freshwater aquatic ecosystem guidelines for Na, concentrations show that the water was unsuitable for human consumption at sites 16 in the wet season, and 17 in both seasons according to DWAF (1996b). These sites were associated with industrial activity and subsequent effluent discharge into the aManzimnyama Canal. In general, principal inputs of nutrients (NH_4, P, S, Na, K, Mg, Ca and Cu) were often associated with industrial and residential land use (sites 8, 9, 16, 17 for NH_4 in the wet season; site 9 for P in both seasons; sites 3, 5, 6, 14, 16 and 17 for S in both seasons; sites 16 and 17 for Ca and Mg in the wet season; sites 16 and 17 in the dry season for Na and K. The significance of riparian vegetation in controlling general nutrient chemistry of water bodies is well documented in watershed studies (Jarvie *et al*., 2008; Lowrance *et al*., 1984; Tran *et al*., 2010). The findings of this study were no different in that the role of nature reserves/riparian habitat (represented by sites 4, 10 and 13) as natural filters in the environment were clearly demonstrated by the reduced concentrations of selected nutrients (particularly NH_4, P and S) detected/measured at these sites across both seasons.

In terms of basic water quality determinants, pH at sites 6 in the dry season, 17 in the wet season, and 14 and 15 across both seasons fell outside the expected range for natural freshwater systems in South Africa (DWAF, 1996a). These sites were associated with industrial activity/effluent releases. COD concentrations in surface waters usually occur at values of 20 mg/L or less in unpolluted waters, which implies some degree of pollution at sites 16 and 17 in the dry season (Chapman, 1992). The contaminant records at these sites were again associated with industrial effluent discharge into the aManzimnyama Canal from surrounding industry.

When present, heavy metals (Al, Hg, Pb and Cr) generally exceeded the freshwater target values for aquatic environments as outlined in DWAF (1996a). Similarly, when present, trace metals V and Ni were at concentrations which rendered the water unsuitable for consumption by humans and animals (DWAF, 1996b). Hg in the system was detected at industrial sites 2 in the wet season, and sites 9 and 16 in the dry season. The consistent presence of Hg in sites 1 – 6 (uMbilo River) in the dry season was unknown – possibly relating to the introduction of Hg containing compounds at the source through illegal dumping activities (photographic evidence in **Figure 3.2**). This is further corroborated by the gradual decrease in Hg concentration in the downstream direction from site 1 to site 6. A similar trend is observed for Pb, V and Cr at sites 1 – 6, however, the possibility of geochemical origin of V and Cr cannot be dismissed as these do not show a downstream decrease in concentration as in the case of Hg and Pb. V, Pb and Cr inputs were also associated with industrial effluent discharge at sites 16 and 17 of the aManzimnyama Canal.

Microbiological data revealed the poor sanitary state of all three freshwater systems in both seasons (DWA, 1996b). Anomalously high combined values of EC and TC were recorded at sites 16 and 17 in the dry season, and sites 11 and 12 in the wet season. High coliform counts are often a common characteristic of residential areas accounting for the high count at site 11. High values are associated with industrial sites 12, 16 and 17, which could be a direct consequence of industrial effluent discharge and some untreated sewage entering the system directly from these sites. The slightly elevated total coliform count at site 10 after the nature reserve in the wet season was reflective of high organic carbon content of runoff water from such areas (Schoonover and Lockaby, 2006).

Specific inter-elemental relationships and spatiotemporal variability of water quality at sample sites were explored through multivariate statistics (Principal Component Analysis – PCA), and depicted in relevant principal component bi-plots (**Figures 3.3a** to **c**).

Figure 3.2: Evidence of illegal dumping at site 1 (uMbilo River) (Source: Moodley, 2013).

3.5.2 SPATIOTEMPORAL WATER QUALITY VARIATIONS

Principal Component Analysis (PCA) was conducted on physico-chemical data for the dry and wet seasons to determine which parameters contributed significantly to water quality variations in the river catchments. PCA is a powerful pattern recognition technique which attempts to explain the variance of large datasets of inter-correlated variables using a small set of Principal Components (PC's) (Sudevi and Lokesh, 2012). The principal components enable the isolation of dominant underlying processes operating within the hydrological systems – including anthropogenic or mineral sources (Ammar and Abderrahmane, 2010). Considering the large numbers of variables studied (22), the first two component loadings were isolated and plotted on the PC1-PC2 axes planes for greater clarity (**Figures 3.3a** to **c**) (Parinet *et al*., 2004). The first two principal components cumulatively represented 60.67% of the total variance for the wet season, 79.19% of the total variance for the dry season and 56.97% for combined seasons (**Table 3.3**).

In the dry season, PC1 accounted for 53.35% of the total variance and was positively and largely contributed by Ca, Cond., Mg, S, TC, TDS, Na, NH_4, K and EC; and negatively by Ni. This component distinguished the importance of mineral related parameters (Ca, Cond., Mg, TDS and K) and anthropogenic sewage related parameters (S, TC, NH_4 and EC) over geochemical weathering inputs (Ni). PC2 in the dry season accounted for 25.84% of the total variance and was positively and largely contributed by Ni; and negatively by V, Pb, Hg, Cu, Cr and Al. This component in all likelihood measured the preponderance of geochemical weathering inputs (Ni) over anthropogenic industrial inputs of heavy metals (V, Pb, Hg, Cu, Cr and Al).

During the wet season, PC1 accounted for 44.05% of the total variance and was mainly contributed positively by Ca, Cond., K, Mg, Na, S and TDS; and negatively by COD, P and TC. This component appeared to distinguish the importance of mineral related parameters (Ca, Cond., K, Mg, Na, S and TDS) over anthropogenic sewage related parameters (COD, P and TC). PC2 in the wet season accounted for 16.62% of the total variance and was contributed positively mainly by COD, P, EC and NH_4; and negatively mainly by Al, BOD, Cu and Hg. This component showed the importance of anthropogenic sewage related parameters (COD, P, EC and NH_4) over organic related parameters (BOD) and industry related heavy metal inputs (Al, Cu and Hg).

For combined wet and dry seasons, PC1 accounted for 35.38% of the total variance and was positively and largely contributed by Ca, Cond., Mg, Na, S and TDS; and negatively by P. This component appeared to distinguish the long term importance of mineral related (Ca, Cond., Mg, Na, S and TDS) parameters over nutrients (P) for the systems. PC2 for combined seasons represented 21.59% of the total variance and was positively and largely contributed by DO, Cr, Hg, Ni and V; and negatively by NH_4, Na and K. This component illustrated the prevalence of industrial heavy metal inputs (Cr, Hg, Ni and V) and organic related parameters (DO) over nutrients (NH_4, Na and K).

Table 3.3: Loadings of Principal Components 1 and 2.

	DRY SEASON		WET SEASON		COMBINED SEASONS	
VARIABLES	**PC1**	**PC2**	**PC1**	**PC2**	**PC1**	**PC2**
Al	0.15	-0.29	0.22	-0.37	0.19	0.17
BOD	0.10	-0.24	0.23	-0.26	0.13	-0.16
COD	0.20	0.03	-0.14	0.36	0.15	0.16
Ca	0.28	0.12	0.32	0.12	0.33	-0.12
Cond.	0.27	0.15	0.32	0.15	0.32	-0.17
Cr	0.21	-0.26	-	-	0.19	0.33
Cu	0.17	-0.34	0.21	-0.38	0.20	0.15
DO	0.08	0.06	-0.08	0.19	0.05	0.37
EC	0.26	0.13	-0.10	0.24	0.26	0.13
Hg	0.17	-0.24	-0.01	-0.23	0.16	0.34
K	0.27	0.15	0.27	0.16	0.18	-0.22
Mg	0.27	0.15	0.32	0.14	0.33	-0.14
NH_4	0.27	0.16	0.21	0.22	0.05	-0.39
Na	0.27	0.15	0.32	0.15	0.28	-0.24
Ni	-0.16	0.34	-	-	-0.03	0.25
P	-0.09	0.17	-0.12	0.32	-0.09	-0.17
Pb	0.17	-0.34	-0.06	0.03	0.06	0.13
S	0.28	0.13	0.33	0.12	0.33	-0.16
TC	0.27	0.15	-0.11	0.26	0.25	0.08
TDS	0.27	0.15	0.30	0.11	0.30	0.04
V	0.16	-0.34	0.25	0.15	0.21	0.22
pH	0.01	-0.17	0.05	0.03	0.01	-0.07
% Variance	**53.35**	**25.84**	**44.05**	**16.62**	**35.38**	**21.59**

The relationships between sites and water quality variables are displayed in the PCA bi-plots along the PC1-PC2 axes planes (**Figures 3.3a** to **c**), where measure of fit is indicated by arrow length in relative to variable placement, and distance between sampling sites approximating the (dis)similarity of water chemistry between sites as a function of Euclidean distance (Walsh and Wepener, 2009). The smaller the angles between arrows, the more strongly correlated the variables (Moser *et al*., 2010). Arrows at 90° to each other indicate uncorrelated variables, whilst arrows plotted in opposite directions indicate negatively correlated variables (Moser *et al*., 2010). This allowed for detailed spatiotemporal evaluation of catchment sites on the basis of significant water quality variations at each of the sites.

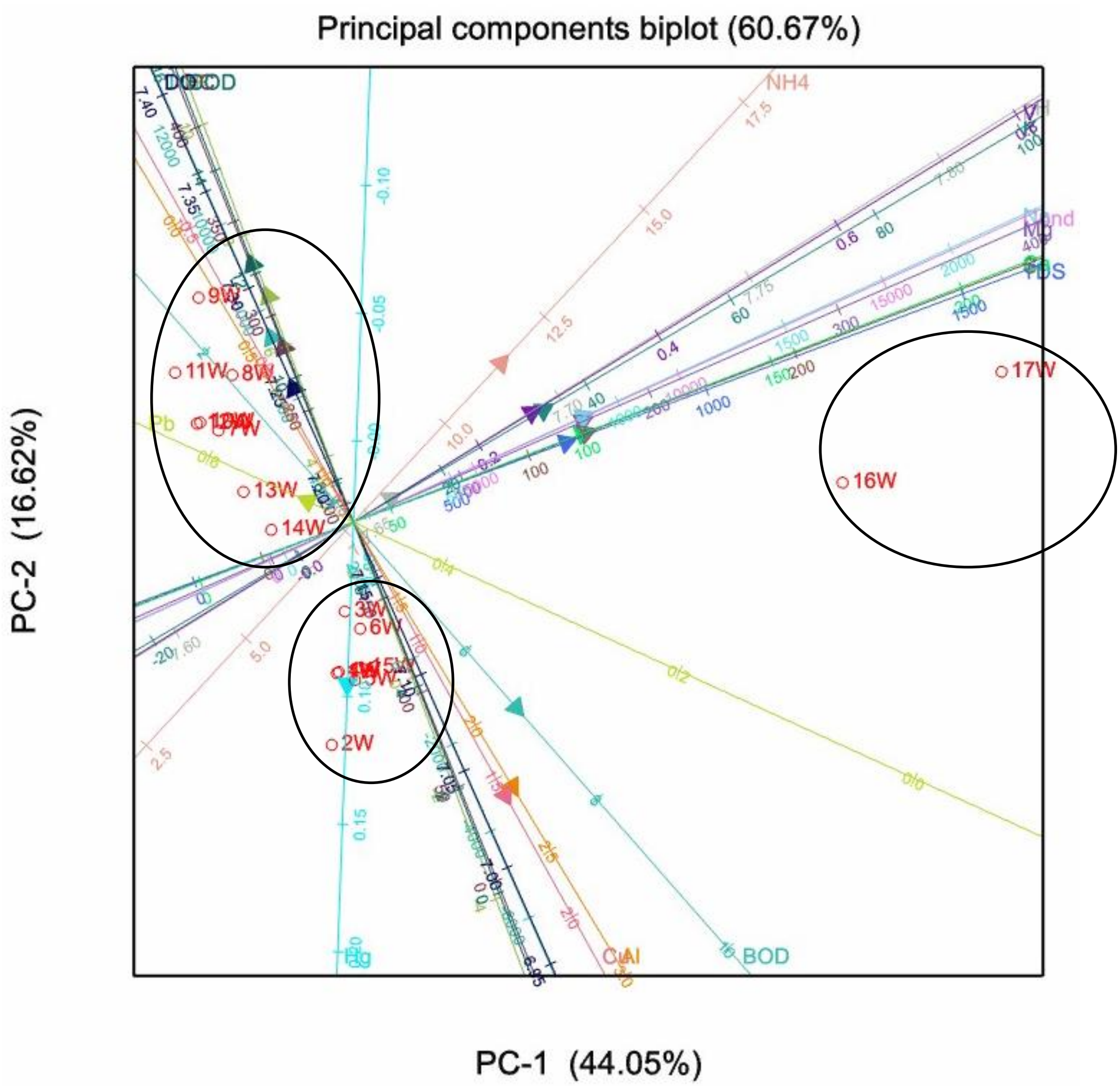

Figure 3.3a: PCA bi-plot for water quality variables in the wet season.

As depicted in **Figure 3.3a**, the PCA bi-plot for the wet season described 60.67% of variation in the data, with 44.05% represented by the first principal component and 16.62% by the second principal component. Sites along the uMbilo and uMhlatuzana Rivers were separated along the PC2 axis, with separation mostly influenced by Al, Cu and Hg (greater loading for uMbilo River and site 15 after the confluence with the uMhlatuzana River), and organic related BOD, COD, DO, P, EC and TC (greater loading for uMhlatuzana River). This suggested that both river systems were separated on the basis of varying anthropogenic influence through sewage discharge – corresponding to PC2 in the prior PCA analysis. Sample sites in the uMhlatuzana River (sites 7 – 14) were clustered and hence similar to each other in terms of water quality. Sites 1 – 6 (uMbilo River) and site 15 (after the confluence with the uMhlatuzana River) were clustered and hence similar to each other in terms of water quality, suggesting a greater influence of the uMbilo River on the water quality of site 15 after the confluence. Evidently, the wet season PCA bi-plot showed spatial dissimilarity in terms of the catchment river systems, with sites 16 and 17 (aManzimnyama Canal) showing a distinct separation from the remaining catchments along the PC1 axis, and is mostly influenced by greater loading of TDS, S, Ca, Mg, Cond., Na, V, NH_4 and pH. This separation corresponded to varying mineral related parameters of PC1 as explained in the previous PCA analysis. No apparent trends in water quality based on specific land use patterns were indicated in the PCA for the remaining catchment sites. The wet season bi-plot further illustrated strong positive correlations between Cond., TDS, S, Ca, Mg, Na, V, NH_4 and pH which mainly influenced the water quality of the aManzimnyama Canal – possibly explaining the nature of effluent discharge into the canal from surrounding industrial activities. The plot also showed positive correlations between Al, BOD and Cu; and positive correlations between EC, TC, P, DO and COD (which were inversely correlated with Al, Cu and BOD on the basis of linear direction) – all of which were most influential on the water quality of the uMbilo and uMhlatuzana Rivers. The unusual inverse correlation between BOD and microbiological parameters (TC and EC) could be explained by the positive correlation between P and the microbiological parameters (TC and EC), as P is typically negatively correlated with BOD as evident in the PCA bi-plot.

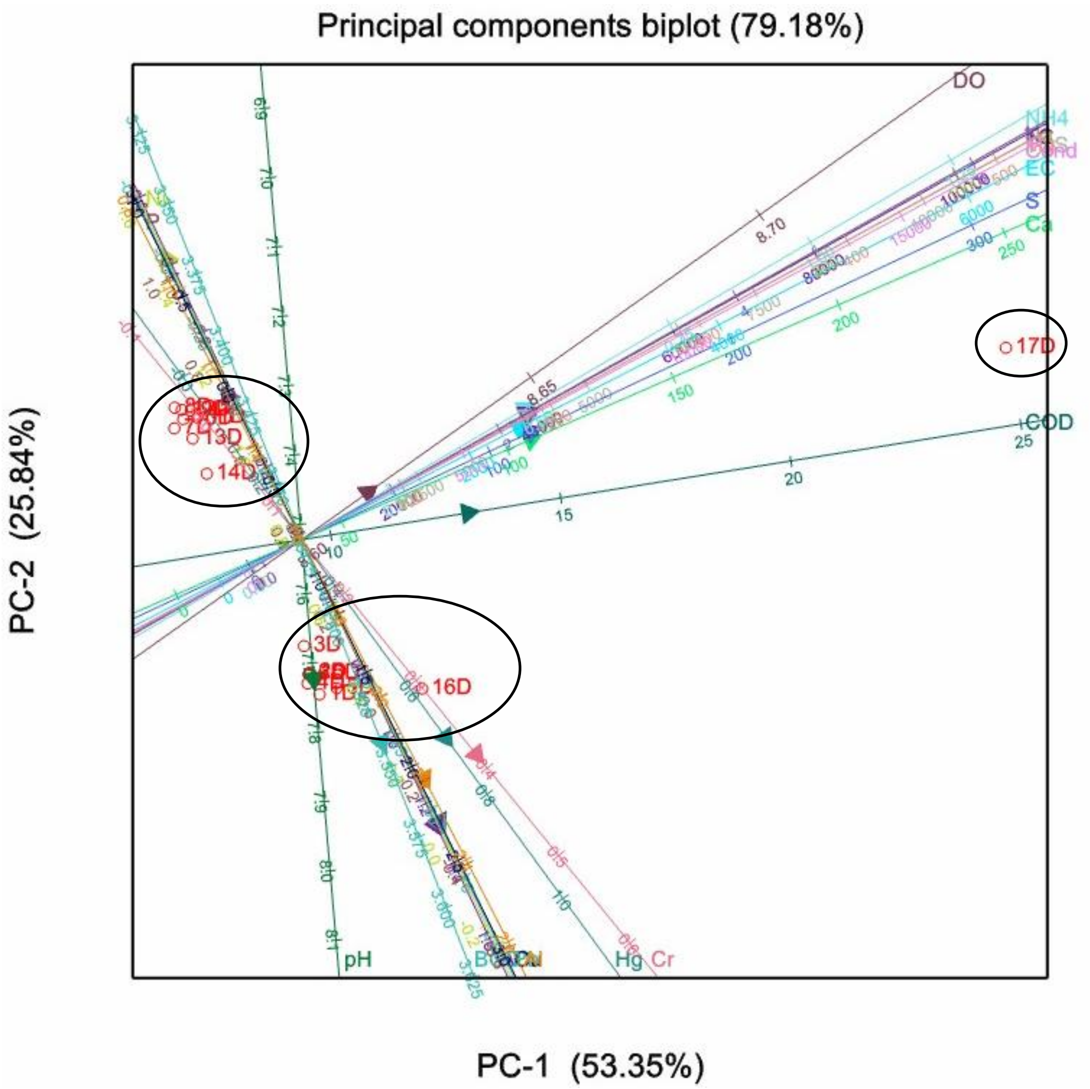

Figure 3.3b: PCA bi-plot for water quality variables in the dry season.

The PCA bi-plot for the dry season (**Figure 3.3b**) described 79.19% of variation in the data, with 53.35% represented by the first principal component and 25.84% by the second principal component. As in the case of the wet season, sample sites in the uMhlatuzana River (sites 7 – 14) were clustered and hence similar to each other in terms of water quality. Sites 1 – 6 (uMbilo River) and site 15 (after the confluence with the uMhlatuzana River) were clustered and hence similar to each other in terms of water quality, suggesting a greater influence of the uMbilo River on the water quality of site 15 after the confluence. In contrast to the wet season, site 16 of the aManzimnyama Canal displayed similar water quality to the sites of the uMbilo River catchment. Sites along the uMbilo and uMhlatuzana Rivers, and aManzimnyama Canal (site 16 only) were separated along the PC2 axis, with separation mostly influenced by Hg, Cr, Al, BOD, pH, Pb, V and Cu (greater inputs for uMbilo River, site 15 after the confluence with uMhlatuzana River, and site 16 of the aManzimnyama Canal), and Ni and P (greater loading for uMhlatuzana River). This suggested that the sites of the river systems were separated on the basis of varying anthropogenic influence – corresponding to PC2 in the prior PCA analysis. Site 17 of the aManzimnyama Canal is separated to a large degree from the remaining sites along the PC1 axis, with separation largely attributed to COD, S, EC, Cond., NH_4, TDS, TC, DO, Na, Mg and K (greater loading at site 17 relative to remaining sites). This suggested separation on the basis of varying mineral and anthropogenic influence – corresponding to PC1 in the prior PCA analysis. As in the case of the wet season, no apparent trends in water quality based on specific land use patterns were indicated in the PCA for the remaining catchment sites. The dry season bi-plot further illustrated strong positive correlations between Cond., EC, TC, TDS, S, Ca, Mg, Na, NH_4 and DO which mainly influences the water quality of the aManzimnyama Canal – possibly explaining the nature of effluent discharge into the aManzimnyama Canal from industrial activities in the dry season. The plot also showed positive correlations between Hg, Cr, Al, BOD, pH, Pb, V and Cu; which were all inversely correlated with Ni – all of which were most influential on the water quality of the uMbilo and uMhlatuzana Rivers, and site 16 of the aManzimnyama Canal.

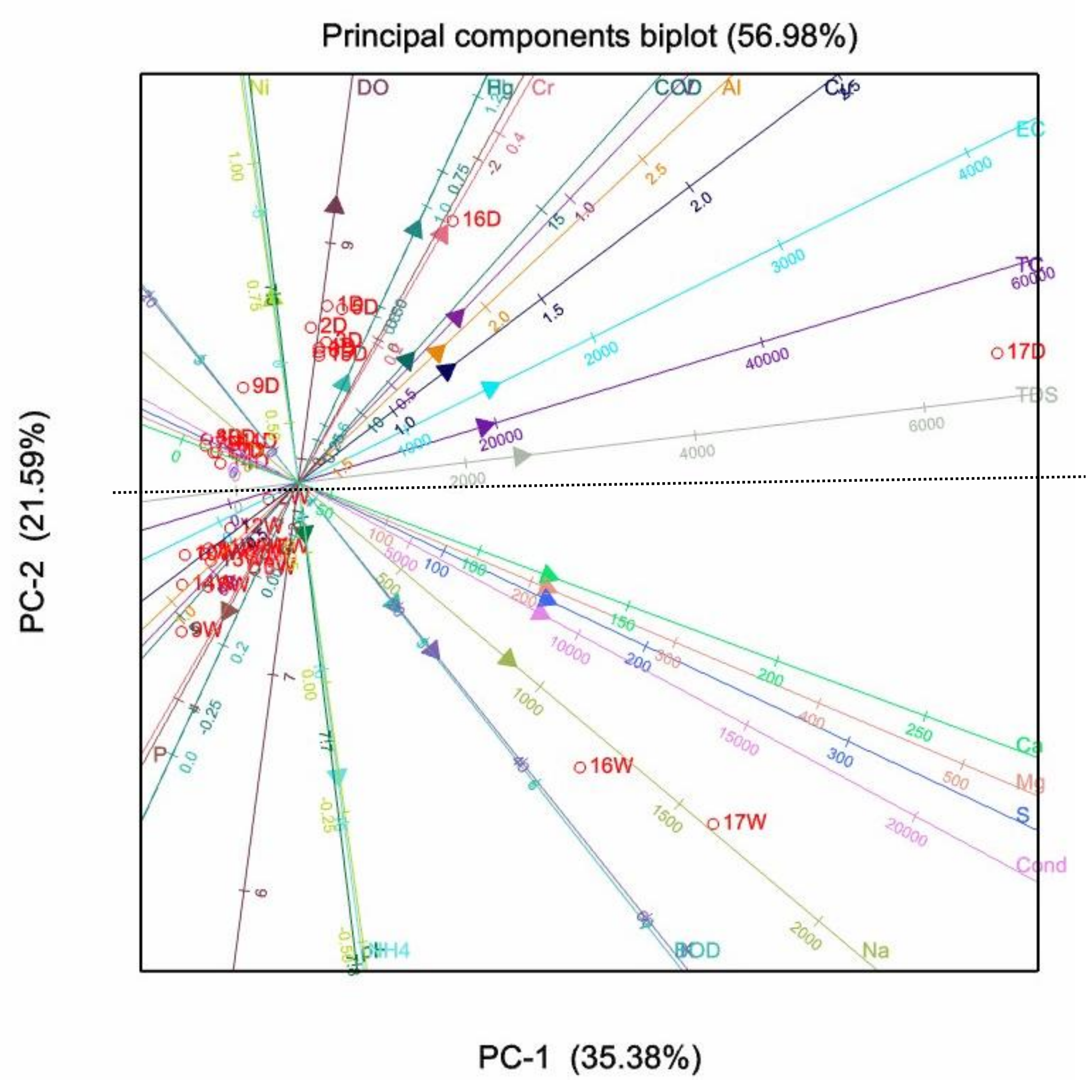

Figure 3.3c: PCA bi-plot for water quality variables in the combined seasons.

Figure 3.3c depicted strong seasonal variations (seasonal separation indicated by dashed line parallel to the PC2 axis) in water quality between selected sites in the uMhlatuzana and uMbilo Rivers along the PC2 axis which primarily related to organic (DO, NH_4) and heavy metal parameters (Cr, Hg, V, Ni) – as explained in previous PCA analysis. The most distinct variations noted in terms of temporal water quality are those for sites 16 and 17 along the PC2 axis which showed a large degree of seasonal spatial dissimilarity on the basis of Euclidean distances between corresponding wet and dry season sites. This was mainly attributed to variations in seasonal loadings of NH_4, Cond., TDS, COD, Na, Ca, Mg, S, EC and TC at site 16; and variations of seasonal loading in TDS, COD, Na, NH_4, EC and TC for site 17.

3.5.3 INFLUENCE OF CATCHMENT WATER QUALITY ON THE BAYHEAD CANAL

Results of additional sampling in the Bayhead Canal of the Durban Harbour after the catchment confluences are depicted in **Table 3.4** below. Chemical concentrations in the Bayhead Canal were used to generate interpolated images for visual interpretation (**Figure 3.4**). Interpolations were created using ArcGIS 9®.

Table 3.4: Concentrations of the Bayhead Canal for dry (*D*) and wet (*W*) seasons.

SEASONAL PARAMETERS		SITES							
		18	19	20	21	22	23	24	25
pH	*D*	7.39E+00	7.79E+00	7.99E+00	8.17E+00	7.90E+00	7.80E+00	7.77E+00	7.80E+00
	W	7.47E+00	7.37E+00	7.44E+00	7.83E+00	7.69E+00	7.72E+00	7.68E+00	7.75E+00
Cond.*	*D*	1.50E+04	3.22E+04	3.00E+04	3.00E+04	4.89E+04	4.84E+04	5.14E+04	5.07E+04
	W	2.05E+04	3.99E+04	3.98E+04	2.80E+04	4.86E+04	4.87E+04	4.70E+04	4.91E+04
TDS**	*D*	9.12E+03	1.14E+04	9.25E+03	9.15E+03	2.17E+04	2.28E+04	2.24E+04	2.21E+04
	W	8.73E+03	1.14E+04	1.50E+04	1.05E+04	2.08E+04	2.43E+04	1.82E+04	2.48E+04
DO**	*D*	8.62E+00	8.62E+00	8.73E+00	8.59E+00	8.58E+00	8.75E+00	8.60E+00	8.54E+00
	W	6.99E+00	7.10E+00	7.10E+00	7.07E+00	6.97E+00	7.03E+00	6.92E+00	6.95E+00
BOD**	*D*	3.30E+00	3.32E+00	3.33E+00	3.25E+00	3.27E+00	3.04E+00	3.02E+00	2.59E+00
	W	4.54E+00	4.51E+00	3.80E+00	6.69E+00	3.44E+00	5.30E+00	5.59E+00	2.06E+00
COD**	*D*	7.86E+00	4.14E+00	3.96E+00	6.14E+00	6.30E+00	6.22E+00	7.40E+00	7.10E+00
	W	5.05E+00	7.70E+00	4.66E+00	7.94E+00	6.84E+00	4.66E+00	3.68E+00	4.34E+00
Na**	*D*	8.64E+02	2.51E+03	2.46E+03	2.52E+03	3.26E+03	3.55E+03	3.84E+03	4.61E+03
	W	2.50E+03	3.60E+03	3.61E+03	2.51E+03	4.25E+03	4.26E+03	4.14E+03	4.21E+03
NH_4**	*D*	1.61E-01	8.03E-01	1.09E+00	1.35E+00	6.10E-01	1.01E+00	7.64E-01	1.07E+00
	W	2.46E+01	4.11E+01	4.32E+01	1.16E+01	3.33E+01	2.09E+01	2.99E+01	2.85E+01
Cu**	*D*	1.53E+00	6.00E-02	6.50E-02	6.00E-02	7.50E-02	5.50E-02	6.00E-02	6.00E-02
	W	1.02E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Ca**	*D*	2.27E+02	3.61E+02	3.29E+02	3.20E+02	5.49E+02	5.40E+02	5.42E+02	5.34E+02
	W	2.68E+02	4.43E+02	4.55E+02	3.38E+02	5.15E+02	5.31E+02	5.07E+02	5.29E+02
K**	*D*	0.00E+00	9.24E+02	9.22E+02	9.08E+02	9.26E+02	9.15E+02	8.95E+02	8.94E+02
	W	1.30E+02	2.68E+02	2.72E+02	1.55E+02	3.37E+02	3.44E+02	3.09E+02	3.33E+02
Mg**	*D*	4.28E+02	6.52E+02	5.88E+02	5.62E+02	9.37E+02	1.04E+03	1.07E+03	9.11E+02
	W	4.64E+02	9.24E+02	8.87E+02	6.46E+02	9.51E+02	9.70E+02	9.30E+02	1.19E+03
P**	*D*	0.00E+00	4.85E-01	5.80E-01	3.80E-01	3.00E-01	1.35E-01	3.15E-01	1.35E-01
	W	4.30E-01	4.52E+00	4.54E+00	4.29E+00	3.36E+00	3.33E+00	3.08E+00	3.39E+00
S**	*D*	2.74E+02	5.65E+02	4.88E+02	4.98E+02	8.55E+02	8.39E+02	8.61E+02	8.40E+02
	W	3.26E+02	7.48E+02	7.80E+02	5.97E+02	9.06E+02	7.94E+02	7.91E+02	8.27E+02
Al**	*D*	2.64E+00	1.17E+00	1.21E+00	1.13E+00	1.23E+00	1.14E+00	1.17E+00	1.13E+00
	W	1.66E+00	5.25E-01	5.25E-01	5.15E-01	5.20E-01	5.20E-01	1.15E-01	9.45E-01
Hg**	*D*	1.29E+00	5.25E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
V**	*D*	7.80E-01	1.87E+00	1.81E+00	1.86E+00	2.08E+00	2.10E+00	2.12E+00	2.07E+00
	W	9.90E-01	0.00E+00	0.00E+00	0.00E+00	6.45E-01	8.20E-01	7.85E-01	8.80E-01
Pb**	*D*	9.60E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.00E-02
Ni**	*D*	4.45E-01	2.38E+00	2.40E+00	2.39E+00	2.31E+00	2.36E+00	2.35E+00	2.42E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cr**	*D*	3.85E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
EC***	*D*	1.80E+02	0.00E+00	1.00E+01	5.00E+00	0.00E+00	0.00E+00	1.00E+00	0.00E+00
	W	3.13E+02	4.00E+01	3.00E+01	4.40E+01	1.30E+02	1.10E+02	1.00E+02	5.50E+01
TC***	*D*	3.10E+02	0.00E+00	2.50E+01	5.10E+01	7.00E+00	2.00E+00	6.53E+02	2.00E+02
	W	4.17E+03	1.30E+03	3.48E+02	6.71E+02	6.00E+03	1.10E+03	2.50E+03	3.85E+03

*Represented as µS/cm. **Represented as mg/L. ***Represented as colonies per 100mL.

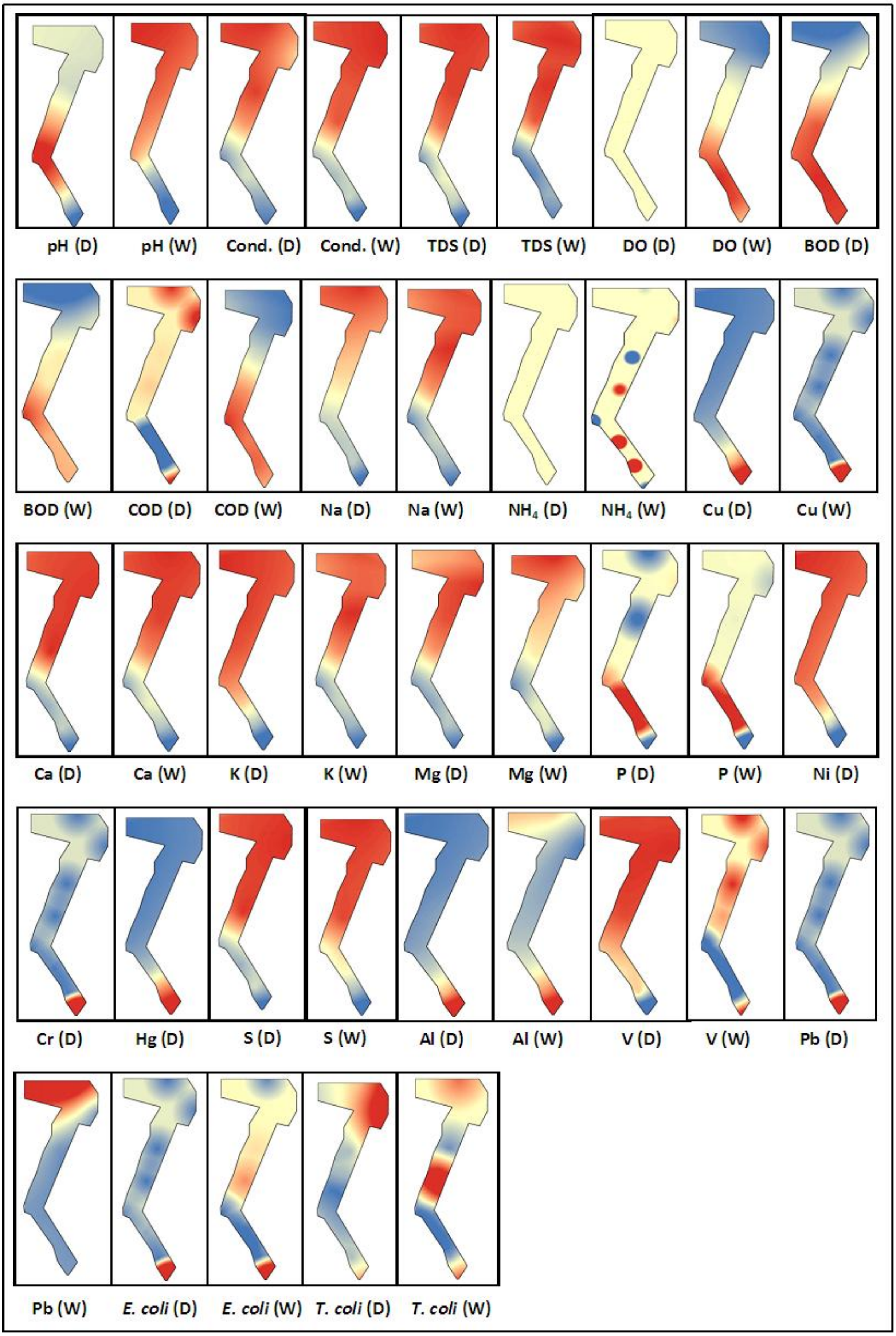

Figure 3.4: Interpolated images of Bayhead Canal chemical data – blue indicates low values transitioning to yellow indicating medium values, and red indicating high values. No Ni, Cr and Hg was detected in the wet season.

Chemical analyses of water quality variables in the Bayhead Canal of the Durban Habour showed that the aManzimnyama Canal is most influential on the Bayhead Canal chemistry at the confluence with the loading of DO (wet season), BOD (both seasons), COD (both seasons), Cu (both seasons), Al (both seasons), *E. coli* (both seasons), total coliforms (both seasons), V (wet season), Pb (dry season), Hg (dry season) and Cr (dry season) at the confluence. The uMhlatuzana/uMbilo Canal appeared to contribute to loadings of pH (dry season), DO (wet season), BOD (both seasons), COD (wet season), P (both seasons), and total coliforms (wet season) at the confluence of the Bayhead Canal. Overall, it appeared that the aManzimnyama Canal is responsible for a greater degree of chemical loading in the Bayhead Canal as compared to the uMbilo/uMhlatuzana catchment inflows. The fact that marine waters of the port itself tend to control dissolved Na, K, Mg, TDS and Cond. values is not unusual, as this phenomenon is characteristic of marine waters (DWAF, 1995). On the other hand, elevated values of Ni, V and S which appears to be controlled by the marine waters of the port, is more likely associated with anthropogenic pollution originating from port activities itself. Whilst the marine guideline values for S and V are unavailable, Ni concentrations for the dry season exceeded the prescribed value of 0.025 mg/L, indicative of anthropogenic pollution most likely of port origin. Whilst the interpolated images provides an indication of the influence of the freshwater canal inflows on the Bayhead Canal, it is difficult to accurately quantify the effects of the freshwater inflows on chemical patterns in the Bayhead Canal, as the chemicals are highly variable with factors such as temperature, water turbulence and volume and biological productivity (DWAF, 1996a). More detailed and scientific evaluation of chemical behaviour associated with the Bayhead Canal can be obtained through detailed, chemical specific hydrodynamic wave modelling.

3.6 CONCLUSION

A diverse variety of activities characterize the catchments of the Durban Harbour – primarily intense anthropogenic alteration and modification of the landscape through industry, wastewater treatment works and urbanization over the past few decades. The influence of human activities on these catchments accounts for substantial spatial and temporal water quality variability across catchments as illustrated in the PCA bi-plots and individual component loadings. Anthropogenic catchment activities have also shown to affect water quality of the receiving Bayhead Canal of the Durban Harbour with respect to selected physico-chemical parameters – with the highly industrialized aManzimnyama catchment being most influential. Although not all possible water quality variables were analyzed, this study has been very comprehensive in that it has assessed the impacts of a wide range of physical and chemical parameters, as well as microbiological aspects which have allowed for subsequent spatiotemporal characterization of the catchments. The study demonstrated that there is no doubt that intensification of anthropogenic activities and processes operating within the catchments have caused a general deterioration of nutrient, heavy metal and microbiological water quality across all land use types on the basis of water quality variables that were analyzed. Specific land use types are shown to affect the river's water quality in different ways. Combined ammonia and phosphorous concentrations emanating from the different land use types were typically high, with the levels of ammonia and phosphorous causing hypertrophic conditions thus rendering sections of the river as unsuitable aquatic habitats. Further analysis of water quality variables reveal disturbing amounts of pathogenic microbes associated with all land use types rendering the sanitary quality of the systems as unacceptable. Whilst the nature reserves display a limited purifying capacity with regard to certain nutrients, the anthropogenic stresses placed on the catchment ecosystems as a whole renders the water source as severely polluted across all land use types.

CHAPTER FOUR

SEASONAL DISCHARGE AND CHEMICAL FLUX VARIATIONS OF RIVERS FLOWING INTO THE BAYHEAD CANAL OF DURBAN HARBOUR, SOUTH AFRICA

This chapter is developed as a research article and has been submitted for publication to the *International Journal of Environmental Research*.

4.1 ABSTRACT

The uMhlatuzana, uMbilo and aManzimnyama river catchments located on the eastern seaboard of the KwaZulu-Natal province, South Africa, form the core of urbanization and industrialization and contribute the only natural freshwater inflows to the Bayhead Canal portion of the Durban Harbour. In this study, seasonal discharges and physico-chemical water properties were used to quantitatively determine the material mass transport capacity of the river systems on the basis of hydrographic inputs and chemical loading from surrounding land use sectors. Mass transport of total dissolved solids (TDS), ammonia (NH_4), phosphorous (P), aluminium (Al), calcium (Ca), copper (Cu), chromium (Cr), mercury (Hg), potassium (K), magnesium (Mg), sodium (Na), nickel (Ni), lead (Pb), sulphur (S) and vanadium (V) were determined for each river. Results indicated that land use, seasonality and river flow were significant determinants of material loading in the rivers and the receiving port waters. The spatiotemporal distribution patterns of chemical fluxes indicated that industrial activity associated with the aManzimnyama Canal contributed the most with regards to TDS, NH_4, Ca, K, Mg, Na, S and V loading in both wet and dry seasons, as well as Al, Cu, Hg and Pb during the dry season. Similarly, industrial activity associated with the uMbilo/uMhlatuzana Canal at the lower reaches accounted for the highest P, Al, Cu and Pb fluxes in the wet season only. Fluxes of these parameters are used to explain observed elemental concentrations and patterns in the port waters of the Bayhead Canal into which they flow.

Key words

Discharge, chemical flux, Durban Harbour

4.2 INTRODUCTION

Studies of material fluxes within river systems are important and have been shown to provide important scientific applications such as utilizing material cycles to understand catchment and coastal interactions (Cruzado *et al*., 2002; Sigleo and Frick, 2007; Xincheng and Huanting, 2001). The material fluxes of rivers are strongly related to river discharge which is a function of several climatic and geological characteristics of the river basin, and this essentially controls the timing and amount of water reaching adjoining river systems and ultimately the coast (Sigleo and Frick, 2007). Consequently, knowledge of river flow and discharge is important in coping with present and future environmental changes of hydrological systems (Cruzado *et al*., 2002).

In recent years there has been a rapid decline in freshwater quantity and quality of rivers due primarily to unsustainable land use practices (Li *et al*., 2008). Human-induced changes, in particular land use management, have significant impacts and relationships on the transport and delivery of sediment, pollutants and nutrients, with implications on stream chemistry and water quality (Dauer *et al*., 2000; Farnsworth and Milliman, 2003; Bullard, 1966; Wilkinson and McElroy, 2007; Weijters *et al*., 2009). These alterations may have strong negative implications on the biodiversity of terrestrial, freshwater and marine ecosystems (Weijters *et al*., 2009).

The impacts of catchment related activities and processes on the water quality of associated river systems and the areas into which they ultimately drain, emphasises the need for careful management of the catchment. As such, a comprehensive study of the material mass transport capacity of the river systems from the source is important in understanding the cycles of seasonal fluxes and variable loads and the ways in which these influence observed physical and chemical water quality patterns of the aquatic environments into which they drain. In this study, such an attempt was made to explain the seasonal material mass transport capacity of three systems namely the uMhlatuzana, uMbilo and aManzimnyama Rivers of Durban, KwaZulu-Natal province, all of which contribute freshwater inflows to the Bayhead Canal of the Durban Harbour. This was related to land use and seasonality for each of the systems, in an attempt to understand the observed water quality trends from source through to sink. The study served as a useful indication of natural and anthropogenic catchment influences on the material mass transport capability of the rivers from the source, and contributed to a broader understanding of water quality changes in each of the river systems.

4.3 STUDY AREA

The uMhlatuzana, uMbilo and aManzimnyama River catchments comprise three major fluvial systems draining into the Bayhead Canal of the Durban Harbour primarily through rainfall runoff from various catchment land use sectors. The land use types of the broader catchment area comprise light and heavy industry, residential sectors, and naturally vegetated areas (MER/ERM, 2011). The catchments, being located in a summer rainfall area, experiences peak river discharge in the summer months between December and February and a reduced winter (June to August) discharge (MER/ERM, 2011). The uMbilo river catchment has an approximate area and length of 67 km^2 and 35 km respectively (reaching as far inland as the suburb of Gillits), the larger uMhlatuzana river catchment has an approximate area and length of 113 km^2 and 50 km respectively (reaching as far inland as Assagay), and the much smaller aManzimnyama river catchment which has a total area and length of approximately 15 km^2 and 5.5 km respectively (MER/ERM, 2011). All three rivers flow into the port waters through associated canals as depicted in **Figure 4.1**.

4.4 MATERIALS AND METHODS

Sampling locations were established on the basis of land use change as depicted in **Figure 4.1**, and was verified through topographic maps and ground truthing *via* site visits.

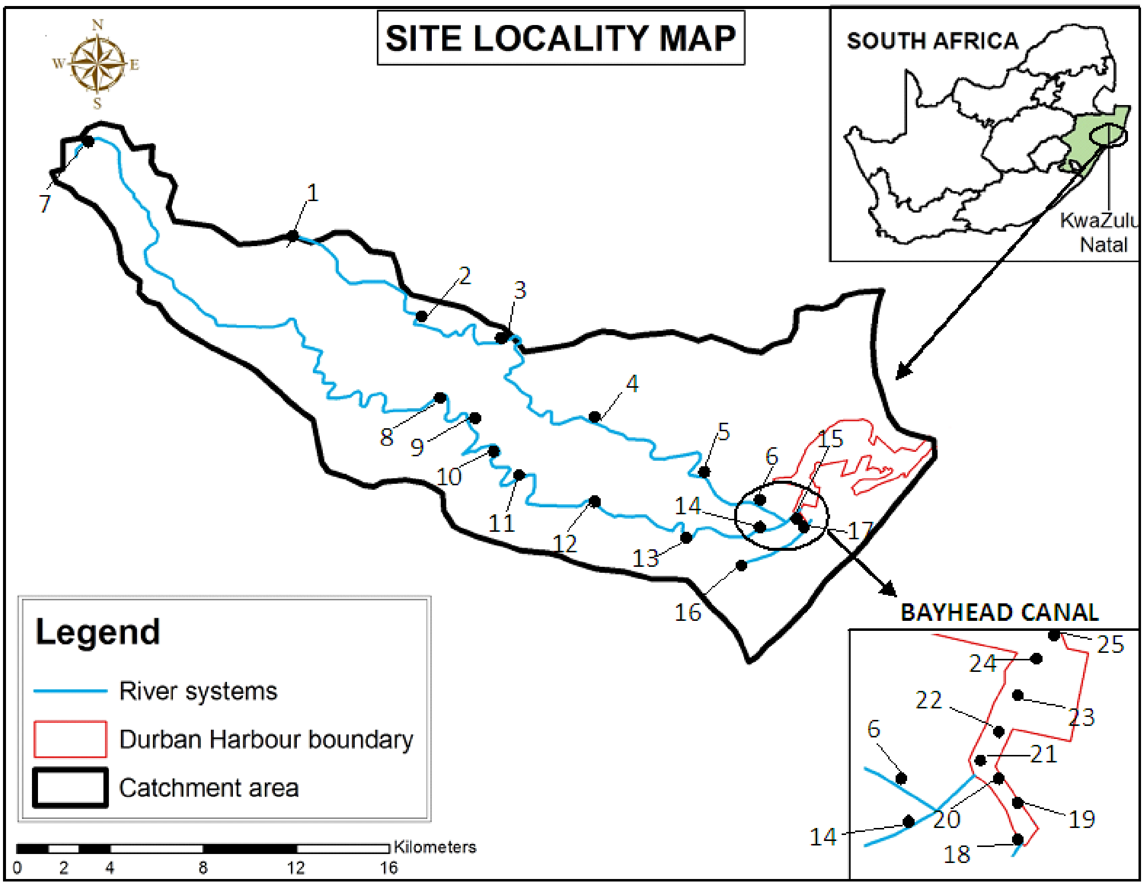

Figure 4.1: Catchments of the three rivers and the Durban Harbour with sampling sites depicted (Source: Moodley, 2013).

A total of 17 sites were sampled seasonally between December 2011 and September 2012. An indication of sampling events in relation to seasonal rainfall distribution patterns during the sampling period is indicated in **Figure 4.2** below:

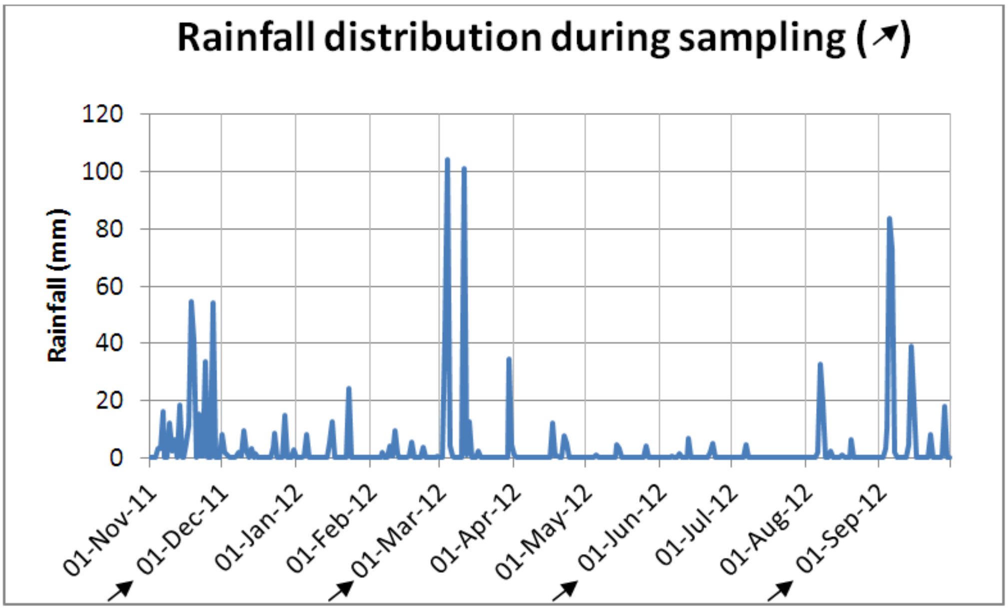

Figure 4.2: Rainfall distribution patterns in relation to four sampling events: 1st Dec 2011 (summer – wet season), 1st March 2012 (autumn – dry season), 1st Jun 2012 (winter – dry season) and 1st Sep 2012 (spring – wet season). (*Source*: SASRI, 2013).

An additional 8 sample sites were selected at equal intervals in the Bayhead Canal of the Durban Harbour (sites 18 – 25 in **Figure 4.1**), and was simultaneously sampled in order to assess the influence of the catchment river fluxes on concentrations of variables in the Bayhead Canal of the Durban Harbour. The sample locations of **Figure 4.1** are described **Table 4.1** below:

Table 4.1: Description of sample sites on the basis of land use (Source: Moodley, 2013).

uMbilo River	
Site	**Land use description**
1	Source (Sparse residential area)
2	Interface of industrial and residential area (sited downstream of industrial area)
3	Interface of residential area and nature reserve (sited downstream of residential area)
4	Interface of nature reserve and residential area – also impacted on by the Waste Water Treatment Works (WWTW) (sited downstream of nature reserve)
5	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
6	Interface of industrial area and confluence with uMhlatuzana River (sited downstream of industrial area)

uMhlatuzana River	
Site	**Land use description**
7	Source (Sparse residential area)
8	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
9	Interface of industrial area and nature reserve (sited downstream of industrial area)
10	Interface of nature reserve and residential area – also impacted on by WWTW (sited downstream of nature reserve)
11	Interface of residential and industrial area (sited downstream of residential area)
12	Interface of industrial area and nature reserve (sited downstream of industrial area)
13	Interface of nature reserve and industrial area (sited downstream of nature reserve)
14	Interface of industrial area and confluence with uMbilo River (sited downstream of industrial area)
uMbilo/uMhlatuzana Canal confluence	
Site	**Land use description**
15	Sited at confluence
aManzimnyama Canal	
Site	**Land use description**
16	Source (Low density industrial area)
17	Interface of industrial area and confluence to Bayhead Canal (sited downstream of industrial area)
Bayhead Canal of Durban Harbour	
Sites	**18, 19, 20, 21, 22, 23, 24, 25** (equidistant)

Reconnaissance survey results showed that material concentrations were fairly homogeneous across the channels due to relatively low discharge and highly turbulent flows, hence seasonally collected water samples were taken at approximately mid-channel and mid-depth at each site. Dry and wet season concentrations were thus obtained for total dissolved solids (TDS), ammonium ions (NH_4), phosphorous (P), sodium ions (Na), sulphur (S), copper (Cu), calcium (Ca), magnesium (Mg), chromium (Cr), aluminium (Al), nickel (Ni), lead (Pb), vanadium (V), mercury (Hg), and potassium ions (K) from the sample derived filtrate.

Analysis of P, S, Cu, Ca, Mg, Cr, Al, Ni, Pb, V and Hg was conducted through atomic adsorption Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis whilst TDS was measured using an electronic TDS meter.

An ion-selective electrode system comprising a polyvinylchloride (PVC) membrane sensitive to ammonium ions was used to analyze the concentration of ammonia in the sample and Na and K cation concentrations was quantitatively determined using a flame photometer following the procedures described in Ngila (2008).

The discharges (Q) at each sampling location were determined as a product of the measured channel cross-sectional area (A) and current velocity (V) at each sample site Chapman (1992):

$$Q = V \times A \qquad (1)$$

Thereafter, the nutrient flux (Φ) or the amount of suspended and dissolved matter passing through the sample location was established as a product of discharge (Q) and nutrient concentration (C) as reflected below (Chapman, 1992):

$$\Phi = Q \times C \qquad (2)$$

4.5 RESULTS AND DISCUSSION

The seasonal variations in the material fluxes of measured parameters for the wet and dry seasons are illustrated in **Table 4.2**, and were explored statistically using Analysis of Variance (ANOVA). Corresponding chemical concentrations and discharge rates are represented in **Figures 4.3(a)** and **(b)** for comparative evaluation. In addition, chemical concentrations in the Bayhead Canal (**Table 4.3**) were used to generate interpolated images using ArcGIS 9®, to visually distinguish the effects of catchment material fluxes on the water quality of the Bayhead Canal (**Figure 4.4**).

Table 4.2: Material fluxes for dry and wet seasons.

DRY SEASON FLUXES (g/s)															
Sites	**TDS**	**NH_4**	**P**	**Al**	**Ca**	**Cu**	**Cr**	**Hg**	**K**	**Mg**	**Na**	**Ni**	**Pb**	**S**	**V**
1	1.50E-01	1.00E-04	0.00E+00	4.30E-03	1.52E-02	3.20E-03	7.00E-04	1.10E-03	0.00E+00	3.60E-03	0.00E+00	1.00E-03	2.20E-03	1.30E-03	1.70E-03
2	4.89E-01	1.00E-04	0.00E+00	1.12E-02	5.80E-02	8.40E-03	1.10E-03	2.70E-03	0.00E+00	2.28E-02	0.00E+00	2.60E-03	5.60E-03	3.10E-03	4.60E-03
3	9.10E+00	5.00E-04	2.37E-02	4.97E-02	7.76E-01	3.80E-02	4.60E-03	1.14E-02	0.00E+00	1.45E-01	7.60E-02	1.38E-02	2.51E-02	4.77E-01	2.04E-02
4	9.86E+00	1.30E-03	0.00E+00	1.20E-01	1.78E+00	9.21E-02	1.12E-02	2.74E-02	0.00E+00	5.20E-01	0.00E+00	2.87E-02	6.06E-02	2.05E-01	5.00E-02
5	1.46E+01	1.80E-03	0.00E+00	1.08E-01	1.78E+00	8.24E-02	2.17E-02	2.37E-02	0.00E+00	4.66E-01	0.00E+00	2.59E-02	5.47E-02	5.88E-01	4.50E-02
6	2.87E+01	2.30E-03	0.00E+00	2.13E-01	3.08E+00	1.62E-01	2.00E-02	4.60E-02	0.00E+00	9.30E-01	0.00E+00	5.22E-02	1.08E-01	8.98E-01	8.86E-02
7	2.38E-01	1.00E-04	0.00E+00	2.50E-03	2.45E-02	1.00E-04	0.00E+00	0.00E+00	0.00E+00	9.80E-03	0.00E+00	2.30E-03	0.00E+00	0.00E+00	0.00E+00
8	2.47E-01	1.00E-04	0.00E+00	2.30E-03	4.22E-02	1.00E-04	0.00E+00	0.00E+00	0.00E+00	1.07E-02	0.00E+00	2.80E-03	0.00E+00	0.00E+00	0.00E+00
9	1.71E+01	3.60E-03	1.89E-01	1.76E-01	2.02E+00	3.10E-03	0.00E+00	4.93E-02	0.00E+00	4.93E-01	0.00E+00	1.10E-01	0.00E+00	1.20E-01	0.00E+00
10	9.46E+00	1.50E-03	0.00E+00	8.85E-02	1.00E+00	2.60E-03	0.00E+00	0.00E+00	0.00E+00	4.17E-01	0.00E+00	8.36E-02	0.00E+00	0.00E+00	0.00E+00
11	4.90E+01	8.70E-03	3.44E-01	3.60E-01	6.33E+00	9.50E-03	0.00E+00	0.00E+00	0.00E+00	1.63E+00	0.00E+00	2.83E-01	0.00E+00	2.01E-01	0.00E+00
12	1.42E+01	3.30E-03	8.18E-02	7.20E-02	1.93E+00	3.40E-03	0.00E+00	0.00E+00	0.00E+00	2.51E-01	0.00E+00	8.25E-02	0.00E+00	9.53E-02	0.00E+00
13	1.81E+02	3.86E-02	7.28E-01	1.22E+00	2.46E+01	3.37E-02	0.00E+00	0.00E+00	0.00E+00	6.22E+00	0.00E+00	1.01E+00	0.00E+00	1.07E+00	0.00E+00
14	3.95E+01	7.60E-03	4.93E-02	2.59E-01	6.87E+00	6.90E-03	0.00E+00	0.00E+00	0.00E+00	1.79E+00	0.00E+00	1.83E-01	0.00E+00	6.94E-01	0.00E+00
15	1.23E+02	9.80E-03	0.00E+00	1.21E+00	2.23E+01	9.27E-01	1.12E-01	2.60E-01	0.00E+00	4.64E+00	0.00E+00	2.82E-01	6.16E-01	5.26E+00	5.07E-01
16	5.39E-01	1.00E-04	0.00E+00	3.50E-03	1.11E-01	2.70E-03	7.00E-04	1.80E-03	0.00E+00	2.49E-02	0.00E+00	8.00E-04	1.80E-03	3.98E-02	1.40E-03
17	1.19E+04	1.39E+00	0.00E+00	2.28E+00	2.78E+02	1.72E+00	4.52E-01	7.70E-01	6.60E+00	5.37E+02	1.13E+03	5.35E-01	1.14E+00	3.46E+02	9.05E-01
Mean	**7.30E+02**	**8.66E-02**	**8.33E-02**	**3.64E-01**	**2.06E+01**	**1.82E-01**	**3.68E-02**	**7.02E-02**	**3.88E-01**	**3.26E+01**	**6.64E+01**	**1.59E-01**	**1.18E-01**	**2.09E+01**	**9.55E-02**
SD	**2.88E+03**	**3.40E-01**	**1.90E-01**	**6.20E-01**	**6.67E+01**	**4.50E-01**	**1.10E-01**	**1.90E-01**	**1.60E+00**	**1.30E+02**	**2.74E+02**	**2.60E-01**	**3.00E-01**	**8.38E+01**	**2.40E-01**
WET SEASON FLUXES (g/s)															
Sites	**TDS**	**NH_4**	**P**	**Al**	**Ca**	**Cu**	**Cr**	**Hg**	**K**	**Mg**	**Na**	**Ni**	**Pb**	**S**	**V**
1	1.49E+00	1.46E-01	1.50E-03	4.03E-02	5.48E-02	2.45E-02	0.00E+00	0.00E+00	0.00E+00	2.81E-02	0.00E+00	0.00E+00	1.54E-02	7.39E-02	0.00E+00
2	2.46E+00	1.62E-01	1.50E-03	4.76E-02	2.15E-01	2.86E-02	0.00E+00	1.50E-02	0.00E+00	9.52E-02	0.00E+00	0.00E+00	2.54E-02	1.41E-01	0.00E+00
3	4.52E+01	1.45E+00	6.16E-01	2.83E-01	4.78E+00	1.79E-01	0.00E+00	0.00E+00	0.00E+00	1.05E+00	1.03E-01	0.00E+00	3.24E-02	2.66E+00	0.00E+00
4	5.13E+01	2.08E+00	6.55E-02	6.30E-01	9.49E+00	3.97E-01	0.00E+00	0.00E+00	0.00E+00	2.26E+00	0.00E+00	0.00E+00	3.47E-02	2.82E+00	0.00E+00
5	4.81E+02	9.61E+00	3.29E+00	3.43E+00	6.72E+01	2.18E+00	0.00E+00	0.00E+00	0.00E+00	1.98E+01	0.00E+00	0.00E+00	7.67E-01	3.06E+01	0.00E+00
6	5.03E+02	2.08E+01	3.89E+00	3.85E+00	6.57E+01	2.43E+00	0.00E+00	0.00E+00	0.00E+00	2.06E+01	0.00E+00	0.00E+00	5.48E-01	2.83E+01	0.00E+00
7	5.86E-01	4.88E-02	1.75E-02	4.80E-03	9.50E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.64E-02	0.00E+00	0.00E+00	3.60E-03	2.69E-02	0.00E+00
8	5.94E-01	7.93E-02	1.26E-02	4.10E-03	7.53E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.25E-02	0.00E+00	0.00E+00	6.00E-04	5.40E-03	0.00E+00
9	4.67E+01	2.73E+00	3.68E+00	1.04E-01	4.12E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.39E+00	0.00E+00	0.00E+00	5.58E-02	1.38E+00	0.00E+00
10	2.48E+01	1.16E+00	7.78E-01	9.09E-02	2.63E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.01E+00	0.00E+00	0.00E+00	2.74E-02	3.30E-01	0.00E+00
11	9.12E+01	2.26E+00	2.05E+00	2.90E-01	1.36E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.47E+00	0.00E+00	0.00E+00	9.30E-03	1.62E+00	0.00E+00
12	3.34E+01	8.20E-01	7.69E-01	1.07E-01	4.05E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.21E+00	0.00E+00	0.00E+00	7.56E-01	7.92E-01	0.00E+00
13	6.55E+02	1.13E+01	1.28E+01	2.54E+00	8.33E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.57E+01	0.00E+00	0.00E+00	1.02E+00	8.47E+00	0.00E+00
14	9.15E+02	2.20E+01	1.46E+01	2.20E+00	1.43E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.96E+01	0.00E+00	0.00E+00	6.19E-01	4.73E+01	0.00E+00
15	1.63E+03	3.28E+01	1.78E+00	1.33E+01	3.07E+02	8.22E+00	0.00E+00	0.00E+00	0.00E+00	7.94E+01	0.00E+00	0.00E+00	8.30E-01	1.52E+02	0.00E+00
16	1.48E+01	1.44E-01	1.16E-02	1.62E-02	1.55E+00	1.01E-02	0.00E+00	0.00E+00	8.95E-02	2.70E+00	1.36E+01	0.00E+00	1.80E-03	1.90E+00	0.00E+00
17	3.13E+03	4.01E+01	3.28E-01	5.29E+00	5.20E+02	3.15E+00	0.00E+00	0.00E+00	3.46E+02	9.36E+02	5.45E+03	0.00E+00	4.70E-01	7.10E+02	2.91E+00
Mean	**4.49E+02**	**8.69E+00**	**2.63E+00**	**1.90E+00**	**7.22E+01**	**9.77E-01**	**0.00E+00**	**9.00E-04**	**2.03E+01**	**6.73E+01**	**3.21E+02**	**0.00E+00**	**3.07E-01**	**5.81E+01**	**1.71E-01**
SD	**8.22E+02**	**1.27E+01**	**4.39E+00**	**3.38E+00**	**1.40E+02**	**2.12E+00**	**0.00E+00**	**4.00E-03**	**8.39E+01**	**2.25E+02**	**1.32E+03**	**0.00E+00**	**3.70E-01**	**1.72E+02**	**7.10E-01**

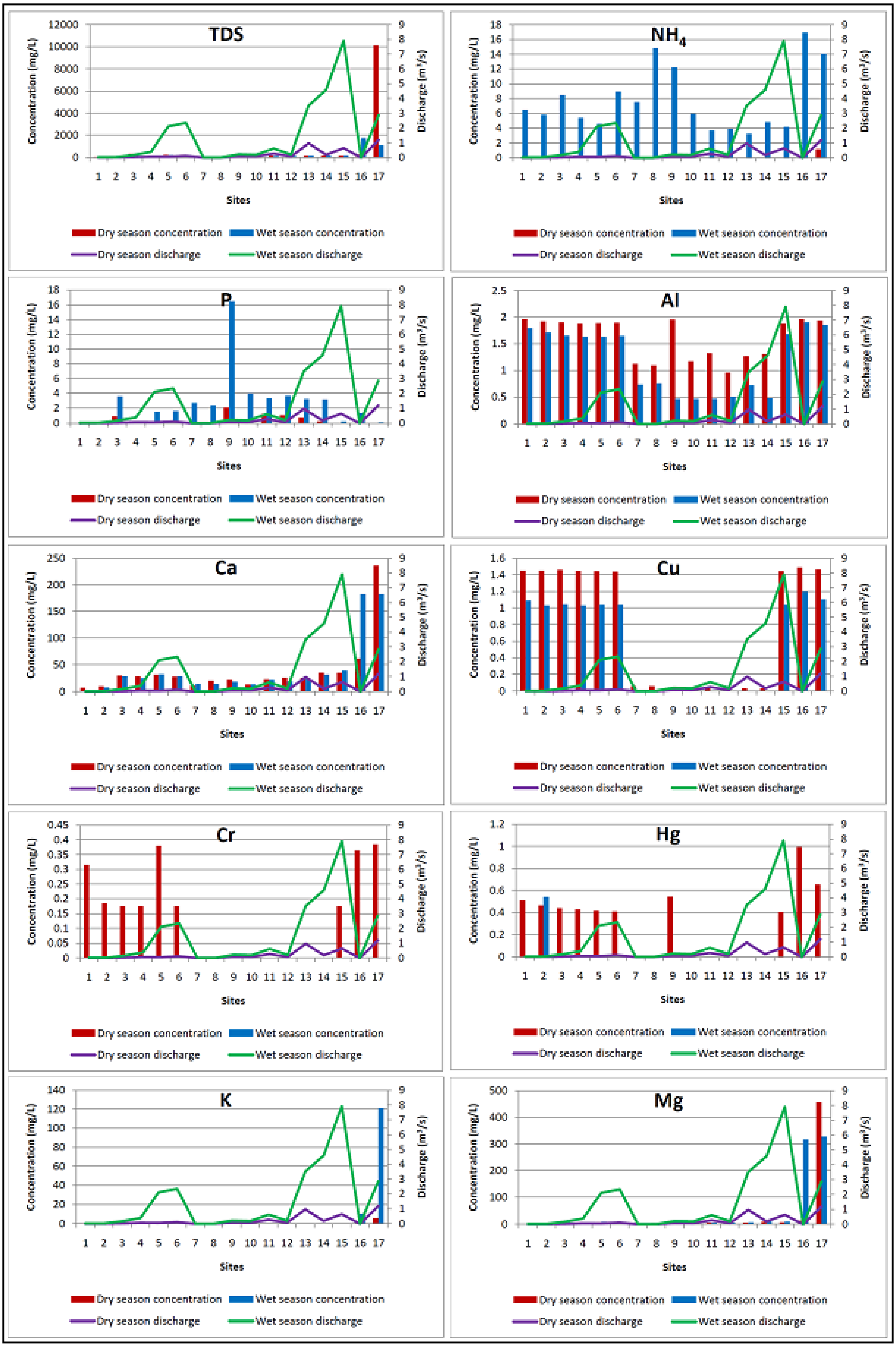

Figure 4.3(a): Seasonal concentrations and discharge rates.

Figure 4.3(b): Seasonal concentrations and discharge rates.

Table 4.3: Chemical concentrations at sample locations in the Bayhead Canal for dry and wet seasons.

DRY SEASON CONCENTRATIONS														
Sites	**TDS**	**Na**	**NH_4**	**Cu**	**Ca**	**K**	**Mg**	**P**	**S**	**Al**	**Hg**	**V**	**Pb**	**Ni**	**Cr**
18	9.12E+03	8.64E+02	1.61E-01	1.53E+00	2.27E+02	0.00E+00	4.28E+02	0.00E+00	2.74E+02	2.64E+00	1.29E+00	7.80E-01	9.60E-01	4.45E-01	3.85E-01
19	1.14E+04	2.51E+03	8.03E-01	6.00E-02	3.61E+02	9.24E+02	6.52E+02	4.85E-01	5.65E+02	1.17E+00	5.25E-01	1.87E+00	0.00E+00	2.38E+00	0.00E+00
20	9.25E+03	2.46E+03	1.09E+00	6.50E-02	3.29E+02	9.22E+02	5.88E+02	5.80E-01	4.88E+02	1.21E+00	0.00E+00	1.81E+00	0.00E+00	2.40E+00	0.00E+00
21	9.15E+03	2.52E+03	1.35E+00	6.00E-02	3.20E+02	9.08E+02	5.62E+02	3.80E-01	4.98E+02	1.13E+00	0.00E+00	1.86E+00	0.00E+00	2.39E+00	0.00E+00
22	2.17E+04	3.26E+03	6.10E-01	7.50E-02	5.49E+02	9.26E+02	9.37E+02	3.00E-01	8.55E+02	1.23E+00	0.00E+00	2.08E+00	0.00E+00	2.31E+00	0.00E+00
23	2.28E+04	3.55E+03	1.01E+00	5.50E-02	5.40E+02	9.15E+02	1.04E+03	1.35E-01	8.39E+02	1.14E+00	0.00E+00	2.10E+00	0.00E+00	2.36E+00	0.00E+00
24	2.24E+04	3.84E+03	7.64E-01	6.00E-02	5.42E+02	8.95E+02	1.07E+03	3.15E-01	8.61E+02	1.17E+00	0.00E+00	2.12E+00	0.00E+00	2.35E+00	0.00E+00
25	2.21E+04	4.61E+03	1.07E+00	6.00E-02	5.34E+02	8.94E+02	9.11E+02	1.35E-01	8.40E+02	1.13E+00	0.00E+00	2.07E+00	0.00E+00	2.42E+00	0.00E+00
MEAN	**1.60E+04**	**2.95E+03**	**8.57E-01**	**2.46E-01**	**4.25E+02**	**7.98E+02**	**7.74E+02**	**2.91E-01**	**6.53E+02**	**1.35E+00**	**2.27E-01**	**1.84E+00**	**1.20E-01**	**2.13E+00**	**4.81E-02**
SD	**6.74E+03**	**1.13E+03**	**3.63E-01**	**5.19E-01**	**1.30E+02**	**3.23E+02**	**2.44E+02**	**1.94E-01**	**2.26E+02**	**5.22E-01**	**4.67E-01**	**4.44E-01**	**3.39E-01**	**6.82E-01**	**1.36E-01**
WET SEASON CONCENTRATIONS															
Sites	**TDS**	**Na**	**NH_4**	**Cu**	**Ca**	**K**	**Mg**	**P**	**S**	**Al**	**Hg**	**V**	**Pb**	**Ni**	**Cr**
18	8.73E+03	2.50E+03	2.46E+01	1.02E+00	2.68E+02	1.30E+02	4.64E+02	4.30E-01	3.26E+02	1.66E+00	0.00E+00	9.90E-01	0.00E+00	0.00E+00	0.00E+00
19	1.14E+04	3.60E+03	4.11E+01	0.00E+00	4.43E+02	2.68E+02	9.24E+02	4.52E+00	7.48E+02	5.25E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20	1.50E+04	3.61E+03	4.32E+01	0.00E+00	4.55E+02	2.72E+02	8.87E+02	4.54E+00	7.80E+02	5.25E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
21	1.05E+04	2.51E+03	1.16E+01	0.00E+00	3.38E+02	1.55E+02	6.46E+02	4.29E+00	5.97E+02	5.15E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
22	2.08E+04	4.25E+03	3.33E+01	0.00E+00	5.15E+02	3.37E+02	9.51E+02	3.36E+00	9.06E+02	5.20E-01	0.00E+00	6.45E-01	0.00E+00	0.00E+00	0.00E+00
23	2.43E+04	4.26E+03	2.09E+01	0.00E+00	5.31E+02	3.44E+02	9.70E+02	3.33E+00	7.94E+02	5.20E-01	0.00E+00	8.20E-01	0.00E+00	0.00E+00	0.00E+00
24	1.82E+04	4.14E+03	2.99E+01	0.00E+00	5.07E+02	3.09E+02	9.30E+02	3.08E+00	7.91E+02	1.15E-01	0.00E+00	7.85E-01	0.00E+00	0.00E+00	0.00E+00
25	2.48E+04	4.21E+03	2.85E+01	0.00E+00	5.29E+02	3.33E+02	1.19E+03	3.39E+00	8.27E+02	9.45E-01	0.00E+00	8.80E-01	4.00E-02	0.00E+00	0.00E+00
MEAN	**1.67E+04**	**3.64E+03**	**2.91E+01**	**1.28E-01**	**4.48E+02**	**2.69E+02**	**8.70E+02**	**3.37E+00**	**7.21E+02**	**6.66E-01**	**0.00E+00**	**5.15E-01**	**5.00E-03**	**0.00E+00**	**0.00E+00**
SD	**6.27E+03**	**7.47E+02**	**1.04E+01**	**3.61E-01**	**9.71E+01**	**8.30E+01**	**2.21E+02**	**1.32E+00**	**1.82E+02**	**4.59E-01**	**0.00E+00**	**4.37E-01**	**1.41E-02**	**0.00E+00**	**0.00E+00**

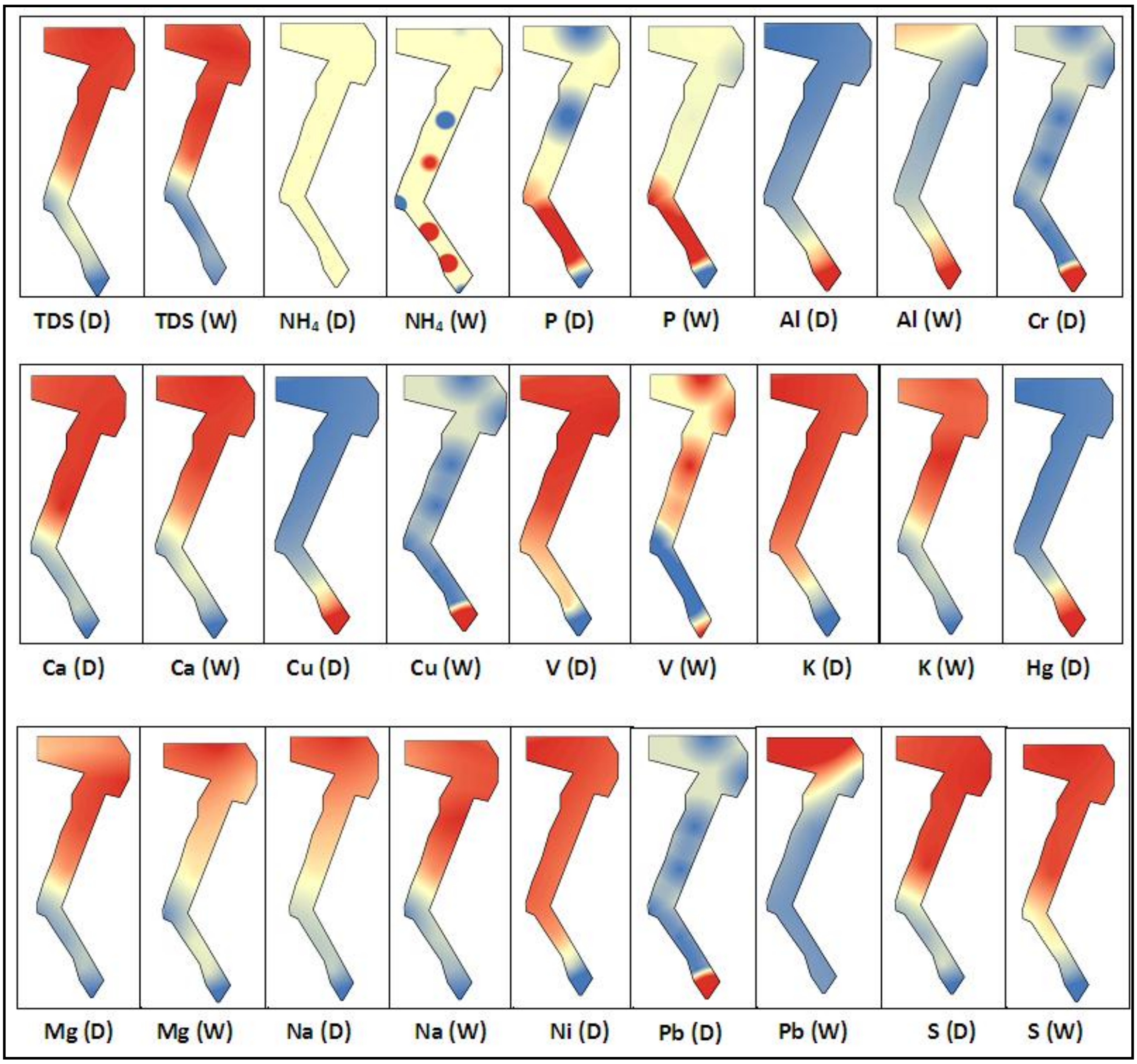

Figure 4.4: Interpolated images of Bayhead Canal chemical data – blue indicates low values transitioning to yellow indicating medium values, and red indicating high values. Cr, Hg and Ni were undetected in the wet season.

4.5.1 TDS FLUX

The average flux of TDS was found to be slightly higher for the dry season as compared to the wet season (**Table 4.2**), with no significant differences in sites across seasons (ANOVA, *p>0.05*). Site 17 displayed an anomalous increase for the dry season which was primarily attributed to a substantial increase in TDS concentration emanating from the high density industrial area of the aManzimnyama catchment (**Figure 4.3a**). Other than sites 6, 14 and 16 in the wet season, there was limited correspondence of seasonal fluxes with seasonal discharge rates, in that the mean dry season flux of TDS appeared to be higher than the wet season values. This could be a direct consequence of limited dry season discharge rates which allowed for an increase in dissolved elemental concentrations and the subsequent higher TDS concentrations observed (**Figure 4.3a**). The lower discharge rates of the dry season in relation to the wet season is further substantiated by rainfall distribution patterns during sampling events of this study as depicted in **Figure 4.2**, where it was evident that lower rainfall events immediately preceded dry season sampling events on 1st March and 1st June 2012, whilst higher rainfall events preceded wet season sampling events on 1st December 2011 and 1st September 2012. Examination of TDS concentrations in the Bayhead Canal of the Durban Harbour showed a limited effect of canal freshwater inflows on the Bayhead Canal TDS concentrations at the confluences (**Figure 4.4**). This was not unexpected as the Bayhead Canal is a large marine-influenced body of water with several orders of magnitude larger than the river discharge.

4.5.2 NH_4 FLUX

The average flux of NH_4 was found to be significantly higher for sites in the wet season as compared to the dry season (ANOVA, *p<0.05*). This was attributed to a combination of higher wet season discharge and subsequent NH_4 loading into the systems following increased runoff from all catchment land use zones (**Figures 4.2** and **4.3a**). The sources of increased NH_4 loading was attributed to runoff derived ammonia compounds from residential fertilizers and industrial activities (DWAF, 1996a), and was evident at sites 3, 6, 8, 14 and 16. With reference to NH_4 loading, all sites exceeded the DWAF (1996a) prescribed target of 0.007 mg/L for aquatic life, rendering the systems unsuitable habitats for aquatic organisms. Sites 6, 14, 15 and 17 yielded anomalously high NH_4 fluxes in the wet season which were reflective of industrial influences whilst site 13, at the interface of the nature reserve and industrial land use zone also yielded a high wet season flux. Elevated discharge rates were observed at these sites in the wet season as a consequence of canalization and greater impervious surfaces at these sectors. Despite the elevated flux at site 17 in both seasons, there appeared to be a limited effect of the aManzimnyama canal inflows on NH_4 concentrations in the Bayhead Canal after the confluence (**Figure 4.4**). This was possibly a direct consequence of dilution effects of the much larger Bayhead Canal. Similar observations were made for the confluence of the uMbilo/uMhlatuzana and Bayhead canals in both seasons. Increases in NH_4 concentration were observed within the Bayhead Canal itself in the dry season which related to point sources from storm water and sewer outfalls draining directly into the Bayhead Canal as indicated in **Figure 4.5** below. All sites in the Bayhead Canal exceeded the DWAF (1995) NH_4 target value of 0.02 mg/L in the coastal zone, highlighting the extent to which the water had become unsuitable for primary consumers.

Figure 4.5: Storm water outflows (black piping) in the Bayhead Canal between both freshwater confluences (Source: Moodley, 2013).

4.5.3 P FLUX

As in the case of NH_4, **Table 4.2** shows that P fluxes were found to be significantly higher across sites in the wet season as compared to the dry season (ANOVA, $p<0.05$). This was attributed to higher wet season P concentrations derived from increased surface runoff (**Figure 4.2**), which was possibly charged with P containing compounds from residential and industrial land use at sites 3, 6, 8 and 16 (DWAF, 1996a). Similar trends are evident internationally with impervious urban catchment influence and increased surface runoff (Lee and Bang, 2000; Tong and Chen, 2002). P loading into the systems at all sites except 1, 2, 4, 5, 6, 7, 8, 10, 15, 16 and 17 in the dry season, exceeded the 0.025 mg/L freshwater guideline value rendering the systems toxic and hypertrophic (DWAF, 1996a). Anomalously high fluxes were recorded at sites 13 and 14 in the wet season, primarily as a consequence of high discharge rates at these sites as depicted in **Figure 4.3 (a)**. The influence of the aManzimnyama and uMbilo/uMhlatuzana Canal fluxes on P concentrations at the respective confluences of the Bayhead Canal was minimal across both seasons (**Figure 4.4**). As in the case of NH_4, the increase in P concentrations in the Bayhead Canal was attributed to a direct consequence of point source pollutant loading through sewer outfalls and storm water discharges directly into the Bayhead Canal (**Figure 4.5**). DWAF (1995), states that the US-EPA target marine water quality range for P is 0.0001 mg/L. When present, P concentrations in the Bayhead Canal exceeded this limit.

4.5.4 Al FLUX

As depicted in **Table 4.2**, the average wet season Al flux was higher than the average dry season values with no significant differences in sites across seasons (ANOVA, $p>0.05$). An anomalously high Al flux was associated with site 15 in the wet season, which was attributed to a high Al concentration in conjunction with a high wet season discharge (**Figure 4.3 (a)**). The high concentration at this site reflected combined contributions of the uMbilo and uMhlatuzana river systems, whilst the high discharge at this site was a result of greater discharge through river canalization in these sectors. Al concentrations at all sites exceeded the prescribed Al freshwater quality range of 0.005 to 0.01 mg/L for aquatic habitats in both seasons (DWAF, 1996a). The consistent presence of Al in sites 1 – 6 (uMbilo River) in both seasons was unknown – possibly relating to the anthropogenic introduction of Al containing compounds at the upstream site 1 as evident in **Figure 4.6**. The substantial increase in fluxes at sites 5, 6 and 17 in the wet season was mainly due to an increase in wet season discharge. **Figure 4.4** shows that the aManzimnyama and uMbilo/uMhlatuzana inflows were influential on Al concentrations in the Bayhead Canal, but to a lesser extent for the uMbilo/uMhlatuzana Canal in the dry season. Despite the lower Al flux contributions of the aManzimnyama Canal in relation to the uMbilo/uMhlatuzana Canal in both seasons, the zone of influence was greater at the confluence for the aManzimnyama Canal. This might be indicative of point source loading of Al from surrounding industry in close proximity to the confluence of the aManzimnyama and Bayhead Canals.

Figure 4.6: Evidence of illegal dumping at upstream site 1 (uMbilo River) (Source: Moodley, 2013).

4.5.5 Ca FLUX

The average Ca fluxes were found to be higher for the wet season as compared to the dry season (**Table 4.2**), with no significant differences in sites across seasons (ANOVA, $p>0.05$). This was mainly attributed to elevated flux levels at sites 5, 6, 13, 14, 15 and 17 in the wet season. **Figure 4.3(a)** shows minimal inter-seasonal variations in Ca concentrations at these sites, with the higher wet season discharges most influential on flux levels. The highest flux values were recorded at sites 14 and 15 in the wet season and at site 17 in both seasons. The increase in sites 14 and 15 was again attributed to high water discharge emanating as a consequence of the impervious canal in conjunction with higher rainfall. The canalized site 17 showed similar behavior, with the much higher values a direct consequence of industrial input in both seasons as reflected in **Figure 4.3(a)**. This was supported by Robson and Neal (1997), who found that despite diffuse sources of Ca, there is always an additional industrial contribution. Analysis of Ca concentrations in the Bayhead Canal revealed a limited effect of freshwater inflows on Ca concentrations in the Bayhead Canal at the confluences (**Figure 4.4**). This was expected as the Bayhead Canal is a large marine-influenced body of water with several orders of magnitude and is therefore characteristic of elevated Ca concentrations (DWAF, 1995).

4.5.6 Cu FLUX

Average Cu fluxes were found to be higher in the wet season with no significant differences in sites across seasons (ANOVA, *p>0.05*) (**Table 4.2**). Cu concentrations exceeded the aquatic life guideline value of 0.0014 mg/L at all sites and seasons other than site 7 – 14 in the wet season (DWAF, 1996a). The consistent presence of Cu in sites 1 – 6 (uMbilo River) in both seasons was unknown – possibly relating to the introduction of Cu containing compounds at the upstream site 1 as in the case of Al (**Figure 4.6**). Highest fluxes were recorded at sites 5, 6, 15 and 17 in the wet season. Marginal variations in Cu concentrations between both seasons at these sites lend confidence to wet season discharge governing the higher wet season fluxes (**Figure 4.3 (a)**). Despite the lower Cu flux contribution of the aManzimnyama Canal in the wet season in relation to the uMbilo/uMhlatuzana Canal, the zone of influence was greater at the confluence of the aManzimnyama Canal in both seasons (**Figure 4.4**). As in the case of Al, this could be indicative of point source loading of Cu from surrounding industry in close proximity to the confluence of the aManzimnyama and Bayhead Canals. According to DWAF (1995), the target marine water quality range of Cu for primary consumers is 0.005 mg/L. With the exception of sites 19 – 25 in the Bayhead Canal in the wet season, all other sites in the Bayhead Canal exceeded this limit.

4.5.7 Cr FLUX

The average dry season fluxes of Cr were found to be higher than the wet season (**Table 4.2**), with no significant differences in sites across seasons (ANOVA, *p>0.05*). Cr concentrations at sites 1 – 6 and sites 15 – 17 in the dry season exceeded the target freshwater quality range of 0.012 mg/L for aquatic life (DWAF, 1996a). The highest flux in the dry season occurred at site 17 before the confluence of the Bayhead Canal as a consequence of increased industrial inputs from the associated aManzimnyama catchment (**Figure 4.3 (a)**). This is substantiated by the fact that Cr salts are extensively used by most chemical manufacturing and metal industries (DWAF, 1996a). Other water quality studies have also found that elevated Cr concentrations in the natural environment were almost entirely influenced by contributions from industrial sources (Robson and Neal, 1997). The effect of fluxes at site 17 in the dry season on the water quality of the Bayhead Canal is illustrated in **Figure 4.4**, where it was shown that the maximum zone of influence occurred at the confluence of the aManzimnyama and Bayhead canals. No Cr was detected in the Bayhead Canal in the wet season (**Table 4.2**). However, with reference to the DWAF (1995) water quality standards, the concentration of Cr at site 18 near the confluence of the Bayhead and aManzimnyama canals greatly exceeded the target marine water quality limit of 0.008 mg/L for primary producers in the dry season.

4.5.8 Hg FLUX

Dry season average fluxes of Hg were found to be marginally higher than the wet season as indicated in **Table 4.2**, with no significant differences in sites across seasons (ANOVA, $p>0.05$). Sites 2 in the wet and dry seasons, as well as sites 1 – 6, 9 and 15 – 17 in the dry season exceeded the target freshwater habitat guideline value of 0.00004 mg/L for Hg (DWAF, 1996a). The consistent presence of Hg in sites 1 – 6 (uMbilo River) in the dry season was not clearly understood and possibly related to the introduction of Hg containing compounds at the upstream site 1 as in the case of Al and Cu (**Figure 4.6**). As in the case of Cr, the highest flux in the dry season was found to be at site 17 before the confluence of the Bayhead Canal. This could be related to industrial loading of Hg from the associated aManzimnyama catchment (**Figure 4.3 (a)**), as Hg is commonly used in industrial processes (DWAF, 1996a). This effect was transferred to the dry season water quality of the Bayhead Canal as illustrated in **Figure 4.4**, where it was shown that the maximum zone of influence occurs at the confluence of the aManzimnyama and Bayhead canals after site 17. No Hg was detected in the Bayhead Canal in the wet season, which was probably attributed to the complete absence of Hg inflows into the Bayhead Canal from the respective catchment canals in the wet season (**Table 4.2**). Hg concentrations at sites 18 and 19 (**Table 4.3**), exceeded the prescribed marine water quality guideline of 0.0003 mg/L for primary producers in the dry season (DWAF, 1995).

4.5.9 K FLUX

The average K fluxes were found to be higher for the wet season as compared to the dry season (**Table 4.2**), with no significant differences in sites across seasons (ANOVA, $p>0.05$). This was mainly attributed to elevated flux recorded at site 17 in the wet season, which was directly related to an anomalous peak in K concentration at this site in conjunction with the elevated wet season discharge as indicated in **Figure 4.3 (a)**. The increase in K concentration at site 17 in the wet season was more than likely associated with industrial input from the aManzimnyama catchment. Despite the elevated K flux at site 17 in both seasons, **Figure 4.4** shows that the K fluxes emanating from the aManzimnyama Canal before the confluence had a limited effect on K concentrations in the Bayhead Canal. As in the case of TDS and Ca, this was a consequence of the dilution effect of a much larger marine water body (DWAF, 1995).

4.5.10 Mg FLUX

The average Mg fluxes were found to be higher for the wet season with no significant differences in sites across seasons (ANOVA, $p>0.05$). This was mainly attributed to elevated flux levels at sites 5, 6, 13, 14, 15 and 17 in the wet season – as in the case of Ca values (**Table 4.2**). There was minimal inter-seasonal variations between concentrations at most sites, with the high wet season discharges dictating the flux levels as depicted in **Figure 4.3 (a)**. The highest value recorded at site 17 in the wet season reflected a combination of elevated Mg concentration through industrial input, acting in conjunction with a higher wet season discharge at the site. Despite the much higher fluxes of the aManzimnyama Canal in relation to the uMbilo/uMhlatuzana Canal before the confluences in both seasons, there was a limited effect of catchment inflows on the Mg concentrations in the Bayhead Canal at the confluence with the aManzimnyama Canal (**Figure 4.4**) as was the case with TDS, Ca and K.

4.5.11 Na FLUX

The average wet season Na flux was higher as compared to the dry season (**Table 4.2)**, with no significant differences in sites across seasons (ANOVA, $p>0.05$). This was primarily attributed to distinct increases at sites 16 and 17 in the wet season – a direct result of increased loading through industrial inputs coupled with a higher wet season discharge (**Figure 4.3 (b)**). The absence of Na in the uMbilo/uMhlatuzana Canal implied no Na flux transfer into Bayhead Canal from the uMbilo/uMhlatuzana catchment. However, the elevated Na fluxes recorded for both seasons at site 17 before the confluence of the aManzimnyama and Bayhead canals had minimal effects on Na concentrations in the Bayhead Canal after the confluence (**Figure 4.4**).

4.5.12 Ni FLUX

The average dry season fluxes of Ni were found to be significantly higher than the wet season at sites across seasons (ANOVA, $p<0.05$) (**Table 4.2**). Whilst there was minimal variation in Ni concentrations for the sites along the uMhlatuzana River in the dry season (sites 7 – 14), there was a distinct increase in Ni flux at site 13 (nature reserve) evidently related to leaching and the higher discharge at this site (**Figure 4.3(b)**). Despite the slightly higher flux of Ni emanating at site 17 from the aManzimnyama Canal as compared to site 15 of the uMbilo/uMhlatuzana Canal before the confluence with the Bayhead Canal, this increase had a limited effect on Ni concentrations in the Bayhead Canal. This can be attributed to Ni predominantly derived from port related activities as evident in **Figure 4.4**. The target marine water quality range of Ni for primary producers is 0.025 mg/L (DWAF, 1995). All sites in the dry season exceeded this limit.

4.5.13 Pb FLUX

The average wet season Pb flux was found to be marginally higher than the corresponding dry season value as indicated in **Table 4.2**, with no significant differences in sites across seasons (ANOVA, $p>0.05$). The highest Pb fluxes were associated with sites 17 in the dry season and sites 13 and 15 in the wet season. The increase in site 17 in the dry season was a direct indication of an increased Pb concentration associated with industrial input of the aManzimnyama catchment as depicted in **Figure 4.3 (b)**. The flux increases at sites 13 and 15 in the wet season was directly related to the elevated wet season discharges. With the exception of sites 7 – 14 in the dry season, all sites exceeded the freshwater guideline of 0.0012 mg/L for aquatic environments in both seasons (DWAF, 1996a). As illustrated in **Figure 4.4**, the elevated dry season flux of Pb at site 17 before the confluence with the Bayhead Canal accounted for a higher Pb concentration after the confluence (site 18) in relation to the corresponding wet season value. As with previous elements, the Pb fluxes emanating from the uMbilo/uMhlatuzana Canals in both seasons had a limited effect on Pb concentrations in the Bayhead Canal. According to the South African Water Quality Guidelines for Coastal and Marine Waters, the target marine water quality for Pb for primary producers is 0.012 mg/L (DWAF, 1995). Site 18 in the dry season and site 25 in the wet season exceed this range, implicating aManzimnyama Canal inflows and port sources of Pb respectively as contaminant sources.

4.5.14 S FLUX

The average wet season flux of S was found to be higher than the corresponding dry season values (**Table 4.2**), with no significant differences in sites across seasons (ANOVA, $p>0.05$). This was primarily due to increased fluxes associated with sites 5, 6, 14, 15 and 17 in the wet season. Increases at sites 5 and 6 were associated with an elevated wet season discharge (**Figure 4.3 (b)**). Such was the case for sites 14 and 15 in the wet season which was characterised by a substantially higher discharge owing to an impervious underlying canal surface at these sites. The substantial increase in S fluxes at site 17 in the wet season was a function of a high wet season S concentration through industrial input; in conjunction with a higher wet season discharge. The high S loading of site 17 in fact greatly exceeded the long term freshwater guideline value of 50 mg/L (Canadian Environmental Quality Guidelines (CEQG), 2005) but displayed little influence on S concentrations of the Bayhead Canal (**Figure 4.4**). Whilst it was evident that S concentrations tend to increase towards the port waters implicating port activities as a possible source of S loading into the Bayhead Canal, limited effects of uMbilo/uMhlatuzana inflows on S concentrations in the Bayhead Canal in the wet season were recorded. This was supported by the fact that there appeared to be higher S flux emanating from site 15 (uMbilo/uMhlatuzana Canal) before the confluence with the Bayhead Canal in the wet season as compared to the dry season (**Table 4.2**).

4.5.15 V FLUX

Despite the increased average dry season V concentrations, the average wet season V fluxes were found to be higher primarily relating to an elevated wet season discharge (**Table 4.2** and **Figure 4.3(b)**), with no significant differences in sites across seasons (ANOVA, $p>0.05$).

The highest V flux was recorded at site 17 in the wet season and was substantially higher in relation to remaining sites in both seasons. This was a direct result of elevated V loading due to industrial input from the aManzimnyama catchment in the wet season, in conjunction with a higher wet season discharge as evident in **Figure 4.3 (b)**. Industrial inputs may be attributed to the fact that V is commonly used in steel and metallurgical industries (WHO, 2000). The consistent presence of V in sites 1 – 6 (uMbilo River) in the dry season was unknown – possibly relating to the introduction of V containing compounds upstream at site 1 (**Figure 4.6**). The high wet season V flux at site 17 before the confluence with the Bayhead Canal possibly explained the elevated V concentration after the confluence in the wet season. In contrast, there was a limited effect of uMbilo/uMhlatuzana Canal inflows on V concentrations in the Bayhead Canal in the wet season – most likely relating to the absence of V at site 15 before the confluence. The higher dry season flux emanating from site 15 accounted for elevated V concentrations in the Bayhead Canal for the dry season after the confluence of the uMbilo/uMhlatuzana and Bayhead canals (**Figure 4.4**). In the absence of relevant South African guidelines for V in the coastal zone, DWAF (1995) states the EEC (after UK) international target value of 0.1 mg/L. With the exception of sites 19 – 21 in the wet season, all other sites in the Bayhead Canal exceeded this limit in both seasons.

4.6 CONCLUSION

The catchments of the uMbilo, uMhlatuzana and aManzimnyama River systems have been subject to intense human development over the past few decades largely accounting for the spatial and temporal variability of water quality. The study showed that the intensification of anthropogenic activities and processes operating within the catchment, primarily through industry, have caused a general deterioration of selected physico-chemical water quality parameters across all land use types on the basis of the parameters analyzed. The following summarizes key findings relating to the water quality of the study area:

- When present, nutrients (NH_4 and P) and trace metals (Cu, Hg, Pb and Cr) exceeded prescribed South African freshwater and marine guidelines;
- Al exceeded prescribed South African freshwater guidelines. No South African marine water quality guidelines were available for Al; and

- V and Ni exceeded South African marine water quality guidelines. No South African freshwater guidelines were available for these metals.

In all the above cases, the relevant water quality guidelines categorized the systems as unsuitable for supporting aquatic life.

In terms of material fluxes for parameters analyzed, the following summarizes the key findings:

- Anomalously high discharge rates due to canalised portions of the river systems at sites 5, 6, 13, 14, 15 and 17 in the wet season generally accounted for elevated dissolved chemical fluxes of parameters at these sites when present;
- In contrast, anomalously high fluxes were noted for NH_4 (sites 8 and 9 in the wet season), P (site 9 in the wet season), Al (site 9 in the dry season), Cr (sites 1, 5 and 15 in the dry season), Hg (site 2 during both seasons and sites 1, 9 and 15 in the dry season), Ni (site 8 in the dry season), Pb (site 12 in the wet season) as a direct consequence of increased chemical loading into the systems mainly from residential and industrial land use associated with most of these sites; and
- High fluxes of Al, Cu, Hg (dry season) and V (dry season) were associated with sites 1 – 6 (uMbilo catchment), which resulted in elevated fluxes of these metals at site 15 at the confluence of the uMbilo and uMhlatuzana river catchments. The source of the consistent presence of these elements in sites 1 – 6 (uMbilo River) was not known – but was possibly related to the anthropogenic introduction of these elements at the upstream site.

Additionally, analyses of the material mass transport capacities of the respective catchment canals just before the confluence with the Bayhead Canal of the Durban Bay Harbour showed minimal influence on chemical concentrations of the port waters for TDS, Na, NH_4, Ca, K, Mg, P, Ni, V and S, due to the disparate size difference of the two environments and suggesting the origin of these chemicals in the Bay to emanate from the port activities itself. The chemical fluxes emanating from the aManzimnyama Canal were most influential on Cu, Cr, Hg, V, Pb and Al concentrations in the Bayhead Canal near the confluence.

Although not all possible water quality variables were analyzed nor was analysis done in conjunction with detailed hydrodynamic modelling of the Bayhead Canal, this study has been very useful in highlighting possible impacts of catchment land use and associated canal inflows on the water quality of the river systems, as well as on that of the Bayhead Canal in terms of the material mass transport capacity of the associated inflows.

CHAPTER FIVE

EFFECTS OF LAND USE ON WATER QUALITY AND DIATOM COMMUNITIES IN THE FLUVIAL CATCHMENTS OF DURBAN HARBOUR, KWAZULU-NATAL, SOUTH AFRICA

This chapter is developed as a research article and has been submitted for publication to the *Journal of Geographical Sciences*.

5.1 ABSTRACT

This study presents data on diatom species, distributions and abundance along three freshwater systems contributing inflows to the Bayhead Canal of the Durban Harbour. Diatom communities along predetermined sampling sites in the uMhlatuzana, uMbilo and aManzimnyama river catchments, and the Bayhead Canal, were examined seasonally and related to changes in water quality gradients through correlation with physico-chemical water quality parameters. A total of 4 diatom taxa were accounted for in the wet season and 2 taxa in the dry season, with *Thalassiosira weissflogii* (Grunow) constituting the most dominant taxon in both seasons. Total diatom densities (*TDD*) were found to have significant positive correlations with dissolved phosphorous in both seasons ($p<0.05$). Seasonal diatom enumeration showed highest diatom densities in the dry season suggesting favourable conditions for diatom growth during this period. Physico-chemical analysis of bed sediments showed that substrate composition generally favoured diatom growth during both seasons. Nonetheless, low seasonal diatom counts observed across sites are likely a direct consequence of deteriorations in physico-chemical water quality, particularly due to the presence of toxic metals (Aluminium – *Al*, Mercury – *Hg*, Lead – *Pb* and Chromium – *Cr*), which were negatively correlated with *TDD*. The general water quality across sites also showed deteriorations in nutrients (Ammonia – NH_4, Phosphorous – *P* and Copper – *Cu*) and microbiological counts (*E. coli* and Total coliforms) with values that frequently exceeded prescribed water quality guidelines – particularly associated with industrial and residential land use along the greater catchment area. The study was useful in highlighting the responses of diatoms to water quality gradients and their subsequent use as water quality indicators.

Key words

Water quality, land use, pollution, diatoms, Durban Harbour

5.2 INTRODUCTION

Diatoms comprise autotrophic unicellular organisms at the base of aquatic food chains and form important components of algal assemblages in freshwater bodies (de la Rey *et al*., 2004). They are one of the most commonly used biological monitoring indicators and environmental assessment tools for river systems, and are often successfully used as water quality indicators owing to their strong responses to environmental change, availability throughout the year, high levels of diversity and short life cycles allowing for the rapid identification of these changes (Schletterer *et al*., 2011).

The use of diatoms in reflecting both the present and past water quality within the environment is facilitated by the continuous integration and reflection of various physical and chemical stressors including but not limited to pH, heavy metals, calcium, magnesium, phosphorus, salinity, substratum, current velocity and light (de la Rey *et al*., 2004; Taylor *et al*., n.d.(b)). In fact, several international studies reveal important relationships between environmental parameters (including substrate sediment size and physico-chemical parameters) in aquatic ecosystems and the distribution, abundance and size of diatom species assemblages, thereby contributing to their success as water quality indicators (Blackburn *et al*., 2009; McQuoid and Nordberg, 2003; Mendes *et al*., 2009; Singh *et al*., 2010; Uthicke and Nobes, 2008).

Whilst diatom responses to water quality variables have been explored to some degree in South Africa (de la Rey *et al*., 2008a; de la Rey *et al*., 2008b; Taylor *et al*., 2007b), no prior attention has been given to the catchments used in this study. As such, this study is useful in forming a baseline study for future water quality assessments in the area, and is useful in determining diatom responses to water quality gradients for catchments occurring in predominantly similar eco-regions.

5.3 STUDY AREA

The uMhlatuzana and uMbilo Rivers, and aManzimnyama Canal of KwaZulu-Natal, South Africa, comprise three freshwater systems which flow into the Bayhead Canal of the Durban Harbour (**Figure 5.1**). The catchments of these freshwater systems are subject to a range of human influence and activities, with more than 70% of these catchments classified as urban, 6% as agriculture and 23% as natural (DEAT, 2001). The broader catchment region is characterized by a warm sub-tropical climate with increased rainfall in the summer months (MER/ERM, 2011). The total catchment area of all three river systems is approximately 195 km^2, and is characterized by relatively flat topography (MER/ERM, 2011). The catchment geology is dominated by tertiary sediments including Berea red sands and beach sands at the lower reaches, with shallow soils occurring on weathering rock for much of the catchment area (WRC, 2002).

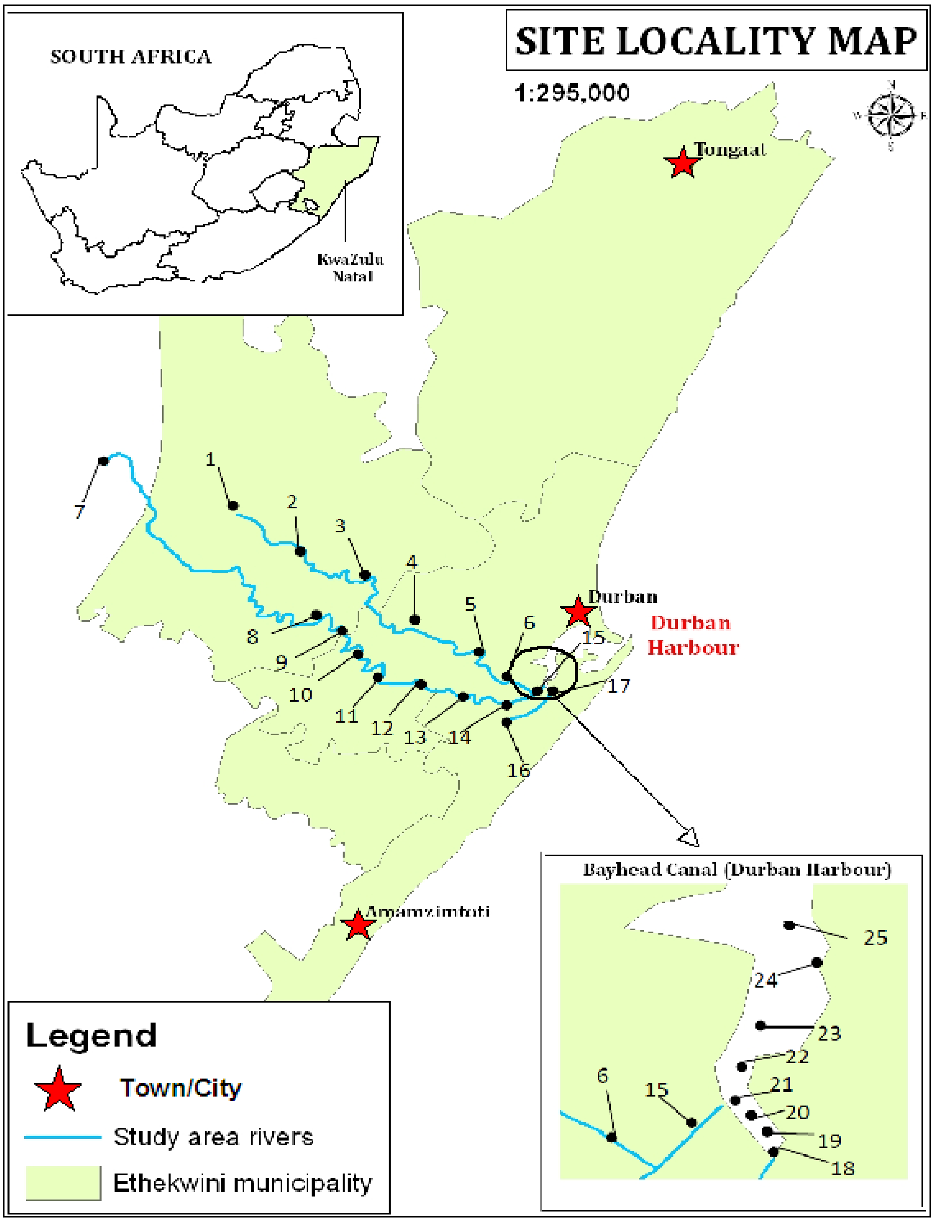

Figure 5.1: Geographic location of study area and sample sites. Insert: The Bayhead Canal and its associated sampling sites (Source: Moodley, 2013).

5.4 MATERIALS AND METHODS

Sampling sites were chosen along each freshwater system on the basis of land use change as illustrated in **Figure 5.1**. Sampling involved the collection of (i) diatoms, (ii) water and (iii) in-stream sediment at the same sites. For water and diatom sample collection, four field surveys were conducted seasonally between December 2011 and September 2012 and the analyses were grouped into wet and dry season results. Due to the fact that sediment tends to record and reflect long-term pollution trends in aquatic bodies as compared to the overlying water column, two field surveys were conducted for sediment in December 2011 and June 2012, which were also grouped into wet and dry season sampling respectively.

Benthic diatom samples were carefully collected from the upper portion of river bed sediment from shallow, slow flowing sections of the river with sufficient light penetration using methods outlined in Naicker (2006). Diatom slides were then prepared using the acid digestion technique with HCl and $KMnO_4$ (Naicker, 2006). Diatom enumeration was accomplished using a Zeiss Primo Star microscope (Carl Zeiss Micromaging GmbH, Germany – Model 41550), and identification using various guidelines (Bate *et al*., 2004; Cholnoky, 1960; Round, 1991; Schoeman, 1979; Schoeman and Archibald, 1976).

Water samples were analyzed for several physico-chemical and biological parameters including pH, Total Dissolved Solids (TDS), conductivity (Cond.), ammonium ions (NH_4), Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), sodium (Na), potassium (K), magnesium (Mg), aluminium (Al), lead (Pb), sulphur (S), calcium (Ca), total coliforms (TC) and *E. coli* (EC) using standard methods (Ngila, 2008).

In-stream surface grab sediment samples were analyzed for several metals using inductively coupled plasma optical emission spectroscopy (ICP-OES) including Al, As, Ca, Cu, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Se, V and Zn (Ngila, 2008). In addition, the percent organic matter and fine sediment was quantitatively determined using standard methods (SASRI, 2012).

Water quality parameters were compared to the reference standards as outlined by the South African Department of Water Affairs and Forestry (DWAF, 1996a and b).

Seasonal variations in diatom taxa and physico-chemical water quality parameters were explored statistically through Analysis of Variance (ANOVA) whilst seasonal diatom densities in response to water quality parameters were studied using Pearson's correlation coefficient (r) (**Table 6.3**). All statistics were performed using the Microsoft Excel® data statistics package.

5.5 RESULTS AND DISCUSSION

Measured physico-chemical parameters for water and sediment during the wet and dry seasons are illustrated in **Tables 5.2** and **5.3** respectively. Representative samples in **Figure 5.1** correspond to the land use activities indicated in **Table 5.1** below:

Table 5.1: Description of sample locations and corresponding catchment land use types (Source: Moodley, 2013).

uMbilo River	
Site	**Land use description**
1	Source (Sparse residential area)
2	Interface of industrial and residential area (sited downstream of industrial area)
3	Interface of residential area and nature reserve (sited downstream of residential area)
4	Interface of nature reserve and residential area – also impacted on by the Waste Water Treatment Works (WWTW) (sited downstream of nature reserve)
5	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
6	Interface of industrial area and confluence with uMhlatuzana River (sited downstream of industrial area)
uMhlatuzana River	
Site	**Land use description**
7	Source (Sparse residential area)
8	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
9	Interface of industrial area and nature reserve (sited downstream of industrial area)
10	Interface of nature reserve and residential area – also impacted on by WWTW (sited downstream of nature reserve)
11	Interface of residential and industrial area (sited downstream of residential area)
12	Interface of industrial area and nature reserve (sited downstream of industrial area)
13	Interface of nature reserve and industrial area (sited downstream of nature reserve)
14	Interface of industrial area and confluence with uMbilo River (sited downstream of industrial area)
uMbilo/uMhlatuzana Canal confluence	
Site	**Land use description**

15	Sited at confluence
aManzimnyama Canal	
Site	**Land use description**
16	Source (Low density industrial area)
17	Interface of industrial area and confluence to Bayhead Canal (sited downstream of industrial area)
Bayhead Canal of Durban Harbour	
Sites	**18, 19, 20, 21, 22, 23, 24, 25** (equidistant)

Table 5.2: Variations in water quality parameters for the dry (D) and wet (W) seasons with guideline values (GV) also indicated. Highlights indicate exceedances of GV.

		FRESHWATER SITES																	MARINE SITES								MEAN	SD
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25		
pH	D	7.56E+00	7.29E+00	7.17E+00	7.70E+00	7.58E+00	8.31E+00	6.96E+00	7.42E+00	6.92E+00	7.25E+00	7.17E+00	7.24E+00	7.54E+00	8.41E+00	8.62E+00	7.34E+00	7.40E+00	7.39E+00	7.79E+00	7.99E+00	8.17E+00	7.90E+00	7.80E+00	7.77E+00	7.80E+00	7.62E+00	4.40E-01
	W	7.57E+00	7.67E+00	7.21E+00	7.33E+00	7.47E+00	7.89E+00	7.75E+00	7.58E+00	7.59E+00	7.54E+00	7.58E+00	7.52E+00	7.61E+00	8.20E+00	8.06E+00	7.34E+00	8.08E+00	7.47E+00	7.37E+00	7.44E+00	7.83E+00	7.69E+00	7.72E+00	7.68E+00	7.75E+00	7.64E+00	2.40E-01
	GV	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	6-8a	7.9-8.2b	7.9-8.2b	7.9-8.2b	7.9-8.2b	7.9-8.2b	7.9-8.2b	7.9-8.2b	7.9-8.2b	N/A	N/A
Cond. µS/cm	D	1.58E+02	1.95E+02	8.15E+02	3.61E+02	5.96E+02	5.96E+02	2.54E+02	2.79E+02	4.46E+02	2.94E+02	4.18E+02	4.40E+02	4.37E+02	4.66E+02	4.43E+02	6.97E+02	1.58E+04	1.50E+04	3.22E+04	3.00E+04	3.00E+04	4.89E+04	4.84E+04	5.14E+04	5.07E+04	1.32E+04	1.93E+04
	W	1.55E+02	2.05E+02	6.17E+02	3.11E+02	5.33E+02	5.01E+02	2.10E+02	2.58E+02	4.87E+02	2.96E+02	3.43E+02	3.70E+02	4.35E+02	4.64E+02	4.81E+02	1.35E+04	1.59E+04	2.05E+04	3.99E+04	3.98E+04	2.80E+04	4.86E+04	4.87E+04	4.70E+04	4.91E+04	1.43E+04	1.95E+04
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	N/A	N/A
TDS (mg/L)	D	6.80E+01	8.40E+01	3.50E+02	1.55E+02	2.56E+02	2.56E+02	1.09E+02	1.20E+02	1.91E+02	1.26E+02	1.80E+02	1.89E+02	1.88E+02	2.00E+02	1.92E+02	3.00E+02	1.01E+04	9.12E+03	1.14E+04	9.25E+03	9.15E+03	2.17E+04	2.28E+04	2.24E+04	2.21E+04	5.64E+03	8.34E+03
	W	6.65E+01	8.85E+01	2.65E+02	1.34E+02	2.29E+02	2.16E+02	9.03E+01	1.11E+02	2.09E+02	1.27E+02	1.48E+02	1.59E+02	1.87E+02	2.00E+02	2.07E+02	1.75E+03	1.10E+03	8.73E+03	1.14E+04	1.50E+04	1.05E+04	2.08E+04	2.43E+04	1.82E+04	2.48E+04	5.56E+03	8.52E+03
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	N/A	N/A
DO (mg/L)	D	8.62E+00	8.69E+00	8.48E+00	8.47E+00	8.69E+00	8.62E+00	8.42E+00	8.64E+00	8.56E+00	8.68E+00	8.63E+00	8.50E+00	8.67E+00	8.66E+00	8.71E+00	8.42E+00	8.74E+00	8.62E+00	8.62E+00	8.73E+00	8.59E+00	8.58E+00	8.75E+00	8.60E+00	8.54E+00	8.61E+00	9.49E-02
	W	7.05E+00	7.07E+00	7.07E+00	7.09E+00	7.07E+00	7.10E+00	7.20E+00	7.25E+00	7.02E+00	7.58E+00	7.13E+00	7.38E+00	7.57E+00	7.04E+00	7.09E+00	7.04E+00	7.19E+00	6.99E+00	7.10E+00	7.10E+00	7.07E+00	6.97E+00	7.03E+00	6.92E+00	6.95E+00	7.12E+00	1.67E-01
	GV	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	5-6c	-	-	-	-	-	-	-	-	N/A	N/A
BOD (mg/L)	D	3.52E+00	3.53E+00	3.52E+00	3.56E+00	3.54E+00	3.48E+00	3.41E+00	3.39E+00	3.27E+00	3.38E+00	3.47E+00	3.47E+00	3.49E+00	3.50E+00	3.45E+00	3.50E+00	3.53E+00	3.30E+00	3.32E+00	3.33E+00	3.25E+00	3.27E+00	3.04E+00	3.02E+00	2.59E+00	3.37E+00	2.17E-01
	W	6.84E+00	5.82E+00	5.33E+00	5.14E+00	5.37E+00	5.08E+00	1.99E+00	1.60E+00	1.51E+00	1.51E+00	1.50E+00	5.23E+00	5.23E+00	1.51E+00	4.69E+00	5.81E+00	8.61E+00	4.54E+00	4.51E+00	3.80E+00	6.69E+00	3.44E+00	5.30E+00	5.59E+00	2.06E+00	4.35E+00	1.97E+00
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	N/A	N/A
COD (mg/L)	D	6.74E+00	7.22E+00	7.42E+00	6.06E+00	8.04E+00	6.38E+00	8.90E+00	7.44E+00	9.10E+00	9.00E+00	5.30E+00	8.10E+00	5.98E+00	7.92E+00	5.44E+00	2.70E+01	2.31E+01	7.86E+00	4.14E+00	3.96E+00	6.14E+00	6.30E+00	6.22E+00	7.40E+00	7.10E+00	8.33E+00	5.24E+00
	W	3.47E+00	6.64E+00	7.08E+00	4.67E+00	3.13E+00	7.01E+00	1.34E+01	1.22E+01	1.47E+01	7.41E+00	9.54E+00	8.93E+00	6.23E+00	2.90E+00	5.22E+00	4.18E+00	5.46E+00	5.05E+00	7.70E+00	4.66E+00	7.94E+00	6.84E+00	4.66E+00	3.68E+00	4.34E+00	6.68E+00	3.12E+00
	GV	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	20d	-	-	-	-	-	-	-	-	N/A	N/A
Na (mg/L)	D	0.00E+00	0.00E+00	2.92E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.60E+02	8.64E+02	2.51E+03	2.46E+03	2.52E+03	3.26E+03	3.55E+03	3.84E+03	4.61E+03	9.83E+02	1.52E+03
	W	0.00E+00	0.00E+00	6.05E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.61E+03	1.91E+03	2.50E+03	3.60E+03	3.61E+03	2.51E+03	4.25E+03	4.26E+03	4.14E+03	4.21E+03	1.30E+03	1.75E+03
	GV	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	100e	-	-	-	-	-	-	-	-	N/A	N/A
NH_4 (mg/L)	D	1.19E-02	1.47E-02	2.39E-02	1.87E-02	3.26E-02	2.04E-02	2.10E-02	1.70E-02	3.55E-02	2.27E-02	3.21E-02	4.33E-02	4.02E-02	3.82E-02	1.55E-02	4.18E-02	1.19E+00	1.61E-01	8.03E-01	1.09E+00	1.35E+00	6.10E-01	1.01E+00	7.64E-01	1.07E+00	3.39E-01	4.72E-01
	W	6.49E+00	5.82E+00	8.51E+00	5.40E+00	4.58E+00	8.94E+00	7.52E+00	1.48E+01	1.22E+01	5.92E+00	3.66E+00	3.91E+00	3.23E+00	4.81E+00	4.16E+00	1.69E+01	1.41E+01	2.46E+01	4.11E+01	4.32E+01	1.16E+01	3.33E+01	2.09E+01	2.99E+01	2.85E+01	1.46E+01	1.22E+01
	GV	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.007a	0.02b	0.02b	0.02b	0.02b	0.02b	0.02b	0.02b	0.02b	N/A	N/A
Cu (mg/L)	D	1.45E+00	1.45E+00	1.46E+00	1.45E+00	1.45E+00	1.44E+00	6.00E-02	6.00E-02	3.50E-02	3.50E-02	3.50E-02	4.50E-02	3.50E-02	3.50E-02	1.45E+00	1.49E+00	1.47E+00	1.53E+00	6.00E-02	6.50E-02	6.00E-02	7.50E-02	5.50E-02	6.00E-02	6.00E-02	6.17E-01	7.06E-01
	W	1.09E+00	1.03E+00	1.05E+00	1.03E+00	1.04E+00	1.04E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.04E+00	1.20E+00	1.11E+00	1.02E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.26E-01	5.34E-01
	GV	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.0014a	0.05b	0.05b	0.05b	0.05b	0.05b	0.05b	0.05b	0.05b	N/A	N/A
Ca (mg/L)	D	6.92E+00	9.97E+00	2.98E+01	2.80E+01	3.13E+01	2.75E+01	1.12E+01	2.04E+01	2.25E+01	1.33E+01	2.33E+01	2.58E+01	2.55E+01	3.48E+01	3.47E+01	6.18E+01	2.36E+02	2.27E+02	3.61E+02	3.29E+02	3.20E+02	5.49E+02	5.40E+02	5.42E+02	5.34E+02	1.62E+02	2.02E+02
	W	2.44E+00	7.73E+00	2.81E+01	2.47E+01	3.20E+01	2.82E+01	1.46E+01	1.41E+01	1.85E+01	1.35E+01	2.21E+01	1.93E+01	2.38E+01	3.13E+01	3.89E+01	1.83E+02	1.83E+02	2.68E+02	4.43E+02	4.55E+02	3.38E+02	5.15E+02	5.31E+02	5.07E+02	5.29E+02	1.71E+02	2.06E+02
	GV	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	15d	-	-	-	-	-	-	-	-	N/A	N/A
K (mg/L)	D	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.62E+00	0.00E+00	9.24E+02	9.22E+02	9.08E+02	9.26E+02	9.15E+02	8.95E+02	8.94E+02	2.56E+02	4.18E+02
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.06E+01	1.21E+02	1.30E+02	2.68E+02	2.72E+02	1.55E+02	3.37E+02	3.44E+02	3.09E+02	3.33E+02	9.12E+01	1.34E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	N/A	N/A
Mg (mg/L)	D	1.62E+00	3.92E+00	5.58E+00	8.16E+00	8.17E+00	8.29E+00	4.48E+00	5.19E+00	5.50E+00	5.56E+00	5.98E+00	3.34E+00	6.45E+00	9.07E+00	7.24E+00	1.38E+01	4.57E+02	4.28E+02	6.52E+02	5.88E+02	5.62E+02	9.37E+02	1.04E+03	1.07E+03	9.11E+02	2.70E+02	3.87E+02
	W	1.25E+00	3.43E+00	6.17E+00	5.88E+00	9.43E+00	8.83E+00	2.52E+00	4.21E+00	6.21E+00	5.19E+00	5.62E+00	5.76E+00	7.34E+00	1.08E+01	1.01E+01	3.18E+02	3.28E+02	4.64E+02	9.24E+02	8.87E+02	6.46E+02	9.51E+02	9.70E+02	9.30E+02	1.19E+03	3.08E+02	4.20E+02
	GV	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	100d	-	-	-	-	-	-	-	-	N/A	N/A
P (mg/L)	D	0.00E+00	0.00E+00	9.10E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.11E+00	0.00E+00	1.27E+00	1.09E+00	7.55E-01	2.50E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.85E-01	5.80E-01	3.80E-01	3.00E-01	1.35E-01	3.15E-01	1.35E-01	3.49E-01	5.25E-01
	W	6.50E-02	5.50E-02	3.61E+00	1.70E-01	1.57E+00	1.67E+00	2.69E+00	2.36E+00	1.65E+01	3.98E+00	3.33E+00	3.66E+00	3.24E+00	3.18E+00	2.25E-01	1.37E+00	1.15E-01	4.30E-01	4.52E+00	4.54E+00	4.29E+00	3.36E+00	3.33E+00	3.08E+00	3.39E+00	2.99E+00	3.20E+00
	GV	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.025a	0.0001b	0.0001b	0.0001b	0.0001b	0.0001b	0.0001b	0.0001b	0.0001b	N/A	N/A
S (mg/L)	D	5.75E-01	5.25E-01	1.83E+01	3.21E+00	1.03E+01	8.01E+00	0.00E+00	0.00E+00	1.34E+00	0.00E+00	7.40E-01	1.27E+00	1.11E+00	3.52E+00	8.20E+00	2.21E+01	2.94E+02	2.74E+02	5.65E+02	4.88E+02	4.98E+02	8.55E+02	8.39E+02	8.61E+02	8.40E+02	2.24E+02	3.29E+02
	W	3.29E+00	5.07E+00	1.56E+01	7.31E+00	1.46E+01	1.21E+01	4.14E+00	1.01E+00	6.18E+00	1.69E+00	2.62E+00	3.77E+00	2.42E+00	1.03E+01	1.92E+01	2.24E+02	2.49E+02	3.26E+02	7.48E+02	7.80E+02	5.97E+02	9.06E+02	7.94E+02	7.91E+02	8.27E+02	2.54E+02	3.47E+02
	GV	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	50f	-	-	-	-	-	-	-	-	N/A	N/A
Al (mg/L)	D	1.97E+00	1.92E+00	1.91E+00	1.88E+00	1.89E+00	1.90E+00	1.13E+00	1.10E+00	1.96E+00	1.18E+00	1.33E+00	9.60E-01	1.27E+00	1.31E+00	1.89E+00	1.97E+00	1.94E+00	2.64E+00	1.17E+00	1.21E+00	1.13E+00	1.23E+00	1.14E+00	1.17E+00	1.13E+00	1.53E+00	4.41E-01
	W	1.80E+00	1.72E+00	1.66E+00	1.64E+00	1.64E+00	1.65E+00	7.35E-01	7.60E-01	4.65E-01	4.65E-01	4.70E-01	5.10E-01	7.25E-01	4.80E-01	1.69E+00	1.91E+00	1.86E+00	1.66E+00	5.25E-01	5.25E-01	5.15E-01	5.20E-01	5.20E-01	1.15E-01	9.45E-01	1.02E+00	6.06E-01
	GV	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	0.01a	-	-	-	-	-	-	-	-	N/A	N/A
Hg (mg/L)	D	5.10E-01	4.65E-01	4.40E-01	4.30E-01	4.15E-01	4.10E-01	0.00E+00	0.00E+00	5.45E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.05E-01	9.95E-01	6.55E-01	1.29E+00	5.25E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.83E-01	3.54E-01
	W	0.00E+00	5.40E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.16E-02	1.08E-01
	GV	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.00004a	0.0003b	0.0003b	0.0003b	0.0003b	0.0003b	0.0003b	0.0003b	0.0003b	N/A	N/A
V (mg/L)	D	7.85E-01	7.85E-01	7.85E-01	7.85E-01	7.90E-01	7.90E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.90E-01	7.90E-01	7.70E-01	7.80E-01	1.87E+00	1.81E+00	1.86E+00	2.08E+00	2.10E+00	2.12E+00	2.07E+00	8.70E-01	7.90E-01
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.02E+00	9.90E-01	0.00E+00	0.00E+00	0.00E+00	6.45E-01	8.20E-01	7.85E-01	8.80E-01	2.06E-01	3.79E-01
	GV	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1e	0.1b	0.1b	0.1b	0.1b	0.1b	0.1b	0.1b	0.1b	N/A	N/A
Pb (mg/L)	D	9.80E-01	9.65E-01	9.65E-01	9.50E-01	9.60E-01	9.60E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.60E-01	1.02E+00	9.70E-01	9.60E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.88E-01	4.85E-01
	W	6.85E-01	9.15E-01	1.85E-01	9.00E-02	3.65E-01	2.35E-01	5.55E-01	1.20E-01	2.50E-01	1.35E-01	1.50E-02	3.60E+00	2.85E-01	1.35E-01	1.05E-01	2.15E-01	1.65E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.00E-02	3.24E-01	7.21E-01
	GV	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.0012a	0.012b	0.012b	0.012b	0.012b	0.012b	0.012b	0.012b	0.012b	N/A	N/A
Ni (mg/L)	D	4.50E-01	4.50E-01	5.30E-01	4.45E-01	4.55E-01	4.65E-01	1.07E+00	1.37E+00	1.23E+00	1.12E+00	1.04E+00	1.05E+00	1.10E+00	9.25E-01	4.40E-01	4.60E-01	4.55E-01	4.45E-01	2.38E+00	2.40E+00	2.39E+00	2.31E+00	2.36E+00	2.35E+00	2.42E+00	1.20E+00	7.99E-01
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.2e	0.025b	0.025b	0.025b	0.025b	0.025b	0.025b	0.025b	0.025b	N/A	N/A
Cr (mg/L)	D	3.15E-01	1.85E-01	1.75E-01	1.75E-01	3.80E-01	1.75E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.75E-01	3.65E-01	3.85E-01	3.85E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.09E-01	1.49E-01
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.012a	0.008b	0.008b	0.008b	0.008b	0.008b	0.008b	0.008b	0.008b	N/A	N/A
EC (colonies/ 100 mL)	D	3.00E+02	3.00E+01	1.23E+02	2.70E+02	2.00E+01	1.50E+01	9.80E+01	1.05E+02	1.30E+02	6.50E+01	1.25E+03	6.75E+02	3.10E+02	1.60E+01	4.00E+00	2.10E+03	5.60E+03	1.80E+02	0.00E+00	1.00E+01	5.00E+00	0.00E+00	0.00E+00	1.00E+00	0.00E+00	4.52E+02	1.17E+03
	W	4.05E+02	7.50E+01	1.95E+02	1.00E+02	9.50E+01	1.90E+01	1.95E+02	4.45E+02	2.15E+02	1.65E+02	2.90E+02	4.85E+02	1.90E+02	5.90E+01	5.80E+01	4.50E+01	2.03E+02	3.13E+02	4.00E+01	3.00E+01	4.40E+01	1.30E+02	1.10E+02	1.00E+02	5.50E+01	1.62E+02	1.33E+02
	GV	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	0g	-	-	-	-	-	-	-	-	N/A	N/A
TC (colonies/ 100 mL)	D	1.33E+03	3.60E+02	5.66E+02	4.35E+02	1.65E+02	1.50E+01	1.61E+03	1.46E+03	1.04E+03	3.80E+02	6.15E+03	2.73E+03	3.65E+02	2.20E+01	2.70E+01	1.01E+04	9.51E+04	3.10E+02	0.00E+00	2.50E+01	5.10E+01	7.00E+00	2.00E+00	6.53E+02	2.00E+02	4.92E+03	1.89E+04
	W	5.55E+02	4.30E+02	6.60E+02	1.59E+03	5.20E+02	6.90E+01	2.23E+03	2.61E+03	5.28E+03	5.51E+03	2.40E+04	4.14E+03	3.58E+03	4.79E+02	4.93E+02	1.95E+02	9.37E+02	4.17E+03	1.30E+03	3.48E+02	6.71E+02	6.00E+03	1.10E+03	2.50E+03	3.85E+03	2.93E+03	4.76E+03
	GV	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	0-5e	-	-	-	-	-	-	-	-	N/A	N/A

–: Guidelines not available; **a**: After DWAF (1996a); **b**: After DWAF (1995); **c**: After Chidya *et al*. (2011); **d**: After Chapman (1992); **e**: After DWAF (1996b); **f**: After CEQG (2005); **g**: After Gray (1994); **N/A**: Not applicable.

Table 5.3: Variations in sediment quality parameters for the dry (D) and wet (W) seasons with guideline values (GV) also indicated. Highlights indicate exceedances of GV.

		FRESHWATER SITES																	MARINE SITES							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Al (mg/kg)	***D***	4.81E+02	1.03E+03	6.98E+02	4.91E+02	6.05E+02	7.96E+02	2.54E+03	5.75E+02	7.23E+02	3.30E+02	1.32E+03	6.78E+02	7.61E+02	3.75E+02	5.33E+02	1.61E+03	1.59E+03	1.33E+03	1.18E+03	1.46E+03	5.87E+02	1.22E+03	8.60E+02	1.05E+03	1.02E+03
	W	9.91E+02	2.09E+03	6.95E+02	3.63E+02	8.00E+01	4.37E+01	2.59E+03	2.27E+03	8.62E+02	9.86E+02	6.58E+02	8.18E+02	7.49E+01	7.56E+01	5.67E+02	1.67E+03	1.63E+03	2.19E+03	7.94E+02	1.08E+03	1.15E+03	1.02E+03	6.50E+02	8.49E+02	7.55E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
As (mg/kg)	***D***	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.80E-01	0.00E+00	0.00E+00	2.10E-01	6.60E-01	5.60E-01	8.55E-01	0.00E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.62E+01	3.76E+01	2.07E+01	3.40E+01	1.53E+01	3.30E+01	1.95E+01	1.69E+01	3.34E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**
Ca (mg/kg)	***D***	1.55E+02	7.87E+02	7.67E+02	3.03E+02	6.31E+02	6.39E+02	3.11E+03	5.73E+02	3.54E+02	3.66E+02	7.43E+02	4.50E+02	4.56E+02	4.96E+02	4.69E+03	3.13E+03	5.96E+03	2.02E+04	2.09E+04	6.51E+03	1.15E+04	2.37E+04	2.97E+04	2.99E+04	2.53E+04
	W	5.05E+02	6.74E+02	1.02E+03	1.40E+02	0.00E+00	0.00E+00	6.38E+02	9.86E+03	7.30E+02	8.06E+02	3.63E+02	5.48E+02	0.00E+00	0.00E+00	4.44E+02	6.21E+03	2.35E+03	7.02E+03	1.02E+04	1.76E+04	1.84E+04	4.06E+04	3.72E+04	3.68E+04	3.04E+04
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cu (mg/kg)	***D***	1.99E+00	6.41E+00	5.20E+00	6.66E+00	8.85E+00	3.95E+00	2.50E+00	3.95E+00	1.56E+02	2.64E+00	5.16E+00	3.17E+00	4.09E+00	3.16E+00	4.74E+00	3.03E+01	1.82E+02	1.66E+01	7.14E+00	4.50E+00	1.17E+01	6.71E+00	5.54E+00	7.65E+00	4.57E+00
	W	0.00E+00	4.44E+00	0.00E+00	0.00E+00	4.90E+01	9.57E+00	5.46E+01	8.45E+01	6.61E+01	6.81E+01	5.57E+01	5.83E+01	7.76E+01	7.81E+01	8.06E+01	0.00E+00	1.76E+01	3.59E+01	0.00E+00	0.00E+00	5.92E-01	2.57E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**108b**	**108b**	**108b**	**108b**	**108b**	**108b**	**108b**	**108b**
Cr (mg/kg)	***D***	0.00E+00	1.46E+00	1.64E+00	0.00E+00	0.00E+00	4.20E-01	4.61E+00	2.02E+00	2.10E-01	0.00E+00	2.56E+00	0.00E+00	0.00E+00	0.00E+00	7.50E-02	1.09E+01	3.24E+01	6.11E+00	1.57E+00	2.00E+00	7.30E-01	3.50E-02	0.00E+00	0.00E+00	0.00E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**160c**	**160c**	**160c**	**160c**	**160c**	**160c**	**160c**	**160c**
Fe (mg/kg)	***D***	1.08E+03	1.63E+03	1.32E+03	9.90E+02	1.28E+03	1.52E+03	2.53E+03	1.74E+03	1.05E+03	7.73E+02	1.64E+03	1.36E+03	1.35E+03	7.01E+02	1.16E+03	2.79E+03	3.45E+03	1.61E+03	1.14E+03	1.94E+03	7.39E+02	9.88E+02	9.28E+02	1.24E+03	1.02E+03
	W	1.65E+03	4.87E+03	2.58E+03	6.09E+02	1.26E+03	1.08E+03	5.14E+03	4.56E+03	2.74E+03	3.07E+03	2.35E+03	3.34E+03	9.61E+02	6.24E+02	1.97E+03	2.74E+03	1.77E+03	4.19E+03	1.09E+03	1.69E+03	1.94E+03	1.28E+03	8.37E+02	1.42E+03	1.22E+03
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mg (mg/kg)	***D***	5.61E+01	3.19E+02	3.69E+02	1.53E+02	2.55E+02	2.93E+02	2.71E+02	2.69E+02	1.70E+02	8.90E+01	2.35E+02	1.86E+02	2.35E+02	1.61E+02	3.11E+02	7.01E+02	1.11E+03	1.07E+03	9.00E+02	7.52E+02	4.97E+02	8.49E+02	1.01E+03	1.16E+03	9.17E+02
	W	6.95E+01	6.05E+02	2.32E+02	3.62E+01	0.00E+00	0.00E+00	1.94E+02	1.50E+03	1.78E+02	1.96E+02	1.59E+02	2.33E+02	5.61E+00	5.52E+00	2.26E+02	6.45E+02	1.65E+03	1.90E+03	6.47E+02	9.68E+02	1.08E+03	1.46E+03	1.06E+03	1.29E+03	1.08E+03
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn (mg/kg)	***D***	1.27E+01	2.56E+01	2.22E+01	1.01E+01	7.18E+01	4.29E+01	3.43E+01	6.18E+01	3.78E+01	8.42E+00	8.62E+01	3.05E+01	4.10E+01	3.49E+01	1.52E+02	1.25E+02	1.61E+03	8.08E+01	1.57E+01	2.62E+01	8.73E+01	2.61E+01	1.71E+01	6.94E+01	6.31E+01
	W	0.00E+00	1.11E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.65E+01	5.25E+03	7.39E+01	8.85E+01	5.22E+01	5.38E+01	2.97E+00	3.00E+00	9.90E+01	6.00E+00	3.48E+02	2.46E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ni (mg/kg)	***D***	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.64E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.31E+00	4.53E+01	0.00E+00	0.00E+00	0.00E+00	3.50E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	W	0.00E+00	1.94E+01	4.65E+00	0.00E+00	1.09E+02	1.13E+02	9.01E+01	8.77E+01	1.22E+02	1.28E+02	1.32E+02	1.35E+02	1.38E+02	1.40E+02	1.31E+02	5.94E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.78E+00	2.04E+00	4.12E+00	1.86E+00
	GV	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	-	-	-	-	-	-	-	-
P (mg/kg)	***D***	3.56E+01	4.44E+01	5.57E+01	1.03E+02	7.58E+01	8.06E+01	7.94E+01	5.11E+01	9.06E+01	3.09E+01	1.84E+02	9.39E+01	8.77E+01	4.15E+01	7.69E+01	1.53E+02	1.95E+02	1.82E+02	1.62E+02	1.44E+02	8.86E+01	1.75E+02	1.84E+02	2.41E+02	1.85E+02
	W	2.06E+00	2.43E+01	9.03E+00	1.43E+01	1.84E+01	1.61E+01	1.42E+02	2.51E+02	1.95E+02	2.44E+02	1.38E+02	1.87E+02	6.09E+01	6.19E+01	1.19E+02	1.67E+02	4.17E+02	1.64E+02	7.89E+01	1.36E+02	1.34E+02	1.91E+02	1.33E+02	1.42E+02	1.27E+02
	GV	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**	**N/D**
Pb (mg/kg)	***D***	6.00E-01	2.78E+00	5.17E+00	2.28E+00	2.95E+00	3.44E+00	1.07E+00	3.34E+00	5.23E+01	1.70E-01	5.41E+00	2.14E+00	4.41E+00	7.85E-01	1.63E+00	4.04E+01	3.74E+01	8.93E+00	4.59E+00	4.96E+00	2.96E+00	2.90E+00	1.72E+00	3.55E+00	5.15E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.04E+01	2.03E+01	6.19E+01	7.17E+01	6.34E+01	6.65E+01	6.00E+01	6.59E+01	5.16E+01	5.22E+01	6.23E+01	0.00E+00	0.00E+00	6.61E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**112e**	**112e**	**112e**	**112e**	**112e**	**112e**	**112e**	**112e**
S (mg/kg)	***D***	2.37E+00	2.03E+01	1.47E+01	4.42E+00	1.88E+01	1.24E+01	8.20E+01	1.10E+00	3.41E+01	7.90E+00	5.65E+01	0.00E+00	6.34E+00	6.54E+00	5.62E+01	1.11E+02	2.28E+02	4.17E+02	3.09E+02	1.42E+02	1.30E+02	3.01E+02	4.14E+02	3.22E+02	3.48E+02
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.60E+01	2.33E+02	1.12E+02	1.27E+02	6.49E+01	9.22E+01	3.11E+01	4.99E+01	6.32E+01	0.00E+00	3.09E+01	3.23E+02	0.00E+00	0.00E+00	1.07E+02	5.41E+02	2.98E+02	1.82E+02	3.00E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Se (mg/kg)	***D***	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.75E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	-	-	-	-	-	-	-	-
V (mg/kg)	***D***	6.00E-01	8.03E+00	4.30E+00	1.06E+00	4.04E+00	3.09E+00	7.15E+00	3.86E+00	1.24E+00	7.10E-01	4.01E+00	2.81E+00	2.25E+00	3.20E-01	1.61E+00	8.17E+00	8.56E+00	7.05E+00	3.24E+00	8.16E+00	2.12E+00	4.77E+00	4.38E+00	6.18E+00	3.25E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.68E+01	7.60E+01	7.58E+01	7.07E+01	6.51E+01	6.55E+01	6.47E+01	6.63E+01	5.38E+01	5.44E+01	6.35E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	-	-	-	-	-	-	-	-
Zn (mg/kg)	***D***	0.00E+00	2.13E+01	1.97E+01	2.98E+01	1.18E+01	9.51E+00	0.00E+00	2.50E+00	2.75E+01	9.60E-01	3.84E+01	7.45E+00	1.61E+01	9.55E-01	4.66E+00	7.80E+01	1.17E+02	2.35E+01	1.28E+01	7.98E+00	4.26E+00	1.41E+01	2.55E+00	6.84E+00	3.20E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.78E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.87E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**271h**	**271h**	**271h**	**271h**	**271h**	**271h**	**271h**	**271h**
Organic matter (%)	***D***	6.00E-01	1.05E+00	1.10E+00	5.00E-01	4.00E-01	6.00E-01	2.00E+00	1.00E-01	7.50E-01	6.00E-01	1.45E+00	6.50E-01	8.50E-01	5.50E-01	3.50E-01	6.00E-01	1.75E+00	3.00E-01	8.50E-01	1.15E+00	4.00E-01	1.00E+00	5.00E-01	4.00E-01	6.50E-01
	W	2.00E+00	1.90E+00	1.50E+00	1.70E+00	1.30E+00	1.90E+00	3.00E+00	3.20E+00	2.00E+00	1.50E+00	3.80E+00	2.30E+00	1.70E+00	1.60E+00	1.30E+00	2.80E+00	1.90E+00	2.30E+00	3.00E+00	2.20E+00	2.00E+00	1.90E+00	1.70E+00	1.70E+00	2.00E+00
	GV	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	**1.25-3i**	-	-	-	-	-	-	-	-
Fines (silt and clay) (%)	***D***	6.00E+00	7.00E+00	6.00E+00	6.00E+00	5.50E+00	6.00E+00	1.50E+01	6.50E+00	5.50E+00	6.50E+00	1.30E+01	6.50E+00	5.25E+01	6.00E+00	5.50E+00	5.50E+00	6.50E+00	6.50E+00	6.50E+00	6.50E+00	6.50E+00	6.00E+00	6.00E+00	6.50E+00	6.00E+00
	W	4.00E+00	4.00E+00	4.00E+00	4.00E+00	4.00E+00	4.00E+00	1.90E+01	1.20E+01	4.00E+00	4.00E+00	8.00E+00	4.00E+00	4.00E+00	4.00E+00	4.00E+00	6.00E+00	5.00E+00	4.00E+00	7.00E+00	5.00E+00	7.00E+00	8.00E+00	4.00E+00	4.00E+00	5.00E+00
	GV	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	**19i**	-	-	-	-	-	-	-	-

Guideline values (GV) are Probable Effect Levels (PEL) from the Canadian quality guidelines for freshwater and marine sediments. **N/D**: Not detected; **–:** Guidelines not available; **a**: After CCME (1999a); **b**: After CCME (1999b); **c**: After CCME (1999c); **d**: After CCME (1999d); **e**: After CCME (1999e); **f**: After CCME (2009); **g**: After CCME (1999f); **h**: After CCME (1999g); **i**: After Singh *et al*. (2010).

Table 5.4: Pearson correlation matrix for physico-chemical characteristics and Total Diatom Densities (*TDD*). Highlighted cells indicate statistically significant correlations with *p*<0.05 or *p*>0.05.

a) Dry season

	TDD	*pH*	*Cond.*	*TDS*	*DO*	*BOD*	*COD*	*Na*	*NH_4*	*Cu*	*Ca*	*K*	*Mg*	*P*	*S*	*Al*	*Hg*	*V*	*Pb*	*Ni*	*Cr*	*EC*	*TC*
TDD	1.000																						
pH	-0.065	1.000																					
Cond.	0.110	0.329	1.000																				
TDS	-0.014	0.275	0.983	1.000																			
DO	-0.048	0.376	0.138	0.159	1.000																		
BOD	-0.069	-0.130	-0.823	-0.819	-0.007	1.000																	
COD	-0.146	-0.314	-0.168	-0.097	-0.274	0.176	1.000																
Na	0.147	0.339	0.991	0.961	0.107	-0.863	-0.191	1.000															
NH_4	0.235	0.332	0.824	0.779	0.217	-0.621	0.021	0.838	1.000														
Cu	-0.255	0.025	-0.409	-0.345	-0.069	0.459	0.352	-0.430	-0.519	1.000													
Ca	0.086	0.325	0.995	0.988	0.148	-0.798	-0.114	0.979	0.827	-0.370	1.000												
K	0.315	0.400	0.939	0.863	0.136	-0.728	-0.296	0.947	0.829	-0.500	0.918	1.000											
Mg	0.085	0.306	0.992	0.987	0.172	-0.794	-0.123	0.972	0.827	-0.368	0.996	0.908	1.000										
P	0.499	-0.381	-0.094	-0.130	-0.078	0.011	-0.182	-0.085	-0.082	-0.415	-0.110	-0.018	-0.114	1.000									
S	0.100	0.325	0.999	0.985	0.145	-0.809	-0.157	0.986	0.821	-0.597	0.997	0.935	0.993	-0.101	1.000								
Al	-0.092	-0.116	-0.421	-0.347	-0.030	0.386	0.313	-0.452	-0.383	0.862	-0.373	-0.535	-0.366	-0.121	-0.389	1.000							
Hg	-0.035	-0.192	-0.270	-0.208	-0.174	0.271	0.474	-0.302	-0.218	0.750	-0.208	-0.373	-0.206	-0.152	-0.251	0.891	1.000						
V	0.184	0.469	0.896	0.850	0.112	-0.650	-0.162	0.895	0.782	-0.082	0.891	0.901	0.881	-0.236	0.898	-0.192	-0.070	1.000					
Pb	-0.252	0.025	-0.419	-0.355	-0.072	0.463	0.360	-0.439	-0.327	0.999	-0.380	-0.509	-0.378	-0.411	-0.407	0.863	0.751	-0.092	1.000				
Ni	0.333	0.250	0.848	0.766	0.110	-0.736	-0.355	0.866	0.737	-0.769	0.816	0.931	0.809	0.156	0.840	-0.740	-0.569	0.689	-0.776	1.000			
Cr	-0.268	-0.087	-0.333	-0.253	-0.050	0.382	0.537	-0.363	-0.211	0.916	-0.277	-0.464	-0.273	-0.421	-0.318	0.846	0.822	-0.085	0.915	-0.710	1.000		
EC	-0.120	-0.248	-0.099	-0.021	-0.011	0.232	0.783	-0.131	0.227	0.293	-0.042	-0.243	-0.033	-0.062	-0.087	0.219	0.320	-0.143	0.296	-0.302	0.460	1.000	
TC	-0.135	-0.154	-0.004	0.076	0.131	0.152	0.656	-0.037	0.339	0.263	0.048	-0.158	0.068	-0.121	0.008	0.184	0.247	-0.061	0.263	-0.224	0.409	0.954	1.000

b) Wet season

	TDD	*pH*	*Cond.*	*TDS*	*DO*	*BOD*	*COD*	*Na*	*NH_4*	*Cu*	*Ca*	*K*	*Mg*	*P*	*S*	*Al*	*Hg*	*V*	*Pb*	*EC*	*TC*
TDD	1.000																				
pH	-0.067	1.000																			
Cond.	0.098	0.002	1.000																		
TDS	0.093	0.026	0.965	1.000																	
DO	-0.358	-0.094	-0.466	-0.456	1.000																
BOD	0.086	-0.020	0.099	-0.013	-0.077	1.000															
COD	0.160	-0.074	-0.297	-0.287	0.261	-0.473	1.000														
Na	0.094	-0.005	0.994	0.946	-0.475	0.137	-0.313	1.000													
NH_4	0.047	-0.188	0.867	0.779	-0.420	-0.023	-0.150	0.879	1.000												
Cu	-0.027	-0.098	-0.377	-0.417	-0.175	0.594	-0.399	-0.324	-0.305	1.000											
Ca	0.086	-0.001	0.998	0.961	-0.477	0.106	-0.310	0.996	0.869	-0.362	1.000										
K	0.085	0.038	0.990	0.968	-0.439	0.072	-0.279	0.980	0.860	-0.401	0.985	1.000									
Mg	0.070	-0.006	0.994	0.959	-0.459	0.082	-0.297	0.989	0.874	-0.373	0.994	0.981	1.000								
P	0.633	-0.117	0.060	0.075	-0.065	-0.457	0.605	0.030	0.136	-0.520	0.052	0.064	0.062	1.000							
S	0.080	-0.007	0.995	0.952	-0.456	0.097	-0.278	0.986	0.878	-0.392	0.994	0.983	0.991	0.074	1.000						
Al	-0.094	-0.047	-0.383	-0.405	-0.102	0.538	-0.345	-0.330	-0.308	0.970	-0.370	-0.404	-0.364	-0.544	-0.399	1.000					
Hg	-0.154	0.046	-0.151	-0.133	-0.043	0.155	-0.005	-0.155	-0.151	0.229	-0.165	-0.141	-0.151	-0.187	-0.149	0.231	1.000				
V	0.076	0.253	0.649	0.662	-0.363	0.203	-0.310	0.690	0.466	-0.014	0.649	0.675	0.631	-0.153	0.592	0.004	-0.113	1.000			
Pb	-0.121	-0.099	-0.315	-0.288	0.349	0.147	0.178	-0.324	-0.333	-0.031	-0.327	-0.305	-0.316	-0.017	-0.318	-0.029	0.172	-0.225	1.000		
EC	0.017	-0.187	-0.385	-0.337	0.351	-0.101	0.393	-0.367	-0.298	-0.068	-0.398	-0.348	-0.398	0.025	-0.404	-0.038	-0.137	-0.025	0.530	1.000	
TC	-0.086	-0.084	-0.084	-0.038	0.068	-0.466	0.333	-0.093	-0.121	-0.346	-0.090	-0.064	-0.089	0.192	-0.090	-0.356	-0.109	0.006	-0.027	0.324	1.000

5.5.1 PHYSICO-CHEMICAL WATER QUALITY ALONG LAND USE ZONES

Table 5.2 summarizes the measured water quality parameters from all sampling sites during the wet and dry seasons. An indication of the corresponding standard deviations for measures across sites and a comparison against prescribed guideline values are also presented. Notable dispersions of selected variables (Cond., TDS, Na, Ca, K, Mg and S) across sites in each season are represented by the high standard deviations showing high spatial variability of these chemical constituents. This was more than likely attributed to increased marine influence on chemical concentrations of these parameters as indicated in by the elevated values in sites 18 – 25 of the Bayhead Canal in the Durban Harbour.

Analysis of Variance (ANOVA) showed statistically significant differences in NH_4, P, DO, BOD, Hg, Al, V, Ni and Cr for sites across seasons (ANOVA, *$p<0.05$*). Remaining variables analyzed showed no statistically significant variations in sites across seasons (ANOVA, *$p>0.05$*). Significant changes in dissolved nutrients (NH_4 and P) across seasons was a direct consequence of substantial runoff derived nutrient contamination from surrounding land use into the catchment systems as represented by the higher wet season mean values in **Table 5.2** – similar conclusions were drawn by Shah *et al*. (2007) in a water quality study conducted for catchments during the dry season and following rain events. The substantial seasonal changes in DO was represented by distinct reductions in wet season DO (summer months) as a consequence of elevated water temperature and a subsequent increase in oxidative processes of organic matter (Abdel-Satar, 2005). This also possibly explained the significantly higher average BOD concentrations in the wet season as compared to the average dry season values. The average dry season concentrations of trace metals analyzed (Hg, Al, V, Ni and Cr) were significantly higher than the wet season values, which was attributed to in-stream evaporative concentration effects of these metals in the water column as a consequence of low tributary inflows and precipitation input as noted in a similar study by Raj and Azeez (2009).

Recommended guideline levels of measured variables for the freshwater (sites 1 – 17) and marine water sites (sites 18 – 25) are also represented in **Table 5.2**, with highlights indicating exceedances of guideline levels. General deteriorations in water quality was observed for most trace metals (Al, Hg, V, Pb, Ni and Cr) and nutrient parameters (Ca, Mg, Na, S, Cu, NH_4 and P) which when present, in most instances, exceeded prescribed guideline levels. Principal land use contributors of these parameters were industrial (sites 9, 16, 17) and residential land use types (sites 3, 5, 6, 8). Inputs of trace metals and nutrients in the Bayhead Canal of the Durban Bay Harbour, which often exceeded prescribed marine target values when present (for NH_4, P, Cu, Hg, V and Pb), was more than likely due to a combination of storm water outfalls in the Bayhead Canal and freshwater catchment inflows. Additionally, when present, P occurred at concentrations which classified the freshwater systems as hypertrophic and toxic for human and animal consumption (DWAF, 1996a). Microbiological counts across all land use types greatly exceeded acceptable standards for human consumption and domestic use, which rendered the sanitary quality of the water source as unacceptable. pH showed slight deviations from prescribed target values at sites 14 and 15 in both seasons, which were associated with industrial land use and were slightly alkaline. pH levels in marine sites (sites 18 – 25) also marginally deviated from the prescribed target values. Conductivity and TDS was associated with anomalous increases across most freshwater sites (3, 5, 9, 11, 12, 13, 14, 15, 16 and 17) which were mainly associated with industrial and residential land use characterized by high combined concentrations of ions in solution. Analytical measures of DO at all sites exceeded the minimum prescribed range of 5 – 6 mg/L required to support an aquatic population, thereby indicating the availability of sufficient DO for biota (Chidya *et al*., 2011). Concentrations of COD at all sites fell less than the prescribed range of 20 mg/L, with the exception of sites 16 and 17 in the dry season associated with industrial inputs and effluent discharge into the aManzimnyama Canal. The quantified amounts of Na at sites 16 (wet season) and 17 (wet and dry season), associated with industrial inputs along the aManzimnyama Canal, substantially exceeded the acceptable water standard range of 0 – 100 mg/L for human consumption as stipulated by DWAF (1996b). Similarly, K concentrations at sites 16 and 17 in the wet season exceeded the natural background concentration of 10 mg/L indicating anthropogenic influence through industrial discharges. Elevated values of Na, K, Cond. and TDS in the marine waters of the Bayhead Canal (sites 18 – 25) can be expected due to naturally higher levels of dissolved ions in solution.

Correlation analysis (Spearman rank correlation) carried out for physico-chemical water parameters are represented in the correlation matrices for wet and dry seasons in **Table 5.4**. As these correlation matrices comprise a combination of catchment sampling sites, the resulting correlation coefficients must be interpreted with caution as these are reflective of both temporal and spatial variations (Vega *et al*., 1998). Nonetheless, some seasonal inter-elemental relationships can be readily interpreted:

- Positive correlations between Cond. and TDS, Na, NH_4, Ca, K, Mg, S, V in both seasons ($p<0.05$) –of which all the elements form major ions in solution within the aquatic environment. Additionally, most of these parameters are responsible for water mineralization (Vega *et al*., 1998);
- Positive correlations between BOD and Cu ($p<0.05$ in both seasons), and BOD and Al ($p>0.05$ in the dry season and $p<0.05$ in the wet season); and COD, EC, TC in both seasons ($p<0.05$ in the dry season and $p>0.05$ in the wet season) – suggesting common sources as also reflected in a study by Ghrefat *et al*. (2011) involving sediment metal contamination investigations in the Kafrain Dam, Jordan;
- Negative correlation between Cond. and DO in the wet season ($p<0.05$) –suggesting that most dissolved ions were of organic origin and subject to chemical oxidation processes (Abdel-Satar, 2005).

When compared to Mg, Ca showed significant positive correlations ($p<0.05$) with more parameters of geological origin, showing the preponderance of Ca over Mg in the sedimentary material (Abdel-Satar, 2005).

5.5.2 Diatom distribution and ecology along land use zones

As depicted in **Figures 5.2** and **5.3**, four diatom taxa (*Thalassiosira weissflogii*, *Navicula salinicola*, *Amphora subacutiuscula*, *Navicula cryptocephala*) were identified from 25 habitats (17 freshwater and 8 marine habitats) which were subject to a range of land use throughout the freshwater catchments. The average count of the *Thalassiosira weissflogii* taxon was higher in the dry season with no significant differences to the wet season count (ANOVA, $p>0.05$). In contrast, average counts of the *Navicula salinicola* and *Amphora subacutiuscula* taxa were higher in the wet season with no significant differences to the dry season values (ANOVA, $p>0.05$). Average counts of the *Navicula cryptocephala* taxon were the same for both wet and dry seasons. The numerically dominant taxon was *Thalassiosira weissflogii* which was most abundant at site 9 in the wet season which was associated with industrial land use, and represented by the highest combined levels of nutrients P and NH_4. The remaining taxa were generally poorly represented (mostly absent) across all sample sites in both seasons, and were present in low counts in the Bayhead Canal (sites 20, 23 and 24). The overall diatom abundance and diversity in this study was low when compared to diatom studies both internationally and regionally (Blinn and Bailey, 2001; Hall, 2012; Singh *et al*., 2010; Walsh and Wepener, 2009), suggesting deteriorations in the river systems of the study area with regard to selected physico-chemical parameters. This could possibly be attributed to cumulative effects of high levels of toxic Cu, Hg, Cr, Pb and Al which were negatively correlated with total diatom densities in both seasons ($p>0.05$) (**Table 5.4**), and frequently exceeded target water quality ranges for growth and reproduction of aquatic species. The Pearson correlation matrix of seasonal physico-chemical water parameters including total diatom density (*TDD*) is represented in **Table 5.4**. *TDD* showed significant positive correlations with P in both seasons ($p<0.05$). Other studies have shown that *TDD* were found to be more closely associated with environmental variables such as water temperature, air temperature, relative humidity and rainfall – and showed significant negative correlations with these variables (e.g. Singh *et al*., 2010). This was possibly attributed to slightly higher average diatom counts in the dry season which is characterized by low rainfall, air and water temperatures, relative humidity and rainfall.

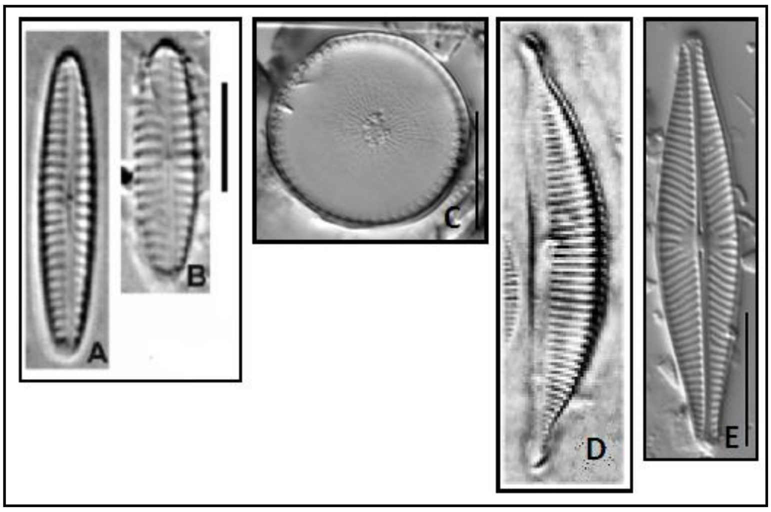

Figure 5.2: Identified diatom taxa across sample sites. A, B: *Navicula salinicola* (Maidana *et al*., 2011; C: *Thalassiosira weissflogii* (Kociolek, 2011); D: *Amphora subacutiuscula* (Wachnicka and Gaiser, 2011); E: *Navicula cryptocephala* (Potapova, 2011). Scale bars (where present) represent 10 µm.

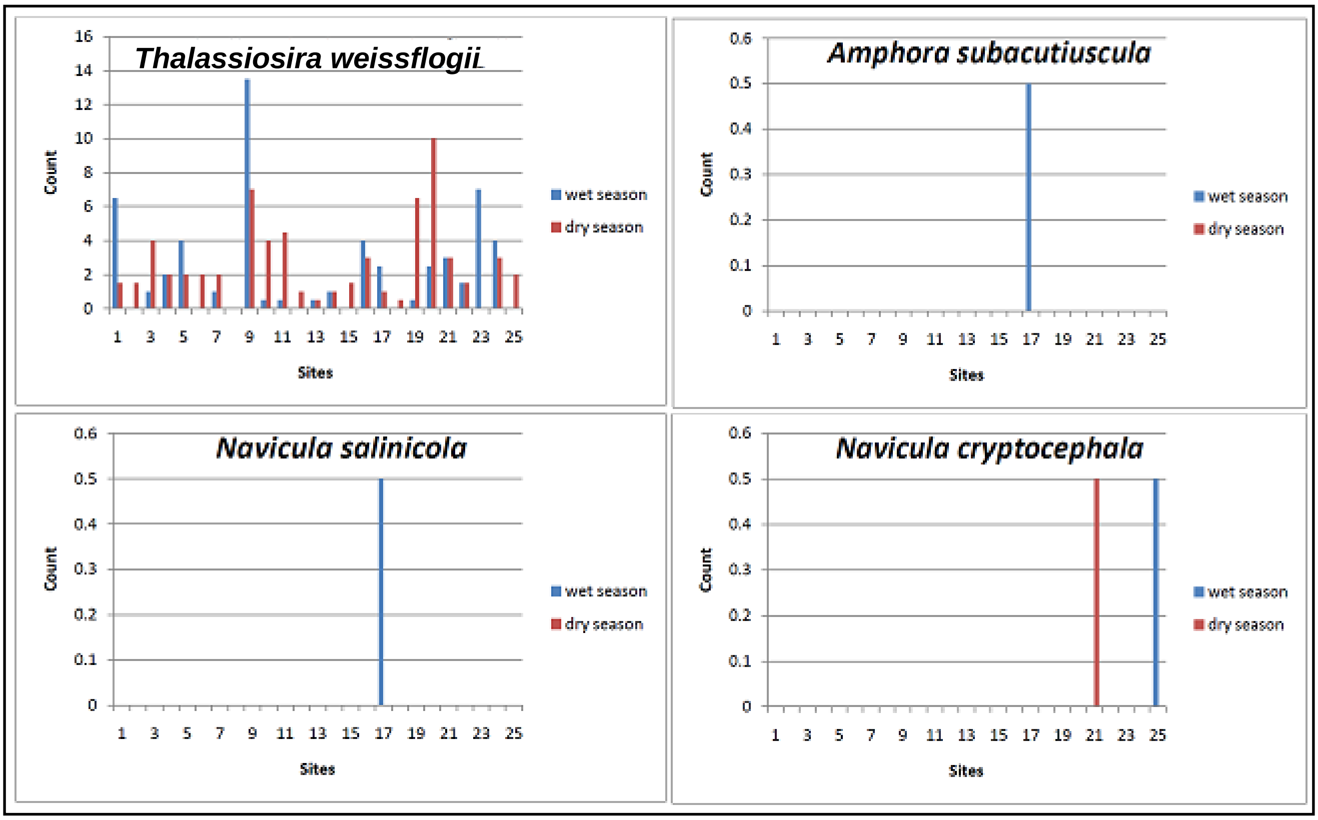

Figure 5.3: Individual counts of diatom taxa across sample sites.

Analysis of seasonal soil physico-chemical characteristics at the sample locations were compared against relevant guideline/control values (**Table 5.3**) to determine substrate suitability for the growth of diatoms. Results showed that parameters were generally well within the prescribed sediment target values for aquatic environments – with the exception of organic soil content (OM) in the dry season, and As (sites 7 – 10, 12, 13 and 15) and Ni (sites 5 – 15) in the wet season, which exceeded the prescribed guideline values and therefore suggesting that these parameters had a low stimulatory effect on diatom growth and reproduction at these sites. P readings also indicated good quality nutrient rich soil for diatom growth. This lends credibility to the assertion relating to the ability of the soil substrate to stimulate diatom growth in the dry season.

5.6 CONCLUSION

The study revealed deteriorations in nutrient (NH_4, P, and Cu), trace metal (Al, Hg, V, Pb, Ni and Cr) and microbiological (*E. coli* and Total coliforms) water quality across most land use types which frequently exceeded prescribed guideline values when present. The study also demonstrated that diatom densities showed strong positive relationships with dissolved P in both seasons, suggesting that this is an important nutrient governing the distribution and abundance of diatoms in the Bayhead Canal of the Durban Bay Harbour and its catchments. The study also revealed that whilst substrate suitability generally favoured diatom growth, low counts of diatom taxa found across all sites and seasons are indicative of the drastic deterioration in water quality. The low diatom counts in this study can be related to toxic concentrations of trace metals analyzed (Cu, Hg, Cr, Pb and Al), all of which were negatively correlated with diatom densities. However, it should be noted that there is a possibility that environmental variables outside of those analyzed such as water temperature, air temperature, relative humidity and rainfall may also be influential on diatom distributions and abundance. Nonetheless, it is clear that the findings of this study point to aquatic systems in an advanced state of degradation, necessitating drastic remedial measures be implemented for restoration of these river systems.

CHAPTER SIX

SPATIOTEMPORAL EVALUATION OF HEAVY METAL CONTAMINATION IN RIVER SEDIMENTS OF THE DURBAN HARBOUR CATCHMENTS, SOUTH AFRICA

This chapter is developed as a research article and has been submitted for publication to the journal *Frontiers of Earth Science*.

6.1 ABSTRACT

The levels of environmental pollution in surface sediments of three major river catchments characterized by industrial and residential land uses (the uMhlatuzana, uMbilo and aManzimnyama rivers) contributing inflows to the Bayhead Canal of the Durban Harbour are presented here. The following heavy metals in the surface sediment were analyzed: Al, As, Ca, Cu, Cr, Fe, Mg, Mn, Ni, P, Pb, S, Se, V and Zn. The contamination status of these systems was then ascertained using the Enrichment Factor (EF) and Contamination Factor (CF) Indices. EF results indicated that most heavy metals were of natural origin except As, Ca, Cu, Mn, Ni, Pb, S, V and Zn across sites which were primarily associated with industrial and residential land use types. The CF showed moderate to considerable contamination of As, Ca, Mn, Ni, Pb and S in sediments primarily associated with industrial and residential land use types. Spatiotemporal characterization of sample sites in relation to metal content using Cluster Analysis, allowed for the identification of three major clusters in the both seasons characterized by different levels of pollution. Additionally, Principal Component Analysis was used to distinguish between the natural and anthropogenic occurrence of heavy metals in the systems and allowed for the identification of three groupings in the seasonal loading plots: Group 1 consisting of As, Cu, Cr, Mg, Mn, Ni, P, Pb, S, Se, V, Zn, fine sediment and OM were representative of anthropogenic contributions from industrial and residential land use; Group 2 consisting of Fe and Al of natural origin; and Group 3 consisting of Ca represented natural sources by seawater incursion. Analysis of bed sediment in the Bayhead Canal of the Durban Harbour showed that the industrialized aManzimnyama catchment inflows were most influential in governing heavy metal content of surface sediment near the confluence in both wet and dry seasons.

Key words

Sediment, geochemistry, land use, pollution, Durban Harbour

6.2 INTRODUCTION

Analysis of sediments remains a favourable method of heavy metal pollution detection in surface waters since heavy metals seldom remain in the water column but are often readily adsorbed to fine particulates and sediment and temporarily sequestrated in the aquatic environment until remobilized (Charkhabi *et al*., 2008). Heavy metals can be very toxic at low concentrations which can prove to be hazardous to general ecosystem health and functioning (Olubunmi and Olorunsola, 2010). Moore *et al*. (2009) further state that of the various pollutants, heavy metals are in fact considered to be amongst the most toxic, persistent and abundant in aquatic ecosystems, the effects of which can be exponentially increased through biomagnification. Some of the impacts associated with toxic metal discharges on aquatic ecosystems often include reductions in overall biotic diversity due to the elimination of most species, as well as a general reduction in the number of individuals in aquatic communities with survival of only a few tolerant species (Gower, 1980). Furthermore, the inherent capability of certain toxic metals such as mercury to bio-accumulate in the tissues of fish and other organisms high in the food chain can result in serious health implications when consumed by humans (Rubin, 2001). The dynamic geochemical nature of heavy metals, particularly the accumulation of metallic contaminants in aquatic bed sediment, has caused much concern at an ecological level and has subsequently resulted in several contamination assessments involving heavy metals in the environment (Addo *et al*., 2011; Liu *et al*., 2005; Moore *et al*., 2009; Yahaya *et al*., 2009). This situation is exacerbated by rapid industrial development and subsequent impacts on the environment, such that human activity has accelerated the risk of environmental pollution by elevating concentrations of heavy metals in aquatic environments far beyond the levels of natural occurrence or geochemical background concentrations associated with the underlying geological substrate (Manjunatha *et al*., 1996).

The geochemical background concentrations of heavy metals in the upper continental crust, commonly referred to as “Clarke values”, form the basis of discriminating between natural and anthropogenic sources of sediment contaminants and have become particularly useful in heavy metal contaminant detection for river sediment in the absence of appropriate sediment quality guidelines as in the case in South Africa (Sukdeo, 2010). Several studies have successfully applied geochemical background concentrations through the use of universally accepted geochemical indices such as the Enrichment Factor (EF) Index and Contamination Factor (CF) Index, in an attempt to analyze and characterize metal enrichment in aquatic sediment, which has subsequently allowed for the effective discrimination of natural and anthropogenic heavy metal occurrence (Chakravarty and Patgiri, 2009; Kaushik *et al*., 2009; Liu *et al*., 2005; Manjunatha *et al*., 1996; Olivares-Rieumont *et al*., 2005; Sekabira *et al*., 2010; Varol, 2011; Wang *et al*., 2012).

The Enrichment factor Index evaluates the magnitude of metal enrichment of an element in the environment as a result of anthropogenic influence, and is useful in indicating the extent to which measured concentrations of heavy metals exceed the natural geochemical background concentrations (Varol, 2011). The Enrichment Factor index is represented by the following equation, in accordance with Varol (2011):

$$\textit{Enrichment Factor (EF)} = \frac{[\textit{Concentration of Metal}] / [\textit{Concentration of Fe}]}{[\textit{Clarke value of Metal}] / [\textit{Clarke value of Fe}]} \qquad (1)$$

Fe is commonly used as the reference metal for the following reasons as identified by Varol (2011):

- Its natural abundance in fine solid substrates;
- Its similar geochemical composition to most heavy metals; and
- Its homogeneous natural concentration with distribution patterns.

As EF values increase, so too does the levels of anthropogenic influence, with 0 < EF < 10 often indicating natural metal sources from initial soil or parent rock and EF > 10 often associated with anthropogenic sources of metals (Moore *et al*., 2009). However, Varol (2011) further identifies 7 classes of Enrichment Factors:

- EF < 1, No enrichment;
- 1 < EF < 3, Minor enrichment;
- 3 < EF < 5, Moderate enrichment;

- 5 < EF < 10, Moderately severe enrichment;
- 10 < EF < 25, Severe enrichment;
- 25 < EF < 50, Very severe enrichment; and
- EF > 50, Extremely severe enrichment.

The Contamination Factor (CF) Index is used to assess sediment contamination by comparing metal concentrations in the surface crustal layer with the natural background occurrence in uncontaminated surface sediment and is given by the following ratio as identified in Varol (2011):

$$\textit{Contamination Factor (CF)} = (C_{\textit{heavy metal}}) / (C_{\textit{background}}) \qquad (2)$$

Where:

C is the metal concentration of a given element.

Varol (2011) further identifies the following classes of contamination for pollution characterization:

- CF < 1, Low contamination;
- 1 < CF < 3, Moderate contamination;
- 3 < CF < 6, Considerable contamination; and
- CF > 6, Very contaminated.

In this study, an attempt is made to characterize the spatiotemporal distributions of catchment land use on the basis of heavy metals analyzed, and to evaluate the contamination status of heavy metals in the sediment of three major catchment river systems contributing freshwater inflows to the Bayhead Canal of the Durban Harbour – the uMhlatuzana, uMbilo and aManzimnyama river catchments. The approach for the characterization of heavy metal contamination was based on seasonality and land use change along the catchments which allowed for comparative evaluation as a consequence of natural and anthropogenic contributions. Additionally, the sediment contamination status of the Bayhead Canal of the Durban Harbour was assessed through the examination of heavy metals in the surface sediment at equidistant, predetermined locations along the Bayhead Canal, in an attempt to assess the influence of catchment contributions on the overall sediment quality of the receiving environment (Bayhead Canal). This study is useful in serving as an effective baseline determination of anthropogenic catchment influence and the subsequent contamination status of the associated catchment river systems, as well as the Bayhead Canal of the Durban Harbour into which they flow.

6.3 STUDY AREA

The uMbilo, uMhlatuzana and aManzimnyama River catchments of KwaZulu-Natal, South Africa, represent predominantly urbanized catchment systems that drain into the Bayhead Canal of the Durban Harbour as corresponding canals at the confluence as depicted in **Figure 6.1**. The geology of the catchments is variable and comprises granites and gneisses of the Basement Complex, sandstones of the Natal Group, glacial tillite and shales of the Dwyka and Ecca Groups and minor Karoo dolerite intrusions (MER/ERM, 2011). The geology of the Durban Harbour comprises faulted Karoo sediments of the Dwyka and Ecca Groups, overlain by a shallow veneer of Cretaceous sediments that thicken eastward beneath the Bluff (MER/ERM, 2011). The broader catchment area occurs in a summer rainfall area with an average summer rainfall of 1054 mm between the months of December and February (MER/ERM, 2011).

6.4 MATERIALS AND METHODS

The locations of the sampling sites were chosen along the river systems at the interface of each land use type in order to account for the changes in catchment land use. As such, the sampling was reflective of the influence of land use management on in-stream sediment quality. Site identification was achieved through topographic maps and aerial photographs, and validated *via* ground truthing site visits. Additional sampling was conducted at equidistant intervals in the Bayhead Canal to assess the effects of catchment inflows on the sediment quality of the Bayhead Canal of the Durban Harbour. The location of sampling sites in the context of the study area is shown graphically in **Figure 6.1** and is described in **Table 6.1** below.

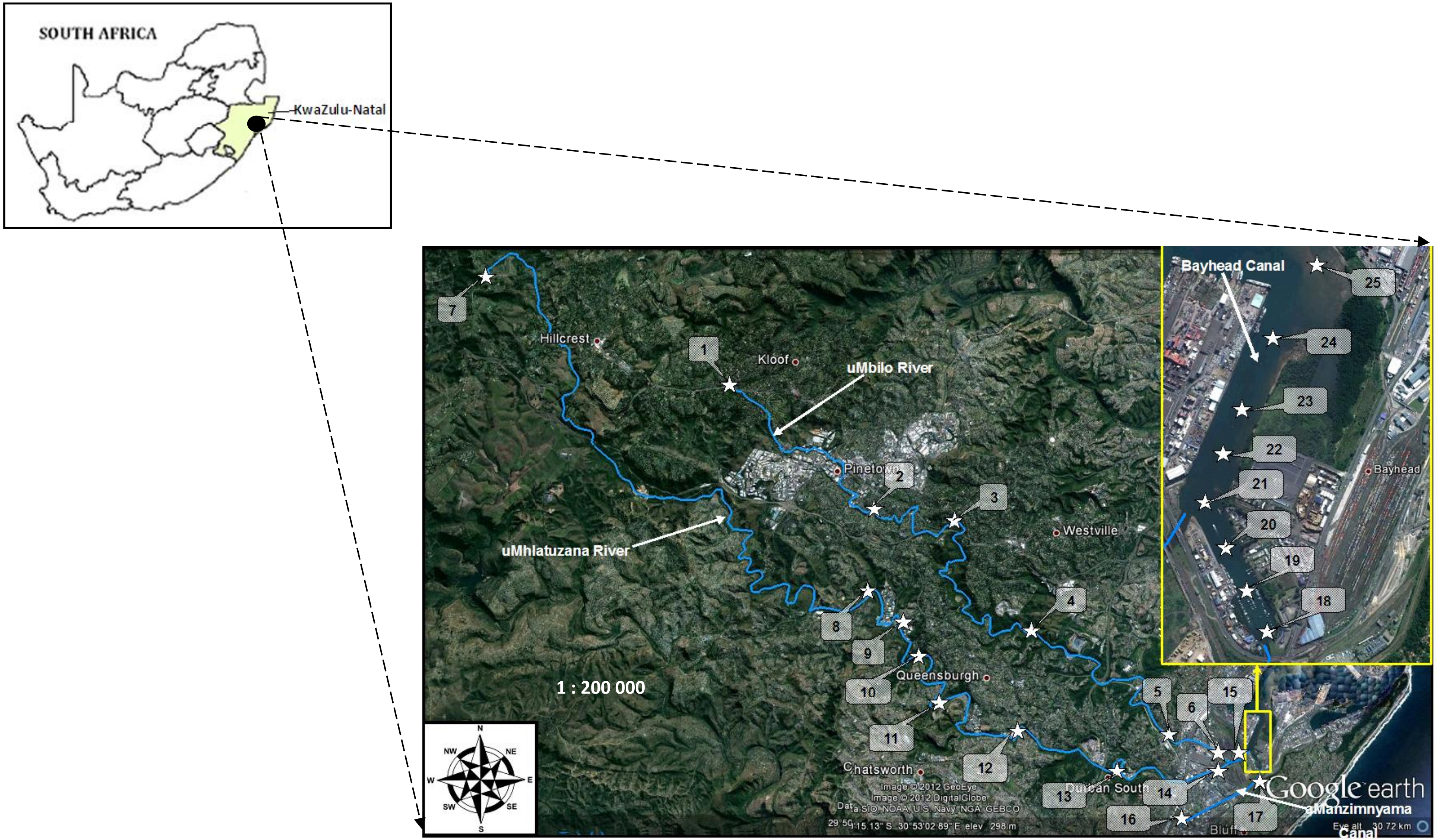

Figure 6.1: Contextualization of study area with sampling sites illustrated (Source: Moodley, 2013).

Table 6.1: Description of sample sites on the basis of land use (Source: Moodley, 2013).

uMbilo River	
Site	**Land use description**
1	Source (Sparse residential area)
2	Interface of industrial and residential area (sited downstream of industrial area)
3	Interface of residential area and nature reserve (sited downstream of residential area)
4	Interface of nature reserve and residential area – also impacted on by the Waste Water Treatment Works (WWTW) (sited downstream of nature reserve)
5	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
6	Interface of industrial area and confluence with uMhlatuzana River (sited downstream of industrial area)
uMhlatuzana River	
Site	**Land use description**
7	Source (Sparse residential area)
8	Interface of residential and industrial area – also impacted on by WWTW (sited downstream of residential area)
9	Interface of industrial area and nature reserve (sited downstream of industrial area)
10	Interface of nature reserve and residential area – also impacted on by WWTW (sited downstream of nature reserve)
11	Interface of residential and industrial area (sited downstream of residential area)
12	Interface of industrial area and nature reserve (sited downstream of industrial area)
13	Interface of nature reserve and industrial area (sited downstream of nature reserve)
14	Interface of industrial area and confluence with uMbilo River (sited downstream of industrial area)
uMbilo/uMhlatuzana Canal confluence	
Site	**Land use description**
15	Sited at confluence
aManzimnyama Canal	
Site	**Land use description**
16	Source (Low density industrial area)
17	Interface of industrial area and confluence to Bayhead Canal (sited downstream of industrial area)
Bayhead Canal of Durban Harbour	
Sites	**18, 19, 20, 21, 22, 23, 24, 25** (equidistant)

Due to the fact that sediment tends to display long-term pollution trends in an aquatic body as compared to water itself, two field surveys were conducted for sediment sampling in December 2011 and June 2012, which were also grouped into wet and dry season sampling respectively. Surface sediment samples were collected at each site and analyzed for several heavy metals including aluminium (Al), arsenic (As), calcium (Ca), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), phosphorous (P), lead (Pb), sulphur (S), selenium (Se), vanadium (V) and Zinc (Zn). Analysis of these heavy metal ions was attained through atomic adsorption Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). In addition, the percent organic matter and fine sediment was quantitatively determined using standard sediment analysis methods as prescribed by SASRI (2012).

6.5 RESULTS AND DISCUSSION

Analytical findings: The variations of parameters defining in-stream sediment quality measured during the wet and dry seasons are illustrated in **Table 6.2**.

Statistical analysis: Seasonal variations in sediment quality parameters were explored statistically through Analysis of Variance (ANOVA). Pearson's correlation coefficient (r) was used to assess inter-elemental relationships for measured parameters (**Tables 6.4a** and **b**). Cluster Analysis (CA) was used to detect spatiotemporal site variations across catchment sampling sites using measured parameters for both seasons (**Figures 6.5a** and **b**). Principal Component Analysis (PCA) was applied to the measured sediment concentrations in order to distinguish between potential natural and anthropogenic sources of pollution in the wet and dry seasons (**Figures 6.6a** and **b**). All statistics were performed using the Microsoft Excel® and Genstat® data statistics packages.

Assessment of sediment contamination: The Enrichment Factor (EF) and Contamination Factor (CF) indices were used to assess and characterize sediment contamination in relation to applicable geochemical background concentrations, the results of which are illustrated in **Figures 6.4a** and **b**.

Effects of catchment land use on receiving environments: Sediment heavy metal concentrations in the Bayhead Canal of the Durban Harbour were used to generate interpolated images using ArcGIS 9® (**Figure 6.2**). This allowed for visual interpretation of the effects of catchment inflows on the heavy metal distributions in the sediment of the Bayhead Canal.

Table 6.2: Variations in sediment concentrations (mg/kg) for the dry (D) and wet (W) seasons with guideline values (GV) also indicated (highlights indicate exceedances of GV).

		FRESHWATER SITES																	MARINE SITES								SEASONAL MEAN VALUES
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	
Al	*D*	4.81E+02	1.03E+03	6.98E+02	4.91E+02	6.05E+02	7.96E+02	2.54E+03	5.75E+02	7.23E+02	3.30E+02	1.32E+03	6.78E+02	7.61E+02	3.75E+02	5.33E+02	1.61E+03	1.59E+03	1.33E+03	1.18E+03	1.46E+03	5.87E+02	1.22E+03	8.60E+02	1.05E+03	1.02E+03	9.54E+02
	W	9.91E+02	2.09E+03	6.95E+02	3.63E+02	8.00E+01	4.37E+01	2.59E+03	2.27E+03	8.62E+02	9.86E+02	6.58E+02	8.18E+02	7.49E+01	7.56E+01	5.67E+02	1.67E+03	1.63E+03	2.19E+03	7.94E+02	1.08E+03	1.15E+03	1.02E+03	6.50E+02	8.49E+02	7.55E+02	9.98E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**N/A**
As	*D*	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.80E-01	0.00E+00	0.00E+00	2.10E-01	6.60E-01	5.60E-01	8.55E-01	0.00E+00	1.23E-01
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.62E+01	3.76E+01	2.07E+01	3.40E+01	1.53E+01	3.30E+01	1.95E+01	1.69E+01	3.34E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.87E+00
	GV	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**17a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**41.6a**	**N/A**
Ca	*D*	1.55E+02	7.87E+02	7.67E+02	3.03E+02	6.31E+02	6.39E+02	3.11E+03	5.73E+02	3.54E+02	3.66E+02	7.43E+02	4.50E+02	4.56E+02	4.96E+02	4.69E+03	3.13E+03	5.96E+03	2.02E+04	2.09E+04	6.51E+03	1.15E+04	2.37E+04	2.97E+04	2.99E+04	2.53E+04	7.65E+03
	W	5.05E+02	6.74E+02	1.02E+03	1.40E+02	0.00E+00	0.00E+00	6.38E+02	9.86E+03	7.30E+02	8.06E+02	3.63E+02	5.48E+02	0.00E+00	0.00E+00	4.44E+02	6.21E+03	2.35E+03	7.02E+03	1.02E+04	1.76E+04	1.84E+04	4.06E+04	3.72E+04	3.68E+04	3.04E+04	8.90E+03
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**N/A**
Cu	*D*	1.99E+00	6.41E+00	5.20E+00	6.66E+00	8.85E+00	3.95E+00	2.50E+00	3.95E+00	1.56E+02	2.64E+00	5.16E+00	3.17E+00	4.09E+00	3.16E+00	4.74E+00	3.03E+01	1.82E+02	1.66E+01	7.14E+00	4.50E+00	1.17E+01	6.71E+00	5.54E+00	7.65E+00	4.57E+00	1.98E+01
	W	0.00E+00	4.44E+00	0.00E+00	0.00E+00	4.90E+01	9.57E+00	5.46E+01	8.45E+01	6.61E+01	6.81E+01	5.57E+01	5.83E+01	7.76E+01	7.81E+01	8.06E+01	0.00E+00	1.76E+01	3.59E+01	0.00E+00	0.00E+00	5.92E-01	2.57E+00	0.00E+00	0.00E+00	0.00E+00	2.97E+01
	GV	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**197b**	**108b**	**108b**	**108b**	**108b**	**108b**	**108b**	**108b**	**108b**	**N/A**
Cr	*D*	0.00E+00	1.46E+00	1.64E+00	0.00E+00	0.00E+00	4.20E-01	4.61E+00	2.02E+00	2.10E-01	0.00E+00	2.56E+00	0.00E+00	0.00E+00	0.00E+00	7.50E-02	1.09E+01	3.24E+01	6.11E+00	1.57E+00	2.00E+00	7.30E-01	3.50E-02	0.00E+00	0.00E+00	0.00E+00	2.67E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**90c**	**160c**	**160c**	**160c**	**160c**	**160c**	**160c**	**160c**	**160c**	**N/A**
Fe	*D*	1.08E+03	1.63E+03	1.32E+03	9.90E+02	1.28E+03	1.52E+03	2.53E+03	1.74E+03	1.05E+03	7.73E+02	1.64E+03	1.36E+03	1.35E+03	7.01E+02	1.16E+03	2.79E+03	3.45E+03	1.61E+03	1.14E+03	1.94E+03	7.39E+02	9.88E+02	9.28E+02	1.24E+03	1.02E+03	1.44E+03
	W	1.65E+03	4.87E+03	2.58E+03	6.09E+02	1.26E+03	1.08E+03	5.14E+03	4.56E+03	2.74E+03	3.07E+03	2.35E+03	3.34E+03	9.61E+02	6.24E+02	1.97E+03	2.74E+03	1.77E+03	4.19E+03	1.09E+03	1.69E+03	1.94E+03	1.28E+03	8.37E+02	1.42E+03	1.22E+03	2.04E+03
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**N/A**
Mg	*D*	5.61E+01	3.19E+02	3.69E+02	1.53E+02	2.55E+02	2.93E+02	2.71E+02	2.69E+02	1.70E+02	8.90E+01	2.35E+02	1.86E+02	2.35E+02	1.61E+02	3.11E+02	7.01E+02	1.11E+03	1.07E+03	9.00E+02	7.52E+02	4.97E+02	8.49E+02	1.01E+03	1.16E+03	9.17E+02	4.94E+02
	W	6.95E+01	6.05E+02	2.32E+02	3.62E+01	0.00E+00	0.00E+00	1.94E+02	1.50E+03	1.78E+02	1.96E+02	1.59E+02	2.33E+02	5.61E+00	5.52E+00	2.26E+02	6.45E+02	1.65E+03	1.90E+03	6.47E+02	9.68E+02	1.08E+03	1.46E+03	1.06E+03	1.29E+03	1.08E+03	6.17E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**N/A**
Mn	*D*	1.27E+01	2.56E+01	2.22E+01	1.01E+01	7.18E+01	4.29E+01	3.43E+01	6.18E+01	3.78E+01	8.42E+00	8.62E+01	3.05E+01	4.10E+01	3.49E+01	1.52E+02	1.25E+02	1.61E+03	8.08E+01	1.57E+01	2.62E+01	8.73E+01	2.61E+01	1.71E+01	6.94E+01	6.31E+01	1.12E+02
	W	0.00E+00	1.11E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.65E+01	5.25E+03	7.39E+01	8.85E+01	5.22E+01	5.38E+01	2.97E+00	3.00E+00	9.90E+01	6.00E+00	3.48E+02	2.46E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.52E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**N/A**
Ni	*D*	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.64E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.31E+00	4.53E+01	0.00E+00	0.00E+00	0.00E+00	3.50E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.98E+00
	W	0.00E+00	1.94E+01	4.65E+00	0.00E+00	1.09E+02	1.13E+02	9.01E+01	8.77E+01	1.22E+02	1.28E+02	1.32E+02	1.35E+02	1.38E+02	1.40E+02	1.31E+02	5.94E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.78E+00	2.04E+00	4.12E+00	1.86E+00	5.44E+01
	GV	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	**50d**	-	-	-	-	-	-	-	-	**N/A**
P	*D*	3.56E+01	4.44E+01	5.57E+01	1.03E+02	7.58E+01	8.06E+01	7.94E+01	5.11E+01	9.06E+01	3.09E+01	1.84E+02	9.39E+01	8.77E+01	4.15E+01	7.69E+01	1.53E+02	1.95E+02	1.82E+02	1.62E+02	1.44E+02	8.86E+01	1.75E+02	1.84E+02	2.41E+02	1.85E+02	1.14E+02
	W	2.06E+00	2.43E+01	9.03E+00	1.43E+01	1.84E+01	1.61E+01	1.42E+02	2.51E+02	1.95E+02	2.44E+02	1.38E+02	1.87E+02	6.09E+01	6.19E+01	1.19E+02	1.67E+02	4.17E+02	1.64E+02	7.89E+01	1.36E+02	1.34E+02	1.91E+02	1.33E+02	1.42E+02	1.27E+02	1.27E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**N/A**
Pb	*D*	6.00E-01	2.78E+00	5.17E+00	2.28E+00	2.95E+00	3.44E+00	1.07E+00	3.34E+00	5.23E+01	1.70E-01	5.41E+00	2.14E+00	4.41E+00	7.85E-01	1.63E+00	4.04E+01	3.74E+01	8.93E+00	4.59E+00	4.96E+00	2.96E+00	2.90E+00	1.72E+00	3.55E+00	5.15E+00	8.04E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.04E+01	2.03E+01	6.19E+01	7.17E+01	6.34E+01	6.65E+01	6.00E+01	6.59E+01	5.16E+01	5.22E+01	6.23E+01	0.00E+00	0.00E+00	6.61E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.39E+01
	GV	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**91.3e**	**112e**	**112e**	**112e**	**112e**	**112e**	**112e**	**112e**	**112e**	**N/A**
S	*D*	2.37E+00	2.03E+01	1.47E+01	4.42E+00	1.88E+01	1.24E+01	8.20E+01	1.10E+00	3.41E+01	7.90E+00	5.65E+01	0.00E+00	6.34E+00	6.54E+00	5.62E+01	1.11E+02	2.28E+02	4.17E+02	3.09E+02	1.42E+02	1.30E+02	3.01E+02	4.14E+02	3.22E+02	3.48E+02	1.22E+02
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.60E+01	2.33E+02	1.12E+02	1.27E+02	6.49E+01	9.22E+01	3.11E+01	4.99E+01	6.32E+01	0.00E+00	3.09E+01	3.23E+02	0.00E+00	0.00E+00	1.07E+02	5.41E+02	2.98E+02	1.82E+02	3.00E+02	1.06E+02
	GV	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**N/A**
Se	*D*	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.75E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.00E-03
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	GV	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	**2.9f**	-	-	-	-	-	-	-	-	**N/A**
V	*D*	6.00E-01	8.03E+00	4.30E+00	1.06E+00	4.04E+00	3.09E+00	7.15E+00	3.86E+00	1.24E+00	7.10E-01	4.01E+00	2.81E+00	2.25E+00	3.20E-01	1.61E+00	8.17E+00	8.56E+00	7.05E+00	3.24E+00	8.16E+00	2.12E+00	4.77E+00	4.38E+00	6.18E+00	3.25E+00	4.04E+00
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.68E+01	7.60E+01	7.58E+01	7.07E+01	6.51E+01	6.55E+01	6.47E+01	6.63E+01	5.38E+01	5.44E+01	6.35E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.93E+01
	GV	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	**130g**	-	-	-	-	-	-	-	-	**N/A**
Zn	*D*	0.00E+00	2.13E+01	1.97E+01	2.98E+01	1.18E+01	9.51E+00	0.00E+00	2.50E+00	2.75E+01	9.60E-01	3.84E+01	7.45E+00	1.61E+01	9.55E-01	4.66E+00	7.80E+01	1.17E+02	2.35E+01	1.28E+01	7.98E+00	4.26E+00	1.41E+01	2.55E+00	6.84E+00	3.20E+00	1.84E+01
	W	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.78E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.87E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.22E+00
	GV	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**315h**	**271h**	**271h**	**271h**	**271h**	**271h**	**271h**	**271h**	**271h**	**N/A**
OM (%)	*D*	6.00E-01	1.05E+00	1.10E+00	5.00E-01	4.00E-01	6.00E-01	2.00E+00	1.00E-01	7.50E-01	6.00E-01	1.45E+00	6.50E-01	8.50E-01	5.50E-01	3.50E-01	6.00E-01	1.75E+00	3.00E-01	8.50E-01	1.15E+00	4.00E-01	1.00E+00	5.00E-01	4.00E-01	6.50E-01	7.66E-01
	W	2.00E+00	1.90E+00	1.50E+00	1.70E+00	1.30E+00	1.90E+00	3.00E+00	3.20E+00	2.00E+00	1.50E+00	3.80E+00	2.30E+00	1.70E+00	1.60E+00	1.30E+00	2.80E+00	1.90E+00	2.30E+00	3.00E+00	2.20E+00	2.00E+00	1.90E+00	1.70E+00	1.70E+00	2.00E+00	2.09E+00
Fines (%)	*D*	6.00E+00	7.00E+00	6.00E+00	6.00E+00	5.50E+00	6.00E+00	1.50E+01	6.50E+00	5.50E+00	6.50E+00	1.30E+01	6.50E+00	5.25E+01	6.00E+00	5.50E+00	5.50E+00	6.50E+00	6.50E+00	6.50E+00	6.50E+00	6.50E+00	6.00E+00	6.00E+00	6.50E+00	6.00E+00	8.64E+00
	W	4.00E+00	4.00E+00	4.00E+00	4.00E+00	4.00E+00	4.00E+00	1.90E+01	1.20E+01	4.00E+00	4.00E+00	8.00E+00	4.00E+00	4.00E+00	4.00E+00	4.00E+00	6.00E+00	5.00E+00	4.00E+00	7.00E+00	5.00E+00	7.00E+00	8.00E+00	4.00E+00	4.00E+00	5.00E+00	5.68E+00

Guideline values (GV) are Probable Effect Levels (PEL's) from the Canadian quality guidelines for freshwater and marine sediments. **–:** Guidelines not available; **N/A:** Not applicable; **a**: After CCME (1999a); **b**: After CCME (1999b); **c**: After CCME (1999c); **d**: After CCME (1999d); **e**: After CCME (1999e); **f**: After CCME (2009); **g**: After CCME (1999f); **h**: After CCME (1999g).

6.5.1 LAND USE IMPACTS ON SEDIMENT GEOCHEMISTRY

Measured sediment quality parameters in the wet and dry seasons are indicated in **Table 6.2**. Analysis of Variance (ANOVA) showed statistically significant differences in As, Fe, Ni, OM, Pb, V and Zn for sites across seasons (ANOVA, $p<0.05$), with higher wet season averages associated with all these parameters except for Zn. This could be attributed to excess wet season chemical loading through runoff-derived contaminants from surrounding land use (Shah *et al.*, 2007). Remaining sediment quality parameters showed no statistically significant variations in sites across seasons (ANOVA, $p>0.05$).

In the absence of relevant South African Sediment Quality Guidelines (SQG's) for aquatic ecosystems, the Canadian SQG's defined by the Probable Effect Levels (PEL's) for the protection of aquatic life/environmental and human health provides a suitable basis for comparative evaluation of measured sediment concentrations in relation to environmentally acceptable target values, which are highlighted in **Table 6.2** for the freshwater (sites 1 – 17) and marine sites (sites 18 – 25). Heavy metal concentrations that exceed the PEL's are often expected to be associated with adverse biological effects (Ho *et al.*, 2010). Results showed that the measured concentrations of most metals across all sample sites and seasons were of an acceptable standard for supporting the aquatic ecosystems of the study area. Exceptions were noted for As (sites 7 – 10, 12, 13 and 15) and Ni (sites 5 – 15) in the wet season, which were primarily associated with industrial and residential land use inputs.

In order to effectively interpret the sediment concentration patterns and principal catchment contributors of heavy metals in the sediment of the receiving Bayhead Canal of the Durban Harbour, interpolated images of sediment concentrations from additional sampling in the Bayhead Canal were created using ArcGIS 9® (**Figure 6.2**). Results showed that the aManzimnyama Canal was most influential on the Bayhead Canal sediment geochemistry at the confluence in terms of Al (both seasons), Cu (both seasons), Cr (dry season), Fe (both seasons), Mg (both seasons), Mn (wet season), P (wet season), Pb (both seasons), S (both seasons), V (dry season), and Zn (both seasons) – most of which are considered to be highly toxic metals commonly associated with industrial operations. The uMbilo/uMhlatuzana Canal showed some influence on sediment geochemistry in the

Bayhead Canal in terms of Cu and Ni in the dry season. Increases in Al, Fe, V and OM content in the Bayhead Canal between the confluences of the uMbilo/uMhlatuzana and aManzimnyama Canals in the dry season were most likely related to storm water outflows in this region (**Figure 6.3**). Overall, it appeared that the aManzimnyama Canal inflows were most influential on the observed sediment geochemistry in the Bayhead Canal as compared to the uMbilo/uMhlatuzana catchment contributions. On the other hand, elevated values of Ca (both seasons), Mg (both seasons), Ni (wet season), P (dry season), S (both seasons) and, to a limited extent, V (dry season) appeared to be controlled by the marine waters of the port, suggesting a combination of natural and anthropogenic sources originating from port activities itself.

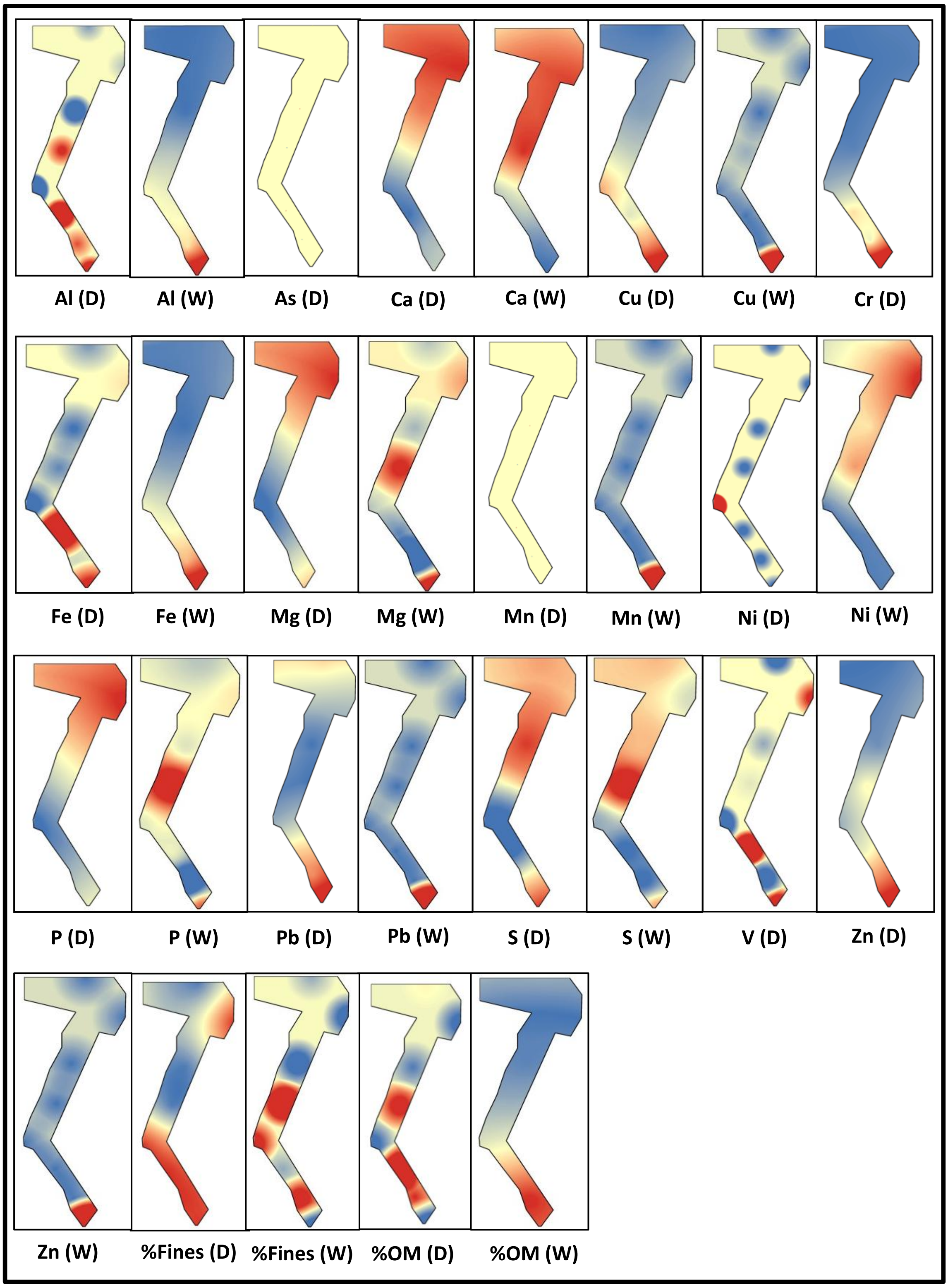

Figure 6.2: Interpolated images of Bayhead Canal sediment data – blue indicates low values transitioning to yellow indicating medium values, and red indicating high values.

Figure 6.3: Storm water outflows (black piping) in the Bayhead Canal between both freshwater confluences (Source: Moodley, 2013).

6.5.2 ASSESSMENT OF SEDIMENT CONTAMINATION USING GEOCHEMICAL INDICES

In order to assess the magnitude of possible metal enrichment, the mean metal concentrations at sample sites in the study area were used to calculate Enrichment Factors (EF) using normalisation to Fe, the scores of which are shown in **Figures 6.4a** and **b**. EF's provide an excellent tool to distinguish between natural and anthropogenic metal sources (Aprile and Bouvy, 2008). Moore *et al*. (2009) states that EF's between 0 and 10 is often an indication of natural metal sources from initial soil or parent rock, whilst EF's greater than 10 tends to be associated with anthropogenic sources of metals. Results showed that metal EF's across most sites ranged between 0 and 10 in both seasons, therefore suggesting natural sources. Exceptions were noted for several metals associated with the sites and seasons listed in **Table 6.3**. Additionally, following the categories of EF's identified by Varol (2011), metal EF's highlighted in red showed extremely severe enrichment at the associated sites and seasons, with EF's > 50 (**Table 6.3**). It was evident that high contamination levels of these heavy metals were generally associated with residential and industrial catchment sites, which have undoubtedly contributed to the severe contamination status of the systems on the basis of calculated EF's for these metals.

Table 6.3: Sites with EF's > 10 suggesting anthropogenic introduction of metals at these sites. Highlighted seasonal metal EF's indicate extremely severe enrichment at corresponding sites according to the classification system by Varol (2011).

Site	Season	Metal	EF
3	Dry	Pb	12.24
4	Dry	Zn	11.40
5	Wet	Cu	27.78
	Wet	Ni	54.07
	Wet	Pb	50.60
	Wet	V	20.32
6	Wet	Ni	65.39
	Wet	Pb	58.74
	Wet	V	23.46
7	Wet	As	70.43
	Wet	Pb	37.63
	Wet	Ni	10.96
8	Wet	As	82.46
	Wet	Cu	13.24
	Wet	Mn	57.57
	Wet	Pb	49.14
	Wet	Ni	12.02
9	Wet	As	75.55
	Dry	Cu	106.12
	Dry	Pb	155.66
	Wet	Cu	17.23
	Wet	Pb	72.31
10	Wet	As	110.75
	Wet	Cu	15.85
	Wet	Ni	26.06
	Wet	Pb	67.69
11	Wet	As	65.11
	Wet	Cu	16.93
	Wet	Pb	79.79
12	Wet	As	98.80
	Wet	Cu	12.47
	Wet	Ni	25.26
	Wet	Pb	61.66
13	Wet	As	202.91
	Wet	Cu	57.68
	Wet	Ni	89.75
	Wet	Pb	167.79
	Wet	V	18.66
14	Wet	As	270.83
	Wet	Cu	89.40
	Wet	Ni	140.22
	Wet	Pb	261.42
	Wet	V	29.06
15	Wet	As	169.54
	Wet	Cu	29.22
	Wet	Ni	41.56
	Wet	Pb	98.83
	Wet	V	10.75
16	Dry	Pb	45.25
	Dry	Zn	10.59
17	Dry	Cu	37.68
	Dry	Mn	23.33
	Dry	Pb	33.88
	Dry	Se	50.73
	Dry	Zn	12.85
18	Dry	Ca	17.28
	Dry	Pb	17.33
	Dry	S	25.90
19	Dry	Ca	25.25
	Dry	Pb	12.58
	Dry	S	27.11
	Wet	Ca	12.89
20	Wet	Ca	14.35
21	Dry	Ca	21.44
	Dry	Cu	11.31
	Dry	Pb	12.52
	Dry	S	17.59
	Wet	Ca	13.06
22	Dry	Ca	33.04
	Dry	S	30.47
	Wet	Ca	43.69
	Wet	S	42.27
23	Dry	Ca	44.08
	Dry	S	44.61
	Wet	Ca	61.22
	Wet	S	35.60
24	Dry	Ca	33.21
	Dry	S	25.97
	Wet	Ca	35.70
	Wet	S	12.82
25	Dry	Ca	34.17
	Dry	Pb	15.78
	Dry	S	34.12
	Wet	Ca	34.32
	Wet	S	24.59

On the basis of Contamination Factors (CF's) for heavy metals analyzed in the dry season, the contamination classification according to Varol (2011) showed that Cu in site 9, as well as Mn and Pb in site 17 showed moderate contamination levels, whilst Pb in site 9 showed considerable contamination. The wet season showed higher levels of contamination which included considerable to high contamination for As in sites 7 – 15, moderate contamination for Ca in sites 22 – 24, moderate contamination for Cu in sites 8 and 13 – 15, moderate contamination for Ni in sites 5 – 15, moderate to considerable contamination for Pb in sites 5 – 15, and moderate contamination for S in site 22. The higher wet season contamination levels possibly related to excess chemical loading from surrounding land use through higher levels of surface runoff. The findings of the calculated CF's confirmed anthropogenic pollution at these sites which highlights the need for immediate remedial actions to restore the ecological state of these catchment systems.

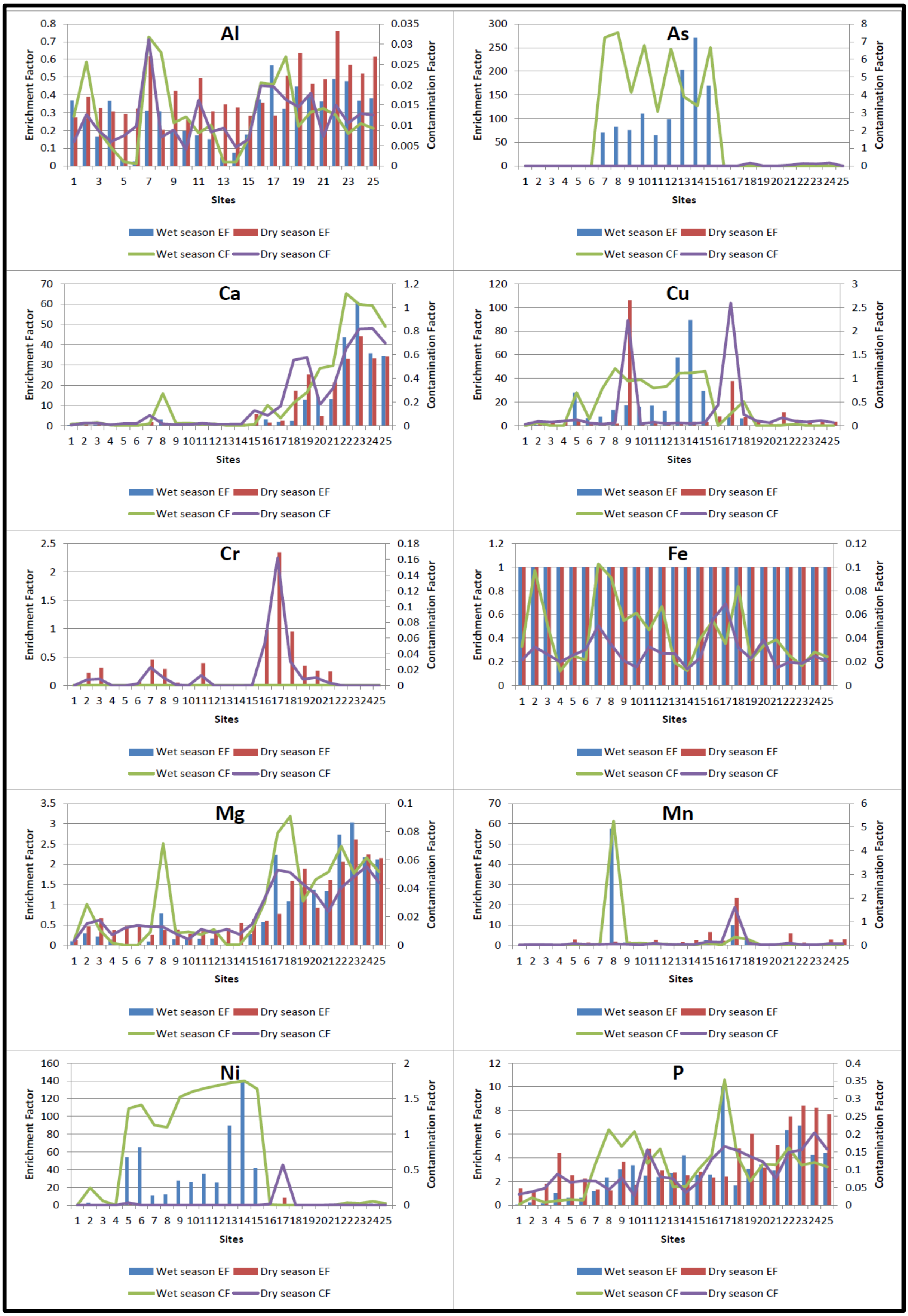

Figure 6.4(a): Seasonal Enrichment Factor (EF) and Contamination Factor (CF) values.

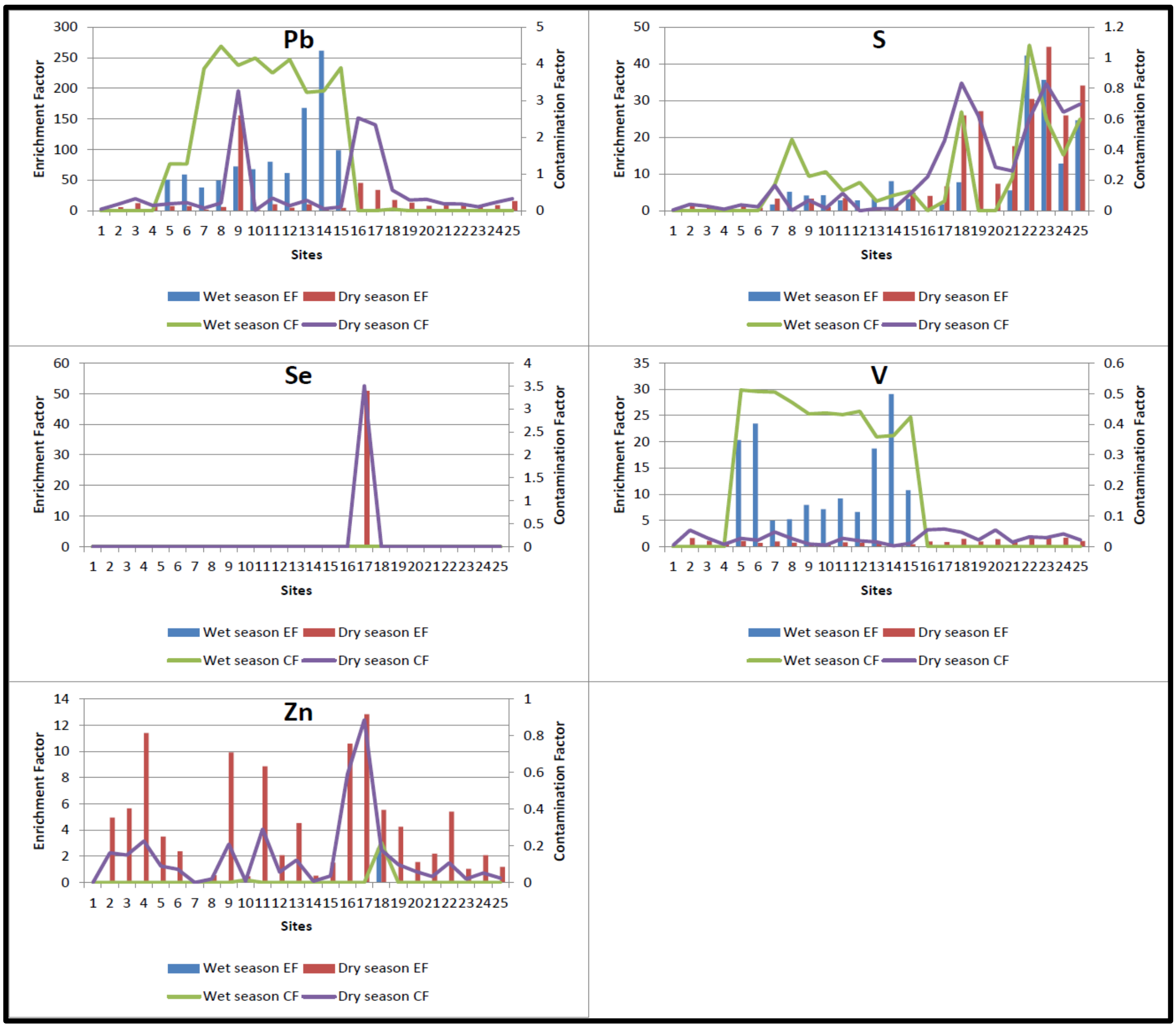

Figure 6.4(b): Seasonal Enrichment Factor (EF) and Contamination Factor (CF) values.

6.5.3 Inter-elemental relationships

The correlation matrices for the wet and dry seasons are represented in **Tables 6.4a** and **b**, and provides useful information on inter-elemental associations and carrier substances (Harikumar and Jisha, 2010). Significant positive correlations (*p<0.05*) were observed for 50 pairs of metals in the dry season and 27 pairs of metals in the wet season, indicating possible common sources or similar geochemical behaviour of these metals (Ghrefat *et al*., 2011). With the exception of As, Ca and S in the dry season, and Zn in the wet season, most metals showed good to significant positive correlations with the sediment organic matter content (*p<0.05* for OM with Al (both seasons), Cr (dry season), Fe (both seasons), Mn (dry season), Ni (dry season), Se (dry season) and V (dry season); and the fine sediment fraction (*p<0.05* for fines with Al, As and Fe in the wet season) indicating the influence of organic matter and fine sediments on heavy metal accumulation (Harikumar and Jisha, 2010).

Table 6.4 (a) and (b): Pearson correlation matrix for measured sediment parameters in the dry and wet seasons. Highlighted cells indicate statistically significant correlations with *p*<0.05 or *p*>0.05.

a) Dry season

	Al	*As*	*Ca*	*Cu*	*Cr*	*Fe*	*Mg*	*Mn*	*Ni*	*P*	*Pb*	*S*	*Se*	*V*	*Zn*	*OM*	*Fines*
Al	1.000																
As	0.130	1.000															
Ca	0.214	**0.775**	1.000														
Cu	0.177	-0.106	-0.103	1.000													
Cr	**0.475**	-0.075	-0.051	**0.703**	1.000												
Fe	**0.733**	-0.180	-0.196	**0.456**	**0.826**	1.000											
Mg	**0.449**	**0.652**	**0.846**	0.197	**0.413**	0.274	1.000										
Mn	0.275	-0.086	-0.030	**0.742**	**0.939**	**0.660**	0.367	1.000									
Ni	0.263	-0.102	-0.044	**0.743**	**0.931**	**0.646**	0.348	**0.994**	1.000								
P	**0.486**	**0.600**	**0.759**	0.206	0.337	0.258	**0.862**	0.302	0.275	1.000							
Pb	0.250	-0.126	-0.129	**0.854**	**0.567**	**0.488**	0.175	**0.471**	**0.459**	0.227	1.000						
S	0.379	**0.729**	**0.944**	0.068	0.193	0.031	**0.926**	0.160	0.144	**0.826**	0.038	1.000					
Se	0.264	-0.094	-0.034	**0.744**	**0.927**	**0.637**	0.352	**0.993**	**0.998**	0.279	**0.448**	0.153	1.000				
V	**0.782**	0.262	0.236	0.186	**0.559**	**0.770**	**0.600**	0.377	0.369	**0.489**	0.256	**0.399**	0.360	1.000			
Zn	0.376	-0.120	-0.138	**0.708**	**0.887**	**0.746**	0.314	**0.796**	**0.786**	0.373	**0.723**	0.086	**0.774**	**0.491**	1.000		
OM	**0.717**	-0.254	-0.162	0.318	**0.479**	**0.583**	0.054	**0.421**	**0.440**	0.145	0.181	-0.026	**0.452**	**0.458**	0.398	1.000	
Fines	0.073	-0.117	-0.172	-0.101	-0.065	0.051	-0.181	-0.053	-0.054	-0.071	-0.094	-0.181	-0.047	-0.081	-0.025	0.198	1.000

b) Wet season

	Al	*As*	*Ca*	*Cu*	*Fe*	*Mg*	*Mn*	*Ni*	*P*	*Pb*	*S*	*V*	*Zn*	*OM*	*Fines*
Al	1.000														
As	0.175	1.000													
Ca	0.020	-0.373	1.000												
Cu	-0.033	**0.857**	**-0.485**	1.000											
Fe	**0.876**	**0.431**	-0.188	0.190	1.000										
Mg	**0.543**	-0.289	**0.634**	-0.313	0.258	1.000									
Mn	**0.403**	**0.410**	-0.004	0.362	0.368	0.339	1.000								
Ni	-0.321	**0.754**	**-0.532**	**0.878**	-0.022	**-0.602**	0.112	1.000							
P	**0.458**	0.307	0.181	0.223	0.341	**0.591**	0.327	-0.005	1.000						
Pb	-0.023	**0.942**	**-0.459**	**0.929**	0.267	**-0.426**	0.340	**0.908**	0.219	1.000					
S	0.215	0.001	**0.734**	-0.038	0.114	**0.639**	0.200	-0.207	0.364	-0.073	1.000				
V	-0.177	**0.764**	**-0.511**	**0.834**	0.075	**-0.538**	0.252	**0.945**	0.030	**0.891**	-0.179	1.000			
Zn	0.348	-0.121	-0.037	0.054	0.302	**0.434**	-0.003	-0.170	0.097	-0.144	0.332	-0.165	1.000		
OM	**0.483**	0.204	-0.067	0.073	**0.453**	0.161	0.372	0.008	0.238	0.210	0.018	0.109	0.059	1.000	
Fines	**0.594**	**0.419**	0.025	0.185	**0.497**	0.115	0.387	0.062	0.230	0.306	0.160	0.263	-0.110	**0.637**	1.000

6.5.4 Spatiotemporal Variation of Heavy Metals

Cluster Analysis (CA) was used to determine similar groups between sampling points in both seasons with the corresponding dendograms and associated linkeage distances depicted in **Figures 6.5a** and **b** for the dry and wet seasons respectively. CA has shown to be useful in identifying zones with similar levels of pollution (Charkhabi *et al*., 2008; Gupta *et al*., 2009; Mahmood *et al*., 2011; Pejman *et al*., 2009; Salah *et al*., 2012; Zhang *et al*., 2009; Zhou *et al*., 2007).

In the dry season, the sampling sites were divided into 3 major cluster groups as follows (**Figure 6.5a**):

- Cluster 1: Sampling sites 1, 10, 14, 3, 5, 8, 6, 12, 13, 15, 4, 21, 2, 20, 7, 11, 16 and 9;
- Cluster 2: Sampling sites 18, 22, 23, 24, 19 and 25; and
- Cluster 3: Sampling site 17.

In the wet season, the sampling sites were also divided into 3 major cluster groups as follows (**Figure 6.5b**):

- Cluster 1: Sampling sites 1, 10, 14, 3, 4, 16, 19, 20, 21, 2, 17, 22, 23, 25, 24 and 18;
- Cluster 2: Sampling sites 5, 6, 9, 11, 10, 12, 15, 13 and 14; and
- Cluster 3: Sampling sites 7 and 8.

These clusters in both seasons were identified as major groups due to the large linkage distances at which they combine with each other which is indicative of large Euclidean distances between the sampling distances in each of the groups (Ryberg, 2006). In the dry season, the linkage distance at which clusters 1 and 2 combines is less than the distance at which cluster 3 combines with remaining data showing a greater degree of similarity of sample sites in clusters 1 and 2 as compared to the sites in cluster 3. In contrast, the linkage distances at which clusters 2 and 3 combines is greater than the distance at which cluster 1 combines with the remaining data showing a greater degree of similarity of sample sites in clusters 2 and 3 as compared to the sites in cluster 1 for the wet season. Examination of the cluster groups revealed that differences between groups may be attributed to the levels of heavy metal contamination as the groupings showed good conformity with variations in sediment quality parameters and contamination levels between sites.

In the dry season, cluster 3 (comprising of site 17 only) showed some of the highest contamination levels for most heavy metals analyzed including Al, Cu, Cr, Fe, Mg, Mn, Ni, P, Pb, Se, V and Zn. In most cases, the levels of contamination were much higher when compared to contamination levels of other sites (**Figures 6.4a** and **b**). This cluster is associated with the dense industrial zone of the aManzimnyama Canal and is subsequently regarded as the most polluted zone of all investigated sample sites based on the data findings. Sample sites associated with cluster 2 showed contamination levels higher than cluster 1 and lower than cluster 3, and therefore represented a cluster of intermediate contamination. All of the sites in cluster 2 were also representative of marine influenced sites which was similar in terms of sediment geochemistry. Cluster 1 represented sample sites which showed amongst the lowest contamination levels on the basis of heavy metals analyzed. This cluster is therefore associated with sample sites regarded as the least polluted.

In the wet season, cluster 3 (comprising sites 7 and 8) showed some of the highest contamination levels for most heavy metals analyzed including Al, As, Cu, Fe, Mn, P, Pb and V (**Figure 6.4a** and **b**), and therefore constituted some of the most polluted zones of all sample sites investigated. As in the case of the dry season, the sample sites of cluster 2 showed contamination levels higher than cluster 1 and lower than cluster 3, and therefore represented zones of intermediate contamination. Cluster 1 represented sample sites which showed amongst the lowest contamination levels on the basis of heavy metals analyzed. This cluster is therefore associated with sample sites regarded as the least polluted. The sites of cluster 1 also included most marine influenced sites which were similar in terms of sediment geochemistry.

The spatiotemporal analysis of heavy metals through CA is useful in that sampling sites of concern can be targeted for ongoing monitoring thereby reducing monitoring costs without missing much information (Salah *et al*., 2012).

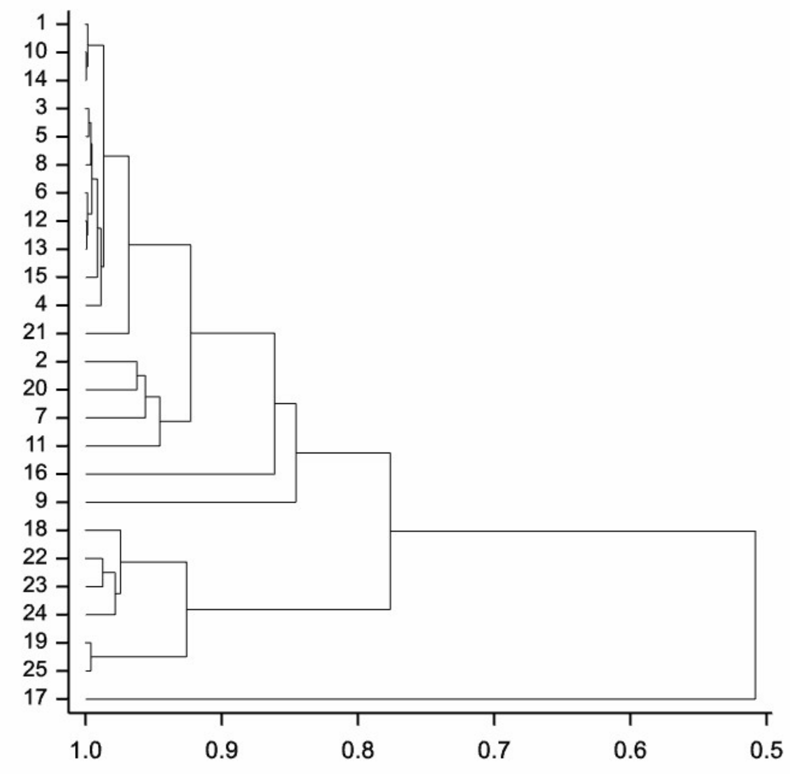

Figure 6.5(a): Dry season dendogram illustrating CA results on the basis of the sediment quality of sampling stations of the Bayhead Canal and catchments of the Durban Harbour.

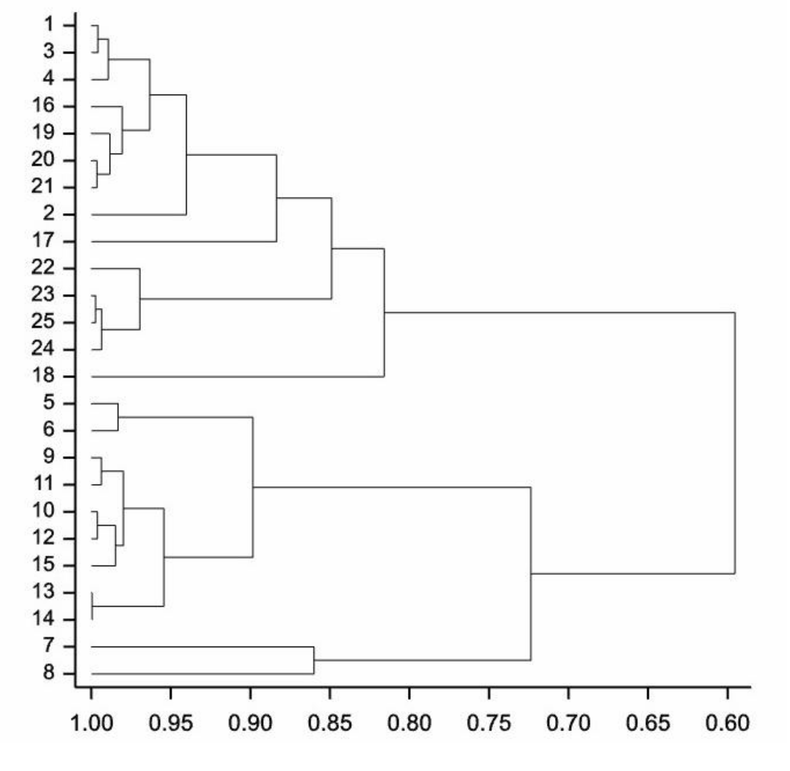

Figure 6.5(b): Wet season dendogram illustrating CA results on the basis of the sediment quality of sampling stations of the Bayhead Canal and catchments of the Durban Harbour.

6.5.5 POTENTIAL SOURCES OF HEAVY METALS

Principal Component Analysis (PCA) was conducted on sediment heavy metal concentrations, organic matter values and percent fine sediment (silt and clay fraction) in order to obtain information on geochemical relationships and potential sources. It is in fact well documented that the use of PCA as a statistical model has proven useful in obtaining information on cluster patterns of parameters in order to gain an understanding on pollutant chemistry and sources (Agunbiade *et al*., 2010; Diaz-de Alba *et al*., 2011). PCA reduces data dimensionality and indicates relationships between variables by explaining the correlation of large data sets by a small number of Principal Components (PC's) (Vega *et al*., 1998). Therefore, the first two component loadings were extracted for the sediment variables in both seasons and is represented in the loading plots in **Figures 6.6a** and **b**, and cumulatively represented 98.92% of the total variance in the dry season and 82.95% of the total variance in the wet season.

The PC loading plot for both seasons showed 3 distinct groupings: Group 1 comprising As, Cu, Cr, Mg, Mn, Ni, P, Pb, S, Se, V, Zn, fine sediment and OM; Group 2 comprising Fe and Al; and Group 3 comprising Ca. The metals of Group 1 are toxic to human life and the ecosystem and most likely represented anthropogenic sources from the Waste Water Treatment Works (WWTW) as well as industrial and residential land use. The metals of Group 2 are natural to the environment and was probably introduced by natural events such as soil erosion (Agunbiade *et al*., 2010). The third grouping consisting of Ca only possibly represented natural sources influenced by seawater incursion.

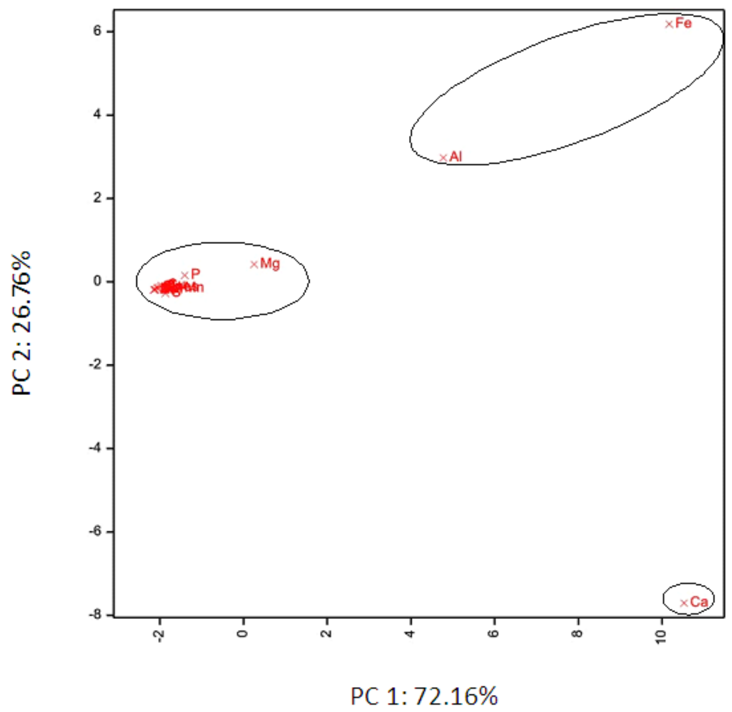

Figure 6.6(a): Dry season loading plot of the first two PC's illustrating heavy metal groupings (sources).

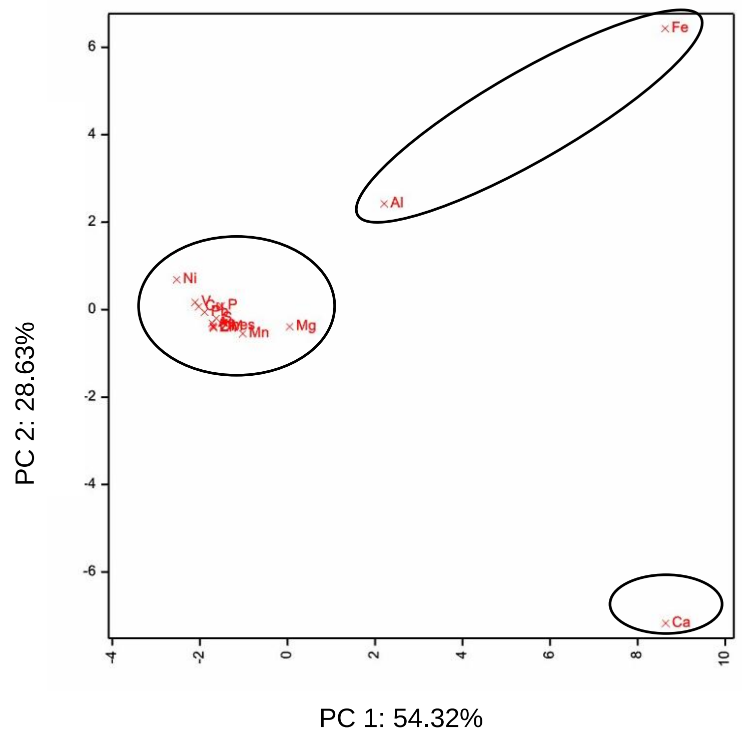

Figure 6.6(b): Wet season loading plot of the first two PC's illustrating heavy metal groupings (sources).

6.6 CONCLUSION

This study revealed the following:

- Specific land use types are shown to affect the river's sediment quality in different ways. Whilst most catchment sites showed low to moderate levels of heavy metal contamination, it is evident that anthropogenic land use, in particular residential and industrial areas, has accounted for severe heavy metal contamination levels in certain catchment sites with regard to selected heavy metal parameters;
- Wet season measures of heavy metal parameters were generally higher than the dry season measures, suggesting greater inputs into the systems through higher wet season surface runoff;
- Anthropogenic land use associated with sites 7, 8 and 17 accounted for some of the highest heavy metal contamination levels in the surface sediments of these sites, suggesting that these sites be specifically targeted for remedial action and ongoing monitoring; and
- Despite the fact that sediment parameters in the Bayhead Canal were not analyzed in conjunction with detailed hydrodynamic modeling, results showed that the highly industrialized aManzimnyama catchment was most influential on heavy metal concentrations of surface sediment at the confluence of the Bayhead Canal. This highlighted the impacts of catchment land use and associated canal inflows on the sediment quality of the Bayhead Canal into which they flow.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS AND KEY FINDINGS OF THIS STUDY

The aim of this study was specifically set out to evaluate the general water quality, sediment quality and material mass transport capacity of three freshwater systems contributing inflows to the Bayhead Canal of the Durban Harbour using a range of biological and analytical monitoring techniques – the uMbilo, uMhlatuzana and aManzimnyama river systems of KwaZulu-Natal. In order to demonstrate the way in which the aim and objectives of this study was addressed, a general synopsis of the key chapters (synthesized as individual papers) and findings thereof are highlighted below:

- In understanding the spatiotemporal variability of water quality (**Chapter 3**), water samples were collected and analyzed for several physico-chemical parameters on the basis of land use change and seasonality. The spatiotemporal (dis)similarity in water quality was then statistically explored through the use of PCA, which showed that human influence accounted for substantial variability in sample sites across seasons. This chapter also compared measured water quality parameters against prescribed South African Water Quality Guidelines, where it was shown that the rivers were polluted and contaminated across most land use types on the basis of selected nutrients and pathogenic microbes. Furthermore, the effects of catchment land use inflows on the Bayhead Canal of the Durban Harbour was explored through statistical interpolations using ArcGIS Version 9®, which revealed that the aManzimnyama Canal was most influential on chemical concentrations of the Bayhead Canal at the confluence.
- In **Chapter 4**, an attempt was made to quantitatively determine the material mass transport capacity of all three river systems on the basis of seasonal hydrographic inputs and measured physico-chemical concentrations at the same predetermined locations, in order to identify principal determinants of material loading. Findings showed that land use, seasonality and river flow were important in governing material loading in the river systems, as well as the Bayhead Canal of the Durban Harbour into which the rivers flow. In particular, it was noted that the dissolved

chemical fluxes associated with industrial activity at the confluences of the canal inflows was responsible for observed chemical concentrations in the Bayhead Canal itself.

- In exploring the use of diatoms as bio-indicators of water quality, **Chapter 5** presented data on diatom species and abundance along all three river systems in relation to seasonality and land use change. Further sampling was conducted in the Bayhead Canal at regular intervals. The study found extremely low diatom counts across all sites, with only 4 taxa accounted for in the wet season and 2 in the dry season. This was representative of aquatic systems in an advanced state of degradation as a consequence of anthropogenic influence. Diatom communities were correlated with measured water quality parameters from the same sampling sites which showed significant positive correlations with dissolved P ($p<0.05$) in both seasons, suggesting that this was an important nutrient governing the distribution and abundance of diatoms in the study area and also highlighting the potential use of diatoms as water quality indicators, particularly in terms of P.
- In order to gain further insight into the levels of environmental pollution associated with the Bayhead Canal of the Durban Harbour and its catchments, **Chapter 6** presented data on several heavy metals from in-stream surface sediment on the basis of land use change and seasonality in these systems. When compared to international guidelines on sediment quality, it was found that most parameters fell within prescribed limits. However, further investigation into contamination levels using Enrichment and Contamination Factor indices showed contamination of several heavy metals associated primarily with industrial and residential land use types. The use of multivariate statistics, namely PCA and CA, was used to identify sources of heavy metals and zones characterized by different levels of pollution respectively. Additionally, the analysis of surface sediment in the Bayhead Canal of the Durban Harbour showed that the industrialized aManzimnyama catchment inflows were most influential in governing the heavy metal content of surface sediment near the confluence in both wet and dry seasons.

A summary of the key findings from each of the abovementioned chapters is presented below:

- Despite the purification capacity displayed by the pristine natural environments such as nature reserves in the study area, the overall intensification of anthropogenic activities and processes operating in the catchments of the Durban Harbour have caused a general deterioration in nutrient, heavy metal and microbiological water quality across all land use types on the basis of this study. This has resulted in substantial spatiotemporal water quality variability across all sample sites as illustrated in the PCA bi-plots and individual component loadings presented in **Chapter 3**;
- When present, concentrations of dissolved ammonia and phosphorous exceeded prescribed freshwater guideline values thereby rendering the freshwater systems as toxic, hypertrophic and unsuitable aquatic habitats for sustaining aquatic biota;
- Disturbing amounts of pathogenic microbes associated with all land use types rendered the sanitary quality of the systems unacceptable;
- The dissolved chemical fluxes emanating from the aManzimnyama Canal were responsible for distinct increases in Cu, Cr, Hg, V, Pb and Al concentrations in the Bayhead Canal near the confluence;
- ANOVA showed no significant differences for most dissolved chemical fluxes in sites across seasons ($p>0.05$). Exceptions were noted for NH_4, P and Ni ($p<0.05$). In the case of NH_4 and P, this was attributed to higher wet season concentrations derived from increased surface runoff. In the case of Ni, this was attributed to a distinct increase in Ni flux at site 13 (nature reserve) in the dry season, evidently related to leaching and the higher discharge at this site;
- In terms of water quality, ANOVA showed statistically significant differences in NH_4, P, DO, BOD, Hg, Al, V, Ni and Cr concentrations in sites across seasons (ANOVA, $p<0.05$). Again, significant changes in dissolved nutrients (NH_4 and P) were due to substantial runoff derived nutrient contamination from surrounding land use in the wet season. Distinct reductions of DO was associated in the wet season as a consequence of elevated water temperature and a subsequent increase in oxidative processes of organic matter, which also explained higher wet season BOD values.

The concentrations of certain metals (Hg, Al, V, Ni and Cr) were found to be substantially higher in the dry season owing to in-stream evaporative concentration effects;

- The water quality of the Bayhead Canal of the Durban Harbour showed that catchment inflows had a high degree of influence on physico-chemical parameters in the receiving Bayhead Canal. In most instances, this was most notable at the confluence of the aManzimnyama and Bayhead Canals, suggesting anthropogenic contributions of industry along the aManzimnyama Canal;
- Despite the sediment quality meeting international target values for most heavy metals analyzed, a high degree of contamination was associated with several potentially toxic metals such as As, Cu, Ni, P, Pb, V and Se. These high contamination levels were predominantly confined to industrial and residential land use types in both seasons;
- In terms of sediment parameters, ANOVA showed statistically significant differences in As, Fe, Ni, OM, Pb, V and Zn for sites across seasons (ANOVA, $p<0.05$). This was attributed to excess wet season chemical loading through runoff-derived contaminants from surrounding land use;
- PCA (**Chapter 6**) showed three groupings of heavy metal sources in both seasons for measured sediment parameters based on the seasonal loading plots: Group 1 consisting of As, Cu, Cr, Mg, Mn, Ni, P, Pb, S, Se, V, Zn, fine sediment and OM were representative of anthropogenic contributions from industrial and residential land use; Group 2 consisting of Fe and Al were considered to be of natural origin; and Group 3 consisting of Ca only represented natural sources by seawater incursion; and
- In terms of sediment quality, Cluster Analysis (CA) (**Chapter 6**) allowed for the identification of three major clusters in the both seasons characterized by different levels of pollution: (i) Sites which were the least polluted – mostly catchment sites in the dry season and marine sites of the Bayhead Canal in the wet season; (ii) Sites which were moderately polluted – primarily marine sites of the Bayhead Canal in the dry season and catchment sites in the wet season; and (iii) Sites which were most

polluted – industry associated with the aManzimnyama Canal in the dry season and residential zones upstream of the uMhlatuzana River in the wet season.

It should be remembered that due to the complex interplay between biotic and abiotic components in ecological systems, it becomes increasingly difficult to precisely discriminate between natural and anthropogenic activities that govern the quality of receiving catchment systems. Nonetheless, it is evident that anthropogenic land use across all spatial and temporal scales, in particular industry, is a principal source of contamination in the systems of this study. This has resulted in the poor state of the Durban Harbour catchments and necessitates the need for urgent intervention to ensure the remediation and optimal biological functioning of the system. This in turn can allow the system to support ecological processes, and in turn the aquatic and terrestrial fauna and flora dependent on the system for its survival.

7.2 RECOMMENDATIONS

The river catchments of the Bayhead Canal of the Durban Harbour face severe chemical and microbiological degradation with an increase in nutrients, pathogens and certain heavy metals rendering the aquatic habitat as unsuitable. Despite a national water policy legal framework considered to be one of the most progressive in the world, implementation has failed to be conveyed throughout the country (Gowlland-Gualtieri, 2007; Malzbender *et al*., 2005). This is evident with high levels of environmental pollution associated with anthropogenic activities within the catchment systems, particularly industry. Subsequently, the following recommendations are made to improve the ecological state of these systems:

- The determination of zones and contaminants of concern should be used to better inform water managers and planners to correctly prioritize stressed zones for on-going monitoring in an attempt to restore the ecological state of the systems whilst saving on monitoring time and costs;
- With the continued growth and expansion of industrial activities contributing to pollutant and nutrient loading into the river systems, it is important that the principles of pollution prevention and use of cleaner production technologies be investigated and implemented into industrial processes where economically feasible.

This includes but is not limited to consideration of on-site effluent treatment through appropriate technologies, and the reuse and recycling of industrial by-products and wastewater before considering the collective discharge of effluent/wastewater into the natural environment;

- Given the natural purification capacity observed for the nature reserves and riparian habitat with respect to selected physico-chemical parameters, further measures should be implemented at a catchment level to protect such areas e.g. implementing measures to control illegal dumping activities and investigating the establishment of buffers around such areas to optimise its restorative capacities;
- Systematic and detailed studies focussing on the use of bio-monitoring and physico-chemical data collection of sediment and water in each of the river systems should continue, so as to ensure that the systems are measured against prescribed targets and the need for its efficient management is facilitated. This will contribute to an understanding of the long term management and utilization of the catchment systems; and
- Further research should focus on implementation of policies and best management practices in relation to specific catchment characteristics (e.g. hydrology, erosion potential etc.), in order to minimize further catchment impairment. Additionally, these should be applied at a community level for testing and guidance of restoration policies (Tsvetkova, 2007).

At a national policy implementation level, the following recommendations are made through identification of key challenges in the management of the country's freshwater resources as identified by Adler *et al*. (2007):

- There is a need for capacity building and skills development in the water management sector which can be achieved through public education and awareness, coaching and mentoring, community planning and regulatory guidelines, all of which can encourage the proactive enforcement of water frameworks and policies;
- There is a pressing need for strengthening cooperative governance which can be attained through mechanisms such as establishing linkages between government institutions with autonomous and interdependent players tasked with preventing

fragmentation and separation of water management structures in government (Knuppe, 2011). This will also facilitate greater levels of information exchange and cooperation between sectors such as land use planning, nature conservation and the greater society; and

- There is a greater need for proper legal definitions in South African legislation such that industrial sectors do not escape through "loopholes" in the country's legislation. Adler *et al*. (2007) uses the example of mineral residue not defined as a waste and is therefore stockpiled and results in environmental pollution and hazards. Furthermore, there is a need to better define water quality standards so as to ensure better monitoring and enforcement. An example is the lack of legislation dictating hydrocarbon limits for discharge into the natural environment.

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APPENDICES

APPENDIX A: RIVER VELOCITY AND AREA ALONG CATCHMENT SAMPLING SITES

	VELOCITY (m/s)						AREA m^2						DISCHARGE (m^3/s)	
SITE	Spring	Summer	[a]Average (Wet season)	Autumn	Winter	[c]Average (Dry season)	Spring	Summer	[b]Average (Wet season)	Autumn	Winter	[d]Average (Dry season)	Wet Season ([a] x [b])	Dry Season ([c] x [d])
1	9.00E-02	1.00E-01	9.50E-02	6.00E-02	4.00E-02	5.00E-02	1.73E-01	3.00E-01	2.37E-01	6.70E-02	2.10E-02	4.40E-02	2.25E-02	2.20E-03
2	8.00E-02	1.00E-01	9.00E-02	7.00E-02	5.00E-02	6.00E-02	2.00E-01	4.17E-01	3.09E-01	1.30E-01	6.40E-02	9.70E-02	2.78E-02	5.82E-03
3	1.30E-01	2.00E-01	1.65E-01	8.00E-02	4.00E-02	6.00E-02	6.67E-01	1.40E+00	1.03E+00	6.00E-01	2.67E-01	4.34E-01	1.71E-01	2.60E-02
4	1.50E-01	2.00E-01	1.75E-01	1.00E-01	7.00E-02	8.50E-02	1.60E+00	2.80E+00	2.20E+00	1.00E+00	5.00E-01	7.50E-01	3.85E-01	6.38E-02
5	3.00E-01	6.00E-01	4.50E-01	1.00E-01	8.00E-02	9.00E-02	2.40E+00	6.93E+00	4.67E+00	8.00E-01	4.67E-01	6.34E-01	2.10E+00	5.70E-02
6	2.00E-01	6.00E-01	4.00E-01	1.00E-01	7.00E-02	8.50E-02	4.67E+00	7.00E+00	5.84E+00	2.00E+00	6.40E-01	1.32E+00	2.33E+00	1.12E-01
7	9.00E-02	1.30E-01	1.10E-01	7.00E-02	6.00E-02	6.50E-02	5.10E-02	6.70E-02	5.90E-02	4.30E-02	2.40E-02	3.35E-02	6.49E-03	2.18E-03
8	1.00E-01	1.30E-01	1.15E-01	9.00E-02	5.00E-02	7.00E-02	4.00E-02	5.30E-02	4.65E-02	3.20E-02	2.70E-02	2.95E-02	5.35E-03	2.07E-03
9	1.50E-01	2.00E-01	1.75E-01	1.20E-01	1.00E-01	1.10E-01	1.20E+00	1.35E+00	1.28E+00	1.08E+00	5.50E-01	8.15E-01	2.23E-01	8.97E-02
10	1.00E-01	1.30E-01	1.15E-01	9.00E-02	6.00E-02	7.50E-02	1.60E+00	1.80E+00	1.70E+00	1.20E+00	8.00E-01	1.00E+00	1.96E-01	7.50E-02
11	5.00E-01	8.00E-01	6.50E-01	5.00E-01	4.00E-01	4.50E-01	8.00E-01	1.10E+00	9.50E-01	7.09E-01	5.00E-01	6.05E-01	6.18E-01	2.72E-01
12	3.00E-01	4.00E-01	3.50E-01	2.00E-01	2.50E-01	2.25E-01	5.60E-01	6.40E-01	6.00E-01	4.00E-01	2.67E-01	3.34E-01	2.10E-01	7.50E-02
13	4.00E-01	6.00E-01	5.00E-01	3.00E-01	1.90E-01	2.45E-01	6.00E+00	8.00E+00	7.00E+00	4.67E+00	3.20E+00	3.94E+00	3.50E+00	9.64E-01
14	5.00E-01	7.50E-01	6.25E-01	3.00E-01	1.00E-01	2.00E-01	4.00E+00	1.07E+01	7.35E+00	1.33E+00	6.40E-01	9.85E-01	4.59E+00	1.97E-01
15	4.00E-01	8.00E-01	6.00E-01	2.00E-01	1.50E-01	1.75E-01	8.33E+00	1.80E+01	1.32E+01	5.33E+00	2.00E+00	3.67E+00	7.90E+00	6.41E-01
16	1.50E-01	2.00E-01	1.75E-01	1.00E-01	8.00E-02	9.00E-02	3.00E-02	6.70E-02	4.85E-02	3.00E-02	1.00E-02	2.00E-02	8.49E-03	1.80E-03
17	4.00E-01	5.00E-01	4.50E-01	3.50E-01	2.50E-01	3.00E-01	5.33E+00	7.33E+00	6.33E+00	4.43E+00	3.40E+00	3.92E+00	2.85E+00	1.17E+00

APPENDIX B: MEASURED WATER QUALITY PARAMETERS FOR SUMMER

Site	pH	Cond	TDS	DO	BOD	COD	Na	NH_4	Cu	Ca	K	Mg	P	S	Al	Hg	V	Pb	Ni	Cr	EC	TC
1	8.45E+00	1.17E+02	5.00E+01	5.87E+00	1.07E+01	1.00E-01	0.00E+00	1.21E+01	1.20E-01	2.30E-01	0.00E+00	5.00E-01	0.00E+00	1.29E+00	1.30E+00	0.00E+00	0.00E+00	1.37E+00	0.00E+00	0.00E+00	5.30E+02	8.30E+02
2	8.13E+00	1.64E+02	7.10E+01	5.92E+00	8.59E+00	6.35E+00	0.00E+00	7.66E+00	0.00E+00	4.36E+00	0.00E+00	2.42E+00	0.00E+00	2.74E+00	1.12E+00	1.08E+00	0.00E+00	1.83E+00	0.00E+00	0.00E+00	6.00E+01	7.70E+02
3	7.64E+00	4.65E+02	2.00E+02	5.81E+00	7.58E+00	5.80E+00	0.00E+00	1.06E+01	0.00E+00	2.72E+01	0.00E+00	6.82E+00	0.00E+00	9.68E+00	1.03E+00	0.00E+00	0.00E+00	3.70E-01	0.00E+00	0.00E+00	1.00E+01	5.10E+02
4	7.82E+00	2.75E+02	1.18E+02	5.94E+00	7.15E+00	2.30E+00	0.00E+00	8.46E+00	0.00E+00	1.98E+01	0.00E+00	6.11E+00	0.00E+00	4.02E+00	9.90E-01	0.00E+00	0.00E+00	1.80E-01	0.00E+00	0.00E+00	1.30E+02	3.10E+03
5	7.59E+00	4.38E+02	1.88E+02	5.81E+00	7.64E+00	1.10E+00	0.00E+00	5.45E+00	0.00E+00	3.12E+01	0.00E+00	9.95E+00	0.00E+00	1.01E+01	9.60E-01	0.00E+00	0.00E+00	7.30E-01	0.00E+00	0.00E+00	1.00E+01	7.40E+02
6	8.51E+00	3.51E+02	1.51E+02	5.88E+00	7.12E+00	5.25E+00	0.00E+00	1.01E+01	0.00E+00	2.10E+01	0.00E+00	8.04E+00	0.00E+00	7.84E+00	9.70E-01	0.00E+00	0.00E+00	4.70E-01	0.00E+00	0.00E+00	1.00E+01	1.10E+02
7	8.25E+00	1.79E+02	7.75E+01	6.03E+00	8.60E-01	1.69E+01	0.00E+00	4.64E+00	0.00E+00	1.00E+01	0.00E+00	2.61E+00	0.00E+00	8.28E+00	1.47E+00	0.00E+00	0.00E+00	1.11E+00	0.00E+00	0.00E+00	1.40E+02	4.20E+03
8	8.06E+00	2.27E+02	9.80E+01	6.08E+00	1.80E-01	1.45E+01	0.00E+00	5.03E+00	0.00E+00	1.55E+01	0.00E+00	5.91E+00	0.00E+00	2.02E+00	1.52E+00	0.00E+00	0.00E+00	2.40E-01	0.00E+00	0.00E+00	2.90E+02	4.50E+03
9	8.38E+00	3.54E+02	1.52E+02	5.77E+00	0.00E+00	1.83E+01	0.00E+00	5.67E+00	0.00E+00	1.34E+01	0.00E+00	8.86E+00	0.00E+00	5.92E+00	9.30E-01	0.00E+00	0.00E+00	5.00E-01	0.00E+00	0.00E+00	2.20E+02	1.03E+04
10	8.05E+00	2.69E+02	1.16E+02	6.71E+00	0.00E+00	7.05E+00	0.00E+00	6.66E+00	0.00E+00	1.20E+01	0.00E+00	7.35E+00	0.00E+00	3.38E+00	9.30E-01	0.00E+00	0.00E+00	2.70E-01	0.00E+00	0.00E+00	1.00E+02	1.07E+04
11	8.06E+00	3.42E+02	1.47E+02	5.92E+00	0.00E+00	9.20E+00	0.00E+00	6.27E+00	0.00E+00	1.65E+01	0.00E+00	8.10E+00	0.00E+00	5.24E+00	9.40E-01	0.00E+00	0.00E+00	3.00E-02	0.00E+00	0.00E+00	5.00E+02	4.80E+04
12	7.96E+00	2.84E+02	1.22E+02	6.42E+00	7.46E+00	7.85E+00	0.00E+00	6.66E+00	0.00E+00	1.51E+01	0.00E+00	6.94E+00	0.00E+00	6.53E+00	1.02E+00	0.00E+00	0.00E+00	7.20E+00	0.00E+00	0.00E+00	2.00E+02	7.20E+03
13	7.84E+00	4.04E+02	1.74E+02	6.81E+00	7.48E+00	4.85E+00	0.00E+00	5.34E+00	0.00E+00	2.15E+01	0.00E+00	9.98E+00	0.00E+00	3.48E+00	1.45E+00	0.00E+00	0.00E+00	5.70E-01	0.00E+00	0.00E+00	2.30E+02	7.00E+03
14	8.27E+00	4.08E+02	1.76E+02	5.76E+00	0.00E+00	0.00E+00	0.00E+00	5.34E+00	0.00E+00	2.15E+01	0.00E+00	1.08E+01	0.00E+00	9.63E+00	9.60E-01	0.00E+00	0.00E+00	2.70E-01	0.00E+00	0.00E+00	1.10E+02	9.50E+02
15	8.26E+00	4.48E+02	1.92E+02	5.88E+00	6.38E+00	2.20E+00	0.00E+00	6.03E+00	0.00E+00	3.30E+01	0.00E+00	5.21E+00	0.00E+00	1.01E+01	1.01E+00	0.00E+00	0.00E+00	2.10E-01	0.00E+00	0.00E+00	9.00E+01	9.60E+02
16	7.73E+00	2.64E+04	3.22E+03	5.67E+00	8.58E+00	2.15E+00	3.21E+03	3.23E+01	2.80E-01	3.33E+02	2.11E+01	6.27E+02	0.00E+00	4.33E+02	1.41E+00	0.00E+00	0.00E+00	4.30E-01	0.00E+00	0.00E+00	0.00E+00	3.00E+02
17	8.84E+00	8.22E+02	3.54E+02	5.96E+00	1.42E+01	5.00E+00	0.00E+00	1.45E+01	1.30E-01	2.65E+01	0.00E+00	7.98E+00	0.00E+00	4.37E+01	1.40E+00	0.00E+00	0.00E+00	3.30E-01	0.00E+00	0.00E+00	2.20E+02	1.64E+03
18	7.67E+00	9.96E+03	1.46E+03	5.66E+00	6.14E+00	3.18E+00	1.13E+03	1.34E+01	0.00E+00	1.85E+02	0.00E+00	2.41E+02	0.00E+00	1.71E+02	1.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.00E+02	8.30E+03
19	7.32E+00	4.83E+04	4.09E+03	5.83E+00	6.00E+00	6.80E+00	3.30E+03	4.10E+01	0.00E+00	5.56E+02	2.71E+02	1.08E+03	0.00E+00	1.03E+03	1.05E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.00E+01	2.60E+03
20	7.49E+00	4.83E+04	1.23E+04	5.78E+00	4.55E+00	4.15E+00	3.37E+03	2.65E+01	0.00E+00	5.90E+02	2.90E+02	1.14E+03	0.00E+00	1.11E+03	1.05E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.00E+01	6.60E+02
21	7.66E+00	4.80E+04	1.58E+04	5.77E+00	1.04E+01	8.40E+00	3.26E+03	8.13E+00	0.00E+00	5.67E+02	2.81E+02	1.10E+03	0.00E+00	1.07E+03	1.03E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.00E+01	1.30E+03
22	7.65E+00	4.72E+04	1.20E+04	5.58E+00	3.80E+00	5.75E+00	3.27E+03	9.54E+00	0.00E+00	5.18E+02	2.67E+02	1.03E+03	0.00E+00	9.83E+02	1.04E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.60E+02	1.20E+04
23	7.75E+00	4.51E+04	1.58E+04	5.61E+00	7.52E+00	1.60E+00	3.11E+03	1.19E+01	0.00E+00	5.34E+02	2.54E+02	1.05E+03	0.00E+00	7.85E+02	1.04E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.20E+02	2.20E+03
24	7.60E+00	4.18E+04	3.48E+03	5.62E+00	8.14E+00	3.20E+00	2.98E+03	1.31E+01	0.00E+00	4.89E+02	2.07E+02	9.69E+02	0.00E+00	7.18E+02	2.30E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.00E+02	5.00E+03
25	7.68E+00	4.52E+04	1.49E+04	5.54E+00	1.03E+00	1.20E+00	3.07E+03	6.66E+00	0.00E+00	5.23E+02	2.42E+02	1.21E+03	0.00E+00	7.68E+02	1.89E+00	0.00E+00	0.00E+00	8.00E-02	0.00E+00	0.00E+00	1.10E+02	7.70E+03

APPENDIX C: MEASURED WATER QUALITY PARAMETERS FOR SPRING

Site	pH	Cond	TDS	DO	BOD	COD	Na	NH_4	Cu	Ca	K	Mg	P	S	Al	Hg	V	Pb	Ni	Cr	EC	TC
1	6.68E+00	1.93E+02	8.30E+01	8.22E+00	2.98E+00	6.84E+00	0.00E+00	8.70E-01	2.06E+00	4.65E+00	0.00E+00	2.00E+00	1.30E-01	5.29E+00	2.29E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.80E+02	2.80E+02
2	7.20E+00	2.46E+02	1.06E+02	8.21E+00	3.05E+00	6.92E+00	0.00E+00	3.98E+00	2.06E+00	1.11E+01	0.00E+00	4.44E+00	1.10E-01	7.40E+00	2.31E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.00E+01	9.00E+01
3	6.78E+00	7.68E+02	3.30E+02	8.32E+00	3.08E+00	8.36E+00	1.21E+00	6.41E+00	2.09E+00	2.89E+01	0.00E+00	5.51E+00	7.22E+00	2.15E+01	2.28E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.80E+02	8.10E+02
4	6.84E+00	3.46E+02	1.49E+02	8.23E+00	3.13E+00	7.04E+00	0.00E+00	2.33E+00	2.06E+00	2.95E+01	0.00E+00	5.64E+00	3.40E-01	1.06E+01	2.28E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.00E+01	7.00E+01
5	7.35E+00	6.28E+02	2.70E+02	8.32E+00	3.09E+00	5.16E+00	0.00E+00	3.70E+00	2.08E+00	3.28E+01	0.00E+00	8.90E+00	3.13E+00	1.90E+01	2.31E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.80E+02	3.00E+02
6	7.27E+00	6.51E+02	2.80E+02	8.31E+00	3.04E+00	8.76E+00	0.00E+00	7.78E+00	2.08E+00	3.53E+01	0.00E+00	9.62E+00	3.33E+00	1.64E+01	2.33E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.80E+01	2.80E+01
7	7.24E+00	2.41E+02	1.03E+02	8.36E+00	3.12E+00	9.92E+00	0.00E+00	1.04E+01	0.00E+00	1.92E+01	0.00E+00	2.43E+00	5.38E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.50E+02	2.50E+02
8	7.09E+00	2.89E+02	1.24E+02	8.42E+00	3.01E+00	9.96E+00	0.00E+00	2.46E+01	0.00E+00	1.27E+01	0.00E+00	2.50E+00	4.71E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.00E+02	7.10E+02
9	6.80E+00	6.19E+02	2.66E+02	8.26E+00	3.01E+00	1.10E+01	0.00E+00	1.88E+01	0.00E+00	2.35E+01	0.00E+00	3.55E+00	3.30E+01	6.43E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.10E+02	2.50E+02
10	7.02E+00	3.22E+02	1.38E+02	8.44E+00	3.02E+00	7.76E+00	0.00E+00	5.18E+00	0.00E+00	1.49E+01	0.00E+00	3.02E+00	7.96E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.30E+02	3.10E+02
11	7.10E+00	3.44E+02	1.48E+02	8.34E+00	2.99E+00	9.88E+00	0.00E+00	1.05E+00	0.00E+00	2.77E+01	0.00E+00	3.13E+00	6.65E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.00E+01	9.00E+01
12	7.08E+00	4.56E+02	1.96E+02	8.33E+00	3.00E+00	1.00E+01	0.00E+00	1.15E+00	0.00E+00	2.35E+01	0.00E+00	4.57E+00	7.32E+00	1.01E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.70E+02	1.07E+03
13	7.37E+00	4.65E+02	2.00E+02	8.32E+00	2.98E+00	7.60E+00	0.00E+00	1.11E+00	0.00E+00	2.61E+01	0.00E+00	4.69E+00	6.48E+00	1.35E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.50E+02	1.50E+02
14	8.12E+00	5.20E+02	2.23E+02	8.31E+00	3.01E+00	5.80E+00	0.00E+00	4.28E+00	0.00E+00	4.11E+01	0.00E+00	1.08E+01	6.35E+00	1.10E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.00E+00	8.00E+00
15	7.85E+00	5.13E+02	2.21E+02	8.29E+00	2.99E+00	8.24E+00	0.00E+00	2.28E+00	2.08E+00	4.47E+01	0.00E+00	1.49E+01	4.50E-01	2.82E+01	2.36E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.60E+01	2.60E+01
16	6.94E+00	6.29E+02	2.70E+02	8.41E+00	3.04E+00	6.20E+00	0.00E+00	1.56E+00	2.11E+00	3.28E+01	0.00E+00	8.92E+00	2.73E+00	1.56E+01	2.40E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.00E+01	9.00E+01
17	7.31E+00	3.09E+04	1.84E+03	8.42E+00	3.02E+00	5.92E+00	3.82E+03	1.36E+01	2.08E+00	3.39E+02	2.42E+02	6.49E+02	2.30E-01	4.55E+02	2.31E+00	0.00E+00	2.04E+00	0.00E+00	0.00E+00	0.00E+00	1.86E+02	2.34E+02
18	7.26E+00	3.10E+04	1.60E+04	8.31E+00	2.94E+00	6.92E+00	3.87E+03	3.57E+01	2.04E+00	3.51E+02	2.59E+02	6.86E+02	8.60E-01	4.81E+02	2.31E+00	0.00E+00	1.98E+00	0.00E+00	0.00E+00	0.00E+00	2.60E+01	3.20E+01
19	7.41E+00	3.14E+04	1.88E+04	8.37E+00	3.02E+00	8.60E+00	3.90E+03	4.12E+01	0.00E+00	3.30E+02	2.65E+02	7.68E+02	9.04E+00	4.66E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20	7.39E+00	3.13E+04	1.76E+04	8.42E+00	3.04E+00	5.16E+00	3.85E+03	5.99E+01	0.00E+00	3.20E+02	2.53E+02	6.34E+02	9.07E+00	4.50E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.00E+01	3.60E+01
21	8.00E+00	8.00E+03	5.14E+03	8.36E+00	2.97E+00	7.48E+00	1.76E+03	1.50E+01	0.00E+00	1.09E+02	2.88E+01	1.91E+02	8.58E+00	1.24E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.80E+01	4.20E+01
22	7.73E+00	5.00E+04	2.96E+04	8.35E+00	3.08E+00	7.92E+00	5.23E+03	5.70E+01	0.00E+00	5.12E+02	4.07E+02	8.72E+02	6.71E+00	8.29E+02	0.00E+00	0.00E+00	1.29E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
23	7.68E+00	5.23E+04	3.27E+04	8.45E+00	3.08E+00	7.72E+00	5.41E+03	2.99E+01	0.00E+00	5.28E+02	4.34E+02	8.90E+02	6.65E+00	8.02E+02	0.00E+00	0.00E+00	1.64E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
24	7.75E+00	5.22E+04	3.30E+04	8.22E+00	3.04E+00	4.16E+00	5.30E+03	4.67E+01	0.00E+00	5.25E+02	4.11E+02	8.91E+02	6.15E+00	8.64E+02	0.00E+00	0.00E+00	1.57E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
25	7.82E+00	5.29E+04	3.46E+04	8.35E+00	3.09E+00	7.48E+00	5.35E+03	5.03E+01	0.00E+00	5.35E+02	4.24E+02	1.17E+03	6.77E+00	8.86E+02	0.00E+00	0.00E+00	1.76E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

APPENDIX D: MEASURED WATER QUALITY PARAMETERS FOR WINTER

Site	pH	Cond.	TDS	DO	BOD	COD	Na	NH_4	Cu	Ca	K	Mg	P	S	Al	Hg	V	Pb	Ni	Cr	EC	TC
1	7.57E+00	1.88E+02	8.10E+01	8.69E+00	3.05E+00	6.52E+00	0.00E+00	2.30E-02	2.90E+00	9.13E+00	0.00E+00	3.24E+00	0.00E+00	2.90E-01	3.94E+00	1.02E+00	1.57E+00	1.96E+00	9.00E-01	6.30E-01	6.00E+01	6.00E+01
2	7.31E+00	2.74E+02	1.18E+02	8.74E+00	3.10E+00	8.92E+00	0.00E+00	2.80E-02	2.90E+00	1.71E+01	0.00E+00	7.54E+00	0.00E+00	1.05E+00	3.84E+00	9.30E-01	1.57E+00	1.93E+00	9.00E-01	3.70E-01	2.00E+01	2.00E+01
3	6.59E+00	7.98E+02	3.43E+02	8.64E+00	3.11E+00	7.08E+00	5.84E+00	4.60E-02	2.92E+00	2.86E+01	0.00E+00	6.59E+00	0.00E+00	1.38E+01	3.81E+00	8.80E-01	1.57E+00	1.93E+00	1.06E+00	3.50E-01	6.00E+00	3.20E+01
4	7.24E+00	3.81E+02	1.64E+02	8.56E+00	3.15E+00	6.60E+00	0.00E+00	3.50E-02	2.89E+00	3.69E+01	0.00E+00	9.45E+00	0.00E+00	2.65E+00	3.76E+00	8.60E-01	1.57E+00	1.90E+00	8.90E-01	3.50E-01	3.40E+02	3.70E+02
5	7.04E+00	6.72E+02	2.89E+02	8.79E+00	3.14E+00	8.72E+00	0.00E+00	6.40E-02	2.89E+00	3.86E+01	0.00E+00	1.10E+01	0.00E+00	1.10E+01	3.78E+00	8.30E-01	1.58E+00	1.92E+00	9.10E-01	7.60E-01	3.00E+01	3.00E+01
6	7.19E+00	7.03E+02	3.03E+02	8.65E+00	3.06E+00	8.64E+00	0.00E+00	3.90E-02	2.88E+00	4.06E+01	0.00E+00	1.20E+01	0.00E+00	8.70E+00	3.80E+00	8.20E-01	1.58E+00	1.92E+00	9.30E-01	3.50E-01	3.00E+01	3.00E+01
7	7.02E+00	2.52E+02	1.09E+02	8.52E+00	3.13E+00	1.09E+01	0.00E+00	4.00E-02	0.00E+00	9.79E+00	0.00E+00	3.59E+00	0.00E+00	0.00E+00	8.40E-01	0.00E+00	0.00E+00	0.00E+00	2.13E+00	0.00E+00	6.00E+00	1.60E+01
8	7.50E+00	3.06E+02	1.31E+02	8.73E+00	3.04E+00	7.32E+00	0.00E+00	3.20E-02	0.00E+00	2.13E+01	0.00E+00	5.26E+00	0.00E+00	0.00E+00	8.40E-01	0.00E+00	0.00E+00	0.00E+00	2.74E+00	0.00E+00	2.00E+01	2.00E+01
9	6.69E+00	4.42E+02	1.90E+02	8.68E+00	3.05E+00	5.40E+00	0.00E+00	6.90E-02	0.00E+00	2.22E+01	0.00E+00	5.36E+00	4.21E+00	2.68E+00	2.29E+00	1.09E+00	0.00E+00	0.00E+00	2.45E+00	0.00E+00	1.10E+02	4.80E+02
10	7.21E+00	3.00E+02	1.29E+02	8.82E+00	3.06E+00	8.68E+00	0.00E+00	4.30E-02	0.00E+00	1.35E+01	0.00E+00	5.13E+00	0.00E+00	0.00E+00	8.20E-01	0.00E+00	0.00E+00	0.00E+00	2.23E+00	0.00E+00	6.00E+01	6.00E+01
11	6.85E+00	4.55E+02	1.96E+02	8.75E+00	3.02E+00	6.04E+00	0.00E+00	6.10E-02	0.00E+00	2.65E+01	0.00E+00	6.02E+00	2.53E+00	1.48E+00	1.31E+00	0.00E+00	0.00E+00	0.00E+00	2.08E+00	0.00E+00	7.00E+02	5.40E+03
12	6.91E+00	4.54E+02	1.95E+02	8.62E+00	3.03E+00	1.02E+01	0.00E+00	8.40E-02	0.00E+00	2.71E+01	0.00E+00	0.00E+00	2.18E+00	2.54E+00	1.31E+00	0.00E+00	0.00E+00	0.00E+00	2.09E+00	0.00E+00	5.00E+01	5.00E+01
13	7.24E+00	4.54E+02	1.95E+02	8.76E+00	3.01E+00	4.88E+00	0.00E+00	7.90E-02	0.00E+00	2.56E+01	0.00E+00	6.07E+00	1.51E+00	2.22E+00	1.18E+00	0.00E+00	0.00E+00	0.00E+00	2.20E+00	0.00E+00	2.00E+01	3.00E+01
14	8.09E+00	4.70E+02	2.02E+02	8.89E+00	3.07E+00	7.92E+00	0.00E+00	7.20E-02	0.00E+00	3.78E+01	0.00E+00	9.58E+00	5.00E-01	7.03E+00	1.22E+00	0.00E+00	0.00E+00	0.00E+00	1.85E+00	0.00E+00	2.00E+00	6.00E+00
15	8.13E+00	4.75E+02	2.04E+02	8.81E+00	3.04E+00	5.36E+00	0.00E+00	2.90E-02	2.89E+00	4.45E+01	0.00E+00	6.83E+00	0.00E+00	6.68E+00	3.77E+00	8.10E-01	1.58E+00	1.92E+00	8.80E-01	3.50E-01	4.00E+00	2.20E+01
16	6.81E+00	8.57E+02	3.68E+02	8.45E+00	3.05E+00	2.82E+01	0.00E+00	8.10E-02	2.98E+00	8.06E+01	0.00E+00	2.02E+01	0.00E+00	2.96E+01	3.93E+00	1.99E+00	1.58E+00	2.03E+00	9.20E-01	7.30E-01	4.20E+03	2.01E+04
17	7.11E+00	1.09E+04	5.55E+03	8.78E+00	3.08E+00	2.41E+01	1.92E+03	2.49E-01	2.93E+00	1.68E+02	0.00E+00	2.49E+02	0.00E+00	1.59E+02	3.88E+00	1.31E+00	1.54E+00	1.94E+00	9.10E-01	7.70E-01	1.90E+02	2.10E+02
18	7.18E+00	9.29E+03	4.84E+03	8.71E+00	2.98E+00	7.76E+00	1.73E+03	3.15E-01	2.90E+00	1.59E+02	0.00E+00	2.35E+02	0.00E+00	1.41E+02	3.90E+00	8.40E-01	1.56E+00	1.92E+00	8.90E-01	7.70E-01	3.30E+02	5.20E+02
19	7.45E+00	4.95E+04	1.38E+04	8.82E+00	3.06E+00	2.28E+00	4.69E+03	1.60E+00	0.00E+00	5.22E+02	1.85E+03	8.83E+02	9.70E-01	8.49E+02	1.00E+00	1.05E+00	3.74E+00	0.00E+00	4.75E+00	0.00E+00	0.00E+00	0.00E+00
20	7.48E+00	4.98E+04	1.28E+04	8.93E+00	3.09E+00	4.96E+00	4.64E+03	2.17E+00	0.00E+00	5.27E+02	1.84E+03	8.96E+02	1.16E+00	7.98E+02	1.07E+00	0.00E+00	3.62E+00	0.00E+00	4.79E+00	0.00E+00	0.00E+00	2.00E+01
21	7.60E+00	5.07E+04	1.38E+04	8.63E+00	2.97E+00	5.96E+00	4.81E+03	2.69E+00	0.00E+00	5.33E+02	1.82E+03	8.99E+02	7.60E-01	8.62E+02	9.20E-01	0.00E+00	3.71E+00	0.00E+00	4.78E+00	0.00E+00	0.00E+00	2.00E+00
22	7.71E+00	4.99E+04	1.47E+04	8.54E+00	3.09E+00	6.52E+00	4.57E+03	1.18E+00	0.00E+00	5.46E+02	1.83E+03	9.24E+02	6.00E-01	8.58E+02	1.03E+00	0.00E+00	3.57E+00	0.00E+00	4.62E+00	0.00E+00	0.00E+00	2.00E+00
23	7.56E+00	4.99E+04	1.62E+04	8.79E+00	3.11E+00	6.96E+00	4.69E+03	1.99E+00	0.00E+00	5.20E+02	1.81E+03	1.12E+03	2.70E-01	8.08E+02	9.60E-01	0.00E+00	3.50E+00	0.00E+00	4.71E+00	0.00E+00	0.00E+00	2.00E+00
24	7.53E+00	4.97E+04	1.62E+04	8.63E+00	3.08E+00	7.76E+00	4.69E+03	1.47E+00	0.00E+00	5.14E+02	1.77E+03	8.74E+02	6.30E-01	8.59E+02	9.80E-01	0.00E+00	3.52E+00	0.00E+00	4.69E+00	0.00E+00	2.00E+00	6.00E+00
25	7.71E+00	4.95E+04	1.59E+04	8.54E+00	3.10E+00	6.52E+00	4.86E+03	2.12E+00	0.00E+00	5.07E+02	1.79E+03	8.74E+02	2.70E-01	8.00E+02	9.30E-01	0.00E+00	3.51E+00	0.00E+00	4.84E+00	0.00E+00	0.00E+00	0.00E+00

APPENDIX E: MEASURED WATER QUALITY PARAMETERS FOR AUTUMN

Site	pH	Cond	TDS	DO	BOD	COD	Na	NH_4	Cu	Ca	K	Mg	P	S	Al	Hg	V	Pb	Ni	Cr	EC	TC
1	7.54E+00	1.28E+02	5.50E+01	8.55E+00	3.98E+00	6.96E+00	0.00E+00	8.00E-04	0.00E+00	4.71E+00	0.00E+00	0.00E+00	0.00E+00	8.60E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.40E+02	2.60E+03
2	7.26E+00	1.15E+02	5.00E+01	8.63E+00	3.95E+00	5.52E+00	0.00E+00	1.30E-03	0.00E+00	2.83E+00	0.00E+00	3.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.00E+01	7.00E+02
3	7.75E+00	8.31E+02	3.57E+02	8.32E+00	3.92E+00	7.76E+00	0.00E+00	1.80E-03	0.00E+00	3.10E+01	0.00E+00	4.56E+00	1.82E+00	2.28E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.40E+02	1.10E+03
4	8.15E+00	3.40E+02	1.45E+02	8.38E+00	3.96E+00	5.52E+00	0.00E+00	2.30E-03	0.00E+00	1.90E+01	0.00E+00	6.86E+00	0.00E+00	3.76E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.00E+02	5.00E+02
5	8.11E+00	5.19E+02	2.23E+02	8.58E+00	3.94E+00	7.36E+00	0.00E+00	1.10E-03	0.00E+00	2.40E+01	0.00E+00	5.33E+00	0.00E+00	9.66E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.00E+01	3.00E+02
6	9.43E+00	4.89E+02	2.09E+02	8.59E+00	3.89E+00	4.12E+00	0.00E+00	1.80E-03	0.00E+00	1.43E+01	0.00E+00	4.57E+00	0.00E+00	7.31E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
7	6.89E+00	2.55E+02	1.09E+02	8.31E+00	3.68E+00	6.90E+00	0.00E+00	1.90E-03	1.20E-01	1.27E+01	0.00E+00	5.37E+00	0.00E+00	0.00E+00	1.41E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.90E+02	3.20E+03
8	7.34E+00	2.52E+02	1.08E+02	8.55E+00	3.74E+00	7.56E+00	0.00E+00	2.00E-03	1.20E-01	1.95E+01	0.00E+00	5.12E+00	0.00E+00	0.00E+00	1.35E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.90E+02	2.90E+03
9	7.15E+00	4.49E+02	1.92E+02	8.44E+00	3.48E+00	1.28E+01	0.00E+00	1.90E-03	7.00E-02	2.28E+01	0.00E+00	5.63E+00	0.00E+00	0.00E+00	1.63E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.50E+02	1.60E+03
10	7.28E+00	2.88E+02	1.23E+02	8.53E+00	3.69E+00	9.32E+00	0.00E+00	2.40E-03	7.00E-02	1.31E+01	0.00E+00	5.99E+00	0.00E+00	0.00E+00	1.53E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.00E+01	7.00E+02
11	7.48E+00	3.81E+02	1.64E+02	8.51E+00	3.91E+00	4.56E+00	0.00E+00	3.10E-03	7.00E-02	2.00E+01	0.00E+00	5.93E+00	0.00E+00	0.00E+00	1.34E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.80E+03	6.90E+03
12	7.56E+00	4.25E+02	1.83E+02	8.38E+00	3.91E+00	6.00E+00	0.00E+00	2.50E-03	9.00E-02	2.44E+01	0.00E+00	6.68E+00	0.00E+00	0.00E+00	6.10E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.30E+03	5.40E+03
13	7.84E+00	4.20E+02	1.81E+02	8.57E+00	3.96E+00	7.08E+00	0.00E+00	1.30E-03	7.00E-02	2.54E+01	0.00E+00	6.83E+00	0.00E+00	0.00E+00	1.36E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.00E+02	7.00E+02
14	8.73E+00	4.61E+02	1.98E+02	8.43E+00	3.92E+00	7.92E+00	0.00E+00	4.40E-03	7.00E-02	3.18E+01	0.00E+00	8.56E+00	0.00E+00	0.00E+00	1.40E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.00E+01	3.80E+01
15	9.11E+00	4.11E+02	1.80E+02	8.61E+00	3.85E+00	5.52E+00	0.00E+00	2.00E-03	0.00E+00	2.49E+01	0.00E+00	7.64E+00	0.00E+00	9.72E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.00E+00	3.20E+01
16	7.87E+00	5.36E+02	2.31E+02	8.39E+00	3.94E+00	2.58E+01	0.00E+00	2.50E-03	0.00E+00	4.30E+01	0.00E+00	7.42E+00	0.00E+00	1.46E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.00E+00	1.20E+01
17	7.69E+00	2.06E+04	1.47E+04	8.69E+00	3.98E+00	2.21E+01	0.00E+00	2.14E+00	0.00E+00	3.04E+02	1.12E+01	6.65E+02	0.00E+00	4.29E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.10E+04	1.90E+05
18	7.60E+00	2.07E+04	1.34E+04	8.53E+00	3.61E+00	7.96E+00	0.00E+00	7.20E-03	1.50E-01	2.95E+02	0.00E+00	6.21E+02	0.00E+00	4.07E+02	1.37E+00	1.73E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.00E+01	1.00E+02
19	8.12E+00	1.49E+04	9.03E+03	8.42E+00	3.57E+00	6.00E+00	3.20E+02	5.10E-03	1.20E-01	2.00E+02	0.00E+00	4.21E+02	0.00E+00	2.81E+02	1.33E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
20	8.50E+00	1.02E+04	5.69E+03	8.53E+00	3.57E+00	2.96E+00	2.80E+02	5.80E-03	1.30E-01	1.31E+02	0.00E+00	2.80E+02	0.00E+00	1.77E+02	1.34E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.00E+01	3.00E+01
21	8.74E+00	9.20E+03	4.50E+03	8.55E+00	3.53E+00	6.32E+00	2.38E+02	2.50E-03	1.20E-01	1.07E+02	0.00E+00	2.25E+02	0.00E+00	1.34E+02	1.34E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.00E+01	1.00E+02
22	8.08E+00	4.78E+04	2.87E+04	8.61E+00	3.45E+00	6.08E+00	1.95E+03	3.92E-02	1.50E-01	5.52E+02	2.26E+01	9.49E+02	0.00E+00	8.52E+02	1.42E+00	0.00E+00	5.80E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.20E+01
23	8.03E+00	4.69E+04	2.93E+04	8.71E+00	2.97E+00	5.48E+00	2.40E+03	3.12E-02	1.10E-01	5.60E+02	2.06E+01	9.57E+02	0.00E+00	8.69E+02	1.32E+00	0.00E+00	6.90E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.00E+00
24	8.00E+00	5.31E+04	2.85E+04	8.56E+00	2.95E+00	7.04E+00	2.99E+03	5.89E-02	1.20E-01	5.69E+02	1.95E+01	1.28E+03	0.00E+00	8.62E+02	1.35E+00	0.00E+00	7.10E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.30E+03
25	7.88E+00	5.18E+04	2.82E+04	8.54E+00	2.08E+00	7.68E+00	4.36E+03	2.60E-02	1.20E-01	5.61E+02	0.00E+00	9.48E+02	0.00E+00	8.80E+02	1.33E+00	0.00E+00	6.30E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.00E+02

APPENDIX F: SEASONAL DIATOM COUNTS (NO. PER 0.1 mL)

Site	Spring				Summer				TDD no.ml-1	Autumn				Winter				TDD no.ml-1
	A	B	C	D	A	B	C	D	(W)	A	B	C	D	A	B	C	D	(D)
1	11	0	0	0	2	0	0	0	65	1	0	0	0	2	0	0	0	15
2	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	15
3	0	0	0	0	2	0	0	0	10	1	0	0	0	7	0	0	0	40
4	4	0	0	0	0	0	0	0	20	4	0	0	0	0	0	0	0	20
5	0	0	0	0	8	0	0	0	40	2	0	0	0	2	0	0	0	20
6	0	0	0	0	0	0	0	0	0	3	0	0	0	1	0	0	0	20
7	0	0	0	0	2	0	0	0	10	4	0	0	0	0	0	0	0	20
8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
9	1	0	0	0	26	0	0	0	135	7	0	0	0	7	0	0	0	70
10	0	0	0	0	1	0	0	0	5	3	0	0	0	5	0	0	0	40
11	0	0	0	0	1	0	0	0	5	7	0	0	0	2	0	0	0	45
12	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	10
13	1	0	0	0	0	0	0	0	5	1	0	0	0	0	0	0	0	5
14	2	0	0	0	0	0	0	0	10	2	0	0	0	0	0	0	0	10
15	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	15
16	0	0	0	0	8	0	0	0	40	6	0	0	0	0	0	0	0	30
17	0	0	0	0	5	1	1	0	35	2	0	0	0	0	0	0	0	10
18	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	5
19	0	0	0	0	1	0	0	0	5	13	0	0	0	0	0	0	0	65
20	0	0	0	0	5	0	0	0	25	16	0	0	0	4	0	0	0	100
21	6	0	0	0	0	0	0	0	30	6	0	0	1	0	0	0	0	35
22	0	0	0	0	3	0	0	0	15	0	0	0	0	3	0	0	0	15
23	0	0	0	0	14	0	0	0	70	0	0	0	0	0	0	0	0	0
24	0	0	0	0	8	0	0	0	40	5	0	0	0	1	0	0	0	30
25	0	0	0	0	0	0	0	1	5	3	0	0	0	1	0	0	0	20

A – *Thallassiosira weissflogii* (Grunow) Fryxell & Hasle; B – *Navicula salinicola* Hustedt; C – *Amphora subacutiuscula* Schoeman; D – *Navicula cryptocephalia* Kutzing

APPENDIX G: ANOVA ANALYSES FOR CHEMICAL FLUXES IN SITES ACROSS SEASONS

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
TDS flux (Dry)	17	12397.18	729.2461	8288941
TDS flux (Wet)	17	7626.53	448.6194	675008.9

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	669386.2	1	669386.2	0.149351	0.701714	4.149097
Within Groups	1.43E+08	32	4481975			
Total	1.44E+08	33				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
NH_4 flux (Dry)	17	1.4695	0.086441	0.112927
NH_4 flux (Wet)	17	147.6901	8.687653	159.9085

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	628.8372	1	628.8372	7.859412	0.008519	4.149097
Within Groups	2560.343	32	80.01072			
Total	3189.18	33				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
P flux (Dry)	17	1.4158	0.083282	0.035988
P flux (Wet)	17	44.6912	2.628894	19.25435

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	55.08118	1	55.08118	5.710753	0.022922	4.149097
Within Groups	308.6455	32	9.645171			
Total	363.7266	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Al flux (Dry)	17	6.18	0.363529	0.38869
Al flux (Wet)	17	32.2279	1.895759	11.39079

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	19.95568	1	19.95568	3.388212	0.074953	4.149097
Within Groups	188.4716	32	5.889738			
Total	208.4273	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Ca flux (Dry)	17	350.7169	20.63041	4453.971
Ca flux (Wet)	17	1226.86	72.16824	19541.84

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	22577.26	1	22577.26	1.881767	0.179675	4.149097
Within Groups	383933	32	11997.91			
Total	406510.3	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Cu flux (Dry)	17	3.0952	0.182071	0.206158
Cu flux (Wet)	17	16.6192	0.9776	4.505778

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5.37937	1	5.37937	2.283295	0.140587	4.149097
Within Groups	75.39097	32	2.355968			
Total	80.77034	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Cr flux (Dry)	17	0.624	0.036706	0.012185
Cr flux (Wet)	17	0	0	0

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.011452	1	0.011452	1.879696	0.179908	4.149097
Within Groups	0.194963	32	0.006093			
Total	0.206415	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Hg flux (Dry)	17	1.1934	0.0702	0.03642
Hg flux (Wet)	17	0.015	0.000882	1.32E-05

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.040842	1	0.040842	2.242001	0.144107	4.149097
Within Groups	0.582936	32	0.018217			
Total	0.623778	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
K flux (Dry)	17	6.6	0.388235	2.562353
K flux (Wet)	17	346.0895	20.35821	7041.89

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3389.798	1	3389.798	0.962402	0.333942	4.149097
Within Groups	112711.2	32	3522.226			
Total	116101	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Mg flux (Dry)	17	554.5738	32.62199	16896.6
Mg flux (Wet)	17	1144.352	67.31484	50583.47

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	10230.55	1	10230.55	0.303217	0.585697	4.149097
Within Groups	1079681	32	33740.04			
Total	1089912	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Na flux (Dry)	17	1130.076	66.47506	75111.13
Na flux (Wet)	17	5463.703	321.3943	1746668

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	552362.4	1	552362.4	0.606399	0.441868	4.149097
Within Groups	29148460	32	910889.4			
Total	29700823	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Ni flux (Dry)	17	2.6992	0.158776	0.068824
Ni flux (Wet)	17	0	0	0

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.214285	1	0.214285	6.227034	0.01793	4.149097
Within Groups	1.101184	32	0.034412			
Total	1.315469	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Pb flux (Dry)	17	2.014	0.118471	0.091216
Pb flux (Wet)	17	5.2164	0.306847	0.137497

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.301628	1	0.301628	2.637613	0.114171	4.149097
Within Groups	3.659411	32	0.114357			
Total	3.961039	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
S flux (Dry)	17	355.6525	20.92074	7019.142
S flux (Wet)	17	988.4192	58.14231	29612.83

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	11776.29	1	11776.29	0.642951	0.428559	4.149097
Within Groups	586111.5	32	18315.98			
Total	597887.8	33				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
V flux (Dry)	17	1.6237	0.095512	0.058363
V flux (Wet)	17	2.91	0.171176	0.498124

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.048664	1	0.048664	0.174896	0.67859	4.149097
Within Groups	8.903785	32	0.278243			
Total	8.952449	33				

APPENDIX H: ANOVA ANALYSES FOR WATER PARAMETERS IN SITES ACROSS SEASONS

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
pH (Dry)	25	190.49	7.6196	0.195529
pH (Wet)	25	190.94	7.6376	0.058302

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00405	1	0.00405	0.031911	0.858975	4.042652
Within Groups	6.091952	48	0.126916			
Total	6.096002	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Cond (Dry)	25	329295	13171.8	3.72E+08
Cond (Wet)	25	356666	14266.64	3.78E+08

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	14983433	1	14983433	0.039941	0.84244	4.042652
Within Groups	1.8E+10	48	3.75E+08			
Total	1.8E+10	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
TDS (Dry)	25	140984	5639.36	69621171
TDS (Wet)	25	139017.3	5560.692	72604910

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	77358.18	1	77358.18	0.001088	0.973826	4.042652
Within Groups	3.41E+09	48	71113041			
Total	3.41E+09	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
DO (Dry)	25	215.23	8.6092	0.008999
DO (Wet)	25	178.07	7.1228	0.027788

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	27.61731	1	27.61731	1501.471	7.1E-38	4.042652
Within Groups	0.882888	48	0.018394			
Total	28.5002	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
BOD (Dry)	25	84.13	3.3652	0.047193
BOD (Wet)	25	108.7	4.348	3.886075

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	12.0737	1	12.0737	6.139271	0.016792	4.042652
Within Groups	94.39842	48	1.966634			
Total	106.4721	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
COD (Dry)	25	208.26	8.3304	27.43357
COD (Wet)	25	167.04	6.6816	9.718714

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	33.98177	1	33.98177	1.829323	0.182545	4.042652
Within Groups	891.6548	48	18.57614			
Total	925.6366	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Na (Dry)	25	24576.92	983.0768	2309875
Na (Wet)	25	32600.61	1304.024	3056009

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1287590	1	1287590	0.479917	0.491798	4.042652
Within Groups	1.29E+08	48	2682942			
Total	1.3E+08	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
NH_4 (Dry)	25	8.4775	0.3391	0.223197
NH_4 (Wet)	25	364.05	14.562	147.8234

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2528.636	1	2528.636	34.16	4.33E-07	4.042652
Within Groups	3553.118	48	74.0233			
Total	6081.754	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Cu (Dry)	25	15.415	0.6166	0.499056
Cu (Wet)	25	10.65	0.426	0.2847

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.454105	1	0.454105	1.158791	0.287097	4.042652
Within Groups	18.81014	48	0.391878			
Total	19.26424	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Ca (Dry)	25	4044.79	161.7916	40773.67
Ca (Wet)	25	4271.27	170.8508	42449.48

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1025.864	1	1025.864	0.024653	0.875893	4.042652
Within Groups	1997356	48	41611.57			
Total	1998381	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
K (Dry)	25	6389.62	255.5848	174592.8
K (Wet)	25	2279.6	91.184	17995.76

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	337845.3	1	337845.3	3.508466	0.067152	4.042652
Within Groups	4622126	48	96294.29			
Total	4959971	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Mg (Dry)	25	6747.35	269.894	149700.8
Mg (Wet)	25	7700.74	308.0296	176532.9

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	18179.05	1	18179.05	0.111448	0.739956	4.042652
Within Groups	7829609	48	163116.8			
Total	7847788	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
P (Dry)	25	8.715	0.3486	0.275724
P (Wet)	25	74.73	2.9892	10.2441

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	87.1596	1	87.1596	16.57054	0.000174	4.042652
Within Groups	252.4759	48	5.259914			
Total	339.6355	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
S (Dry)	25	5593.2	223.728	108270.2
S (Wet)	25	6351.3	254.052	120472.6

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	11494.31	1	11494.31	0.1005	0.752605	4.042652
Within Groups	5489827	48	114371.4			
Total	5501321	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Al (Dry)	25	38.33	1.5332	0.194131
Al (Wet)	25	25.505	1.0202	0.366905

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.289613	1	3.289613	11.72692	0.00127	4.042652
Within Groups	13.46487	48	0.280518			
Total	16.75448	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Hg (Dry)	25	7.085	0.2834	0.125295
Hg (Wet)	25	0.54	0.0216	0.011664

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.856741	1	0.856741	12.51088	0.000909	4.042652
Within Groups	3.287022	48	0.06848			
Total	4.143763	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
V (Dry)	25	21.76	0.8704	0.623792
V (Wet)	25	5.14	0.2056	0.143449

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5.524488	1	5.524488	14.40094	0.000414	4.042652
Within Groups	18.41376	48	0.38362			
Total	23.93825	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Pb (Dry)	25	9.69	0.3876	0.234884
Pb (Wet)	25	8.095	0.3238	0.519374

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.05088	1	0.05088	0.134916	0.715003	4.042652
Within Groups	18.10217	48	0.377129			
Total	18.15305	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Ni (Dry)	25	30.11	1.2044	0.638036
Ni (Wet)	25	0	0	0

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	18.13224	1	18.13224	56.83767	1.1E-09	4.042652
Within Groups	15.31287	48	0.319018			
Total	33.44511	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Cr (Dry)	25	2.715	0.1086	0.022299
Cr (Wet)	25	0	0	0

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.147425	1	0.147425	13.22252	0.000674	4.042652
Within Groups	0.535176	48	0.01115			
Total	0.682601	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
EC (Dry)	25	11307	452.28	1376017
EC (Wet)	25	4061	162.44	17784.42

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1050090	1	1050090	1.506801	0.225614	4.042652
Within Groups	33451227	48	696900.6			
Total	34501318	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
TC (Dry)	25	123103	4924.12	3.58E+08
TC (Wet)	25	73217	2928.68	22691806

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	49772260	1	49772260	0.26142	0.61149	4.042652
Within Groups	9.14E+09	48	1.9E+08			
Total	9.19E+09	49				

APPENDIX I: ANOVA ANALYSES FOR SEDIMENT PARAMETERS IN SITES ACROSS SEASONS

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Al (Dry)	25	23843	953.72	251207.6
Al (Wet)	25	24952.2	998.088	508120.7

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	24606.49	1	24606.49	0.064811	0.800135	4.042652
Within Groups	18223881	48	379664.2			
Total	18248487	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
As (Dry)	25	3.065	0.1226	0.073207
As (Wet)	25	246.6	9.864	207.5307

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1186.186	1	1186.186	11.42739	0.001446	4.042652
Within Groups	4982.495	48	103.802			
Total	6168.68	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Ca (Dry)	25	191320	7652.8	1.09E+08
Ca (Wet)	25	222508	8900.32	1.78E+08

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	19453827	1	19453827	0.135502	0.714412	4.042652
Within Groups	6.89E+09	48	1.44E+08			
Total	6.91E+09	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Cu (Dry)	25	495.18	19.8072	2063.909
Cu (Wet)	25	743.272	29.73088	1094.46

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1230.993	1	1230.993	0.779512	0.381691	4.042652
Within Groups	75800.84	48	1579.184			
Total	77031.84	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Cr (Dry)	25	66.74	2.6696	44.65273
Cr (Wet)	25	0	0	0

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	89.08455	1	89.08455	3.990106	0.051453	4.042652
Within Groups	1071.665	48	22.32636			
Total	1160.75	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Fe (Dry)	25	35969	1438.76	432267.5
Fe (Wet)	25	54981	2199.24	1798751

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	7229123	1	7229123	6.480557	0.014172	4.042652
Within Groups	53544453	48	1115509			
Total	60773576	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Mg (Dry)	25	12338.1	493.524	133117.4
Mg (Wet)	25	15419.83	616.7932	364993.6

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	189941.2	1	189941.2	0.762646	0.38685	4.042652
Within Groups	11954664	48	249055.5			
Total	12144605	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Mn (Dry)	25	2792.92	111.7168	98742.9
Mn (Wet)	25	6290.97	251.6388	1091381

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	244727.1	1	244727.1	0.411263	0.52438	4.042652
Within Groups	28562981	48	595062.1			
Total	28807708	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Ni (Dry)	25	49.6	1.984	81.77049
Ni (Wet)	25	1361.244	54.44976	3728.856

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	34408.2	1	34408.2	18.05908	9.8E-05	4.042652
Within Groups	91455.04	48	1905.313			
Total	125863.2	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
P (Dry)	25	2840.7	113.628	3694.3
P (Wet)	25	3172.89	126.9156	9043.497

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2207.004	1	2207.004	0.346528	0.558845	4.042652
Within Groups	305707.1	48	6368.899			
Total	307914.1	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Pb (Dry)	25	201.035	8.0414	185.9886
Pb (Wet)	25	596.861	23.87444	883.5323

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3133.564	1	3133.564	5.859754	0.019323	4.042652
Within Groups	25668.5	48	534.7605			
Total	28802.07	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
S (Dry)	25	3045.67	121.8268	20917.68
S (Wet)	25	2641.2	105.648	18867.78

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3271.92	1	3271.92	0.164478	0.686869	4.042652
Within Groups	954851	48	19892.73			
Total	958122.9	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Se (Dry)	25	0.175	0.007	0.001225
Se (Wet)	25	0	0	0

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.000612	1	0.000612	1	0.322325	4.042652
Within Groups	0.0294	48	0.000613			
Total	0.030013	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
V (Dry)	25	100.96	4.0384	6.849964
V (Wet)	25	732.6	29.304	1164.431

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	7979.382	1	7979.382	13.62505	0.00057	4.042652
Within Groups	28110.75	48	585.6406			
Total	36090.13	49				

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
Zn (Dry)	25	460.865	18.4346	703.009
Zn (Wet)	25	30.48	1.2192	32.90405

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3704.625	1	3704.625	10.06811	0.002632	4.042652
Within Groups	17661.91	48	367.9565			
Total	21366.54	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
% OM (Dry)	25	19.15	0.766	0.205358
% OM (Wet)	25	52.2	2.088	0.3911

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	21.84605	1	21.84605	73.25256	3.19E-11	4.042652
Within Groups	14.315	48	0.298229			
Total	36.16105	49				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
% Fines (Dry)	25	216	8.64	88.4275
% Fines (Wet)	25	142	5.68	11.47667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	109.52	1	109.52	2.192501	0.145219	4.042652
Within Groups	2397.7	48	49.95208			
Total	2507.22	49				

APPENDIX J: PCA LOADING PLOTS FOR WATER QUALITY PARAMETERS ON THE BASIS OF CATCHMENT SITES ONLY

DRY SEASON

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Al	0.1476	-0.2875	-0.1705	0.4323	-0.0240	0.0065	0.0570	0.4904	0.3660	-0.1561	0.1339	0.4433	0.1982	0.0161	0.0864	0.0356	0.0106	0.0856	0.0249	0.0398	0.0610	0.0285
BOD	0.0961	-0.2440	0.2140	-0.4194	0.5434	0.2070	-0.4300	0.2716	0.1530	0.1676	0.2316	-0.0684	0.0467	-0.0151	-0.0057	0.0017	-0.0034	-0.0188	-0.0024	-0.0032	-0.0087	-0.0092
COD	0.2001	0.0322	-0.3377	-0.2891	-0.4865	0.0846	-0.4007	0.1220	-0.1350	0.3274	-0.2499	0.0876	0.3069	0.0131	0.1641	0.1016	0.0127	0.0932	0.0270	0.0212	0.0680	0.0146
Ca	0.2757	0.1207	0.0079	-0.0152	-0.0491	0.1857	-0.0318	-0.0937	-0.0027	0.2750	0.0647	0.5065	-0.6971	-0.1051	-0.0429	0.0481	-0.0610	0.0359	-0.0286	0.0504	-0.1005	0.0805
Cond	0.2717	0.1468	0.0447	0.0267	0.0604	0.0099	0.1040	-0.0076	0.0549	0.1096	-0.0486	0.0218	0.1460	0.3448	0.1768	-0.3417	0.1422	-0.1043	-0.1867	0.2607	-0.5704	-0.3492
Cr	0.2100	-0.2583	-0.0745	-0.0496	-0.0471	-0.2073	-0.2551	-0.6411	0.5735	-0.1590	-0.0703	0.0044	0.0149	0.0064	0.0085	0.0153	0.0036	0.0106	0.0010	-0.0066	0.0053	0.0017
Cu	0.1659	-0.3391	-0.0092	0.0401	0.0735	-0.0674	0.1539	-0.1640	-0.2943	0.1462	0.1136	0.0476	0.0297	-0.1359	0.0458	-0.0198	-0.1913	0.2727	-0.0041	0.0085	0.2931	-0.6733
DO	0.0798	0.0567	0.5231	0.4473	-0.1111	-0.4108	-0.5331	0.0688	-0.1928	0.0860	-0.0259	-0.0159	-0.0271	-0.0054	-0.0111	-0.0020	-0.0049	-0.0125	-0.0040	-0.0015	-0.0079	-0.0095
EC	0.2617	0.1349	-0.1089	-0.1184	-0.0034	0.1244	-0.2541	-0.0682	-0.3715	-0.7008	0.2442	0.1604	0.0015	0.2611	-0.1089	-0.0190	0.0166	0.0322	0.0200	0.0273	0.0696	-0.0213
Hg	0.1731	-0.2378	-0.3516	0.1828	-0.2574	0.0430	-0.1162	0.1941	0.0276	0.0346	0.2825	-0.5708	-0.3367	-0.0193	-0.2140	-0.1130	-0.0324	-0.1872	-0.0493	-0.0353	-0.1154	-0.0645
K	0.2698	0.1520	0.0546	0.0244	0.0593	-0.0242	0.1177	0.0433	0.0665	0.0011	-0.0081	-0.2016	0.0358	0.0033	-0.0945	0.4118	-0.1035	0.2120	0.6998	0.2367	-0.2308	-0.0327
Mg	0.2711	0.1490	0.0521	0.0195	0.0445	-0.0078	0.1055	0.0548	0.0696	0.0190	-0.0035	-0.0877	-0.0562	0.1805	0.2258	0.2328	0.2388	0.0340	-0.0128	-0.8109	-0.0095	-0.1232
NH_4	0.2689	0.1574	0.0476	0.0257	0.0548	0.0017	0.0835	0.0449	0.0864	0.0487	-0.0293	-0.2185	-0.1302	0.0594	0.2474	-0.4885	0.2855	0.2845	0.1605	0.1773	0.4924	0.2173
Na	0.2699	0.1518	0.0541	0.0245	0.0609	-0.0238	0.1188	0.0424	0.0646	0.0090	-0.0097	-0.1910	0.0599	-0.0133	-0.1672	0.4837	0.0932	0.2138	-0.6401	0.2878	0.1410	0.0840
Ni	-0.1614	0.3379	-0.0580	0.0109	-0.1308	-0.0944	-0.0131	-0.1868	0.1076	0.2635	0.8057	0.0698	0.2226	0.0225	0.0666	0.0241	0.0212	0.0431	0.0199	0.0076	0.0446	0.0201
P	-0.0887	0.1728	-0.3414	0.5310	0.4102	0.4283	-0.2758	-0.2589	-0.0950	0.1381	-0.1332	-0.0705	0.1028	-0.0156	0.0539	0.0517	0.0078	0.0324	0.0088	-0.0165	0.0178	0.0016
Pb	0.1652	-0.3406	-0.0146	0.0402	0.0653	-0.0663	0.1318	-0.1516	-0.3008	0.1274	0.0954	0.0120	0.1870	0.0013	-0.1370	-0.1758	-0.0573	0.4233	-0.0646	-0.1936	-0.3482	0.5097
S	0.2764	0.1299	0.0287	0.0125	0.0403	0.0160	0.0921	-0.0315	0.0239	0.1642	-0.0707	0.1510	0.2736	-0.1393	-0.7142	-0.1896	0.2242	-0.2999	0.1069	-0.1244	0.1680	-0.0585
TC	0.2716	0.1519	0.0050	-0.0166	0.0318	0.0037	0.0249	0.0033	-0.0566	-0.2137	0.0617	-0.0509	0.1352	-0.8072	0.3190	-0.0832	-0.0285	-0.1787	-0.0604	-0.0235	-0.1705	0.0371
TDS	0.2711	0.1486	0.0481	0.0260	0.0600	-0.0016	0.1087	0.0095	0.0586	0.0726	-0.0353	-0.0538	0.1080	0.2249	0.0814	-0.0961	-0.8036	-0.2680	-0.0640	-0.0852	0.1906	0.1723
V	0.1616	-0.3432	-0.0034	0.0493	0.0795	-0.0669	0.1547	-0.1569	-0.2898	0.1361	0.0991	0.0415	0.0278	0.1538	0.2801	0.2698	0.2813	-0.5587	0.1045	0.1908	0.1373	0.2171
pH	0.0144	-0.1673	0.5101	0.1081	-0.4009	0.6922	0.0627	-0.1331	0.0826	-0.0487	0.0682	-0.0866	0.1271	0.0030	0.0206	0.0107	0.0067	0.0075	0.0054	-0.0015	0.0169	-0.0058
% variation	53.3500	25.8400	8.6400	4.6400	3.0300	2.1000	1.5000	0.3000	0.2700	0.1600	0.1200	0.0400	0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
latent roots	11.7364	5.6840	1.9001	1.0212	0.6676	0.4630	0.3296	0.0650	0.0587	0.0344	0.0272	0.0097	0.0027	0.0002	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

WET SEASON

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Al	0.2225	-0.3702	0.0549	0.1368	0.0710	0.0342	0.1977	-0.1396	0.0052	0.2544	0.1699	0.0109	0.2424	0.0546	0.2207	0.7189	0.0455	0.0367	0.0417	0.0288
BOD	0.2279	-0.2597	-0.3091	0.1705	0.0538	-0.0071	0.1228	-0.0398	0.3038	0.0798	0.3542	-0.4291	-0.5378	-0.0769	-0.0274	-0.1703	0.0251	-0.0217	-0.0004	-0.0465
COD	-0.1417	0.3611	0.1156	0.1508	0.3928	0.0151	0.0358	-0.2446	-0.0459	0.6601	-0.1373	-0.3369	0.0977	0.0077	-0.0605	-0.1123	-0.0339	-0.0046	-0.0186	0.0130
Ca	0.3201	0.1239	0.0476	0.0080	-0.1175	0.0078	-0.1188	0.1145	0.0002	0.0760	-0.0425	-0.0686	-0.0299	0.7255	0.5010	-0.1985	0.0334	0.0518	0.0461	0.0538
Cond	0.3223	0.1467	-0.0065	0.0238	-0.0386	0.0399	-0.0932	0.0349	-0.0099	-0.0268	-0.0135	-0.0666	0.0952	-0.2350	-0.0179	-0.0197	-0.3652	0.6320	0.4818	-0.1600
Cu	0.2125	-0.3826	0.0795	0.1295	0.0485	0.0692	0.1989	-0.0488	0.1166	0.2345	0.1412	0.4187	0.3577	0.0155	-0.1619	-0.5542	-0.0867	-0.0102	-0.0462	0.0345
DO	-0.0834	0.1868	-0.4009	-0.0707	-0.3341	-0.2476	-0.3400	-0.5712	0.1332	0.1293	0.2920	0.1913	0.1393	0.0350	0.0174	0.0192	0.0056	0.0017	0.0036	-0.0008
EC	-0.0978	0.2445	-0.3825	0.3550	0.0882	0.0803	0.3956	0.0189	-0.3536	-0.3452	0.2902	-0.1562	0.3295	0.1453	-0.0157	-0.0573	-0.0261	0.0031	-0.0105	0.0196
Hg	-0.0083	-0.2271	-0.0476	0.0250	0.5560	0.3889	-0.5830	-0.2098	-0.0599	-0.2753	0.0837	-0.0254	0.0680	0.0944	0.0036	-0.0220	-0.0026	0.0009	-0.0007	0.0027
K	0.2660	0.1569	-0.2322	-0.2157	0.1884	0.0798	0.2114	-0.1395	0.1781	-0.0880	-0.2515	0.1247	-0.0329	0.0528	-0.0985	0.0763	-0.1884	-0.5069	0.4735	0.2094
Mg	0.3206	0.1407	0.0172	0.0441	-0.0650	0.0351	-0.1318	0.0569	-0.0439	-0.0223	0.0153	-0.0840	0.1181	-0.3197	0.2954	0.0002	-0.5099	-0.3598	-0.4573	-0.1935
NH4	0.2062	0.2222	0.2892	0.2417	0.2274	-0.2059	0.0715	-0.2303	-0.3428	-0.0668	0.2066	0.4571	-0.4808	-0.0467	0.0473	0.0249	0.0466	-0.0074	0.0178	-0.0381
Na	0.3218	0.1477	-0.0136	0.0248	-0.0323	0.0472	-0.0947	0.0262	-0.0283	-0.0338	-0.0161	-0.0817	0.1371	-0.4208	0.1912	-0.1056	0.4727	0.0645	-0.0543	0.6147
P	-0.1193	0.3159	0.2921	0.1029	0.2434	-0.1575	0.0167	0.1726	0.6909	-0.2073	0.3307	0.0647	0.1749	0.0182	0.0725	0.0751	0.0116	0.0056	0.0086	0.0017
Pb	-0.0639	0.0292	-0.4986	0.3630	0.1721	-0.1264	-0.2469	0.5121	0.0498	0.2617	-0.1694	0.3518	-0.0719	-0.0450	0.0399	0.1154	0.0154	0.0058	0.0105	-0.0002
S	0.3253	0.1248	0.0142	0.0265	-0.0454	0.0290	-0.0943	0.0599	-0.0171	0.0080	-0.0197	-0.0630	0.1859	-0.0527	-0.1723	-0.0101	0.5518	-0.2235	0.1329	-0.6468
TC	-0.1147	0.2584	0.0022	-0.0618	-0.2330	0.7981	0.0656	0.0925	0.0597	0.2172	0.2666	0.2259	-0.1747	-0.0377	0.0302	0.0723	0.0269	-0.0020	0.0115	-0.0185
TDS	0.2977	0.1116	0.1430	0.1486	-0.1779	-0.0135	-0.2398	0.1533	-0.0502	0.0350	0.1285	-0.1106	0.0091	0.2696	-0.6901	0.1967	-0.1378	-0.0496	-0.1545	0.2795
V	0.2492	0.1532	-0.2565	-0.2438	0.2145	0.0819	0.2492	-0.1592	0.2025	-0.0931	-0.2778	0.1508	-0.0566	0.1204	-0.1384	0.0997	0.0877	0.3909	-0.5319	-0.0962
pH	0.0525	0.0327	-0.1086	-0.6667	0.2760	-0.1881	-0.0022	0.3199	-0.2575	0.1937	0.4677	0.0050	0.0535	-0.0012	-0.0159	-0.0105	-0.0074	0.0049	-0.0007	0.0113
% variation	44.0500	16.6200	9.1300	7.8000	5.6800	4.3900	4.2500	3.3000	2.4700	1.1800	0.6800	0.3000	0.1000	0.0300	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
latent roots	8.8100	3.3240	1.8258	1.5610	1.1354	0.8775	0.8506	0.6606	0.4936	0.2369	0.1369	0.0593	0.0207	0.0064	0.0009	0.0003	0.0000	0.0000	0.0000	0.0000

COMBINED SEASONS (WET AND DRY)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Al	0.1855	0.1742	0.3512	0.0706	-0.2541	0.0785	-0.2839	0.0309	0.2844	0.1801	0.0172	0.2932	0.1313	-0.0311	0.3400	-0.5244	0.1223	0.0481	0.1702	0.0053	0.0000	-0.0026
BOD	0.1279	-0.1625	0.3547	0.0797	-0.3865	-0.0880	0.2641	-0.2508	0.4520	-0.0667	-0.1587	-0.2594	-0.2696	0.2425	-0.2383	0.1238	0.0080	-0.1165	0.1271	-0.0159	-0.0205	0.0033
COD	0.1453	0.1634	-0.3287	-0.1951	0.0333	0.3328	0.0283	-0.5689	0.0389	0.2755	-0.3104	-0.1173	0.3431	0.1909	-0.0772	-0.0760	-0.0324	0.1157	0.0375	0.0145	0.0175	-0.0050
Ca	0.3342	-0.1242	-0.0512	0.0790	0.0483	-0.0208	-0.0263	0.0704	-0.0173	0.1835	0.0007	-0.3146	0.1512	-0.2764	0.0178	-0.1637	-0.1779	-0.7178	-0.1428	0.1530	0.0289	0.0685
Cond	0.3234	-0.1747	-0.0151	0.1081	0.0562	0.0349	0.0415	0.1144	-0.0613	0.0830	0.0541	-0.0610	0.0037	0.0383	-0.0298	0.0049	0.0455	0.1377	0.0475	-0.2213	0.6031	-0.6149
Cr	0.1917	0.3321	0.0512	-0.2044	0.1067	0.0942	-0.0787	0.1224	-0.1715	-0.1168	-0.3089	-0.3600	-0.4542	0.1843	0.5036	0.0587	0.0357	-0.0184	-0.0073	-0.0018	0.0056	0.0006
Cu	0.1982	0.1500	0.3424	-0.2241	-0.1627	-0.0002	-0.2758	0.1548	0.0589	-0.0873	-0.2151	0.0059	0.3694	-0.1577	-0.1392	0.4445	0.0297	0.1279	-0.4337	0.0418	0.0396	-0.0042
DO	0.0491	0.3690	-0.0097	0.3277	0.2294	0.0404	0.1262	0.1955	0.0765	0.1011	-0.2238	0.1245	-0.2122	0.1592	-0.4374	-0.3115	0.0998	0.0004	-0.4384	-0.0453	-0.0305	0.0083
EC	0.2566	0.1268	-0.3115	-0.0418	-0.1372	-0.1510	0.0167	-0.2193	0.1322	-0.1390	-0.1270	0.1382	-0.3472	-0.7067	-0.0702	-0.0139	0.0577	0.1660	0.0325	-0.0106	0.0083	-0.0054
Hg	0.1566	0.3385	0.0754	-0.1825	-0.0270	0.2394	-0.0778	-0.1661	0.0241	0.2244	0.7348	-0.0015	-0.2632	0.0436	-0.1406	0.1809	-0.0437	-0.0646	-0.0971	-0.0125	-0.0054	0.0033
K	0.1795	-0.2244	0.2029	0.1376	0.3122	0.2469	0.2446	-0.3612	0.0679	-0.4350	0.1111	0.2230	0.0244	-0.0096	0.3103	-0.0414	-0.0865	0.0179	-0.3773	0.0601	-0.0120	0.0106
Mg	0.3321	-0.1406	-0.0707	0.0905	0.0171	-0.0373	0.0107	0.1386	-0.0519	0.0938	0.0539	-0.0277	-0.0176	0.1024	-0.0377	0.0273	-0.0179	0.2615	0.0625	0.5966	-0.5033	-0.3545
NH4	0.0526	-0.3918	0.0055	-0.2114	-0.0476	0.2350	-0.1668	0.0015	-0.1583	0.2803	-0.2676	0.5464	-0.3520	0.1005	-0.0585	0.1646	0.0600	-0.2631	-0.0381	-0.0181	-0.0291	0.0045
Na	0.2806	-0.2363	0.0837	0.1365	0.0988	0.1477	0.0771	0.1033	-0.1488	0.1588	0.0617	-0.1632	-0.0121	-0.0537	-0.0703	0.0243	0.3886	0.2976	0.1079	0.1424	0.2318	0.6164
Ni	-0.0345	0.2453	-0.0834	0.5465	0.0921	0.1178	0.1303	0.0496	0.2257	0.2461	-0.0871	0.1686	0.0807	-0.0739	0.2823	0.5511	0.0162	-0.1188	0.1840	0.0073	-0.0048	-0.0023
P	-0.0947	-0.1712	-0.2705	-0.2961	0.1684	0.3843	0.0105	0.4084	0.6588	-0.0793	0.0410	-0.1006	-0.0116	-0.0430	0.0171	-0.0248	0.0352	0.0358	-0.0157	0.0042	-0.0056	0.0032
Pb	0.0610	0.1315	0.0862	-0.3941	-0.0999	-0.1454	0.7747	0.1914	-0.0707	0.2398	0.0007	0.1916	0.1297	-0.0632	0.1537	-0.0336	0.0317	-0.0110	-0.0480	0.0055	0.0019	-0.0004
S	0.3321	-0.1561	-0.0335	0.0760	0.0214	-0.0012	0.0051	0.1052	-0.0461	0.0850	0.0388	-0.0805	0.0726	0.0051	0.0294	0.0201	-0.1189	0.1322	-0.0003	-0.7295	-0.5042	0.0708
TC	0.2487	0.0755	-0.3441	-0.0547	-0.0755	-0.2669	-0.0489	-0.0223	0.0660	-0.3057	0.1323	0.1578	0.1543	0.3157	0.0387	0.0748	0.6096	-0.2903	-0.0169	-0.0499	-0.0419	0.0018
TDS	0.2968	0.0358	-0.2551	0.0024	-0.0927	-0.2645	-0.0657	0.1300	0.1185	-0.0838	0.0246	0.2366	-0.0162	0.3209	0.0315	0.0308	-0.6071	0.1158	0.0050	0.0891	0.2584	0.3259
V	0.2116	0.2213	0.2391	-0.1289	0.3301	0.1813	0.0501	0.0902	-0.0934	-0.3477	-0.0866	0.1667	0.1086	-0.0529	-0.3424	0.0165	-0.0991	-0.1700	0.5857	-0.0043	-0.0344	0.0005
pH	0.0080	-0.0664	0.1863	-0.2020	0.6238	-0.5356	-0.1477	-0.1970	0.2804	0.3012	-0.0180	0.0009	-0.0480	0.0048	0.0335	0.0574	0.0620	0.0449	0.0304	-0.0126	0.0043	-0.0014
%variation	35.3800	21.5900	13.8900	9.0700	5.1100	4.1700	3.6600	2.0800	1.5200	1.4400	0.7400	0.4600	0.2800	0.2100	0.1600	0.1000	0.0800	0.0400	0.0300	0.0000	0.0000	0.0000
latent roots	7.7841	4.7506	3.0557	1.9946	1.1237	0.9170	0.8051	0.4578	0.3345	0.3169	0.1631	0.1005	0.0619	0.0452	0.0347	0.0223	0.0178	0.0081	0.0057	0.0005	0.0001	0.0000

APPENDIX K: PCA LOADING PLOTS FOR ALL SAMPLING SITES ON THE BASIS OF SEDIMENT QUALITY PARAMETERS

DRY SEASON

LOADINGS

SITES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
1	0.1854	0.2340	0.1411	0.2614	0.4935	-0.0890	-0.2042	0.0975	0.0959	0.0130	0.0256	-0.1869	0.2077	-0.2328	0.0714	0.0799	0.0621	0.3334	-0.3264	-0.0096	0.0384	0.2576	0.1972	0.1338	0.1412
2	0.2180	0.1430	-0.1518	-0.0240	-0.1900	-0.1095	-0.3568	0.1185	0.1494	-0.3601	-0.3298	0.3641	-0.2198	-0.2763	0.0073	0.0172	-0.0180	0.0328	0.1843	0.2702	-0.0691	0.1580	-0.1123	0.2164	0.0553
3	0.2246	0.1099	0.0641	-0.0674	-0.5534	0.0079	-0.1531	0.0744	0.0171	-0.1397	-0.0920	-0.2234	-0.0504	0.0436	0.4358	0.0605	0.0273	0.0945	-0.2846	-0.3306	0.1040	-0.0253	0.1631	-0.2816	0.0052
4	0.2043	0.1906	0.0751	0.1415	-0.0157	0.0084	0.6170	0.1611	0.1754	-0.4732	-0.2463	-0.2456	0.0578	0.1284	-0.2695	-0.0769	0.0059	0.0533	0.0361	0.0474	0.0403	-0.0832	-0.0103	-0.0023	-0.0141
5	0.2206	0.1322	0.1573	-0.0682	-0.0962	-0.0168	0.0605	0.0882	-0.1403	0.2241	-0.2247	0.4597	0.6123	-0.0768	-0.1277	0.0364	0.0126	-0.0207	-0.1083	-0.1700	0.1390	-0.1109	-0.2685	-0.0557	-0.0729
6	0.2151	0.1566	0.0458	-0.0066	-0.1537	-0.0533	-0.0294	0.0381	-0.2410	0.0396	0.1176	-0.0297	0.0937	-0.1163	-0.3397	0.0545	-0.0417	-0.4286	0.1353	-0.1216	-0.3419	0.2089	0.5497	0.0056	0.0439
7	0.2284	-0.0058	-0.5681	0.0066	0.2147	-0.2631	-0.3638	-0.0038	-0.1360	-0.1901	0.0380	-0.1641	0.1526	0.3185	-0.2157	-0.0507	0.0121	-0.0338	0.0328	-0.1115	0.1154	-0.2054	-0.0754	-0.1989	-0.0706
8	0.2063	0.1725	0.4324	0.1140	0.0572	0.0303	-0.1916	0.0639	-0.0391	0.0304	0.1801	0.1909	-0.5032	0.3576	-0.3250	-0.0305	0.0043	0.0125	-0.1504	-0.2250	0.0235	-0.0356	-0.2187	0.0265	-0.0024
9	0.2019	0.1891	-0.2885	-0.0543	0.1106	0.9045	-0.0389	-0.0573	-0.0164	0.0212	0.0023	0.0191	-0.0235	-0.0104	-0.0046	-0.0006	0.0033	0.0017	-0.0107	-0.0146	-0.0002	0.0003	0.0026	-0.0056	0.0015
10	0.2196	0.1335	0.2021	0.2241	0.2149	-0.0210	-0.1230	0.0379	0.1198	0.2998	-0.3372	-0.2469	-0.0658	0.0030	0.3296	-0.0948	-0.0211	-0.3841	0.3110	0.0664	-0.0740	-0.2904	-0.0578	-0.0214	-0.1902
11	0.2099	0.1580	-0.4497	-0.1235	0.1249	-0.2411	0.4315	0.1938	0.0107	0.3395	0.0347	0.1404	-0.3656	-0.1471	0.1564	0.0623	0.0207	-0.0703	-0.1657	-0.2160	-0.0178	0.0751	-0.0699	0.0745	0.0178
12	0.2074	0.1822	0.0709	0.1038	0.1011	-0.0604	0.1814	-0.0377	-0.4008	-0.1473	0.2935	0.2949	0.0326	0.2624	0.4297	0.0189	-0.0863	0.1307	0.2155	0.3544	0.0124	0.0527	0.1068	-0.1944	0.0273
13	0.2070	0.1837	-0.0380	0.0052	-0.0728	-0.1328	0.0748	-0.8331	0.4120	0.0761	0.0639	0.0999	0.0360	0.0500	-0.0361	-0.0056	0.0040	0.0216	-0.0157	0.0018	-0.0106	0.0155	0.0559	-0.0145	0.0128
14	0.2307	0.0751	0.0494	-0.0873	-0.2130	-0.0425	0.0175	-0.2073	-0.4535	0.1273	0.0802	-0.4861	-0.0379	-0.2421	-0.1136	0.0880	-0.0182	0.1362	0.1087	0.1553	0.0583	0.0896	-0.4326	0.1955	0.0615
15	0.1920	-0.2231	0.0981	0.0267	0.1044	0.0042	0.0360	-0.0707	-0.0889	-0.1235	0.1711	0.1083	-0.1859	-0.6005	-0.1242	-0.2364	0.1233	0.0858	-0.0350	0.0193	0.1142	-0.4152	0.1375	-0.3393	-0.1074
16	0.2350	-0.0170	-0.0057	-0.0471	-0.2061	0.0090	-0.0506	0.3535	0.4954	0.1107	0.6206	-0.0798	0.2059	-0.0175	-0.0034	-0.0203	-0.0124	-0.0255	0.1486	0.1752	0.0136	-0.0682	-0.1208	0.0786	-0.0263
17	0.2188	-0.1146	0.2415	-0.8564	0.3054	-0.0293	-0.0136	0.0069	0.0655	-0.0927	-0.0924	-0.0783	0.0028	0.1020	0.0600	-0.0063	-0.0008	0.0085	0.0237	0.0371	-0.0401	0.0328	0.0775	0.0099	0.0218
18	0.1672	-0.2721	0.0035	0.0792	-0.0222	0.0292	0.0185	0.0740	0.1276	0.2778	-0.2023	-0.0162	-0.1241	0.0589	-0.2302	0.5179	-0.0986	0.2131	0.1714	0.1843	0.1752	0.2322	0.1160	-0.4208	-0.1269
19	0.1629	-0.2790	-0.0084	0.0961	0.0036	0.0258	0.0246	-0.0107	0.0239	0.0050	-0.0498	-0.0270	0.0398	0.0552	0.0290	-0.3827	0.1963	-0.2541	-0.3331	0.2340	-0.2543	0.4620	-0.2764	-0.3254	-0.0033
20	0.2034	-0.1939	-0.0764	0.0249	-0.2102	-0.0038	-0.0036	0.0534	-0.0873	0.3405	-0.1918	0.0202	-0.0272	0.2570	-0.0934	-0.3594	0.1014	0.3117	-0.1503	0.2912	-0.0090	-0.2139	0.3561	0.3351	0.0483
21	0.1640	-0.2774	0.0170	0.0785	0.0289	0.0288	0.0268	-0.0760	-0.0502	-0.1559	0.0548	0.0232	-0.0107	-0.0116	0.0674	0.1016	-0.4485	-0.3880	-0.3308	0.1097	0.4499	0.0527	0.0849	0.3199	-0.2194
22	0.1606	-0.2825	-0.0141	0.1009	0.0349	0.0217	0.0309	-0.0390	-0.0078	-0.1092	0.0071	0.0288	0.0532	0.0088	0.0782	0.3067	-0.3099	0.1699	-0.1845	-0.0732	-0.7004	-0.2800	-0.1352	0.0891	-0.0672
23	0.1574	-0.2874	0.0224	0.1125	0.0383	0.0343	0.0322	-0.0143	0.0332	-0.0032	-0.0468	0.0337	0.0145	0.0225	0.0517	0.0601	-0.0358	-0.1625	0.1235	-0.1176	0.1279	-0.1054	-0.0450	-0.0158	0.8819
24	0.1595	-0.2843	0.0228	0.1014	0.0227	0.0345	0.0510	-0.0655	-0.0558	-0.1504	0.0584	0.0579	0.0254	0.0756	0.1193	0.3235	0.7450	-0.0910	0.0996	-0.1369	0.0365	0.0242	0.0210	0.2977	-0.1835
25	0.1596	-0.2841	0.0093	0.1007	0.0368	0.0276	0.0361	-0.0247	0.0067	-0.0226	0.0040	0.0313	0.0403	-0.0181	0.0857	-0.3770	-0.2385	0.2697	0.4303	-0.5017	0.0290	0.3415	-0.0038	0.1202	-0.1679

WET SEASON

LOADINGS

SITES

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
1	0.2261	0.1933	0.0436	-0.1498	0.0349	0.1438	0.4073	-0.2338	-0.0099	-0.1371	-0.0429	0.0542	0.3793	0.3785	0.0547	0.0813	-0.2001	-0.1836	0.1649	0.2214	-0.2415	-0.0745	-0.3027	-0.1353	0.0252
2	0.2091	0.2371	-0.0023	-0.0806	0.0022	0.0818	0.0135	0.0333	-0.0946	-0.4220	0.1304	0.0988	0.1735	0.3013	-0.1807	0.0122	0.3039	0.4233	-0.1429	-0.1197	0.3819	0.1343	0.0927	0.1944	0.0400
3	0.2448	0.1554	-0.0091	0.1674	-0.0527	0.0262	-0.1224	0.1872	-0.0342	-0.3781	0.3974	0.1013	-0.2293	-0.1379	-0.0610	-0.0905	0.0604	-0.2068	-0.0323	0.1467	-0.4579	-0.2684	0.0091	0.2961	0.0065
4	0.2165	0.2143	0.0365	-0.1724	0.0498	0.1425	0.3584	-0.2420	0.0861	0.0461	0.2867	0.1392	-0.5133	-0.2012	0.1269	-0.0003	-0.2450	-0.0386	0.1387	-0.1440	0.2335	0.2292	0.1549	-0.0505	-0.0119
5	-0.0626	0.0773	0.5025	-0.2183	-0.2635	0.1286	0.2878	0.6898	-0.1171	0.1766	0.0095	0.0074	0.0037	-0.0001	-0.0007	0.0050	0.0034	0.0062	-0.0016	0.0039	0.0043	0.0025	-0.0044	-0.0139	0.0001
6	-0.0692	0.0578	0.4821	0.0205	-0.6572	0.0808	-0.2966	-0.4759	0.0426	-0.0626	-0.0128	0.0045	-0.0045	0.0025	0.0015	-0.0043	-0.0052	-0.0064	0.0020	-0.0048	-0.0036	-0.0019	0.0043	0.0131	0.0004
7	0.2026	0.2447	0.0238	-0.0615	0.0231	0.0756	0.2762	-0.1737	-0.0101	0.0639	-0.4808	-0.3868	-0.1617	-0.2998	-0.1509	-0.0454	0.3374	0.1616	-0.1687	0.1618	-0.1809	-0.1288	0.0961	0.0551	0.0045
8	0.2265	-0.1377	-0.0020	-0.1845	-0.2299	-0.8878	0.2152	-0.0233	-0.0187	-0.0552	0.0434	0.0214	0.0118	-0.0199	-0.0027	0.0076	0.0188	0.0119	-0.0176	-0.0016	-0.0011	-0.0075	0.0239	-0.0118	-0.0003
9	0.2262	0.2028	0.0080	0.1720	0.0017	-0.0477	-0.0697	0.0091	0.0058	0.3485	0.0186	-0.1255	0.3493	0.0876	0.0121	-0.0053	-0.1386	-0.2079	0.1462	0.0973	0.0398	0.1403	0.5825	0.3787	-0.0784
10	0.2256	0.2043	0.0069	0.1641	0.0105	-0.0495	-0.0608	-0.0231	0.0658	0.4434	-0.1282	0.5720	0.0806	-0.1854	-0.0839	0.0491	0.0137	0.1685	-0.0512	-0.1153	0.0209	-0.1186	-0.3886	0.2340	0.1185
11	0.2085	0.2347	-0.0011	0.1942	-0.0305	-0.0561	-0.1429	0.0902	0.0476	0.0842	0.3552	-0.5158	0.1930	-0.2767	-0.0061	0.0395	0.0200	0.0154	0.1131	0.0318	0.2438	0.0816	-0.4264	-0.2085	-0.0913
12	0.2108	0.2285	-0.0143	0.2285	-0.0321	-0.0546	-0.1918	0.1210	0.0426	0.0913	-0.0119	0.2181	-0.1146	0.1679	0.0548	0.1373	0.0826	0.1334	-0.1324	0.2288	-0.1432	0.0783	0.2831	-0.6867	0.0407
13	-0.0957	0.0673	0.4851	0.0846	0.4113	-0.1648	-0.0316	0.0366	0.6081	-0.2930	-0.1413	0.0948	0.0990	-0.1563	-0.0105	0.0279	-0.0095	-0.0433	0.0699	0.0831	0.0626	0.0572	0.0392	0.0127	-0.0532
14	-0.0983	0.0662	0.4772	0.1210	0.4768	-0.1819	-0.0414	-0.2253	-0.5605	0.1451	0.1712	-0.0814	-0.0993	0.1441	0.0039	-0.0283	0.0231	0.0474	-0.0776	-0.0714	-0.0787	-0.0659	-0.0249	-0.0066	0.0542
15	0.2195	0.2149	0.0018	0.1489	-0.0228	-0.1041	-0.2065	0.1876	-0.0031	-0.1321	-0.4544	-0.1920	-0.3380	0.3677	0.1433	-0.1272	-0.2451	-0.1638	0.0655	-0.3350	0.0817	0.0068	-0.1770	0.0758	0.0109
16	0.2495	-0.1358	0.0752	-0.0261	0.0390	0.1178	0.0823	-0.0598	0.1310	0.0609	0.0960	0.0301	0.2343	-0.0204	0.1656	-0.3086	0.2084	-0.2726	-0.3600	-0.5058	0.0233	-0.2786	0.1105	-0.2213	-0.1891
17	0.2397	-0.0278	0.0370	-0.7342	0.1845	0.0348	-0.4799	0.0014	0.1524	0.2129	0.0813	-0.0766	-0.0853	0.1266	-0.0480	-0.0146	0.0477	0.0178	0.0159	0.1162	-0.0908	-0.0252	-0.0508	0.0332	0.0113
18	0.2596	-0.0934	0.0439	-0.1495	0.0602	0.0730	-0.2076	0.0522	-0.4662	-0.3175	-0.2955	0.1973	0.2239	-0.4874	0.0822	0.0304	-0.1663	-0.1198	0.1079	0.0156	0.0932	0.1373	0.0653	-0.1295	-0.0518
19	0.1999	-0.2466	0.0761	0.0608	0.0134	0.0822	0.0246	0.0081	0.0740	-0.0243	0.0318	-0.1649	0.0004	-0.0146	-0.1652	0.4812	-0.3389	-0.0857	-0.5834	-0.0334	0.0041	0.1016	-0.0085	0.0838	0.3282
20	0.1973	-0.2506	0.0749	0.0826	0.0089	0.0744	0.0216	0.0145	0.0839	-0.0034	0.0382	-0.1155	0.0849	-0.0274	0.1116	0.1270	0.0518	0.4136	0.3488	-0.4331	-0.5087	0.2648	0.0428	0.0082	0.0864
21	0.1988	-0.2484	0.0736	0.0840	0.0118	0.0740	0.0121	0.0088	0.0193	-0.0058	-0.0030	-0.0673	-0.0620	0.0319	0.0485	0.2076	-0.1007	0.2109	0.3416	0.0698	0.3008	-0.7174	0.1643	-0.0442	0.1220
22	0.1834	-0.2695	0.0745	0.1154	0.0106	0.0617	0.0333	-0.0158	-0.0426	0.0565	-0.0502	0.0743	-0.1793	0.1322	0.0925	0.3894	0.5892	-0.4085	0.1732	0.0940	0.1404	0.2004	-0.1239	0.0886	-0.1037
23	0.1813	-0.2719	0.0748	0.1252	0.0042	0.0587	0.0418	-0.0052	0.0120	0.0490	-0.0100	0.0263	-0.0572	0.0650	-0.7256	-0.4264	-0.0296	-0.1371	0.2009	0.0324	0.0582	0.1349	-0.0087	-0.1609	0.1973
24	0.1848	-0.2677	0.0741	0.1195	0.0028	0.0607	0.0304	0.0086	0.0361	0.0227	0.0102	-0.0254	-0.0065	0.0274	0.5213	-0.4689	0.0322	0.1521	-0.1320	0.3871	0.0994	0.1664	-0.0868	0.1177	0.3528
25	0.1850	-0.2674	0.0740	0.1191	0.0066	0.0609	0.0308	-0.0038	-0.0112	0.0386	-0.0233	0.0306	-0.1094	0.1032	-0.0735	-0.0426	-0.2286	0.2743	-0.1608	0.2121	-0.0216	0.0522	-0.0957	0.0869	-0.7866

APPENDIX L: CA SIMILARITY MATRICES FOR SEDIMENT QUALITY PARAMETERS ACROSS ALL SAMPLE SITES

DRY SEASON

1	----											
2	93.2	----										
3	97.7	98.3	----									
4	98.8	93.7	98.1	----								
5	98.2	97.8	99.8	98.7	----							
6	98.4	97.2	99.6	98.8	99.8	----						
7	87.2	95.4	92.6	87.5	92.1	92.9	----					
8	98.2	97.8	99.6	97.8	99.6	99.7	92.6	----				
9	87.5	83.9	88.4	89.1	88.5	88.6	78.1	87.6	----			
10	99.9	92.9	97.5	98.7	98.0	98.0	85.6	97.8	87.2	----		
11	93.2	95.1	96.5	96.6	96.9	97.4	93.8	95.8	86.9	92.4	----	
12	98.8	96.5	99.3	99.3	99.7	99.8	91.7	99.4	88.4	98.4	97.3	----
13	98.8	96.2	99.3	99.5	99.6	99.9	91.5	99.2	89.3	98.5	97.4	99.9
14	99.8	92.4	97.5	98.9	97.9	98.0	85.4	97.6	87.6	99.9	92.7	98.4
15	98.9	94.9	98.8	99.1	99.1	99.3	89.6	98.8	88.3	98.8	95.9	99.4
16	77.4	89.7	87.7	82.3	86.1	86.5	89.6	85.8	83.5	76.1	91.2	84.7
17	31.7	48.2	45.8	39.3	44.6	44.1	49.9	43.5	49.6	30.4	52.5	41.4
18	69.9	79.2	78.7	74.2	78.0	78.1	79.6	76.6	67.2	69.7	81.6	76.5
19	85.3	87.3	89.9	88.4	89.7	90.2	86.5	88.3	79.3	85.3	91.4	89.2
20	86.8	96.2	94.5	89.5	94.0	94.0	95.8	93.4	80.4	86.2	95.5	92.8
21	96.1	93.2	97.0	96.8	97.2	97.2	88.0	96.4	87.0	96.3	94.4	97.1
22	79.5	83.4	85.0	82.9	84.9	85.0	82.5	83.1	73.4	79.5	86.9	84.2
23	74.1	77.4	79.6	77.6	79.6	79.7	75.9	77.8	67.7	74.4	81.2	78.7
24	66.1	73.2	74.1	71.1	74.0	74.1	72.7	72.0	61.7	66.1	77.8	73.0
25	82.1	83.7	86.6	85.3	86.6	87.0	82.8	85.0	76.2	82.1	88.5	86.2
	1	2	3	4	5	6	7	8	9	10	11	12

13	----											
14	98.6	----										
15	99.5	99.0	----									
16	85.5	76.4	82.8	----								
17	42.7	31.2	41.1	70.7	----							
18	76.8	70.5	78.3	82.3	52.5	----						
19	89.7	86.2	91.6	84.9	49.8	91.9	----					
20	92.6	86.4	91.9	93.0	56.0	88.8	94.1	----				
21	97.2	96.7	98.6	82.6	42.6	85.9	95.2	92.6	----			
22	84.4	80.3	86.2	80.7	45.2	97.7	95.7	90.6	92.7	----		
23	78.9	75.3	82.1	75.0	40.9	96.8	95.6	86.8	89.8	98.7	----	
24	73.1	67.2	75.4	74.3	41.9	97.6	90.5	84.6	84.2	97.8	97.8	----
25	86.5	83.1	89.1	81.4	46.4	91.6	99.6	91.9	93.5	95.5	96.6	91.4
	13	14	15	16	17	18	19	20	21	22	23	24

25	----

25

WET SEASON

	1	2	3	4	5	6	7	8	9	10	11	12
1	----											
2	94.8	----										
3	99.6	95.8	----									
4	99.2	90.3	98.6	----								
5	82.7	73.9	82.3	84.3	----							
6	84.9	75.7	84.6	86.5	98.3	----						
7	65.5	73.4	66.4	60.4	74.0	71.5	----					
8	46.3	55.8	48.1	41.9	58.3	53.3	86.0	----				
9	73.2	72.8	74.1	72.1	89.6	86.4	92.6	82.1	----			
10	66.4	67.1	67.4	65.0	83.3	79.9	94.2	84.6	98.8	----		
11	76.4	74.6	77.2	75.8	93.1	90.9	90.0	77.8	99.4	96.9	----	
12	68.3	69.2	69.7	67.0	84.9	82.5	94.2	83.2	98.9	99.6	97.8	----
13	74.2	66.3	74.0	75.8	94.4	90.5	80.5	68.8	95.4	92.6	96.8	93.3
14	74.2	66.3	74.0	75.9	94.8	90.8	80.1	68.5	95.4	92.3	96.9	92.9
15	68.2	65.8	68.9	67.9	87.7	83.4	90.6	80.8	98.3	98.4	97.5	98.6
16	97.0	97.2	97.3	94.7	77.3	79.4	69.8	55.0	73.9	68.3	75.7	69.4
17	86.1	87.3	86.6	84.5	69.2	69.8	62.6	58.2	69.8	65.2	69.9	64.6
18	76.1	83.5	77.6	71.9	57.2	56.2	60.1	57.0	61.3	57.6	60.8	56.6
19	98.4	93.1	98.4	98.3	82.0	84.2	63.4	49.3	73.0	66.3	75.9	68.0
20	96.1	93.5	96.4	95.1	78.4	80.6	64.2	52.7	72.1	65.9	74.4	67.3
21	95.2	93.5	95.7	93.9	77.1	79.2	64.7	54.6	72.0	66.0	74.0	67.2
22	79.1	76.9	79.7	78.3	62.2	64.2	50.0	48.3	59.8	54.3	60.5	54.4
23	88.2	83.1	88.5	88.2	72.2	74.5	54.4	48.0	65.7	59.5	67.7	60.4
24	88.9	86.0	89.6	88.3	72.1	74.3	57.0	50.6	66.5	60.5	68.5	61.6
25	90.4	86.4	90.9	90.2	73.9	76.2	57.8	50.7	68.1	62.0	70.0	62.9

	13	14	15	16	17	18	19	20	21	22	23	24
13	----											
14	100.0	----										
15	96.9	96.5	----									
16	69.5	69.5	66.9	----								
17	63.5	63.6	62.2	94.3	----							
18	52.2	52.6	53.9	83.9	84.5	----						
19	73.8	73.8	67.9	97.9	91.1	79.3	----					
20	70.4	70.5	66.2	98.4	93.6	82.5	99.2	----				
21	69.3	69.5	65.7	98.0	93.7	84.9	98.5	99.6	----			
22	55.6	56.2	52.5	84.2	83.2	80.1	86.0	89.1	92.2	----		
23	64.8	65.2	59.7	90.5	86.3	79.0	93.7	95.4	96.7	97.7	----	
24	64.6	64.8	60.4	92.5	89.0	81.0	94.7	97.1	98.0	96.3	99.4	----
25	66.5	66.8	61.9	92.8	88.6	81.8	95.2	96.6	98.0	97.4	99.7	99.3

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