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THE IMPACT OF SUB-CATCHMENT ACTIVITY ON RIVER WATER QUALITY: A CASE STUDY OF MBABANE RIVER IN THE EZULWINI VALLEY, SWAZILAND.

BY

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In

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ABSTRACT

The water quality of a river is influenced by the catchment's characteristics. The Mbabane River sub- catchment in the eZulwini Valley, Swaziland has catchment activities which are potential sources of both point and non point pollution. The effect on the water quality of the river has not been integrated though monitoring is done only on the point source of pollution. The river is a surface water source for potable water production and is used for domestic and agricultural uses. This study assessed the impacts of the existing activities on the water quality of the Mbabane River through assessment of temporal and spatial variation in water quality of the Mbabane River, analysis of historical data, identify factors influencing water quality and to outline the aspects of sub-catchment management plan. Seven sites were selected along the river at strategic points. Assessment was carried out late January to mid March 2009. The analysis consisted of *in situ* and laboratory analysis of samples using standard methods. Parameters selected for the assessment were Temperature, pH, Alkalinity, ammonia (as ammonia), Phosphorous (as orthophosphate), dissolved Oxygen, biological Oxygen demand (BOD), chemical Oxygen Demand (COD) and faecal coliforms. At all sampling sites faecal coliforms and chemical Oxygen demand were the significant pollutants exceeding the pollution limits with ranges of 230 – 6900 FC counts/100mℓ and 11-141mg/ℓ respectively. Ammonia and phosphorous were below the pollution limits at all sites with highest values 0.26 and 0.80 mg/ℓ respectively. Chemical oxygen demand and biochemical oxygen demand showed inverse relation with dissolved oxygen. Faecal coliforms were the significant water quality pollutant at the Control Point. COD was the significant pollutant at Site B. ammonia was seen to be a significant pollutant at all site downstream of Site B. The percentage oxygen deficiency ranged form 13 – 42% in sites upstream of eZulwini wastewater plant and ranged between 27 – 45% in down stream of the wastewater plant. Available historical data showed an increase in levels of parameters in the effluent from the eZulwini wastewater plant.

Key Words: Spatial and Temporal Variation, Water Quality Management, Mbabane River Sub-catchment.

DECLARATION

I **BONISWA WISDOM DLADLA** here by do declare that all work done in this study originates from my own work and that all secondary sources referred to in this work have been duly acknowledged and therefore this thesis is submitted for an awarded of the degree of Masters of Science Degree in Integrated Water Resources Management tenable in the Department of Civil Engineering of the University of Zimbabwe

Signature ……………………………..

Date…… ……………………

DEDICATION

TO MY WIFE AND CHILDREN FOR THEIR PATIENCE THROUGH THIS TIME AWAY FROM THEM:

The Strategic Plan for One's Life Guides Their Every Move.

"The Future is in Today's Initiative, This is only the Beginning"
BDL

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My Creator and LORD the Almighty GOD I do not exist outside your courts and for giving me "Proverbs 6" that gave strength through sleepless nights.

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To the Maphosa families who cared for me in Zimbabwe and made it my second home, God richly bless you.

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ACRONYMS AND ABBREVIATION

COP – Catchment Outline Plan

DFID – Department for International Development

DWAF - Department of Water Affairs & Forestry South Africa

GAO - United States General Accounting Office

IWRM - Integrated Water Resources Management

LIMS – Laboratory Information Management System

NWA – National Water Authority (Swaziland)

SWSC – Swaziland Water Service Corporation

SZWP - Swaziland Water Partnership

UN – United Nations

WHO – World Health Organisation

INTRODUCTION

1.0 Introduction

Water is essential for all socio-economic development and for maintaining healthy ecosystems; however freshwater sources have experienced increased stress due to ever rising demand and degenerate use, as well as by growing pollution worldwide (UN water, 2006). The water quality of a river is influenced by the catchment characteristics with various imposed pollution loads. The pollution loads imposed on a river system consists of three components, direct/point wastewater discharge, diffuse/non – point contribution in seepage and runoff water from the catchment and background contribution from natural sources (Hema and Muthalagi, 2009). These three aspects must be considered in catchment water quality management plan.

Surface waters have for a long time been considered as a convenient receiver of wastes, such is the case with Mbabane River, Swaziland. The entry of wastewater into water bodies disrupts the quality of the ecosystem and this use (abuse) of surface waters conflicts with all other intended uses of that water such as domestic use, recreational and stock watering and this characterises Mbabane River (Bartram and Balance, 1996; Dakova *et al.*, 2000; Hranova, 2002). This therefore means that the quality of water has a bearing on the economy of the riparian population and therefore it gains economic value (Harmancioğlu *et al.*, 1999).

Urban civilisation has been characterised by potable water supply and systems coupled with growth in industries, transport and energy generation. These activities result in production of wastewater with inadequate or no treatment facility, which creates a situation where water and environmental quality is negatively impacted leading to possible conflicts due to the upstream – downstream dimensions (Vesilind *et al.*, 1990; Lundqvist., 2000). Urbanisation in Swaziland has resulted in rural-urban migration (since 1980) resulting in development of informal settlements with in inadequate or no waste disposal facilities in areas around Mbabane and Manzini including eZulwini (The World Bank, 2002).

The management of water resources is complex with urgent problems related to overexploitation of water resources, the lack of an adequate water supply infrastructure in many parts of the world. Water pollution is therefore not only an issue of water quality and contaminant emission, it traces back to the source of the pollution, defines its effect and the need to control or avoid the pollution (Huang and Xia, 2001; Koutsoyiannis, et al., 2009).

1.1 Background

As the need for energy in Swaziland grew the Luphohlo dam was constructed for hydropower generation and was completed in 1984. The Dam was constructed along the Lusushwana River abstracting $10m^3/s$ at peak hydropower generation, releasing this water in to the Mvutsini River, a tributary of the Mbabane River (Kowalkowski *et al*., 2007). According to Baldwin *et al.* (2009) dams affect the river system below the dam, changing characteristics such as temperature, flow and morphology. Swaziland like many African countries has some urban and rural areas built in close proximity to one another. Most urban centres in Swaziland have centralised wastewater collection systems serving 51.5% of the urban population. The rest of the urban populations have onsite wastewater disposal systems. Rural and peri-urban areas utilise mainly pit latrines and septic tanks in these systems serving 36.5% rural population (WHO, 2000). Mbabane the capital city treats its wastewater in a new wastewater plant situated in the eZulwini Valley five kilometers outside the capital and the plant discharges the effluent into the Mbabane River.

The eZulwini peri-urban area is characterised by intensive agricultural activity along the riparian areas of the Mbabane River. According to Dorner *et al*. (2007) agricultural non-point sources have been seen to be a major cause of deterioration in the water quality of lakes and rivers. The residents of the eZulwini peri-urban area also keep livestock such as cattle and goats, and according to Sinclair *et al*. (2009) this activities contribute to the microbial loading on rivers especially during the rainfall seasons.

High-gradient water courses enable good re-aeration of water bodies, assisting in better self cleansing ability. However the risk of pollution loading may be intolerable for low flows or for rivers flowing on gentle slopes (Kowalkowski *et al.,* 2007). Such is the eZulwini Valley where the wastewater is discharged into the Mbabane River.

1.2 Problem Statement

The presence of a number of various point and non-point sources of pollution around the Mbabane River may have a synergistic effect on the water quality of the river. The National Water Authority of Swaziland has a monitoring programme that focus on the wastewater from the eZulwini Wastewater plant and the Swazi Sun wastewater system. The focus is mainly on point source. The presence of both point and non-points possible sources of pollution in the sub-catchment justified the need to conduct an integrated assessment of the possible negative impacts on the river water quality.

1.3 Justification

The use of the Mbabane River by the riparian population especially those using the water for domestic purposes necessitates the need to have the river assessed for its ability to carry the pollutants while maintain water of suitable quality for its intended use. The human need for water is not only a function of quantity but also of the quality of the water (Kowalkowski *et al*., 2007). There is need to understand the variations of raw water quality as it has a bearing on the risk associated with the final use of the water particularly abstraction for potable water production (WHO, 2006). Potable water for areas such as Luyengo, Bhunya and Matsapha in Swaziland obtain their water from raw water abstracted on the Lusushwana River down stream of its confluence with the Mbabane River (Kowalkowski *et al*., 2007).

1.4 Objectives

The main objective of the study was to assess the impact of existing sub-catchment activities on the water quality of the Mbabane River, Swaziland in its relation to down stream users.

1.4.1 Specific objective were:

- To make a preliminary assessment of the temporal and spatial variation in water quality of the Mbabane River
- To assess selected physical and chemical parameters at site B and compare the parameters at the sampling site over the past three years (2006 – 2008) from historical data provided by National Water Authority Laboratory.
- To explore the use of Descriptive Numerical Analysis in relating parameters for in-depth analytical interpretation of results.
- To make use of the analysis to identify the influential factors of water quality along the river corridor
- To outline a sustainable management plan for the Mbabane River.

LITERATURE REVIEW

2.1 Introduction

Fresh water is a finite resource, essential for agriculture, industry, and human existence (Bartram and Balance, 1996). It is apparent that water quality and water quantity are inextricably linked, however water quality deserves special attention because of its direct implication in public health and quality of life (Viessman and Hammer, 1999). Human civilisation has led to dynamic shifts in the patterns of water use, resulting in inevitable discharge of liquid and solid wastes into water bodies resulting in adverse effects upon the receiving water bodies (Song and Kim, 2006). Surface waters are an essential part of our natural environment but due to the activities of humans the quality of surface waters is rapidly deteriorating (Li *et al.,* 2007). Increased populations continue to place pressure on both surface and ground water sources due to increased discharge of wastewater into river corridors, degrading their water quality (Kannel *et al.,* 2007).Water pollution causes water quality deterioration, ineffective use of water resources, ultimately affecting economic and social activities and impacts negatively on the ecological environment (Zhang, 2008).

Kannel *et al.* (2007) noted that major pollution sources in many rivers include industries processing of agricultural products, textiles, extensive agricultural activity using excessive fertiliser and pesticides and wastewater treatment works. The latter two aspects are characteristic of the eZulwini Valley, Swaziland.

2.2 Water Quality Management

Change in the water quality of water bodies is not an issue unique to the 21st century. Nature herself is sometimes guilty of causing changes in water quality (Miller and Tetlow, 1989). As water management entered the 21st century, there was a need for a new water quality management paradigm to achieve ‘sustainable development’ (Poo *et al.,* 2007). Water quality management falls in place with the increased cry for better management of natural resources against human impact (Ward *et al.,* 1990).

Water quality management is possible only within a legal framework and many countries have for a long time had rudimentary and outdated water legislation hampering the effectiveness of water quality management (Bartram and Balance, 1996; Ongley, 2000). The management of water resources in Swaziland has been previously managed on an ad hoc basis utilising various legislative instruments spread across various ministries with no coordination. The water sector reform brought about the new Water Act of 2003, which replaced the Water Act of 1967. This resulted in the country having a harmonised and clear national policy on water use and management (Mlilo *et al.*, undated).

Water quality observations date back more than 100 years, but the need for the systematic management of water quality has become eminent because of the recognition that hydrologic processes affect water quality. This has led to the demand for the better understanding of the process and approaching it within a structured water quality management programme (Harmancioğlu, *et al.,* 1999; GAO, 2001).

Involvement of all stakeholders in identification of discharges to receiving waters is crucial for the success of any water quality management programme (Lee and Jones-Lee, 1999). On a similar note Ongley (2000) stated that the addition of indigenous knowledge to scientific knowledge leads to better water quality management decisions. For effective water quality management, it is important to have access to the latest water quality data, making data an additional component to water quality management (Huang and Xia, 2001; Miami Conservancy, 2005). However on-site water quality assessment is often expensive and time consuming and this becomes a barrier in availability of data (Yang *et al.,* 2000). The establishment of the new National Water Authority with an overall role to manage water resource aspects will hopefully provide more coordination of available data and information among water sector players.

Water quality management programmes can follow three basic formats as defined by Chapman (1996), that is:

Monitoring - Long-term, standardized measurements and observation of the aquatic environment in order to define status and trends.

Survey - A finite duration, intensive programmes to measure and observe the quality of the aquatic environment for a specific purpose.
Surveillance - Continuous, specific measurement and observation for the purpose of water quality management and operational activities

The benefits of a well designed and executed Water Quality Management programme is that critical management decisions are made timely, and are based on comprehensive and appropriate data, with each aspect of the programme focusing on relevant water quality issues (Chapman, 1996).

2.3 Water Quality in Rivers

River discharge has been used extensively as a covariate in water quality assessment and in the development of water quality criteria for rivers being evaluated for disposal of wastewater, based on low discharge conditions. However the is variation in constituent concentration and stream discharge among parameters with varying interactions in different rivers (Chapman, 1996; Esterby, 1996).

This is can be attributed to the fact that water in streams and rivers is influenced by a variety of factors such as drought or dry season which result in fluctuations in water quality (Cho *et al.,* 2004; Atasoy *et al.,* 2006). This can be observed in the variation of the impact that wastewater can have on receiving waters at the same loading volume. At a given discharge there could be none or minimal effect, but when the discharge is low the same loading volume can have significantly degrading impact (Assaf and Saadeh, 2008).

The selection of water quality assessment parameters depend on the needs and objectives of the assessment (Bartram and Balance, 1996). Primary parameters such as temperature, pH and dissolved oxygen are essential as they influence reactions in water and the later important for sustaining aquatic life, (Chapman 1996; DWAF, 1996). Other parameters are selected based on the needs of the water quality assessment.

2.3.1 Temperature

Temperature is a critical water quality parameter, since it directly influences the amount of dissolved Oxygen that is available to aquatic organisms. Water bodies undergo temperature variations along with normal climatic fluctuations. These variations occur seasonally and, in some water bodies, over periods of 24 hours (Chapman, 1996).

The temperature of water is influenced by many factors but it may exceed recommended criteria due to exposures to radiation (Washington State, 1998). The accumulation of daily temperature above the critical level has shown that it is a crucial factor in the distribution of aquatic species and also influences the rate of reactions occurring within the a water body. Water temperature is therefore a critical parameter for any water resources management programme (Rivers-Moore and. Jewitt, 2007; Zhang, 2008). In deep rivers the vertical temperature profile can be stable with a gradual drop in temperature as depth increases (Tanajura and Belyaev, 2009).

2.3.2 pH

pH, or the "potential of hydrogen", is a measure of the concentration of hydrogen ions in the water. This measurement indicates the acidity or alkalinity of the water. On the pH scale (0-14), a reading of seven is considered to be "neutral". Readings below seven indicate acidic conditions, while readings above seven indicate the water is alkaline, or basic. Naturally occurring fresh waters have a pH range between six and eight. The pH of the water is important because it affects the solubility and availability of nutrients, and how they can be utilized by aquatic organisms. The pH is an important variable in water quality assessment as it influences many biological and chemical processes within a water body and all processes associated with water supply and treatment (Chapman, 1996).

The pH levels in surface waters can render the water unusable for all or some activities (Washington State, 1998). The pH of water preferably should not vary by ± 0.5 outside the background range and by ± 1.0 in the natural occurring range

(DeCesare and Connors, 2002). Surface water pH can be relatively higher in low discharge since water is rich in solutes characteristic of ground water (Calles *et al*., 2007). pH can sensitively indicate variations in water quality and is affected by dissolved substances (Yang *et al*., 2008).

2.3.3 Total Alkalinity

Alkalinity is the acid-neutralising capacity of water and is usually expressed in mg/ℓ. When the water has no buffering capacity total alkalinity and acidity are inter-related with pH. However, as most natural waters contain weak acids alkalinity is usually determined as well as pH in water quality assessment (Chapman, 1996).

Total alkalinity, the concentration of bases in water is composed mainly of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydroxyl (OH^-) ions and is expressed as mg/ℓ of CaCO3 (Dougherty *et al*., 2007). Total Alkalinity is affected by changes in flow regimes (Brydsten *et al*., 1990) and its natural variability is linked to the presence or absence of carbonate rock (Kney and Brandes, 2007). It can also be affected by the denitrification process in water which increases alkalinity in river water (Kannel *et al*., 2007).

2.3.4 Ammonia

In the environment, inorganic nitrogen occurs in a range of oxidation states as nitrate ($NO3^-$) and nitrite (NO^{2-}), the ammonium ion (NH_4^+) and molecular nitrogen (N_2). In aqueous solution, un-ionized ammonia exists in equilibrium with the ammonium ion. Total ammonia is the sum of these two forms (Chapman, 1996).

The ammonium ion (NH_4^+) is a reduced form of inorganic nitrogen derived mostly from aerobic and anaerobic decomposition of organic material (DWAF, 1996). In rivers ammonia losses tend to be associated with surface runoff and erosion rather than subsurface flow (Heathwaite *et al*., 1996). In wastewater treatment effluent the ammonium ion along with urea tends to prevail above other nitrogen compounds (Kannel *et al*., 2007).

2.3.5 Phosphorous

Phosphorous is crucial to the stimulation of plant growth; Phosphorus is an essential nutrient for living organisms and exists in water bodies as both dissolved and particulate species. In natural waters and in wastewaters, phosphorus occurs mostly as dissolved orthophosphates (PO_4^{3-}) and polyphosphates, and organically bound phosphates (Chapman, 1996). *"Orthophosphate, is that phosphorus which is immediately available to aquatic biota which can be transformed into an available form by naturally occurring processes" (*DWAF, 1996).

Phosphate and nitrates are the main nutrients required for phytoplankton growth, and consequently eutrophication, which depends on their abundance. The increase of phosphorous in water bodies can be attributed to artificial introduction due to human activity (Chapman 1996; Chen *et al.*, 2007). Eutrophication can be a serious problem when nutrient levels are high with low renewal rate. The Mbabane River in the eZulwini Valley receives additional phosphates and nitrates from both point and non-point sources.

2.3.6 Dissolved Oxygen

Dissolved oxygen is the amount of oxygen dissolved in water, measured in milligrams per litre (mg/ℓ). This component in water is critical to the survival of various aquatic lives in streams, such as fish. The ability of water to hold oxygen in solution is inversely proportional to the temperature of the water. For example, the cooler the water temperature, the more dissolved oxygen it can hold. Dissolved Oxygen can vary seasonally or in 24 hour depending on the temperature and the biological activity (Chapman, 1996).

Dissolved oxygen is one of the parameters that influence the biodegradation rate in water bodies (Reckhow, 1994). Dissolved oxygen can either impair or support use for aquatic life depending on its concentration (DeCesare and Connors, 2002). Dissolved oxygen is affected by entry of organic matter in to rivers especially from runoff during and after a rainfall event (Kannel *et al.,* 2007).

2.3.7 Biological Oxygen demand and Chemical Oxygen Demand

Biological Oxygen Demand (BOD) is a measure of how much oxygen is used by microorganisms in aerobic oxidation, or the breakdown of organic matter. Usually, the higher the amount of organic material found in the stream, the more oxygen is used for aerobic oxidation. BOD depletes the amount of dissolved oxygen available to other aquatic life. This measurement is obtained over a period of five days, and is expressed in mg/ℓ.The levels of BOD in receiving waters is directly increased by the discharge of wastes high in organic matter, resulting in localized areas of Dissolved Oxygen depletion (Chapman, 1996). These organic wastes emanate from municipal sewage, industrial wastewater and non-point source pollutants and lead to problems of water access to downstream users (Poo *et al*., 2007). This scenario is characteristic of the Mbabane River in the eZulwini Valley where downstream users are at risk of upstream pollution, (Nkambule, 2001)

Chemical Oxygen Demand (COD) is the oxygen equivalent of the organic matter that will require the use of oxygen to be broken down. COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and in the effluents from sewage and industrial plants (Chapman, 1996). Chemical Oxygen Demand is useful for the determination of wastewater quality requirement discharged into receiving waters in order to limit their impact and can be used as an index for organic pollution (DWAF, 1996; Chen *et al*., 2007).

2.3.8 Faecal Coliforms

Faecal coliforms bacteria are microscopic organisms that live in the intestines of all warm blooded animals, and in animal wastes or faeces eliminated from the intestinal tract. Faecal coliforms bacteria may indicate the presence of disease carrying organisms which live in the same environment as the faecal coliforms bacteria. The measurement is expressed as the number of organisms per 100 mℓ sample of water (FC/100mℓ).

To assess possible faecal pollution faecal coliform count is used as it indicates the presence of faecal bacteria in water bodies. The Washington State (1998) reported that the primary cause of use impairment in streams is faecal coliforms. According to MNM Consultants (2002) high coliform counts are responsible for the impairment of use of surface waters in Swaziland. Faecal pollution can escalate in the summer warm and dry months (Assaf and Saadeh, 2008). This was also confirmed by Sinclair *et al*. (2009) who observed that during low flows the outlet discharge of streams assessed exceeded the national standards set for faecal coliform counts.

2.4 Temporal and Spatial Variation

For effective water-quality assessment and management a reflection of the temporal variation characteristics is very important (Huang and Xia, 2001).Temporal variation is the assessment of the effect of time on pollution such as the seasonal pattern and its effect on the constituent's relationship (Kannel *et al.,* 2007). Variation in water quality is caused by natural process and anthropogenic sources (Li *et al.,* 2007).

The analysis of spatial point patterns came to prominence in geography in the late 1950s and early 1960s, when a spatial analysis paradigm began to take firm hold within the discipline (Gatrell *et al.,* 1996). Researchers borrowed freely from plant ecology literature, adopting techniques that had been used there in the description of spatial patterns and applying them to other contexts (Gatrell *et al.,* 1996). The spatial extent of pollution is critical as the mixing of pollutants occurs over a given distance. From a water quality management perspective accurate assessment of spatial and temporal variation of pollutant loadings in streams within a watershed is essential (Elshorbagy *et al.,* 2006). The risk associated with pollution depends on both the extent of the temporal and spatial variation of the pollutant (Remesan and Panda, 2008)

2.5 Statistical analysis

The temporal and spatial variation analysis only reflects part of the pollution impact factor. Statistical analysis and expert judgment can be used to transform data into information and provide a data base that is a reference point for the analysed data for meaningful decision support (Huang and Xia (2001); Schneider *et al.,* 2003; Brouwer and De Blois, 2008). Furthermore, statistical analysis can be used to get a broader understanding of the interaction between water quality parameter and isolating pollution impacts in relation to their source, therefore assisting in solving various pollution problems (Atasoy *et al.,* 2006; Strobl and Robillard, 2008).

2.6 Climate Change and water Quality

Global change studies have gathered information on the effects of climate change and factors predisposing the population to risk (Liu *et al.,* 2008). Knowledge of the effects of climate change is difficult to understand due to the complexity of climate. The presentation of different opinions and hypothesis needs to achieve a balance, with a complete perspective not just the summarization of information (Koutsoyiannis *et al.,* 2009).

The construction of reservoirs has enabled the withdrawal of water resources from a river system reducing the amount of water available to the down stream ecosystem. Climate has the capability to increase the impact of that reservoirs have already had downstream ecosystems and users (Lundqvist, 2000). The impacts of climate change need to be tracked through long term monitoring programmes focusing on the variation in water quality in river, lakes and wetlands (Kiparsky and Gleick, 2003). According to predictions by Matondo *et al. (*2004) most of the river basins in Swaziland will have a reduction in the amount of available water resources. The impact of future catchment management objectives should incorporate climate change, water quality and quantity. Changes in water bodies are already evident, such as increase in water temperature due to in increase in atmospheric temperature (Janssen *et al.,* 2005; Rivers-Moore and Jewitt 2007)

2.7 Integrated Water Resource Management and Water Quality

To ensure adequate quality and quantity of water within a river system the Integrated Water Resources Management (IWRM) approach is required (Rivers-Moore and Jewitt, 2007). The Swaziland Water Act was developed based on the IWRM principle therefore ensuring that water resources will be conserved, developed, used, and managed in a sustainable, efficient and equitable manner, Mlilo *et al.* undated). IWRM provides a platform for addressing transboundary issues including those pertaining to water quality (Huang and Xia 2001; McKinney, 2003). IWRM ensures that regulatory instruments cover water quality and water resource protection this is crucial in the management of Mbabane River with different sectors at sub-catchment and different countries (South Africa, Swaziland and Mozambique) represented at catchment level (UN, 2005).

STUDY AREA

3.1 Background

Swaziland is a small, land locked country located in south-south-eastern Africa. She is boarded mainly by the Republic of South Africa and by Mozambique on a small stretch to the east. The country has a maximum north south length of 193 kilometres and a maximum east-west width of 145 kilometres. Swaziland covers approximately 17,400 square kilometres and is divided into four climatic regions namely: the Highveld which receives the highest rains in the country followed by the middleveld, Lubombo and Loweveld, with the later being the driest region in the country with annual rain fall over the past decade less the 400mm (U.S. Army Corps, 1981). The total renewable water resources of the country are estimated at 4.51 km^3/year, with 1.87 km^3/year or 42 percent originating from South Africa (WHO, 2000). The country has five major rivers namely Lomati, Komati, Mbuluzi, Usuthu and Ngwavuma (*Appendix 1*).

3. 2 The Swazi Water Sector

Over the past decade the water sector in Swaziland has gone through much reform, with the Water Act of 2003 (which repealed the Water Act of 1967) and the current Draft Water policy which aims to meet the provision relating to water and environment as outlined in the country's constitution adopted in 2005 (SZWP, 2008). Furthermore the Water Act of 2003 established the National Water Authority (NWA) which is now the national custodian of the nation's water resources. Amongst its current responsibilities, the NWA has been tasked with the development of a Water Resources Master Plan to guide the development and utilization of water resources in the country.

3.3 Mbabane River

The perennial Mbabane River is the main drainage channel for the capital city of Swaziland, Mbabane, located in the North West. The mean annual rainfall in the river sub catchment is 1500mm and the rainy season occurs in the months of September to mid February. The winter/dry season falls in the months of June to August. The meteorological station has predicted a shift in weather patterns (shorter rainy seasons and wetter winters).

Mbabane River in the eZulwini Valley has three main tributaries Mvutsini River which carries along with it water from the hydropower station, and Mkhondolwane and Mzimnene Rivers toward the terminal end of the Mbabane River. The regional location of the Study area is shown in Figure 1 and Figure 2 shows 13.23 km reach of the Mbabane River, its tributaries and the sub-catchment activities.

The river banks are lined with extensive domestic dwellings and agricultural fields, mainly growing maize. The rural built-up areas have increased, comprising mainly of single rental rooms sharing pit toilets. The largely uncontrolled spread of development, much of it on steep land, is causing environmental degradation and the pollution of natural water sources, particularly on Swazi National Land (SNL) immediately outside the jurisdictions of Mbabane and eZulwini urban areas (The World Bank, 2002). The fields are close to the river banks and in some places, there is no river reserve. River water is used for irrigation of crops when the rains are in short supply. The banks of the river have visible signs of extensive erosion, resulting in siltation along the course of the river. This has changed the river course in some places. Other activities along the river include sand excavation of river sand for construction, which increases the erosion of the river banks. Car wash businesses are also present and are made possible by the ease of access to the river bank. Water from the river is used to wash the cars and the soapy water flows back into the river. Along the river corridor there is a wastewater plant which treats wastewater from the capital city and discharges the treated effluent into the Mbabane River.

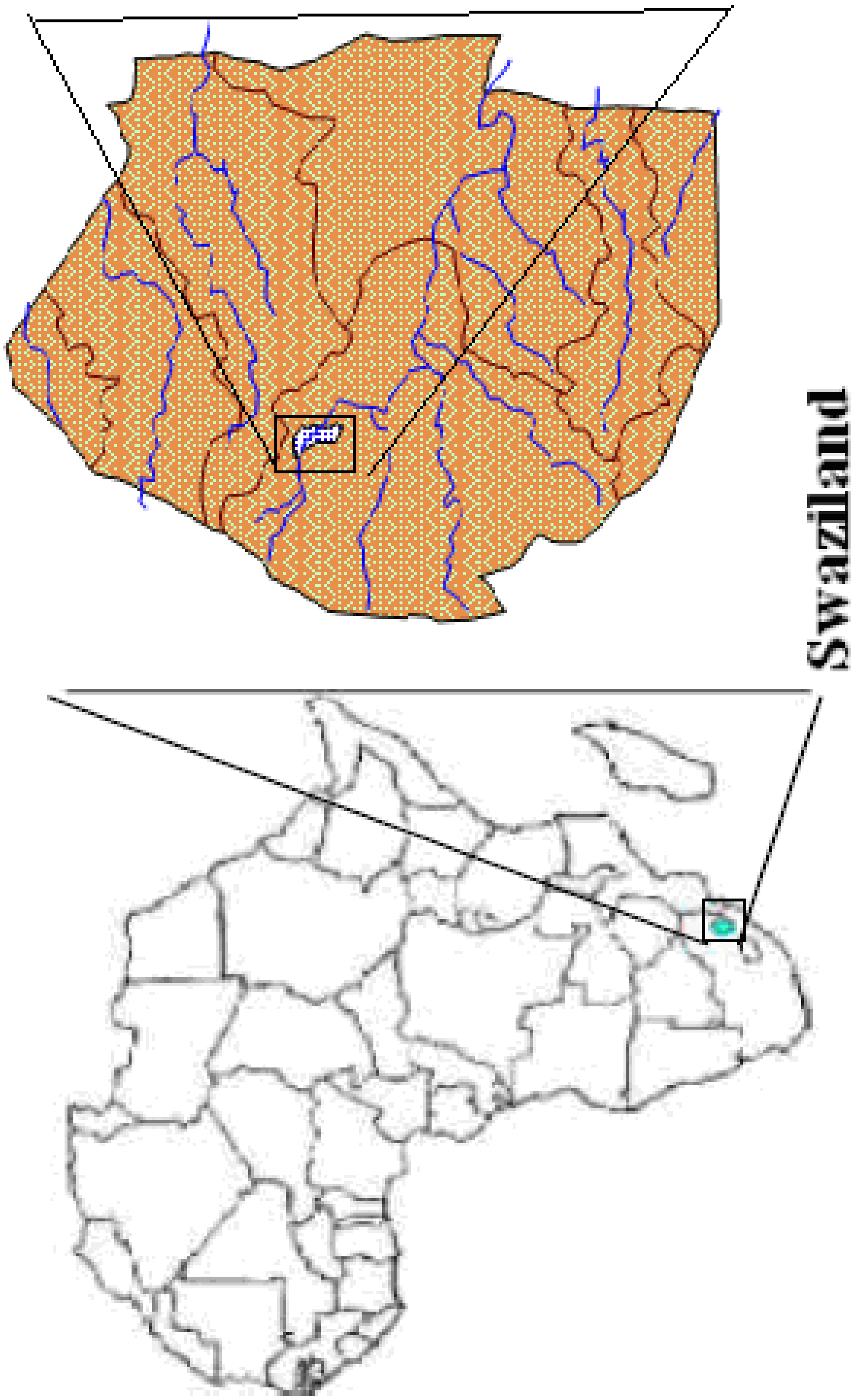

Figure 1: Study Area in relation to Regional location

Expanded view Figure 2

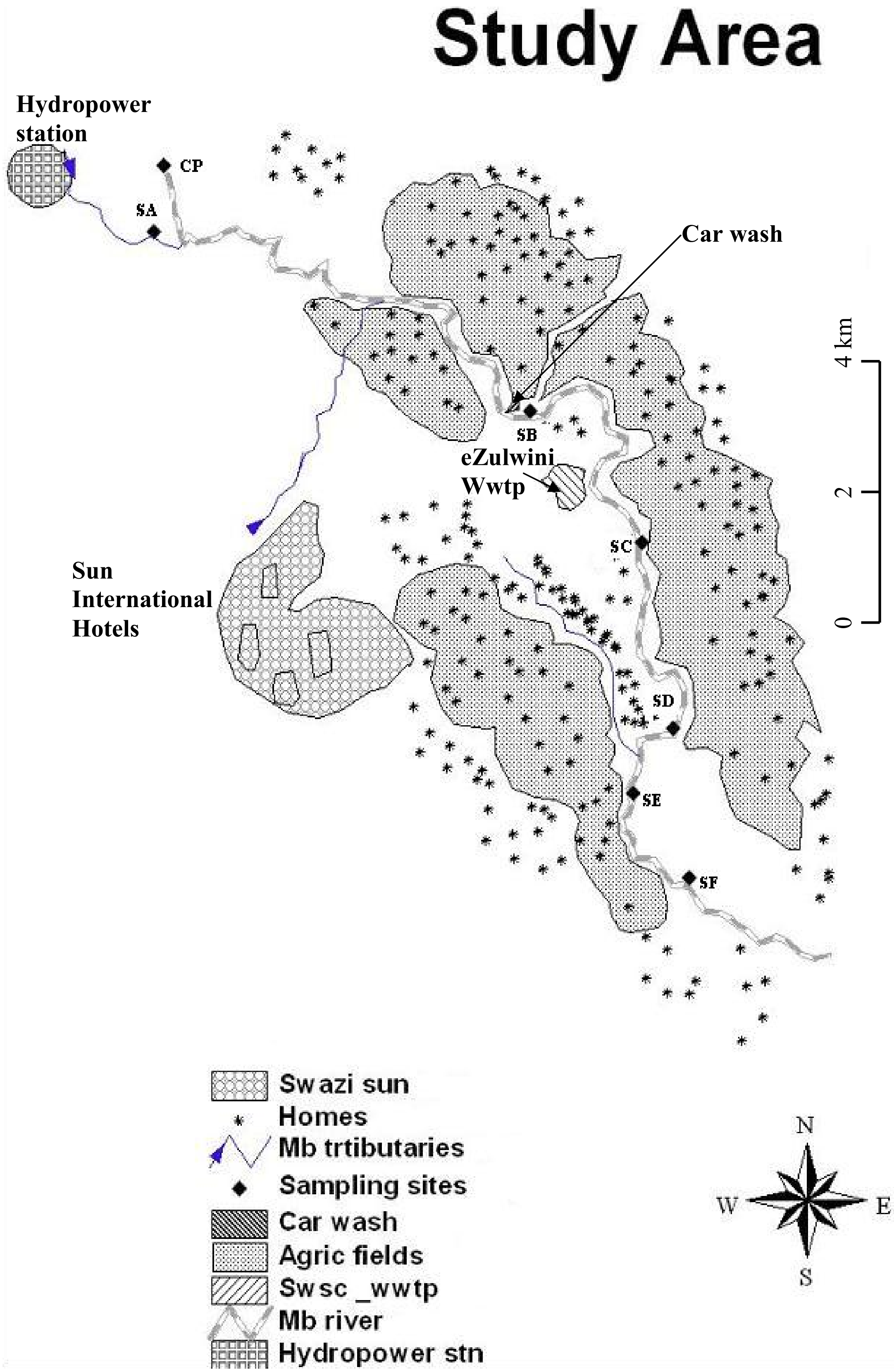

Figure 1: Study area showing sampling sites

MATERIALS AND METHODS

4.0 Introduction

The assessment of the water quality of surface water bodies depends on the designated beneficial use of the water body. The assessment takes into account local conditions such as the natural background levels of the parameters of the pollution event(s) being studied. The assessment of the water quality of a river receiving wastewater must consider that the main source of the river has a bearing on the rivers capabilities to absorb any further pollution impacts. The activities upstream of a discharge point can lower the receiving water quality before the wastewater discharge point reducing the rivers ability to absorb the extra pollution load (Juanico and Friedler, 1999). Water quality assessment is done on a dynamic system with various interactions among the systems spatial elements coupled with changes in structure and function of the system over time (Zhang, 2008). The use of models has enabled the study of complex dynamic system; however models are at present not significantly used in water quality management (Elshorbagy and Ormsbee, 2005).

4.1 Sampling

The study made use of 500mℓ polypropylene bottles for physico-chemical parameter analysis and 500mℓ pre-treated glass bottles were used for biological sampling, the later being stored in a cooler box during transportation and all samples were refrigerated until testing at 4-5 ^{o}C. The sampling consisted of identification of sampling sites, sampling procedure, identification of laboratory facilities, methods of laboratory analysis and analysed parameters.

4.1.2 Sampling sites

For the study, six sites were selected but during the course of the study, the results identified a gap that needed a seventh site to enable better interpretation of results. The sites were selected at strategic but easily accessible places, based on the presumption that there was a measurable problem at that location along the Mbabane River.

Two sites were selected upstream of the eZulwini wastewater plant (CP, SB) and three sites chosen down stream of the wastewater discharge point (SC, SD, SE). Two other sites were chosen, one on the head water tributary and the other below the confluence of Mbabane River and Lusushwana River (SA and SF respectively). The control point was selected based on the fact that is located before any of the discharge points in the eZulwini Valley and according to Nkambule (2001) by the time the water comes to this site any pollution from the capital city (upstream) would have mixed well with river water and the distance would have sufficed for self cleansing of the river. Table 1 shows the chainage of each site from the control point and its GPS coordinates.

Table 1: Sampling site Details

Site	Km	GPS Coordinates		Comments
Control Point (CP)	0.00	S26°22’37.31”	E31°09’44.00”	The site forms the head water control point for the survey for the 13.23 km river reach.
Site A (SA)	0.70	S27°22’51.26”	E31°09’37.07”	located 0.33km on the Mvutjini River before its confluence with the Mbabane River
Site B (SB)	5.91	S26°23′44.8″	E31°11’32.60”	Located after the confluence of Mbabane River with Mkhondolwane River and is 2.33 km before the WWTP.
Site C (SC)	8.81	S26°24′21.80″	E31°12′01.60″	Located 0.57 km after the WWTP just down stream of a human bridge. Riparian agricultural activity is evident.
Site D (SD)	10.93	S26°25′09.80″	E31°12′11.00″	Agricultural activity is also evident at the riparian area of the site. Siltation in the river is evident just above the site
Site E (SE)	12.02	S26°25′28.90″	E31°11′58.80″	The Mzimnene River confluence with Mbabane River occurs 0.7 km before Site. Signs of river sand excavation on banks
Site F (SF)	13.18	S26°25′49.47″	E31°12′14.44″	Located on the Lusushwana River of which Mbabane River is tributary.

4.1.2 Sampling procedure

Sampling for the study was done once a week and the sampling campaign was for a period of 8 weeks. The sampling started in mid summer (27th January 2009) and ended at beginning of autumn (17th March 2009). At each sampling site, both physico-chemical and microbiological samples were collected.

Sampling time was between 0900hrs and 1200hrs every week on Tuesday. The sampling period coincided with the hydropower operations and the maximum effluent outfall from the wastewater plant. Single grab samples were taken from the river at approximately 20 cm from the water surface and when sites were not accessible a sampling device designed by the National Water Authority was used to collect the sample. According to DWAF (1996) in shallow or fast-flowing water, a grab sample should be taken immediately below the water surface.

4.1.3 Laboratory Facilities

Two laboratories were chosen for laboratory analysis this was done to run cross laboratory check. The chosen laboratories were the National Water Authority laboratory under the newly formed National Water Authority (NWA) where physiochemical analysis was done and the Analytic laboratory under Swaziland Water Services Corporation (SWSC) where microbiological analysis was done.

4.1.4 Methods of *in situ* and laboratory analysis

Analysis of parameters was done *in situ* and in the laboratory using the following Standard Methods (2000). *In situ* measurement of Dissolved Oxygen and Temperature were done using a WTW Oxi 330i Meter with a low-maintenance probe which operates for up to six months between membrane changes. Galvanic probe needs no warm-up time. The meter was NEMA 6 and IP67 rated. (*Appendix 2*)

Physiochemical analysis was done at the NWA laboratory using the LOVIBOND® - Photometer PC MULTIDIRECT for analysis of water. The PC MultiDirect is a modern, microprocessor-controlled photometer with a user friendly keyboard and large graphic display. It features a broad selection of pre-programmed methods based on the proven range of Lovibond® reagent tablets, liquid reagents, vial tests and powder reagents (VARIO Powder Packs). (*Appendix 3*). Quality control was done by laboratory cross check with SWSC utilising Standard Methods. For the purpose of this study the PC MultiDirect was suitable though it not a standard method.

BOD measurement was done using the OXITOP® BOD sensor. The classical application field for the OxiTop® Control measuring heads and controller is the BOD_x determination (BOD_x = Biochemical Oxygen Demand for the time x). The evaluation of biological degradability (e.g. test according to OECD 301F) is also part of this field. (*Appendix 4*)

4.1.5 Analysed Parameters

The selection of parameters was based on their relation with the possible parameters present in wastewater, agricultural runoff and anticipated waste from domestic activity. This was done to compare the levels of these parameters in the receiving waters before and after the possible points of entry of the possible pollution. This made it possible to assess the impact of the wastewater, runoff and tributary discharge on the receiving water quality. A summary of the analysed parameters is shown in Table 2.

4.2 Quality Assurance

To prevent cross contamination with previous samples none sterile bottles for physic-chemical samples were rinsed once with the sample waters. For some sites a sampler designed by the laboratory was used to collect samples. The sampler was also rinsed once each time it was used to reduce cross contamination between samples. Care was taken not to lower the sampler mouth to the sediment which would collect sediments and contaminate sample. The sampler was a simple tool designed to collect approximately 500mℓ of a sample. The sampler was cast into the water toward the centre of river and after it had drawn water it was pulled in and the sample was poured into sample bottles (*Appendix5*).

Table 2: Analysed Parameters and method used

PARAMETER	METHOD	UNITS
Temperature	Measured *in Situ* using Dissolve Oxygen Meter WTW Oxi 330i	^oC
pH	PC Multi-Direct Lovibond Photometer selecting Method 330 - pH – Value 6.5 – 8.4	pH Value
Total Alkalinity	Multi-Direct Lovibond Photometer selecting Method 30 - Alkalinity Range 5 – 200 mg/ℓ	mg/ℓ $CaCO_3$
Ammonia (NH_4^+)	a PC Multi-Direct Lovibond Photometer selecting Method 60	mg/ℓ N.
phosphorous(PO_4^{3-})	PC Multi-Direct Lovibond Photometer selecting Method 320 – Phosphate, ortho LR with tablet, Range 0.05 – 4mg/	mg/ℓ PO_4
Dissolved Oxygen (DO)	*in situ* using Dissolve Oxygen Meter WTW Oxi 330i Kit in mg/ℓ	mg/ℓ
Biological Oxygen Demand	OXITOP® BOD sensor in a closed system	mg/ℓ.
Chemical Oxygen Demand	Colorimetry (low range 0 – 150mg/ℓ) at wave length 420nm	mg/ℓ COD LR.
Faecal Coliform	Membrane filtration, incubation for 24hrs at 44.5 ^oC on m-FC agar	FC /100mℓ of water

The Temperature and Dissolved Oxygen measurement was done *in site* using the WTW Oxi 330i Kit which gave both reading simultaneously. The meter was given time to stabilise before reading were taken. Care was taken to prevent samples from being oxygenated leading to wrong DO reading. All instruments were calibrated a week before the sampling campaign. Laboratory vials were cleaned and care was taken to zero the meter before each test, a full analysis procedure can be seen in Appendix 3. Samples were analysed within 24 hours and stored in refrigerator (at 4–5^oC) if not analysed on the day of sampling.

4.3 Analysis of Results

The analysis of water from a grab sample represents a very short time period (one hour) for many chemical measurements, such as ammonia. Nevertheless, when river discharge is stable, a grab sample is also supposed to be stable for at least a day, if not more, for parameters such as nutrients, dissolved oxygen, pH, conductivity, calcium and bicarbonate (Chapman, 1996).

4.3.1 Water Quality Standards

The parameters were analysed against Schedule One, Water Quality Objectives (Regulations 2 and 3) and Schedule Two, Effluent Standards (Regulations 2 and 4) of the Swaziland Water Pollution Control Regulations, 1999 (ELAW, 2009) the Standard values are shown in Table 2.

Table 3: River Water Quality Standards

Parameter	Unit	Surface water	Effluent
Temperature	^{o}C		35
pH	pH units	6.5 - 8.5	5.5 - 9.5
Dissolved Oxygen (O)	mg/ℓ O	4	Minimum 75%
Chemical Oxygen Demand	mg/ℓ O	10	75
Biological Oxygen Demand	mg/ℓ O	5	10
Ammonia (NH_4^+)	mg/ℓ N	0.6	
PhophatePO_4^{3-}	mg/ℓ PO_4^{3-}	2	2
Faecal Coliform	per 100mℓ	01-10	10

4.3.2 River Discharge

In the study of river water resources the rivers hydrological regime is the governing factor, i.e. their discharge variability (Chapman, 1996). Discharge can be estimated from the product of the velocity and the cross-sectional area of the river. It should be measured at the time of sampling and preferably at the same position as water samples are taken (Bere, 2007). For the this study it was not possible to make flow records at each site due to the budget and time slot allocated to the study by the National Water Authority Laboratory and the river did not have a gauging station. This study made use of daily discharge of a river within the same catchment which is at the same flow stage as the Mbabane River to illustrate the variation of discharge as both rivers fall in the same rainfall canopy. The data was coupled with estimate flows of the hydropower station output which regulates the rivers base flow.

4.3.3 Temporal and Spatial analysis

To carry out temporal analysis the spatial variation was assumed to be fixed at a particular site. For Spatial variation the time was fixed to a day. Chapman (1996) stated that the conditions in a stream can be considered stable over a period of 1 hr to 24 hours if the river discharge is stable. The Mbabane River is regulated by the presence of a hydropower station upstream which has managed releases from the dam therefore regulating the amount of discharge in the Mbabane River. The sampling on this study was done within two hours within which the river conditions could be considered stable.

4.3.4 Statistical Analysis

The Pearson Correlation Coefficient and Linear Regression in Ms Excel 2003 were used to measure the significance of known and possible relationships among assessed parameters.

4.3.5 Historical Data

Historical Data was obtained from the National Water Authority Laboratory for the period March 2005 – June 2008. Although the Data had many gaps, some information from the analysis could be gathered about the state of the river and the effluent quality. The data obtained was only for Site B which was located upstream of the eZulwini wastewater plant. The data enabled comparison of past water quality corresponding to the same study period.

4.3.6 Descriptive Numerical Analysis of Results

Descriptive methods have been described by Esterby (1996) as the trend analysis methods "which do not involve either formal hypothesis testing or estimation and include graphical methods and summary statistics". And can be used from the initial inspection of data to results presentation.

4.3.6.1 Oxygen Saturation

The American Society of Civil Engineers Formula (1960) was used for descriptive numerical analysis of Dissolved Oxygen Saturation to assess the DO deficiency trend.

$$\mathbf{DO_{sat} = 14.652 - 0.41022T + 0.0079910T^2 - 0.000077774T^3} \qquad \mathbf{(1)}$$

Where: DO_{sat} – Dissolved Oxygen Saturation concentration in mg/ℓ
T – Water Temperature.

Equation one was used to assess the expected (saturation) Dissolved Oxygen concentration at any given time for the given water temperature. The calculated value was measured compared to the actual (measured) dissolved Oxygen concentration recorded at the site and the dissolved Oxygen deficit was calculated and presented as percentage Dissolved Oxygen deficiency. The values were compared against Chemical Oxygen Demand which is used as a measure or organic pollution (Chapman, 1996). For organic pollution Chemical Oxygen Demand can be useful as a pollution index (Chen *et al.,* 2007).The equation was used with the assumption that temperature is the significant factor for DO_{sat} concentration in the Mbabane River. There use of this assumption is justifiable and was demonstrated by Tesfaye (2007). Deviations from the Expected value could be attributed to other factors such as COD.

RESULTS AND DISCUSSION

5.0 Introduction

This section of this document presents the results and their discussion. The mean values of analysed parameters are presented in Table 4. The mean values were obtained from 30 – 40 data units of each parameter. The results represent the water quality of the Mbabane during the assessment period between January and March 2009.

Table 4: Mean of Measured Parameters

Site	**Temp. ^{0}C**	**pH**	**TA (mg/ℓ)**	**NH_4^+ (mg/ℓ)**	**PO_4^{3-} (mg/ℓ)**	**DO (mg/ℓ)**	**BOD (mg/ℓ)**	**COD (mg/ℓ)**	**FC / 100mℓ**
CP	20.6	6.92	25.75	0.11	0.25	6.35	1.0	3.25	3237.5
SA	23.3	7.19	24.67	0.07	0.26	5.60	4.0	19.75	1645.00
SB	22.6	6.98	20.86	0.09	0.26	6.06	2.3	26.50	1458.75
SC	23.3	7.16	27.43	0.09	0.39	5.84	1.5	12.38	2096.25
SD	23.8	7.12	23.43	0.11	0.30	5.84	3.3	11.50	1643.75
SE	23.4	6.90	28.50	0.13	0.35	5.59	1.0	6.50	1202.50
SF	24.5	7.19	22.33	0.05	0.19	5.85	2.0	15.25	1692.50

Figure 3 shows the estimated temporal variation in discharge of the Mbabane River over the sampling period. The graph has a base flow of 10 m^3/s discharged at maximum out put of the hydropower station. According to Brydesten *et al*. (1990) dams enable the distribution of flow over a year to maintain hydropower power plants. Miller, (2001) and Shen *et al.* (2005) used the dam outflows in a similar manner to represent the mean daily flows below the dam. Jourdonnais *et al.* (1990) noted that dams can be able to regulate lake volumes and river flow levels, releasing water at specified volumes such as for hydropower generation even during dry winters. The variation is representative of discharge from station GS15 upstream of the Luphohlo Dam which illustrates the effect of rainfall events during the sampling period as the hydrograph from the river data showed peaks on the rainfall events recorded during the study period.

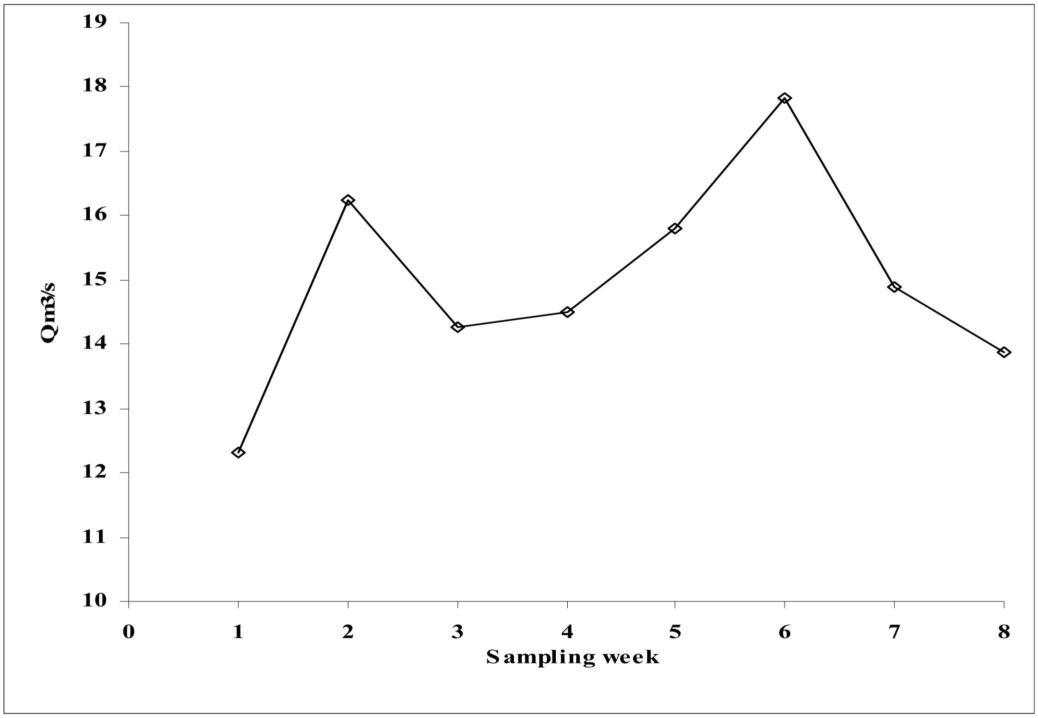

Figure 2: Temporal Variation in discharge

5.1 Temporal Water Quality Variation

This section presents and discusses the temporal variation of parameters at the Control Point, Sites A to F. The temporal variation was over 8 sampling weeks and discussed in relation to the estimated discharge of the river over the same period.

5.1.1Temperature

The Temperature (Figure 4) showed a random trend over the sample period within a range of 22 to 25.7 ^{o}C. All sites in the first half of testing period (week one - four) showed an increase in temperature with a peak on the second week and a decline toward the end. However Site A showed a decline from the first sampling week till the fourth week. This could be attributed to the fact that the waters at Site A were predominantly from the hydropower power station. The temperature of the water could be influenced by the thermal stratification in the dam. This observation is supported by Baldwin *et al.* (2009) who stated that dams affect the riverine system below the dam, changing characteristics such as temperature, flow and morphology.

According to Zimmerman and Dortch (1989) the deleterious effects of the Hydropower operation scenarios can be ameliorated using a flexible seasonal release plan based on knowledge of river water quality and likely meteorological conditions.

The temperature in the second half of the sampling campaign showed a uniform trend among all sites within a range of 21.7 to 25.7 ^{o}C, the control site CP fell outside the range with its own range which was 19.8 to 22.1 ^{o}C. This variation from the other sites could be attributed to the sites location under a tree canopy provided by a dense forest.

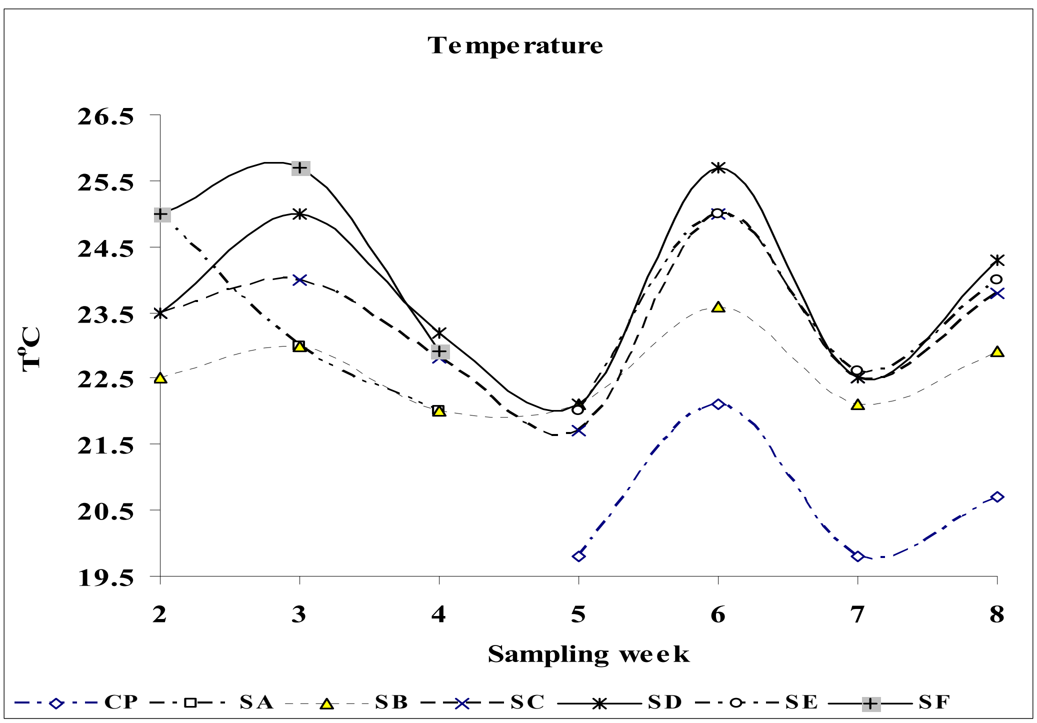

Figure 3: Temporal Variation of Temperature

The temperatures of inland waters in South Africa (a regional representation) generally range from 5 – 30 ^{o}C. Thermal characteristics of running waters are dependent on various features of the region and catchment area (DWAF, 1996). The temperature variation exhibited by Mbabane River was within range of rivers in neighboring South Africa.

5.1.2 pH

Figure 5 shows the temporal variation of pH in the Mbabane River within the upper and lower set limits (8.6 and 6.5). The first half of the sampling campaign showed a uniform trend among sites with the exception of Site A which showed a steeper decrease in pH and steep increase toward the end of the first half of the sampling campaign. This could be attributed to the greater volume of water at the site was originating from the hydropower plant and thus the semi-stagnant state of the water within the dam could be leading to the difference in the pH of the water.

During the second half of the sampling campaign, most sites had measured pH values below the lower limit and this could be attributed to the dilution of the ions in the water that influence pH or the disturbance of sediments which can result in the release of sediments leading to reactions that lower the pH. Site C was an exception with pH levels maintained above minimum standard (6.5). This could be attributed to the wastewater having had a buffering effect on the acidic nature of the water during the second half of the sampling campaign, but was not enough to maintain the pH downstream as the water pH dropped by Site D. However the river showed recovery by Site E at pH 6.48.

The Control Point showed an irregular pattern which could be explained by activities that were occurring upstream where water from the river was used for washing at the river banks. Figure 3 and 5 showed that pH had an inverse relationship with the river discharge. These similar results were observed by Calles *et al*. (2007), *i.e.* that when discharge increases there was a drop in pH.

According to DeCesare and Connors (2002) water quality conditions, which do not meet criteria but are “naturally occurring” (e.g., low pH in some areas) do not constitute violations of the standards. However pH levels have a role in the form in which parameters exist in water i.e. high pH results in the higher relative proportion of the toxic NH_3 molecule instead of the ionic NH_4^+ therefore affecting the aquatic equilibrium, (Chapman, 1996). On the contrary low levels of pH can cause the release of toxic metals present in sediments (DWAF, 1996).

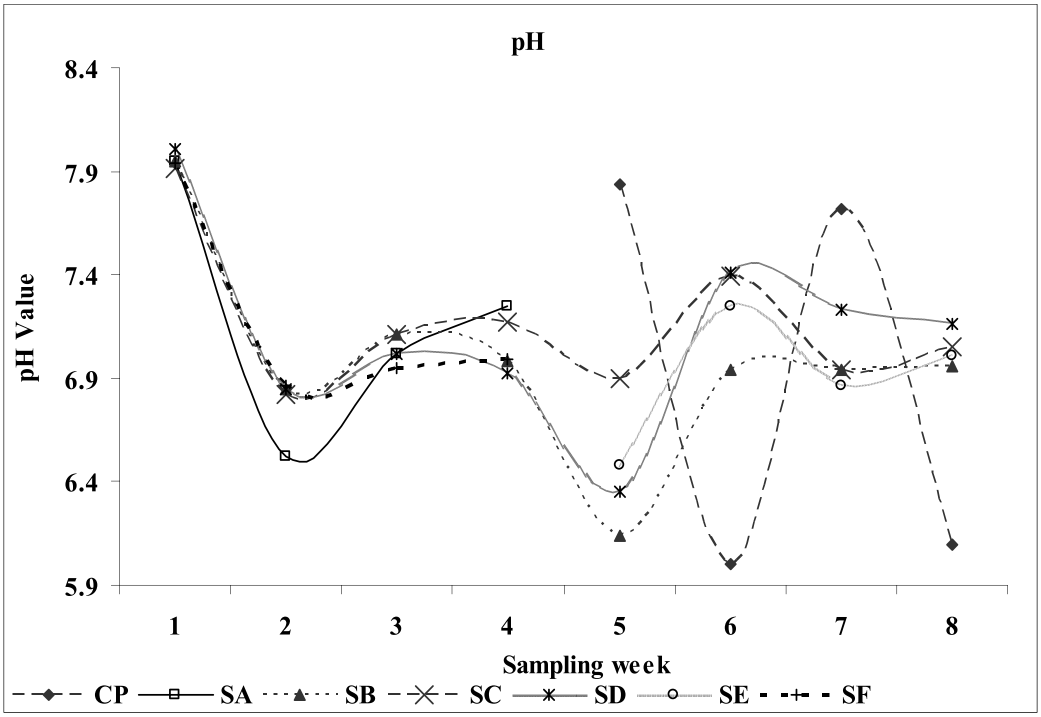

Figure 4: Temporal Variation pH

5.1.3 Total Alkalinity

The total alkalinity (Figure 6) showed a random trend for the assessment period. Site CP had the lowest peak reading of 14mg/ℓ $CaCO_3$ and Site C located down stream of the wastewater outfall had the highest peak at 45mg/ℓ $CaCO_3$. This implied that the wastewater had a positive impact on alkalinity, this corresponds with the effect the wastewater discharge had on pH as explained in sub-section 5.1.2.

Sites A and E showed a difference in the variation of alkalinity. At Site A the variation could be attributing to the activity in the dam which also affects pH of water. Variation of alkalinity at Site E could be affected by the entry of water from the Mzimnene River which has its confluences with Mbabane River Upstream of Site E.

In a study of the impact of municipal sewage on river water quality Lewis (1986) measured the alkalinity before and after the wastewater outfall and found that the value of alkalinity was 292 mg/ℓ before the outfall and 312 mg/ℓ 100m after the wastewater outfall.

These results also showed that wastewater increased the alkalinity concentration in receiving waters as observed in the Mbabane River. It can be concluded that the wastewater increases the basic nature of the receiving waters. If the water is acidic, wastewater can have a positive impact of neutralizing the receiving waters.

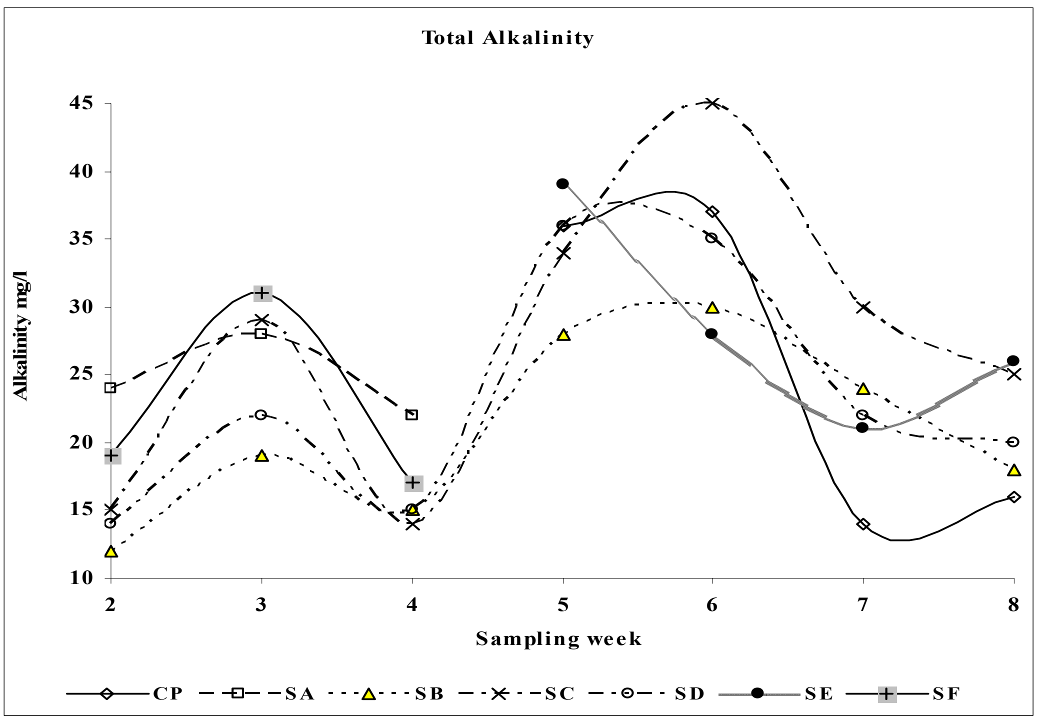

Figure 5: Temporal variation of Total Alkalinity

5.1.4 Ammonia

The Temporal variation of ammonia (NH_4^+) is shown in Figure 7. The figure showed that for the duration of the assessment ammonia was recorded below the standard 0.6 mg/ℓ N. Concentration for the first half of the sampling campaign were generally lower than those of the second half. Sites B, C and D showed the same random trend with peaks on the week two and six.

Figures 3 and 7 show the variation of discharge and ammonia. The relative picks can be observed at the same time intervals (weeks two and six). Chapman (1996) stated that an increase in discharge results in a dilution of the variables at constant loading i.e. from point source pollution. The ammonia values however in this data showed an increase with increase in discharge.

This could be attributed to the agricultural activity on the river banks. Ammonia is a constituent of fertiliser and the increase could be attributed to the carriage of fertiliser by runoff during the rainfall events on the days of sampling. This means that the ammonia concentration during or after an immediate rainfall event is affected by contribution of ammonia loading from the non-point sources (agricultural fields) especially during the growing season which coincided with the study period.

High pH results in the higher relative proportion of the toxic NH_3 molecule instead of the ionic NH_4^+. Figure 5 and 7 are in agreement with DWAF (1996) as the higher pH values corresponded to lower ammonia levels and *vice versa*. The results therefore do not account for total ammonia in the water, but show the variation in relation to Discharge and pH.

The higher level of ammonia in at Site A (SA) can be attributed to the reservoir catchment activity. In a study conducted by Liu and Yu (1992) it was shown that dams tend change water quality parameter such as increase in ammonia concentration. This could explain the results obtained from at Site A.

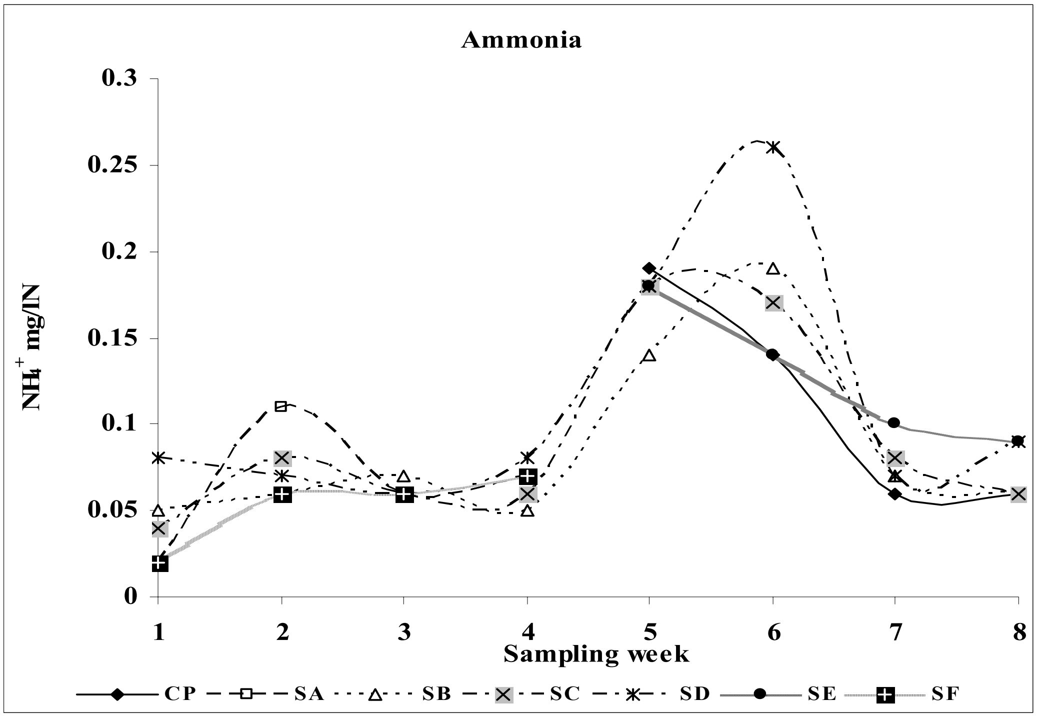

Figure 6: Temporal variation of Ammonia

5.1.5 Phosphorous

The temporal variation of Phosphorous is shown in Figure 8.The figure showed that for the duration of the assessment phosphorous was recorded below the standard 2mg/ℓ. The variation of Phosphorous showed a similar trend among sampling sites with lower value in the first half of the sampling campaign. Site C located after the wastewater outfall showed relatively higher trend values than all other sites. This indicated that the wastewater had an effect on the level of Phosphorous in the river.

The variation of Phosphorous showed a positive relation to variation in discharge with a peak at all sites on Week Six and generally followed the trend of discharge as seen in Figures 3 and 8. This could be attributed in the same reason as with ammonia since both Phosphorous and ammonia are constitutes of fertiliser and are carried by runoff into rivers during rainfall events.

The highest average value in the data set was 0.594 mg/ℓ PO_4, which was almost a quarter of the standard value. According to DWAF (1996) the waters of Mbabane River even after wastewater discharge according to the test results had levels of PO_4^{3-} as those found in pristine waters. Common concentrations of phosphorous in South

African river are between 10 and 50mg/ℓ and up to 200mg/ℓ in enclosed saline waters.

However the riparian agricultural activity may impact on the river water quality as the wastewater plant output increases especially during the crop growing season. According to Yang *et al.* (2000) eutrophication in rivers results from the accelerated fertilisation of surface waters arising from phosphorous pollution associated with discharge of wastewater and agricultural drainage. In a study of the Berg River, South Africa De Villiers (2007) showed that profile peaks of Nitrogen and Phosphorous compounds occurred during high runoff conditions, consistent with a diffuse pollution of water resources from agricultural runoff. The same was observed in this assessment of the Mbabane River.

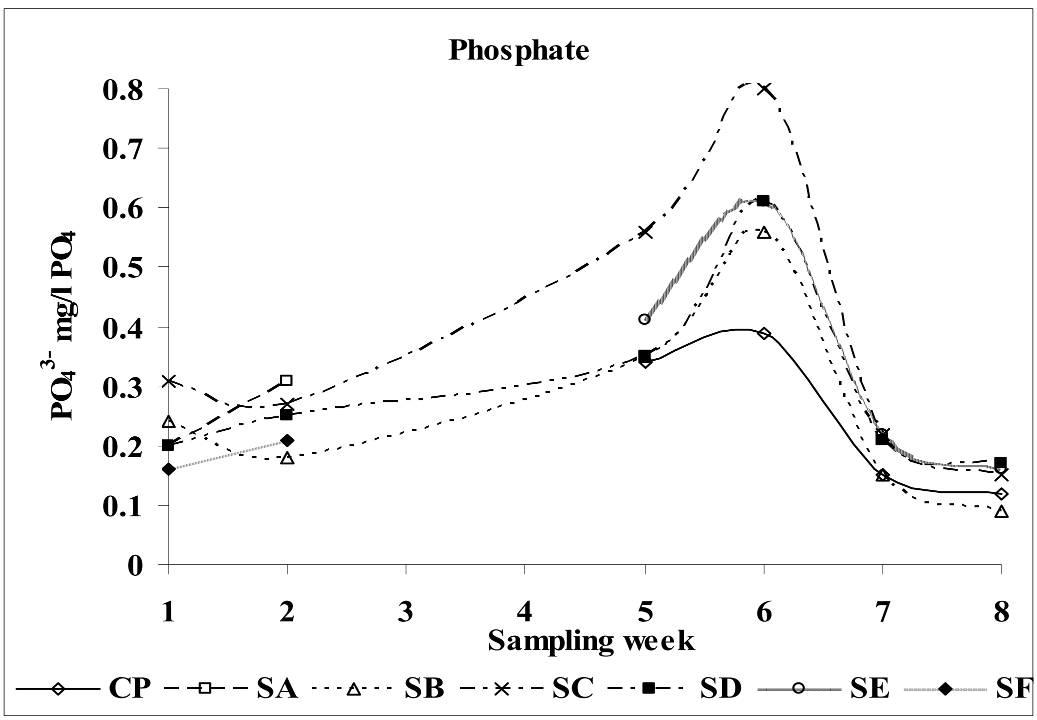

Figure 7: Temporal Variation of Phosphorous

5.1.6 Dissolved Oxygen

The temporal variation of dissolved Oxygen (DO) for all sites is depicted in Figure 9. The data set started on the third sampling week. The DO for all sites through out the sampling campaign was recorded above the standard value (4mg/ℓ). Kannel *et al.* (2007) stated that an increase in river discharge from a rainfall event carries with it by runoff organic matter which reduces the Dissolved Oxygen by biodegradation due to increases respiration off organisms. This could have been the possible cause for the decrease in dissolved Oxygen with increase in discharge as seen from Figures 3 and 9.

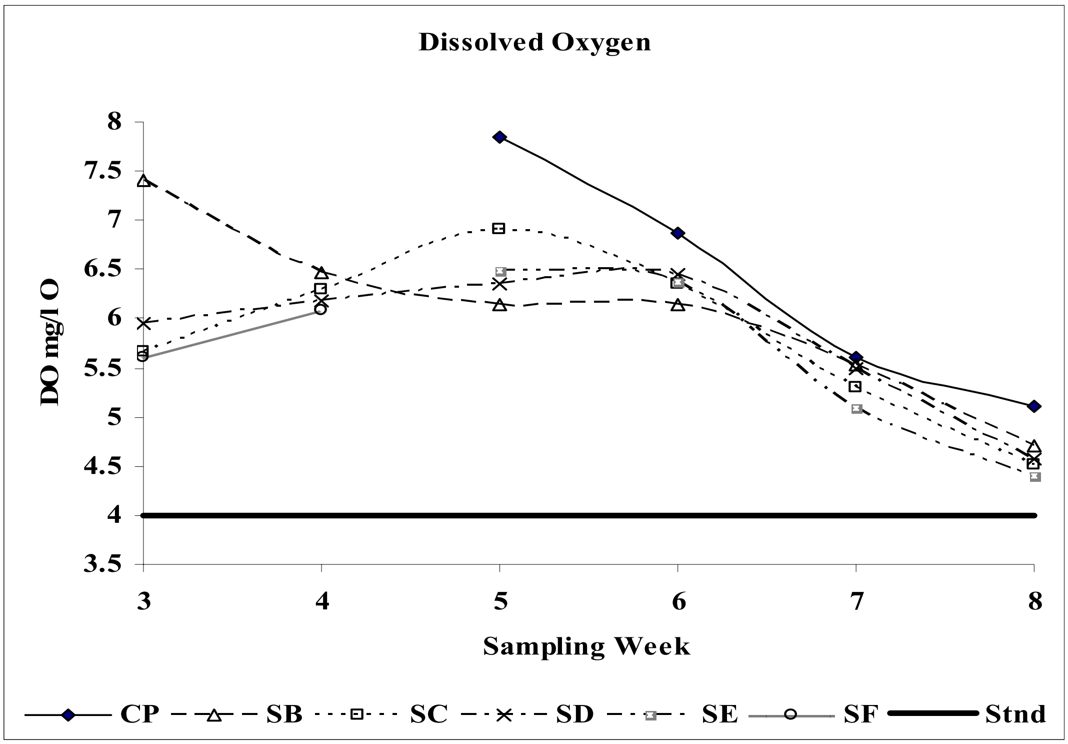

Figure 8: Temporal Variation of DO of all test sites

5.1.7 Biological Oxygen Demand and Chemical Oxygen Demand

The temporal variation of Biological Oxygen Demand is shown in Figure 10. The Figure is a scattered data set, but it can be seen that the BOD levels were higher in the first half of the sampling campaign corresponding to lower DO levels. It can be seen that BOD is also affected by the trend in the discharge, with BOD levels corresponding with lower discharge and *vice versa*. This could be attributed to the dilution effect of the increased discharge leading to lower BOD mg/ℓ in the sample.

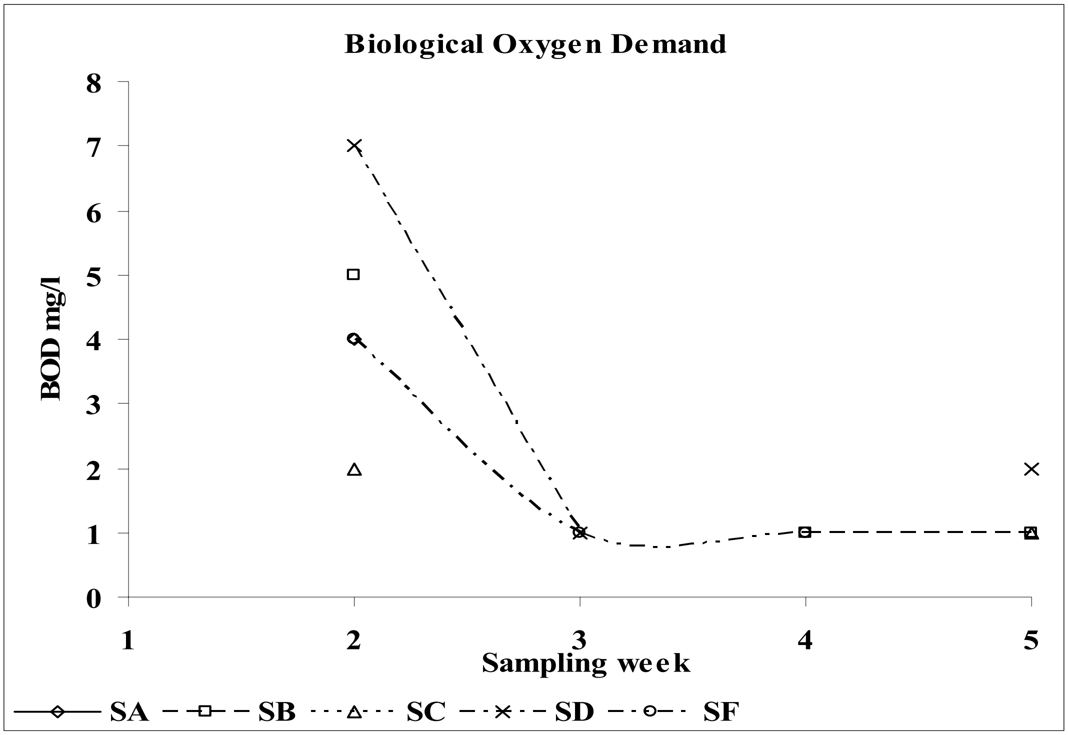

Figure 9: Temporal Variation Biological oxygen Demand

The temporal variation of COD is shown in Figure11. It can be seen that the COD concentration were predominantly above the standard value (10mg/ℓ) in the first half of the sampling campaign with a significant note of Site B on the first sampling week with a value out of the graph range at 141mg/ℓ COD. This high value could be attributed to the car wash business that was operational at the sampling site.

Site A showed relatively higher values of COD. This could be linked to dam activities (such as sedimentation, convection currents), which influence the quality of water flowing at the site. Site C located after wastewater outfall showed higher reading, this showed that the wastewater discharge had a negative impact on the water quality of the river by increasing the COD concentration in receiving waters. The impact can be seen in comparison of Figure 9 and 11 which show that the increase in COD caused a decrease in the levels of DO in the receiving water.

The COD trend when compared to the discharge trend showed that there was an inverse relation between the two (Figure 3 and 11). In the first half of the sampling campaign the discharge lows corresponded to COD highs and *vice versa*. The same trend can be seen in the second half of the sampling campaign. It could suggest that the levels of COD fell below the standard value on the second half because the discharge increases. The increase river discharge results in dilution of COD resulting in lower readings in the second half of the sampling campaign.

The concentrations of COD observed in surface waters range from 20 mg/ℓ or less in unpolluted waters to greater than 200 mg/ℓ in waters receiving effluents (Chapman, 1996). For this study of the Mbabane River the COD concentrations showed that they were influenced by the river discharge. During dry winter months the COD concentrations can constantly be higher than the standard value.

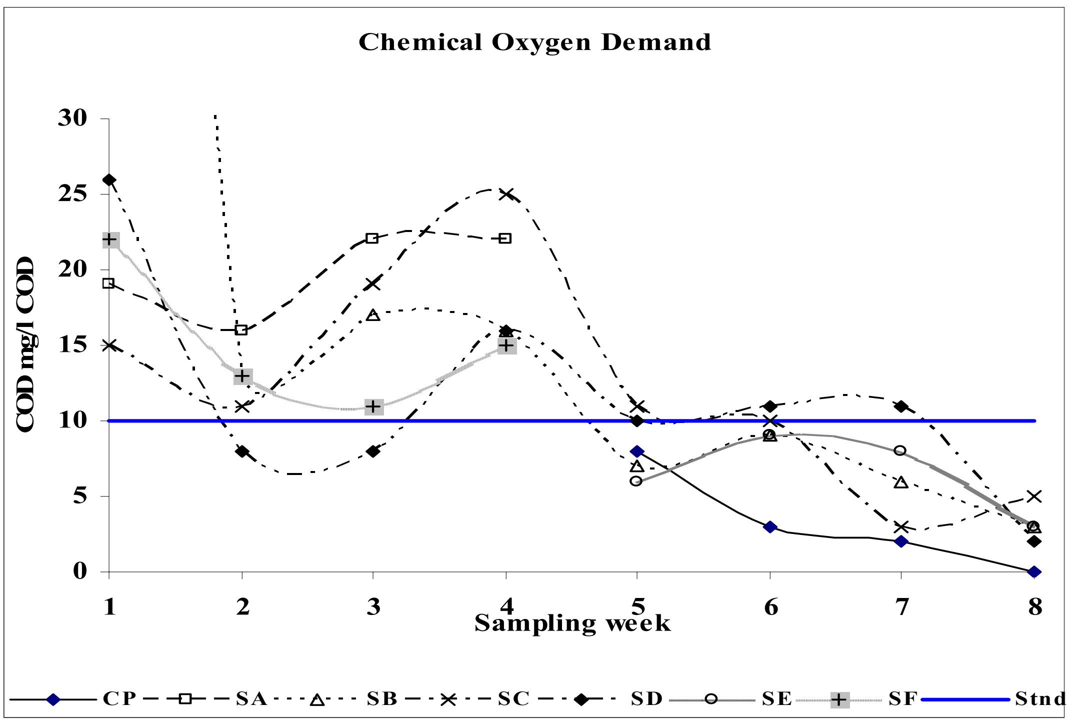

Figure 10: Temporal Variation Chemical Oxygen Demand

5.1.8 Fecal Coliform

The variation of Fecal coliform (FC) in the Mbabane River can be seen in Figure 12. The standard value for FC is exceeded at all sites with the lowest value recorded was 10 times the standard value. Highest values were 6900 FC/100mℓ at CP and 6300 FC/100mℓ at Site SC. Sites generally showed higher values of FC as the first sampling point after wastewater outfall from the plant. With the exception of Site CP, the trend of FC showed an inverse relation with the river discharge though the peaks are the same. At lower discharge the FC values are high as can be seen from the first half of the sampling campaign in reference to Figures 3 and 12. This could be attributed to the dilution effect of the increase in river discharge diluting the FC counts per 100mℓ. The same was observed by Sinclair *et al.* (2009) that during low flows faecal coliform counts were higher than in high discharge which is the same as in this study. At site CP the increase in FC counts could be attributed to the residential areas located upstream of the point.

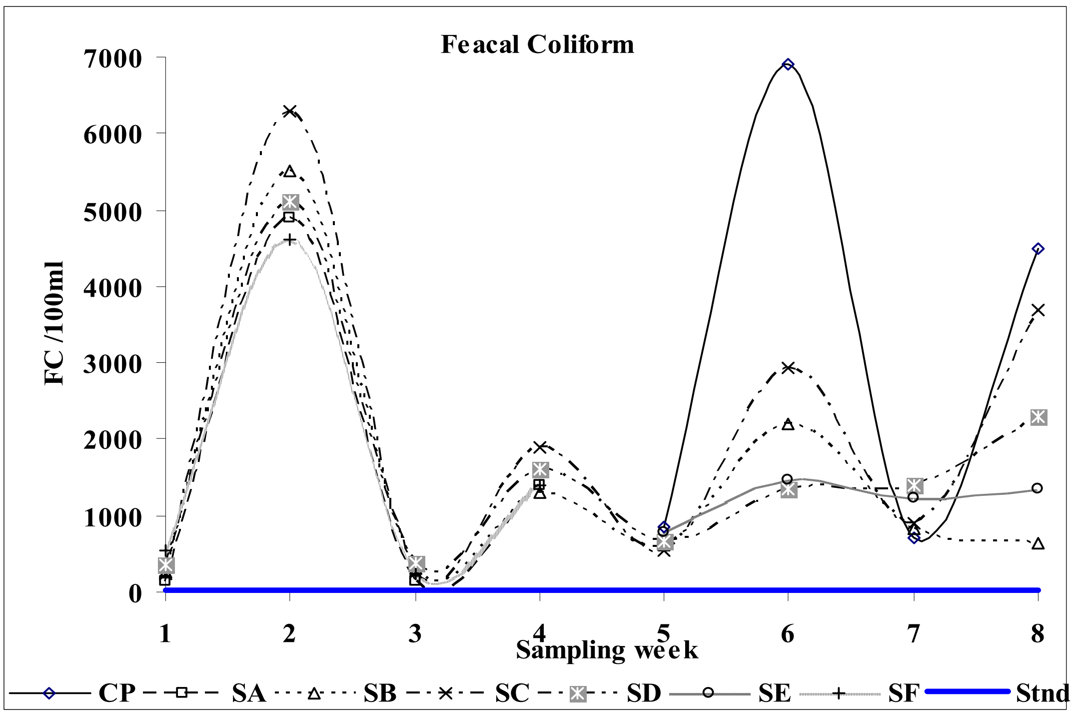

Figure 11: Temporal Variation Faecal Coliform

Temporal assessment of river water quality is affected by variation in rainfall and runoff from surrounding activities along the river (Carlisle, 2009). River flow variability due to rainfall and runoff can explain the differences in temporal variation of variable concentration and trends over time. To unravel this dynamics it is important to obtain fine scale flow data such as daily or hourly flows (Chang, 2008)

5.2 Spatial Variation

Spatial variation was done to assess the difference in parameter concentration at all sites. Comparison is possible between upstream and downstream sites. It enabled the identification of key areas of pollution along the river reach. The graph represents the spatial variation from Site CP (0 km) to Site E (12 km). Spatial variation was done for all sites sampled on the campaign along the 12km reach.

5.2.1 Spatial variation of Temperature

Temperature (Figure13) showed random variation from the headwaters to down stream. The temperature variation between sites showed that the sites which were sampled at the end of each campaign showed a relatively high temperature than those sampled first. This could be due to the exposure of the water to a longer heat absorption period hence at time of sampling they have a higher temperature.

The spatial variation could be as a result of the time between sampling points, approximately 20 minutes with total sampling time at 2hours from Control Point to Site E. Site CP is located within a forest where as all other sites are exposed to the thermal radiation of the sun, which resulted in better energy absorption that increased the water temperature. This was also observed by Douglas and Swank (1975) that stream under a cover tend to be shielded from sunlight affecting the water temperature even during summer months.

The sites downstream had more radiation exposure time, resulting in higher temperatures. River-Norris and Jewitt (2007) observed that the water temperature changes as a river flows though different climatic regions with variation in atmospheric temperature. The Mbabane River source is in the Highveld and the study area is in the Middleveld where temperatures are warmer.

DeCesare and Connors (2002) stated that water temperature due to discharge should not change by $\pm 1.7^{o}$C. All sites recorded a deviation in temperature less than $\pm 1.7^{o}$C from the average value with the exception of Site D with a positive deviation of 1.9^{o}C.

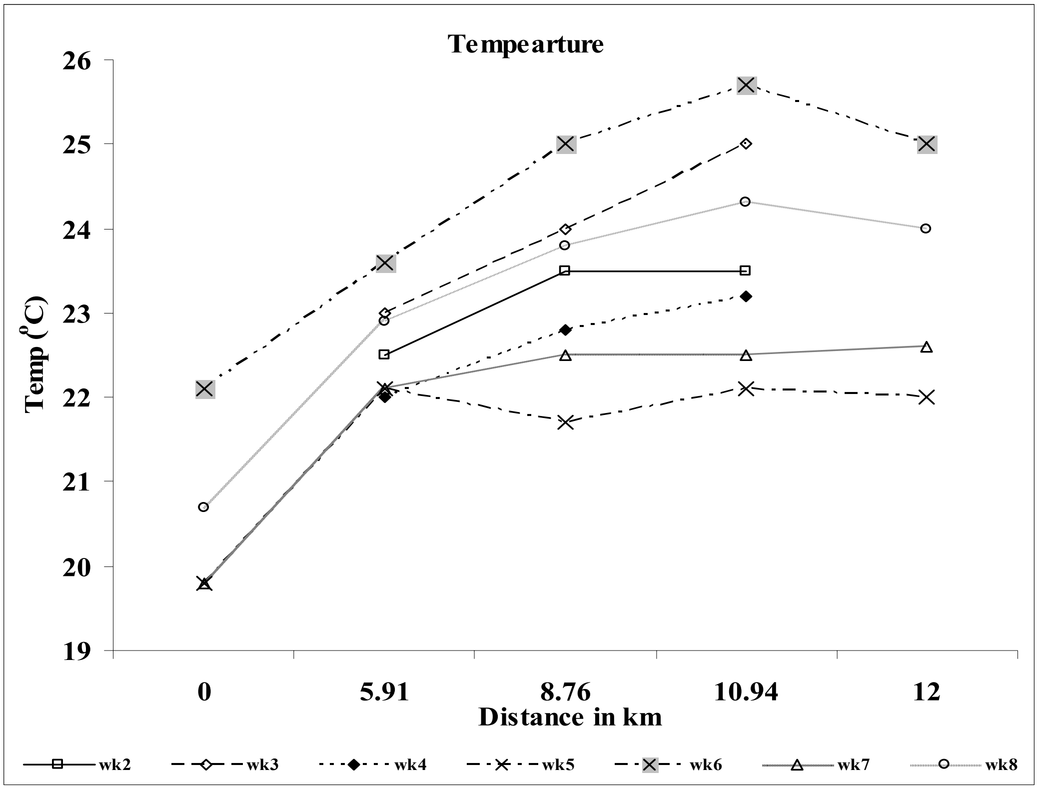

Figure 12: Spatial variation of Temperature

5.2.3 Spatial variation of pH

The spatial variation of pH is shown in Figure 14. The pH variation showed similarity in the head waters and downstream. When pH is high upstream it was high downstream and *vice versa*. The pH increases at Site C after the wastewater outfall, and it can be clearly seen on Week five, indicating the significant impact of wastewater on the pH levels in the receiving waters.

The average pH at Sites CP and B was 6.91, 6.98 respectively before wastewater outfall. There was an observed average increase in pH after the wastewater outfall with Site C and D averaging 7.16 and 7.11 respectively. The Average pH downstream showed recovery of the receiving water quality before wastewater outfall as Site E had an average pH of 6.91 the same as observed at Site CP.

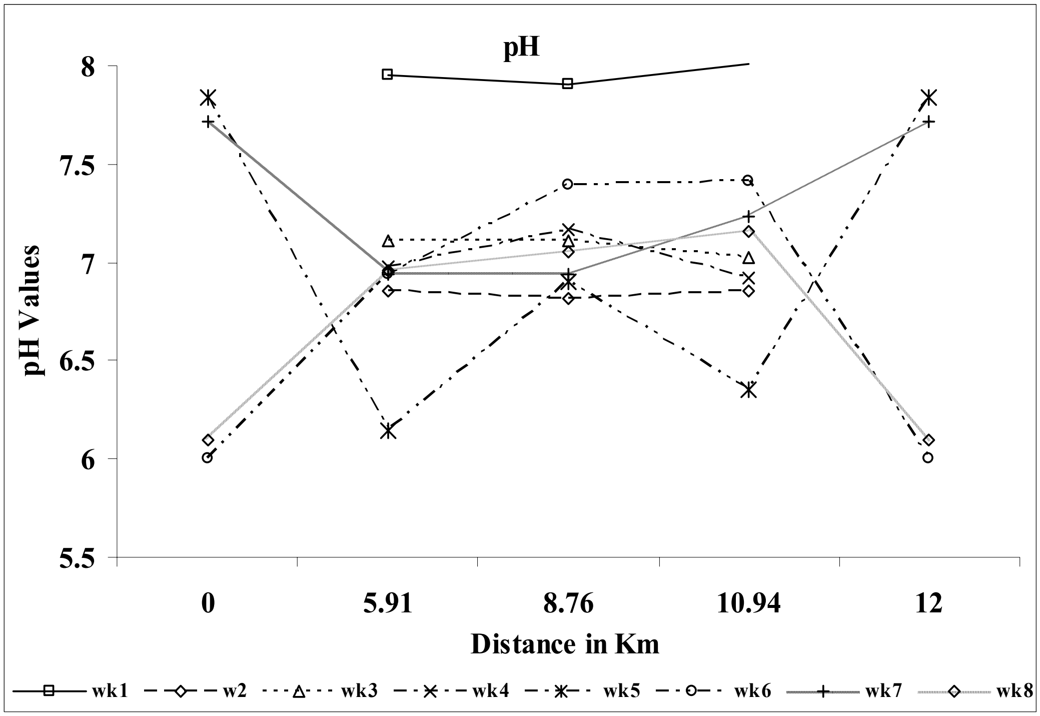

Figure 13: Spatial variation of pH

5.2.3 Spatial variation of Total Alkalinity (TA)

The observed spatial variation of total alkalinity during the sampling campaign is shown in Figure 15. The spatial variation showed significant increase at Site C signifying that the wastewater discharge in the river had a bearing on the alkalinity concentration within the river. Figure 14 and 15 show the relationship between pH and total alkalinity, that higher peaks in total alkalinity corresponding with high peaks in pH, the relationship more distinct at Site C

The was an average 31.1 % rise in Total Alkalinity after the wastewater outfall and a recovery of 14.6 % down stream at Site D. The average alkalinity before the wastewater outfall was 25.8 and 20.8mg/ℓ observed at site CP and SB. Sites C and D after the wastewater outfall alkalinity averaged 27.42 and 23.42mg/ℓ respectively with the highest value (46mg/ℓ) recorded at Site C.

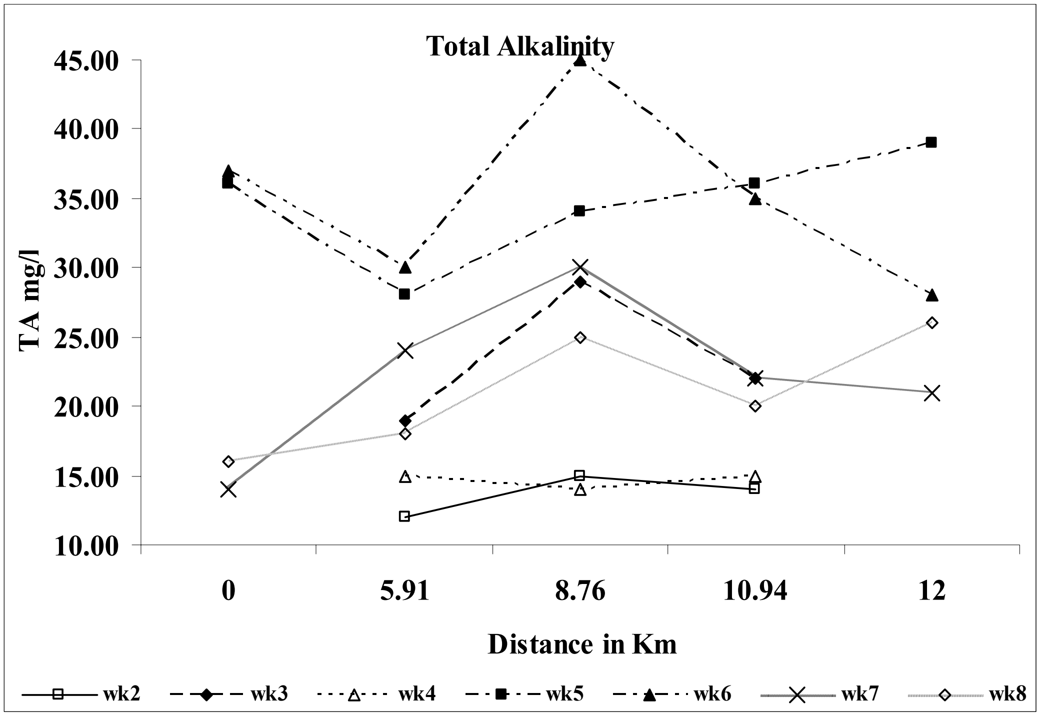

Figure 14: Spatial Variation of Total Alkalinity

5.2.4 Spatial variation of Ammonia

Spatial variation of ammonia is shown in Figure 16. The variation of ammonia showed higher levels of ammonia at Site D. This could be attributed to Site D being the possible mixing zone for the wastewater discharge leading to higher readings than Site C located only 0.54km after the wastewater outfall. The proximity of agricultural fields could also be contributing factor due to runoff carrying ammonia based fertilisers into the river.

The average ammonia concentration before the wastewater outfall was 0.11 and 0.08 mg/ℓ at sites CP and B respectively. Sites C, D and E located after the wastewater outfall averaged 0.09, 0.11 and 0.11 mg/ℓ respectively. The highest value observed was at Site D. In a study of the Impact of a Municipal Wastewater Effluent on Water Quality Lewis (1986) observed the same trend, that ammonia above the wastewater outfall averaged lower (0.01mg/ℓ) relative to the average downstream (1.7mg/ℓ) of the wastewater outfall below the mixing zone.

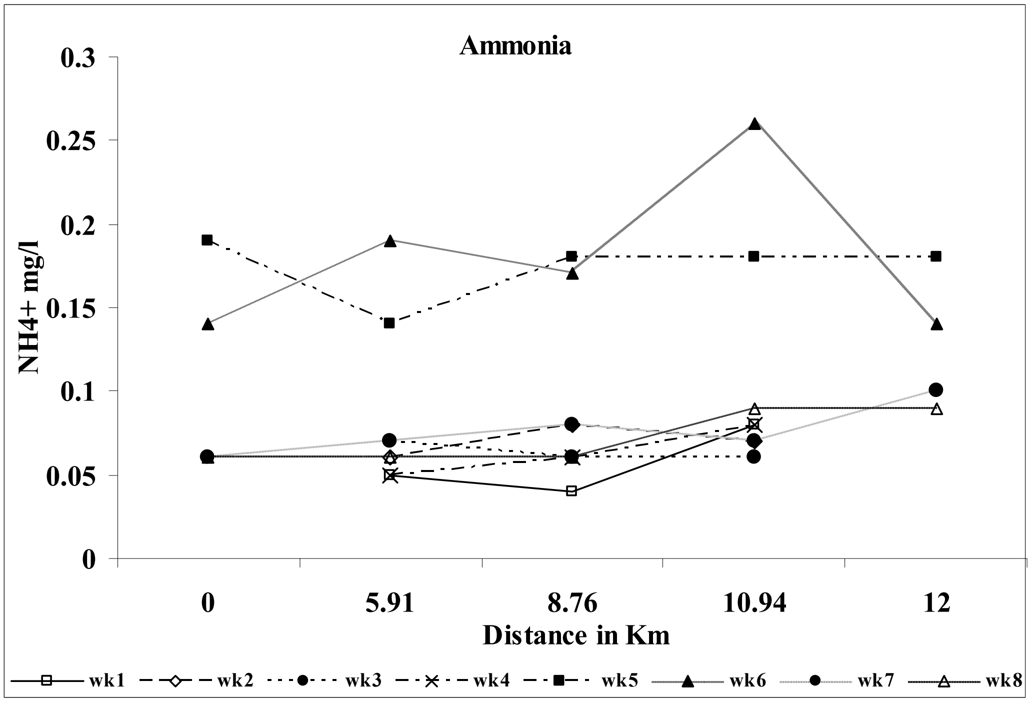

Figure 15: Spatial Variation of Ammonia

5.2.5 Spatial variation of Phosphorous

The spatial variation of Phosphorous (Figure 17) indicated that there was an increase in the Phosphorous concentration at Site C after wastewater outfall. The Phosphorous concentrations were generally low at headwaters CP (0.25mg/ℓ) and Site B (0.26mg/ℓ) and generally higher even beyond Site C (0.38mg/ℓ). This could be attributed to the treatment plant discharge as well as the agricultural fields present close and along Site C, D (0.29mg/ℓ) and E (0.35mg/ℓ).

The slight increase in both ammonia and phosphorous at Site E could be attributed to the discharge of water from Mzimmnene River which receives waste from domestic and agricultural activity and the waste is discharged at it's confluence with the Mbabane River upstream of Site E. The phosphorous concentration after the wastewater outfall increased by 47.1% and there was observed recovery of river with a 22.5% decrease down stream.

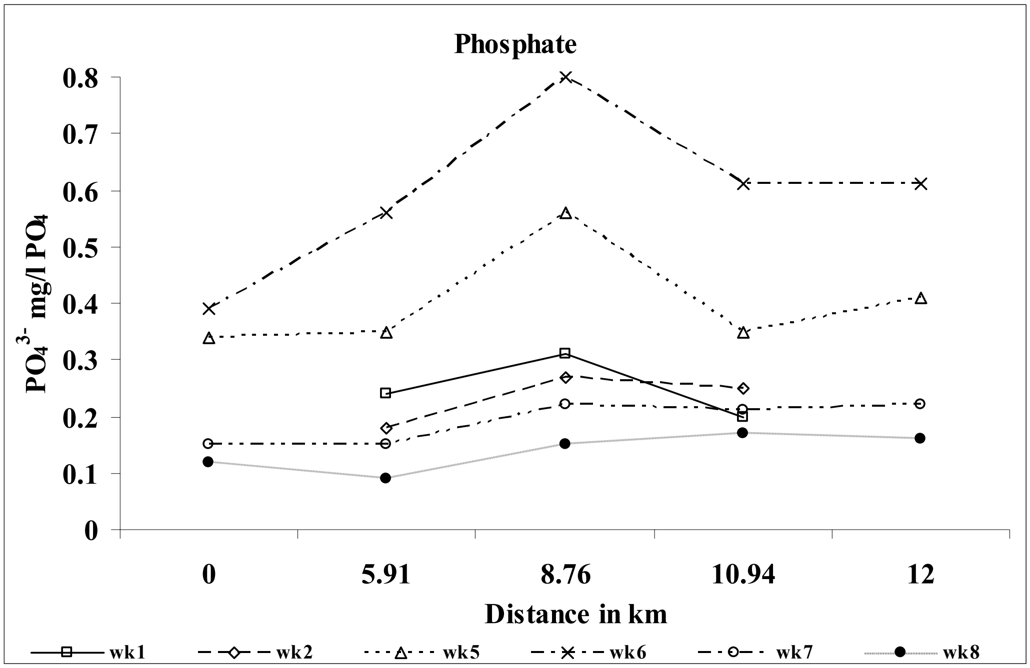

Figure 16: Spatial Variation of Phosphorous

5.2.6 Spatial variation of Dissolved Oxygen

Figure 18 shows the spatial variation of DO along the Mbabane River. It can be seen that the Dissolved Oxygen concentrations were higher upstream and began to decrease as the river flowed downstream. Week seven and eight showed a trend of the decline in DO concentrations along the river. The reduction in DO concentrations downstream of the Control point could be attributed to the discharge of pollutants from point and nonpoint sources such as tributaries carrying oxygen demanding constituents, agricultural residues in runoff, car wash activity and the wastewater discharge.

Site CP was located under forest canopy shielding it from the sun's thermal radiation this results in lower temperatures at the site. This allowed for better oxygen solubility in the water. The down stream points are more exposed to the thermal radiation and have higher temperatures resulting in decrease in solubility of oxygen. A similar observation on the effect of temperature on DO was made by Dougherty *et al. (*2007) where it was seen that cooler temperatures lead to seasonal highs in DO in reservoirs and rivers. The observed decrease in DO after the wastewater outfall was 3.7% and however the was a noted recovery in of the DO concentrations further downstream with 1.9% increase in DO concentration. The lowest DO level was recorded at Site E (4.40mg/ℓ). The level of DO at Site B could be as a result of the waters from the Mkhondolwane River coming with water low in DO. The receiving water quality in terms of DO meets the standard value of 4 mg/ℓ having maximum average value of 6.74mg/ℓ.

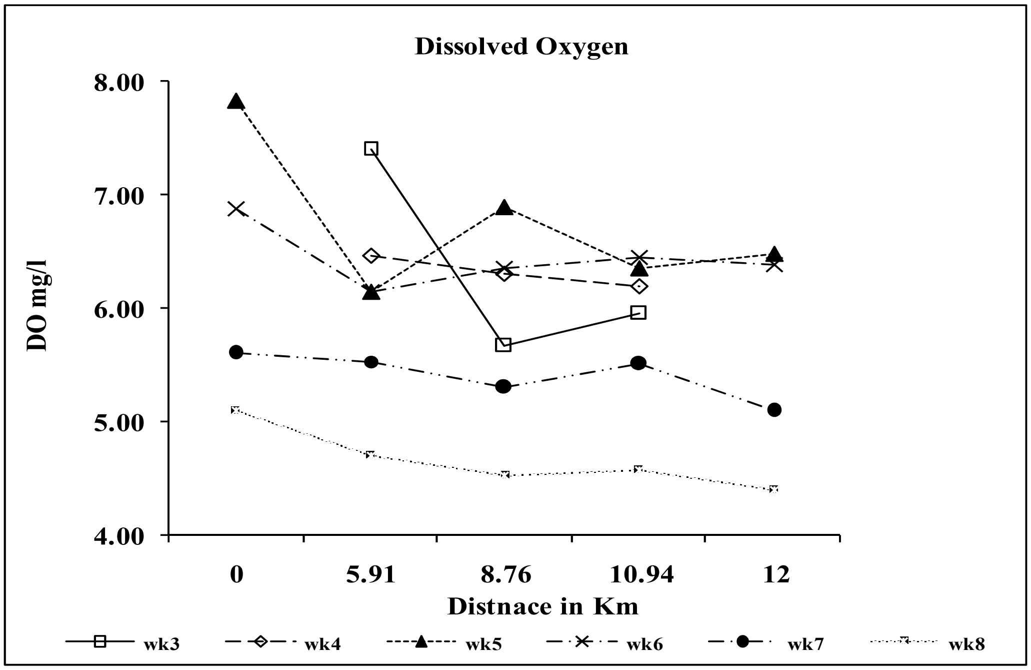

Figure 17: Spatial Variation of Dissolved Oxygen

5.2.7 Spatial variation of Biological Oxygen Demand and Chemical Oxygen Demand

The spatial variation of BOD is shown in Figure19. It is seen from the variation that BOD was higher before and after the wastewater outfall point. This was strange as expectation was that it would be higher at Site C. This anomaly could be due to the Mkhondolwane River discharging higher BOD waters into the Mbabane before Site B leading to higher BOD concentrations at Site B. Site D could be explained by the possible Distance required for mixing of the wastewater and the river waters; it could be that Site D was the mixing zone resulting in high BOD values than at Site C.

The degradation of materials such as BOD is dependent on other parameters such as temperature and oxygen the mix and concentration of micro-organisms (Reckhow, 1994). This could explain the high BOD concentrations at Site D which for most parameters could the mixing zone. The results however from assessment were to sparse to make meaningful deduction

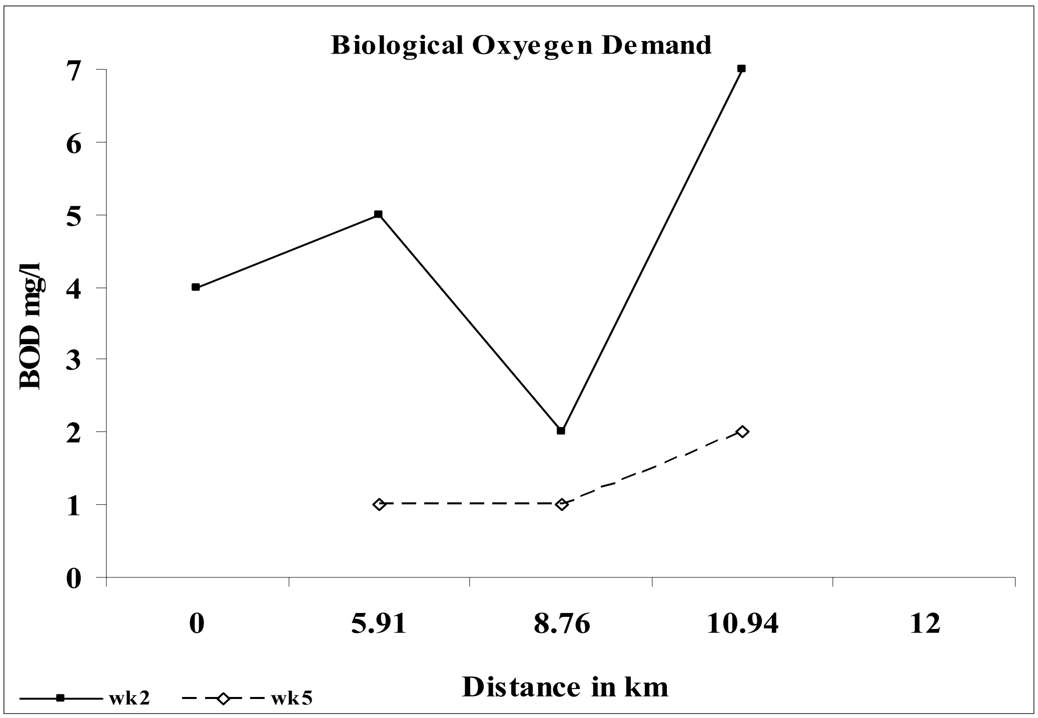

Figure 18: Spatial variation of Biological Oxygen Demand

The spatial variation of COD is shown in Figure 20. The variation showed an increasing trend from the headwaters and general decrease from Site C. The trend showed may account for the inverse trend showed by DO which could be as a result of the demand for oxygen by COD.

The increase in COD could be attributed to the pollution activities which were taking place at Site B (car wash) and upstream of Site C (wastewater outfall). The decline could be due to the river natural self cleansing ability which corresponds to further decrease in DO as it is demanded by COD. The rise in COD after the wastewater outfall was at 18% the recovery of the river from COD was observed to be at 43.5% by Site E.

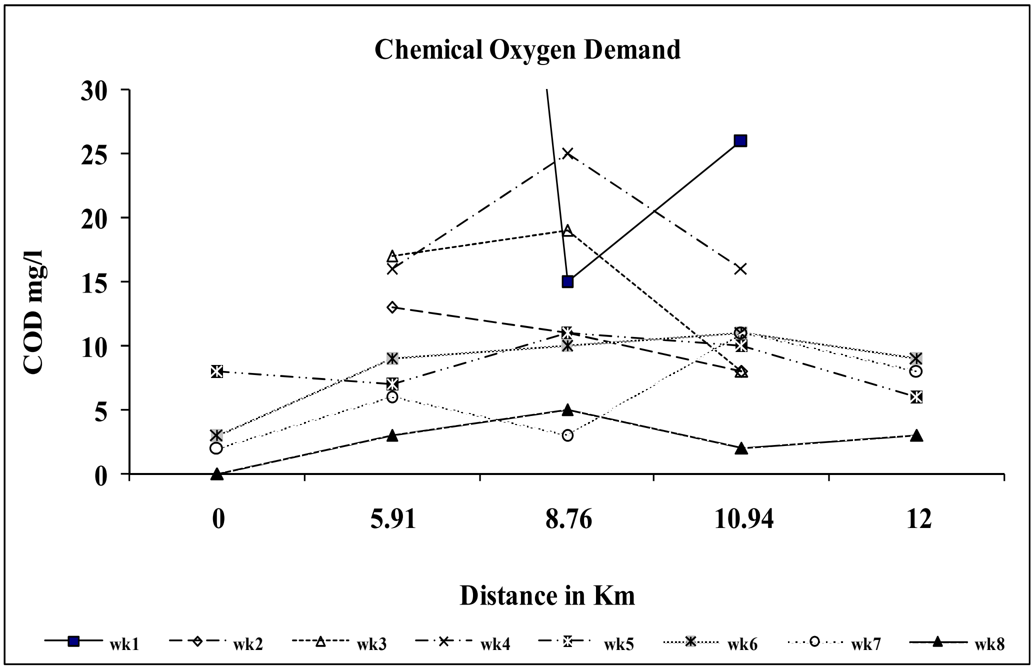

Figure 19: Spatial Variation of Chemical Oxygen Demand

5.2.8 Spatial variation of Faecal Coliforms

The spatial variation of Faecal Coliforms is shown in Figure 21. The variation showed high faecal coliforms counts at the headwater Site CP. This could be attributed to the clustered domestic dwellings located approximately 2km upstream of site CP. The area did not have access to a centralized wastewater system and most homes had pit latrines.

Due to the general steep slope of the area seepage of waste from toilets may possibly be infiltrating into the river. Another possible contribution of faecal coliforms could have possibly been due to the operations of the old wastewater plant which has not been decommissioned.

The faecal coliforms count showed a peak at Site C. This could be attributed to the introduction of wastewater into the river from the eZulwini wastewater plant. At Site E downstream the slight increase observed could be due to entry of waters from the Mzimmnene River which also has clustered homesteads on both sides hence receiving waste that it discharges in to the Mbabane River. There is a 43.7 % increase in faecal coliform counts after the wastewater outfall and there is an observed 21.6% fall further downstream.

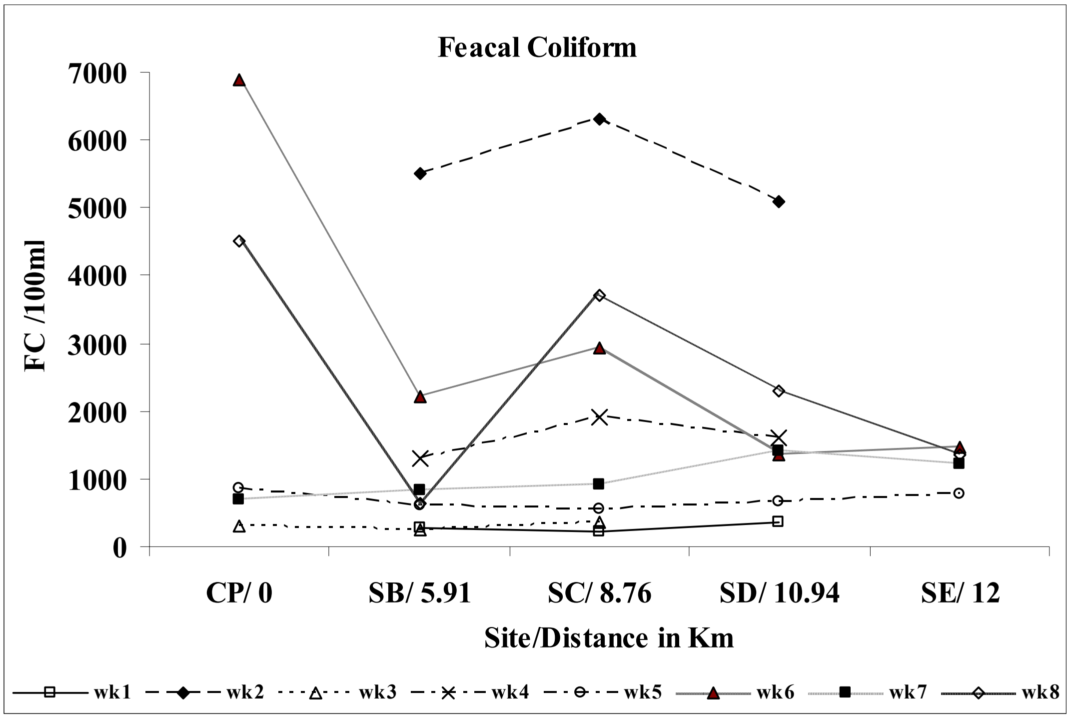

Figure 20: Spatial Variation of Faecal Coliform

5.3 Statistical Analysis of Assessment Results

The temporal and spatial variation analysis discussed in the previous sections only reflects part of the impact factor leaving out the interactions among the pollution parameters. In this section statistical analysis was used to quantify the correlation within the parameters and the significance of those relationships. Correlations are critical to understand as they can help to predict possible scenarios in water quality. For example growth of algae and other microscopic plants found floating on the surface of the water is stimulated by light, temperature, nutrients such as nitrogen and phosphorus, and pH conditions.

The basic statistical analysis of the data set from the preliminary assessment of the Mbabane River for the period 27th January 2009 to 17th March 2009 is shown in Table

5. The table shows the variable mean, data range, standard deviation and the confidence interval at 0.05. Parameters used in the assessment showed no significant correlation with discharge except for ammonia and dissolved Oxygen with r = 0.80 and 0.86 respectively at $p < 0.05$.

Table 5: Mean values with Standard Deviation for all parameters

Parameter	Mean	Data Range	Standard Deviation	Confidence interval
Temperature (^{o}C)	23.00	19.8 - 25.7	1.51	23 ± 0.53
pH (pH values)	7.07	6.0 - 8.01	0.5	7.07 ± 0.16
TA (mg/ℓ)	24.10	12.0 - 45.0	8.59	24.1 ± 3.02
Ammonia (mg/ℓ)	0.09	0.02 - 0.26	0.05	0.09 ± 0.02
Phosphorous (mg/ℓ)	0.30	0.09 - 0.80	0.17	0.30 ± 0.06
DO (mg/ℓ)	5.91	4.40 - 7.84	0.84	5.91± 0.30
BOD (mg/ℓ)	4.40	2.0 - 7.0	1.82	4.4 ± 1.59
COD (mg/ℓ)	14.55	0.00 - 141	21.57	14.55 ± 6.68
FC (counts/100mℓ)	1817.50	140 - 6900	1868.2	1817.5 ± 578.95

Note: *Significance at $p<0.05$

Table 6 shows the correlation matrix calculated from the combination of all sampling sites. The table shows the correlation with significance at $p<0.05$ marked by asterisk (*), all other correlations were found to be less significant at p Values greater than 0.05. Kannel *et al*. (2007) stated that correlation coefficients from combined data from various stations should be used with caution as they are affected simultaneously by spatial and temporal variations. Because of this weakness, site specific correlations matrices were computed to reduce the effect of spatial and temporal variation.

Table 6 showed that eleven out of the 36 pairs were significant. Four pairs showed high correlation (above r = 0.7) with significance and the remaining showed low correlation but at $p < 0.05$. Yang *et al*. (2008) stated that pH is affected by dissolved substances. This could explain the significance in correlation between pH and COD. However, Yang *et al.* (2008) also stated that there is a non linear relation between pH and COD which could explain the low r value (= 0.400) and $r^2 = 0.16$ values. Kannel *et al*. (2007), also obtained significant correlations between pH and both BOD and COD at r = 0.669 and 0.730 respectively at $p<0.05$.

Table 6: Correlation Matrix for preliminary Assessment of Mbabane River

Parameters	**Temp**	**pH**	**TA**	**NH_4^+**	**PO_4^{3-}**	**DO**	**BOD**	**COD**
pH	0.058	-	-	-	-	-	-	-
TA	0.130	-0.045	-	-	-	-	-	-
NH_4^+	0.038	-0.246	0.747*	-	-	-	-	-
PO_4^{3-}	0.352	-0.044	0.740*	0.788*	-	-	-	-
DO	-0.211	0.072	0.369*	0.514*	0.676*	-	-	-
BOD	0.490	0.734*	-0.711*	-0.569	-0.672	-0.250	-	-
COD	0.181	0.400*	-0.163	-0.209	-0.041	0.392*	0.936*	-
FC	0.107	-0.480*	-0.221	0.039	-0.015	-0.073	-0.485	-0.203

Note: *Significance at $p<0.05$

For the preliminary assessment of the Mbabane River, the correlation coefficient was higher for pH and BOD than pH and COD at r = 0.734 and 0.400 respectively. This was in agreement with Kannel *et al. (*2007) who also stated that the correlation between pH and BOD could be due to the decomposition of nitrogenous organic matter by microorganism, resulting in increases in both pH and alkalinity and the formation of ammonia. This can also explain the significant correlation between total alkalinity and ammonia. From this discussion one can infer that the negative correlation between pH and ammonia is true though insignificant r = -0.246, in that a rise in pH favors an increase in the relative proportion of non ionic ammonia molecule (NH_3) in water. This is in agreement with Li *et al*. (2007) also obtained negative correlation between pH and ammonia.

Phosphorous and Dissolved Oxygen showed correlation with r = 0.676 (R2 = 0.45, p = 0.001), according to Kannel *et al. (*2007) high sorption of phosphorus occurs at high dissolved oxygen concentrations, this could explain the correlation. Kannel *et al.* (2007) further explains that this sorption occurs at pH range 2-3 and 6 -8 the latter range as can be seen in table 5 is the pH range observed in the Mbabane River during the assessment period.

COD and BOD showed high correlation at r = 0.936 (R^2= 0.876, p = 0.001), Hossain *et al.* (2008) also observed a significant correlation between COD and BOD with r = 0.69 and p = 0.01. Kannel *et al.* (2007) noted that the correlation between COD and BOD is due to the fact that they are closely related to organic contamination. According to Goel *et al* (2008) BOD can be estimated from COD if a significant correlation can be established on a specific case. For this study the results from the linear trend line equation give BOD = 0.2922COD – 1.5922. This is very useful as COD test give a quick estimation of carbonaceous contents within a water sample (Goel *et al.,* 2008). The results also show that the organic matter in the river is mainly non biodegradable (COD:BOD = 4). BODS showed negative correlation with DO though it was not significant in this study, Kannel *et al.* (2007) stated that this is due to the fact oxidation of organic matter occurs at the expense of oxygen.

5.3.1 Correlations at the Control Point

Table 7 shows the correlation matrix at the Control Point. A comparison of Tables 6 and 7 showed that at specific sites the correlation values increased among analyzed relationships. However only four pairs showed significance and these were temperature and FC (with correlation coefficient r = 0.975, R^2 = 0.95 and p = 0.024). This could be attributed to the fact that faecal colifroms are themorphilic and therefore respond to changes in temperature. This was in agreement with Assaf and Saadeh (2008) who observed that faecal coliform counts presented higher values in warmer summer months

Faecal Coliform and pH also showed a significant correlation (with r = 0.956, R^2 = 0.91 and p = 0.044) similar result were observed by Hossain *et al.* (2008) with r= 0.21 at p <0.05 from these results it can be inferred that faecal coliforms are directly affected by an increase or decrease in pH. Total Alkalinity and Phosphorous r = 0.981 (R^2 = 0.96, p = 0.019). Ammonia and dissolved Oxygen r = 0.986 (R^2 =0.97 p = 0.013), this could be linked to the oxidation of ammonia which exist in equilibrium with ammonia in water (Tesfaye, 2007). DWAF (1996) states that ammonia toxicity is affected by the dissolved Oxygen concentration, in view of this an increase in DO and ammonia in water can possibly lead to toxic conditions when oxidation occurs. Faecal Coliforms were represented in two significant correlations this makes it a significant water quality parameter at the Control Point

Table 7: Correlation Matrix for Site CP

Parameters	Temp	pH	TA	NH_4^+	PO_4^{3-}	DO	BOD	COD
pH	-0.870	-	-	-	-	-	-	-
TA	-0.566	-0.062	-	-	-	-	-	-
NH_4^+	0.077	0.245	0.935	-	-	-	-	-
PO_4^{3-}	0.466	-0.048	0.981*	0.885	-	-	-	-
DO	0.016	0.354	0.909	0.986*	0.885	-	-	-
BOD	-	-	-	-	-	-	-	-
COD	-0.316	0.613	0.726	0.915	0.682	0.943	-	-
FC	0.975*	-0.956*	0.305	-0.030	0.318	-0.119	-	-0.429

Note: *Significance at $p<0.05$

5.3.2 Correlations at Site B

Table 8 shows the correlation matrix at Site B before the wastewater outfall. The table shows that only four parameter pairs were significant. The significant correlations were pH and COD (with $r = 0.814$, $R^2 = 0.66$ and $p = 0.010$), Total Alkalinity and Ammonia (with $r = 0.865$, $R^2 = 0.74$ and $p = 0.01$), Ammonia and Phosphorous (with $r = 0.926$, $R^2 = 0.85$ and $p = 0.007$) and between DO and COD (with $r = 0.904$, $R^2 = 0.81$ and $p = 0.013$). The reasons for these relationships are discussed in section 5.31. The matrix presents COD and ammonia in two significant correlation making them possible important water quality assessment parameters at Site B.

5.3.3 Correlations at Site C

Site C correlation matrix is shown by Table 9. The site is located 0.5km downstream of wastewater outfall. Only one pair in analyzed pairs had a significant relationship.

The pair was ammonia and Phosphorous (with r = 0.863, R^2 = 0.74 and p = 0.026) making the two parameter significant water quality assessment parameters at Site C.

Table 8: Correlation Matrix for Site B

Parameters	Temp	pH	TA	NH_4^+	PO_4^{3-}	DO	BOD	COD
pH	0.401	-	-	-	-	-	-	-
TA	0.285	-0.429	-	-	-	-	-	-
NH_4^+	0.505	-0.469	0.865*	-	-	-	-	-
PO_4^{3-}	0.553	-0.180	0.742	0.926*	-	-	-	-
DO	0.069	0.097	-0.046	0.085	0.848	-	-	-
BOD	0.982	0.370	-0.645	-0.410	-	-	-	-
COD	-0.037	0.814*	-0.459	-0.312	-0.043	0.904*	0.189	-
FC	0.071	-0.185	-0.433	0.040	0.032	-0.048	0.992	-0.250

Note: *Significance at p<0.05

Table 9: Correlation Matrix for Site C

Parameters	Temp	pH	TA	NH_4^+	PO_4^{3-}	DO	BOD	COD
pH	0.671	-	-	-	-	-	-	-
TA	0.303	0.486	-	-	-	-	-	-
NH_4^+	-0.071	-0.248	0.733	-	-	-	-	-
PO_4^{3-}	0.303	0.186	0.814	0.863*	-	-	-	-
DO	-0.278	0.156	0.259	0.704	0.836	-	-	-
BOD	-	-	-	-	-	-	-	-
COD	0.002	0.278	-0.399	-0.259	0.371	0.466	-	-
FC	0.375	-0.393	-0.393	0.006	-0.153	-0.411	-	-0.242

Note: *Significance at p<0.05

5.3.4 Correlations at Site D

Table 10 shows the correlation matrix of Site D pairs. The matrix presents only two parameter pairs with significant correlation. The presented correlation are total alkalinity and ammonia (with r = 0.861, R^2 = 0.74 and p = 0.012) and ammonia and

Phosphorous (with r = 0.951, R^2 = 0.90 and p = 0.003). What can be inferred from the matrix is that ammonia is significant water quality assessment parameter at Site D

The positive and significant correlations between phosphorous and ammonia could be attributed to the point and non point sources of pollution. Between Total Alkalinity and ammonia the correlation could be influenced by the relationship between pH and alkalinity in influencing reaction in water bodies.

Table 10: Correlation Matrix for Site D

Parameters	Temp	pH	TA	NH_4^+	PO_4^{3-}	DO	BOD	COD
pH	0.663	-	-	-	-	-	-	-
TA	0.100	-0.124	-	-	-	-	-	-
NH_4^+	0.303	-0.086	0.861*	-	-	-	-	-
PO_4^{3-}	0.575	-0.085	0.744	0.951*	-	-	-	-
DO	0.004	-0.299	0.506	0.535	0.818	-	-	-
BOD	-0.175	0.121	-0.670	-0.288	-	-	-	-
COD	-0.269	0.587	0.039	-0.064	-0.035	0.759	-	-
FC	-0.060	-0.246	-0.575	-0.196	-0.173	-0.656	-	-0.406

Note: *Significance at $p<0.05$

5.3.5 Correlations at Site E

The correlation matrix is shown in Table 11. Only one pair from the analysis showed significance Temperature and pH (with r = -0.956, R^2 = 0.91 and p = 0.044) making the two parameter significant water quality assessment parameters at Site E.

The correlation analysis across all site showed a negative correlation between Dissolved Oxygen and faecal coliforms though not significant this could be linked to the need of oxygen for respiration.

Table 11: Correlation Matrix for Site E

Parameters	Temp	pH	TA	NH_4^+	PO_4^{3-}	DO	BOD	COD
pH	-0.956*	-	-	-	-	-	-	-
TA	-0.356	0.271	-	-	-	-	-	-
NH_4^+	-0.323	0.369	0.902	-	-	-	-	-
PO_4^{3-}	0.389	-0.216	0.421	0.681	-	-	-	-
DO	-0.072	0.219	0.679	0.919	0.889	-	-	-
BOD	-	-	-	-	-	-	-	-
COD	0.130	0.165	-0.149	0.291	0.675	0.615	-	-
FC	0.888	-0.818	-0.745	-0.679	0.062	-0.393	-	0.154

Note: *Significance at $p<0.05$

5.4 Analysis of the Historical Data at Site B

The following section presents historical data obtained from the National Water Authority over the period march 2006 to 2008. The data available was for Site B and the eZulwini effluent. Figures 22 to 26 are plots of the historical data of available parameters at Site B and their concentrations in the eZulwini effluent.

The historical temporal variation in temperature is shown in Figure 22. It can be seen from the figure the temperature of the effluent varies in the same pattern as that of the water temperature over the data set period. The temperature varied with the season as the seasonal temperature influences the temperature of both effluent and river water. The winter temperature can be as low as 13°C showing which has an impact on the reactions that occur in the river.

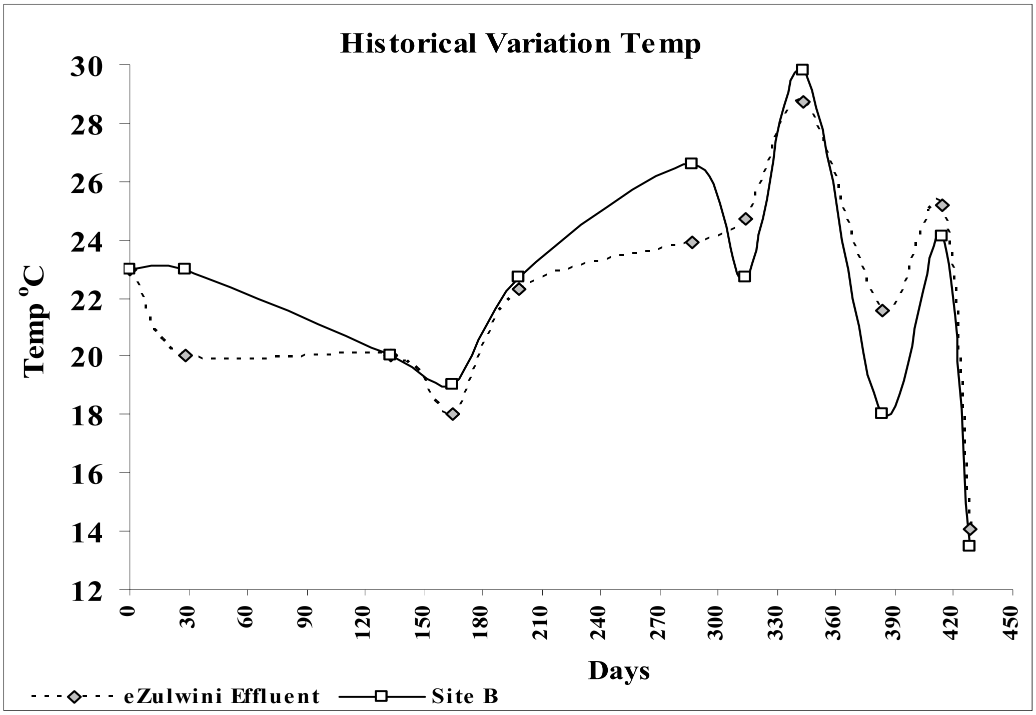

Figure 21: Historical Variation of Temperature

Figure 23 shows the historical variation of ammonia in the effluent and at Site B upstream of the wastewater outfall. From the figure there is a general increase in ammonia in the effluent from the treatment plant. Site B showed a high pick in ammonia on the last data point; this could be attributed to rainfall event as there was change in the reference river hydrograph.

The values observed from the historical data corresponding to the same period as this study fell in the same range (0.05 – 0.19mg/ℓ) observed during the preliminary assessment period of this study with an exception of observation taken on day 282 (0.29mg/ℓ). The results in the data set showed that the concentrations of ammonia in the receiving water were below the standard limit of 0.6mg/ℓ with exception of 3.3mg/ℓ recorded on day 354. The ammonia concentrations are high during the rainy season from October to March this could be attributed to runoff from the agricultural fields.

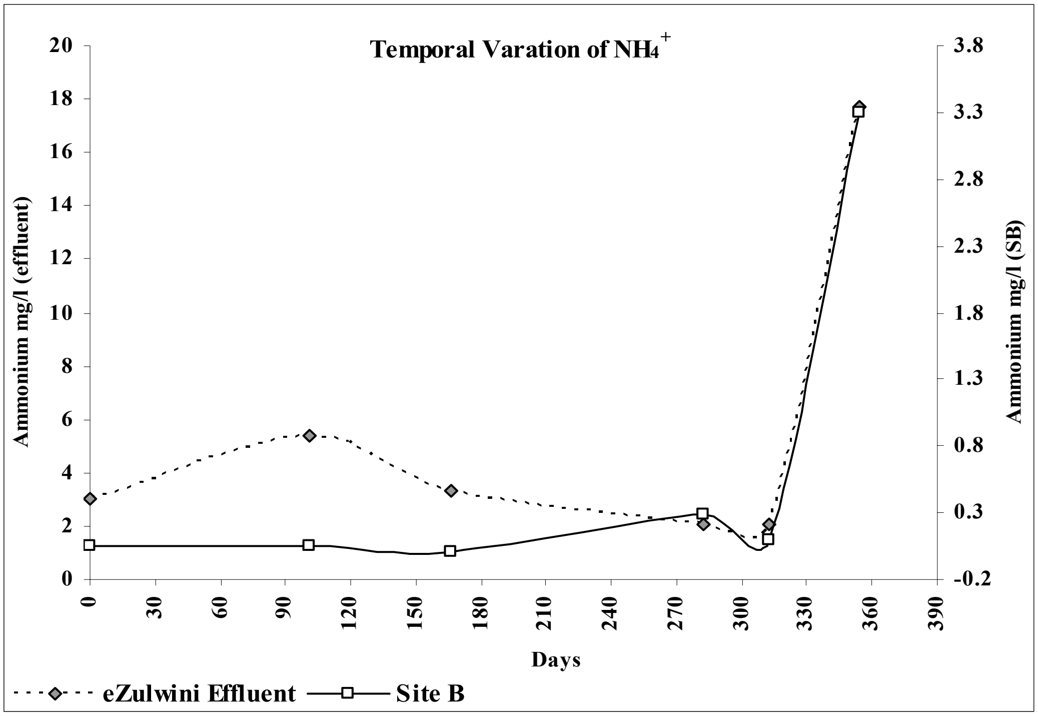

Figure 22: Historical Variation of Ammonia

Figure 24 shows the variation of phosphorous over the historical data set for effluent and Site B. The values observed from the historical data corresponding to the same period as this study fell in the same range (0.09 – 0.38mg/ℓ) as that was observed during the preliminary assessment period of this study. The results also show that the concentrations of Phosphorous in the receiving waters were below the standard limit of 2mg/ℓ.

Figure 25 shows the historical temporal variation of dissolved Oxygen for the data set. The historical data showed that the receiving water quality in terms of dissolved Oxygen was above the standard minimum of 4mg/ℓ even the effluent dissolved Oxygen was above the receiving water quality minimum standard. This study however showed that DO concentrations decreased immediately after the wastewater outfall. (Figure 18).

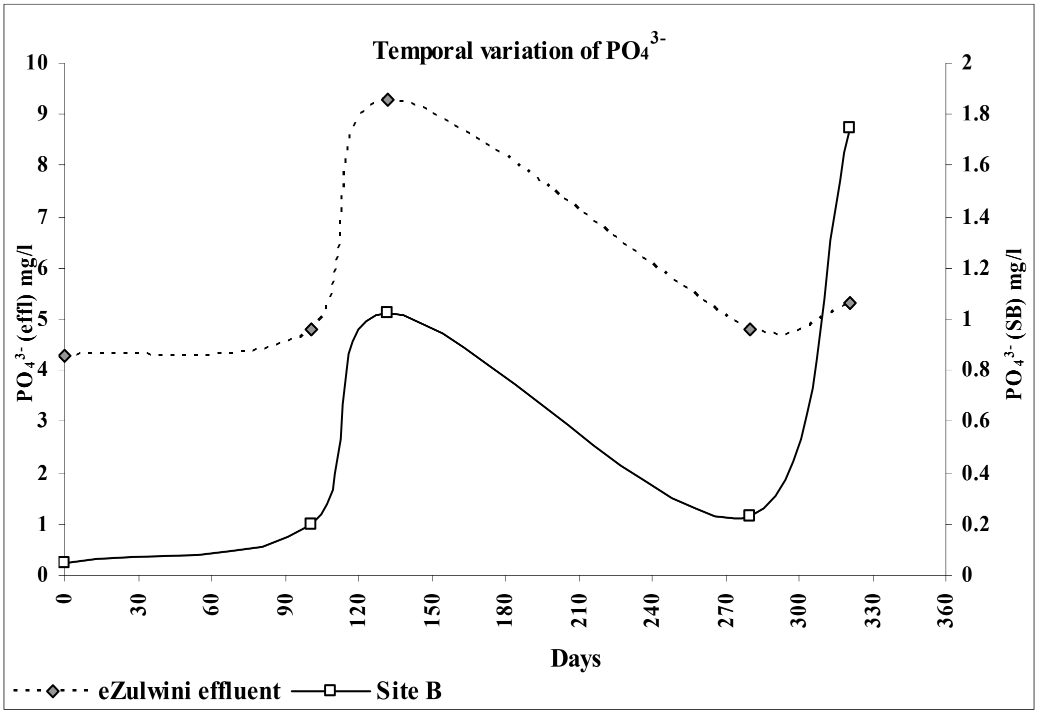

Figure 23: Historical Variation of Phosphorous

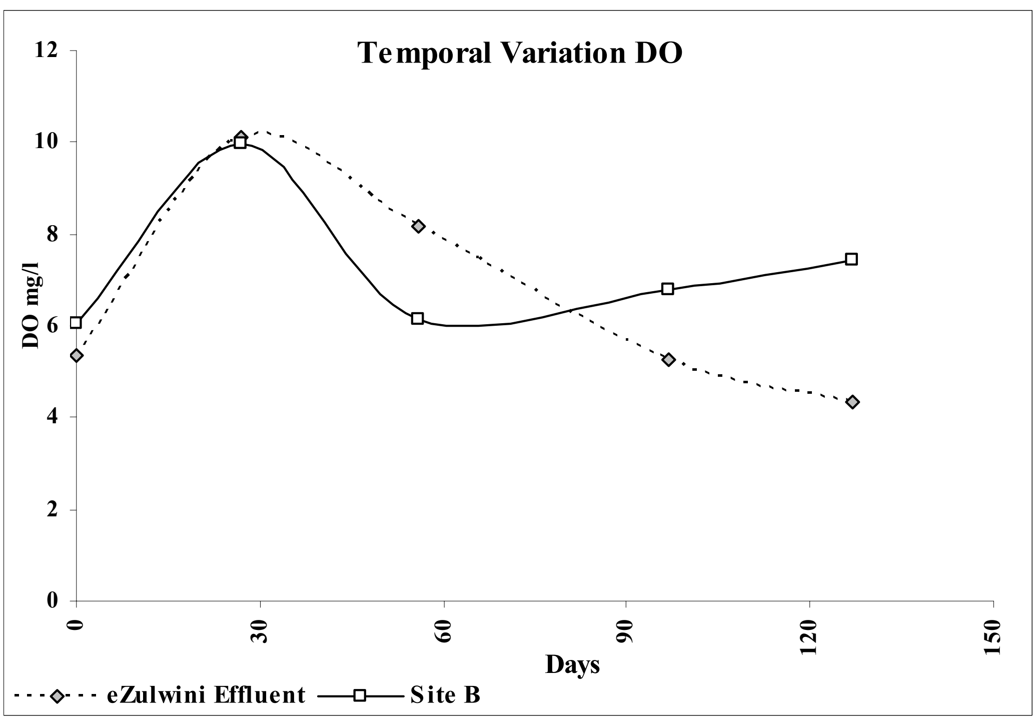

Figure 24: Historical Variation of Dissolved Oxygen

Figure 26hows the variation of Chemical Oxygen Demand in the effluent and Site B. The variation of COD in the effluent and receiving waters is seen to be the same from the data set. The COD concentrations were observed to be high at site B in the months August to November 2007 and generally the historical data had a COD range wider than that observed for the same site during the study period, (10 – 68.2) which is a sign of the activity taking place at the site that of washing cars.

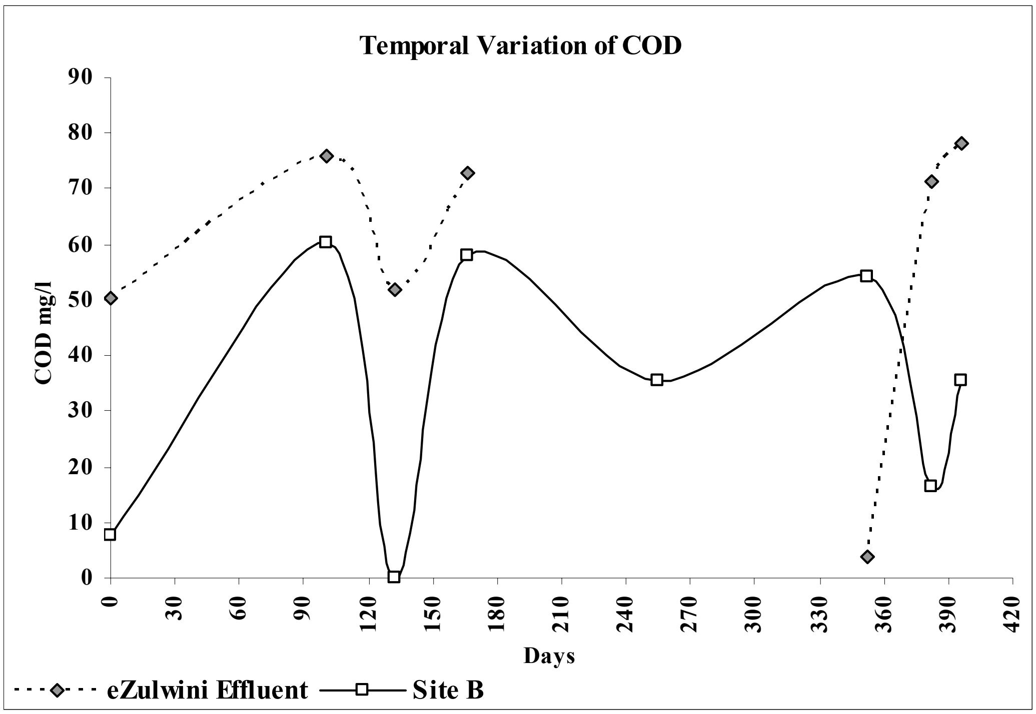

Figure 25: Historical Variation of COD

Figure 27 shows the trend of Phosphorous in the effluent with time. The record starts from March 2006 to June 2008. The figure shows that there is a general increase of phosphorous in the effluent. This could be attributed to increases in incoming wastewater from the Capital Mbabane. The increase in not smooth but it can be observed from the trend line that the phosphorous concentrations are increasing. This trend may need to be monitored as phosphorous (measured as orthophosphate) is a limiting nutrient to growth of algae and when present in large quantities can result in algal bloom.

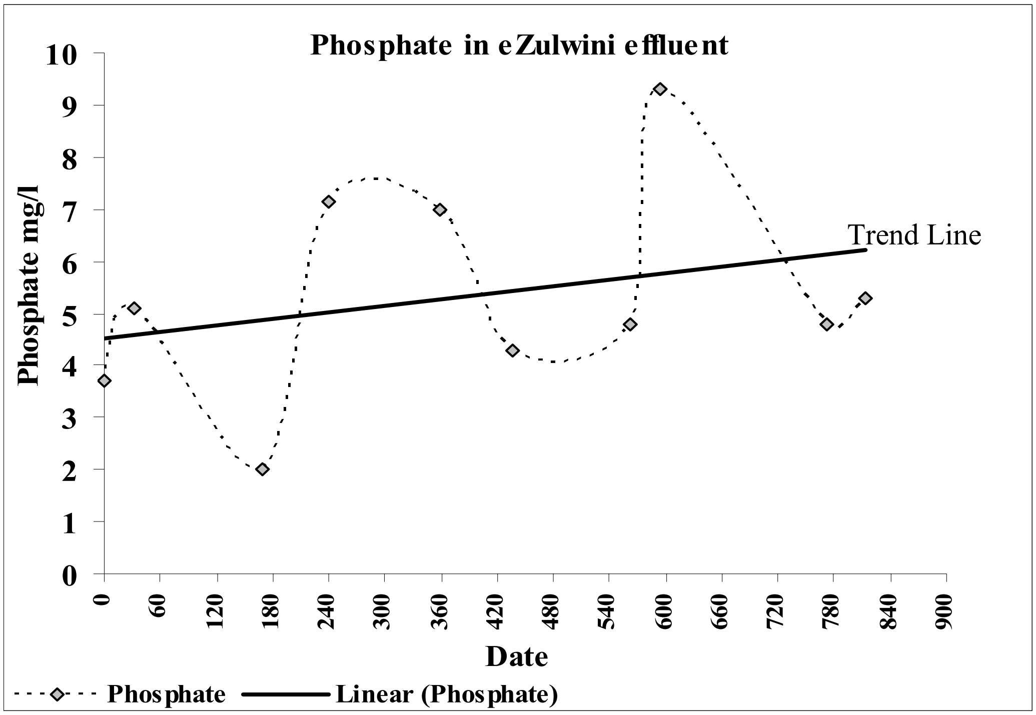

Figure 26: Variation of Phosphorous in Effluent from Wastewater Plant

5.5 Numerical Analysis of Dissolved Oxygen Saturation

The results of the site specific analysis of percent Dissolved Oxygen deficit (%DO def) using the Dissolved Oxygen saturation equation are shown below. The saturation results as stated in section 4.3.6 were related to the Chemical Oxygen Demand (COD) at the each specific site.

The further analysis of the relationship of COD and Dissolved oxygen Saturation at Site CP is shown in Figure28. It can be seen from the figure that COD at site CP had an inverse relation with Dissolved oxygen percentage deficiency the Pearson correlation coefficient confirmed the negative relation with $r = -0.896$, though the relation ship was not significant at $p = 0.10$. Other factors that can be considered to affect the expected DO concentrations could be sediment demand for oxygen, as well as ammonia nitrogen oxidation.

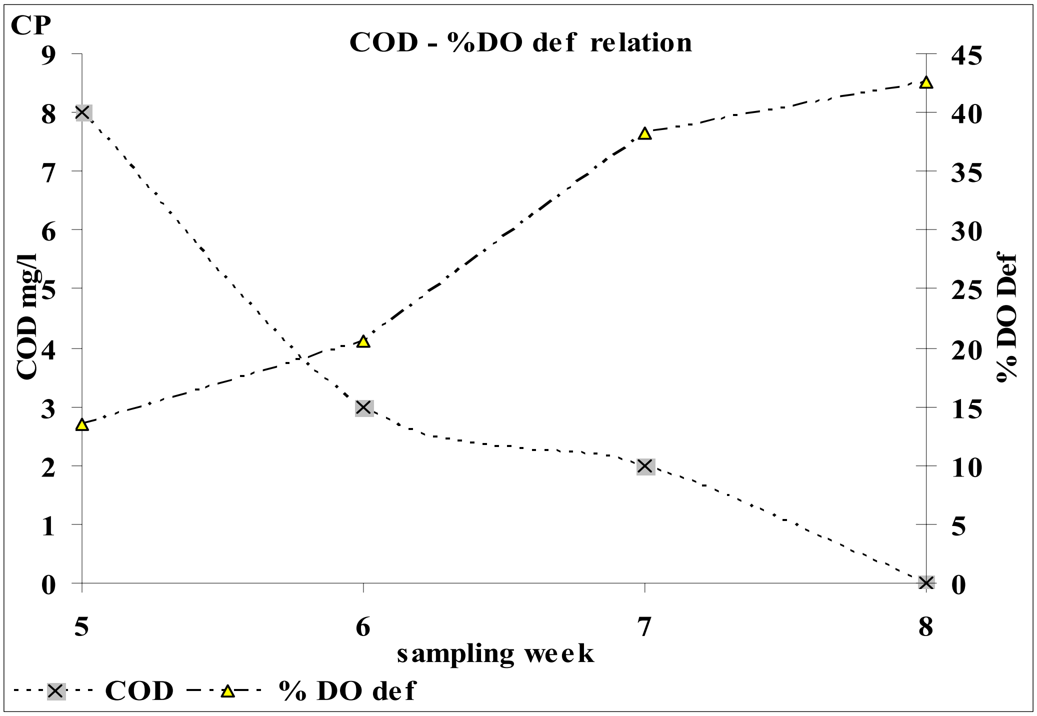

Figure 27: COD relation with %DO deficiency – CP

Figure 29 shows the COD relation with %DO def at Site B where there is a car wash. From the Figure it can be seen that when COD concentrations are high the %DO deficiency is low. The temporal variation observed depicts the expected trend with COD removal corresponding to a reduction in Dissolved Oxygen. However the Data is for periods one week apart.

Figure 30 shows the COD relation with %DO deficiency at Site C below the wastewater outfall. The trend of %DO deficiency at Site C was observed to be different from those of upstream site. The %DO deficiency had a wave trend starting with a crest. This could be attributed to the high concentrations of organic matter introduced by the wastewater into the receiving waters.

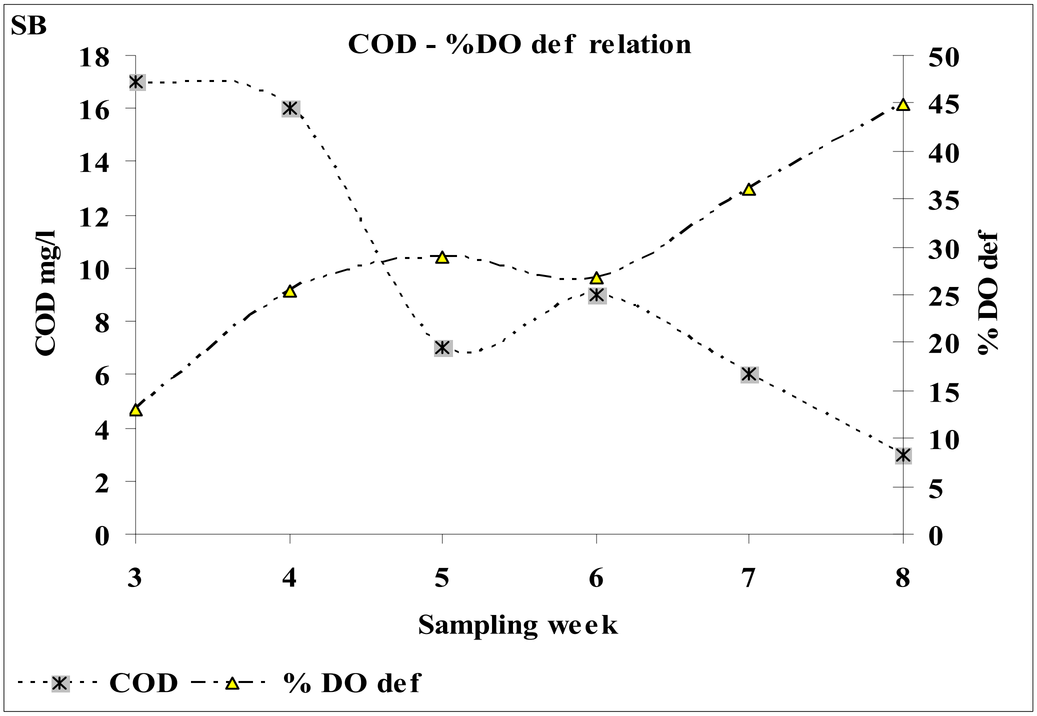

Figure 28: COD relation with %DO deficiency – Site B

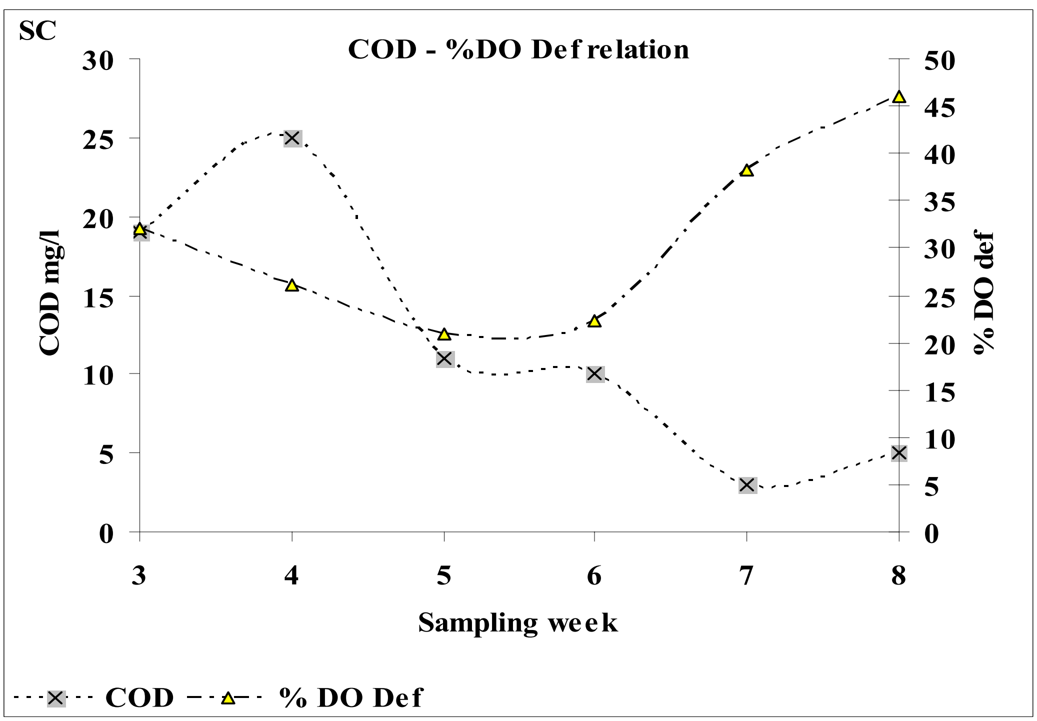

Figure 29: COD relation with %DO deficiency – Site C

The COD relation with %DO deficiency for Site D is shown in Figure 31. From the figure it can be seen that the COD concentrations went up but did not significantly alter the %DO deficiency in the water. This could be due to the fact that Site D could be a mixing zone where the water is mixed well with the effluent, it also possible that the DO concentrations were sufficient to deal with the COD concentrations without significantly affecting the DO concentrations in the receiving waters.

The second increase in the COD changed the %DO deficiency which signified the demand of oxygen by COD. The DO concentrations respond to the increase in COD which is reflected in the rise in %DO deficiency.

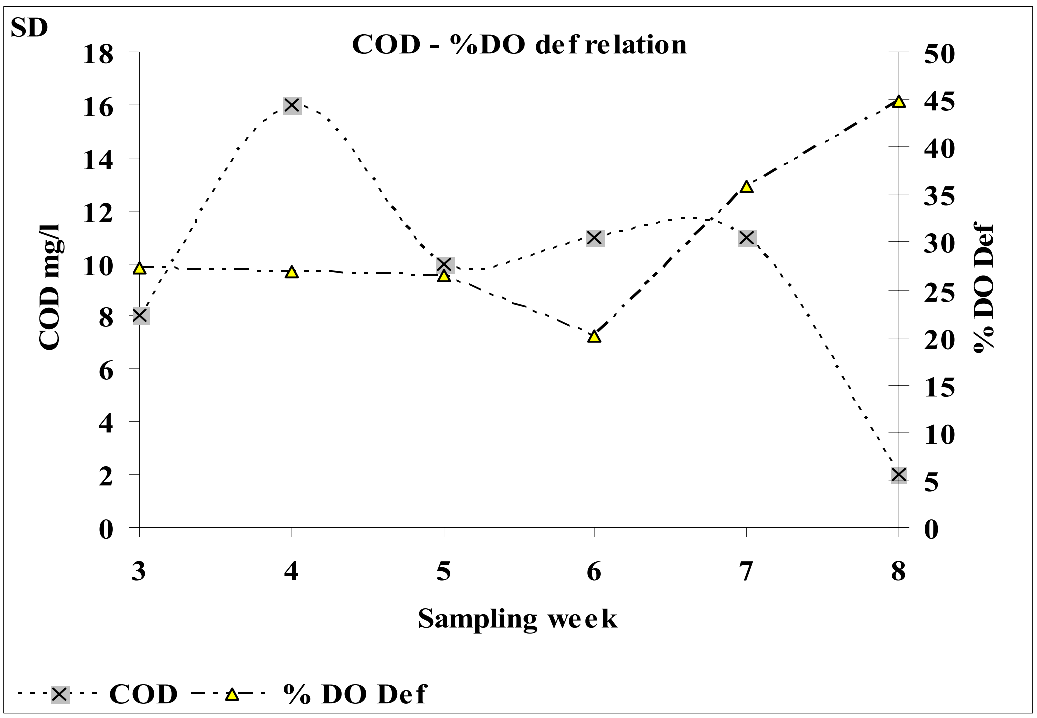

Figure 30: COD relation with %DO deficiency – Site D

The relation of COD and %DO deficiency at Site E is shown in Figure 32 at this point the trend in %DO deficiency is like the one observed at the upstream sites. This could signify a normalisation in the COD relationship which is seen to be affected at Site C and D

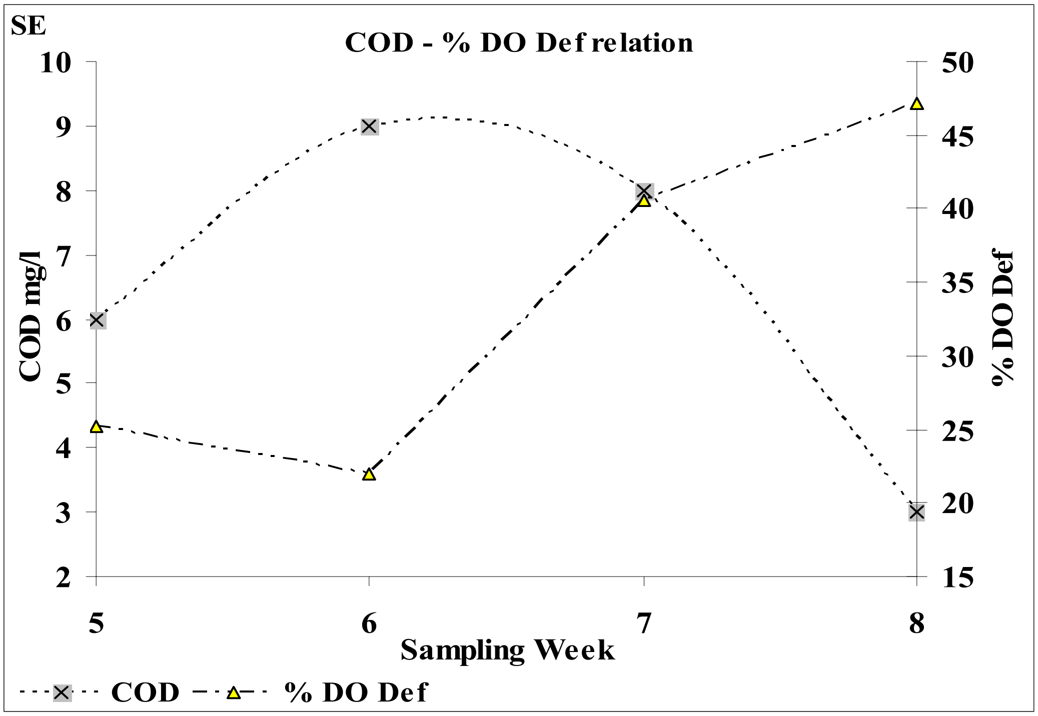

Figure 31: COD relation with %DO deficiency – Site E

5.5 Factors Influencing Water Quality

The water quality of the Mbabane River was affected by many factors in the form of point source and non-point sources. This section aims to summaries these factors identified during the study period and highlight their significant to the water quality in the Mbabane River.

5.5.1 Rainfall and Runoff

Rainfall leads to the production of runoff which carries waste that is deposited on land in to the Mbabane River. The lack of proper dumpsites in the study area has negative implications on the water quality of the river. The tributaries of the Mbabane River pass through high density residential areas, increasing the risk of pollution from varying activities along the banks of the river. The eZulwini Valley is a peri-urban area, was not serviced by centralized wastewater collection systems. Most of the domestic dwellings have pit toilets and septic tanks.

5.5.2 Agricultural Activity

The existence of agricultural activity at the banks of the river increase the effect of runoff as the fertiliser is washed into the river channel. The level of knowledge or fertiliser application and the farming methods influence the amount of fertiliser carried in to the river. Activities such as cattle rearing contribute to the quality of the river water especially in the rainy season when livestock waste is carried by runoff into the river channel. The river is a drinking spot for the cattle in the area and they leave droppings at the river banks.

5.5.3 Point source pollution from Tributaries and Wastewater plant

Activities taking place in the tributaries of the Mbabane River deposit organic and other wastes which are discharged in to the Mbabane River at the point of confluence. The presence of the eZulwini Wastewater plant has an added water quality influence as there is continuous point source discharge of wastewater. As the population in Mbabane grows there will be more wastewater production and its seasonal variation quantity and quality is a critical factor. The tributaries form point source pollution coupled with the wastewater treatment plant. The presence of business activity that utilizes the water directly such as car wash has a direct impact on the water quality at the point of business and downstream.

5.5.4 Hydropower Plant

The hydropower station also has a significant effect on the quality of the water in the Mbabane River. The hydropower station regulates the discharge of the river and there fore influences transportation of pollutants down stream. The variation in loading from the wastewater plant needs to be balanced with operations of the hydropower plant. The water from the dam is from a different river system. The quality of water in a river and in a dam is different due to factors such as depth, velocity etc. therefore the quality of water in the Dam influences the water quality in the Mbabane River. A seasonal turn over which could lead to high concentrations of organic matter release from the dam could disturb the receiving water quality of the river. Furthermore Climate change predictions by Matondo *et al.* (2004) indicate that water resource available to Swaziland will be reduced and this will affect the storage dams across the country. It is crucial that the dam operations are managed properly and the release of water is accounted for to ensure proper management of the volumes within the dam.

5.5.5 Water Sector Change

The introduction of the Swazi Water Act of 2003 and the formation of the National Water Authority provides a structure through which water pollution control can be handled. The present drafting of the Integrated Water Resources Master (IWRM) Plan will provide platform to handle water pollution. One of the challenges that water sector management faces is the lack of data to enable better decision making. The data gaps in water quantity and quality need to be closed by use of models and sharing of data among stakeholders.

Mbabane River needs an Integrated Water Resource Management Plan since it has a lot of competing activities which utilize the services that the river provides. The Management plan should taken into account all the stakeholders, namely the farming community, the residents along the main river and tributaries, the business activities which benefit directly or indirectly from the river and the wastewater treatment plant. The plan should also account for both the quantity and quality of the water flowing in the catchment. The water quality monitoring programme for the river needs to be intensified as the wastewater plant output increases especially during low flows.

5.6 Outline of Mbabane River Sustainable Management Plan

To achieve sustainable Management of the Mbabane River catchment it must be done within the IWRM framework. Mlilo *et al.* (undated) stated that IWRM at its core recognizes the river catchment as the unit of resource management, which is the base on which the Swaziland Water Act of 2003 is developed. The future management of the Mbabane River can not be achieved by one sector. A UN (2005) report stated that water related problems can not be solved or reversed by the conventional single –

sector approaches and that in cases like these, the IWRM approach makes identifying and implementing effective solutions much easier.

5.6.1 Legal and Institutional Framework

5.6.1.1 Legal Framework

The main legal instruments governing water resources in Swaziland are the Water Act (2003), the Swaziland Environmental Act (1992), and The Swaziland Electricity Act (2007). There latter is important because of the presence of the hydropower station in the sub-catchment.

5.6.1.2 Institutional Framework

The Mbabane River is part of a transboundary Catchment (South Africa, Swaziland and Mozambique) of the Great Usuthu River. It is therefore critical to identify the international framework that influences the local plan. The key water management institutions as sited in the Water Act, (2003) are; National Water Authority with roles for planning, policy formulation and monitoring water use, and the Joint Water Commission, which deals with transboundary water issues. At implementation level institutions include the Water Apportionment Board, which is a temporal body that will carry out functions of river basin authorities until such time as the river catchment basin authorities are established and Water Users Associations, which are bodies made up of the water users dealing with water issues at user levels. Government Ministries include the Ministry of Health and Social welfare that has a role in rural sanitation, the Ministry of Natural resources, the Ministry of Housing, Rural and Urban development and the Ministry of Agriculture and Cooperatives.

At the catchment level, the involvement of the following stakeholders is critical. Mbabane City Council, which is responsible for activities upstream in the capital city. The Swaziland Water Services Corporation, which supplies potable water and collects wastewater from the capital and transmits it to the eZulwini wastewater works need to work closely with the Swaziland Electricity Company, which operates the Luphoholo hydropower station. The eZulwini Traditional Leaders and Water Use Associations are also key stakeholders in the catchment as well as the industries and business located around the Mbabane River and its tributaries.

5.6.2 Outline of the Plan

The following outline of the Plan is adapted from the "*Guidelines for the Preparation of Catchment Outline Plans (COP) In Zimbabwe*" (SWACO and Associates, *2005).*

5.6.2.1 Definition of the Environmental Baseline

In the definition of the environmental baseline there is need to describe the natural and socio-economic resources of the catchment comprising the following main aspects: the basic catchment hydrology, manifested through rainfall, gauged stream flows, the potential for the occurrence of groundwater aquifers and evaporation; the biophysical environment consisting of the geology and soils, fisheries, vegetation and conservation areas; the socio-economic environment; and the water quality status of the catchment.

In the understanding of catchment hydrology the involvement of the Meteorological Department is crucial. This department has the historical weather data and is custodian of the instruments of measurement. However the is no meteorological station in the eZulwini Valley and there is need to establish one so that data may be relevant to the catchment.

Mbabane River has no gauging station, this makes evaluation of the quantity of water in the sub catchment difficult and measurement of pollutant loading difficult. The operations of the hydropower plant regulate the volumes of water in the catchment. However there is need to have measuring tools such as flow meters to assess the contribution of the tributaries in to the flow of the Mbabane River.

Current monitoring taking place in the catchment is targeting point source and is focused on the physiochemical aspect, there is need to carry out bio assessments to establish the ecological health of the river. The lithology of the area needs to be assessed to establish the contribution of groundwater in terms of the water quality especially during the dry season and assistance can be provided by the Geology Department. The soils of the area need to be tested to establish the fertiliser requirements for the growing season to prevent excess use of fertiliser this can be done with guidance for the Soils Department in the Ministry of Agriculture and Cooperatives. The involvement of university research institutions in aquatic biology is required to establish the habitats that exist within the catchment and the effects the catchment activities have on these habitats

The socio-economic environment of the eZulwini Valley comprises of settlements, water and sanitation development, agriculture, tourism and general infrastructure development. The business community in the eZulwini Valley has a role to play in the economic environment of the eZulwini Valley especially those that benefit directly from the services of the water body. The Traditional leaders in the eZulwni Valley are responsible for allocation of land on Swazi Nation Land (held in trust for the Swazi Nation by The King). Their role in placement of settlements and agricultural fields determines the activities that take place near the river banks. The hotel industry is mainly concentrated in the eZulwini Valley, these facilities produce a lot of wastewater and the main hotel the Sun International has its own treatment works which releases effluent into Mbabane River via its tributary. The presence of hot water springs within the catchment has an effect on the quality of water and the operation of these tourism facilities established around them is crucial and their involvement in the plan is vital. Sanitation in the rural parts of the eZulwini Valley is handled by the Ministry of Health and records of the sanitation status need to be evaluated and studies to confirm this can be carried out.

Currently water quality monitoring within the catchment is focused on point sources such as the wastewater plants at Sun International Hotel and eZulwini wastewater plant. What is important is that Swaziland Water Service Corporation, Swaziland Environmental Authority, National Water Authority need to continually work together in the monitoring of the Mbabane River sharing available data, and human resources.

5.6.2.2 Data Analysis

Data analysis involves the evaluation of the water demands for all social and economic sectors of the catchment comprising the following main consumer groups: Rural and urban settlements; Agricultural irrigation and livestock consumption; Inter-catchment transfers; International obligations, and the reserve.

The eZulwini Valley has both rural and urban settlement; the contribution of rural settlements is covered in section *5.6.2.1 bullet 4*. The urban Area is under the eZulwini Town Board which has plans to construct a land fill in the area. The operation within the town must be coordinated within the Mbabane River Sustainable Management Plan.

Mbabane River is a source of irrigation water for fields in close proximity to the river. Livestock also come to the river to drink. These activities as has been mentioned in this document have a bearing on the water quality especially during the growing season where there are rainfall events. The irrigation requirements become critical during the low flow in the rainfall dry months.

The water coming from the hydropower dam is from a dam constructed in another sub-catchment with its own unique characteristics. The effects of the inter-catchment withdrawal from Lusushwana down stream need to be monitored to ensure that environmental flows are met.

As already mentioned that the Mbabane River is part of an international catchment its operation and management affect the international obligations of the country in terms of the quality and quantity of water that exists the country to Mozambique.

The amount of water available to the catchment water users needs to be quantified so as to establish the reserve that is available in summer and winter dry months. It is critical as has been mentioned that the measuring of flow in the river is important. The water quantity alone can not satisfy the water requirements the quality of the water is also important.

5.6.2.3 Strategic Water Resources Management Framework

To establish an effective plan there is need to identify priorities for the implementation of COP. The institutions mentioned in the plan need to meet to establish a steering committee to look into the state of play and make recommendations on the way forward. There is also need to establish a framework of capable institutions with clearly defined roles in the implementation of the COP, these institutions exist, the is however need for coordination

Water Quality Management requires a lot of data which at times is available but not shared or not retrievable since it is not managed properly. Software such as LIMS can be networked between participating organizations and can be locked for editing to prevent data manipulation by non-authorized personnel.

The involvement of all relevant and interested stakeholders is important and a mechanisms for stakeholder involvement and conflict resolution needs to be established. Training in this area is available and organizations such as the country water partnership can assist in the training programmes for both users and the institutions within the catchment.

Without adequate communication and infrastructure support (roads, telecommunications &, power supplies) it is difficult to manage natural resources. Fortunately the eZulwini Valley is easily accessible and has transverse roads, telecommunication and power lines. These services are critical in terms of communication and operations of the COP

The strategic framework must define clear water management indicators and targets as a basis for monitoring. This study has outlined a few of the management indicators that need to be considered. The recommendation in Section 6.3 can give more clarity into the critical management indicators in the sub- catchment. Monitoring and review mechanisms such as consistent monitoring within clear objectives gives the appropriate data required and at the frequency needed. Monitoring activities need not be routine as seasons vary and during low flows water quality may be significantly altered. Environmental audits can be used to evaluate and review the performance of the monitoring activity within the catchment.

All management activities require financial resources; therefore there is need for a broad budgetary provision and an indication of financing options. This can be sourced through government and other organizations such as UNEP. For small economies self sustenance of river catchments is usually not feasible however the organisations involved can link up to come up with the most possible structure to implement the plan.

A framework for the analysis of risks (climatic, economic, political and other), including measures to reduce or manage them is required. Matondo *et al. (*2004) have conducted a climate change study of Swaziland and this need to be considered in the COP. The input of the data obtained from the study can be used in projections of the catchment resources. Predictions of climate change are negative in terms of water quantity availability and this is a threat to the Mbabane River Sub-Catchment.

SUMMARY, CONCLUSION AND RECOMENDATIONS

6.0 Summary

From the study Mbabane River can be described as a river at high risk of pollution from the activities in the catchment with extensive agriculture, wastewater discharge and hydropower outfall all contributing to the water quality of the river. Faecal coliform is the most significant pollutant in all the parameters selected for the assessment of Mbabane River with the lowest record at more ten times the stand value of 20 coutns/100mℓ of sample. Chemical Oxygen Demand is the second highest pollutant in the river systems among the parameters selected. However the results of the assessment are not conclusive since other parameters such as heavy metals, turbidity and total dissolved solids etc. were not analyzed.

The study showed that the temperature range was 19.8 - 25.7 ^{o}C. pH was within the range of set standards on surface water quality 6.5 -8.5 pH values at all sites. Ammonia was below the set limit of 0.6mg/ℓN at all sites even during rainfall events. Phosphorous was below he set limit of 2.0mg/ℓ PO_4 at all sites. Dissolved oxygen was seen to be above the set minimum of 4mg/ℓ, the highest oxygen deficiency was observed at Site C below the eZulwini effluent outfall. Biochemical Oxygen Demand, the set limit exceeded at Site D down stream of the waste water outfall. Chemical Oxygen Demand was exceeded at all sites at low flows and was below set limits of 10mg/ℓ during increased flow. Faecal Coliform limit of 20FC/100mℓ was exceeded at all sites and highest values were observed at Site C 500m after the wastewater outfall.

6.1 Conclusions

The temporal variation in water quality in the Mbabane River was influenced by the discharge within the river. The water from the hydropower dam at Site A had distinct characteristics which were different from the other sampling sites. The marked difference was seen in the temporal variation of Temperature which was different when compared to the other sites. pH concentrations in the river were generally within the standard limits but were negatively affected by high discharge. Total alkalinity, Ammonia and Phosphorous varied with discharge in the river; during low flows total alkalinity was low and *vice versa*. Dissolved oxygen showed a variation that was reflective of the fluctuation in Chemical Oxygen Demand and Biological Oxygen Demand concentrations which were significantly affected by the river discharge as well as discharge from the tributaries of the Mbabane River.

The spatial variation showed that the temperature gradient was increasing in a downstream direction. This was however attributed to the exposure time as the samples were not taken at one time. Results show a relationship between pH levels upstream and downstream which were affected by the site B and C. Total alkalinity was observed to be generally higher after the wastewater plant which showed the significance of the treatment plant in influencing the concentration of alkalinity in the river. Ammonia and Phosphorous showed a general increase downstream this was attributed to the existence of agricultural fields in close proximity to river banks. Dissolved Oxygen was generally higher upstream than downstream where most of the catchment activities occur.

Historical data provided an insight into the prevailing trend in the parameters selected for the assessment of the water quality of the Mbabane River. From the data it can be seen that there is great seasonal variation in all parameters. The Phosphorous concentration in the eZulwini effluent showed a general increase with time and this should be monitored as phosphorous is a limiting nutrient to growth of algae.

The direct relationship of Chemical Oxygen Demand with Dissolved oxygen was numerically analysed. As is commonly accepted the trends showed that COD has a bearing on the %DO deficiency. However other under laying factors could be attributed to the levels of the %DO deficiency as the correlation between DO and COD was not significant at all sites.

Mbabane River is characterised by a number of different activities which lead to point and non point sources of pollution. The river discharge is regulated by the hydropower station operation and all these different aspects make Mbabane River a good site to pilot an integrated water resource management plan.

6.2 Recommendations

Mbabane River needs to have a management plan which will guide operations of both the hydropower plant and the Wastewater plant which are major institutions influencing the quality of water in the Mbabane River.

The finalisation of the National IWRM plan must map a way forward in terms of water quality assessment protocols for most rivers receiving wastewater and located along agricultural and industrial activity.

6.3 Areas for Further Research

Water quality research by the use of network analysis of the river is required because it enables the assessment of the impact of the tributaries, which contribute a varied quantity and quality of water into the Mbabane River. This can assist in better understanding of the spatial conditions contributing to the quality of the Mbabane River in the eZulwini Valley.

The use of models is required to simulate management scenarios that can be applied. Models are decision support tools which simulate complex environmental scenarios. Models such as QUAL2K, STELLA have the capacity to combine water quantity and quality data to show the effect of the variation in both, this makes scenario application less risky for planners.

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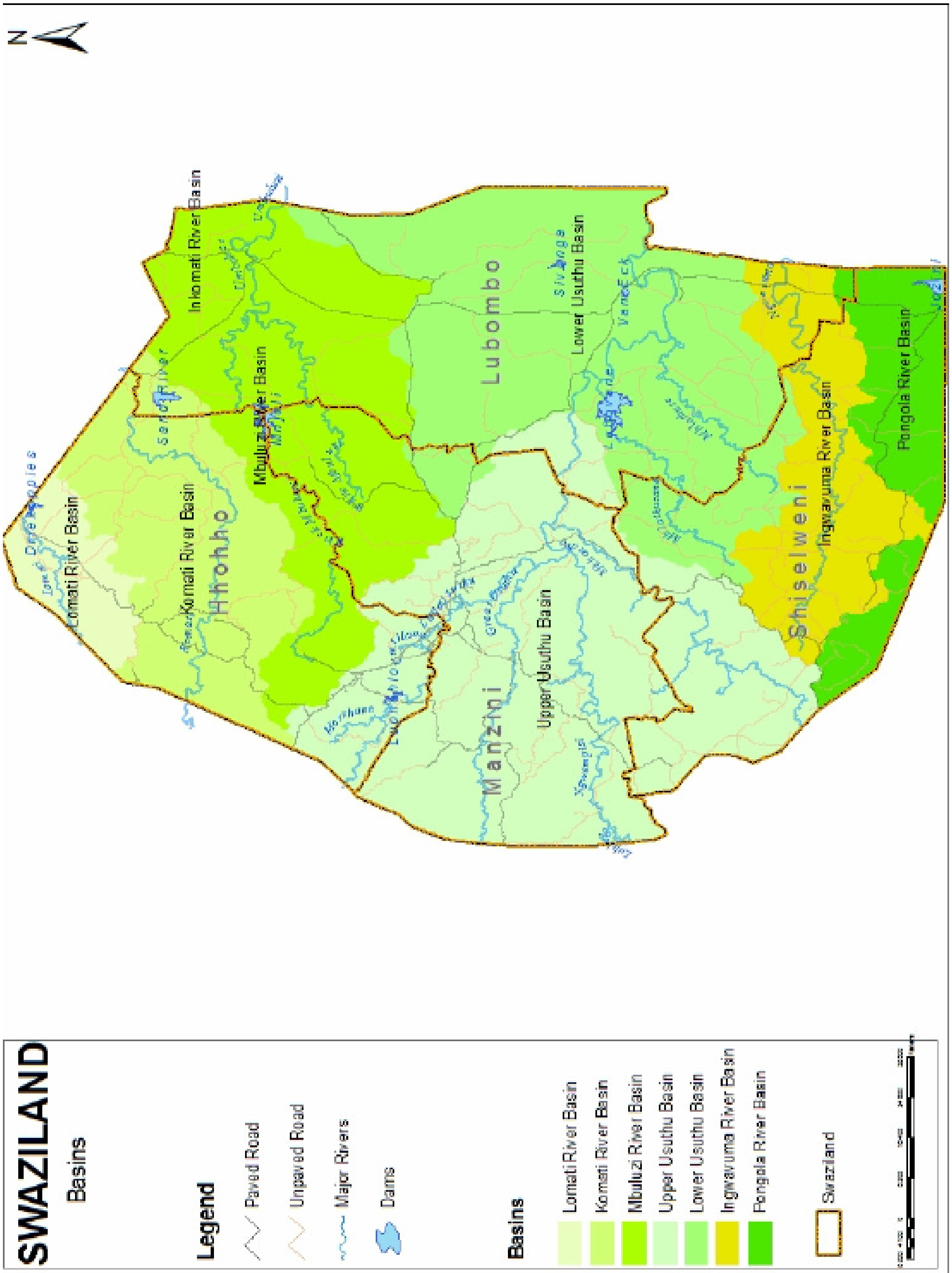
Appendix 1 – River Basin of Swaziland



Appendix 2 - WTW Oxi 330i Meter

Description - WTW Oxi 330i Waterproof, Battery Powered Dissolved Oxygen Meter Kit

Low-maintenance probe operates for up to six months between membrane changes. Galvanic probe needs no warm-up time 2000 hour battery life makes kits ideal for use in remote locations.

Waterproof and shock-resistant dissolved oxygen (DO) and biological oxygen demand (BOD) meters are NEMA 6 and IP67 rated. Meters feature data logging, salinity correction, calibration alarm, 2000 hour battery life, low-battery indication, a real-time clock, a locking probe connector, auto-read drift control, and automatic air pressure/temperature compensation. A 500-GLP data set memory is enhanced by a time controlled function that logs data at intervals from 5 seconds up to 60 minutes. Both DO and BOD kits are optimized for water and wastewater applications. Models 53105-14 features a digital RS-232 interface and an analog (0 to 2 V) output.

Appendix 3 – Lovibond Meter

LOVIBOND® - Photometer PC MULTIDIRECT for analysis of water

Description - PC MultiDirect

The PC MultiDirect is a modern, microprocessor-controlled photometer with a user friendly keyboard and large graphic display. It features a broad selection of pre-programmed methods based on the proven range of Lovibond® reagent tablets, liquid reagents, vial tests and powder reagents (VARIO Powder Packs).

Moreover, you can also store your own methods. The calibration option, including software-supported adjustment, means that the PC MultiDirect photometer can be used as a testing instrument.

The 7 standard rechargeable batteries (supplied) allow portable use. These standard batteries are available all over the world and are easy to change. An intelligent, integrated charge controller allows battery charging (using the supplied power pack) whilst the instrument is in operation. The PC MultiDirect can also be operated without power pack using alkalinemanganese batteries.

The complete unit including the test and battery compartments are fully watertight, ensuring that water does not come into contact with the electronic components.

Appendix 3 – continued – examples of how LOVIBOND test is done

Method 320 – Phosphate,
ortho LR with tablet

Range 0.05 – 4mg/ℓ $CaCO_3$

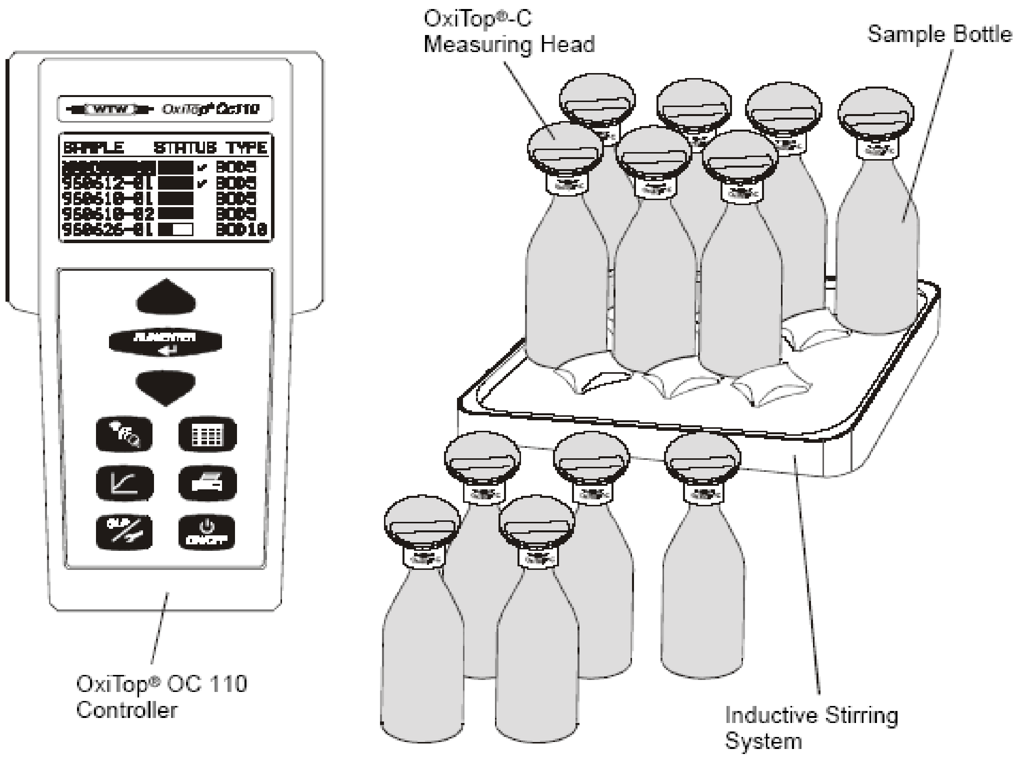
1. Fill a clean vial (24 mm Ø) with **10 mℓ of water sample,** close the vial with the cap tightly.
2. place the vial in the sample chamber making sure that the ⧖ marks aligned
3. Press **Zero** key
4. Remove the vial from the sample chamber.
5. Add **one PHOPHATE No.1** tablet straight from the foil to the water sample and crush the tablet using a clean stirring rod.
6. Add **one PHOPHATE No.2** tablet straight from the foil to the water sample and crush the tablet using a clean stirring rod.
7. Close the vial with the cap tightly and swirl the vial several times until tablet is dissolved.
8. Place the vial in the sample chamber making sure that the ⧖ marks aligned.
9. Press **TEST** key – wait for reaction period (10 min)

   Results are shown in the display as ortho-Phospahte in mg/ℓ PO_4

Appendix 4 – The OxiTop® Control System

The OxiTop Control system

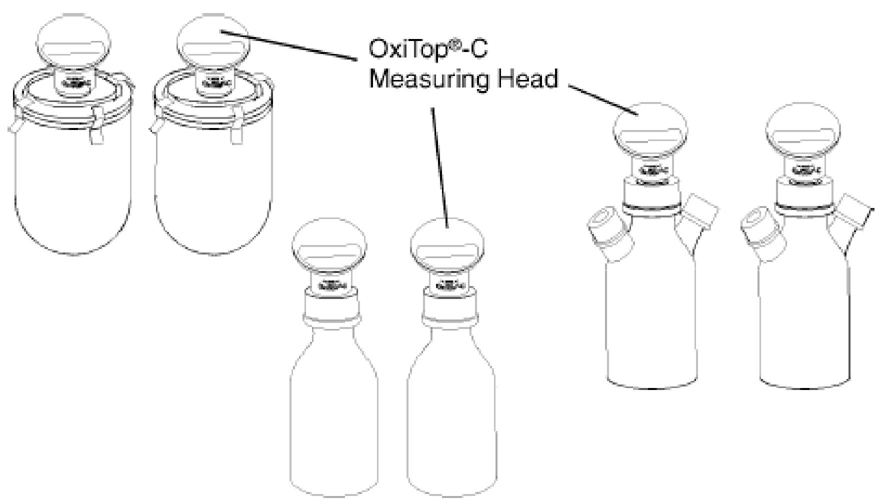
The classical application field for the OxiTop® Control measuring heads and controller ist the BOD_x determination (BOD_x = Biochemical Oxygen Demand for the time x). The evaluation of biological degradability (e.g. test according to OECD 301F) is also part of this field.



Appendix 4 - continued

With different sample vessels, the OxiTop®-C measuring heads in conjunction with the OxiTop® Controller 110 can also be used in other areas such as

- Evaluation of respiration and toxicity in earth, sludge, waste and sediment (e.g. extraction of earth contaminated according to recovery concepts)
- Evaluation of the respiration rate of cell cultures
- Microbiological growth and stress examinations
- Measurement of anaerobic degradation processes (e.g. biogas evaluation)



Appendix 4 - continued

The measuring principle

The respirometric measurement is a pressure measurement. If oxygen is consumed in a closed vessel at a constant temperature, a negative pressure develops. If a gas is released, an overpressure develops.
The OxiTop®-C measuring head measures and stores this pressure for the whole duration of a measurement once started.

The OxiTop® OC110 controller collects the pressure values from the measuring heads and processes them.
The formula shown below is the basis for all calculations for the BOD using the values from the OxiTop®-C measuring head.

$$BOD = \frac{M(O_2)}{R \cdot T_m} \cdot \left(\frac{V_t - V_l}{V_l} + \alpha \frac{T_m}{T_0} \right) \cdot \Delta p(O_2)$$

$M(O_2)$	Molecular weight (32000 mg/mol)
R	Gas constant (83.144 l·mbar/mol·K)
T_0	Reference temperature (273.15 K)
T_m	Measuring temperature
V_t	Bottle volume (nominal volume in ml)
V_l	Sample volume in ml
•	Bunsen absorption coefficient (0.03103)
• $p(O_2)$	Difference of the oxygen partial pressure (mbar)

The interpretation of the pressure differences in the temporal course depends on the measured material and its preparation and on the sample manipulation (e. g. intermediate aerations) during the measuring period.

Appendix 5 – National Water Authority sampler