Water Quality Trends in the Eerste River, Western Cape, 1990-2005.

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A minithesis submitted in partial fulfillment of the requirements for the degree of Magister Scientiae, Integrated Water Resources Management in the Faculty of Natural Science, University of the Western Cape.

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June 2006

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KEYWORDS

Water Quality
Temporal trends
Seasonal Mann-Kendall test
Regression analysis
Spatial trends
pH
Electrical Conductivity
Nitrogen
Phosphorus
Chemical oxygen demand

ABSTRACT

The Eerste River is a river system which has, over the years, been subjected to human interference. The purpose of this study was to investigate temporal and spatial trends in the water quality of the Eerste River between 1990 and 2005. Data accumulated by the City of Cape Town (CCT) and the Department of Water Affairs and Forestry (DWAF) at eight sampling stations along the course of the Eerste River, and one on the Plankenbrug tributary, were analysed to identify the trends. The water quality parameters analysed were pH, electrical conductivity (EC), nitrogen, phosphorus and chemical oxygen demand (COD). These parameters were selected particularly because they are considered key indicators of water quality.

In order to discern temporal trends in the data, the non-parametric Seasonal Mann-Kendall Test for trend and parametric regression analysis were used. Significant trends were assumed to exist if the p-values of the Seasonal Mann-Kendall test statistic and the slope coefficient were different from zero at a significance level of 5% ($p< 0.05$).
In the investigation of spatial trend, regression analysis and the analysis of variance (ANOVA) were used.

The study results reveal that the major trends in the water quality of the Eerste River are more spatial than temporal. This is because very few, isolated, significant long term trends were detected from the available data by both analyses. The increasing trends of electrical conductivity; nitrate and nitrite; and phosphates, at some of the stations, though the slope coefficients from the regression analysis were small, point to deteriorating water quality over time at those stations.

The spatial analysis of the sites showed that the water quality in the river system was deteriorating significantly with distance downstream, albeit in a step-wise manner. The deteriorating quality of water in the Eerste River was concluded to be driven by human activities, including fish farming in a dam upstream of the Swartbrug Bridge, the polluted Plankenbrug River, the Stellenbosch Waste Water Treatment Works (SWWTW) through the Veldwagters tributary, farming non point sources of pollution and the poor quality Kuils River. Therefore, greater attention ought to be paid to these activities to ameliorate their impact on the Eerste River.

June 2006

DECLARATION

I declare that *Water quality trends in the Eerste River, Western Cape, 1990-2005* is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Faith Ngwenya Date: June 2006

Signed ………………………………

ACKNOWLEDGEMENTS

Firstly, I would like to extend my gratitude to Mr. Lewis Jonker for his support and guidance throughout the period of the degree.

Secondly, I am deeply indebted to my mentor, Prof. Lincoln Raitt for his unwavering support, encouragement and guidance during the writing of this mini-thesis.

My sincere gratitude goes to Dr. Dirk van Driel and Mr. Robert Siebritz of the City of Cape Town, and Ms. Wilna Kloppers and Mr. Larry Ferguson of the Department of Water Affairs and Forestry (Belville) for their assistance with obtaining the data and information used in this work.

Many thanks to Mr. Fredrick Calitz and Ms. Marde Booyse of the Agricultural Research Council for their help with the SAS regression analyses.

Thanks also to Dr Claudia Libiseller of the Linkoping University, Sweden, for her assistance with the interpretation of the Seasonal Mann-Kendall test results.

Finally, I am grateful to Ndodana, my boys, my family and friends for their love and unwavering support as I walked this journey.

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND

Rivers are waterways of strategic importance across the world, providing main water resources for domestic, industrial, and agricultural purposes. This is particularly true for South Africa, a country that relies heavily on surface water resources to sustain its growing population and economy. In this part of the world, surface water is inherently unevenly distributed with almost 60% of the country categorised as arid to semi arid (Nomquphu, 2005; Mack *et al*, 2004; DWAF, 2004a). Since there are hardly any freshwater lakes in South Africa, the only exploitable surface water is confined to rivers (O'Keeffe *et al*, 1992). There is plenty evidence of this reliance on rivers in South Africa, and it includes the extensive damming and interbasin transfers (IBT's) such as the Orange-Fish, Thukela-Vaal, Riviersonderend-Berg River, and the Usutu-Vaal (Nomquphu, 2005; Lusher & Ramsden 1992).

The quality of water in many rivers in South Africa continues to deteriorate at unprecedented rates, and in the process compromising the health of aquatic ecosystems, as well as the well being and livelihoods of some water users (O'Keeffe *et al*, 1992). Catchment based land activities generate waste that is delivered into and transported by rivers. The diversity of catchments and their rivers is often reflected by an assortment of water quality problems including eutrophication, increased salinity, increased turbidity, acidification and toxicity.

The deteriorating quality of water in rivers presents a major challenge to South Africa. It is perceived to be one of the major impediments to South Africa's capability to provide sufficient water of appropriate quality to meet its current needs and to ensure sustainable water provision for the future (Otieno & Ochieng, 2004). The quality of water directly affects its availability and use, such that the poorer the quality of water, the less water there is available to support various uses (DWAF, 2004b).

The concern for water quality has often led to an increasing demand for water quality monitoring (Antonopoulos *et al*, 2001). Measuring of water quality conditions in time and space as a means of defining water resource problems has a long history in South Africa (DWAF, 2004c; DWAF, 1999). For example, the Department of Water Affairs and Forestry's (DWAF) National Monitoring Programme, whose main objectives were to provide ambient water quality data and information for water resource planning, management and pollution control, has been underway since the late 1960's (Van Vliet & Nell, 1986). Notably, environmental monitoring of water quality has and continues to play an integral part in water resources management at all levels (national, provincial and local) with many water resource professionals subscribing to the principle that "if you can't measure it, you can't manage it" (Nomquphu, 2005; DWAF, 2004c). Chapter 14 of the National Water Act (RSA, 1998) currently provides for water resource monitoring, for purposes of data gathering, information generation and dissemination.

The Department of Water Affairs and Forestry (2004b) forward the view that, in spite of all the attention that has been given to water quality, it has yet to take its rightful place in the integrated management of water resources. Nomquphu (2005) reinforces this assertion by arguing that, notwithstanding the hypothesized continuous degradation of the nation's water resources, and extensive monitoring programmes that have been in place for decades, there are still no clear indicators of the rate of degradation in the country's waters. This deficiency of information, diagnosed by DWAF (2004c) as the "data rich but information poor syndrome" is an unfortunate reality in light of the large expenditure devoted to the routine monitoring of water quality.

Therefore, it is critical to improve knowledge on the water quality of the various river systems by seeking out relevant and reliable, temporal and spatial information from existing time series data resulting from water quality monitoring programmes and make it accessible as a basis for effective and efficient water quality management.

1.1 THE RESEARCH PROBLEM

The Eerste River in the Western Cape is a river that supports a number of uses including agriculture and domestic use. The river currently supplements bulk water supply to the town of Stellenbosch (RHP, 2005). Therefore, the quality of its water requires a high degree of protection. However, along its course, the river traverses an array of land uses that are indicated to progressively impact negatively on the quality of its water (DWAF, 1993; Hendricks, 2003; Joseph, 2003). These land uses include; agricultural areas with intensive irrigation and forestry (DWAF, 2004b), industrial and domestic use in highly urbanised residential areas in its upper and lower zones (DWAF, 2004b; Somers & Nel, 2003).

Dr Dirk van Driel (2005) of the Scientific Services Branch of the City of Cape Town (CCT) observes that there have been some evident changes in the water quality of the Eerste River over the years. Seemingly, the river, which flows on Table Mountain Sandstone in its upper reaches, and Malmesbury Shale and Cape Granite in its lower reaches (DWAF, 1993), was acidic at some point in time, with a pH of about 4.5, its water soft, and naturally "black". However, with the onslaught of urbanisation those traits changed dramatically. At present the pH is said to be neutral and the water much harder (Van Driel, 2005).

Previous research of water quality trends in the Eerste River was carried out by the Department of Water Affairs and Forestry (DWAF) in 1993. In that study, DWAF sought to compile information on the water quality of the Eerste River with a view to understand the processes that influence its water quality. This particular study was based on the assessment of time series plots of 12 year data for electrical conductivity, pH, chloride, nitrate, ammonia, and phosphate, at four stations located on the river during the period starting in 1977 to 1989. This study was not a detailed assessment and therefore did not employ trend tests. On the basis of the time series assessment, DWAF (1993) concluded that no long term trends were evident in the river system. In the assessment for spatial trend, DWAF (1993) compared the water quality data for the upper reaches to that of the lower reaches of the river, and reported a steady decline in water quality. This decline was ascribed to point and non-point sources of pollution in the catchment.

This study explores data accumulated between 1990 and 2005 to investigate long term and spatial trend in water quality data with respect to the pollution indicator variables; pH, electrical conductivity (EC), nitrogen, phosphorus and chemical oxygen demand (COD) in the Eerste River.

1.3 AIMS & OBJECTIVES

1.3.1 Aims

The aims of the study are:

1. To investigate significant long term trends in the surface water quality of the Eerste River between 1990 and 2005.
2. To investigate the nature of spatial trend in water quality, that is, if the water quality degrades or improves downstream during the study period.

1.3.2 Research objectives

The specific research objectives are:

1. To investigate long term trend in the water quality data using the non- parametric Seasonal Mann-Kendall Test for Trend.
2. To evaluate long term trend in the water quality data using regression analysis.
3. To assess spatial trend in the Eerste River during the study period.
4. To identify possible cause(s) of deterioration or improvement in water quality in the Eerste River.

1.3.3 Research questions

In pursuing the objectives of the study, the following questions provide focus,

1 Has the water quality deteriorated or improved with time?
2 Does the water quality deteriorate or improve with distance?
3 What are the main sources of pollution in the river?

1.4 STUDY DESIGN

The study is informed by a comprehensive review of peer reviewed publications concerned with water quality trend detection, and is based on the statistical analysis of secondary time series data. Standard regression analysis and the Seasonal Mann-Kendall test are used to analyse the data in order to identify and characterise the long-term temporal and spatial trends therein. The particular variables of interest are: pH, electrical conductivity (EC), nitrogen, phosphorus, and chemical oxygen demand (COD). The data were obtained for eight monitoring stations along the course of the Eerste River and one station on the Plankenbrug tributary. Two of the stations (EK13 and EK14) on the Eerste River were monitored by the City of Cape Town while the rest were monitored by the Department of Water Affairs and Forestry between 1990 and 2005. For the raw data refer to Appendix 1.

The study sites were selected to ensure relatively even spatial coverage of the river. Furthermore, the major land uses in the catchment, which are hypothesised to influence water quality, these include agriculture, industrial, formal & informal residential settlements and wastewater treatment works (WWTW) are considered in the selection of study sites.

The water quality parameters used in the study were selected for the below mentioned reasons. pH and electrical conductivity are important indicators of water quality Golterman *et al*, (1997). pH is generally viewed as an indicator of acidification in a sample of water (EEA, 1996). Dallas & Day (2004) state that for naturally acid, black water systems, such as those of the south western Cape, continuously low values of pH are perhaps the best single measure of integrity and therefore invaluable in the assessment of their water quality. Electrical conductivity is a measure of the total amount of dissolved material in a water sample (Dallas & Day, 2004). DWAF (1998) classifies pH and electrical conductivity as Group A indicators. They define Group A indicators as those that are considered critical and must always be monitored from source and right through the distribution system in water for domestic supplies (DWAF, 1998).

The nitrogen, phosphorus and chemical oxygen demand, were selected for the study because they are typical indicators of water pollution (Pegram & Gorgens, 2001). Nitrogen and phosphorus, though naturally occurring, can be indicative of anthropogenic pollution and are considered to be the most limiting nutrients. They control the degree of eutrophication in South Africa (Dallas & Day, 2004). Their presence has been implicated in the excessive growth of aquatic plants in inland water bodies (Pegram & Gorgens, 2001, Davies & Day, 1998). Chemical oxygen demand is useful as an indicator of water pollution because its measure determines the quantities of organic matter found in water.

The period of 15 years was selected on the basis of data availability, and also the knowledge that when investigating long term trends, a period of over 10 years is preferable (Cox *et al*, 2005). The reasoning being that with a shorter time scale, for example five to seven years, one may detect linear trends and assume those trends to be continuous when they may in fact have later reversed direction. Therefore, a longer time period allows for the consideration of non-linear trends (Cox *et al*, 2005).

For the detection of monotonic temporal trends, the parametric regression analysis using the SAS version 8.2 (SAS, 1999) statistical package; and the non parametric Seasonal Mann-Kendall Test, MULTIMK/PARTMK available online: www.mai.liu.se/~cllib/welcome/pmktest.html (Libiseller, 2002), are used. For spatial trend, regression analysis and analysis of variance (ANOVA) using the SAS version 8.2 (SAS, 1999) are employed. A more detailed exposition of the methods is given in Chapters 3.

The study will be useful for describing the quality of the water in the Eerste River as well as the identification of possible and persistent polluting activities.

1.5 THE EERSTE RIVER

1.5.1 Description of the river

The Eerste River, shown in Figure 1.1, is generally a rocky and narrow river whose head waters arise in the Jonkershoek Mountains in the Jonkershoek Forest Reserve (Somers & Nel, 2003; DWAF, 1993). From its source, the river flows in a north westerly direction to Stellenbosch, and then south to where it discharges into False Bay at Macassar (DWAF, 1993).

The Eerste River is approximately 40km long with a catchment of 420km² (DWAF, 1993). The river comprises a mountain stream zone (Jonkershoek), of reach of 7km long from its headwaters; the upper zone, which starts 5km from the lower end of the Jonkershoek valley to its confluence with the Plankenbrug River in Stellenbosch; and the lower zone which stretches from Stellenbosch to the estuary at False Bay (DWAF, 1993). In its lower zone, the Eerste River is joined by the Veldwagters, Blouklip, and Kuils rivers.

The Eerste River typically exhibits fluctuations in stream flows, with low flows in summer and increased flows in the winter season. The winter season in the Western Cape is the rainfall season as is typical of the Mediterranean climate that characterises this province.

1.5.2 Regulation of the river

The Kleinplaas Dam, which has regulated the Eerste River since 1981 (DWAF, 1993), on the Jonkershoek tributary of the Eerste River serves as a balancing and diversion dam in a tunnel transfer system between the Theewaterskloof Dam and the Stellenboschberg tunnel outlet (DWAF, 2004b). At the inflow into the dam, water is abstracted and then stored in the two municipal dams in Stellenbosch, for the town's water supply (DWAF, 2004b; DWAF, 1993). The system supplies water to irrigation farmers as well as the City of Cape Town's water treatment works at Blackheath and Faure (DWAF, 2004b).

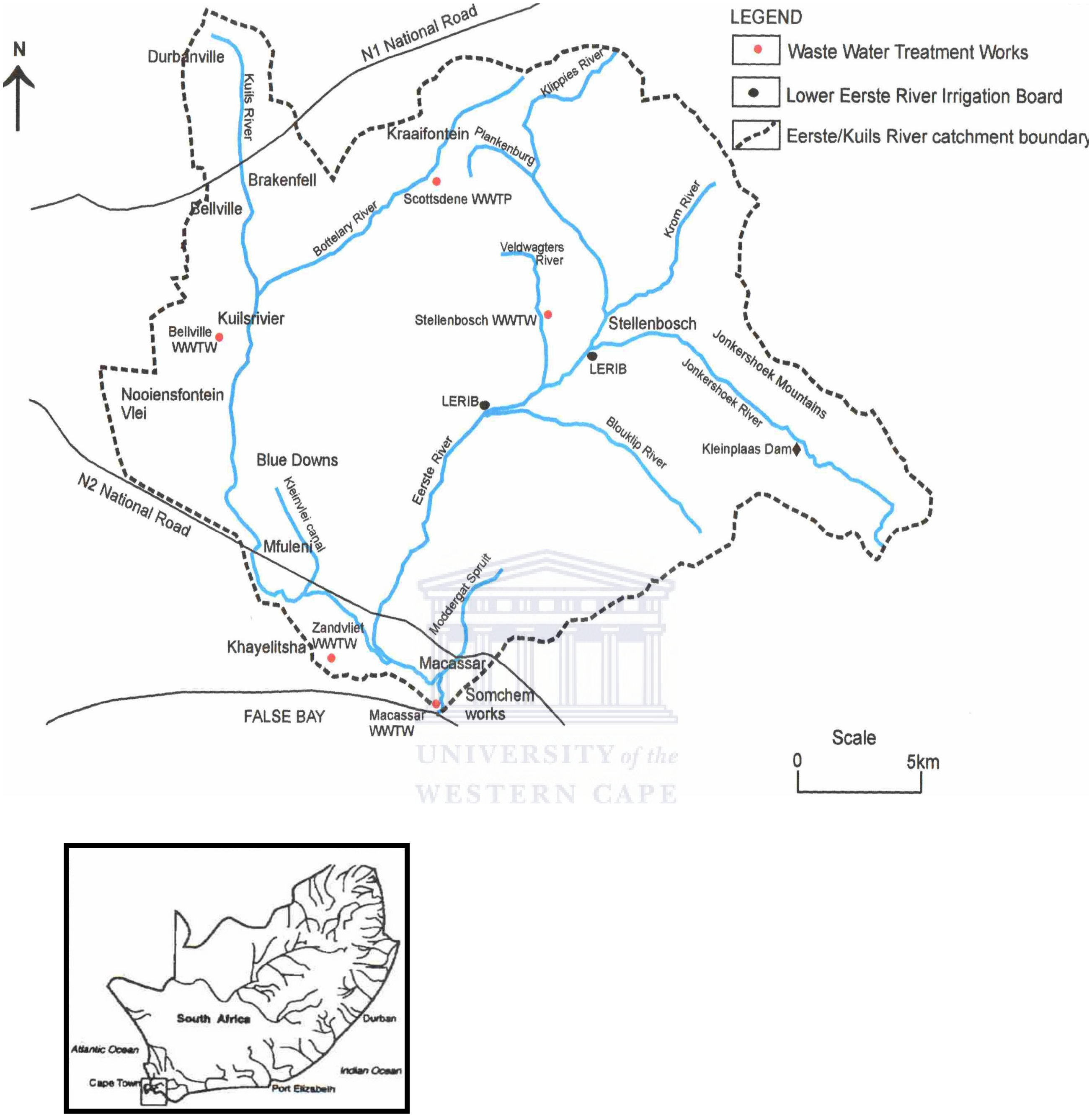

FIGURE 1.1 LOCATION OF THE EERSTE RIVER

Map adapted from Petersen (2002), Harrison (1998) &DWAF (1993)

1.5.3 Water quality of the river

The Eerste River receives the country's highest recorded rainfall of 4000mm and is considered pristine in its upper reaches (DWAF, 2004b). The water quality is indicated to deteriorate downstream, starting at the Eerste River's confluence with the Plankenbrug River. The Plankenbrug River, whose water quality is classified as poor, carries a high load of pollutants emanating from stormwater and waste water from the Khayamandi informal settlement and Stellenbosch (RHP, 2005).

Downstream of its confluence with the Plankenbrug tributary, the Eerste River receives treated municipal effluent (8.4 million cubic metres/ annum) from the Stellenbosch Waste Water Treatment Works through the Veldwagters tributary (RHP, 2005; DWAF, 2004b; DWAF, 1993). This treated effluent contributes not only to the changes in water chemistry, but also to changes in flow regime in the summer season (DWAF, 1993).

Further down its lower reaches, the Eerste River is joined by the heavily polluted Kuils River system. The Kuils River receives treated effluent from the Bellville (14.7 million cubic metres/ annum) and Zandvliet (16.8 million cubic metres/ annum) waste water treatment works. At the estuary at Macassar, it further receives treated effluent (13.3 million cubic metres / annum) from the Macassar Waste Water Treatment Works before discharging into False Bay (RHP, 2005; DWAF, 2004b).

1.6 LIMITATIONS OF THE STUDY

There was a large number of missing and below detection limit values in the water quality data, as well as a general lack of consistency in the frequency of monitoring. While missing data are not a big problem in trend testing particularly when they are random, below detection limit values usually are (Darken, 1999). This is because they result in low outliers which often cause skewness in data, and thus render statistical techniques such as regression inappropriate.

Furthermore, the lack of accurate and corresponding flow data made flow adjustment on the variables impossible, meaning that for those variables such as conductivity whose concentration may be influenced by flow, the observed trends may not be an accurate representation of the actual trend and should therefore be read into with caution.

1.7 OVERVIEW

The study is arranged into five chapters followed by appendices. The second chapter is a discussion of statistical methods currently used in water quality trend assessments and an exploration of water quality studies using some of these methods.

Chapter three addresses the actual statistical methods, namely the Seasonal Mann-Kendall test and regression analysis, which are used to test the research hypotheses. Furthermore, the data set; its acquisition and preparation; and the actual water quality variables used are discussed.

In the fourth chapter, the results of the temporal and spatial trend analyses of individual variables at each station are presented and discussed. Possible explanations for the observed trends are also given.

The fifth chapter presents the summary, conclusions and recommendations.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

Rivers are vital and vulnerable freshwater systems that are critical for the sustenance of all life. However, the declining quality of the water in these systems threatens their sustainability and is therefore a cause for concern. Since the early 19th century, the rapid growth of industry and the introduction of sewer systems to service a rapidly growing population have resulted in widespread pollution of entire river systems (SEPA, 1996). The damage is so extensive that very few, if any, have remained in their natural condition (Ngonye & Machiwa, 2004).

Rivers are longitudinal functional units whose flow is unidirectional, as explained by the 'river continuum' concept (Davies & Day, 1998). This concept considers rivers as characterised by physical and chemical conditions that are progressively and continuously modified downstream from the headwaters to the sea (Davies & Day, 1998). Whilst the attributes and constituents of water vary naturally within and between rivers, almost all surface water bodies tend to exhibit some degree of natural intra and inter annual variation (King *et al*, 2003).

However, the natural variation of water quality in time and space is greatly affected by land based activities in the different river catchments (Buck *et al*, 2004). Since rivers arise from surface runoff, they mobilise and transport pollutant matter from both natural and anthropogenic sources that they interact with along their course. The pollutants that may be held in solution or as particulate matter (Dallas & Day, 2004; Tong & Chen, 2002) are therefore, often reflective of catchment activity (King *et al,* 2003; Ferrier & Edwards, 2002; Davies & Day, 1998).

The deteriorating quality of surface water is an area of concern in both the scientific and public arenas. The result of this concern has been an increased demand for reliable water quality information (Antonopoulos *et al*, 2001; Hirsch *et al*, 1991). Most countries have comprehensive networks for monitoring chemical constituents, physical attributes and some even use biomonitoring techniques, to ensure that all aspects of water quality are monitored (King *et al*, 2003). The consequence of which has been the gradual accumulation of long term data and an interest in examining these data for trends (Hirsch *et al*, 1991).

The interest in water quality trends stems firstly, from the intrinsic interest in the question of changing water quality out of concern for the environment, secondly, from the availability of substantial amounts of data to warrant such analysis (Antonopoulos *et al*, 2001), thirdly, from the view that detecting temporal trends is or should be one of the main objectives of environmental monitoring (Libiseller & Grimvall, 2002; Smith *et al*, 1996), and lastly, that the ability to detect trends is a principal tool for effective and sustainable water quality planning, control, and management (Ferrier & Edwards, 2002; Antonopoulos *et al*, 2001).

The process through which water quality information is produced has become more targeted in the recent past (Griffith *et al*, 2001). The last two decades have seen a flurry of studies investigating trends, both temporal and spatial, particularly in the developed nations. These studies have been informed by meticulously researched, investigated, reviewed and improved statistical analyses suitable for distinguishing the more persistent changes in water quality from random fluctuations (Libiseller & Grimvall, 2002; McBride & Loftis, 1994). Scholars like Smith *et al* (1996); McBride & Loftis (1994); Hirsch *et al* (1991); Helsel & Hirsh (1991); to name a few, have emerged as key figures in the research, development and application of statistical techniques that are 'appropriate' for trend testing in water resources data.

This chapter presents a synthesis of literature on statistical procedures and techniques currently in use to detect long term trends in water quality data.

2.2 STATISTICAL ANALYSIS OF WATER QUALITY

The use of statistical techniques in aquatic environmental monitoring is a relatively new subject (Hamed & Rao, 1998). Statistical tests are currently considered invaluable in the design and analysis of the results of monitoring programmes (Antonopoulos *et al*, 2001; McBride & Loftis, 1994). Routine water quality monitoring programmes often serve many purposes, but are primarily aimed at assessing the environmental state of water and detecting trends (EEA, 1996). Often, monitoring programmes produce a wealth of long term time series data. Statistical tests are the principal means used in the analysis of these time series data to "…arrive at a deeper understanding of the causal mechanisms that generated it…" (Kendall *et al,* 1983).

A time series generally has four components: a trend or long term movement; oscillations about the trend, of greater or less regularity; a seasonal effect and an irregular or random component (Kendall *et al*, 1983). Quantitative statements about time series data are obtained from the series by decomposing it into its individual components (Mattikalli, 1996). Of key interest in this study is the trend component.

2.3 TESTING FOR TREND IN WATER QUALITY DATA

Detecting temporal trend in water quality data is a subject that is currently very topical in the water research fraternity (Hess *et al*, 2001; Hamed & Rao, 1998; Helsel & Hirsch, 1991; Hirsch *et al,* 1991).

A trend in water quality data is defined as a monotonic change in a particular constituent with time (Helsel & Hirsch, 1991), the causes of which may or may not be known. The purpose of trend testing is to investigate whether the measured values of a water quality constituent are increasing or decreasing over time in statistically significant terms (Onoz & Bayazit, 2003; Helsel & Hirsch, 1991). When checking for an increase or decrease in variable values, statistically it means determining whether the probability distribution from which they arise has changed with time (Antonopoulos *et al*, 2001; Helsel & Hirsch, 1991).

Trend detection involves statistical testing of the null hypothesis that there is no trend with time, the alternative hypothesis being that there is an overall increase or decrease in a constituent with time at some specified significance level (Onoz & Bayazit, 2003; Zipper *et al*, 1998). The significance level is the probability of incorrectly rejecting the null hypothesis when it is in fact true (McBride & Loftis, 1994; Helsel & Hirsch, 1991). The traditional default significance value usually used in statistics is 5% (Griffith *et al*, 2001; Helsel & Hirsch, 1991). A statistically significant trend is obtained when a smaller p value than the significance level (0.05) is obtained (Griffith *et al*, 2001).

When selecting the trend detection method to follow, several considerations must be made. These considerations include, taking into account the characteristics of the data itself; the type of trend expected (monotonic or step); the general category of statistical methods to employ (parametric or non parametric); adherence of data to assumptions of normality, independence, linearity, as required by various analytical procedures; as well as the objectives of the study (Darken *et al*, 2002; Qian *et al*, 2000; Hirsch *et al*, 1991).

2.3.1 Characteristics of water quality data

Water quality data exhibit many characteristics that complicate trend analysis and influence the choice of analysis procedures (Darken, 1999; Helsel & Hirsch, 1991). A mere application of analysis procedures that assume that data possess characteristics that they may in fact not, often results in the incorrect interpretation of the actual situation and therefore, add no value to the analysis at hand (Helsel & Hirsch, 1991).

Helsel & Hirsch (1991), state that all statistical methods, from simple summarisation methods to the more complex procedures should recognise the characteristics of most water resources data outlined below;

- No negative values are possible, the lower boundary is zero.
- Outliers, that is, those values that are considerably higher or lower than most of the data occur regularly.
- Due to the two characteristics above, positive skewness occurs. Skewness is an indication of the departure of the distribution from the normal symmetrical curve. The

data are positively skewed if the curve has a longer right tail and are negatively skewed if it has a longer left tail. In many cases water quality data are positively skewed, indicating the presence of many relatively low values and a few high values (Grabow *et al*, 1999).

The measure of skewness is known as the coefficient of skewness. In perfectly normally distributed data, the coefficient of skewness is zero. Values that are greater than one, point to a degree of skewness that ought to be addressed (Grabow *et al*, 1999).

- Owing to the three characteristics above, non-normal distribution of data often occurs. Most inferential methods, or parametric methods including linear regression, are founded on the assumption of a normal (Gaussian) distribution and yet water quality data and their regression residuals are often 'distinctly non-normally distributed' (Vant & Smith, 2004; Lietz, 2000; Darken, 1999; Zipper *et al,* 1992).

  Tests for normality include the Shapiro-Wilk test (test statistic, W) and the Kolmogorov-Smirnov (test statistic D) among a few other tests. The Shapiro- Wilk test statistic (W) which is frequently used, ranges from zero to one, with low p-values (smaller than 0.05) resulting in the rejection of the hypothesis of normality (Grabow *et al*, 1999). Values that are greater than 0.05 suggest that there is insufficient evidence to reject the null hypothesis, and lead to the assumption that the data are indeed from a normal distribution.

- Censored data. This refers to observations that fall below or above some threshold, often occurring because of imprecision in laboratory analytic techniques when measuring minute or very large quantities (Darken, 1999). The magnitudes of water quality observations that occur beyond technically possible detection limits are often unknown. In linear regression, this amounts to incomplete information that cannot be used effectively (Darken, 1999; Zipper *et al*, 1992). Whilst the IDT (1989) have suggested that censored values can be eliminated by assigning a value of half the detection limit to each of the affected records, Cox *et al* (2005) argue that in their experience this method results in low outliers. Low outliers often result in skewness. Therefore, they propose that the detection limit itself be used instead (Cox *et al*, 2005).

- Seasonal patterns are common in water resources data, as most concentrations in surface water respond to seasonal changes in stream flow and catchment inputs (Helsel & Hirsch, 1991).

- Serial correlation also known as autocorrelation is another common feature of long term water quality data whose extent is a critical consideration. Serial correlation is a situation where water samples carry over information from one sample to the next, such that data have redundant information and less information for the same number of independent observations (Grabow *et al*, 1999). This is usually a result of monitoring the same station at very close time intervals (McBride & Loftis, 1994). For example, data that is collected more frequently than monthly tends to lose its independence (Cox *et al*, 2005, McBride & Loftis, 1994). The power of statistical tests is a function of independent sample size. Therefore, if data lose their independence, the tests become prone to falsely rejecting the null hypothesis of no trend (Type I error), leading to a wrong conclusion of the presence of a trend (McBride & Loftis, 1994).

  According to Grabow *et al* (1999) the easiest way to eliminate autocorrelation, is to aggregate or average the data into longer time steps (data reduction). Alternatively, one could employ the Seasonal Kendall Test with the covariance sum method to allow for serial dependence. However, when serial correlation is negligible, tests such as the Seasonal Kendall Test may be applied in their original form (Darken *et al*, 2002).

- Covariance. This is a situation where the behaviour of the variables under study is influenced by other and uncontrolled variables. For example, the concentration of some water quality variables, such as conductivity is influenced by stream flow. Therefore, two analyses must be carried out on the data; one on the non-flow adjusted data and another on flow adjusted data where flow data are available, to determine whether a trend detected is genuine or a result of flow. Analysis of trend on flow adjusted variables eliminates the influence of flow, thereby, giving a more reliable trend (Vant & Smith, 2004; Griffith *et al*, 2001; Zipper *et al*, 1998).

- Another feature of time series data that complicates analysis is unequal sampling, which is often viewed as equal sampling intervals with missing data (Darken 1999). In multiple station studies, multiple starting and ending dates complicate trend analysis. Therefore, in order to correctly interpret data, the water quality records must be concurrent and yet long enough to discern true trends. Hirsch *et al* (1991) state that when one is doing a study of data, for instance, from 1970 to 1985, a record that starts in 1972 or ends in 1983 need not be excluded from the study, similarly a record with a two year gap need not be disqualified from the study.

The water quality characteristics discussed above often present problems in trend analysis particularly when conventional parametric techniques such as linear regression are used (Lietz, 2000; Darken, 1999; Zipper *et al*, 1992). However, Zipper *et al*, (1992) state that in spite of the limitations identified thus far, linear regression has been observed to be capable of detecting water quality trends, particularly where those trends were well defined.

2.3.2 Types of trend

Two types of trend are considered for hypothesis testing and trend estimation in literature; these are the monotonic and step trends (Qian *et al,* 2000; Darken, 1999; Hirsch *et al*, 1991).

2.3.2.1 *Monotonic trend*

Monotonic trend occurs when a response variable changes with a concomitant change in the explanatory variable. The change is unidirectional over time and the hypothesis in this case does not specify whether this shift is continuous, linear, in one or more discrete steps, or in any particular pattern (Zipper *et al*, 1998; Hirsch *et al*, 1991). If no prior hypothesis of a time change is known, or if records from multiple stations are being analysed in a single study, then monotonic trend procedures are appropriate (Hirsch *et al* 1991).

For monotonic trend, the hypothesis that the data shifts monotonically is often tested with regression analysis of the water quality variable as a function of time (Hirsch *et al*, 1991). The alternative test is the nonparametric Mann-Kendall test for trend (Hirsch *et al*, 1991). A number of variations of the Mann Kendall test are currently in use, these include the Seasonal Kendall Test with its variations, the covariance sum test, or the covariance eigenvalue test (Darken, 1999).

2.3.2.2 *Step trend*

The step trend occurs when a variable changes from one constant level to another constant level (Darken, 1999; Hirsch *et al*, 1991). The assumption made is that the locations (means or median values) of data collected before and after a specific time are distinctly different. The trend hypothesis tested here is more specific than with the monotonic trend in that it requires that certain facts be known before examining the data (Hirsch *et al*, 1991). Step trend procedures are particularly useful in two instances; firstly, when there is a relatively large gap in time separating data into two distinct groups (Darken, 1999; Hirsch *et al*, 1991). While there is no hard and fast rule as to the length of the gap, a time gap of over a third of the study period warrants the use of the step trend procedures (Hirsch *et al*, 1991). Secondly, if an event that is likely to have resulted in change in water quality is known, then two time periods are considered, that is the before and after the incident. Examples of such events include the introduction of point or non point sources of pollution, or a ban of certain polluting activities.

Step trend techniques include the two-sample t-test with the associated estimates of change in magnitude based on the difference in sample means. The alternative is the Mann-Whitney-Wilcoxon Rank sum test and the Hodges-Lehmann estimator of trend magnitude (Darken, 1999; Hirsch *et al*, 1991).

2. 4 METHODS FOR DETECTING TREND

Whilst many techniques are available for trend detection and estimation in environmental data (Griffith *et al*, 2001, Hess *et al*, 2001) none are published as standard tests for assessing water quality data (Griffith *et al*, 2001). However, many have been proposed (Qian *et al,* 2000) and established through common practice (Griffith *et al*, 2001). The various trend detection tests fall under two broad categories, the parametric and the non-parametric methods (Hess *et al*, 2001; Hamed & Rao 1998; Hirsch *et al*, 1991).

2.4.1 Parametric methods

Parametric statistical tests are those tests that are based on estimates of statistical parameters such as mean and standard deviation. Parametric statistical methods are based on linear regression and therefore check only for linear or monotonic trend. They assume that the random variable (water quality constituent) is independent and follows the normal distribution 'or very nearly so' (Onoz & Bayazit, 2003; Grabow *et al*, 1999; Helsel & Hirsch, 1991). A normal distribution is bell shaped, but as has been asserted in the discussion above, water quality data are often skewed and therefore seldom normally distributed.

However, when the data do follow a normal distribution and are independent, parametric methods are perceived to be the most powerful tests, far more powerful than their nonparametric counterparts at any significance level (Darken, 1999; Hamed & Rao, 1998; Zipper *et al*, 1992; Hirsch *et al*, 1991). However, if the data do not follow normal distribution, the parametric tests tend to lose their power to detect trends (Hirsch *et al*, 1991). Examples of parametric tests include the ordinary least squares also known as linear regression, the t-test and the rank sum test.

Transformations have been carried out on data to make them more linear, symmetric and normally distributed (see for example Verhallen *et al*, undated; Cox *et al*, 2005) and, thus more suited to parametric methods. However, Hirsch *et al* (1991) argue that transformations are not always recommended, particularly with multiple record data. They state that data transformations are subjective; because data can easily be manipulated until a desired or preconceived result is achieved (Hirsch *et al*, 1991).

2.4.1.1 *Linear Regression*

Simple linear regression is an important and commonly used parametric method for identifying monotonic trend in a time series (Zipper *et al*, 1992; Helsel & Hirsch, 1991). It is used to describe the relationship between one variable with another or other variables of interest. It is often performed to obtain the slope coefficient of a water quality variable on time. The slope coefficient is tested under the null hypothesis that it is equal to zero. Regression has the advantage that it provides a measure of significance based on the hypothesis test on the slope or correlation coefficient; and also gives the magnitude of the rate of change (Hirsch *et al*, 1991).

2.4.1.1 *T-Test for difference between means*

The t-test is a simple trend detection method that is often used by researchers with very basic training in statistics (Hess *et al*, 2001). It is based on whether a statistically significant difference exists between the means first half of data and last half (Hess *et al*, 2001). The mean of second half of data is simply subtracted from the mean of the first half of data. The statistical significance at 95% confidence interval is then calculated. However, Hess *et al* (2001) state that the t-test is only valid when observations are random and stress that t-tests ought to be used with extreme caution in serially correlated data.

Onoz & Bayazit (2003) used Monte Carlo simulation to investigate the relative power of the parametric t-test, in comparison with the non parametric Mann-Kendall test. They found the t-test to be slightly more powerful under normal probability distribution, decreasing in power ratio with an increase in the coefficient of skewness. However, for moderately skewed distributions, they observed the t-test to be nearly as powerful as the Mann-Kendall test. They then used the two tests on water quality data of 25 to 65 years at 107 sites in various river basins in Turkey. They found that both tests detected trend in 29 series; at two sites trends were detected by the t-test only; at two other sites by the Mann Kendall test only; and at four sites the two tests gave different results. Onoz & Bayazit (2003) then concluded that the two tests could be used interchangeably in practical applications with identical results.

2.4.2 Non-parametric methods

These are hypothesis tests that are distribution free (Zipper *et al* 1992), not requiring the assumption that data follow any particular distribution and not restricted to linear trend (Onoz & Bayazit, 2003). Non parametric tests demand independence of data and use rank order statistics only. They extract trend information based on the relative magnitudes of the data, but do not quantify the size of change (Hamed & Rao 1998; Helsel & Hirsch 1991). Tests including the Seasonal Kendall Slope Estimator and the Sen's slope estimator are available to quantify the trends (Libiseller, 2002; Zipper *et al*, 1992).

Non-parametric tests are thought to be more powerful than their parametric counterparts for non-normally distributed data, and are therefore useful in water resources data (Yue *et al*, 2002; Lietz, 2000; Helsel & Hirsch 1991). When dealing with normally distributed data, these tests are said to be as powerful as their parametric counterparts (Lietz, 2000; Hirsch *et al*, 1991). There are two basic non-parametric tests for trend analysis, the Mann Kendall and the Spearman's rho test (Onoz & Bayazit, 2003). These tests are discussed in subsequent sections.

The decision to use either the parametric or non-parametric tests is based on the considerations of power and efficiency (Hirsch *et al*, 1991). Power is defined as the probability to reject the null hypothesis (no trend) when it is truly false (McBride & Loftis, 1994). Therefore in order to be useful, the tests chosen should have good power to detect environmentally important trends (Griffith *et al*, 2001).

Monte Carlo simulation analyses used by Hirsch *et al* (1991) to compare the performance of both the parametric and non-parametric methods under various probability distribution conditions revealed that the non-parametric methods suffer minute disadvantages in terms of power and efficiency when data are normally distributed. However, when data depart slightly or largely from normality then modest and significant advantages are observed respectively.

2.4.2.1 *The Mann-Kendall Test*

The Mann-Kendall test is a widely used non-parametric test of association between two variables (Yue *et al*, 2002; Hamed & Rao, 1998). The test is generally used for the detection of trend in time series data (Hess *et al*, 2001; Hamed & Rao, 1998). According to Helsel & Hirsch (1991), this test may generally be stated as a test for monotonic change, where the central values (mean or median) tend to either increase or decrease with time.

The basic principle of the Mann-Kendall test is to examine the signs of all pair wise differences of the observed values, ranked in chronological order (Darken, 1999; Hamed & Rao 1998; Libiseller & Grimvall, 2002). Since the test uses the relative magnitude of data (based on rank order) and not the actual values of the data, they have the advantage that they are able to cope with outliers, missing values and values below detection limits (Onoz & Bayazit, 2003; Libiseller, 2002; Helsel & Hirsch, 1991). The test does however; assume independence and randomness in data and this is a disadvantage in the presence of serial correlation (Hamed & Rao, 1998; Darken *et al*, 2002).

Some variations of the Mann Kendall test have been developed over the years since its initial inception in 1981 (Libiseller, 2002). One version is the Seasonal Kendall test.

2.4.2.2 *The Seasonal Kendall Test*

The Seasonal Kendall Test is a modified version of the non-parametric Mann-Kendall test for monotonic trend, developed by Hirsch and others in 1982 (Libiseller, 2002; Hess *et al*, 2001). It carries all the robust statistical properties offered by its predecessor and can be performed on raw data; or on residuals of the time series before and after the effects of flow have been removed (Zipper *et al*, 1992). The Seasonal Kendall test is particularly popular with studies done for United States Geological Survey, for example Griffith *et al*, (2001); Lietz, (2000); Schertz *et al,* (1991); and Hirsch *et al*, (1991) used it to detect trends in water quality data in various areas. Helsel & Hirsch (1991) are often cited as reference in studies using the Seasonal Kendall test for trend (Vant & Smith, 2004; Raike *et al*, 2003; Libiseller & Grimvall, 2002; Griffith *et al*, 2001; Darken *et al*, 2002; Darken, 1999; Zipper *et al*, 1992).

The Seasonal Kendall test for trend is capable of analysing time series data for the likely presence of an upward or downward trend, at a specified significance level, while accounting for the effects of seasonality (Helsel & Hirsch, 1991). As with other nonparametric tests, the Seasonal Kendall test for trend deals only with the ranks and signs of data and not the actual data values (Smith *et al*, 1996). The Seasonal Kendall test is founded on the rationale that water quality is cyclical, varying with the seasons in the year. Therefore, to eliminate the possibility of seasonality invoking trend, and also to reduce variability when there is a seasonal effect, comparisons are made strictly between data from similar seasons, blocking out the other seasons (Darken, 1999; Schertz *et al*, 1991).

If a month is considered a season, then for example, one January value is compared to the January value of the following year and so on in an iterative manner, no comparisons are made across months. If the later value is larger than the one before it, a plus is recorded, if on the other hand the later value is smaller, then a minus is recorded. The plus sign is then converted to +1, the negative sign to -1 and the zero left as a 0. The statistic (S_i) for each month is then computed as the difference between the total number of +1 and the total number -1 for each season (Helsel & Hirsch 1991; Schertz *et al* 1991). The variance of the individual test statistics (S_i) is then computed (Darken, 1999).

The information from all the seasons is then aggregated by summing the individual monthly statistics (S_i) and their variances to give the overall statistic (S) and the overall variance (Darken, 1999; Helsel & Hirsch, 1991). The trend hypothesis is then tested by invoking a normality approximation of the standardised test statistic (Darken, 1999; Helsel & Hirsch 1991, Zipper *et al*, 1992). A positive Mann-Kendall statistic means an increasing trend, and a negative one means a decreasing trend. The p value associated with the statistic describes the significance of the trend (Schertz *et al* 1991).

The Seasonal Kendall test for trend is limited to monotonic trends, it does not fare well when trend changes direction and it is not robust against serial correlation (Cox *et al*, 2005; Darken *et al*, 2002). Its scope is limited to indicating the likely presence or absence of a trend and provides no information about the rate of change of the trend. Furthermore, it is technically invalid if detection limits change (Cox *et al*, 2005; Darken *et al*, 2002; Qian *et al*, 2000; Darken, 1999; Zipper *et al*, 1992; Helsel & Hirsch, 1991). Hamed & Rao (1998) suggest a modified Mann Kendall test, which is 'inert' in the presence of autocorrelation. Similarly, Darken *et al* (2002) recommend the use of the covariance sum method that allows some deviation from independence in place of the original Seasonal Kendall test to deal with serial correlation.

In 2002, Dr Claudia Libiseller of the Department of Mathematics at the Linkoping University in Sweden wrote a computer programme, the MULTIMK/PARTMK available online at http://www.mai.liu.se/~cllib/welcomed/pmktest.html for performing the Seasonal Mann-Kendall test for monotonic trend on multivariate data at multiple monitoring stations.

2.4.2.3 The Spearman's Rho.

The Spearman's rho, also known as the Spearman's Partial Rank Correlation (SPRC) is a non-parametric coefficient of rank correlation between two variables (X, Y) used to determine whether or not an association exists between the two variables (Hess *et al*, 2001). However a possible third variable Z may be responsible for the correlation between X and Y and thus its effects need to be removed so that the degree of correlation between the two can be quantified (Hess *et al*, 2001). According to Helsel & Hirsch (1991) the Spearman's rho can be understood to be a linear correlation coefficient computed on the ranks of the data.

Yue *et al* (2002) observed that for some unknown reason the Spearman's Rho, being another rank based non-parametric test for monotonic trend detection, seems to be seldom used compared to the Mann Kendall tests. In investigating this problem, they sought to determine the relative power of the two tests. Yue *et al* (2002) carried out simulation experiments using the Monte Carlo technique and found that while the two tests have similar if not 'indistinguishable' power, that power is influenced by distribution type and skewness in the time series. Furthermore, they found the power of the tests to be governed by the magnitude of the trend (the bigger the size of the trend, the more powerful the test), the sample size (as the sample size increases, the tests gains more power), and the amount of variation within the time series (as the variation increases in the time series, the power of the test decreases).

2.5 WATER QUALITY STUDIES INVOLVING THE USE OF TREND TESTS

A number of studies have been carried out on surface water bodies across the globe to investigate if any discernible patterns can be observed in their water quality over lengthy periods of time. A survey of literature revealed that some researchers are using non-parametric procedures to avoid being caught up in the complications of data sets and assumptions of probability distribution. Griffith *et al*, (2001) in their study, established that out of the 19 temporal trend studies that they reviewed, 12 employed the Seasonal Kendall test. In this study, the Seasonal Kendall test was observed to be frequently used as was modified regression (see Table 1). In this section case studies involving different methods are explored.

Table 2. 1. Water Quality Studies investigating trend.

Author(s)	**Test used**
Cox et al, 2005	Censored regression
Vant & Wilson, 2004	Seasonal Kendall
Raike *et al*, 2003	Seasonal Kendall
Interlandi & Crockett, 2003	Basic time series assessment
Parr & Mason, 2003	Spearman's Rho
Antonopoulos, 2001	Spearman's Rho
Grimwall *et al*, 2000	Basic time series assessment
Qian *et al*, 2000	Seasonal trend decomposition that uses local regression analysis
Zipper *et al*, 1998	Seasonal Kendall
Bhangu & Whitfield, 1997	the sign test
Smith *et al*, 1996	Seasonal Kendall
Mattikalli, 1996	Multiple linear regressions
MacDonald, 1995	Linear regression
Zipper *et al*, 1992	Seasonal Kendall

2.5.1 Studies of temporal trend using the regression analysis

Macdonald *et al* (1995) undertook a study to investigate annual and seasonal trends of soluble nitrogen and phosphorus data accumulated at a sampling station on the River Ythan in the United Kingdom between 1980 and 1992. They used regression analysis to investigate monotonic trend in the river. They opted for the parametric regression analysis because they had no prior hypothesis on the quality of the water in the River Ythan and because the sample size used was rather small and unbalanced since the data was collected from one sampling point. From their analysis, MacDonald *et al* (1995) found significant increasing trend in nitrogen concentrations, and high variability in phosphorus that did not exhibit any significant trend.

In another study, Mattikalli (1996) undertook a time series analysis of water quality data for the River Glen in south-eastern England, accumulated at 14 stations between 1976 and 1990. For the study Mattikalli (1996) developed an approach involving multiple regressions to quantify the seasonal and annual trends in the data. This particular technique was developed to handle missing records and irregularly sampled data. The research revealed a rise in the highly variable concentrations of total oxidized nitrogen.

Cox *et al* (2005) undertook a study to investigate the condition and trends in the water quality of major rivers and estuaries flowing into the Great Barrier Reef (GBR), North Queensland in Australia. They developed a method based on a censored regression technique to investigate the trends in data accumulated between 1992 and 2001, at 133 sampling stations. However, to take into account the assumptions of parametric tests, Cox *et al* (2005) log-transformed the data (to improve normality), and assumed data points to be independent (data was collected monthly). Seasonality was included in the model by fitting standard sine and cosine curves to the data. The advantages offered by the censored regression technique were that it allowed for the detection of non-monotonic trend, incorporated changes in detection limit, incorporated covariates and was also able to detect small trends with precision. Cox *et al* (2005) found several long term linear trends at many sites. However, they reported that these trends as not consistent across the whole region.

A study was carried out by Verhallen *et al* (undated) on the Vechte River basin (on the German-Dutch borders) to investigate long term trend in annual data of total nitrogen and total phosphorus with a view to infer future trends. Linear regression on log-transformed concentration data was used to process the time series of the nutrients from 1977 to 2000. From their analysis, Verhallen *et al*, (undated) observed significant declining trends in total phosphorus concentrations.

A study of the Neuse River Estuary, North Carolina, was carried out by Qian *et al* (2000) to analyse nutrient concentration data accumulated between 1979 and 1998. They applied a seasonal trend decomposition method that uses local regression analysis to investigate long term and seasonal trends in the river and estuary. The study revealed that while there were minor increases in nitrogen concentrations at upstream locations during the period of study, these changes did not reflect downstream and in the estuary. Furthermore, they observed that the significant decreases in phosphorus concentration were consistent downstream owing to the phosphorus ban in 1988.

Another study undertaken in the Schuylkill River, Pennsylvania in the United States by Interlandi & Crockett (2003) used multiple regression models to investigate trends in water chemistry (1973 to 1999) and land use (1982 to 1997). In developing the regression models, Interlandi & Crockett (2003) surveyed the data to assess normality of data distribution to determine their suitability for use in regression analysis. All the variables met the conditions of the Shapiro-Wilk test for normality. The multiple regression models indicated long-term trends of increased nutrient flux and other solutes over the past century particularly in urbanised catchments.

The studies outlined above make use of the parametric regression technique to investigate temporal trend in water quality data. However, owing to the complexities presented by water quality data characteristics including seasonality, non-normality, non-linearity, missing values and many more, some researchers have developed or modified the ordinary linear regression technique in order to curtail the limitations therein. Moreover, others use transformations to make the data conform to the requirements of regression techniques. The studies generally point to increasing trends in nitrogen in rivers and decreasing trends in phosphate (owing to the ban of phosphate based detergents) such that nitrogen seems to be the major driver of nutrient enrichment.

2.5.2 Studies of temporal trend using the Seasonal Kendall Test

Vant and Smith (2004) undertook a study to investigate long term trends in the water quality of rivers in the Waikato Region of New Zealand. They used the Seasonal Kendall test for trend to analyse records of 19 water quality variables taken at 110 monitoring stations in the region from 1987 to 2002. Ten of these stations were located on the Waikato River itself, and the rest distributed across the Waikato Region’s other rivers and streams. Vant & Smith embraced the Seasonal Kendall test on the strength that water quality data possess characteristics that render parametric tests ‘generally not appropriate’ and that this particular test is distribution free so they did not need to test the data for probability distribution. They observed trends of significant decreases in pH, dissolved oxygen, turbidity, and increases in conductivity, visual clarity, total nitrogen and total phosphorus. With respect to decreasing pH and increasing conductivity, they observed that this was a trend that has been observed throughout New Zealand, and concluded that the causal mechanisms were not just at regional level but at national level as well.

Raike *et al* (2003) carried out a study to detect trend in nutrient data monitored in rivers and lakes in Finland between 1975 and 2000. The objective of their study was to investigate if the water protection measures that were in place had decreased nutrient and chlorophyll *a* concentrations in the rivers. Using the Seasonal Kendall test for trend, they found that there were increasing trends in nutrients in those rivers passing through agricultural areas, while a decline in chlorophyll *a* was observed in a few places. They then concluded that these observed increasing trends in nutrients were responsible for the eutrophication that was becoming prominent in the surface waters of Finland. Besides agriculture, municipalities and industry were perceived contribute to excessive nutrient loading in the rivers.

Smith *et al* (1996) used the Seasonal Kendall test to detect trend for 14 physical and chemical parameters at 77 river sites distributed across New Zealand's North and South Islands. Their justification for using the Seasonal Kendall test was that, firstly, water quality data were often not normally distributed, thus casting doubt on the use of regression techniques. Secondly, the seasonality aspect of water quality data would not be accounted for in regression analyses. The results of their analysis revealed that there was a general improvement in water quality, especially in the South Island. This was seen in decreasing trends of biological oxygen demand, nitrogen and phosphorus.

Zipper *et al* (1992) undertook a study to evaluate changes in the water quality on an area drained by four river systems in south-western Virginia. They employed the Seasonal Kendall test for trend on data covering a period of about 20years from 1970-1989. They selected the Seasonal Kendall test for trend to avoid the complexities of data characteristics including skewness, non-linearity and non-normality.

Zipper *et al* (1992) considered data for 8 water quality variables; dissolved oxygen (DO), biochemical oxygen demand (BOD), pH, filterable residue (FR), non-filterable residue (NFR), total Kjeldahl nitrogen (TKN), total phosphates (TP), and faecal coli forms (FC) accumulated at 38 monitoring stations in the four river systems. They observed declining trends in water quality with regards to BOD and NFR for 25 stations. This trend was interpreted to mean significant improvements in water quality. With respect to TP, TKN and FR small declines in water quality were observed.

In another study of long term trends in surface water quality, Zipper *et al* (1998), employing the Seasonal Kendall test for trend, analysed time series data for dissolved oxygen (DO), biological oxygen demand (BOD), pH, total residue (TR), non filterable residue (NFR), total Kjeldahl nitrogen (TKN), total phosphorus (TP) and faecal coli form (FC) accumulated for 187 monitoring stations in Virginia's rivers, from 1966 to early 1997. They observed that significant trends indicating improvements in water quality exceeded those indicating deterioration for BOD, TP, FC, NFR, and DO across the state of Virginia. Increasing trends for TKN outnumbered the decreasing trends, suggesting deteriorating water quality in that regard.

The studies outlined above make use of the Seasonal Kendall test for trend on the basis of its non parametric nature and its relatively robust nature against various probability distributions of data. Its ability to handle the effects of seasonality is also cited as another reason for its use in a number of trend studies. The results of these tests suggest that the water quality in the rivers understudy is deteriorating with respect to nitrogen.

2.5.3 Studies of temporal trend using the Spearman's Rho

Parr & Mason (2003) undertook a study of long term trends in lowland rivers in the United Kingdom between 1958 and 1990, using the Spearman's Rank Correlation. They found that there was a significant decline in dissolved oxygen in eight rivers in Sussex and Suffolk. Chloride concentrations were on the rise during that period. An estimated 70% of total nitrogen (TN) in the rivers under study was ascribed to diffuse sources such as agricultural runoff, precipitation and urban waste. Furthermore, agriculture, domestic sewage and industrial detergents were found to be responsible for 43%, 24% and 19% respectively, of soluble reactive phosphorus found in the rivers. They also observed that rivers in East Anglia exhibited their lowest water quality during 1988-90, and then concluded that this deterioration was due to a combination of drought, agricultural runoff and inadequate sewage treatment facilities.

Antonopoulos *et al* (2001) undertook a study to examine long term trends in the water quality data of a monitoring station on Greek section of the Strymon River, a transboundary river in the Greek and Balkan area. The observed water quality of the Strymon River was hypothesized to be a function of upstream anthropogenic activity from Bulgaria and the Former Yugoslav Republic of Macedonia (FYROM). In order to meet the objective of their study, Antonopoulos *et al* (2001) used data for nine variables; temperature, electrical conductivity, dissolved oxygen, sulphates, sodium and potassium, magnesium, calcium, nitrate and total phosphate. They then used the Spearman's rank correlation coefficient and the student's t-test distribution to characterise trends for monthly water quality data accumulated between 1980 and 1997. However, prior to running the trend test, they used the chi-square and the Kolmogorov-Smirnov tests to determine the probability distribution of the data as a means to determining the appropriate model to fit. The trend analysis revealed upward trends in electrical conductivity, dissolved oxygen, sulphates, sodium and potassium and nitrate and no trend in magnesium, calcium and total phosphate.

The two studies that use the Spearman's rho select it for its non-parametric nature which makes it impartial to probability distribution assumptions. The increasing trends observed in these studies also point to deteriorating water quality in the rivers.

2.5.4 Studies of temporal trend using other techniques

The Scotland Environmental Protection Agency (SEPA) (1996) used time series assessments to track historical trends in the water quality of Scotland's rivers. They observed that in the early 19th Century, the rivers in Scotland were "clean, in healthy condition". However, six decades later, widespread pollution was witnessed in the entire river system in Britain, including estuaries, coastal water, and ground water. The pollution was associated with urban infrastructural development and rapid growth of industry. In the early 1900s, gross levels of pollution were observed downstream of significant conurbations and concentrations of industries. Improvements were observed from 1951 when legislation to control new discharges into the rivers was introduced, and in 1965 when The Rivers Act was enacted.

Time series studies of water quality of the Rhine River, near the border between Germany and Netherlands, revealed that nitrate concentrations trebled between the 1950’s and the 1980’s (Grimwall *et al*, 2000). Phosphate concentrations increased fivefold at the same site during that period. The increasing trend then changed direction and declined when point sources were eliminated and detergents containing phosphates were phased out (Grimwall *et al*, 2000).

Bhangu & Whitfield (1997) used the sign test, a non-parametric test to investigate the presence of trend in a water quality time series of 21 water quality variables accumulated for the Skeena River, British Columbia over a period of 8 years. The trend assessment suggested that there were no significant trends for any of the water quality variables tested.

Other techniques have been used to detect trend, these include basic time series assessments which are invaluable in the identification of temporal trends. The studies discussed in this section also point to progressive deterioration in water quality over time.

2.6 CONCLUSION

The assessment of literature from around the world depicts widespread concern over the deterioration of the world’s surface water quality in both space and time. The driving mechanisms behind the degradation of water quality include both natural and anthropogenic influences. Scientific and public awareness of degrading water quality continues to grow and with it the demand for knowledge of the complex interactions within the water cycle. This knowledge is primarily acquired through the monitoring of water resources and assessing the resultant time series data for trends.

Trend testing of water quality data provides useful information that ensures a sound appreciation of the cause and effect processes within a catchment. The ability to understand the changing environment and predict future scenarios is fundamental in achieving sustainable management of water resources. However, to attain this understanding, it is critical to be able to detect practically significant trends.

This review reveals that an array of statistical techniques is currently in use across the world to produce information on long-term trends in water quality. However, the selection of the appropriate method (parametric versus non-parametric) is influenced mainly by the data characteristics and the type of trend expected (monotonic versus step).

The justification of the use of different trend detection techniques is often centered on the knowledge that water quality data often exhibits characteristics that render some techniques inappropriate. The complexities that often characterize water quality data and influence the choice of test for trend include serial dependence, non-normal distribution and skewness. In some of the studies reviewed here, the authors do not bother to check the water quality data for probability distribution and automatically opt for non-parametric methods.

Non-parametric methods such as the Seasonal Kendall test for trend are a current ‘industry standard’, favoured by many scholars. They are considered as being more powerful, robust and better suited to water quality data than parametric tests. This is because they can be applied to data from any probability distribution. To the contrary, the parametric methods require that data follow probability distributions such as the normal or log normal distribution. If the data do adhere to the assumptions of linearity, normality and independence, then parametric methods exhibit greater power to detect trends than the non parametric methods. Linear regression is a popular parametric technique that has been observed to discern trends particularly when they are well defined.

Before the data are analysed for trend, it is critical to interact with the data so that their characteristics are well understood and not taken for granted. Firstly, this interaction with the data may include graphics, such as scatter plots, for visual interpretation and to aid the development of assumptions such as serial correlation and seasonality. Secondly, data ought to be tested for normality and skewness. Tests such as the coefficient of skewness; the Shapiro-Wilk test (test statistic, W) and the Kolmogorov-Smirnov (test statistic D) are among many that can be used to investigate the probability distribution of the data and thus aid the selection of appropriate trend detection methods, that is, parametric versus non-parametric. Other researchers prefer to use transformations so that non normal data can fit their parametric regression models of choice.

Thirdly, a lot of emphasis is placed on the importance of flow adjustment on water quality variables. Those closely involved with temporal trend analysis recommend that where possible, the effects of flow should be removed prior to testing for trend. At the core of this recommendation is the fact that the concentrations of variables, for example, electrical conductivity are a function of flow, such that changes in river flow regime may, through dilution and wash off, mask actual trends.

Finally, from the literature assessment, it seems that the techniques of choice for trend detection are the Seasonal Kendall test for trend and regression analysis subject to the data adhering to the assumptions required.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter addresses the methods used to accomplish the specific objectives of the study. Two statistical analyses, the Seasonal Mann-Kendall test and regression were employed to test for monotonic trend in the long term water quality data for the Eerste River for a period of approximately 15 years from 1990 to 2005. Regression analysis was further used in the analysis of spatial trend. The water quality variables under consideration were pH, electrical conductivity, nitrogen, phosphorus, and chemical oxygen demand. These were selected for the study period from databases maintained by the Department of Water Affairs and Forestry (DWAF) and the City of Cape Town (CCT). The two entities accumulated data for the eight monitoring stations on the Eerste River and one on the Plankenbrug River, for a period inclusive of the study period (see Raw Data in Appendix 1).

3.2 DATA ACQUISITION

Water quality data were obtained in electronic format (Excel files) from DWAF and the CCT. DWAF accumulated the water quality data in their routine monitoring programme (Ferguson, 2005). To the contrary, the CCT monitored the Eerste River specifically for "reference purposes [sic]" (Siebritz, 2006). The data from DWAF were compiled from grab samples that were analyzed at the South African Bureau of Standards laboratory following standard procedures (Kloppers, 2005). The data from the CCT were analysed using standard procedures by their Scientific Services Department (Siebritz, 2005). Both datasets contained a number of sites and variables, from which a subset of nine sites and five variables, were selected for the study. It was necessary to combine the data from the two entities as a means of ensuring a somewhat even spatial coverage of the Eerste River.

3.2.1 Water quality monitoring stations

The monitoring sites EK 13 and EK14 are the two stations on the Eerste River that were monitored by the City of Cape Town. EK13 is located at the N2 freeway while EK 14 is located in Dorp Street in Stellenbosch. The earliest record from the two stations is dated

January 1991. However, the City of Cape Town stopped monitoring EK 14 two years ago in 2003 (van Driel, 2005) with the last observation in the dataset recorded for March 2003. The data set from the Department of Water Affairs and Forestry (DWAF) for the seven stations used in the study starts in May 1990 and continues beyond the study period. Table 3.1 and Figure 3.1 give locational and spatial orientation.

Table 3.1 List of monitoring stations, their location and respective monitoring entity.

Distance (km)	Station	Monitoring entity	Location	Geographic Location
0	ER720A1	DWAF	Under Swartbrug Bridge	Latitude 33 56 00 ; Longitude 18 55 05
5.9	ER720B	DWAF	Before suspension bridge	Latitude 33 56 30; Longitude 18 53 25
9.7	EK14	CCT	Dorp Street	±
*	PR720B	DWAF	Plankenbrug river, below Khayamandi	±
11.6	ER720C	DWAF	At Stellenbosch Farmers Winery Cricket grounds	Latitude 33 56 45; Longitude 18 50 45
14.2	ER720D	DWAF	At Goetvertrouw Farm	Latitude 33 57 20; Longitude 18 49 00
22.4	ER720E	DWAF	At Kompanje's Drift (Meerlust)	±
26.9	EK13	CCT	On the N2 freeway	±
30.5	ER720F	DWAF	At Sjiek Josef'se Kramat	±

± Geographic location not available

Note that approximate and not actual distances between the stations are used in the study.

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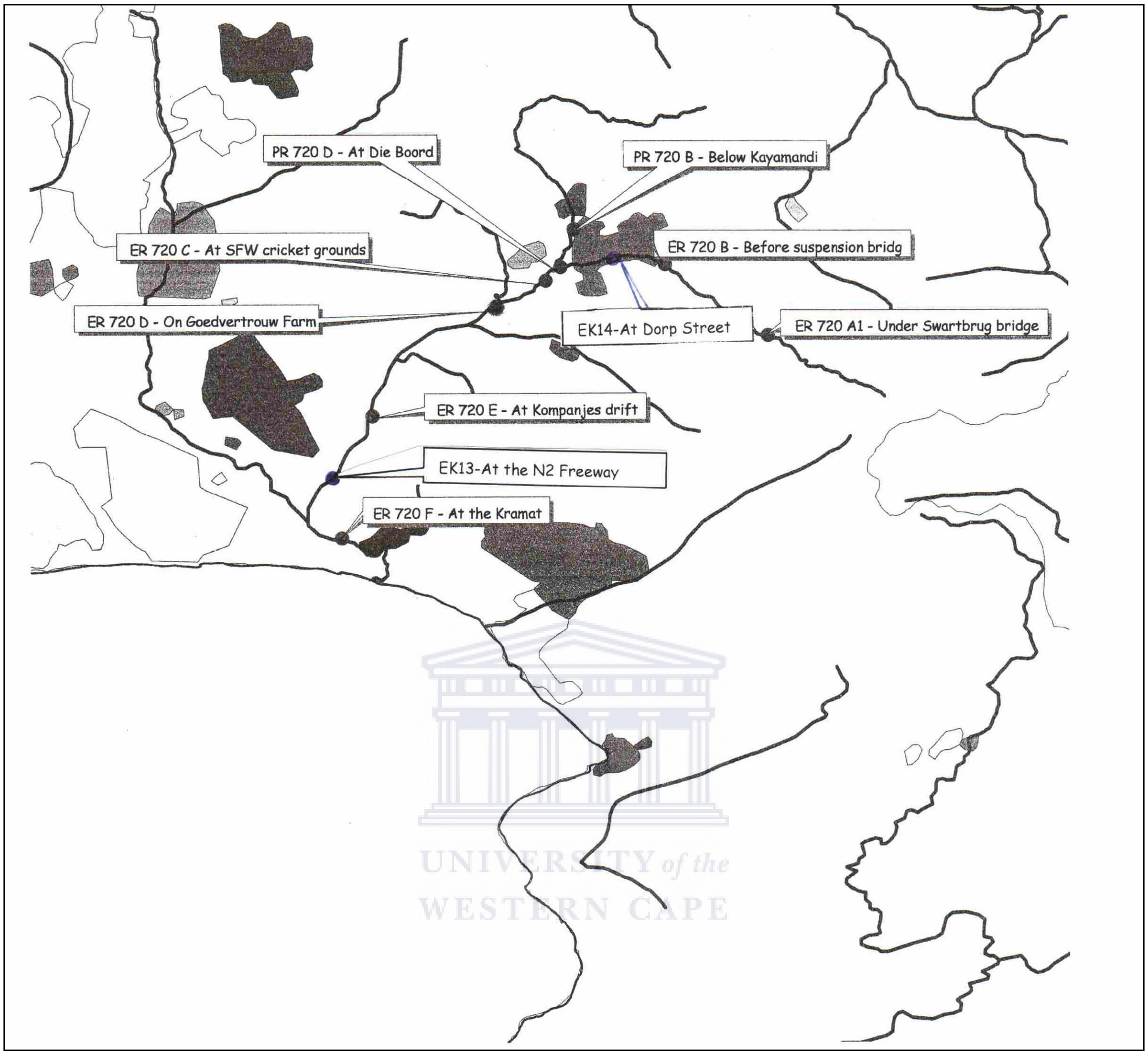
[*] denotes a station on the Plankenbrug River, tributary to the Eerste River.

Figure 3.1 Sampling stations on the Eerste River



3.2.2 Water quality variables

The five water quality variables that were selected for the study are outlined below.

3.2.2.1 pH

pH is an indicator of acidification and is often used in the general characterisation of water quality (Golterman *et al*, 1997; EEU, 1996). It is defined as a measure of hydrogen ion activity and an indicator of hydrogen ion concentration present in water (DWAF, 1996). When the concentration of hydrogen ions [H^+] increases, a more acidic solution results, and is indicated by a decrease in pH values. On the other hand, when the concentration of hydrogen ions [H^+] decreases, a more alkaline solution results and is indicated by increasing pH values. Such changes in pH affect stream water chemistry (Dallas & Day, 2004).

The pH of a sample of water determines the chemical species in which many elements are found in that sample (Dallas & Day, 2004). Thus, it affects the solubility and toxicity of both metals and non metallic ions in water (Dallas & Day, 2004; DWAF, 1996). When pH falls below neutral, metal such as mercury, lead and manganese become highly toxic. However, when pH values are higher than eight, non-metallic ions can be converted into toxin. For example the ammonium ion can be converted to highly toxic ammonia (Dallas & Day, 2004; King *et al*, 2003). As a result, pH affects the fitness of water for ecological, agricultural, industrial and domestic use (Pegram & Gorgens 2001).

The typical pH range for most surface water in South Africa is 6 to 8 (Dallas & Day 2004; DWAF, 1996). However, fresh waters that drain catchments such as the south western Cape, may experience pH values as low as 3.9 due to the influence of organic acids leaching from the vegetation such as fynbos (Dallas & Day 2004; King *et al,* 2003, DWAF, 1996). Fynbos produces large amounts of secondary plant compounds, polyphenolics, which decompose to form humic and other weak organic acids (Dallas & Day 2004). Rivers in South Africa are seldom naturally very alkaline (Dallas & Day, 2004).

While the pH in natural waters is influenced by geology and biotic activities, human induced acidification may result from low pH point source effluent produced by chemical, pulp and paper, tanning and leather industries; acid mine drainage and atmospheric pollution associated with acid rain (Dallas & Day, 2004; Davies & Day 1998; Zipper *et al*, 1992).

3.2.2.2 *Electrical Conductivity (EC)*

Electrical conductivity (EC) is defined as a measure of the ability of a sample of water to conduct an electric current. This ability to conduct electric current is due to the presence of ions such as sodium, chloride, potassium, calcium, magnesium and other such ions. It is the concentration of these ions that influences the ability of water to conduct electric current (Dallas & Day 2004; Davies & Day, 1998; Du Preez *et al*, 2000).

EC measures the total amount of material that is dissolved in a sample of water and is therefore often used in the general characterisation of water quality (Dallas & Day 2004). EC is used as proxy to total dissolved solids (TDS), it is directly proportional to TDS with a conversion factor ranging from 5.5 to 7.7 (the average conversion factor for most water is 6.5 and the exact factor depends on the ionic composition of the water). Higher values of EC are reflective of higher TDS levels (Du Preez *et al*, 2000).

In natural waters, the EC is often a function of geological formation. However, the total amounts of salts accumulate downstream as both natural and anthropogenic processes such as domestic, industrial effluent, surface runoff make their contribution (Du Preez *et al*, 2000). EC is measured in purer water, whilst salinity is measured in more saline waters where concentrations could be higher than field conductivity instruments can measure (King *et al*, 2003).

3.2.2.3 *Nitrogen*

Nitrogen occurs abundantly in nature. It is an essential macronutrient for plant growth and an indicator of eutrophication. In both polluted and unpolluted water, inorganic nitrogen may be present in many forms. The commonly measured forms are nitrates, nitrites, ammonium, and ammonia (Dallas & Day, 2004; King *et al*, 2003; Davies & Day, 1998). Nitrates are the end products of aerobic stabilisation of organic nitrogen (Dallas & Day, 2004). Sources of nitrogen include fertilisers and agricultural runoff. Nitrogen can contribute to excessive algal blooms and growth of aquatic plants (Pegram & Gorgens, 2001).

3.2.2.4 *Phosphorus*

Phosphorus is also an essential macronutrient for numerous life processes and an indicator of eutrophication (Dallas & Day, 2004). Phosphorus occurs naturally at low concentrations in unimpacted surface water, and originates from the weathering of igneous rocks, soil leaching and organic matter (DWAF, 1996; King *et al*, 2003). Phosphorus occurs in many organic and inorganic forms, most commonly in dissolved form as the inorganic phosphate ion (PO_4^{3-}) (Dallas & Day, 2004). Soluble Reactive Phosphorus (SRP) or orthophosphate is an approximation of the phosphorus that is immediately available to aquatic biota and can be transformed into any available form by natural processes. Therefore, it is seldom found in quantity in unpolluted water (Dallas & Day, 2004). Total phosphorus (TP) is a measure of the total phosphorus potentially available to biological systems.

Phosphorus is considered to be one of the limiting nutrients in South Africa's freshwater systems, more limiting than nitrogen (Dallas & Day, 2004). Increases in phosphorus can result in increased biological activity and lead to excessive algal blooms and the growth of aquatic plants (Pegram & Gorgens, 2001). Excessive growth of macrophytes and algae is usually a greater problem in standing water bodies than moving water. In running waters, the retention time may be too short for the algae to grow to higher densities.

Anthropogenic activities generate high concentrations of phosphorus. The greatest proportion is generated from agricultural activities and delivered into river environments by surface runoff and from point sources such as waste water treatment works (WWTW) (Davies & Day 1998; Zipper *et al*, 1998).

3.2.2.5 *Chemical Oxygen Demand*

Chemical oxygen demand (COD) is a measure of the oxidation of reduced chemicals in water (King *et al*, 2003). It is commonly used to indirectly measure the amount of organic compounds in water. The measure of COD determines the quantities of organic matter found in water. This makes COD useful as an indicator of organic pollution in surface water.

3.3 DATA PREPARATION FOR THE REGRESSION ANALYSES WITH SAS.

The data were arranged chronologically from day one in Julian days, taking into account leap years, to the last record in the data set and formatted to the specifications of the SAS Version 8.2 (SAS, 1999) statistical programme. For example, the package requires that no record is left blank, instead dots be used in place of the missing data values. Approximate distances between the sites were also included in the subset, for spatial analysis. The spreadsheet was then sent to the Agricultural Research Council in Stellenbosch for temporal and spatial trend testing. However, prior to testing the data for trend, the data were assessed in SAS version 8.2 (SAS, 1999) to determine their probability distribution.

3.3.1 Probability distribution of water quality variables.

The UNIVARIATE procedure of the SAS version 8.2 (SAS, 1999) statistical package was used to describe the water quality data. The UNIVARIATE procedure provided details of missing values, extreme values (outliers), quantiles, central location, basic statistical measures and tests for normality and skewness. The tests for normality and skewness are particularly important in ascertaining the validity of trend detection methods (Grabow *et al*, 1999). Most inferential methods, or parametric methods including linear regression, are founded on the assumption of a normal (Gaussian) distribution (Vant & Smith, 2004; Lietz, 2000; Grabow *et al*, 1999Darken, 1999; Zipper *et al,* 1992). Therefore, they tend to lose their power to detect trends when data depart from normality (Hirsch *et al*, 1991).

Tests for normality investigate the null hypothesis that data values are a random sample from a normal distribution. The decision to reject the null hypothesis of normality is based on the probability or p-value associated with the test statistic (DCEE, undated). In the case of the research data used herein, four statistics and their probability values were computed from four tests, the Shapiro-Wilk with its test statistic (W) and p-value (PR<W); the Kolmogorov-Smirnov with its test statistic (D) and p-value (PR>D); the Cramer-von Mises with its test statistic (W-Sq) and p-value (PR>W-Sq;) and the Anderson-Darling with its test statistic (A-Sq) and p-value (PR>A-Sq).

Taking the Shapiro-Wilk test statistic as an example, the null hypothesis of normality is rejected when the p-value (PR<W) is less than the 0.05 significance level. This would suggest that the data are not from a normal probability distribution. However, if the p value is greater than the 0.05 significance level, then there is 95% confidence that there is insufficient evidence to conclude that the data are not normally distributed. Therefore, the conclusion would be that the sample data are from a normal distribution (DCEE, undated).

Skewness is another indication of the departure of data from the normal probability distribution. Normally distributed data have an absolute skewness value of zero. Any value of skewness that is larger than one, points to a large degree of skewness that needs to be addressed (Grabow *et al*, 1999)

Over and above the coefficient of skewness and the test for normality, the UNIVARIATE procedure yielded histograms, box plots and normal probability plots to assist in the interpretation of the probability distribution. Outlined below are the results of the UNIVARIATE procedure on pH, electrical conductivity (EC), nitrates & nitrites, phosphates and chemical oxygen demand (COD).

3.3.1.1 *pH*

The results from the UNIVARIATE procedure on pH showed a low coefficient of skewness of -0.0203; and a Shapiro-Wilk test statistic (W) of 0.984 whose p-value is <0.0001. Although the histogram and box plot were near symmetrical, the results in their entirety indicated that the pH data depart slightly from a normal distribution.

3.3.1.2 *Electrical Conductivity*

The results from the UNIVARIATE procedure on electrical conductivity showed a relatively low coefficient of skewness of 0.247, and a Shapiro-Wilk test statistic (W) of 0.923 whose p-value is <0.0001. The histogram, box plot were near symmetrical, whilst the normal probability graph was curvilinear. The entire results indicate that the electrical conductivity data are not normally distributed.

3.3.1.3 *Nitrates & Nitrites*

The results from the UNIVARIATE procedure on nitrates and nitrites showed a high coefficient of skewness of 3.298 and a Shapiro-Wilk test statistic (W) of 0.774 whose p-value is <0.0001. The histogram, box plot were asymmetrical, whilst the normal probability plot graphed a curvilinear line. These results indicate that the nitrates and nitrites data are positively skewed and not normally distributed.

3.3.1.4 *Phosphates*

The results from the UNIVARIATE procedure on phosphates showed a very high coefficient of skewness of 20.0354 and a Shapiro-Wilk test statistic (W) of 0.1967 whose p-value is <0.0001. The histogram and box plot were asymmetrical and positively skewed with a long right tail, whilst the normal probability plot graphed a broken, stepped line. These results indicate that the data for phosphates are distinctly not normally distributed.

3.3.1.5 *Chemical Oxygen Demand*

The results of the UNIVARIATE procedure on chemical oxygen demand showed a high coefficient of skewness of 5.107 and a Shapiro-Wilk test statistic (W) of 0.7015 whose p-value is <0.0001. The histogram and box plot were asymmetrical, and positively skewed whilst the normal probability plot graphed a broken and stepped line. These results indicate that the chemical oxygen demand data depart significantly from normal distribution.

3.4 DATA PREPARATION FOR THE SEASONAL MANN-KENDALL TEST.

The data of interest were extracted from the raw data sets and maintained in Microsoft Excel format so that it was compatible with the programme used. The Seasonal Mann-Kendall test that is used, accepts only single values for a season, so the data was organized into single monthly observations. Where two observations were recorded for the month, the average of the two was used as the monthly value. However, in the presence of three values, the median value was used to represent the month. The reason for using the median value was that unlike the mean value, the median is minimally affected by the magnitude of a single observation and is determined only by the relative order of observations. Therefore, their resistance to outliers justifies their use in water quality data (Darken, 1999; Helsel & Hirsch, 1991). No station had more than three observations.

Since the Seasonal Mann-Kendall test accepts only a single observation per season (month), this was in itself taken to be a way of reducing data, thus correcting for serial or autocorrelation. Longer time steps than daily and bi weekly reduce interdependence among the records (Grabow *et al*, 1999).

The data were assessed to detect any outlying values as well as obvious erroneous values, for example if pH were recorded as 15 then one would immediately discard it as an erroneous value. While no erroneous values were observed, there were a few outlying values which, following Zipper *et al* (1998), and Helsel & Hirsch (1991) were maintained. Most of the low outliers were a result of below detection limit observations.

Following recommendations of the Intelligent Decision Technologies (IDT, 1989) the values that were observed below the detection limit were assigned values of half the detection limit. The detection limit values for each parameter were obtained with the data from the monitoring entities.

There were a large number of missing values in the data set. For instance, in the whole of 1997, the City of Cape Town recorded only 2 observations at both of the stations (EK13 and EK14) that they monitored. DWAF has no records for any of the parameters at stations ER720A1 and ER720C in 2001. However, the missing values were left blank because the programme used, requires that missing values be left blank. Missing values do not present major problems as long as they are randomly distributed (Darken, 1999).

Those values where the number of decimal places seemed to increase in the records as was the case with electrical conductivity towards the end of the study period, the records were rounded to two decimal places to conform with the convention used in the bulk of the study period. This was done to promote consistency.

Precise data for discharge corresponding to sampling was not available from either the Department of Water Affairs and Forestry or the City of Cape Town. Therefore, the effects of flow on the data could not be removed.

The results of the tests for normality and skewness that were generated with the SAS package (SAS, 1999) substantiated the theory that water quality data seldom follow a normal distribution. Therefore, the results lent credence to the use of the non-parametric Seasonal Mann-Kendall test for trend.

3.5 HYPOTHESES AND METHODS

To detect trend in the data, two statistical methods were used; the parametric linear regression tests with SAS Version 8.2 (SAS, 1999) and the non-parametric Seasonal Mann-Kendall Test.

The Research Hypotheses

In order to detect trend in the water quality data, the following trend hypothesis were stated;

1. The null hypothesis H_0 : There in no trend of a water quality variable with time and in space.
2. The alternative hypothesis H_1: There is significant upward or downward trend of a water quality with time and in space.

3.5.2 Regression analyses with the SAS Version 8.2 (SAS 1999)

The parametric regression analyses were employed to test the presence of trend in the water quality data of the Eerste River over the 15 year period. The analyses were done by the Agricultural Research Council (ARC) in Stellenbosch. For the spatial analysis, analysis of variance (ANOVA) and the regression procedure (REG) in SAS version 8.2 (SAS, 1999) were used. The analysis of variance was used to determine if the sites were significantly different from one another with respect to pH, electrical conductivity, nitrogen, phosphorus, and chemical oxygen demand. The regression procedure (REG) was carried out to detect any significant spatial trend in the data.

For detecting temporal trend, the regression procedure (REG) was carried out on the individual water quality variables with time, in days at each site. However, having determined that the data violated the assumptions of normality and linearity, the regression model that was used for temporal trend was considered inappropriate. This is because parametric tests are said to lose their power to detect trends when distribution assumptions are violated (Hirsch *et al*, 1991). However, since Zipper *et al* (1992) observed that in spite of its limitations, conventional linear regression has been found to be capable of detecting temporal trend, particularly where those trends are well defined, the results from the regression analysis were not disregarded. Instead they were incorporated and cautiously interpreted with those of the alternative non-parametric Seasonal Mann-Kendall Test (see Chapter 4 for discussion of results).

3.5.3 The Seasonal Mann-Kendall Test

A programme for Seasonal Mann-Kendall tests written by Libiseller (2002) [Available Online] www.mai.liu.se/~cllib/welcome/pmktest.html was used to investigate the presence of statistically significant temporal trends in each water quality variable over time. This programme is particularly suited to the study for a number of reasons. Firstly, having ascertained that the data are not from a normal distribution, a non-parametric test, because of its impartiality to distribution assumptions, was considered more suitable for the study. It has been reported that when data depart slightly or largely from normality then modest and significant advantages are observed when using non-parametric methods (Hirsch *et al*, 1991). Secondly, being a Seasonal Mann-Kendall test for trend, it incorporated some water quality data characteristics such as seasonality, multiple monitoring sites, multiple variables and covariates representing natural fluctuations.

Thirdly, the use of single values for each month was assumed to sufficiently deal with serial correlation (Cox *et al*, 2005, McBride & Loftis, 1994). Furthermore, the research hypotheses being tested are embedded in the programme. Lastly, the programme runs in Excel and does not require programming knowledge by the user, making it simple and user friendly. Therefore, since the data was in Excel format, it required inputting of the treated data into the raw data worksheet and then running the test. The results of the test are presented in the next chapter.

CHAPTER 4
RESULTS AND DISCUSSION

4. 1 INTRODUCTION

Statistical analyses were conducted for the purpose of identifying water quality trends in the Eerste River. This chapter is a presentation and discussion of the results from both the standard regression analysis and Seasonal Mann-Kendall test on the individual water quality variables at each of the monitoring stations over the study period. The Seasonal Mann-Kendall statistics (MK) and their respective p values (probability), the regression slope and its respective p values for each variable at each of the stations are presented in Tables 4.2 to 4.6.

It should be reiterated at this point that the results of the regression analysis are applied with great caution. This is because the data were characterized by skewness, non-linearity, non-normality and a possible lack of independence (data was organized in cumulative days), and thus violated the assumptions required for linear regression. When the assumptions required for linear regression are not met, the method tends to lose its power to detect trend (Hirsch *et al*, 1991). However, where trends are well defined, linear regression is said to be capable of detecting them, in spite of its limitations (Zipper *et al*, 1992). Therefore, because of the uncertainty with linear regression, greater reliability is awarded to the Seasonal Mann- Kendall test, which is specifically suited to water quality data because of its impartiality to probability distribution, requiring only that data be monotonic regardless of whether or not it is linear.

For both the regression and Seasonal Mann-Kendall tests, trends were considered statistically significant if the p value was less than 0.05 ($p < 0.05$). Note that for both tests, a positive statistic indicates an increasing trend whilst those preceded by the negative sign (-), indicate declining trends at the respective stations. Note also, that the shaded values in Tables 4.2 to 4.6 highlight the significant p-values.

The results from the regression analysis of water quality data for trend with distance down the river are also presented here. It should be noted that the station PR720B, on the

Plankenbrug River is deliberately excluded from the spatial analysis because it is not on the main channel of the Eerste River. Plots from the analysis of variance (ANOVA) of each water quality variable on approximate distance are presented in Figures 4.2 to 4.6.

4.2 ANALYSES OF pH

4.2.1 Temporal Trends in pH

The results from the Seasonal Mann-Kendall test, presented in Table 4.2 reveal that there are no significant trends in pH values at any of the stations during the study period. To the contrary, the regression analysis, also presented in Table 4.2, detected significant, though very small, increases in pH at all but one station. Interestingly, both tests reveal that at station EK13 (on the N2 Freeway) there is an insignificant decline in pH.

Distance (km)	Station	Location	Seasonal Mann-Kendall Test		Regression Analysis	
			MK Statistic	p-value	Slope	p-value
0	ER720A1	Under Swartbrug Bridge	0.2169	0.8283	0.00017	0.0001
5.9	ER720B	Before suspension bridge	1.5827	0.1135	0.00013	<0.0001
9.7	EK14	Dorp Street	1.7720	0.0764	0.00014	0.00010
	PR720B	Plankenbrug river, below Khayamandi	1.1044	0.2694	0.00007	0.00710
11.6	ER720C	At Stellenbosch Farmers Winery Cricket grounds	0.5624	0.5739	0.00006	0.04200
14.2	ER720D	At Goetvertrouw Farm	1.4180	0.1562	0.00007	0.02100
22.4	ER720E	At Kompanje's Drift (Meerlust)	1.2138	0.2248	0.00005	0.01100
26.9	EK13	On the N2 freeway	-0.3511	0.7255	-0.00003	0.21070
30.5	ER720F	At Sjiek Josef'se Kramat	1.4303	0.1526	0.00011	0.00030

Table 4.2 Results of the temporal analyses of pH at the study sites on the Eerste River using the Seasonal Mann-Kendall test and the standard regression analysis.

4.2.2 Spatial Trends in pH

The regression analysis of pH on distance indicates a significant (<0.0001) and increasing (0.022) trend from the upper zone of the Eerste River (Under Swartbrug Bridge) to the lower zone (At Sjiek Josef'se Kramat). The ANOVA to compare if the sites were significantly different showed some significant differences as shown by the letters. Note that stations with the same letter are not significantly different from each other. The progressive increases in mean pH values are concomitant with increasing distance downstream as shown in Figure 4.2.

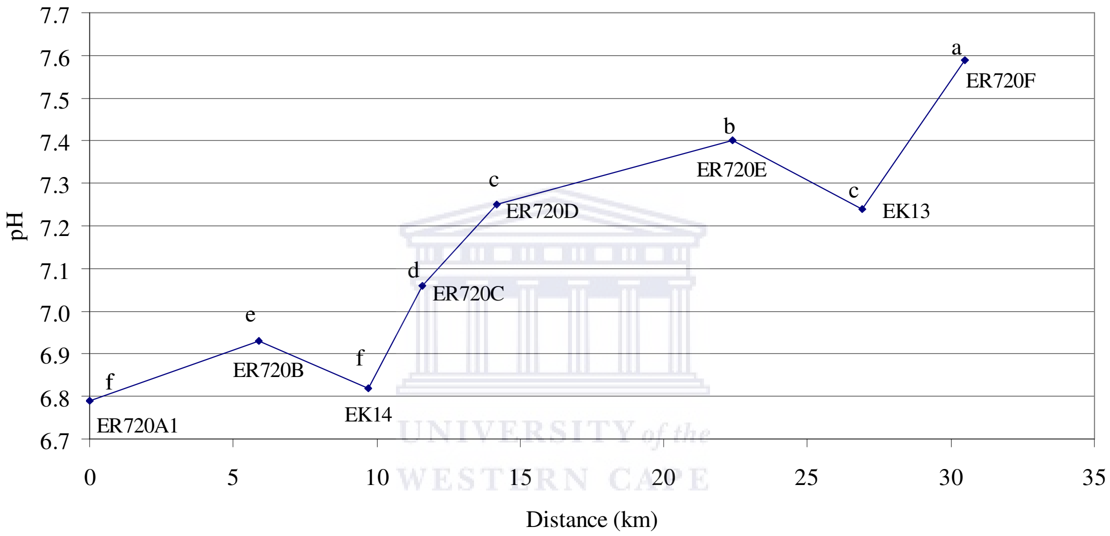


Figure 4.2. A graph showing an overall increasing trend in pH at the study sites with increasing distance down the Eerste River.

A decline in pH is first observed between ER720B (before the suspension bridge) and EK14, in Dorp Street, Stellenbosch. A few kilometres downstream, at the Stellenbosch Farmers Winery cricket grounds (ER720C), the pH is observed to rise abruptly. The plausible reason for this change is that the Plankenbrug River discharges water of higher pH into the Eerste River in this region. Over the study period the mean pH of the Plankenbrug River at station PR720B (below Khayamandi) is 7.5, over 0.5 pH units higher than the pH values observed ER720A1, ER720B and EK14 which are located upstream of the Eerste-Plankenbrug confluence.

Beyond the Eerste-Plankenbrug confluence, the pH continues to rise (ER720D). This rise could be due to the cumulative effects from upstream and also influence of the Stellenbosch Waste Water Treatment Works which discharges treated effluent into the Eerste River through the Veldwagters tributary. The station ER720D is located at Goetvertrouw Farm, at the confluence of the Veldwagters River and the Eerste River.

A second decline in pH is observed between Kompanje's drift (ER720E) and EK13 (on the N2 freeway). However, between EK13 and ER720F (at the Sjiek Josef'se Kramat) the pH values tend to rise. It is possible that this increasing trend is a result of water of higher pH entering the Eerste River from the Kuils River system.

4.3 ANALYSES OF ELECTRICAL CONDUCTIVITY

4.3.1 Temporal trends in Electrical Conductivity

Table 4.3 is a summary of results from the statistical analyses of electrical conductivity (EC). Both the Seasonal Mann-Kendall and regression analyses detected similar and significant trends in electrical conductivity at three stations, namely, ER720D, EK13 and ER720F. The stations, ER720D, located at Goetvertrouw Farm and EK13, located on the N2 freeway exhibit increasing trend, while ER720F at Sjiek Josef'se Kramat exhibits decreasing trend.

The regression analysis further detected increasing trends at ER720A1 (under the Swartbrug Bridge), EK14 (in Dorp Street, Stellenbosch) and ER720C (at the Stellenbosch Farmers Winery cricket grounds).

The most plausible explanations for the increasing trend at ER720D are that there is some significant contribution from the incoming discharge of the Plankenbrug River as well as that the Stellenbosch Waste Water Treatment Works has probably been discharging progressively poor effluent into the river. At EK13, the trend could be the result of non point sources in the environs of the station. The declining trend in EC at ER720F comes as a surprise because the 'heavily polluted Kuils River' enters the Eerste River upstream of this point.

Distance (km)	Station	Location	Seasonal Mann-Kendall Test		Regression Analysis	
			MK Statistic	p-value	Slope	p-value
0	ER720A1	Under Swartbrug Bridge	0.8651	0.3869	0.00534	0.0004
5.9	ER720B	Before suspension bridge	1.4083	0.1590	0.00050	0.0502
9.7	EK14	Dorp Street	1.8236	0.0682	0.00130	0.0442
	PR720B	Plankenbrug river, below Khayamandi	0.0462	0.9631	-0.00133	0.4314
11.6	ER720C	At Stellenbosch Farmers Winery Cricket grounds	1.7696	0.0768	0.00117	0.0253
14.2	ER720D	At Goetvertrouw Farm	2.0720	0.0386	0.00248	0.0179
22.4	ER720E	At Kompanje's Drift (Meerlust)	0.9191	0.3580	0.00026	0.7700
26.9	EK13	On the N2 freeway	2.1715	0.0066	0.00432	<0.0001
30.5	ER720F	At Sjiek Josef'se Kramat	-2.1996	0.0278	-0.00268	0.0118

Table 4.3 Results of the temporal analyses of electrical conductivity (EC) at the study sites on the Eerste River using the Seasonal Mann-Kendall test and the standard regression analysis.

4.3.2 Spatial trends in Electrical Conductivity

The regression analysis of electrical conductivity on distance indicated a significant (<0.0001) and increasing (1.873) trend from the upper zone of the Eerste River (Under Swartbrug Bridge) to the lower zone (At Sjiek Josef'se Kramat). The ANOVA to compare if the sites are significantly different showed some significant differences. Those stations with same letter are not significantly different from each other. Figure 4.3 shows that the mean values of electrical conductivity tend to increase in steps with distance downstream.

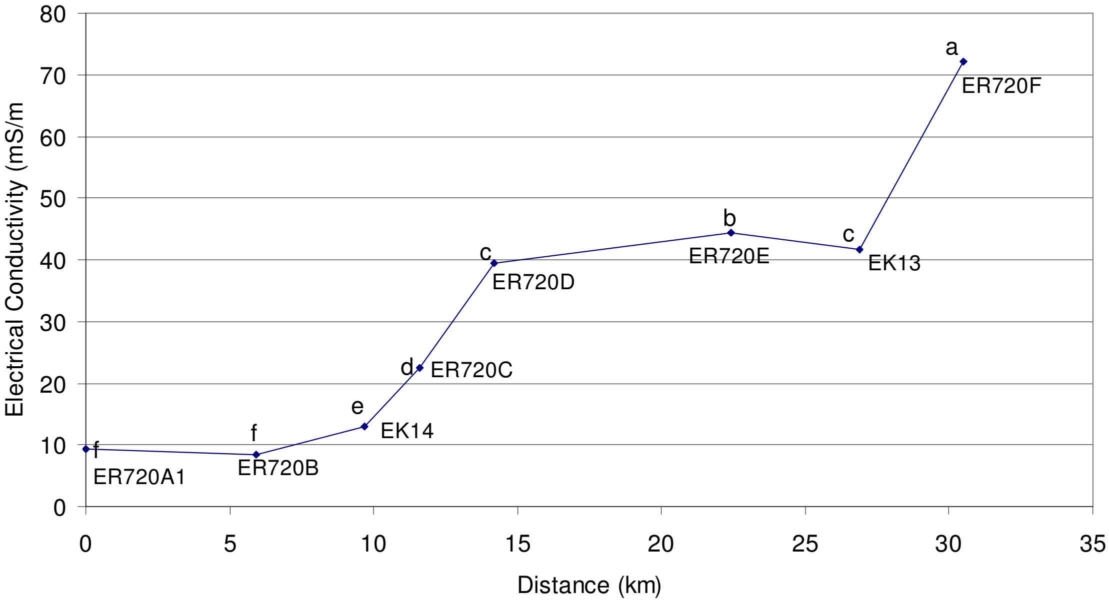


Figure 4.3 A graph showing an overall increasing trend in electrical conductivity at the study sites downstream the Eerste River.

A significant rise in electrical conductivity is initially observed between stations EK14 and ER720C. These two stations are located approximately 9.7km (in Dorp Street Stellenbosch) and 11.6km (Stellenbosch Farmers Winery cricket grounds), respectively, from the uppermost station ER720A1 (under Swartbrug Bridge). The initial rise observed at EK14 could be the result of surface runoff and storm water conveyed into the Eerste River from the surfaces of the town of Stellenbosch.

The next rise in EC, observed at ER720C, could be a result of substantial quantities of pollutants from the Plankenbrug River entering the Eerste River just upstream of this station, which is located at the Stellenbosch Farmers Winery cricket grounds. The Plankenbrug River generally carries high pollutant loads from storm water and waste water discharges from both the Khayamandi informal settlement and the industrial area of Stellenbosch (RHP, 2005). The mean value of electrical conductivity computed for station PR720B, on the Plankenbrug River, over the entire period of study was 73 mS/m which is much higher than the mean values the bulk of the stations.

Between the station ER720C (at the Stellenbosch Farmers Winery cricket grounds) and ER720D (Goetvertrouw Farm), electrical conductivity continues to rise. Station ER720D is located at the confluence of the Eerste River and the Veldwagters tributary. The probable source of the rise in EC is the Stellenbosch Waste Water Treatment Works which is said to be discharging approximately 8.4Million m^3/year of treated effluent into the Eerste River (RHP, 2005) through the Veldwagters tributary.

The last and abrupt rise in electrical conductivity is observed towards the mouth of the river in a region where the heavily polluted Kuils River discharges into the Eerste River (RHP, 2005).

4.4 ANALYSES OF NITRATES AND NITRITES

4. 4.1 Temporal trends in nitrates & nitrites.

Table 4.4 presents the results of the analyses of nitrates & nitrites for long term trend. Both the regression analysis and the Seasonal Mann-Kendall test detected significant increasing trends at EK13 at the N2 freeway, and ER720F at Sjiek Josef'se Kramat. However, the regression analysis further detected a slight declining trend in nitrates and nitrites at station EK14 (in Dorp Street).

The cause of the significant increasing trend in nitrates and nitrites at EK13 is probably, farming nonpoint sources of pollution. The most likely cause of the increasing trend in nitrate and nitrite at Sjiek Josef'se Kramat (EK720F) is high nutrient loads from the Kuils River which discharges into the Eerste River just upstream of this station.

It was noted that both tests detected decreasing trend in nitrates and nitrites at the station EK14 in Dorp Street in Stellenbosch, even though with the Seasonal Mann-Kendall test this decrease was not significant (0.0583). One would have expected to detect significant increases of nutrients from the wash off of large quantities of nutrient matter from urban activity into the river.

Distance (km)	Station	Location	Seasonal Mann-Kendall Test		Regression Analysis	
			MK Statistic	p-value	Slope	p-value
0	ER720A1	Under Swartbrug Bridge	1.7179	0.0858	0.00054	0.178
5.9	ER720B	Before suspension bridge	1.2377	0.2158	0.00002	0.0908
9.7	EK14	Dorp Street	-1.8934	0.0583	-0.00008	0.0108
	PR720B	Plankenbrug river, below Khayamandi	-0.1623	0.8710	0.000005	0.9375
11.6	ER720C	At Stellenbosch Farmers Winery Cricket grounds	0.4568	0.6478	-0.00004	0.3303
14.2	ER720D	At Goetvertrouw Farm	-0.1128	0.9102	-0.00017	0.5614
22.4	ER720E	At Kompanje's Drift (Meerlust)	-0.9432	0.3455	0.00008	0.606
26.9	EK13	On the N2 freeway	2.8238	0.0047	0.00039	<0.0001
30.5	ER720F	At Sjiek Josef'se Kramat	2.0262	0.0427	0.00052	<0.0001

Table 4.4 Results of the temporal analyses of nitrates and nitrites at the study sites on the Eerste River using the Seasonal Mann-Kendall test and the standard regression analysis.

4.4.2 Spatial trends of Nitrates & Nitrites

The regression analysis of nitrates and nitrites on distance indicated a significant (<0.0001) and increasing (0.0632) trend from the upper zone of the river (Under Swartbrug Bridge) to the lower zone (At Sjiek Josef'se Kramat). The ANOVA to compare if the sites are significantly different showed some differences between the sites. The mean values of nitrates and nitrites tended to fluctuate downstream as shown in Figure 4.4. Note that the stations with same letter are not significantly different from each other.

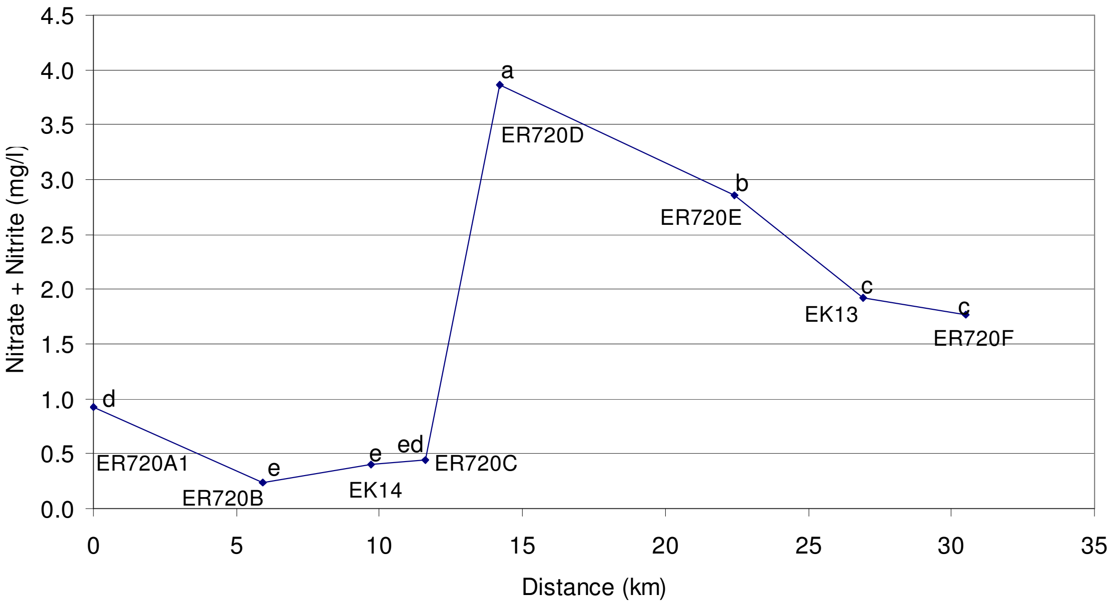


Figure 4.4 A graph showing a fluctuating though increasing trend in nitrate & nitrite at the study sites along the Eerste River.

At ER720A1, under Swartbrug bridge the nitrates and nitrites start off higher than at ER720B (before the suspension bridge), EK14 (Dorp Street) and ER720C, at the Stellenbosch Farmers Winery cricket grounds. A fish farm located upstream of station ER720A1, is probably responsible for the higher concentration of nitrates and nitrites at that station. Interestingly, EK14, which is located in the town of Stellenbosch, shows relatively low nitrates and nitrites concentrations.

Between the stations, ER720C and ER720D in Goetvertrouw Farm, the nitrates and nitrites concentration rises abruptly and then declines all the way down to the last station, ER720F. The sharp rise in concentration is probably due to treated effluent entering the river through the Veldwagters River, from the Stellenbosch Waste Water Treatment Works.

The declining trend observed from ER720E, to EK13 and ER720F point to improving water quality in this section of the Eerste River. The Kuils River, which is expected to carry high pollution loads, comes in just upstream of ER720F. Seemingly, it does not cause any more deterioration in the quality of water at this point. This is possibly because the Kuils River forms an extensive wetland, which may be responsible for the removal nitrate and nitrite, prior to joining the Eerste River.

4.5 ANALYSES OF PHOSPHATES

4.5.1 Temporal trends in Phosphates

Table 4.5 presents results from the statistical analyses of phosphates with time. Both the regression analysis and the Seasonal Mann-Kendall test detected increasing trends in phosphates at stations ER720A1, under the Swartbrug Bridge; EK 13, at the N2 Freeway; and PR720B, downstream of Khayamandi, on the Plankenbrug River. The Seasonal Mann-Kendall test further detected a decreasing trend at EK14, in Dorp Street, whilst the regression analysis detected an increase at ER720B, before the suspension bridge**.**

The significant increasing trend of phosphates at station ER720A1 suggests that there is some polluting activity on the Jonkershoek River upstream of this station. It is a possibility that the phosphates are coming from a dam; located upstream of the Swartbrug Bridge, where there is fish farming.

The significant increasing trend in phosphates at station PR720B, on the Plankenbrug River, can be ascribed to stormwater and waste water discharges from Khayamandi and Stellenbosch (RHP, 2005). The increase in phosphates at EK13, at the N2 Freeway, which is upstream of the Eerste-Kuils river confluence, is likely to be the effect of farming non-point sources of pollution.

The decreasing trend in phosphates at station EK14 in Dorp Street seems to be concomitant with that of nitrates at this particular station.

Distance (km)	Station	Location	Seasonal Mann-Kendall Test		Regression Analysis	
			MK Statistic	p-value	Slope	p-value
0	ER720A1	Under Swartbrug Bridge	2.0579	0.0395	0.00012	0.0070
5.9	ER720B	Before suspension bridge	1.8999	0.0574	0.0003	0.0102
9.7	EK14	Dorp Street	-2.2923	0.0218	-0.000006	0.4486
	PR720B	Plankenbrug river, below Khayamandi	2.5525	0.0106	0.00013	0.0382
11.6	ER720C	At Stellenbosch Farmers Winery Cricket grounds	0.7886	0.4303	0.00007	0.0567
14.2	ER720D	At Goetvertrouw Farm	0.9227	0.3561	$4.75\text{x}10^{-7}$	0.999
22.4	ER720E	At Kompanje’s Drift (Meerlust)	0.7555	0.4499	0.00004	0.6707
26.9	EK13	On the N2 freeway	3.2256	0.0012	0.00025	<0.0001
30.5	ER720F	At Sjiek Josef’se Kramat	0.8021	0.4225	0.00009	0.3714

Table 4.5 Results of the temporal analyses of phosphates at the study sites on the Eerste River using the Seasonal Mann-Kendall test and the standard regression analysis.

4.5.2 Spatial trends in Phosphates

The regression analysis of phosphates on distance indicated significant (<0.0001) and increasing (0.048) trend from the upper zone of the river (Under Swartbrug Bridge) to the lower zone (At Sjiek Josef’se Kramat). The ANOVA to compare if the sites are significantly different showed that the mean values of phosphates tend to fluctuate downstream as shown in Figure 4.5. Note that the stations with the same letter are not significantly different from each other.

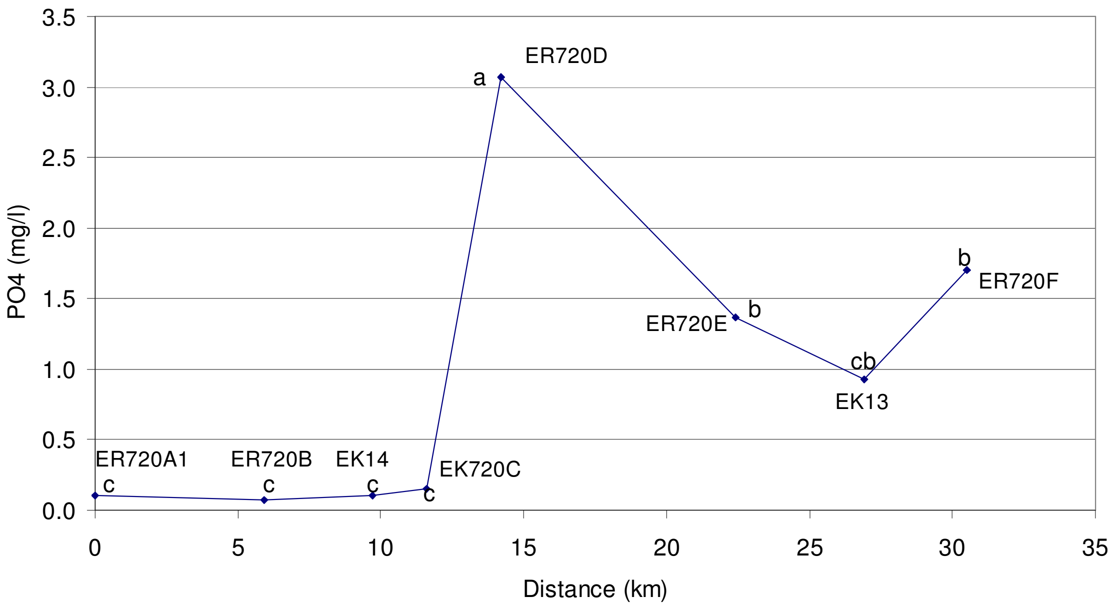


Figure 4.5. A graph showing a fluctuating though increasing trend in phosphate at the study sites along the Eerste River.

The phosphates tend to increase sharply between ER720C and ER720D in a manner similar to that of nitrates and nitrites (Figure 4.4). The cause of this increasing trend is probably the effluent from the Stellenbosch waste water treatment works. The phosphates then decline at Kompanje's Drift (ER720E) and the N2 Freeway (EK13). However, the phosphates rise abruptly at ER720F, after the Eerste-Kuils river confluence at the Sjiek Josef'se Kramat. While the influence of the Kuils River is apparent in the abrupt rise at ER720F, the rise is not as high as expected. By comparison, the peak that is observed at ER720D is somewhat expected because of the waste water treatment effluent discharged (Stellenbosch) into the river. The most plausible reason for the relatively lower concentration of phosphate is that the wetland on the Kuils River takes up the phosphates before its confluence with the Eerste River.

4.6 ANALYSES OF CHEMICAL OXYGEN DEMAND

4.6.1 Temporal trends in Chemical Oxygen Demand.

Table 4.6 is a presentation of results of the analyses of chemical oxygen demand (COD) with time. Both the Seasonal Mann-Kendall test and regression analysis detected significant decreasing trends in COD at stations ER720E in Kompanje's Drift; and ER720F, at Sjiek Josef'se Kramat. However, the regression analysis detected significant increasing trends at stations ER720B, at the suspension bridge that is upstream of Stellenbosch and at ER720C at the Stellenbosch Farmers Winery cricket grounds.

Distance (km)	**Station**	**Location**	**Seasonal Mann-Kendall Test**		**Regression Analysis**	
			MK Statistic	**p-value**	**Slope**	**p-value**
0	ER720A1	Under Swartbrug Bridge	1.0141	0.3105	0.00074	0.6993
5.9	ER720B	Before suspension bridge	-1.1138	0.2653	0.00326	0.0012
9.7	EK14	Dorp Street	0.0902	0.9281	-0.00032	0.724
	PR720B	Plankenbrug river, below Khayamandi	1.6103	0.1073	-0.00195	0.6496
11.6	ER720C	At Stellenbosch Farmers Winery Cricket grounds	1.5386	0.1238	0.00325	0.0007
14.2	ER720D	At Goetvertrouw Farm	-0.3608	0.7182	-0.00028	0.892
22.4	ER720E	At Kompanje's Drift (Meerlust)	-2.3072	0.0210	-0.00327	0.018
26.9	EK13	On the N2 freeway	0.3970	0.6913	0.00015	0.8301
30.5	ER720F	At Sjiek Josef'se Kramat	-2.9108	0.0036	-0.00791	<0.0001

Table 4.6 Results of the temporal analyses of chemical oxygen demand at the study sites on the Eerste River using the Seasonal Mann-Kendall test and the standard regression analysis.

4.6.2 Spatial trends in Chemical Oxygen Demand.

The regression analysis of chemical oxygen demand on distance, indicated a significant (<0.0001) and increasing (0.7032) trend from the upper zone of the river (Under Swartbrug Bridge) to the lower zone (At Sjiek Josef'se Kramat). The ANOVA to compare if the sites are significantly different showed that the mean values of chemical oxygen demand tend to increase in steps downstream as shown in Figure 4.6. Note that the stations with the same letter are not significantly different from each other.

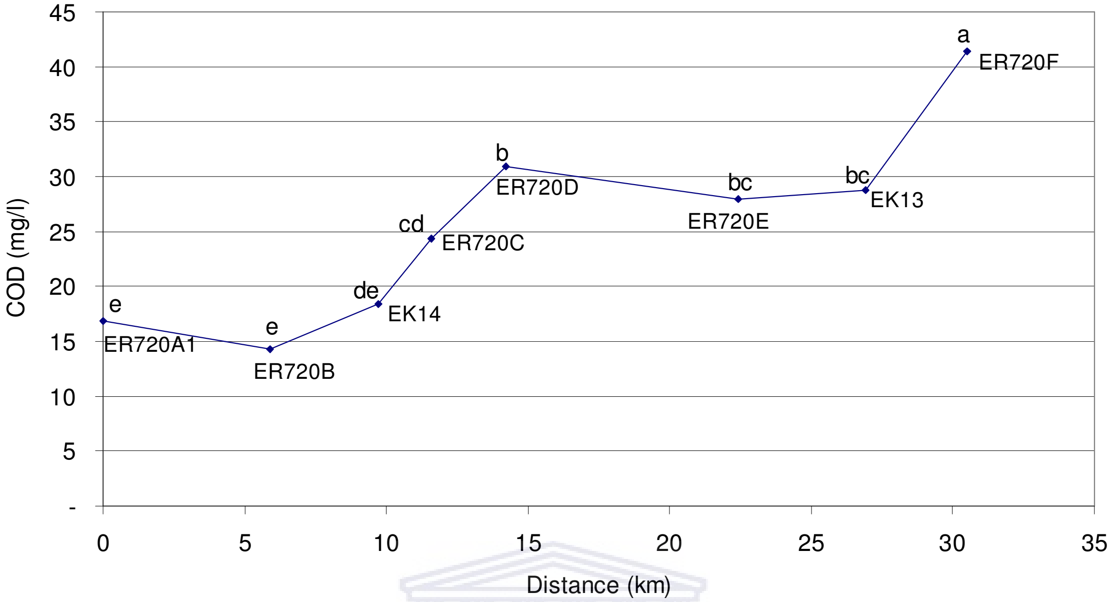


Figure 4.6. A graph showing an overall increasing trend in chemical oxygen demand at the study sites downstream the Eerste River

In Figure 4.6 above, the COD at station ER720A1 at the Swartbrug Bridge starts off higher than the station ER720B (before the suspension bridge) located downstream of it. This is probably because of the fish farming activities upstream of ER720A1. Beyond ER720B, the COD increases in the river when it passes through Stellenbosch (EK14), further rising (ER720C) after the Eerste River meets the Plankenbrug River, whose mean COD is 24mg/l at PR720B, before it discharges into the Eerste River. The COD concentration continues to rise at ER720D where the Stellenbosch Waste Water Treatment Works discharges treated effluent through the Veldwagters tributary. Between ER720D and EK13, the COD remains relatively constant. However, towards the mouth of the river, the chemical oxygen demand rises after the Eerste-Kuils River confluence probably as a result of high levels of organic matter contained in the discharge of the Kuils River.

4.7 SUMMARY OF RESULTS

The study analysed monthly water quality data for five water quality parameters gathered at eight monitoring stations on the Eerste River and one on the Plankenbrug River over a 15-year period. The results show that a mix of significant negative and positive long-term trends is present in the water quality of the Eerste River. This revelation is particularly true with respect to the indicator variables, pH, electrical conductivity, nitrate & nitrite, phosphate and chemical oxygen demand, selected for purposes of trend detection in the river. The possible primary drivers of water quality degradation identified are; fish farming in a dam upstream of the Swartbrug Bridge, the Plankenbrug River, the Stellenbosch Waste Water Treatment Works (SWWTW), farming non-point sources of pollution and the Kuils River which conveys pollutants from it catchment..

The pH results reveal that there are no significant long term trends in pH at any of the sites. The results of the regression analysis, though considered dubious because the data violated the assumptions for regression analysis, show very slight but significant temporal trends. While the pH generally oscillated between 6 and 8 pH units, a range that is typical of well buffered fresh waters, it is a far cry from the 3.9 that was associated with the ‘unimpacted’ surface waters of the south western Cape reported by Dallas & Day (2004), Davies & Day (1998) and DWAF (1996). In the analysis of spatial trend, the pH was observed to be increasing significantly (0.022; p-value <0.0001) with distance from the upper zone to the lower zone of the Eerste River.

Electrical conductivity was generally observed to be a mix of temporal trends during the period studied. The stations, ER720D at Goetvertrouw farm and EK13 on the N2 freeway, exhibited significant increasing trends with time. The last station, ER720F at the Sjiek Josef’s Kramat, in the lower zone of the Eerste River, showed a significant declining trend in electrical conductivity with time. In space, electrical conductivity showed a significant (1.873; p-value, <0.0001) increasing trend down stream the river. From the analysis of variance (ANOVA) results, it was inferred that the pollution of the Plankenbrug River, the Stellenbosch WWTW through the Veldwagters tributary and the polluted Kuils River were the major drivers of the trend.

Significant increasing temporal trends in nitrates and nitrites were observed at the last two stations, EK13 and ER720F. The possible drivers of these trends are nonpoint sources of pollution from farming activities (EK13) and the polluted Kuils River. However, the results of station EK14 in Dorp Street, Stellenbosch were unexpected. Both the Seasonal Mann-Kendall test and regression analyses detected decreasing temporal trend in nitrates and nitrites at this station, even though with the Seasonal Mann-Kendall p-value, this trend was not significant. The decrease means that with respect to nitrates and nitrites the water quality at that station is improving. This is an interesting development since one would expect to detect the effects of surface wash off of significant quantities of nutrient matter from urban activity (Stellenbosch) into the river.

In the spatial analysis, a significant increasing (0.0632; p-value <0.0001) trend was detected for nitrates and nitrites from the upper to the lower zone of the Eerste River. The ANOVA revealed an abrupt rise in nitrate & nitrite concentrations at ER720C (at the Stellenbosch Farmers Winery cricket ground) approximately 11, 6km downstream from the first station ER720A1, at the Swartbrug Bridge. This hike was attributed to the influence of the Plankenbrug River and the Stellenbosch Waste Water Treatment Works, which discharges treated effluent into the river through the Veldwagters River at ER720D (Goetvertrouw Farm).

Both tests were able to pick up increasing temporal trends in phosphate concentration well upstream of Stellenbosch at station ER720A1. This station is just downstream of a dam where fish farming activities occur. Other increasing long term trends were observed on the Plankenbrug River (PR720B) and at station (EK13) at the N2 freeway. However, where non point sources, in particular the urban residential and industrial areas, were expected to make a significant contribution to nutrient loads in the river, no increasing trends were found (station EK14 at Dorp Street, Stellenbosch). Instead, in a behavior similar to that of the nitrates and nitrites, the phosphates showed a decreasing trend.

The spatial trend of phosphate was observed to be generally similar to that of the nitrate and nitrites except at ER720F. Therefore, the causal mechanisms were assumed to be the same. At ER720F, located at Sjiek Josef'se Kramat towards the mouth of the Eerste

River, the phosphate concentrations were observed to rise with the entry of the Kuils River. In a nutshell, the spatial trend of phosphate was observed to be increasing significantly (0.048; p-value <0.0001).

For chemical oxygen demand (COD) with time, the predominant significant trends observed were declining ones. These were observed in the lower zone of the Eerste River at stations ER720E and ER720F. With regards to the behavior of COD downstream the river, a significant and positive trend (0.703; p-value <0.0001) was observed. The gradual inclines were initially observed at EK14, in the town of Stellenbosch, further rising at the rivers confluence with the Plankenbrug and Veldwagters rivers. From Goetvertrouw Farm, the COD was observed to decrease slightly until its confluence with the Kuils River.

From a practical perspective, significant increasing temporal trends of pH, electrical conductivity, nitrate and nitrite, phosphate and chemical oxygen demand are indicative of deteriorating water quality. In the Eerste River, the temporal trends though present are generally mixed, showing more deterioration in water quality than improvements at individual, isolated sampling sites. The temporal trends are therefore not consistent in the entire river. This is true for all water quality constituents except for pH. The Seasonal Mann Kendall test did not detect any trend at all in pH at any of the sites, while the regression analysis detected overall increasing though minute trends in the entire river. The spatial trends point to an overall deteriorating water quality with approximate distance downstream with respect to all the constituents. The spatial trend is by no means a smooth broad motion, as shown by the ANOVA, rather, it is characterised by steps, peaks and declines that proved to be very useful in the identification of the sources of pollution in the Eerste River.

CHAPTER 5

SUMMARY, CONCLUSIONS & RECOMMENDATIONS

5.1 SUMMARY AND CONCLUSIONS

Rivers are longitudinal functional units, whose flow is unidirectional. They are characterised by physical and chemical conditions that are progressively and continuously modified along their reaches and over time (Davies & Day, 1998). However, the changing quality of water in rivers, particularly when deteriorating, compromises its availability and use. For this reason greater attention is being paid to water quality information. An understanding of the temporal and spatial changes in the water quality of rivers is critical for water resource protection and management. This need to understand river water quality has often taken the form of data gathering which is costly and on its own gives very little, if any, information to underpin effective water resource management. Therefore, the ability to convert this available data into information that can be used in the management and protection of water resources becomes of fundamental importance.

The validity and applicability of various statistical techniques to water resources data for purposes of information generation, has resulted in a lot of interest in the water research fraternity. One decision support tool that has gained prominence is the non-parametric Seasonal Mann-Kendall test for trend. This test is considered to be particularly suited to water quality data because water quality data are seldom normally distributed, linear, and independent, and thus violate the assumptions required for parametric tests. Linear regression techniques require that the data be from a normal distribution, be linear and independent for them to be appropriate and reliable. To the contrary, the Seasonal Mann-Kendall tests are impartial to probability distribution and linearity, demanding only that data be monotonic and independent.

In 1993, the Department of Water Affairs and Forestry undertook a study to compile information on the water quality of the Eerste River. This was with a view to understand the processes which influence its water quality. This particular study was based on the assessment of time series data plots of 12 year data for the period 1977 to 1989. Whilst the study was not a detailed trend study, it revealed that no long term trends were evident in the river system. Furthermore, with regards to spatial trend, DWAF (1993) reported a steady decline in water quality. This decline was ascribed to point and non-point sources of pollution in the catchment.

The aim of this study was to investigate temporal and spatial trends in available water quality data of the Eerste River, from 1990 to 2005. The water quality variables used to achieve this aim were pH, electrical conductivity, nitrogen, phosphorus and chemical oxygen demand. In meeting the objectives of the study, raw water quality data was obtained from the City of Cape Town (CCT) and the Department of Water Affairs and Forestry (DWAF). The data were analysed for temporal trend using the Seasonal Mann-Kendall test and standard regression analysis.

Prior to testing for trend, the data were formatted to the specifications of the Seasonal Mann-Kendall test and regression analysis and then tested for normality. It was found that the data were not from a normal distribution and therefore violated the assumptions required for analysis with parametric methods. Despite this knowledge, linear regression was used to detect trend and observe just how different the results of the two tests would be. The reasoning being that, as was observed by Zipper *et al*, (1992) linear regression is capable of detecting trends where they are well defined, in spite of its limitations as a parametric method.

There generally was substantial congruence in the results of the two tests. Both tests were able to pick up similar significant temporal trends for electrical conductivity at three out of nine stations, nitrates and nitrites at two out of nine stations, phosphates at three out of nine stations and chemical oxygen demand at two out of nine stations. However, the major disparity was the pH result, where the regression analysis picked up significant trends and the Seasonal Kendall-Test did not. Notably, all the slope coefficients of the regression lines were, in practical terms, very small.

From the temporal analyses, it emerged that there has not been a clear-cut overall deterioration in the water quality of the entire Eerste River over time. The temporal trends that were observed were a mix of no trend, significant increases, and decreases in variable concentrations, which were isolated and localised at the different stations. Some stations, showed no temporal trends in most of the variables over time (ER720B and ER720C) suggesting that there have not been any discernible changes in water quality in that part of the river. Other stations exhibited improvements in water quality as was the case with EK14 (Dorp Street, Stellenbosch) with significant decreasing trends in phosphates. Other stations showed deteriorating water quality, these include ER720D (Goetvertrouw Farm) and EK13 (at the N2 Freeway) with increasing trends in electrical conductivity. The station with the most increasing temporal trends was EK13.

The inclusion of spatial trend assessment for defining the water quality of the Eerste River proved to be very useful. This is because the spatial trends were more apparent and their probable causes easier to identify than the temporal trends. Overall, the five variables exhibited significant increasing trends with approximate distance downstream. The analysis of variance (ANOVA) used to investigate the differences between the stations, showed generally increasing trends of the mean values of the variable concentrations from the uppermost station (ER720A1) to the last one on the lower zone of the river. These observed increases are indicative of deteriorating water quality with increasing distance downstream.

The observed spatial trends culminated in the identification of a fish farm on the Jonkershoek River, the polluted Plankenbrug River, the Stellenbosch Waste Water Treatment Works though the Veldwagters tributary, farming non point sources of pollution and the polluted Kuils River as the major catchment activities with direct impact on the water quality of the Eerste River.

It would seem that, the pollution in the Plankenbrug River and Stellenbosch Waste Water Treatment Works through the Veldwagters River which were identified by the Department of Water Affairs and Forestry (1993) as some of the major impacts on the water quality of the Eerste River, continue to be problematic. Therefore, if the water quality situation in the Eerste River is to be remedied then the pollution sources identified herein, are the places to start.

5.2 RECOMMENDATIONS

The water quality of the Eerste River is influenced by catchment activities. The major sources of pollution that were identified, namely, the fish farm, on the Jonkershoek River; the Plankenbrug River; the Stellenbosch Waste Water Treatment works; and the Kuils River are point sources that can be controlled. The non point sources of pollution are more complex to deal with. As part of efforts to improve water quality management in the Eerste River the following recommendations are made.

- Upgrading the wetlands along the Kuils River to cope with the effluent being released into the river from waste water treatment works.

- Upgrading the Stellenbosch waste water treatment works to increase its efficiency to treat effluent and thus reduce its impact on the Eerste River.

When addressing the “data rich but information poor syndrome” (DWAF, 2004c) the Department of Water Affairs and Forestry needs to re-evaluate the current water quality monitoring system of the Eerste River.

The reliability of the information produced by statistical analyses is only as reliable as the data from which it is generated. Greater commitment to consistency, frequency and accuracy is critical when accumulating the data. When dealing with frequency, it is important to note that observations that are accumulated too frequently, for instance weekly or bi weekly, tends to compromise data independence. Therefore, for purposes of temporal trend detection, monthly observations are considered sufficient (Cox *et al*, 2005, McBride & Loftis, 1994). It is also important to be consistent and accurate when collecting the data in order to curtail the limitations presented by missing, inaccurate and insufficient data.

It emerged from the literature survey that when investigating long term trend, the effects of flow need to be removed (Vant & Smith, 2004; Griffith *et al*, 2001; Zipper *et al*, 1998; Smith *et al*, 1996; Zipper *et al*, 1992). This is because the concentration of some water quality variables is greatly influenced by stream flow. The mechanisms in action being dilution (causing the concentrations to decrease with an increase in flow) and wash off (causing the concentrations to increase with an increase in flow). Dilution affects parameters such as dissolved solids, while wash off affects parameters such as suspended solids and total phosphates (Smith *et al*, 1996). Therefore, when investigating trend, it is critical that these effects be removed so that the actual underlying trends are discerned (Zipper *et al*, 1992). But to do this, flow data corresponding to the sampling activity ought to be available. Therefore, it is recommended that discharge data corresponding to sampling times at the sampling points be accumulated as part of the water quality data.

Further research recommended for the Eerste River

- A study to investigate the relationship between changes in catchment land use and changes in the water quality of the Eerste River over a long period of time is recommended. Such a study would provide greater detail of the predominant drivers of water pollution in the Eerste River catchment.

- A predictive study to model or forecast future trends and provide estimates of the rates of change in water quality is also recommended as a basis for water quality management strategies.

- A comprehensive study to investigate the impacts associated with the fish farming activities in the upper reaches of the Eerste River on its water quality is recommended.

- It would also be worthwhile to investigate the impacts of possible constructed wetlands for the Plankenbrug and Veldwagters tributaries. Constructed wetlands have emerged as very useful soft engineering techniques for the mitigation of both point and non point sources of pollution. Moore *et al* (2002) carried out field assessments to investigate the effectiveness of a constructed wetland in the mitigation of the orthophosphate, chlopyrifos, in a tributary to the Lourens River, in the Western Cape. They found that the constructed wetland, reduced by 15%, 54% and 70% (in dry weather) and 78%, 75% and 84% (in wet weather) the total suspended solids, orthophosphate and nitrate that were entering it (Moore *et al,* 2002).

The Eerste River is an important river that supports many uses. The present study found its water quality to be characterised by a mix of long-term trends. Some of the study sites showed improving water quality, some deteriorating water quality and others showed no changes at all. The spatial trends that were observed were well defined, showing degrading water quality from the upper reaches to the lower reaches of the river. The observed trends were inferred to be driven by point and non-point sources of pollution.

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APPENDICES

Appendix 1: Raw Water Quality Data

Station	date	pH	electrical conductivity	nitrates+ nitrites	phosphates	COD
ek13	1/17/1991	7.5	50	0.6	0.9	30
ek13	2/7/1991	7.6	30	0.9	0.9	10
ek13	3/8/1991	7.7	40	0.3	0.2	25
ek13	4/4/1991	7.4	40	0.6	0.5	25
ek13	5/23/1991	7.3	40	0.8	1	32
ek13	7/4/1991	7.3	40	3.8	0.2	30
ek13	8/9/1991	6.9	25	1.2	0.3	34
ek13	9/6/1991	7.7	49	1	0.3	15
ek13	10/24/1991	7.5	30	0.4	0.3	25
ek13	11/15/1991	7.9	28	0.7	0.2	44
ek13	12/6/1991	7.6	50	1.4	0.3	20
ek13	1/16/1992	7.6	30	0.3	0.2	20
ek13	2/14/1992	7.3	24	0.5	0.2	20
ek13	3/12/1992	7	34	0.6	1.2	20
ek13	4/9/1992	7.9	38	0.7	0.1	30
ek13	5/14/1992	6.6	30	0.6	0.1	25
ek13	6/11/1992	7	25	1.2	0.2	23
ek13	7/17/1992	6.9	27	0.8	0.3	15
ek13	8/20/1992	7.7	30	1	0.7	22
ek13	9/10/1992	7.7	28	0.5	0.1	47
ek13	10/15/1992	7.4	45	1.3	0.6	25
ek13	11/12/1992	7.4	25	0.8	0.2	20
ek13	12/4/1992	7.5	29	0.6	0.5	24
ek13	1/18/1993	7.4	20	0.6	0.3	20
ek13	2/19/1993	7.7	34	1.3	0.5	25
ek13	3/5/1993	7.6	28	0.4	0.2	15
ek13	4/1/1993	7.2	58	7.1	2.5	57
ek13	5/7/1993	7.5	20	0.3	0.1	20
ek13	6/4/1993	7	15	0.9	0.1	15
ek13	7/16/1993	7.4	20	1.1	0.2	30
ek13	8/6/1993	7.1	18	1	0.05	20
ek13	9/3/1993	7.4	20	0.4	0.2	25
ek13	10/8/1993	6.9	24	0.5	0.3	30
ek13	11/5/1993	7.5	38	1.8	0.6	15
ek13	12/2/1993	7.4	29	0.3	0.7	15
ek13	1/13/1994	7.2	21	0.7	0.6	30
ek13	2/11/1994	7.5	33	0.05	0.4	39
ek13	3/11/1994	6.7	20	0.2	0.1	20
ek13	4/15/1994	7	25	0.7	0.6	25
ek13	5/20/1994	6.8	17	0.4	0.2	45
ek13	6/23/1994	6.6	17	1.4	0.2	20
ek13	7/15/1994	6.6	52	2.1	0.5	45
ek13	8/12/1994	6.8	43	1.5	0.5	30

Station	**date**	**pH**	**electrical conductivity**	**nitrates+nitrites**	**phosphates**	**COD**
ek13	9/16/1994	6.8	52	2.6	0.9	35
ek13	10/14/1994	6.9	20	0.8	0.2	20
ek13	11/11/1994	6.7	31	1	0.4	25
ek13	12/1/1994	6.9	25	0.8	0.4	37
ek13	1/20/1995	7	64	0.4	0.6	20
ek13	2/2/1995	7.3	68	0.6	0.5	30
ek13	3/9/1995	7.3	57	0.4	0.5	35
ek13	4/21/1995	6.5	17	2.9	0.2	25
ek13	5/12/1995	7	51	4	1.3	47
ek13	6/8/1995	6.8	29	0.4	0.4	20
ek13	8/25/1995	7.4	31	0.7	0.6	23
ek13	9/15/1995	7.3	28	1.3	0.05	23
ek13	10/6/1995	7.2	21	1.3	0.2	20
ek13	11/9/1995	7.4	20	1.3	0.1	20
ek13	12/7/1995	7.2	27	1.1	0.4	20
ek13	1/22/1996	7.4	59	4.2	2	30
ek13	2/16/1996	6.8	28	1.8	0.4	20
ek13	3/14/1996	7.4	30	0.8	0.7	29
ek13	4/18/1996	7	19	0.3	1	100
ek13	5/9/1996	6.7	30	0.1	0.05	27
ek13	6/13/1996	7.4	22	0.7	0.4	20
ek13	7/4/1996	7.2	21	0.9	.	28
ek13	8/23/1996	7	51	3.4	0.5	45
ek13	9/20/1996	7	42	1.2	0.4	35
ek13	10/11/1996	7.1	32	1.7	0.4	90
ek13	11/14/1996	7.1	42	2.7	0.5	75
ek13	8/28/1997	7.5	47	0.5	0.7	40
ek13	11/20/1997	7.3	44	.	0.83	30
ek13	1/21/1998	7.6	60	1.51	1.8	35
ek13	2/9/1998	7.7	68	5.04	1.63	.
ek13	2/22/1998	7.7	68	5.04	1.63	.
ek13	4/20/1998	7.4	60	1.7	2.9	47
ek13	7/23/1998	7.5	46	1.6	0.9	25
ek13	10/21/1998	7.5	49	1.6	1.73	25
ek13	2/9/1999	7.7	68	5.04	1.63	33
ek13	2/22/1999	.	.	.	.	.
ek13	5/26/1999	7.5	54	6.5	2.026	24
ek13	7/15/1999	7.5	34	1.99	0.646	12
ek13	9/9/1999	7.7	43	2.68	.	34
ek13	10/13/1999	7.7	41	2.646	0.659	15
ek13	11/16/1999	7.6	77	1.969	1.058	24
ek13	1/18/2000	7.6	58	2.21	1.503	45
ek13	2/16/2000	7.8	64	0.716	.	17
ek13	3/23/2000	7.6	51	2.833	1.606	24
ek13	5/2/2000	7.4	37	4.864	1.088	14
ek13	6/6/2000	7.6	39	1.752	1.155	21
ek13	7/18/2000	7.4	32	1.089	0.171	19
ek13	8/31/2000	7.5	38	1.867	0.676	25

Station	date	pH	electrical conductivity	nitrates+nitrites	phosphates	COD
ek13	9/21/2000	7.5	40	1.552	0.67	30
ek13	10/19/2000	7.9	40	2.301	1.613	.
ek13	11/16/2000	7.5	105	1.869	0.997	34
ek13	1/18/2001	7.6	60	5.051	2.172	27
ek13	2/15/2001	4.2	58	2.9	1.562	27
ek13	3/15/2001	7.6	50	1.727	1.726	24
ek13	4/5/2001	7.5	58	4.073	2.238	26
ek13	5/3/2001	7.5	65	3.92	1.489	6
ek13	6/7/2001	7.5	40	1.784	0.804	28
ek13	7/5/2001	7.5	25	1.963	0.319	41
ek13	7/9/2001	7.5	40	1.784	0.804	28
ek13	8/2/2001	7.4	48	1.913	0.651	24
ek13	9/6/2001	7.7	30	1.175	0.497	39
ek13	10/4/2001	7.2	43	1.788	0.549	21
ek13	11/1/2001	7.9	42	1.9	0.483	37
ek13	12/6/2001	7.5	57	9.815	2.248	29
ek13	1/24/2002	7.7	44	1.37	0.653	17
ek13	2/21/2002	7.5	56	3.003	1.156	21
ek13	3/14/2002	7.3	60	4.229	1.936	50
ek13	4/18/2002	7.5	44	3.332	1.997	61
ek13	5/23/2002	7.1	35	2.809	1.232	32
ek13	6/20/2002	7.2	40	1.584	0.651	38
ek13	7/18/2002	7.3	41	1.384	0.402	38
ek13	8/22/2002	7	45	1.32	0.836	48
ek13	9/19/2002	7.2	44	2.047	0.454	48
ek13	10/24/2002	7.2	44	2.907	1.08	31
ek13	11/21/2002	7.1	41	0.803	0.84	27
ek13	12/12/2002	7.5	69	6.289	2.667	55
ek13	1/23/2003	6.6	46	2.92	1.874	34
ek13	2/20/2003	6.9	28	1.623	1.482	17
ek13	3/18/2003	6.7	26	2.553	1.365	27
ek13	4/10/2003	6.9	29	2.364	0.35	14
ek13	5/15/2003	6.3	52	2.551	1.114	29
ek13	6/12/2003	6.4	44	2.432	2.072	26
ek13	7/24/2003	6.8	47	2.725	1.554	25
ek13	8/21/2003	6.1	37	1.807	0.398	42
ek13	9/18/2003	6	46	1.474	0.791	11
ek13	10/16/2003	7.6	30	0.946	1.346	10
ek13	11/13/2003	7	49	3.195	1.793	21
ek13	12/18/2003	6.7	40.7	4.635	1.702	32
ek13	1/15/2004	7	43.2	0.177	2.995	34
ek13	2/12/2004	7	54.3	1.113	1.79	10
ek13	3/11/2004	7.3	43.8	3.723	1.878	47
ek13	4/15/2004	6.6	48.7	4.366	2.536	24
ek13	5/13/2004	7.4	60.9	3.046	2.044	27
ek13	6/10/2004	7.4	54.2	3.436	1.635	22
ek13	7/8/2004	7.2	42.6	2.243	1.171	32
ek13	8/5/2004	7.1	42	2.706	1.401	36

Station	date	pH	electrical conductivity	nitrates+nitrites	phosphates	COD
ek13	9/2/2004	7.3	46.6	1.822	0.617	19
ek13	10/14/2004	7	58.1	1.891	1.098	40
ek13	11/11/2004	7.4	62.2	3.62	1.622	5
ek13	12/9/2004	7.4	73.5	0.987	2.216	34
ek13	1/13/2005	7.5	80.1	1.681	2.014	15
ek13	2/10/2005	7.5	97.6	3.336	1.613	15
ek13	3/10/2005	7.4	65.7	2.286	2.613	34
ek13	4/14/2005	7.6	76.8	2.86	3.141	12
ek13	5/12/2005	7.3	47.5	3.526	2.143	47
ek13	6/9/2005	6.9	25.2	0.68	0.375	16
ek13	7/14/2005	8	52.2	1.867	0.716	6
ek13	8/4/2005	7	35.8	0.818	0.472	27
ek14	1/17/1991	6.5	10	0.1	0.1	7
ek14	2/7/1991	6.8	8	0.7	0.1	5
ek14	3/7/1991	7	10	0.1	0.1	15
ek14	4/4/1991	6.4	13	0.3	0.05	5
ek14	5/23/1991	5.7	2	0.8	0.1	15
ek14	7/4/1991	6.8	10	0.3	0.1	10
ek14	8/9/1991	6.2	8	0.4	0.1	2
ek14	9/6/1991	6.9	10	0.3	0.1	5
ek14	10/24/1991	6.8	10	0.2	0.1	20
ek14	11/15/1991	6.7	11	0.4	0.1	44
ek14	12/6/1991	6.5	12	0.3	0.1	20
ek14	1/16/1992	6.5	10	0.4	0.05	20
ek14	2/14/1992	6.7	8	0.3	0.1	20
ek14	3/12/1992	6.2	12	0.4	0.1	20
ek14	4/9/1992	7.2	10	0.2	0.1	15
ek14	5/14/1992	6.4	8	0.4	0.05	20
ek14	6/11/1992	6.3	10	0.4	0.1	20
ek14	7/17/1992	6.9	8	0.3	0.1	15
ek14	8/20/1992	7.2	10	0.4	0.3	22
ek14	9/10/1992	7	10	0.2	0.05	20
ek14	10/15/1992	6.7	12	0.8	0.1	10
ek14	11/12/1992	6.5	10	0.3	0.05	12
ek14	12/4/1992	7	9	3	0.05	15
ek14	1/18/1993	7.1	10	0.5	0.1	15
ek14	2/19/1993	7.1	10	0.2	0.1	6
ek14	3/5/1993	7.1	12	0.4	0.05	10
ek14	4/1/1993	6.5	12	0.05	0.1	12
ek14	5/7/1993	6.4	10	0.2	0.05	10
ek14	6/4/1993	6.6	10	0.6	0.1	15
ek14	7/16/1993	6.6	10	0.4	0.1	20
ek14	8/6/1993	6	8	0.7	0.05	10
ek14	9/3/1993	6.8	10	0.2	0.05	15
ek14	10/8/1993	6.5	12	0.4	0.1	15
ek14	11/5/1993	7.3	14	0.7	0.1	15

Station	**date**	**pH**	**electrical conductivity**	**nitrates+nitrites**	**phosphates**	**COD**
ek14	12/2/1993	6.7	11	0.2	0.1	15
ek14	1/13/1994	6.8	12	0.9	0.4	20
ek14	2/11/1994	7.1	18	0.05	0.1	15
ek14	3/11/1994	6.4	10	0.3	0.1	15
ek14	4/15/1994	6.6	10	0.5	0.1	20
ek14	5/20/1994	6.5	12	0.5	0.1	15
ek14	6/23/1994	6	9	1	0.05	23
ek14	7/15/1994	5.8	14	0	0.1	25
ek14	8/12/1994	6.4	10	0.3	0.1	20
ek14	9/16/1994	6.3	13	0.4	0.1	20
ek14	10/14/1994	6.3	11	0.8	0.05	20
ek14	11/11/1994	6.6	17	0.4	0.1	20
ek14	12/1/1994	6.2	15	0.5	0.05	22
ek14	1/20/1995	6.2	13	0.4	0.05	20
ek14	2/2/1995	6.6	16	0.8	0.05	20
ek14	3/9/1995	6.4	11	0.5	0.1	20
ek14	4/21/1995	6.1	12	2.9	0.05	25
ek14	5/12/1995	6.2	16	0.5	0.8	20
ek14	6/8/1995	6.3	13	0.3	0.05	20
ek14	8/25/1995	7.7	8	0.6	0.05	20
ek14	9/15/1995	7.3	11	0.3	0.05	20
ek14	10/6/1995	7.2	12	0.6	0.1	20
ek14	11/9/1995	7.1	11	0.7	0.05	20
ek14	12/7/1995	7	17	0.6	0.1	71
ek14	1/22/1996	6.7	20	0.7	0.1	20
ek14	2/16/1996	6.2	14	1.7	0.05	20
ek14	3/14/1996	6.4	14	0.4	0.2	20
ek14	4/18/1996	6.2	8	0.2	0.5	110
ek14	5/9/1996	6.4	15	0.2	0.05	20
ek14	6/13/1996	6.8	10	0.4	0.1	20
ek14	7/4/1996	6.9	11	0.5	.	25
ek14	8/23/1996	6.3	12	0.5	0.1	30
ek14	9/20/1996	6.4	8	0.5	0.1	20
ek14	10/11/1996	6.2	5	0.4	0.4	75
ek14	11/14/1996	7	11	0.8	0.3	35
ek14	8/28/1997	7.6	10	0.3	0.1	25
ek14	11/20/1997	7.2	11	.	0.16	13
ek14	1/21/1998	7.5	13	0.51	0.08	15
ek14	2/9/1998	8	12	0.101	0.041	.
ek14	2/22/1998	8	12	0.101	0.041	.
ek14	2/23/1998	0	.	.	.	.
ek14	4/20/1998	7.5	10	0.53	0.03	13
ek14	7/23/1998	7.5	10	0.51	0.31	10
ek14	10/21/1998	7.5	12	0.42	0.1	10
ek14	2/9/1999	8	12	0.101	0.041	27
ek14	2/22/1999	.	.	.	.	.

Station	date	pH	electrical conductivity	nitrates+nitrites	phosphates	COD
ek14	2/23/1999	.	.	.	.	.
ek14	5/26/1999	7.6	16	0.25	0.045	13
ek14	7/15/1999	7.7	16	0.29	0.164	12
ek14	9/9/1999	7.6	11	0.22	0.103	19
ek14	10/13/1999	7.5	12	0.291	0.036	2
ek14	11/16/1999	7.4	15	0.154	0.019	8
ek14	1/18/2000	7.4	12	2.205	0.027	45
ek14	2/16/2000	7.3	17	0.069	0.168	8
ek14	3/23/2000	7.6	11	0.079	0.025	12
ek14	5/2/2000	7.4	9	0.044	0.012	13
ek14	6/6/2000	7.6	11	0.095	.	16
ek14	7/18/2000	7.5	63	0.076	.	17
ek14	8/31/2000	7.2	98	0.225	0.029	22
ek14	9/21/2000	7.5	12	0.326	0.074	22
ek14	10/19/2000	7.6	12	0.208	0.035	.
ek14	11/16/2000	7.3	11	0.133	0.05	21
ek14	1/18/2001	7.5	10	0.122	0.038	12
ek14	2/15/2001	4.1	11	0.067	0.032	13
ek14	3/15/2001	7.7	8	0.059	0.181	10
ek14	4/5/2001	7.1	10	0.049	0.026	12
ek14	5/3/2001	7.4	15	0.16	0.059	10
ek14	6/7/2001	7.6	13	0.149	0.035	14
ek14	7/5/2001	7.4	6	0.197	0.049	16
ek14	7/9/2001	7.6	13	0.149	0.035	14
ek14	8/2/2001	7.4	13	0.531	0.277	11
ek14	9/6/2001	7.7	62	0.125	0.02	10
ek14	10/4/2001	6.7	10	0.369	0.029	6
ek14	11/1/2001	7.9	11	0.251	0.056	13
ek14	12/6/2001	7.3	12	0.274	0.033	4
ek14	1/24/2002	7.7	15	0.132	0.73	40
ek14	2/21/2002	7.2	14	0.121	0.055	17
ek14	3/14/2002	7.3	15	0.147	0.14	21
ek14	5/23/2002	6.3	6	0.074	0.098	24
ek14	6/20/2002	7	11	0.199	0.06	16
ek14	7/18/2002	6.9	12	0.31	0.043	17
ek14	8/22/2002	6.7	13	0.338	0.082	15
ek14	9/19/2002	7.1	13	0.328	0.016	24
ek14	10/24/2002	6.9	13	0.189	0.043	6
ek14	11/21/2002	6.7	13	0.076	0.03	10
ek14	12/12/2002	6.7	14	0.129	0.04	20
ek14	1/23/2003	6.1	11	0.138	0.019	9
ek14	2/20/2003	6.4	8	0.05	0.049	11
ek14	3/18/2003	6	7	0.06	0.051	18

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720F	2/14/95	7.7	89	0.2	2.07	74
ER720F	3/14/95	7.6	79	0.7	3.12	48
ER720F	4/11/95	7.6	90	0.2	4.00	53
ER720F	5/8/95	7.6	73	1.1	1.80	45
ER720F	6/6/95	7.6	72	1.2	1.43	40
ER720F	7/4/95	7.6	88	1.3	1.22	66
ER720F	8/1/95	7.5	42	1.3	0.42	36
ER720F	8/29/95	7.5	76	2.0	0.85	46
ER720F	9/26/95	7.6	82	0.9	1.28	51
ER720F	10/24/95	7.5	77	1.1	1.40	54
ER720F	11/21/95	7.5	89	1.0	2.10	60
ER720F	12/18/95	7.4	84	4.1	1.60	117
ER720F	1/23/96	7.3	85	0.4	2.84	70
ER720F	2/20/96	7.6	94	0.2	1.72	57
ER720F	3/18/96	7.6	83	0.2	3.11	52
ER720F	4/16/96	7.3	65	2.4	2.12	50
ER720F	5/14/96	7.2	80	1.1	2.00	58
ER720F	6/18/96	7.4	51	1.4	0.20	32
ER720F	7/16/96	7.6	80	2.4	0.80	40
ER720F	8/13/96	7.4	61	1.5	0.51	67
ER720F	9/10/96	7.6	69	1.8	0.68	61
ER720F	10/8/96	7.3	73	2.4	0.94	47
ER720F	11/5/96	7.1	68	1.5	0.94	46
ER720F	12/17/96	7.4	76	0.8	1.86	40
ER720F	2/11/97	7.6	80	1.3	1.38	50
ER720F	3/25/97	7.3	79	1.4	1.07	53
ER720F	5/6/97	7.4	68	2.6	1.21	46
ER720F	6/17/97	7.4	53	1.6	0.88	34
ER720F	7/28/97	7.5	76	2.6	1.02	52
ER720F	9/9/97	7.5	77	1.8	0.91	43
ER720F	10/21/97	7.1	83	0.6	2.13	48
ER720F	12/2/97	7.4	69	1.0	1.45	52
ER720F	1/27/98	7.5	78	0.2	1.97	32
ER720F	3/10/98	7.3	75	0.2	1.26	50
ER720F	5/4/98	7.4	71	1.4	1.19	38
ER720F	6/29/98	7.5	81	2.5	1.13	52
ER720F	1/26/99	7.3	84	0.2	3.46	57
ER720F	3/1/99	7.3	75	0.6	1.36	49
ER720F	4/12/99	7.7	73	0.7	2.40	29
ER720F	5/17/99	7.8	75	2.3	2.78	37
ER720F	6/22/99	7.4	38	0.8	0.48	26
ER720F	8/10/99	7.5	66	1.8	0.25	32
ER720F	9/14/99	7.6	58	1.2	0.41	30
ER720F	10/25/99	7.5	76	1.0	1.15	34
ER720F	12/6/99	7.4	80	0.4	2.40	46
ER720F	1/24/00	7.0	79	0.2	4.05	48
ER720F	2/28/00	7.3	74	0.3	4.20	38
ER720F	3/27/00	7.6	76	1.0	1.70	28
ER720F	5/15/00	7.3	70	1.9	2.31	48
ER720F	6/27/00	7.7	75	2.1	0.76	30

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720F	8/7/00	7.6	78	2.1	1.15	45
ER720F	9/11/00	7.4	57	2.7	1.10	34
ER720F	12/4/00	7.6	80	0.6	2.10	28
ER720F	3/6/01	7.8	78	0.5	2.58	10
ER720F	5/28/01	7.6	68	1.8	1.37	33
ER720F	1/22/02	7.6	68	1.8	1.38	22
ER720F	6/26/02	8.0	62	2.6	0.81	10
ER720F	8/21/02	8.4	76	1.8	0.58	32
ER720F	1/13/03	8.3	60	2.3	0.03	24
ER720F	2/25/03	8.3	63	2.3	2.70	32
ER720F	4/10/03	8.1	76	2.4	1.70	44
ER720F	5/7/03	8.1	69	3.2	1.00	24
ER720F	5/27/03	8.2	66	2.6	2.20	10
ER720F	6/30/03	7.9	68	4.2	1.80	52
ER720F	7/28/03	7.7	63	4.6	1.90	52
ER720F	9/3/03	7.4	59	2.2	0.68	46
ER720F	10/13/03	7.8	69	2.3	1.50	20
ER720F	11/11/03	7.7	73	2.2	4.10	40
ER720F	1/13/04	7.8	71	4.7	4.30	44
ER720F	2/18/04	8.0	68	1.5	3.40	68
ER720F	4/28/04	7.4	67	1.5	0.03	10
ER720F	5/31/04	9.0	73	3.4	3.90	36
ER720F	7/20/04	7.5	70	3.5	1.70	32
ER720F	8/30/04	7.7	85	2.8	1.50	10
ER720F	10/12/04	8.4	75	4.8	1.40	26
ER720F	11/22/04	7.5	80	6.2	2.20	24
ER720F	3/15/05	8.0	69	4.7	2.60	32
ER720F	5/18/05	6.8	18	0.8	0.40	45
ER720F	7/11/05	7.0	81	2.2	1.50	10
ER720F	9/14/05	7.5	73	0.4	1.8	24

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720E	2/14/95	7.6	62	2.3	3.92	34
ER720E	3/14/95	7.4	39	2.0	1.88	25
ER720E	4/11/95	7.4	53	3.7	2.20	31
ER720E	5/9/95	7.3	36	3.1	1.39	29
ER720E	6/6/95	7.4	37	3.1	0.92	22
ER720E	7/4/95	7.5	41	3.1	0.60	28
ER720E	8/1/95	7.3	17	0.7	0.13	10
ER720E	8/29/95	7.5	39	2.1	0.56	30
ER720E	9/26/95	7.6	40	2.6	0.51	21
ER720E	10/24/95	7.5	40	2.4	0.79	22
ER720E	11/21/95	7.4	51	5.8	2.40	28
ER720E	12/18/95	7.3	44	0.4	1.70	55
ER720E	1/23/96	7.2	53	4.5	2.08	32
ER720E	2/20/96	7.4	55	3.3	1.86	39
ER720E	3/18/96	7.5	49	2.5	1.31	26
ER720E	4/16/96	7.0	32	2.5	0.83	26
ER720E	5/14/96	7.3	42	3.7	1.90	22
ER720E	7/16/96	7.4	43	1.9	0.24	22

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720E	8/13/96	7.1	40	1.3	0.22	115
ER720E	9/10/96	7.4	33	1.6	0.25	29
ER720E	10/8/96	7.0	37	2.7	0.50	21
ER720E	11/5/96	7.1	35	2.7	0.56	40
ER720E	12/17/96	7.3	41	2.4	1.25	48
ER720E	2/11/97	7.4	45	3.6	1.77	64
ER720E	3/26/97	7.4	44	3.6	1.61	25
ER720E	5/6/97	7.0	41	6.6	1.91	36
ER720E	6/17/97	7.1	33	1.8	0.37	24
ER720E	7/28/97	7.2	42	2.7	0.65	22
ER720E	9/9/97	7.4	51	1.4	0.39	45
ER720E	10/21/97	7.4	55	2.9	1.57	42
ER720E	12/2/97	7.4	37	3.4	1.18	28
ER720E	1/27/98	7.4	51	1.8	2.08	10
ER720E	3/10/98	7.7	59	1.7	3.06	28
ER720E	5/4/98	7.4	47	2.4	1.39	29
ER720E	6/29/98	7.4	42	2.5	0.61	39
ER720E	8/17/98	7.6	44	2.9	0.47	32
ER720E	9/28/98	7.4	38	4.2	1.24	27
ER720E	11/4/98	7.4	33	0.8	0.31	26
ER720E	12/7/98	7.2	51	5.0	2.02	10
ER720E	1/26/99	7.2	65	8.2	2.84	35
ER720E	3/1/99	7.5	65	1.3	2.42	35
ER720E	4/12/99	7.4	51	5.9	2.80	21
ER720E	5/17/99	7.3	48	6.8	2.18	25
ER720E	6/22/99	6.9	25	0.4	0.23	22
ER720E	8/10/99	7.4	41	1.9	0.32	36
ER720E	9/14/99	7.4	54	1.2	0.20	38
ER720E	10/25/99	7.3	40	2.0	0.79	10
ER720E	12/6/99	7.6	64	3.1	2.22	20
ER720E	1/24/00	7.4	49	1.3	2.47	24
ER720E	2/28/00	7.5	61	1.5	2.80	55
ER720E	5/15/00	7.4	50	0.2	2.01	28
ER720E	6/27/00	7.4	48	4.6	1.16	26
ER720E	8/7/00	7.1	42	1.9	0.58	10
ER720E	9/11/00	7.2	29	1.4	0.31	26
ER720E	12/4/00	7.4	55	0.6	2.43	25
ER720E	1/23/01	7.3	55	8.3	2.85	29
ER720E	3/6/01	7.4	55	1.9	2.46	25
ER720E	5/28/01	7.2	45	3.4	1.20	25
ER720E	9/3/01	7.6	40	1.3	0.36	30
ER720E	1/22/02	7.2	39	2.0	0.90	10
ER720E	6/26/02	7.5	35	2.1	0.60	10
ER720E	8/21/02	7.8	41	1.6	0.35	10
ER720E	9/30/02	7.5	36	2.0	0.40	10
ER720E	1/13/03	7.6	48	1.7	0.62	63
ER720E	2/25/03	7.5	39	2.2	1.40	40
ER720E	4/10/03	7.6	50	2.7	1.70	40
ER720E	5/7/03	7.6	49	1.0	3.10	32
ER720E	5/27/03	7.4	41	1.9	0.82	10
ER720E	6/30/03	7.5	50	4.8	1.50	10

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720E	7/28/03	7.4	35	6.1	0.67	28
ER720E	9/3/03	7.4	35	1.0	0.19	10
ER720E	10/13/03	7.4	40	2.1	0.71	10
ER720E	11/11/03	7.6	43	6.0	3.00	40
ER720E	1/13/03	7.5	46	5.6	4.10	20
ER720E	2/18/04	7.6	46	1.9	1.70	20
ER720E	4/28/04	7.9	68	4.2	2.20	28
ER720E	5/31/04	8.6	56	5.3	0.21	20
ER720E	7/20/04	7.3	43	5.6	3.80	10
ER720E	8/30/04	7.4	43	1.9	0.26	20
ER720E	10/12/04	8.0	44	4.6	0.98	34
ER720E	11/22/04	7.5	53	5.0	1.20	28
ER720E	3/15/05	7.5	57	3.5	3.40	36
ER720E	5/18/05	7.0	9	0.5	0.17	28
ER720E	7/11/05	6.9	37	1.9	0.72	10
ER720E	9/14/05	7.4	39.2	0.8	0.8	10

ER720D	2/14/95	7.7	49	1.1	1.80	32
ER720D	3/14/95	7.3	33	8.4	3.90	27
ER720D	4/11/95	7.3	41	11.3	3.60	32
ER720D	5/8/95	7.3	31	2.8	1.78	10
ER720D	6/6/95	7.0	31	3.7	1.86	10
ER720D	7/4/95	7.6	38	3.1	0.94	30
ER720D	8/1/95	7.2	10	0.5	0.12	10
ER720D	8/29/95	7.5	36	2.3	0.31	28
ER720D	9/26/95	7.6	36	4.0	1.07	25
ER720D	10/24/95	7.4	35	1.4	1.10	24
ER720D	11/21/95	7.2	48	8.1	2.00	42
ER720D	12/18/95	6.7	19	1.1	0.27	66
ER720D	1/23/96	6.9	29	4.4	1.67	32
ER720D	2/20/96	7.2	48	6.5	2.43	37
ER720D	3/18/96	7.6	43	3.2	2.24	30
ER720D	4/16/96	6.8	28	2.0	1.55	32
ER720D	5/14/96	7.0	35	5.2	1.80	24
ER720D	6/18/96	6.8	16	0.9	0.60	26
ER720D	7/16/96	7.5	39	1.8	0.29	24
ER720D	8/13/96	7.0	23	0.9	0.14	63
ER720D	9/10/96	7.1	38	0.6	0.62	69
ER720D	10/8/96	7.2	37	2.6	0.85	37
ER720D	12/17/96	6.9	28	1.0	0.78	84
ER720D	2/11/97	7.4	44	3.9	2.85	22
ER720D	3/25/97	6.6	38	4.4	3.74	10
ER720D	5/6/97	6.7	29	3.5	1.56	31
ER720D	6/17/97	7.1	33	2.3	1.16	44
ER720D	7/28/97	7.3	40	3.6	1.08	28
ER720D	9/9/97	7.4	39	1.6	0.80	21
ER720D	10/21/97	6.9	47	4.8	3.15	42
ER720D	12/2/97	7.4	28	3.8	1.39	26
ER720D	1/27/98	7.3	50	5.2	4.32	10
ER720D	3/10/98	7.3	58	5.7	78.00	34
ER720D	5/4/98	7.2	56	12.2	4.94	27

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720D	6/29/98	7.3	37	3.8	1.06	25
ER720D	8/17/98	7.5	38	3.7	0.81	10
ER720D	9/28/98	7.0	41	4.8	2.09	108
ER720D	11/4/98	7.2	32	1.5	0.90	20
ER720D	12/7/98	7.1	45	7.5	2.59	38
ER720D	1/26/99	6.8	62	18.4	6.40	43
ER720D	3/1/99	7.5	58	7.0	4.12	63
ER720D	4/12/99	7.0	34	7.1	2.84	23
ER720D	5/17/99	6.7	39	6.6	2.92	53
ER720D	6/22/99	7.0	15	0.9	0.46	22
ER720D	8/10/99	7.3	35	2.2	0.03	20
ER720D	9/14/99	7.3	29	1.8	0.31	10
ER720D	10/25/99	7.0	42	4.7	2.88	24
ER720D	12/6/99	7.1	67	8.6	5.40	38
ER720D	1/24/00	7.1	38	4.6	2.92	20
ER720D	2/28/00	7.0	43	2.1	2.80	24
ER720D	3/27/00	6.9	39	2.2	1.90	10
ER720D	5/15/00	7.0	38	0.3	3.20	24
ER720D	6/27/00	7.5	43	5.0	1.66	10
ER720D	8/7/00	7.0	41	1.5	0.83	10
ER720D	11/09/00	7.4	33	2.7	0.64	24
ER720D	12/4/00	7.5	48	3.8	2.31	10
ER720D	1/23/01	7.3	41	3.4	7.40	24
ER720D	5/28/01	7.5	39	2.3	1.11	26
ER720D	9/3/01	7.7	35	2.1	0.54	38
ER720D	1/22/02	7.5	37	2.3	0.99	10
ER720D	6/26/02	7.6	31	2.0	0.66	10
ER720D	8/21/02	7.7	39	0.3	0.67	10
ER720D	9/30/02	7.3	37	5.5	1.30	40
ER720D	4/10/03	7.7	52	3.4	3.30	32
ER720D	5/7/03	7.7	50	1.7	2.40	20
ER720D	5/27/03	7.1	48	7.0	3.10	36
ER720D	6/30/03	7.6	53	7.4	4.20	24
ER720D	7/28/03	7.2	36	2.0	0.77	48
ER720D	9/3/03	7.2	26	1.5	0.34	26
ER720D	10/13/03	7.4	38	4.8	1.50	20
ER720D	11/11/03	7.4	44	6.2	4.70	20
ER720D	1/13/04	7.1	54	9.0	7.00	143
ER720D	2/18/04	6.8	39	0.2	1.60	64
ER720D	4/28/04	7.4	71	5.3	3.10	20
ER720D	5/31/04	8.7	63	8.9	0.59	36
ER720D	7/20/04	7.3	42	5.9	8.20	10
ER720D	8/30/04	7.3	40	2.2	0.84	10
ER720D	10/12/04	7.9	48	5.2	2.10	30
ER720D	11/22/04	7.6	44	1.5	1.40	24
ER720D	3/15/05	7.4	53	1.3	9.50	36
ER720D	5/18/05	7.2	7	0.2	0.18	24
ER720D	7/11/05	6.6	32	0.2	1.10	10
ER720D	9/14/05	7.3	41.3	0.15	2.8	57

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720C	5/15/90	7.3	27	0.5	0.05	20
ER720C	5/22/90	6.9	14	0.2	0.05	29
ER720C	6/26/90	7.5		2.2	0.05	
ER720C	7/3/90	7.5	25	0.5	0.07	20
ER720C	8/7/90	7.5	29	0.5	0.05	27
ER720C	8/14/90	7.5	31	0.4	0.15	21
ER720C	9/19/90	7.4	32	0.5	0.05	15
ER720C	9/25/90	7.3	33		0.10	34
ER720C	11/13/90	7.2	31	1.0	0.60	52
ER720C	11/20/90	7.6	25	1.0	0.50	16
ER720C	1/29/91	6.9	11	0.2	0.05	20
ER720C	2/5/91	7.0	9	0.2	0.05	20
ER720C	3/12/91	6.7	11	0.2	0.05	28
ER720C	3/18/91	7.0	11	0.2	0.05	20
ER720C	4/23/91	7.7	37	0.6	0.03	10
ER720C	4/29/91	6.9	16	6.8	0.03	10
ER720C	6/3/91	6.2	19	0.9	0.03	10
ER720C	7/16/91	6.6	25	0.4	0.03	20
ER720C	7/22/91	7.0	28	0.1	0.03	20
ER720C	8/26/91	7.0	29	0.4	0.03	10
ER720C	9/3/91	7.9	17	0.1	0.03	10
ER720C	10/7/91	7.1	28	0.6	0.03	10
ER720C	10/14/91	6.9	26	0.4	0.03	10
ER720C	11/19/91	6.8	34	0.8	0.03	23
ER720C	11/26/91	7.1	26	2.0	0.03	
ER720C	2/3/92	6.9	10	0.1	0.03	
ER720C	3/4/92	6.3	14	0.1	0.03	20
ER720C	3/30/92	3.6	30	0.1	0.03	10
ER720C	5/4/92	6.2	10	0.3	0.03	
ER720C	6/1/92	6.3	48	0.1	0.03	20
ER720C	6/30/92	6.5	18	0.1	0.03	10
ER720C	7/28/92	6.8	7	0.1	0.03	
ER720C	8/25/92	6.7	17	0.4	0.03	36
ER720C	9/21/92	6.7	19		0.03	36
ER720C	10/20/92	7.0	16		0.03	10
ER720C	11/17/92	6.8	17	0.1		24
ER720C	12/14/92	6.3	12	0.1	0.03	32
ER720C	2/8/93	6.7	11	0.1	0.03	28
ER720C	3/9/93	6.8	33	0.1	0.03	36
ER720C	4/20/93	6.3	9	0.1	0.03	26
ER720C	5/11/93	6.8	35	0.1	0.03	18
ER720C	6/7/93	6.7	23	0.4	0.03	10
ER720C	7/5/93	6.9	29	0.3	0.06	26
ER720C	8/2/93	6.6	15	0.4	0.07	10
ER720C	8/30/93	6.3	25	0.2	1.10	40
ER720C	9/29/93	6.7	32	0.8	0.03	28
ER720C	10/25/93	6.6	17	0.4	0.03	10
ER720C	11/22/93	6.6	20	0.2	0.03	10
ER720C	12/20/93	7.0	17	0.2	0.05	10
ER720C	1/24/94	7.2	10	0.2	0.03	10
ER720C	2/21/94	7.1	11	0.2	0.03	28

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720C	3/21/94	6.9	10	0.2	0.03	25
ER720C	4/25/94	7.4	13	0.2	0.03	26
ER720C	5/24/94	7.3	12	0.2	0.03	27
ER720C	6/21/94	7.2	17	0.7	0.09	20
ER720C	7/18/94	7.2	11	0.2	0.03	10
ER720C	8/15/94	7.5	25	0.2	0.03	39
ER720C	9/13/94	7.6	26	0.2	0.03	10
ER720C	10/11/94	7.5	23	0.2	0.03	27
ER720C	11/7/94	7.5	20	0.2	0.03	20
ER720C	11/28/94	7.3	13			20
ER720C	12/5/94	7.6	26	0.2	0.03	10
ER720C	1/17/95	7.3	11	0.3	0.03	10
ER720C	2/14/95	7.2	15	0.2	0.03	30
ER720C	3/14/95	6.9	11	0.2	0.03	25
ER720C	4/11/95	7.2	17	0.2	0.03	10
ER720C	5/9/95	7.3	17	0.2	0.03	10
ER720C	6/6/95	7.5	16	0.2	0.03	10
ER720C	7/4/95	7.6	22	0.2	0.03	10
ER720C	8/1/95	6.9	7	0.2	0.03	10
ER720C	8/29/95	7.6	30	0.7	0.03	26
ER720C	9/26/95	7.6	22	0.5	0.03	10
ER720C	10/24/95	6.9	22	0.2	0.03	24
ER720C	11/21/95	7.4	18	0.4	0.06	20
ER720C	12/18/95	6.7	16	0.4	0.09	82
ER720C	1/23/96	6.6	17	0.2	0.03	54
ER720C	2/20/96	7.4	24	0.2	0.03	21
ER720C	3/18/96	7.6	22	0.2	0.03	10
ER720C	4/16/96	7.1	15	0.2	0.03	24
ER720C	5/14/96	7.1	23	0.2	0.03	10
ER720C	6/18/96	6.8	12	0.5	0.03	22
ER720C	7/16/96	7.4	31	0.6	0.03	10
ER720C	8/13/96	7.1	22	0.3	0.06	57
ER720C	9/10/96	7.6	30	0.7	0.09	23
ER720C	10/8/96	7.6	30	0.6	0.03	10
ER720C	11/5/96	6.9	33	2.9	0.81	28
ER720C	2/11/97	7.2	21	0.2	0.03	10
ER720C	3/25/97	7.1	13	0.2	0.03	10
ER720C	5/6/97	7.3	19	0.2	0.03	50
ER720C	6/17/97	6.9	25	0.2	0.03	26
ER720C	7/28/97	7.4	33	2.1	0.10	10
ER720C	9/9/97	7.6	32	0.5	0.03	10
ER720C	10/21/97	7.2	28	0.2	0.03	10
ER720C	1/27/98	7.2	17	0.2	0.03	10
ER720C	3/10/98	6.8	21	0.2	0.03	48
ER720C	5/4/98	7.1	12	0.2	0.03	10
ER720C	3/1/99	7.4	24	0.2	0.03	10
ER720C	4/12/99	6.9	12	0.2	0.03	10
ER720C	8/10/99	6.5	25	0.2	0.03	58
ER720C	10/25/99	7.1	26	0.2	0.03	10
ER720C	12/6/99	7.4	60	0.8	0.11	26
ER720C	1/24/00	7.1	20	1.0	0.06	10

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720C	2/28/00	6.7	35	0.2	2.90	61
ER720C	3/27/00	6.8	17	0.2	0.06	22
ER720C	5/15/00	6.6	22	0.2	0.03	46
ER720C	9/11/00	7.4	25	0.7	0.03	22
ER720C	8/21/02	7.8	33	0.4	0.03	44
ER720C	9/30/02	7.2	30	0.2	0.03	28
ER720C	1/13/03	7.2	24	0.4	0.03	59
ER720C	4/10/03	7.0	36	0.2	0.05	56
ER720C	5/7/03	7.4	32	0.2	0.03	28
ER720C	5/27/03	7.2	34	0.2	0.03	20
ER720C	6/30/03	7.1	37	0.2	0.03	20
ER720C	7/28/03	7.0	22	1.0	0.03	32
ER720C	9/3/03	7.2	20	0.5	0.03	114
ER720C	10/13/03	6.9	29	0.2	0.03	32
ER720C	11/11/03	7.0	25.0	0.2	0.07	10
ER720C	1/13/04	6.7	25	0.2	1.20	63
ER720C	2/18/04	6.6	16	0.2	0.03	64
ER720C	4/28/04	7.6	51	1.7	6.60	45
ER720C	5/31/04	8.5	36	0.2	0.07	32
ER720C	7/20/04	7.2	28	0.2	0.03	56
ER720C	8/30/04	7.1	30	0.2	0.03	20
ER720C	10/12/04	7.8	35	0.5	0.03	30
ER720C	11/22/04	7.0	34	0.2	0.03	10
ER720C	3/15/05	7.3	20	0.2	0.13	36
ER720C	5/18/05	7.1	5	0.2	0.03	10
ER720C	7/11/05	6.8	19	0.2	0.13	10
ER720C	9/14/05	7.2	7.33	0.15	0.06	10

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720B	2/2/94	6.7	7.2	0.2	0.33	26
ER720B	2/21/94	7.0	7.3		0.03	10
ER720B	3/21/94	6.6	7.7			10
ER720B	6/7/94	6.6	6.9			21
ER720B	7/4/94	6.7	7.7			10
ER720B	8/2/94	6.9	8.2			10
ER720B	9/26/94	7.0	8.9			10
ER720B	11/28/94	5.9	3.5			10
ER720B	2/14/95	6.9	7.7	0.2	0.03	10
ER720B	3/14/95	7.0	7.7	0.2	0.03	10
ER720B	4/11/95	6.9	8.2	0.2	0.03	10
ER720B	5/9/95	7.0	9.0	0.2	0.03	10
ER720B	6/6/95	7.1	7.9	0.2	0.03	10
ER720B	7/4/95	7.0	8.3	0.2	0.03	10
ER720B	8/1/95	6.5	3.9	0.2	0.03	10
ER720B	8/29/95	7.0	7.6	0.2	0.03	10
ER720B	9/26/95	7.1	9.7	0.2	0.03	10
ER720B	10/24/95	7.1	8.0	0.2	0.03	10
ER720B	11/21/95	7.1	8.7	0.2	0.06	10
ER720B	12/18/95	6.7	8.6	0.2	0.05	27
ER720B	1/23/96	6.8	9.0	0.2	0.03	10

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
ER720B	2/20/96	7.0	8.6	0.2	0.03	10
ER720B	3/18/96	6.9	8.6	0.2	0.03	10
ER720B	4/16/96	6.8	8.0	0.2	0.03	10
ER720B	5/14/96	6.9	8.5	0.2	0.03	10
ER720B	6/18/96	6.4	5.9	0.2	0.03	10
ER720B	7/16/96	6.9	8.3	0.2	0.03	10
ER720B	8/13/96	6.6	5.9	0.2	0.03	29
ER720B	9/10/96	6.7	6.0	0.2	0.03	10
ER720B	10/8/96	6.9	7.6	0.2	0.03	10
ER720B	11/5/96	6.7	7.5	0.3	0.03	10
ER720B	12/17/96	6.8	8.6	0.3	0.03	10
ER720B	2/11/97	7.0	7.7	0.2	0.03	10
ER720B	3/25/97	6.9	8.0	0.2	0.03	10
ER720B	5/6/97	6.6	7.8	0.2	0.03	10
ER720B	6/17/97	6.8	7.6	0.2	0.03	10
ER720B	7/28/97	6.8	8.1	0.2	0.03	10
ER720B	9/9/97	6.8	7.1	0.2	0.03	10
ER720B	10/21/97	7.0	8.8	0.7	0.03	10
ER720B	12/2/97	6.9	8.3	0.4	0.03	10
ER720B	1/27/98	6.8	8.2	0.2	0.03	10
ER720B	3/10/98	7.0	9.2	0.2	0.03	10
ER720B	5/4/98	6.8	8.4	0.2	0.03	10
ER720B	6/26/98	6.8	8.2	0.2	0.03	10
ER720B	1/26/99	6.8	8.8	0.2	0.03	10
ER720B	3/1/99	6.9	8.7	0.2	0.03	10
ER720B	04/12/99	6.8	9.2	0.2	0.03	10
ER720B	5/17/99	6.9	10.1	0.2	0.03	10
ER720B	6/22/99	6.2	5.0	0.3	0.03	10
ER720B	8/10/99	6.7	7.9	0.4	0.03	10
ER720B	9/14/99	6.5	5.8	0.2	0.03	10
ER720B	10/25/99	6.9	8.8	0.2	0.03	10
ER720B	12/6/99	7.1	8.6	0.2	0.03	10
ER720B	1/24/00	6.7	8.0	0.2	0.03	10
ER720B	2/28/00	6.8	8.2	0.2	0.03	10
ER720B	3/27/00	6.7	8.3	0.2	0.03	10
ER720B	5/15/00	6.9	8.1	0.2	0.03	10
ER720B	6/27/00	6.9	8.8	0.2	0.03	10
ER720B	8/7/00	6.7	9.4	0.2	0.03	10
ER720B	9/11/00	6.6	7.2	0.2	0.03	10
ER720B	12/4/00	7.1	8.7	0.2	0.03	10
ER720B	1/23/01	6.7	7.6	0.4	0.03	10
ER720B	3/6/01	6.2	7.9	0.2	0.03	10
ER720B	5/28/01	6.5	9.8	0.2	0.06	10
ER720B	9/3/01	6.9	9.1	0.2	0.03	10
ER720B	1/22/02	6.8	12.6	0.2	0.06	10
ER720B	6/26/02	6.7	8.7	0.3	0.06	10
ER720B	8/21/02	7.8	8.7	0.3	0.03	10
ER720B	9/30/02	7.0	10.1	0.2	0.03	32
ER720B	1/13/03	6.7	6.5	0.2	0.03	55
ER720B	2/25/03	7.0	6.5	0.2	0.13	28
ER720B	4/10/03	7.0	10.7	0.2	0.10	40

ER720B	5/7/03	7.2	10.6	0.2	0.09	10
ER720B	5/27/03	7.0	9.2	0.2	0.14	10
ER720B	6/30/03	7.3	10.4	0.2	0.19	24
ER720B	7/28/03	7.7	7.8	0.2	0.03	10
ER720B	9/3/03	7.4	6.0	0.4	0.05	10
ER720B	10/13/03	7.1	9.8	0.2	0.14	80
ER720B	11/11/03	7.4	9.0	0.2	1.10	28
ER720B	1/13/04	7.3	7.8	0.2	0.55	24
ER720B	2/18/04	7.1	7.4	0.2	0.20	36
ER720B	4/28/04	7.1	30.9	0.2	0.08	24
ER720B	5/31/04	8.5	10.5	0.2	0.18	36
ER720B	7/20/04	7.7	9.3	0.2	0.10	10
ER720B	8/30/04	7.3	8.6	0.2	0.03	10
ER720B	10/12/04	7.9	8.4	0.9	0.03	10
ER720B	11/22/04	7.0	8.8	0.2	0.03	10
ER720B	3/15/05	7.7	7.8	0.8	0.26	40
ER720B	5/18/05	7.2	3.0	0.2	0.03	10
ER720B	7/11/05	6.9	7.6	0.2	0.03	10
ER720B	9/14/05	7.2	8.53	0.15	0.025	10

Station	**Date**	**pH**	**Electrical conductivity**	**Nitrate + Nitrite**	**Phosphate**	**COD**
ER720A1	2/14/95	6.9	7	0.2	0.03	10
ER720A1	3/14/95	7.0	7	0.2	0.03	10
ER720A1	4/11/95	6.8	8	0.2	0.03	10
ER720A1	5/9/95	6.7	7	0.2	0.03	10
ER720A1	6/6/95	6.7	5	0.2	0.03	10
ER720A1	7/4/95	6.8	6	0.2	0.03	10
ER720A1	8/1/95	6.4	3	0.2	0.03	10
ER720A1	8/29/95	6.6	6	0.2	0.03	10
ER720A1	9/26/95	7.0	6	0.2	0.03	10
ER720A1	10/24/95	6.9	6	0.2	0.03	10
ER720A1	11/21/95	6.9	6	0.2	0.03	10
ER720A1	12/18/95	6.9	7	5.3	0.07	74
ER720A1	1/23/96	6.9	7	0.2	0.03	22
ER720A1	2/20/96	6.9	7	0.2	0.03	67
ER720A1	3/18/96	6.8	8	0.2	0.03	10
ER720A1	4/16/96	6.7	7	0.2	0.03	32
ER720A1	5/14/96	6.9	8	0.2	0.03	10
ER720A1	6/18/96	5.5	4	0.2	0.03	10
ER720A1	7/16/96	6.5	6	0.2	0.03	10
ER720A1	8/13/96	6.0	4	0.2	0.03	10
ER720A1	9/10/96	6.6	6	0.2	0.03	23
ER720A1	10/8/96	6.8	5	0.2	0.03	10
ER720A1	11/5/96	6.6	6	0.2	0.03	26
ER720A1	12/17/96	7.0	7	0.2	0.03	10
ER720A1	2/11/97	6.8	7	0.2	0.03	48
ER720A1	3/25/97	6.7	7	0.3	0.03	10
ER720A1	5/6/97	6.8	7	0.2	0.03	10
ER720A1	6/17/97	6.4	5	0.2	0.03	10
ER720A1	7/28/97	6.6	6	0.2	0.03	10
ER720A1	9/9/97	6.7	6	0.2	0.03	10
ER720A1	10/21/97	6.8	7	0.2	0.03	10
ER720A1	12/2/97	6.7	6	0.2	0.03	10

ER720A1	1/27/98	6.7	7	0.2	0.03	10
ER720A1	3/10/98	6.9	8	0.2	0.03	20
ER720A1	5/4/98	6.8	7	0.2	0.03	10
ER720A1	6/29/98	6.7	6	0.2	0.03	10
ER720A1	1/26/99	6.8	8	0.2	0.03	10
ER720A1	3/1/99	6.7	8	0.2	0.03	10
ER720A1	4/12/99	6.7	9	0.2	0.03	10
ER720A1	5/17/99	7.0	8	0.2	0.03	10
ER720A1	6/22/99	6.0	4	0.2	0.03	24
Station	**Date**	**pH**	**Electrical conductivity**	**Nitrate + Nitrite**	**Phosphate**	**COD**
ER720A1	8/10/99	6.6	6	0.2	0.03	10
ER720A1	9/14/99	6.3	4	0.2	0.03	10
ER720A1	10/25/99	6.6	6	0.2	0.03	10
ER720A1	12/6/99	6.8	7	20.3	0.03	10
ER720A1	1/24/00	6.7	7	0.2	0.03	10
ER720A1	2/28/00	6.8	8	2.2	0.03	22
ER720A1	3/27/00	6.7	8	0.2	0.09	10
ER720A1	9/30/02	7.8	68	2.2	1.1	47
ER720A1	9/3/03	7.3	58	10.8	2.4	54
ER720A1	4/28/04	7.3	9	0.2	0.1	28
ER720A1	11/22/04	7.4	6.65	0.15	0.025	10
ER720A1	3/16/05	7.7	7			36
ER720A1	5/18/05	7.3	2.91	0.15	0.1	10
ER720A1	7/11/05	7.3	51.2	0.15	0.08	10
ER720A1	9/14/05	7.3	5.37	0.15	0.08	10

PR720B	2/2/94	7.3	64	0.2	0.19	85
PR720B	2/21/94	7.2	77		0.45	125
PR720B	3/21/94	7.2	82			101
PR720B	6/7/94	7.2	90			68
PR720B	7/4/94	7.3	59			29
PR720B	8/2/94	7.5	56			48
PR720B	9/26/94	7.6	66			40
PR720B	11/28/94	7.2	59			42
PR720B	2/14/95	7.6	76	0.2	0.55	120
PR720B	3/14/95	7.3	92	0.2	0.56	77
PR720B	4/11/95	7.2	80	0.2	1.70	86
PR720B	5/8/95	7.3	72	0.2	0.12	39
PR720B	6/6/95	7.5	64	0.2	0.03	57
PR720B	7/4/95	7.6	113	0.2	0.03	34
PR720B	8/1/95	7.5	70	2.6	0.10	29
PR720B	8/29/95	7.4	60	1.7	0.06	26
PR720B	9/26/95	7.6	85	0.8	0.03	39
PR720B	10/24/95	7.3	59	0.9	0.10	40
PR720B	11/20/95	7.4	84	0.2	0.08	30
PR720B	12/18/95	6.9	39	0.6	0.54	133
PR720B	1/23/96	7.2	84	0.2	0.68	61
PR720B	2/20/96	7.3	79	0.2	0.33	55
PR720B	3/18/96	7.5	77	0.2	0.11	32
PR720B	4/16/96	7.3	52	0.2	0.06	38

Station	Date	pH	Electrical conductivity	Nitrate + Nitrite	Phosphate	COD
PR720B	6/18/96	7.2	56	3.5	0.23	48
PR720B	7/16/96	7.5	72	1.7	0.12	48
PR720B	8/13/96	7.2	42	0.8	0.18	87
PR720B	9/10/96	7.5	56	1.3	0.18	61
PR720B	10/8/96	7.4	55	1.2	0.10	38
PR720B	11/5/96	7.3	63	0.8	0.09	30
PR720B	12/17/96	7.0	51	0.4	0.24	124
PR720B	2/11/97	7.3	85	0.2	0.14	46
PR720B	3/25/97	7.2	90	0.2	0.20	51
PR720B	5/6/97	7.7	65	0.2	0.22	30
PR720B	6/17/97	7.3	63	1.3	0.10	88
PR720B	7/28/97	7.4	67	0.6	0.03	32
PR720B	9/9/97	7.7	65	0.7	0.03	39
PR720B	10/21/97	7.2	88	0.2	0.07	36
PR720B	12/2/97	7.5	94	0.2	0.03	50
PR720B	1/27/98	7.3	88	0.2	0.21	22
PR720B	3/10/98	7.2	70	0.2	0.21	56
PR720B	5/4/98	7.3	73	0.2	0.25	39
PR720B	6/29/98	7.1	110	0.4	0.03	47
PR720B	1/26/99	7.2	84	0.2	0.60	41
PR720B	3/1/99	7.1	105	0.2	1.40	62
PR720B	4/12/99	7.0	90	0.2	2.68	62
PR720B	5/17/99	7.1	73	0.2	0.47	33
PR720B	6/22/99	7.2	72	0.8	0.11	40
PR720B	8/10/99	7.3	75	1.5	0.18	36
PR720B	9/14/99	7.4	68	1.9	0.20	42
PR720B	10/25/99	7.2	73	0.4	0.03	22
PR720B	12/6/99	7.5	125	0.2	0.32	52
PR720B	1/24/00	7.3	90	0.2	1.47	62
PR720B	2/28/00	7.1	84	0.2	0.38	126
PR720B	3/27/00	7.0	93	0.2	2.20	373
PR720B	5/15/00	7.2	68	0.2	0.33	32
PR720B	6/26/00	7.3	91	0.2	0.09	44
PR720B	8/8/00	7.3	100	0.7	0.08	45
PR720B	9/11/00	7.3	80	1.5	0.14	44
PR720B	10/23/00	6.9	80	0.2	0.35	26
PR720B	12/4/00	7.4	91	0.2	1.04	60
PR720B	1/23/01	7.2	88	0.2	1.63	97
PR720B	3/6/01	7.9	87	0.2	3.48	76
PR720B	4/23/01	6.8	53	0.2	0.16	61
PR720B	5/28/01	7.2	92	3.3	0.10	54
PR720B	7/24/01	8.2	54	2.8	0.05	10
PR720B	9/3/01	7.7	52	1.2	0.21	30
PR720B	10/15/01	7.6	62	0.6	0.12	28
PR720B	12/13/01	7.5	79	0.2	0.12	28
PR720B	1/22/02	7.3	60	0.6	0.06	22
PR720B	3/11/02	7.4	79	0.3	0.34	28
PR720B	5/6/02	7.4	41	1.0	0.36	52
PR720B	6/24/02	7.5	84	1.0	0.18	47
PR720B	8/21/02	8.2	62	3.8	0.09	24
PR720B	10/14/02	7.5	69	0.2	0.12	36
PR720B	2/25/03	7.4	81	0.2	0.84	56

PR720B	4/10/03	7.5	114	0.2	1.40	169
PR720B	5/7/03	7.6	78	0.2	1.10	105
PR720B	5/27/03	7.9	87	0.2	0.28	56
PR720B	6/30/03	7.2	48	0.2	1.20	149
PR720B	7/28/03	7.2	35	0.2	0.18	72
PR720B	9/3/03	7.3	69	1.8	0.18	177
PR720B	10/13/03	7.2	35	1.3	0.10	84
PR720B	11/11/03	7.3	59	0.2	0.27	64
PR720B	1/13/04	7.3	84	0.2	2.50	40
PR720B	2/18/04	7.2	81	0.2	0.85	36
PR720B	4/28/04	7.5	62	0.2	0.18	45
PR720B	5/31/04	8.6	71	0.2	0.19	10
PR720B	7/20/04	7.5	77	0.2	0.14	10
PR720B	8/30/04	7.3	98	0.2	0.88	48
PR720B	10/12/04	7.8	14	1.9	0.12	26
PR720B	11/22/04	7.8	79	0.2	0.19	10
PR720B	3/15/05	7.6	76	0.2	3.40	36
PR720B	5/18/05	7.5	32	1.6	0.38	10
PR720B	7/11/05	7.6	69	0.2	0.27	10
PR720B	9/14/05	7.6	71.1	0.7	0.17	10