

Analysis of Temporal and Spatial changes in major dissolved salts in the Vaal River system over a 40 year period

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Preface

The research contained in this thesis was completed by the candidate while based at the Centre for Environmental Studies at the University of Pretoria, South Africa.

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

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DECLARATION OF AUTHORSHIP

I, Samson Oghenemauro Akpotu declare that the thesis which I hereby submit for the degree Master of Science in Water Resource Management at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.



Signature:

Date: 20 October 2021

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List of Abbreviations

° C – Degrees Celsius

Ca – Calcium

CO₃ – Carbonate

DWAF – Department of Water Affairs and Forestry

DWS – Department of Water and Sanitation

EC – Electrical Conductivity

HCO₃ – Hydro carbonate

K – Potassium

Mg – Magnesium

Na – Sodium

NCMP – National Chemical Monitoring Programme

SO₄ – Sulfate

TAL – Total Alkalinity

TDS – Total Dissolved Salts

TSS – Total Suspended Solids

WWTW – Wastewater Treatment Works

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Abstract

In this study, the fluctuation and variation in salinity composition of the Vaal River and its catchment area was investigated between 1975-2015. Long-term data sets gathered from a 40-year span collected across nine monitoring station in the study catchment area was analysed. The statistical tool applied for the data analysis is the Maucha diagram, as well as the Origin software used in plotting graphs. These graphs revealed several trends and patterns. The graphs and the Maucha diagrams reflected long-time changes in salts composition and concentration in the water of the Vaal River and its catchment area over a 40-year period. From the data analysed, the graphs plotted, and the Maucha diagrams, the salinity of the Vaal River was majorly total alkalinity (TAL) and sulfate (SO₄) dominated, with a substantial amount of Calcium (Ca²⁺). However, the concentration of other salts remained relatively constant during the duration of study. Analysis of 5-year averages of TAL, SO₄ and total dissolved solids (TDS) concentration showed that zones and sub-catchment uniquely impacted variation in salinity levels and composition. Furthermore, salinity levels and composition in zones 1 and 4 were greatly impacted by water from the Lesotho Highlands and the Orange River, respectively. The salinity level changes of the Vaal River were mainly attributed to anthropogenic sources such as pollution from (mining) industries, increased urbanisation, economic expansion, paving of roads, increasing population, water transfer in and out of the river's catchment area and irrigation outflow from agricultural activities. Based on the salinity concentration of the Vaal River and the effect on humans and the environment, routine continuous monitoring and sampling programmes are recommended to be carried out by the National government. This will help to make informed decision on managing the salinity levels of the Vaal River and mitigating any negative attendant consequence of increased salinity.

Chapter 1: Introduction

1.1 Background Information

Water bodies historically, especially rivers have been degraded globally over time. Rivers, typical serves as sinks for domestic, agricultural, and industrial wastes (Akpotu and Moodley, 2018b). As a result, over the last few decades, the term “healthy rivers” have gained prominence particularly in industrial areas (Cole and Weihe, 2015). Due to the limited supply of fresh water globally, water resources are unfortunately over recycled and reused. In South Africa, water resources management is of critical concern as South Africa is as a “water stressed” country. This situation is further aggravated by its geographical location in a semi-arid region of the world. A study by Nicholson, Funk et al. (2018) placed the average annual rainfall in South Africa as 455.96 mm, when compared to tropical regions Ghana and Nigeria with annual averages of 1169 and 1197 mm, respectively, it is rather low. South Africa’s water resources are extremely limited and falls below the global average of approximately 860 nm. Thus, the scarcity of water resources has led to intensive use of water and water recycling, a situation that if left unchecked amongst other factors may result in the progressive salinisation of many South Africa rivers (Le Maitre, Colvin et al. 2009). Other factors such as the discharge of poorly managed/treated municipal waste and industrial effluents, mine water discharges, agricultural and municipal run-offs, high evaporation rates, high erosion and siltation rates are also top contributors to salinization (Rahman, Penny et al. 2019). The surface water yield in South Africa is approximately $52\ 000 \times 10^6\ \text{m}^3\ \text{yr}^{-1}$ with a water demand of $29\ 000 \times 10^6\ \text{m}^3\ \text{yr}^{-1}$, which exceeds water yields (Bosch, Schulze et al.). Hence, the need for a comprehensive long-term plan for monitoring river salinity should be instituted. The importance of long-term monitoring of river salinity was emphasized in an article published Van Niekerk et al. (2009). In this article, the authors collected, analysed and modeled data for several years which were applied indetermning long-term changes in salinity taking place in South African rivers. Additionally, the information gathered from the research was crucial in making informed policy decision on water resources management by the government towards the preservation of the ecosystem. The detection/monitoring of changes in salinity levels of rivers is crucial because it adversely affects flora and fauna, resulting in loss of biodiversity, and a subsequent decline in ecosystem goods and services. Additionally, salt enrichment reduces the water’s fitness for various non-ecological water uses.

The salinity levels of South Africa rivers over the past 7 decades have been monitored by the Department of Water and Sanitation (DWS), previously referred to the Department of Water Affairs (DWA) through the National Chemical Monitoring Programme (NCMP). The robust scientific data generated is critical in decision making for effective water resources strategies and management. The data generated through such monitoring programmes, can be used to assess the river quality, quantity, health, establish appropraite rehabilitation strategies, and evaluate atmospheric factors influencing water resources(Cilliers and Adams, 2016). There are several routes through which a river is progressively

salinised, and these includes input from sewages, atmospheric pollution, acid mine drainage, industrial effluents, and dry-land farming through stripping of vegetative cover and irrigation. However, the latter 2 factors are major contributors to increased river salinization (Braune and Roger 1987).

The Vaal river is very important because this is the most hard-working river in South Africa. It is located in a highly industrialised and very populated area of the country and receives a high amount of industrial waste respectively. Like any other river in South Africa, the Vaal River has witnessed a consistent decline in water quality over time, which can be attributed to eutrophication and salinisation. This is evidenced by the presence of excessive phytoplankton and macrophytes such as water hyacinth in vast section of the river mostly during spring and winter seasons (Roos and Pieterse, 1995 (Jordaan and Bezuidenhout 2013)). The Upper Vaal Catchment Rivers are mostly characterised by fairly low dissolved solids, as well as bicarbonates (Van Vliet and Nell, 1986). However, the water quality deteriorate rapidly downstream as salts and solids are added from agriculture, human and industrial effluents. The middle Vaal River (Vaal to Bloemhof Dam and its tributaries (West Rand and South Witwatersrand) are characterised by high dissolved solids from mostly non-point sources (Roos and Pieterse, 1995) (Tempelhoff 2009). High salinity and deteriorating water quality could affect downstream use such as potable water supply, industrial and irrigation application. Du Preez et al. (2000) investigated the water quality of the Lower Vaal River and its tributaries. The result confirmed a steady decline in water quality over the past 2 decades and further deterioration was expected in the near future. The poor water quality of the lower Vaal River was anticipated because it receives most of the wastewater from Gauteng province, South Africa's most populous and industrialised province. The lower Vaal River is also a source of water for a vast percentage of South Africa's irrigation land (Le Roux et al., 2007). The salinisation of the Vaal River has tremendous environmental and economic implication for South Africa, hence, salinity concentration should be continuously monitored.

Therefore, this research seeks to expand on the research carried out by Van Niekerk et al. (2009), that mainly focused on electrical conductivity (EC) changes in the Vaal River and its tributaries. The changes in salinity levels and composition over a 40-year period of the Upper Vaal, Middle Vaal, and Lower Vaal River will be determined. The start point for the sample collection and analysis will be the Lower Vaal (Orange River, Douglas, Riet), followed by the Middle Vaal (Vaal Dam to Bloemhof Dam), and finally the Upper Vaal (Vaal region to Barrage).

1.2 Aim of the Research

The research is aimed at studying the spatial and temporal changes in salinity and salt composition of the Vaal River system over a 40-year period (1975-2015). Outcomes can in future be used to determine possible sources of specific salts contributing to the salt loads in the Vaal River system.

1.3 Specific Objectives

- To determine the variation in salinity composition over an extensive time frame placing

emphasis on the major salts found in the Vaal River and over a 40-year period (1975-2015).

- To ascertain, determine and explain likely factors in and around the Vaal River Catchment (Vaal Dam, Wilge River, Douglas Barrage) that may affect and contribute in no small measure to variation in salinity composition which spans a period of 40 years (1975-2015).

1.4 Research Scope

The scope of this research will be limited to the salinity composition and salinity properties of the Vaal River water quality as one of the major contributing factors affecting water quality. There are numerous studies in literature on the Vaal River and its tributaries with focus on other factors contributing to the deteriorating water quality. Hence, it will not be included in this study. The essence of the study is the temporal and spatial changes in salinity composition of the Vaal River and its tributaries.

1.5 Expected Outcomes

The findings from this research based on long-term salinity and chemical composition changes in the Vaal River will aid stakeholders such as academia, government, and citizens to understand the impact and potential sources of salinisation on water quality and determine the extent of the Vaal River pollution. This will also aid in policy formulation and strategy towards the efficient utilisation and management of the Vaal River water resources. Furthermore, the information generated will aid in future modelling/prediction of the pollution load of the Vaal River.

Chapter 2: Literature Review

2.1. Introduction

In this chapter, several physical and chemical parameters resulting from human and anthropogenic activities that impacts aquatic life and water quality will be reviewed. Furthermore, an *exposé* will be carried out to determine the various sources of pollution (of the Vaal River) and its impact on aqueous environment.

2.2. Salinisation Overview

The issue of salinisation is not limited to South Africa alone. Globally, it is estimated that approximately 7% of the earth has significant high salt content which arises from both natural and anthropogenic sources (Rose and Rose, 2004). These parts of the earth have restricted application. Rivers with high salinity levels have reduced overall application, and associated problems includes reduction in farmland fertility which affects crop production; water quality degradation issues which makes the water unsuitable for recreational, domestic, agricultural, and industrial use (Van Rensburg et al., 2011). This causes water supply issues and substantial financial losses. An understanding of the effect and causes of salinisation is crucial in crafting effective management strategies. Over the past 5 decades, South African rivers have been known to have significant levels of salinity which affects water quality (Le Roux et al., 2007). High level of salinity in rivers can be attributed to anthropogenic activities or natural geologic effects (Du Preez et al., 2000).

Salinisation as a process occurs over a period of time, and it is defined as an increase in the concentration of dissolved inorganic salts and general chemical components (such as Total Dissolved Solids [TDS]) in an aqueous environment relative to its original baseline values (Mirzavand et al., 2020; Smedema, 2004). Salinity can be influenced by either natural or anthropogenic factors.

Salinity levels in water can be classified in different ways based on parameters such as source of salt and value limits used (Freeze and Cherry, 1979; Le Roux et al., 2007). However, two of the most used parameters are Electrical Conductivity (EC) and Total Dissolved Solids (TDS). The parameters EC and TDS can be converted to each other and vice-versa with equation 2.1.

$$TDS \left(\frac{mg}{l} \right) = EC \left(\frac{mS}{m} @ 25^{\circ}C \right) \times 6.5 \quad (2.1)$$

EC metres makes an assumption that the standard instrument setting is correct and may be unaware that an indirect measurement may be taking place. To effect this correction, the value 6.5 in equation 2.1 is a general value used and typically vary from 5 – 7 in South Africa depending on the model and manufacturer of the meter (Van Niekerk et al., 2014).

In South Africa, very low natural levels of TDS have been recorded in Waterkloof and Swartboskloof of 10 – 27 mg/L and 17 – 37 mg/L, respectively (Van Rensburg et al., 2011). Contrastingly, extremely high TDS values have been reported in the Sak River of approximately 84000 mg/L (Dallas and Day,

2004). On the average, most South African rivers have TDS values that exceeds 1000 mg/L, and this may be attributed to both anthropogenic and natural factor (Dallas and Day, 2004).

However, in the Lower Vaal River and its tributaries, the high salinity values recorded were attributed to high soil salinity resulting from extensive irrigation (Le Roux et al., 2007). The salinity level of the Vaal River has steadily been on the rise over time. In 1998, (Davies and Day, 1998) reported an annual increase in TDS concentration of the Vaal River by 2.5 mg/L and the increase was attributed to highly saline mine effluent deposits. Salinity may be regarded as toxic at high concentrations (Sampaio et al., 2002). Increasing salinity of South African Rivers should be an issue of national concern.

2.2.1 Salinity Types

Salinisation of water resources are majorly from 2 sources (i) natural phenomenon otherwise referred to as primary salinity and (ii) anthropogenic/man-made causes otherwise known as secondary salinity (Mirzavand et al., 2020).

2.2.1.1 Primary Salinity

Primary salinity in water is a naturally occurring phenomenon. It results from the release of salts through deposition by climatic factors such as the aeolian/rainfall deposit or by the weathering of naturally occurring saline rocks (Nell and Van Huyssteen, 2014). This type of salinity occurs in environments with inadequate rainfall and high rates of evapotranspiration (Krishan, 2019; Le Roux et al., 2007). A combination of high rate of evapotranspiration and inadequate rainfall results in a subsequent decrease in water volume and an increase in the concentration of river salts. The effects of primary salinisation are visible in semi-arid or arid region due to high evapotranspiration rate and low rainfall. Some part of the Vaal River is located in Gauteng (a semi-arid climatic region) with very low annual rainfall of a few centimetres (Le Roux et al., 2007) which can be a hotbed for salinization due to its high industrial activity and population.

2.2.1.2 Secondary Salinity

Secondary salinity of rivers occurs from anthropogenic activities resulting in direct addition of saline water through industrial effluent or agricultural activities *via* saline water irrigation (Egamberdieva et al., 2010). Secondary salinity is localised, and it includes the following:

- (a) Dryland/non-irrigated salinity frequently occurs due to change in land use (vegetation or livestock farming) and management which results in an imbalance in water and salt levels of the landscape (Jolly et al., 2008). This results in immobilisation of the stored salts due to decrease in water usage and evapotranspiration. Also, the exposure of natural saline soil may result in dryland salinity which reduces the water infiltration capacity of soils (Kreitler, 1993).
- (b) Industrial salinity results from industrial activities mainly mining. High concentration of salts are present in industrial effluents from mining. Improper disposal of mining effluent may result

in increased river salinity. Most South Africa rivers have high salinity levels due to mining as well as abandoned mines from the pre-regulation era (Hohne and Hansen, 2008).

- (c) Irrigation salinity is the most common type of secondary salination (Malash et al., 2008). Water from irrigation can infiltrate through non-saturated zones contaminating ground aquifer and can also flow into rivers. This ultimately results in increased salt levels of the ground water and shallow river water through high rate of evapotranspiration (Van Weert et al., 2009).
- (d) Urban salinity results from development activities in urban areas (Wilson, 2003). Human sewage contains high levels of salts which contributes immensely to the salinity level of the river it is discharged in. Other likely sources of salts are from building materials, leaking pipes and watering of parks (Pluske et al., 2004). The water used for these activities enters the sewer and ultimately end up in rivers, thereby increasing salt concentration.

2.3 Effect of Physico-Chemical Parameters on Water Quality

The determination of water quality can be assessed holistically by considering the amount of physical, biological, and chemical parameters present in the water (Pluske et al., 2004). Water quality assessment and monitoring is of utmost importance because it determines the suitability of water for different application, helps to track the source of pollutants (natural or anthropogenic) and assists in formulating remediation strategy (Akpotu and Moodley, 2018a). Physico-chemical parameters includes, electrical conductivity (EC), TDS, cations, anions, and salinity.

2.3.1 Electrical Conductivity (EC), Total Dissolved Salts (TDS), Ionic Salts/Salinity

The total concentration of dissolved materials in water can be expressed/measured as TDS, salinity, and conductivity (Zinabu et al., 2002). Conductivity defines the capacity of water to conduct electrical charge. TDS (mg/L) concentration of water, is expressed as the value of dissolved substances in water capable of conducting electrical charge (Williams and Sherwood, 1994). The definition makes a presumption that all the dissolved solids in water are capable of carrying electrical charges (Freeze and Cherry, 1979). Several authors have established a correlation between conductivity and TDS and these terms are often used interchangeably (Van Niekerk et al., 2014). A measurement of EC gives an accurate estimate of TDS. A conversion of EC to TDS was carried out by (Walton, 1989). An increase in electrical conductivity of water is directly proportional to an increase in ion concentration (Rebello et al., 2020). The conversion of TDS to EC is because EC values are easy to obtain. Often EC is preferred because it easier to obtain EC values as compared to TDS. The conductivity value and TDS of a pristine river is dependent mainly on geological influence, water flow patterns and decomposed plant materials (Kreitler, 1993). Other sources of TDS in water include industrial effluents and agricultural run-off (Hohne and Hansen, 2008). The TDS concentration or river salinity may be affected also by rainfall distribution patterns as well as evapotranspiration (Yechieli and Wood, 2002).

Ionic (cations and anions) compounds are typically found in river (water). Cations found in rivers include cadmium, nickel, lead, magnesium, iron, and chromium. Anions such phosphate, nitrate, sulphate, potassium, chlorides, carbonates, and bicarbonates have been detected in rivers (Jaji et al., 2007).

2.3.2 Effects of Nutrients (Ionic Salts) on Water Quality

Nutrients are essential for plant growth and most nutrient are not toxic. However, high concentration of certain nutrients (phosphorus and nitrogen) in water can result in the eutrophication of a water body. Eutrophication arises from nutrient enrichment of water bodies, which results in the growth of unwarranted algae and plants, leading to an imbalance in water ecosystem (Hilton et al., 2006).

2.3.2.1 Phosphorus/phosphates

One of the most important nutrients on earth is phosphorus and it is an essential component of the human DNA (Akbaş et al., 2013). In water bodies, phosphorus is present as both particulate and dissolved matter (Parry, 1998). The dissolved form of phosphorus are polyphosphate and orthophosphates. Organically, phosphorus exists as phosphate ions. Its pathway into rivers is through run-off, contamination of ground water and through lateral movement (Withers and Jarvie, 2008).

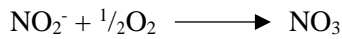
Phosphorus can enter rivers through natural/anthropogenic sources. The natural sources of phosphorus into water bodies/rivers includes atmospheric deposition, organic material decay and rock weathering (Mainstone and Parr, 2002). However, the nature of the weathered rock determines the quantity of phosphorus in water. Igneous rock which are more crystalline in nature are hardly weathered, therefore, it is expected that surrounding rivers will have very low levels of phosphorus. Contrastingly, sedimentary rocks are easily weathered and deposited in the river. Furthermore, the phosphorus content in sedimentary water/rock are organic in nature and are easily released by bacteria (Withers and Jarvie, 2008). Concentration ranges (0.005 – 0.020 mg/L) of phosphorus in fresh water (South African Rivers) have been obtained in previous studies (Wiechers and Heynike, 1986; Mason, 2002).

Anthropogenic sources of phosphorus in rivers are mainly due to human activities such as domestic and industrial effluents, live-stock production, and run-off from fertilizer application in farming (Withers and Jarvie, 2008). However, a very high amount of phosphate in rivers is typically from detergent in domestic sewage. Detergents contains very high levels of phosphates.

At low levels phosphorus is not harmful to aquatic organism and the environment. However, if present at elevated concentration in water together with nitrate, it will result in eutrophication. Eutrophication can cause indirect toxicity to organisms through the promotion of the growth of toxic algae (Chapman, 1996). Nonetheless, at very high concentration over $0.100 \text{ mg-P L}^{-1}$, phosphorus may become toxic in rivers (Carpenter et al., 1998).

2.3.2.2 Nitrate/Nitrogen

Nitrate is produced from the oxidation of nitrite or ammonia. It is highly stable and abundant in terrestrial and aquatic habitat (Alahi and Mukhopadhyay, 2018). Nitrate has a +5 oxidation state which is from highly oxidised nitrogen. Under aerobic condition through nitrification, ammonia is first oxidised to nitrite and subsequently to nitrate.



Nitrate removal from aqueous environment is very essential because appropriate concentration alongside phosphorus causes nutrient enrichment of water. There are two methods that can be applied for the removal of nitrate from water (i) through the application of macrophytes and algae as biotic assimilators (Chen et al., 2016), and (ii) through denitrification under very low oxygen conditions with bacteria reduces nitrate to nitrite and subsequently to nitrogen gas (Alahi and Mukhopadhyay, 2018).

The source of nitrate in rivers can either be natural or anthropogenic. Natural sources of nitrate can be through atmospheric deposition from the nitrogen cycle (Mayer et al., 2002). Other natural sources of nitrate include through volcanic eruption, weathering of igneous rocks, soil, plants, and animal debris (Panno et al., 2008). Nitrate have been found in rivers in concentration ranging from 0.4 mg/L (in pristine rivers) and greater than 4 mg/L (in highly impacted rivers). However, in South Africa similar concentrations (0.5 – 10 mg/L) have been found in pristine and highly impacted rivers, respectively.

Anthropogenic sources of nitrate present in rivers are from different land use by human beings. The major source of nitrate in river from human activity is through agricultural run-off and municipal sewage discharge (Panno et al., 2008). Other anthropogenic activities that generate significant amounts of nitrates are the combustion of agricultural products and fossil fuel.

Elevated levels of nitrates are dangerous for aquatic organism with the maximum threshold set at 2 to 3.6 mg NO₃⁻/L (Villiers and Thiar, 2007). In South Africa, the regulatory authority sets the maximum threshold at 0.5 to 2.5 mg NO₃⁻/L (DWAF, 1996). Nitrate concentration may vary in rivers due to temporal and spatial orientation. An increase in nitrate concentration is observed temporarily during the agriculture season. Usually, there is an uptick in nitrate concentration during spring and winter, and a decline in other seasons as a result of higher nitrate uptake increased biological productivity (Mason, 2002). In summer, nitrate concentration is significantly low because of utilisation by plants and higher rate of evapotranspiration. In contrast, during winter evapotranspiration rate is significantly reduced and consequently, nitrate is leached from soils into rivers. However, a study conducted by Villiers and Thiar (2007) in South Africa, showed that nitrate levels in rivers were directly from run-off which coincide with fertiliser application from the planting season.

High nitrate concentration affects river water quality. The presence of nitrate in water is dependent on the physico-chemical parameters such as pH, DO and temperature (Vajravelu et al., 2018). Nitrate concentration greater than 4 mgNO₃⁻/L have been implicated in promoting algal bloom growth as well as eutrophication (DWAF, 1996) which results in depletion of oxygen levels and less sunlight penetration. Nitrate may not be so toxic to aquatic organism at low concentration, but it becomes toxic as its concentration increases. Amphibians, invertebrate, and fishes becomes sensitive at concentrations of 73 to 7752 mg NO₃⁻/L, 24 to 3070 mg NO₃⁻/L and 847 to 9344 mg NO₃⁻/L, respectively. The toxic effect of nitrate at elevated levels includes deformities, high stress level, stunted growth, high rate of mortality, low reproduction rate and lethargy (Addiscott and Benjamin, 2004). In humans, nitrate concentration of 100 mg/L present a potent danger to human health. Nitrate has been implicated in methemoglobinemia. This is a condition in minors which digestive bacteria reduced nitrate to nitrite resulting in the alteration of haemoglobin to produce methaemoglobin (Addiscott and Benjamin, 2004).

2.3.2.3 Potassium (K⁺)

Potassium is a naturally occurring element found in soils and in the core of the earth. In water, potassium does not occur at elevated concentrations, because it does not have the mobility of sodium (Nikanorov and Brazhnikova, 2009). However, it is an important micronutrient facilitating the growth of plants and aquatic organisms (Rodríguez-Navarro, 2000).

2.3.2.4 Sodium (Na⁺)

Unlike potassium ion, sodium ion has high mobility and solubility in aqueous environment (Kang et al., 2021). Sodium is present naturally in water as part of different salt compounds trapped at the bottom of water. Another great source of sodium in water is limestone deposits. Sodium is released into water when a mass of limestone is weathered over time (Nikanorov and Brazhnikova, 2009).

2.3.2.5 Calcium (Ca²⁺)

The origin of Ca²⁺ is from sedimentary rocks such as gypsum, limestone, and dolomite (Nikanorov and Brazhnikova, 2009). Carbonic acid found in water readily dissolves dolomite and limestone, releasing an enormous amount of calcium (Zavarzin, 2002).

2.3.2.6 Magnesium (Mg²⁺)

Just like Ca²⁺, Mg²⁺ is present in water due to the weathering and dissolution of dolomites and other sedimentary rocks (Tipper et al., 2008). In water Mg²⁺ are found as carbonates or present with calcium (Wimpenny et al., 2011).

2.3.2.7 Carbonate

Carbonates in water originates from the weathering or dissolution of rocks over time such as dolomite, limestone and magnetite with carbon(IV)oxide as a catalyst (Han and Liu, 2004). Carbonate present in water can either be hydro carbonate (HCO₃⁻) or carbonate ions (CO₃). The pH of water is determined by which carbonate is present in such water body. High amount of HCO₃⁻ concentration in water is an indication that the pH of water is between 7 to 8.5. A pH greater than 8.5 signifies the presence of high

CO₃ concentration in water. Thus, implying the water is dominated by Ca₂⁺. However, if the pH of water is below 5, it shows that HCO₃⁻ is not present in significant amount. The presence of carbonate in water ensures that water has inherent buffering capability. These carbonate ions act as alkaline and thus neutralises pH and ensuring that the ionic balance of the water is maintained (Jacobson et al., 2002).

2.3.3 Effect of pH

pH is essential in determining water quality. Hydronium (H⁺), carbonate (CO₃²⁻), and bicarbonate (HCO₃⁻) ion concentration are essential parameters in the determination of water quality of a river. pH is defined as the hydrogen ion concentration and it is measured on a scale of 0 - 14. A value of $0 \leq 7$ is acidic, 7 is neutral, and $7 \geq 14$ is basic. This scale is used to read alkalinity or acidity of water bodies (Dutta et al., 2015). The pH of surface water or rivers is regulated by several factors such as the presence of humic and fulvic acids, HCO₃⁻, CO₃²⁻ and CO₂. pH ranges of 3 – 11 have been recorded in South African rivers (Abel, 1996). However, the ideal pH range for fresh water is 5 – 9, because this pH range supports life for a vast array of aquatic organisms (Abel, 1996).

The pH of surface water is influenced by several factors such as atmospheric deposition, cation exchange capacity, temperature, dissolved solids, biological activities, organic/inorganic matter, vegetative cover along river course and geological influences. The rock on which a river flows may significantly affect the pH to acidity or alkalinity. Another important factor that can change the pH of a river is seasonal variation. Typically, in spring, there is usually an increase in pH levels of rivers due to photosynthetic process (the abstraction of CO₂) of aquatic flora (Maberly et al., 2015). This may lead to the river being acidic or alkaline at different seasons of the year, which brings about pH fluctuation. A balanced pH is required for the maintenance of “river health” and the thriving of aquatic organisms. Nature has an inbuilt river coping mechanism to buffer extreme pH. This ensures that the pH of a river is stable at all times through its buffering capacity (Dutta et al., 2015). However, the buffering capacity of a river can be destroyed if effluent with extreme pH is dumped into such river.

Despite the changes in river due to natural processes, the greatest threat to surface water quality globally may be attributed to human activities. Activities such as farming and industrial effluents have the potential to radically alter the pH of a river, resulting in it being too alkaline or acidic. Surface run-off from fertiliser application in farms have been shown to increase the eutrophic potential of rivers (Jarvie et al., 2006). However, most industrial effluents result in acidic pollution. In South Africa, the acidification of rivers is not a new phenomenon. Over the past few decades, South African rivers have become increasingly acidic due to acid mine drainage issues (Naicker et al., 2003). Acidification of rivers results in the destruction of the river ecosystem and buffering capacity which differs from river to river. Furthermore, it severely restricts river use, resulting in loss of numerous economic opportunities from river ecosystem goods/services and land use.

The effect of pH river water quality cannot be over emphasised. A very low pH signifies the abundance of hydronium ion which increases the electrical conductivity of the water. Metal complexes in water are formed at high pH which reduces bioavailability and mobility. However, at low pH, there is an alteration in the toxicity of metal species present in water due to increase in ion mobility. Furthermore, precipitation may lead to the release of toxic metals species.

2.4 Vaal River System Description

The Vaal River catchment is a very large catchment, and the river flows all year round, however, fluctuation in flow variation occur due to seasonal changes. The Vaal River is divided into the upper Vaal, middle Vaal and the lower Vaal. Each part of the Vaal is unique in its usage. The Vaal River is the second largest river in South Africa after the Orange River. It is the most hard-working river in South Africa (Tempelhoff 2009). The river is the most regulated and developed in Southern Africa (Roos and Pieterse 1994). The Vaal River rises on western hill of the Drakensburg mountains and flows for approximately 900 km traversing the inner land plateau before it links with the Orange River and subsequently draining into the Atlantic Ocean. The main tributaries of the Vaal River drain the Maluti, Witwatersrand, and Drakensburg mountains in the south, north and east, respectively. In summer (January to March), the River discharges about 300 m³/S; which supports economic activities within the catchment to the value of approximately USD 100 billion per year, through the storage dams at Bloemhof with a volume of 1200 million m³ and Vaal at 2200 million m³. The mean annual evapotranspiration rate is approximately 1300 mm and rainfall are about 600 mm. However, the Drakensberg escarpment has the highest rainfall of approximately 800 – 1000 mm and an evaporation rate of 1250 mm. Evaporation and rainfall intensifies towards the west with values of 300 mm and 2250 mm, respectively (Jury 2016).

The climate experienced is subtropical dry savannah with discharges and rainfall fluctuating from year to year (Tadross et al., 2007). Approximately 20% of the Vaal River and its tributaries is drained from the Orange-Vaal basin. The origin of the Vaal River main course is at Breyten, Mpumalanga. Breyten has an elevation of 1770 m and its major tributaries originates close to Bethlehem and Harrismith along the Eastern Escarpment Mountains with an annual rainfall of approximately 700mm. The Vaal River travels from its origin for 1425 km before it joins the Orange River. Approximately 775 km of the Vaal River is the border of the Free State, spanning from Kimberly in the west to Meyerville to the east.

The list of locations of major dams in the Vaal River catchment are respectively presented in Table 2.1 and Figure 2.1. The river is highly regulated through these *small* dams which conserve water for irrigation. The water in the dams are periodically released into the Orange River. No other catchment in South Africa supports industrial, agricultural, urban, and mining industries to this magnitude. These activities release high level effluent discharge into the River.

Table 2.1: Major Dams in The Vaal River Catchment [Source: (Braune and Roger, 1987)].

Dam Name	River/Tributary	Surface Area (ha)	Capacity (10⁶m³)
Grootdraai	Vaal River	3879	358.6
Sterkfontein	Nuwe Jaarsspruit	6937	2656
Vaal Dam	Vaal River	32107	2535
Vaal Barrage	Vaal River	1700	56.7
Boskop	Mooi	378	20.7
Koppies	Renoster	1367	41.2
Allemanskraal	Sand	2697	174.3
Erfenis	Vet	3308	224.1
Bloemhof	Vaal River	23427	1269.2
Vaalharts	Vaal River	2142	51.2
Spitskop	Harts	2496	61.3
Rustfontein	Modder	1162	75.4
Krugersdrift	Modder	1876	76.7
Tierpoort	Kaffir	911	34.5
Kalkfontein	Riet	4550	321.8
Douglas Weir	Vaal River	799	17.2

2.4.1 Geology

The Vaal region is characterised by different types of sedimentary and metamorphic rocks of different ages (Van Riet Lowe, 1952). At the Black Reef, there is an extensive deposit of old quartzites. Dolomite is the second most abundant rock of the Chuniespoort group and the Hekpoort andesite and Daspoort quartzites with the Black Reef quartzites and the rocks of the Transvaal Sequence. In the Eccia group of the Karoo sequence, younger sedimentary rock overlays the older quartzite rocks. Dolerite from the Karoo age also encroached into Eccia group. However, there are recently formed sedimentary rock from the tertiary to current age, present mainly in the west of the drainage routes. Although only a small section of the area is underlain by dolomite, there have been occurrences of subsidences and sink holes (Braune and Roger, 1987).

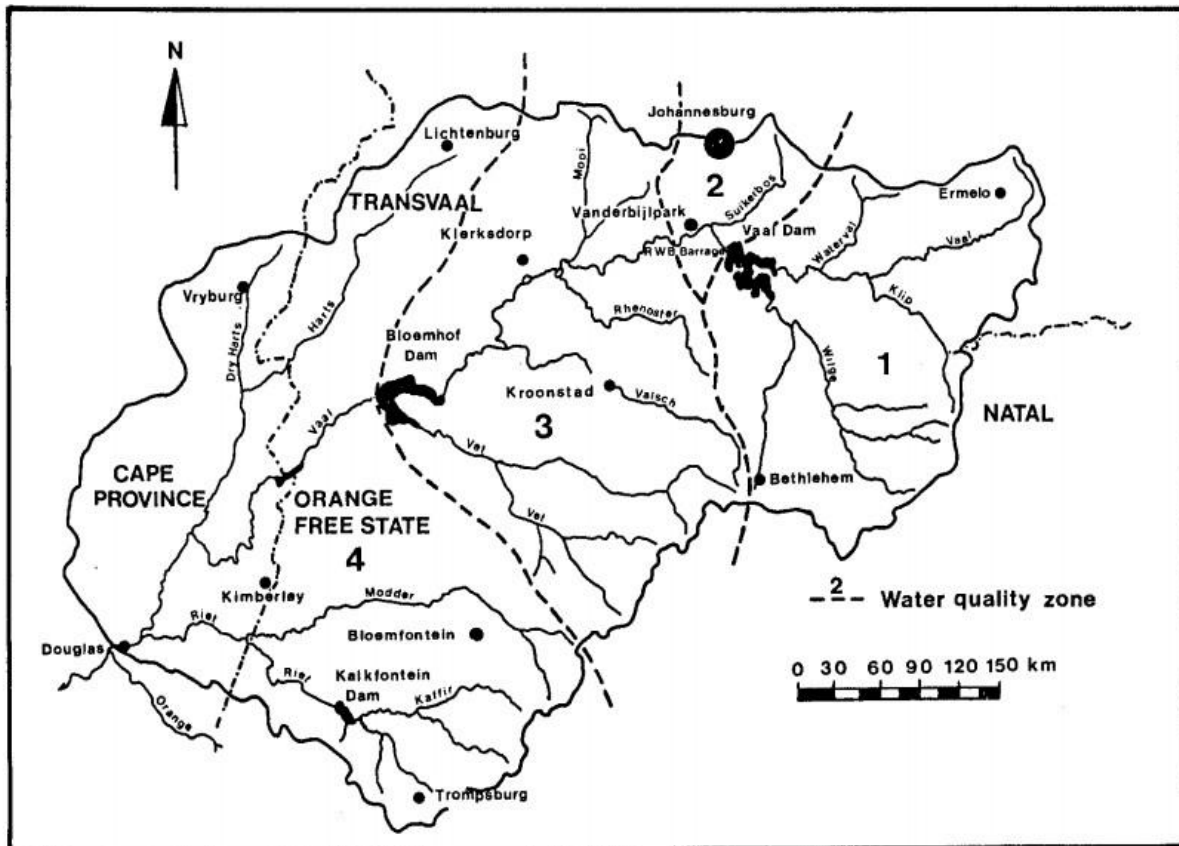


Figure 2.1: Vaal River Catchment indicating 4 zones based on water quality (Braune and Roger, 1987)

2.4.2 Soil

Around the entire stretch of the Vaal region, there are 5 major agricultural soil types (Van Riet Lowe, 1952). In the south-west part, there is the Lindley and Gelykvlakte association which has between 30 – 60% clay content in the A-horizon. In the B-horizon, the Lindley soil series have clay contents between 30 -35%. Other soil series include the Kroonstad series and the Wesleigh series. These soils possess a very sandy E- horizon, and the collapse of the soil is typically attributed to the differential wetting of the E-horizon. The saturation of the E-horizon is associated with clayey material beneath the horizon. There is also the Shorrocks association soil which contains a considerable amount of clay sediments. The northern part of the Vaal is characterised by several soils such as the Blinkklip, lithosols and the Shorrocks series. Also present is the Makatini series, which has high levels of clay. Lastly, is the Devon series which contains very high content of clay sediments (Van Riet Lowe, 1952).

2.4.3 Land Use

The land use of the Vaal region is centred around the River. The Vaal River catchment has a number of dams. The River also has several small barrages which is used to regulate water for irrigation.

The Vaal catchment receives approximately 8% of the mean annual rainfall of South Africa but it has the highest number of human beings, and concentration of industrial, agricultural, urban, power

generation and mining in South Africa. The Vaal River catchment produces approximately 55% of South Africa gross domestic product and is home to about 42% of the South Africa urban dwellers. The mining from this region represents approximately 79% of the total mining operation in South Africa. Most oil-from-coal production and power generation are done in this region. This region produces about 42% of the country's total agricultural produce and have 155000 hectares of irrigated lands. The distribution of the economic activities over the catchment requires that the catchment is divided into four zones on the basis of water quality. This River also have many recreational spots and it is often regarded as the main artery of the South African heartland".

Zone 1: This zone is otherwise referred to as the Vaal Dam catchment. In this zone, agriculture (dryland cultivation and animal grazing), mining and fuel processing activities takes place. The water quality is great for all the economic/commercial activities in this zone. The best quality of water is found in this zone and the water is known to deteriorate in quality further downstream (Braune and Roger 1987).

Zone 2: This zone is referred to as the Vaal Barrage sub-catchment. The water quality in this zone is poor as the river drains the highly industrialised Witwatersrand area. The total runoff from the Vaal Barrage is 11% from industries, 14% from mines and 75% from sewage. In this Barrage, agriculture activities have little or no bearing on water quality. However, increased salinity and eutrophication are the major water quality issues (Braune and Roger 1987).

Zone 3: This zone is the Bloemhof catchment. Major contributors to this catchment are domestic sewage, industrial waste from mining which impacts water quality. In this catchment, there is the presence of high amounts of sulphate and a resultant contribution to alkalinity. The high TDS value in this part of the River is due to the immense contribution from the tributaries draining the northmost part of the catchment which are polluted severely from industrial effluent and intensive mining activities (Braune and Roger 1987).

Zone 4: The Douglas weir catchment has contribution from high level irrigation from agriculture along the tributaries of the Plodder, Hart and Riet which affects water quality. This represents the downstream of the Vaal River and has carry on pollution from Bloemhoff dam. It has significant amount of chloride, low sulphate which has been replaced with alkalinity, chloride and bicarbonates issues due to irrigation overflow. However, dilution from the Orange River renders its pollution negligible (Braune and Roger 1987).

2.4.4 Land use and water quality issues in the catchment

There are several land uses that affects the quality of the Vaal River catchment. This includes mining, power generation and fuel production, urban and industrial development, agriculture, conservation, and recreation.

Mining, Power and Fuel Production: Approximately 79% of South Africa's mining is done within the Vaal catchment area. The region is also known to be the "home" for a large proportion of the oil-from-coal industries (Jury, 2016).

2.4.4.1 Coal and Gold Mining

Coal mining around the Vaal and Oliiphant rivers catchment is majorly underground and only a few open cast mines can be found. Most of the mines are found in Witbank, Ermelo and Mpumalanga. Coal mining impact water quality through the increase of sulphates, acidity, and TDS which can be attributed to the open mine technique used in coal extraction. However, the underground technique also has its issues. A collapse of the overburden could potentially lead to ground water pollution. There is the issue of the accumulation of ground water in pits and the overflow into surface water which is problematic. This overflow is typically red in colour and comprises of iron and has low levels of pH and oxygen (McCarthy and Pretorius, 2009).

Most of the gold mines in South Africa are present in and around the Vaal River catchment (Vaal barrage, Bloemhof and Vaal dam). Gold mining results in water pollution due to oxidation of pyrite in gold to H_2SO_4 and Fe. This causes mines to have very high salt levels and low pH. Soda ash used for the control of surface water acidity if not controlled properly may result in pollution issues. Another concern from gold mining is cyanide pollution when it is discharged into the Vaal River.

2.4.4.2 Power Generation/Fuel Production

Potential pollution of the Vaal River may arise from fuel production (Du Plessis, 2017). Currently, SASOL I discharge its effluent very close to Vaal River Barrage (Tempelhoff 2009). Inorganic pollutants such as fluoride, and other non-degradable organic substances are all by-product of fuel processing. Other avenues of pollution from the power generation to the Vaal River includes the possibility of oil spills or the discharge of alkaline ash water. Atmospheric pollution and enhanced metal corrosion are other associated issues from power generation, which severely impacts flora and fauna in the Vaal River.

2.4.4.3 Urban and industrial development

The Vaal catchment and its supply area houses 42% of the urban population of South Africa and is responsible for 56% of the total industrial production (Raubenheimer et al 1985)(Du Plessis 2017). The largest concentration of these activities is in the Pretoria-Witwatersrand-Vereeniging (PWV) complex which falls mainly in the Barrage catchment. Pollution of water resources through industrial and municipal effluents, solid waste disposal and other diffuse sources is the major problem relating to this land use.

2.5 Eutrophication

Due to municipal and industrial waste being discharged in the Vaal River, the River has undergone massive nutrient enrichment overtime. This is clearly evident in the Vaal Barrage and Dam. This also

causes a high TDS and high salinity levels.

Solid wastes and sewage from municipalities are also a source of pollution to the Vaal River. These wastes are source of inorganic salts and organic pollutants. The leachate from the wastes could seep into the Vaal River and over time have affected the water quality of the Vaal River.

Forestry and Agriculture: Approximately 42% of South Africa's agricultural production is around the Vaal River catchment. The farming activities includes livestock, crop and intensive cultivation (Braune and Roger, 1987).

Irrigation: Approximately 22% of the water use in the Vaal catchment is used for irrigation which significantly affects water quality of the River. This has led to increased salinity of the Vaal River Barrage. This is evidenced in the salinity and TDS levels downstream the Vaal River (Braune and Roger 1987).

Based on run-off from irrigation, nutrients load from fertilised farms can cause eutrophication in the Vaal River. Another source of nutrient pollution is through animal feeding. Pesticides from farms can seep into the Vaal River. This is prominent in the Barrage and at Douglas (Braune and Roger, 1987)

Chapter 3: Methodology

3.1 Study Area

This research was carried out in a supposed saline tributary catchment of the Vaal River. The Vaal River has a catchment of approximately 192000 km². It spans across 3 provinces; Gauteng; Free State; and Mpumalanga. The Southern border of Gauteng Province is the Vaal River, which separates Gauteng from the Free State Province. To the west, the Vaal river shares a border with Gauteng and North-West Province; to the east, the river shares a border with the Mpumalanga province and to the north the Limpopo province. Gauteng is situated on the Highveld which is a high-altitude grassland with an elevation of 4921 feet or 1500 m above sea level. There are undulating grasslands and parallel ridges between Pretoria and Johannesburg. The north of Gauteng experiences a subtropical due to its lower altitude and dry savanna, however, the South (Johannesburg) is relatively cooler. The province has an annual average rainfall of 26 inches (650 mm). Gauteng Province is the most densely populated area in South Africa with an estimated population of about 10 million. It is also home to about 20 wastewater treatment plants and 600 wet industries and a quite a number of mines contributing to the pollution of fresh water (Tempelhoff et al., 2007). The North-West province is made of very flat lands/plains, grassland, and scattered trees. It stretches from the dry Molopo River to the Southern border of the North-West province which is the Vaal River. It is the home of the Magaliesberg mountain range, an extensive belt of land in the northeast spanning 130 km from Pretoria to Rustenburg. It has a semi-arid climate with temperature ranging from 3 to 21 °C in winter and 17 to 31 °C in summer. This province experiences an annual rainfall of 14 inches (360 mm) which occur during summer (October to April). Some part of the Mpumalanga province is in the Highveld region of South Africa, while other regions are in the Lowveld. It is a plateau that sits about 4000 – 6000 feet (1200 – 1800 m) in the west above sea level. This province is also home to the Drakensberg mountains which is 7500 feet (2300 meters) above sea level. The Drakensberg escarpment receives most of the rainfall and other areas receive mild rainfall (767 to 878 mm). The Highveld areas experience severe frost throughout the year, while the Lowveld areas are frost free. The climate in the Lowveld is subtropical due to its proximity to the Indian Ocean. However, the Highveld is relatively much cooler. Annual temperature ranges from 1 to 15 °C in winter and 15 to 29 °C in the summer.

3.2 Sampling Site Selection

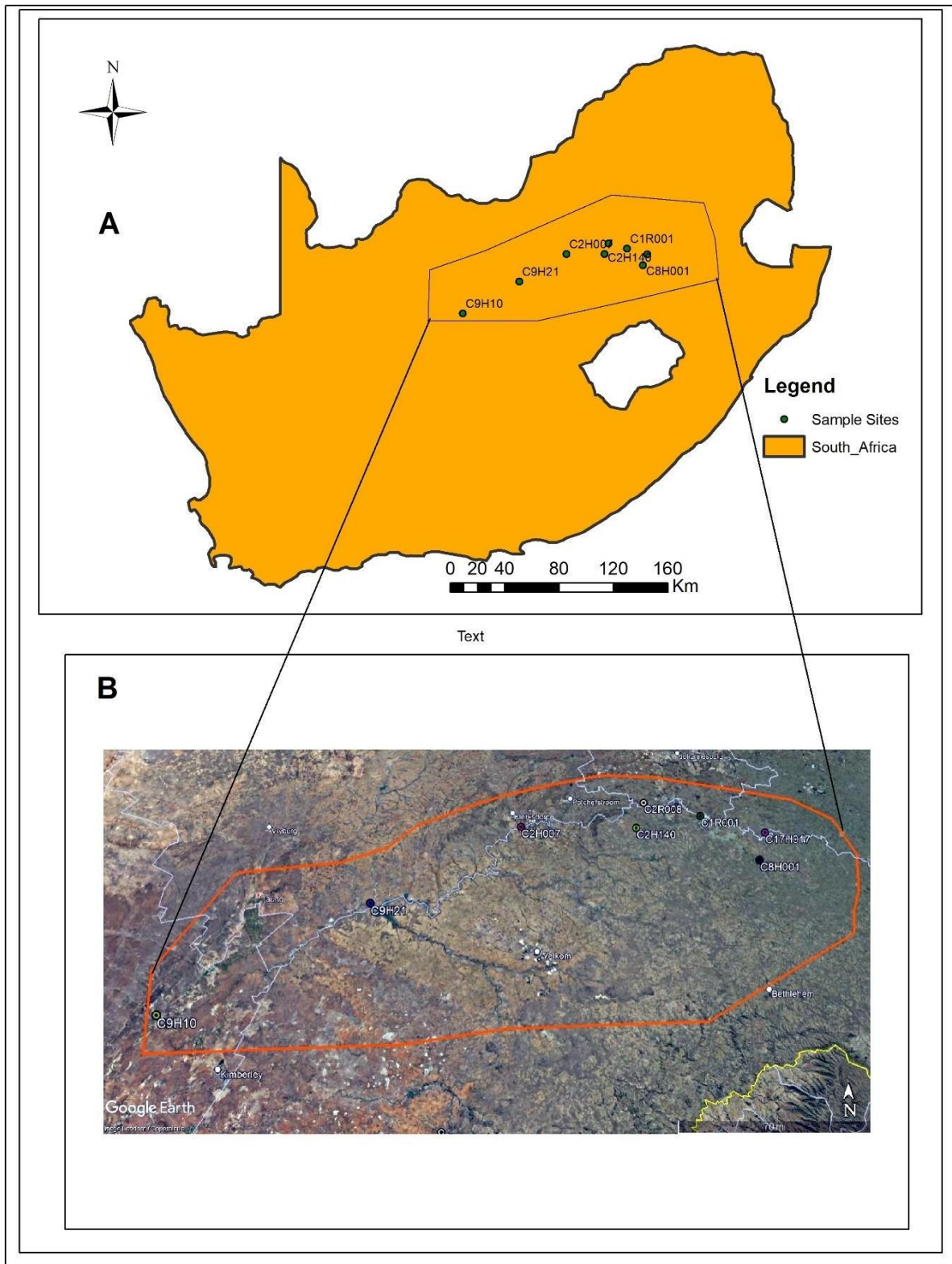
The data utilised in this research study was obtained from the Department of Water and Sanitation (DWS). For the most part, samples were collected daily or after 2 days for the entire study duration. The data analysed in this study was as a result of sampling multiple locations along the Vaal River and its tributaries. Various parameters were monitored in nine stations within the boundaries of the study location (the Vaal River and its tributaries). These monitoring stations are listed below (Table 3.1; Figure 3.1):

Table 3.1: Monitoring sites and coordinates

Sample Code	Sampling sites	Coordinates	
		Longitudes	Latitudes
Upper course			
C8H001	Wilge River at Frankfurt	28.49	-27.27389
C17H017	Villers at Flood section on Vaal River	28.59389	-27.02314
C1R001	Vaal Dam at Vaal River	28.1167	-26.8834
Middle course			
C2R008	Vaal Barrage on Vaal River (Lower end of Vaal Triangle)	27.68472	-26.76556
C2H140	Vaal River at Woodlands/Goose Bay Canyon	27.59194	-27.01011
C2H007	Pilgrims Estate at Orkney on Vaal River	26.69808	-27.01011
C9H21	Vaal River below Bloemhof Dam	25.59616	-27.65489
Lower course			
C9H10	Vaal River 0.85 Km downstream of Vaal-Harts irrigation return flow	24.27167	-28.40583
C9R003	Douglas Barrage on Vaal River (Last point before confluence with the Orange River)	23.83694	-29.04333

The review/analysis of data will commence at the Wilge River monitoring station (CH8001), which is the most upstream in the study area's catchment. It receives water from the Lesotho Highlands and at the station the water quality is near pristine and can be used as a gauge or marker for the water quality for the whole catchment. From the C8H001 upstream monitoring station, the Vaal River flows midstream to the C1R001 and C9H21 monitoring stations, which are the Vaal dam wall and Bloemhof dam, respectively. Onwards, the flow continues to the Lower Vaal (downstream) which are the C9H10 Vaal-Harts irrigation return flow and the C9R003 Douglas Barrage (Orange River confluence) monitoring stations, respectively. The last monitoring station receives water from the Orange River which affects its salinity.

The systematic monitoring approach proposed in this study was to ensure that the variation in salinity over a long period of time, as well as possible causes/origin of salinity along the course of the Vaal River are properly investigated.



**Figure 3.1: (a) Map of South Africa and monitoring stations in the Vaal River and its catchment
 (b) Terrain Image of the monitoring station generated from Google Earth**

3.3 Data Management

The data obtained from the DWS had to be refined before use. This meant the data was converted into a proper format (grouped into a 5-year averages) to ensure concise interpretation. Furthermore, it should be noted that data that were outside the time frame of the research was deleted to avoid unnecessary complications as they are not in tandem with the objectives of the study. Also, several bits of information present in the DWS data such as temperature, pH were omitted because they were not within the scope of the study. Thus, a highly refined data set were used in plotting graphs, interpreted, and deduce valuable information on salinisation.

3.4 Approach

Time series graphs will be used to depict long term TDS changes at the monitoring stations. Furthermore, Maucha diagrams will be used to depict salt composition changes over time. This will be carried out using 5-year averages which will reflect changes in TDS and indicates the salts responsible for such changes and the times such changes took place.

3.5 Data Interpretation

The data sets span a period of forty years (1975-2015). The data sets obtained at each monitoring station were classed based on a 5-year interval. The data for the individual monitoring station for a 5-year time frame was calculated with the aid of a Maucha diagram.

Maucha Diagrams: This is a powerful tool developed by Maucha (Maucha, 1932), it is used in analysing total ionic concentrations in a water sample. It is the graphical representation of major anions and cations in water (M).

In a typical Maucha diagram plot, main anions are plotted on the left side, whereas cations are plotted on the right side. It was abundantly evident from the Maucha diagrams that salt composition at the monitoring stations varied significantly over the course of the 40-year period. Salts with concentration that were significantly different overtime included TDS, total alkalinity (TAL), and sulphates. These salts were selected as a reflection of changes with time and were further analysed and investigated. The following salts: TDS, Ca, SO₄, Mg, K, TAL, Na, and Cl had individual graphs of their 5-year averages plotted.

A comparative analysis of the Maucha diagrams and the various plots against each other over a 40-year period showed visible changes in salinity composition at the individual monitoring stations and the reasons explained in the next chapter. The composition and concentration of salts/ions in the Vaal River varied considerably which may be attributed to numerous factors such as evaporative concentration extent, amount of precipitation received, and geology of the catchment.

Chapter 4: Results

4.1 Introduction

The results obtained from the analysis of 9 sampling sites from the Vaal River system were grouped based on the river course *viz*: upper (zone 1); middle (zone 2) and lower River (zone 3) stream. Remarkable changes were observed both temporarily and spatially in TDS, sulfate, total alkalinity (TAL) and other salts concentration over the study period of 40 years (1975-2015). The river course also reflects long-term changes in salinity from individual monitoring stations.

4.2 River Upper stream (Zone 1): C8H001, C17H017 and C1R001 sections

4.2.1 C8H001 Wilge River Monitoring Station

This monitoring station is the commencement point of the study catchment area and is classified as part of zone 1 of the river system. This zone is characterised by good water quality, and it serves as a crucial supplier of water into the Vaal River. Water from the Lesotho Highlands and the Sterkfontein dam scheme contributes to the water in the Vaal River upstream. Furthermore, this zone is also characterised by agricultural activities (dryland cultivation and animal grazing), fuel processing and mining with minimum return flow into the river (Braune and Roger, 1987(Tempelhoff 2009)). The Maucha diagram (Figure 4.1) and the average 5-year salt change (Figure 4.2) shows the variation in concentration of salts and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, Cl, TAL and TDS) over a period of 40 years.

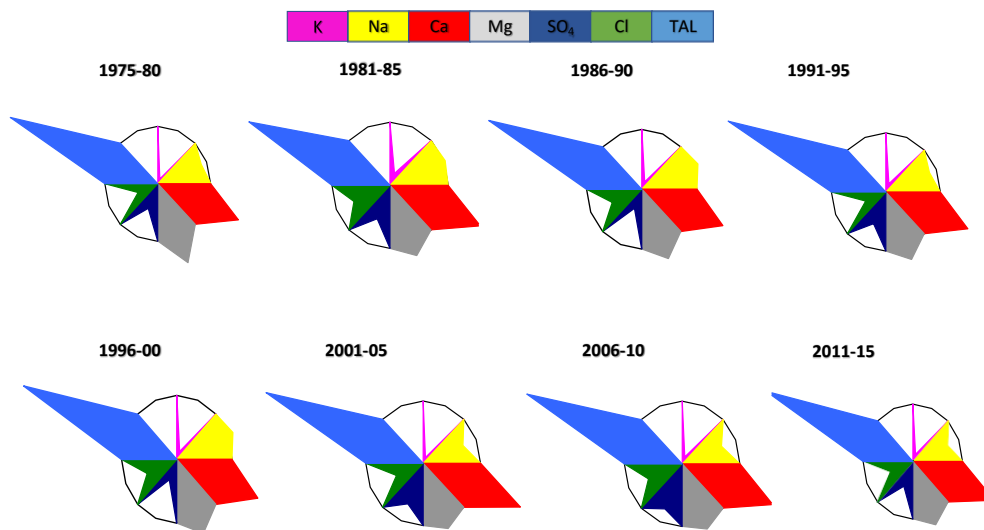
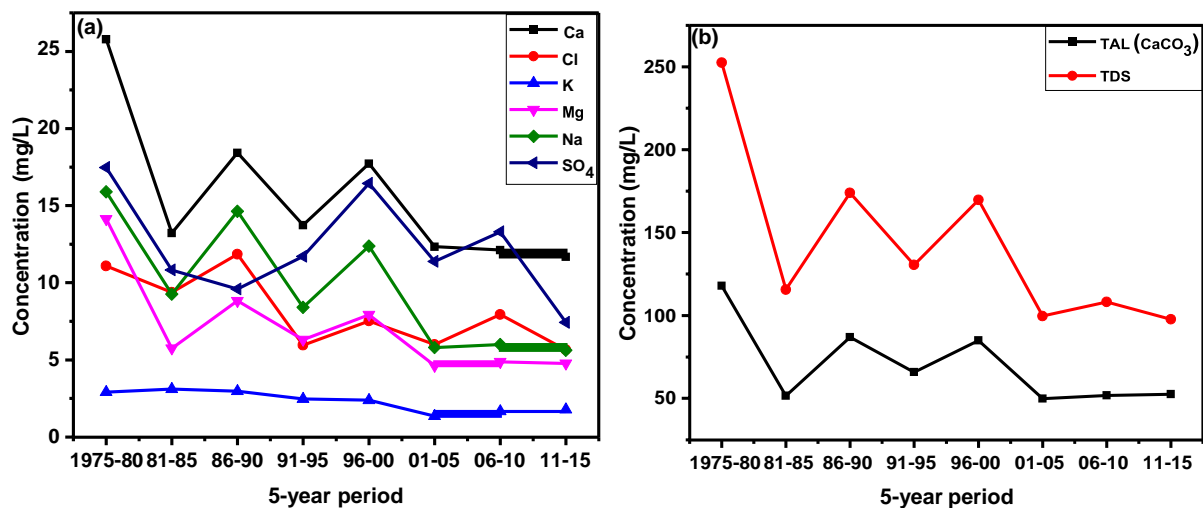


Figure 4.0.1: Maucha diagram at C8H001 Wilge River



**Figure 4.2: Graphical representation of salt average 5-year changes over the period 1975-2015
C8H001Wilge River**

From the result (Figures 4.1, 4.2 and Table 4.1), the major contributor to TDS was TAL, other significant contributors included SO₄ and Ca.

Interesting observations were recorded for the temporal study over the 40-year period (Table 4.2). An example is the high concentration of all salts at the start (1975) of the monitoring period with a decline in concentration over the years. Between 1981-1985, there was a sharp decline in the concentrations of all salts from the highs recorded between 1975-1980. Nonetheless, despite the sudden drop, there was an increase and subsequent decrease in salts (TDS) alternating 5-year average periods/cycle. Increase in concentration occurred between 1986-90, 1996-00 and 2006-2010, while alternate corresponding decreases were observed between 1981-85, 1991-95, 2001-05, and 2011-2015. Another interesting observation was that percentage ratio of ions remained constant over the years (Table 4.2). The percentage ratio of ions remained relatively constant over the study period and showed minor increases and decreases (Table 4.1).

Table 4.1: Percentage composition of individual salts in the Maucha diagram to TDS concentration C8H001 Wilge River

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	12.6	5.40	1.42	6.89	7.75	8.51	57.5
1981-85	12.8	9.09	3.01	5.58	8.99	10.5	50.0
1986-90	12.0	7.73	1.94	5.76	9.55	6.26	56.7
1991-95	12.0	5.21	2.16	5.52	7.34	10.2	57.5
1996-00	11.9	5.04	1.60	5.32	8.29	11.0	56.9
2001-05	12.3	6.01	1.36	4.63	5.80	11.4	49.9
2006-10	12.5	8.12	1.71	4.99	6.14	13.6	53.0
2011-15	13.0	6.32	2.00	5.33	6.29	8.29	58.7

Table 4.2: 5-year averages of ions at C8H001 Wilge River

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	25.8	11.1	2.90	14.1	15.9	17.5	117.9	205.2
1981-85	13.2	9.38	3.11	5.76	9.28	10.8	51.6	103.2
1986-90	18.4	11.9	2.96	8.83	14.6	9.60	87.0	153.3
1991-95	13.7	5.97	2.48	6.31	8.41	11.7	65.9	114.6
1996-00	17.7	7.53	2.39	7.94	12.4	16.5	85.0	149.5
2001-05	12.3	6.01	1.36	4.63	5.80	11.4	49.9	91.4
2006-10	12.1	7.95	1.67	4.88	6.01	13.3	51.9	97.8
2011-15	11.7	5.66	1.79	4.78	5.64	7.43	52.6	89.6

4.2.2. C17H017 Villers at Flood section on Vaal River Monitoring Station

This station is a little further downstream from the Wilge River and it falls within zone 1 of the study catchment area. Therefore, it is expected that the water quality in C17H017 should be relatively good, but of a slightly lesser quality when compared to CH8001. The Maucha diagram (Figure 4.3) and the average 5-year salt change (Figure 4.4) shows the variation in concentration and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

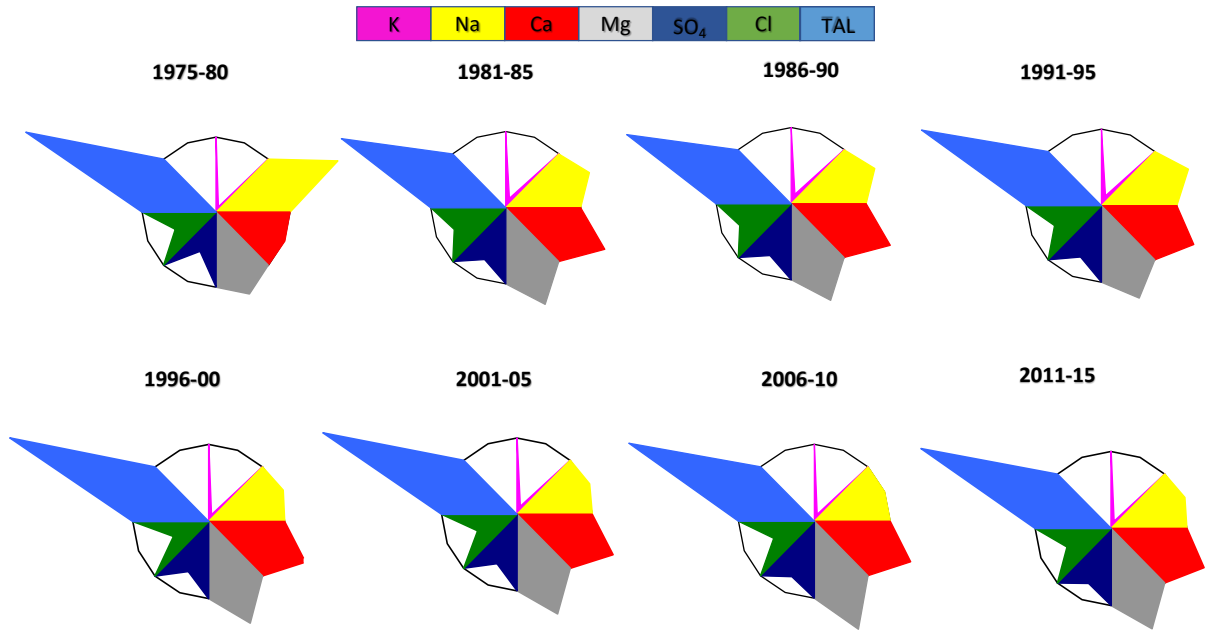


Figure 4.3: Maucha diagram at C17H017 Villers at Flood section on Vaal River

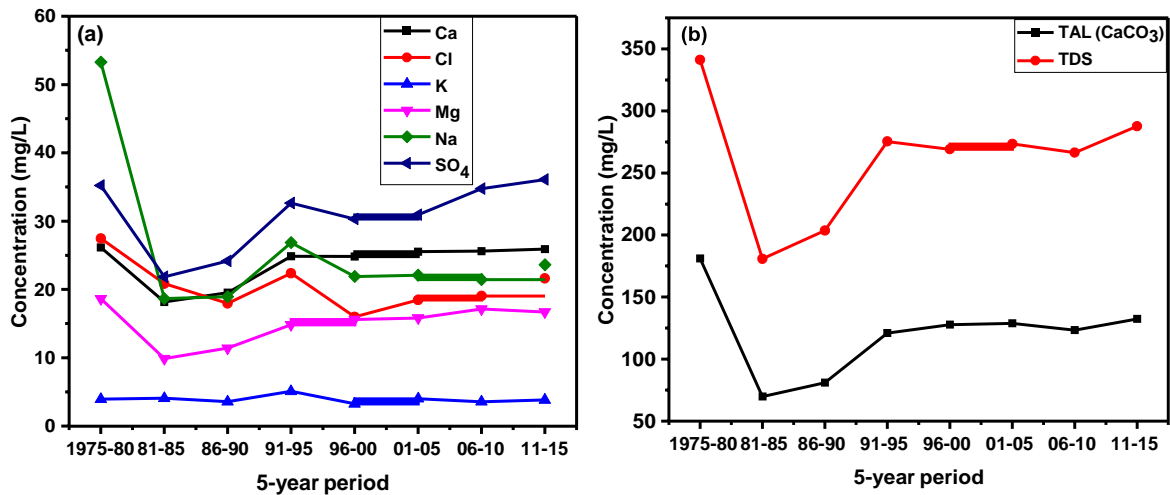


Figure 4.4: Graphical representation of salt changes over an average 5-year period at C17H017 Villers at Flood section on Vaal River

From the results (Figure 4.3; Tables 4.3 and 4.4), a similar trend was observed when compared to CH8001. The major contributor to salinity was TAL and TDS, other significant contributors included SO₄, Na and Ca with the least contributor as K. A similar trend was observed when compared to salinity in CH8001. Between 1975-80, the concentration of all salts was at their highest levels, however, between 1981-85, a sudden drop in the concentration of all salt was observed and it more pronounced in TDS and TAL. From 1986-90, the concentration of salts remained relatively constant and stabilised throughout the remaining study with very little fluctuation.

Table 4.3: Percentage composition of individual salts in the Maucha diagram to TDS concentration at C17H017 Villers at Flood section on Vaal River

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	7.57	7.94	1.14	5.40	15.4	10.2	52.4
1981-85	11.14	12.8	2.50	6.05	11.5	13.4	42.7
1986-90	11.07	10.2	2.21	6.46	10.7	13.7	45.8
1991-95	10.04	9.04	2.06	6.00	10.8	13.2	48.8
1996-00	10.37	6.68	1.36	6.52	9.15	12.7	53.3
2001-05	10.4	7.52	1.64	6.44	9.00	12.6	52.4
2006-10	10.5	7.79	1.46	7.01	8.77	14.2	50.3
2011-15	9.96	8.32	1.48	6.42	9.09	13.9	50.9

Table 4.4: 5-year averages of ions C17H017 Villers at Flood section on Vaal River

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	26.2	27.5	3.94	18.7	53.3	35.2	181.0	345.8
1981-85	18.2	20.9	4.07	9.87	18.7	21.9	69.6	163.2
1986-90	19.5	18.0	3.57	11.4	18.9	24.2	80.9	176.5
1991-95	24.8	22.4	5.10	14.9	26.9	32.7	120.8	247.6
1996-00	24.8	16.0	3.26	15.6	21.9	30.3	127.6	239.5
2001-05	25.5	18.5	4.02	15.8	22.1	30.9	128.8	245.7
2006-10	25.6	19.1	3.58	17.2	21.5	34.8	123.2	244.9
2011-15	25.9	21.6	3.84	16.7	23.6	36.1	132.3	260.0

4.2.3 C1R001 Vaal Dam on Vaal River Monitoring Station

This is the third monitoring site at the dam wall below the other two sites. C1R001 is classified in zone 1 of the of the study catchment area. The Maucha diagram (Figure 4.5) and the average 5-year salt change (Figure 4.6) shows a slight variation in concentration and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

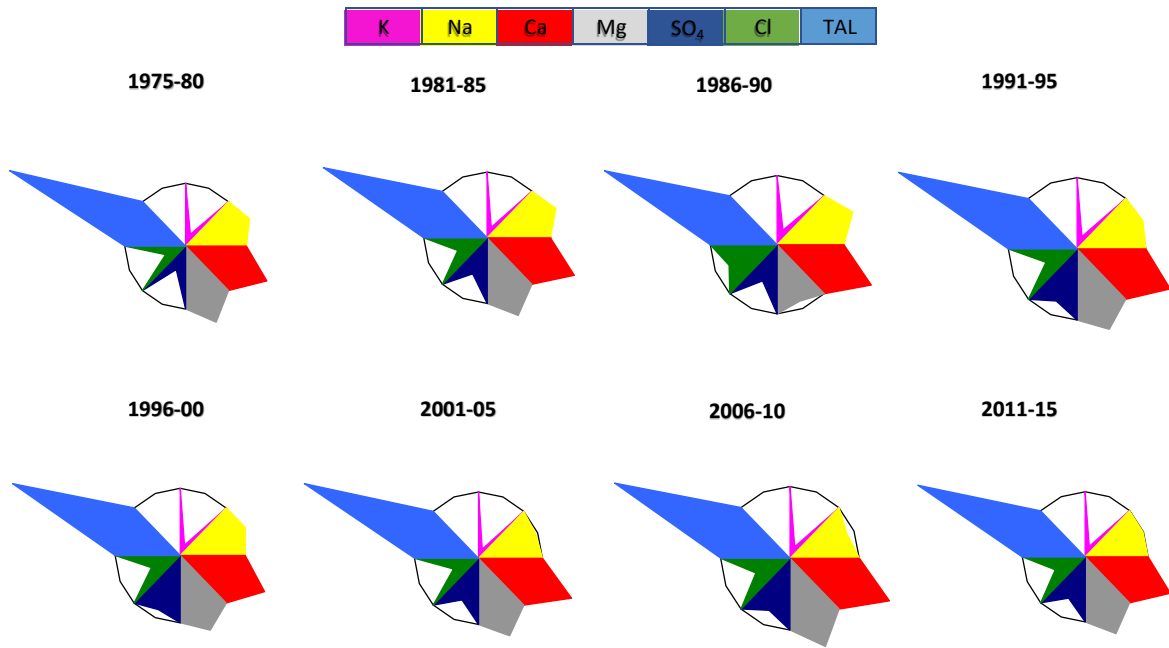


Figure 4.5: Maucha diagram at C1R001 Vaal Dam on Vaal River Monitoring Station

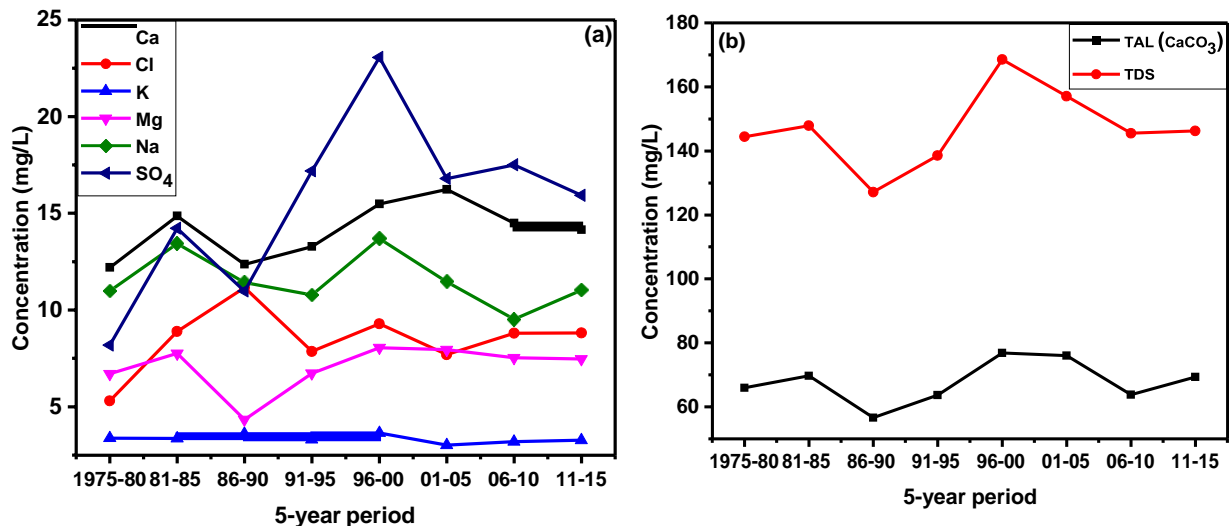


Figure 4.6: Graphical representation of salt changes over an average 5-year period at C1R001 Vaal Bank on Vaal Dam on Vaal River

From the result obtained (Tables 4.5 and 4.6), the major contributor to salinity in this study catchment area was TAL and sulfate. It was observed between 1996-2000, there was an increase in the concentration of all salts, however, this was more pronounced in TAL, TDS and SO₄. Of interest is the peak in sulfate concentration between 1996-2000. Other significant contributors to salinity were Na and Ca. Despite the rise in concentration of all salts between 1996-2000, the salinity composition percentage remained relatively stable throughout the entire 40 years duration of the study with very little fluctuation. This observation contrasted with that recorded in CH8001 and C17H017, where there was a sudden increase in salt concentration between 1975-80 and relative stability thereafter.

Table 4.5: Percentage composition of individual salts in the Maucha diagram to TDS concentration at C1R001 Vaal Dam on Vaal River

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	10.8	4.70	3.00	5.95	9.75	7.27	58.5
1981-85	11.2	6.73	2.54	5.87	10.2	10.8	52.7
1986-90	11.2	10.1	3.26	3.93	10.3	9.93	51.3
1991-95	10.8	6.40	2.69	5.48	8.79	14.0	51.8
1996-00	10.3	6.19	2.43	5.36	9.13	15.4	51.2
2001-05	11.7	5.53	2.17	5.71	8.24	12.1	54.6
2006-10	11.6	7.05	2.57	6.03	7.63	14.0	51.1
2011-15	10.9	6.78	2.52	5.75	8.48	12.3	53.3

Table 4.6: 5-year averages of ions at C1R001Q01 Vaal Dam on Vaal River

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	12.2	5.3	3.4	6.70	11.0	8.2	66.0	112.8
1981-85	14.9	8.9	3.36	7.8	13.4	14.2	69.7	132.2
1986-90	12.4	11.2	3.60	4.3	11.4	11.0	56.7	110.5
1991-95	13.3	7.9	3.30	6.73	10.8	17.2	63.7	122.8
1996-00	15.5	9.3	3.65	8.1	13.7	23.1	76.9	150.1
2001-05	16.2	7.70	3.02	7.9	11.5	16.8	76.0	139.2
2006-10	14.5	8.80	3.20	7.5	9.50	17.5	63.9	124.9
2011-15	14.1	8.8	3.28	7.47	11.0	15.9	69.3	130.0

4.3 Upper River Course five yearly average concentrations of TDS, TAL, and SO₄

The salinity composition of the Vaal River and its tributaries was mainly dependent on the concentration of SO₄, TAL and TDS.

4.3.1 Upper River Course: C8H001, C17H017, and C1R001 5-yearly average TDS concentration

TDS concentration of 5 yearly averages of the monitoring stations C8H001, C17H017 and C1R001 is presented in Figure 4.7. At the monitoring station C8H001, there was an overall decrease in TDS concentration across the entire 40-year span of the study. The highest 5-year average TDS value (Table 4.1) was recorded between 1975-1980 and was followed by a subsequent sudden dip in the 1981-1985 timeframe. The lowest TDS 5-year average concentration was recorded in the 2011-2015 timeframe. However, from the recorded 5-year TDS averages from 1986 onwards, there was alternating increase and decrease in TDS concentration. C17H017 had a higher 5-year average TDS concentration (Figure 4.7 and Table 4.3) as compared to C8H001. In a reversal of the 5-year average TDS concentration trend for C8H001 and C17H017, C1R001 (Figure 4.7) had the lowest 5-year average TDS concentration

values across the entire duration of the study. Contrastingly, 5-year average TDS values of C1R001 rose steadily across the timeframe of the study with the highest value recorded between the 1996-2000 timeframe. The 5-year average TDS concentration was relatively low despite it being the most downstream of the samples analysed in zone 1.

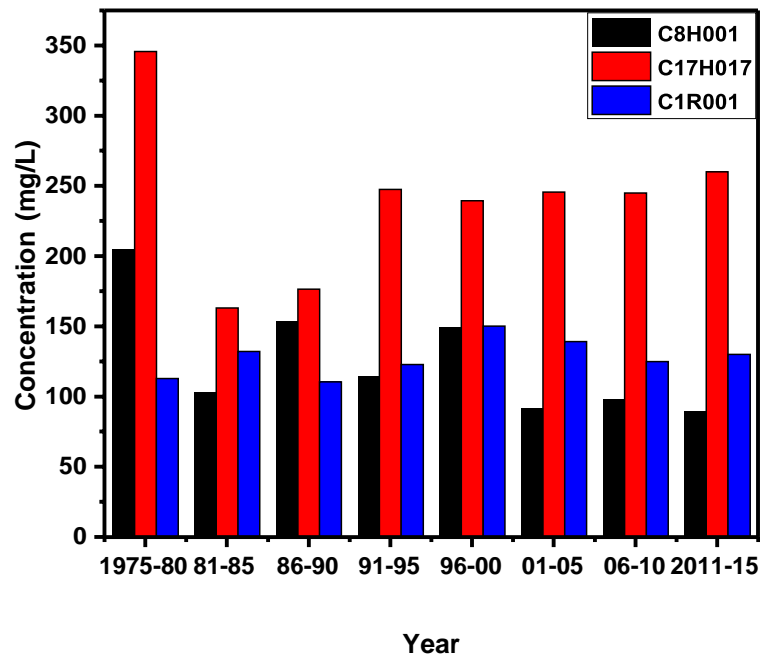


Figure 4.7: Five-year average TDS concentration at C8H001, C17H017 and C1R001 monitoring stations

4.3.2 Upper River Course: C8H001, C17H017, and C1R001 5-yearly average TAL concentration

The 5-year average concentration for TAL had a similar trend to TDS for C8H001, C17H017 and C1R001 monitoring stations. At the monitoring station C8H001, there was an overall decrease in TAL concentration across the entire 40-year span of the study. The highest 5-year average TAL value (Table 4.1, Figure 4.8) was recorded between 1975-1980 with a sharp decline over the next 5-year average time frame (1981-1985), and the lowest value recorded in the 2011-2015 timeframe. Thereafter, the 5-year averages for TAL became relatively stable over the last 3 decades of the study. A similar trend was observed for the monitoring station C17H017. C17H017 had the highest TAL concentration in zone 1 (river upstream). C1R001 5-year average TAL concentration (Figure 4.8) had a similar trend to the 5-year average TDS concentration. The highest 5-year average TAL concentration was recorded between 1996-2000 and the lowest obtained between 1986-1990. However, in comparison to the other 2 monitoring sites, the changes in C1R001 TAL concentration was minimal and the value relatively stable over the 40-year study period.

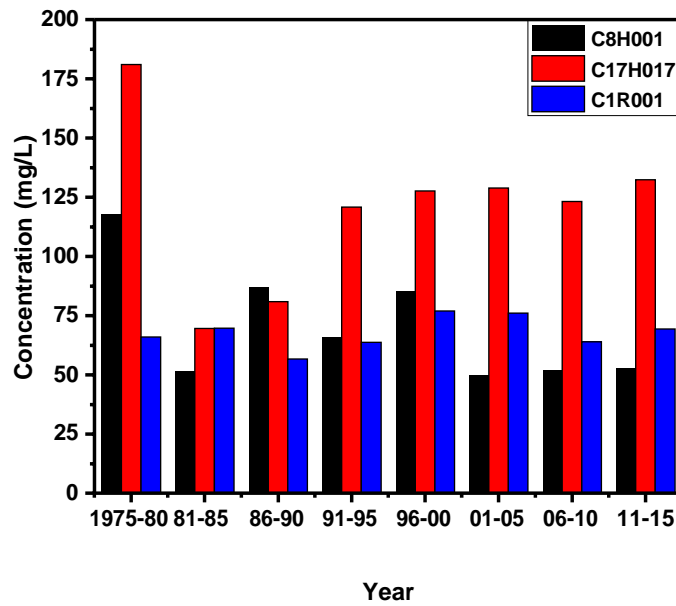


Figure 4.8: Five-year average TAL concentration at C8H001, C17H017 and C1R001 monitoring stations

4.3.3 Upper River Course: C8H001, C17H017, and C1R001 5-yearly average SO₄ concentration

The 5-year average concentration for SO₄ had a similar trend to TDS and TAL for C8H001, C17H017 and C1R001 monitoring stations. At the monitoring station C8H001, there was an overall decrease in SO₄ concentration across the entire 40-year span of the study. The highest 5-year average SO₄ value (Table 4.1, Figure 4.9) was recorded between 1975-1980 with a sharp decline in concentration in the next 5-year period (1981-1985). The lowest SO₄ concentration was recorded between 2011-2015. C17H017 (Figure 4.9) had the highest SO₄ concentration as compared to the other 2 sites in zone 1 (river upstream). A similar phenomenon was recorded for TDS and TAL concentration in C17H017 monitoring station. The highest and lowest SO₄ concentration was recorded in 1975-1980 and 1996-2000, respectively.

C1R001 5-year average SO₄ concentration (Figure 4.9) had a similar trend to the 5-year average TDS and TAL concentration. However, in contrast to C8H001 and C17H017 SO₄ concentration, the highest 5-year average SO₄ concentration for C1R001 was recorded between 1996-2000 and the lowest between 1975-1980.

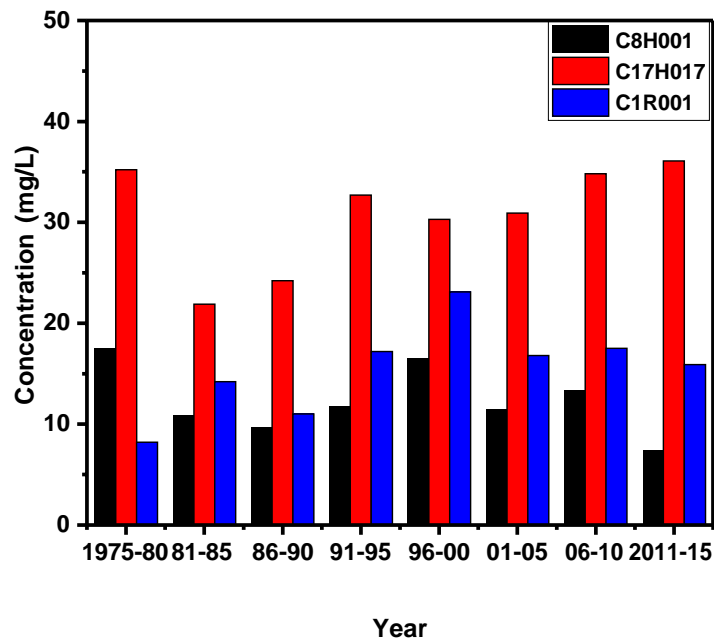


Figure 4.9: Five-year average sulfate concentration at C8H001, C17H017 and C1R001 monitoring stations

4.4 River Middle stream (Zone 2): C2R008, C2H1404, C2H007 and C9H21 sections

4.4.1 C2R008 Vaal Barrage on Vaal River (Lower end of Vaal Triangle)

C2R008 is the first monitoring station in the Vaal River midstream section, and it is classified in zone 2 of the study catchment area. This zone is referred to as the Vaal barrage sub-catchment. In this zone, the water quality is poor as the river drains the highly industrialised Witwatersrand area.

The Maucha diagram (Figure 4.10) and the average 5-year salt change (Figure 4.11) shows the variation in concentration of salts and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

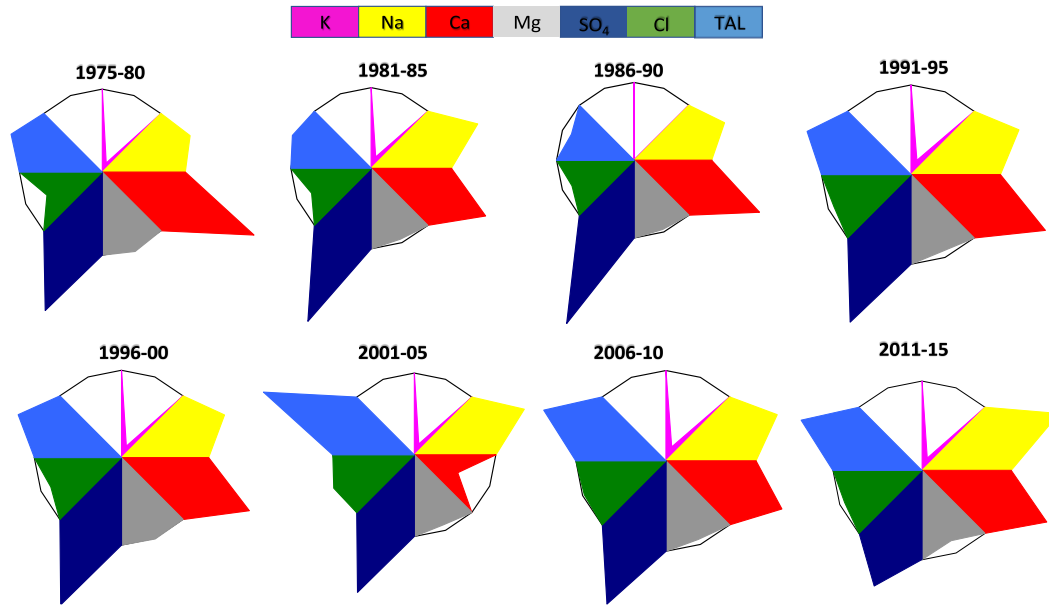


Figure 4.10: Maucha diagrams C2R008 Vaal Barrage on Vaal River (Lower end of Vaal Triangle)

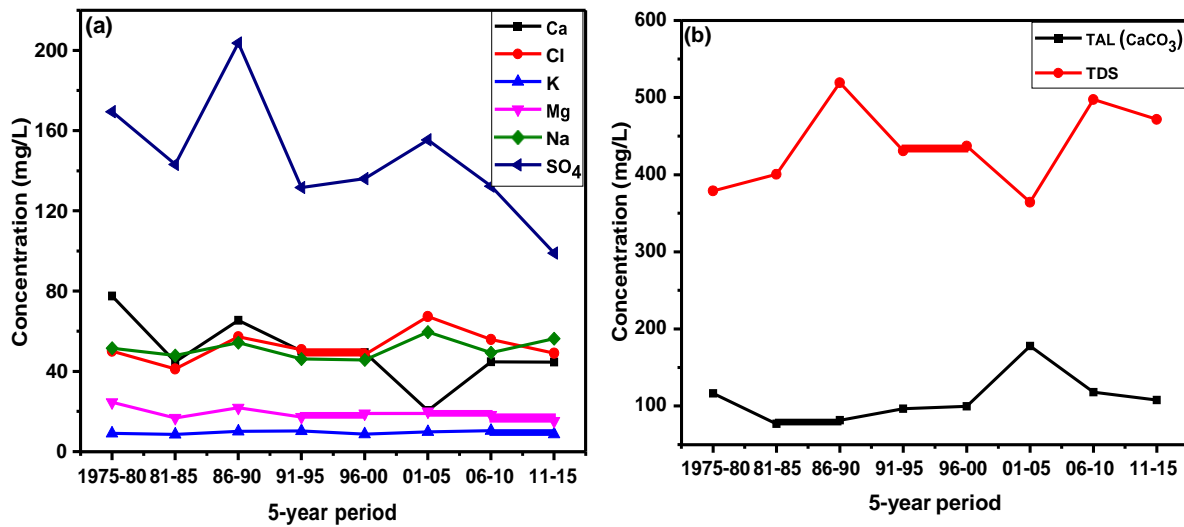


Figure 4.11: Graphical representation of salt changes over an average 5-year period at C2R008 Vaal Barrage on Vaal River near Barrage Wall

From the result (Figures 4.10 and 4.11 and Table 4.7), the major contributor to salinity was sulfate and TAL. Interestingly, it was observed that sulfate was the significant contributor to salinity at this site in contrast to zone 1 where TAL was the main contributor.

Over the course of the 40-year period (Table 4.8), it was noted that the concentration levels of all the salts were relatively stable with the exception being sulfate. However, minor changes were observed between 1981-1985, where salt concentration levels dropped slightly from the initial highs experienced

between 1975-1980. Nonetheless, the levels of salts increased appreciably (most notably sulfate) in 1986-90, thereafter, the concentration of all salts becomes stabilized. However, there was a remarkable drop in sulfate concentration which occurred between 2011-2015. Furthermore, percentage ratio of all salt remains relatively constant over the years (Table 4.7) showing minor increases and decreases (Table 4.8) in salt levels.

Table 4.7: Percentage composition of individual salts in the Maucha diagram to TDS concentration at C2R008: Vaal Barrage on Vaal River (Lower end of Vaal Triangle)

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	15.6	10.0	1.83	4.93	10.3	34.0	23.4
1981-85	11.8	10.9	2.25	4.42	12.6	37.7	20.3
1986-90	13.2	11.6	2.05	4.43	11.0	41.2	16.5
1991-95	12.4	12.6	2.57	4.28	11.5	32.6	24.0
1996-00	12.1	11.9	2.13	4.68	11.2	33.4	24.5
2001-05	4.01	13.2	1.92	3.93	11.7	30.4	34.9
2006-10	10.4	13.0	2.50	4.28	11.5	30.8	27.5
2011-15	11.7	12.9	2.28	4.01	14.8	26.0	28.4

Table 4.8: 5-year averages of ions at C2R008 Vaal Barrage on Vaal River near Barrage Wall

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	77.6	50.1	9.20	24.6	51.5	169.4	116.6	498.9
1981-85	44.8	41.2	8.53	16.8	47.9	143.2	77.1	379.6
1986-90	65.4	57.3	10.1	21.9	54.2	203.7	81.8	494.4
1991-95	50.2	50.8	10.4	17.2	46.2	131.5	96.8	403.3
1996-00	49.4	48.3	8.66	19.0	45.7	136.0	99.8	406.9
2001-05	20.5	67.4	9.83	20.05	59.6	155.4	178.0	510.7
2006-10	44.8	55.9	10.5	18.4	49.4	132.3	118.0	429.3
2011-15	44.6	49.0	8.69	15.3	56.3	99.0	108.0	380.9

4.4.2 C2H1404: Vaal River at Woodlands/Goose Bay Canyon

This station is a little further downstream from the Vaal Barrage and it is classified as part of zone 2 of the study catchment area. Therefore, it is expected that the water in C2H1404 should be similar to that in C2R008 but with a lower quality. The Maucha diagram (Figure 4.12) and the average 5-year salt change (Figure 4.13) shows the variation in concentration, and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

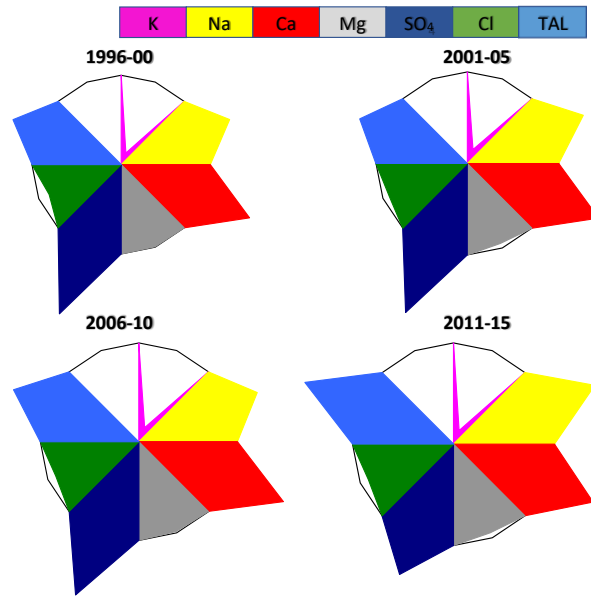


Figure 4.12: Maucha diagrams of C2H1404: Vaal River at Woodlands/Goose Bay Canyon

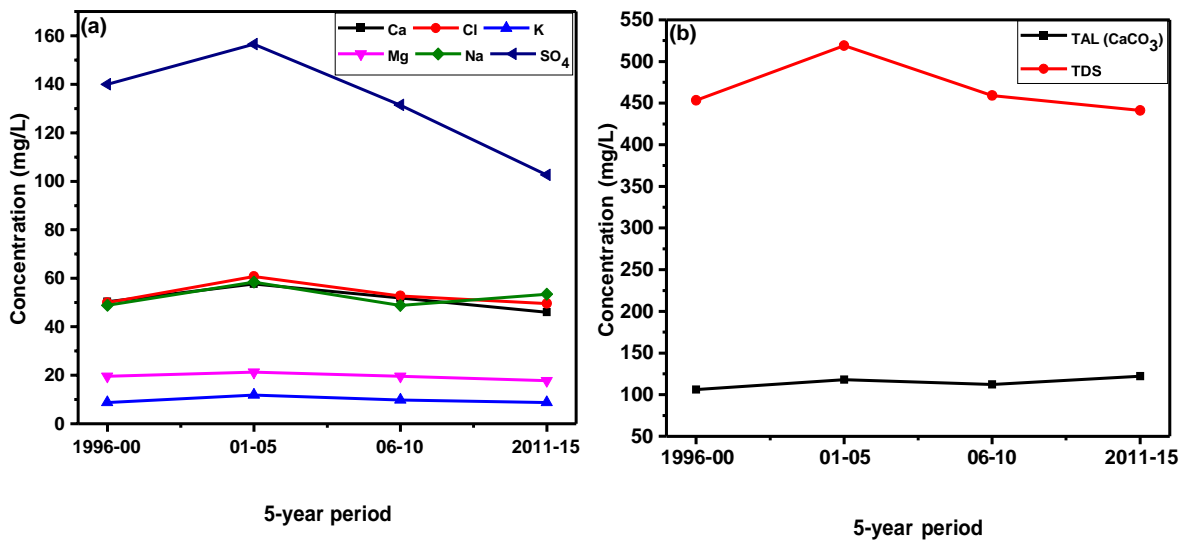


Figure 4.13: Graphical representation of salt changes over an average 5-year period at C2H1404 Vaal River at Woodlands/Goose Bay Canyon

From the result (Figures 4.12 and 4.13), the major contributor to salinity was TAL, SO₄ and TDS. It was observed that unlike in zone 1, the concentration (relative ratio) of SO₄ levels to salinity was quite high but the value was lower as compared to that obtained in C2R008. It was also observed that sulfate was a significant contributor to salinity and the concentration levels was higher than in zone 1.

Over the course of the 20-year period (Table 4.9), it was noted that except for sulfate the concentration levels of all the salts were relatively stable. The sulfate concentration showed a decrease from 2005 to

2015. However, minor changes were observed between 2001-2008, where salt concentration levels

increased slightly from 1996-2000. Thereafter, the concentration of all salts became stabilised. Except for sulfate, the percentage ratio of salts remained relatively constant over the years (Table 4.10) showing minor increases and decreases in salt levels.

Table 4.9: Percentage composition of individual salts in the Maucha diagram to TDS concentration at C2H1404 Vaal River at Woodlands/Goose Bay Canyon

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1996-00	11.9	11.8	2.07	4.61	11.5	33.1	25.0
2001-05	11.9	12.5	2.44	4.38	12.1	32.3	24.3
2006-10	12.2	12.4	2.31	4.58	11.4	30.8	26.3
2011-15	11.5	12.4	2.19	4.42	13.3	25.6	30.5

Table 4.10: 5-year averages of ions at C2H1404 Vaal River at Woodlands/Goose Bay Canyon

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1996-00	50.4	49.9	8.76	19.5	48.9	139.9	106.0	423.4
2001-05	57.6	60.8	11.8	21.2	58.4	156.5	117.9	484.3
2006-10	51.8	52.7	9.84	19.5	48.7	131.4	112.1	426.1
2011-15	46.0	49.6	8.78	17.7	53.4	102.5	122.2	400.2

4.4.3 C2H007: Pilgrims Estate at Orkney on Vaal River

This is the third monitoring station in zone 2 of the catchment area and it is further downstream from the Vaal Barrage. The water in this monitoring station is expected to be of a lesser quality when compared to the other 2 stations which may be attributed to increased gold mining in the area. The Maucha diagram (Figure 4.14) and the average 5-year salt change (Figure 4.15) shows the variation in concentration and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

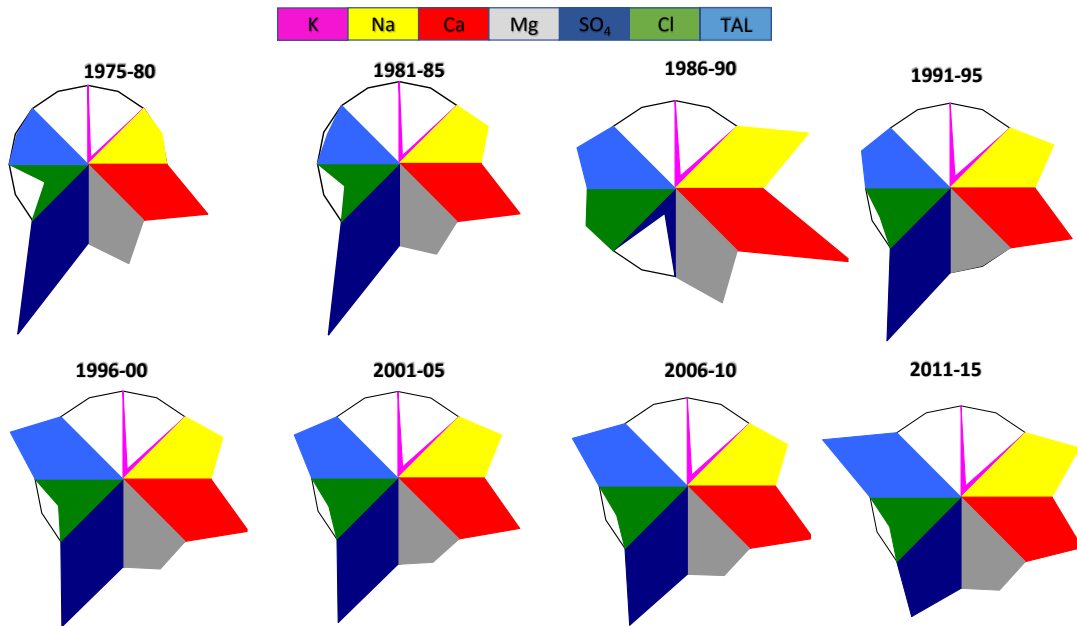


Figure 4.14: Maucha diagrams of C2H007: Pilgrims Estate at Orkney on Vaal River

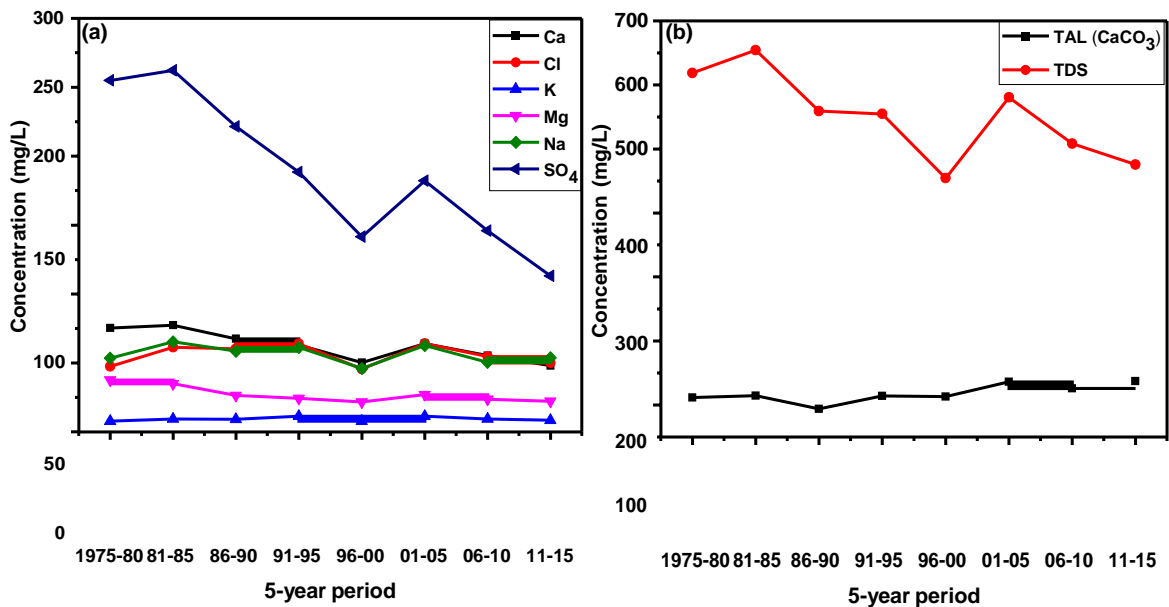


Figure 4.15: Graphical representation of salt changes over an average 5-year period at C2H007 Pilgrims Estate 272 at Orkney on Vaal River

From the result (Figures 4.14 and 4.15), the major contributor to salinity was TAL and SO₄. It was observed that the concentration of SO₄ to salinity levels was very high, it was higher than the values obtained in all of zone 1 and also in zone 2 (C2H1404 and C2R008). Sulfate accounted for almost 50% of the salinity recorded in this monitoring station.

Over the course of the temporal 40-year study period (Table 4.11), it was noted that the concentration levels of most salts were relatively stable. However, sulfate levels changed significantly. The highest

levels of sulfate were recorded between 1981-1985, thereafter sudden drops in sulfate levels were recorded until 1996-2000. During 2001-2005, there was a sudden spike in sulfate concentration and a subsequent decline occurring during the next 10 years. However, for other salts except sulfate their concentration was relatively stable. Furthermore, percentage ratio of salts except sulfate remained relatively constant over the years (Table 4.12) showing minor increases and decreases in salt levels.

Table 4.11: Percentage composition of individual salts in the Maucha diagram to TDS concentration at C2H007: Pilgrims Estate at Orkney on Vaal River

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	12.8	8.90	1.33	6.41	9.08	43.3	18.9
1981-85	12.4	9.84	1.49	5.61	10.5	41.9	18.3
1986-90	12.6	11.2	1.71	4.93	10.9	41.2	17.4
1991-95	12.0	12.2	2.15	4.60	11.6	35.8	21.7
1996-00	11.8	10.7	1.83	5.12	10.8	33.2	26.5
2001-05	11.7	11.7	2.06	4.92	11.4	33.3	24.9
2006-10	11.9	11.8	2.00	5.10	10.8	31.4	27.0
2011-15	11.1	11.6	1.97	5.15	12.4	26.1	31.6

Table 4.12: 5-year averages of ions at C2H007 Pilgrims Estate 272 at Orkney on Vaal River

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	75.4	47.6	7.84	37.7	53.4	255.1	111.5	588.5
1981-85	77.4	61.5	9.32	35.1	65.4	262.2	114.4	625.3
1986-90	67.6	60.2	9.17	26.5	58.6	221.6	93.8	537.5
1991-95	62.9	64.0	11.3	24.2	61.3	188.4	114.1	526.2
1996-00	50.3	45.7	7.81	21.8	45.9	141.6	112.9	426.0
2001-05	64.1	64.2	11.3	26.9	62.6	182.2	136.2	547.5
2006-10	55.3	54.7	9.29	23.7	50.5	146.0	125.8	465.4
2011-15	48.0	50.1	8.52	22.3	53.9	113.2	137.1	433.1

4.5 Zone 3: River Midstream

4.5.1 C9H21: Vaal River below Bloemhof Dam

This monitoring station is the only one in zone 3 and it is referred to as the Bloemhof catchment.. The Maucha diagram (Figure 4.16) and the average 5-year salt change (Figure 4.17) shows the variation in concentration and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

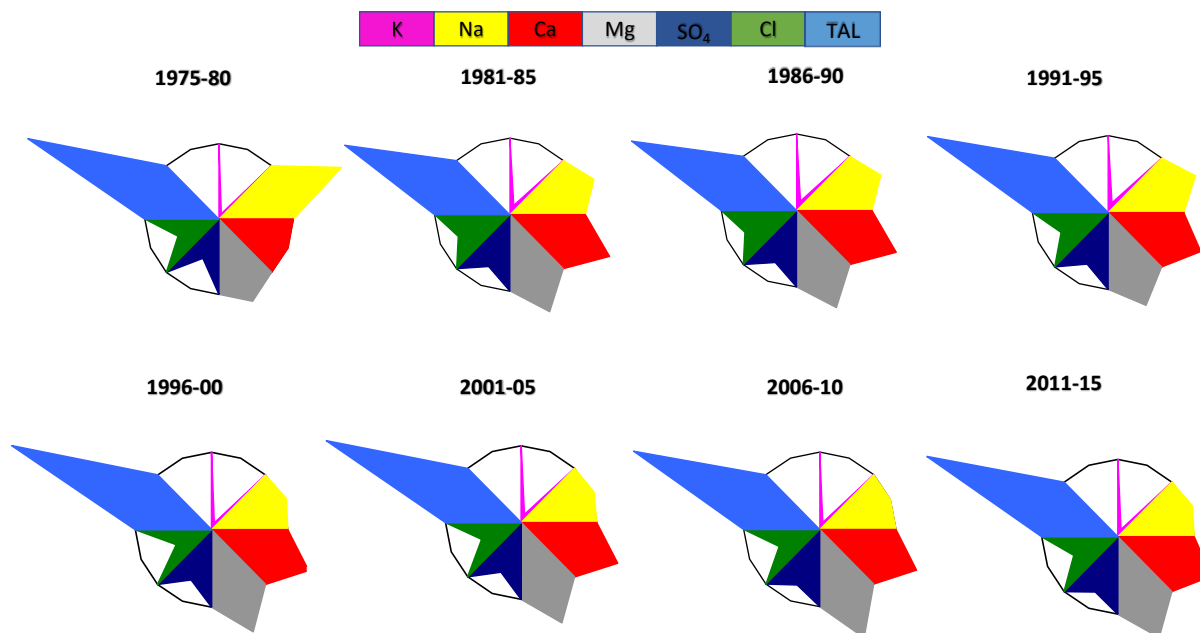


Figure 4.16: Maucha diagrams of C9H21 Vaal River below Bloemhof Dam

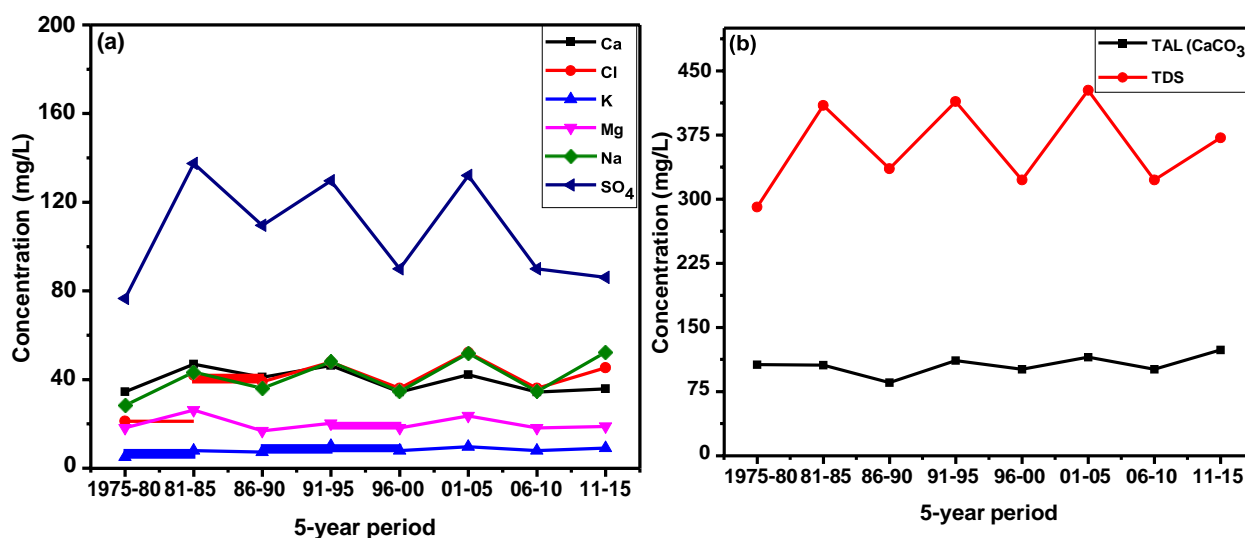


Figure 4.17: Graphical representation of salt changes over an average 5-year period at C9H021 Bloemhof Dam on Vaal River Down Stream Weir

From the result (Figures 4.16, Table 4.13), the major contributor to salinity was TAL and SO₄. It was observed that the concentration of SO₄ to salinity levels were very high and was higher than the values obtained in zone 1 but lower than the values recorded in zone 2. Sulfate accounted for a third of the salinity recorded in the Bloemhof dam monitoring station. Sulfate concentration was relatively stable

throughout the entire study duration.

Over the course of the temporal 40-year study period (Table 4.14), it was noted that the concentration levels of all the salts were relatively stable. However, minimal increases/decreases in salt concentrations were recorded in alternating 5-year cycles with slightly higher concentration recorded during 2011-2015. The highest concentrations for all salts were recorded 2001-2005 and this was very profound for sulfate. For the most part, the percentage ratio of all salts except Na and Ca remained relatively constant over the years (Table 4.14) showing minor increases/decreases.

Table 4.13: Percentage composition of individual salts in the Maucha diagram at C9H021 Bloemhof Dam on Vaal River Down Stream Weir

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	11.9	7.31	1.77	6.28	9.77	26.4	36.6
1981-85	11.5	10.2	1.96	6.42	10.6	33.5	25.8
1986-90	12.2	11.6	2.19	5.03	10.8	32.7	25.5
1991-95	11.2	11.6	2.46	4.88	11.6	31.3	26.9
1996-00	10.7	11.2	2.49	5.64	10.7	27.9	31.3
2001-05	9.89	12.2	2.29	5.53	12.2	30.9	27.0
2006-10	10.7	11.2	2.49	5.64	10.7	27.9	31.3
2011-15	9.65	12.2	2.46	5.10	14.1	23.2	33.3

Table 4.14: 5-year averages of ions at C9H021 Bloemhof Dam on Vaal River Down Stream Weir

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	34.5	21.3	5.14	18.2	28.4	76.7	106.4	290.5
1981-85	47.0	42.0	8.02	26.3	43.4	137.5	105.7	409.9
1986-90	41.0	39.1	7.34	16.9	36.1	109.6	85.6	335.6
1991-95	46.4	48.0	10.2	20.2	48.1	129.8	111.2	414.0
1996-00	34.4	36.1	8.04	18.2	34.6	90.0	100.9	322.3
2001-05	42.2	52.3	9.77	23.6	52.0	132.1	115.3	427.2
2006-10	34.4	36.1	8.04	18.2	34.6	89.96	101.0	322.3
2011-15	35.8	45.4	9.13	19.0	52.4	86.1	123.5	371.4

4.5.2 Middle Zone, five yearly average concentrations of TDS, TAL, and SO₄

The salinity composition of the Vaal River and its tributaries was mainly dependent on the concentration of SO₄, TAL and TDS.

4.5.3 Middle River Course: C2R008, C2H1404 and C2H007C9H21 5-yearly average TDS concentration

TDS concentration of 5 yearly averages of the monitoring stations C2R008, C2H1404, C2H007 and C9H21 is presented in Figure 4.18. At the monitoring station C2R008, there was a slight net overall decrease in TDS concentration across the entire 40-year span of the study. The highest 5-year average

TDS value (Table 4.7) was recorded between 2001-2005 and the lowest was recorded between the 1981-1985 timeframe. However, TDS value over the span of 40 years can be said to be relatively stable. The TDS concentration of C2H1404 was relatively stable throughout the entire duration of the study. However, the highest 5-year average TDS concentration (Figure 4.13 and Table 4.9) in C2H1404 was recorded between 2001-2005 and the lowest between 2011-2015. The 5-year average TDS concentration C2H007 (Figure 4.15 and Table 4.11) was highest between 1981-1985 and the lowest between 1986-1990. Besides the massive dip experienced in the 5-year TDS value between 1986-1990, the TDS 5-year average value recorded was relatively stable over the period of study. Initially, the 5-year average TDS values was low at the beginning of the study (1975-1980) but it increased gradually with the peak occurring between 2001-2005. However, the 5-year TDS average over the duration of the study became relatively stable with slight increase/decrease during certain period of the study.

Generally, the 5-year average TDS concentration in zones 2 and 3 was greater as compared to the values obtained in zone 1. It was also observed that the 5-year average TDS value in zones 2 and 3 was relatively stable, however, there are intermittent increases/decreases in 5-year average value. Lastly, the highest 5-year TDS average was recorded in C2H007, followed by C2R008, C2H1404 and the least was C9H21.

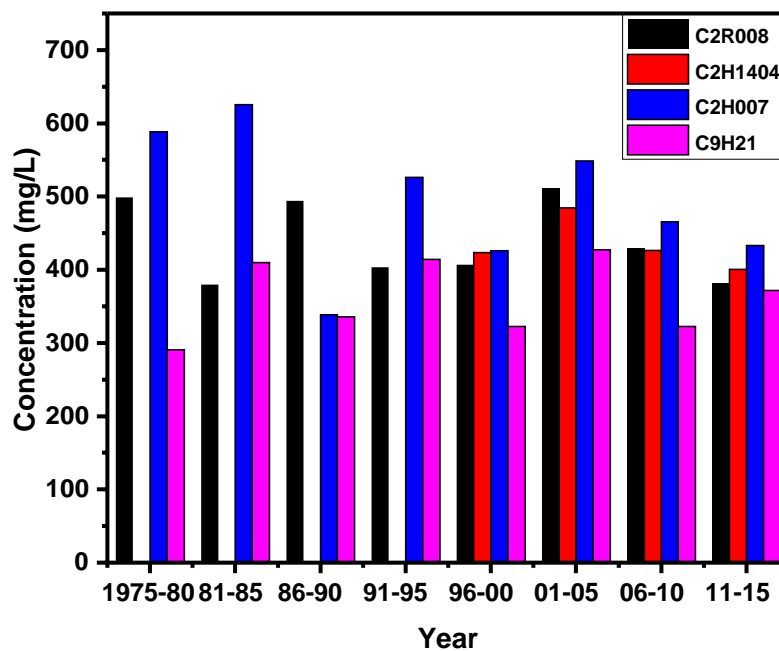


Figure 4.18: Five-year average TDS concentration at C2R008, C2H1404, C2H007 and C9H21 monitoring stations

4.5.4 Middle River Course: C2R008, C2H1404, and C2H007 and C9H21 5-yearly average SO₄ concentration

Sulfate concentration of 5 yearly averages of the monitoring stations C2R008, C2H1404, C2H007 and C9H21 is presented in Figure 4.19. At the monitoring station C2R008, there was an overall decrease in sulfate concentration across the entire 40-year duration of the study. The highest 5-year average sulfate concentration was observed between 1986-1990 and the lowest between 2011-2015. However, the values were relatively stable over the study timeframe. C2H1404 (Figure 4.19) 5-year average sulfate concentration increased between from 2001-2005 and subsequently declined over the next 10 years timeframe. C2H007 (Figure 4.19) 5-year average sulfate concentration increased between the 1981-1985 timeframe and subsequently declined consistently during the last 30 years of the study. C2H007 is the monitoring station with the highest 5-year average sulfate concentration, with the highest concentration recorded between 1981-1985. C9H21 5-year average sulfate concentration witnessed an increase between 1981-1985 which was the highest and the lowest recorded between 1975-1980 which was when the study commenced. Generally, the 5-year average sulfate concentration in zones 2 and 3 was greater as compared to the values obtained in zone 1. It was also observed that the 5-year average sulfate value in zones 2 and 3 was relatively stable, however, there were intermittent increases/decreases in 5-year average values. Lastly, the highest 5-year sulfate average was recorded in C2H007, followed by C2R008, C2H1404 and the least was C9H21. This was a similar trend observed in 5-year average TDS level analysis.

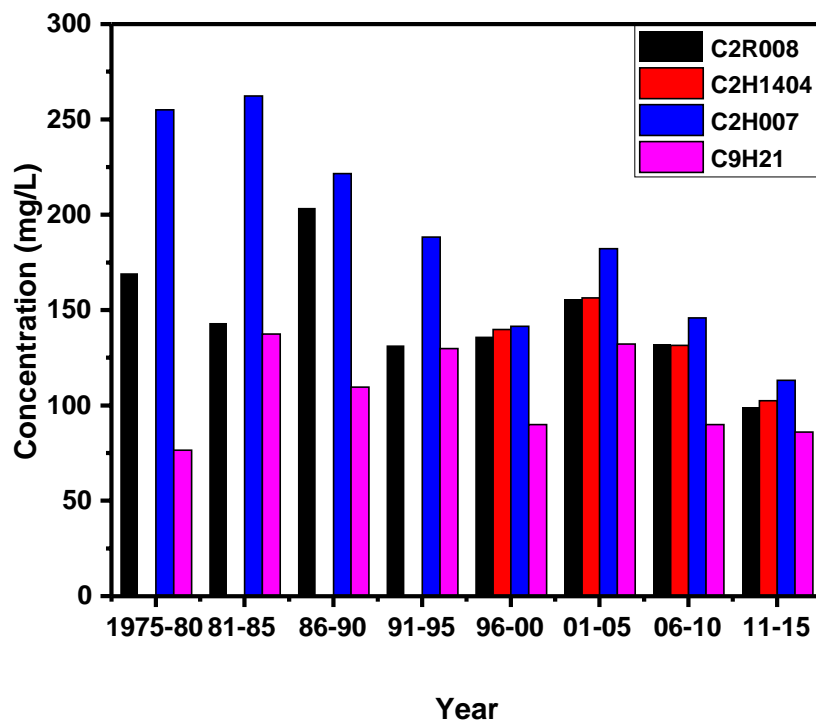


Figure 4.19: Five-year average sulfate concentration at C2R008, C2H1404, C2H007 and C9H21 monitoring stations

4.5.5 Middle River Course: C2R008, C2H1404, C2H007 and C9H21 5-yearly average TAL concentration

The 5-year average concentration for TAL had a similar trend to TDS and sulfate for C2R008, C2H1404, C2H007 and C9H21 monitoring stations. At the monitoring station C2R008, TAL concentration remained relatively constant across the entire 40-year span of the study except between 2001-2005 where a sharp increase in concentration was observed. The highest 5-year average TAL value (Figure 4.20) was recorded between 2001-2005, and the lowest value recorded in the 1981-1985 timeframe. C2H1404 had high TAL concentration in zone 2 (river midstream) with the highest concentration occurring between 2001-2005 and the lowest between 1981-1985. C2H007 5-year average TAL concentration had a similar trend to the 5-year average TDS and sulfate concentration. The highest 5-year average TAL concentration was recorded between 2011-2015 and the lowest obtained between 1986-1990. The 5-year average concentration was relatively stable and increased gradually over the course of the 40-year period. C9H21 5-year average TAL concentration was relatively stable throughout the entire study duration. However, the highest and lowest 5-year average TAL concentration was recorded between 2011-2015 and 1996-2000, respectively. Conclusively, the 5-year average TAL concentration was higher in the monitoring stations present in zones 2 and 3 as compared to zone 1. Lastly, the highest 5-year TAL average was recorded in C2R008, followed by C2H007, C2H1404 and the least was C9H21.

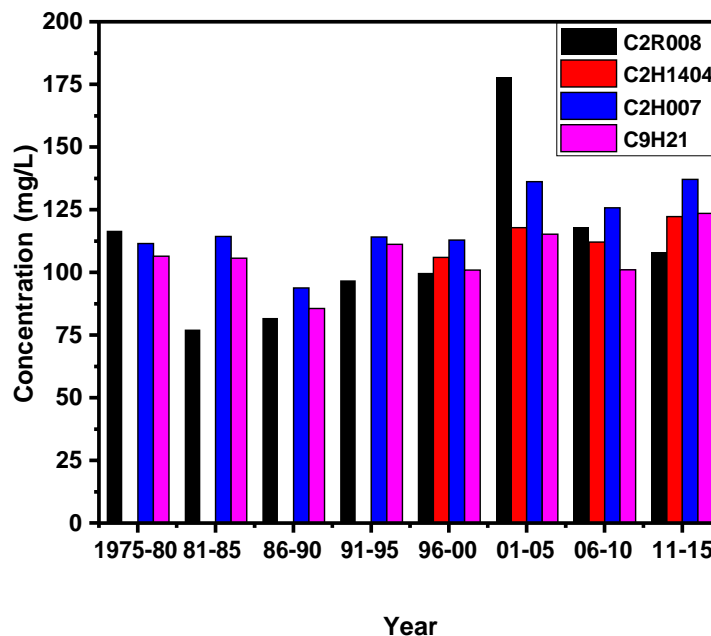


Figure 4.20: Five-year average TAL concentration at C2R008, C2H1404, C2H007 and C9H21 monitoring stations

4.6 Downstream (Zone 4): (C9H10 and C9R003) sections

4.6.1 C9H10 Vaal River Downstream of Vaal-Harts Irrigation Flow

C9H10 is the first monitoring station at the downstream section of the river and it is classified in zone 4 of the study catchment area. This zone is referred to as the Douglas Weir catchment.

The Maucha diagram (Figure 4.21) and the average 5-year salt change (Figure 4.22) shows the variation in concentration of salts and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

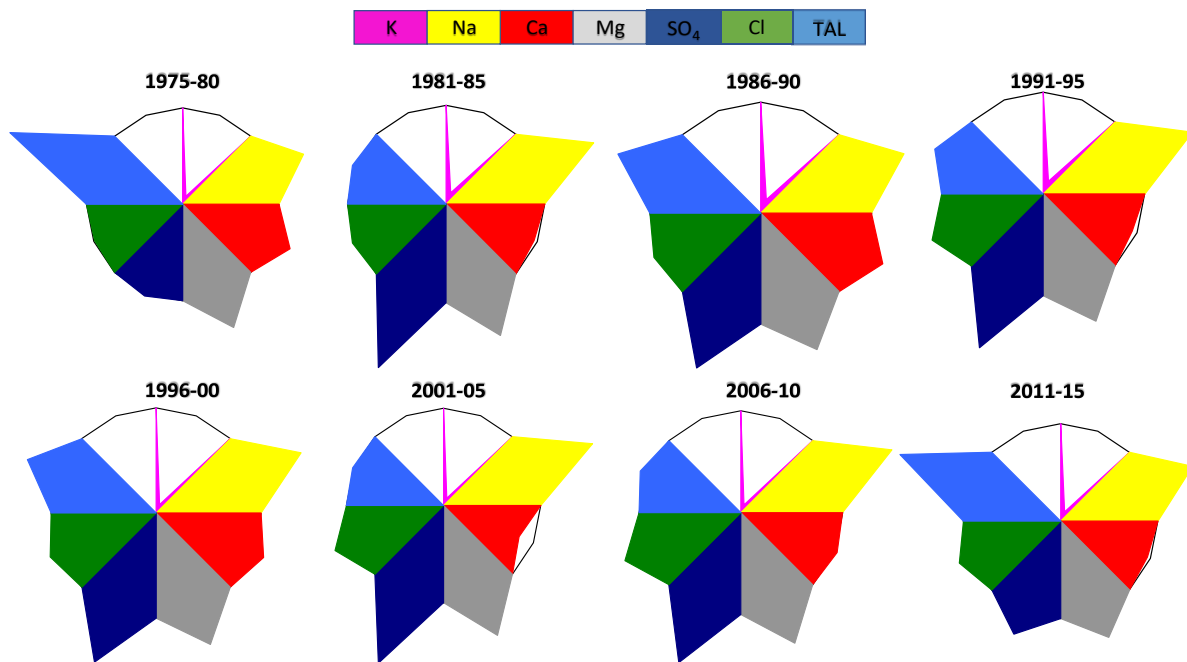


Figure 4.21: Maucha diagram at monitoring station C9H10 Vaal River Downstream of Vaal-Harts Irrigation Flow

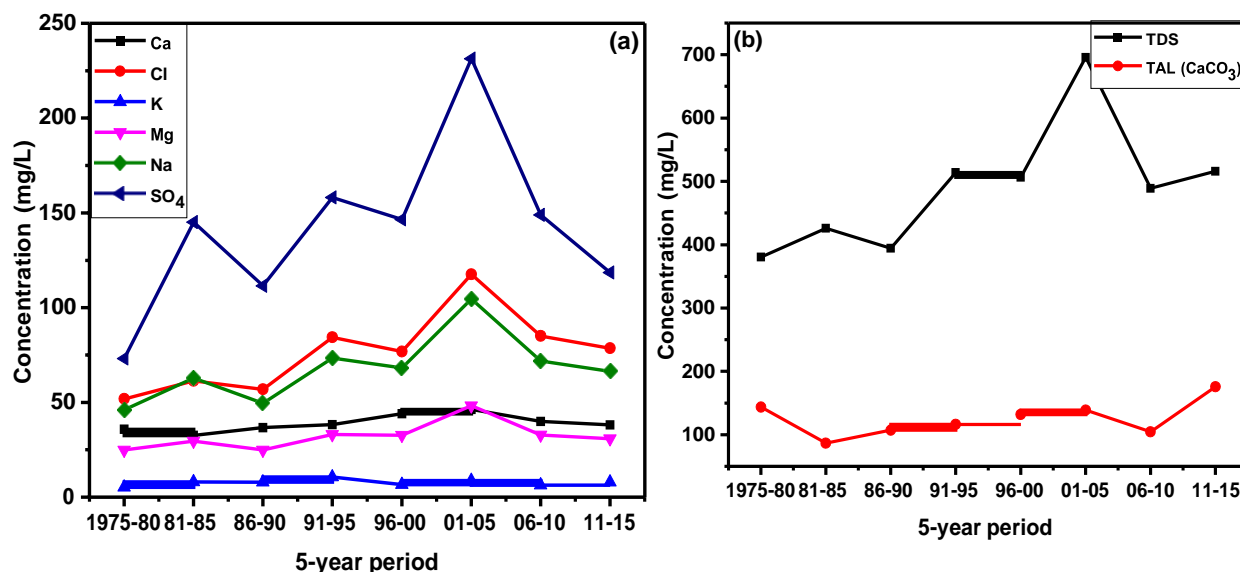


Figure 4.22: Graphical representation of salt changes over an average 5-year period at C9H010 C9H10 Vaal River Downstream of Vaal-Harts Irrigation Flow

From the result (Tables 4.15 and 4.16), the major contributor to salinity was TAL and SO₄. It was observed that the contribution of SO₄ to salinity levels was very high, however, it was slightly lower than the sulfate values recorded in zones 2 and 3. Sulfate accounted for almost one-third of the salinity recorded in this monitoring station.

Over the course of the temporal 40-year study period (Table 4.16), it was noted that the concentration levels of all the salts were relatively stable except for an increase in concentration recorded between 2001-2005. However, sulfate levels changed significantly as there was a drastic increase in sulfate levels between 1981-1985 and 2001-2005 timeframes. Na and Cl followed the same trend. Thereafter, from 2006 onwards there was a reduction in sulfate levels. Over 40 years duration, there was an increase in TDS that was mostly driven by increased sulfate, sodium and chloride concentrations.

Table 4.15: Percentage composition of individual salts in the Maucha diagram C9H010 Wilmea Vaal Gamagara Confluence of Harts and Vaal River

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	9.39	13.6	1.37	6.53	12.1	19.2	37.7
1981-85	7.65	14.4	1.90	6.93	14.7	34.0	20.3
1986-90	9.31	14.4	2.00	6.30	12.5	28.3	27.2
1991-95	7.43	16.4	2.06	6.44	14.3	30.8	22.6
1996-00	8.70	15.2	1.30	6.44	13.5	28.9	26.0
2001-05	6.64	16.9	1.27	6.93	15.0	33.3	20.0
2006-10	8.17	17.4	1.30	6.71	14.7	30.4	21.3
2011-15	7.37	15.2	1.54	5.98	12.9	23.0	34.1

Table 4.16: 5-year averages of ions at Percentage composition of individual salts in the Maucha diagram C9H10 Vaal River Downstream of Vaal-Harts Irrigation Flow

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	35.7	51.8	5.20	24.8	46.2	73.1	143.6	380.5
1981-85	32.6	61.4	8.10	29.5	62.8	145.0	86.6	425.9
1986-90	36.7	56.8	7.91	24.9	49.5	111.5	107.2	394.4
1991-95	38.2	84.4	10.6	33.1	73.4	158.0	116.2	513.9
1996-00	44.1	76.9	6.69	32.6	68.2	146.5	131.8	506.7
2001-05	46.2	117.6	8.84	48.2	104.6	231.3	138.8	695.6
2006-10	40.0	85.0	6.34	32.8	71.9	148.8	104.2	489.1
2011-15	38.0	78.6	7.94	30.9	66.3	118.5	175.7	515.9

4.6.2 Downstream (Zone 4): C9R003 Douglas Barrage on Vaal River

C9R003 is the final monitoring station at the downstream of the river and it is classified in zone 4 of the study catchment area. This zone is referred to as the Douglas Weir catchment. This monitoring station represents the point before the confluence of the Orange River.

The Maucha diagram (Figure 4.23) and the average 5-year salt change (Figure 4.24) shows the variation in concentration of salts and salinity changes in major dissolved ions (K, Na, Ca, Mg, SO₄, TAL and TDS) over a period of 40 years.

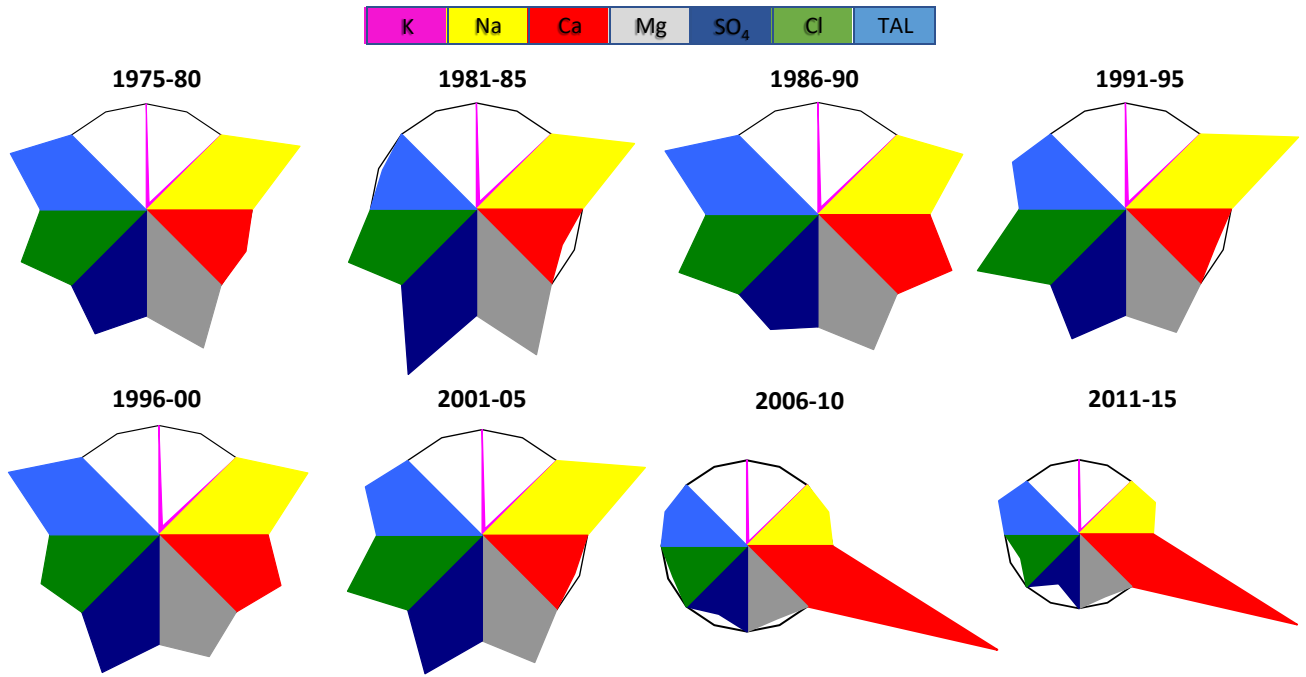


Figure 4.23: Maucha diagrams C9R003 Douglas Barrage on Vaal River (Last point before confluence with the Orange River)

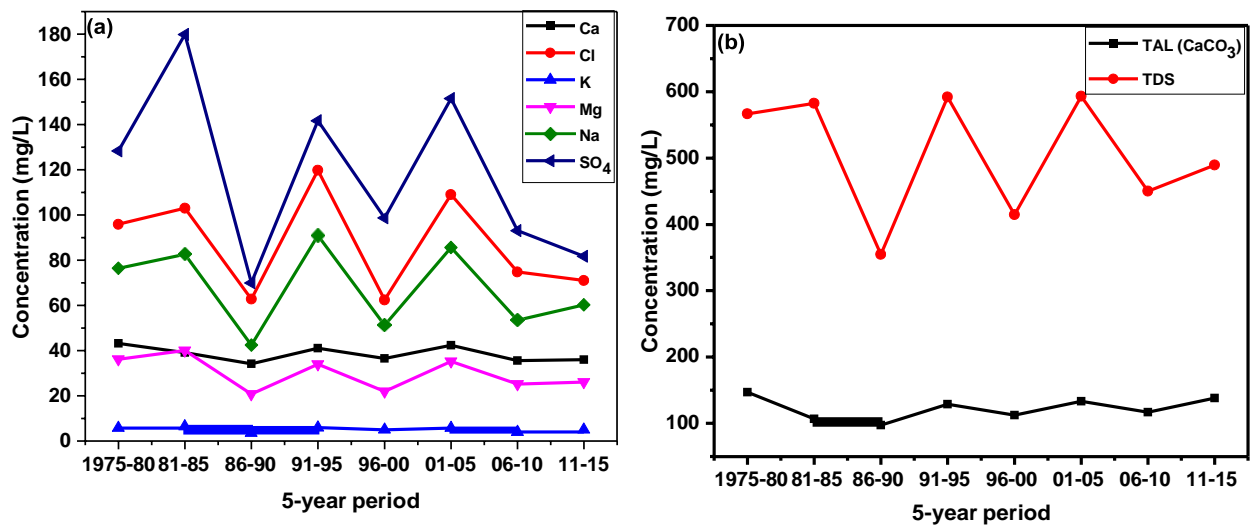


Figure 4.24: Graphical representation of salt changes over an average 5-year period at C9R003 Douglas Barrage on Vaal River (Last point before confluence with the Orange River)

From the result (Tables 4.17 and 4.18), the major contributor to salinity was TAL and a substantial amount Ca and SO₄. It was observed that the contribution of Ca to salinity levels was substantially higher as compared to all the other monitoring stations in zones 1, 2 and 3. Sulfate levels was also significant but was lower when compared to the values recorded in C9H10 and other zones. It accounted for 10-30% of total salinity which represents a major increase in the values recorded from other monitoring stations.

Over the course of the temporal 40-year study period (Table 4.18), it was noted that the concentration levels of all the salts were relatively stable except for Ca, TDS and SO₄. These salts experienced significant increase in concentration levels from 1981-1985, 1991-1995 and 2001-2005. These concentration increases were accompanied by corresponding alternate decreases in the following five-year period.

Table 4.17: 5-year averages of ions at Percentage composition of individual salts in the Maucha diagram C9R003: Douglas Barrage on Vaal River (Last point before confluence with the Orange River)

Year	Ca (mg/L)	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SO ₄ (mg/L)	TAL (CaCO ₃) (mg/L)	ΣTotal (mg/L)
1975-80	43.2	95.9	5.85	36.2	76.5	128.3	147.1	533.1
1981-85	39.1	103.0	6.60	40.1	82.7	179.9	106.8	558.2
1986-90	34.2	62.8	3.65	20.9	42.4	70.0	97.4	331.4
1991-95	41.1	119.8	6.06	34.1	91.0	141.7	129.1	562.8
1996-00	36.6	62.5	5.07	22.1	51.3	98.7	112.7	388.9
2001-05	42.4	109.1	5.80	35.2	85.7	151.5	133.3	563.1
2006-10	35.6	74.8	4.07	25.2	53.6	93.1	116.8	403.2
2011-15	36.0	71.1	5.03	26.2	60.3	81.8	138.3	418.7

Table 4.18: Percentage composition of individual salts in the Maucha diagram C9R003: Douglas Barrage on Vaal River (Last point before confluence with the Orange River)

Year	Ca (%)	Cl (%)	K (%)	Mg (%)	Na (%)	SO ₄ (%)	TAL (CaCO ₃) (%)
1975-80	8.11	18.0	1.09	6.79	14.3	24.1	27.6
1981-85	7.00	18.5	1.18	7.18	14.8	32.2	19.1
1986-90	10.3	18.9	1.1	6.29	12.8	21.1	29.4
1991-95	7.3	21.3	1.08	6.06	16.2	25.2	22.9
1996-00	9.41	16.1	1.3	5.68	13.2	25.4	29.0
2001-05	7.53	19.4	1.03	6.26	15.2	26.9	23.7
2006-10	35.6	18.6	1	6.26	13.3	23.1	29.0
2011-15	36.0	17.0	1.2	6.25	14.4	19.5	33.0

4.6.4 C9H10 and C9R003 five yearly average concentrations of TDS, TAL, and SO₄

4.6.5 Five yearly average concentrations of TDS, TAL, and SO₄

The salinity composition of the Vaal River and its tributaries was mainly dependent on the concentration of SO₄, TAL and TDS.

4.6.6 Down River Course: C9H10 and C9R003 average TDS concentration

TDS concentration of 5 yearly averages of the monitoring stations C9H10 and C9R003 is presented in Figure 4.25. The TDS value is reflective of the water quality and state of the river. At the monitoring station C9H10, there was a slight net overall increase in TDS concentration across the entire 40-year

span of the study. The highest 5-year average TDS value was recorded between 2001-2005 and the lowest was recorded between the 1975-1980 timeframe. However, TDS value over the span of 40 years can be said to be relatively stable. The TDS concentration of C9R003 was relatively stable throughout the entire duration of the study. Nonetheless, the highest 5-year average TDS in C9R003 was recorded between 1991-1995 and the lowest between 1975-1980.

Generally, the 5-year average TDS concentration in zone 4 was greater as compared to the values obtained in zones 1 and 2 but lesser than in zone 3. It was also observed that the 5-year average TDS value in zone 4 was relatively stable, however, there are intermittent increases/decreases in 5-year average value. Lastly, the highest 5-year TDS average was recorded in C9H10 as compared to C9R003.

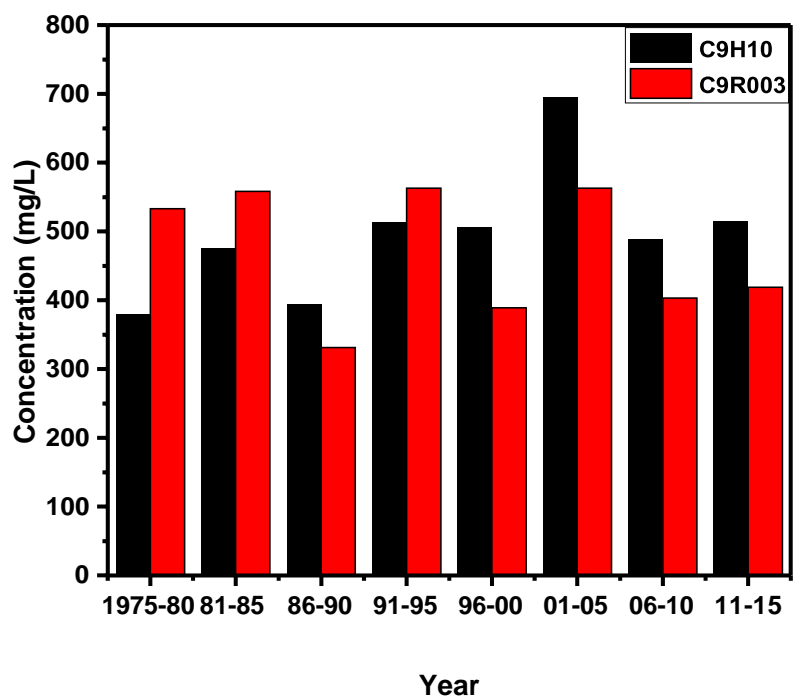


Figure 4.25: Downstream Five-year average TDS concentration at C9H10 and C9R003 monitoring stations

4.6.7 Down River Course: C9H10 and C9R003 average sulfate concentration

Sulfate concentration of 5 yearly averages of the monitoring stations C9H10 and C9R003 is presented in Figure 4.26. At the monitoring station C9H10, there was an overall increase in sulfate concentration across the entire 40-year of the study. The highest 5-year average sulfate concentration was observed between 2001-2005 and the lowest between 1975-1980. Except for the sudden increase in 5-year average concentration levels, the values were relatively stable over the study timeframe. C9R003 (Figure 4.26) 5-year average sulfate concentration increased between 1981-1985 and subsequently decreased and increased in alternate 5-year average period from 1986-2010. The highest 5-year average sulfate concentration was observed between 1981-1985 and the lowest between 1986-1990.

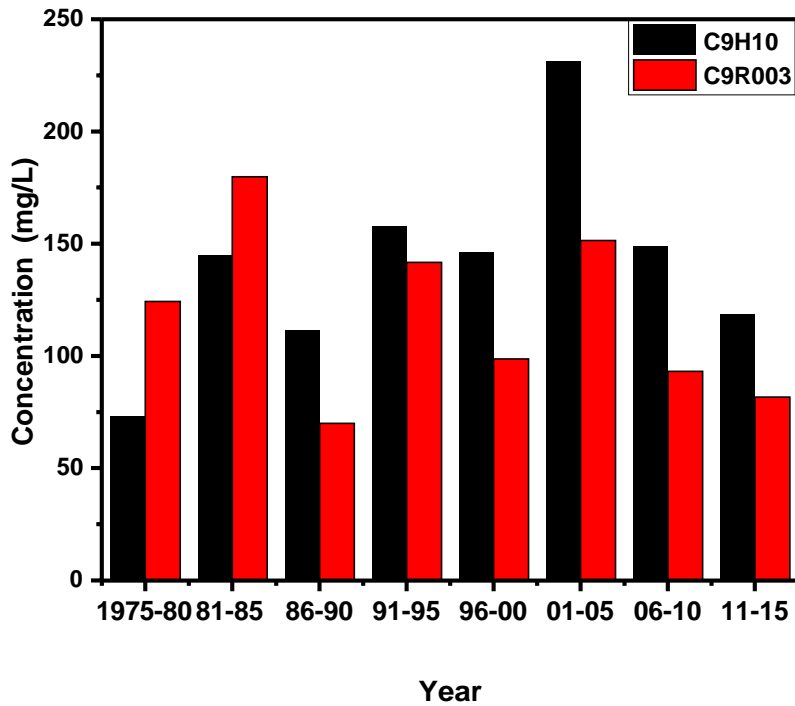


Figure 4.26: Downstream Five-year average sulfate concentration at C9H10 and C9R003 monitoring stations

4.6.8 Down River Course: C9H10 and C9R003 average TAL concentration

The 5-year average concentration for TAL had a similar trend to TDS and sulfate for C9H10 and C9R003 monitoring stations. At the monitoring station C9H10, TAL concentration (Figure 4.27) fluctuated across the entire 40-year span of the study with the peak occurring between the 2011-2015 timeframe and lowest concentration levels occurring between 1981-1985. C9R003 (Figure 4.27) had a higher TAL concentration in zone 4 (river downstream) as compared to C9H10. The highest 5-year average TAL concentration for C9R003 occurred between 1975-1980 and the lowest between 1986-1990. Conclusively, the 5-year average TAL concentration was higher in the monitoring stations present in zone 4 as compared to zone 1 but lesser than in zones 2 and 3.

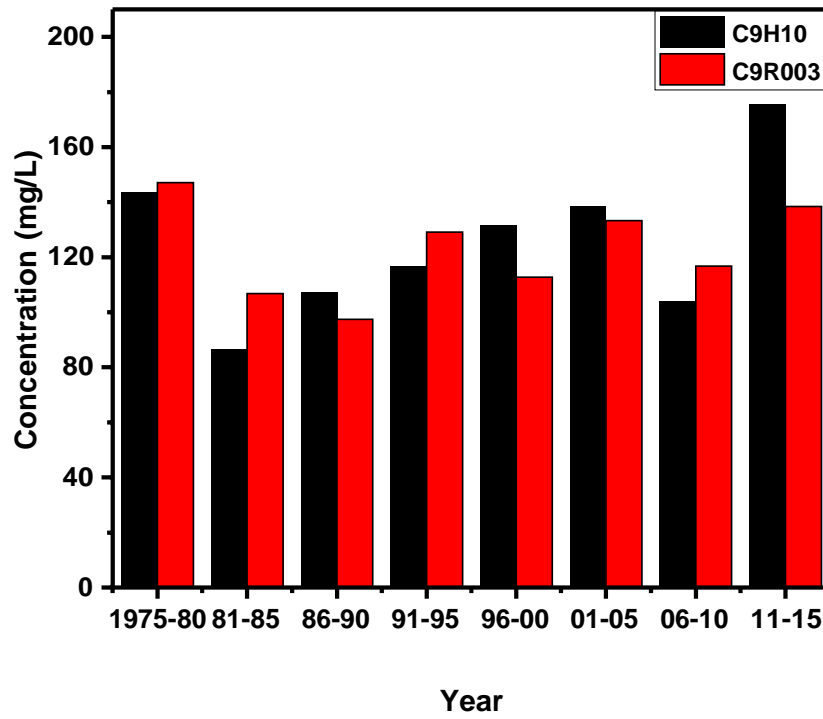


Figure 4.27: Downstream Five-year average TAL concentration at C9H10 and C9R003 monitoring stations

Chapter 5: Discussion and Conclusion

5.1 Introduction

This chapter discusses, the effect of time on salinity concentration and composition in the monitoring stations and unique zones of the Vaal River and its tributaries. Thus, providing insights into the relationship between time and overall salinity of the Vaal River. Furthermore, the relationship between salinity composition and concentration along the course of the Vaal River was examined. From the results obtained and its analysis, the 3 major salts that majorly contributed to salinity composition and concentration of the Vaal River and its tributaries over time in this study are TAL, SO₄ and to a lesser extent Ca.

5.2 Zone 1 (River Upstream)

5.2.1 C8H001: Wilge River Monitoring Station

This study site is in the river upstream and present in zone 1. The water here is of near-natural quality, and it serves as a critical source of water supply to the Vaal River. Due to river use and activities such as agriculture and mining, the water quality has been known to deteriorate further downstream (Braune and Roger, 1987). Based on the Maucha diagrams for C8H001 Monitoring Station (Figure 4.1 and 4.2), it is visibly clear that TDS was high at the beginning of the study period in 1975 and a sharp drop off occurred between 1981-1985. This was followed by a rise in the next 5 years and a sharp decline again between 1991-1995. It was observed that TDS stabilised after the year 2000. This stabilisation in the salinity level at this monitoring station may be due to the in-flow and mixture of water from the Lesotho Highlands Water (Lepono et al., 2003). This pattern was repetitive throughout the entire study duration. For TAL, the percentage contribution towards salinity followed a similar trend and mirrors the pattern of TDS. The TDS and TAL concentration overall decreased during the 40-year period of the study. The salinity composition of C8H001 (Wilge River) is a TAL dominated system.

5.2.2 C17H017: Villers at Flood section on Vaal River Monitoring Station

This monitoring station is in zone 1 and it represents the Vaal River catchment inflow into the Vaal dam. Based on the data obtained from the Maucha diagrams (Figure 4.3 and 4.4), there was a sharp drop off at the initial phase of the study, a trend similar to C8H001. After this drop, concentration of salts increased steadily and stabilised over the remaining period of the study. In C17H017, TAL also dominated salinity, however, the percentage of sulfate increased marginally during the 40-year study duration.

5.2.3 C1R001: Vaal Dam on Vaal River Monitoring Station

This monitoring station is in zone 1, it is the furthest downstream and it is situated in Vaal dam close to the dam wall. Analysis of the data from the Maucha diagrams (Figure 4.5 and 4.6) shows that salinity was dominated by TAL and to a little extent sulfate. From the analysed data, it was observed that the salts concentration was relatively stable throughout the entire duration of the study. However, for all salts there was an increase in concentration which coincided with increased salinity between 1996-2000.

This phenomenon may be attributed to the occurrence of drought around that time of the study (Showers 2002). It is speculated that after that dry spell, rainfall resumed, and the river recovered, and the salinity stabilised. Another reason for the stability may be because this is a dam and salt levels are not expected to drastically change in relation to season/time.

5.2.4 Upper River Course: C8H001, C17H017, and C1R001 5-yearly average TDS concentration

TDS is an essential parameter in water quality studies, and it is a key indicator that reflects the state/quality of a water body (Weber-Scannell and Duffy, 2007). Other water quality parameters are dissolved oxygen (DO), pH, nutrient (phosphorus and potassium) and temperature (Teodosiu et al., 2015). The 5-year TDS average concentration of the monitoring stations in the upper course of the river and its tributaries are presented (Figure 4.7). In the monitoring station C8H001, the 5-year average showed an overall decline in the TDS concentration over a 40-year span of the study. There was a massive drop in 5-year average between 1981-1990 (10 years) before TDS became stabilised. A similar trend was observed in the C17H017 monitoring station. In contrast to the other 2 sites, the C1R001 Vaal dam monitoring station 5-year TDS average value was relatively constant throughout the entire duration of the study. Despite it being the furthest of the monitoring station in zone 1, it had a relatively low 5-year average TDS concentration. This may be attributed to the C1R001 monitoring station being a dam. The 5-year average value of TDS obtained for the monitoring stations in zone 1 as compared to the other zones is reflective of a higher water quality.

5.2.5 Upper River Course: C8H001, C17H017, and C1R001 5-yearly average TAL concentration

Total alkalinity (TAL) measures the concentration/levels of the entirety of alkaline substance dissolved in water capable of attracting and releasing hydrogen ions (Lee et al., 2006). It reflects the water ability to resist a change in pH. TAL, ultimately consist of hydroxide, carbonate, and primarily bicarbonate. TAL is largely driven by the geology in the catchment. This was the most dominant contributor to salinity in the upstream of the river. The 5-year TAL average concentration of the monitoring stations in the upper course of the river and its tributaries are presented in Figure 4.8. In the monitoring station C8H001, the TAL was initially high (1975-1980) and a subsequent decrease was followed in the next 5-year period. This was a trend that was observed for TDS in the upper river course. However, TAL concentration was relatively constant throughout the entire duration of the study. C17H017 had a similar pattern to C8H001, it initially had a high TAL concentration but stabilised over the course of study. This monitoring station had the highest TAL concentration of all the stations in zone 1. However, in C1R001, the 5-year TAL average was initially low (1975-1980) and it increased with time. The 5-year TAL average was relatively constant throughout the entire duration of the study. Despite it being the furthest of the monitoring station in zone 1, it had a relatively low 5-year average TAL concentration. This may be attributed to the C1R001 monitoring station being a dam.

5.2.6 Upper River Course: C8H001, C17H017, and C1R001 5-yearly average SO₄ concentration

Sulfate is the second most abundant major anion in hard water reservoir. It may be naturally occurring in water through atmospheric deposition, rock weathering or from industrial or municipal discharges (Ren et al., 2017). Amongst the 2 major contributor to salinity, sulfate had the lowest 5-year average levels but nonetheless, it was very impactful on the overall salinity composition. The 5-year sulfate average concentration of the monitoring stations in the upper course of the river and its tributaries are presented in Figure 4.9. In the monitoring station C8H001, the 5-year sulfate concentration was initially high (1975-1980) and it reduced during the next 5-year average period. Thereafter, the 5-year sulfate average concentration became relatively stable with very little fluctuation. This was a trend that was also observed for TDS and TAL 5-year averages in C8H001 monitoring station. C17H017 had a similar pattern to C8H001, it initially had a high sulfate concentration but stabilised over the course of study. This monitoring station had the highest sulfate level in zone 1, a trend that was previously spotted for TDS and TAL. However, in C1R001, the 5-year TAL average was initially low (1975-1980) and it increased with time and the peak occurring between 1996-2000. Besides this high 5-year sulfate average between 1996-2000, the sulfate 5-year average values were relatively constant throughout the entire duration of the study. This increase in 5-year sulfate average concentration may be attributed to drought during that period. However, rainfall occurrence during the next 5-year average period ensured that the sulfate concentration became stabilised. Despite it being the furthest downstream of the monitoring stations in zone 1, it had a relatively low 5-year average sulfate concentration. This trend was spotted for TAL and TDS and may be attributed to C1R001 monitoring station being a dam. Zone 2 (River Midstream)

5.2.7 C2R008: Vaal Barrage on Vaal River (Lower end of Vaal Triangle Monitoring Station)

This monitoring station is the first site midstream, and it is present in zone 2 (the Vaal barrage sub-catchment). The water quality in this region is poor as it receives effluents from the highly industrialised Witwatersrand area. As a result of this, water quality in this zone has increased salinity as compared to zone 1 and it is affected by eutrophication. Based on the Maucha diagrams for C2R008 Monitoring Station (Figure 4.10 and Table 4.7), TAL and sulfate were the major contributors to salinity. This was a deviation from the monitoring stations in zone 1, where TAL dominated salinity. This is not unexpected due to large amount of domestic, industrial, and mining activities in this region as it is densely populated. The concentration of all salts stayed relatively constant throughout the entire duration of the studies except during the 1986-1990 timeframe.

5.2.8 C2H1404: Vaal River at Woodlands/Goose Bay Canyon Monitoring Station

This monitoring station is the second in zone 2 and it is expected to have similar water quality to C2R008. Based on the Maucha diagrams for C2H1404 Monitoring Station (Figure 4.12 and Table 4.9), it is visibly clear that the percentage contribution of TAL and sulfate contributed towards salinity. The contribution from sulfate towards salinity was higher than TAL and TDS. The concentration of all the

salts remained relatively constant throughout the entire duration of the study except during a brief stint between the 2001-2005 timeframe. This pattern was similar to what was observed in C2R008 as salinity moved from TAL dominated to being sulfate dominated. However, the concentration of sulfate was lower in this monitoring station as compared to C2R008.

5.2.9 C2H007: Pilgrims Estate at Orkney on Vaal River Monitoring Station

This monitoring station is the last in zone 2. As can be inferred from the Maucha diagram from the C2H007 monitoring station (Figure 4.14 and Table 4.11), sulfate and TAL were major contributors to salinity. The monitoring station became more progressively sulfate dominated, as the river flow more downstream. The concentration of all salts remained constant throughout the entire duration of the study except for sulfate and TDS. There was sudden drop off from the initial start point of the study to 1996-2000 where the sulfate and TDS levels became stabilised. This value was higher than the value recorded in C2H1404 monitoring station.

5.2.10 Zone 3 (River Midstream)

5.2.11 C9H21: Vaal River below Bloemhof Dam Monitoring Station

This monitoring station is the only one in zone 3. This monitoring station is located in the Bloemhof catchment. This zone is an extension of zone 2, and water quality is impacted from industrial waste from mining which generates a high amount of sulfate (Braune and Roger, 1987). As can be inferred from the Maucha diagram from the C9H21 monitoring station (Figure 4.16 and Table 4.13), sulfate and TAL were major contributors to salinity. The station had a similar trend to the stations in zone 2 which were mostly sulfate dominated. The high sulfate value is due to immense contribution from the tributaries draining the northmost part of the catchment polluted due to industrial (mining) activities. The concentration of the salts in the station was relatively constant over the duration of the study with minimal fluctuations in salt levels. However, the sulfate concentration was lower in this zone as compared to zone 2 (monitoring station below Bloemhof dam).

5.2.12 River Midstream (Zone 2 and 3): C2R008, C2H1404, C2H007 and C9H21 5-yearly average TDS concentration

The 5-year TDS average concentration of the monitoring stations in the middle course (zones 2 and 3) of the Vaal River and its tributaries are presented (Figure 4.18). In the monitoring station C2R008, the 5-year average showed a slight decline in the TDS concentration over the 40-year span of the studies. The 5-year average TDS value was relatively constant throughout the duration of the study. A similar trend was observed in the C2H1404 monitoring station. In contrast to the other 2 sites, the C2H007 monitoring station 5-year average TDS value increased during 1981-1985 and stabilised thereafter. This monitoring station had the highest TDS value in this zone. This may be attributed to high volume of industrial activity (mining) in this zone. The 5-year TDS average of C9H21 had a similar trend to C2H007 monitoring station as there was a massive increase in 5-year TDS average concentration between 1981-1985 before it stabilised.

5.2.13 River Midstream (Zone 2 and 3): C2R008, C2H1404, C2H007 and C9H21 5-yearly average TAL concentration

The 5-year TAL average concentration of the monitoring stations in the middle course of the river and its tributaries are presented (Figure 4.19). In the monitoring station C2R008, the TAL was initially high (1975-1980), and a subsequent decrease was followed in the next 5-year period. A sharp increase in the 5-year average concentration occurred around 2001-2005 before it stabilised. The sudden increase experienced may be attributed to drought. C2H1404 5-year average was relative stable over the duration of the study. C2H007 and C9H21 5-year averages had a similar trend to C2H1404 and had relatively stable 5-year averages throughout the entire duration of the study.

5.2.14 River Midstream (Zone 2 and 3): C2R008, C2H1404, C2H007 and C9H21 5-yearly averagesulfate concentration

The 5-year sulfate average concentration at the monitoring stations in zones 2 and 3 are presented (Figure 4.20). The 5-year averages for C2R008 and C2H1404 showed an overall decline in sulfate concentration over the duration of the study. C2H007 5-year sulfate averages followed a similar trend to the monitoring stations in zone 2, however, there was a very steep decline in the sulfate levels over the decades. In contrast, the 5-year average for C9H21 witnessed a net increase over the decade and the values was relatively stable throughout the study duration.

5.3 Zone 4 (River downstream) C9H10 and C9R003

5.3.1 C9H10: Vaal River below Bloemhof Dam Monitoring Station

This is the first monitoring station downstream of Harts. It is present in zone 4, a zone referred to as the Douglas Weir Catchment. Water may be of low quality in this station because it has carry-on pollution from the Bloemhoff dam (Braune and Roger, 1987). In this zone, high level irrigation occurs from extensive agricultural activities. This zone is characterised by increased TAL, bicarbonate and chloride from the irrigation overflow. Based on the results from the analysis of the Maucha diagrams for C9R003 Monitoring Station (Figure 4.22), TAL, and sulfate contributed to the salinity levels at this station. The sulfate level in this zone was at par with that obtained in zones 2 and 3. However, noteworthy is the increase in Cl and Na levels which exceeded values in zones 2 and 3, attributable to irrigation overflow. Over the study duration, the concentration of all salts was mostly relatively constant with slight fluctuations in alternate 5-year period.

5.3.2 C9R003: Douglas Barrage on Vaal River Monitoring Station

Based on the Maucha diagrams for C9R003 Monitoring Station (Figure 4.24), TAL, and to a lesser extent Ca and sulfate contributed to the salinity at this station. The sulfate level in this zone was significantly lower than in zones 2 and 3 with a corresponding increase in Ca concentration exceeding values in zones 2 and 3. The reduced sulfate and TDS levels in this site can be attributed to irrigation water transfer from the Orange River which also increases TAL concentration. Over the study duration, the concentration of all salts was mostly relatively constant with slight fluctuations in alternate 5-year period.

5.3.3 River Downstream (Zone 4): C9H10 and C9R003 5-yearly average TDS concentration

The 5-year TDS average concentrations of the monitoring stations in the river downstream (zone 4) of the river and its tributaries are presented (Figure 4.25). In the C9H10 Vaal River below Bloemhof Dam monitoring station, the 5-year average showed a slight decline in TDS concentration over the 40-year span of this study. The 5-year average TDS values were relatively constant throughout the duration of the study. A similar trend was observed in the C9R003 monitoring station. The highest 5-year average for both monitoring stations occurred between 2001-2005 and the lowest between 1986-1990.

5.3.4 River Downstream (Zone 4): C9H10 and C9R003 5-yearly average sulfate concentration

The 5-year sulfate average concentrations of the monitoring stations in the river downstream (zone 4) of the Vaal River and its tributaries are presented (Figure 4.26). In the monitoring station C9H10, the 5-year average showed a slight decline in the sulfate concentration over the 40-year span of the studies. The 5-year average sulfate value was relatively constant throughout the duration of the study. A similar trend was observed in the C9R003 monitoring station. The highest 5-year average for both monitoring stations occurred between 2001-2005 and the lowest between 1986-1990.

5.3.5 River Downstream (Zone 4): C9H10 and C9R003 5-yearly average TAL concentration

The 5-year TDS average concentrations of the monitoring stations in the river downstream (zone 4) of the river and its tributaries are presented (Figure 4.27). In the monitoring station C9H10, the 5-year average showed a slight increase in the TAL concentration over a 40-year span of the studies due to the admixture of water from the Orange River. The 5-year average TAL concentration value was relatively constant throughout the duration of the study. A similar trend was observed in the C9R003 monitoring station.

5.4 Conclusion

Based on the results obtained from the analysed data, it can be concluded that the composition and concentration of TAL, TDS and SO₄ in the study area underwent significant changes over the 40-year period of this study. It can be inferred that variation in salt composition of the (river) study area may be due to the following:

- Effluent runoff from increasingly modified urban habitat of the catchment study area
- Effluent runoff from the ever increasing extensive agricultural/irrigation set up
- Effluent runoff from majorly industrial activity (mining)
- Extra sources of water from outside the study area catchment (Orange River) with a different salt composition besides the water present in the catchment
- A combination of anthropogenic effects on the catchment area water sources as the 40-year duration of the study progressed

Remarkable changes in the concentration of TDS, TAL, SO₄ and nominally Ca occurred over time during the 40-year duration of the study.

C8H001, C17H017 and C1R001 monitoring station showed a marginal decrease in TDS and TAL concentration, but a slight uptick in SO₄ concentration was also observed. This is expected as these monitoring sites (zone 1) has the best quality of water because of little to no industrial and agricultural activity takes place here. Holistically, the observed decline does not indicate the quality of water was improving at these stations, on the contrary over time it may get worse as more polluted water pollution enter the study catchment area. In line with the variation of salt change overtime, salinity in zone1 was mostly TAL dominated which changed in the zones further downstream. Climatic conditions such as too much or too little rainfall affects salts concentration. This phenomenon occurred in some monitoring station but was clearly visible in TDS concentration in C17H017. A lack of rainfall between 1975-1980 resulted in increased TDS concentration (Showers 2002). Also, the impact of Rand Water on the salinity composition in C1R001 can not be overlooked because the water treatment facility transfers a high volume of treated water into urban area in Gauteng and its environs. This water transferred from the Vaal dam to other catchment as an added source of water, significantly impacts the concentration of salts in C1R001 monitoring station and environs keeping the concentration of salts relatively constant and low.

Water quality in zones 2 (C2R008, C2H1404 and C2H007) and 3 (C9H21) had a similar trend to zone 1, however, there was a marginal increase in TDS concentration; a significant increase in SO₄ concentration; and a corresponding decline in TAL concentration. The increase in SO₄ concentration was due to the industrial activity (mining) - mostly acid mine drainage waste. The drainage from the mines leaches sulphates into the water catchment sources which is predominantly reflected in C2R008, C2H1404 and C2H007 monitoring stations. Salinity in this zone is sulfate dominated. In zones 2 and 3, factors such as increasing population, rapid urbanization around Witbank/Ermelo, Vereeniging, Witwatersrand axis and industrialization (mining and electricity production) may have impacted concentration of salts (TDS, TAL and SO₄) in the study catchment area water sources.

In zone 4, intense agricultural activity and irrigation outflow is responsible for the concentration of salts in this zone of the river. Hence, the high concentration of Na and Cl is a result of this factor. However, increase in sulfate concentration was due to upstream sources. Furthermore, water from the Orange River mix and dilutes the salt concentration in the lowest section of zone 4.

From the analysed data, over the past 4 decades (1975-2015), it can be opined that the Vaal River catchment area is severely impacted by pollution from anthropogenic sources. The composition and concentration of salts in the Vaal River and its tributaries were impacted by anthropogenic influences, although natural drivers such as droughts, floods and geology also play a major role. The levels of TAL present in the water mostly due to natural sources. South Africa is a growing economy and against this

backdrop developmental projects are a must. These projects along with poor enforcement of environmental regulation will further exacerbate the salinity issues of the Vaal Rivers and its tributaries. The industries in this (Vaal) region are liable for the declining water quality of the Vaal River over the past 4 decades and should be responsible in proffering adequate solution alongside the municipalities, institutions and environment regulators. Solution should be a multi-pronged hybrid approach combining technical and non-technical (management) resources in combating excess pollution. Technical solutions such as adequate treatment of mining related runoff and industrial effluent as well as adequate treatment of municipal waste by the municipality will be a good commencement point. Furthermore, the municipalities should ensure effective regulation and coordination of waste treatment before discharge into the Vaal River and also ensure better management of agricultural return flows in lower parts of the Vaal River. Therefore, the quality of the Vaal River should be monitored routinely. This monitoring programme should be expanded to include biological and chemical (organics and inorganics) test. Effective monitoring of the water quality of the Vaal River should be carried out for salt concentration and composition, this will be useful to scientist, policy makers and the government in making informed decision on the best management strategy and sustainable practice for the Vaal River catchment for the continual benefit of humans.

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