

The impacts of irrigation by industrial effluent on the groundwater resource in Zwelitsha-King Williamstown, Eastern Cape

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PREFACE AND ACKNOWLEDGEMENTS

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ABSTRACT

The greatest water quality problem in the Buffalo River catchment area is the discharge of effluent from waste water treatment works and industries around Zwelitsha-King Williamstown. The Da Gama Textile factory has caused significant pollution on the Buffalo River, resulting in the widespread death of fish. This disaster occurred when holding dams over-flowed during periods of intense rain. Groundwater contaminated by industrial effluents, have impact on agriculture irrigation, drinking utilities, soil and agricultural systems. So, it is essential to assess the status of industrial effluent and distribution and dispersion of chemical parameters in the environment of the vicinity of industrial areas before discharging to prevent and control groundwater pollution. The main aim for this study was to determine the impacts of irrigation with industrial waste water (Da Gama Textile) on the groundwater quality in Zwelitsha-King Williamstown. This central aim was supported by investigating a) the historical and current water quality status of the surface water of the Buffalo River; b) the current industrial waste water quality from the textile industry; and c) the influence of the industrial effluent on the surface and groundwater.

Water quality data (2002 to present) were obtained from surface and groundwater monitoring stations within the Buffalo River catchment to assess the long-term water quality patterns. Multivariate statistical methods such as Analysis of Variance (ANOVA) and Principal Component Analysis (PCA) were used. The key findings were that the groundwater quality has deteriorated due to the salinity and suspended solids inputs from the industrial area through effluent irrigation.

The historical and current water quality status of the surface water of the Buffalo River showed an overall decrease. The only exception was for PO_4^{2-} that displayed an increasing trend in the surface water sites.

The data further showed that the effluent has high TSS, EC, PO_4^{2-} and COD concentrations. The effluent irrigation activities have caused a notable increase in the EC and TSS of the groundwater as observed in the groundwater sites results. However, the surface water of the Buffalo River downstream of the textile industry does not have elevated TSS and EC compared to upstream. There is however an overall increase in PO_4^{2-} , which may be indicative of the groundwater transporting the effluent PO_4^{2-} into the river through groundwater-surface water interaction.

The contamination further moves to the Buffalo River as the PO_4^{2-} showed an increasing trend. The salinity of the water was also found to be increased and causing water quality problems from the discharge of textile effluents. On-going monitoring of the ground and surface waters in the study area should be continued at higher frequency and with more than the current four common water quality variables included in the monitoring. Future studies should also focus on

the impact of heavy metals on the environmental aspects associated with the irrigation with industrial effluent.

Keywords: Buffalo River, Eastern Cape Province, water quality, impacts, groundwater, pollution

ABBREVIATIONS AND ACRONYMS

ANOVA	: Analysis of Variance
As	: Arsenic
BH 1-6	: Borehole 1-6
BOD	: Biological Oxygen Demand
Ca	: Calcium
Cd	: Cadmium
Cl	: Chloride
Co	: Cobalt
COD	: Chemical Oxygen Demand
CES	: Centre for Environmental Studies
Cr	: Chromium
Cu	: Copper
°C	: Degrees Celsius
DO	: Dissolved Oxygen
DoE	: Department of Environment
DWAF	: Department of Water Affairs and Forestry
DWS	: Department of Water and Sanitation
EC	: Electrical Conductivity
EPA	: Environmental Protection Agency
Fe	: Iron
FEPA	: Federal Environmental Protection Agency
GPS	: Global Positioning System
Hg	: Mercury
K	: Potassium
Km	: Kilometre
Mg	: Magnesium
Mg/L	: Milligram per Litre
Mn	: Manganese
mS/m	: milliSiemens per metre
Na	: Sodium
NEQS	: National Environmental Quality Standards
NO ₂ ⁻	: Nitrite
NO ₂ ⁻ -NO ₃ ²⁻	: Nitrite-Nitrate
NO ₃ ²⁻	: Nitrate
NH ₃	: Ammonia

NH ₄ ⁺	: Ammonium as nitrogen
PB	: Lead
PCA	: Principle Component Analysis
PCB	: Polychlorinated biphenyl
PCRWR	: Pakistan Council of Research in Water Resources
pH	: hydrogen ion concentration
PO ₄ ²⁻	: Orthophosphate
RHP	: River Health Programme
RQIS	: Resource Quality Information Services
SABS	: South African Bureau of Standards
SADC	: Southern African Development Community
SANS	: South African National Standards
SAR	: Sodium Adsorption Ratio
S ²⁻	: Sulphide
SO ₄	: Sulphate
SPSS	: Statistical package for the social sciences
SS	: Suspended Solids
TDS	: Total Dissolved Solids
TSS	: Total Suspended Solids
UNEP	: United Nations Environment Programme
US	: United States
USEPA	: United States Environmental Protection Agency
WHO	: World Health Organisation
WMS	: Water Management System
WWTWs	: Waste water Treatment Works
Zn	: Zinc

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CHAPTER 1 INTRODUCTION

1.1 Background

All over the world, there is a natural concern of the shortage of consumable water (Ghisi *et al.*, 2006). The most sources of water pollutants within the developing nations are industrial waste (chemical and thermal wastes), municipal wastes (generally effluent containing human wastes, cleaning soaps) and agricultural waste (animal wastes, pesticides and fertilizers) (Fatoki *et al.*, 2012). According to Fatta-Kassinos *et al.* (2011) issues related to administration and management of waste water are the most problematic areas.

Effluents containing huge volumes of natural organic matter and nutrients have a negative effect on the receiving environment area due to the failing and poorly maintained infrastructure (Buechler *et al.*, 2013). The status of the receiving aquatic system has been deteriorating at an alarming rate due to the extreme amount or poor quality of the waste water effluents (Kanu and Achi, 2011).

In the United States (US), more than half the volumes of all water contamination and the most hazardous pollutants are from industrial pollution (Blomquist, 1994). The waste-containing water, or effluent, is released into streams, lakes, or ocean, which in turn distributes the contaminants (Mansfeldt *et al.*, 2020). In 1996, the U.S. Environmental Protection Agency (EPA) revealed that approximately 40% of the nation's surveyed estuaries, streams and lakes were too contaminated for such basic uses as swimming, fishing and drinking (Stoddard *et al.*, 2003).

The biggest polluter within the world is the oil industry followed by the clothing industry (Levy and Kolk, 2002). According to Kar *et al.* (2012) the textile industry is responsible for one-fifth of the world's industrial water contamination and utilizes 20,000 chemicals, numerous of them carcinogenic, for making clothing. This makes the industry one of the greatest environmental polluters (Naylor, 1995). Pre-treatment, colouring, printing, and wrapping up operations are among the different stages of the industrial textile manufacturing process that results in the poor status of the industrial effluent and ultimate pollution of the water bodies that are at the receiving end (Wang *et al.*, 2011; Madhav *et al.*, 2018).

Groundwater contamination around industrial and urban centres is caused by the discharge of untreated effluents and municipal waste that is rich in nitrates, heavy metals and dissolved and suspended solids (Bhadra, 2013). Therefore, research on the water quality of these textile industries is important to implement fitting processes, e.g. pre-treatment of effluents,

prior to it being released into the environment (Bouwer and Idelovitch, 1987). Kakkar (1990) examined contamination caused by industrial effluents in numerous places of India. He found that severe damage to the agricultural land and groundwater resources within 3 km buffer zone of the Bandi River was as a result of the discharge of effluents.

The major contaminants in effluents from the textile industry are the dyes used for colouring and the concern is the enormous quantity of effluent released into the water bodies. Noel and Rajan (2015) observed that dye effluent contaminates the surface water and groundwater, subsequently, making it unsafe for irrigation and drinking. Chemicals that may well be harmful, carcinogenic or mutagenic to living organisms are contained within the dye effluent (Carmen and Daniela, 2012). Irrigation with water containing waste may diminish soil hydraulic conductivity and infiltration rate and also affect the quality (David and Ranjan, 2015).

Effluent irrigation is sustainable on condition that legitimate administration practices are followed (Hogg *et al.*, 1997). Effluent irrigation for disposal purposes is for the most part considered to have the least ecological impact for a municipal disposal problem (Hogg *et al.*, 1997). Sustainability in these cases might be viewed as longevity of the environment at large as compared to the long term effects of using the disposal site (Bishop, 1995; Tollefson and Hogg, 1997). Water of good quality is saved for domestic purposes whereas irrigation activities are receiving minimum quality water such as sewage and industrial effluent (Bouwer and Idelovitch, 1987). Waste water contains basic supplements for plant growth besides being a generally cheap source of irrigation water (Pescod, 1992). A naturally more secure alternative for waste water disposal is by land application as compared to coordinate release into surface water bodies (Asano and Cotruvo, 2004).

In Zimbabwe, a disposal method such as waste water irrigation is common in peri-urban areas, and it is seen as an arranged reuse of waste water (Buechler *et al.*, 2013). Earliest irrigation ventures include big-scale grassland irrigation utilizing treated effluent. Deep-rooted crop types are exceedingly compelling in nitrogen absorption and storage nitrogen (Vaisman *et al.*, 1981). Adverse environmental impacts such as soil and groundwater contamination may become prominent after prolonged irrigation with waste water.

Research and literature on long-term effects of waste water irrigation on groundwater is inadequate. Most studies have focused on impacts on crop productivity and efficiency and trace metal accumulation. (Oloya and Tagwira 1996; Rattan *et al.*, 2005; Xu *et al.*, 2010; Bao *et al.*, 2014; Wu *et al.*, 2017; Jampani *et al.*, 2018). The continuous application of large volumes of partially treated or untreated waste water in urban and peri-urban areas has

adversely affected farmers who use polluted water bodies as sources of irrigation (Keraita and Drechsel, 2004). In addition, studies in the Lake Victoria Basin found that the wetlands receiving waste water from multiple industrial sources through the accumulation of heavy metals had the highest levels recorded (Nabulo *et al.*, 2008).

Adverse biological, physical or chemical effects on fruits and vegetables have been observed if irrigated using partially or pre-treated waste water rather than raw effluent water (Emongor and Ramolemana, 2004; Heidarpour *et al.*, 2007; Wang *et al.*, 2011). However, studies have found that the nutrient loads in water reservoirs are enriched by the nutrients from waste water-irrigated pastures (Nhapi *et al.*, 2003). Freshwater resources in Southern Africa were found to be under increasing pressure from contamination and water quality may be a developing concern, especially in urban regions and near industrial centres (SADC, 1996; (UNEP), 2000; Swaminathan, 2010). Jenkins (1972) and SADC (1996) distinguished that with the developing urban and industrial use of the water in 3rd world countries, more high volumes of natural and inorganic wastes are discharged back into the water resources driving to a more reduced water quality of the water resources. Given the elevated levels of pollutants from agriculture, industry and households in southern Africa, water resources are not able to viably purify themselves (SADC, 1996). An emerging problem of unmonitored diffuse source run off is going unnoticed as compared to the popular industrial and municipal waste that contribute to nutrient loading of inland waters (Magadza, 2002). The release into surface water bodies of untreated or inadequately treated effluents from households, industries, and zoo technical farms is one of the main causes of different pollutants occurring in the water (Verlicchi and Grillini, 2020).

The most noteworthy water quality problem in the Buffalo River catchment area is the release of effluent from waste water treatment plants and industries around Zwelitsha-King Williamstown (Van Ginkel *et al.*, 1996). In 1946, Da Gama Textiles was developed comprising of a huge single textile mill in Zwelitsha-King Williamstown and it is a big producer of bleached, polished, dyed and printed fabric materials (Van Ginkel *et al.*, 1996). The company utilizes a different blend of manufacturing innovation including intertwining, washing, bleaching, whitening, dyeing, printing, heat treatments and others, numerous of which necessitate vapour for their process (Van Ginkel *et al.*, 1996). Groundwater contamination is commonly related with the use of waste water from industrial sources such as textile and tanneries (Karthik and Gopalakrishnan, 2014).

One of the studies has named the Da Gama textile industry as one of the main contributors to the salt content of the Buffalo River and the Laing Dam (Van Ginkel *et al.*, 1996). The exact contribution has never been evaluated and quantified satisfactorily (van Veelen and

van Heerden, 1994). The impact of the run-off from these irrigated lands has not been measured (Van Ginkel *et al.*, 1996). The Department of Water Affairs and Forestry (DWAF) (1999) assessed that 88% of the salts load flowing into the Mlakalaka stream from other than common sources originate from the industrial factories. The Da Gama Textile factory has caused major contamination of the Buffalo River, resulting in the predominant death of fish (RHP, 2004). This catastrophe happened when holding dams over-flowed amid periods of extreme rain, (CES), (2003). The community of the kwa Tshatshu village had complained of their cattle dying through drowning or being stuck in contaminated effluent-rich mud around the Mlakalaka stream in the vicinity of the Da Gama textile industry (RHP, 2004).

The textile effluent at Da Gama is at first contained in evaporation ponds, and is then sprayed onto land adjacent to the Mlakalaka tributary, from which much of the effluent runs directly into the Buffalo River and infiltrate to the groundwater (Van Ginkel *et al.*, 1996). A major issue is the bad condition of the stormwater drainage system. These structures were planned to keep stormwater from entering the irrigated lands and the tailings dam and to channel storm water around the tailings dam to the Mlakalaka Stream. The system does not operate effectively, which results in run-off from the catchment causing the tailings dam to overflow during one severe rainfall event (van Veelen and van Heerden, 1994).

1.2 Problem statement and rationale for the study

According to (Bharti, 2013), agriculture irrigation, potable water, soil, aquatic and agricultural systems are affected by groundwater that is contaminated by textile effluents. So, before discharging and to prevent and control the groundwater contamination it is fundamental to survey and evaluate the dispersion and distribution of the contaminants within the environment of the vicinity of industrial area and the status of the industrial effluent (Bharti, 2013). The country's freshwater resources have now declined due to increased pollution caused by mining, urbanization, agriculture, afforestation, power generation and industry (Ashton *et al.*, 2008). The Buffalo River is of economic significance to the Eastern Cape Province. Dams such as Bridle Drift, Rooikrantz, Maiden and Laing are fed by the Buffalo River to supply for domestic and agricultural needs (Van Ginkel *et al.*, 1996). The river's catchment communities such as Mdantsane, Izele town, Bisho, Zwelitsha-King Williamstown, East London and Berlin were to be supplied for by the dams that were built as impoundments along the course of the river (Yahaya *et al.*, 2018).

The anthropogenic activities in these locations are predisposing factors to the discharge of agricultural, domestic and industrial wastes into the river (O'Keeffe *et al.*, 2015). The main sources of pollution for this river are the leached poisonous wastes from the dump site

location close to Zwelitsha and hazardous wastes from an ancient tannery textile mill (Yahaya *et al.*, 2018). A major resource within the area may be the Buffalo River; however the water adjacent and downstream of these industries is coloured, turbid and the vegetation shows to be scorched (O'Keeffe *et al.*, 2015). The water is used for irrigation of vegetables, construction development, cleaning, drunk by birds and animals, and children using it for recreational purposes (O'Keeffe *et al.*, 2015).

There are studies that have been done on the effects of industrial/textile waste water on the adjacent Buffalo River and not on the receiving groundwater resource (O'Keeffe *et al.*, 2015). In general, the available and accessible data (information) come from scattered investigations, which were carried out by individuals and by exceptionally few scientific projects concerned with African waters. Few reviews and audits exist on the state of pollution of African inland and coastal waters (Bandowe *et al.*, 2014) and there is a considerable decline in the groundwater quality (Nagarajan, 2012).

Existing literature show that research on long-term impacts of waste water irrigation is limited. To date, trace metal accumulation and impacts on crop productivity studies have been the main focus, for (example Oloya and Tagwira, 1996). However, Nhapi *et al.* (2003) found that nutrient flows from waste water-irrigated pastures increased the nutrient loads in water reservoirs for surface water studies.

A few water quality issues within the Buffalo River catchment have been examined in previous studies. Previous pollution investigations on the river and its estuary incorporate physicochemical and microbiological qualities (Dallas, 2008; Chigor *et al.*, 2013), assessment of levels of heavy metals (RHP, 2004), pesticides (Fatoki and Awofolu, 2003; Yahaya *et al.*, 2018) and total petroleum hydrocarbons (Adeniji *et al.*, 2017) in different environmental media. The aims of the physico-chemical study conducted by Chigor *et al.* (2013) were to assess the distribution of PCBs within the surface water of Buffalo River and additionally to assess the level of wellbeing hazard to people.

Reed and Thornton (1969) established that the major source ($\pm 61\%$) of salinisation originates from natural geological weathering, whereas $\pm 27\%$ came from industrial origins (textile and tannery). Textile effluent contains high concentrations of water colorants, dissolved salts, organic wastes, insecticides, pesticides, chemical wastes, alkalis, sodium and detergents (Buckley *et al.*, 1983). The study prepared by Osode (2007) assessed the productivity of the different waste water treatment works for the removal of chemical and microbiological contaminants in order to establish the relationship between the quality of the final effluents and that of the receiving water bodies. The results showed that health effects

were potentially associated with significantly higher occurrences of the target pathogens detected during the water quality monitoring period (Osode, 2007).

Limited studies have been conducted to examine groundwater contamination by waste water irrigation (e.g. Gallegos *et al.*, 1999) moreover; significant literature exists on the impacts of soil aquifer treatment systems and groundwater recharge utilizing effluent on chemical and microbiological quality of water (e.g. Bouwer *et al.*, 1980; Nema *et al.*, 2001).

Main issue in this catchment is that the industrial effluents are discharged into the Buffalo River and streams almost exclusively without adequate treatment which results in nutrient enrichment, the accumulation of toxic compounds in biomass and sediments, loss of dissolved oxygen in water and other nuisances (Dunbabin and Bowmer, 1992).

1.3 Research aim

The main aim for this study was to determine the impacts of irrigation with industrial waste water (effluent) (Da Gama Textile) on the surface water and groundwater quality in Zwelitsha-King Williamstown.

The objectives for this study were to:

- To investigate the historical and current water quality status of the surface water of the Buffalo River
- To investigate and examine the current industrial waste water quality from the textile industry;
- To evaluate the effects of the industrial waste water on the groundwater and surface water quality of the Buffalo River.

1.4 Structure and outline of the dissertation

Chapter One: Introduction

This chapter provides a general introduction to the study by describing the background to the study and providing a clarification of the research problem. Furthermore, the chapter will discuss the key question that the study pursues to answer.

Chapter Two: Literature Review

This chapter focuses on the existing literature in particular the current status of the impact of irrigation with industrial effluent on different water resources. Definitions of the key concepts and terms will be covered under this chapter.

Chapter Three: Research Methodology

This chapter provides a justification for the use of quantitative approach and also describe the research method/approach, data collection and data analysis procedures as well the strategies used to ensure the strength of the study findings.

Chapter Four: Results and Discussion

The chapter interprets analyses data and discusses the research findings based on detailed presentation of the research data in relation to the research problem and compared to the literature review and theoretical framework.

Chapter Five: Conclusion and Recommendations

This chapter concludes the study. It will give a synthesis of the study, highlighting and reflecting on the current state of the water quality. The chapter will make appropriate recommendations to inform the water quality management issues, irrigation practices, and for future research as the objective is to consider issues for further investigation to reduce the pollution in the catchment.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

One of the most essential strategic alternatives for renewable water in many nations is the use of treated waste water for different purposes, particularly for people who are affected by a shortage of conventional water sources (Scott *et al.*, 2004; Qadir *et al.*, 2010;).The life of human beings and other different organisms that are dependent on freshwater assets for their survival has been threatened by means of the devastating industrial activities that cause groundwater contamination (Arora *et al.*, 2014). The discharge of untreated industrial effluents is the major cause of groundwater pollution (Singh *et al.*, 2004; Wu *et al.*, 2015).

Ezemonye and Kadiri (2000) understood that in Africa, industrial discharge and run-off continue to pollute the coastal water bodies. The soil is provided with water, nitrogen and phosphorus as well as organic matter after irrigation with sewage effluents (Devkota and Schmidt, 2000).

Changes in the ecology and quality of receiving water bodies are largely affected by the discharge of industrial effluents (Umeham *et al.*, 2012). The textile processing waste water is recorded as the most polluted sources among all industrial commercial sectors when taking into effect both the magnitude and composition (Rusan *et al.*, 2007). The dye waste water has been found to be poisonous to various crop and vegetation at the same time as scientists have documented destructive outcomes of various industrial effluents on the growth of flora (Rusan *et al.*, 2007).

According to Tolba (1982), the quality and quantity of water in most African countries is poor, the nutrition and sanitation is the worst and diseases are mostly prevalent. Unfortunately, most African inland waters have few water quality studies or research (Palmer *et al.*, 2015).

The period of application determines the extent of build-up of metals in waste water -irrigated soils (Palaniswami and Sree Ramulu, 1994; Bansal and Sugiarto, 1999). The environmentally safer choice has been identified as land application of waste water as compared to direct discharge into surface water bodies (Bouwer *et al.*, 1980). A concept of waste water irrigation is comparable to pre-treated waste water being passed through the unsaturated zone into deep aquifers and is also related to slow-rate soil aquifer treatment (Bouwer *et al.*, 1980). Literature and research studies on long-term period influences of waste water irrigation on groundwater are limited (Zema *et al.*, 2012). The main emphasis of

documented studies has a propensity to be on trace metal accumulation and impacts on crop productivity (Oloya and Tagwira, 1996).

Due to the speedy industrialisation and subsequent contamination of groundwater and surface sources, due to the speedy industrialisation and subsequent contamination of groundwater and surface sources, water quality management has become very challenging. (Tong and Elimelech, 2016). The far reaching impact on human fitness has added with it the much needed attention on water pollution and its control. Textile industries utilize a massive amount of water and generate a massive quantity of waste water, which is normally released into a common effluent manhole sewer in an industrial area (Bharti *et al.*, 2013). Toxic contaminants may infiltrate down through the soil profile and reach the groundwater, which in the end cause the health risks amongst human being and livestock as a result of daily intake (Bharti *et al.*, 2013). Contamination of surface water, as well as soil and groundwater is due to the presence of soluble solids, suspended solids (SS), organic matter, and toxic constituents in industrial effluents (Bhagure and Mirgane, 2011).

Application of effluent to arable lands additionally entails definite environmental and agricultural hazards (Al-Jaloud *et al.*, 2007). Wallach *et al.* (2005) stated that effluent differs from fresh water by higher contents of dissolved organic matter, electrolytes, suspended solids, and Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). These mixed parts in effluent can have an effect on soil hydraulic and physical properties (Al Omron, 2012). Physical blockage of pores by suspended material is as a result of adverse effects that may lead to decreased hydraulic conductivity and infiltration rates (Wallach *et al.*, 2005).

2.2 Impact of industrial pollution on groundwater and surface water quality: overview

The major sources of pollution are industries and the various level of pollutant can be discharged into the environment either directly or indirectly (Glyn and Gary, 1996). However, discharged effluents from industries have other chemicals equally present which are poisonous to human and toxic to aquatic life (Kupechella and Hyland, 1989).

Industrial water pollution is a serious problem in a worldwide context (Duda, 1993). It has been recommended to be the main cause of sickness and death globally. Naidoo (2005) cited that pollution may originate from an exact single source called a point source, such as industrial processes, mining activities and sewage effluents or from sources that are not easily located called non-point sources, such as from runoff, agricultural land and traffic. The author further said that industries are the most common primary source of pollution around the world, producing massive quantities of liquid effluents that regularly find their way to water bodies. Sources of industrial effluents range from pulp and paper mills, textile manufacturing using dyes and noxious cleaning chemicals and steel industries (Naidoo, 2005). Industrial pollutants can also adjust the stream environment and thereby have an effect on aquatic life (Hancock, 2002). Industrial water pollution can also affect a stream ecosystem with reference to hydrogen ion concentration (pH), temperature, dissolved oxygen (DO) and turbidity, which in turn have an effect on the organisms living in the water (Bhateria and Jain, 2016). Industrial effluents discharged in Lagos, Abaekuta showed a high level of turbidity, oil and grease, faecal coliform and iron were very high in the sampling sites that were part of a study on water quality of Ogun River (Nigeria) (Ado *et al.*, 2014; Jaji *et al.*, 2007).

Surface and groundwater may be contaminated by numerous sources (Brusseau, and Artiola, 2019). The bad quality of water in urban areas is caused by the careless disposal of industrial effluents and other wastes (Mathuthu *et al.*, 1997). The end points of effluents discharged from industries are usually the water bodies in most areas of the developing world (Yahaya *et al.*, 2018). The use of effluent for irrigation is not without issues and, except if well managed, can bring about the pollution of underlying aquifers (Gallegos *et al.*, 1999).

The use of raw river water for drinking purposes is popular in developing countries that do not have access to potable water (Ademoroti, 1988). These groups of people are usually affected by effluents generated by the industries which are the major sources of pollution (Ademoroti, 1988).

Deterioration of water quality due to industrial effluent and municipal sewage discharge has been documented in literatures (Qadir *et al.*, 2008). The contamination of Cauvery River in India by heavy metals such as (lead (Pb), chromium (Cr), zinc (Zn)), was reported and it was attributed to agricultural, industrial and anthropogenic activities around the river (Begum *et al.*, 2009). High level of mercury (Hg) was found in reptiles, amphibians and invertebrates which showed a strong influence from industrial effluent (Zhou *et al.*, 2008).

Analysis of the characteristic qualities of five textile industries effluent in Kaduna (Nigeria) was conducted and high levels of COD, TSS, BOD, ammonia (NH₃), and sulphide (S²⁻) that exceeded the Federal Environmental Protection Agency (FEPA) limit by several fold was reported (Yusuf and Sonibare, 2004). The concentration of effluent discharge was reported to be within the limits when the characteristics of selected effluents from industries in Ikeja, Lagos (Nigeria) were analysed (Sangadoyin, 1995). Groundwater contamination was evident as a result of continuous disposal of industrial effluents on land, which has restrained potential to assimilate the pollution load (Gothwal, and Shashidhar, 2015). Manzoor *et al.* (2006) reported that the groundwater quality of open boreholes as well as deep boreholes deteriorates to a considerable extent and the water from such sources has excessive salt concentration.

When considering the reuse of industrial waste water, for any final purpose, it is essential to consider the type of industry as well as the nature of the effluents generated. In order to meet environmental standards and be economically competitive, industries take nowadays different measures that contribute to achieve these goals. Reducing waste at source, minimizing the use of water, and recycling/reusing waste water are the main measures implemented by industries (Liu and Haynes, 2011).

2.3 International studies

The disposal of waste water to non-perennial rivers in a semi-arid and arid climate of Israel is related to intolerable environmental risks (Faechem *et al.*, 1983). Hence, land treatment through irrigation with effluent is advantageous, as experienced for numerous years in Israel. A study was conducted at the Challawa River, Kano State, Nigeria and it was found out that the concentrations of heavy metals within the water and sediment samples were greater than the World Health Organization (WHO) guideline values for the protection of aquatic ecosystem (WHO, 1984). This is expected because of its location near tanneries and textile industries (Akan *et al.*, 2009). A study was conducted in Panipat City, India and it was found that textile waste water was the main source of water pollution through leaching (Choudhary, 2014). Effluent is the major source for irrigation in Haryana state, irrigation with contaminated groundwater containing different amounts of heavy metals resulted in increased concentrations of metals in the agricultural soil (Malik and Bharti, 2007).

Surface water bodies, irrigation fields and surrounding land were impacted upon due to the direct effluent discharges from industries in the Gulf of Mannar, India (Krishna *et al.*, 2009). This had an influence on the microbiological quality, physico-chemical properties, heavy metals, trace metals and of drinking water in the region (Selvam *et al.*, 2015).

The waste water of Faisalabad, Pakistan is released without any treatment into the Ravi and the Chenab Rivers through drainage systems (Kahlowan *et al.*, 2006). Seepage from these drains is the major source of groundwater contamination (Rehman and Cheema, 2016). The concentration of physicochemical and biological parameters for most of the waste water discharged from the industries exceeded their permissible limits resulting in the groundwater quality of the city not being suitable for consumption (PCRWR, (2002). Waste water from different industrial plants had a negative effect on the DO and TDS of the Kabul River (Qadir *et al.*, 2008). The outcomes of the study were that measures should be put in place so that all the waste water coming from the industrial sources should be properly treated as an essential part of its production and manufacturing system before disposing them into the river (Kiran *et al.*, 2012).

The industries positioned along this river are responsible for the Illegal discharges of industrial effluent into the Mukuvisi River in Zimbabwe and its tributaries (Nyamangara, 2008; Chimuriwo, 2016). The capacity for monitoring by the relevant authorities in Zimbabwe is limited, whereas the penalty for polluting rivers is far lower compared to the value of processing the effluent (Nyamangara *et al.*, 2008).

The deteriorating water quality within the Manyame catchment, which includes Mukuvisi River and Lake Chivero is due to the disposal of sewage and industrial effluent into these rivers (Marshall, 1994). Poor water quality significantly increases expenditures of treating the water for domestic use and no longer only impacts negatively on the aquatic fauna (Greichus *et al.*, 1978).

2.4 Impact of irrigated effluent on surface and groundwater

Crops are provided with water and nutrients as a result of irrigation with effluent (Rusan *et al.*, 2007). Furthermore, it provides a convenient means of sewage disposal through land treatment and prevents potential environmental and health hazards caused by the uncontrolled flow of waste water (Rusan *et al.*, 2007). The gap between water supply and demand could be served through treated waste water reclamation (Asano, 1998). The nutrients contained in the effluent replace artificial fertilizers requirements in irrigated areas, thus can increase productivity (Oron, 2000).

For many centuries, the disposal of sewage to land has been implemented in Europe (Wolman, 1977). The only method of treatment was land disposal (Metcalf *et al.*, 1991) and in the practice, unacceptable levels of pollution were reached by many rivers as the disposal of waste on land became more popular. However this approach to controlling water has largely ceased due to the occurrence of a range of waste water treatment options that are available currently (Vazquez-Montiel *et al.*, 1996).

Preliminary treatment before the discharge of effluents to surface waters (water resources) is current practice in many countries (Ferrar *et al.*, 2013). However, more emphasis has been placed on reclaiming waste waters in various ways: industrial and non-potable reuse as well as agricultural irrigation has been indicated as the most common types of reuse (Shannon *et al.*, 1986; Crook and Okun, 1987). The agricultural use of waste water effluents demonstrates the additional advantage of nutrient recycling in crop irrigation in relation to other types of reuse (Toze, 2006). Moreover, an effortless and cheap pre-treatment is needed because effluent irrigation generally requires less strict water quality standards (Qadir *et al.*, 2008).

The potential problems and benefits of land application of waste waters have been scrutinised by Bouwer and Chaney (1974), and the double benefit of using waste water irrigation (water and nutrients) is well documented. Nevertheless, waste water contains more pollutants than the original source of water and these may be possibly detrimental, depending upon the waste water aspects and regulation practices.

For instance, significant environmental complications such as nitrate leaching, build-up of toxic elements in soils and plants, and human health hazards from pathogenic microorganisms may develop. It is of significant importance to match response rates with the hydraulic loading to ascertain successful results during effluent irrigation. Reduction of pollution by expanding the effectiveness of nitrogen use can be maintained by management practices based on an understanding of the transformations in waste water irrigation systems (Vazquez-Montiel *et al.*, 1996).

Discharge of the textile effluent to the nearby water body(s) alters the biological, chemical and physical nature of the water bodies. The effluent further seeps into the aquifer, decreases the oxygen level in water leading to death of the aquatic biota and bio magnification (Abubacker and Kirthiga, 2017).

2.5 Irrigation with industrial effluent as a way of disposal

From the 1860s and 1870s, the method of irrigation as a way of disposal has been used considerably, especially on sewage farms (Schraufnagel, 1959). Irrigation strategies consisting of ridge, furrow and spray are the most typically used methods to eliminate the waste water (Schraufnagel, 1959). These systems may require extra land to be far from factories, dwellings, or public roads and are more likely to develop into a nuisance (Schraufnagel, 1959). Disposal with the aid of spray irrigation is a current improvement in terms of waste disposal for most countries. Waste is sprayed onto the land, generally via revolving nozzles (Hillel, 1987).

In the developed countries, restrictions are made on crops allowed to be grown, stringent water quality and treatment requirements are observed and reclamation is scheduled (Angelakis *et al.*, 1999). Countries which include Germany, Israel, and America (especially the states of Arizona and California) are practicing controlled and managed irrigation re-use (Ayers and Westcot, 1985). Re-use in developing countries occurs without powerful controls and safeguards, but there are a few exceptions to this exercise whereby there are regulations put in place. (Strom, 1985; Ambrose and Lynn, 1986; Shuval *et al.*, 1986). In Zimbabwe, waste water irrigation is common in the peri-urban parts, in which it is mostly observed as a disposal method rather than deliberate waste water reclamation (Jimenez and Asano, 2008). In Zimbabwe, treated effluent was used for irrigation of large-scale pasture fields in previous years (Xu *et al.*, 2010). For developing nations, in particular in areas wherein vegetables are eaten raw, stabilization ponds are preferred means of handling the health effects of waste water irrigation (Bartone and Arlosoroff, 1987). The big problem is the disposal of sewage water and industrial waste (Boadi and Kuitunen, 2002).

The discharge of untreated or partially treated waste water into the environment has resulted in the freshwater supplies being impaired and deteriorated (Fakayode, 2005). The poor quality of the water affects the downstream users due to the continuous discharge of effluents to the environment (Kanu and Achi, 2011). A way of controlling industrial discharges into the environment is through safeguarding the quality of freshwater supplies and to reduce freshwater use by the industries (Kraemer *et al.*, 2001). Treatment of the effluent is of paramount importance before it is discharged to the environment to minimise the impact (Sibanda *et al.*, 2015).

The nature of the industrial effluents has caused serious problems for the industries. Industrial effluent discharged into the environment introduces a high percentage of colour, salinity and COD problems (Buckely *et al.*, 1992). Most of the soluble salts that are supplemented to the soil during irrigation ultimately reach the shallow groundwater and increase the salt content in shallow domestic boreholes and springs. They eventually become part of the return flow of groundwater to nearby rivers and streams (Hogg *et al.*, 1997). Land treatment techniques for disposal purposes are employed under dry as well as humid climates (Bouwer and Chaney, 1974; Pound *et al.*, 1983).

According to (Pound and Crites, 1973; Shuval *et al.*, 1986), irrigation with effluent has been practiced for centuries. Shortage of water stimulated research on different aspects of the subject in Israel, where valuable information on effluent irrigation has also been gained (Feigin *et al.*, 2012). If proper management practices are followed, effluent irrigation can be sustainable (Hogg *et al.*, 1997).

Advantages of irrigation with effluent

There are various potential benefits of irrigation with effluent such as protection of water resources, prevention of coastal pollution, recovery of nutrients for agriculture, augmentation of river flow, savings in waste water treatment, groundwater recharge, and sustainability of water resource management (Angelakis and Bontoux, 2001). Utilisation for irrigation frees high quality water for other users where other sources of water are scarce (Feigin *et al.*, 2012). The most reasonable and applicable method for reuse is through the irrigation of parks and other landscape areas (Feigin *et al.*, 2012).

Safe and low-cost treatment and disposal of waste water; the conservation of water and recharge of groundwater reserves; and the use of nutrients in the effluent for productive purposes are some of the many potential benefits offered by the use of textile effluent for irrigation purposes (Angelakis *et al.*, 2003). Additional benefits could be offered by the

irrigation of trees. Crop or forestry irrigation may be adopted primarily for treatment and disposal purposes in areas where water is relatively plentiful. Irrigation with effluent can bring advantages to tourism (e.g. golf course irrigation agriculture) and agriculture (e.g. crop irrigation) (Feigin *et al.*, 2012).

Disadvantages of irrigation with effluent:

Trace organic toxic substances such as pesticides may be in the effluent (Bond, 1998). Increases in the inorganic soluble salt content of the water with the principal ions being picked up are sodium, chloride and bicarbonates (Feigin *et al.*, 2012). The total salt content (salinity) and the sodicity of the water increase (Feigin *et al.*, 2012).

Effluents comprise of different levels of plant macronutrient elements, especially nitrogen and phosphorus. These should be taken into consideration as a source for groundwater contamination (Pound and Crites, 1973). The concentration of trace elements may also increase, mainly from specific industrial waste water (Feigin *et al.*, 2012). The level of toxicity or harmfulness of the textile effluents varies among industries (Kiriakidou *et al.*, 1999). Pathogenic microorganisms (bacteria and viruses) are present, even though their concentration in effluent is reduced throughout the normal reclamation process (Harwood *et al.*, 2005).

One of the biggest threats to the environment is the textile industry (Choudhury, 2014). The numerous procedures implemented in the textile industries create large amounts of liquid, solid and gaseous wastes (Ghaly *et al.*, 2014). The textile waste water effluent contains high amounts of agents causing damage to the environment and human health including suspended and dissolved solids, BOD, COD, chemicals, odour and colour (Arya and Kohli, 2009).

Some risk factors have longer term impacts which increase with continued use of recycled effluent (e.g. saline effects on soil), while others are short term and vary in severity depending on the potential for human, animal or environmental contact (e.g., microbial pathogens) (Feachem *et al.*, 1983; Goel and Kulkarni, 1994).

2.6 Impact of textile industry effluent on surface and groundwater

The textile production is considered to be one of the world's most polluting industries since a vast amount of chemicals (e.g. detergents, soaps, etc.) are needed in some of the industrial processing stages (Gravelet-Blondin *et al.*, 1997). Furthermore, in the KwaZulu-Natal coastal area, textile effluents are considered to be one of the most problematic especially in terms of colour, TDS, COD and salinity (Gravelet-Blondin *et al.*, 1997). Effluent irrigation is not new for many countries in arid or semi-arid regions (Mizyed, 2013). It presents problems that differ in important aspects from those involved in the use of water from streams and from groundwater sources (Niemczynowicz, 1999).

Environmental degradation over long period for surface and groundwater quality is induced by the discharge of highly contaminated effluent accelerated by overexploitation of existing water resources (Phiri *et al.*, 2005). A study conducted in Noyyal River indicated that the water quality deterioration of groundwater was as a result of continuous discharge of non-treated and semi treated effluent (Prabha *et al.*, 2013). The effluent was reported to be characterized by high load of BOD, COD, colour, heavy metals, TDS and Suspended Solids (SS) and bad odour, over long period of time. Moreover the water becomes unsuitable for irrigation and even for drinking (Hari *et al.*, 1994; Tufekci *et al.*, 1998). Groundwater pollution is eminent as well as loss of soil productivity (Prabha *et al.*, 2013).

A study to assess the quality of the Cauvery River water and adjacent groundwater was conducted in India (Venkatramanan, 2013). Bicarbonate was identified as the dominant anion and sodium was the dominant cation for both surface and groundwater. Most of the surface water samples were found to be within the limits for drinking water quality standards of India; additionally most of the groundwater samples were unsuitable based on the concentration of major ions (RamyaPriya and Elango, 2018). Both surface water and groundwater near the coast were found to be poor, both for drinking and irrigation purposes, whereas the groundwater quality in locations nearer to the confluence of tributaries and textile industrial areas was also of poor quality (RamyaPriya and Elango, 2018).

Mukherjee and Nelliya (2006) noted that the industries in Mettupalayam Taluk, Tamil Nadu disposing their effluents on land have polluted the shallow open boreholes and also the salt content of the soil has started building up slowly; furthermore the farmers of the adjacent farmlands have also complained. This study revealed that groundwater pollution has been caused by the continuous disposal of industrial effluents on land, which has restricted ability to assimilate the pollution load (Mukherjee and Nelliya, 2006). Sampling results showed that the quality of groundwater in shallow open boreholes surrounding the industrial locations had

worsened, and the application of the effluent for irrigation has caused an increased salinity in soils (Mukherjee, 2008).

Another study in Bangalore City in India aimed at identifying the groundwater contamination (Shankar *et al.*, 2008). The investigations reveal that most of the study area was highly contaminated due to the excessive concentrations of one or more water quality parameters such as nitrates, total hardness, calcium, magnesium, total dissolved solids, sulphates and fluorides, which have rendered nearly 77% of the water samples tested to be not fit for consumption (non-potable) (Parameshwari and Kalpanadevi, 2006).

Research for the impact assessment on surface and groundwater was conducted in Tirupur (India's textile valley) and it concluded that the quality of water was poor from the deeper aquifers especially the TDS and TSS parameters (Pranaw *et al.*, 2014). Generally, the water was not suitable for the textile industry and for drinking purposes (Prabha *et al.*, 2013). A study conducted whereby textile effluent was utilised for irrigation in Roswell, New Mexico since 1946 (Koerner and Haws, 1979) revealed that the concentration of nitrate in groundwater increased as a result of irrigation with waste water effluent, in addition, no substantial amounts of trace elements were found in the groundwater (Tang *et al.*, 2004).

A study close to Faisalabad was carried out which investigated the physico-chemical components of the textile effluents and groundwater samples (Nasir *et al.*, 2016). The results discovered that there is a substantial impact on groundwater quality caused by effluents discharged from the textile industries (Taj *et al.*, 2013).

The research carried out by Shivkumar and Biksham (1995) in the industrial parts of India proposed that an increase in the concentration of heavy metals in groundwater was caused by highly variable pH of the industrial waste water that can percolate heavy toxic metals from the sediments, soils and rocks. Some effluents have been considered for reuse in irrigation (Angelakis *et al.*, 2003). The presence of nutrients (e.g. nitrogen, phosphorus and magnesium (Mg)) in some textile effluents, highly appreciated by crops, highlights the potential of this industrial sector to reuse its waste water (Wu *et al.*, 2015). Moreover, textile industries are great water consumers, which results in large volumes of effluents generated, equally important for irrigation (Yusuff and Sonibare, 2004).

High values of TSS and organic loads are expected from waste water effluents from natural fibres such as cotton (Correia *et al.*, 1994). Nitrogen is only present in large quantities within dyeing and printing waste water (Bisschops, and Spanjers, 2003). The textile effluents comprise of trace metals like arsenic (As), Cr, Cu and Zn, which are capable of damaging

the environment (Ghaly *et al.*, 2014). Suspended solids concentrations can combine with oily scum and interfere with oxygen transfer mechanism in the air-water interface; this aspect plays an important role in harming the environment (Laxman, 2009).

2.7 Industrial pollution in the Buffalo River catchment

Zwelitsha Township in King Williamstown has some of the oldest industries in the Eastern Cape Province (Chigor *et al.*, 2013), which consist mainly of textile industries. The Da Gama Textile Company (Pty) Ltd factory, close to Zwelitsha undertakes a whole range of textile manufacturing activities from spinning and weaving to dyeing and completing printing (Kilvington, 1996). The impact of the run-off from these irrigated lands has not been measured (Van Ginkel *et al.*, 1996). The manufacturing unit at the factory started out in 1946 and employed more than 1,852 people. The township of Zwelitsha was established after the factory was built and it was envisioned that the industry would ultimately employ 700 individuals (Kilvington, 1996). The staff complement at Da Gama textile is currently reported to be 720 (Dayimani, 2020).

The water quality of the water systems in the Zwelitsha-King Williamstown industrial area has been negatively affected by untreated effluents from the industrial activities (Yahaya *et al.*, 2018). This is of concern for the water quality of the Buffalo River as it is informed as a primary water resource within the Eastern Cape Province (Van Ginkel *et al.*, 1996). Notwithstanding its importance there are limited data available on contaminants in surface and groundwater and their possible effects on the aquatic ecosystem and humans (Yahaya *et al.*, 2018).

All the industries that generate waste water and discharged into the Buffalo River catchment were obligated to conform to the general effluent standard and the special 1 mg/L phosphate standard. Da Gama industry utilizes different techniques of irrigation schemes to get rid of their effluent (Van Ginkel *et al.*, 1996). The impact of excess run-off from the irrigation schemes in the event of local rainfall occasions have not been determined; however it has been projected that as much as 88% of the salt load entering the river, apart from natural sources, is coming from the industry (Van Ginkel *et al.*, 1996). Effluents are discharged into the rivers almost solely lacking proper treatment, that's probably to have an effect on the water quality of the receiving environment and eventually into the Buffalo River (Van Ginkel *et al.*, 1996). Industrial effluent discharged upstream additionally in all likelihood contributes significantly to the poor state of the Buffalo River (Chigor *et al.*, 2013). The Da Gama textile factory has retaining (tailings) dams where industrial effluent (dyes) are stored ultimately discharging into the Buffalo River (Palmer, 1991). The over-flowing of the holding dams has

occurred during excessive rainfall events resulting in pollution of the Buffalo River and causing extensive fish kills (Palmer, 1991).

The water quality of the middle and lower reaches of the Buffalo River has been a major concern (Zokufa *et al.*, 2001). Laing Dam is located downstream of Zwelitsha-King Williamstown, and receives treated domestic and industrial effluent from the surrounding industries and Waste Water Treatment Works (WWTWs) (Van Ginkel *et al.*, 1996). The last detailed situation analysis of the Buffalo River was carried out by Van Ginkel *et al.* (1996) using current data and information; to define and outline the water quality guidelines for different users; to design a water quality monitoring system; and to make management recommendations to reduce the impacts of pollution in the river. Mokone-Somoro (2006) conducted research on the impacts of industrial effluent on the pH, temperature, DO and turbidity and impacts on the macroinvertebrates. The general microbiological quality of the effluents discharged from the WWTWs did not comply with the water quality limits in respect of pathogens such as, *Vibrio cholera* and coliphages (Momba, *et al.*, 2006). Some of the pollution point sources for specific water bodies were identified as WWTWs (Teklehaimanot *et al.*, 2014). Another study carried out by Palmer and O'Keeffe (1990) found out that the biota downstream of dams in the Buffalo River catchment is modified due to altered physico-chemical variables.

Preceding contamination studies on the Buffalo River and the estuary assessed physico-chemical and microbiological quality (Dallas, 2008; Chigor *et al.*, 2013), pesticides (Fatoki and Awofolu, 2003; Yahaya *et al.*, 2018) and total petroleum hydrocarbons (Adeniji *et al.*, 2017). These results show that the bacteriological qualities of the Buffalo River and dams were poor, and suggest that sewage was dumped into the Buffalo River during the study period (Chigor *et al.*, 2013); the results for the pesticides study appear to show that the exposure levels of the compounds were safe for humans and animals (Yahaya *et al.*, 2018); the petroleum study revealed that the TPHC concentrations were found to be extremely higher in the spillage sites and greatly industrialized areas.

The Buffalo River was included in the 2008 state of the nation report for the South African river systems that are classed as eutrophic or having the potential to become eutrophic in the near future due to their poor water quality (Oberholster and Ashton, 2008; Allanson and Jackson, 1983; O'Keeffe, 1989; Pieterse and Janse Van Vuuren, 1997). The Buffalo River was one of the rivers included in this list. Limited research has been carried out to investigate groundwater contamination by waste water irrigation in the study area. However, it is well documented that irrigation of effluents impacts groundwater recharge and soil

aquifer treatment systems as well as the chemical and microbiological water quality (Bouwer *et al.*, 1980; Gallegos *et al.*, 1999;; Nema *et al.*, 2001).

Palmer (1991) studied the extent and intensity of the effects of impoundments on selected physical, chemical and biotic conditions in an impounded southern African river. Laing Dam is a surface-releasing impoundment which receives treated sewage and industrial effluent from the urban and industrial complex of Zwelitsha-King Williamstown. The study found that impoundments in the Buffalo River caused an upstream shift of the thermal and suspended organic conditions, and the distribution of blackfly species.

Yahaya *et al.* (2018) investigated the insufficient evidence about phenolic by-products by establishing the distribution of these phenolic derivatives along the course of Buffalo River and delivered information on the possible health risk from exposure. It was evident from the results that the occurrence of organic contaminants in the Buffalo River could have an important health impact.

2.8 Previous studies in the Buffalo River catchment

For many years there has been distress about the water quality, especially in the middle and lower reaches of the Buffalo River (Zokufa *et al.*, 2001). Laing Dam is located downstream of Zwelitsha-King Williamstown, and gets treated domestic and industrial effluent from the surrounding industries and waste water treatment works (Van Ginkel *et al.*, 1996). Previous research has been carried out within the Buffalo River whereby a water quality situation analysis was carried out (Van Ginkel *et al.*, 1996). The study was conducted using current data and information; to define and outline the water quality guidelines for different users; to design a water quality monitoring system; and to make management recommendations to reduce the impacts of pollution in the river (Van Ginkel *et al.*, 1996). Previous pollution investigations on the Buffalo river and its estuary encompass physicochemical and microbiological qualities (Dallas, 2008; Chigor *et al.*, 2013), pesticides (Fatoki and Awofolu, 2003; Yahaya *et al.*, 2018) and total petroleum hydrocarbons (Adeniji *et al.*, 2017) in various environmental media. According to Hart (1982) the water quality is degraded from a naturally elevated baseline condition (Thornton *et al.*, 1967, Reed and Thornton, 1969) as a result of industrial, domestic and agricultural effluent, but the relative contributions to mineralisation and eutrophication are not known. It was found that the nutrients in the Buffalo River cannot be accounted for, even though there were industries that were discharging waste water into the river (Selkirk and Hart 1984). A state of the nation report on an overview of the current status of water quality and eutrophication in South African Rivers and reservoirs was done in 2008 (Oberholster and Ashton, 2008). Selkirk and Hart (1984) also investigated the

sensitivity of the major impoundments in the Buffalo River catchment to eutrophication. Limited research has been carried out to investigate groundwater contamination by waste water irrigation (e.g. Gallegos *et al.*, 1999). However, substantial literature exists on the impacts of soil aquifer treatment systems and groundwater recharge with the usage of effluent on chemical and microbiological quality of water (e.g. Bouwer *et al.*, 1980; Nema *et al.*, 2001). There are not any studies that have catered their focus at the impact of irrigation with industrial effluent on groundwater in the Zwelitsha area near Da Gama textile industry.

2.9 Industrial pollution in other countries

Israel

The disposal of waste water to non-perennial rivers in a semi-arid and arid climate is related to intolerable environmental risks (Faechem *et al.*, 1983). Hence, land treatment through irrigation with effluent is advantageous, as experienced for numerous years in Israel.

Nigeria

A study was conducted at the Challawa River, Kano State, Nigeria and it was found out that the concentrations of heavy metals within the water and sediment samples were greater than the WHO guideline values for the protection of aquatic ecosystem. This is expected because of its location near tanneries and textile industries (WHO, 1984; Akan *et al.*, 2009).

India

A study was done in Panipat city India. In the study, it was divulged that textile effluent is the main source of water contamination by leaching. As it is the major source for irrigation in Haryana state, irrigation with contaminated groundwater containing variable amounts of heavy metals results in increase in concentration of metals in the agricultural soil (Malik and Bharti, 2007).

Effluents from the industries in the Gulf of Mannar, South Coast of Tamil Nadu, India are reportedly being directly discharged onto surrounding land, irrigation fields and surface water bodies forming point and non-point sources of contamination for groundwater in the study area. The study looked at the determination of physico-chemical properties, trace metals, heavy metals and microbiological quality of drinking water (Selvam *et al.*, 2017).

Pakistan

The waste water of Faisalabad is being disposed without any treatment into rivers, the Ravi and the Chenab through drainage system that include Madhuana and Paharang drains and city municipal channels. Industrial and sewerage waste water is polluting the surface and groundwater of Faisalabad city daily (Kahlown *et al.*, 2006). Seepage from these drains is the major source of groundwater contamination and is causing problems to its uses (Rehman, 2013). The concentration of physicochemical and biological parameters for most of the waste water discharged from the industries can be exceeding their permissible limits. The groundwater quality of the city is not suitable for consumption due to the fact the concentration of physicochemical constituents was quite high from the permissible limits (PCRWR, 2002).

Another study was conducted in Nullah to assess the probable hazards associated with the untreated effluent being discharged from a number of the main industrial units on the River Kabul's water quality (Qadir *et al.*, 2008). This study also focussed on the estimation of the waste water characteristics of some major important industrial units like sugar mills, paper mills, ghee (butter) mills and textile mills and so forth, within the vicinity of this river and their effects on the Dissolved Oxygen (DO) and Total Suspended Solids (TSS) concentrations (Qadir *et al.*, 2008). This study suggested that all the waste water coming from the industrial sources should be properly treated as an essential part of its production and manufacturing system before disposing them into the river (Kiran *et al.*, 2019).

Saskatchewan-Canada

Monitoring information from two big effluent irrigation initiatives (projects) in Saskatchewan have shown that the soil bio-system is changed with the application of sewage effluent. Irrigation is sustainable, provided proper management practices are followed. An irrigation sustainable project was developed in Saskatchewan to assess the long term impact and sustainability of effluent irrigation practices (Tollefson and Hogg, 1997). This project was established to examine existing monitoring information from the major effluent irrigation to assist in setting guidelines for future effluent irrigation projects and tasks (Hogg *et al.*, 1997).

Zimbabwe

Industries positioned along the Mukuvisi River illegally discharges industrial effluent into this river and its tributaries (Chimuriwo, 2016). Sometimes formal industries also dump effluent

into the Mukuvisi River or its tributaries (Nyamangara, 2008). The penalty for polluting rivers in Zimbabwe is far lower compared to the value of processing the effluent, and capacity for monitoring by the relevant authority is limited. The disposal of sewage and industrial effluent into the rivers has been blamed for the deteriorating water quality within the Manyame catchment, which includes the Mukuvisi River and Lake Chivero (Marshall, 1994). Poor water quality no longer only influences negatively on the aquatic fauna but also significantly increases expenditures of treating the water for domestic use. There is excessive metal content that is attributed to unlawful discharge of industrial effluent from the industries that are located along the river and its tributaries, coupled with exceptionally low flow rates of water which favour the flocculation and sedimentation of the clay-sized particles often associated with heavy metals (Greichus *et al.*, 1978).

CHAPTER 3 METHODOLOGY

3.1 Description of the study area

3.1.1 Location

The Buffalo River is considered to be a small system with a catchment area of 1276 km² and is 125 km in length (Figure 1). The Buffalo River drains from the headwater stream in the mountain of the Amatole Mountains at an altitude of 1200 m where it passes through Zwelitsha-King Williamstown and Mdantsane (RHP, 2004). From its eye and headwaters, the river flows downhill through ancient woodlands in a deeply carved stream, flanked by rock cliffs that reach up to 120 m in height. After only 7 km the river drains into the small, century-old Maiden Dam and 4 km downstream of the Maiden Dam, into the much bigger Rooikrantz Dam. Two fundamental tributaries from the west join the centre section of the Buffalo River (Mggakwebe simply upstream of Zwelitsha-King Williamstown and the Ngqokweni tributary at Zwelitsha) (Palmer, 1991).

Yellowwoods is the major tributary which flows from the north into Laing Dam (Palmer, 1991). From Laing Dam, the Buffalo River flows eastwards for 40 km to Bridle Drift Dam, the biggest impoundment in the river (Palmer, 1991). Small streams on the northern bank direct runoff into Bridle Drift Dam from Mdantsane. From Bridle Drift Dam, the Buffalo River flows through low altitude coastal forest for 20 km, before flowing into the Indian Ocean through the estuary harbour of East London (RHP, 2004). The layout of the study area and the sample collection sites are shown in Figure 1 and 2 and Tables 2 and 3. Table 3 depicts the site location of all the monitoring boreholes that have been sampled at the study area; and Table 2 shows the site locations of all the surface water sites. The study was carried out in the river and tributaries that drain into the Buffalo River industrial and in effluent containment facilities of the industry. Small streams at the northern bank convey runoff directly into Bridle Drift Dam from Mdantsane. From Bridle Drift Dam, the Buffalo River flows through low altitude coastal forest for 20 km, before coming into the Indian Ocean through the estuary harbour of East London (RHP, 2004).

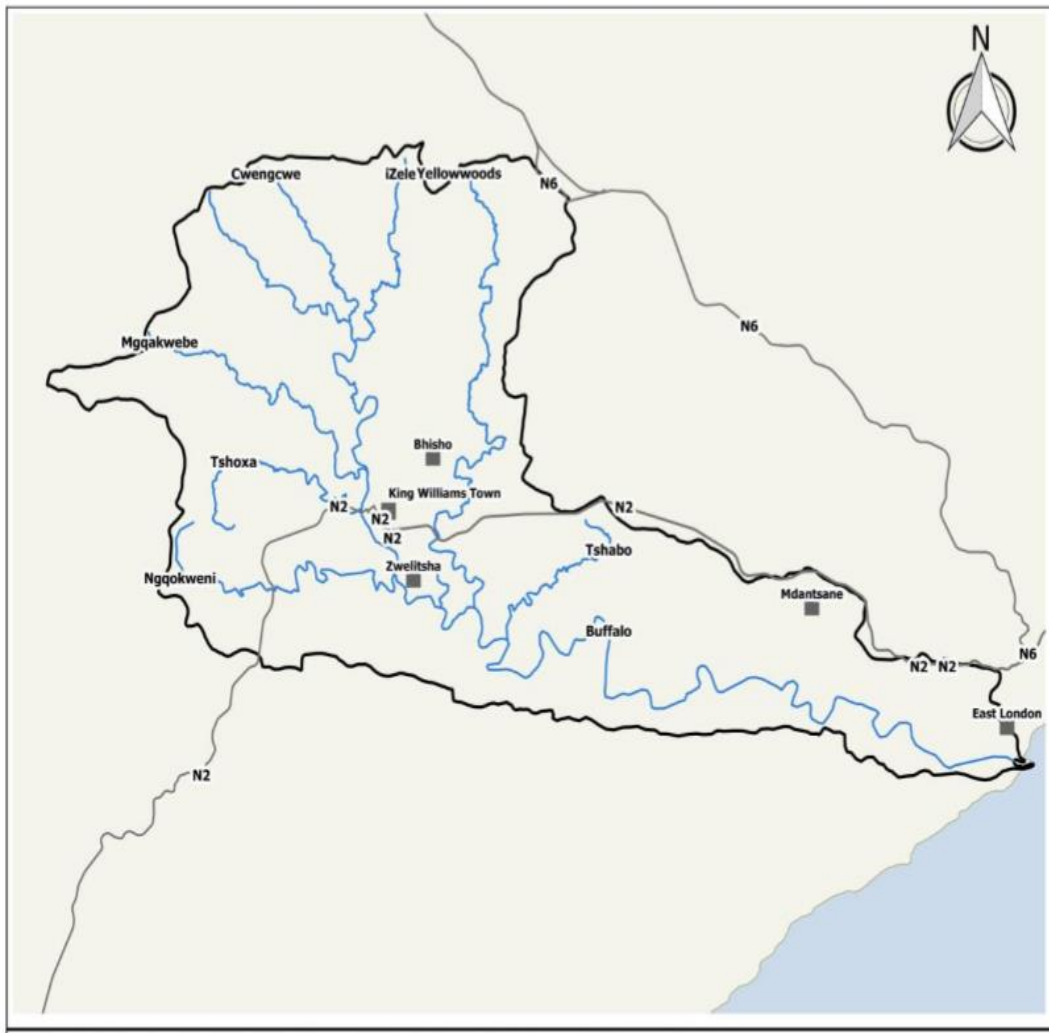


Figure 1: Overview of the catchment boundaries of the study area

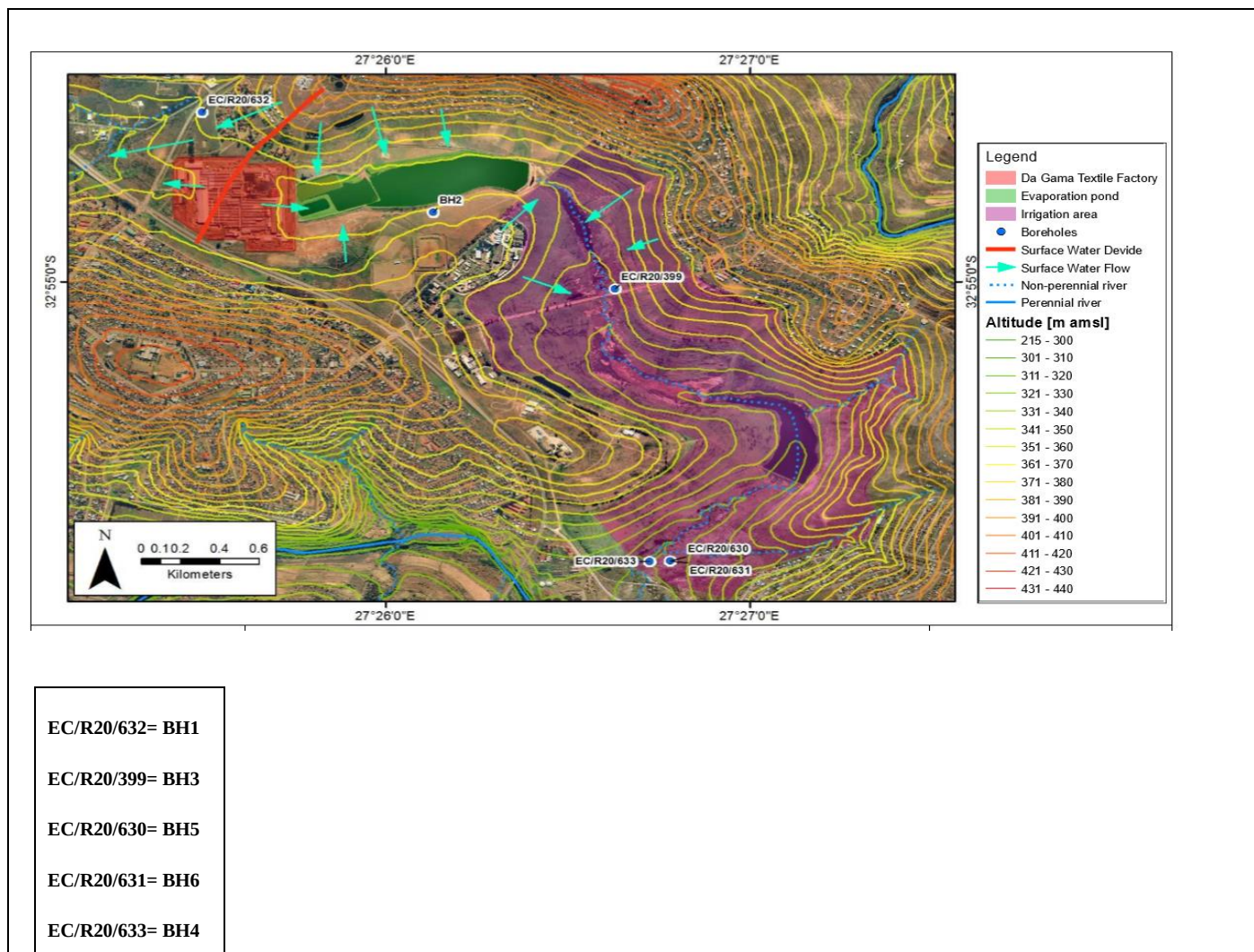


Figure 2: Overview of Da Gama Textile industry and the area irrigated with effluent. The position of the boreholes and gradient towards the Buffalo and tributaries are also indicated (Google Earth imagery)

3.1.2 Description of the Climate and Runoff

The Buffalo River Catchment is characterised by a warm and temperate weather. According to the RHP (2004) the temperatures range between 8 and 39°C with an annual mean of 21°C. The mean annual temperature is 18°C with the inland temperatures fluctuating between -2° and 42°C. The Buffalo River catchment falls within the summer rainfall region of South Africa and the summer rainfall is about double that of the winter season. The higher zone offers 40% of the runoff for the entire catchment as the mean annual rainfall over the entire catchment is 736 mm (Van Ginkel *et al.*, 1998).

3.1.3 Description of the Geology and Geomorphology

The Balfour Formation and Middleton Formation (Adelaide Subgroup, Beaufort Group) are the main geological formation of the Buffalo River Catchment (Figure 3) (Van Der Walt, 1980; Partridge and Maud, 1987; Johnson *et al.*, 2006). Interchanging layers of grey, fine-grained sandstone and greenish-grey, bluish-grey or greyish-red mudstone (Middleton Formation only) are the main characteristics of the Adelaide Subgroup. The dykes, sills and inclined sheets of the Jurassic age dolerite have intruded these sedimentary rocks. Soils with negligible development, usually on tough or weathering rock (Leptosols, Regosols, Calcisols, Durisols) are the dominant in the catchment (Johnson *et al.*, 2006). Soils with a marked clay conglomerate occur closer to the estuary (Luvisols, Planosols, Solonetz) (Johnson *et al.*, 2006). The geology of the study area is defined on 1:250 000 geology sheet 3226 King Williams Town (Figure 3).

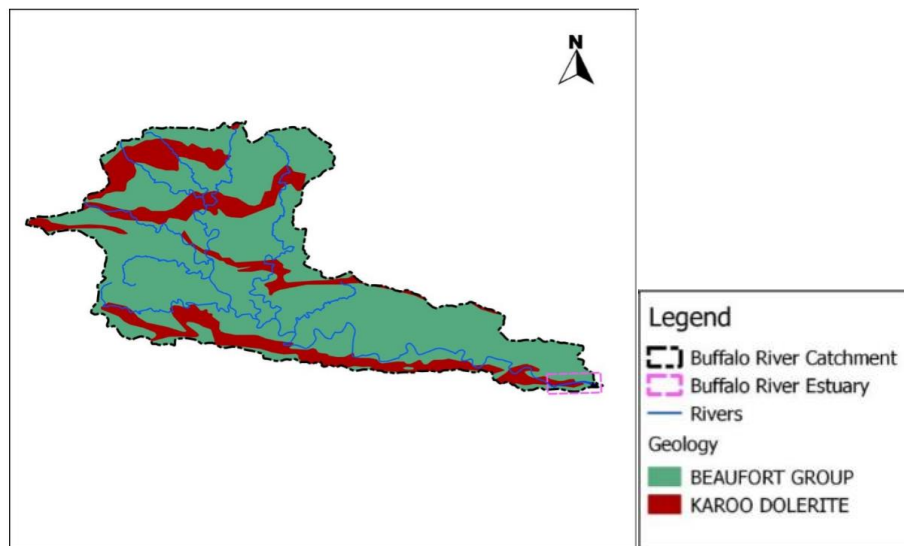


Figure 3: Geology of the Buffalo River Catchment

3.2 Research Design

The study involved analysing the water quality of the discharge effluents from the Da Gama textile industry in Zwelitsha-King Williamstown. Discharge effluent was sampled once a week at the evaporation ponds, settling tanks and the tailings dam of the industry. Sampling was also conducted in selected boreholes and surface water sites along the Buffalo River catchment and within the vicinity of the industry. The Da Gama textile industry specifically discharges its treated effluents into the open field via sprinkle and flood irrigation. This study was commenced to assess the industrial effluents for physicochemical characteristics at the various holding dams and discharge point and evaluate the quality of groundwater in the

surrounding area so as to know if the industrial effluents had any impact on the present water quality status of such water.

3.2.1 Data collection

For this study, secondary data were used. Historical data records from six South African Department of Water and Sanitation (DWS) monitoring stations within the Buffalo River catchment were obtained from the DWS Resource Quality Information Services (RQIS, 2019; Silberbauer, 2019). Data for six borehole sites were obtained from the Da Gama textile industry groundwater monitoring reports (SRK, 2015). The Da Gama effluent water quality data were acquired from the effluent monitoring reports (SRK, 2015). The water quality data collected and analysed from the river monitoring stations included electrical conductivity (EC in mS/m), sodium (Na), Ammonia (NH_3), Ammonium as nitrogen (NH_4), Nitrite /Nitrate as nitrogen (NO_2^- - NO_3^{2-}), orthophosphate (PO_4^{2-}) pH, total suspended solids (TSS) and chemical oxygen demand (COD) in mg/L. The borehole samples were analysed for the same parameters as surface water except for Cl, SO_4^{2-} and COD. The Da Gama factory effluent water quality parameters that were measured included pH, EC, Na, Ca, Mg NH_3 , PO_4^{2-} , COD and TSS. The water quality data collected and analysed from the monitoring sites are presented in Table 1.

3.2.2 Site Selection

a) Surface water

Surface water sites had been selected in line with their role in terms of the industrial vicinity and the proximity to the Buffalo River. A total of six sites were selected on the Buffalo River main channel and the associated tributaries (refer to Figure 4 and Table 2). The GPS co-ordinates were documented for every single sampling site. Samples have been collected by the DWS (2002) to (2019) at the flow gauging weirs. At some sites, samples have been taken under other DWS water quality compliance monitoring projects. The textile industry collects water samples at the effluent discharge points whereby irrigation is taking place via sprinkler or flood method. This data is then included into the DWS database as part of compliance monitoring reporting from the industry. Effluent discharge collection points such as the evaporation ponds, settling tanks and the return water dam were also sampled with the associated flow being recorded.

Table 1: Water quality parameters available for the three different types of water sources utilised in this study.

Water quality parameter	Buffalo River	Borehole	Textile effluent
pH	X	X	X
Electrical conductivity (EC) (mS/m)	X	X	X
Calcium (Ca) (mg/L)			X
Magnesium (Mg) (mg/L)			X
Sodium (Na) (mg/L)	X	X	
Chloride (Cl) (mg/L)		X	
Sulphate (SO ₄) (mg/L)		X	
Nitrate-Nitrite (NO ₂ ⁻ /NO ₃ ²⁻) (mg/L)	X	X	
Ammonia (NH ₃) (mg/L)	X		X
Ammonium (NH ₄ ⁺) (mg/L)	X	X	
Ortho-phosphate (PO ₄ ²⁻) (mg/L)	X		X
Total suspended solids (TSS) (mg/L)	X	X	X
Chemical oxygen demand (COD) (mg/L)	X		X

Table 2: Site information for the surface water gauge stations.

SITE NAME	DWS MONITORING ID	LATITUDE	LONGITUDE	Description
US1	1000010299	-32.83125	27.37883	Upstream of the textile industry (reference site)
US2	100002455	-32.87186	27.38475	Upstream of the textile industry
US3	100002466	-32.900139	27.40416	Upstream of the textile industry
DS1	1000002458	-32.93227	27.43919	Downstream of the textile industry
DS2	1000002474	-32.93500	27.44666	Downstream of the textile industry
DS3	1000002477	-32.93810	27.46631	Downstream of the textile industry

b) Groundwater (Boreholes)

There are six existing monitoring boreholes namely (BH1, BH2, BH3, BH4, BH5 and BH6) that were evaluated for data analysis (refer to Figures 2, 4 and Table 3). Borehole BH1 was drilled up-gradient from the remaining monitoring wells, in order to serve as background groundwater quality. Boreholes BH5, BH6 and BH4 were established to monitor outflow groundwater quality from the irrigated area, shallow groundwater flow (potential perched flow) as well as deeper groundwater flow. Borehole BH3 is situated inside the irrigated area and BH2 is situated below (down-gradient) the evaporation pond.

Interruptive monitoring has been taking place at these boreholes from 2013 up to date. Data collection was done from 2013 to 2019. The period 2013 to 2015 was considered as historical. Data were collected on a quarterly basis four times a year to represent the summer, autumn, winter and spring seasons. This was to allow sampling throughout the wet and dry seasons. There was sufficient water within the monitoring boreholes which allowed

for sampling with a submersible pump. Only one monitoring borehole (BH2) was sampled using the bailing method, as the submersible pump was obstructed by the borehole casing.

Table 3: Sampled monitoring boreholes positions and associated site information.

Location	Borehole ID	DWS site ID	Latitude	Longitude	Depth (m)	Groundwater level (mbgl)
Up-gradient (Background)	BH1	EC/R20/632	-32.90782	27.42494	28.35	7.36
Below evaporation pond-shallow	BH2	BH2	-32.91303	27.43551	8.00	3.20
Irrigation area	BH3	EC/R20/399	-32.91703	27.44383	27.00	3.13
Outflow zone-shallow	BH4	EC/R20/633	-32.93118	27.44541	13.70	2.56
Outflow zone-deep	BH5	EC/R20/630	-32.93116	27.44636	40	4.16
Outflow zone-shallow	BH6	EC/R20/631	-32.93115	27.44636	12.20	1.54

Map of the Groundwater and Surfacewater sites

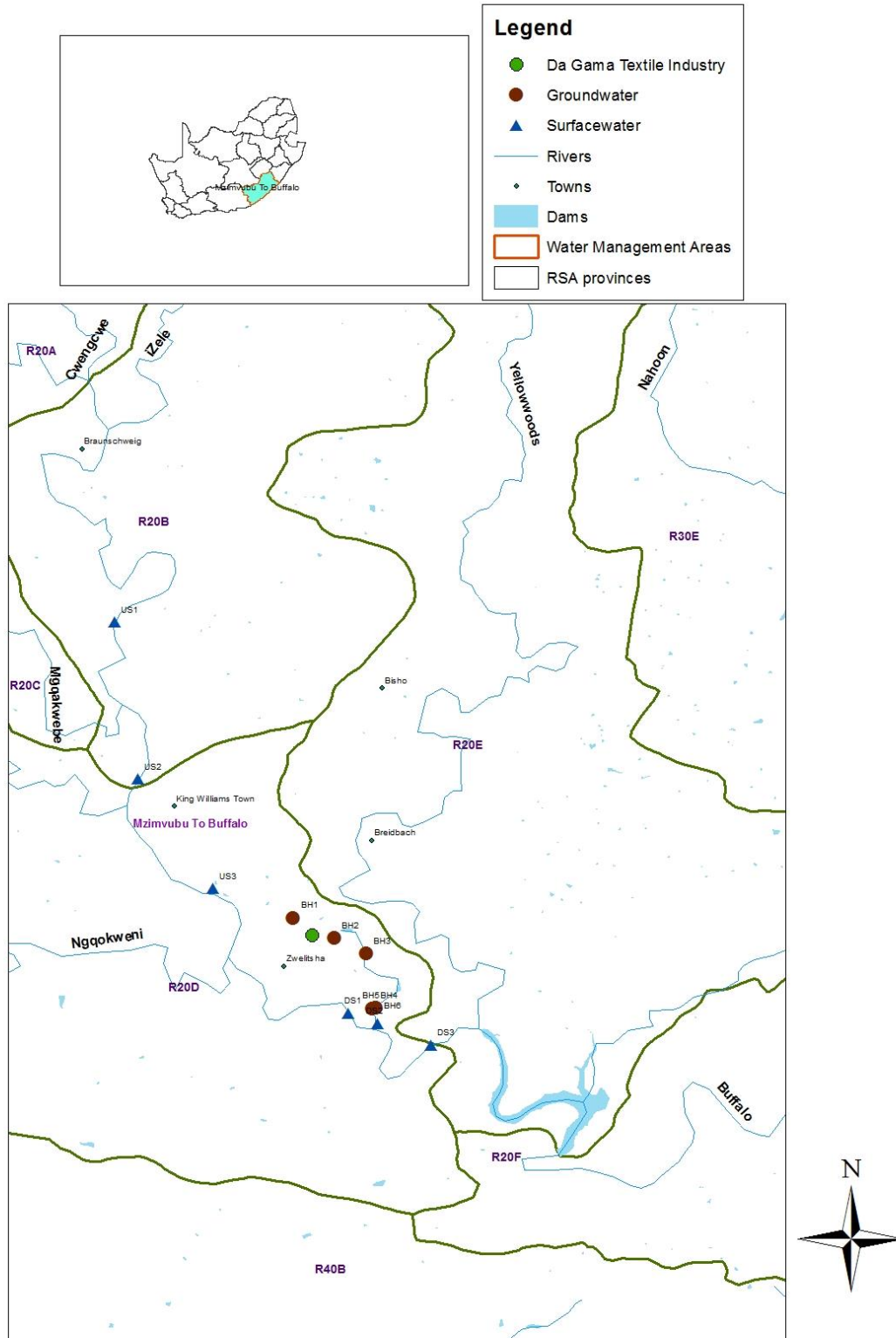


Figure 4: Position of the surface water (Buffalo River), groundwater (borehole) and textile industry samplings sites.

c) Textile plant effluent

The textile industry collected water samples on a weekly basis at the effluent discharge points where irrigation is taking place via sprinkler or flood method. These data are then included into the DWS database as part of compliance monitoring reporting from the industry. Effluent discharge collection points such as the evaporation ponds, settling tanks and the tailings dam were also sampled with the associated flow being recorded.

3.3 Data analysis

Univariate summary statistics (mean, standard deviation and range) and trend analyses were conducted using Microsoft Excel. The means of each site were compared to one another using the non-parametric Kruskal Wallis test. The significance was taken as $p < 0.05$. The statistical significance between two or more groups of an independent variable on a continuous dependent variable is determined using the Kruskal Wallis test. This test is also a rank-based non-parametric test. All analyses were conducted using GRAPHPAD PRISM software version 9. For the purposes of this study historical data were regarded as the first two years of the data set and current data were based on the rest of the data set. The time series assessment was done. The available data for each variable were averaged to annual records to determine trends in surface water quality at all sites from 1999 to 2019 and 2013 to 2019 for the groundwater quality sites. For the groundwater data, historical period was noted as 2013 to 2015; whereas for the surface water, the historical data period was from 2003 to 2005.

Line graphs of the mean standard deviation of each variable were created to visually assess the general trends and possible changes in water quality from 1999 to 2019 of all the data sets. The historical data for surface water and groundwater sites will be compared using trend graphs plotted on GRAPHPAD PRISM.

Univariate Analysis

Analysis of variance (ANOVA) was used to determine whether there were statistically significant differences in water physico-chemistry. The $p < 0.05$ was selected as indicating significant differences, calculated using GRAPHPAD PRISM version 9. ANOVA is a statistical method for the analysis of one variable as a factor of interest. However, it also enables generalisation of the two sample t-test, used to decide whether two samples have the same mean (Snedecor and Cochran, 1989).

Principal Component Analysis

One of the most frequently used multivariate data analysis of large data set is the Principal Component Analysis (PCA). PCA creates orthogonal transformation to convert a set of observations of possibly interrelated variables into a set of values of linearly uncorrelated variables referred to as principal components (Mohammed *et al.*, 2011). In PCA, the variety of principal components is less than or equal to the number of original variables (Jolliffe, 1973). This transformation is defined in one of these manner that the foremost principal component has the biggest possible variance (that is, accounts for as much of the variability in the data as possible), and each succeeding component in turn has the highest variance possible under the constraint that it be orthogonal to (i.e., uncorrelated with) the preceding components (Pripp, 2013). PCA is sensitive to the relative scaling of the original variables (Doukas *et al.*, 2012). A PCA starts by building the correlation matrix for data. Eigen values and eigen matrix will be provided through the diagonalizing the matrix (Hoyle and Rattray, 2004). Since the variance explained by each eigen vector is proportional to its eigen value, and only those eigen vectors with eigen values greater than one (1) be selected as significant independent variables (components). Determination of the most interrelated parameter for each component will enable identification of the sources of pollution (Jackson, 1993).

3.4 Ethical considerations

Due to the nature of this research, the study does not have any ethical implications. The research was conducted in a manner that animals or plants were not harmed. The zero ethics approval was provided by the Faculty of Natural and Agricultural Sciences (NWU-01348-20-A9). The applicable methodology and procedures, and appropriate ways of gathering data to present the investigation outcomes and interpret them accordingly resulting in demonstration of information in a coherent structure were followed. Appropriate standards and values at all these steps while conducting the study were followed and observed.

3.5 Methodological limitations

The water quality data for all the gauging stations are incomplete. Little or no data exists earlier than March 1992. From March 1992 onwards the data is adequate, however with some gaps. Some of the effluent flow readings were also erroneous for some periods. Some of the groundwater stations were destroyed and data collection was discontinued. This was either by the local communities through vandalism, or building infrastructure had been erected on top of the boreholes. Temporal variability in water quality (e.g. seasonal changes,

influence of groundwater particularly during the dry season) could not be assessed. For the groundwater data, historical period was noted as 2013 to 2015; whereas for the surface water, the historical data period was from 2003 to 2005.

3.6 Methodological boundaries

Data obtained from the Water Management System (WMS) had gaps. This could be due to a period of no data collection by the Department of Water and Sanitation; moreover this resulted in the data period being affected.

CHAPTER 4 RESULTS AND DISCUSSION

The chapter describes the results from the various methods described in the previous chapter. Of note was that the data was analysed with the aim of evaluating the current status of water quality in Zwelitsha King Williams's town and also trying to establish if the textile industry has an impact on the surface water and groundwater of this area. For conducting the data analysis of the dataset, tests were performed in GRAPHPAD PRISM. This Chapter therefore sought to present, discuss and interpret the results from a survey that was done looking at the various aspects that may have contributed to or influenced the water quality of the groundwater and surface water of the Buffalo River catchment. The time series assessment was done. The available data for each variable were averaged to annual records to determine trends in surface water quality at all sites from 1999 to 2019 and 2013 to 2019 for the groundwater quality sites.

Line graphs of the mean standard deviation of each variable were created to visually assess the general trends and possible changes in water quality from 1999 to 2019 of all the data sets.

Due to gaps in the data which was caused by the data collection that was not consistent for the similar months at every site for a particular year the annual average for each site was used for statistical analyses. For the purposes of comparing historical data to current data, the first two years of the available data set were used as historical data and the remainder represented the current water quality data at each site.

4.1 Buffalo River sites

4.1.1 Site US1

The water quality trends for the period 2003 to 2019 are shown in Figure 5. The pH values showed a slight decrease over the period, although the conductivity showed a slight increase. Sodium showed a slight decrease (notably only data available between 2003 and 2007). The nutrients showed a decreasing trend, except for PO_4^{2-} which showed a slight increase. Chemical oxygen demand showed a decreasing trend (Figure 5). Total suspended solids increased significantly for the three years of data availability (2016-2019).

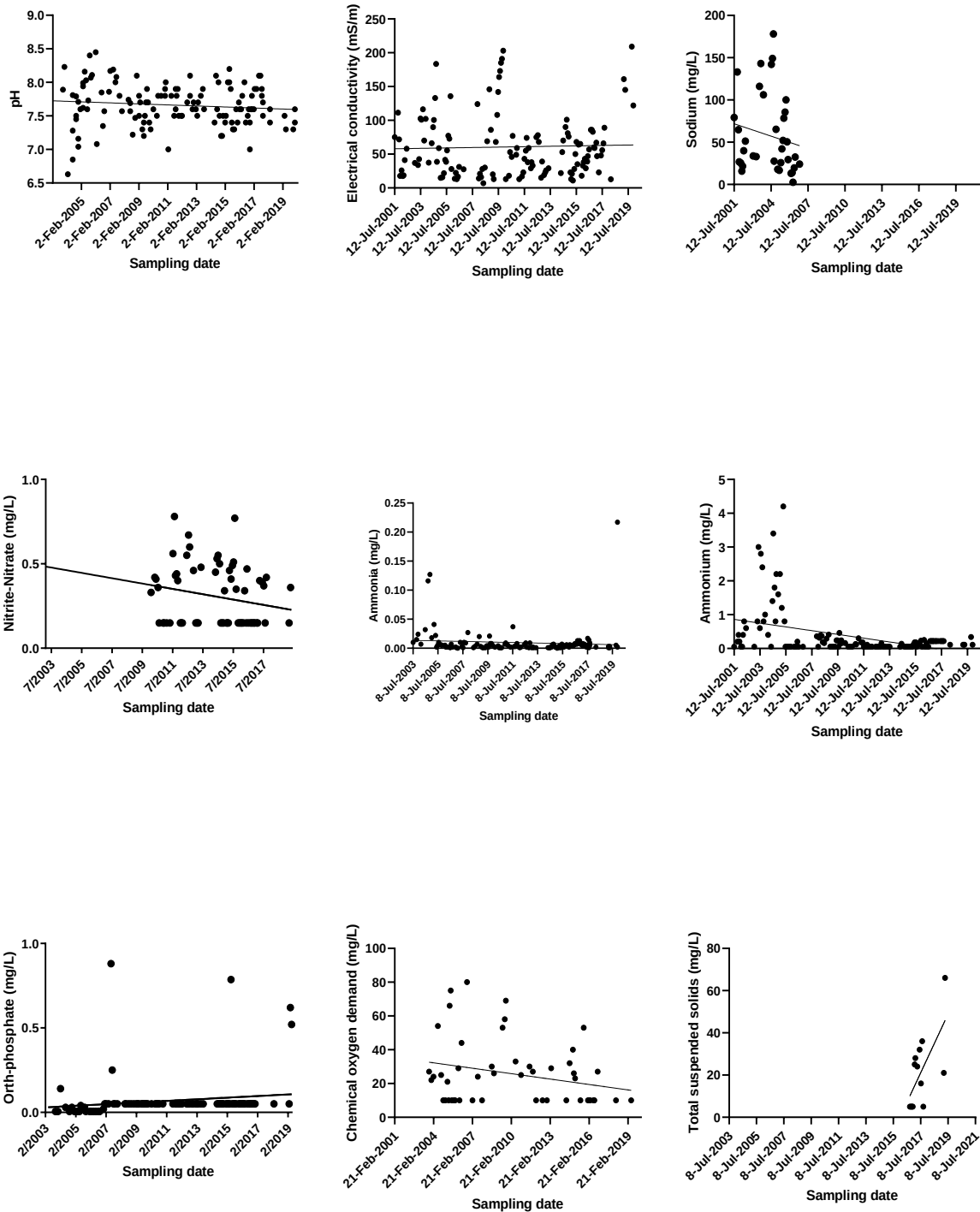


Figure 5: Trends in selected water quality variables measured at Site US1 from 2003 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for pH and EC (Table 4). The $\text{NO}_2\text{-NO}_3^{2-}$ levels decreased significantly without any statistical significance between the historical and current periods, while the PO_4^{2-} increased significantly (Table 4). There was significance difference in the means of Na, NH_3 , NH_4^+ and COD as $p < 0.05$.

4.1.2 Site US2

The water quality trends for the period 2003 to 2019 are shown in Figure 6. The pH values and EC showed a slight decrease over the period, while the Na showed a decrease (notably only data available between 2003 and 2007). The nutrients showed a significant decreasing trend, as well as the COD. The TSS increased over time.

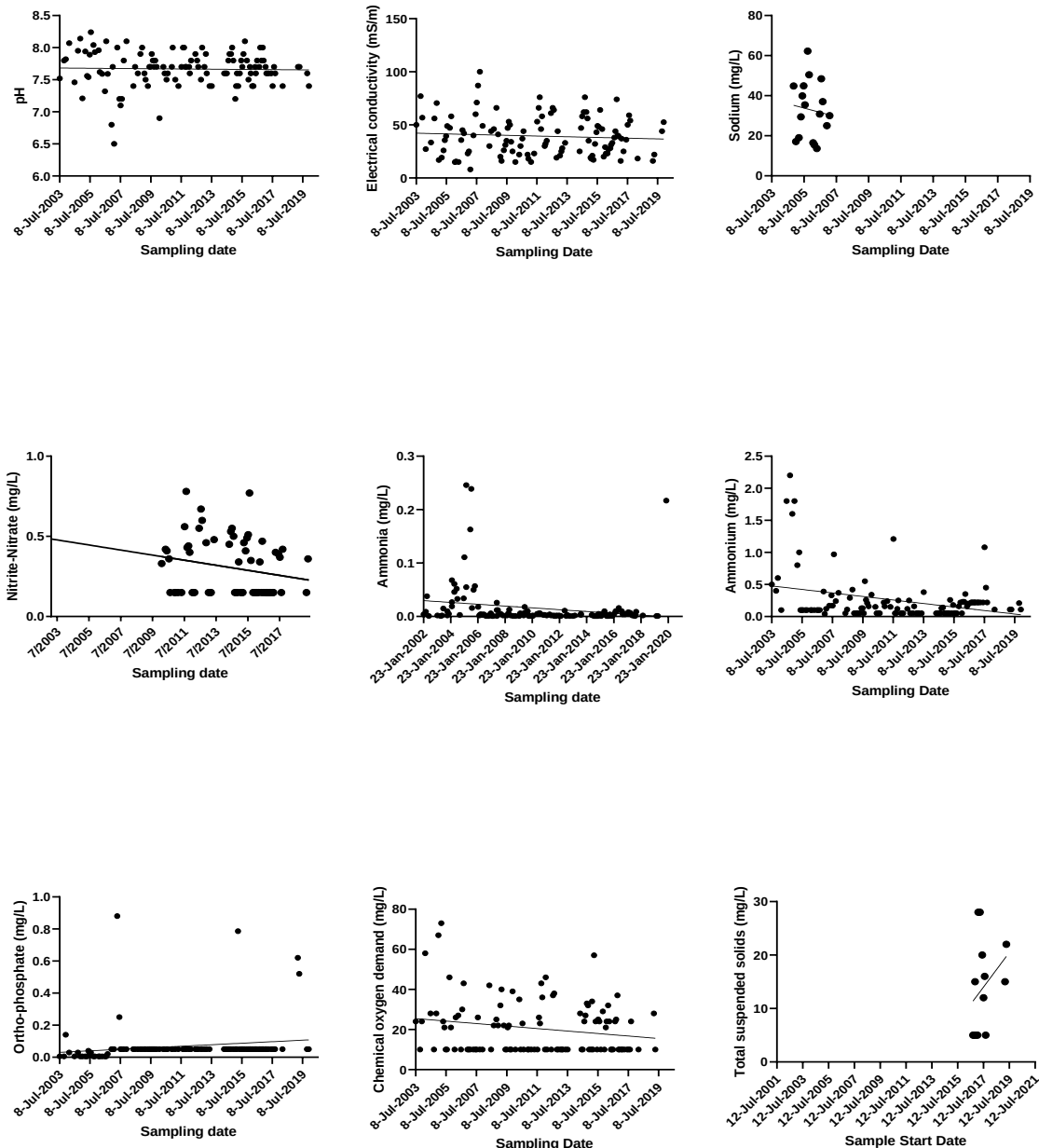


Figure 6: Trends in selected water quality variables measured at Site US2 from 2003 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for pH and EC (Table 4). The NO_2^- - NO_3^{2-} and COD levels decreased significantly between the historical and current periods, while the PO_4^{2-} slightly increased (Table 4). There was significance difference in the means of NH_3 and NH_4^+ as $p < 0.05$.

4.1.3 Site US3

The water quality trends for the period 2003 to 2019 are shown in Figure 7. The pH values showed a slight increase, while the EC showed a slight decrease over the period. There were no values recorded for Na during the entire period. The nutrients showed a decreasing trend, including COD (Figure 7).

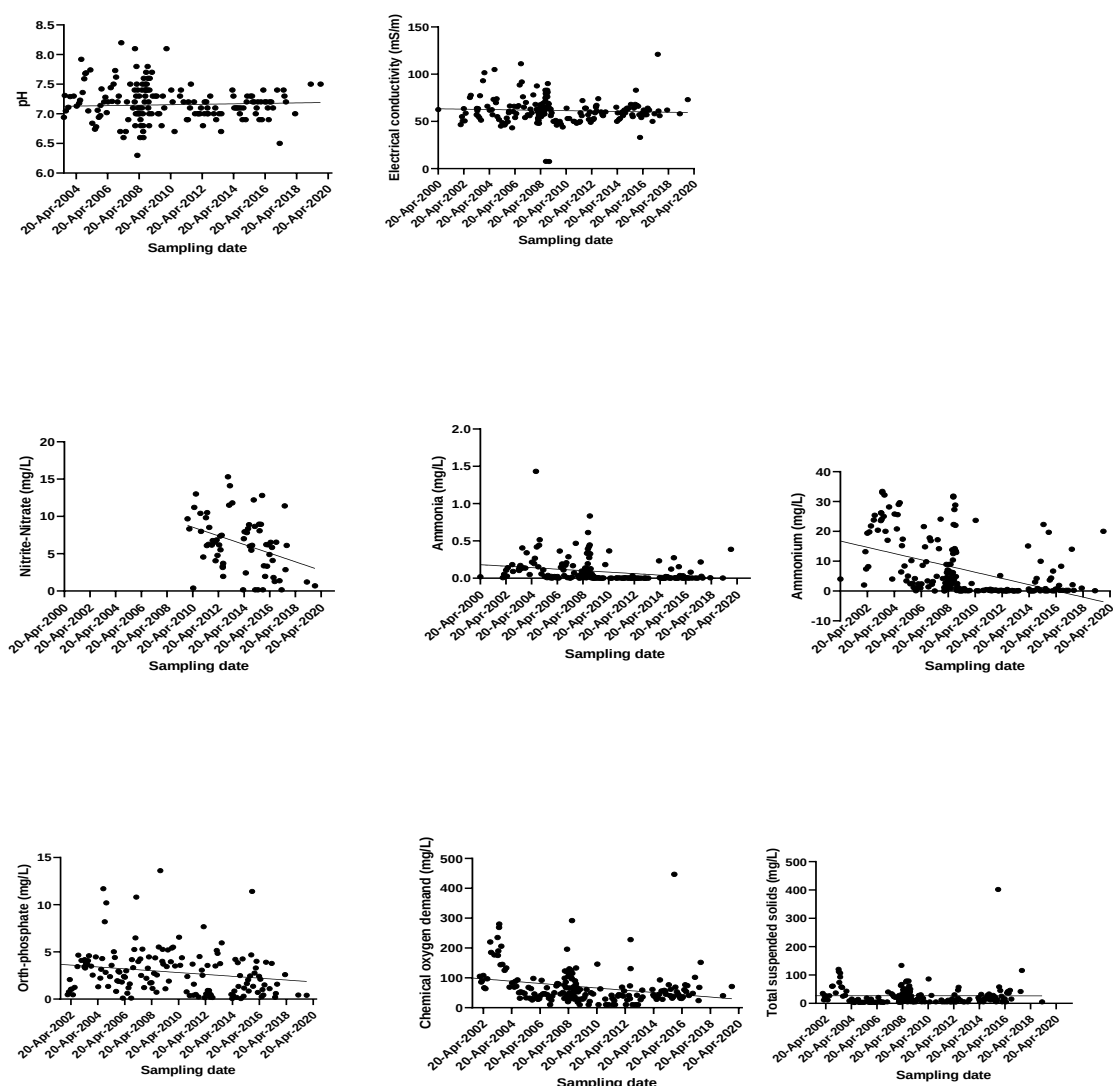


Figure 7: Trends in selected water quality variables measured at Site US3 from 2003 to 2019. Note there is no graph for Na as it was not recorded during the entire period. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for pH and EC (Table 4). There was no historical data recorded for Na and NO_2^- - NO_3^{2-} for this site. The

NH_4^+ , COD and TSS levels showed a significant decrease ($p < 0.05$) between the historical and current periods, while the PO_4^{2-} increased significantly and there was no significant difference. There was significance difference in the means of NH_3 , as $p < 0.05$.

4.1.4 Site DS1

The water quality trends for the period 2003 to 2019 are shown in Figure 8. The pH values showed a slight increase, while the EC showed a slight decrease over the period. Sodium showed a increase (notably only data available between 2011 and 2012). The nutrients showed a notably decreasing trend, except for PO_4^{2-} which increased significantly over time. The COD showed a significant decreasing trend (Figure 8).

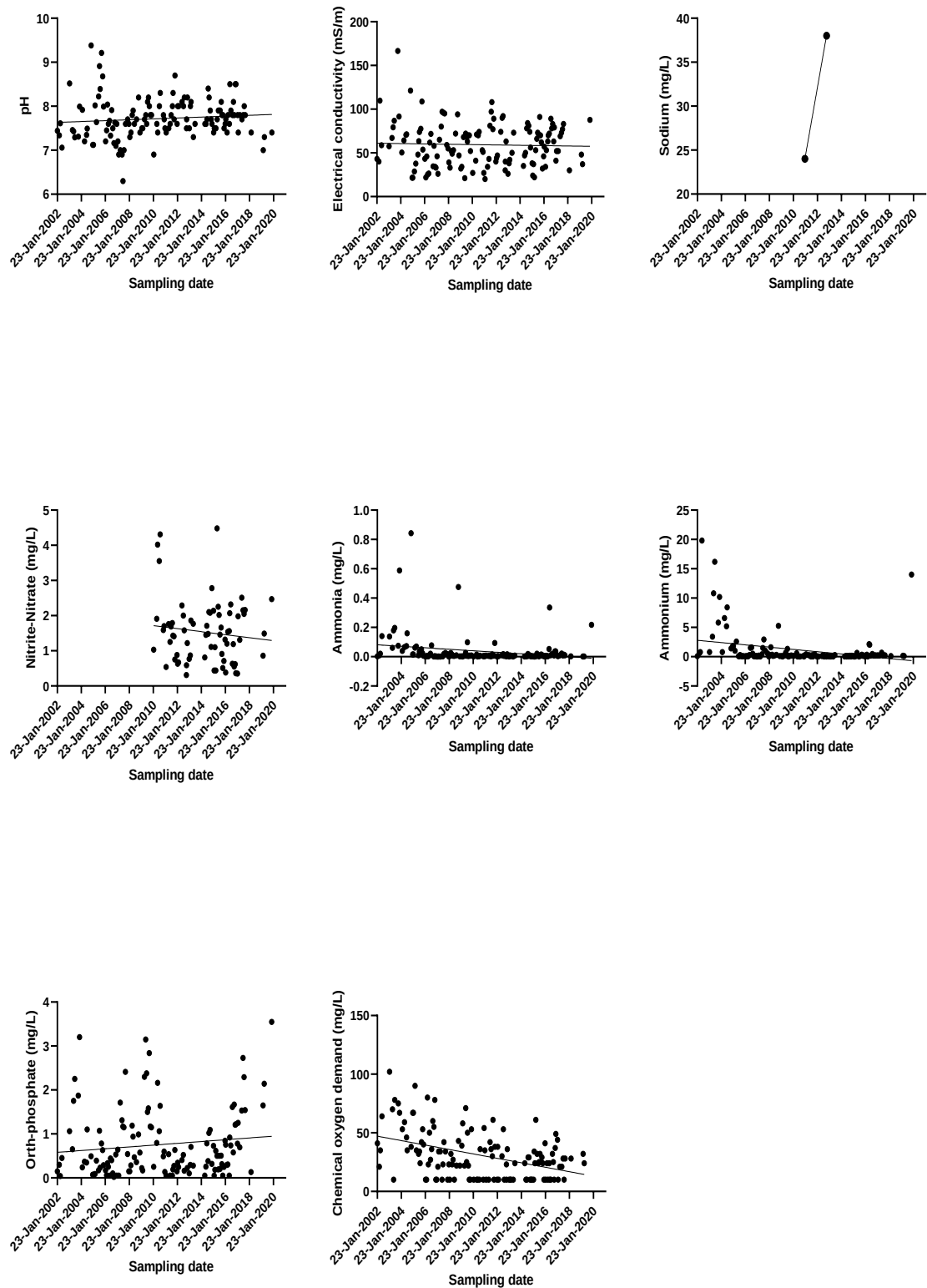


Figure 8: Trends in selected water quality variables measured at Site DS1 from 2003 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A multi comparison test was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for pH, while the EC showed a slight decrease (Table 5). There was no historical data recorded for Na and NO_2^- - NO_3^{2-} . The NH_4^+ and COD levels decreased significantly between the historical and current periods, while the PO_4^{2-} increased significantly. Total suspended solids did not have data recorded for this site (Table 5). There was significance difference ($p < 0.05$) in the means of EC, NH_3 , and COD.

4.1.5 Site DS2

The water quality trends for the period 2003 to 2019 are shown in Figure 9. The pH and EC values showed a slight increasing trend over the period. The nutrients showed a decreasing trend except for NH_3 , while the PO_4^{2-} did not show much variation over time.

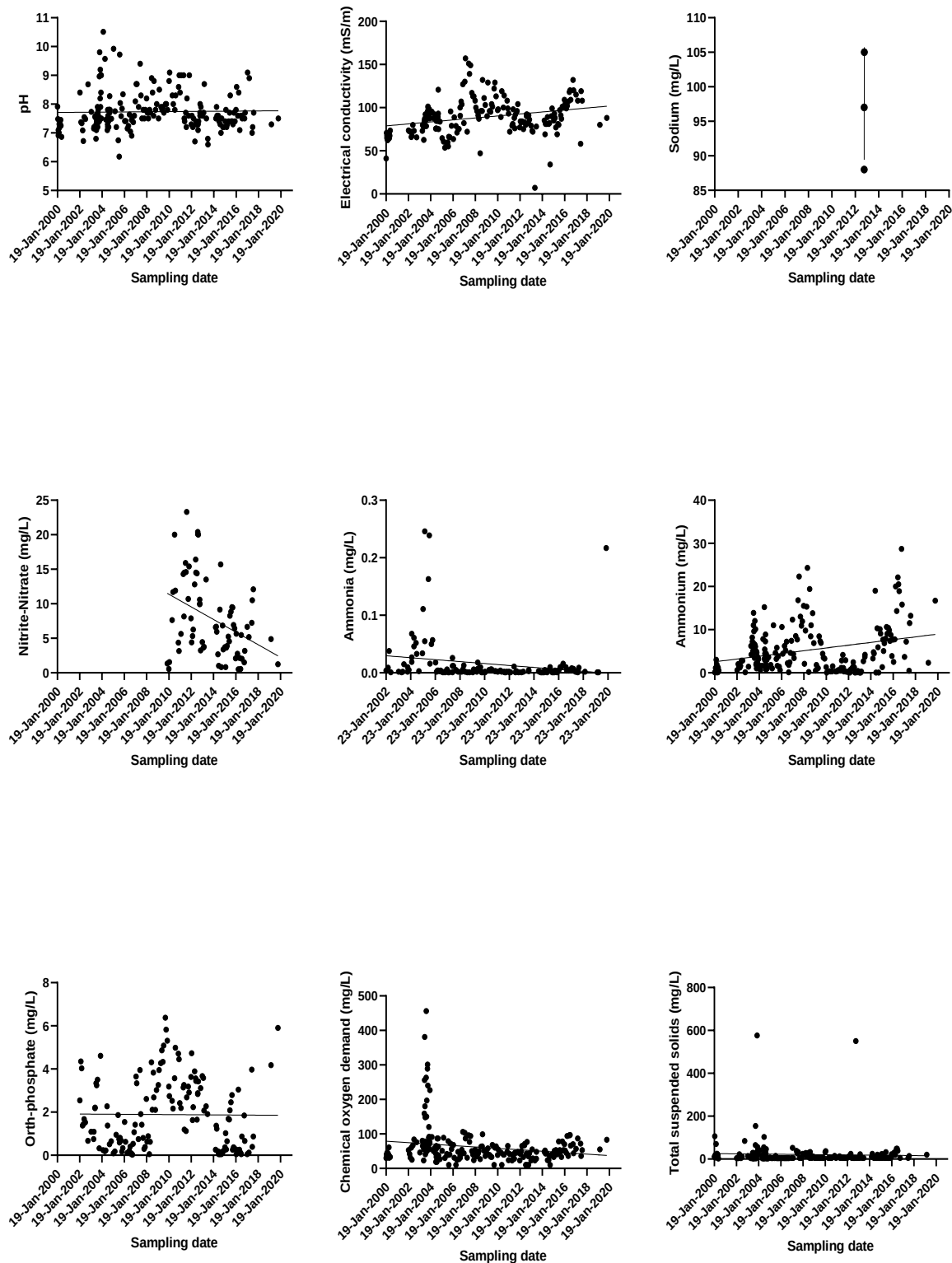


Figure 9: Trends in selected water quality variables measured at Site DS2 from 2003 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test for the historical and current water quality data and it revealed that there were no significant differences for pH and NH_4^+ (Table 5). There was no historical data recorded for Na and NO_2^- - NO_3^{2-} for this site. The EC, NH_3 , COD and TSS levels decreased significantly between the historical and current periods, while the PO_4^{2-} increased significantly (Table 5). There was significance difference ($p < 0.05$) in the means of EC and COD.

4.1.6 Site DS3

The water quality trends for the period 2003 to 2019 are shown in Figure 10. The pH values showed a slight decrease, while the EC did not show much variation over the period. Sodium showed a increase (notably only data available between 2011 and 2012). The nutrients showed a decreasing trend, except for NH_3 while the COD decreased significantly over time.

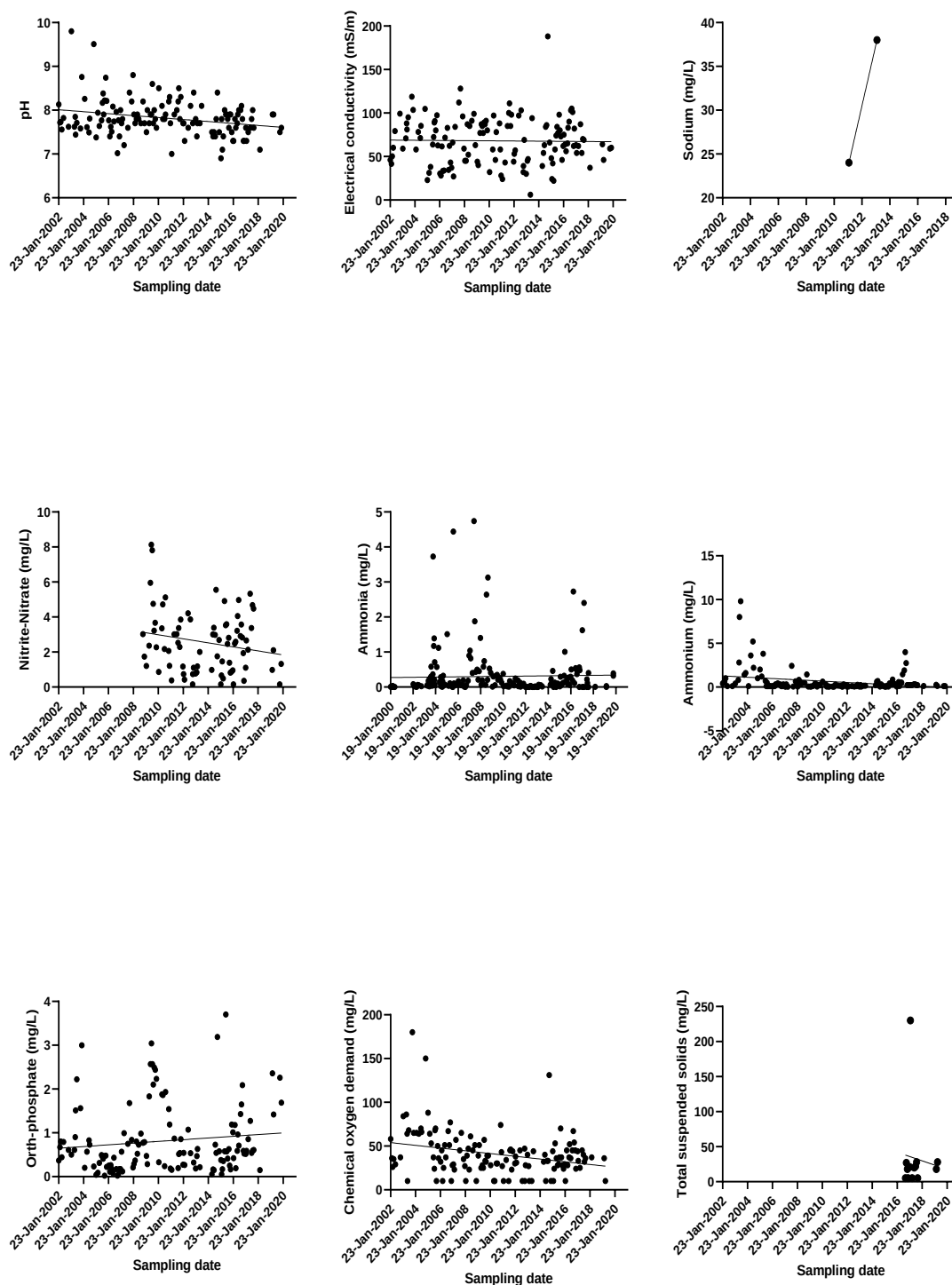


Figure 10: Trends in selected water quality variables measured at Site DS3 from 2003 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

4.1.7 Integrated assessment of the water quality

The data were subjected to PCA analyses for the Buffalo River (Figure 11) and groundwater (Figure 13) samples separately. The PCA bi-plot for the Buffalo River samples explained 87% of the variation in the data on the first two axes. The water quality at Sites US1, US2 and Site DS1 were distinctly different from the other sites. For the two upstream sites (US1 and US2) the higher pH distinguished them from the other sites while low COD and TSS concentrations distinguished Site DS1. Sites US3 and DS2 were characterised by high EC, COD and nutrient concentrations. These are in accordance with the water quality parameters that are of concern in the textile effluent (see Table 4). Site DS3 was influenced mainly by high TSS concentrations.

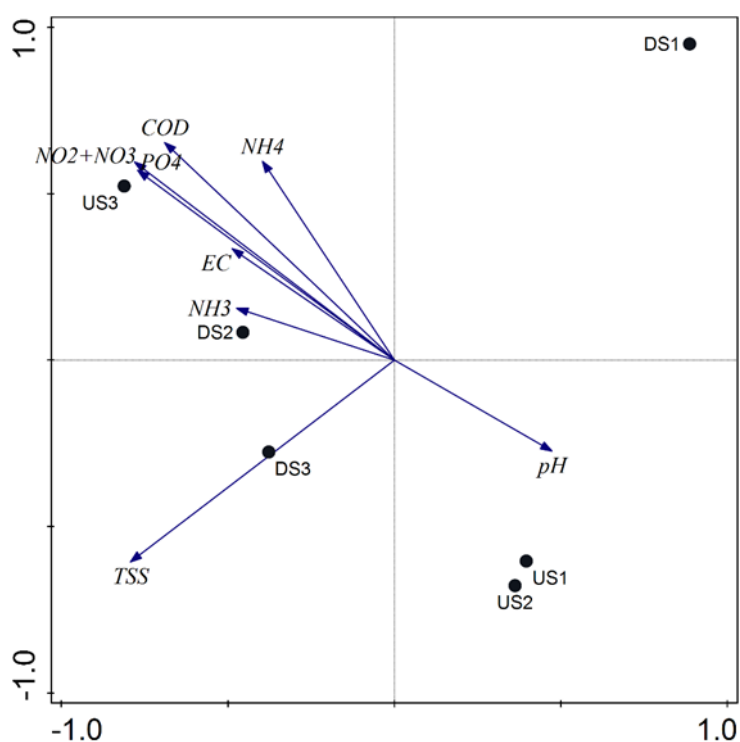


Figure 11: Principal component analysis of the water quality at the six sites in the Buffalo River. The first two axes explain 87.4% of the variation in the data with 51.4% and 36% on the first and second axes respectively.

A multi comparison test was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for pH and EC (Table 5). Sodium increased significantly over time; however it was not statistically significant. There was no historical and current data recorded for NO_2^- - NO_3^{2-} . The NH_3 , NH_4^+ and COD levels decreased significantly ($p < 0.05$) between the historical and current periods,

while PO_4^{2-} showed some significant increase (Table 5). There was significance difference ($P<0.05$) in the means of NH_3 and COD.

Table 4: Summary statistics of the historical and current water quality of selected sites in the Buffalo River. Data are presented as mean $\pm$ standard deviation, with minimum and maximum values in parentheses. For the purposes of this study historical data were regarded as the first two years of the data set and current data were based on the rest of the data set. Significant differences ($p<0.05$) between the historical and current data sets are indicated with an asterisk.

Parameters	Site US1		Site US2		Site US3	
	Historical	Current	Historical	Current	Historical	Current
pH	7.7 $\pm$ 0.19 (7.4-7.9)	7.6 $\pm$ 0.11 (7.5-7.9)	7.7 $\pm$ 0.98 (7.63-7.85)	7.6 $\pm$ 0.12 (7.4-7.8)	7.02 $\pm$ 0.24 (6.8-7.4)	7.2 $\pm$ 0.14 (6.98-7.4)
Electrical conductivity (mS/m)	62.7 $\pm$ 20.6 (33.2–80.9)	59.8 $\pm$ 30.3 (33-125)	42.34 $\pm$ 12.87 (27.38-53.37)	39.08 $\pm$ 9.64 (21.4-52.63)	65.06 $\pm$ 2.0(62.5-67.4)	61.3 $\pm$ 9.3 (47.8-79.7)
Na (mg/L)	173.8 $\pm$ 230.8* (31.5- 518)	36.34 $\pm$ 11.5* (28.2-44.5)	No Data	27.5 $\pm$ 6.61 (19-37)	No Data	No Data
NO_2^- - NO_3^{2-} (mg/L)	1.59 $\pm$ 0.68 (0.93-2.29) NO DATA	0.21 $\pm$ 0 (0.21-0.21)	No Data	0.32 $\pm$ 0.07 (0.19-0.38)	No Data	9.5 $\pm$ 3.5 (6-13)
NH_3 (mg/L)	0.04 $\pm$ 0.05* (0.01-0.11)	0.01 $\pm$ 0* (0-0.01)	0.03 $\pm$ 0.04* (0-0.09)	0.005 $\pm$ 0.002* (0- 0.01)	0.16 $\pm$ 0.14* (0.03-0.35)	0.09 $\pm$ 0.09* (0-0.25)
NH_4^+ (mg/L)	1.0 $\pm$ 0.85* (0.21- 2.0)	0.13 $\pm$ 0.06* (0.06-0.22)	0.78 $\pm$ 0.76* (0.13-1.87)	0.17 $\pm$ 0.8* (0.09-0.28)	16.7 $\pm$ 7.55(6.7-24.4)	6.11 $\pm$ 5.03 (0.15-15.3)
PO_4^{2-} (mg/L)	0.02 $\pm$ 0.09 (.01-0.03)	0.82 $\pm$ 0.09 (0.01-0.34)	0.02 $\pm$ 0.16 (0.01-0.05)	0.08 $\pm$ 0.05 (0.05-0.20)	2.98 $\pm$ 1.58 (1.13-4.7)	3.55 $\pm$ 2.26 (1.65-9.56)
COD (mg/L)	31.1 $\pm$ 5.5* (25.4–36.4)	19.84 $\pm$ 4.3* (13.2-24.3)	29.84 $\pm$ 11.42 (22-46.25)	19.38 $\pm$ 4.3 (13.2-24.25)	116.7 $\pm$ 50.3 (61.09 -178.83)	61.4 $\pm$ 21.5 (27-107.4)
TSS (mg/L)	No Data	14.08 $\pm$ 0.59 (13.67-14.50)	No Data	16.56 $\pm$ 16.34 (5.00-28.11)	34.49 $\pm$ 27.07 (6.55-69.75)	24.83 $\pm$ 14.42 (6.55-50.25)

Table 4: (continued): Summary statistics of the historical and current water quality of selected sites within the Buffalo River.

Parameter	Site DS1		Site DS2		Site DS3	
	Historical	Current	Historical	Current	Historical	Current
pH	7.76 ±0.32 (7.4-8.13)	7.76 ±0.49 (7.13-9.25)	7.4 ± 0.18 (7.24-7.66)	7.9 ±0.41 (7.4-8.95)	7.98 ±0.15 (7.79-8.15)	7.77 ± 0.15 (7.54-8.01)
Electrical conductivity (mS/m)	70.9 ± 16.45* (53.5-91.5)	55.84 ±11.28* (30-72.14)	70.4 ±10.8* (61.05-85.6)	96.1 ±15.67* (66.9-121.3)	71.35 ± 17.56 (49.5-88.5)	65.06 ± 10.97 (48.2- 81.1)
Na (mg/L)	No Data	31±7 (24-38)	No Data	97 ±6.9 (88-105)	No Data	50±34.3 (8-144)
NO ₂ ⁻ -NO ₃ ²⁻ (mg/L)	No Data	1.470 ±0.89 (0.31-4.48)	No Data	6.51 ±5.56 (0.52-23.3)	No Data	2.46±1.72 (0.15-8.13)
NH ₃ (mg/L)	0.13 ±0.11* (0.04-0.24)	0.02 ± 0.0*2 (0-0.07)	0.81 ± 0.14 (0-0.29)	0.44 ± 0.38 (0.08-1.16)	1.64 ± 1.24* (0.63-3.14)	0.33 ± 0.28* (0.11-1.09)
NH ₄ ⁺ (mg/L)	4.6 ± 2.92 (0.80-7.87)	0.64 ± 1.21 (0.1-4.8)	0.05 ± 0.49(0.01-0.11)	0.09 ± 0.05 (0.01-0.20)	1.68 ±1.19 (0.63-3.14)	0.33 ± 0.28 (0.11-1.09)
PO ₄ ³⁻ (mg/L)	0.74 ± 0.71 (0.24-1.8)	0.81 ±0.68 (0.13-2.45)	0.01 ± 0 (0.01-0.01)	0.06 ±0.04 (0.01-0.10)	0.49 ±0.41 (0.06-1.02)	0.79 ± 0.51 (0.14-2)
COD (mg/L)	0.17 ±0.14* (0.03-0.35)	0.02 ±0.03* (0-0.08)	65.33 ±52.8* (35.5-144.3)	51.15 ± 10.4* (37.6-76.5)	59.26 ± 24.23* (38.75-94.3)	35.09 ± 4.15* (28.6-42)
TSS (mg/L)	No Data	No Data	23.2 ± 10.71 (11.23-37.25)	19.57 ± 17.88 (4-67.87)	No Data	32.29 ± 17.16 (20.17-44.43)

4.1.8 Comparison between river sites

Comparisons (using the one-way ANOVA non-parametric Tukey test) of the water quality (for the surface water, the historical data period was from 2003 to 2005 while the rest of the dataset was considered as current) between the six sites in the Buffalo River are presented in the box and whisker plots in Figure 12. The full data sets including both the historical and current were used to run this test. The pH values at Site US3 were significantly lower (Figure 12) than all the other upstream and downstream sites. The EC at Site US2 was significantly lower compared to all sites, while the EC at Site DS2 was significantly higher compared to all the sites. Sodium was not measured at sites US3; while it was higher at site DS2 (Figure 12). The TSS concentrations at sites US3 and DS3 were significantly higher than at the other sites (Figure 12).

The pH significance differences were observed between site US1 and US3; US2 and US3; US3 and DS1; US3 and DS2; US3 and DS3 as $p < 0.05$. Electrical conductivity significance difference ($p < 0.05$) was shown between sites US1 and US2; US1 and DS2; US2 and US3; US2 and DS1; US2 and DS2; US2 and DS3; US3 and DS2; DS1 and DS2; DS2 and DS3.

For Na, all the sites did not show any significant difference as they were above the threshold of $p < 0.05$. For $\text{NO}_2\text{-NO}_3^{2-}$, there was a significant difference observed between site US1 and US3; US1 and DS2; US3 and DS1; DS1 and DS2 as $p < 0.05$.

For NH_3 , there was a significant difference observed between site US1 and DS2; US2 and DS2; US3 and DS2; DS1 and DS2; DS2 and DS3 as $p < 0.05$ (Figure 12). It was noted that site DS2 was significantly different from all the other sites. For Ammonium, there was a significant difference observed between site US1 and US3; US1 and DS3; US2 and DS2; DS2 and DS3; US3 and DS3. For PO_4^{2-} , all sites showed significance difference ($p < 0.05$) except for US1 and US2; and DS1 and DS3. For COD, there was a significant difference observed between sites; all sites showed significant difference except for US1 and US3; US1 and DS3; US2 and DS1. For TSS all the sites did not show any significant difference as they were above the threshold of $p < 0.05$ (Figure 12).

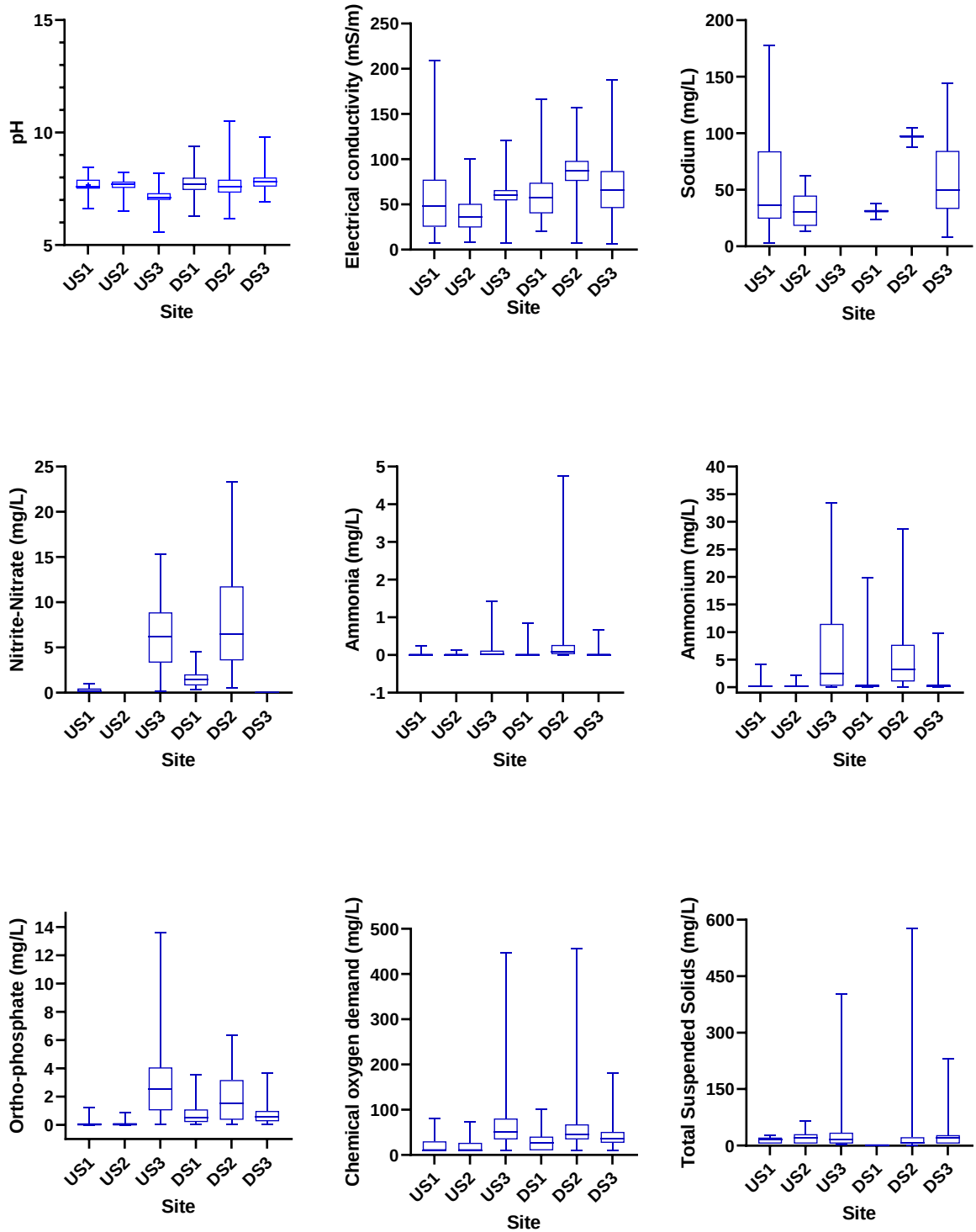


Figure 12: Box and whisker plots of selected water quality parameters at six sites in the Buffalo River. The bars represent the median (line) and 5th and 95th percentiles. The box indicates the interquartile range. Significant differences ($p < 0.05$) between sites are indicated in the text.

4.1.9 Integrated assessment of the water quality

The PCA bi-plot for the groundwater quality data explained 98% of the variation in the data (Figure 13). The water quality at Site BH1 is dominated by EC as a result of higher Na and Cl concentrations. In general, the pH at BH1 and BH2 was higher than the other sites. High NH_4^+ concentrations were responsible for the water quality at the remaining sites being distinctively different.

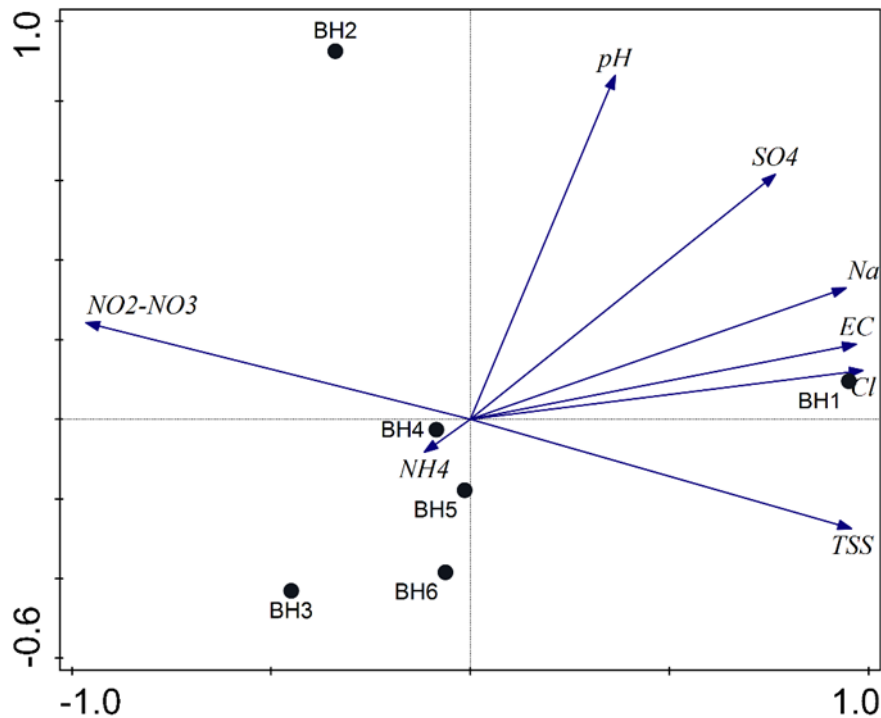


Figure 13: A Principal component analysis bi-plot indicating the association between the respective six sites of the groundwater with regard to changes in the water quality parameters. The total variation explained is 98.4% with 90.3% on the first axis and 8.1% on the second axis.

4.2 Groundwater sites

4.2.1 Site BH1

The water quality trends for the period 2013 to 2019 are shown in Figure 14. The pH values showed a decrease, while the EC showed a slight increase over the period. Sodium showed an increase. The nutrients showed a decreasing trend (NH_4^+), whereas NO_2^- - NO_3^{2-} showed a slight increase over time.

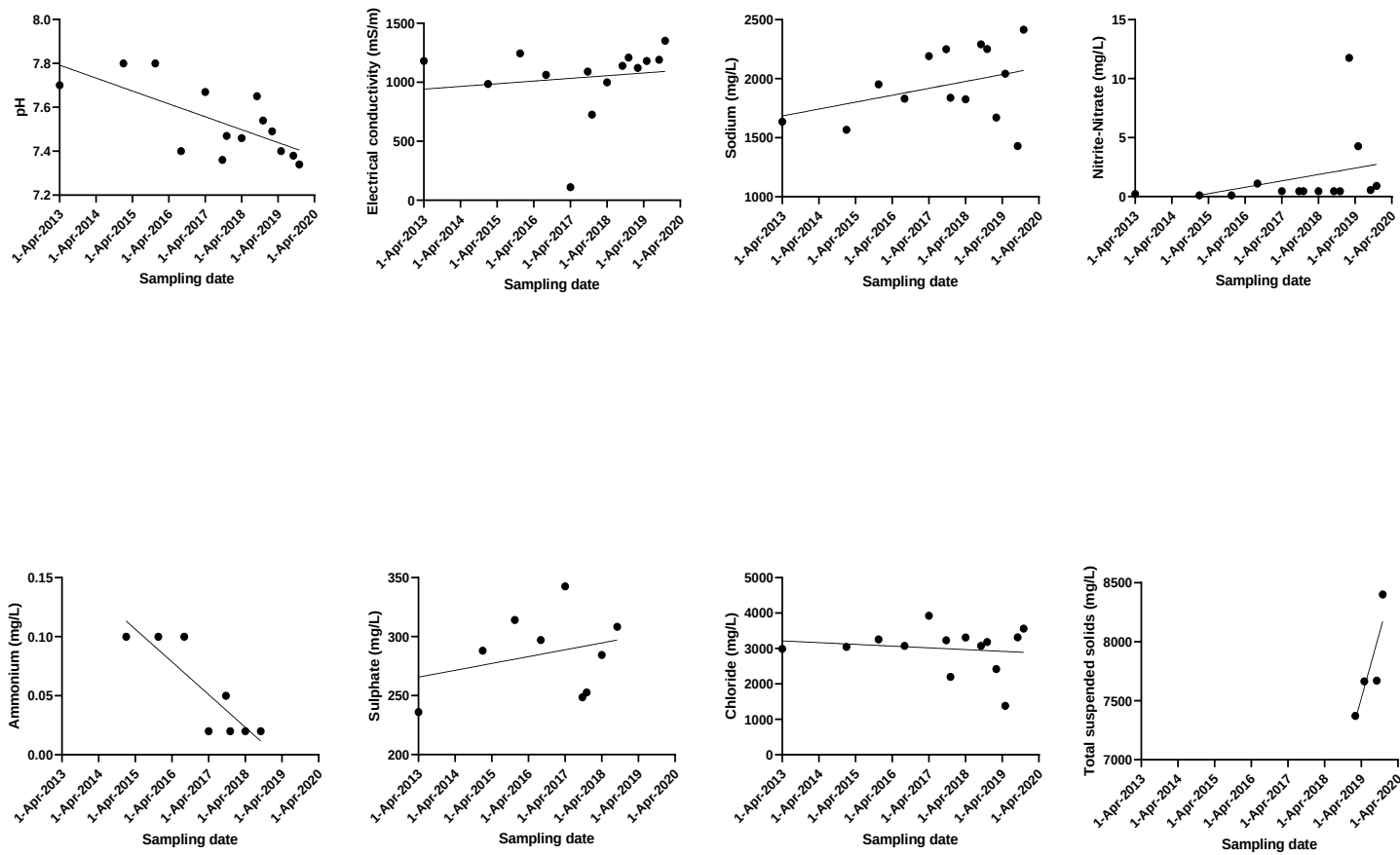


Figure 14: Trends in selected water quality variables measured at Site BH1 from 2013 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for EC, NO_2^- - NO_3^{2-} , NH_4^+ , SO_4^{2-} , Cl and TSS (Table 6). The EC and Cl levels decreased significantly, while Na and NO_2^- - NO_3^{2-} levels increased significantly between the historical and current periods. The SO_4 showed a slight increase, but this was not statistically significantly different. The TSS did not have any historical data (Table 6). There was significance difference ($p < 0.05$) in the means of pH.

4.2.2 Site BH2

The water quality trends for the period 2013 to 2019 are shown in Figure 15. The pH values and EC showed a significant decrease over the period. Sodium showed a decreasing trend. The nutrients showed a significant decreasing trend (NH_4^+), while the NO_2^- - NO_3^{2-} showed an increasing trend. Chloride and SO_4^{2-} showed a slight decrease, while TSS increased significantly over time.

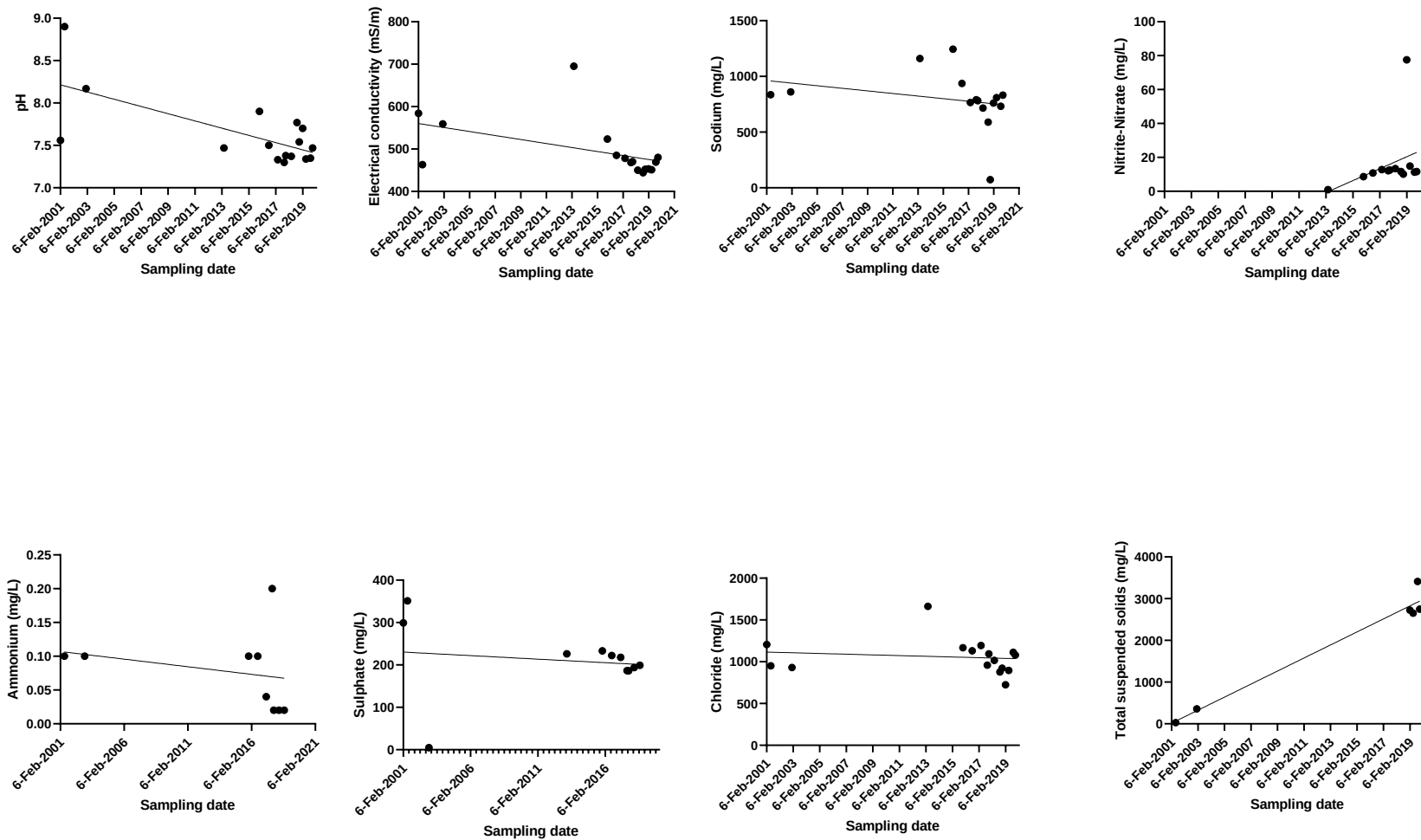


Figure 15: Trends in selected water quality variables measured at Site BH2 from 2013 to 2019. Trend lines depicted are based on linear regression of the data over sampling period

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there was significance difference ($p < 0.05$) in the means of pH and EC (Table 6). There were no significant differences for Na, and SO_4^{2-} (Table 6). Ammonium showed a slight decrease but it was not statistically significant. The EC, Na, and Cl levels decreased significantly, while Na and NO_2^- - NO_3^{2-} , levels increased significantly ($p < 0.05$) between the historical and current periods. The TSS did not have any historical data (Table 6).

4.2.3 Site BH3

The water quality trends for the period 2013 to 2019 are shown in Figure 16. The pH and EC values showed a slight increase over the period, while the Na showed a slight decrease. The nutrients showed a significant decreasing trend (NH_3), while the NO_2^- - NO_3^{2-} slightly increased. The TSS increased significantly over time.

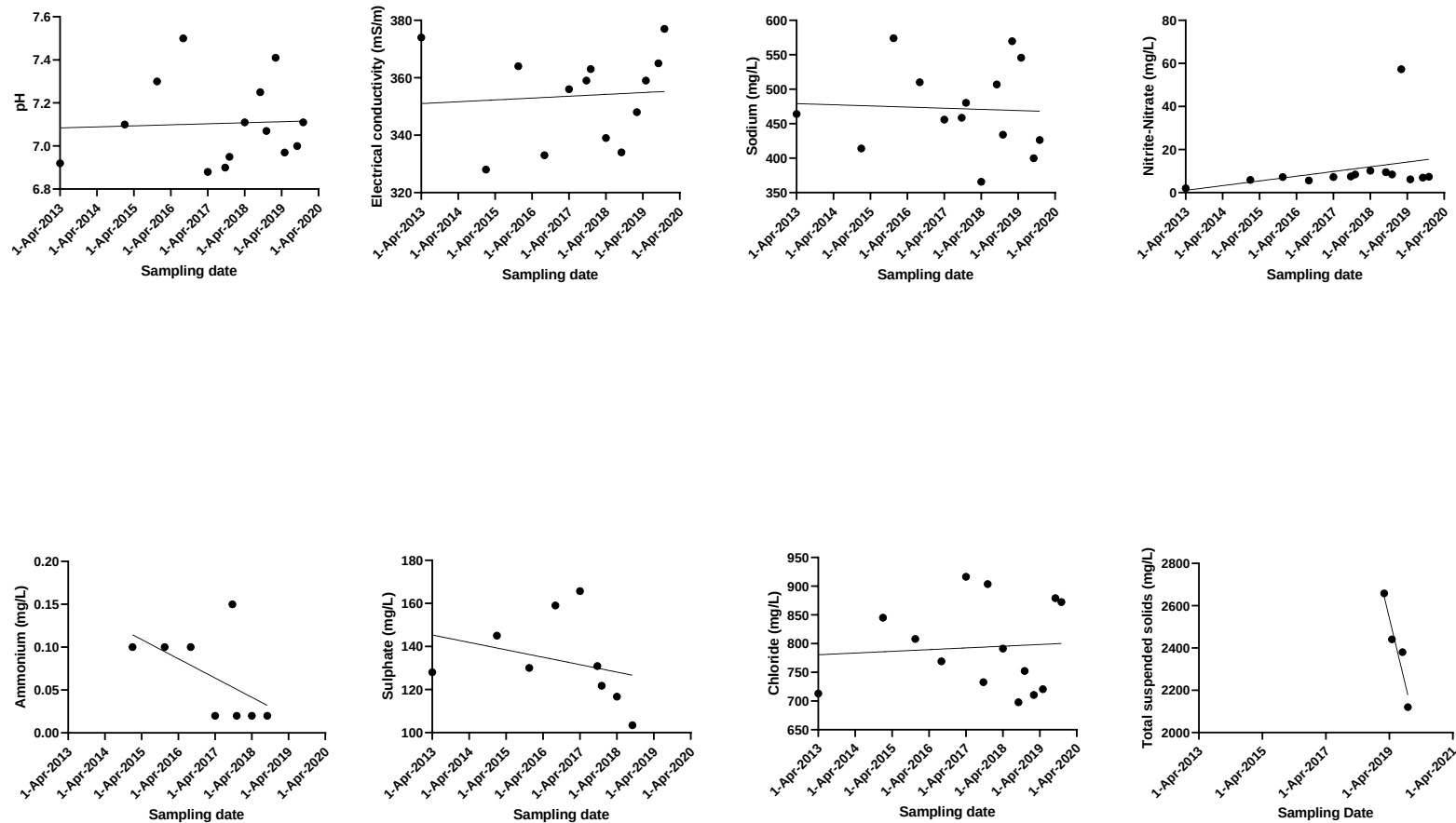


Figure 16: Trends in selected water quality variables measured at Site BH3 from 2013 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A multi comparison test was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for all the parameters (Table 6). The NH_4^+ levels decreased significantly, while NO_2^- - NO_3^{2-} increased ($p < 0.05$) between the historical and current periods. The TSS did not have any historical data (Table 6).

4.2.4 Site BH4

The water quality trends for the period 2013 to 2019 are shown in Figure 17. The pH values slightly increased while the EC showed a significant decrease over the period. Sodium showed a slight decrease. The nutrients showed a significant increasing trend, while SO_4^{2-} and Cl showed a decreasing trend. The TSS decreased significantly over time (notably only data available in 2019).

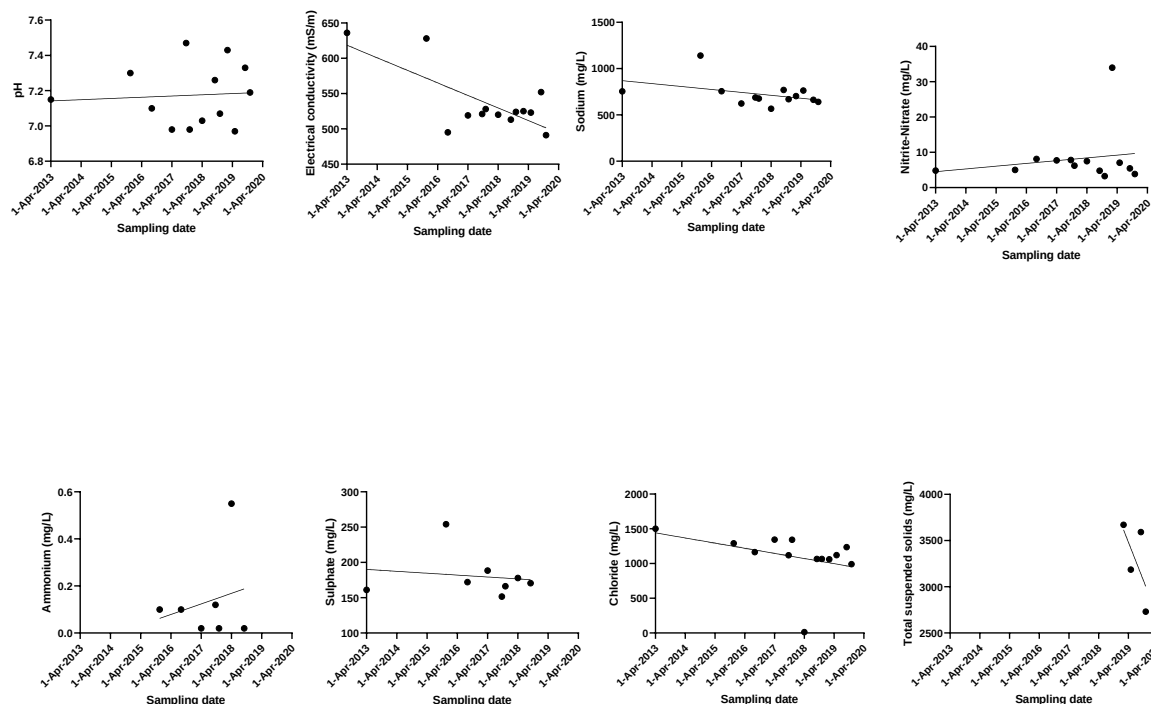


Figure 17: Trends in selected water quality variables measured at Site BH4 from 2013 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for pH, Na, NO_2^- - NO_3^{2-} , NH_4^+ , SO_4^{2-} , Cl and TSS (Table 7). The EC, Na, Cl, SO_4^{2-} , levels decreased significantly, while NO_2^- - NO_3^{2-} and NH_4^+ levels increased significantly between the historical and current periods. The TSS did not have any historical data (Table 7). There was significance difference ($p < 0.05$) in the means of EC.

4.2.5 Site BH5

The water quality trends for the period 2013 to 2019 are shown in Figure 18. The pH values slightly increased while the EC showed a significant decrease over the period. Sodium showed a significant decrease. The nutrients showed a significant increasing trend. Sulphate and Cl showed a decreasing trend. The TSS decreased significantly over time (notably only data available in 2019).

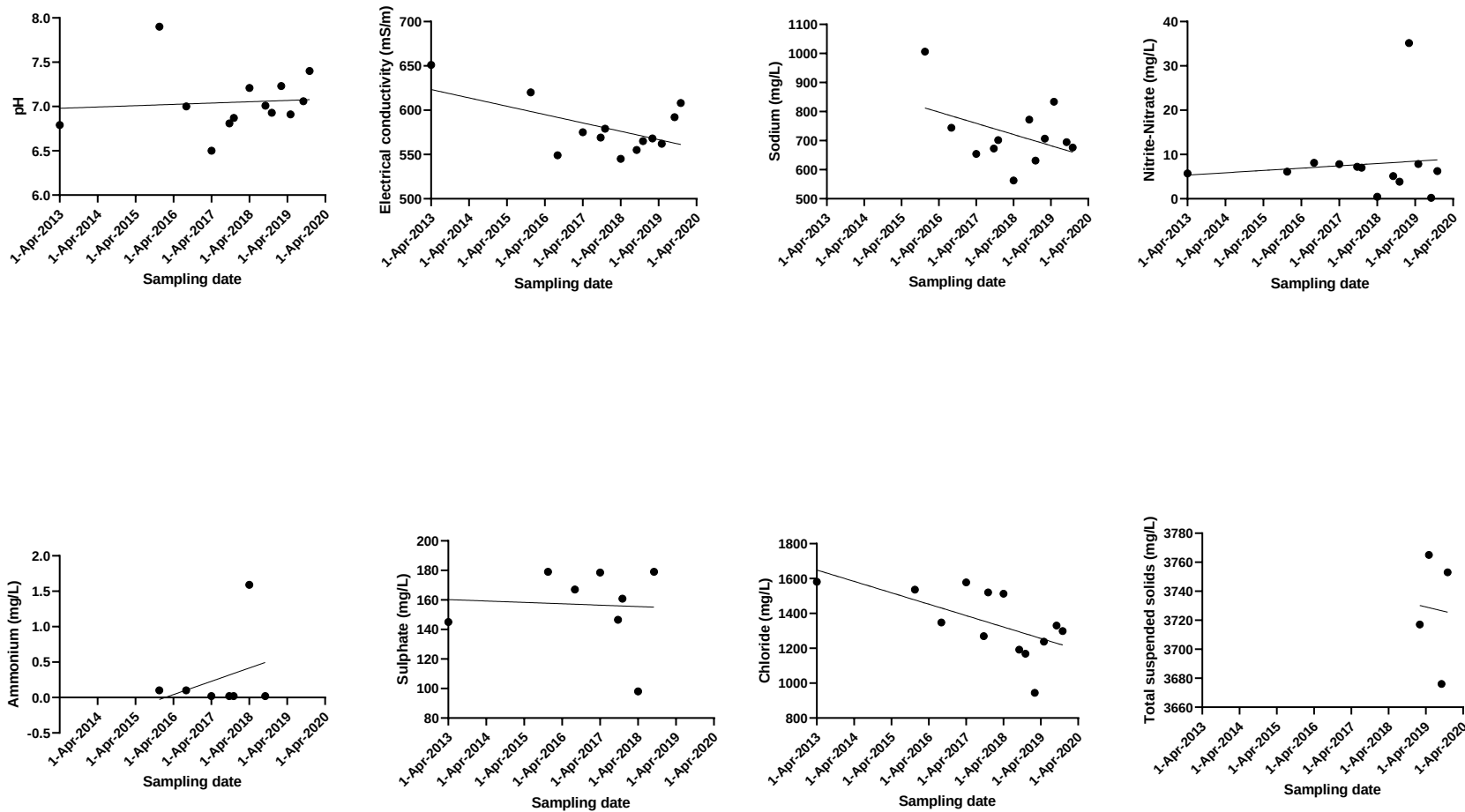


Figure 18: Trends in selected water quality variables measured at Site BH5 from 2013 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for pH, Na, NO_2^- , NO_3^{2-} , NH_4^+ , SO_4^{2-} , Cl and TSS (Table 7). The pH, EC, Na and Cl levels decreased significantly, while NO_2^- - NO_3^{2-} and NH_4^+ levels increased significantly ($p < 0.05$) between the historical and current periods. The TSS did not have any historical data (Table 7). There was significance difference ($p < 0.05$) in the means of EC.

4.2.6 Site BH6

The water quality trends for the period 2013 to 2019 are shown in Figure 19. The pH values slightly increased while the EC showed a significant decrease over the period. Sodium showed a significant decrease. The nutrients showed a significant increasing trend. Sulphate and Cl showed a decreasing trend. The TSS decreased significantly over time (notably only data available in 2019).

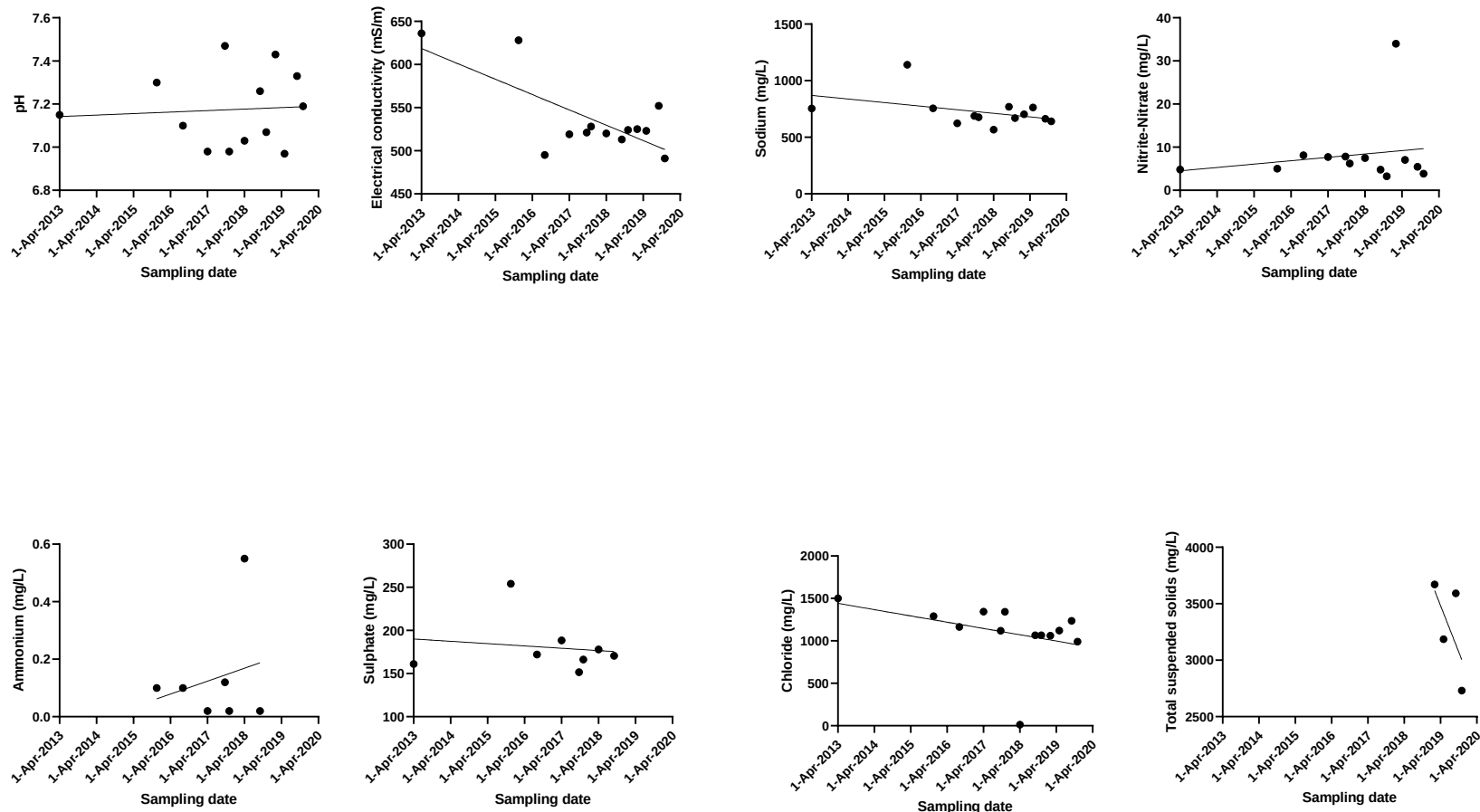


Figure 19: Trends in selected water quality variables measured at Site BH6 from 2013 to 2019. Trend lines depicted are based on linear regression of the data over sampling period.

A one-way Anova was performed using the Tukey test. A comparison between the historical and current water quality revealed that there were no significant differences for all the parameters (Table 7). The EC, Na, NH_4^+ and Cl levels decreased significantly, while NO_2^- - NO_3^{2-} levels increased significantly ($p < 0.05$) between the historical and current periods. The TSS did not have any historical data (Table 7).

Table 5: Summary statistics of the historical and current water quality of selected groundwater sites within the Buffalo River catchment. Data are presented as mean $\pm$ standard deviation, with minimum and maximum values in parentheses. For the purposes of this study historical data were regarded as the first two years of the data set and current data were based on the rest of the data set. Significant differences ($p < 0.05$) between the historical and current data sets are indicated with an asterisk.

Parameter	Site BH1		Site BH2		Site BH3	
	Historical	Current	Historical	Current	Historical	Current
pH	7.7 $\pm$ 0.06* (7.70-7.8)	7.47 $\pm$ 0.11* (7.34-7.67)	7.7 $\pm$ 0.3* (7.47-7.90)	7.46 $\pm$ 0.16* (7.30-7.77)	7.1 $\pm$ 0.19 (6.92-7.3)	7.10 $\pm$ 0.20 (6.88-7.50)
Electrical conductivity (mS/m)	1136 $\pm$ 134.9 (985–1244)	1016.6 $\pm$ 338.5 (111-1352)	609.3 $\pm$ 121.3* (523.5-695)	463.6 $\pm$ 14.14*(444-485)	355.3 $\pm$ 24.19 (328-374)	353.3 $\pm$ 14.5 (333-377)
Na (mg/L)	1718 $\pm$ 205.5 (1567-1952)	2002.6 $\pm$ 306.2(1429-2414)	1202.5 $\pm$ 58.69 (1161-1244)	707.99 $\pm$ 226.6 (73.7-937)	484 $\pm$ 81.85 (414-574)	468.5 $\pm$ 61.7 (365.7-569.7)
Cl(mg/L)	3097 $\pm$ 141.6 (2990-3258)	2970.3 $\pm$ 710.3 (1383-3924)	1415 $\pm$ 350.7 (1167-1663)	1000.6 $\pm$ 138.8 (724.1-1194.5)	788.7 $\pm$ 68.1 (713-845)	795.1 $\pm$ 82.5 (697.9-916.4)
SO_4^{2-}	279.3 $\pm$ 39.7 (236-314)	288.9 $\pm$ 35.4 (248.6-342.6)	229.3 $\pm$ 4.95 (226-233)	200.8 $\pm$ 15.5 (186-222)	134.3 $\pm$ 9.29 (128-145)	132.9 $\pm$ 24.6 (103.5-165.7)
$\text{NO}_2^-/\text{NO}_3^{2-}$ (mg/L)	0.14 $\pm$ 0.07 (0.10-0.22)	1.94 $\pm$ 3.45 (0.45-11.76)	4.76 $\pm$ 5.43 (0.92-8.60)	18.06 $\pm$ 19.78 (10.2-77.6)	5.03 $\pm$ 2.7 (2.0-7.2)	12.24 $\pm$ 15(5.6-57.3)
NH_4^+ (mg/L)	0.10 $\pm$ 0 (0.10-010)	0.04 $\pm$ 0.03 (0.02- 0.10)	0.10 $\pm$ 0 (0.10-0.10)	0.07 $\pm$ 0.07 (0.02-0.20)	0.10 $\pm$ 0 (0.10-0.10)	0.06 $\pm$ 0.06 (0.02-0.15)
TSS (mg/L)	No Data	7776.8 $\pm$ 438.8 (7372-8401)	No Data	2883.8 $\pm$ 353.9 (2651-3411)	No Data	2399.8 $\pm$ 221.4 (2120-2658)

Table 5: (continued): Summary statistics of the historical and current water quality of selected groundwater sites within the Buffalo River catchment.

Parameters	Site BH4		Site BH5		Site BH6	
	Historical	Current	Historical	Current	Historical	Current
pH	7.2 ±0.11(7.15-7.30)	7.16 ±0.18 (6.97-7.47)	7.4 ± 0.18 (7.24-7.66)	6.99 ±0.24 (6.50-7.40)	7.02 ±0.26 (6.83-7.20)	7.10 ± 0.21 (6.86-7.55)
Electrical conductivity (mS/m)	632 ±5.66* (628-636)	519.2 ±16.27* (491-552)	635.5 ±21.92* (620-651)	569.7 ±18.5* (545-608)	582.5±2.12 (581-584)	512.5 ± 150.8 (88.1-1352)
Na (mg/L)	947.5 ±273.7* (754-1141)	683.3 ± 62.5* (566.6-769.2)	1006 ±32* (1006-10006)	695.4±71.9* (562.7-833.5)	784.5 ±195.(646-923)	664.25 ± 205.9 (109.6-898.7)
Cl (mg/L)	1396±148.5 (1291-1501)	1047.2 ± 361.9 (12.59-1344.9)	1558.5 ±31.8 (1536-1581)	1309.1 ± 182.6 (944.2-1577.9)	1414±48.1 (1380-1448)	1133.9 ±380.9 (161.4-1584.6)
SO ₄	207.5 ±65.8 (161-254)	171.1 ±12.2* (151.6-188.4)	162 ±24.04 (145-179)	155.0 ± 30.44 (98-179.1)	142.5 ±23.3(126-159)	143.9 ± 52.73 (40.9-342.6)
NO ₂ ⁻ /NO ₃ ²⁻ (mg/L)	4.9 ±0.14 (4.8-5.0)	8.70 ± 8.55(3.24-33.9)	5.9 ±0.28 (5.7-6.10)	8.09 ±9.40 (0.23-35.14)	3.8 ±1.69 (2.60-5.0)	8.12±9.31 (1.44-35.49)
NH ₄ ⁺ (mg/L)	0.10 ±0 (0.10-010)	0.14± 0.21 (0.02-0.55)	0.10 ±0 (0.10-010)	0.30 ± 0.64 (0.02-1.59)	0.10 ±0 (0.10-010)	0.03 ± 0.03(0.02-0.10)
TSS (mg/L)	No Data	3294 ±432.3 (2730-3671)	No Data	3727 ± 40.1 (3676-3765)	No Data	3753.5± 407.6 (3186-4078)

4.2.7 Comparison between groundwater sites

Comparisons of the water quality between the six groundwater sites in the Buffalo River catchment are presented in the box and whisker plots in Figures 20. The comparison was done for entire data set (both the historic and current datasets). For the groundwater data, historical period was noted as 2013 to 2015; whereas the rest was taken as current period. The pH values at Site BH6 were significantly higher (Figure 20) than all the sites outside and within the irrigated areas as well as the downstream sites. The EC and Na at Site BH1 were

significantly higher compared to all the other sites (Figure 20). For the nutrients, BH1 showed the lowest mean (NO_2^- - NO_3^{2-}) as compared to the other sites. The concentration of Cl and SO_4^{2-} at site BH1 (which is the upstream borehole) was noted to be significantly higher than all the other sites. The TSS values at Site BH1 were also significantly higher compared to the other sites.

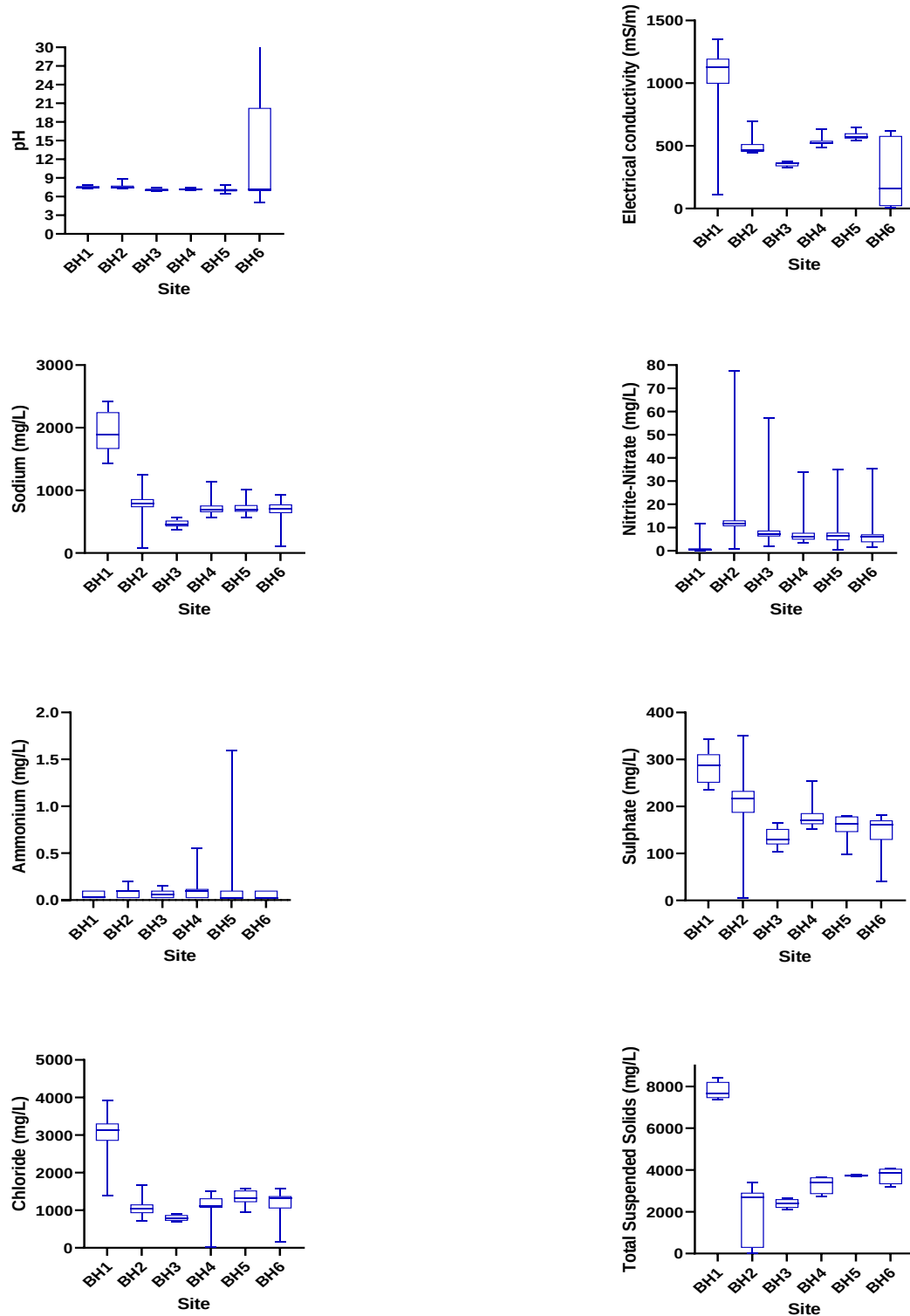


Figure 20: Box and whisker plots of selected water quality parameters at six groundwater sites within the Buffalo River catchment. The bars represent the median (line) and 5th and 95th percentiles. The box indicates the interquartile range. Significant differences ($p < 0.05$) between sites are indicated in the text.

4.2.8 Integrated assessment of the water quality

A PCA ordination of the water quality representing both the surface water (Buffalo River) and groundwater (borehole) was constructed (Figure 21). The bi-plot represents 96.9% of the variation in the data on the first two axes (Figure 21). There was a clear distinction between the water quality of the Buffalo River and the borehole samples. This was primarily due to the much higher EC and TSS recorded in the borehole samples. The two most upstream rivers sites were associated with higher pH values while the downstream sites had elevated NH_4^+ concentrations.

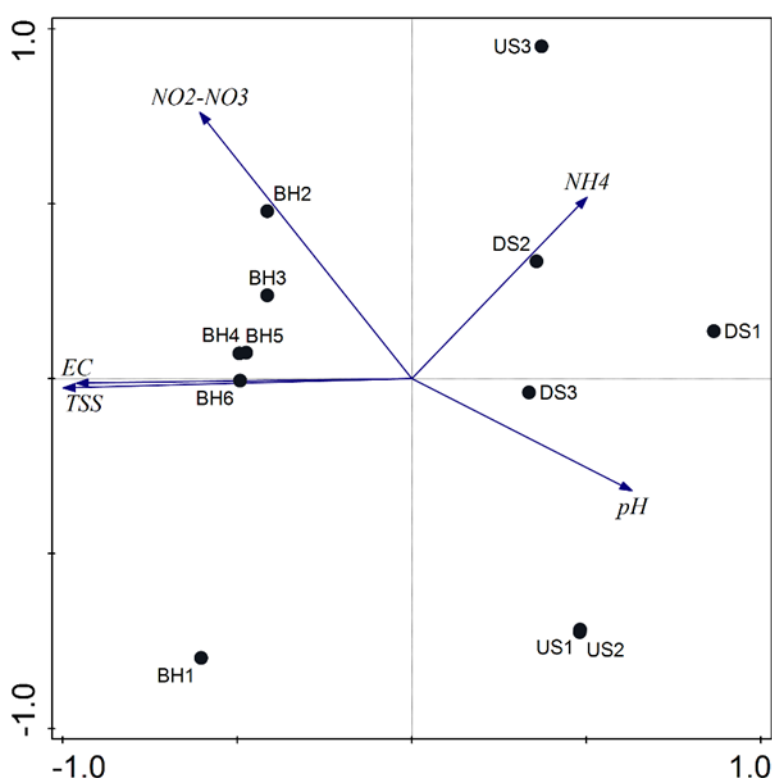


Figure 21: Principal component analysis of the water quality at the surface water (Buffalo River) and groundwater (borehole) sites. The first two axes explain 96.9% of the variation in the data with 92% and 4.9% explained on the first and second axes respectively.

Textile industrial effluent discharged from the Da Gama textile factory is presented in Table 8. The pH ranged between 9.9 and 13.1 with a mean of 12, while the EC ranged between 237 and 1019 mS/m with a mean of 370 mS/m. Sodium concentration was found at a higher level as it ranged between 1247 and 6522 mg/L with a mean of 2229 mg/L. The nutrients (NH_3) ranged between 7 and 71.6 mg/L; while PO_4^{2-} ranged from 13 to 59 mg/L with a mean

value of 31 mg/L. Chemical oxygen demand for the textile effluent was recorded between 1.21 and 2086 mg/L with a mean of 1398 mg/L.

Table 6: Summary statistics of the textile waste water discharged from the settling tanks of the Da Gama industry water quality. Data are presented as mean $\pm$ standard deviation, with minimum and maximum values in parentheses from 2015 to 2019.

pH	EC	Na	NH ₃	PO ₄ ²⁻	COD	TSS	Ca	Mg
12 $\pm$ 0.84 (9.9-13.1)	370.5 $\pm$ 141 (237-1019)	2229 $\pm$ 1002 (1247-6522)	3.5 $\pm$ 13.4 (7-71.6)	31 $\pm$ 12 (13-59)	1398 $\pm$ 368.4 (1.21-2086)	90.5 $\pm$ 41.9 (19-287)	7 $\pm$ 23.5 (1-173.4)	6 $\pm$ 16.4 (2-121.4)

4.3 Discussion

4.3.1 pH

According to Dallas and Day (2004) pH is viewed as one of the most generally carried out and significant measurements in natural waters. As you go downstream of the river, the temperature generally increases; however the pH of water is greatly dependent on the biological activity (Dallas and Day, 2004). Drinkable levels of pH range from 4 to 11 and they have minimal side effects. A specific catchment area's water pH and alkalinity is influenced by the geochemistry and geological stratigraphy within that drainage area (Smart, 1998). Industrial effluents and increased biological reaction activities due to STW effluents can lead to pH change (Zuma, 2010). If not buffered properly, low pH levels can allow for the formation of toxic substances, leading to species diversity and structure alterations. The buffering capacity of an ecosystem is important for sustenance of aquatic life and is measured through alkalinity/hardness (DWAf, 1996). The study conducted by Zuma (2010) revealed the measured values of mean pH of 6.96 over the entire sampling period. This pH is slightly acidic as compared to the values obtained in this current study.

The pH values recorded in this study do not concur with the study done by Day (1993); which showed that the water resources (surface water) in the Republic of South Africa are rarely naturally alkaline with a pH >9; for instance the pH for the surface water sites ranged from 7.1 to 7.8 for US3 and DS3 respectively. The highest mean pH was recorded at site BH2 (7.6), while the lowest was at site BH5 (7.05); which evidently demonstrate that the groundwater of the selected study area is slightly basic in nature. BH2 is more basic than BH5. This could have been due to an increase in temperature that results in higher rates of chemical reactions in the water (Barron *et al.*, 2012). These results differ with the findings of

a study conducted in Chittagong, Bangladesh (Uddin *et al.*, 2020) where the pH values ranged from 5.3 to 6.72, making the water acidic. A mean range of 7.79 to 8.97 was found by a study done by Momba *et al.* 2006 for some rivers in the Buffalo City and Nkonkobe districts of the Eastern Cape Province. Palmer (1991) found that the upper reaches of the Buffalo River catchment had a slightly acidic to neutral pH of 6.1 to 7.5.

Comparison of surface water historical with current data shows a decreasing trend for sites US1, US2 and DS3; and an increasing trend for sites US3 and DS2. However; for the groundwater sites an increasing trend for BH3, BH4, BH5 and BH6 and a decreasing trend for BH2 and BH1 were observed. The increasing trend for the groundwater might be due to the effects of the textile effluent as this is noticed on the boreholes within the irrigation area.

The pH values in this research are slightly lower than those stated by Chigor *et al.* (2013) for the Buffalo River whereby the pH ranged from 6.6 to 10.7. This could be as a result of the pollution emanating from land use activities such as untreated waste water effluents, industrial effluents and agricultural run-off observed in the Buffalo River drainage area. For example, high bacteriological quantities e.g. faeces-indicating bacteria such as *E.coli* were detected in the Buffalo River and the surrounding dams, giving indications that sewage was being dumped at some point in the river (Chigor *et al.*, 2013). It was also noted that the bacteriological counts were high, with a wide range of total and faecal coliforms (Chigor *et al.*, 2013).

The target water quality range guideline for agricultural activities (irrigation) water varies between 6.5 and 8.4, but this could vary depending on the soil type (DWAF, 1996d; Jeong *et al.*, 2016). Soil pH within this range does not show key complications with either absence of plant nutrients or toxic levels of elements (DWAF, 1996d). According to DWAF (1996a) and Dallas and Day (2004), for a specific site of day, the pH readings should not be allowed to vary from the range of the background pH, by > 0.5 of a pH unit, or by > 5 % for aquatic ecosystems. The pH value of between 5 and 9.7 is stipulated as recommended limits for drinking water by the SANS 241:2015 (SABS, 2015). The pH values acquired in this study for both the surface water and groundwater sites were all within the SANS 241: 2015 recommendations (SABS, 2015). The mean pH values recorded ranged from 7.1 to 7.8.

4.3.2 Electrical conductivity

According to Robinson *et al.* (2003) a capability of water to conduct an electrical current is known as the electrical conductivity. The EC of water is directly equivalent to the TDS concentration (Rhoads, 1996). Electrical conductivity and TDS are important parameters to measure the salinity risk of water.

The rocks' mineral composition, size of the watershed and other sources of ions normally regulate the EC in freshwater ecosystems (Hudson-Edwards *et al.*, 2003; Nielsen *et al.*, 2003). The dissolution of carbonate into river basins is as a result of limestone contributing to higher EC in the surface water (Roelofs, 1991; O'Keeffe., 1989). Reed and Thornton (1969) established that the main source ($\pm 61\%$) of salinisation originates from natural geological weathering, whereas $\pm 27\%$ came from industrial origins (textile and tannery) in the Buffalo River catchment. High concentrations of water colorants, dissolved salts, organic wastes, insecticides, pesticides, chemical wastes, alkalis, sodium and detergents are some of the constituents of textile effluent (Buckley *et al.*, 1983). The biological, chemical and physical nature of the water bodies is altered by the discharge of textile effluent to the nearby water bodies. Some death of fish and aquatic biota is as a result of the effluent that further seeps into the aquifer and decreases the oxygen level (Abubacker and Kirthiga, 2017).

The mean values of EC obtained for this study (Buffalo River) ranged from 39.9 to 89.7 mS/m. Electrical conductivity levels of 88.8 and 92.2 mS/m were recorded at some sites of the Buffalo River from a study conducted by Zuma (2010); while Maseti (2005) recorded slightly lower values of 70 mS/m. all these values were found to be in line with the values recorded for this study.

In contrast, a study done by Chigor *et al.* (2013) for the Buffalo River showed the values of EC from 40.23 to 40.67 mS/m. These values are extremely lower than the values obtained in the current study. For the groundwater sites; the EC ranged from 353.8 to 1042.2 mS/m for sites BH3 and BH1 respectively. Comparison of surface water historical with current data showed a decreasing trend for all the sites except site DS2; moreover a decreasing trend was also observed for all the groundwater sites. The increasing trend at site DS2 might be influenced by other external land use factors such as the close proximity to the waste water treatment works.

The South African water quality guideline for domestic purposes' target water quality range for EC is 70 to 170 mS/m and it indicates that the water has a distinguishable brackish taste

but it is tolerated (DWAF, 1996a). There are no health effects that are likely except for taste and aesthetics. A slight salty taste may be detected above the concentration of 45 mS/m as a minimum threshold for dissolved salts in water (DWAF, 1996b; Langeneggar, 1990). For EC that is less than 45 mS/m, there is no health effects associated with such (DWAF, 1996b).

All sites exceeded the water quality range guidelines except for DS2. All the groundwater sites exceeded these limits (DWAF, 1996a). This statement supports results of another study on the neighbouring Keiskamma River, whereby the EC exceeded the limits set by the South African water quality guideline for domestic purposes (Fatoki *et al.*, 2003). Nonetheless; all the surface water sites were found to be within the SANS 241: 2015 limits whereby the EC should be less or equal to 170 mS/m (SABS, 2015).

Electrical conductivity in the present study clearly shows that almost all the sampling sites' EC are not desirable for drinking (except for site DS2). The groundwater quality map of South Africa indicates that the study area should have EC range of 150 - 370 mS/m (Murray *et al.*, 2012). All the groundwater sites do not fall within this range.

4.3.3 Sodium

Sodium ion is abundant in water due to the high solubility of its salts and the earth crust's abundance of sodium-containing mineral deposits (Dallas and Day, 2004). Areas with abundance of sodium mineral deposits or areas with sea or estuarine water intrusions typically contains higher concentrations of minerals and salts for groundwater as compared to surface waters (WHO, 1984). The toxic effects of acid pH values on fish increase as the concentrations of Ca, Cl and Na decrease (Dallas and Day, 2004).

The quality of the Cauvery River water and adjacent groundwater was assessed in India (Venkatramanan, 2013). For both surface and groundwater; bicarbonate was identified as the dominant anion and sodium was the dominant cation. Most of the groundwater samples were unsuitable for drinking based on the concentration of major ions; moreover, most the surface water samples were found to be within the limits for drinking water quality standards of India (RamyaPriya and Elango, 2018). Poor drinking and irrigation water was identified for both groundwater and surface water near the coast, whereas the groundwater quality in locations nearer to the confluence of tributaries and textile industrial areas was also of poor quality (RamyaPriya and Elango, 2018).

A study in Chinnalapatti, India had the groundwater concentration of Na that varied between 4.24 and 6.34 mg/l (Noel and Rajan (2015). The mean values recorded for this study range

from 0.52 to 128 mg/L; the lowest value was recorded at site DS3 (0.52 mg/L) while the highest value was recorded at site US1 (128 mg/L). The mean values obtained for this study (surface water) are higher than those of Noel and Rajan (2015); however they are less than the groundwater results as the groundwater sites, the mean values ranged from 471.8 to 1942 mg/L for BH3 and BH1 respectively. Comparison between historic and current data could only be done for site US1 as it is the only site that had a complete dataset. The majority of the groundwater sites showed a decreasing trend except for site BH1 which showed an increasing trend.

It is however worth noting that site BH1 is located upstream of the textile industrial activities. High salinities affect the suitability of water for irrigation; for example, high sodium concentrations damage the clay particle structure and permeability of soils (DWAF, 1996a). The South African water quality guidelines for domestic water use have a target water quality range of 0-100 mg/L for Na. This range does not have any aesthetic or health effects (DWAF, 1996b). For irrigation, the target water quality range for sodium is 70 mg/L and all the sites were falling outside this range (DWAF, 1996a). According to the SANS 241 standards of 2015, the limit for Na is 200 mg/L and all the groundwater sites exceeded these limits (SABS, 2015); however, all the surface water sites were within these limits.

4.3.4 Chloride

Different compounds of chlorides, like ammonium chloride, are widely used in industry for controlling pH. It is also used as bleaching and disinfecting agent (Toedt *et al.*, 2005). Health implications of chlorides are that they may exert a mild diuretic effect.

The assessment done at Chinnalapatti, India revealed the groundwater Cl values ranging from 210 to 391 mg/L (Noel and Rajan, 2015). These values are lower than the mean values recorded for this study range, which is from 793.7 to 2998 mg/L for sites BH3 and BH1 respectively. This variable was only sampled and analysed for at the groundwater sites only. Comparison of groundwater historical with current data showed a decreasing trend for all the sites except for BH3.

The target water quality range for domestic water is 0-100 mg/L. There are no aesthetic or health effects associated with this range. The threshold for corrosion acceleration in domestic appliances is at 50 mg/L. All the sites were in exceedance of the South African drinking water guidelines for domestic use and the SANS: 241: 2015 as they were found to be not permissible for drinking.

4.3.5 Sulphate

Sulphate is one of the most common ions found in natural waters (Dallas and Day, 2004). Sulphate gives a salty or unpleasant taste to water (DWAF, 1996b). Sulphur is an essential component of proteins and is thus an essential element in living systems. In most natural waters, sulphate ions tend to occur in lower concentrations than either bicarbonate or chloride ions. Toxicity is not associated with sulphates (DWAF, 1996b).

The groundwater mean values for a study conducted in Chinnalapatti (Noel and Rajan, 2015), India indicated the ranges from 82 to 171 mg/L; these values were lower than those obtained in the current study whereby the mean ranges recorded ranged from 133.4 to 285.7 mg/L for sites BH3 and BH1 respectively. Comparison of groundwater historical with current data showed an increasing trend at two sites (BH1 and BH6), while a decreasing trend was observed at BH2, BH3, BH4 and BH5. The sites located within the irrigation area show a decreasing trend; indicating that the textile effluent might have little or no influence to the groundwater quality.

To comply with the SANS 241:2015, SO_4^{2-} values must not exceed 250 mg/L. Site BH1 fell outside of this limit. The predominance of SO_4^{2-} in association with Na, K, Ca or Mg is dependent on the threshold of SO_4^{2-} which falls in the range of 200-400 mg/L (DWAF, 1996a). It is important to note that SO_4^{2-} was only sampled and analysed in the groundwater samples.

4.3.6 Nitrite-Nitrate

Inter-conversion occurs between nitrates and nitrites as they occur together in the environment. Under oxidising conditions nitrite is transformed into nitrate, which is far more common in the aquatic environment than nitrite and the most stable positive oxidation state of nitrogen (DWAF, 1996a). Human and animal waste, industrial effluents, agricultural wastes and seepage of fodder through drainage systems are the main sources for deposition of nitrate water (Hooda *et al.*, 2000; Van Drecht *et al.*, 2003)). The 'blue baby' syndrome is caused by drinking water that gets contaminated with nitrates; can prove fatal to infants that drink formula milk and also causes digestive tract cancers (L'hirondel, 2002; Chant *et al.*, 2011). Eutrophication is caused by NO_3^{2-} which assists in the growth of algae (Boeykens *et al.*, 2017). For water quality assessment, NO_3^{2-} in surface water is an important factor (McCasland *et al.*, 1985; Mensinga *et al.*, 2003)). Bacterial reduction from gastrointestinal tract to nitrite is a major health concern mainly from NO_3^{2-} in drinking water after conversion of these elements (McCasland *et al.*, 1985).

A study on Bangalore City's groundwater contamination by nearby textile industries revealed that most of the study area was extremely polluted. The contamination was as a result of high nitrates amongst other parameters, which rendered nearly 77% of the water samples tested to be unfit for consumption (non- potable) (Parameshwari and Kalpanadevi, 2006). A study was conducted whereby textile effluent was utilised for irrigation in Roswell, New Mexico since 1946 (Koerner and Haws, 1979) revealed that the concentration of nitrate in groundwater increased as a result of irrigation with waste water effluent (Tang *et al.*, 2004). A study conducted in Amaravathi River basin (Sivakumar *et al.*, 2011) in India showed that the $\text{NO}_2\text{-NO}_3^{2-}$ were between 0.5 and 37 mg/L. These levels were higher than the mean values recorded for this study which ranged from 0.15 to 6.51 mg/L for US1 and DS2 respectively. Moreover they were higher than values recorded for the groundwater sites which ranged from 1.6 to 16 mg/L for sites BH1 and BH2. Comparison of surface water historical with current data showed a decreasing trend for the only site that had data. All the groundwater sites revealed an increasing trend; this could be as a result of land use activities such as runoff or leaching from fertilized soil, waste water, landfills, animal feedlots, septic systems, or urban drainage etc.

The target water quality range from the South African water quality guidelines for domestic purpose is from 0 to 6 mg/L and there is no adverse health effects (DWAF, 1996b). Site US1 was within the limits for domestic use (DWAF, 1996b), while the other sites fell outside of these standards. Target water quality range for South African water quality guideline for aquatic ecosystem and irrigation use were not in place.

4.3.7 Ammonia

Ammonia is a common pollutant which generally occurs in either the free, un-ionized form (NH_3) or as ammonium ions (NH_4^+) and is associated with sewage and industrial effluents (Galvao *et al.*, 2013). Handy and Poxton (1993) have established that the toxicity of ammonia is directly related to the concentration of the un-ionized form and that the ammonium ion has little or no toxicity, although it does contribute to eutrophication. Concentrations of below 0.1mg/L are typical for ammonia and ammonium compounds in natural waters. The major sources of inorganic nitrogen which enters aquatic systems are surface runoff from the surrounding catchment area, the discharge of effluent streams containing human and animal excrement, agricultural fertilizers and organic industrial wastes. Even in high concentrations (most nutrients are not toxic), but when present in aquatic systems in these high concentrations, they may have a significant impact on the structure and functioning of biotic communities; exceptions include nitrogen-derivatives ammonia and nitrite, and occasionally nitrate (Dallas and Day, 2004).

A study conducted by Yusuff and Sonibasre (2005) in Kaduna state River basin, Nigeria showed that NH_3 values ranged from 1.82 to 2.72 mg/L. These values were higher than the mean values recorded for this study which ranged from 0.012 to 0.6 mg/L for sites US2 and DS3 respectively. The groundwater sites were not sampled and analysed for NH_3 . Comparison of surface water historical with current data showed a decreasing trend for all the sites. This clearly shows that the Buffalo River is not affected by the disposal of the textile effluent from the Da Gama textile industry. The drinking water quality standard (SANS 241:2015) limit for ammonia is 1.5mg/L. All sites sampled during this study were within these limits. This is in contrast to findings of NH_3 levels reported in effluent of five textile industries in Kaduna (Nigeria) that exceeded the Federal Environmental Protection Agency (FEPA) limit by numerous fold was described (Yusuf and Sonibare, 2004).

4.3.8 Ammonium

Low NH_4^+ nitrogen concentration of less than 0.2 mg/L is common in surface waters which are not polluted with organic wastes (Morrison *et al.*, 2001). The mean values recorded for this study ranged from 0.09 to 8.8 mg/L for DS2 and US3 respectively; while the groundwater sited mean values ranged from 1.6 to 16 mg/L for BH1 and BH2 respectively.

Comparison of surface water historical with current data showed a decreasing trend for all the sites except for site DS2. Majority of the groundwater sites showed a decreasing trend except for sites BH4 and BH5. Site DS2 might have other external factors which could be emanating from the WWTWs located nearby this site. At a wider catchment level, the agricultural return flows contribute to the nutrient loading (Dabrowski and De Klerk, 2013).

Values of between 1 and 10 have possibility of taste effects taste and smell complaints from consumers; and the disinfection by chlorine can be compromised (DWAf, 1996b). The SANS 241 standards of 2015 indicate that NH_4^+ should not exceed 1.5 mg/L; sites US3 and DS1 exceed this limit (SABS, 2015); moreover, all the groundwater sites were within these limits. The South African guidelines for water quality: domestic use, water quality range for NH_4^+ is 0-1 mg/L. This does not have any health or aesthetic effects. The irrigation target water quality range is less or equal to 7 mg/L (DWAf, 1996a); all sites were within these limits, except for site DS2. Exceedances for site DS2 could be because of the fact that this site is situated closer to a waste water treatment works.

4.3.9 Orthophosphate

Waters that receive sewage, and leaching or runoff from cultivated land are likely to have higher concentrations of phosphorus (Dallas and Day, 2004). One of the limiting factors in

aquatic environments is PO_4^{2-} (Osode and Okoh, 2009). However, orthophosphate concentrations above 0.1 mg/L in surface water resources usually result in increased eutrophication (Zhang and Rao, 2012). As phosphates bind to most soils and sediment, surface waters receive most of their P in surface flows rather than in groundwater (Correll, 1999).

According to Sivakumar *et al.* (2011), study done in Amaravathi River basin in India showed that the values recorded ranged from 0.8 to 30 mg/L and were higher than the mean values recorded for this study which ranged from 0.06 to 3.4 mg/L for sites US2 and US3 respectively. Comparison of surface water historical with current data showed an increasing trend for all the sites. According to Oberholster *et al.* (2014), nutrient enrichment is as a result of excessive increase of nutrients which can be linked to improper functioning or dysfunctional sewage treatment plants.

The South African guidelines do not specify the target water quality ranges for phosphate in water for domestic use, irrigation and recreational purposes (DWAF, 1996a; DWAF, 1996b; DWAF, 1996d). However, according to the SANS 241:2015, orthophosphate can be greater than 1 but less than 10 mg/L. The values recorded during this study were all within these limits. However, the levels were greater than concentrations reported by Chigor *et al.* (2013) for orthophosphate which ranged between 0.01 and 1.72 mg/L. A previous study conducted by Van Ginkel *et al.* (1996) revealed the median phosphate concentrations were less than 0.1 mg/L in the middle reaches of the Buffalo River, which are lower than the levels measured during this study.

4.3.10 Chemical oxygen demand

Chemical oxygen demand is defined as the amount of oxygen required to oxidise all the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant (DWAF, 1996a). The COD is used as a routine measurement for effluents and also a measure of the amount of oxygen likely to be used in the degradation of organic waste (Dallas and Day, 2004). Measurement of the biochemical oxygen demand (BOD) or the COD are useful for determining water quality requirements of effluents discharged into aquatic systems, in order to limit their impact; moreover they impact negatively on aquatic ecosystems (Kanu and Achi, 2011). The COD indicates the level of toxicity and the presence of biological resistant substances in water (Chaurasia and Tiwari, 2011). Industrial effluents are the main source of high COD in natural receiving waters (Buckely 1992; Wallach *et al.*, 2005).

A study conducted by Yusuff and Sonibare (2005) in Kaduna state River basin, Nigeria showed that the values ranged from 1067 to 2430 mg/L; and these were extremely higher than the mean values recorded for this study which ranged from 0.06 to 75.2 mg/L for sites DS1 and US3 respectively. Comparison of surface water historical with current data showed a decreasing trend for all the sites. This could indicate that the textile effluent that is disposed of by Da Gama textile industry might not have any impact on the COD concentration of the Buffalo River. The groundwater sites were not sampled and analysed for this variable. The South African water quality guidelines do not specify the COD concentrations for domestic, recreational, aquatic ecosystems, and agricultural purposes (DWAf, 1996a, DWAf, 1996b; DWAf, 1996c). The COD guidelines is available for industrial purposes and range from 0 –10 mg/L (DWAf, 1996c).

Raw water from the textile and tannery industries is expected to have a COD of between 2760-29110 mg/L (Swartz *et al.*, 2017). According to Swartz *et al.* (2017), the parameter COD is widely used to test the level of quality in effluents (i.e. COD is produced in almost all textile processes and can be used as a quality indicator). These concentrations are much higher than the 1400 mg/L of CODs in the Da Gama textile effluent measured during this study. Roy *et al.* (2010) found that the COD levels were very high in the range of 800-2304 mg/L, which is higher compared to the values recorded in this study. The high value of COD indicates the toxicity of the effluents and it may be due to the presence of non-biodegradable dyeing chemicals, softeners and detergents discarded during the process (Yusuff and Sonibare, 2004).

4.3.11 Total suspended solids

The TSS concentration of a water sample is measured gravimetrically and expressed as mg/L (Gray *et al.*, 2009) and is a measure of the amount of material suspended in water (Guo, 2006). High values of TSS and organic loads are expected from textile industries effluents from natural fibres such as cotton (Correia *et al.*, 1994).

A study conducted by Uddin *et al.* (2017) showed the mean groundwater values ranging from 690 to 2536 mg/L for an investigation conducted in Chittagong in Bangladesh. These values are higher than the surface water results which have the mean ranging from 14.1 to 32.3 mg/L for site US1 and DS3 respectively; while the groundwater sites recorded values from 1987 to 7777 mg/L for sites BH2 and BH1 (higher than the Chittagong study). Groundwater sites could not be compared (historical vs current) due to lack of historical data. Comparison of historical surface water quality data with current conditions showed a decreasing trend for the two sites for which data were available (US3 and DS2). The levels

recorded in this study were lower to studies where industrial effluents from Lagos and Abaekuta were discharged into the Ogun River (mean of 1205 mg/L) (Ado *et al.*, 2014; Jaji *et al.*, 2007). The groundwater TSS levels recorded in this study were higher compared to the study conducted on the Noyyal River where the levels were ranging from 222 to 896 mg/L (Pranaw *et al.*, 2014). An impact assessment on surface and groundwater was conducted in Tirupur (India's textile valley) and it concluded that the quality of water was poor mainly due to high TSS concentrations in the groundwater (Pranaw *et al.*, 2014). These concentrations were lower to the TSS measured in groundwater samples from this study. Generally, the water was not suitable for the textile industry and for drinking purposes (Prabha *et al.*, 2013).

The limits for TSS are not listed on the SANS 241:2015 and the South African water quality guidelines for domestic use (SABS, 2015; DWAF, 1996a). Water quality guidelines for aquatic ecosystems in South Africa specify a target water quality range whereby any increase in TSS concentration (or turbidity) should be less than 10% of the background TSS concentrations at a specific site and time. This is applicable for sites where the background TSS concentration is less than 100 mg/L (Dallas and Day, 2004). There are limited data available on historical concentrations of TSS for the study area. However, based on the two year historical data for sites US1 and DS2 it would appear that there is a slight increase in TSS at Site US3 and a decrease in TSS at Site DS2 (Table 4).

4.3.12 Impact of the irrigation of Da Gama effluent on the ground- and surface water quality

The water quality of the discharged effluent was observed to have high concentration of EC, TSS, PO_4^{2-} and COD. The high EC might be associated with the release of chemical salts from the textile industry as well as the overflow of the settling dam. Presence of biologically resistant organic substances is indicated by high COD in water (Sawyer, 1978). The elevated values of COD in this study were similar to the study of Olayinka and Alo (2004) who found high values of COD (204-2000 mg/L) in water close to textile effluent discharge. The irrigation of this effluent caused an increase in notably the EC and TSS of the groundwater most likely through leaching, percolation and runoff from the effluent irrigated land (Beltran, 1999).

A study in Tamil Nadu's Mettupalayam Taluk industries revealed that continuous disposal of industrial effluents on land, which has restricted the ability to assimilate the pollution load and in turn, this has resulted in groundwater pollution (Mukherjee and Nellyat, 2006). The application of the effluent for irrigation has caused an increased salinity in soils and the

quality of groundwater in shallow open boreholes surrounding the industrial locations had worsened (Mukherjee, 2008). Other studies for example by Tafesse *et al.* (2015) indicated that the lowest concentration of TSS was found in the sample of textile industry; however, they did not meet the legislative requirements of National Environmental Quality Standards (NEQS) limits in Hattar industrial estate, Haripur. Sathiyaraj *et al.* (2017) also found the TSS values of textile effluents of Erode, Pallipalayam, and Bhavani of Tamil Nadu were high in the range of 222-896 mg/L. These studies confirm the results obtained in this study which revealed that high TSS concentrations can enter the groundwater via surface irrigation. However, even in a small amount, the presence of TSS in groundwater does indicate the impact of industrial effluents in the close proximity (Tariq *et al.*, 2006).

In this study the textile effluent was irrigated onto the land. This resulted in high TSS, and EC levels in the groundwater. The findings from this study are supported by different studies done internationally such as a study by Joshi and Santani (2012) which reported that EC and TSS in industrial effluents were above the permissible limits set by NEQS in India. The results of this study agreed with the findings of Tariq *et al.* (2006) for a study in Peshawar (Pakistan) which indicated the effluent TSS levels between 125 to 1980 mg/L and the groundwater TSS levels between 1.80 to 2.10 mg/L which did not meet the NEQS standards. Another study in Punjab town of Pakistan (Nasrullah *et al.*, 2006) revealed high levels of TSS in both the industrial effluent (140.5 to 1670 mg/L) and the groundwater samples (1.78 to 2.09 mg/L). According to Sial *et al.*, (2006) the Hattar industrial estate in Pakistan showed results with very high EC and TSS which exceed the NEQS of Pakistan.

The textile waste water effluent contains high amounts of agents causing damage to the environment including salts, suspended and dissolved solids (Arya and Kohli, 2009). Irrigation with effluent has some risk factors that have longer term impacts which increase with continued use of recycled effluent (e.g. saline effects on soil), while others are short term and vary in severity depending on the potential for human, animal or environmental contact (e.g., microbial pathogens) (Feachem *et al.*, 1983; Goel and Kulkarni, 1994). A major threat to ecological integrity and human well-being is soil pollution with heavy metals due to discharge of untreated urban and industrial waste water (Mahmood and Malik, 2014).

Furthermore, an increase of such metals in soils and various crops, which ultimately resulted in clinical problems in human beings, is from the extensive use of textile effluent for irrigation purpose (Butt *et al.*, 2005). Contamination of soil and plant system with heavy metals emanates from the long term irrigation of farm lands with effluent (Salakinkop and Hunshal, 2014). Effects on the soil quality deteriorating, with less microbial activities, high salinity and heavy metals accumulation over time are some of the threats associated with the application

of waste water as irrigation water for agriculture (Shammi *et al.*, 2016). Toxic levels for plants and animal health can be reached if these effluents are continuously used for irrigation for long periods of time (Kirkham, 1983).

The study in Dimbaza and Nkonkobe (Eastern Cape, South Africa) indicated that the deterioration of the groundwater was as a result of constant discharge of non-treated and partially treated effluent that is characterized by high load of heavy metals, TDS and SS, over long period of time. Moreover the water becomes unsuitable for irrigation and even for drinking (Momba *et al.*, 2006). Groundwater pollution is eminent as well as loss of soil productivity (Prabha *et al.*, 2013).

There is an overall increase in PO_4^{2-} in the Buffalo River, which may be indicative of the groundwater transporting the effluent PO_4^{2-} into the surface water. This is possible from the concept of surface water-groundwater interaction. Previous studies of the Buffalo River show that natural deterioration in water quality was more severe caused by inflow from urban and industrial effluents and the phosphate exceeded 1 mg/L recommendation at two sites (Kempster *et al.*, 1980; Palmer, 1991). This indicates that high levels of PO_4^{2-} is a continuous phenomenon of the Buffalo River and is influenced by the discharge industrial effluent. This confirms that the practice of waste water effluent irrigation can act as a source of pollutants to shallow groundwater and nearby surface water (Turner *et al.*, 2019); therefore the groundwater in the Buffalo River catchment has been impacted upon by the irrigation effluent. According to Awomeso *et al.* (2010) a study in Ibeshe (Nigeria) showed PO_4^{2-} levels of 1.0-6.02 mg/L in the surface water body. These levels were found to be higher than the USEPA standards which state that PO_4^{2-} value of 0.1 mg/L is recommended in surface water, the result obtained in this study is far above this standard indicating the pollution of the stream (USEPA, 1986). A study by Ahmed *et al.* (2011) reported that PO_4^{2-} levels in effluents in Karnatoli River (Bangladesh) ranged from 0.54 to 19.88 mg/L. These values are also in line with the values recorded for this study's surface water sites.

Phosphate levels from a Chittagong (Bangladesh) study conducted by Jamaluddin and Nizamuddin (2012) indicated that the levels of the effluent (2.79 to 253.96 mg/L) do not comply with the Bangladesh-Department of Environment recommendations/limits. These values were higher than the levels recorded in this study (13-59 mg/L). Domestic detergent and industrial sewage effluents represent important sources of PO_4^{2-} in natural water (Taha *et al.*, 2004). Moreover, high PO_4^{2-} value of a stream could also lead to oxygen reduction with subsequent effect on aquatic organisms. Runoff water from areas of phosphate rocks may contain high concentrations of PO_4^{2-} and the PO_4^{2-} may be introduced into groundwater from the industrial wastes as well as agricultural drainage (Taha *et al.*, 2004). Over

enrichment of PO_4^{2-} can lead to algae bloom, because of the excess nutrients (Jamaluddin and Nizamuddin, 2012).

Elevated levels of PO_4^{2-} can lead to extensive growth of the phytoplankton and macroalgae (Armitage *et al.*, 2005). Eutrophication problems might also arise in the Buffalo River catchment which might cause algal growth problems in the near future (Thornton *et al.*, 1967; Selkirk and Hart, 1984; Schwab *et al.*, 1988).

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study was undertaken to better understand the current situation in the surface water and groundwater in the vicinity of the textile industry in Zwelitsha-King Williamstown. The central aim for this study was to determine the impacts of irrigation with industrial waste water (Da Gama Textile) on the groundwater quality in Zwelitsha-King Williamstown. This aim was achieved as it can be concluded that the textile industry has affected the groundwater in terms of high EC and TSS and ultimately the surface water quality of this study area; however, it is also well known that the Eastern Cape province experienced severe droughts since 2015 (Ramahlalela *et al.*, 2015). In October 2019, the Eastern Cape Province was declared a drought disaster region following pronounced water shortages in many urban and rural areas (Ramahlalela *et al.*, 2015).

- The data shows that the effluent has high TSS, EC, PO_4^{2-} and COD. The effluent irrigation activities have caused an increase in notably the EC and TSS of the groundwater as observed in the groundwater sites results. However, the surface water of the Buffalo River downstream of the textile industry does not have elevated levels of TSS and EC compared to upstream. There is however an overall increase in PO_4^{2-} , which may be indicative of the groundwater transporting the effluent PO_4^{2-} into the river through groundwater-surface water interaction; however, the runoff from the agricultural fields and the effluent discharges from the waste water treatment works could also have an effect on the elevated PO_4^{2-} levels.
- The contamination further moves to the Buffalo River as the PO_4^{2-} showed an increasing trend. The salinity of the water was also found to be increased and causing water quality problems from the discharge of textile effluents. The objectives for this research were to investigate the historical and current water quality situation of the surface water of the Buffalo River. This was done using the comparison Tukey test which showed the significance difference between sites; however, the PO_4^{2-} was observed to be showing an increasing trend in the surface water sites.
- Under the existing circumstances the disposal of effluent through irrigation has had significant effect on the fitness for use of water in the Buffalo River in terms of salts and PO_4^{2-} . The effect has been noted to be in a negative manner. As it stands, none of the groundwater is currently used for domestic purposes, and as all the communities in the area are served with treated water from the Laing Dam (Palmer, 1991).

- The irrigated effluent has an effect on the groundwater through increased EC and TSS, but does not seem to influence the EC and TSS of the Buffalo River. The study has revealed that both groundwater and surface water have been affected in a negative way.

5.2 Recommendations

Future water quality studies may include the analysis of more physico-chemical parameters that are common for all the aspects such as surface water, groundwater and the effluent to be evaluated. Moreover, it is recommended to utilise tracer studies for analysis of irrigation water contamination of groundwater and surface waters, flow models such as Modflow and GIS simulations. Further examination of extent of surface-ground water interaction in relation to reaction changes and fluctuations using large number of samples must be promoted for obtaining long-term and future assessment of contamination.

Future studies should focus on the impact of heavy metals, environmental, health and safety associated with the irrigation with industrial effluent. Disposal of effluent through irrigation should be phased out, although this should be done such that the surrounding community of Zwelitsha-King Williamstown would have time to adjust to this.

Suspended solids and COD removal by means of a proper treatment works should be implemented as soon as is possible in order to minimise the risk of contamination and to protect the soil. The irrigation application rate should be reduced. This can be achieved by reducing the effluent flow by re-using and recycling the effluent in the factory. The Da Gama textile industry can achieve this through the implementation of a zero liquid discharge (ZLD) system.

Soil surveys should be done to verify the current levels of contamination and to recommend remedial measures. The quality of the upper soils directly influences the quality of rainwater that recharges the groundwater and constituents can leach out of the soil and be transported to the groundwater, further reducing the quality of the groundwater. Further research is recommended during spring and autumn for the sampling of soil, and groundwater piezometers for analyses of nutrients and major ions. Parameters monitored can include effluent flow and chemistry, groundwater (shallow and deep) level and chemistry, surface water (river and springs) chemistry, distribution of salts in the soil profile, soil heavy metal content and crop yield.

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