

**Geochemical analysis of stream responses to changes in land development
and seasonal variation, Western Cape, South Africa**

by

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Abstract

It is generally accepted that poor riparian land-use practices, commonly associated with agricultural, urban and industrial sectors, have a negative effect upon the geochemical state of streams. The Western Cape of South Africa has experienced both a rapid increase in its population, and a severe drought. These factors have highlighted the need to investigate the effect of riparian land-use practices specific to the rivers and estuaries of the Western Cape, which leads to the research question: What is the effect of riparian land-use practices, taking into account seasonal change, upon the Rooiels Estuary, the Eerste River and the Lourens River?

A year-long monitoring study was conducted on nutrient and cation fluxes within the Eerste and Lourens River streams. This was done to delineate ion sources and geochemical responses to seasonal change and land-use practices. The anthropogenic influence on these streams was evident from the principal component analysis. Nitrate loading from agricultural land-use practices was highest during the wet season, indicative of a diffusive source. Ammonium and Na loading within the Lourens River wetland were highest during the dry season, indicative of a point source. Urban structure weathering within urban developed sections proved to be a large source of Ca and Mg affecting stream electrical conductivity and carbonate alkalinity. Nutrient retention under base flow conditions was site specific, the highest located in natural stream sections and the lowest in restructured stream segments. Research conducted on nutrient retention was preliminary, thus the need for further research within the field of nutrient retention in sub-Saharan African streams, under fluctuating climatic conditions and differential anthropogenic influences, persists.

In conclusion, the freshwater systems of the False Bay region, South Africa, are notably affected by anthropogenic influences. Thus, to maintain the state of freshwater systems, management of the riparian zones, river structures and anthropogenic practices should focus on limiting the anthropogenic impact.

Opsomming

Daar word algemeen aanvaar dat swak oewere-grondgebruikspraktyke, wat algemeen verband hou met landbou-, stedelike en nywerheidsektore, 'n negatiewe uitwerking het op die geochemiese toestand van strome. Die Wes-Kaap van Suid-Afrika het beide 'n vinnige toename in sy bevolking ervaar en terselde tyd 'n ernstige droogte. Hierdie faktore het die behoefte beklemtoon om die effek van oewerlandgebruikspraktyke, wat spesifiek vir die riviere en riviermondings van die Wes-Kaap is, te ondersoek, wat lei tot die navorsingsvraag: Wat is die effek van oewerlandgebruikspraktyke, met inagneming van seisoenale verandering, op die Rooiels-riviermonding, die Eersterivier en die Lourensrivier?

'N Jaarlange moniteringsstudie is uitgevoer oor voedingstowwe en katione in die Eerste en Lourensrivierstrome. Dit is gedoen om iononbronne en geochemiese reaksies op seisoensverandering en grondgebruikspraktyke te definieer. Die antropogene invloed op hierdie strome was duidelik geïdentifiseer uit die hoofkomponent-analise. Nitraat van landbougrondgebruikspraktyke was die hoogste gedurende die nat seisoen, wat aandui dat dit 'n diffuse bron is. Ammoniumkonsentrasies en natriumkonsentrasies binne die Lourensrivier-vleiland was die hoogste gedurende die droë seisoen, wat aandui dat dit 'n puntbron is. Stedelike struktuur verwerking binne stedelike ontwikkelde afdelings was 'n groot bron van Ca en Mg wat elektriese geleidingsvermoë en karbonaat alkaliniteit beïnvloed. Nutriëntretensie onder basisvloei toestande was plekspesifieke, die hoogste in natuurlike stroomafdelings en die laagste in herstruktureerde stroomsegmente. Navorsing oor nutriëntretensie was voorlopig, en die behoefte aan verdere navorsing op die gebied van nutriëntretensie in Suid Afrika, onder fluktuierende klimaatstoestande en differensiële antropogene invloede, bly voort.

Ten slotte word die varswaterstelsels van die Valsbaai-streek, Suid-Afrika, veral beïnvloed deur menslike invloede. Om die toestand van varswaterstelsels te handhaaf, moet die bestuur van die oewersones, rivierstrukture en menslike praktyke dus fokus op die beperking van die menslike impak.

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1. Chapter 1 Introduction

1.1. Background

The City of Cape Town and the surrounding region are primarily dependent on surface water as a main source for agricultural, domestic and industrial water use (City of Cape Town, 2018). As part of the freshwater system, rivers are used as the major transport system for water to the agricultural system and in some cases between water reservoirs. Rivers ultimately also act as the transport mechanism between freshwater systems and the ocean via estuaries. In general, if the state of local rivers deteriorates, it will have immense effects on both the freshwater supply system and the coastal region.

Rivers and estuaries form part of complex open systems, sensitive to several external factors, such as climate and land-use practices (Bussi et al., 2017). The processes taking place within the riparian zone and the catchment greatly affect these systems. Urban development caused by the influx of people to this region place strain on the rivers. Linked to the influx of more people, are the expansion of urban areas and higher demands on both the agricultural and the industrial sector. This, in turn, affects rivers systems. Urban expansion next to river systems require certain changes to be made to the river system to protect the new development. This often includes artificial bank stabilisation, channelisation and riparian vegetation removal (Newcomer Johnson et al., 2016). A constantly growing agricultural sector leads to the clearing of more indigenous vegetation and higher nutrient loading on the catchment for crop development. Similarly, the industrial sector produces more waste, in the forms of dust and harmful effluents, to keep up with increasing demands.

Environmental factors, such as the climatic conditions of the region, affect these systems in several ways. Within the river system, several internal processes are dependent on the external conditions and processes, such as ambient temperature, catchment run-off rates and nutrient loading (Hale et al., 2016). These external conditions follow seasonal cycles, causing internal processes to be affected within the same time cycle. However, in the case of an extreme weather event such as a flood or a drought, it is expected that internal processes will be adversely affected (Mirza, 2003).

In the case of nutrient loading of the river system, climatic conditions, development and land-use processes have an impact on nutrient concentrations within the river system. If nutrient loading is excessive and internal processes cannot manage the nutrient influx, the river system can experience eutrophication leading to mass biological mortalities and general deterioration

of river health, and eventually causing nutrient loading of the coastal regions as well (Nyenje et al., 2010). Nutrients such as nitrate and phosphate are fundamental for the growth of biological organisms, microbial community and the riparian vegetation of streams (Flemming et al., 2016). The microbial community together with hydrological processes and chemical processes are the main elements in managing nutrient levels within river systems. These factors contribute to the ability of rivers to retain and store nutrients entering the system, thus decreasing nutrient loading on the coastal environment as well as keeping the fresh water in a usable state (Thomas et al., 2001). The efficiency of these three factors are sensitive to change caused by external factors such as the climatic conditions and the surrounding environment.

To an extent, this topic is unexplored within the freshwater structures of the Western Cape of South Africa. These factors are rarely being considered in the decision-making process regarding the management strategies for river and estuary systems. Thus, it is important to establish an understanding of how these river systems will react to the continuous change they are experiencing during land development and climatic change.

1.2. Research question

The magnitude of human impacts, land characteristics and changes in the climate, on nutrient loading, ecological processes and geochemical responses within streams and estuaries of sub-Saharan Africa, requires research to fully quantify and understand. The lack of research and understanding surrounding these freshwater systems within South Africa will lead to mismanagement and the deterioration of these freshwater resources.

1.3. Aims and objectives

This study consists of three studies focusing on the estuaries and rivers of the False Bay region, South Africa (Appendix A, Figure 1). As each study evolved, new questions were raised, forming the basis for the next study.

The initial study aimed to delineate the effects of environmental factors such as the weather and ocean on the geochemistry of the Rooiels Estuary over an extended period of six years. To achieve the aim, the following objectives were set:

- Monitor the Rooiels Estuary on an annual basis for six consecutive years.
- Compare the data to historic literature from the Rooiels Estuary.
- Compare the data to natural external factors including precipitation, ambient temperature and oceanic factors such as tides.

The results from the Rooiels Estuary study led to the second study. to delineate the effect of anthropogenic land-use practices in conjunction with natural factors such as precipitation on the geochemistry of rivers within the False Bay region, South Africa. To achieve the aim, the following objectives were set:

- Delineate the influence of different land-use practices on the Eerste and Lourens Rivers and identify different sources of pollution in the rivers.
- Determine the effect of the weather on the geochemical signal of these land-use practices for the duration of a full seasonal cycle.
- Compare the Eerste and Lourens Rivers to the pristine Steenbras River to determine the overall state of these rivers.

The results of the Eerste and Lourens Rivers study led to the third study: to delineate factors influencing nutrient retention within the Eerste River. To achieve this aim, the following objectives were set:

- Determine what sections of the Eerste and Lourens Rivers exhibited nutrient retention, which nutrients were retained, and what factors influenced the nutrient retention.
- Quantify nutrient retention within natural river sections and anthropogenically affected river sections using tracer tests.
- Isolate different environments and variables to provide a direct insight into the effects that climate variables such as water flow velocity and water temperature, as well as developmental factors such as stream structure and land-use practices, have on nutrient retention and storage within stream environments.

1.4. Limitations

The nature of the Rooiels Estuary study resulted in several limitations regarding sampling methodology and study area.

1. The data was collected by undergraduate students. This forced the sampling methodology to be simple and easily reproducible; however, it limited the parameters that were sampled. Data was primarily collected using handheld probes to ensure accurate reproducible data, thus the parameters sampled were limited to parameters that could be sampled using the above-mentioned probes.
2. The river section above the Rooiels Estuary is inaccessible because of thick vegetation and steep topography.
3. A time constraint related to the nature of the undergraduate field trip only allowed for sampling once every year.

Within the Eerste and Lourens Rivers study, some of the limitations related to the Rooiels Estuary were addressed. The River study did, however, have its own limitations.

1. The Eerste River could not be sampled in its entirety. The lower section of the Eerste River runs through informal settlements and sampling it proved to be a safety concern. This limited the Eerste River sampling to the upper catchment of the river, excluding the estuary located at Macassar beach.
2. The Kleinplaas Dam located in the Eerste River controlled flow in the Eerste River to some extent.
3. The Lourens River mouth was inaccessible until 2018.

The experimental study had several limitations hindering the study from achieving the objectives.

1. The tracer test could only be conducted within baseflow conditions of the Eerste River, placing a time constraint on the study.
2. The biofilm for the flume experiment had to be cultivated within the Eerste River stream, under low flowing conditions to prevent the growing beds from flushing away. This limited the cultivation of the biofilm to summer conditions.
3. Regulating the temperature within the flume proved to be challenging and could only be achieved after the time frame of the study was over.

The limitations surrounding the project played a large role in the structure of the project. Several aspects of the study were limited because of these limitations including: the study area and the parameters that could be sampled.

1.5. Structure

This thesis manuscript addresses the main aims of the manuscript in three chapters. Chapter 4 focuses on the Rooiels Estuary and the external factors affecting the geochemistry of the estuary. Chapter 4 includes the findings of six years of geochemical monitoring conducted by undergraduate students.

In Chapter 5 the study area is changed from the anthropogenically unaffected Rooiels Estuary to the river systems of the Eerste and Lourens Rivers. These two rivers are located within cultivated regions of False Bay, South Africa. This chapter focuses directly on the geochemical responses of streams to land-use practices and seasonal change.

Chapter 6 focuses on nutrient retention within the Eerste River stream. This chapter includes two experimental procedures. The first experiment was conducted within the Eerste River and focuses on differences between nutrient retention in channelised and natural river sections. The second experiment was conducted within a flume. The flume was used to recreate a natural river environment with controllable climatic variables, such as water flow velocity and water temperature. This aimed to directly determine the effects of these variables on nutrient retention within channelised river sections by biological biofilms. Both these experiments were, however, still in their infancy and provide merely an insight into the possibility for future research surrounding these questions on a local level.

2. Chapter 2 – Literature review

The future in terms of freshwater availability within the Western Cape of South Africa is currently unsecured. The local government of the Western Cape of South Africa declared the Western Cape a disaster area in 2017. This was caused by the worst drought in the area since 1904. South Africa was already classified by New (2002) as a water-limited country. According to New (2002), the region is and will continue to face water scarcity and water quality problems, because of continuous development in both the social and economic sectors. Climate change will increase the stress on the water resources of this region. Several climate models have indicated drier and warmer conditions for the Western Cape (New 2002; Engelbrecht et al., 2009).

2.1. Climate

Climatic change, a global issue, is creating an unknown future, filled with challenges and change. The start of the industrial age marked the beginning of the release of large amounts of greenhouse gasses. Linked with the release of these anthropogenically produced greenhouse gasses are increasing global temperatures. Increased temperatures result in increased evaporation rates, thus requiring higher precipitation rates to maintain the moisture balance (New, 2002).

Climate change will have different effects on different climatic regions. In semi-arid regions it is expected that climate change will intensify the hydrological cycle and thus increase the intensity of already extreme events, such as extended droughts, larger precipitation events and increases in the average temperature. Within Mediterranean climate zones the effects of climate change are expected to be severe as these regions are the most susceptible to the effects of climatic change. Within these regions different effects are expected, including increased temperatures and reduced vegetation. It is also expected to increase the effects of anthropogenic development, causing water shortages, agricultural losses and increased risks of forest fires. The Western Cape of South Africa, being a Mediterranean zone with semi-arid conditions, is expected to have a decrease in precipitation (MacKellar, New and Jack, 2014).

The scale and magnitude of the climate change the Western Cape will face is uncertain, however, climate projection models have provided several predictions for this region. These include increased maximum and average annual temperatures coupled with more heat waves and higher minimum temperatures. Precipitation patterns will also change to reduced average

precipitation coupled with more frequent and intensified extreme weather events. These extreme events include floods, droughts and storm surges (Western Cape Department of Environmental Affairs and Development Planning, 2017; Ziervogel et al., 2014). MacKellar, New and Jack (2014) found rain days to have decreased by 11.3 days for the duration of a 50-year period as well as significant increases between $0.015^{\circ}\text{C}/\text{annum}$ and $0.027^{\circ}\text{C}/\text{annum}$ in maximum temperatures. Precipitation rates in the South Western Cape of South Africa are estimated to decrease by 20% by 2070–2100, based on a Conformal-cubic Atmospheric module (CCAM) and an A2 scenario (Engelbrecht et al., 2009). This will be associated with more extreme precipitation events (Engelbrecht et al., 2013).

2.2. Development

Climatic change is, however, not the only challenge faced by rivers, as continuous development surrounding the riverbanks is destroying the natural riparian vegetation and sections are channelised. Riparian vegetation has a large influence on nutrient retention, as it does not only take up nutrients, but also affects the in-stream ecological features of streams, such as water temperature, stream flow and light availability (Sabater et al., 2000), which, in turn, affect the benthic community. With the removal of riparian vegetation, the process of nutrient retention is more dependent on the benthic community and the hyporheic zone (Bukaveckas, 2007), by eliminating all nutrient uptake by the riparian vegetation itself. Channelisation also affects the flowing water to bottom surface area ratio. In the case of natural streams, the bottom surface area, exposed to the flowing water, tends to be larger than in channelised streams. This smaller interaction area can reduce nutrient retention (Alexander et al., 2000). Channelisation also removes natural curves and bends in the streams, causing a loss in hyporheic exchange, because of a lack in differential flow patterns (Rhoads et al., 2003).

Development within the agricultural sector is having increasing effects on stream health (Foley et al., 2005; Vörösmarty et al., 2010). The main cause for decreases within stream health, linked to a developing agricultural sector, is caused by the clearing of land and excessive nutrient and pesticide loading. Land clearing, including the removal of riparian vegetation, decreases nutrient retention within soils and root zones and destabilises soil layers, allowing high concentrations of nutrients, sediments and pesticides to be transported into the stream by means of surface run-off (Burrell et al., 2014).

Similar to the agricultural sector, urban development decreases river health by land clearing, yet with the difference of creating large, impermeable surfaces. These surfaces accumulate high

concentrations of metals, salts and nutrients (Nyenje et al., 2010). With the first precipitation after any dry period, the accumulated metals, salts and nutrients flush into the river system. When infrastructure within urban regions is developed too close to riverbanks, the rivers become a threat to the infrastructure, because of flood risks and ground stability. To overcome this threat on the infrastructure, riverbanks are stabilised by either channelising the river or building the banks with rock-filled gabions. The channelised or semi-channelised sections of rivers tend to lack vegetation to some extent, and in addition natural meandering, pools and rapids are removed from the rivers. Decreases in stream meandering and hydrogeological structures will affect the residence time of nutrients, thus limiting the interaction between the nutrients, vegetation, sediments and benthic microbial communities (Newcomer Johnson et al., 2016). Removal of the vegetation increases the amount of light available to the water column. This contributes to the overall trophic state of the river by contributing to photosynthesis of the algae community as well as increasing the water temperature (Burrell et al., 2014).

2.3. Nutrients

Nutrients such as nitrate and phosphate are an essential food source for biological organisms within freshwater systems (Dodds and Smith, 2016). Without nutrients, vegetation and the microbial community, dependent on the freshwater body as their source of nutrients, will be limited in growth. On the contrary, if excess nutrients are present within the waterbody the biological community will flourish to the extent of the whole system being affected negatively (Smith, Tilman and Nekola, 1998). Thus the biological productivity is directly related to the nutrient loading within the waterbody. This can be classified by the trophic state of the waterbody. The trophic state is classified within four categories, namely: oligotrophic, mesotrophic, eutrophic and hypereutrophic (Dodds and Smith, 2016).

Oligotrophic conditions can be associated with low nutrient concentrations resulting in low primary productivity and algal production. Thus, the water is typically rich in oxygen and clear and can support large vertebrates such as fish and amphibians. Mesotrophic conditions can be associated with intermediate nutrient concentration. This creates more suitable environments for macrophytes; however, the water is still clear and oxygen rich. Eutrophic conditions are associated with high nutrient concentrations. Under eutrophic conditions aquatic plants flourish; however, so do algae. As the algae die, microbes degrade the organic matter from the dead algae. This results in an increase in microbial biomass. The increase in microbial biomass results in increased respiration, depleting the waterbody of oxygen and causing high biological mortality rates (Smith, Tilman and Nekola, 1998). The hypereutrophic state is associated with

extremely high nutrient concentrations, resulting in frequent algae blooms. This causes oxygen-depleted water with limited life. These waters are often dark in colour and are unsafe for human consumption (Smith, Tilman and Nekola, 1998).

Nutrient sources are often dependent on the riparian environment. Nutrient sources can be classified into two distinct groups: point sources and diffused sources (De Villiers, 2007). Nutrients originating from point sources enter the river at specific locations associated with a localised source. These sources include storm water outlets, water treatment sites, effluents released by industrial processes, ground water infiltration etc. Non-point sources or diffused sources are associated with nutrients entering the waterbody via extended areas such as agricultural fields and industrial sectors as well as natural processes such as rock weathering and decomposition of biomass. In the case of diffusive source nutrient loading, nutrients are often dependent on a method of transportation to reach the waterbody. Nutrients are transported by surface run-off from the source to the stream during precipitation events. In the case of dry periods, nutrients tend to accumulate in the soils, causing sudden high nutrient loading in the waterbody when precipitation does take place (Whitehead et al., 2009). The soil's nutrient holding capacity in agricultural fields are highest during dry periods because soils become water saturated, decreasing the nutrient uptake capacity of the soils (Labuschagne et al., 2006). This increases the likelihood of nutrient transport to streams during wetter times.

Within a stream, nutrients tend to follow cycles based on their physical and chemical properties. During this process nutrients spiral between the mobilised inorganic state and immobilised organic state within the water column (Figure 2.1) (Bouwman et al., 2013).

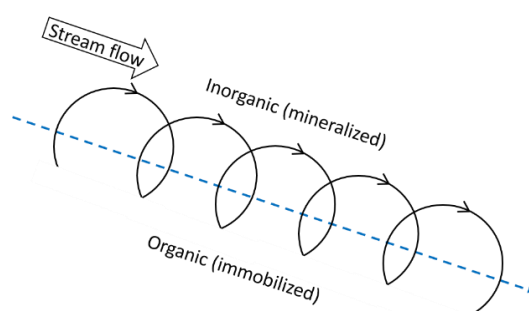


Figure 2.1: Diagram depicting nutrient cycling between the mobile inorganic phase and the immobile organic phase within a stream (Baker and Webster, 2017).

Nitrate is an essential nutrient added to agricultural fields in the form of ammonium nitrate. Within the nitrate cycle, ammonium is also present as a reduced state of nitrate. Both nitrate and ammonium enter the waterbody by atmospheric deposition or anthropogenic sources such as the agricultural sector (Figure 2.2) (Baker and Webster, 2017). After entering the river water, the nitrate or ammonium might either be taken up by the microbial community or transported to the ocean (Thomas et al., 2001). Biological uptake transforms nitrate and ammonium into organic nitrogen (Figure 2.2). Nitrate and ammonium are then essentially stored and retained as organic nitrogen, thus removed out of the water, until remineralisation takes place during the biodegradation process of the organic biomass (Tank, Reisinger and Rosi, 2017). Under anoxic conditions denitrifying microbes reduce nitrate to atmospheric nitrogen, thus also removing nitrate from the water column (Tank, Reisinger and Rosi, 2017).

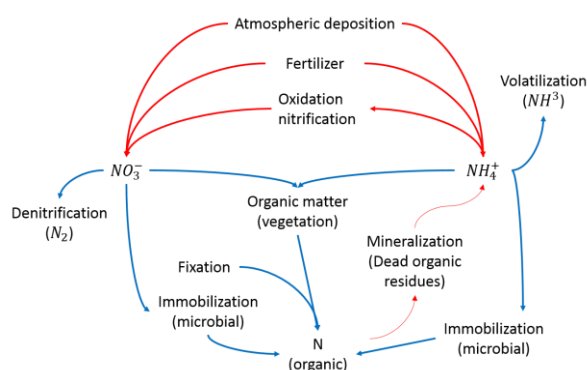


Figure 2.2: The nitrogen cycle, including main sources of nitrate and ammonium as well as primary speciation. Adapted from Thomas et al. (2001).

The main sources of phosphate are of anthropogenic origin, such as the agricultural sector (Luszcz, Kendall and Hyndman, 2017) as well as of natural origin, such as from rock weathering (Taunton, Welch and Banfield, 2000). After phosphate enters the water column, it can be immobilised by the microbial community. Similar to the nitrate cycle, phosphate is released back into the water column during the decomposition of the organic matter, thus remineralising the phosphorous to mobile inorganic phosphate. Compounds that contain phosphorus are generally being insoluble, and will precipitate out under the correct conditions, ultimately being removed from the water column (Vymazal, 2007). Phosphate is also readily adsorbed on to sediment particles at the stream bottom (Hall, Bernhardt and Likens, 2002).

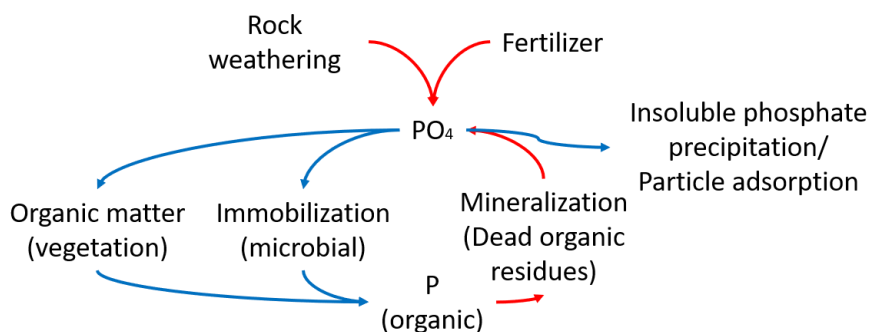


Figure 2.3: The phosphorous cycle including main sources of phosphate and uptake mechanism via microbial organisms and adsorption as described by Vymazal, (2007).

Nutrient retention or storage is not limited to only uptake by biological organisms, but chemical and hydrological processes will also be part of the process. Nutrient retention by the hyporheic zone is influenced by the hydraulic conductivity of the bottom sediment. In the case of sediment with high hydraulic conductivity, more interaction between the hyporheic zone and the stream water is allowed, thus allowing better nutrient retention (Thomas et al., 2001). This interaction is also facilitated by processes that cause temporary water retention, for instance debris dams, turbulent eddies and morphological structures.

2.4. Biofilm

Biofilm can be described as the benthic, microbial community consisting of algae and bacteria found on the surface sediments and the upper layer of the hyporheic zone and benthic zone of streams and freshwater bodies (Prieto et al., 2016). The algae cells similar to plants conduct photosynthesis, where carbon is transformed into organic matter by energy gained from sunlight (Flemming et al., 2016). During the life cycle of microalgae as well as benthic bacteria, macronutrients like nitrate and phosphate as well as micronutrients are needed to facilitate the growth of the organisms.

Biofilm differ from similar organisms in the planktonic state mainly by the fact that they are attached and not in the suspended, planktonic state (Watnick and Kolter, 2000). This characteristic of biofilm makes it essential in the process of nutrient retention. In the case of planktonic microorganisms, when growth is accelerated by the addition of nutrients to the hosting waterbody, the trophic state of the waterbody increases leading to eutrophication (Nyenje et al., 2010). Biofilm can help mediate this process by taking up the excess nutrients in the water column and storing it within the benthic zone. In addition to nutrient uptake by the

biofilm, it also decreases nutrient release from the hyporheic zone, by resuspension, by stabilising the sediments at the bottom of the water column (Drummond et al., 2016).

The growth cycle of biofilm is divided into four phases of growth before detachment. The initial stage consists of microorganisms in the planktonic state attaching to suitable surfaces within an optimal environment (Flemming et al., 2016). During this stage, the organism will determine the most suitable location on the surface to establish itself. In the second stage of the life cycle, the organism forms a stable association with the attachment surface. During the third stage, a microcolony develops between the attached cells and the biofilm starts to develop and mature. Within the final stage of the biofilm growth cycle, the biofilm achieves maturity. If environmental conditions surrounding the biofilm change and become unfavourable, the microorganisms might detach or die. The detached cells, in the planktonic state, will reattach to favourable surfaces if better environmental conditions are found. During the stage of detachment, nutrients that had been taken up during the growth cycle are released back into the water column together with nutrients that were stored within the now unstable sediment layer to which the biofilm was attached (Flemming et al., 2016). Thus, for optimal nutrient storage by biofilm, the environmental condition needs to be stable and suitable for biofilm growth (Drummond et al., 2016).

Biofilm growth and thus nutrient uptake is vastly dependent on the physical environment of the biofilm. Factors such as light availability, water temperature, water flow rate and nutrient availability all affect the growth rate and growth cycle of the biofilm (Sabater et al., 2007). How these factors affect the biofilm varies based on the type of biofilm present. Under a eutrophic state, light availability to the biofilm is limited because of dense planktonic microorganisms blocking out the light, thus limiting the energy source of the biofilm. A similar effect can be seen under dense vegetation cover vs direct sunlight or deeper waters (Villeneuve, Montuelle and Bouchez, 2009). Water flow velocity affects the biofilm in different ways. Under high turbulent flow conditions, the biofilm is hindered from attaching to suitable surfaces, whereas stiller waters are more suitable for biofilm growth. The water flow velocity also determines the interaction time between the biofilm and nutrients suspended within the water column. In the case of low nutrient loading, faster flows might prevent suitable nutrient uptake by the biofilm. However, under high nutrient loading, stagnant or slower flowing water might cause nutrient saturation of the biofilm (Price and Carrick, 2016). This will accelerate eutrophication within such a waterbody.

3. Chapter 3 – Methodology

Due to the nature of this thesis, each result chapter contains a summarised methodology suitable for publication. Here follows the technical methodology excluded from the summarised versions as well as a detailed methodology for Chapter 6 – Experimental analysis.

3.1. Sample collection and preparation

Throughout Chapters 4 to 6, the electrical conductivity, pH and oxidation reduction potential were measured by means of electrical handheld probes. The handheld probes used in Chapters 4 and 5 are individually discussed within the respective chapters. The handheld probe methodology used in Chapter 6 – Experimental analysis, is the same as the methodology used within Chapter 5. The Extech EC500 Waterproof ExStik II was used to measure the electrical conductivity, pH and water temperature and the Extech RE300 ExStik ORP was used to measure the oxidation reduction potential. Triple point calibration was done on the Extech EC500 Waterproof ExStik II probe prior to sampling using Hanna instrument calibration ranges for conductivity (84 μ S/cm, 1413 μ S/cm and 12880 μ S/cm) and pH (4.01, 7.01 and 10.01).

No water samples were collected as part of Chapter 4. Sample collection for Chapter 5 was discussed in detail in section 5.4. Chapter 6 – Experimental analysis, required sampling for the nutrients ammonium, phosphate and nitrate as well as the cation bromide. Sample collection was done in triplicate, using 10mL disposable test tubes. Each sample was filtered using 0.22 μ m Millex-GP filters before being refrigerated at 4°C until analysis. Bromide samples were acidified prior to refrigeration, to a pH < 2, using 1M HCl.

3.2. Lab analysis

No lab analysis was required for Chapter 4. Chapter 5 required elemental analysis for calcium, magnesium, sodium and potassium as well as nutrient analysis for nitrate, phosphate and ammonium. Chapter 6 required elemental analysis for bromine and nutrient analysis for nitrate, nitrite, ammonium and phosphate.

3.2.1. Elemental analysis

For elemental analysis, samples were sent to the Central Analytical Facilities of Stellenbosch University. Samples were analysed on an Agilent 7900 ICP-MS. A standard quartz spray chamber and torch configuration were used in conjunction with Ni-plated sampling and skimmer cones. The samples were aspirated using a 0.4ml/min micromist nebuliser. The

instrument was calibrated using USEPA Methods 6020A and 200.8 guidelines and NIST traceable standards were used for calibration and validation.

3.2.2. Nutrients analysis

Ammonium, nitrate, nitrite and phosphate were analysed using a spectrometry technique and a Thermo Scientific Genesys 10UV spectrophotometer. Each nutrient required a unique experimental procedure. Ammonium was analysed using a procedure published by Strickland and Parsons (1972). The method depends on the reaction of ammonium with sodium hypochlorite and phenol in a citrate medium with sodium nitroprusside as a catalyser. This resulted in a blue indophenol forming of which the absorbance was measured at 640nm. The method was originally developed for the analysis of ammonia in 10-cm cells. For this analysis it has been adapted to analyse for ammonium by the use of a NH_4Cl standard as well as for a 1cm cuvette. The adapted method used 40 μL of 1.062M phenol diluted in 95% ethyl alcohol, 40 μL of 0.019M sodium nitroprusside and 100 μL of 0.124M sodium citrate mixed with 0.177M sodium hypochlorite added to 1mL of sample. Samples were left to react for 1 hour before measurements were taken.

Phosphate was analysed using a procedure published by Strickland and Parsons (1972). The method depends on a reaction between phosphate and a composite reagent consisting of molybdic acid, ascorbic acid and trivalent antimony. The reaction forms a complex heteropoly acid that is reduced to form a blue coloration which is measured at 880nm. The method was originally developed for analysis in 10cm cells. For this analysis it has been adapted to be used for 1cm cuvette. The adapted method used 60 μL of 0.306M ascorbic acid, and a 60 μL mixture of 4.454mM ammonium molybdate tetrahydrate, 0.041mM potassium antimonyl tartrate, and 1.93M sulphuric acid as reagents to be added to 1mL of sample. KH_2PO_4 was used as a standard. Samples were left to react for 1.5 hours before measurements were taken.

Nitrite and nitrate were analysed using a procedure published by García-Robledo, Corzo and Papaspyrou (2014). The method first analyses for NO_2^- using a method described in Hansen and Grasshoff (1983). The method used a reagent complex consisting of sulphanilamide dissolved in 12N hydrochloric acid and N-(1-naphthyl)-ethylenediamine dihydrochloride. After the initial reaction NO_3^- is reduced to NO_2^- using vanadium (III) to analyse for the combination of NO_2^- and NO_3^- . The concentration of NO_3^- in the sample is then calculated based on the difference between the two analyses. NaNO_2 was used as a standard for NO_2^- and KNO_3 was used as a standard for NO_3^- .

Each method was calibrated prior to analysis using a standard calibration curve, calculated from a range of ten standards. Curves with R^2 values below 0.995 were rejected and all reagents were freshly prepared before a revised curve was calculated. The method for ammonium provided a R^2 value of 0.997 (Figure 3.1a). The method for phosphate provided a R^2 value of 0.998 (Figure 3.1b). The method for nitrite provided a R^2 value of 0.998 (Figure 3.1c) and the method for nitrate provided a R^2 value of 0.999 (Figure 3.1d).

The detection limit for each method was calculated based on a method described by Shrivastava and Gupta (2011). Equation 3.1 was used to calculate the detection limit for each method using the calibration curves calculated.

Equation 3.1: Statistical detection limit calculated from calibration curves.

$$DL = 3.3 \sigma \div S$$

σ = standard deviation of the response

S = slope of the calibration curve

The resulting detection limit for ammonium was 0.011 μ g/L and 0.643 μ M. The resulting detection limit for phosphate was 0.010 μ g/L and 0.102 μ M. The resulting detection limit for nitrite was 0.004 μ g/L and 0.008 μ M. The resulting detection limit for nitrate was 0.060 μ g/L and 0.962 μ M.

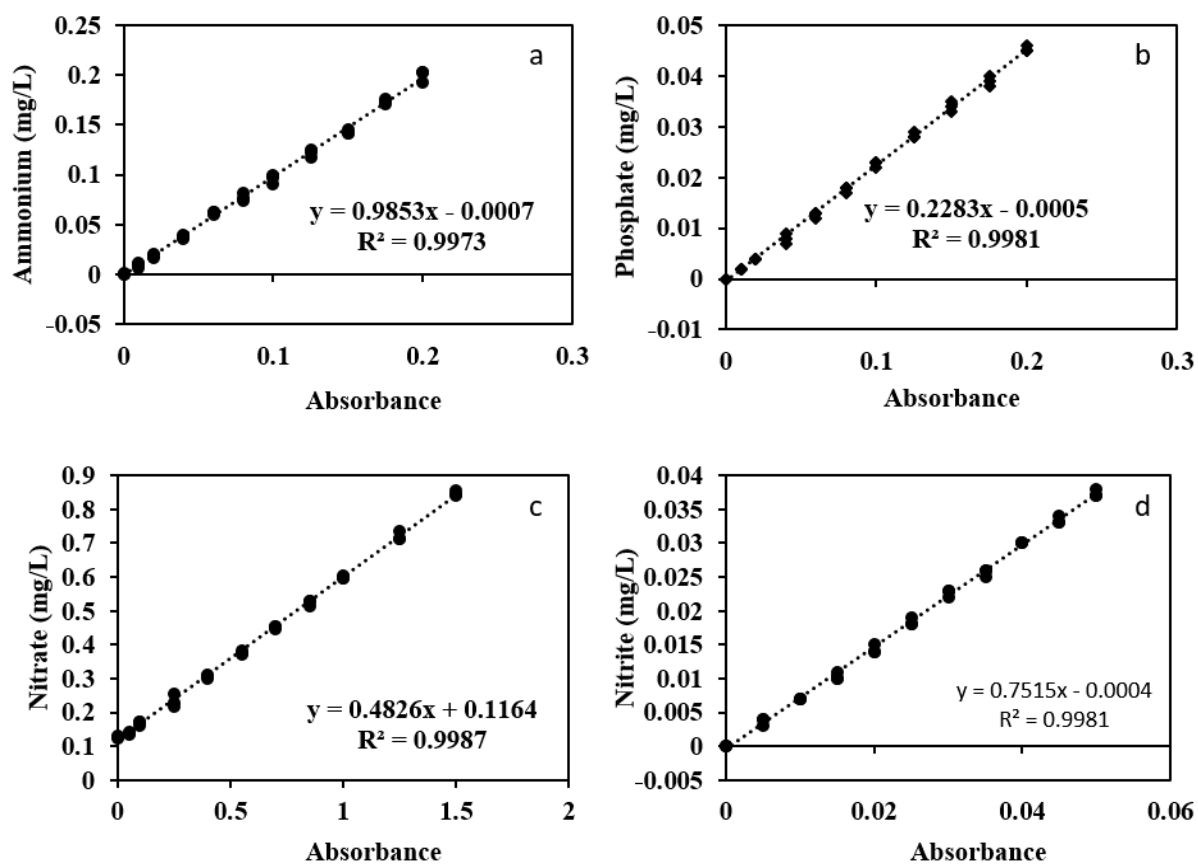


Figure 3.1: Calibration curves calculated for spectrophotometry. a) Ammonium analysis with R^2 value of 0.997. b) Phosphate analysis with R^2 value of 0.998. c) Nitrate analysis with R^2 value of 0.999. d) Nitrite analysis with R^2 value of 0.998.

3.3. Experimental procedure

3.3.1. Short-term nutrient release analysis

The short-term nutrient release experiment was performed based on the method described in Baker and Webster (2017) and Tank, Reisinger and Rosi (2017). The method relied on the addition of nutrient salts as well as a conservative tracer into a stream at a constant rate. Samples are to be taken at predetermined distances below the injection point as soon as the injective has reached the most downstream sampling site.

Nutrients were released in the form of salts. The concentration of the added nutrients was determined based on the stream discharge and stream background concentration of the nutrients. The nutrient addition should be just high enough to be analytically detectable to prevent stream demand saturation. Equation 3.2 was used to calculate the concentration of nutrient salt to be added to the release solute.

Equation 3.2: Determination of the required concentration of the release solute for a short-term nutrient release experiment.

$$C_i = \frac{Q \times C_s}{Q_R}$$

C_i = concentration of release solute

Q = discharge of stream

C_s = target concentration of the stream

Q_R = release rate

The following salts were used as nutrients: KNO_3 for nitrate, KH_2PO_4 for phosphate and NH_4Cl for ammonium. KBr was used as the conservative bromide tracer. Because the salts added increased the electrical conductivity of the stream during addition, the electrical conductivity could be used as an indicator of when the nutrients had reached the most downstream sampling location. Figure 3.2 displays the breakthrough curve of the nutrients at the lowest sampling location. As soon as the increase in electrical conductivity ended and the elevated electrical conductivity was stable, the sampling was initiated.

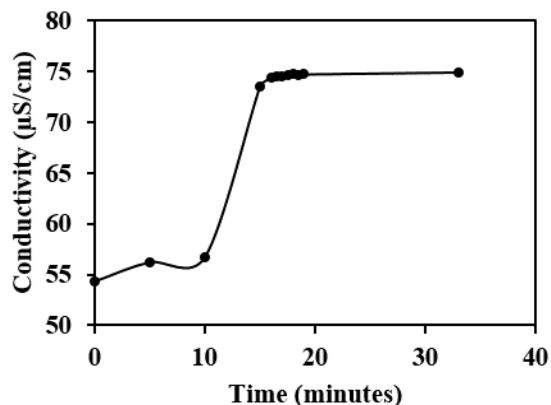


Figure 3.2: Breakthrough curve for the electrical conductivity as part of a short-term nutrient release experiment. The plateau indicated that the release solute reached the end of the sampling section and sampling could be initiated.

Sampling was taken at 20m spacing for a stream length of 80m. Samples were presented as a percentage of upstream concentration over distance (Figure 3.3). This produced a visual representation of the nutrient uptake over distance. Samples were corrected for background concentrations as well as the conservative bromide tracer based on Equation 3.3. This corrected for nutrient addition or dilution caused by lateral inflow over the sampled stream reach.

Equation 3.3: Normalised nutrient concentrations to a conservative tracer within a stream after the addition of a nutrient solute as part of a short-term nutrient release experiment.

$$C_N = \frac{(C_x - C_b)}{(C_t - C_{tb})}$$

C_N = normalised added nutrient concentration

C_x = sampled nutrient concentration

C_b = background nutrient concentration

C_t = sampled tracer concentration

C_{tb} = tracer background concentration

The logarithm of the corrected nutrient concentration at each sampling site was plotted over distance to calculate the longitudinal uptake rate (K_w) for each sample. The longitudinal uptake rate is equal to the slope of the linear equation produced by the plot (Equation 3.4).

Equation 3.4: Determination of the longitudinal uptake rate from normalised nutrient concentrations with a stream as part of a short-term nutrient release experiment.

$$\ln(C_N) = \ln(C_{NO}) - K_w x$$

C_N = normalised added nutrient concentration

C_{NO} = nutrient concentration at release site

K_w = longitudinal uptake rate

x = sampling distance

The longitudinal uptake rate (K_w) was used to calculate the uptake length (S_w), uptake velocity (V_f) and areal uptake (U).

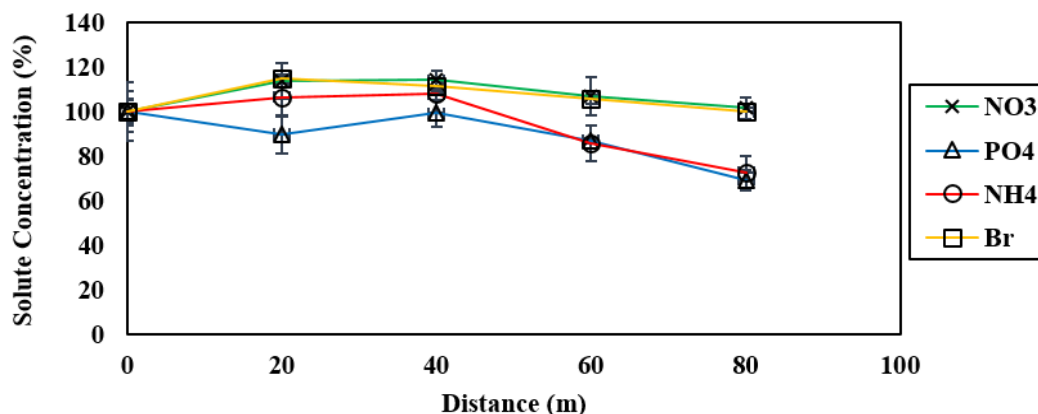


Figure 3.3: Percentage concentrations of reactive nutrients and conservative trace within a stream after the addition of a nutrient solute as part of a short-term nutrient release experiment.

The uptake length represents the distance required for total uptake of an inorganic nutrient and is calculated from the longitudinal uptake rate (equation 3.5). The uptake length is dependent on the stream discharge and velocity, attributes of the stream size. To compare solute dynamics across different streams, the uptake length needs to be corrected for influences caused by the stream size.

Equation 3.5: Determination of the uptake length.

$$S_w = K_w^{-1}$$

The uptake velocity represents the velocity of nutrient removal from the water column via uptake. The uptake velocity describes the biotic nutrient demand relative to the available

nutrients in the stream. The uptake velocity is calculated using the stream discharge and longitudinal uptake rate (Equation 3.6).

Equation 3.6: Determination of the uptake velocity.

$$V_f = QK_w/w$$

The areal uptake represents the nutrient removal per unit area of the stream bed. The areal uptake is used in conjunction with the uptake length and uptake velocity to describe the nutrient uptake within streams. It is calculated as in Equation 3.7.

Equation 3.7: Determination of the areal uptake.

$$U = V_f \times C_b$$

3.3.2. In-lab flume experiment

I built a flume based on the design of De Falco, Boano and Arnon (2016). The flume consisted of a 250cm stream bed channel with a width of 30cm and height of 20cm (Figure 3.4) and was set up at the Department of Earth Sciences, Stellenbosch University. Water was circulated from a 260l reservoir, using a circulation pump capable of pumping 500l/min through the system. Flow through the channel section was regulated using a set of taps controlling the flow path of the water through the system. Water temperature was controlled using a secondary circulation system.

Biofilm was cultivated on top of hessian material sheets inside the Eerste River prior to the analysis. The hessian was stretched over Perspex containers designed to fit inside the flume. The hessian was left inside the river for approximately 14 days to allow the biofilm to grow. The biofilm, situated on the hessian sheets, as well as water were collected from the Eerste River at location L4. The biofilm and water were collected within 1 hour of the start of the analysis and allowed to stabilise prior to nutrient loading. The hessian sheets were secured to the bottom of the channel to form a biofilm layer (Figure 3.4). Nutrient loading took place inside the storage reservoir, where the salts KNO_3 for nitrate, KH_2PO_4 for phosphate and NH_4Cl for ammonium as well as KBr for the conservative bromide tracer were added. Mixing took place inside the tank prior to circulation through the stream bed channel.

Background concentrations were sampled prior to nutrient loading. After nutrient loading, sampling took place on an experimental time scale, starting on an hourly basis and increasing in time as the experiment continued.

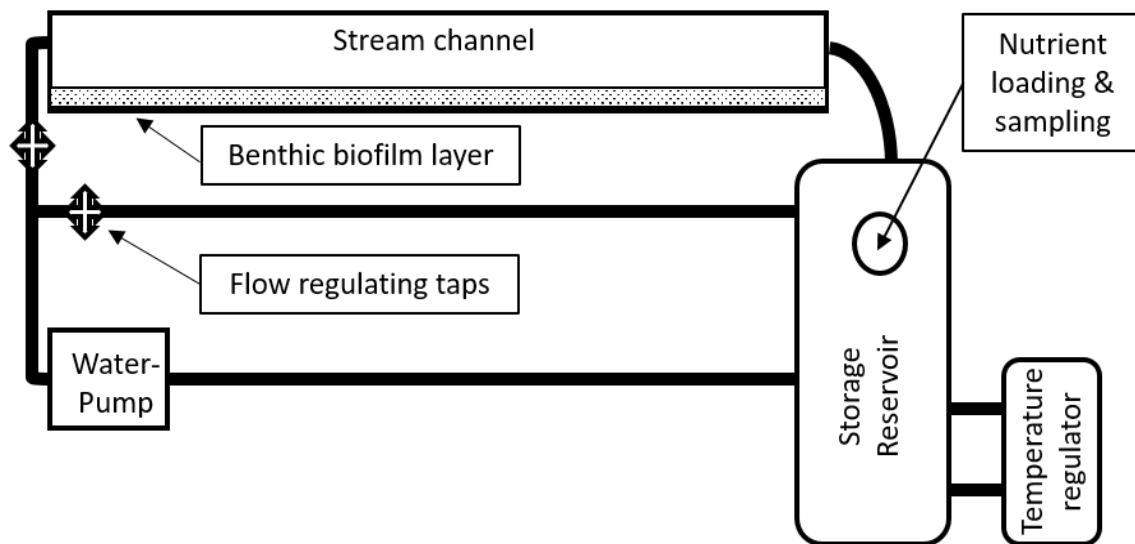


Figure 3.4: Flume experimental design including external temperature regulator, water pump and flow regulating system.

4. Chapter 4 – Geochemical analysis of the Rooiels Estuary, South Africa, via long-term student data collection

Contributions

During the write-up of this paper, I fulfilled the role of primary author and Dr S Fietz of secondary author. Field data collection was done by the second-year geochemistry class of Dr S Fietz from the years 2013 to 2018. During 2014, I took part in this class as a student, and this formed part of the data collection procedure. During 2016–2018, I fulfilled the role of demonstrator for this class during the field data collection. Data was compiled, plotted and analysed by me.

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Abstract

External environmental factors such as precipitation and the ocean play a determining role in the geochemistry of the Rooiels Estuary. The Rooiels Estuary is located on the south western point of False Bay, South Africa. The estuary is of a pristine nature and performs a key environmental role in the False Bay region. Annual sampling of the estuary was conducted for six consecutive years (2013–2018). The sampling was conducted by undergraduate students from Stellenbosch University. From the geochemical data collected, it was found that the estuary is affected by precipitation in the region. Precipitation altered the geochemical signal of the estuary substantially. This was caused by fulvic and humic acids, associated with the natural flora of the region, flushing into the upstream river system via surface run-off. The influence of the ocean was also minimalised during times of higher precipitation as fresh river water flow was increased.

Keywords

Estuary; Tertiary Education; Field Work; Rooiels; Western Cape

4.1. Introduction

Estuaries provide essential ecosystem services (Barbier et al., 2011). They form the connection between freshwater systems and the saline ocean water, thus they form a unique habitat for high numbers of diverse fauna and flora (Worm et al., 2006; Hassani et al., 2017). Estuaries also perform a key role in filtration and detoxification of continental waters before entering the marine realm (Barbier et al., 2011), as well as in flood control (Worm et al., 2006).

Estuaries are under great threat from urban development, anthropogenic pollution and climate change (Lotze et al., 2006). The variability within estuarine environments, at temporal and spatial scale, challenges the thorough understanding of estuarine processes. Currently, a lack of long-term monitoring data on estuarine environments exists in South Africa (Bollmohr et al., 2011).

One such estuary is the Rooiels Estuary located on the south western point of False Bay. The Rooiels Estuary is currently largely unaffected by anthropogenic influences as the only development next to the river system is located to the south of the estuary and consists of minimal urban dwellings. The future condition of the estuary is unclear as development in the region increases. Howland et al. (2000) found that the geochemical condition of the pristine Tweed Estuary was affected by precipitation as fresh river run-off entered the estuary. It has also been found that tidal influences have an effect on the geochemistry of estuaries (Grande et al., 2003). To ensure the health of the estuary, factors influencing the state of the estuary need to be delineated.

Undergraduate students from Stellenbosch University sampled the Rooiels Estuary for six consecutive years (2013–2018). The sampling formed part of their environmental geochemistry course. From an educator's view, the field trip aimed to introduce the students to field work; however, by analysing the collected data, this study aimed to delineate the geochemical responses of the Rooiels Estuary to external environmental factors such as precipitation and the ocean.

4.2. Site description and sampling strategy

For six consecutive years, from 2013 to 2018, the environmental geochemistry students from the Department of Earth Sciences, Stellenbosch University, visited the Rooiels Estuary. The field trips consisted of ca. 40 students each year and always took place during April: 13 April 2013, 12 April 2014, 18 April 2015, 16 April 2016, 1 April 2017 and 21 April 2018. The earlier date in 2017 was due to the university term break period from 8 to 17 April 2017.

The Rooiels Estuary (Figure 4.1) is located at ca. 34.3°S and 18.8°E, next to the small town of Rooiels where the Rooiels River flows into False Bay. The river is approximately 10km long, originates in the Hottentots Holland Mountains and has a catchment of 21km² (Harrison, 1998). The geology of the catchment area is described by Heinecken (1984) as Table Mountain Group (TMG) environment, characterised largely by Table Mountain Sandstone (TMS). Details of the geology surrounding the river and catchment area are extensively described in Boucher (1972). While the state of many of the Western Cape's estuaries have deteriorated due to urban or industrial development and/or invasion of alien plants, the environmental state of the lower Rooiels River appears to be unchanged since early assessments took place in 1938 (O'Callaghan, 1990). The surrounding soils have been described as generally nutrient poor, and mostly acidic, with water typically percolating through rapidly (Boucher, 1972). The river mouth is characterised by a beach (Figure 1a), influenced by both the material deposited by the river and from the sea. We define here as estuary the beach area downstream (west) and the area ca. 100m upstream (east) of the Clarence Drive bridge (Figure 1b). The river upstream of the bridge is ca. 20m wide and ca. 3m deep and flattens to mostly below 1m water depth ca. 20m downstream of the bridge, meandering as shallow river southeast (along Clarence Drive) and then northeast towards the ocean. The river and tributaries lie in the winter rainfall area of South Africa, and we thus assume seasonal variability in flow and discharge. The estuary is temporarily open or closed (Bollmohr et al., 2011). The closed state seems to be the exception though (Department of Water and Sanitation, 2016). During all six years (2013–2018) of this study, the river was open and connected to the ocean at the time of the field trips (first weeks of April).



Figure 4.1: Field trip location. a) Map of Rooiels Estuary and catchment. b) Site view of field trip area: The bridge on the left of the photo indicates the starting point of the sampling area. The estuary connects to the ocean on the right of the photo. The small village of Rooiels can be seen in the background.

Tidal, air temperature and precipitation data were collected for comparison with physicochemical parameters. The tides induce seawater intrusion into the estuary, especially along the meandering river channel. With larger tidal amplitudes, this influence tends to increase. An inflow of seawater up to 1km into the river has been proposed (Department of Water and Sanitation, 2016), but to the best of our knowledge, respective data has not yet been published. According to the tidal data presented in Figure 4.2a, the 2015 field trip was affected by the largest tidal amplitude compared to all other years (South African Navy Hydrographic

Office, 2018). During these field trips, sampling took place between 10:00am and 02:30pm, with the pH and conductivity analysis taking place first, with few exceptions until 12:00pm.

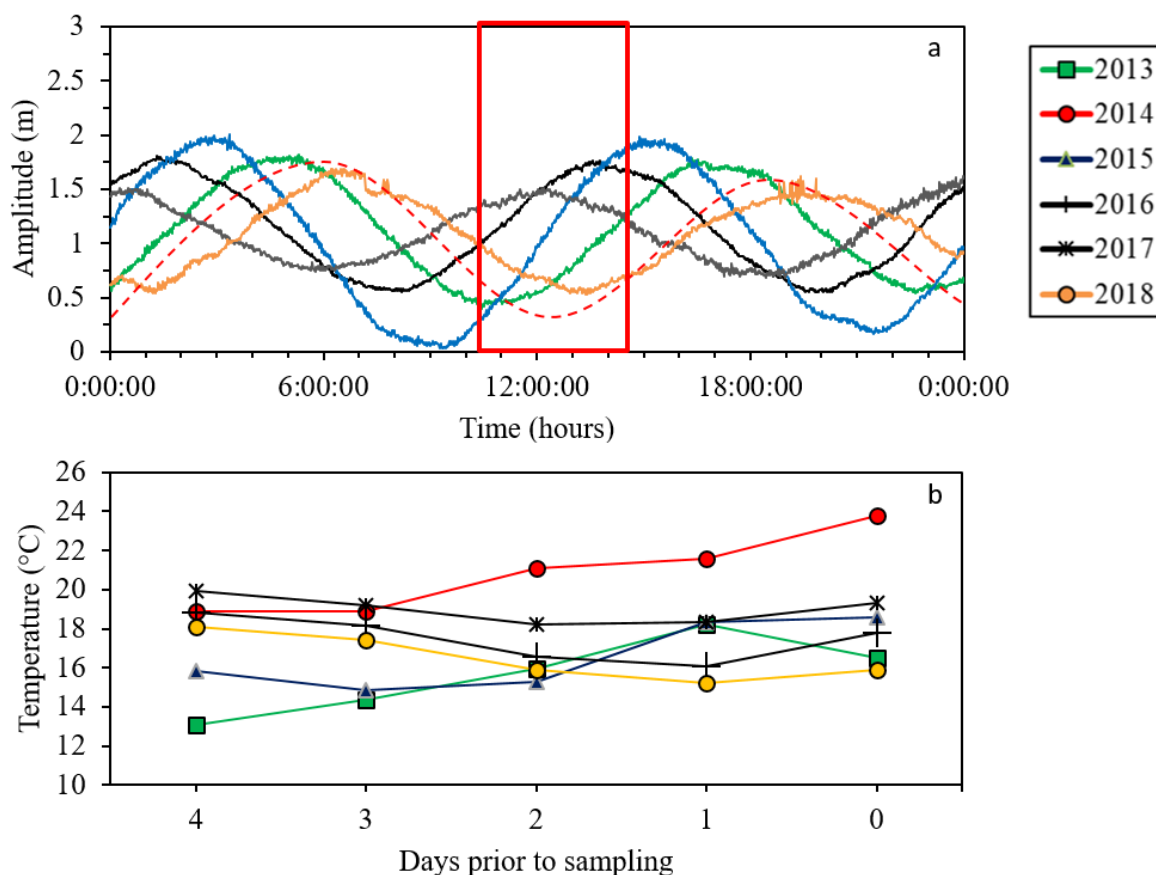


Figure 4.2: Interannual differences in tide height and air temperature. a) Tidal heights during the sampling period indicated by the red square (South African Navy Hydrographic Office, 2018). b) Air temperatures, four days prior to sampling.

Precipitation was also expected to have a notable effect on the estuarine water chemistry, mainly through increased river discharge into the estuary providing fresh water to the system, but also through surface run-off. Sampling took place during autumn (April), just before the region typically experiences its first major winter rain events (Figure 4.3). Cumulative rainfall for the period from 1 January to the date of the field trip was the highest in 2013 and 2014 (111 and 124mm, respectively) and lowest in 2015 and 2017 (29 and 2mm, respectively; Table 1).

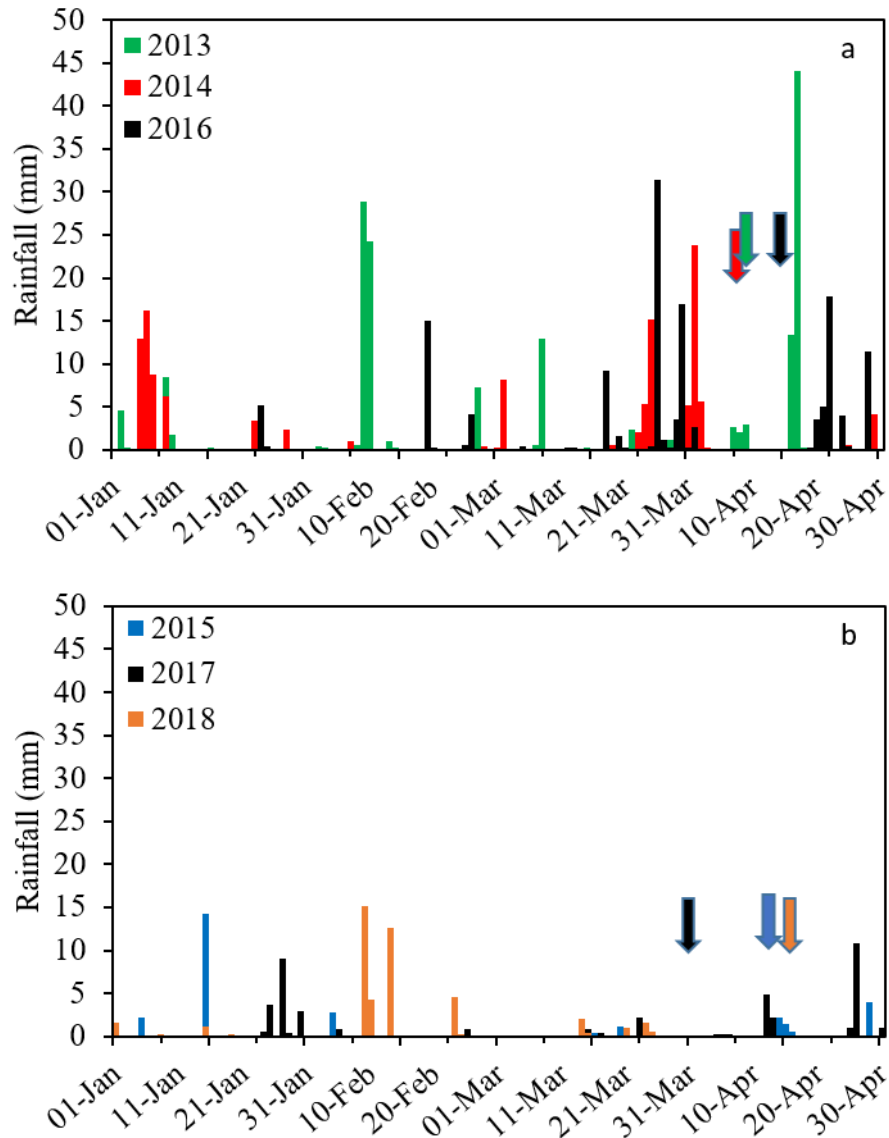


Figure 4.3: Precipitation pattern for the study area from 1 January to 30 April for the years a) 2013, 2014 and 2016 and b) 2015 and 2017. Data obtained from the South African Weather Services (SAWS). Arrows indicate the respective dates of sampling. Cumulative rainfall for the period from 1 January to the date of the field trip is 111mm in 2013, 124mm in 2014, 29mm in 2015, 94mm in 2016, 24mm in 2017 and 47mm in 2018 (Table 1).

4.3. Methodology

A calibrated combo tester (HI98130, Hannah Instruments (Pty) Ltd, SA) was used for measuring pH and water temperature along the river up to the sea. Electrical conductivity was measured with the same calibrated combo tester for all sections with conductivities lower than 20mS cm^{-1} . A CyberScan PCD 650 probe (Eutech InstrumentsTM, Thermo Fisher Scientific Inc., USA) was used for measuring conductivity higher than 20mS cm^{-1} . Oxidation-Reduction Potential (ORP) was analysed using an ExStik® ORP meter (EXTECH RE300, Extech Instruments, USA). Probe calibrations were conducted in field by students. The Rooiels River is a typical black water river (Figure 2c). Water colour was therefore visually assessed by comparing filtered ($0.45\mu\text{m}$ nominal pore size syringe filters) water samples in a glass beaker to a colour chart. Organic matter concentrations in filtered water samples were measured using a Spectroquant® Move 100 Mobile Colorimeter (Merck Millipore, USA). The students also analysed the concentrations of nutrients and potential pollutants, such as nitrate, phosphate, lead, iron and aluminium, using the Spectroquant® Move 100 Mobile Colorimeter and respective test kits (Merck Millipore, USA). The test kits included nitrate ($0.3\text{--}30.0\text{mg L}^{-1}\text{NO}_3\text{-N}$), phosphate ($5.00\text{mg L}^{-1}\text{PO}_4\text{-P}$), lead ($0.010\text{--}5.00\text{mg L}^{-1}\text{Pb}$), iron ($0.005\text{--}5.00\text{mg L}^{-1}\text{Fe}$), and aluminium ($20\text{--}700\mu\text{g L}^{-1}\text{Al}$). The measured concentrations were, however, often below detection limit or yielded unreliable large variability. Despite the easy handling of the instrument and sample processing, measured concentrations could often not be replicated. The use of the portable Spectroquant® Mobile Colorimeter proved to be a valuable teaching tool in the field. We call for caution, though, using it for research purposes. We therefore only include example data in this paper.

Surface flow velocity was measured using a typical citizen science approach, i.e. tracking the time of a floating lemon to pass over a distance of 3–5m. This approach provides a rough estimate and was adopted as flow was often too slow (i.e. $< 0.1\text{m s}^{-1}$) for the mechanical flowmeter (2030R, General Oceanics Inc.). The discharge was estimated using a measuring stick to calculate the cross-sectional area of the river. This approach led to very high variability of discharge values reported by the student teams and the discharge will therefore not be reported here.

With the focus on creating a reliable dataset, the students were given the opportunity to explore and learn within consistent guidelines and analytical protocols. Students were divided into groups of three to four. All groups ideally had to measure every parameter at five or more sampling locations along the river in the estuary. This resulted in at least two and up to ten

reliable measurements per site and year. After the field trip, the students analysed the data that they collected using statistical and graphical techniques they learned during lectures. This includes classifying the water using Gibbs and Pourbaix diagrams (Langmuir, 1997), determining the respective influence of the river and the ocean on the estuary, and explaining trends they observe using literature and external data such as tidal cycles and weather information. A discussion class followed the field trip to show interannual differences and identify analytical issues. The parameters not included in this article were still used in the classes after the field trips to raise awareness of sampling strategy, choice of water sampling depths, instrument choices, etc. All data is available to interested readers for teaching purposes upon request from the corresponding author.

4.4. Results and discussion

Surface water temperatures, in general, showed some correspondence to the air temperature prior to and during the field trip (Figure 4.2a, 4.4a). For instance, the highest air and water temperatures were both observed in 2014. However, surface water temperatures were clearly the lowest in 2015, when air temperatures were found to be within the range of the other years of this study (Figure 4.2b, 4.4a), which indicates that other factors influence the water temperature in the estuary. Surface water temperatures did not change along the estuary, but slightly increased towards the ocean in most years (Figure 4.4a). The main reason for the slight increases in surface water temperatures was likely the shallowing of the river from ca. 3m to ca. 1m approximately 10m downstream of the bridge, and to ca. 0.2m across most of the estuary. The scatter in measured water temperatures observed each year (Figure 4.4a) is related to sampling strategy. While all groups are advised to sample mid-stream, each year some groups sample near shore. The difference in temperature between the cooler, deeper mid-stream water and warmer, shallower near-shore waters is illustrated in Figure 4.4b (year 2017). On their own accounts, groups 4 and 9 collected water from near-shore, while all other groups ventured mid-stream. It is a good example to raise awareness of sampling strategies for long-term monitoring.

Table 4.1: Summary of observations collected upstream of or near the bridge compared to published data for 1993 (Harrison, 1998) and 2001–2003 (Bollmohr et al., 2011). Abbreviations: dO_2 – dissolved oxygen, n – number of samples, OM – organic matter, ORP – oxidation-reduction potential, SE – standard error, Stdv – Standard deviation, TOC – total organic carbon, Water temp. – water temperature ($^{\circ}C$). The rainfall data refers to the cumulative rainfall (mm) from 1 January up until the date of the field trip of the respective years (early April).

		Apr 1978 ^a	Sep 1958 ^b	Dec 1979 ^c	Mar 1981 ^c	1993 ^a		
	Salinity (ppt)	24 [§]	-	26 [§]	28 [§]	Conductivity ($mS\ cm^{-1}$)	40	
	pH	-	6.5	-	6.4	pH	7.8	
					dO_2	($mg\ L^{-1}$)	7.0	
	Water temp. ($^{\circ}C$)	20	21	18	15	Water temp. ($^{\circ}C$)	20	
2001-2003 ^f		2013	2014	2015	2016	2017	2018	
Salinity (ppt)	5.19 ^u	Conductivity ($mS\ cm^{-1}$)	8.8	7.5	35	12	42	35.5
SE	5.7	Stdv	2.0	5.2	5.3	4.7	5.0	6.8
		n	23	22	23	18	20	38
TSS (ppm)	1.0	TDS (ppt)	6.3	4.2	29.0	7.1	38.6	27.5
SE	1.2	Stdv	1.4	4.0	5.2	5.2	4.7	5.3
		n	16	22	23	18	20	38
pH	6.7	pH	6.3	6.4	7.4	6.6	7.4	7.5
SE	1.0	Stdv	0.2	0.5	0.4	0.7	0.6	0.7
		n	23	23	23	18	20	38
TOC %	1.3	OM index (Pt/Cd)	-	298	93	142	-	-
SE	0.5	Stdv	-	112	58	51	-	-
		n	-	8	20	8	-	-
dO_2 ($mg\ L^{-1}$)	8.8	ORP (mV)	-	314	382	324	285	313
SE	1.3	Stdv	-	49	14	19	11	35
		n	-	9	13	18	15	38
Water temp. ($^{\circ}C$)	18	Water temp. ($^{\circ}C$)	19	22	18	20	21	18
SE	4.2	Stdv	0.9	1.9	1.8	2.1	1.5	0.4
		n	25	20	23	18	20	33
		Flow velocity ($m\ s^{-1}$)	0.038	0.024	0.079	0.071	0.067	0.069
		Stdv	0.013	0.027	0.047	0.052	0.030	0.103
		n	25	8	7	15	11	32
		Rainfall (Jan - field trip; mm)	111	124	29	94	24	47
^a estuary, surface water (Grindley, unpublished, in Heinecken, 1982) ^b estuary, surface water (van Wyk, unpublished, in Heinecken, 1982) ^c estuary, surface water (Heinecken, 1982) [§] corresponds to conductivities of ca. 34–37 $mS\ cm^{-1}$ at respective water temperatures ^e Oct/Nov above bridge, surface waters (Harrison, 1998) ^f annual average, estuary, surface waters (Bollmohr et al., 2011) ^u corresponds to conductivity of ca. 8 $mS\ cm^{-1}$ at respective water temperatures								

The measured pH ranged from 5.4 to 8.7 across the estuary and in the different years (Figure 4.4c). Low pH values were observed near the bridge in 2013, 2014 and 2016 (6.3–6.6; Table 4.1). Those values are similar to the pH values of 6.5 and 6.4 found near the bridge previously (Heinecken, 1982; Bollmohr et al., 2011). They are likely a result of humic or fulvic acids produced by the indigenous fynbos flora (Midgley and Schafer, 1992). They might be a result of the stronger precipitation that occurred during the months prior to the field trip in 2013, 2014 and 2016 (Figure 4.2, Table 4.1). Stronger precipitation in the river catchment might lead to more humic or fulvic acids being washed from the shores into the river water (Midgley and Schafer, 1992), and/or a greater share of river water compared to the intrusion of seawater into the estuary. Higher pH values (7.4) were observed during our field trips in 2015, 2017 and 2018 (Table 4.1). Harrison (1998) also measured such high pH values above the bridge in October/November 1993. The pH of the estuary increased in all years downstream towards the ocean (Figure 4.4c), therefore, the higher pH values observed in 2015, 2017 and 2018 as well as in October/November 1993 might indicate a much stronger seawater inflow compared to the years 2013, 2014 and 2016 and 2001–2003 (Bollmohr et al., 2011), assuming typical seawater pH of ca. 8.1 (Gregor, 2012). The larger tidal amplitude in 2015 (Figure 4.2a) likely intensified the seawater inflow.

Strong interannual differences were also observed in the conductivity, with considerably higher conductivities near or upstream of the bridge in the years 2015, 2017 and 2018 (35 and 42, and 35.5 mS cm⁻¹, respectively), compared to the years 2013, 2014 (7.5 and 8.8 mS cm⁻¹, respectively) and 2016 (12 mS cm⁻¹; Table 4.1). Hence, conductivities indicated strong seawater influence in 2015, 2017 and 2018. As mentioned above, during these three years, the region experienced low precipitation during the summer months prior to the sampling compared to the other years (Figure 4.3, Table 4.1). Consequently, the ocean water intrusion might have increased in the estuary and seawater might have become the dominant end-member assuming a typical EC for seawater 45–50 mS cm⁻¹; (Tyler et al., 2017).

The low tide at the time of sampling (Figure 4.2a) led us to expect low seawater influence in 2017. The conductivity increased exponentially from the bridge towards the ocean (Figure 4.4e) in the years 2013 ($r^2 = 0.70$) and 2014 ($r^2 = 0.42$). The increase was insignificant in other years, especially in 2015 and 2018 – years during which the influence of the seawater was probably already very strong near and upstream of the bridge. The flow velocities near or upstream of the bridge, where the river is at least > 2m deep, were very low (< 0.1 m s⁻¹) and can probably not fully withstand seawater pushing upstream. Flow velocities were lowest in

2013 and 2014 and higher in 2015–2018 (Table 4.1). However, due to the scatter resulting from the citizen science approach, these interannual differences were not statistically significant. The lack of difference in flow rate and the fact that measured flows were at least not higher in 2013 and 2014, i.e. the years with summer rainfall, than in 2015 and 2017, suggest though that flow rate is not a suitable parameter to predict the water geochemistry in such a flat estuary.

Another indication of seawater inflow was obtained from the visually determined water colour and the spectrophotometrically determined organic matter index. On a colour scale from 1 to 6, where 1 means “transparent” and 6 “dark”, students characterised the water upstream and near the bridge with colour codes of around 5 in 2013 and 2014, i.e. “brown” (Figure 4.1b), but around 1.5 in 2015, 2016, 2017 and 2018, i.e. “pale/transparent”. Bollmohr et al. (2011) visually characterised the water colour near the bridge as “brown, peat-stained” for the years 2001–2003. In 2013 and 2014, the water colour changed from dark to pale along the estuary and students attributed a “transparent” colour code (colour code ≤ 2) to the water from ca. 200m downstream onwards. This visual assessment of the change in water colour corresponds roughly to the changes observed in conductivity and pH in those years and illustrates adequately the shift in water chemistry along the estuary even for the layman. This visual assessment was supported spectrophotometrically using the portable Spectroquant Colorimeter. The water colour is mostly caused by dissolved organic carbon (e.g. humic or fulvic) compounds forming organo-metal complexes (Midgley and Schafer, 1992). In South Africa, it is indicative of water flowing through a fynbos vegetated catchment and pale-coloured soils (Midgley and Schafer, 1992). The spectrophotometrically determined organic matter index near or upstream the bridge was high in 2014, lower in 2016, and lowest in 2015 (Table 4.1; organic matter content was not determined in 2013, 2017 and 2018, see Methodology). Furthermore, a strong decrease in the organic matter index from the bridge to the river mouth was observed in 2014 (Figure 4.4f). The same type of vegetation that most likely stains the river water also rapidly acidifies it (Midgley and Schafer, 1992), explaining at least partly the low pH observed in 2014. Since the pH was also low in 2016, though, when the river water was characterised as “pale”, and the organic matter content was not particularly high (Table 4.1), other factors that had not been investigated during our field trips, must play a role in the regulation of the pH or the water colour/organic matter content in the Rooiels River.

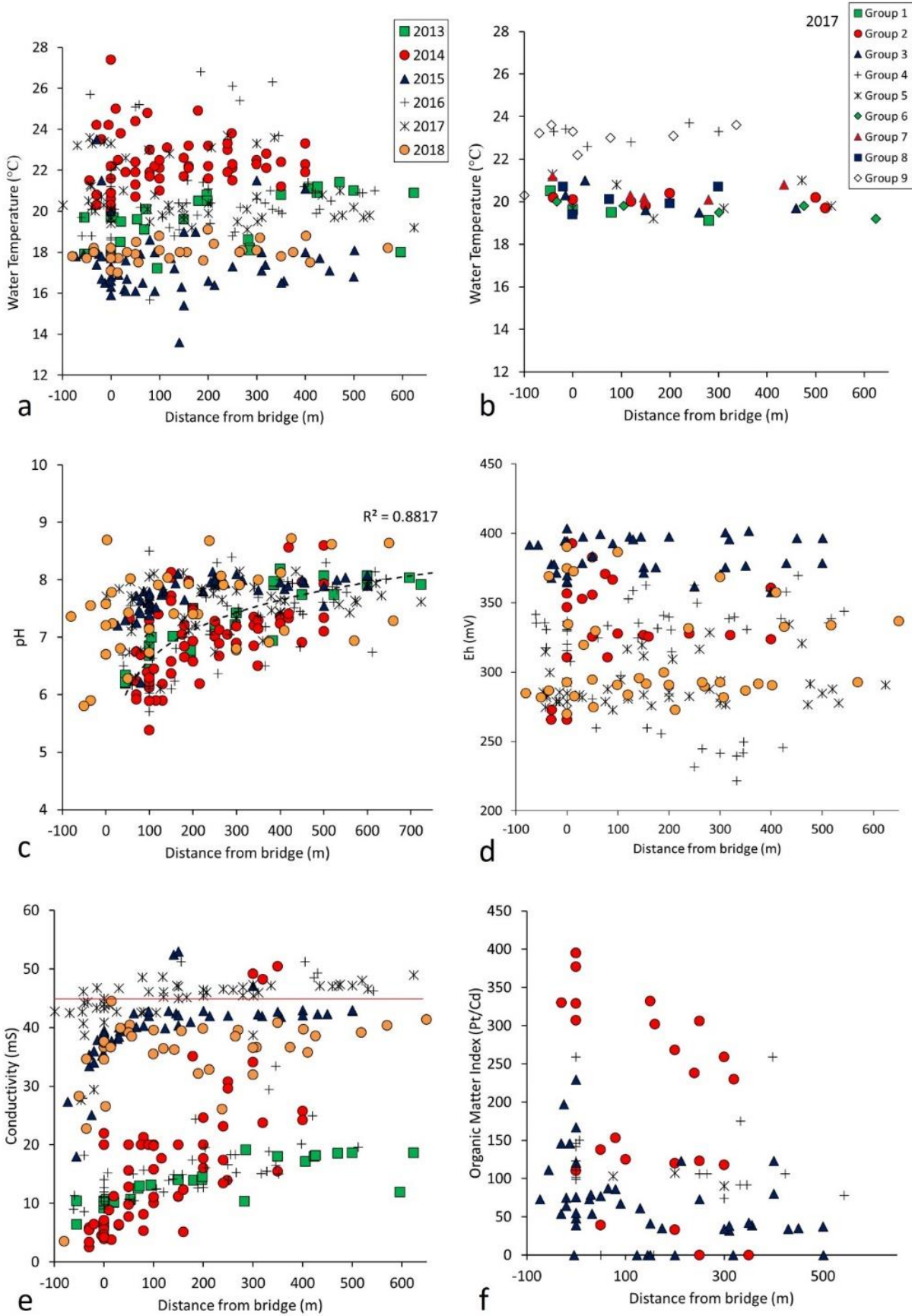


Figure 4.4: Major geochemical parameters reported by the various student teams per year. (a) Surface water temperature. (b) Surface water temperature from the estuary for 2017 only, to visualise the difference in the choice of sampling location between student teams; groups 4 and 9 (diamonds and crosses) reported during the discussion after the field trip that they sampled on the shore rather than in the centre of the river. (c) pH; best-fits of the increase in pH towards the ocean followed logarithmic trends in all years except 2017, but a statistically significant trend was only observed in the year 2013 ($r^2 = 0.88$; black dotted line). (d) Redox-Potential (Eh). (e) Conductivity with the conductivity of ocean water (red line). (f) Organic matter; the instrument (Spectroquant® Move 100 Mobile Colorimeter) was only purchased in 2014.

Interestingly, the redox potential of the water near or upstream of the bridge did not show interannual trends that correspond to the pH, conductivity and/or water colour (Figure 4.4d). Redox potential trends also did not correspond to water temperature trends. For example, highest redox potentials were observed in 2015 (382mV) but lowest in 2017 (285mV). Nonetheless, redox potentials indicated a high degree of oxygenation in all years (Figure 4.5), which corresponds to previous findings across the estuary (Table 1; Heinecken, 1984; Bollmohr et al., 2011). With observed pH values predominantly being higher than 6 and oxidising conditions, the threat of metal dissolution in the Rooiels Estuary and discharge of dissolved heavy metals into False Bay are rather low (Figure 4.5). For example, the concentration of dissolved iron was determined in 2017, and decreased from 0.17mg L^{-1} at the bridge to 0.1mg L^{-1} ca. 150m downstream and 0.04mg L^{-1} close to the river mouth.

This decrease of dissolved iron towards the ocean correlated with the increase in pH ($R^2 = 0.91$) and redox potential ($R^2 = 0.94$). The reader should, however, be aware that the dissolved iron data are snap-shot concentrations that had not been replicated. The dissolved iron was determined using the Spectroquant® Move 100 Mobile Colorimeter coupled with the test kit 1.14761.0001. The test kit had a range of $0.005\text{--}5.000\text{mg L}^{-1}$.

The combination of the educational field excursion with data collection proved to be challenging. The field trip required students to explore and discover the environment and by doing so learning and understanding the complex relationship between the estuary and the surrounding environment. In contrast to the freedom required for the educational part of the excursion, the data collection required strict sampling regimes that had to be duplicated annually. To accommodate the educational aim of the excursion, trade-offs had to be made regarding data collection. Primarily this consisted of allowing students to make mistakes, to allow for future discussion surrounding it. Students often failed to follow precise sampling procedures, and this was reflected in the data. Outliers, however, were easily identified because of the large extent of sampling data.

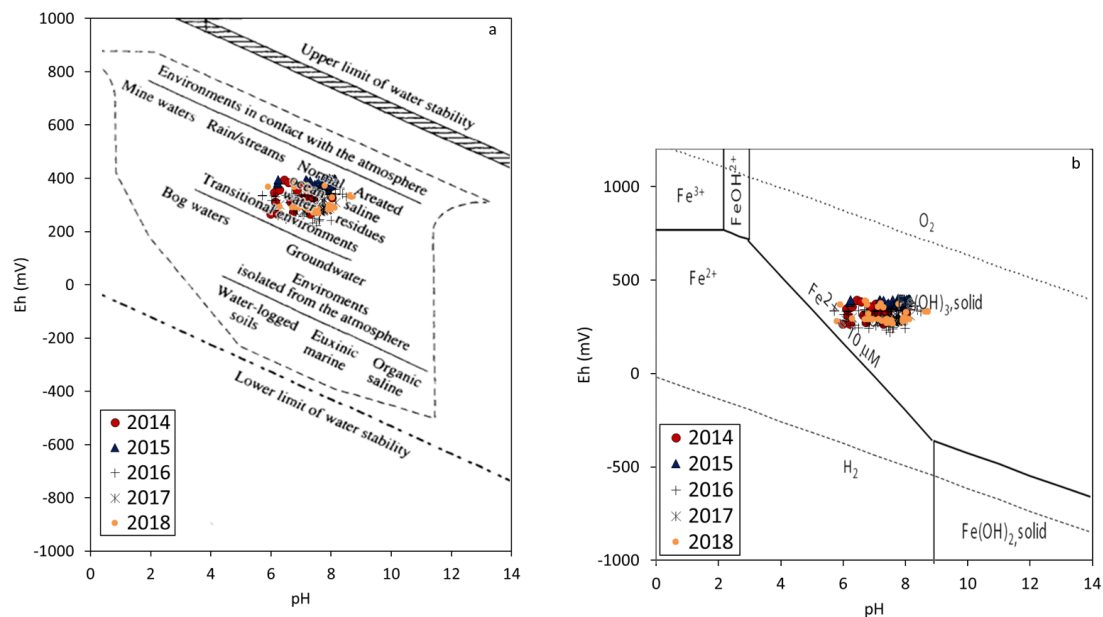


Figure 4.5: a) Eh-pH diagram providing an example of environmental conditions in the estuary (Langmuir, 1997). b) Eh-pH diagram displaying the state of iron under the measured environmental state of the estuary (Kappler and Straub, 2005).

4.5. Conclusion

Geochemical monitoring data from the Rooiels Estuary was analysed to determine the primary external factors affecting the geochemical state of the estuary. The data was collected over a period of six years by second-year students from Stellenbosch University. The data was compared to historic data published by Heinecken (1984) and Bollmorh et al. (2001). The similarity between these historic data and the data collected by the students indicated that the data obtained by the students was representative of the estuary.

The data was further compared to environmental factors such as precipitation, ambient temperature and ocean tides to determine whether or to what extent these external factors influence the estuary. Precipitation appeared to have an important effect. During years with summer precipitation, pH, conductivity and organic matter index indicated humic and fulvic compounds washed into the river water from the surroundings dominated by indigenous fynbos vegetation. During dry periods, in contrast, even the waters close to and upstream of the bridge showed seawater-like conditions. During these drier periods, ocean water reached higher into the estuary, changing the water chemistry in the estuary dramatically. This was likely exacerbated by tidal amplitudes.

Precipitation has a large impact on the geochemical condition of the Rooiels Estuary. Because of the pristine nature of the estuary and the limited number of parameters sampled, it is, however, not apparent how the freshwater system will respond to an increase in pollution from anthropogenic influences on the upstream section with seasonal change. Thus, it will be beneficial to increase the study area to freshwater systems in the same region, which experiences a stronger anthropogenic impact. It will also be beneficial to increase the range of parameters sampled and the sampling frequency to delineate the effect of land development in conjunction with seasonal change on the freshwater systems in the False Bay region.

Acknowledgements

The authors would like to thank the Centre for Geographical Analysis at Stellenbosch University (CGA), The South African Navy Hydrographic Office (SANHO) and South African Weather Services (SAWS) for providing data. Furthermore, we appreciate the contribution of all ca. 200 participating students.

Bibliography

Combined bibliography compiled in Chapter 8 – Bibliography.

5. Chapter 5 – Geochemical response in South African streams to land-use and seasonal change

Contributions

During the write-up of this paper, I fulfilled the role of primary author and Dr S Fietz of secondary author. All field data collection, analysis and interpretation were performed by me, with the exception of data regarding the Steenbras River. The Steenbras River was sampled and analysed by Gustav Rezelman during his BSc Honours 2017.

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Abstract

A year-long geochemical monitoring study in the Eerste and Lourens Rivers was conducted to analyse geochemical stream responses to land use and seasonal change. The $(Ca + Mg)/(Na + K)$ ratios suggest high urban weathering rates affecting stream conductivity and alkalinity. Nutrient sampling delineated nutrient loading by agricultural and industrial land use as well as described nutrient retention within these streams compared to rainfall. Industrial land use released NH_4 as waste water into the streams via point sources. NO_3 originating from agricultural land practices entered the streams via surface run-off dictated by precipitation. Increased discharge and lower water temperature, associated with winter months' reduced nutrient retention, as water-bottom surface interaction times and organic productivity decreased. A principal component analysis concluded that weather-related factors, such as precipitation and water temperature, were primary drivers of differential geochemical signals within anthropogenically unaffected stream reaches. Mineral dissolution was found to be the primary driver of differential geochemical signals within anthropogenically affected stream reaches.

Keywords

Streams; Land-use practices; Seasonal change; Nutrients; Retention; Eerste River; Lourens River; Western Cape

5.1.Introduction

Future freshwater availability in the Western Cape of South Africa is uncertain. The local government of the Western Cape of South Africa declared the Western Cape a disaster area in 2018 (Tandwa, 2018). This was caused by the worst drought in the area since 1904. South Africa had already been classified as a water-limited country prior to 2017. The Western Cape of South Africa will likely continue to face water scarcity and water quality problems, because of continuous development in both the social and economic sectors, with the possibility of added stress caused by climate change (New, 2002). This brought forth the motivation to evaluate the current status of the freshwater reservoirs of the region. River systems are affected, to a large extent, by the surrounding environment (Nyenje et al., 2010); thus, mismanagement can have a profound negative effect on a region's freshwater systems. Two factors that have been found to have a direct influence on the water quality and the surrounding ecological environment of rivers are land development and seasonal change (Vega et al., 1998; Nilsson et al., 2005). For example, land-use and the climate affect both the influx of ions into river systems (Gong et al., 2015) and downstream processes, such as nutrient uptake via biotic organisms (Chen et al., 2010).

The effect of land development is a direct impact caused by anthropogenic processes in the riparian region of the freshwater system. It has been found that urban and agricultural sectors are significant sources of ions caused by the industrial processes associated with these sectors (Jarvie et al., 1997; Kaushal et al., 2016). These processes release cations such as Ca, Mg, K and Na and nutrients such as nitrate and phosphate into the environment, transported by storm water systems or facilitated by surface run-off (Xia et al., 2016). The agricultural sector, a primary source of nutrients, applies ammonium nitrate and several other ions as fertilisers to crops and fields (Vega et al., 1998). Agricultural processes such as tilling further increase nutrient loading as dust particles are released into the atmosphere during this process.

The effect of land-use practices varies according to the climatic conditions as the ions released by the land-use are often dependent on weather factors such as wind and precipitation for transportation to the freshwater systems (Schulz and Peall, 2001). Surface run-off is dependent on the regional precipitation and thus the rain season can be associated with high ion influxes into the river system (De Villiers and Thiart, 2007). In the agricultural sector this effect is further increased as the soil's nutrient uptake capacity is lowest during wetter periods, thus increasing the release of nutrients into the river (Labuschagne et al., 2006). Ion concentrations

within the rivers have also been found to react differently to seasonal change depending on the source of the ions.

Ions originating from point sources opposed to diffusive sources have been found to exhibit different seasonal trends. Stream ion concentrations, from point sources, are higher during dry periods as increased precipitation during wetter periods results in high discharge, resulting in the dilution of the ions (De Villiers, 2007; Xiao et al., 2016). Within the streams, ions react differently; some ions such as Ca, Mg, K and Na tend to be more conservative and nutrients such as ammonium (NH_4^+), nitrate (NO_3^-) and phosphate (PO_4^{3-}) tend to be converted to the immobilised organic state by biotic organisms and/or react with charged particles (Triska et al., 2017).

Because of the reactive nature of nutrients, the impact of nutrient fluxes is often diminished along the rivers. For example, nutrients are retained by the biological community in the river and used as a food source (Schuetz et al., 2016). This process has been found to be affected by both the climate and land-use practices as nutrient retention depends on several factors controlled by the climate and land-use practices, i.e. channelised or natural flow regime, light availability, flow rates and availability of riparian vegetation (Earl, Valett and Webster, 2012; Newbold et al., 2006; Newcomer Johnson et al., 2016).

Minimal research has been done on the effects of climate and land development on stream ion loading within the sub-Saharan African region; thus, the extent of the effect of climate and land-use practices is not clear within the Eerste and Lourens Rivers, located in the False Bay region of South Africa. This study aims to delineate the effect of land development in conjunction with seasonal change on the geochemical conditions of the Lourens and Eerste Rivers. This was achieved by monitoring the rivers for a duration of one seasonal cycle in conjunction with land-use patterns and seasonal conditions.

5.2. Study area

The Eerste River originates in the Jonkershoek Valley on the outskirts of the town Stellenbosch. It flows through the town and stretches for approximately 40km before it flows into the ocean at Macassar beach (Figure 5.2). Upstream, the Eerste River flows through pine plantations, vineyards, indigenous flora and a large urban area. The Eerste River is dammed within the Jonkershoek Valley in the Kleinplaas Dam (Stellenbosch Municipality, 2014). Water is diverted from the Kleinplaas Dam into the Idas Valley Dam and water from the

Theewaterskloof Dam is diverted into the Kleinplaas Dam. The geology surrounding the Eerste River mainly comprises of three rock formations. The origin of the Eerste River is found in quartzitic sandstones from the Peninsula formation. The Peninsula formation forms part of the Table Mountain Group and Cape Super Group, which forms the mountains surrounding the river and thus forming the Jonkershoek Valley (CGS, 1990). Lower down in the valley, phyllite and greywacke, from the Tygerberg formation, part of the Malmesbury Group outcrop together with granite from the Stellenbosch pluton, part of the Cape Granite suite (CGS, 1990).

The Lourens River originates in the Hottentots Holland catchment area to the south east of Helderberg Mountain (Figure 5.2). Approximately 20km downstream it flows through the town of Somerset West before discharging into an estuary at Strand beach. It runs through forestry, vineyards, orchards, indigenous flora and a large urban area that includes a section for industrial use. The geology surrounding the Lourens River, similar to the Eerste River comprises of three main rock formations. Most of the tributaries originate from the sandstones of the Peninsula formation, before running through granites from the Stellenbosch pluton. Lower downstream the Lourens River comes into contact with greywacke and phyllites from the Tygerberg formation.

The Steenbras River originates in the Hottentots Holland Mountain catchment area. The river has been dammed close to the source at the Bo-Steenbras Dam and the Steenbras Dam, after which it flows for approximately 3.8km to the ocean between the towns of Gordons Bay and Rooi-Els. The total length of the river is estimated to be 18.7km with a total catchment of 74km² (Harrison, 1998). The river system is minimally affected by anthropogenic influences. The geology of the Steenbras River consists primarily of the Peninsula formation and is largely similar to the Eerste and Lourens Rivers (Appendix A, Table 1). This is especially evident below the dam where the river forms part of the Steenbras Nature Reserve. The primary reason for the inclusion of this river is for comparison with the Eerste and Lourens Rivers systems. Three sampling sites were sampled by Rezelman (2017). However, because of the similarity of the three sites, the average values for the river will be used.

The climate in the area is Mediterranean and consists of hot, dry and windy summers and cold, wet winters (Stellenbosch Municipality, 2014). Temperatures of the area range between 6°C and 36°C. The highest rainfall takes place during the months of May to August (Roets, 2008) (Figure 5.1).

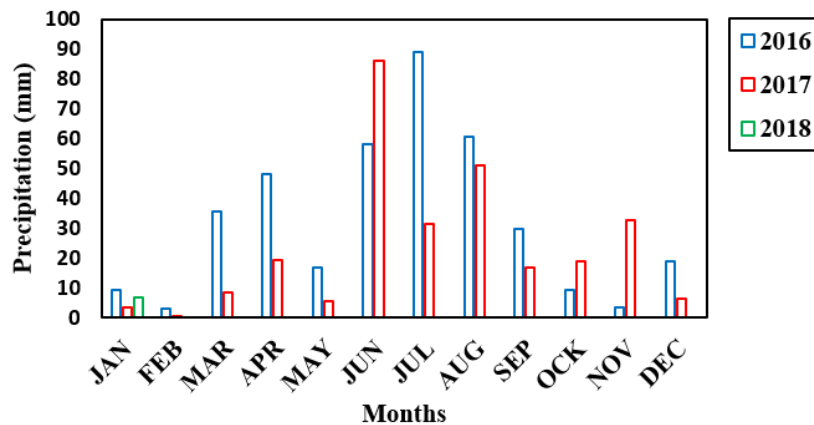


Figure 5.1: Monthly average regional precipitation for the sampling years 2016–2018. Precipitation data was collected from Data station [0021178A3] – Cape Town WO. Coordinate -33.9630 18.6020. Data obtained from the South African Weather Services (SAWS).

5.3. Sampling Methodology

The Eerste and Lourens Rivers were sampled during the months February 2017 to January 2018. Sampling locations were selected based on riparian land-use characteristics. Land-use characteristics were divided into four sections: pristine, agricultural, urban and industrial (see Figure 5.2.2). Each of these land-use practices is distinct in the way it impacts the rivers of interest. Natural regions have a generally small impact on river systems, with little to no riverbank impacts and small natural nutrient loading caused by rock weathering and soil leaching. Agricultural regions have high nutrient loading capacities, coupled with rich riparian vegetation on semi-natural riverbanks. In urbanised regions, riverbanks are impacted to a large degree, as large sections of the river are being channelised to support further development. Large areas of impermeable surfaces are present, increasing nutrient transport to the river systems. Channelising continues into industrial regions, where large amounts of nutrients and metals enter the river systems, generated from industrial processes. Based on these descriptions, four sampling locations were selected within each river. These sampling locations are presented in Figure 5.2.

For interannual comparison, previously collected data sampled at the same locations during March 2016 to September 2016 was included in the study. Additionally, data collected in the Steenbras River during March 2017 to September 2017 was used for regional spatial comparison.

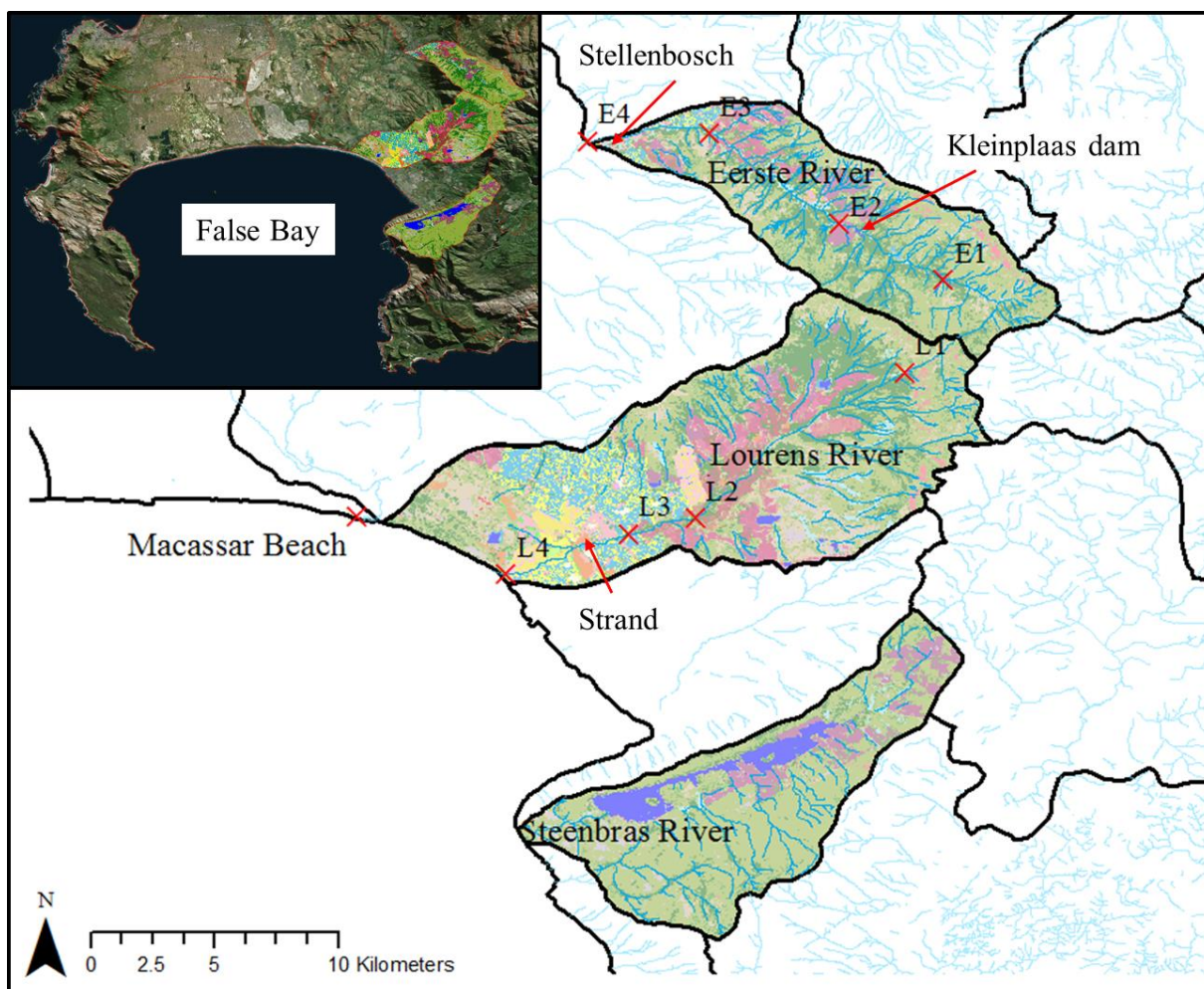


Figure 5.2: Sampling area including land-use patterns. Yellow: urban/industrial; Red: agricultural; Green: Natural. Sampling locations E1–E4 refer to sampling stations in the Eerste River. Sampling locations L1–L4 refer to sampling stations in the Lourens River. Station 1 is located upstream, and consecutive numbers refer to stations downstream.

Locations E1 and L1 had little to no anthropogenic impacts and represented a natural stream section. Location E2 is situated below the Kleinplaas Dam, ca. 0.2km², (Figure 5.2) and was affected by the influx of water from other sources such as the Theewaterskloof Dam as well as small-scale recreational and subsistence trout farming (Britz et al., 2015). Locations E3 and L2, identified as within agricultural lands, were surrounded by vineyards, orchards and forestry. The riverbanks were vegetated and without large anthropogenic influence. Location L3, identified as within an urban environment, had small sections of reconstructed riverbanks surrounded by residential dwellings; however, riverbank reconstruction was underway. Location E4, identified as within an urban/industrial environment, had large sections of

reconstructed riverbanks, surrounded by industrial activities and large residential areas. Riverbank reconstruction was done using gabions. Location L4 is located in a man-made wetland at the mouth of the Lourens River. It was influenced by large industrial processes and urban residential activities. The wetland was rich in riparian vegetation and to a large extent stagnant. Cliff (1982) found the estuary to be influenced by the ocean during summer months, while minimal river flow is present. Additional sampling location information can be obtained in Appendix A (Table 1).

5.3.1. Sampling limitations

Sampling sites were initially selected based on the land-use characteristics across the full lengths of the Eerste and Lourens Rivers. During a study on these rivers conducted by us in 2016, it was found that personal safety was of great concern at the Eerste River section past the town of Stellenbosch. The Eerste River section past Stellenbosch was also found to be highly polluted by the Plankenburg River that flows into the Eerste River just below Stellenbosch as well as the water treatment plant located at Macassar beach. A limitation had to be placed on the study area and the catchment of the Plankenburg River could not be included. Based on the safety factor and the influence of the Plankenburg River, it was decided to monitor only the Eerste River located in catchment G22F and the whole of the Lourens River located in catchment G22J. The Kleinplaas Dam was an uncontrolled factor within the Eerste River. Sampling location E2 was specifically selected to monitor the impact of the Kleinplaas Dam on the Eerste River. The Steenbras River was sampled by Rezelman (2017). The Steenbras River has minimal anthropogenic influences and all the sampling locations, sampled by Rezelman (2017), were of similar nature. Therefore, the Steenbras River was only used as a reference to compare the Eerste and Lourens Rivers.

5.4. Analytical Methodology

The Extech EC500 Waterproof ExStik II was used to measure the water temperature, electrical conductivity and pH of the water. All handheld probe readings were taken on site in triplicate. The alkalinity of each sample was measured using a manual titration method and calculated as the CaCO_3 alkalinity.

Nutrient samples were collected in fivefold using 10mL disposable test tubes. Each sample was filtered using 0.22 μm Millex-GP filters before refrigeration at 4°C. Nutrients were analysed spectrophotometrically, using a Thermo Scientific Genesys 10UV spectrophotometer. Phosphate was analysed using a procedure published by Strickland and Parsons (1972). The method was adapted for 1cm cuvettes (Section 3.2.2.) The detection limit for the phosphate analysis was calculated at 0.10 μM . Ammonium was analysed using a method described in Strickland and Parsons (1972). The method was adapted for 1cm cuvettes (Section 3.2.2.). The detection limit for the ammonium analysis was calculated at 0.64 μM . Nitrate was analysed using a method described in García-Robledo, Corzo and Papaspyrou (2014). The detection limit for the nitrate analysis was calculated at 0.96 μM .

Sample collection for the elemental analysis (Ca, Mg, Na and K) was done in triplicate, using 10mL disposable test tubes. Each sample was filtered using 0.22 μm Millex-GP filters before acidification to $\text{pH} < 2$ using 1M HCl. Samples were analysed on an Agilent 7900 ICP-MS. A standard quartz spray chamber and torch configuration were used in conjunction with Ni-plated sampling and skimmer cones. The samples were aspirated using a 0.4ml/min micromist nebuliser. The instrument was calibrated using USEPA Methods 6020A and 200.8 guidelines, and NIST traceable standards were used for calibration and validation. Detection limits were 0.003mM for Ca, 0.003mM for K, 0.004mM for Mg, and 0.004mM for Na.

5.5. Results and discussion

5.5.1. Spatial and interannual comparison

The Steenbras River, largely unaffected by anthropogenic influences, was a prime example of the natural state of streams in the Western Cape. Therefore the Steenbras River was used as a control to compare the average states of the Eerste and Lourens Rivers to. By relating ion concentrations from the Steenbras River with the Lourens River and the sampled section of the Eerste River, for the seven months from March to September 2017, the anthropogenic influence on the Eerste and Lourens Rivers can be evaluated (Appendix B, Figures 5 & 6).

Table 5.1: Nutrient and cation comparison between the Eerste River, Lourens River and anthropogenically less affected Steenbras River during the year 2017 (Rezelman, 2017).

	Ca (mM)	K (mM)	Na (mM)	NH ₄ (μM)	PO ₃ (μM)	NO ₃ (μM)
Eerste 2017	0,07	0,02	0,39	0,82	0,14	3,69
Lourens 2017	0,17	0,08	2,45	43,62	0,82	22,66
Steenbras 2017	0,06	0,01	0,85	0,53	0,12	1,52

The Lourens River was enriched in ammonium, nitrate, calcium and potassium compared to the Steenbras River, with concentrations far exceeding that of the Steenbras River (Table 5.1). The Eerste River was enriched in nitrate and calcium to a much smaller extent than the Lourens River (Table 5.1). The difference in ion concentrations suggested that the sampled section of the Eerste River was anthropogenically less affected compared to the Lourens River, based on the comparison to the Steenbras River.

The differences in ion concentrations suggested that the Lourens River and the Eerste River were distinct from a typical anthropogenically unaffected river, such as the Steenbras River, within the Western Cape of South Africa. However, because the sampling period for the Steenbras River was limited to the seven months in 2017, it was not certain whether the anthropogenic influence observed within these rivers would always persist. The months sampled in the Steenbras River, March to September, were representative of autumn, winter and spring only. The summer months for 2017 could not be compared. The drought persisting in the region peaked in the year 2017. Conditions outside of the drought and under summer conditions could not be compared.

Table 5.2: Nutrient and cation comparison between the Eerste River and Lourens River for the years 2016 and 2017.

	Ca (mM)	K (mM)	Na (mM)	NH ₄ (μM)	PO ₃ (μM)	NO ₃ (μM)
Eerste 2016	0,09	0,03	0,69	2,53	0,54	41,22
Eerste 2017	0,08	0,02	0,40	0,91	0,12	4,08
Lourens 2016	0,29	0,19	7,73	1,95	1,90	37,23
Lourens 2017	0,17	0,08	2,21	5,99	0,63	22,88

To investigate interannual differences, a comparison was made of the months March to August 2016 and March to August 2017, in the Eerste and Lourens Rivers. On average both the nutrients and sampled cations (Ca, K and Na) were of a much lower concentration during 2017 compared to 2016 (Table 5.2), the exception being ammonium in the Lourens River, with an average concentration of 6μM in 2017 compared to 2μM in 2016. The average value observed for nutrient and cation concentrations within the Lourens River, in both 2016 and 2017, was largely influenced by the highly polluted estuary at the river mouth. The data indicated that during March and April 2017 ammonium concentrations were several magnitudes higher in this location compared to 2016 (Appendix C, Table 2).

The region experienced a severe drought during the sampling years, with 2017 experiencing less precipitation than 2016. The difference observed between the two sampling years highlighted the effect of low precipitation on the state of these rivers. The decrease in precipitation reduced the transportation of ions into the rivers via surface run-off. The decreased transportation, coupled with an increase in nutrient storage capacity of agricultural soils due to drier soils, caused a reduction in the input of ions into the river system (Randall and Mulla, 2001; Labuschagne, Hardy and Agenbag, 2006). The drought also influenced land-use practices. During 2017 the local municipality increased water restrictions, resulting in a decrease in agricultural production to compensate for the shortage in water, and causing a decrease in the amount of fertilisers applied. Similarly, waste water released by urban regions was drastically decreased by limited water use on construction sites, at car washes and for gardening. These constraints decreased the amount of water entering the river systems even more, again reducing ion transport into the rivers, causing the reduced ion concentration observed in 2017 compared to 2016. However, the effect of waste water entering the Lourens River system at the estuary was evident by the increase in ammonium during 2017 compared to 2016. The increase in ammonium suggested a decrease in the dilution capacity of the system.

5.5.2. Seasonal change

Seasonal change within these streams was primarily driven by the ambient temperature and precipitation events. Thus, the primary instream parameters affected by the ambient temperature and precipitation were the surface water temperature and the water flow velocity and discharge. Water depths in both rivers ranged between 0.12m and 1.00m. The shallow water depth increased the effect of the ambient temperature on the water temperature. Water temperatures were highest during the summer months of December to February, reaching a maximum of 30°C in the Eerste River and 27°C in the Lourens River (Figure 5.3a, b). Minimum temperatures were reached during the winter months of June to August, with temperatures around 8°C in both rivers. The discharge and flow velocity were dependent on the precipitation, as run-off increases with precipitation. Discharge and flow velocity were highest during the winter months of June to August and lowest during the summer months of December to February (Figure 5.3c, d, e, f). Because the region experienced out-of-season precipitation events during October and November 2017, elevated discharge and flow velocities were observed during that time (Figure 5.3c, d, e, f). In the Eerste River, the Kleinplaas Dam influenced the downstream stream flow to a large extent. This was most visible at location E2, located just below the dam. Flow was mostly restricted, especially because of the drought the region was experiencing during the study period (Figure 5.3c, e). Directly below the dam the response of the discharge to precipitation was not visible and the discharge was mostly constant at this site. Downstream a reduced response in the discharge was observed to precipitation. In the Lourens River, the wetland was mostly stagnant and no response in discharge was observed to precipitation (Figure 5.3f). No published data of previous discharge and flow velocity within these streams was available for comparison.

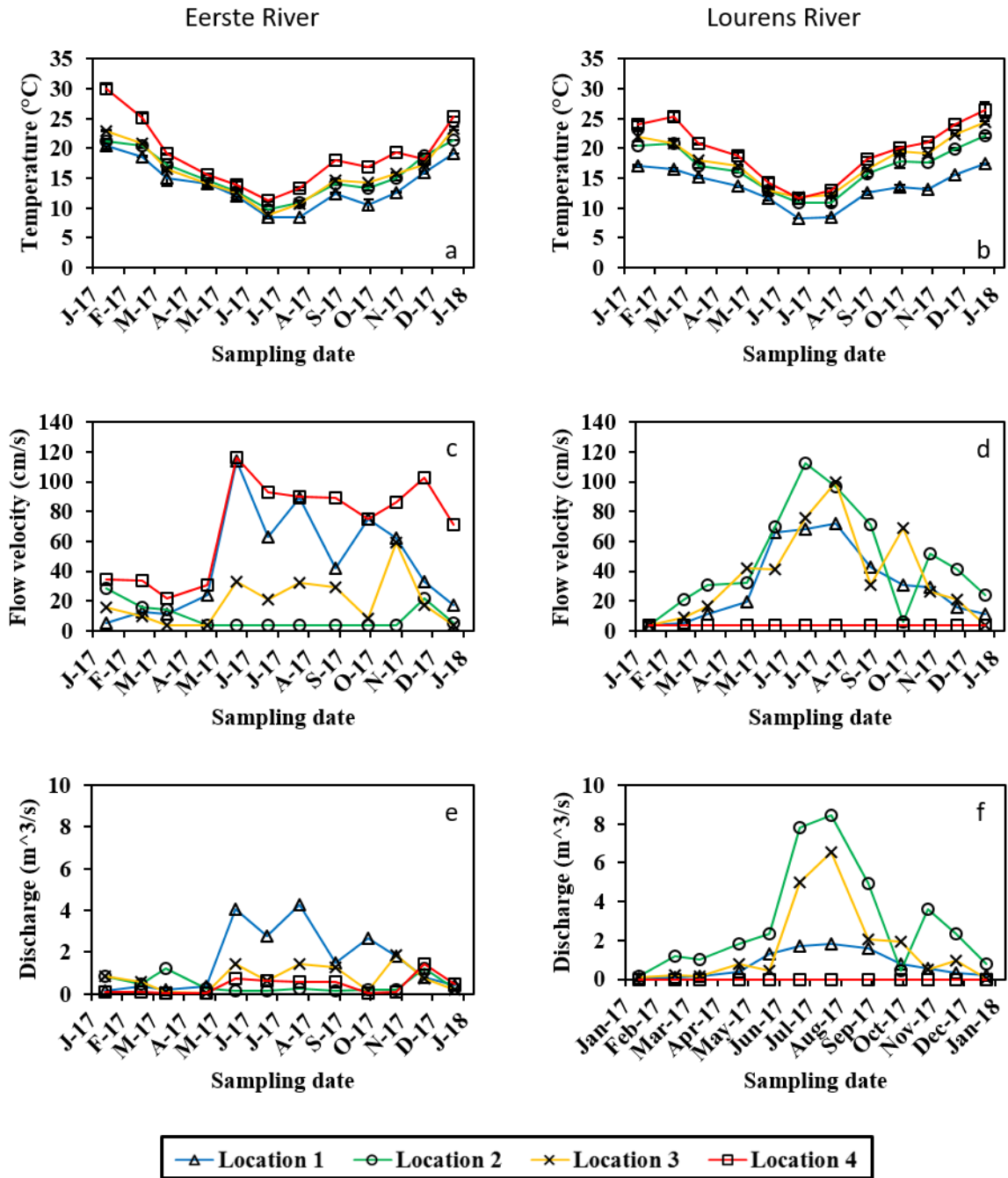


Figure 5.3: Water temperature, discharge and flow velocity for the Eerste River and Lourens River respectively for the year 2017. a-b) Water temperature for the Eerste River and Lourens River. c-d) Flow velocity for the Eerste River and Lourens River. e-f) Discharge for the Eerste River and Lourens River.

5.5.3. Electrical conductivity, carbonate alkalinity and discharge

The electrical conductivity (Figure 5.4a, b) within both streams increased downstream from natural to anthropogenically affected stream sections. Within the natural sections of both rivers, electrical conductivity was generally low and constant, ranging between 24.9 and 57.4 μ S/cm. The Lourens River stream had electrical conductivity values between > 20 000–ca. 120 μ S/cm at the urban/industrially affected stream section. This was several magnitudes higher than the electrical conductivity values observed at the urban/industrial stream section of the Eerste River (193–78 μ S/cm). The downstream increase observed can be attributed to cations released by anthropogenic land-use practices in the lower stream section and the estuary. Within the natural stream section, vegetation cover holds soils rich in minerals in place, limiting the release of particles into the streams. The removal of vegetation cover at agricultural lands and the accumulation of road salts in urban settings introduce large amounts of cations into the streams, increasing the electrical conductivity (So et al., 2016). Within anthropogenically affected stream sections the electrical conductivity was higher during summer months compared to wetter winter months (Figure 5.4a, b). So et al. (2016) attribute the higher electrical conductivity during summer months to increased solubility caused by high water temperatures; however, the increased electrical conductivity can also be attributed to oceanic influences in the estuary as a result of low river flow (Cliff, 1982). The carbonate alkalinity was closely related to the conductivity of the water (Figure 5.4c, d and Figure 5.4a, b) as the amount of dissolved Ca affects both these parameters. The pH in the natural stream sections was generally low compared to the rest of the stream sections (Figure 5.4e, f). This was caused by the presence of humic and fulvic compounds produced by the natural fynbos flora (Midgley and Schafer, 1992). The alkalinity of these streams buffered changes in the pH. This resulted in the pH reacting in changes in the alkalinity. Large decreases in alkalinity was mostly associated with decreases in the pH. The electrical conductivity, carbonate alkalinity and the pH are dependent on the influx of ions into the streams. Thus, large ion influxes can have adverse effects on the general state of these streams.

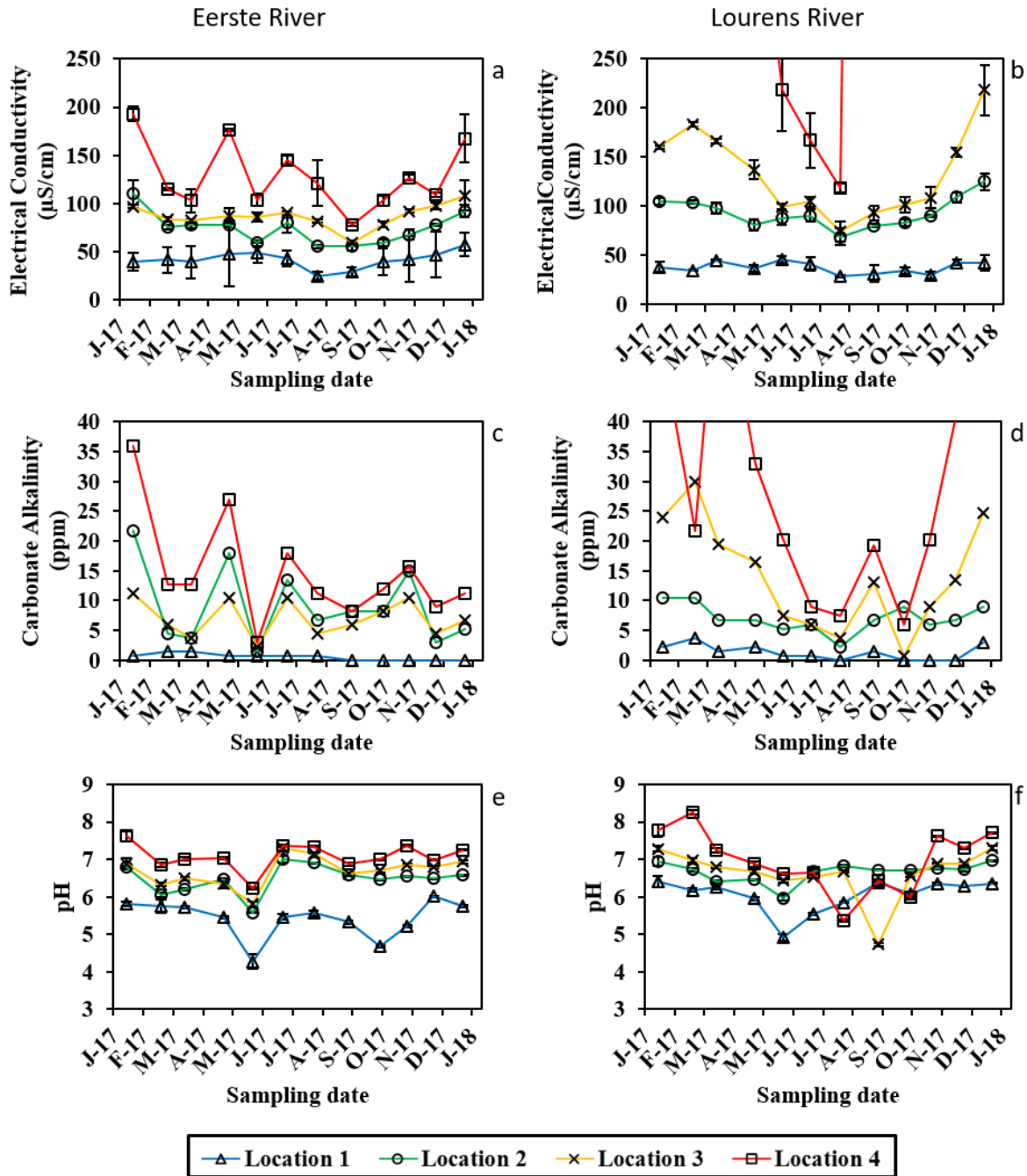


Figure 5.4: Electrical conductivity, carbonate alkalinity and pH for the Eerste River and Lourens River respectively for the year 2017. a-b) Electrical conductivity for the Eerste River and Lourens River. c-d) Carbonate alkalinity for the Eerste River and Lourens River. e-f) pH for the Eerste River and Lourens River. Electrical conductivity and carbonate alkalinity for Location 4, Lourens River, can be found in Appendix B (Figure 2).

5.5.4. Cations (Ca, Mg, Na and K)

The cations Ca, Na, K and Mg followed similar seasonal trends within these river systems, indicating that the same processes were at work controlling the influx of these cations into the streams. The cation concentrations indicate spatial variability between the two streams (Figure 5.5). The sampled sections of the Eerste River generally had lower average cation concentrations compared to the Lourens River (Figure 5.5). Measured ranges for these cations are shown in Figure 5.5a, c, e and f for the Eerste River (Ca 0.01–0.34mM, Mg 0.02–0.13mM, K < 0.005–0.05mM, Na 0.19–0.85mM) and shown in Figure 5.5b, d, f and h for the Lourens River (Ca 0.01–4.44mM, Mg 0.02–18.97mM, K 0.001–2.57mM, Na 0.18–176.25mM). The largest differences between the two rivers were observed at urbanised stream sections, suggesting that the differences were anthropogenically driven. A seasonal trend was observed in both streams as the highest cation concentrations were observed during drier, warmer summer months. This trend was particularly evident within the wetland (L4). Spatially the cation concentrations increase downstream, moving from natural to anthropogenically affected regions. The largest cation increase is observed between the natural and the initial anthropogenically affected river sections (E1 to E2 and L1 to L2, Figure 5.5), with the exception of the man-made wetland (L4). Within the wetland Ca, Mg, K and Na were present, in concentrations several magnitudes higher compared to the rest of the stream sections in both rivers.

Ca, K, Na and Mg are naturally associated with bedrock weathering of silicates and shales (Cerling and Pederson, 2016). The geology of the Eerste and Lourens Rivers consists of silicate from the Peninsula Formation and shales from the Tygerberg Formation forming the source of the Ca, K, Na and Mg in the natural sections of these rivers. Cerling and Pederson (2016) stated that clay minerals weathered from shales by fresh water release sodium and take up calcium, supporting the low Ca + Mg/Na + K ratios observed in the natural regions in the absence of urban produced carbonates (Table 5.3). Mineral dissolution accelerated by higher temperatures during summer months explained the higher cation concentrations that were observed within the anthropogenically unaffected sections of the streams. Furthermore, increased discharge during wetter winter months allowed for dilution of the cations decreasing observed concentrations. The combined effect of higher mineral dissolution during warmer months and dilution during winter months explained the observed pattern in both the Eerste and Lourens River streams.

The downstream increase, observed in the cations of both streams, indicated that anthropogenic processes in the sampled region had a large effect on the average cation concentrations. Kaushal et al. (2016) found that high concentrations of Ca, Mg, K and Na could be associated with anthropogenic processes such as urban dust, produced by transportation and industrial processes, accumulation on impermeable surfaces, agricultural fertilisers and urban karst weathering. Urban karst weathering is associated with the dissolution of urban structures such as concrete bridges, drain pipes and buildings. Dissolution of these structures is accelerated by acidic rain and high water temperatures. High water temperatures accelerate the weathering of urban structures by increasing dilution rates. The downstream increase observed in Ca, Mg, K and Na within the sampled streams (Figure 5.5) suggests that these processes were also present.

Kaushal et al. (2016) also found that Ca and Mg were released in higher quantities compared to Na and K when karst weathering took place as Ca and Mg are two abundant ingredients in concrete. Thus, $(Ca + Mg)/(Na + K)$ ratios can be used to identify anthropogenic ion releases. Within the Eerste and Lourens River streams, $(Ca + Mg)/(Na + K)$ ratios (Table 5.3) increased downstream, thus confirming the anthropogenic influence on the streams. Location L4 was an exception to this finding, as high Na concentrations were introduced into the wetland via tidal influences. The anthropogenic influence on these streams in areas of urban industrial land-use was prominent. With further development, increases in cations should be expected. Together with increased cation concentration, increased electrical conductivity, alkalinity and pH values can also be expected, changing the natural state of the streams.

Table 5.3: $(Ca + Mg)/(Na + K)$ cation ratios based on average cation concentrations within the Eerste River and Lourens River for the year 2017.

	E1	E2	E3	E4	L1	L2	L3	L4
Feb-17	0,14	0,74	0,30	0,57	0,01	0,09	0,24	766,90
Mar-17	0,12	0,30	0,30	0,48	0,01	0,09	0,33	123,19
Apr-17	0,15	0,32	0,34	0,47	0,01	0,07	0,24	36,90
May-17	0,20	0,57	0,31	0,43	0,01	0,08	0,17	1,25
Jun-17	0,17	0,26	0,25	0,32	0,33	0,08	0,06	0,02
Jul-17	0,14	0,51	0,26	0,39	0,01	0,07	0,09	0,23
Aug-17	0,11	0,38	0,26	0,36	0,01	0,04	0,05	0,12
Sep-17	0,11	0,38	0,24	0,29	0,01	0,06	0,08	37,39
Oct-17	0,13	0,41	0,27	0,33	0,01	0,06	0,09	5,30
Nov-17	0,12	0,45	0,29	0,38	0,01	0,07	0,90	2,66
Dec-17	0,09	0,31	0,33	0,39	0,01	0,10	0,19	46,38
Jan-18	0,11	0,32	0,27	0,28	0,01	0,11	0,39	4186,11

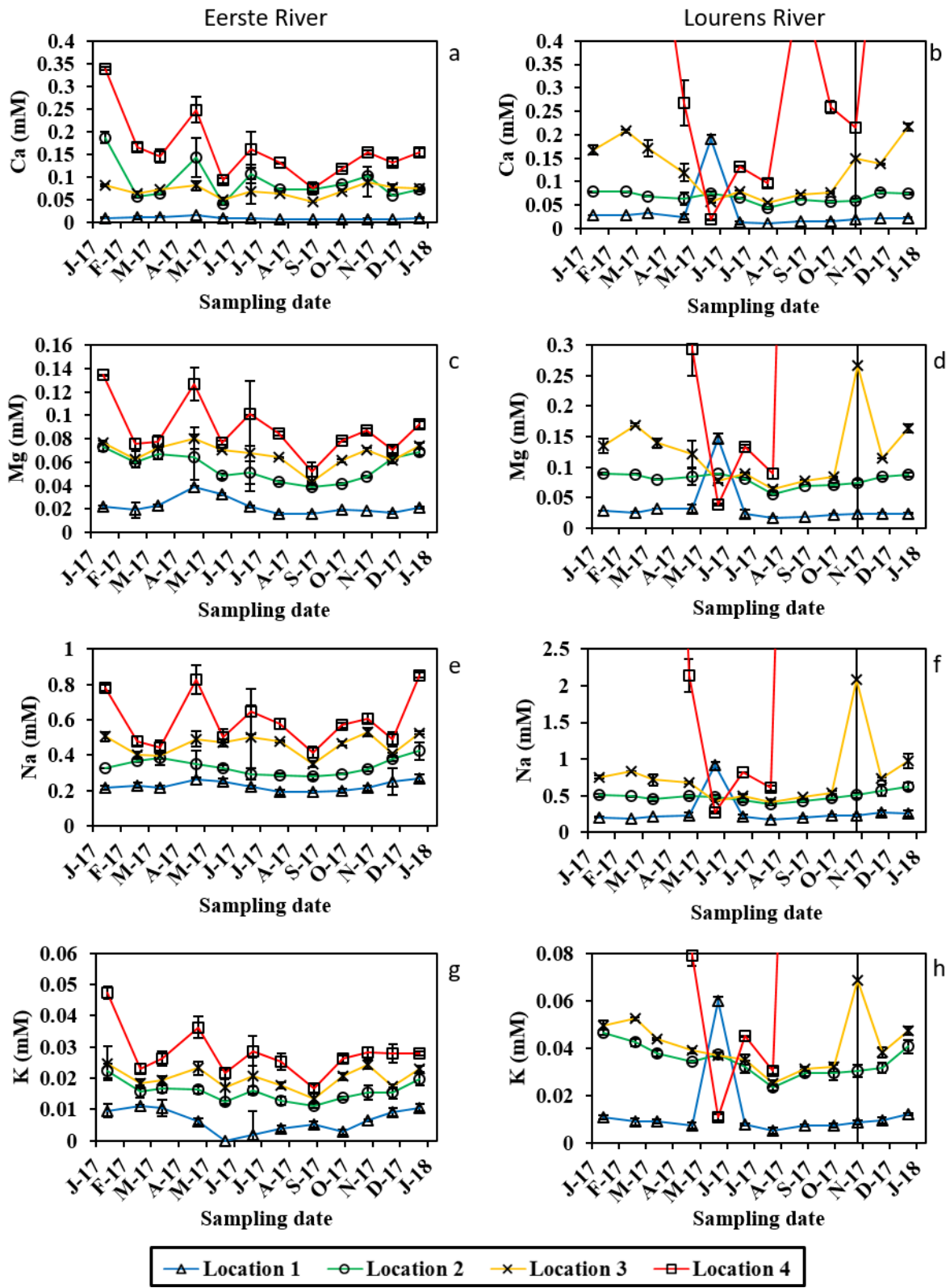


Figure 5.5: Ca, Mg, Na and K concentrations for the Eerste River and Lourens River respectively for the year 2017. a-b) Ca concentration for the Eerste River and Lourens River. c-d) Mg concentration for the Eerste River and Lourens River. e-f) Na concentration for the Eerste River and Lourens River. g-h) K concentration for the Eerste River and Lourens River. Cation profiles for location 4, Lourens River, can be found in Appendix B (Figure 3).

5.5.5. Nutrients fluxes

Ammonium, often being below the statistical detection limit of $0.64\mu\text{M}$ in both rivers, exhibits no statistically significant seasonal trends (Figure 5.6c, d). During the summer months, site specific, higher ammonium concentrations compared to winter months are observed. In the Eerste River, the sites exhibiting these ammonium influxes are locations E2, associated with the Kleinplaas Dam and E4, associated with the urban region of Stellenbosch. The maximum observed ammonium concentration at location E2 was $3.25\mu\text{M}$ during February 2017, and at location E4 $3.18\mu\text{M}$ during December 2017. In the Lourens River, the site exhibiting high ammonium influxes was location L4, located within the man-made estuary. A maximum influx took place during February 2017, with extreme concentration of $1120\mu\text{M}$. However, for the rest of the sampling period ammonium concentrations at location L4 ranged between $72\mu\text{M}$ and $0.05\mu\text{M}$. The extreme ammonium concentrations suggest the inflow of untreated waste water into the estuary. During winter times these concentrations are lowered as fresh water from upstream dilutes the waste water.

Nitrate within the Eerste River showed high seasonal variability, with no significant trend observed (Figure 5.6a). Periodic spikes were observed during spring and autumn, possibly related to nutrients added to vineyards pre- and post-harvest. The Eerste River also had the influence from other agricultural sectors as water from the Theewaterskloof Dam was pumped into the Kleinplaas Dam at location E2. The largest nitrate influxes were observed at location E2, with concentrations reaching up to $14\mu\text{M}$. In the Lourens River (Figure 5.6b), nitrate was present at much higher concentrations, compared to the Eerste River, reaching up to $48\mu\text{M}$ at location L2. The Lourens River's agricultural sector was much larger compared to that of the Eerste River. A seasonal trend was visible, with higher nitrate loading during the winter time. Nitrate influxes were observed at location L2, after which they gradually decreased downstream to location L4. Location L4 experienced a disproportional nitrate loading during March and April, reaching $107\mu\text{M}$ and $99\mu\text{M}$ respectively; however, nitrate concentration decreased to values below $30\mu\text{M}$ in the months that followed. These results can also be explained by the waste water signal observed in ammonium concentrations.

Nitrate, often in the form of ammonium nitrate, was used as an inorganic fertiliser (Vega et al., 1998), thus explaining the high nitrate loading at sampling locations associated with agricultural land-use. Because nitrate concentrations followed similar trends to precipitation (Figure 5.1 and Figure 5.6a, b) it could be deduced that nitrate was transported by surface runoff and originated from diffused sources (Vega et al., 1998). During dry summer months

precipitation affected nitrate surface run-off far less as the soil storage capacity was elevated as a result of low soil moisture and high nutrient demands; however, during wetter months, when the soil moisture was high and low nutrient demands were present, the nutrient storage capacity was low, providing for larger nutrient run-off during precipitation events (Randall and Mulla, 2001; Labuschagne, Hardy and Agenbag, 2006).

Phosphate was present in low concentrations in both rivers and was often below the detection limit ($0.10\mu\text{M}$). Within the Eerste River, no seasonal or spatial trends were observed (Figure 5.6e). Phosphate concentrations ranged between below detection limit and $0.44\mu\text{M}$. In the Lourens River, phosphate concentrations up to $0.42\mu\text{M}$ were observed at location L1, the uppermost part of the river. Higher values were observed during summer times at location L1 (Figure 5.6f). Phosphate originates naturally from the weathering of the mineral appetite in granites (Taunton, Welch and Banfield, 2000) as well as from municipal waste water (Vega et al., 1998). The presence of granites from the Cape Granite suite, located at the source of the Lourens River, explains the presence of elevated phosphate concentrations at location L1. The temporal high phosphate concentrations, associated with location L4, the Lourens River Estuary, can only be explained by the influx of industrial waste water.

Comparing nutrient concentrations at the Lourens River Estuary during 2017 with data obtained in 1998 by Schulz and Peall (2001), it was apparent that the source of nutrient loading in the river had changed. In 1998 the maximum nutrient loading was observed during the winter months (PO_4 $9.2\mu\text{M}$; NO_3 $30\mu\text{M}$), suggesting that the primary source of the nutrients was surface run-off. However, the maximum nutrient concentration observed in the summer months during 2017 (PO_4 $7.5\mu\text{M}$; NO_3 $107\mu\text{M}$), suggests a point source of the nutrients. This suggests that a waste water source had been introduced into the river and was causing high levels of nutrient loading. According to Cliff (1982) effluent flows into the Lourens River Estuary at location L4.

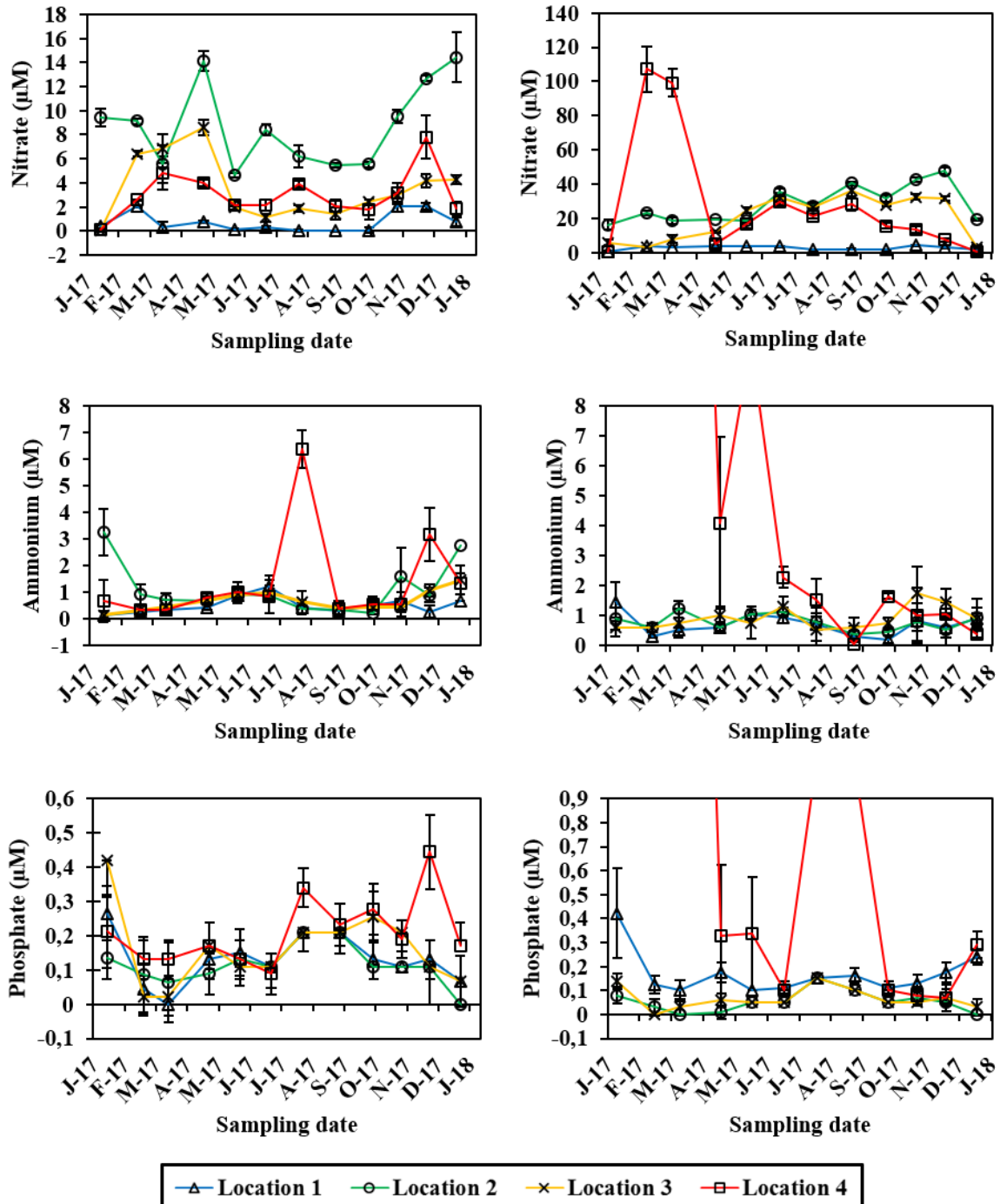


Figure 5.6: Ammonium, nitrate and phosphate concentrations for the Eerste River and Lourens River respectively for the year 2017. a-b) Ammonium concentration for the Eerste River and Lourens River. c-d) Nitrate concentration for the Eerste River and Lourens River. e-f) Phosphate concentration for the Eerste River and Lourens River. Nutrient profiles for Location 4, Lourens River, can be found in Appendix B (Figure 4).

5.5.6. Nutrient retention

Major nutrients (N, P), typically being more susceptible to biological processes than the cations Ca, K, Na and Mg, change between the inorganic and organic phase as part of the nutrient cycles. During the organic phase the nutrients are immobilised and retained from the water column. The nutrient retention observed in the Eerste and Lourens Rivers was river section specific. For example, ammonium uptake was primarily observed during the summer season between location E2 and E3 (Figure 5.7c). Other sections in the Eerste River rarely indicate any ammonium retention. In the Lourens River, ammonium retention was occasionally observed downstream from location L2 (Figure 5.7b). In the Eerste River nitrate retention was primarily observed between locations E2 and E3 (Figure 5.7c). At this section nitrate retention was observed year long; however, it was highest during the summer months, with uptake up to $10\mu\text{M}$. At the lower section, between E3 and E4 (Figure 5.7d), nitrate retention was only observed during the summer months. In the Lourens River, a similar nitrate retention trend was observed. Nitrate retention downstream of location L2 was observed throughout the year, with the highest retention observed during the summer months (Figure 5.7b, d). At location L3 nitrate retention of up to $20\mu\text{M}$ was observed and at location L4 nitrate retention of up to $24.29\mu\text{M}$. The lack of flowing tributaries during the summer months rules out the possibility of nutrient dilution at these locations. No nitrate or ammonium retention took place in the Lourens River Estuary (L4, Figure 5.7d) during March and April, although retention was observed upstream at these times. This suggests that the excessive nutrient loading caused N saturation. N saturation takes place when the nitrogen uptake capacity of the system is depleted, and the nitrogen added into the system equals the nitrogen released by the system (Earl et al., 2012). Chen et al. (2010) suggested that the seasonal summer increase in nitrate uptake was caused by increases in water temperature and biological productivity.

It was evident that the state of the streams influenced the retention of NH_4 and NO_3 . The highest observed nutrient retention was associated with the stream sections rich in vegetation, organic matter and undisturbed river structure. Undisturbed river structures allowed turbulent flow and stagnant segments to co-exist as water flow in the structurally diverse river channels. Bukaveckas (2007) found that increased water residence time, caused by stagnant segments, allowed for longer reaction time with the uptake agent and, in turn, allowed for increased nutrient retention. Reduced discharge during dry summer times allowed for higher residence times compared to winter months. Bouwman et al. (2013) found that organic matter increased the productivity of the benthic biological community, thus increasing nutrient retention. The

riparian vegetation surrounding the Eerste and Lourens Rivers stream sections that displayed nutrient retention, was a large source of organic matter as leaf litter and degrading plant material were present in high quantities. Biotic processes associated with the mineralisation of the benthic organic matter contributes to the retention of nitrate and ammonium (Newbold et al., 2006). The decreasing nutrient retention as observed downstream in the Eerste River was most likely a function of development and additional nutrient loading associated with urban processes. Large sections of riverbanks have been stabilised using gabions. This disturbs both the river structure and riparian vegetation, creating continuous linear flow and reductions in organic matter.

Phosphate retention, present year-long, was observed at the river section above location L2 in the Lourens River (Figure 5.7a). The highest phosphate retention ($34\mu\text{M}$) took place during the summer months. This correlates to higher phosphate loading above location L1. The increase of retention with an increase of phosphate influxes suggests that phosphate is limiting and readily cycled to the organic state or sorbed to particulates. Precipitation has a negative trend related to phosphate retention. This suggests that during higher discharge related to precipitation, phosphate concentrations are diluted, limiting the interaction between the dissolved phosphate and the uptake agent. The estuary, loaded with high concentrations of phosphate, exhibits no phosphate retention. It has been found that phosphate retention within constructed wetlands, such as the Lourens River Estuary, is limited. Phosphate retention is normally facilitated by sorption, precipitation and plant uptake. These mechanisms are fast to be saturated under high phosphate loading (Vymazal, 2007). The concentrations of phosphate below analytical detection limit elsewhere do not allow estimates of phosphate retention; however, these low concentrations possibly suggest rapid phosphate uptake as other nutrients are readily available.

A study done by Schulz & Peall (2001) on the Lourens River Estuary in 1998 suggested that retention of both nitrate and phosphate was present. Nitrate retention was recorded at 70% during the dry period and 84% during the wet period. Phosphate retention was recorded at 54% during the dry period and 75% during the wet period. These findings contradict our results. Nitrate retention during 2017 was 79% during the dry months and 25% during the wet months, excluding the two months of disproportionately high nitrate loading. No phosphate retention was observed. The amount of nitrate retained was, however, similar with a maximum of $25\mu\text{M}$ retained during 1998 and $24\mu\text{M}$ during 2017. The lack in phosphate retention supports the possibility that the estuary has become saturated in phosphate since 1998.

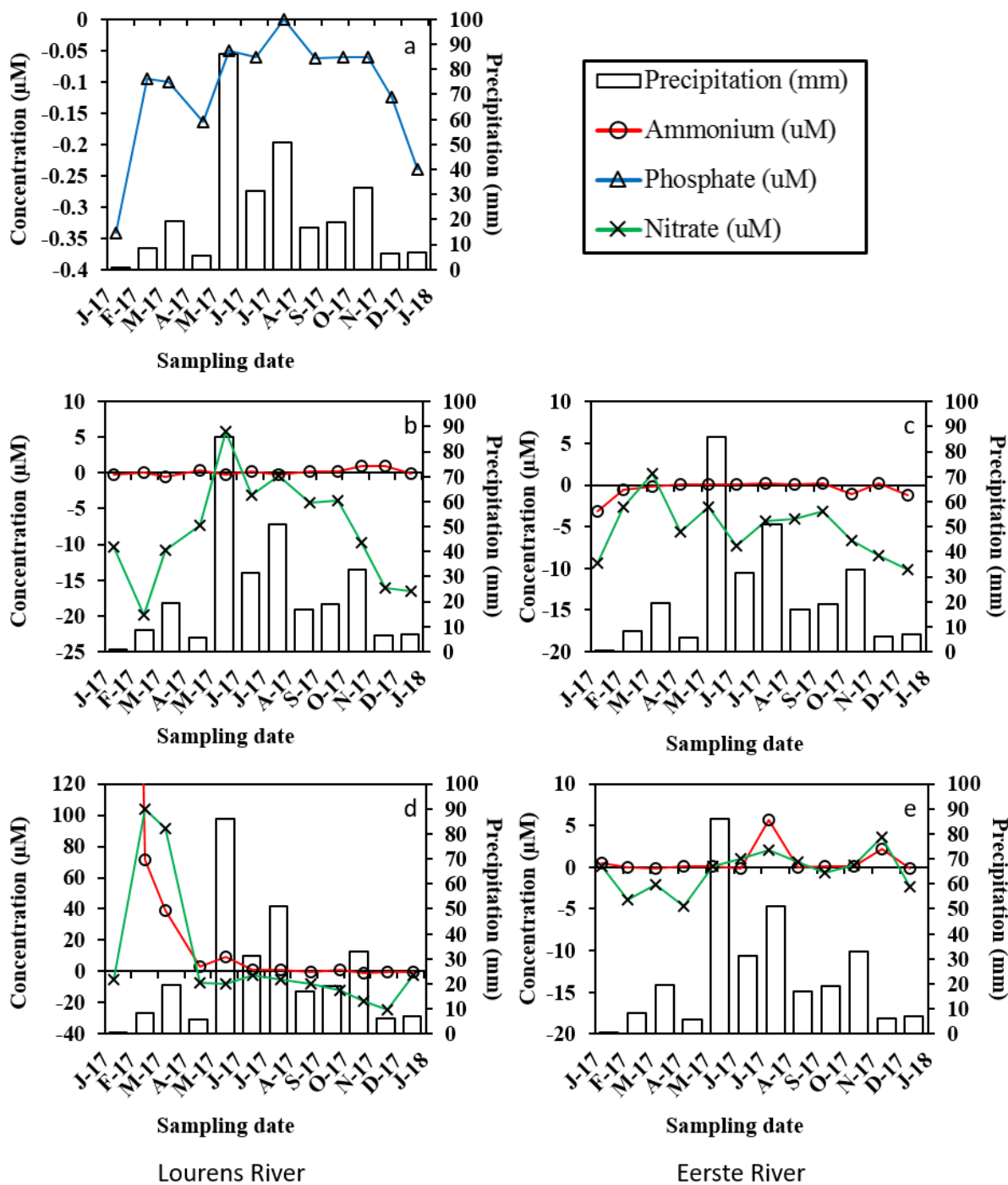


Figure 5.7: Ammonium, nitrate and phosphate retention for the Eerste River and Lourens River respectively for the year 2017 compared to average monthly precipitation. a) Phosphate retention between locations L1 and L2 in the Lourens River. b) Ammonium and nitrate retention between locations L2 and L3 in the Eerste River. c) Ammonium and nitrate retention between locations E2 and E3 in the Lourens River. d) Ammonium and nitrate retention between locations L3 and L4 in the Eerste River. e) Ammonium and nitrate retention between locations E3 and E4 in the Lourens River.

5.5.7. Driving factors for change in chemical composition

To distinguish between the sampling locations in each river, based on the impact that the climate had and the effect of land-use, a factor analysis was done to determine the principal components influencing the variance at each location. Based on the Eigenvalues of the analysis, four factors were selected to explain the variance within these two rivers. From the PCA (Figure 5.8) it was determined that factor 1 can be primarily associated with the dissolution of minerals. Factor 1 explained between 42% and 45% of the variance in the two rivers. Variables contributing to factor 1 included the cations, Mg, Ca, K, Na, the alkalinity and the conductivity. Factor 2 explained between 16% and 18% of the variance and included variables such as precipitation and temperature. Precipitation contributed negatively to this factor while temperature contributed positively. Higher temperatures were associated with lower precipitation in this winter rainfall area. Sampling locations were clearly distinguishable based on the PCA as the effect of factor 1 increased with increasing anthropogenic influences (Figure 5.8).

The variance in natural stream sections were influenced primarily by factor 2, arguably driven by climatic patterns (Figure 5.8). Factors such as precipitation, flow velocity and to some extent temperature contributed to the variance within these locations. Moving downstream, it was evident that the influence of factor 1 increased. Locations E3 and L2, associated with agricultural land-use practices, were still largely influenced by climatic patterns. However, factor 1 was influencing these locations to a similar extent. Locations E4, L3 and L4 were primarily influenced by factor 2 with a smaller percentage of the variance explained by factor 1 (Figure 5.8). This indicated a strong increase in mineral dissolution and pollutant inputs from urban industrial areas. Because similar variance in factor 1 was not seen at the pristine sampling locations, and no major geological changes took place between the pristine and urban/industrial regions, it can be expected that the increase in the mineral concentrations is anthropogenically driven. Location L4 was exceptionally influenced by factor 2 compared to other urban/industrial regions (Figure 5.8c), highlighting the influence of waste water input.

The two primary factors of variance that influenced the rivers were interpreted as climate driven and anthropogenically driven processes. Climate driven processes include factors such as precipitation, discharge and to some extent water temperature, while anthropogenic processes include mineral loading and pollution inputs. It was evident that the influence of anthropogenic processes increased downstream in these rivers, with the change in land-use practices. Essentially, the effect of climatic factors was masked in regions strongly affected by

anthropogenic factors. The data indicated that these rivers are not homogeneous spatially nor temporally. The rivers are affected by seasonal changes, riparian land-use practices and point sources of nutrients and cations. The sampling locations that were selected in both rivers were statistically distinct from one another, based on principal component analysis, suggesting that the downstream increasing anthropogenic influence impacts these rivers to a large extent. Similar results found in the larger adjacent Berg River system also indicated strong influences from the agricultural sector and urban settlements, with the largest effects seen at the highest populated and cultivated regions (De Villiers, 2007).

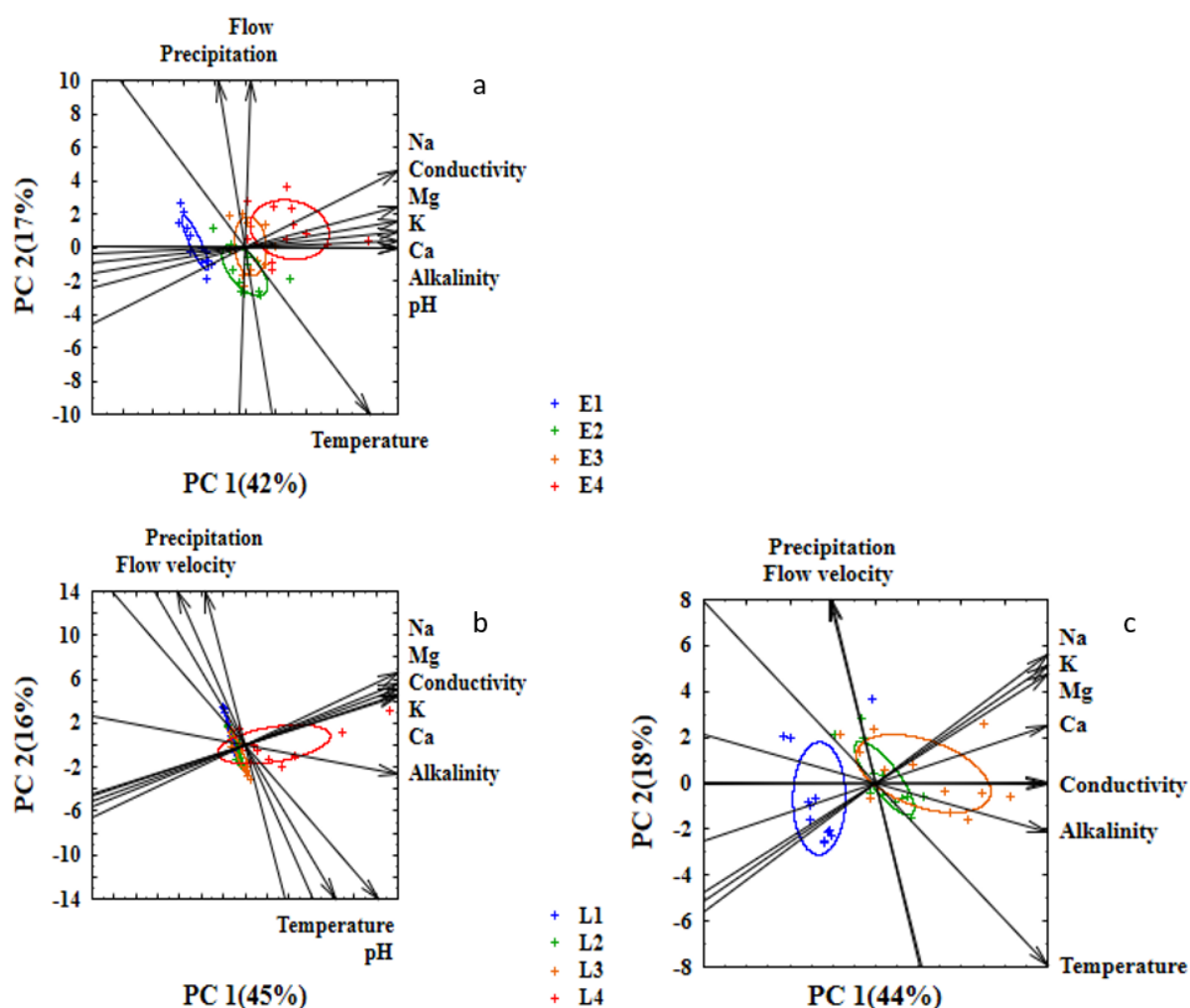


Figure 5.8: Principal component analysis bi-plots of the climatic factors, geochemical parameters and ion concentrations of the Eerste River and Lourens River. a) PCA bi-plot of the Eerste River. b) PCA bi-plot of the Lourens River. c) PCA bi-plot of the Lourens River without the influence of location L4 (wetland) to allow for higher resolution.

5.6. Conclusion

The impact of the climate and land development on these streams located in the Western Cape of South Africa is evident. Cation and nutrient loading in the streams depended largely on the riparian environment. River sections unaffected by anthropogenic land-use practices were primarily affected by the climate as temperature and precipitation affect weathering and ion transport. An increase in anthropogenic influences was linked to an increase in cation concentrations. This was observed in the increase of Ca, Mg, K and Na concentrations as the streams progressed from a natural environment to agricultural and urban/industrial regions. River sections affected by urban/industrial land-use practices displayed high variability in the geochemical state, as per PCA, independent of the climate; however, climate-induced variability was also observed to some extent, as mineral transportation was associated with climatic factors such as precipitation and surface run-off.

Nutrients, ammonium, nitrate and phosphate differed spatially and temporally to the cations (Ca, Mg, K and Na), as the sources of the nutrients differed from those of the cations. Nitrate and ammonium, often used as agricultural fertiliser, were found at higher concentrations in river sections related to agriculture. However, unlike the cations, retention of these nutrients was observed at certain stream sections. Larger uptake in nitrate and ammonium was observed at undisturbed stream sections associated with an abundance of riparian vegetation and wetlands compared to restructured stream sections. Thus, the removal of riparian vegetation by the restructuring of these streams, through the use of bank stabilisation with gabions, proved to hinder the natural nutrient uptake capabilities of these streams. Phosphate was associated with the weathering of granite, specifically in the Lourens River, and municipal waste water. Phosphate was found to be highly reactive, being both adsorbed and retained as a nutrient by biological organisms. Thus, the nutrient concentration was often removed out of the stream within short distances from the source, resulting in concentrations below detection limit.

The drought appeared to decrease ion loading within the streams. As the precipitation was limited during the drought, the transport of ions to the streams was hindered. This resulted in lower ion concentrations compared to years with higher precipitation. It is currently unclear for what time period the drought conditions will persist. In times of higher precipitation, under the current land-use state, the influx of ions into these streams will again increase. The increase in ions might cause eutrophication to take place within these streams. Eutrophication will have a severely negative effect on these streams as is already evident in the Lourens River Estuary.

Thus, great care must be taken to prevent higher ion fluxes to these streams caused by land-use practices and continuous land development.

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Bibliography

Combined bibliography compiled in Chapter 8 – Bibliography.

6. Chapter 6 – Experimental analysis

6.1. Introduction to experimental analyses

Nutrient retention within streams is dependent on the current state of the stream environment and several different factors determine the extent of the retention. Climatic factors such as precipitation and ambient temperature affect stream discharge and water temperature, while riparian factors such as vegetation and stream bank structures affect factors such as nutrient residence time. These factors, coupled with differential nutrient loading, which is dependent on land-use practices and nutrient availability, often make it difficult to evaluate the state of the nutrient retention capacity of streams and how each of these factors influences it.

In section 5.5.6 the nutrient uptake based on differences in nutrient concentrations, related to river sections, was discussed. The discussion evaluated the extent of nutrient retention within different land-use regions and within different climatic conditions. However, the discussion fails to assess the impact each of these factors has on the nutrient retention capacity and ultimately only infer the possible impact of each of these factors on the nutrient retention capacity based on differences observed within different environments.

In this chapter the aim is to assess the loading of factors such as riparian land-use, river structure, discharge, driven by precipitation, and water temperature, affected by vegetation covering and ambient temperature, on nutrient retention within streams. Two experimental procedures were implemented to evaluate these factors. First, a short-term nutrient release experiment was performed within two river sections of the Eerste River to assess the impact of riparian land development and river structure. The second procedure consisted of an in-lab flume study that was initiated to evaluate and assess the impact of differential flow velocities, nutrient loading and water temperature on nutrient retention by a benthic biofilm.

Both of these analyses were conducted as feasibility studies. The main constraint on these studies was time, as both studies were initiated towards the end of the feasible data collection period for this project. Thus, the data discussed in this section serves as preliminary research for a future project.

6.2. Set-up of short-term nutrient release experiment

As stated previously, the main aim of the in-situ tracer analysis was to assess the impact of riparian land development and river structure on nutrient retention. It was suggested that nutrient retention should be elevated in less developed river sections, being rich in riparian vegetation and having a natural river structure, when compared to developed sections of rivers, being channelised and lacking riparian vegetation.

Two experimental sites were located within the Eerste River to test this hypothesis. The first site, referred to as undeveloped, was located within a relatively undisturbed stream section. It exhibited a natural flow regime rich in turbulent flow, meandering and stagnant sections, as well as riverbanks rich in vegetation. The second site, referred to as developed, was located within a more urbanised section of the river. It exhibited restructured riverbanks by use of gabions, coupled with a lack in vegetation and a channel-like structure causing accelerated flow. Both sections exhibited a flourishing benthic community in the form of biofilm.

Two short-term nutrient release experiments were conducted at each of the experimental sites. During the initial experiment, two reactive nutrient salts, ammonium chloride (NH_4Cl) and potassium dihydrogen phosphate (KH_2PO_4), together with a conservative sodium bromide tracer (NaBr), were released at a constant release rate determined by the discharge of the stream. During the second experiment an addition of potassium nitrate (KNO_3) was included in the non-conservative nutrients. Three explanatory values were obtained based on the analysis. These values include the uptake length, the uptake velocity and the areal uptake, each explaining to some extent the nutrient retention capabilities of the experimental site. The methodology regarding this analysis can be found in sections 3.2.2 and 3.2.3.

6.3. Set-up of in-lab flume experiments

Nutrient uptake studies have primarily been conducted under base flow conditions, because of limitations related to the short-term nutrient release experiment. Base flow under normal circumstances is associated with drier seasons. This proved to produce results not necessarily representative of the system over time (Newcomer Johnson et al., 2016). Flow velocity, water temperature and nutrient loading are three parameters dependent on seasonal change. During the rainy season the flow velocity within the streams of the Western Cape of South Africa increases dramatically. This is caused by increased surface run-off during precipitation events that also increase the nutrient loading from non-point sources. In this region, the rainy season occurs during the winter months, causing lower water temperatures. Kadlec and Reddy (2001)

and Earl et al. (2006) found that water temperature and nutrient loading both affect the nutrient uptake capacity.

Nutrient uptake within the developed sections of the Eerste River was also impaired because of the removal of riparian vegetation as seen in section 6.1. This suggests that nutrient uptake within the developed sections of the Eerste River will primarily take place through benthic communities and particulate sorption. The benthic community in the Eerste River largely consists of biofilm that grows on the coarse boulders found in the stream. Thus, a flume was designed to assess the nutrient uptake capacity of the benthic biofilm under changing seasonal parameters, including water temperature, differential flow velocity and nutrient loading.

The flume was designed to mimic the natural environment found in the Eerste River, examined in the monitoring section. It was used to set up an experiment dedicated to investigating nutrient uptake by benthic biofilm in these streams. The flume was based on the designs of De Falco et al. (2016). The methodology regarding this analysis can be found in section 3.2.3.

The cultivation of the benthic biofilm for the flume experiment proved to be challenging and time consuming. This complicated duplication of the experiment for all parameters within the limited timeframe. A preliminary experiment was conducted to evaluate the possibility of conducting the analysis in the future. The preliminary experiment provided a clear outline of possible changes to be made as well as the probability of achieving the objective. The preliminary experiment was conducted with a steady flow rate of 29cm s^{-1} at ambient temperature, without water temperature control. The biofilm introduced into the system was collected from the Eerste River system at location E2 (section).

6.4. Results and discussion

6.4.1. Short-term nutrient release analysis

The initial tests were conducted in the absence of nitrate. Both the undeveloped and developed sections showed uptake of both ammonium and phosphate. In the undeveloped section a 78% decrease of ammonium was measured over the distance of 80m. This relates to an uptake of $11\mu\text{M}$. The average concentration at the start of the section, after the addition of the nutrient, was $16.00\mu\text{M}$ with a standard deviation of 18.45 and the average concentration after 80m was $4.00\mu\text{M}$ with a standard deviation of 1.22. Phosphate showed a decrease of 4%, which related to an uptake of $0.03\mu\text{M}$ over the distance of 80m. The concentration at the start of the section, after the addition of the phosphate, was $0.92\mu\text{M}$ with a standard deviation of 0.00 and the average concentration after 80m was $0.89\mu\text{M}$ with a standard deviation of 0.03. In the developed section, ammonium showed a decrease of 11%, corresponding to an uptake of $0.65\mu\text{M}$. The concentration at the start of the section, after the addition of the nutrient, was $6.33\mu\text{M}$ with a standard deviation of 1.48 and the concentration after 80m was $5.80\mu\text{M}$ with a standard deviation of 0.5. Phosphate showed a decrease of 19% relating to an uptake of $0.25\mu\text{M}$. The concentration at the start of the section, after the addition of the nutrient, was $1.36\mu\text{M}$ with a standard deviation of 0.07 and the concentration after 80m was $1.15\mu\text{M}$ with a standard deviation of 0.03. Based on the uptake observed and the standard deviation of the samples, no significant results could be obtained from the initial test conducted in the undeveloped section of the stream. This was likely caused by experimental errors.

During the second group of tests, in the presence of nitrate, the undeveloped section showed uptake of both ammonium and phosphate. A 27% decrease of ammonium was measured after a distance of 80m. This relates to a decrease of $3.24\mu\text{M}$. The concentration at the start of the section, after the addition of the nutrient, was $11.97\mu\text{M}$ with a standard deviation of 1.10 and the concentration after 80m was $8.72\mu\text{M}$ with a standard deviation of 0.89. Similarly, a 31% decrease of phosphate was measured over the distance of 80m. This relates to a decrease of $0.65\mu\text{M}$. The concentration at the start of the section, after the addition of the nutrient, was $2.13\mu\text{M}$ with a standard deviation of 0.11 and the concentration after 80m was $1.48\mu\text{M}$ with a standard deviation of 0.10. In the developed section, nutrient uptake was only observed for phosphate with a 10% decrease over the distance of 80m. This relates to a decrease of $0.15\mu\text{M}$. The concentration at the start of the section, after the addition of the nutrient, was $1.62\mu\text{M}$ with a standard deviation of 0.05 and the concentration after 80m was $1.46\mu\text{M}$ with a standard

deviation of 0.05. No change in nitrate was evident and the nutrient reacted similarly to the conservative tracer.

The previously described nutrient uptake was not normalised to the conservative tracer and is an overview of the uptake at the two locations. However, based on the nutrient uptake values obtained from the second test it is evident that the undeveloped section had better nutrient uptake. To truly quantify the nutrient uptake at these locations and to eliminate the effects of lateral inflow over the stretch, the logarithmic normalised concentrations of each nutrient need to be calculated. This is explained in section 3.2.2.

Table 6.1: Nutrient retention from the Eerste River within a stream section that is developed (bank restructured and vegetation removed) vs undeveloped stream section (natural vegetation and stream structure). SW – uptake length, Vf – uptake velocity, U – areal uptake. NH₄ and PO₄ represented the background concentrations at the time of sampling.

	Discharge (L/s)	NH ₄ (μ M)	PO ₄ (μ M)	Sw (m)	Vf (m.min ⁻¹)	U (μ M.m ⁻² .min ⁻¹)	
Test 1	Ammonium						
	Undeveloped	35.4	0.98	59.9	10.1	9.9	
	Developed	46.5	0.98	526	0.9	0.9	
	Phosphate						
	Undeveloped	35.4		0.16	200	3	0.5
	Developed	46.5		0.16	434.1	1.1	0.2

Test 2	Ammonium						
	Undeveloped	26.9	1.34	217	2.1	2.9	
	Developed	32.4					
	Phosphate						
	Undeveloped	26.9		0.12	250	1.9	0.2
	Developed	32.4		0.12	500	0.7	0.1

The discussed results focus on the second test as it was found that the initial test could not provide any significant data because of experimental errors. Ammonium uptake was only present within the undeveloped stream sections sampled with an uptake length of 217m (Table 6.1). Within the developed section no ammonium uptake was present – on the contrary, an increase in ammonium was present in the section of the stream. The increase was likely caused by ammonification. A decrease in nitrate associated with the process was not observed as the

standard deviation associated with the nitrate exceeds the increase observed in the ammonium. Mulholland et al. (2008) found that with increasing nitrate availability, biological demand and the overall uptake of nitrogen decreases. Based on a study done, within a similar stream section, by Covino, McGlynn and McNamara (2010), a possible reason for the absence of observed nitrate in the Eerste River was that the uptake length (2534–4140m) for nitrate is much larger than the section sampled in this experiment. Secondly, nitrate uptake was possibly not observed because the nitrogen demand within the stream was saturated by preferential ammonium (Dortch, 1990; Tank, Reisinger and Rosi, 2017).

Phosphate uptake was present in both the developed and undeveloped section of the stream. However, the uptake length in the developed section (500m) was double that of the undeveloped section (250m) (Table 6.1). The uptake velocity and uptake rate in the undeveloped section ($1.9\text{m}\cdot\text{min}^{-1}$, $0.2\mu\text{M}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) was approximately double that of the developed section ($0.7\text{m}\cdot\text{min}^{-1}$, $0.1\mu\text{M}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) (Table 4).

In a study done in Wilson Creek in Kentucky, North America, by Bukaveckas (2007), it was found that the uptake rate and uptake velocity were greatly improved in stream sections that had been restored to a natural state compared to that of channelised sections. This supports the finding from the Eerste River as the restored sections can be compared with the natural section in the Eerste River. Bukaveckas (2007) attributed these differences to an increase in abiotic and biotic activity in natural rivers caused by increased organic matter and longer residence times as stream discharge was decreased. The change in discharge was caused by a change in the river structure, as stagnant pools and meandering were reintroduced into the streams. A decrease in the discharge between developed and undeveloped stream sections was also observed in the analysed reaches of the Eerste River as seen in Table 4, suggesting that the increase in residence time in the undeveloped section might contribute to the observed elevated nutrient uptake. Newcomer Johnson et al. (2016) compiled the work of 79 individual studies from across the world. The study suggested that the average nutrient uptake was increased in streams rich in organic matter, with larger water-bottom surface interaction. The increased nutrient uptake observed in the undeveloped section of the Eerste River support these findings, highlighting the impact of development on the nutrient uptake capacity of streams.

The study done by Newcomer Johnson et al. (2016) suggests that an increase in nutrient uptake was observed for streams that had been restored to a natural state; however, the highest uptake was observed immediately after restoration. Based on the change in the nutrient uptake capacity

from undeveloped to developed stream sections, observed in the Eerste River and the findings of Bukaveckas (2007) and Newcomer Johnson et al. (2016), it is evident that in the case of continuous development and nutrient loading from the agricultural sector, stream restoration will be beneficial. Stream restoration of a restructured stream sections will restore the stream structure to allow for increased residence time of the nutrients as well as increasing the interaction surface. The restoration of riparian vegetation will also increase the amount of organic matter within the stream, allowing for elevated biological activity and sorption (Sabater et al., 2000). This will increase the overall nutrient uptake capacity of the Eerste River, allowing for more positive responses to increased development. As development continues it will also be beneficial if the natural stream structure is preserved.

6.4.2. In-lab flume analysis

The initial experiment provided an understanding of the sensitivity of the system and the internal responses (pH and conductivity) to external factors such as ambient temperature. The experiment was conducted in the hot summer month of November 2017. The ambient temperature and the cooling system of the pump motor increased the water temperature greatly (Figure 6.1d). It could not be mediated due to the temperature control unit not being available at the time. After the system was started and the nutrients were added, the system reached a steady state after approximately 5 hours. The experiment functioned as expected during the first 27 hours, after which the water temperature increased to above 35.9°C. This point initiated a change in several other parameters, including the pH and conductivity of the system. The conductivity suddenly increased from a semi-constant 98 μ S/cm to 104 μ S/cm (Figure 6.1a). At 27 hours the pH responded with an initial decrease from 7.57 to 7.49, after which it increased to 7.64 (Figure 6.1c). So et al. (2016) previously found that an increase in the conductivity might be associated with an increase in ion solubility caused by high water temperatures. The increase in the pH was a response to the increasing conductivity, as newly freed ions bonded with free hydrogen ions in the system. The ORP of the system gradually decreased up to 27 hours after which a sudden decrease in the ORP from 316mV to 306mV was observed (Figure 6.1b). At 35 hours, when the water temperature reached a peak of 38.4°C, the ORP reached a minimum of 300mV. After this point the ORP started to increase again to values as high as 322mV. The initial decrease in the ORP suggests that the oxygen demand of the biofilm was higher than what the system could supply. The biofilm most likely died at around 27 hours,

where the water temperature and the ORP drastically decreased. The increase in conductivity was likely caused by the release of ions as the dead biofilm decomposed.

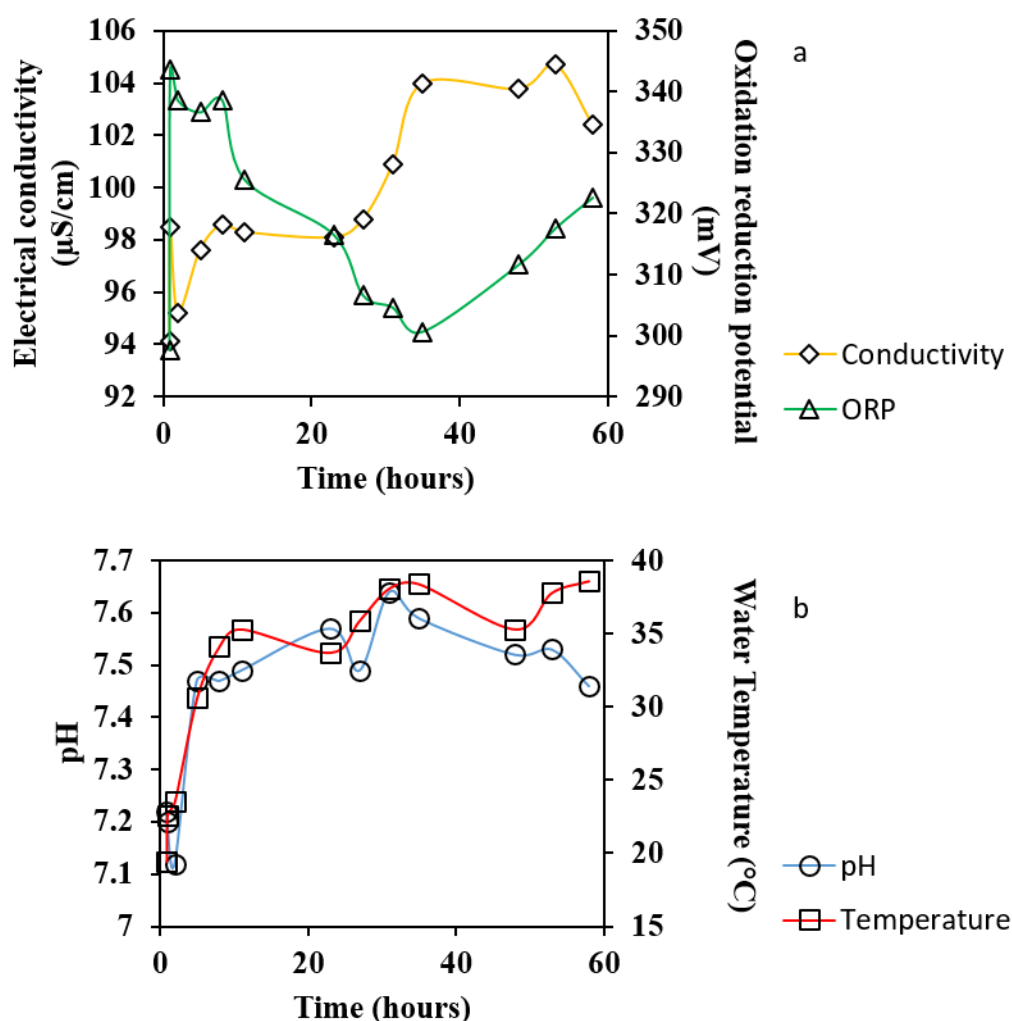


Figure 6.1: a) The electrical conductivity and oxidation reduction potential of the water within the flume during the initial 60-hour experiment. b) The pH and water temperature of the water within the flume during the initial 60-hour experiment.

Ammonium and nitrite also increased greatly after 27 hours (Figure 6.2a). The decomposition of the organic matter possibly caused ammonification (Dodds et al., 2000). This releases organic nitrogen back into the water column as ammonium. The uptake of nitrate vs increase of ammonium was compared to rule out the possibility of nitrate reduction leading to nitrite reduction (Figure 6.2b). This process is highly unlikely and normally takes place within anaerobic conditions. It is evident from this comparison that the uptake of nitrate was not nearly enough to compensate for the increase in ammonium as the process involves a 1:1 ratio between NO_3 and NH_4 . This supports the idea of ammonification because of remineralisation.

Phosphate uptake within the water column was immediate and extensive (Figure 6.2c). Phosphate was almost completely removed out of the water column within the first 5 hours of the experiment. Two possible explanations can be provided for the uptake of phosphate. The first explanation is that the phosphate was adsorbed onto particles within the system, removing it from the water column. Phosphate is readily adsorbed on to charged surfaces such as clay particles or charged mineral surfaces (Bowden et al., 1980) that were likely present at high concentrations in the system. The second explanation is that phosphate was the limiting factor for microbial growth and that the biofilm took up the phosphate as it was introduced into the system. However, because a remineralisation signal was observed after 27 hours yet no change was observed in the phosphate concentration, it was most likely phosphate adsorption that caused the uptake of phosphate in the system. No significant uptake of nitrate was observed although a negative trend was observed. This is similar to the findings of the short-term nutrient release experiment, where nitrate reacted as a conservative ion. Similar to the short-term nutrient addition experiment, nitrate uptake might be slower compared to the uptake of ammonium within these streams as the biofilm favours nitrogen in the ammonium form above the nitrate form (Dortch, 1990). Bromide concentrations within the system were not stable (Figure 6.2c). Because bromide reacts as a conservative ion, the variability of bromide suggests that water mixing within the flume was not optimal and needs to be addressed.

Ultimately, the experiment has proven to be plausible, if the environmental conditions are properly managed. With the temperature control unit installed, the water temperature can be controlled to eliminate biological death due to high water temperatures. Care should be taken to monitor the dissolved oxygen levels and to make sure that sufficient mixing takes place within the system. However, the main aim of examining the effects of water temperature, variable flow velocity and nutrient loading has not yet been achieved.

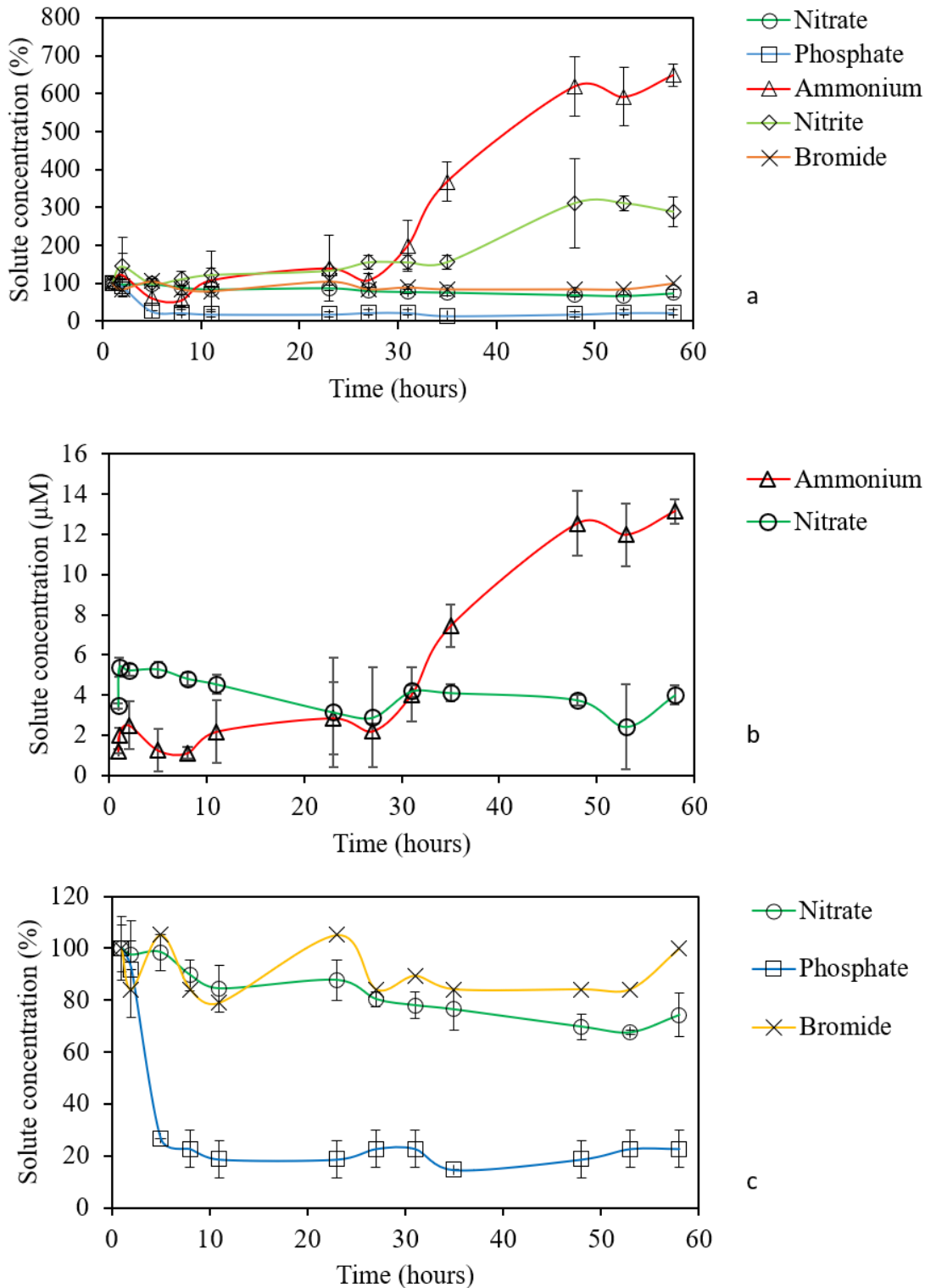


Figure 6.2: a) Nutrient concentration percentages over time based on concentrations after the initial nutrient addition including a conservative bromide tracer. The measured concentrations immediately after the initial addition is referred to as “100%”. Percentage values higher than 100 indicate release of the respective nutrients, and percentage values below 100 indicate removal. b) Nitrate and ammonium concentrations are contrasted in this panel to display potential denitrification. c) Nitrate and Phosphate retention vs the conservative bromide tracer as percentages based on concentrations after the initial nutrient addition.

6.5. Conclusion

Preliminary experimental analysis of nutrient uptake in the Eerste River suggested that the restructuring of the stream might have a negative effect on nutrient uptake in Eerste River stream sections associated with the restructured sections. Thus, great care must be taken to preserve the natural structure of the Eerste River in the process of bank stabilisation, as part of continuous riparian development. Stream restoration will also be beneficial for nutrient uptake at stream sections that have undergone restructuring. The short-term nutrient release results are not conclusive and provide only an early estimate of what can be expected in the case of stream restructuring and continuous development. Further analysis should be conducted within this stream with the focus on quantifying the nutrient uptake within different stream sections under different flow conditions. This should be done over the entirety of the Eerste River within different land-use zones as well as during different seasons.

The in-lab flume experiment proved to be able to recreate a stream environment if the environmental conditions are closely monitored and managed. The preliminary flume experiment provided insight into the effect of water temperature on the benthic biofilm and its capability to take up nutrients as well as the requirements to keep the flume environment stable. Further analysis should be conducted on the nutrient uptake capacity of benthic biofilm under different water flow velocities, water temperatures and nutrient loadings. The flume is currently set up for analysis of parameters. The focus for this project should be to produce benthic biofilm within a controlled environment as described by De Falco et al. (2016).

7. Chapter 7 – Overall Conclusion

Water scarcity has become of great concern in South Africa. According to Botai et al. (2017), the Western Cape is currently experiencing the worst drought since 1904. To secure the water resources of South Africa, great emphasis should be placed on managing the current resources and researching the sustainability of the freshwater systems under constantly changing conditions. The False Bay region located in the Western Cape of South Africa is rich in rivers supporting ecological systems. Understanding the factors impacting these rivers will assist in managing the total freshwater system of the regions.

A six-year monitoring study on the pristine Rooiels Estuary delineated the effects of external environmental factors on the geochemistry of the estuary. The estuary is located on the south eastern side of the False Bay region and is typical of the natural conditions for the region. Monitoring was conducted by undergraduate students from Stellenbosch University. Thus, the parameters monitored in the estuary were limited to parameters that could be measured using handheld probes. The study found that precipitation had a notable effect on the geochemical condition of the estuary. The ocean influence was minimalised during times of high precipitation as freshwater flow increased in the estuary. High precipitation was also associated with lower pH values as humic and fulvic acids associated with the indigenous vegetation flushed into the estuary. Howland et al. (2000) and Grande et al. (2003) found that precipitation had similar effects on estuaries located in Europe. The effect of precipitation on the Rooiels Estuary raised the question of how freshwater systems will be affected if the anthropogenic influence in the region increased.

To delineate the effect of land development in conjunction with seasonal change on the freshwater systems in the False Bay region, a study was done on the rivers located on the eastern side of the False Bay region. The study was conducted during a single seasonal cycle covering the major land-use sectors of the region. The agricultural and industrial sectors notably impacted these rivers. However, the impact of these sectors was linked to seasonal change. Increased surface run-off during the winter season proved to be the primary method of transportation for ions released by these sectors. The same phenomenon was described by De Villiers (2007) in the Berg River, South Africa. De Villiers and Thiart, (2007) found that regions associated with winter rainfall had higher ion concentrations during winter times and

the opposite for summer rainfall regions if the primary source of the ions were diffusive of nature. A strong waste water signal was observed within the Lourens River Estuary. The influence of the waste water source was most prominent during the dry period. During the wet period fresh water from upstream diluted the effect of this waste water point. The effect of land-use in the region is evident in the geochemical condition of these freshwater systems. The freshwater systems did, however indicate some resistance to the inflow of nutrients. Nutrient retention was observed along certain sectors of the sampled rivers. The observed nutrient retention raised the question of what factors control nutrient retention in these freshwater systems.

A short-term nutrient addition test proved that restructuring natural river sections to facilitate development, nutrient retention was greatly impaired in the Eerste River. The extent of the impact is still unclear and the effect of seasonal change has not yet been investigated. Further research should be conducted on the effect of differential nutrient loading and changes in weather factors (e.g. water temperature and flow velocity) on the nutrient retention in these rivers. This should be done in conjunction with further research on the effects of stream reconstruction on nutrient uptake, to accommodate future development.

This project highlighted the impact of anthropogenic land-use practice on the freshwater systems of the False Bay region. Even though the freshwater systems investigated in the project were still in a healthy state, with the exception of the lower Lourens River, the impact of land development in the region should be closely monitored to ensure the health of these systems in the future. With the possible effects of climate change resulting in extreme periodic precipitation events (Mirza, 2003), the effect of surface run-off might be increased resulting in sudden ion loading events. This, coupled with decreasing waste water dilution caused by shorter wet periods, can have devastating effects on the freshwater systems of the False Bay region. Thus, riparian vegetation buffer zones should be increased, waste water inflow into the freshwater systems should be minimalised and river structures should be maintained and restored to ensure a healthy future for the freshwater systems in the False Bay region.

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Appendix A – Study Area

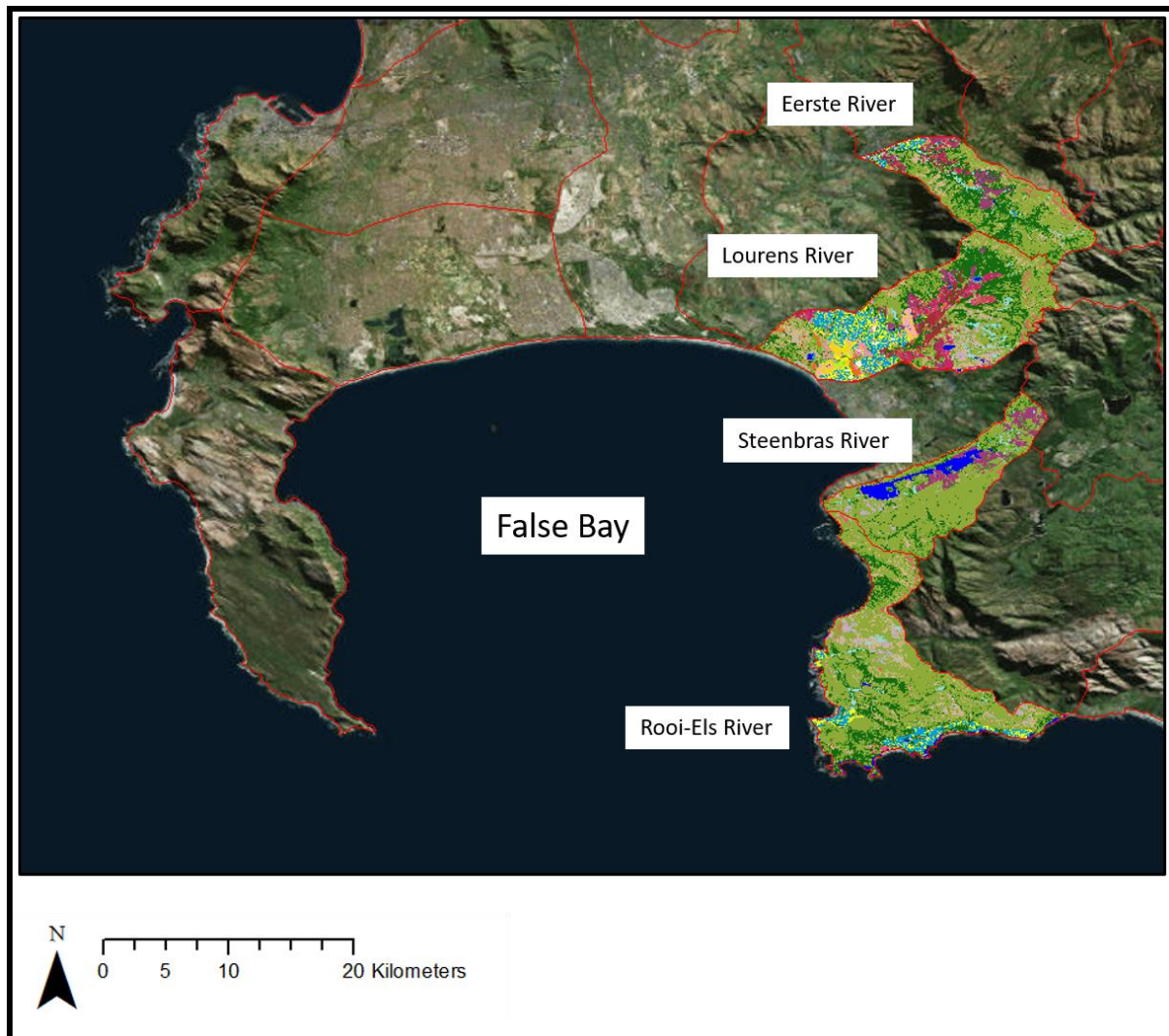


Figure 1: Regional study area including the Rooiels Estuary, Steenbras River, Lourens River and Eerste River.

Table 1: Detailed description of each sampling location for the Steenbras River, Lourens River and Eerste River. The description includes pollution source type, primary land-use characteristics and the geology of the site.

Sampling Location ID	Latitude	Longitude	Primary land-use characteristic	Geology	Primary pollution source
Eerste River 1 (E1)	-33.99378	18.97525	Pristine fynbos	Silicates, Granite	/
Eerste River 2 (E2)	-33.97354	18.93713	Kleinplaas dam	Silicates, Shales and Granite	Point source (dam)
Eerste River 3 (E3)	-33.94047	18.88979	Agricultural lands	Silicates, Shales and Granite	Diffuse source
Eerste River 4 (E4)	-33.94371	18.84452	Urban residential/Industrial	Silicates, Shales and Granite	Diffuse source
Lourens River 1 (L1)	-34.02746	18.96091	Pristine fynbos	Silicates, Granite	/
Lourens River 2 (L3)	-34.07969	18.88446	Agricultural lands	Silicates, Shales and Granite	Diffuse source
Lourens River 3 (L3)	-34.08602	18.86034	Urban residential	Silicates, Shales and Granite	Diffuse source
Lourens River 4 (L4) Estuary	-34.10116	18.81602	Industrial	Silicates, Shales and Granite	Point source (waste water)
Steenbras River 1	-34.19165	18.83598	Pristine fynbos	Silicates	/
Steenbras River 2	-34.19409	18.82623	Pristine fynbos	Silicates	/
Steenbras River 3	-34.19235	18.82243	Pristine fynbos	Silicates	/

Appendix B – Graphs

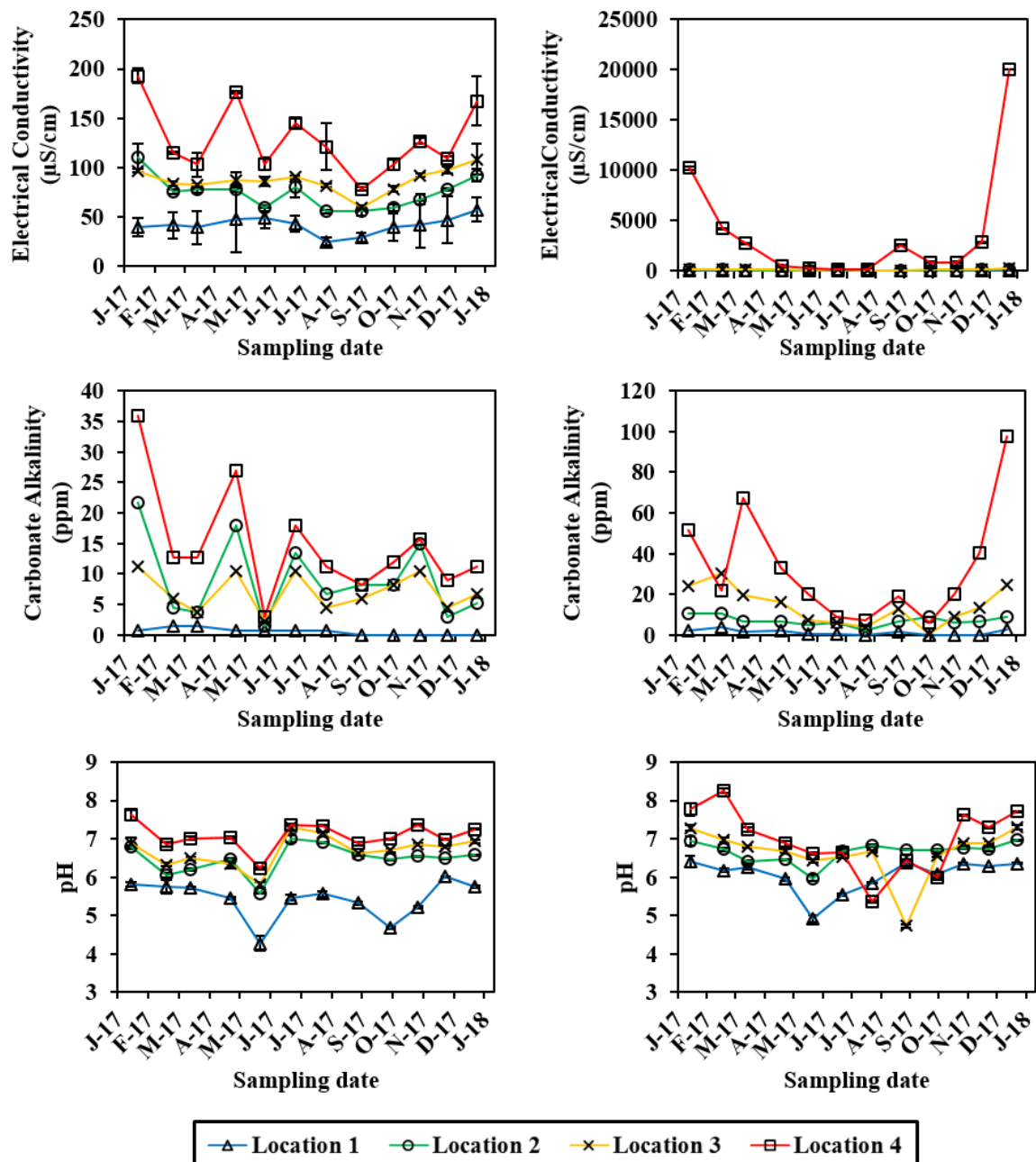


Figure 2: Electrical conductivity, carbonate alkalinity and pH for the Eerste River and Lourens River respectively for the year 2017. a-b) Electrical conductivity for the Eerste River and Lourens River. c-d) Carbonate alkalinity for the Eerste River and Lourens River. e-f) pH for the Eerste River and Lourens River.

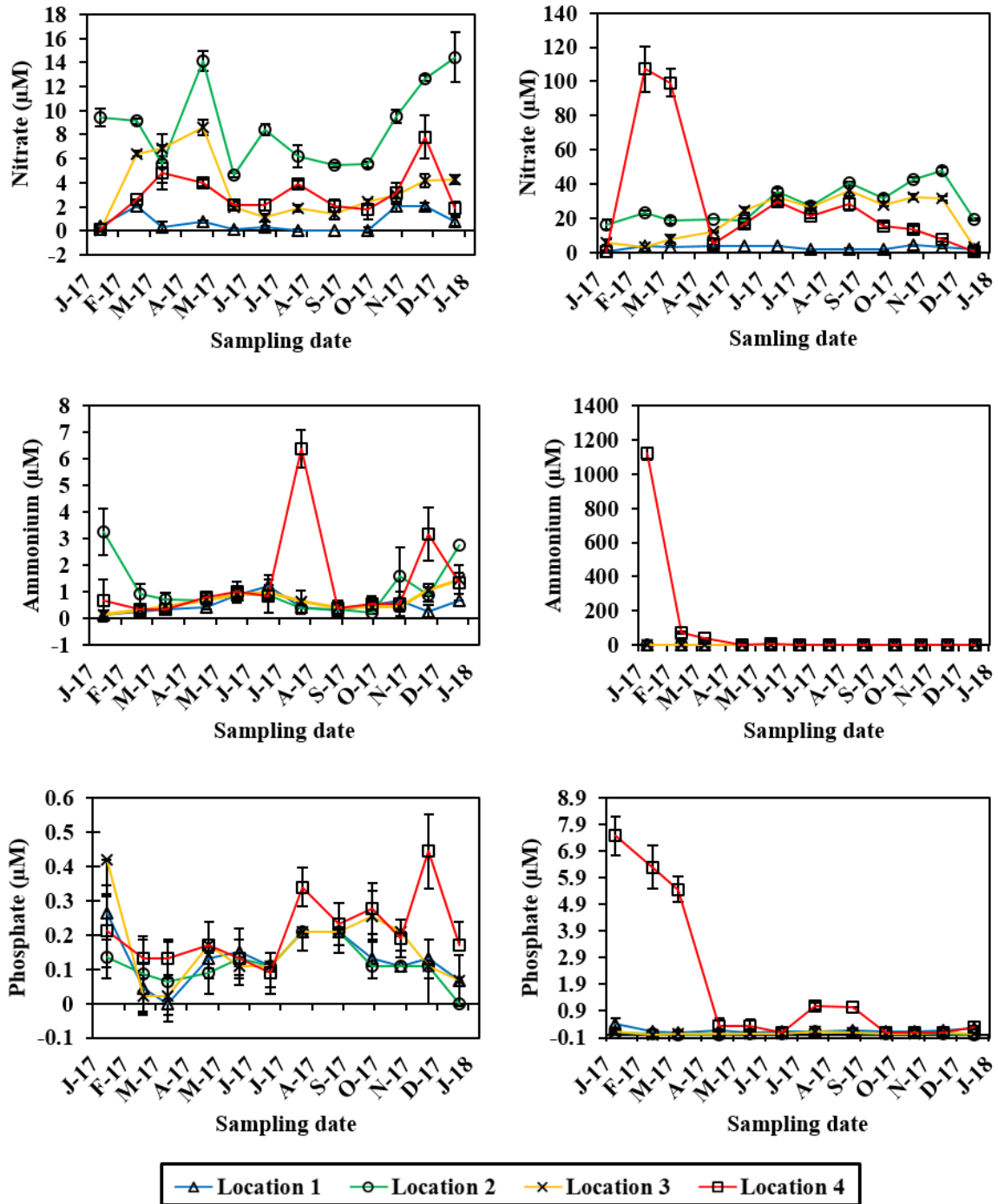


Figure 3: Ca, Mg, Na and K concentrations for the Eerste River and Lourens River respectively for the year 2017. a-b) Ca concentration for the Eerste River and Lourens River. c-d) Mg concentration for the Eerste River and Lourens River. e-f) Na concentration for the Eerste River and Lourens River. g-h) K concentration for the Eerste River and Lourens River.

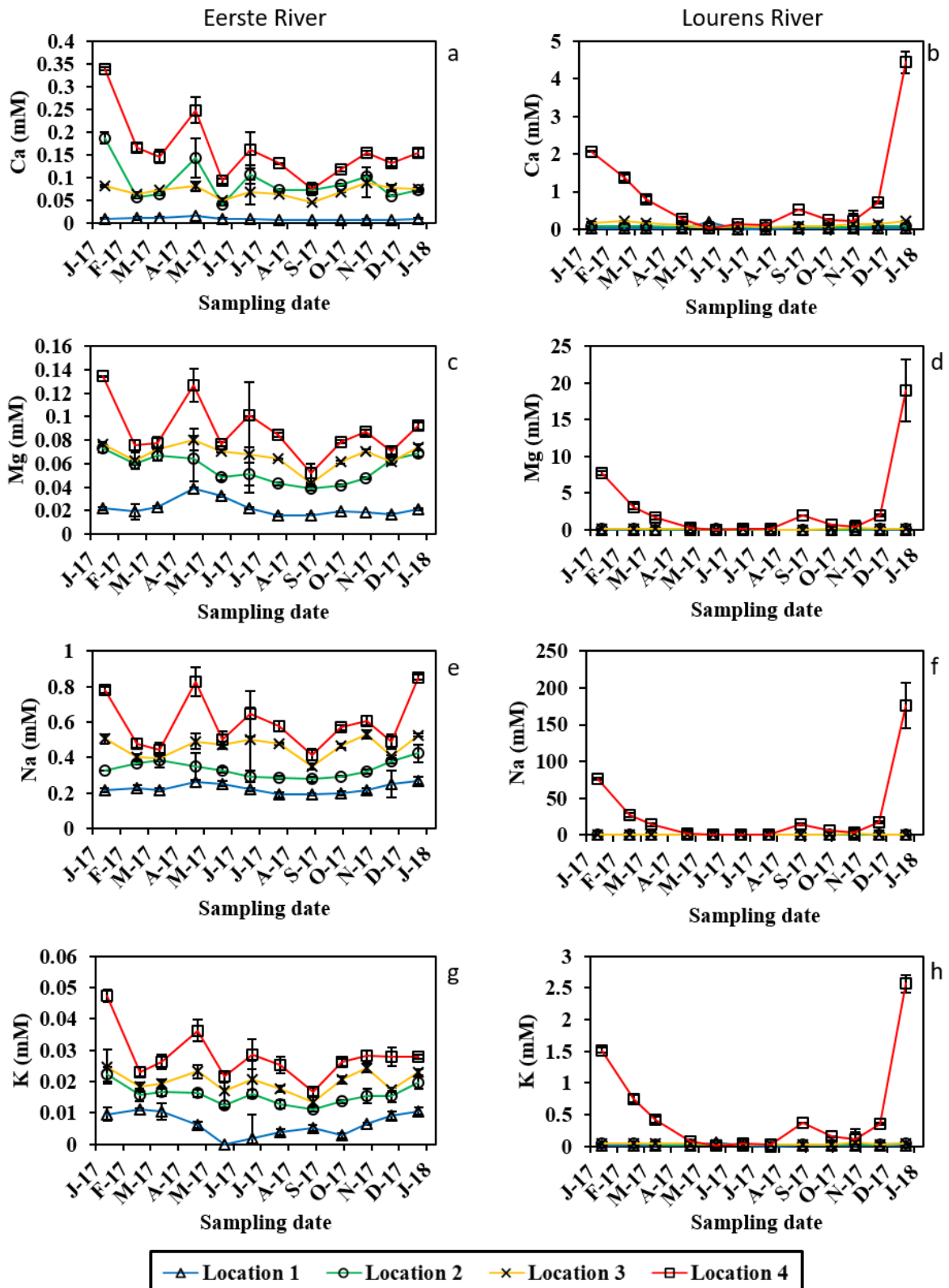


Figure 4: Ammonium, nitrate and phosphate concentrations for the Eerste River and Lourens River respectively for the year 2017. a-b) Ammonium concentration for the Eerste River and Lourens River. c-d) Nitrate concentration for the Eerste River and Lourens River. e-f) Phosphate concentration for the Eerste River and Lourens River.

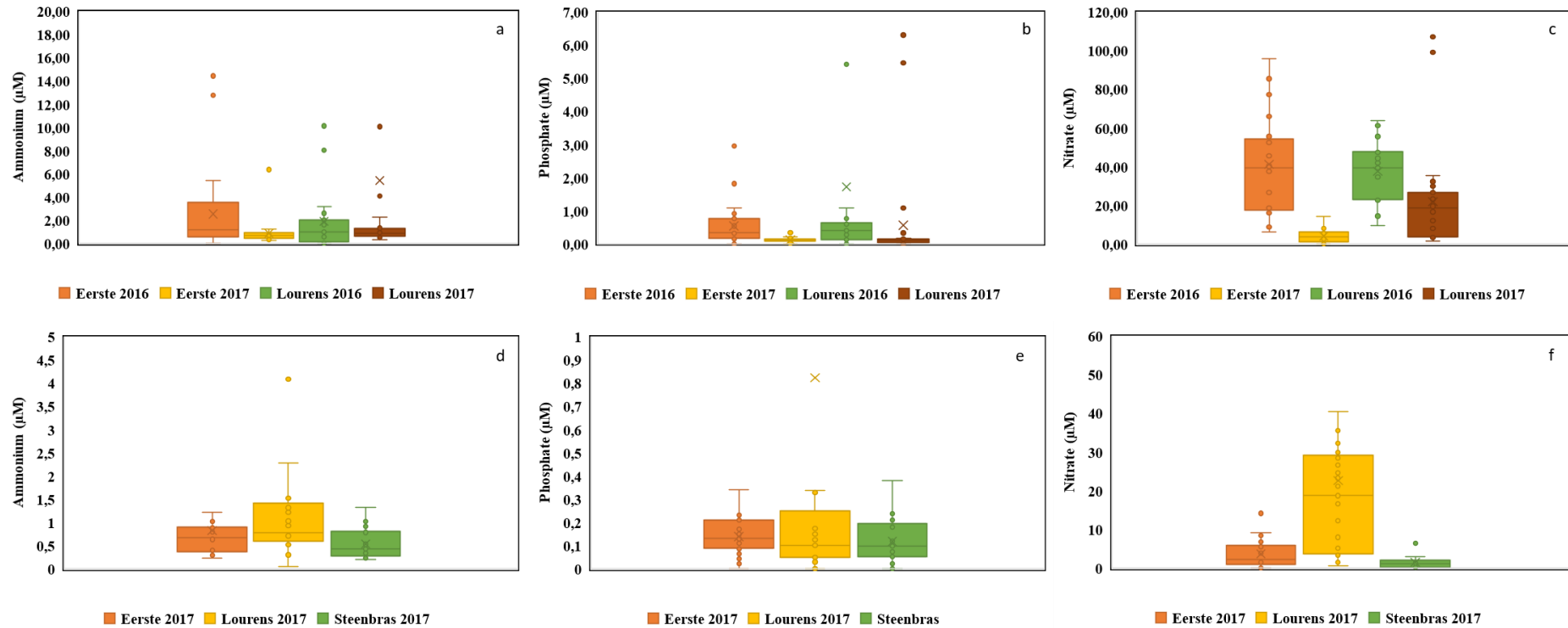


Figure 5: Box plot nutrient comparison for the Lourens River and Eerste River for the months of March to September 2016 and 2017. a) Ammonium comparison between the Lourens River and Eerste River 2016 and 2017. b) Phosphate comparison between the Lourens River and Eerste River 2016 and 2017. c) Nitrate comparison between the Lourens River and Eerste River 2016 and 2017. Box plot nutrient comparison for the Steenbras River, Lourens River and Eerste River for the months of March to September 2017. d) Ammonium comparison between the Steenbras River, Lourens River and Eerste River 2017. e) Phosphate comparison between the Steenbras River, Lourens River and Eerste River 2017. f) Nitrate comparison between the Steenbras River, Lourens River and Eerste River 2017.

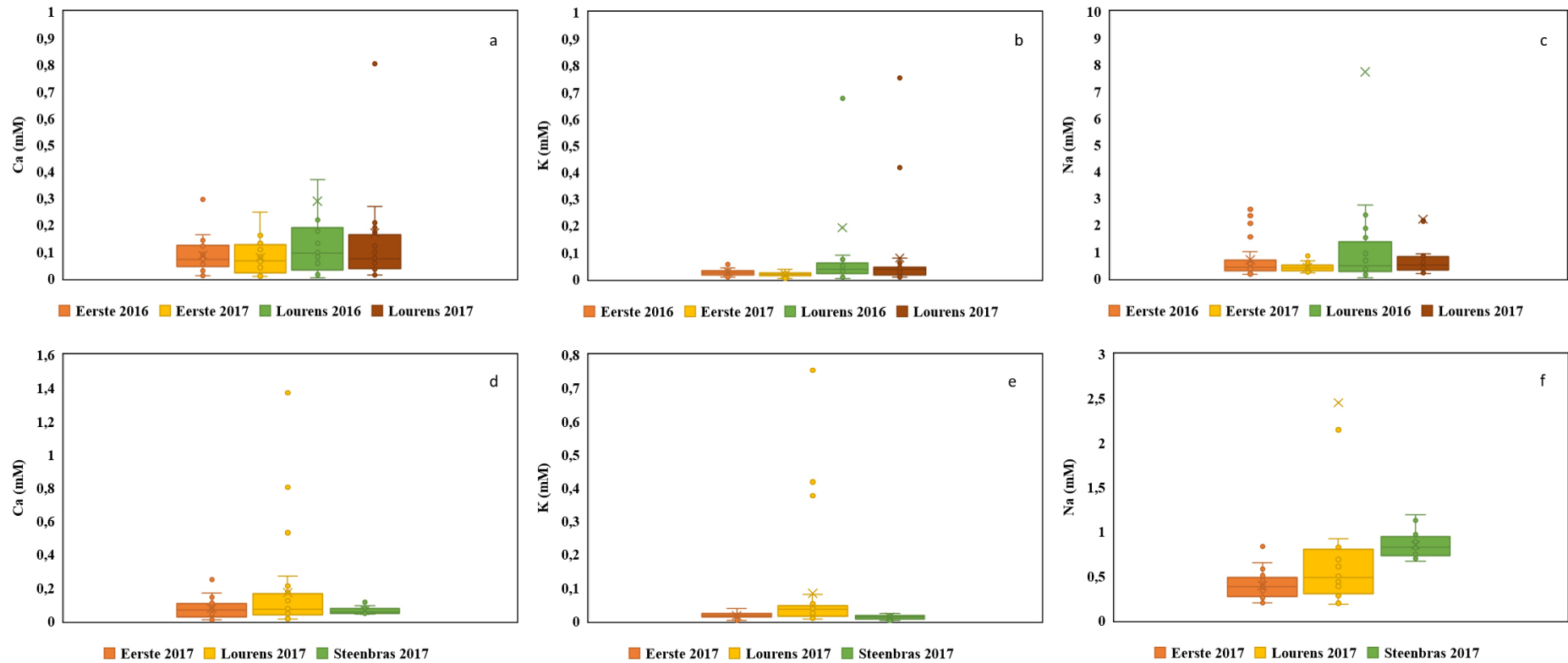


Figure 6: Box plot cation comparison for the Lourens River and Eerste River for the months of March to September 2016 and 2017. a) Calcium comparison between the Lourens River and Eerste River 2016 and 2017. b) Potassium comparison between the Lourens River and Eerste River 2016 and 2017. c) Sodium comparison between the Lourens River and Eerste River 2016 and 2017. Box plot nutrient comparison for the Steenbras River, Lourens River and Eerste River for the months of March to September 2017. d) Calcium comparison between the Steenbras River, Lourens River and Eerste River 2017. e) Potassium comparison between the Steenbras River, Lourens River and Eerste River 2017. f) Sodium comparison between the Steenbras River, Lourens River and Eerste River 2017.

Appendix C – Additional Data

Table 2: Nutrient comparison data for the Eerste River and Lourens River for the months of March to August 2016 and 2017.

Location	Date	Eerste 2016			Eerste 2017			Lourens 2016			Lourens 2017		
		NH4	PO3	NO3	NH4	PO3	NO3	NH4	PO3	NO3	NH4	PO3	NO3
1	Mar	1,18	0,42		0,24	0,04	2,06	0,00	0,00		0,30	0,13	3,50
1	Apr	14,44	0,24	8,87	0,32	0,00	0,35	1,28	0,13		0,52	0,10	3,26
1	May	1,97	0,00		0,44	0,13	0,78	0,60	0,27	23,39	0,60	0,17	3,93
1	June	0,65	0,27	40,32	0,89	0,15	0,10	0,00	0,14	22,58	1,04	0,10	3,90
1	July	0,30	0,00	55,65	1,22	0,11	0,30	2,04	0,00		0,93	0,11	3,57
1	August	3,47	0,00	77,42	0,44	0,21	0,02	0,60	0,32		0,71	0,15	1,54
Average		3,67	0,15	45,56	0,59	0,11	0,60	0,75	0,14	22,98	0,68	0,13	3,29
2	Mar	2,23	0,27	85,48	0,92	0,09	9,13	1,23	0,05		0,60	0,03	23,26
2	Apr	4,02	0,16	18,55	0,71	0,06	5,55	1,13	0,02		1,22	0,00	18,73
2	May	12,76	0,16		0,69	0,09	14,15	3,18	0,20	63,71	0,59	0,01	19,63
2	June	1,07	0,35	6,45	0,91	0,13	4,62	0,15	0,64	34,68	1,03	0,05	18,84
2	July	0,83	0,45	39,52	0,88	0,11	8,43	0,23	0,45	44,35	1,12	0,05	35,51
2	August	0,45	0,55	37,90	0,40	0,21	6,20	0,98	0,64		0,78	0,15	27,04
Average		3,56	0,32	37,58	0,75	0,11	8,01	1,15	0,33	47,58	0,89	0,05	23,83
3	Mar	1,55	0,42	26,61	0,33	0,02	6,43	1,18	0,82		0,60	0,00	3,32
3	Apr	0,55	1,82	16,94	0,45	0,02	6,86	10,13	0,05		0,74	0,03	7,98
3	May	0,97	0,20		0,71	0,17	8,58	2,60	0,24	61,29	1,01	0,06	12,23
3	June	0,60	0,13	95,97	0,92	0,11	1,94	1,58	0,64	39,52	0,76	0,05	24,63
3	July	0,08	2,96	16,13	0,97	0,11	1,11	0,60	0,41	55,65	1,32	0,05	32,35
3	August	0,30	0,95	52,42	0,63	0,21	1,87	0,15	0,77	35,48	0,53	0,15	26,64
Average		0,67	1,08	41,61	0,67	0,11	4,46	2,71	0,49	47,98	0,83	0,06	17,86
4	Mar	1,49	0,27	66,13	0,36	0,13	2,59	8,02	31,47		71,81	6,31	107,25
4	Apr	5,44	0,38	28,23	0,32	0,13	4,80	0,55	5,42		39,58	5,47	99,19
4	May	4,28	0,82		0,79	0,17	3,96	10,49	0,46	9,68	4,09	0,33	5,16
4	June	0,55	0,57		1,02	0,13	2,11	0,00	0,59	14,52	10,07	0,34	16,64
4	July	0,00	0,77	16,13	0,84	0,09	2,16	0,08	1,09	41,94	2,28	0,10	29,90
4	August	1,58	0,91	53,23	6,37	0,34	3,89	0,08	0,77		1,52	1,08	21,21
Average		2,23	0,62	40,93	1,62	0,16	3,25	3,20	6,63	22,04	21,56	2,27	46,56
Total Average		2,53	0,54	41,22	0,91	0,12	4,08	1,95	1,90	37,23	5,99	0,63	22,88

Table 3: Cation comparison data for the Eerste River and Lourens River for the months of March to August 2016 and 2017.

Location	Date	Eerste 2016			Eerste 2017			Lourens 2016			Lourens 2017		
		Ca	K	Na	Ca	K	Na	Ca	K	Na	Ca	K	Na
1	Mar	0,04	0,04	1,56	0,01	0,01	0,23	0,00	0,00	0,00	0,03	0,01	0,19
1	Apr	0,03	0,02	0,55	0,01	0,01	0,22	0,02	0,02	0,23	0,03	0,01	0,22
1	May	0,02	0,01	0,21	0,01	0,01	0,26	0,02	0,01	0,18	0,03	0,01	0,24
1	June	0,01	0,01	0,19	0,01	0,00	0,25	0,02	0,01	0,16	0,19	0,06	0,92
1	July	0,01	0,01	0,16	0,01	0,00	0,22	0,01	0,01	0,13	0,01	0,01	0,22
1	August	0,01	0,01	0,14	0,01	0,00	0,19	0,02	0,01	0,15	0,01	0,01	0,18
Average		0,02	0,01	0,47	0,01	0,01	0,23	0,01	0,01	0,14	0,05	0,02	0,33
2	Mar	0,10	0,05	2,04	0,06	0,02	0,37	0,10	0,07	1,86	0,08	0,04	0,49
2	Apr	0,06	0,02	0,38	0,06	0,02	0,38	0,07	0,04	0,48	0,07	0,04	0,45
2	May	0,05	0,02	0,98	0,14	0,02	0,35	0,06	0,03	0,33	0,06	0,03	0,50
2	June	0,16	0,02	0,30	0,04	0,01	0,33	0,08	0,03	0,38	0,07	0,04	0,48
2	July	0,09	0,01	0,25	0,11	0,02	0,29	0,09	0,04	0,41	0,07	0,03	0,45
2	August	0,05	0,01	0,25	0,07	0,01	0,29	0,08	0,03	0,39	0,04	0,02	0,38
Average		0,08	0,02	0,70	0,08	0,01	0,34	0,08	0,04	0,64	0,07	0,03	0,46
3	Mar	0,10	0,06	2,34	0,06	0,02	0,40	0,37	0,08	2,74	0,21	0,05	0,83
3	Apr	0,06	0,02	0,40	0,07	0,02	0,40	0,17	0,05	0,92	0,17	0,04	0,72
3	May	0,07	0,02	0,37	0,08	0,02	0,49	0,08	0,03	0,42	0,12	0,04	0,68
3	June	0,11	0,03	0,55	0,05	0,02	0,47	0,10	0,03	0,44	0,06	0,04	0,43
3	July	0,06	0,02	0,34	0,07	0,02	0,50	0,13	0,04	0,49	0,08	0,04	0,50
3	August	0,07	0,02	0,39	0,06	0,02	0,48	0,11	0,03	0,48	0,06	0,03	0,42
Average		0,08	0,03	0,73	0,07	0,02	0,46	0,16	0,05	0,92	0,11	0,04	0,60
4	Mar	0,15	0,07	2,58	0,17	0,02	0,48	3,53	3,12	137,45	1,37	0,75	26,63
4	Apr	0,12	0,03	0,47	0,15	0,03	0,45	1,06	0,68	32,54	0,80	0,42	14,33
4	May	0,13	0,03	0,45	0,25	0,04	0,83	0,22	0,09	2,38	0,27	0,08	2,14
4	June	0,30	0,04	0,70	0,09	0,02	0,50	0,22	0,06	1,51	0,02	0,01	0,27
4	July	0,12	0,02	0,41	0,16	0,03	0,65	0,18	0,05	0,66	0,13	0,04	0,82
4	August	0,14	0,03	0,48	0,13	0,03	0,58	0,19	0,04	0,70	0,10	0,03	0,60
Average		0,16	0,04	0,85	0,16	0,03	0,58	0,90	0,67	29,21	0,45	0,22	7,47
Total Average		0,09	0,03	0,69	0,08	0,02	0,40	0,29	0,19	7,73	0,17	0,08	2,21