Impact of Storm Events on the Transport of Solutes and Macronutrients in Mountainous Catchments under Contrasting Land Uses at the Cathedral Peak Research Site, Drakensberg

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Contents

DECLARATION

I declare that this Dissertation is my own, unaided work. It is being submitted for the Master of Science within the School of Geography, Archaeology and Environmental Studies at the University of the Witwatersrand, Johannesburg under the supervision of Dr C.J. Curtis.

This declaration is to certify that the work reported is the Master of Science is my own original and unaided work, unless where specific acknowledgement has been made.

Signed by Aobakwe Lenkwe 464517 Date

ABSTRACT

Streamwater chemistry is influenced by several factors that include: geology, soil-geology interactions, land use, climate change, topography, vegetation, mechanical and chemical weathering. The dominance of these factors when determining the chemistry of streamwater varies from one situation to the other. Four different catchments in the Drakensberg were monitored to identify the processes determining temporal and seasonal patterns in streamwater chemistry. The land uses of the catchment include: CP03 (previously afforested, degraded), CP04 (pristine grasslands), CP06 (pristine grasslands) and CP09 (protection from fire). All the catchments were investigated for differences in major ion concentrations, streamwater temperatures, dissolved organic carbon (DOC), dissolved oxygen, pH, conductivity. There were comparisons made between historical and recent data collected at the Cathedral Peak Research Site. Comparisons were made between CP03 and CP06 to identify effects of storm events on streamwater chemistry. CP03 and CP09 had significant statistical differences in terms of major ions. Land use and stormflow path ways were most influential in determining the streamwater chemistry across catchments.

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ABBREVIATIONS

APES	Animal, Plant and Environmental Sciences
CPRS	Cathedral Peak Research Site
DOC	Dissolved organic carbon
DO	Dissolved oxygen
NPOC	Non-Purgeable Organic Carbon
POC	Particulate organic carbon
SAEON	South African Environmental Observation Network
SAFRI	South African Forestry Research Institute
TDS	Total dissolved solids
TSS	Total suspended solids

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

Overview

> *This chapter provides a brief background on work that has been done concerning the relationship between land use and climate change; the water cycle globally. It also outlines the rationale of the study and the accompanying aims and objectives.*

1.1 Background

One of the scarcest resources in South Africa, with the potential to limit economic development is freshwater (Blignaut and Van Heerden 2009). This is the issue the nation faces even before considering the effects of climate change. The sources of South African freshwater resources include: surface water (77%), return flows (14%) and groundwater (9%) (Maserumule 2010). Since water plays a major role in the growth potential and development of South Africa, wise management of water resources to ensure sustainable growth and resiliency should be integrated across all sectors (Maserumule 2010).

Mountains are of particular importance for the management of water quality and quantity and are often referred to as natural water towers (Nel *et al.* 2013). This is because of the essential and relatively higher volume of freshwater they supply to the lowlands. The discharge that builds up in these mountains is transported along headwater streams and is used further downstream (Lowe and Likens 2005, Viviroli and Weingartner 2008). In South Africa, the Drakensberg mountain range is considered a key water tower and is a strategic water resource area (Nel *et al.* 2013).

There are important relationships between land use and naturally occurring processes that influence stream chemistry. These processes include sedimentation, erosion, wind and rainfall – amount and intensity (Christophersen *et al.* 1990, Harvey and Bencala 1993, White and Blum 1995, Ahearn *et al.* 2004, Fraterrigo and Downing 2008, Park *et al.* 2011, Lee *et al.* 2013). The transporting of materials by rivers has been considered in geochemical budgets for many years (Beck *et al.* 1974, Sholkovitz 1976, Schlesinger and Melack 1981, Hedges *et al.* 1986). This is because the materials being transported give information about the natural processes acting in and around the water body (Meybeck 1982). Many studies have thus used geochemical budgets to give an idea how elaborate the processes acting on water bodies are (Bond 1979).

Human induced changes in climate – rainfall patterns, the occurrence of low and high flows and land use may thus result in changes in the water cycle and consequently impact streamwater discharge and chemistry – quality. Stresses on water resources have indeed increased over the past several decades. For example, there is an increase in the risk of pollution of water resources (Ometo *et al.* 2000, Erol and Randhir 2013). Interest in stream water chemistry studies has largely focused on the effects of land use on water quality and aquatic communities (McDiffett 1993, Fraterrigo and Downing 2008). However, at the global scale, there is a general consensus that human induced climate change is a reality (IPCC 2014) but not much is known about the effect of this change on the water cycle and projections become less and less reliable as we move from the global, to the regional then local scales (Kruger 2006, Maserumule 2010, Davies 2011). In South Africa particularly, there is a knowledge gap in understanding the relationship between climate change, streamflow discharge and streamwater chemistry as well as the interactions of these with land use. This uncertainty keeps water managers from effectively planning or making decisions at the regional and local scales.

Human induced climate change is largely the result of increases in greenhouse gases, particularly CO_2 (Le Quéré *et al.* 2015), which has influenced the carbon cycle. Climate change and land use have an impact on each other. One of the ways in which climate change is expressed is through changes in land cover patterns (Dale 1997, Maserumule 2010), in turn, land use and land cover change can have an impact on the carbon cycle and consequently back on climate. The effects of temporal and spatial variation in both land use and rainfall are factors which are often neglected when considering biogeochemical cycles (Allan *et al.* 1997, Mouri *et al.* 2011, Tu 2013, Mattsson *et al.* 2015).

Major drivers of mountain catchment water chemistry include: land use practices, bedrock mineralogy, weathering processes, hydrological flow paths, fluctuations in discharge, variations between the wet and dry seasons, vegetation type, topography and acid deposition (Goldstein *et al.* 1987, Sueker *et al.* 2001, Mast *et al.* 2011).

Global-scale changes in climate and atmospheric CO_2 will potentially have significant impacts on carbon cycling (Evans *et al.* 2006) and many countries in the Northern Hemisphere are already experiencing the direct effect of elevated CO_2 through increases in dissolved organic carbon (DOC) in streams (Worrall *et al.* 2004, Evans, Chapman, *et al.* 2006, Clark *et al.* 2010, Monteith *et al.* 2015). Indirect effects of increased CO_2 through climate change, in altering rainfall pattern and intensity, are also likely a impact on streamflow chemistry. For example, the intensity of storm flow events may change, consequently altering streamflow chemistry.

This study was aimed at improving the understanding of the links between land use and land use history, rainfall effects and stream chemistry in a key water source area in South Africa. It focused on the assessing the effects of storm events on streamwater chemistry across three land uses. Although several studies have been done in this regard, especially in the Northern Hemisphere, not much research has been done in the Southern Hemisphere, or in South Africa. This study was carried out at the Cathedral Peak Research Site, which is in the Southern Drakensberg region as shown in **Figure 1**. The site consists of fifteen historic research catchments with differing land uses, which made it possible for a study across varying land uses. The catchments included for this study were CP03 (afforested in 1959), CP04 and CP06 (both receiving biennial spring burns) and; CP09 (protection from fire) as shown in **Figure 2**.

1.2 Aims and objectives

The first aim of this study was to investigate the impact of storm events on catchment solute and macronutrient concentrations. The second aim was to determine whether land use history and management lead to differing responses between catchments. It was possible to make these comparisons because of the similarities in the geology, slope and elevations. A third aim was to explore cost effective monitoring tools for assessing dissolved organic carbon in streams.

The objectives are as follows:

- To identify patterns of seasonal change in solute concentrations and compare results between the catchments.

- To identify the changes to macronutrient concentrations that occur during storm events and compare catchments.
- To investigate whether there is a correlation between the colour of the sample water and dissolved organic carbon (DOC) and to explore a simpler method of ascertaining DOC concentrations using UV light.

CHAPTER 2: LITERATURE REVIEW

Overview

This chapter provides a description of headwater streams and factors influencing the chemistry of streams. It also provides insight into the temporal and spatial controls on stream chemistry. It gives more insight into the sources, transport and controls of dissolved organic carbon (DOC), debates around the influence of climate, land use and acid deposition on DOC and the use of absorbance as a measure of DOC.

2.1 The importance of headwater streams

Streams and rivers form part of networks, these networks are reflective of the branching patterns of trees. These networks begin in areas where overland flow converges to form visible channels which are called headwater or first order streams (Lowe and Likens 2005). Head waters in high altitude mountainous catchments often receive a greater amount of rainfall than those further downhill and are thus important for providing recharge of downstream rivers (Scott 1993). The sound management of both water quality and quantity from such systems is of vital economic importance, particularly in a water scarce country such as South Africa (Blignaut and Van Heerden 2009).

Headwater systems are characterised by strong interactions between hydrological, geomorphic and biological processes (Lowe and Likens 2005). These processes differ from stream, channel to channel and terrestrial to aquatic environments (Gomi *et al.* 2002). Some of the services provided by headwater streams include: sediment export regulation, nutrient retention, organic matter processing, maintenance of natural discharge, processing of terrestrial organic matter and the establishment of a chemical signature for water quality in the landscape (Lowe and Likens 2005, Meyer *et al.* 2007). However, the relationship between headwater and downstream systems was previously poorly understood (Hewlett and Hibbert 1967) and as a consequence the roles of the headwater systems were typically underestimated.

More recently the importance of head water streams in influencing lowland streams, including influences on stream chemistry, has been demonstrated (Alexander *et al.* 2007). It is therefore important to understand the inherent chemistry of upland steams, as well as how land use and climate change may impact on this, to understand potential impacts on and how to protect downstream ecosystems (Gomi *et al.* 2002).

Historical studies of the physical and chemical characteristics of catchments concentrated on the influence of geomorphic characteristics such as drainage area, gradient, stream order, turbidity, dissolved oxygen concentration and temperature. More recently, research efforts focused on understanding the elemental dynamics of quantifying diffuse sources of pollutants in catchments (McDiffett *et al.* 1989, Johnson *et al.* 1997). Some, for example Bond (1979), had attempted to identify the presence of patterns or trends in the dynamics of nutrient concentrations related to seasonal changes in stream discharge. Significant attention has been given to the effect of land use on water chemistry. There are a number of factors that influence the export of macronutrients and solutes, these include: land use, discharge pattern, total annual runoff and varying concentration discharge relationships (Huntington *et al.* 1994, Süß 2006). A review of the influences of head water streams on downstream systems has illustrated the value of combining hydrological characteristics with biogeochemical processes of head waters to assess their influences on downstream water quality and quantity, as tool for enabling sound water resources management (Alexander *et al.* 2007).

2.2 What Influences on headwater stream chemistry?

It is essential to know what the drivers of headwater quality and flow conditions are because the information is essential to water management. An improved understanding of the influences of headwaters is a central need to assist policy makers and regulatory authorities (Alexander *et al.* 2007). There is an intrinsic connection between headwaters and solutes in watersheds and streams. Natural processes happening at the catchment scale define the overall supply of elements to a stream and furthermore, provide the framework within which other processes operate (Johnson *et al.* 1997).

The chemistry of headwaters is influenced by several natural factors as well as anthropogenic impacts. These include geology, topography, climate, mechanical and chemical weathering, rainfall rates, rainfall chemistry, vegetation, land use and climate change (Alexander *et al.* 2007, Andersson and Nyberg 2009) soil erosion and anthropogenic effects (Hassan *et al.* 2015).

2.2.1 Component interactions

Rain water composition is assembled through the scavenging of soluble components from the atmosphere (Wang and Han 2011). Rainfall interacts with soil and vegetation. Soil composition dictates the movement of throughfall, whether it is by absolute infiltration or in a form of infiltration excess, subsurface stormflow or saturation excess overland flow (La Torre Torres *et al.* 2011). The drainage ability of a landscape is determined by the combined effects of soil; and vegetation types (Zanchi *et al.* 2015). In areas where infiltration capacity of surface soils is high, overland flow is minimal (Mulholland 1992, 1993, Johnson *et al.* 1997, Chessman and Townsend 2010). Groundwater does not exist in isolation from surface water, both interact in a variety of physiographic and climate landscapes (Sophocleous 2002). There are also interactions between rocks and groundwater, which adds complexity (Kalbus *et al.* 2006, Mondal *et al.* 2010). The water can also pick up suspended particles and dissolved components of rocks, influencing the composition of water. As a consequence, streamwater composition is in part ,a reflection of the geology of the area with which it has had contact (Colorado Geological Survey 2000). In addition, the streamwater chemistry is regulated by several complex instream processes operating over a range of spatial and temporal scales (Johnson *et al.* 1997), that can strongly influence stream water nutrient concentrations. These concepts are expanded in the sections below.

2.3 Natural influences on stream chemistry

2.3.1 Geology

Geology is known to influence streamwater chemistry (Colorado Geological Survey 2000, Chessman and Townsend 2010). Examples of the importance of geology are of: how the weathering of parent material is considered to be an important source of P (Mulholland and Hill 1997), the dominance of an acidic bedrock can result in acid sensitive streamwater which also has a low content of dissolved substances and how upslope soil and bedrock processes influence streamwater chemistry (Mulholland 1992).

2.3.2 Topography

Topography is a physical expression of not only geology but the geological history of an area (Wade 1935). Allan *et al.* (1997) referred to catchments as topographically and hydrologically defined units. The effect of topography is important because it governs how long subsurface water is in contact with bedrock. Steep slopes have increased runoff and decreased contact time with the bedrock because of the gradient of the slope, in contrast, wetlands can intercept more runoff and decrease the velocity of the water (Geen *et al.* 2015). Other factors that topography influences include: soil water content, flow paths residence times and the chemical composition of surface waters (Andersson and Nyberg 2009). Variability in water chemistry could be caused by differences in the structure of the catchment. These structural differences are capable of affecting the ability of surface water and groundwater to convey materials (Mulholland 2004, Lewis and Grimm 2007, Fraterrigo and Downing 2008).

2.3.3 Vegetation

Vegetation type is one of the factors that affect catchment hydrology and has an influence on surface hydrological processes. The extent and type of vegetation can have complex effects on chemical weathering rates and therefore impacting streamwater chemistry (White and Blum 1995). Vegetation affects catchment hydrology through changing surface energy balance and evapotranspiration. Vegetation can either increase or decrease streamflow through their influence on the magnitude of evaporation, infiltration rates and water yields (Zhang *et al.* 2011). Studies have shown that vegetation is important because it retains nutrient inputs and also minimises nutrient losses to the streams (Mulholland and Hill 1997). Vegetation can also influence both the physical habitat of streams through providing shade and the chemical composition of streamwater. This is because overhanging vegetation can change the temperature of streams which directly impacts the biological processes acting in the water body (Merbold *et al.* 2009).

A number of studies have reported that vegetated areas have a positive contribution to water quality (Tong and Chen 2002, Bu *et al.* 2014). The processes govern these contributions vary between vegetation types, however they include: the supply of organic matter to soils, modification of water movement and the stabilisation of soil. All these have an influence on the quality of streamwater (Dosskey *et al.* 2010).

2.4 Rainfall, hydrology and streamwater chemistry

Residence time refers to the amount of time that the particles of a fluid spend in a controlled volume. It has an impact on the concentrations of solutes and the concentrations will therefore vary with residence time (Edwards 1973, Holloway and Dahlgren 2001). The solutes that are commonly used to analyse the effects of residence times include: calcium (Ca^{2+}), sodium (Na^{+}), potassium (K^{+}), magnesium (Mg^{2+}), chloride (Cl^{-}), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and nitrate (NO_3^{-}). Changes in water chemistry are also a function of the availability of solutes and nutrients and their ability to be transported (Mulholland and Hill 1997, Mulholland 2004, Lewis and Grimm 2007, Fraterrigo and Downing 2008). For example, the nutrient dynamics, terrestrial inputs and processes of instream retention and transformation, were found to be significant in explaining why there is a strong seasonality in stream N, phosphorus (P) and DOC concentrations in the West Fork of Walker Branch study in eastern Tennessee (Mulholland 1993, Mulholland and Hill 1997). These processes of retention and transformation can end in the transformation of nutrients which are being transported downstream from inorganic to dissolved organic or particulate forms (Mulholland 1992, Allan *et al.* 1997). There has been a lot of interest around the regulation of P through processes occurring in the riparian zone, this is because excessive phosphorus in waterbodies can result in eutrophication (Dillon and Kirchner 1975, Mulholland 1992).

In a study of the temporal dynamics of streamwater chemistry, nitrate (NO_3^{-}) and sulfate (SO_4^{2-}) concentrations were positively correlated with discharge (Edwards 1973, Rice and Bricker 1995, Ahearn *et al.* 2004). In contrast, Lambert et al. (2014) found that there was an inverse correlation between NO_3^{-} and SO_4^{2-}; and discharge. Results from long-term monitoring programmes have shown that sulfate and phosphate concentrations tend to display seasonality and increased during winter and spring (Hirsh *et al.* 1982, Huntington *et al.* 1994). Another seasonal pattern was observed in the monitoring of the Bospoort Dam, in Rustenburg, North West Province, where phosphate concentrations increased during autumn (Mogakabe and van Ginkel 2008).

Hydrological processes occurring within streams are the drivers behind streamwater chemistry cycles (Ávila *et al.* 1992). There are variations in water quality over space and seasons (Pratt and Chang 2012). Spatial-scale patterns are commonly disturbed by seasonal trends (Buck *et al.* 2004). These processes are capable of both increasing or reducing solute and nutrient concentrations (Mulholland 2004). Discharge varies seasonally (Mulholland 1992), the peak and volume of storm water discharge increases in proportion to increases in rainfall intensities (Hewlett *et al.* 1977).

The distinct patterns in streamwater solutes and macronutrient concentrations can be broken down into: baseflow, stormflow and meltflow (Mouri *et al.* 2011, Mattsson *et al.* 2015). For the purpose of this study, only the baseflow and stormflow was considered, this was because meltflow was a very minor component. Jordan et al. (1997) and Smakhtin (2001) suggested that in the absence of recharge, baseflow is an integral constituent of streamflow with sources such as subsoil water and or shallow subsurface storages. Baseflow water is relatively rich in solutes (Edwards 1973), the nutrient concentrations found in baseflow water can contribute to in-stream biological processes (Mulholland 1992).

During the dry season, streamflow discharge can comprise entirely of baseflow whilst the stormflow discharge is made of both baseflow and stormflow. During the wet season, streamflow predominantly consists of stormflow (Smakhtin 2001, Ahearn *et al.* 2004, Shu and Villholth 2012).

2.5 Stormflows in depth

Baseflow is diluted by stormflow due to increased water volume, which decreases the residence times of the solutes in streams, increasing flow rate which results in shorter reaction periods for solutes (Edwards 1973). As water is discharged, it affects the concentration of solutes. An inverse relationship has been commonly recorded in a large number of studies (Edwards 1973, Mulholland and Hill 1997). The relationship remains one of inverse nature if all other factors acting on the stream are constant. It has been contended that it is possible to use water velocity as an independent variable instead of discharge. This is because the channel characteristics accommodate the changes in discharge (Edwards 1973). Flushing and dilution make up two chemically distinct components of stormflow. The flushing is the period when the first large storm rinses out the solutes that have built up on land during the dry season (Piñol *et al.* 1992). Discharge has been found to be positively correlated to solute concentrations during this period. The dilution occurs in the period after the first large storm. In this period it has been found that discharge is negatively correlated to solute concentrations (Smakhtin 2001, Ahearn *et al.* 2004, Lambert *et al.* 2014). Due to the unique associated streamwater chemistries, it is vital to draw differences between these periods (Ahearn *et al.* 2004).

Ahearn *et al.* (2004) attributed streamwater chemistry variability during the stormflow season to the fact that rainfall gets drained through a highly variable landscape before it makes it into the waterways. The impact of stormflow on streamwater chemistry is important (McDiffett 1993), because the relationship between precipitation and runoff can be used to evaluate climatic effects on solute chemistry (White and Blum 1995).

The presence of these cycles is evidence that streamwater chemistry is variable on a temporal scale and it is essential to understand these processes especially with the threat of climate change (Ávila *et al.* 1992). Yu *et al.* (2015) strongly argued that it was imperative to consider seasonal variation when studying the influence that land use has on streamwater chemistry.

2.5.1 Flow paths

. Hydrologic flow paths play a major role in the determination of water chemistry and in regulating biological communities in headwater streams (Gomi *et al.* 2002, Collins *et al.* 2007). This is because storms hydrologically link the land with waterways. This leads to an increased variation in streamwater chemistry during the stormflow season (Meybeck 1982, Ahearn *et al.* 2004, Mouri *et al.* 2011). Cerro *et al.* (2014) asserted that flow paths that are most dominant during storm events are predominantly responsible for the resulting streamwater chemistry. This means that flow paths dictate the chemistry of the streamwater, both during and after the storm events. Concentrations of solutes, nutrients and DOC will differ depending on flow paths (Elsenbeer *et al.* 1995, Mulholland and Hill 1997). Flow paths, along with residence time, have an impact on the behaviour of solutes and macronutrients (Ávila *et al.* 1992). This is because the residence time of water controls solute and macronutrient concentrations and when accompanied by lengthened transporting this favours the accumulation of more solutes (Maher 2011, Lambert *et al.* 2015). As a consequence, flow path lengths tend to bias solute and macronutrient concentrations (Moulton *et al.* 2000). Variations in water chemistry from one flow path to another can be accounted for through total dissolved solids (TDS) and total suspended solids (TSS). This is because total dissolved and suspended solids vary with time during storm events (Augustijn *et al.* 2011).

The concentration of dissolved solids within a catchment is strongly influenced by both the intensity and frequency of rainfall (Britton *et al.* 1993). It is important to understand how flow paths change during storm events in order to better predict changes in streamwater chemistry (Mulholland 1993). Although there is still much uncertainty about the paths water follows from the point it hits the land and then reappears as streamflow, the manner in which streamflow responds to rainfall events is strongly influenced by flow paths (Mulholland 1993). It is possible for variation to exist both between catchments and temporally within catchments and this is one of the drivers of variation in major ion chemistry in streams (Rice and Bricker 1995, Mulholland and Hill 1997).

Rivers and streams play a central role in regulating the concentrations and forms of nutrients that are exported downstream (Mulholland 2004, Ensign and Doyle 2006). Patterns of nutrient fluxes seem to be mostly controlled by the magnitude of stream discharge and relative contributions of groundwater, overland and interflows (Bond 1979). During rainfall events a rising water table can flush the soil of nutrients (Inamdar and Mitchell 2006), whilst high leaf litter can result in increased nutrient concentration and low flow can result in dilution (Anderson *et al.* 1997). Nutrient export patterns are an expression of near-surface and deep groundwater flow paths, as a function of topography (Collins *et al.* 2007) and the manner in which stormflow responds to intense rainfall depends on storage capacity and the length of flow paths (Gomi *et al.* 2002).

2.6 Biological activity and its influence on streamwater chemistry

Andersson and Nyberg (2009) suggested that biological activity in streams is at its lowest during summer in low flow situations, in Swedish boreal catchments. There are a number of factors that determine the amount of biological activity happening in streams; these include: nutrient availability, hydrodynamics, grazing, temperature, turbidity, riparian shading, bacterial activity, remineralisation of organic material and human impacts (Dodds and Welch 2000, Lu *et al.* 2013). A very important question that has been asked by numerous researchers is about how nutrient concentrations in headwater streams are controlled, this is because these processes are important in terms of stream productivity (Buell and Peters 1988, Mulholland 1992, Mulholland and Hill 1997, Andersson and Nyberg 2009)

2.7 Scales of influence

Mulholland and Hill (1997) argued that catchment processes can be used to explain most of the variability in streamwater chemistry at West Fork of Walker Branch and White Oak Creek, whilst Andersson and Nyberg (2009) suggested that there are landscape factors which are important for the development of streamwater chemistry. Mulholland (2004) argued that the assumption that processes in or near a stream hardly influence water chemistry should be challenged. This is because these processes can have substantial effects on concentrations and fluxes of nutrients in streamwater. This view is supported because viewing such complex relationships in isolation distracts from what is being investigated. For example, aquatic vegetation uses up the nutrients that are found in streamwater. The processes that the plants use to extract the nutrients changes the chemistry of the water and the by-products from the use of the nutrients will have further influence on the water chemistry.

It has strongly been argued that the processes that occur in riparian zones are the most important and they mostly depend on the level of flow (Allan *et al.* 1997, Andersson and Nyberg 2009). It has been further suggested that riparian land use/management practices dictate streamwater chemistry and ecology. And for that reason when considering the effect of land use on streamwater chemistry, the riparian land use is more important than the broader catchment land use (Allan *et al.* 1997). Riparian soils are important contributors of dissolved organic matter during storms. A large number of anaerobic processes happen in the riparian soils (Mulholland *et al.* 1997).

2.8 Impact of burning on stream chemistry

2.8.1 Fire is a natural part of mesic South African grasslands

Although the effects of burning can be short-lived, the burning of biomass can cause hydrochemical changes in soil water, groundwater and surface waters. This could result in the liberation or leaching of nutrients which are being stored in the vegetation above the ground and an increase in surface runoff and erosion, which would cause elevated exports of solids and solutes (Lindell *et al.* 2010). In the long-term, these changes can cause alterations in the way ecosystems look and function.

2.9 Anthropogenic influences on streamwater chemistry

2.9.1 Episodic acidification

Atmospheric deposition is a process where particles are settled onto the landscape (Iavorivska *et al.* 2016). Studies have documented that a large proportion of solutes that are discharged from some catchments may be derived from both wet and dry atmospheric deposition (White and Blum 1995).

One of the most significant issues that were faced between the 1970s and 1980s, in Europe, was the episodic acidification of streams caused by acid deposition (Bonjean *et al.* 2007). Episodic acidification is most common in the rainfall season (Lawrence 2002).

Episodic acidification refers to the short-term decrease in acid neutralising capacity (ANC) of water, which occurs during high flows which are associated with rainfall and snowmelt (Wellington and Driscoll 2004). These episodes can also be caused by the deposition of sea salt, sulfate and nitrate flushes; which are associated with climatic extremes (Lawrence 2002, Evans, Monteith, *et al.* 2006). Episodic acidification may also be brought about by natural processes such as dilution of base cations relative to increases in inorganic acid anions and the flushing of organic acids from soils. Atmospheric deposition of strong inorganic acids such as sulfuric, hydrochloric, phosphoric and nitric acids, is also a possible contributor to acid deposition in streams. Along with that, the variations in hydrologic flow paths may control the extent to which these factors may contribute to episodic acidification (Wellington and Driscoll 2004). The net effect of acid deposition on stream chemistry is to reduce the pH of the water (Harriman and Morrison 1982).

Episodic acidification of streamwater can occur through the mobilisation of organic acids but decreases in pH are associated with increases in SO_4^{-2} and NO_3^- are generally attributable to deposition effects (Lawrence 2002). Episodic acidification is most common during seasons of high precipitation and is least common during summer because evapotranspiration reduces soil moisture. Severe canopy defoliation is capable of increasing NO_3^- concentrations in streamwater (Burns 1996, Lawrence 2002, Evans, Monteith, *et al.* 2006). The loss of forests can effect groundwater, runoff and water quality (Erol and Randhir 2013).

2.10 Long-term change: Climate change and land use

2.10.1 Climate change

Due to global warming, climate change is likely to have significant impacts on the hydrologic cycle and affect water resources. Most, if not all African ecosystems are going to experience increased climate change driven and anthropogenically driven pressures in the future (Merbold *et al.* 2009). Predictions have been made showing the impact climate change will have on both overall and specific geographic regions. It is expected that as climate change progresses, flood and drought incidences are going to increase (Kruger 2006, Davies 2011, Delpla *et al.* 2011). South African temperatures are expected to increase at a rate that is faster than that of the global mean temperature (Maserumule 2010, Davies 2011). It has been projected that eastern South Africa will experience summers with severe rainfall events whilst the south Western Cape is predicted to experience drier winters (Maserumule 2010, Davies 2011).

Climate related mechanisms can directly affect water quality, in both the long-term and short-term scale. These include air temperatures, changes in hydrological factors, changes in vegetation and soil structure (van Vliet and Zwolsman 2008). Climate change can result in significant changes in the variables and processes that affect water quality and freshwater biodiversity (Evans, Monteith, *et al.* 2006, Solheim *et al.* 2010). Although this is the case, the effects of climate change on water quality cannot be thought of in isolation from other anthropogenic drivers of change (Evans, Monteith, *et al.* 2006).

The Drakensberg is a water tower region (Schulze 1974)**,** water tower regions are faced with changing hydrologic regimes which are induced by climate change and will subsequently result in the variation in available water resources (Zhang *et al.* 2015). Water quality and quantity are key environmental indicators and are sensitive to several external disturbances. Infiltration, groundwater recharge, baseflow and runoff can all be influenced by changes inflicted through climate change (Fan and Shibata 2015).

The impacts of global climate change on rainfall cause challenges for the management of freshwater resources all around the world (Fraterrigo and Downing 2008, Park *et al.* 2011). Climate change can influence the amount, variability, seasonality and intensity of rainfall. Changes in rainfall characteristics are likely to influence streamwater chemistry. Stormflow caused by intense rainfall events, are known to affect water chemistry (McDiffett 1993). Donat *et al.* (2013) demonstrated increases in the index for extreme rainfall events at the global scale. An analysis of long term records in South Africa (1912-2015) provides additional evidence that for increasing trends in extreme, more intense rainfall events (Kruger and Nxumalo 2017). A key point is to understand seasonal as well as storm-induced changes in streamwater quality and chemistry (Park *et al.* 2011).

2.10.2 Land use

Terrestrial processes are important regulators of nutrient inputs into streams. These nutrient input concentrations are helpful indicators and can be used to infer the status of nutrient cycling in the terrestrial ecosystems that the streams drain (Mulholland 1992, 2004, Mulholland and Hill 1997) The quantification of land use is a valuable indicator of the state of ecosystems (Allan 2004). The impact of land use on natural systems is often quantified through the evaluation of the relationship between land use and streams (Pratt and Chang 2012). For example, Lee *et al.* (2013) found that nutrient exports had a heightened sensitivity to runoff and land use. It has been suggested that many issues related with water quality are related with the inappropriate use of land and practices within catchments (Bu *et al.* 2014). Tong and Chen (2002) and Jung *et al.* (2008) showed that land use types have a significant impact on water quality parameters. Land use is capable of increasing nutrient loading, through the use of fertilisers (Erol and Randhir 2013). Water that is released from farms into rivers, is often high in phosphates and nitrates (Bu *et al.* 2014). Although land use effects are dependent on scale within catchments (Buck *et al.* 2004), they are clearly capable of having significant impact on water chemistry (Allan *et al.* 1997, Gergel *et al.* 1999).

Understanding the impact of land use on water quality is an important goal for environmental management. Yu *et al.* (2015), however, proposed that the relationship between land use and streamwater is complex. In addition, the variability within the relationship between land use and water quality is high and is also dependent on the scale of the entire watershed (Fraterrigo and Downing 2008). Several factors can also act in a single catchment, and alterations to these can act at varying spatial scales but all have an overarching effect on the condition of in-stream water (Allan 2004).The impact of alterations in land use is that they can influence in-stream conditions through multiple processes which operate at varying spatial scales (Allan *et al.* 1997). In addition, land use changes are capable of not only significantly influencing water quality but also hydrologic processes (Allan 2004, Erol and Randhir 2013), as shown in **Table 1**. To cope with this complexity it has been suggested that small catchments can be used as useful models to monitor and disentangle impacts of changes in land use on stream chemistry from other factors (Allan *et al.* 1997, Silva *et al.* 2012, Erol and Randhir 2013).

Table 1 Mechanisms through which land use influences in-stream conditions (Allan 2004).

Environmental factor	**Effects**
Sedimentation	Increases in turbidity, scouring and abrasion; reduced stream depth heterogeneity.
Nutrient enrichment	Increased biomass and production of autotrophs, decreases in dissolved oxygen combined with increased litter decomposition.
Contaminant pollution	Increased concentrations of heavy metals, synthetics and toxic suspended organics which are associated with sedimentation. These can also be accompanied by increases in mortality rates and deformities.
Hydrologic alteration	Any alterations in runoff-evapotranspiration balance, possibly causing increased flood magnitude and frequency and this often lowers baseflow. Altered channel dynamics, increased erosion.
Riparian clearing/canopy opening	Clearing reduces shading which leads to increases in stream temperatures, light penetration, plant growth and erosion. This also leads to decreased bank stability, litter inputs and retention of nutrients and sediment trapping.

2.10.3 Interactive effects of climate change and land use change

Climate change and land use have an impact on each other at the landscape scale, changes in land-cover patterns have the ability to impact both energy and mass fluxes (Christensen *et al.* 2008). The effect of climate change can be realised through changes in land cover patterns (Dale 1997, Maserumule 2010, Zhang *et al.* 2014). High mountain environments are sensitive to changes in atmospheric pollution and climate (Mast *et al.* 2011).

2.11 Afforestation and streamwater chemistry

A prominent issue with regards to afforestation is the impact it has on surface water quality and quantity. An obvious consequence is the decrease in water quantity in the concerned catchment (Principe *et al.* 2015). It is important to consider soils, geology, topography and deposition within the area being investigated for the effects of afforestation on streamwater chemistry (Waters and Jenkins 1992, Rees and Ribbens 1995).

Establishing evergreen conifers in grassland landscapes is expected to produce strong stream impacts. This is not only because of the increased inputs of organic matter from leaf litter and woody material but heavy shading affects streamwater temperature (Nisbet *et al.* 1995, Principe *et al.* 2015). Any marked shift in vegetation could have important implications in terms of functioning and structure of aquatic ecosystems(Jenkins *et al.* 1990, Mareschal *et al.* 2013, Principe *et al.* 2015).

One land use of concern regarding how it affects streamwater in South Africa is afforestation. There are increasing concerns about the climatic consequences of greenhouse gas emissions. In order to increase the sequestration of carbon dioxide (CO_2), suggestions have been put forward to use afforestation as a tool (Zhao *et al.* 2017). The changes caused by afforestation in the chemical and physical elements of soil (especially carbon (C), nitrogen (N) and phosphorus (P), are of importance. This is because these elements could be used to understand the biological processes and nutrient cycling in terrestrial ecosystems (Zhao *et al.* 2017).

In a study of two forested catchments in the mid-Atlantic region of the eastern USA, Rice and Bricker (1995) observed periodic streamwater chemistry cycles. The highest concentrations of SO_4^{2-} occurred during winter, at a time when discharge was at its lowest (baseflow); whilst calcium and magnesium concentrations peaked during summer (Rice and Bricker 1995).

2. 12 Studies on headwater chemistry in South Africa

In the South African context, high conductivity values were recorded for three outlets along the Berg River, during winter. The opposite was observed for the portion of the river that runs through the Western Cape Province. This is because the province experiences winter rainfall and not summer rainfall like the Free State Province (Clark and Ractliffe 2007). In a study of the hydrochemical response during storm events in South Africa, chloride (Cl^-), phosphate (PO_4^{3-}) and nitrate (NO_3^-) showed seasonal variations due to changes in soil moisture and different responses to discharge. Furthermore, a seasonal difference in ionic storm chemistry was observed (Britton *et al.* 1993)

2.13 Dissolved organic carbon sources, transport and controls

Although it is not sufficiently investigated, the carbon cycling in rivers is important. Dissolved organic carbon is the link between terrestrial and aquatic ecosystems (Yang *et al.* 2017). The process in which terrestrial dissolved organic carbon is produced is biological (Clark *et al.* 2010). Organic matter is one of the key components of streamwater chemistry (Erlandsson *et al.* 2008). The amount of dissolved organic matter in a system is an indication of the catchment scale hydrologic and biogeochemical processes (Qualls and Haines 1992, Mulholland *et al.* 1997). There are significant interactions that occur between dissolved organic matter and inorganic constituents in freshwater and these interactions cannot be ignored (Beck *et al.* 1974). Increased dissolved organic matter in streams results in increased natural acidity (Andersson and Nyberg 2009).

The way organic carbon is transported has not always received a considerable amount of attention and has only recently started to be investigated profusely. Organic carbon plays an important role in many ecological processes and has major consequences on both human and environmental health (Meybeck 1982, Dhillon and Inamdar 2014, Sawicka *et al.* 2016). Organic carbon can be transported in water, in one of two ways: as dissolved organic carbon (DOC); or as particulate organic carbon (POC). The supply and transport of DOC and POC differs and concentrations can vary between day and night (Mulholland 1992). These differences are important and occur at different scales, relative to time. DOC and POC play a key role in ecological processes, like regulating aquatic metabolism and affecting potable water grade. DOC is responsible for regulating the acid-base chemistry of acid sensitive freshwater systems and it governs the complexity, solubility and mobility of trace metals and attenuates light penetration into aquatic ecosystems. POC on the other hand acts as a carrier for the transport of organic chemicals (Meybeck 1982, Dhillon and Inamdar 2014). Organic carbon is not inert, when DOC and POC are released into aquatic ecosystems, they are used as sources of energy by microbial communities (Correll *et al.* 2001).

2.13.1 Temporal controls of DOC

Dhillon and Inamdar (2014) propose that exports of organic carbon from catchments are strongly influenced by storm events - specifically large storm events. This is because DOC is transported when overland flow seeps through the ground;

groundwater level rises into the soil horizon resulting in the increased potential for infiltration (Kim *et al.* 2014). If there is no physical barrier, this will aid the rise of the groundwater Table. Concentrations of DOC and POC decrease as water moves downstream, this happens through a process called spiraling (Correll *et al.* 2001).

Previously, it had been found that concentrations and exports of DOC and POC increase with large storm events (Dhillon and Inamdar 2014). This suggests that riverine DOC and POC may be limited by transport-related processes instead of catchment carbon supply (Moore and Dalva 2001, Yang *et al.* 2017). Their responses are not always similar but even in cases where responses are subtle, the distinctions are important (Dhillon and Inamdar 2014, Lambert *et al.* 2014). Seasonal hydrologic and biochemical conditions of storms have implications on DOC and POC (Holloway and Dahlgren 2001, Dhillon and Inamdar 2014).

2.13.2 Spatial controls of DOC

Dissolved organic carbon concentrations vary with land cover, soil and anthropogenic disturbances. These concentration variations exist due to differences in land cover, soil respiration, soil carbon storage and adsorption (Yang *et al.* 2017). The changing of land use and associated human activities are capable of having profound and long-lasting impacts on the concentration of DOC (Worrall *et al.* 2004, Clark *et al.* 2010, Yang *et al.* 2017).

Vegetation can directly control the production of DOC through residue input to soils or indirectly by affecting transport through hydrological processes (Findlay *et al.* 2001, Yang *et al.* 2017).

2.14 Dissolved organic carbon debates – climate vs. acid deposition vs. land use

The increasing DOC concentration in freshwaters of Europe and North America is the driving force behind many DOC debates. These increases were initially observed almost 30 years ago, similar trends have been documented across large parts of Scandinavia and the United Kingdom (Skjelkvåle *et al.* 2005, Evans, Chapman, *et al.* 2006, Monteith *et al.* 2007, 2015, Clark *et al.* 2010, Evans *et al.* 2012, Curtis *et al.* 2014). There has also been an increase in DOC of the northern boreal lakes over the past thirty years. This phenomenon has been referred to as browning (Edwards 1973, Evans, Chapman, *et al.* 2006, Monteith *et al.* 2007, Finstad *et al.* 2016). One of the hypothesised drivers of increased DOC concentrations is the long-term change in the chemistry of atmospheric deposition that has been recorded across many of the areas in freshwaters of Europe and North America, as a result of reductions in anthropogenic sulfur and sea salt deposition in some locations (Clark *et al.* 2010).

There is an important relationship between land use and processes of naturally occurring organic acids (Oliver *et al.* 1983, Goldstein *et al.* 1987, Christophersen *et al.* 1990). Dissolved organic carbon forms a large part of the carbon export of streams and lakes, it is therefore an important component of the upland carbon balance (Evans, Chapman, *et al.* 2006, Evans, Monteith, *et al.* 2006). The increase in DOC concentrations had a wide-ranging possibility of effects at the global scale. In terms of the local scale, it could influence the transparency of water, acidity, metal transport and effects on potable water (Evans, Chapman, *et al.* 2006, Clark *et al.* 2010, Monteith *et al.* 2015).

A number of potential drivers of increases in DOC have been put forward and these include: recovery from acidification, temperature changes and hydrological change (Evans *et al.* 2005, 2012). It was estimated that rising atmospheric CO_2 levels could account for 1-5% increase that changes in temperature alone could only account for 10-20% DOC increases. Climate change has also been proposed as one of the mechanisms driving the increases in DOC concentrations (Evans, Chapman, *et al.* 2006, Evans, Monteith, *et al.* 2006). Evans *et al.* (2006) argue that, the causes of increasing DOC concentrations in the UK is changing atmospheric deposition and rising temperatures. Although increases in temperature through the decomposition of organic matter result in increases in the production of DOC, this theory cannot be used to explain the entire reason behind DOC increases. It does however, account for a small proportion of the change (Evans, Monteith, *et al.* 2006).

There is not much information highlighting the role Africa plays in the global carbon cycle (Williams *et al.* 2007). The spatial and temporal variability in atmospheric carbon at the continent scale is unknown. It is important to understand this role because Africa supports a large variety of terrestrial ecosystems, has varying climate, geology, species composition and land use (Merbold *et al.* 2009).

2.15 Absorbance as a measure of DOC

For decades dissolved organic carbon has received plenty of attention due to possible impacts on aquatic freshwater ecosystems (Lewis and Tyburczy 1974, Correll *et al.* 2001, Peacock *et al.* 2014). Interest around the subject of DOC is due to the close and detailed association between the optical processes of water and biochemical processes that occur in aquatic environments. The optical properties of water and the biochemical processes that occur in aquatic environments make the relationship between both factors very important (Beck *et al.* 1974, Lewis and Tyburczy 1974). The humic fraction of DOC plays an important role in the functioning of aquatic ecosystems and tannic equivalents can possibly provide a suitable alternate unit for quantifying colour in freshwater (Cuthbert and del Giorgio 1992).

The earliest invention of a reliable method for measuring DOC was in the 1960s. Although the method of using the optical properties of water to measure DOC with a spectrophotometer was developed for the rapid measuring of DOC in sea water, a large amount of work has been done adapting it to different aquatic environments (Menzel and Vaccaro 1964, Lewis and Tyburczy 1974). The use of spectrophotometry for the determination of colour using light energy from within the ultraviolet spectrum was frequently performed at 440 nm (Cuthbert and del Giorgio 1992).

A common laboratory method used to analyse DOC is a test where UV combustion or persulfate, through oxidation, is used to convert organic carbon to carbon dioxide (CO_2). A CO_2 concentration is then generated by using an infrared analyser, the value reported is of organic carbon (Kaplan 1992, Gadmar *et al.* 2002). This method is referred to as the total organic carbon and dissolved organic carbon high temperature method and was also used by Umgeni Water Laboratory when analysing DOC. The method is both costly and laborious; and requires specialist personnel due to some of the safety, health and environmental hazards such as the use of phosphoric acid.

The use of DOC in aquatic ecosystems to understand the compounds that influence the system and biogeochemical roles is important. Since DOC is a representation of the organic compounds that are in solution and is furthermore sensitive to catchment ecology, monitoring the concentration of this compound is important (Jollymore *et al.*

2012). Although the common laboratory method is useful, a quicker and cheaper method for the quantification of DOC is advantageous. The use of UV absorbance have been shown to be an exceptional proxy for DOC concentration (Weishaar *et al.* 2003, Jaffrain *et al.* 2007, Jollymore *et al.* 2012).

CHAPTER 3: STUDY SITE

Overview

> *This chapter provides a detailed description of the study site at which this research was conducted, geology, historical and proposed land use management techniques and the history of monitoring at the site.*

Given the complex interactions among various processes that can influence water chemistry, disentangling the relative impacts of different stressors can be challenging. There have been studies where small watersheds were perturbed in order to investigate the importance of terrestrial processes dictating nutrient concentrations in streams (Mulholland 1992), since terrestrial ecosystems influence streams and rivers (Allan *et al.* 1997). An ideal scenario is where geology, topography, soils and vegetation where initially similar then perturbed – some catchments, in this case, the effect of plantation on water yield. Cathedral Peak offers ideal such a site with catchments that have varying land uses, which allowed for the investigation on how streamwater chemistry was affected by land use.

3.1 Study area description

The Cathedral Peak Research Site (29° 00’ S; 29° 15’ E) in the Drakensberg, Kwa-Zulu Natal, was established in 1938 as the Cathedral Peak Forestry Influences Research Station. The aim of the program was to determine what the effect of various land management practices (e.g. fire regimes and planting exotic conifer plantations) on water supplies was (Nänni 1956). The location of the Cathedral Peak Research Site is shown in **Figure 1**.

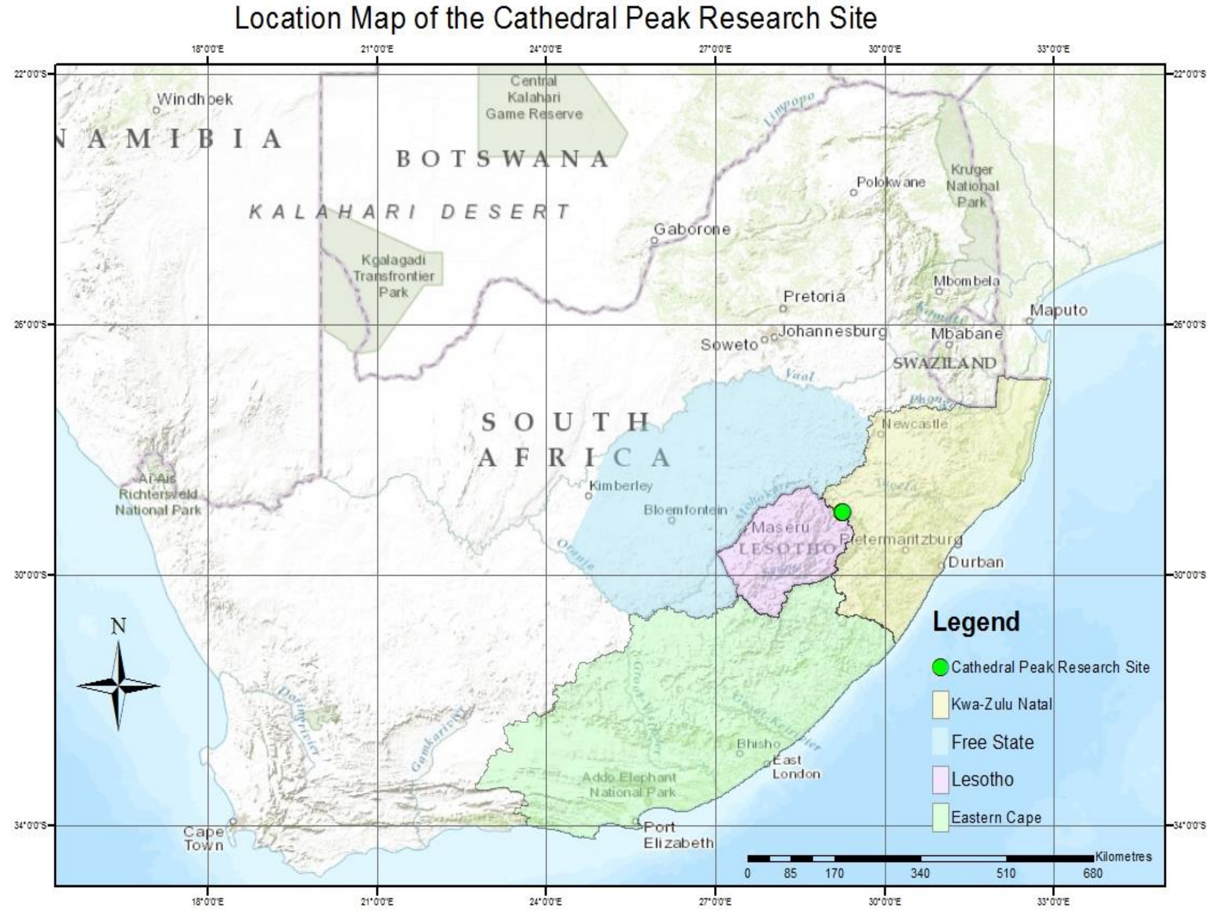

Figure 1 Map showing the location of the Cathedral Peak Research Site.

The research site consists of fifteen catchments numbered 01 to 15, which are located at the head of three isolated Little Berg spurs at an altitude of approximately 1890 m.

Different catchments receive varying land management treatments such as afforestation, burning and protection from burning. Catchment 01 receives biennial spring burns with light summer grazing by livestock, catchments 02 and 03 were previously afforested with *Pinus patula,* catchments 11 to 15 have received regular burning since 1975, catchments 07 and 09 have been protected from fire for about 17 and 30 years respectively (Gush *et al.* 2002). The catchments that were used in this study, indicated by the red circle, are shown in **Figure 2**.

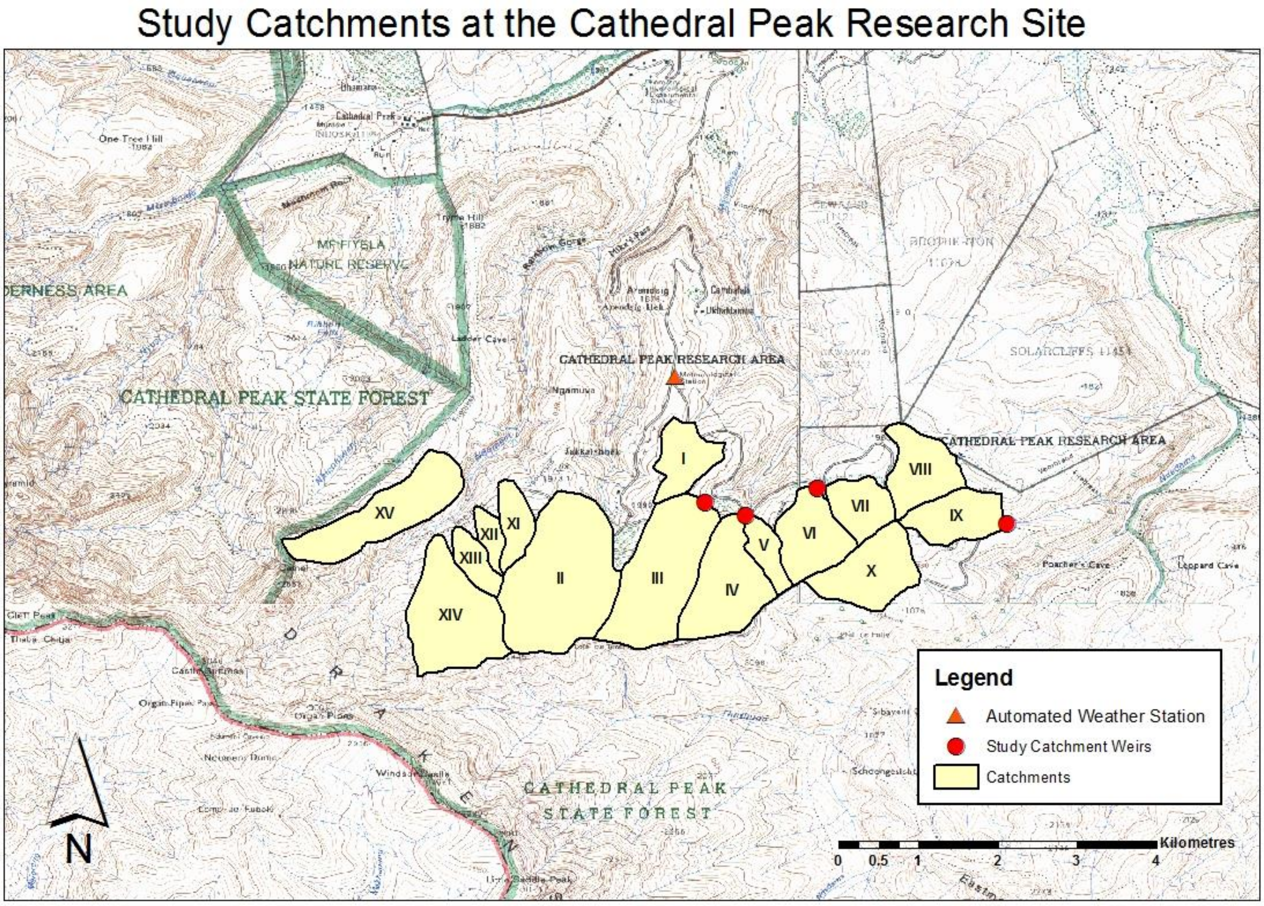

Figure 2 Map showing the study catchments at the Cathedral Peak Research Site. Each catchment represents a standalone catchment.

These include CP03 (degraded - previously afforested) is shown in **Figure 3a**, CP04 and CP06 (pristine grasslands which receive biennial spring burns) are shown in **Figures 3b** and **c** respectively and CP09 (fire protected) is shown in **Figure 3d**. All of the catchments used in this study have perennial streams (Gush *et al.* 2002). These catchments were selected based on their contrasting land uses.

Figure 3 Images showing study catchments: ***(a)*** CP03 – degraded (previously afforested), ***(b)*** CP04 - pristine grasslands (receive biennial spring burns), ***(c)*** CP06 - pristine grasslands (receive biennial spring burns) and ***(d)*** CP09 – protection from fire.

3.1.1 Geology

The southern Drakensberg region is made up of rocks belonging to the Stormberg Group, which is the youngest and uppermost sequence within the Karoo Supergroup and coincides with the early Jurassic. The Clarens Sandstone Formation, which is the uppermost sequence within the Stormberg Supergroup, lies conformably on the red mudstone of the Elliot Formation. The Drakensberg Basaltic Lavas cap the Clarens Sandstone Formation (Nänni 1956, Gush *et al.* 2002).

The lowest point within any of the catchments is well above the Clarens Sandstone Formation. This formation is about 180 m thick at Cathedral Peak and is of Aeolian origin. The thickness of the Drakensberg Basaltic Lavas is just over 1500 m. The

Drakensberg Basaltic Lavas Formation is made up of several flows that followed one another without weathering. The floor of the research area is formed by the lowest flows which rest conformably on the Clarens Sandstone (Nänni 1956, Gush *et al.* 2002). The geology of South Africa is shown in **Figure 4.**

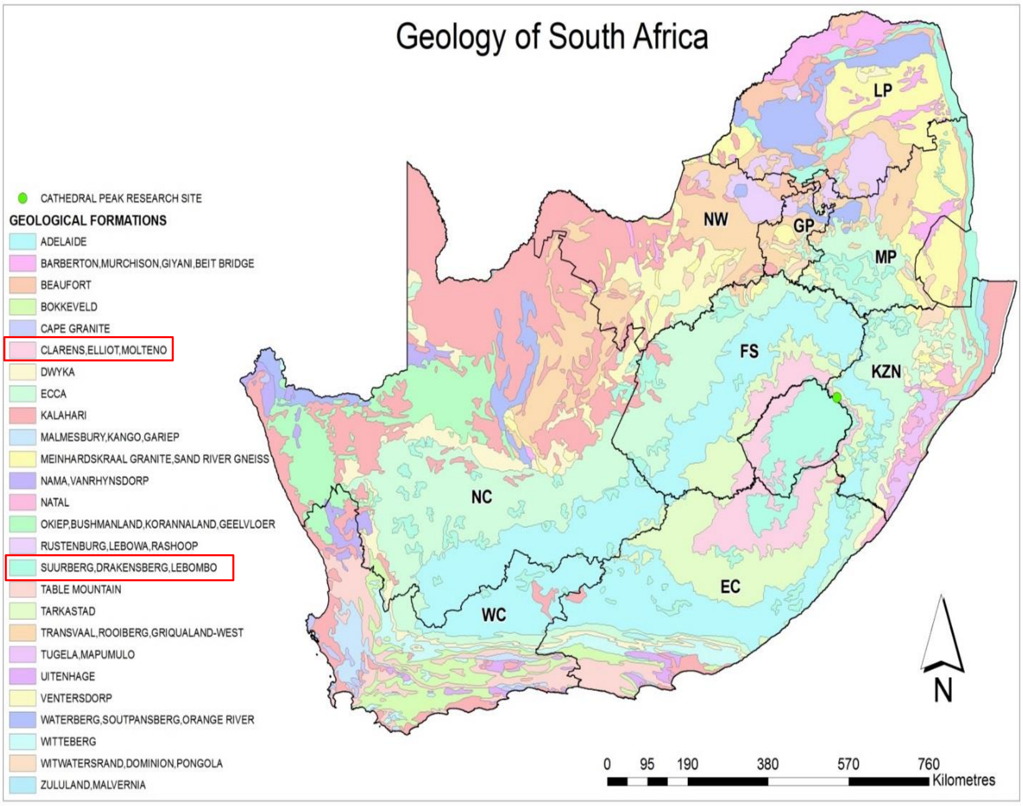

Figure 4 Geology of South Africa (Burger 2013).

The geology also includes three syn-Karoo dolerite dykes, each about 3m wide, running through the research area. One of the dykes trends in a NNW-SSE direction and forms the lower section of the eastern watershed of catchment 02. The other two dykes trend in the NW-SE direction, are roughly parallel and run about 500m apart. It has been claimed that the dykes have no hydrological influence (Nänni 1956, Gush *et al.* 2002).

3.1.2 Vegetation

Acocks (1988) established that the Highland Sourveld in the Drakensberg replaced forest. It is a pure grassveld, which does not have any thorns. The catchments fall within the temperate grassland biome of South Africa. They are dominated by C4 grasses, with C3 grass species occurring on higher and southern facing slopes in some areas. *Leucosidea sericea* and *Buddleia salvifolia* occur in patches along rivers and fire protected areas (Bosch 1979). As part of the experimental design, Catchment 3 was afforested in in 1959. The catchment burnt out in a runaway fire in 1981. After the fire the catchment was sown with *E. curvula* in response to concerns over erosion. It is currently dominated by Pteridium fern. Catchment 9 which has been largely protected from fire barring a few runaway fires, is switching from a C4 grasslands dominated system to Leucosidea *sericea* woodland.

3.2 History of the Cathedral Peak Research Site

The Cathedral Peak Forest Influences Research Station was established in 1938. The objective was to determine the effect of exotic conifer plantations on water supplies across nine catchments. It was proposed to have six catchments planted with *Pinus patula* at eight year intervals. One catchment was to be sporadically grazed for five years followed by complete afforestation. Another catchment was to be completely planted with *Pinus patula*. The ninth catchment was to be protected from burning and grazing for an indefinite period to determine the trend of plant succession and the effect on water supplies. Discharge from all experimental catchments was continuously measured (Nänni 1956).

In **Table 1**, an account of the treatments that were applied to study catchments and the year in which *Pinus patula* was proposed to be planted. *Pinus patula* was never planted in catchments 04 and 06.

Table 2 Résumé of treatments that were proposed to be applied to catchments at the Cathedral Peak Research Station (Nänni 1956, 1959, Gush *et al.* 2002, Toucher *et al.* 2016).

Catch.	**Elevation a.s.l (m)**	**MAP (mm)**	**Area (ha)**	**Proposed treatment**	**To be planted in year:**				
					1959	**1967**	**1975**	**1983**	**1991**
03	1845-2317	1564	138.9	Burning every alternate spring until planted	*Pinus patula*				
04	1845-2226	1420	94.7	Burning every alternate spring until planted					*Pinus patula*
06	1845-2073	1340	67.7	Burning every alternate spring until planted				*Pinus patula*	
09	1822-1982	1257	64.5	Total protection for an indefinite period					

3.2.1 Historical water chemistry data

In 1971 research into water quality of upper mountain catchments was initiated at the South African Forestry Research Institute (SAFRI). Monitoring originated in the south Western Cape at Zachariashoek and was then extended to the Jonkershoek Research Centre (1974) and Lebanon (1978), both in the south Western Cape (van

Wyk 1983). **Table 3** gives an account of the development of spate sampling across the different monitoring sites.

Table 3 Development of spate sampling across the SAFRI monitoring sites (van Wyk 1983, Lesch 1992).

Year	**Where**	**Monitoring method**	**Equipment**	**Comments**
1979	Bosboukloof (Jonkershoek catchment)	Spate sampling	Fredricsen sampler	Problems encountered
1977	Zachariashoek	Economical spate sampling	Using plastic containers on wooden frame	Led to design and implementation of rising and recession spate samplers in 1981.

Monitoring included baseflow, precipitation and spate sampling which were further extended to the CPRS and Witklip in 1981. Precipitation data were collected using a locally designed bulk sampler. The data collection was initiated at Zachariashoek in 1971, Jonkershoek 1979, Lebanon 1982, Witklip 1983 and Cathedral Peak in 1984 (Lesch 1992). Other data that were being collected at each research centre include suspended sediments and bedload export, in 1977 and 1978 respectively. Samples collected in the Kwa-Zulu Natal region were analysed at the Hydrological Research Institute; **APPENDIX A1** gives an outline of data collected at the CPRS, types of sample, sample names, how long monitoring lasted and the file codes used for storing metadata.

3.2.2 Historical water parameters data

The different water quality parameters that were collected at the CPRS and other catchments are shown in **APPENDIX A1**. Although monitoring at the South African Forestry Research Institute was established in 1971, the historical data used in this study only accounts, at varying degrees for monitoring done between 1980 and

1991. Data were collected from 15 catchments; **Table 4** highlights the data that was collected from the catchments associated with this study (III, IV, VI and IX).

Table 4 Historical data collected from catchments with this study, much like APPENDIX C1; the sample types, running time and parameters collected are included in this Table.

CPRS historical data			**Running time**		
Sample category	**Sample type**	**Sample name(s)**	**Start**	**End**	**Data collected**
Grab samples	pH and conductivity	CAT3, 4, 6, 9	1985/10/02	1987/09/23	Date, sample, time, HT, pH, COND, ST/FL, R/FLL
	Chemical analyses	CAT3, 4, 6, 9	1981/11/12	1986/09/03	Date, sample, time, HT, Na, K, Ca, Mg, Cl, SO_4, HCO_3, NO_3, PO_4, pH, COND, NH_4, F, Si, KN, TP, ST/FL
	Suspended sediment	CAT3, 4, 6 CAT9	1980/09/08 1980/10/01	1991/05/29 1990/07/11	Date, sample, time, HT, Vol, FLT/EM, FILT_SLK, Silk, COND, ST/FL
Spate samples	Chemical analyses	CAT3 OP1->4 / AF1->4 CAT4 OP1->3 / AF1, 4 CAT6 OP1, 2 / AF1, 4 CAT9 OP1->3 / AF1	1981/11/09 1981/11/26 1981/11/19 1981/12/08	1988/02/18 1988/07/10 1988/04/06 1988/03/10	Date, sample, time, HT, Na, K, Ca, Mg, Cl, SO_4, HCO_3, NO_3, PO_4, pH, COND, NH_4, F, Si, KN, TP, ST/FL
	Suspended sediment	CAT3 OP1->3, 5, 6 / AF1->4 CAT4 OP1->3 / AF1, 3, 4 CAT6 OP1->3 / AF1, 4 CAT9 OP1->2 / AF1 /OP	1980/09/23 1980/09/23 1980/09/23 1982/01/30	1988/02/21 1988/04/06 1988/03/16 1988/03/10	Date, sample, time, HT, vol, FLT/EM, FILT_SLK, Silk, COND, ST/FL

The n in “OP1 -> n” refers to any of 2-8 samples of the rising limb of the hydrograph, date – date sample was taken, sample – sample name, time – time the sample was taken, HT – height of the gauging weir, COND – conductivity, KN – total nitrogen, TP – total phosphorus, Vol – volume of sample taken (ml and L), ST/FL – weekly volumes of streamflow, R/FLL – weekly volumes of rainfall, FILT_SLK – mass of filter paper plus sediment sample (g), FILTLG – mass of filter paper before filtration (g), OONDDRGS (g and mg) – oven dried sediment, *calculated TSS (mg/L)

CHAPTER 4: METHODS

Overview

This chapter provides a detailed description of the methods that were used to collect and analyse data. A description of the laboratory analyses that were performed is given. The locations, frequency of sampling as well as the devices that were used to collect data are also outlined. A description of all the tests run on the data and further calculations performed is given.

4.1 Sampling objectives

The objectives of field sampling were to:

- Collect monthly streamwater chemistry samples from all study catchments, over a minimum of one year – for chemical analysis of major ions, DOC and assessment of TDS and TSS.
- Collect monthly field measurements of temperature, conductivity, pH and dissolved oxygen for all four catchments.
- Monitor storm water chemistry from two occasions across catchments III and VI for comparison.
- Assess the utility of streamwater colour, through spectral absorbance, as a proxy for DOC.

4.2 Sampling methods

During the collection of water samples in the field, the procedures that were followed were ones that helped reduce the amount of contamination. These procedures included: rinsing out the top part of the filter rig; shown in **Figure 5**; three times with the sample water, rinsing out the bottom section of the filter rig with the filtered sample three times and throwing the rinsing water out, down and not upstream.

Figure 5 Filter rig and pump.

In preparation for sampling, the washing procedures described in **Table 5** were followed for sample bottles that were being reused. New sample bottles were rinsed three times, using the filtered sample being collected.

Table 5 Washing procedures followed for collecting grab samples (UNEP/WHO 1996).

Variable to be analysed	Recommended container	Washing procedure
Acidity, alkalinity, arsenic, calcium, chloride, colour, fluoride, hardness, Magnesium, non-filterable residue, pH, potassium, sulfate, turbidity and conductivity	1L polyethylene	Rinse three times with tap water, once with hydrochloric acid, three times with tap water and three times with distilled water, in that order.

Water samples were filtered on site using a filter rig and pump, through a 0.45 μm membrane filter (Pall, USA). To avoid contamination from residue of earlier samples while filtering, the filter rig was rinsed three times with water from the catchment where a sample was being taken. The filter was changed whenever a new sample was being filtered. The polyethylene sample bottle was also rinsed three times with the filtered sample to ensure that contamination was minimised as per UNEP/WHO (1996). Subsamples of 100 ml were used for major ion analysis and DOC analysis. These were immediately frozen until delivered to the Chemistry Laboratory at North West University for major ion analysis, whilst the DOC sample was chilled, until delivered to the Umgeni Water Laboratory in Pietermaritzburg.

4.2.1 Sampling locations

The sampling sites were consistently selected at the exit point of the catchment, at the outflow of the gauging weir, as shown in **Figure 6**.

Figure 6 Sampling location for CP04, at the outflow of the gauging weir.

To capture storm flow events as per objectives in section 4.1, samples were collected during rainfall events, using an automated ISCO sampler shown in **Figure 7** at CP03 (degraded) and CP06 (pristine grassland) respectively..

Figure 7 An automated ISCO sampler.

4.2.2 Sampling frequency

Sampling was a combination of monthly and episodic data. Catchments III, IV, VI and IX were sampled monthly through the process of grab sampling, from 2014 - 2016. Episodic data refers to data that were collected during the storm events in the rainfall season – programming of the automated ISCO sampler is outlined in **Section 4.2.3**.

Monthly trips were coordinated between Wits and South African Environmental Observation Network to collect these samples. In the case when Wits was unable to go to CPRS, an individual from the SAEON Pietermaritzburg office would collect samples at the study catchments. Although more frequent sampling would have been desirable, in terms of logistics, it was impossible. These catchments lie 20 km up a 4x4 mountain track that may not be driven on when wet.

Episodic samples were collected using automated ISCO samplers (see **Section 4.2.3**), which were located at catchments III and VI.

4.2.3 Sampling devices

A YSI Multiparameter probe was used to collect field measurements, shown in **Figure 8**. These included; pH, dissolved oxygen, conductivity and temperature. The instrument was calibrated no more than 48 hours prior to use. The standard solutions used for calibration were those for conductivity (1413 µS/cm) and pH, (pH 4 and 7 buffer solutions), also shown in **Figure 8**.

Figure 8 The YSI Multiparameter probe used to collect field measurements; and the standard solutions (pH and conductivity) that were used to calibrate it.

The probe was calibrated on-site for dissolved oxygen at each catchment to account for variations in barometric pressure.

In-stream temperature data were collected, from 2014 – 2016, using waterproof iButton data loggers, shown in **Figure 9**.

Figure 9 The iButton data loggers that were used to monitor stream water temperature during the year of monitoring.

These were secured in plastic sample bottles with holes in them to allow for the flow of water. Temperature data were recorded every 15 minutes and the loggers were replaced at least every 85 days. The data collected could have possibly been altered if sediment had entered the container in which they were deployed. In such a case, it would have been challenging to obtain the proper temperature of the water flowing through the container due to the sediment restricting the flow of water.

Auto samplers were used to collect episodic samples, shown in **Figure 7** and have advantages over grab samples in that, an auto sampler can be programmed to collect samples at regular time intervals such as daily or triggered by a rise in the stage or onset of rain. Depending on the frequency the automated ISCO sampler is programmed to collect water samples, it is possible to document an entire storm event. The instruments were triggered to start collecting samples when the initial streamwater level increased by 10 mm, then every 10 mm increase or decrease in water level. Since sample collection was dependent on streamwater level increases, there was no time period but rather 24 sample bottles to be filled over an event. Water level is a convenient measure of whether a sample is being collected during a period of normal or stormflow conditions. It can collect discrete (one sample per bottle) and integrated (several samples per bottle) samples and must be manually emptied.

During a test installation in February 2016, the auto samplers in catchments III and VI were programmed to collect samples with every 5 mm change in streamwater level. The change to every 10 mm was made because the prior resolution did not capture the whole storm event and was too frequent. Water samples were collected during this period and all 48 samples were used for the analyses of TDS, TSS and DOC. The auto samplers were officially installed during the first week of March 2016 and were programmed to collect samples after every 10 mm change in streamwater level.

4.3 Climate and discharge/flow data sources

Climate data were obtained from the SAEON Automated Weather Station within the Cathedral Peak Research Site area at Mike’s Pass, about 2 km from the research catchments. It is a Campbell Scientific Automated Weather Station which processes data on a CR1000 logger. The station outputs 5 minute, hourly and daily data. Data collected includes: wind speed and direction, solar radiation, temperature (air, soil), relative humidity, precipitation, barometric pressure and soil moisture. This is serviced and downloaded by SAEON field staff.

The South African Environmental Observation Network has data loggers installed on V-notch weirs across the four catchments, measuring water pressure every fifteen minutes. The data loggers in catchments III and VI are connected to the auto samplers. Data were extracted daily during the week-long visit in March 2016. Additionally, data from the auto samplers were extracted at the end of every month and if a rainfall event occurred, by a field technician at SAEON.

4.4 Historical data

The samples were collected and then preserved with 10 mg of mercury (II) chloride – except for chloride, the sample bottles were filled and were not to be opened before analysis. Samples were filtered through a prewashed 0.45 µm membrane filter (Whatman GF/C or equivalent). These were the methods used for the analysis of surface, ground and waste waters (van Wyk 1985, van Vliet *et al.* 1989).

The historical data used was drawn from primary data files that were subsequently corrected for missing values. the files were used to calculate mean concentration values for elements in mg/L (cations) or µeq/L (anions) (van Vliet *et al.* 1989).

4.4.1 Data transformation

All missing values “0” and “.” were replaced with “NA”. Data were furthermore organised into season years. A season year spanned from spring to winter.

4.5 Laboratory analyses – current field programme

Grab samples were analysed at North West University, along with samples collected by the ISCO automated sampler. All the samples were analysed for major cations and anions using suppressed ion chromatography. Samples are analysed using two different analysis lines running in parallel; one for the cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and one for the anions (NO_3^-, SO_4^{2-}, Cl^- and PO_4^{3-}). A subsample of 100ml was collected from the original filtered sample and sent to Umgeni Water for DOC analysis.

To monitor the changes in streamwater chemistry during a storm event, a daily visit to the catchments was conducted over a week long period. The trip occurred during the one week with the most rainfall during the entire rainfall season. Water samples that were collected over the week were analysed for TDS, TSS and DOC. This was done to make a comparison between DOC data collected by Umgeni Water and spectral absorbance data analysed in the Animal, Plant and Environmental Sciences (APES) Aquatics laboratory using a spectrophotometer. To analyse the DOC samples, the Umgeni Water Laboratory used the Non-Purgeable Organic Carbon (NPOC) method.

Table 6 gives a summary of all data collected monthly and during storm events and where they were analysed.

Table 6 Outline of data collected and where it was analysed.

Monthly/storm event			
Parameter	**Volume (ml)**	**Condition**	**Laboratory**
Major ions	100	Frozen	North West University
DOC	100	Chilled	Umgeni Water
TDS and TSS	500	Chilled	Wits Sediments
Spectral absorbance	100	Chilled	Wits APES

4.5.1 Total dissolved solids (TDS) and total suspended solids (TSS)

Total dissolved solids are a measure of the amount of material that is dissolved in a water sample. TSS represents both organic and inorganic particulate material in the water column, which are larger than 0.45 µm. Both TDS and TSS are good indicators of physical (erosion of geology, sedimentation) and chemical (pollutants, decomposition of organic matter), degradation of surface water (Augustijn *et al.* 2011).

During the early stages of laboratory work, the method described in the proposal was used to calculate TDS, TS and TSS. Although results were obtained for TSS, some of the results for TDS gave negative masses. To address this issue, a method of carefully preparing the filters had to be adopted.

The following method in **Table 7** describes what was done in order to prepare the filters to filter samples in order to calculate TDS and TSS (USDA 2007).

Table 7 Methods followed to prepare the filters before filtering the samples in order to calculate TSS and TDS (USDA 2007).

Filter preparation	
1.	Ensure that filters are handled with forceps at all times, that the forceps do not at any time damage the filters and if so dispose of the filter. - This is because a fingerprint may weigh 0.0001 g and this adds a 10% error for samples containing 0.0010g of sediment.
2.	Carefully inspect the filters as they are removed from the box. Hold them up to a light to make sure that they do not have any holes.
3.	Weigh each of the aluminum dishes that the filters are going to go into (W_1)
4.	Then record the weight of both the aluminum dish and a filter (W_2)
5.	Rinse filters with deionised water using a squirt bottle; - Do not press the filters too hard with forceps - Ensure that there are no holes when placing them down - Be consistent in using the same side for filtering - Rinse to remove any debris, loose fibres etc. - Rinse for a minimum of 30 seconds
6.	After rinsing the filter, carefully place the filters back into their respective aluminum dishes.
7.	Place the dishes into a hot air oven for 60 minutes at 100-105˚C.
8.	Cool filters prior to weighing - Do not remove filters from the oven unless they are ready to be weighed as they will absorb moisture from the air
9.	Weigh each dish containing a filter on the analytic balance and record the weight on the initial form used (W_3)
10.	Now start with the process of TSS and TDS calculation - Work in a systematic manner so that filters aren't left out in the room for too long

After having had prepared the filters as outlined in **Table 6**, the procedures of calculating both TSS and TDS were followed as indicated below in **Table 7.**

Table 8 Methods that were followed when calculating TSS and TDS respectively (Augustijn *et al.* 2011).

	Total suspended solids (TSS)	**Total dissolved solids (TDS)**
1.	Check and regulate oven to maintain the desired temperature range (103-105°C).	Check and regulate oven to maintain the desired temperature range (103-105°C).
2.	After having weighed the aluminum dish with the rinsed filter in an analytical balance and noted the measured weight (W_3). Start the process of TSS calculation.	Weigh the aluminum dish that is going to be used for the TDS analysis, label accordingly (Wt_1).
3.	Using forceps take the filter and place it on the filter rig to start filtering.	Pass the sample water through the filter, applying suction if necessary.
4.	To ensure mixing, shake the sample bottle. Rinse the filter rig three times with the sample, both before the sample gets filtered and after. Be wary of how much of the sample you use that you have enough for the 500 ml.	Rinse a graduated cylinder with three successive 10 ml portions of distilled water then the filtered sample. Allowing complete drainage between each rinse.
5.	Filter 500 ml through a 0.45 µm pre-weighed filter paper.	Transfer 100 ml (V) of filtered sample into the dish using a graduated cylinder.
6.	Pass the sample water through the filter, applying suction if necessary.	Place the dish into the oven at 103-105°C for at least three hours. Be wary of boiling and splattering of the sample during the evaporation process.
6.	Disconnect the filter rig and use forceps to remove the filter and put it into its respective dish.	Allow the dish to cool before weighing.
7.	Place the dish into the oven.	When cool, weigh the dish (Wt_2).
8.	Dry the filters for one to three hours to get constant mass.	
9.	Weigh the filter and dish as soon as it has cooled to avoid absorption of moisture (W_4).	

Both TSS and TDS were examined for variability during and after storm events. This is because of storm-induced consequences which include but are not limited to: changes in flow rates, erosion and runoff (Park *et al.* 2011). The data analyses tools that were used in this respect are highlighted in **Figure 11**.

4.5.2 Dissolved organic carbon

The correlation between the intrinsic colour of sample waters and dissolved organic carbon was investigated in the APES Laboratory. This was done using spectral absorbance, using a Mapada UV-1100 spectrophotometer shown in **Figure 10**. The results were then compared with the control.

The Mapada UV-1100 spectrophotometer, shown in **Figure 10**, was used to take absorbance readings at wavelengths 254 nm, 360 nm, 400 nm and 546 nm for comparison with DOC measured independently at Umgeni Water.

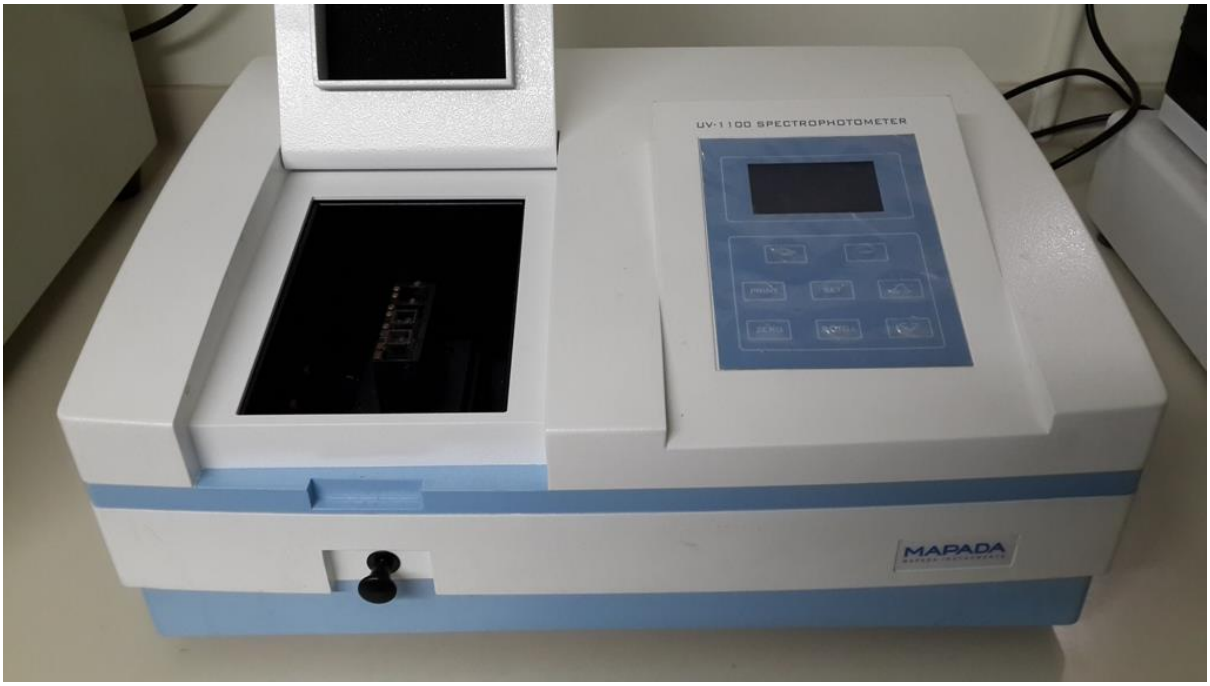

Figure 10 Mapada UV-1100 spectrophotometer used for spectral absorbance analyses.

Source: Gavin Snow

To do the analyses, a blank – deionised water – was put into one of the cuvettes and the sample into the other. The sample cuvettes were rinsed clean with deionised water, in between each analysis.

The relationship between the intrinsic colour of sample waters and dissolved organic carbon was investigated. This was done using spectral absorbance, at the wavelengths of 254 nm, 360 nm, 400 nm and 546 nm. The wavelengths 254 nm and 546 nm; were used because those wavelengths are commonly used in studies of spectral absorbance in natural waters (van Steenderen and van Rossum 1985, Brandstetter *et al.* 1996, Weishaar *et al.* 2003, Austnes *et al.* 2010). Then 360 nm and 400 nm were arbitrarily chosen to fill the gap between 254 nm and 546 nm.

4.6 Data analyses

4.6.1 Monthly data – historical and recent

R was used (R Development Core Team 2008) and *lme4* (Bates *et al.* 2015) to perform a linear mixed effects analysis of the relationship between streamwater chemistry and catchments. The fixed effects were the catchments as each are their own treatment. This analysis was performed because the absence of data, i.e. missing values violated the assumption of independence in an ANOVA. The model expresses the relationships in data in terms of a function. Multiple responses from the same subject cannot be regarded as independent from each other. These catchments were resampled over time and this is characteristic of repeated measures time series analysis. These two violations left the option of using linear mixed effects models, the models are an extension of normal regression models and can control for the non-independence of data points.

First tests were performed to investigate differences between catchments, this was done for historical streamwater chemistry data. This was then followed by a post-hoc test type scenario to test if there was an effect of catchment on the streamwater chemistry concentrations. To do this, two models were created. An effect model **(4.1)** which said there was an effect and a null model **(4.2)** which said there was no effect;

mod.all <- lmer(ob[[chem]] ~ CMT + (1|YR), data = ob, REML = F) **(4.1)**

mod.null <- lmer(ob[[chem]] ~ (1|YR), data = ob, REML = F) **(4.2)**

The models were then compared using a likelihood ratio test (Pinheiro and Bates 2000), P-values were obtained from the ratio test. Other data techniques that were applied in this section are explained in **Figure 11**.

Historical data -> test for differences between catchments and then investigate for effect of catchment on streamwater chemistry.

***lme4* and likelihood ratio test**

Monthly data-> compare catchment means of recent streamwater chemistry data, DOC, pH, conductivity, dissolved oxygen and streamwater temperature.

One-Way ANOVA

Comparing sample constituents ->

comparing DOC, pH, conductivity,dissolved oxygen and streamwater temperature from control catchment with those from other catchments.

Tukey HSD

DOC -> investigate if relationship between DOC and UV radiation is significant

Simple linear regression to predict DOC from absorbance

TSS and TDS -> compare concentrations from CP03 and CP06.

Episodic data -> compare streamwater chemistry concentrations of CP03 and CP06.

Figure 11 Statistical analysis techniques that were applied**.**

The following hypotheses were made when analysing the DOC, conductivity, dissolved oxygen, pH and temperature data:

H_0: $\mu_{CP03} = \mu_{CP04} = \mu_{CP06} = \mu_{CP09}$

H_1: $\mu_{CP03} \neq \mu_{CP04} \neq \mu_{CP06} \neq \mu_{CP09}$

A post-hoc test was run on the data after it had been processed. These tests were used to determine which catchment pairs were significantly different from each other. In cases where there was an abundance of data points, the Tukey procedure (Haynes 2013) was used. This procedure gave more reliable results; the level of reliability is dependent on the number of data points.

CHAPTER 5: RESULTS

Overview

> *This chapter provides the results from the tests and analyses of data used to answer the objectives of this research project. Historical data collected at the CPRS during the 1980s were also analysed and compared to data collected during this study.*

5.1 Major ions

Results from historical data (1981 – 1986) and recent data (2014 – 2016) were compared to investigate differences in major ion concentrations over these periods.

5.1.1 Historical vs. recent data

Calcium

Results obtained from analysing the data collected during 1981 to 1986 and 2014 to 2016 are shown in this section. The historical Ca changes are shown in **Figure 12** (the data used can be found in **APPENDIX B1**).

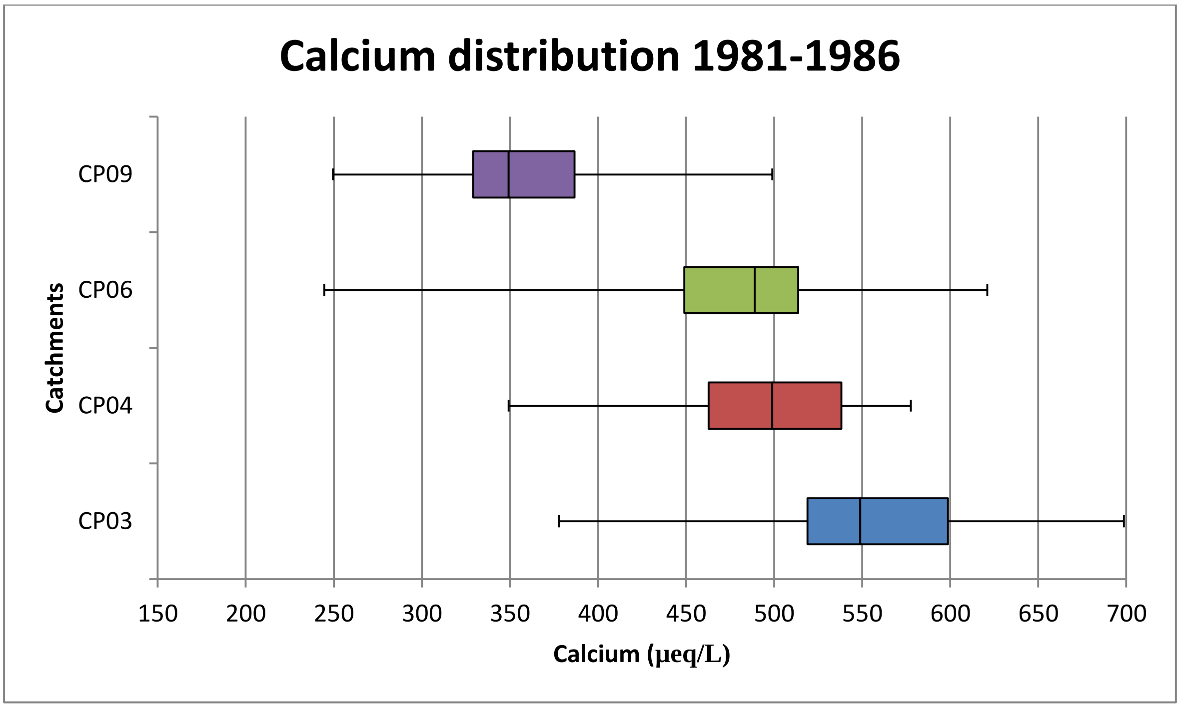

Figure 12 Plot showing historical Ca concentrations across study catchments from 1981 - 1986.

CP09 (protection from fire) had the lowest Ca concentrations whilst CP04 and CP06 (pristine catchments) had similar concentrations and CP03 (previously afforested) had the highest, as shown in **Figure 12**.

The recent data changes are shown in **Figure 13** (data in **APPENDIX B2**).

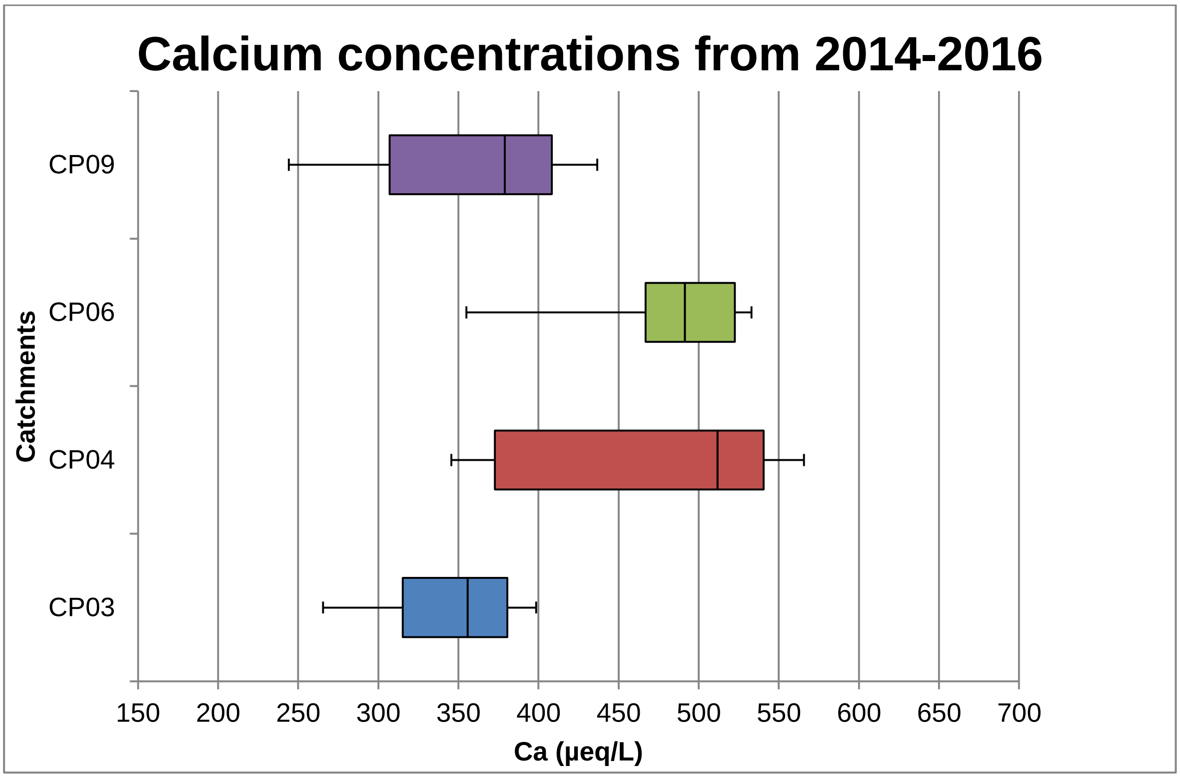

Figure 13 Plot showing recent Ca concentrations across study catchments from 2014 – 2016.

CP04 and CP06 again showed similar Ca concentration ranges. At CP03 Ca concentrations were dramatically reduced from the historical to the recent monitoring programme. At CP09 Ca concentrations dropped from the historical to recent by about 50 µeq/L.

The historical and recent summer data were graphed and shown in **Figure 14** and **15**. Only the summer data were used because the recent only had complete summer season data points, therefore only the summer season was extracted from the datasets.

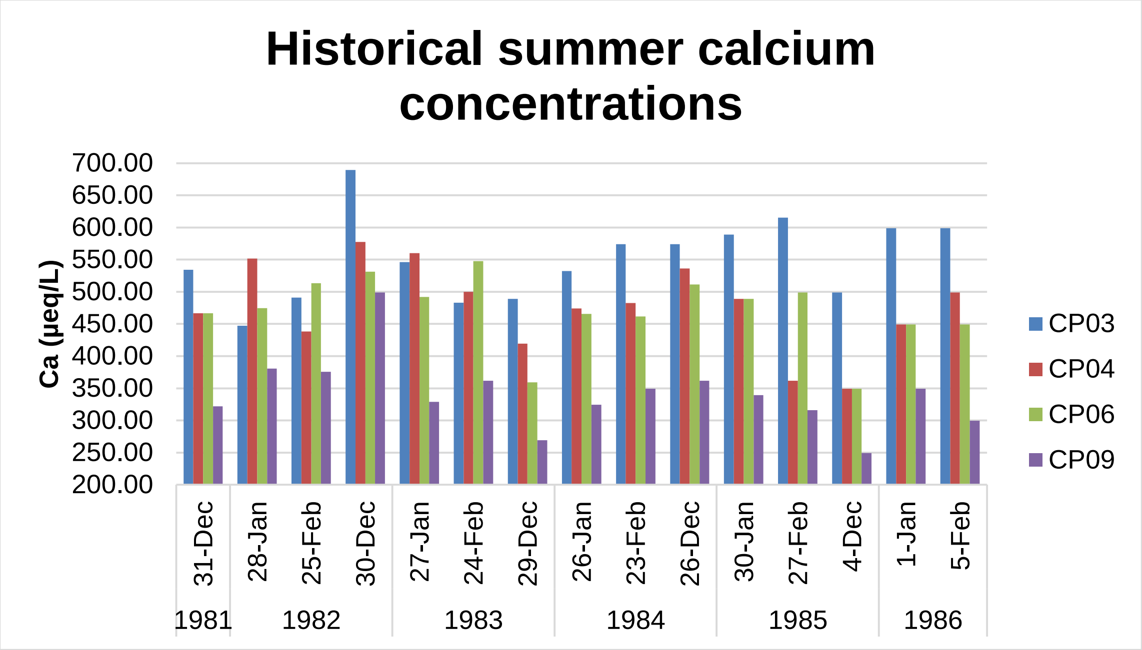

Figure 14 Bar graph showing all summer season data extracted from the historical dataset.

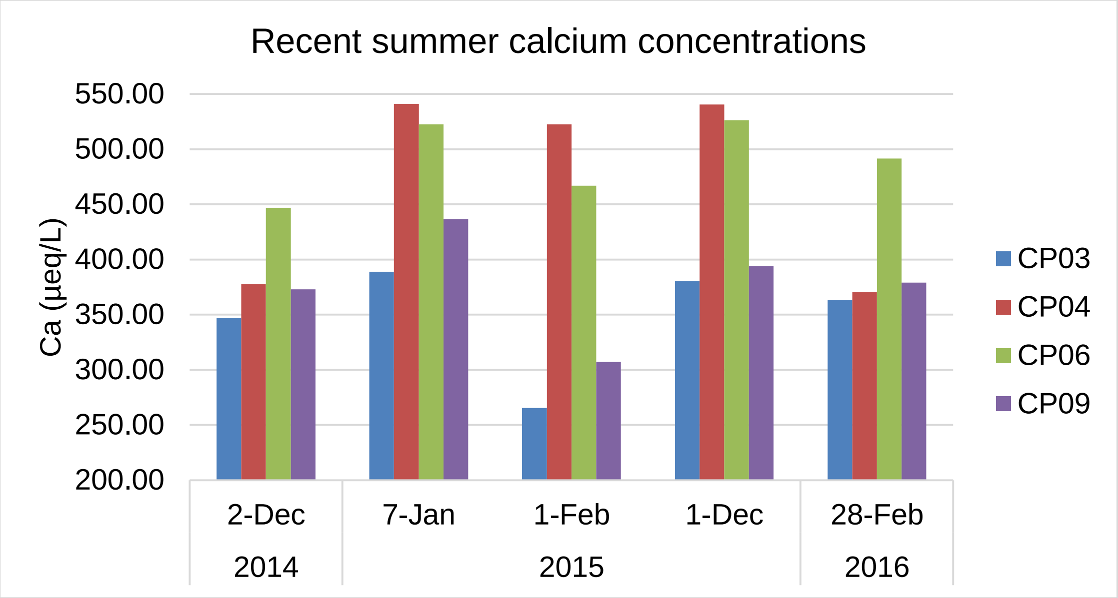

Figure 15 Bar graph showing all summer season data extracted from the recent data set.

CP03 tended to have high Ca concentrations in the historical dataset. In October 1985, there was a controlled fire in CP03 to reduce fuel loads. The table shown in **APPENDIX B1** indicates that there was no immediate change in concentrations but increases were only seen in the middle of summer (1st January 1986) and maintained till February. Since the fire had been controlled, it could have taken the burnt ash and other materials long before it entered the stream and created a noticeable signature. Concentrations of solutes are meant to be diluted by the consistent summer rainfall and so that increase could have been caused by the later effects of fire.

There was an overall decrease in the range of concentrations of Ca from the historical to the recent. CP03 shifted from always having the highest concentration in the 1980s to the lowest in the 2000s.

From 1981 to 1983, CP06 was not being burned whilst CP04 was receiving consistent controlled burns (except 1983 and 1985). During the times when CP04 was receiving fire and CP06 was not, CP04 had higher Ca concentrations. This showed that fire had an influence on the solute concentrations.

CP04 was burned in September 2015 and there was a small increase in the concentration during the first month of summer late in the year. By the end of summer, the concentration had dropped by over 200 µeq/L. The CP04 and CP06 concentrations tended to be comparable except after when the fire had occurred. This shows that land use could be having a significant influence on the streamwater chemistry of these catchments, amongst other factors.

CP09 received and still receives protection from fire. This catchment had the lowest concentrations during the 1980s. Generally, there was no change in the ranges of the data from the historical to recent datasets. In June 2014, there was a fire in CP09 and there was an increase in the Ca concentration in January 2015. There was a possible relationship between increases in concentrations and the rainfall season. Another factor which could have affected the intensity of the signature could have been the extent of each of the associated fires.

A summary of the changes that occurred from the historical to recent datasets was shown in **Table 9**.

Table 9 Outline of the changes in Ca concentration from the historical to recent datasets.

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	377.8	265.4	349.3	345.7	244.6	354.9	249.5	244.1
Q_1	519.0	315.3	462.9	372.8	449.1	466.9	329.1	307.1
Q_2	548.9	355.7	499.0	511.8	489.0	491.5	349.3	379.0
Q_3	598.8	380.5	538.3	540.6	513.7	522.5	386.7	408.4
Max	698.6	398.5	577.7	565.8	621.0	533.0	499.0	436.7

As shown in **Table 9**, the historical data had higher minimum values at CP03, CP04 and CP09 so there was a general drop in minimum Ca concentrations from the historical to recent datasets. CP03 had the most dramatic changes with recent concentrations much lower than historical across all quartiles.

The results obtained from running the linear mixed effects model on the historical data and a one-way ANOVA on the recent data are shown in **Table 10** and **11**, respectively.

Solutes	**Comparisons**	**Chi-squared**	**Df**	**Pr(>Chisq)**	**Signif. code**	**Significant/Insignificant**
Ca	**Differences between catchments**	229.32	3	<2.2E-16***	***	Significant
	Catchment pairs					
	CP0304	26.297	1	2.927E-07	***	Significant
	CP0306	30.469	1	3.392E-08	***	Significant
	CP0309	30.469	1	3.392E-08	***	Significant
	CP0406	30.469	1	3.392E-08	***	Significant
	CP0409	30.469	1	3.392E-08	***	Significant
	CP0609	30.469	1	3.392E-08	***	Significant

There were significant differences between catchments as shown in **Table 10**. These differences were further investigated and it was found that there were significant differences between catchments, therefore catchments had an influence on Ca concentrations.

Table 10 One-way ANOVA results for recent Ca data.

Source	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	F-statistic	P-value
Catchment	3	127068.1057	42356.0352	9.6243	0.0001
Residuals	32	140829.7036	4400.9282		
Total	35	267897.8093			

The p-value corresponding to the F-statistic of one-way ANOVA was lower than 0.05, suggesting that one or more catchment pairs were significantly different. The Tukey HSD test was then run to identify which of the catchment pairs were significantly different from each other. The results from running a Tukey HSD test on the recent Ca data are shown in **Table 12**.

Table 11 Tukey HSD results for recent data.

Catchment pairs	Tukey HSD F statistic	Tukey HSD p-value	Tukey HSD inference
CP04 – CP03	5.8871	0.004628	** p<0.01
CP06 – CP03	6.8558	0.0010053	** p<0.01
CP09 – CP03	0.7293	0.8999947	insignificant
CP06 – CP04	0.9687	0.8999947	insignificant
CP09 – CP04	5.1578	0.0147896	** p<0.05
CP09 – CP06	6.1265	0.0010053	** p<0.01

The p-value corresponding to the F-statistic of one-way ANOVA was lower than 0.01 which suggests that one or more catchment pairs were significantly different.

There were some statistically significant differences between recent catchment pairs as determined by one-way ANOVA (F (3, 32) = 4.7732, p = 0.0001) at α=0.01 and (F (3, 44) = 3.8315, p = 0.0001) at α= 0.05.

The recent Ca concentrations, although not the lowest across the different catchments, was significantly lower than the historical levels. Again, CP09 was very different from the other catchments. This could have been because the riparian vegetation and aquatic ecosystem within each catchment used up Ca in different ways from each other or the catchment was depleted in Ca due to a lack of burning which releases nutrients and other ions. The possible effects of the fire in June 2014 could be responsible for the increased CP09 recent Ca concentrations, as the fire liberated ions and nutrients which reflected in streamwater chemistry concentrations

Magnesium

The graphs showing the changes in magnesium concentrations from 1981 to 1986 were shown in **Figure 16** (data in **APPENDIX B3**).

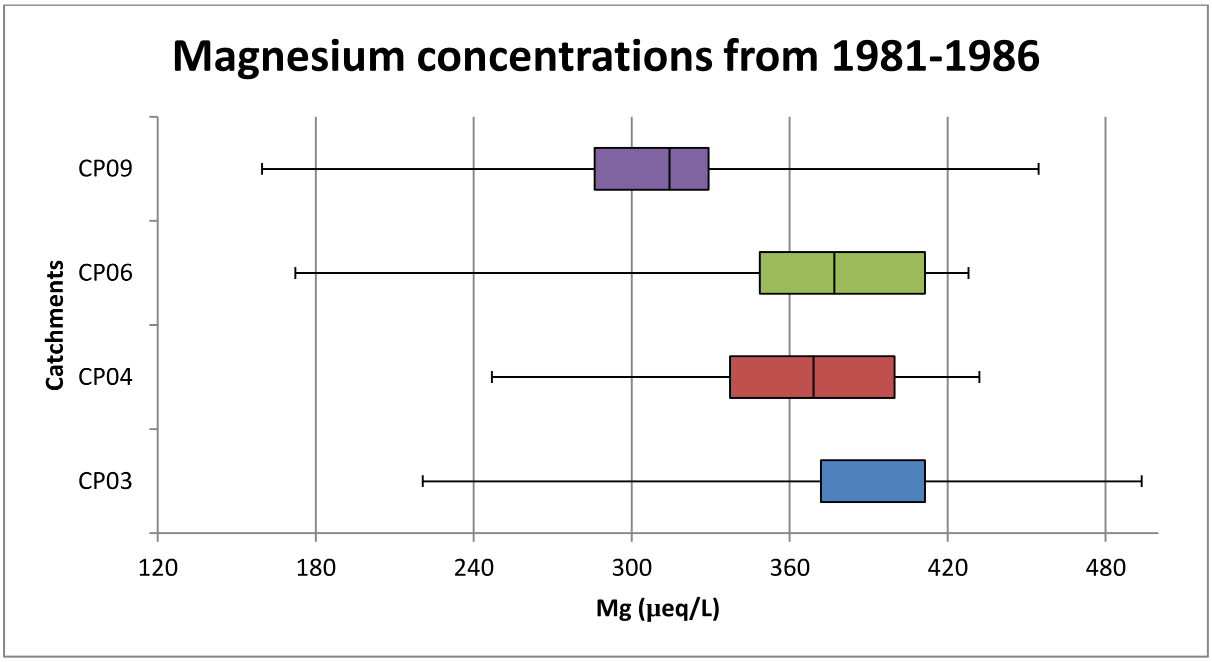

Figure 16 Plot showing historical Mg concentrations across study catchments from 1981 - 1986.

CP04 and CP06 (pristine catchments) had similar Mg concentrations. CP09 (protection from fire) had Mg concentrations which were much lower than the other catchments. CP03 (previously afforested) had concentrations in the ranges of CP04 and CP06.

Figure 17 shows the changes in Mg concentrations from 2014-2016 (data used could be found in **APPENDIX B4**).

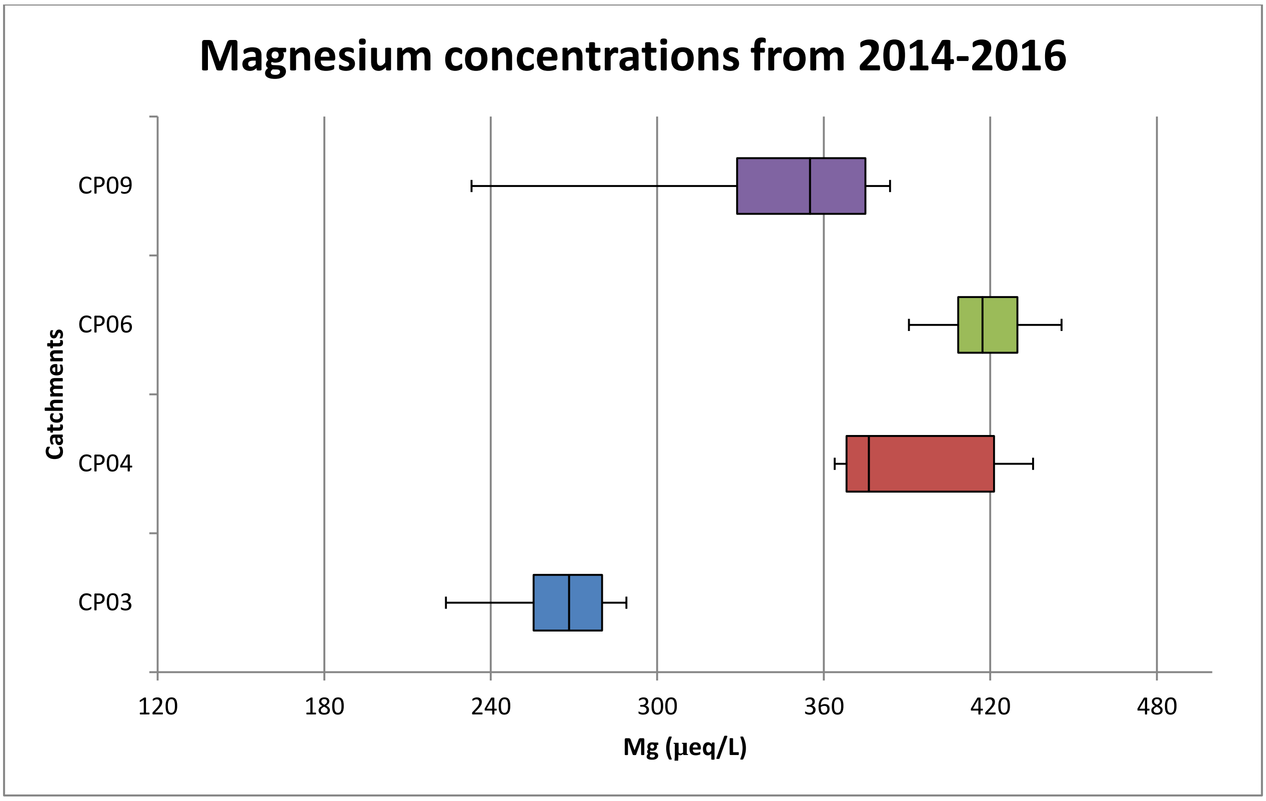

Figure 17 Plot showing recent Mg concentrations across study catchments from 2014 - 2016.

CP04 and CP06 again had similar concentration ranges, as seen in the historical plot (**Figure 16**), the range had increased but the two catchments were still comparable. This could have been due to their similar land uses and management techniques. CP03 had concentrations which were significantly lower than those that were seen in the historical data. This could have been due to amount of time since the fire. Felling and fire release a flush of ions but the effects wear off with time. CP09 concentrations increased from historical to recent datasets and this could possibly be relate to the fire which occurred in 2014

The historical and recent summer data were graphed and shown in **Figure 18** and **19**.

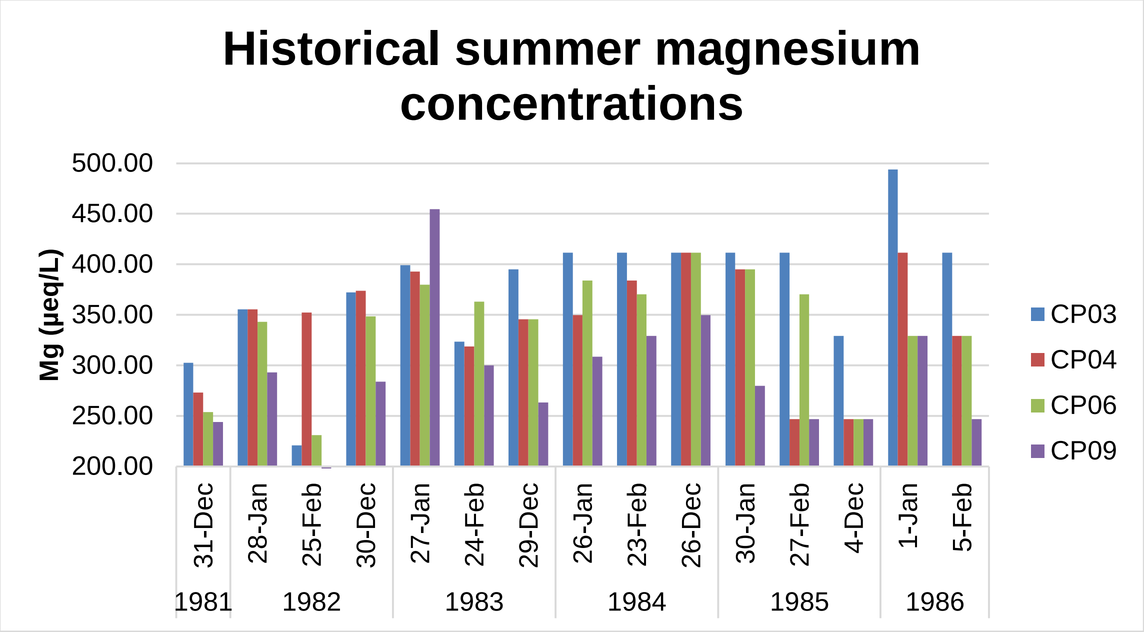

Figure 18 Bar graph showing all summer season data extracted from the historical dataset.

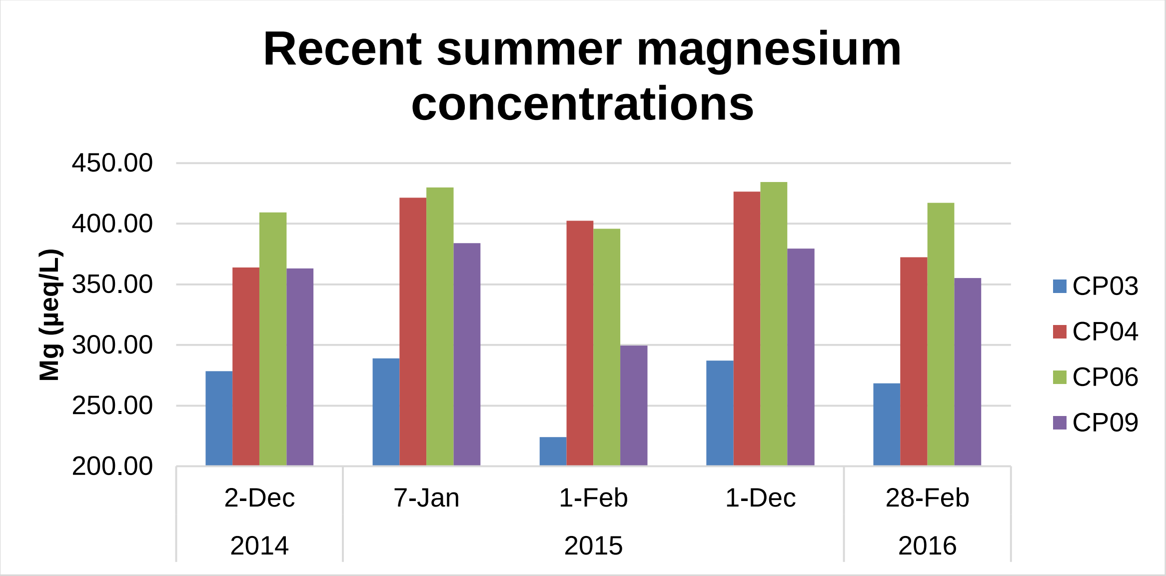

Figure 19 Bar graph showing all summer season data extracted from the recent dataset.

Aside from a high Mg CP03 concentration in 1986, the catchments maintained concentrations that were below or equal to 450 µeq/L. CP03 had concentrations which dropped from the historical to the recent data. It had no concentrations which exceeded 300 µeq/L, as compared to other catchments that had a majority of concentrations in excess of 350 µeq/L in the historical context. The Mg concentrations were higher during the years which fire had been applied (September 1981 and October 1985), the increases did not occur immediately after the fire but a couple of months after.

CP04 had controlled fires applied in August/September of 1981, 1982 and 1984. The Mg concentrations from the years when fire was applied were higher than the times when it had not been applied. CP04 and CP06 have similar land uses and as a consequence had comparable concentrations for most of the time.

Overall CP09 had some of the lowest concentrations overall. In 1983 there was a spike in concentrations.

The recent CP04 and CP06 Mg concentrations remained comparable. There was a fire in CP04 in September 2015, the overall pattern has been that concentrations increased in January after a fire had been applied the year before so the February data could have been from a period of decrease in concentration after that month (data missing).

CP09 was burnt in June 2014 and again the Mg concentrations increased in January of the next year.

A summary of the changes that occurred from the historical to recent datasets is shown in **Table 13**.

Table 12 Outline of the changes in Ca concentrations from the historical to recent datasets.

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	220.7	223.9	246.9	364.0	172.3	390.7	159.6	233.1
Q_1	371.8	255.5	337.3	368.2	348.7	408.4	286.0	328.7
Q_2	411.5	268.3	369.0	376.3	377.0	417.2	314.4	355.1
Q_3	411.5	280.1	399.8	421.4	411.5	429.8	329.2	375.0
Max	493.7	288.9	432.0	435.4	427.9	445.7	454.6	383.9

The historical data had lower minimum and 50% of the maximum values across all the catchments. Overall, CP04 and CP06 had recent data points that were mostly higher than the historical data points. CP03 had generally higher historical magnesium concentrations.

The results obtained from running the linear mixed effects model on the historical data and one-way ANOVA on the recent data are shown in **Table 14** and **15**, respectively.

Table 13 Results obtained from running a linear mixed effects model on the historical data and comparisons between Catchments to see if Catchments were responsible for differences in Mg concentrations.

Solutes	**Comparisons**	**Chi-squared**	**Df**	**Pr(>Chisq)**	**Signif. code**	**Significant/Insignificant**
Mg	**Differences between catchments**	91.888	3	<2.2E-16	***	Significant
	Catchment pairs					
	CP0304	13.288	1	0.0002671	***	Significant
	CP0306	9.5942	1	0.001952	**	Significant
	CP0309	9.5942	1	0.001952	**	Significant
	CP0406	9.5942	1	0.001952	**	Significant
	CP0409	9.5942	1	0.001952	**	Significant
	CP0609	9.5942	1	0.001952	**	Significant

There were significant differences between Catchments as shown in **Table 14**. These differences were further investigated and it was found that there were significant differences between catchment pairs and therefore the catchment treatments had an influence on Mg concentrations.

Table 14 ANOVA results for recent Mg data.

Source	**Degrees of freedom**	**Sum of squares (SS)**	**Mean square (MS)**	**F-statistic**	**P-value**
Catchment	3	119488.7050	39829.5683	40.5701	5.1556E-11
Residuals	32	31415.9930	981.7479		
Total	35	150904.6381			

For the recent data, the p-value corresponding to the F-statistic of one-way ANOVA was lower than 0.05, suggesting that the one or more catchment pairs were significantly different. The Tukey HSD test was then run to identify which of the catchment pairs are significantly different from each other.

The results that were obtained from running a Tukey HSD test on the recent data were shown in **Table 15**.

Table 15 Tukey HSD results for recent Mg data**.**

Catchment pairs	**Tukey HSD F statistic**	**Tukey HSD p-value**	**Tukey HSD inference**
CP04 – CP03	13.1929	0.0010053	** p<0.01
CP06 – CP03	15.8250	0.0010053	** p<0.01
CP09 – CP03	7.9389	0.0010053	** p<0.01
CP06 – CP04	2.6321	0.3616733	insignificant
CP09 – CP04	5.2541	0.0071017	** p<0.01
CP09 – CP06	7.8861	0.0010053	** p<0.01

The p-value corresponding to the F-statistic of one-way ANOVA was lower than 0.01 which suggests that one or more catchment pairs were significantly different.

There were some statistically significant differences between recent catchment pairs as determined by one-way ANOVA (F (3, 32) = 4.7732, p = 5.1556E-11) at α=0.01 and (F (3, 32) = 3.8315, p = 5.1556E-11) at α= 0.05.

There were statistically significant differences between historical Mg data between all the research catchments pairs except for the similar land use catchments, CP06 and CP04.

Sodium

The historical data collected for Na is depicted in **Figure 20 (**data used could be found in **APPENDIX B5**).

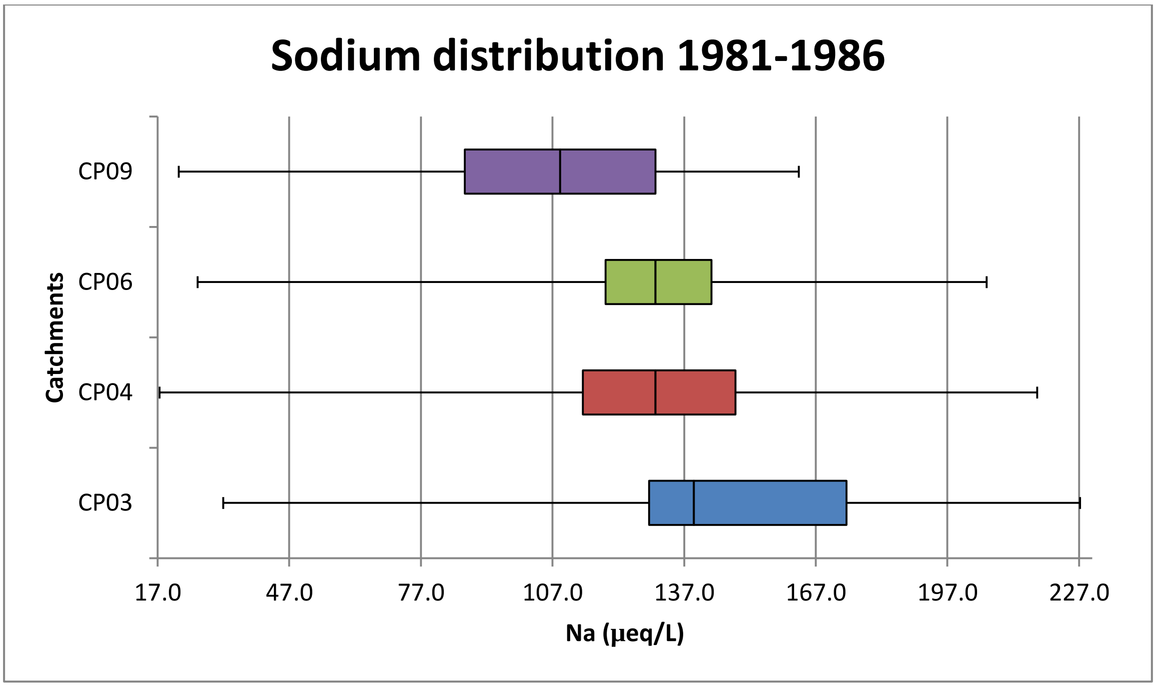

Figure 20 Plot showing historical Na concentrations from 1981 - 1986.

As seen in **Figure 20**, CP03 had some of the highest Na concentrations across all the catchments. CP04 and CP06 had comparable concentrations whilst CP09 had the lowest Na concentrations.

The recent sodium data is represented in **Figure 21** (data used could be found in **APPENDIX B6**).

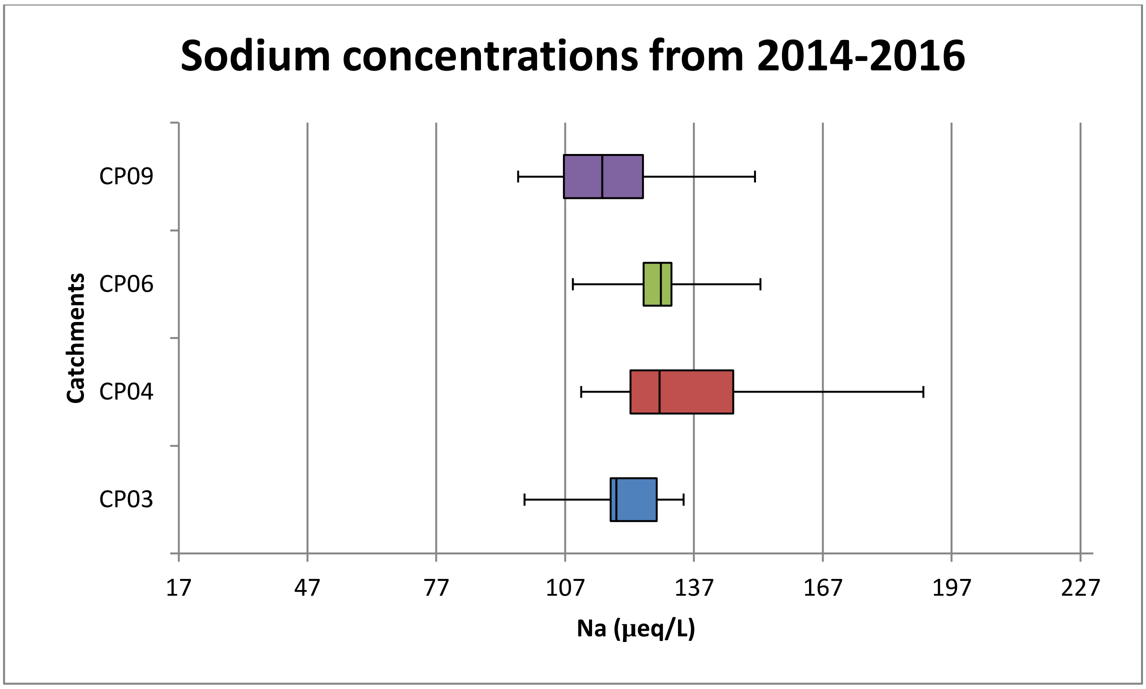

Figure 21 Plot showing recent Na concentrations from 2014 - 2016.

The general relationship between CP04 and CP06 remained the same as was seen in **Figure 20**. These two catchments had similar concentrations. There was an overall decrease in Na concentrations from the historical to recent datasets. CP09 and CP03 were roughly in the same range in the recent dataset.

The historical and recent summer data were graphed and shown in **Figure 22** and **23**.

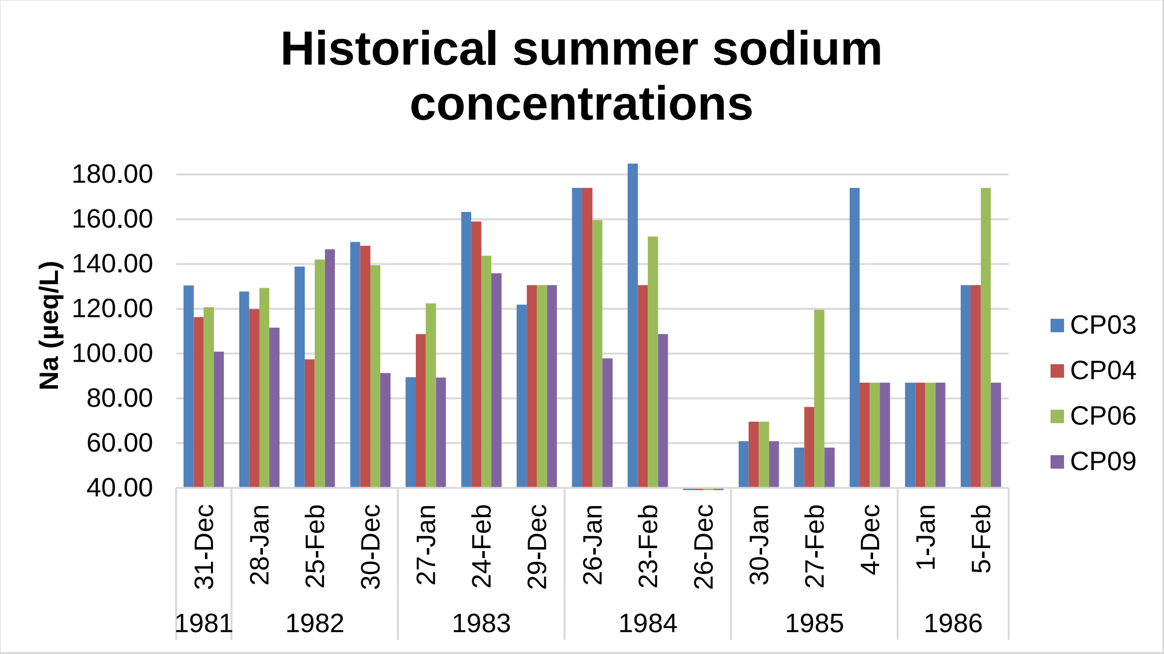

Figure 22 Bar graph showing all summer season data extracted from the historical dataset.

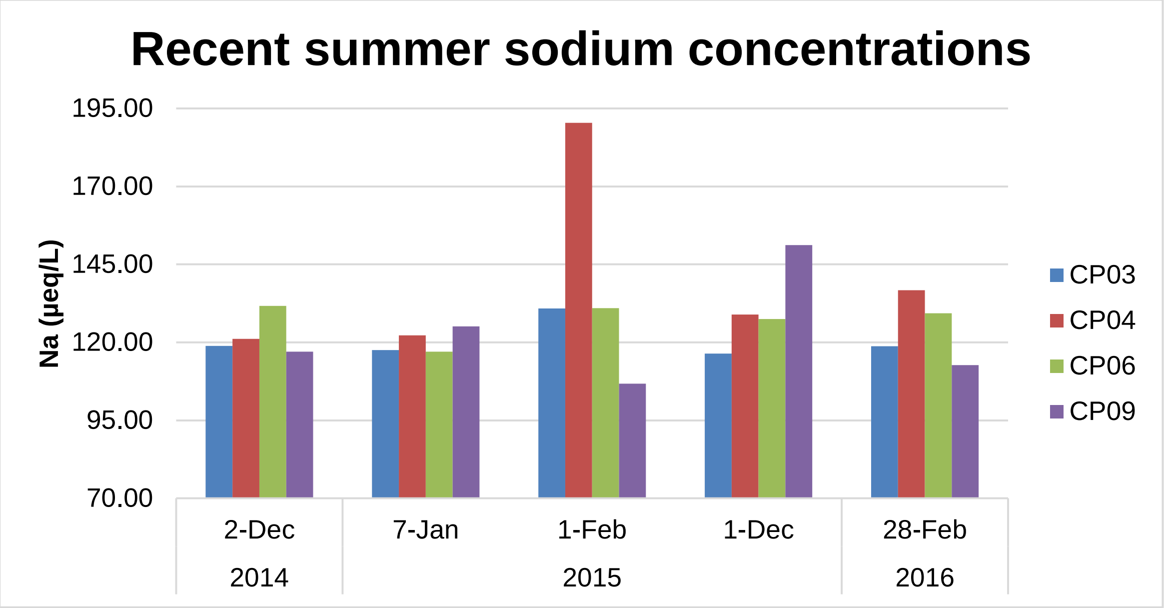

Figure 23 Bar graph showing all summer season data extracted from the recent data set.

CP03 had the most variable historical Na concentrations, it had the highest and lowest values. There were noticeable increases in concentrations months after fires had occurred (September 1981 and October 1985).

CP04 and CP06 had comparable historical concentrations. CP04 had increased concentrations during the times after fire had been applied, the same was true for CP06 but the concentrations remained comparable.

CP09 had relatively low Na concentrations throughout most of the historical dataset. There were instances when the same concentrations were maintained over one or two months.

The extreme values were lower in the historical dataset compared to the recent.

A summary of the changes that occurred from the historical to recent datasets is shown in **Table 17**.

Table 16 Outline of the changes in Na concentration from the historical to recent datasets.

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	31.9	97.6	17.4	110.7	26.1	108.8	21.8	96.0
Q_1	129.0	117.6	113.9	122.2	119.1	125.3	87.0	106.7
Q_2	139.2	118.9	130.5	129.0	130.5	129.3	108.8	115.7
Q_3	174.0	128.3	148.7	146.1	143.3	131.7	130.5	125.1
Max	227.3	134.6	217.5	190.4	205.9	152.5	163.1	151.2

The historical data had the lowest minimum concentrations, there was a major increase in minimum concentrations from the historical to recent datasets. However, there was alsoa decrease in the maximum values. CP04 experienced the biggest changes in concentrations between all the catchments in terms of the minima.

The results obtained from running the linear mixed effects model on the historical data and a one-way ANOVA on the recent data were shown in **Table 18** and **19**, respectively**.**

Table 17 The results obtained from running the linear mixed effects model on the historical and comparisons of Na concentration between catchments to investigate differences between catchment pairs.

Solutes	Comparisons	Chi-squared	Df	Pr(>Chisq)	Signif. code	Significant/Insignificant
Na	**Differences between CMTS**	25.959	3	0.000009727	***	Significant
	Effect of CMT on chemistry					
	CP0304	0.9715	1	0.3243		Insignificant
	CP0306	4.183	1	0.04083	*	Significant
	CP0309	4.183	1	0.04083	*	Significant
	CP0406	4.183	1	0.04083	*	Significant
	CP0409	4.183	1	0.04083	*	Significant
	CP0609	4.183	1	0.04083	*	Significant

There were significant differences between catchments as shown in **Table 18**. These differences were further investigated and it was found that catchments had significant influence on Na concentrations, except when CP03 and CP04 were compared.

Table 18 One-way ANOVA results for recent Na data.

Source	**Degrees of freedom**	**Sum of squares (SS)**	**Mean square (MS)**	**F-statistic**	**P-value**
Catchment	3	2514.7048	838.2349	2.8065	0.0554
Residuals	32	9557.8063	298.6814		
Total	35	12072.5111			

The p-value corresponding to the F-statistic of the one-way ANOVA was higher than 0.05 which suggested that none of the catchment pairs were significantly different in the recent dataset.

There was an overall increase from historical to recent Na data. Historical CP03 Na concentrations had significantly higher values than CP04 and so there was a statistical difference observed. This could be linked to the different land uses, accompanied by the effects of fire on the liberation of Na ions.

Potassium

The historical potassium data is shown in **Figure 24** (data in **APPENDIX B7**).

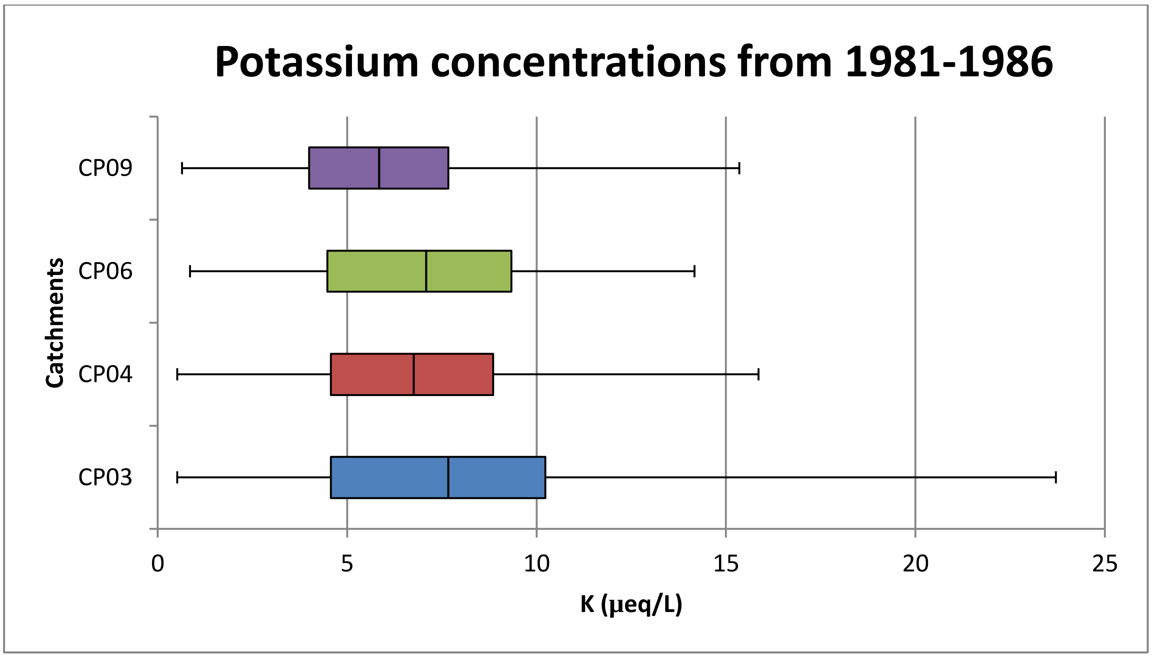

Figure 24 Plot showing historical K concentrations from 1981-1986.

The K concentrations were similar across all the catchments.

The recent data is represented in **Figure 25** (data used was shown in **APPENDIX B8**).

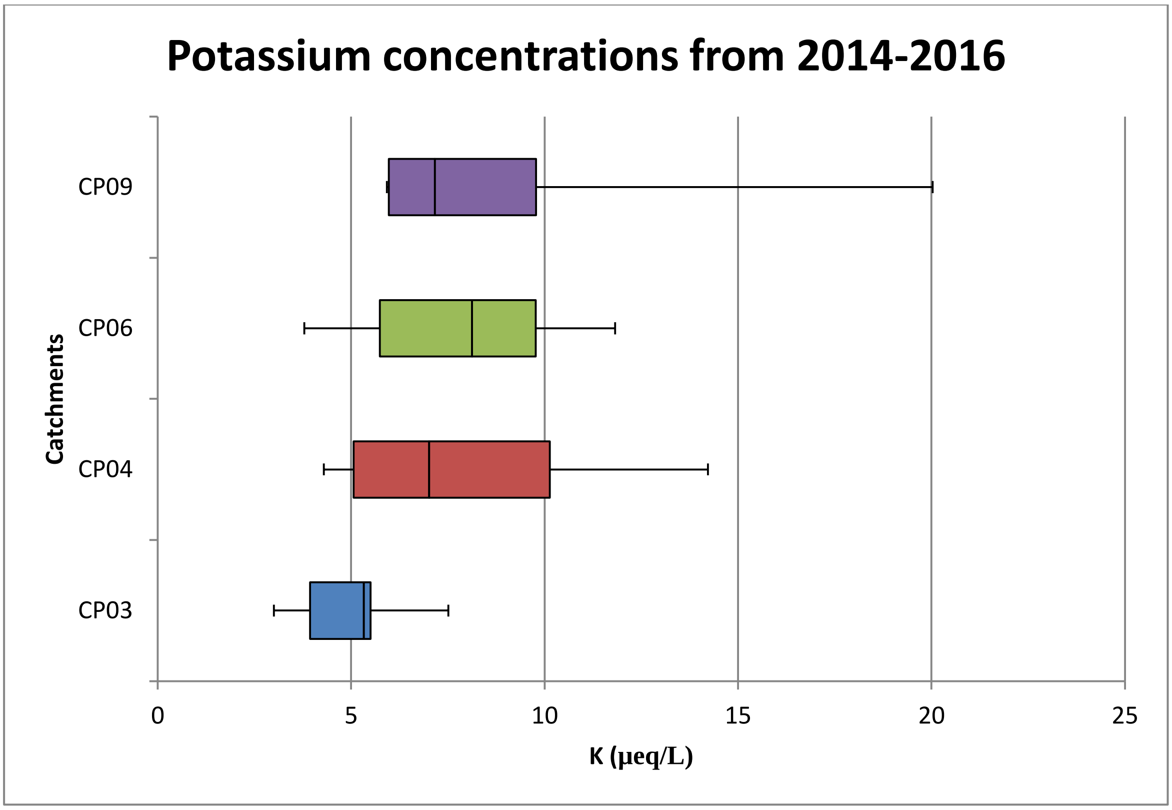

Figure 25 Plot showing recent K concentrations from 2014 – 2016.

As shown in **Figure 25**, CP03 had the lowest K values in comparison to other catchments. High readings vary between CP04 (pristine grasslands) and CP09 (fire protected), all there had comparable concentrations.

The historical and recent summer data were graphed and shown in **Figure 26** and **27**.

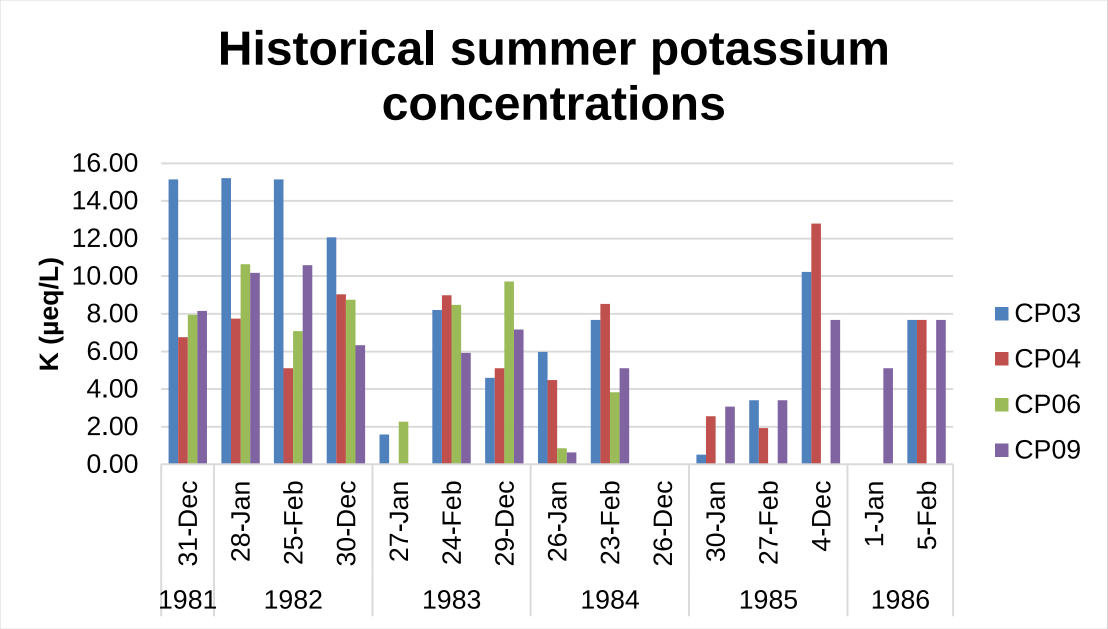

Figure 26 Bar graph showing all summer season data extracted from the historical dataset.

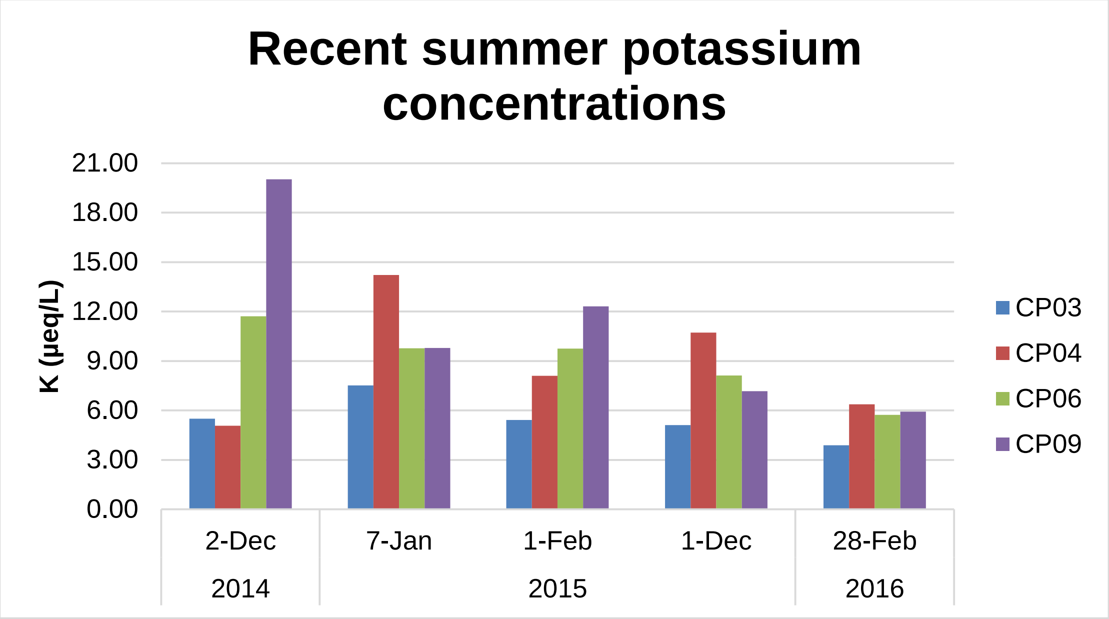

Figure 27 Bar graph showing all summer season data extracted from the recent dataset.

CP03 was burnt in September 1981 and as a consequence K concentrations which were significantly higher than those of other catchments were observed from summer of 1981 through 1982. Concentrations also increased the time period after the fire in October 1985. The same was true for CP04, concentrations increased after fires in 1981 and 1982. Due to missing data a possible increase in K concentration after fire was applied in CP06 could not be shown.

CP09 had varying concentrations, but since there were no fires during the data collection period these changes must have been due to other catchment specific processes acting within the riparian and aquatic ecosystems.

CP03 had consistently low recent K data. There was an increase in K concentrations a few months after the fire in CP09 had occurred in 2014. The concentrations then dropped to those that were comparable to CP03. CP04 and CP06 had varying concentrations despite their similar land uses. After the fire in September 2015, there was an increase in CP04 K concentrations.

A summary of the changes that occurred from the historical to recent datasets is shown in **Table 20.**

Table 19 Outline of the changes in K concentration from the historical to recent datasets.

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	0.5	3.0	0.5	4.3	0.9	3.8	0.6	5.9
Q_1	4.6	3.9	4.6	5.1	4.5	5.7	4.0	6.0
Q_2	7.7	5.3	6.8	7.0	7.1	8.1	5.8	7.2
Q_3	10.2	5.5	8.9	10.1	9.3	9.8	7.7	9.8
Max	23.7	7.5	15.9	14.2	14.2	11.8	15.3	20.0

As shown in **Table 20**, recent data show higher minimum values across all the catchments. The ranges of the catchment were similar.

The results obtained from running the linear mixed effects model on the historical data and a one-way ANOVA on the recent data are shown in **Table 21** and **22**, respectively.

Table 20 Results obtained from running a linear mixed effects model on the historical data and comparisons between catchments to investigate differences between catchment pairs.

Solutes	**Comparisons**	**Chi-squared**	**Df**	**Pr(>Chisq)**	**Signif. code**	**Significant/Insignificant**
K	**Differences between catchments**	4.3128	3	0.2296		Insignificant
	Catchment pairs					
	CP0304	1.6934	1	0.1932		Insignificant
	CP0306	0.9795	1	0.3223		Insignificant
	CP0309	0.9795	1	0.3223		Insignificant
	CP0406	0.9795	1	0.3223		Insignificant
	CP0409	0.9795	1	0.3223		Insignificant
	CP0609	0.9795	1	0.3223		Insignificant

There were no significant differences between catchments.

Table 21 One-way ANOVA results for recent K data.

Source	**Degrees of freedom**	**Sum of squares (SS)**	**Mean square (MS)**	**F-statistic**	**P-value**
Catchment	3	80.9771	26.9924	2.5651	0.0719
Residuals	32	336.7336	10.5229		
Total	35	417.7107			

The p-value corresponding to the F-statistic of the one-way ANOVA for the recent data was higher than 0.05, suggesting that the catchment pairs were not significantly different.

Chloride

Graphs depicting the changes in chloride levels during 1981 - 1986 (data were shown in **APPENDIX B9**) are shown in **Figure 28.**

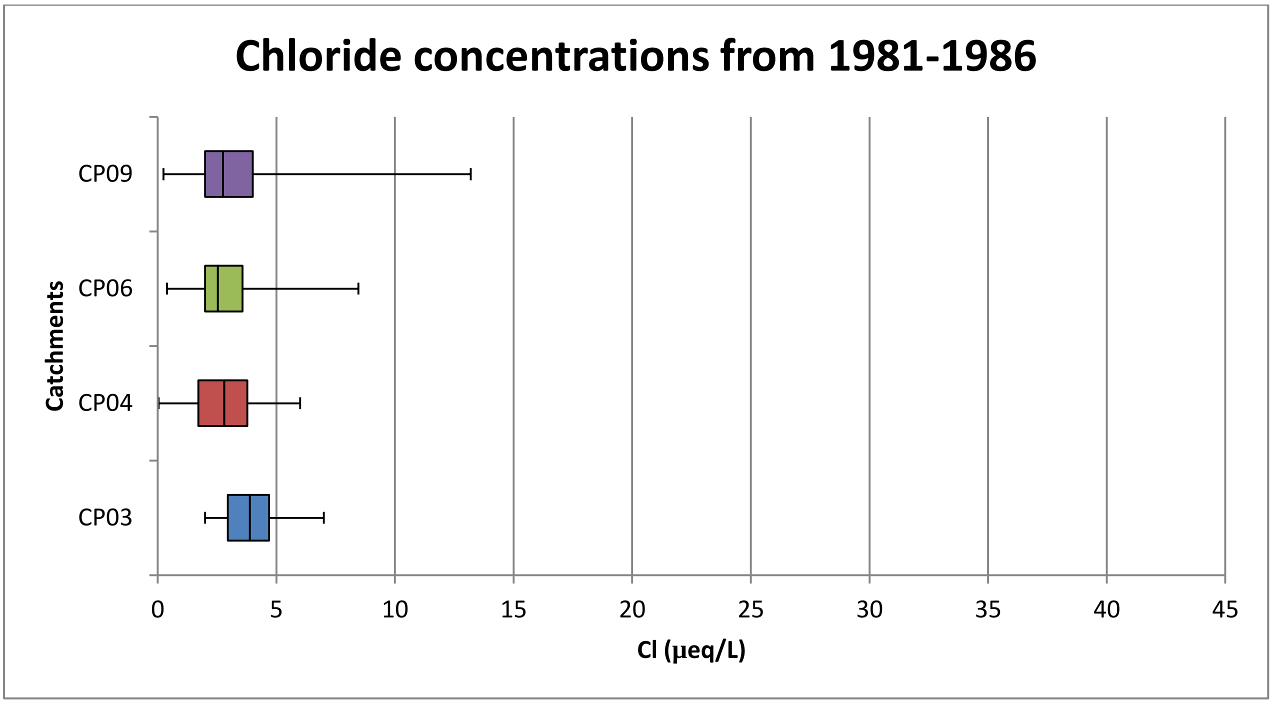

Figure 28 Plot showing historical Cl concentrations from 1981 – 1986.

CP04, CP06 and CP09 had similar Cl concentrations whilst CP03 had concentrations which were slightly higher than the other three catchments.

The recent data is shown in **Figure 29** (data are shown in **APPENDIX B10**).

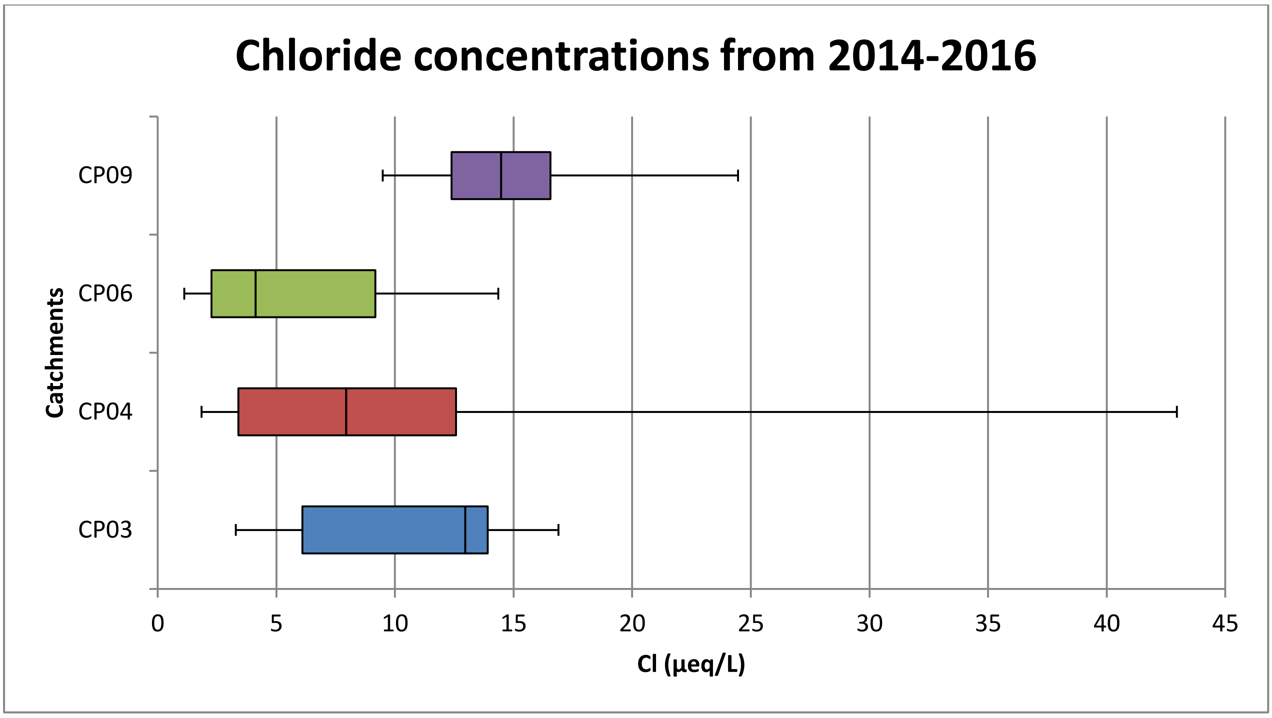

Figure 29 Plot showing recent Cl concentrations from 2014 – 2016.

Chloride concentrations increased from the historical to the recent datasets. CP04 and CP06 had similar Cl concentrations. CP03 and CP09 showed drastic increases in concentrations to almost three times the historical means, although absolute concentrations are still low relative to water bodies in other regions. CP09 also had the same.

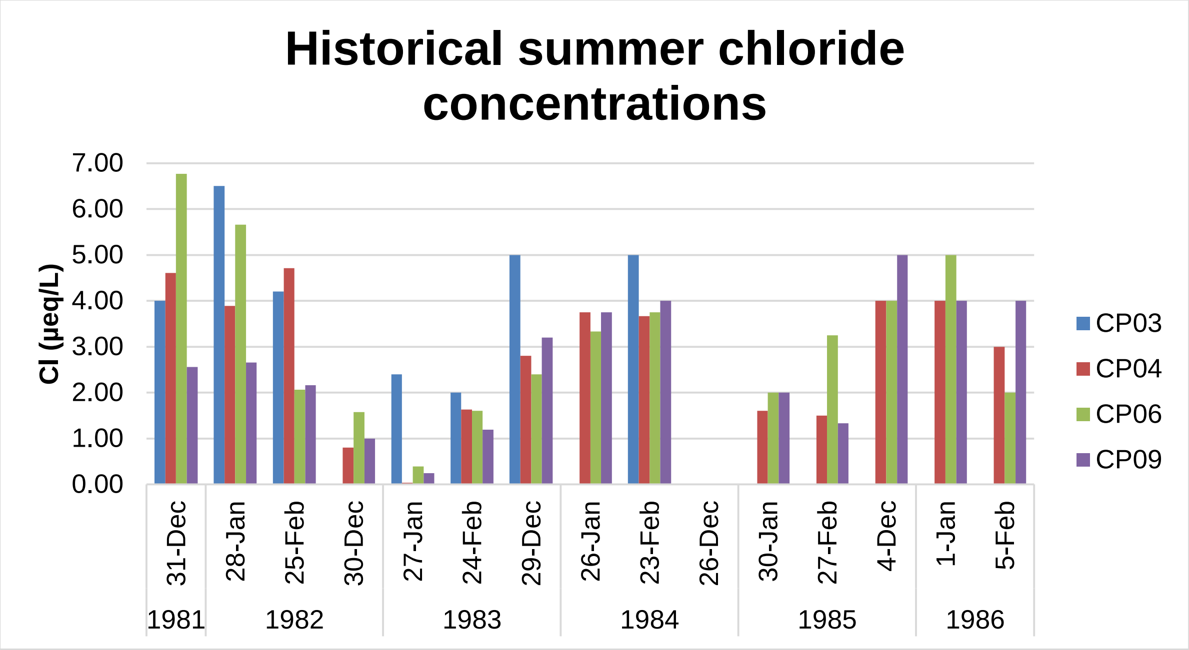

Figure 30 Bar graph showing all summer season data extracted from the historical dataset.

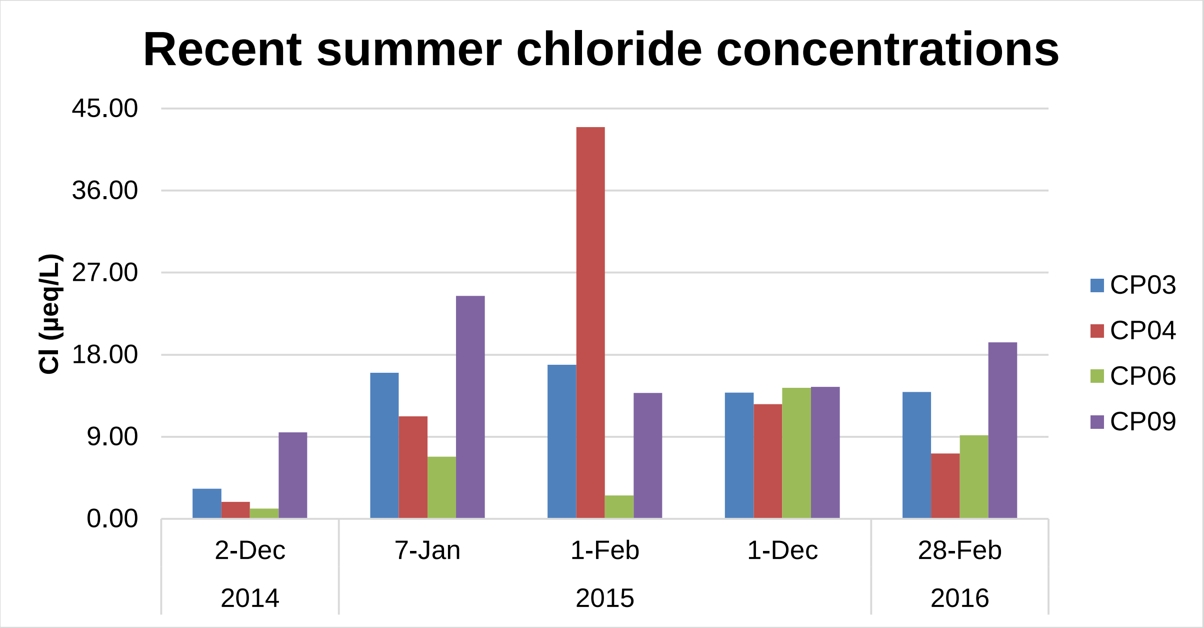

Figure 31 Bar graph showing all summer season data extracted from the recent dataset.

CP03 had increased Cl concentrations after the fire in September 1981. Concentrations were consistently high after then. There were a number of missing values so the nature of the change in the years after the fire was not apparent.

CP06 had been burnt in 1984 and 1985, and also showed an increase in Cl concentrations. In 1985 after CP04 had been burnt, the catchment had concentrations comparable to those of CP06.

CP09 had variable concentrations which could not be attributed to fire since CP09 receives protection from fire).

CP03 mostly had consistent Cl concentrations in the recent dataset. CP04 and CP06 had comparable concentrations, except for the really high concentration in February 2015 – after which concentrations started decreasing. CP09 had increased concentrations after the fire in June 2014 but the concentrations dropped after January 2015.

A summary of the changes that occurred from the historical to recent datasets is shown in **Table 23**.

Table 22 Outline of the changes in Cl from the historical to recent datasets.

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	2.00	3.29	0.04	1.85	0.39	1.11	0.25	9.48
Q_1	2.95	6.09	1.72	3.39	2.00	2.26	2.00	12.39
Q_2	3.89	12.96	2.80	7.95	2.53	4.13	2.75	14.47
Q_3	4.70	13.91	3.78	12.58	3.58	9.17	4.00	16.55
Max	7.00	16.89	6.00	42.95	8.46	14.36	13.20	24.47

Table 23 shows that there was a consistent pattern of higher recent chloride concentrations across all catchments and quartiles.

The results obtained from running the linear mixed effects model on the historical data and a one-way ANOVA on the recent data are shown in **Table 24** and **25**.

Table 23 Results obtained from running a linear mixed effects model on the historical data and comparisons between catchments to investigate differences between catchment pairs.

Solutes	**Comparisons**	**Chi-squared**	**Df**	**Pr(>Chisq)**	**Signif. code**	**Significant/Insignificant**
Cl	**Differences between catchments**	10.462	3	0.01502	*	Significant
	Catchment pairs					
	CP0304	13.327	1	0.0002616	***	Significant
	CP0306	5.1982	1	0.02261	*	Significant
	CP0309	5.1982	1	0.02261	*	Significant
	CP0406	5.1982	1	0.02261	*	Significant
	CP0409	5.1982	1	0.02261	*	Significant
	CP0609	5.1982	1	0.02261	*	Significant

There were significant differences between catchments as shown in **Table 24**. These differences were further investigated and it was found that all the catchment pairs were significantly different from each other.

Table 24 One-way ANOVA results for the recent Cl data.

Source	**Degrees of freedom**	**Sum of squares (SS)**	**Mean square (MS)**	**F-statistic**	**P-value**
Catchment	3	386.8716	128.9572	2.1830	0.1093
Residuals	32	1890.3122	59.0723		
Total	35	2277.1838			

For the recent data, the p-value corresponding to the F-statistic was higher than 0.05, suggesting that catchments were not significantly different at that level of significance

There were significant differences between all the catchment pairs in the historical data and no significant differences between the catchments when the recent data was analysed. Although the boxplots showed that there the differences between the historical data were not that significant and the opposite for the recent data. This could possibly be attributed to the use of the 2 different tests to try accommodate for the presence of missing values in the historical dataset.

Sulfate

The historical SO_4 concentrations are shown in **Figure 32** (associated data in **APPENDIX B11**).

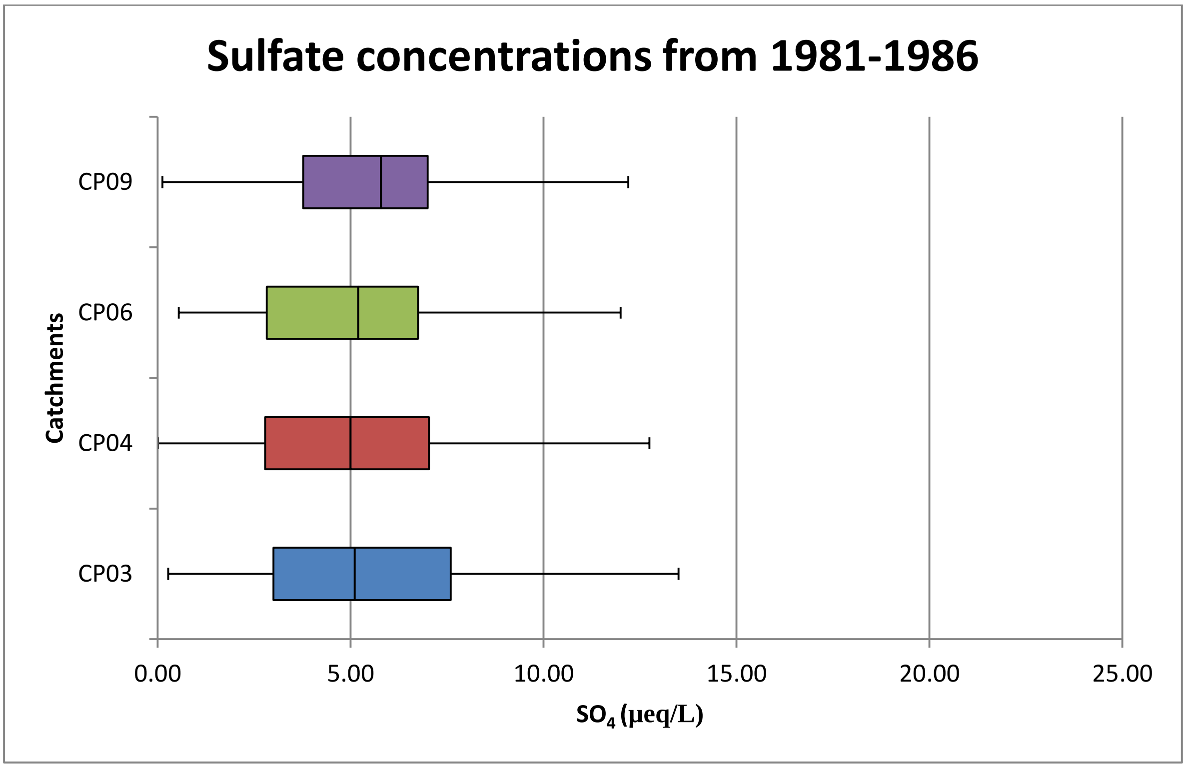

Figure 32 Plot showing historical SO_4 from 1981 – 1986.

CP04 and CP06 had similar SO_4 concentrations. CP03 had the greatest range, followed by CP09.

The recent data is shown in **Figure 33** (associated data found in **APPENDIX B12**).

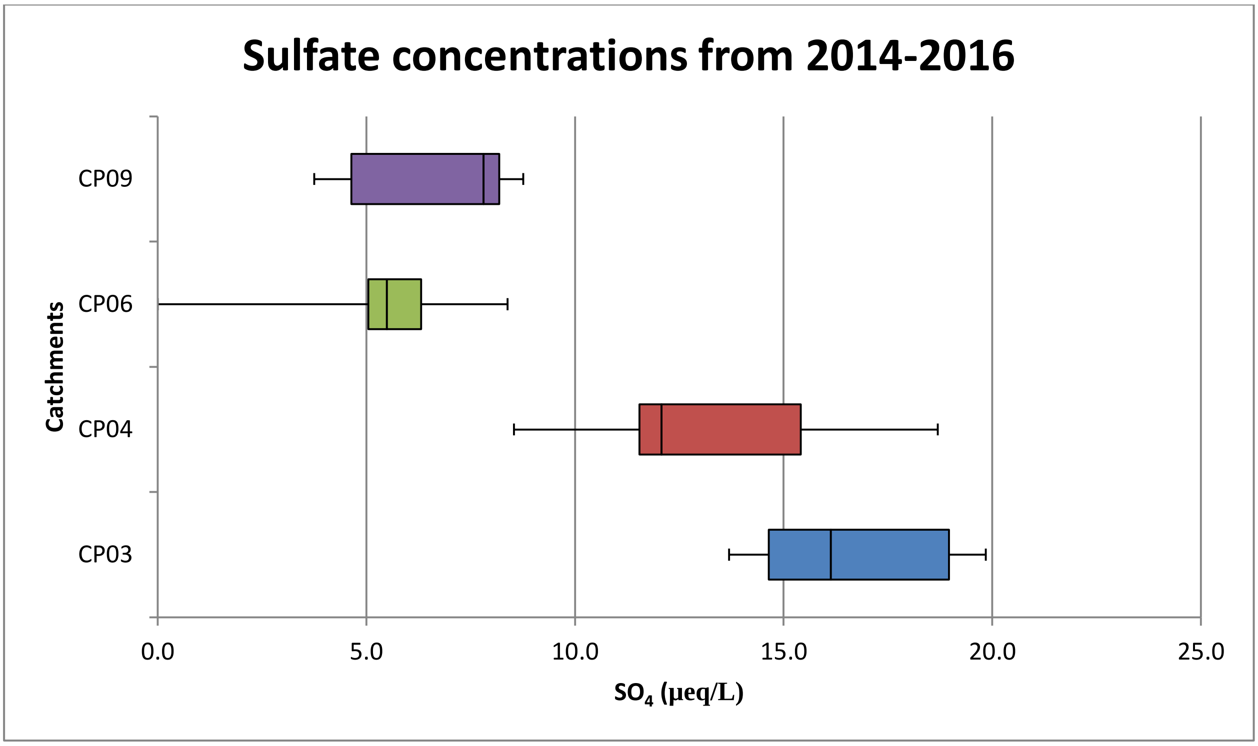

Figure 33 Plot showing recent SO4 concentrations from 2014 – 2016.

The recent SO_4 concentrations were significantly higher in CP03 and CP04. Unlike the historical dataset, CP06 had the lowest concentrations followed by CP09.

The historical and recent summer data are shown in **Figure 34** and **35**.

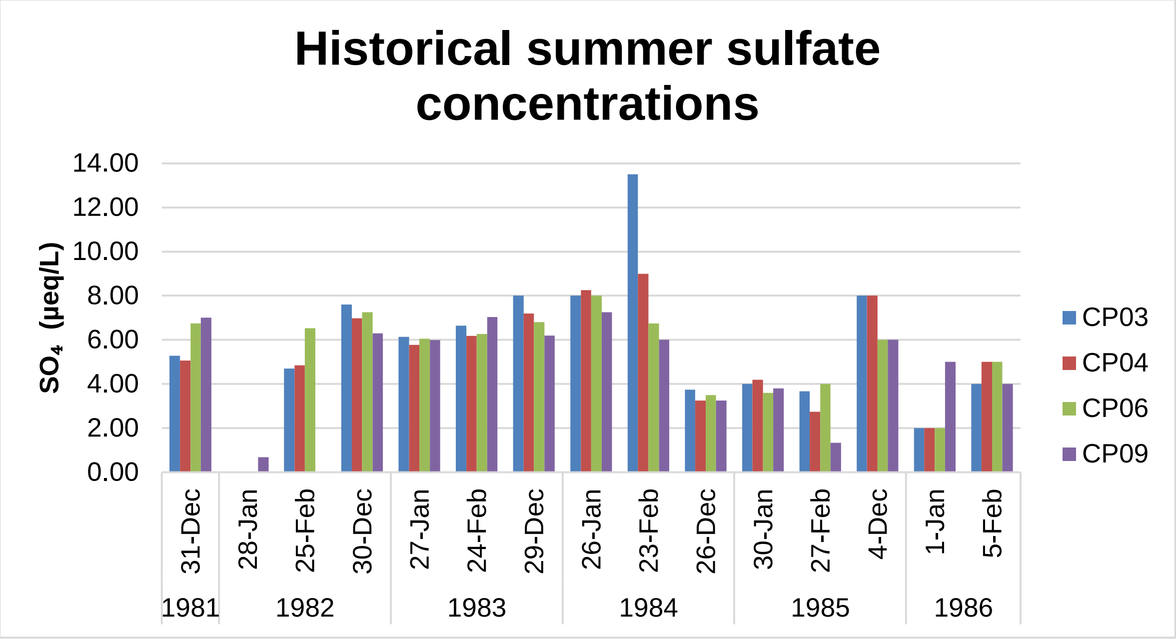

Figure 34 Bar graph showing all summer season data extracted from the historical dataset.

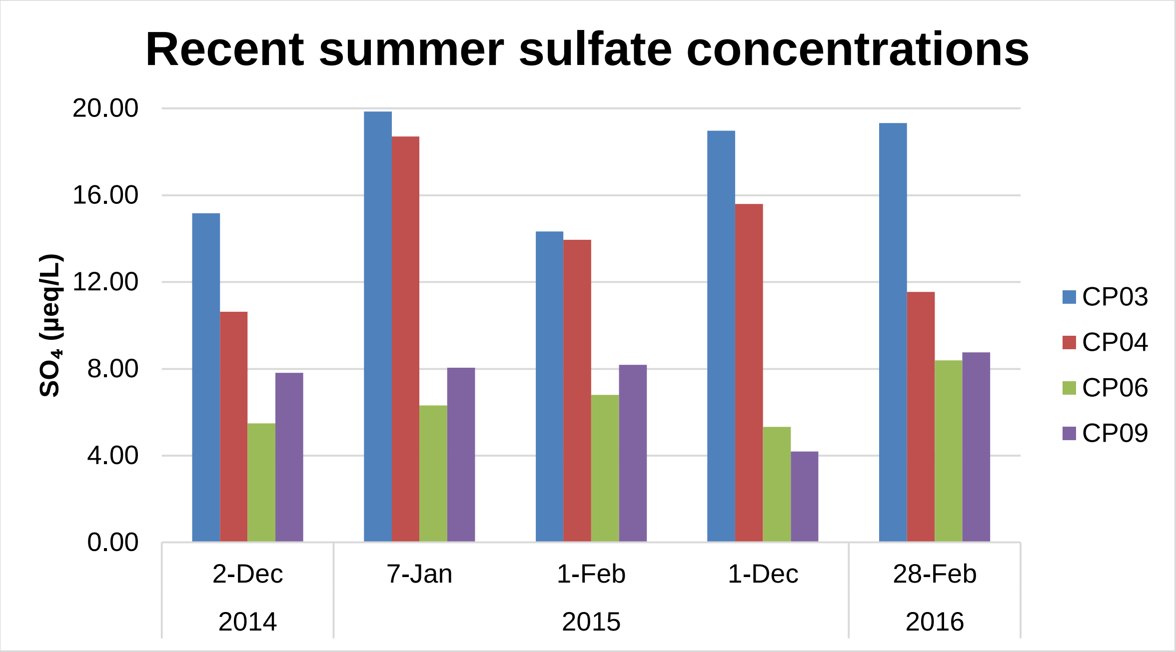

Figure 35 Bar graph showing all summer season data extracted from the recent dataset.

There was a general increase in concentrations from the historical to the recent datasets. CP03 and CP04 had comparable concentrations and that relationship was maintained in the recent dataset as well. CP03 did not have a significantly higher concentration after the fire in 1981 had occurred but did after the fire in 1985 happened. CP06 and CP09 were more comparable in this instance. CP06 tended to have decreased concentrations after fires had occurred.

CP03 had increased recent SO_4 concentrations and had similar concentrations with CP04. Again CP06 and CP09 had comparable concentrations. CP09 did not have concentration increases after the fire in June 2014.

A summary of the changes that occurred from the historical to recent datasets is shown in **Table 27**.

Table 25 Outline of the changes in SO_4 from historical to recent datasets

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	0.28	13.69	0.01	8.54	0.54	0.00	0.13	3.75
Q_1	3.00	14.65	2.79	11.55	2.83	5.05	3.78	4.64
Q_2	5.11	16.13	5.00	12.07	5.20	5.49	5.79	7.81
Q_3	7.60	18.97	7.03	15.41	6.75	6.31	7.00	8.19
Max	13.50	19.85	12.75	18.70	12.00	8.38	12.20	8.76

The recent data generally had higher minimum values than the historic data. In some cases (CP04 and CP09) concentrations doubled from historical to recent datasets. There was an overall increase from the historical to recent datasets.

The results obtained from running the linear mixed effects model on the historical data and one-way ANOVA on the recent data are shown in **Table 28 and 29**, respectively.

Table 26 Results obtained from running a linear mixed effects model on the historical data and comparisons between catchments to investigate differences between catchment pairs.

Solutes	Comparisons	Chi-squared	Df	Pr(>Chisq)	Signif. code	Significant/Insignificant
SO_4	Differences between CMTS	1.7378	3	0.6286		Insignificant
	Effect of CMT on chemistry					
	CP0304	0.5018	1	0.4787		Insignificant
	CP0306	1.0013	1	0.317		Insignificant
	CP0309	1.0013	1	0.317		Insignificant
	CP0406	1.0013	1	0.317		Insignificant
	CP0409	1.0013	1	0.317		Insignificant
	CP0609	1.0013	1	0.317		Insignificant

There were no significant differences in the historic SO_4 concentrations between catchments.

Table 27 One-way ANOVA results for recent SO_4 data.

Source	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	F-statistic	P-value
Catchment	3	777.8253	259.2751	42.8259	2.6008E-11
Residuals	32	193.7332	6.0542		
Total	32	971.5585			

The p-value corresponding to the F-statistic of the one-way ANOVA was lower than 0.05, suggesting that one or more of the catchment pairs were significantly different. A Tukey HSD test was then performed to identify which the pairs were significantly different for the recent data and the results are shown in **Table 30**.

Table 28 Tukey HSD results for recent SO_4 data.

Catchment pairs	**Tukey HSD F statistic**	**Tukey HSD p-value**	**Tukey HSD inference**
CP04 – CP03	4.7036	0.0224129	* p<0.05
CP06 – CP03	14.4988	0.0010053	** p<0.01
CP09 – CP03	12.9694	0.0010053	** p<0.01
CP06 – CP04	9.7952	0.0010053	** p<0.01
CP09 – CP04	8.2657	0.0010053	** p<0.01
CP09 – CP06	1.5295	0.6706130	insignificant

There were some statistically significant differences between recent catchment pairs as determined by one-way ANOVA (F (3, 32) = 4.7732, p = 2.6008E-11) at α=0.01 and (F (3, 32) = 3.8315, p = 2.6008E-11) at α=0.05.

There were no significant differences between catchments in the historical dataset. The recent sulfate dataset had insignificant differences in SO_4 concentrations in the catchment pair CP09 – CP06.

Phosphate

The recent concentration data for PO_4 are shown in **Figure 36** (the data used can be found in **APPENDIX B13**).

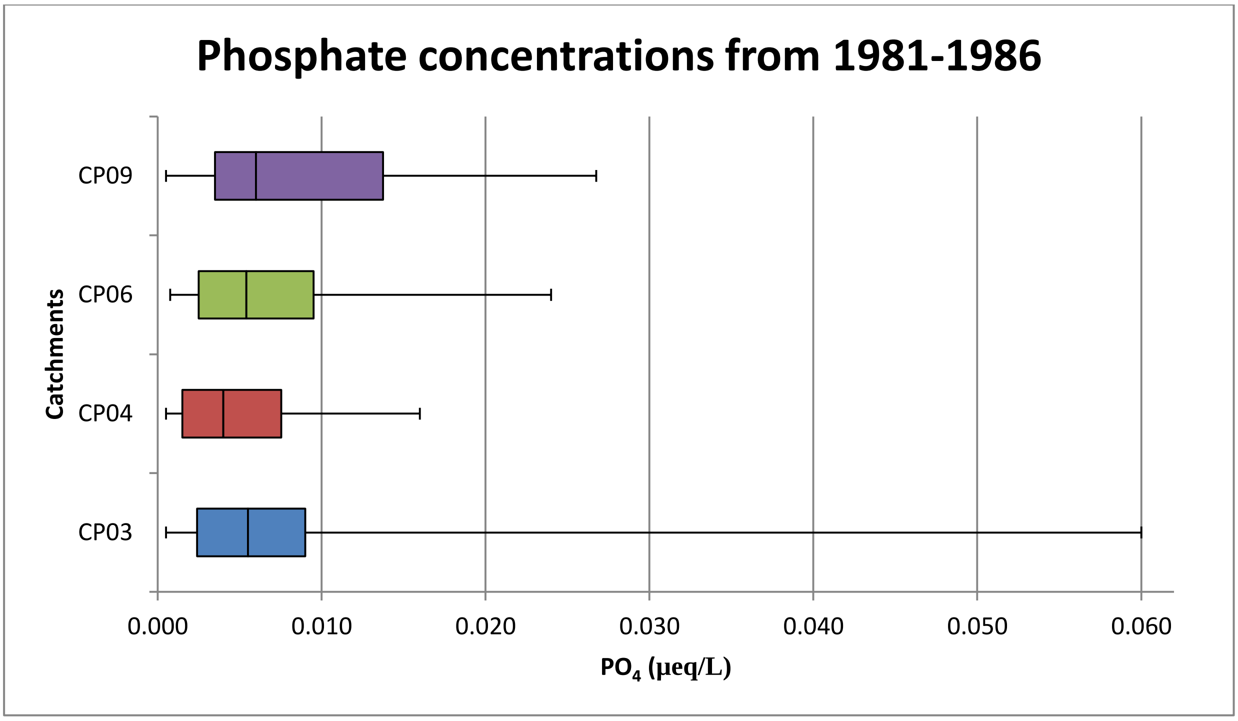

Figure 36 Plot showing historical PO_4 concentrations from 1981 - 1986.

The PO_4 concentrations were low across all the catchments. CP03 and CP09 had similar concentrations whilst CP04 and CP06 were comparable.

The recent data changes in PO_4 are shown in **Figure 37** (data used was shown in **APPENDIX B14**).

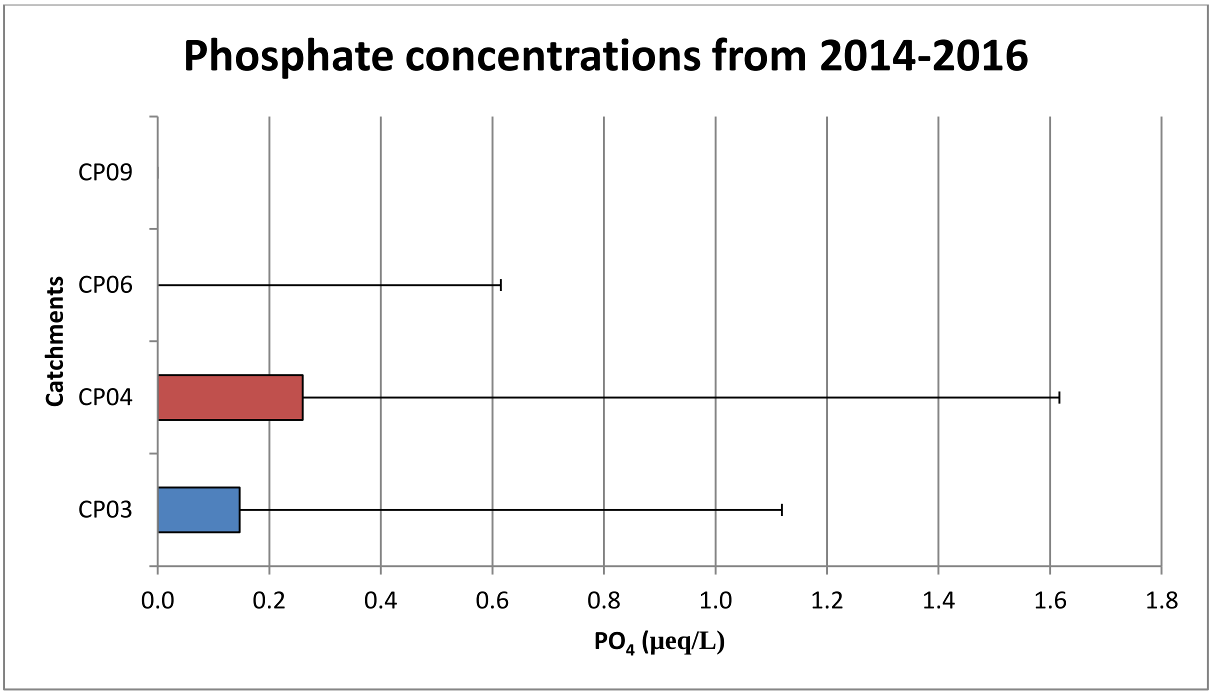

Figure 37 Plot showing recent PO_4 concentrations from 2014 - 2016.

CP09 had readings below detection limits, therefore no points were presented on the time series. CP04 has the highest PO_4 readings whilst CP03 has the lowest. There were a few CP06 readings.

The historical and recent summer data were graphed and shown in **Figure 38** and **39**.

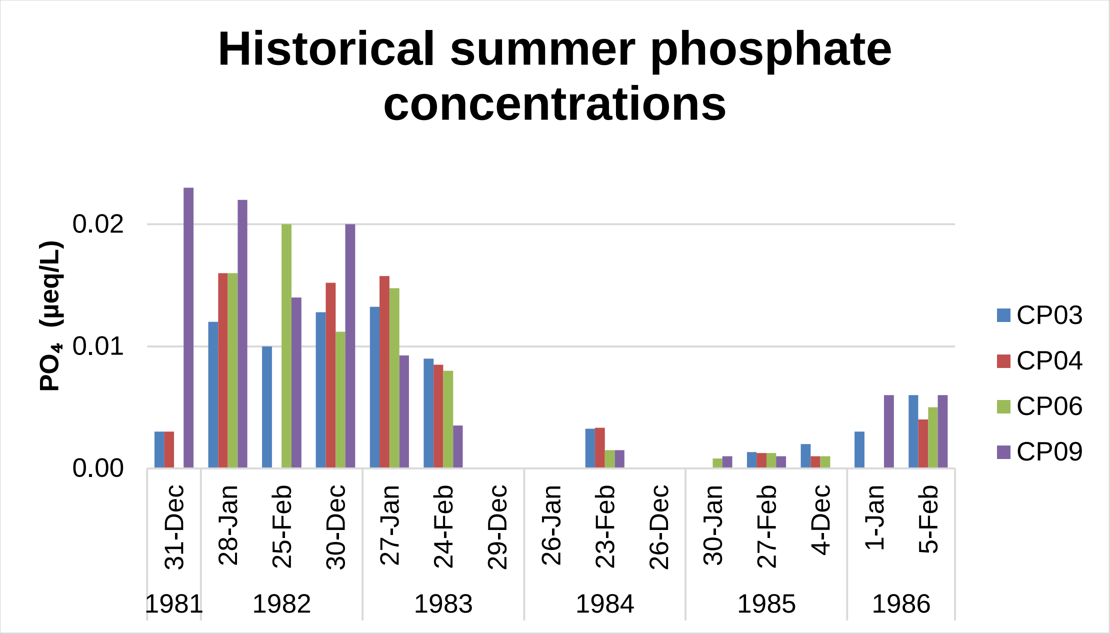

Figure 38 Bar graph showing all summer season data extracted from the historical dataset.

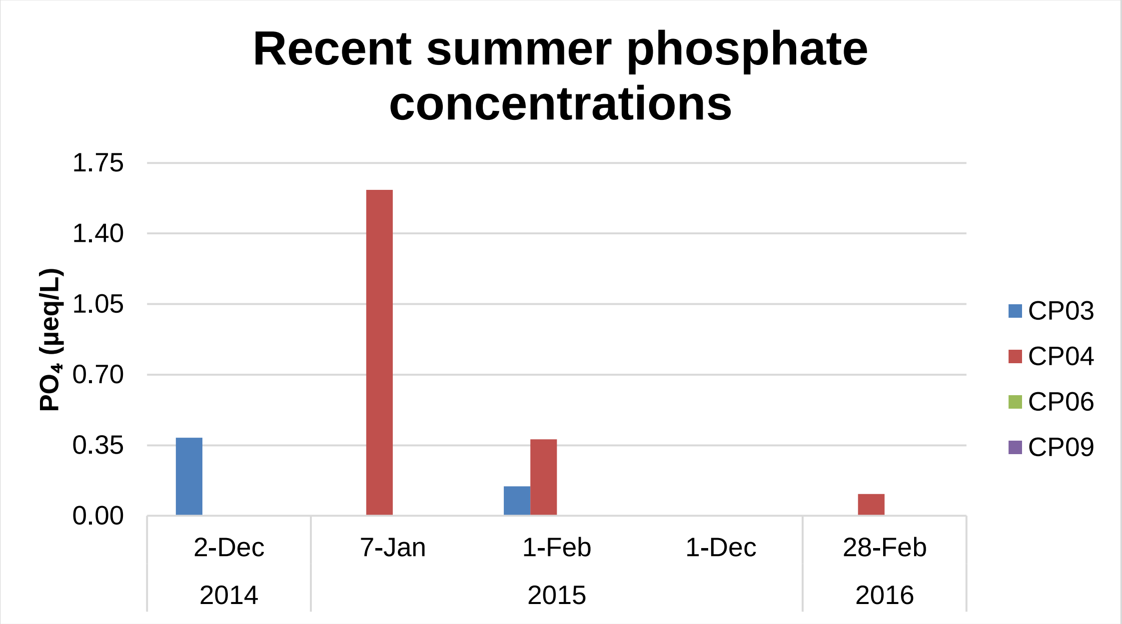

Figure 39 Bar graph showing all summer season data extracted from the recent dataset.

The historical PO_4 concentrations tended to be low, however CP09 had the highest concentrations across the catchments. CP03 had increased concentrations after the fire in 1981, which then dropped afterwards. CP04 and CP06 mostly had comparable concentrations. CP04 had increased concentrations for some time after fires had occurred whilst CP06 decreased concentrations post fires.

Although the recent dataset had an increased concentration range (CP04), the other catchments had concentrations of zero. CP04 had a high PO_4 a few months after there had been a fire in June 2014.

A summary of the changes that occurred from the historical to recent datasets is shown in **Table 31**.

Table 29 Outline of the changes in PO_4 concentrations from historical to recent datasets.

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	0.0005	0.0000	0.0005	0.0000	0.0008	0.0000	0.0005	0.0000
Q_1	0.0024	0.0000	0.0015	0.0000	0.0025	0.0000	0.0035	0.0000
Q_2	0.0055	0.0000	0.0040	0.0000	0.0054	0.0000	0.0060	0.0000
Q_3	0.0090	0.1468	0.0075	0.2600	0.0095	0.0000	0.0138	0.0000
Max	0.0600	1.1188	0.0160	1.6165	0.0240	0.6152	0.0268	0.0000

The ranges of CP03 and CP04 were higher in the recent dataset than in the historical one. The PO_4 were relatively low and some catchments had concentrations which were below detection limits.

The results obtained from running the linear mixed effects model on the historical data and one-way ANOVA on the recent data are shown in **Table 32 and 33**, respectively.

Table 30 Results obtained from running a linear mixed effects model on the historical data and comparisons between catchments to investigate differences in PO_4 between catchment pairs.

Solutes	**Comparisons**	**Chi-squared**	**Df**	**Pr(>Chisq)**	**Signif. code**	**Significant/Insignificant**
PO_4	**Differences between CMTS**	6.6063	3	0.08556	.	Significant
	Effect of CMT on chemistry					
	CP0304	0.3689	1	0.5436		Insignificant
	CP0306	0.0384	1	0.8447		Insignificant
	CP0309	0.0384	1	0.8447		Insignificant
	CP0406	0.0384	1	0.8447		Insignificant
	CP0409	0.0384	1	0.8447		Insignificant
	CP0609	0.0384	1	0.8447		Insignificant

The initial test to investigate if there were any differences between catchments showed that there were significant differences but when investigating where those differences were, there were none between catchment pairs. This could possibly be because the test picked up the differences in PO_4 concentrations, some differences observed between maxima in **Table 31**, but those apparent differences were actually not so different. This could also be related to the number of zeros in the dataset and further offset from outliers.

Table 31 One-way ANOVA results for PO_4 recent data.

Source	**Degrees of freedom**	**Sum of squares (SS)**	**Mean square (MS)**	**F-statistic**	**P-value**
Catchment	3	0.3858	0.1286	1.1303	0.3515
Residuals	32	3.6406	0.1138		
Total	35	4.0264			

For both the historical and recent data, the p-value corresponding to the F-statistic of the one-way ANOVA was higher than 0.05, suggesting that the catchment pairs were not significantly different.

The historical test output said that there were significant differences between catchment but the pairwise comparisons showed that there were no significant differences between the catchments. There were no significant differences between catchments when the recent data was tested. In terms of the recent data, too many of the data points were below detection limits and so it was hard to make any comparisons.

Nitrate

The historical NO_3 changes are shown in **Figure 40** (associated data in **APPENDIX B15**).

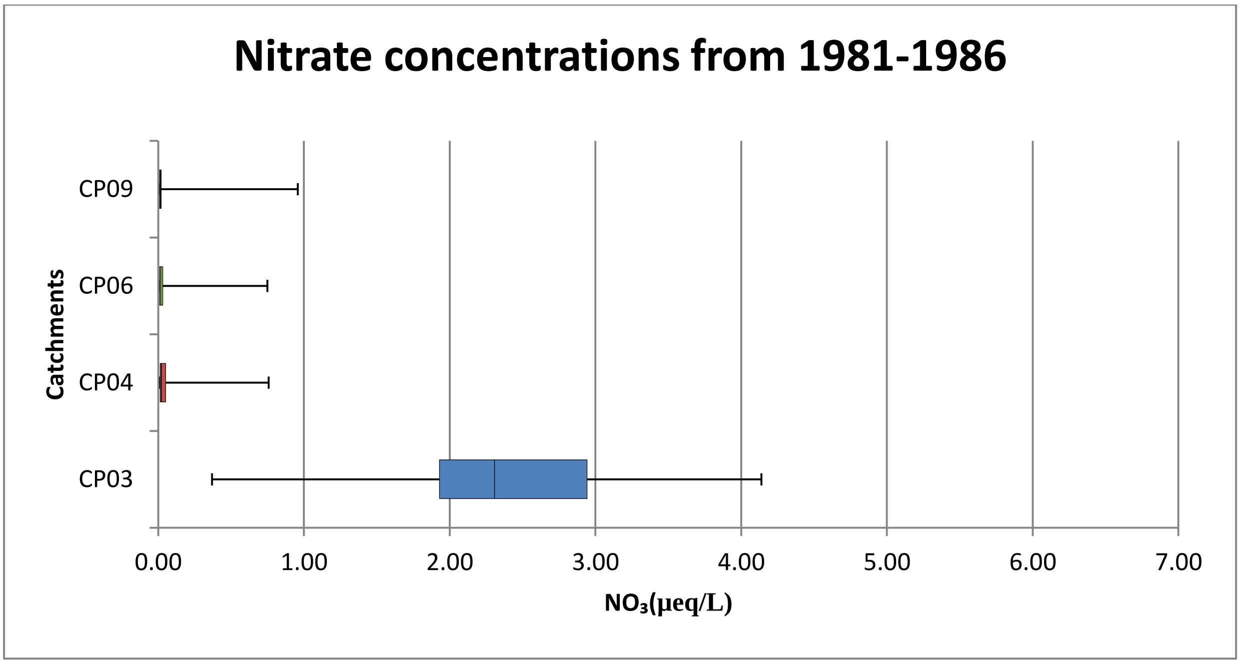

Figure 40 Plot showing historical NO_3 concentrations from 1981 - 1986.

CP03 has some of the highest recorded historical data readings. CP04, CP06 and CP09 had comparable, low NO_3 concentrations.

The recent $\mathbf{NO_3}$ data is shown in **Figure 41** (associated data found in **APPENDIX B16**).

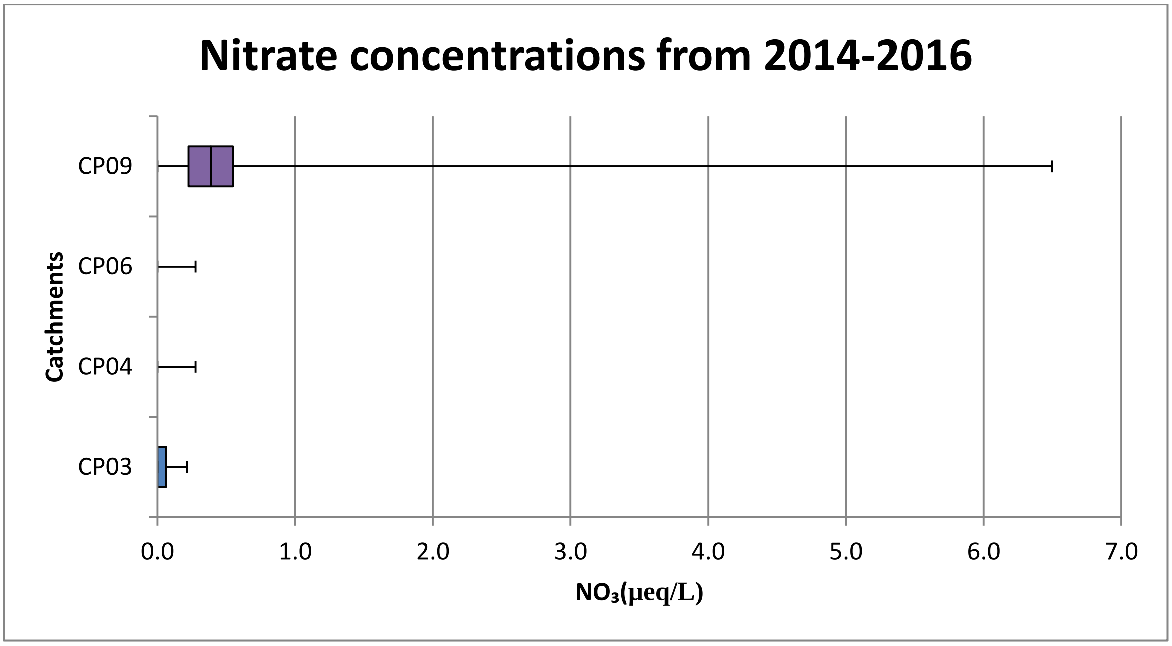

Figure 41 Plot showing recent NO_3 concentrations from 2014 - 2016.

There are few data points shown in **Figure 41** because most of the readings were below detection limits. CP09 has the most readings, followed by CP04, CP03 and then CP06 with a single reading.

The historical and recent summer data were graphed and shown in **Figure 42** and **43**.

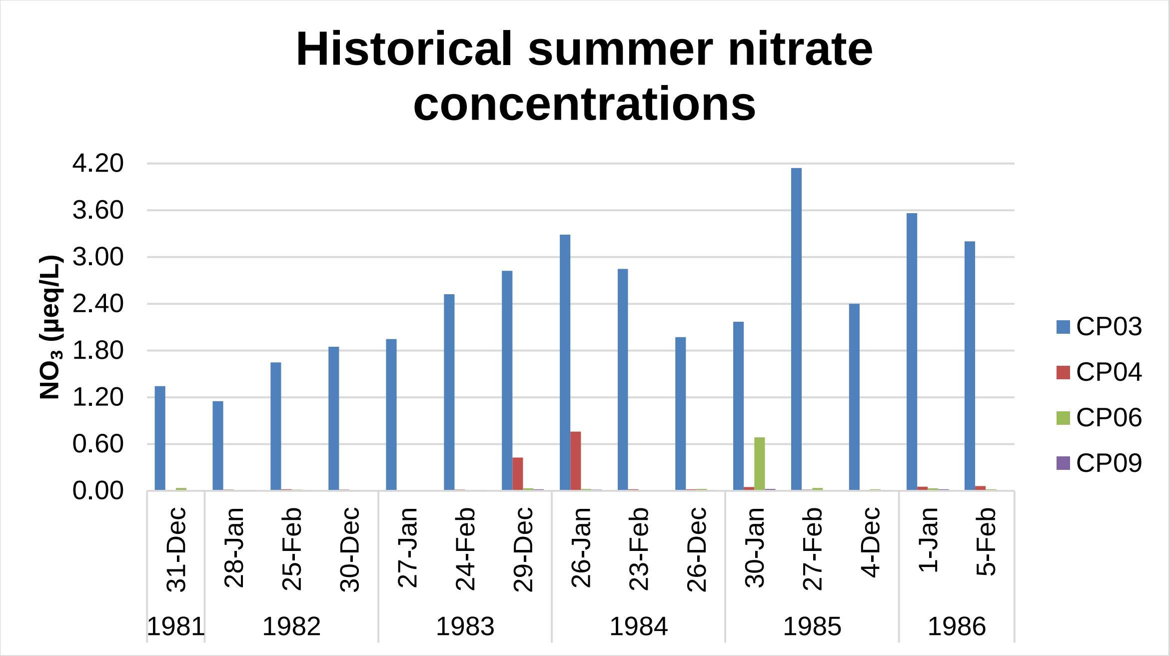

Figure 42 Bar graph showing all summer season NO_3 data extracted from the historical dataset.

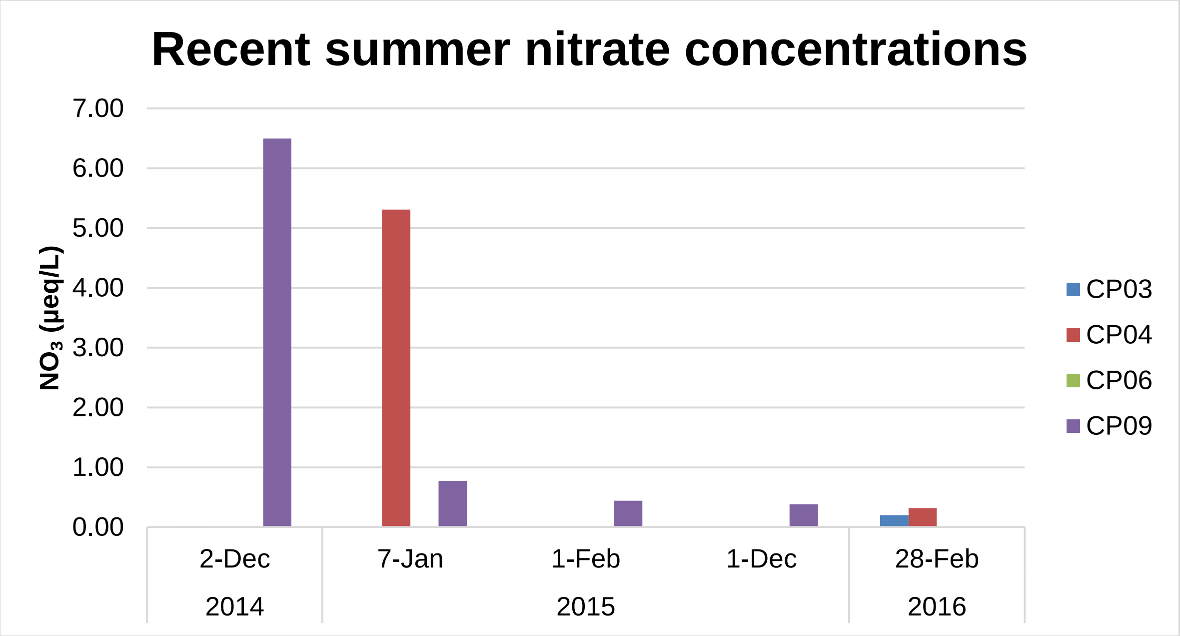

Figure 43 Bar graph showing all summer season NO_3 data extracted from the recent dataset.

CP03 had NO_3 concentrations which were higher than those of the other three catchments. This could have been a signal from the fire in 1981 and was further exacerbated by the fire in 1985.

CP04 and CP06 showed increases in concentration a couple of months after the fires in 1984 and 1985, respectively.

CP09 had very low NO_3 across the entire sampling period.

In terms of the recent data, CP09 had increased NO_3 concentrations a couple of months after the fire in June 2014. The concentrations significantly decreased one summer after the other, from then onwards.CP04 had an one high NO_3 concentration in 2015 but that occurred months before the fire and there were not any other data points within the season to help better understand the signal.

A summary of the changes that occurred from the historical to recent datasets is shown in **Table 34**.

Table 32 Table showing the differences between historical and recent NO_3 data.

	CP03		**CP04**		**CP06**		**CP09**	
	Historical	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**	**Historical**	**Recent**
Min	0.3683	0.0000	0.0045	0.0000	0.0023	0.0000	0.0043	0.0000
Q_1	1.9314	0.0000	0.0140	0.0000	0.0100	0.0000	0.0100	0.2250
Q_2	2.3070	0.0000	0.0225	0.0000	0.0183	0.0000	0.0150	0.3890
Q_3	2.9419	0.0625	0.0500	0.0000	0.0310	0.0000	0.0207	0.5489
Max	4.1400	0.2145	0.7575	0.2774	0.7500	0.2774	0.9575	6.4958

Overall, the recent data set has lower nitrate concentrations than those that were recorded in 1981 - 1986, except for CP09 which has higher concentrations.

The results obtained from running the linear mixed effects model on the historical data and one-way ANOVA on the recent data are shown in **Table 35 and 36**, respectively.

Table 33 Results obtained from running a linear mixed effects model on the historical data and comparisons between catchments to investigate differences between catchment pairs.

Solutes	Comparisons	Chi-squared	Df	Pr(>Chisq)	Signif. code	Significant/Insignificant
NO_3	**Differences between CMTS**	458.02	3	<2.2E-16	***	Significant
	Effect of CMT on chemistry					
	CP0304	207.91	1	<2.2E-16	***	Significant
	CP0306	206.09	1	<2.2E-16	***	Significant
	CP0309	206.09	1	<2.2E-16	***	Significant
	CP0406	206.09	1	<2.2E-16	***	Significant
	CP0409	206.09	1	<2.2E-16	***	Significant
	CP0609	206.09	1	<2.2E-16	***	Significant

There were significant differences between the catchments and catchment pairs, as seen in **Table 35**.

Table 34 One-way ANOVA results for recent NO_3 data.

Source	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	F-statistic	P-value
Catchment	3	6.5629	2.1876	1.1984	0.3261
Residuals	32	58.4163	1.8255		
Total	35	64.9792			

The p-value corresponding to the F-statistic of the one-way ANOVA was higher than 0.05, suggesting that the catchment pairs were not significantly different at that level of significance.

CP03 had some of the highest nitrate levels and therefore has statistically significant differences when compared to the other three catchments in the historical data. In terms of the recent data, there were no statistically significant differences between catchments.

5.2 Monthly DOC

The results from the water samples that were collected and analysed for DOC (mg/L) are shown in **Figure 44**. The graph shows measurements from June 2015 - December 2016, a Table of all the data can be found in **APPENDIX E17**.

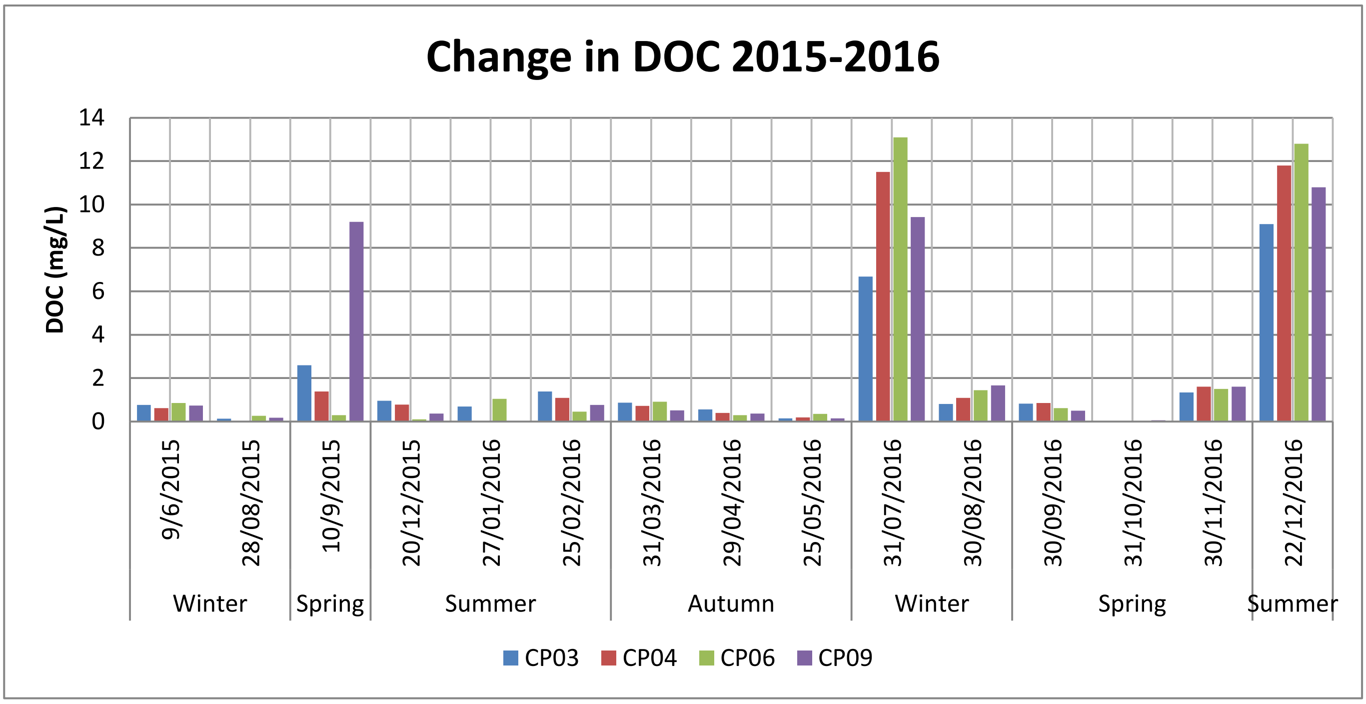

Figure 44 Changes in DOC from 2015 - 2016 across different seasons.

Some of the highest concentrations of DOC are seen at CP06 (pristine grassland) during both summer and spring in 2016, whilst CP04 (pristine grassland) has the second highest concentrations during the same seasons; followed by CP09 (fire protected) and then CP03 (previously afforested, degraded). DOC concentrations > 2 mg/L are reflective of times when there were rainfall events.

CP09 reacted in similar ways to rainfall in spring 2015, winter 2016 and summer 2016 – in terms of the concentration; the response could have been reflective of the way the catchment responded to recharge or rainfall. The same was evident for CP04 and CP06 for spring and winter of 2016.

In September 2015, when water samples were collected, CP04 had recently been burnt, as shown in **Figure 45**.

Figure 45 CP04 after it had recently been burned in 2015/09. **Source: Chris Curtis**

Although that was the case, CP09 has a higher level of DOC and this might be due to the associated land use management technique. Around the same time, CP03 was being worked on because it had silted up, **Figure 46** shows the time when the weir was being worked on.

Figure 46 CP03 during the time the weir was being worked on. **Source: Chris Curtis**

The boxplot that was created using the data collected is shown in **Figure 47**.

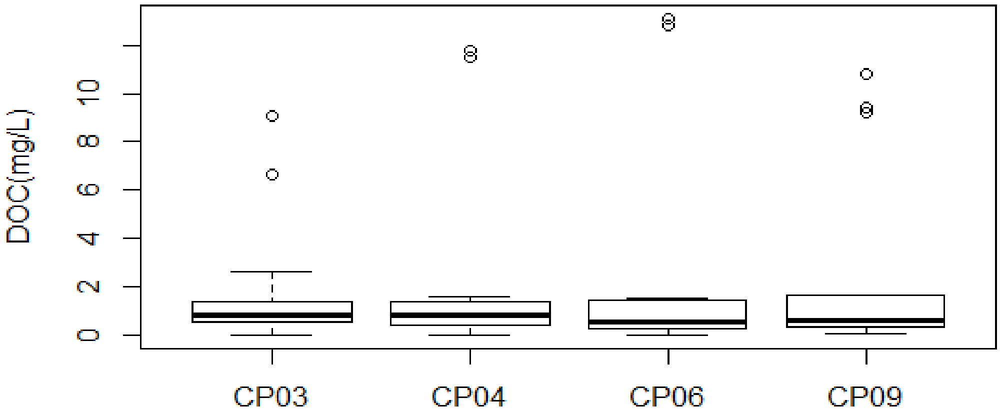

Figure 47 Boxplot generated using DOC data from **APPENDIX B17**

As shown in **Figure 47**, on average, the medians of CP03 and CP04, CP06 and CP09 score the same. The spread of CP09 is a bit larger, followed by CP06, CP04 then CP03. The ranges are quite different, in that, CP03 has a higher range than all the catchments and it decreases to CP04, CP06 and CP09. There are several outliers, with CP06 with one of the highest, followed by CP04, CP09 and CP03; these outliers are reflective of samples that were collected after a rainfall event.

A one-way ANOVA was performed on the DOC data shown in **APPENDIX B17**

The results obtained from running the one-way ANOVA are shown in **Table 37**.

Table 35 One-Way ANOVA test DOC results.

Source	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	F- statistic	P-value
Catchment	3	3.8443	1.2814	0.0867	0.9670
Residuals	52	768.1904	14.7729		
Total	55	772.0347			

$F_{critical} > F_{value,}$ therefore we fail to reject the null hypothesis and the DOC means are equal across catchments.

The p-value corresponding to the F-statistic of the one-way ANOVA was higher than 0.05, suggesting that the catchments were not significantly different for that level of significance.

There are no significant differences between catchments, DOC concentrations are similar.

5.3 Stream temperature, conductivity, dissolved oxygen and pH

5.3.1 Temperature

The following graph (**Figure 48**) shows the daily changes in temperature across the study catchments (data shown in **APPENDIX B18**).

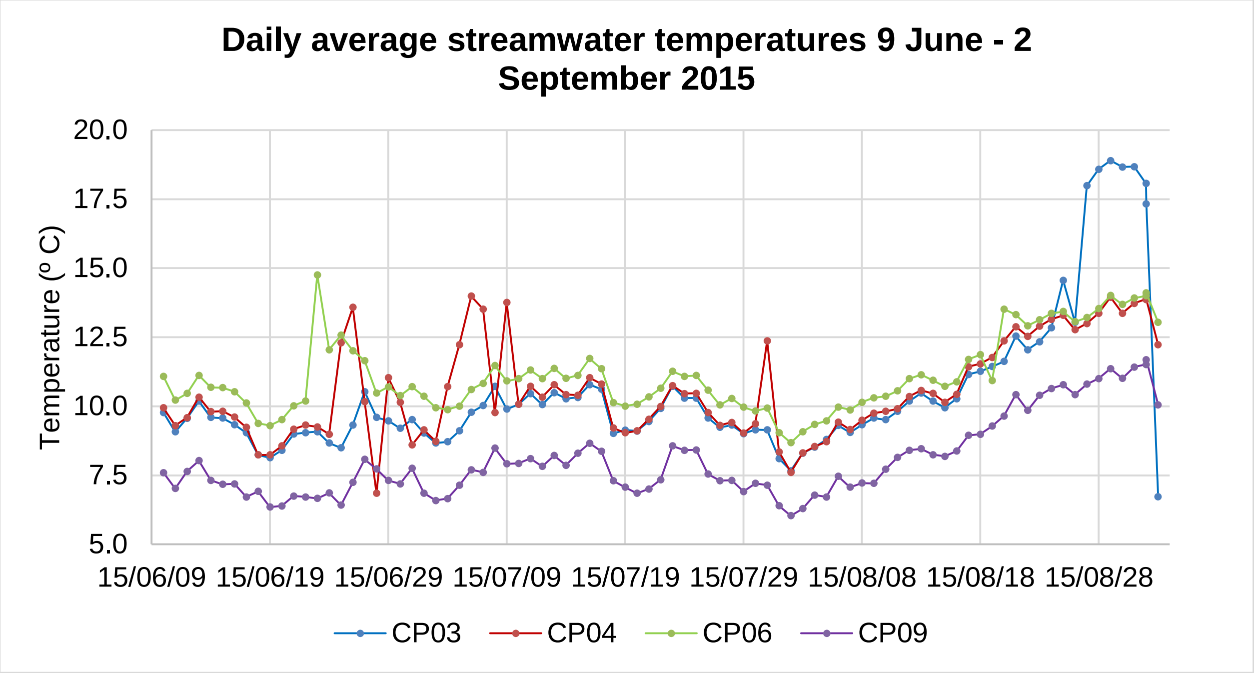

Figure 48 Daily average streamwater temperatures in study catchments over three months.

CP09 had the lowest daily average temperatures, this catchment had received more shading from the riparian vegetation. CP03 and CP04 closely followed each other, with several extreme temperature dips and increases. CP06 has relatively higher average daily temperatures than the other catchments.

The following graph – **Figure 49**, showed the overall pattern that each catchment streamwater temperature had followed.

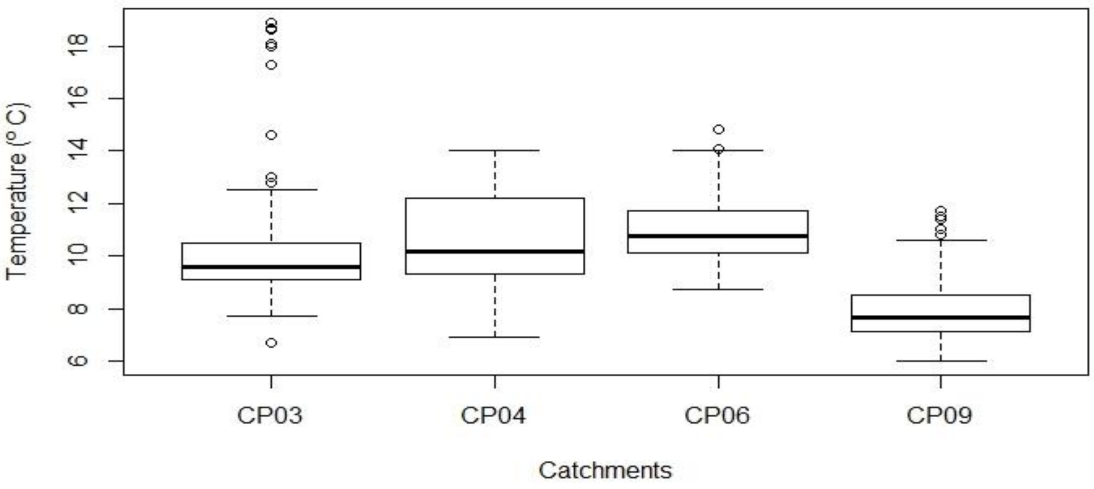

Figure 49 Boxplots showing the streamwater temperature distribution across the different catchments.

As previously mentioned CP09 had the lowest daily average temperatures and therefore had the lowest mean value across the catchments. On average, CP04 and CP06 had similar means whilst CP03 scored just below the two catchments. CP03 also had the most variability in terms of outliers, these increased temperatures could have reflected times when surface water levels had decreased. The decrease in surface water levels resulted in the iButton data loggers being closer to the water surface and thus showing an increased streamwater water temperature signal

The results obtained from running the one-way ANOVA are shown in **Table 38**.

Table 36 Results from running a one-way ANOVA.

Source	**Degrees of freedom**	**Sum of squares (SS)**	**Mean square (MS)**	**F-statistic**	**P-value**
Catchment	3	481.6678	160.5559	45.9777	1.1102e-16
Residuals	340	1187.2941	3.4920		
Total	343	1668.9618			

$F_{statistical} > F_{critical}$, therefore we reject the null hypothesis and the means are not equal across all the catchments.

The p-value corresponding to the F-statistic of the one-way ANOVA was lower than 0.05, suggesting that one or more of the catchment pairs were significantly different. The Tukey HSD test was to identify which catchment pairs were significantly different, the results were shown in **Table 39**.

Table 37 Results from running the Tukey HSD test.

Catchment pairs	Tukey HSD F statistic	Tukey HSD p-value	Tukey HSD inference
CP04 – CP03	0.4212	0.8999947	insignificant
CP06 – CP03	3.1334	0.1212329	insignificant
CP09 – CP03	12.0891	0.0010053	** p<0.01
CP06 – CP04	2.7121	0.2226064	insignificant
CP09 – CP04	12.5104	0.0010053	** p<0.01
CP09 – CP06	15.2225	0.0010053	** p<0.01

The p-value corresponding to the F-statistic of one-way ANOVA was lower than 0.01 which suggests that one or more pairs of treatments were significantly different.

There were some statistically significant differences between group means as determined by one-way ANOVA (F (3, 340) = 4.4357, p = 1.1102E-16) at α=0.01 and (F (3, 340) = 3.6513, p = 1.1102E-16) at α= 0.05.

There are significant differences between the following catchment pairs – **Table 39**: CP09-CP03, CP09-CP04 and CP09-CP06. CP09 is significantly different from all other streams in terms of streamwater temperature.

5.3.2 Conductivity

Conductivity is a measure of the ability of water to pass a current. The following conductivity data that was collected from 2014 – 2016 and is shown in **Figure 50**. The data that was used to draw the graph can be found in **APPENDIX B19**.

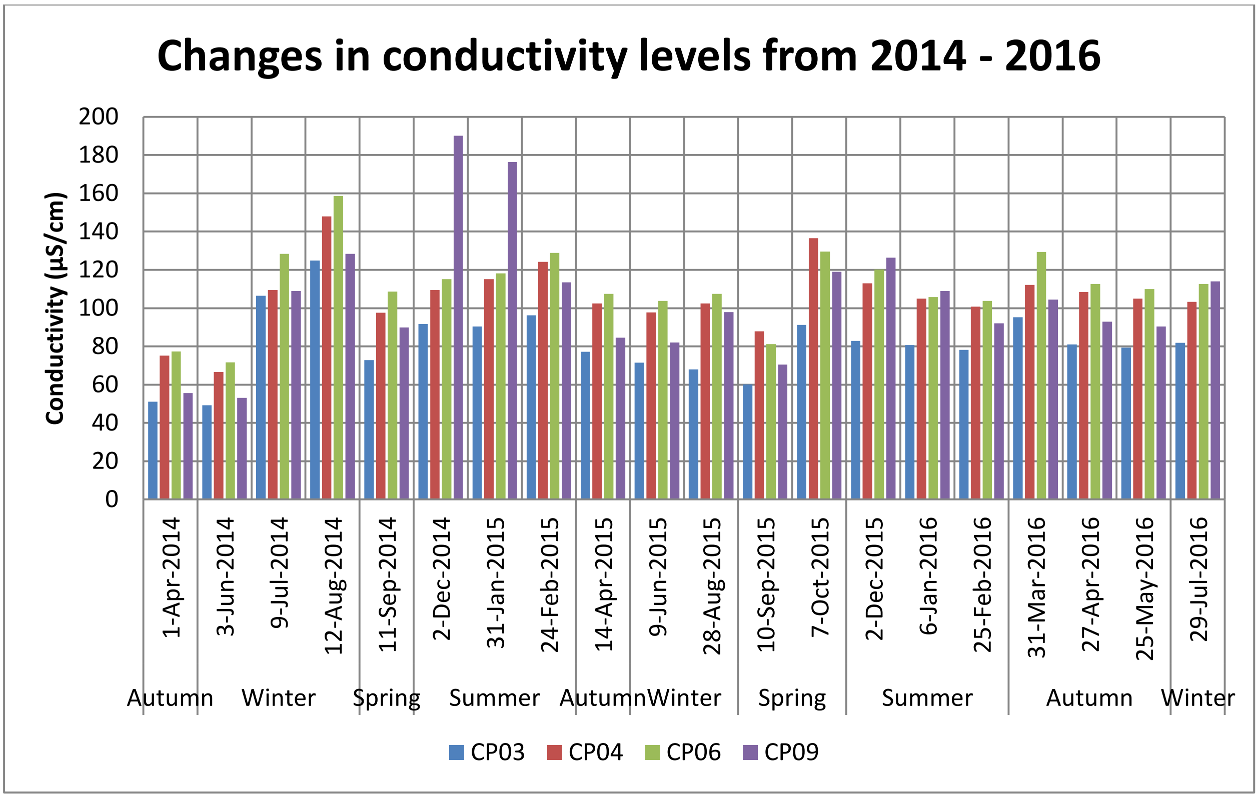

Figure 50 Changes in conductivity levels, which were collected monthly across all catchments.

CP03 always had the lowest conductivity levels across all seasons, these levels could have been in response to land use, groundwater recharge and erosion/weathering. CP04 and CP06 had similar conductivity levels, these two catchments are pristine grasslands which receive biennial spring burns. In some instances, CP09 had conductivity levels that were more variable over the duration of data collection.

The following boxplots – **Figure 51**, shows the distribution of conductivity levels across the study catchments.

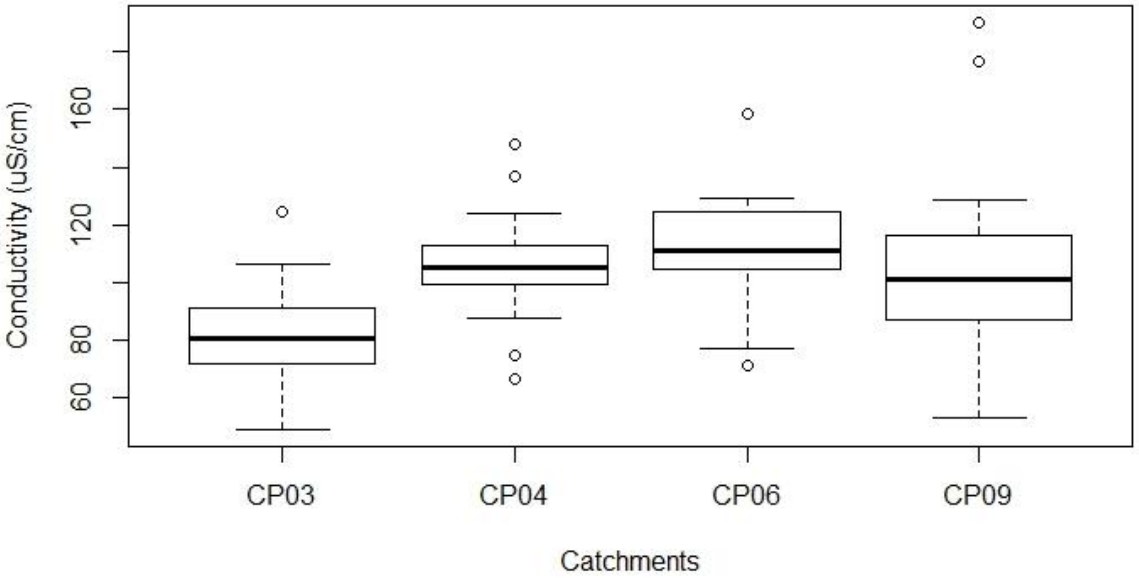

Figure 51 Boxplots showing the distribution of conductivity levels across catchments.

As previously shown, overall CP03 had the lowest conductivity levels across all the catchments. CP03 therefore had a lower mean than all the other catchments. CP04 and CP06 had similar means whilst CP09 had a mean that was higher than CP03 but lower than CP04 and CP06. Both CP03 and CP09 had wider ranges than CP04 and CP06.

The results obtained from running the one-way ANOVA are shown in **Table 40**.

Table 38 Results obtained from running a one-way ANOVA on the data.

Source	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	F- statistic	P-value
Catchment	3	10644.7844	3548.2615	6.4913	0.0006
Residuals	76	41542.9645	546.6180		
Total	79	52187.7489			

The p-value corresponding to the F-statistic of the one-way ANOVA was lower than 0.05, suggesting that one or more catchment pairs were significantly different. A Tukey HSD was performed to show which pairs were different from each other, results were shown in **Table 41**.

Table 39 Results that were obtained from running a Tukey HSD test on the data, to see if any of the catchments showed significantly different conductivities.

Catchment pairs	**Tukey HSD F statistic**	**Tukey HSD p-value**	**Tukey HSD inference**
CP04 – CP03	4.68762899	0.0075089	** p<0.01
CP06 – CP03	5.74504643	0.0010053	** p<0.01
CP09 – CP03	4.48494139	0.0114749	* p<0.05
CP06 – CP04	1.05741743	0.8651765	insignificant
CP09 – CP04	0.20268760	0.8999947	insignificant
CP09 – CP06	1.26010504	0.7855053	insignificant

The p-value corresponding to the F-statistic of the one-way ANOVA was lower than 0.01 which suggested that one or more pairs of treatments were significantly different.

There were some statistically significant differences between group means as determined by one-way ANOVA ($F(3, 76) = 4.5531$, $p = 0.0006$) at $\alpha=0.01$ and ($F(3, 76) = 3.7150$, $p = 0.0006$) at $\alpha= 0.05$.

There were significant differences between three catchment pairs at two different confidence levels (**Table 41**). There were significant differences between CP04 – CP03, CP06 – CP03 and CP09 – CP03,so CP03 was significantly different from all other catchments.

5.3.3 Dissolved oxygen (DO)

The data showing dissolved oxygen concentrations collected from 2014 – 2016 were shown in **Figure 52**, the data that was used to generate graph could be found in **APPENDIX B20**.

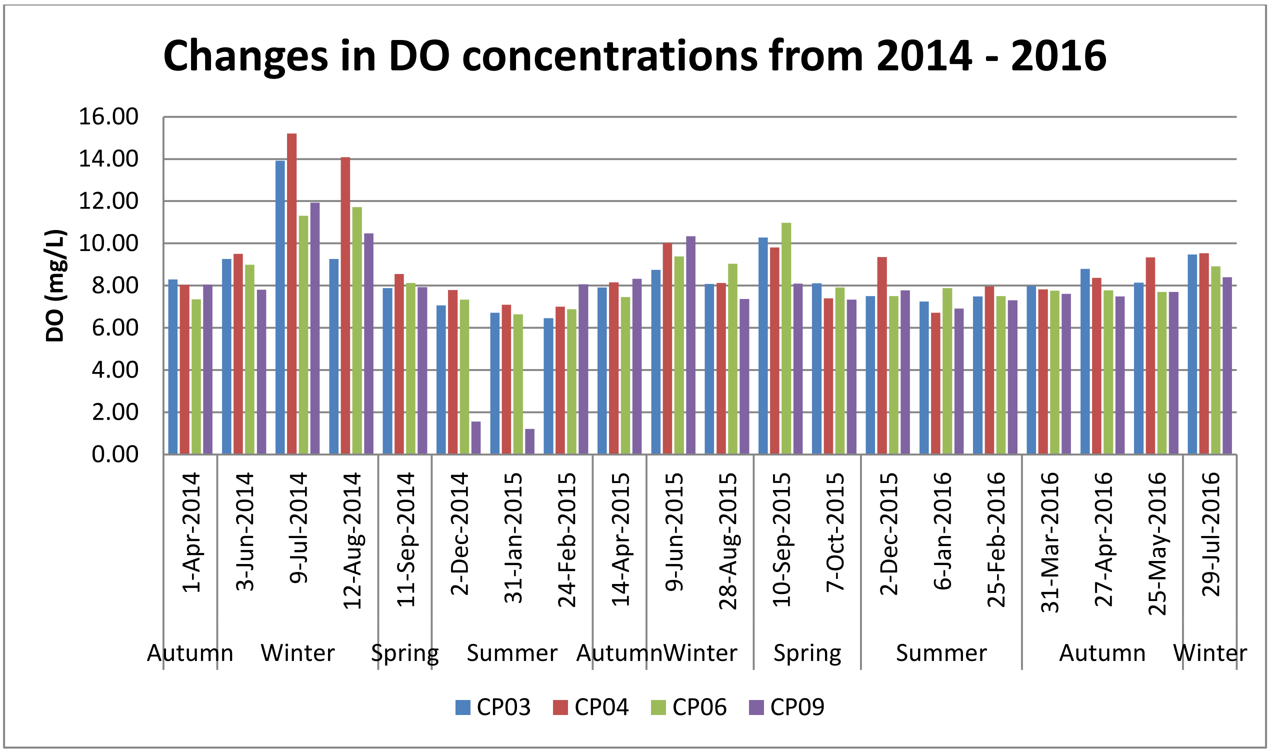

Figure 52 DO concentration data collected using a YSI, collected across study catchments during monthly sampling trips.

Some of the highest DO concentrations were found during winter in 2014, with CP04 showing the greatest levels. The DO concentrations were lower during summer and autumn, with some variation during winter and spring. CP04 also had relatively high DO concentrations whilst CP09 had some of the lowest. CP03 and CP04 do not show much variability. The boxplots for the DO concentration data across catchments were shown in **Figure 53**.

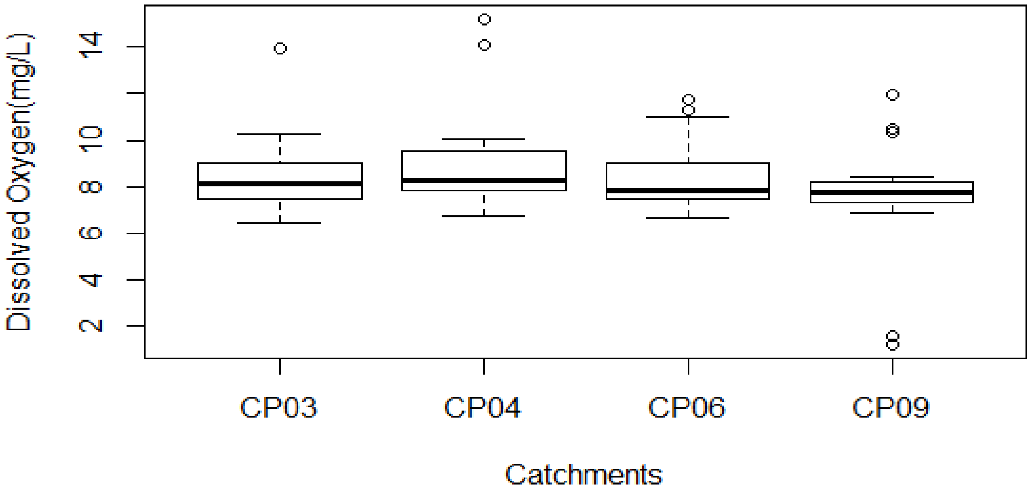

Figure 53 Boxplot showing the data distribution across study catchments.

The data across all the catchments was similarly distributed.

The results obtained from running the one-way ANOVA are shown in **Table 42**.

Table 40 ANOVA results for DOC.

Source	**Degrees of freedom**	**Sum of squares (SS)**	**Mean square (MS)**	**F- statistic**	**P-value**
Catchment	3	20.1794	6.7265	1.7452	0.1649
Residuals	76	292.9248	3.8543		
Total	79	313.1042			

$F_{critical} > F_{statistic}$, therefore we fail to reject the null hypothesis and the DOC means are equal across catchments.

The p-value corresponding to the F-statistic of the one-way ANOVA was higher than 0.05, suggesting that the treatments were not significantly different for those levels of significance.

There was no statistical difference between the catchments.

5.3.4 pH

The pH of the different study catchments from monthly sampling trips were displayed in **Figure 54** (data shown in **APPENDIX B21**).

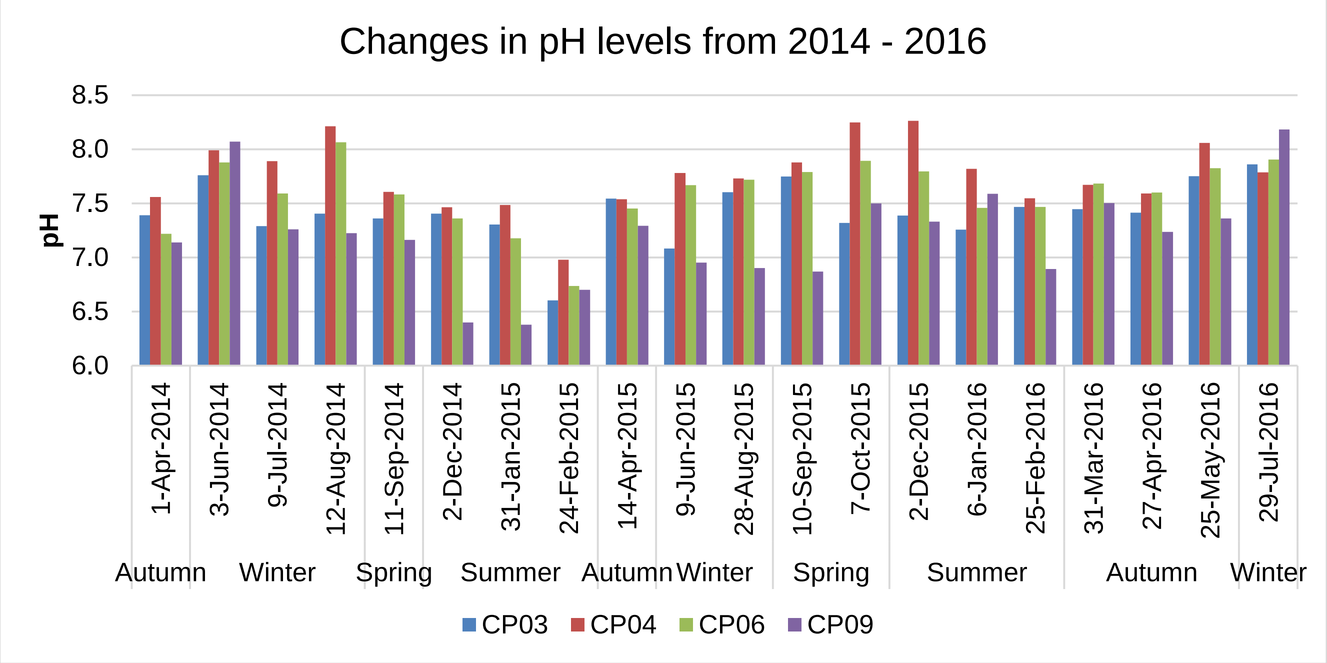

Figure 54 The changes in pH across study catchments from 2014 - 2016.

The highest recorded pH was measured at CP09 during 2014 and 2015 (**Figure 54**). CP09 had a pH which was higher than that of other catchments across the study; during summer and winter.

The distribution of the H + ion concentration data is shown in **Figure 55**.

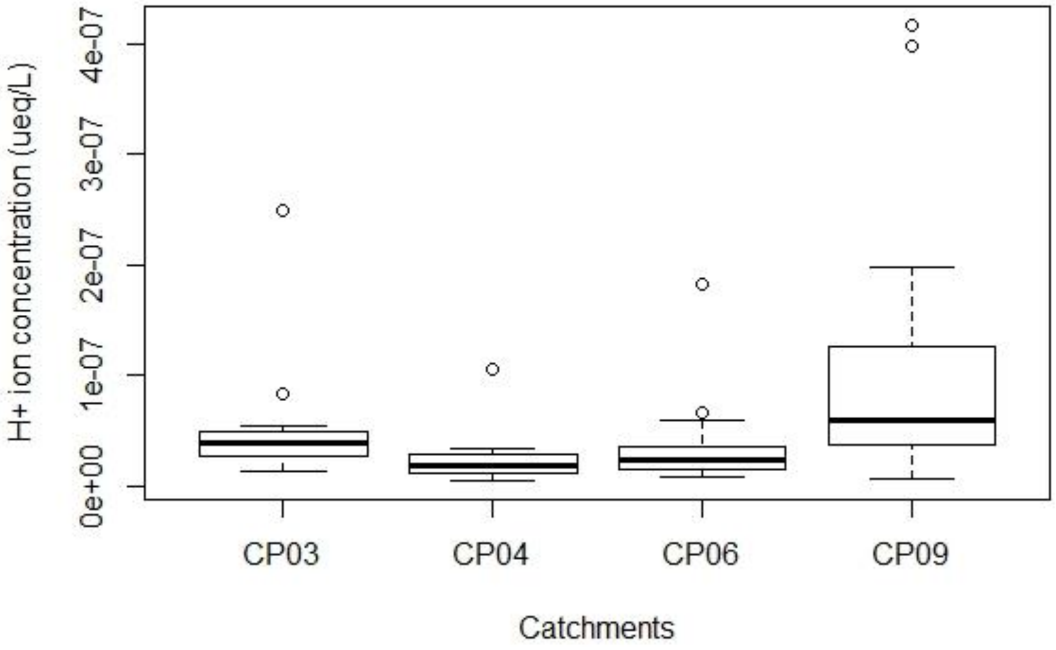

Figure 55 Boxplot showing the distribution of the H+ ion concentration data across catchments from 2014 – 2016.

CP04 and CP06 had similar concentration ranges. CP09 had the highest concentrations followed by CP03.

The results obtained from running the one-way ANOVA are shown in **Table 43**.

Table 41 Results obtained from running a one-way ANOVA.

Source	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	F- statistic	P-value
Catchment	3	7.64E-14	2.548E-14	5.817	0.00124
Residuals	76	3.329E-13	4.380E-15		
Total	79	4.093E-13			

$F_{statistical} > F_{critical}$, therefore we reject the null hypothesis and the means are not equal across all the catchments.

The p-value corresponding to the F-statistic was lower than 0.05, suggested that one or more treatments were significantly different. A post hoc test was run to identify which catchment pairs were significantly different from each other; the results of the Tukey HSD test are shown in **Table 44**.

Table 42 Results from running a Tukey HSD post hoc test.

Catchment pairs	Tukey HSD F statistic	Tukey HSD p-value	Tukey HSD inference
CP04 – CP03	1.727053646	0.6022068	insignificant
CP06 – CP03	0.938959386	0.8999947	insignificant
CP09 – CP03	3.723840029	0.0492412	* p<0.05
CP06 – CP04	0.788094259	0.8999947	insignificant
CP09 – CP04	5.450893675	0.0013549	** p<0.01
CP09 – CP06	4.662799416	0.0079457	** p<0.01

The p-value corresponding to the F-statistic of one-way ANOVA was lower than 0.01 which suggested that one or more pairs of treatments were significantly different.

There were some statistically significant differences between group means as determined by the one-way ANOVA (F (3, 76) = 4.5531, p = 0.00124) at α=0.01 and (F (3, 76) = 3.7150, p = 0.00124) at α= 0.05.

When all the catchments were compared, CP09 had significant differences in relation to other catchments.

5.4 Stormflow data

5.4.1 Total dissolved solids (TDS)

The following graph, **Figure 56**, shows the relationship between flow level and TDS measurements in CP03 (data shown in **APPENDIX B22**).

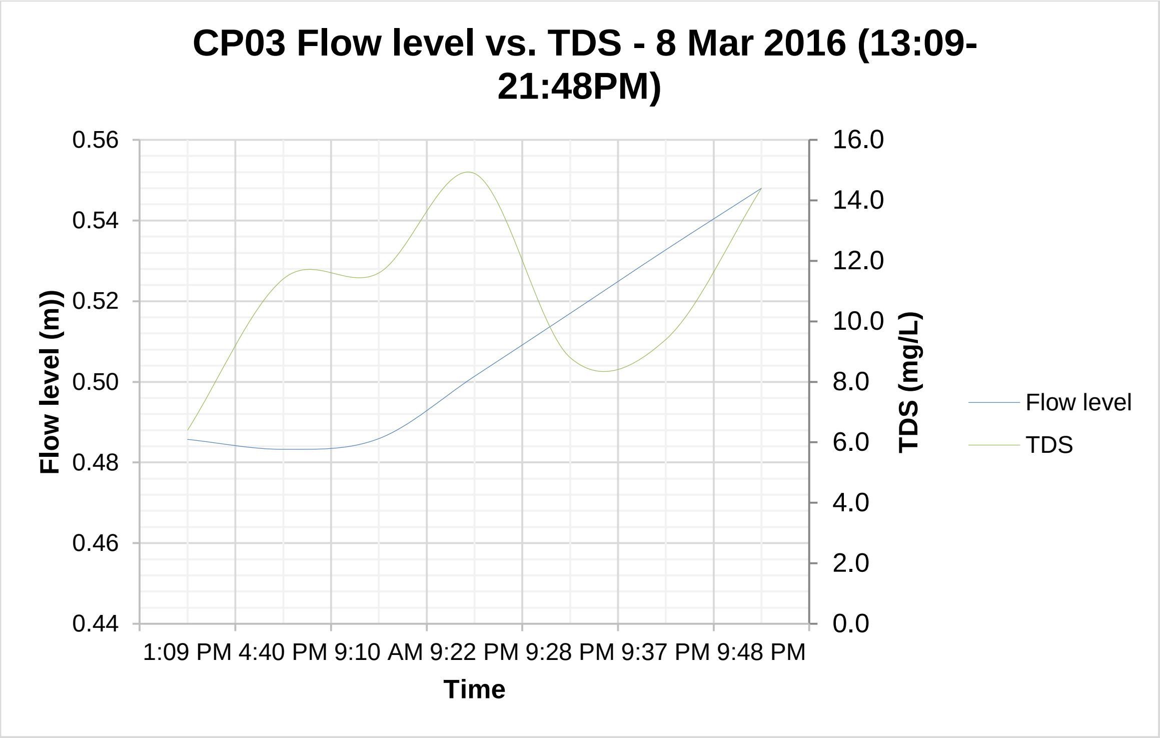

Figure 56 Relationship between flow level and TDS during a storm event 08/03/2016 at CP03.

As seen in **Figure 56**, there was no immediate change in flow level when the ISCO had started sampling. The changes started happening almost half-way though the sampling period and levels increase with time. The TDS measurements increased from the time the storm started, and continued to increase past when the last sample had been collected.

Overall, TDS increased as the flow level increased and here was in peak in load at the start of the flow pulse.

Figure 57 shows the relationship between flow level and TDS measurements in CP06 (data shown in **APPENDIX B23**).

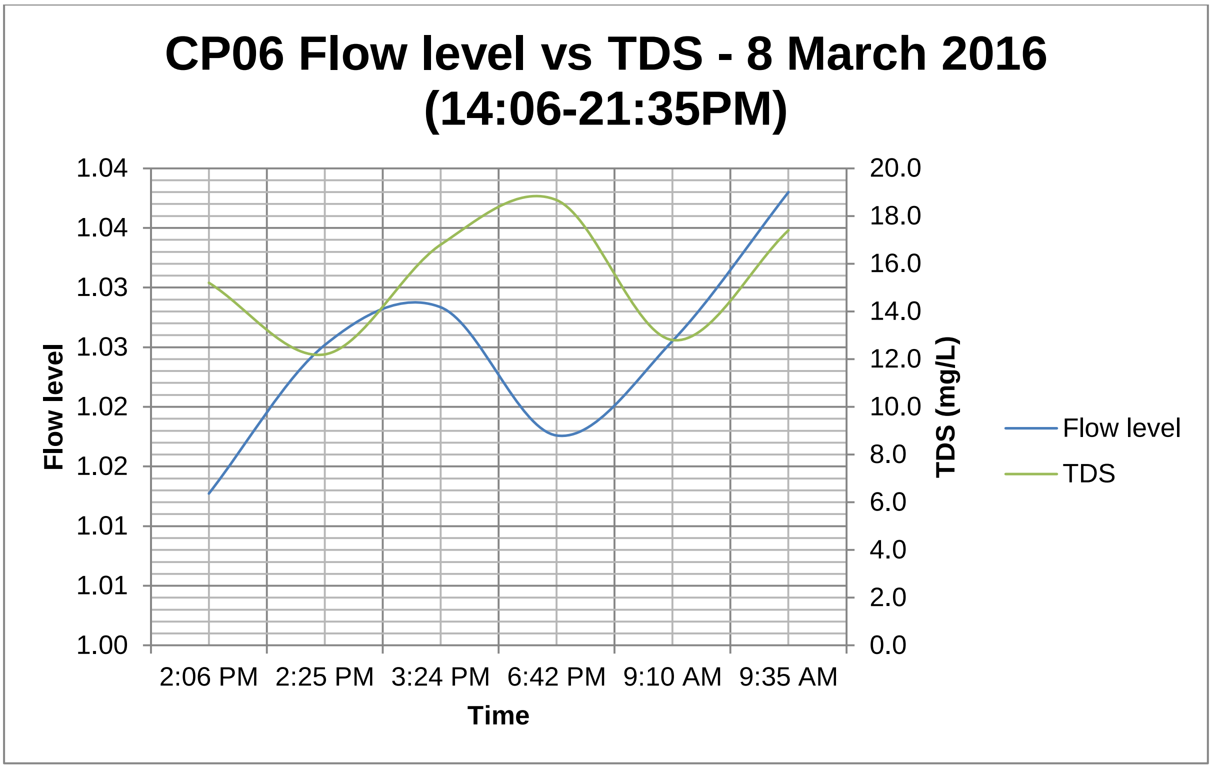

Figure 57 Relationship between flow level and TDS during a storm event 08/03/2016 at CP06.

In terms of CP06, TDS had dropped at the beginning of the monitoring period. It then increased as flow level also increased. This plot was complicated by a preliminary pulse in the flow which subsided and was followed by a larger and more typical pulse.

Overall there was a relationship between TDS and flow level. The TDS increased as flow level increased. Like CP03, CP06 TDS increased, peaked, declined then increased again. CP03 had a different flow level curve from CP06. This could have been caused by the difference in catchment land use. Overland flow could possibly behave differently in CP03 from CP06. The concentration of dissolved solids flowing into the stream increased as flow level and possibly precipitation increased. As the overland flow flushed particles out of the soil and surrounding vegetation, TDS steadily increased. The decrease in flow level (CP06) could have been due to the rainfall decreasing, this however did not mean that the water washed from the land would stop flowing into the stream and could have been coming from further upstream.

5.4.2 Total suspended solids (TSS)

The relationship between flow level and TSS measurements of CP03 was shown in **Figure 58** (data shown in **APPENDIX B22**).

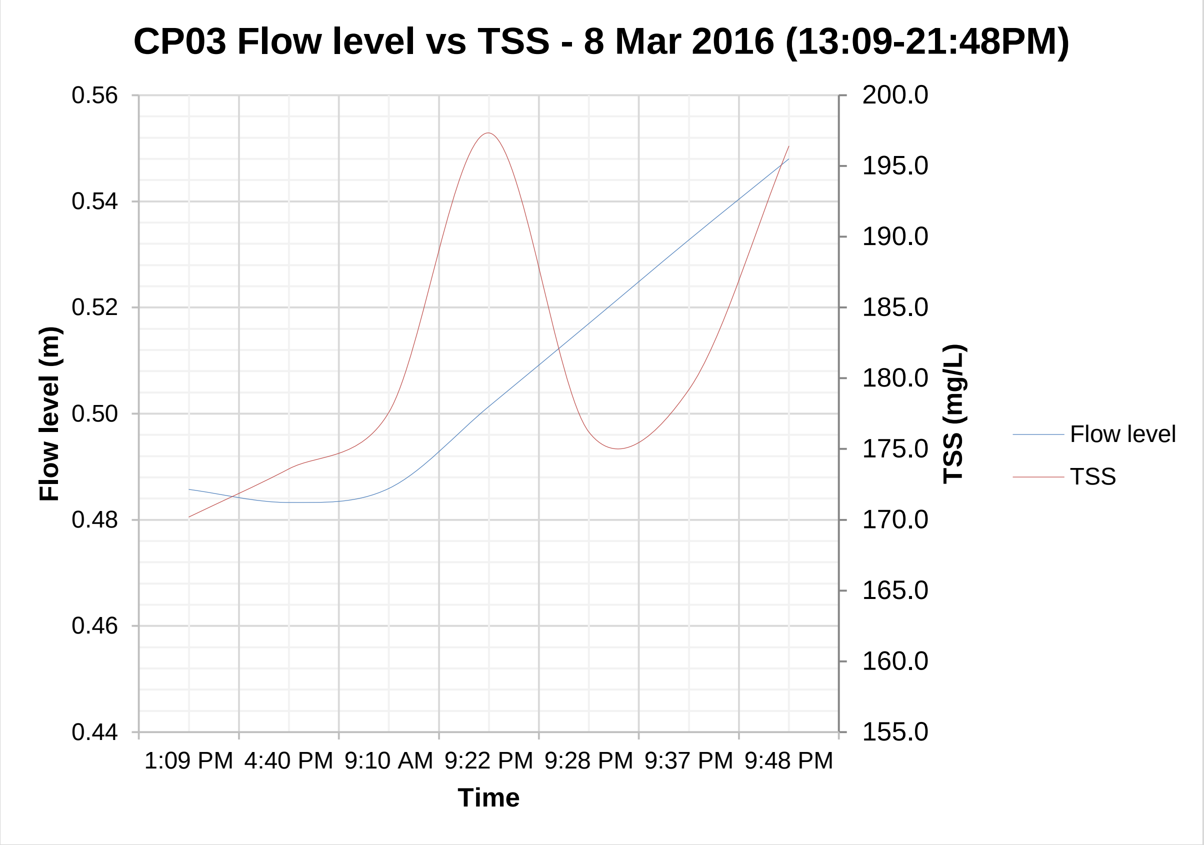

Figure 58 Relationship between TSS and flow level for CP03.

As the flow level increased, TSS rapidly increased as well. There was a similar pattern to TDS, with an early peak, a decline, followed by another increase. There was likely to be a build-up of material between pulses. The start of the surface flow pushed the large load of material into the stream and rapidly dissipated. This was then followed by the usual load associated with flows.

Figure 59 showed the relationship between flow level and TSS measurements of CP06 (data shown in **APPENDIX B23**).

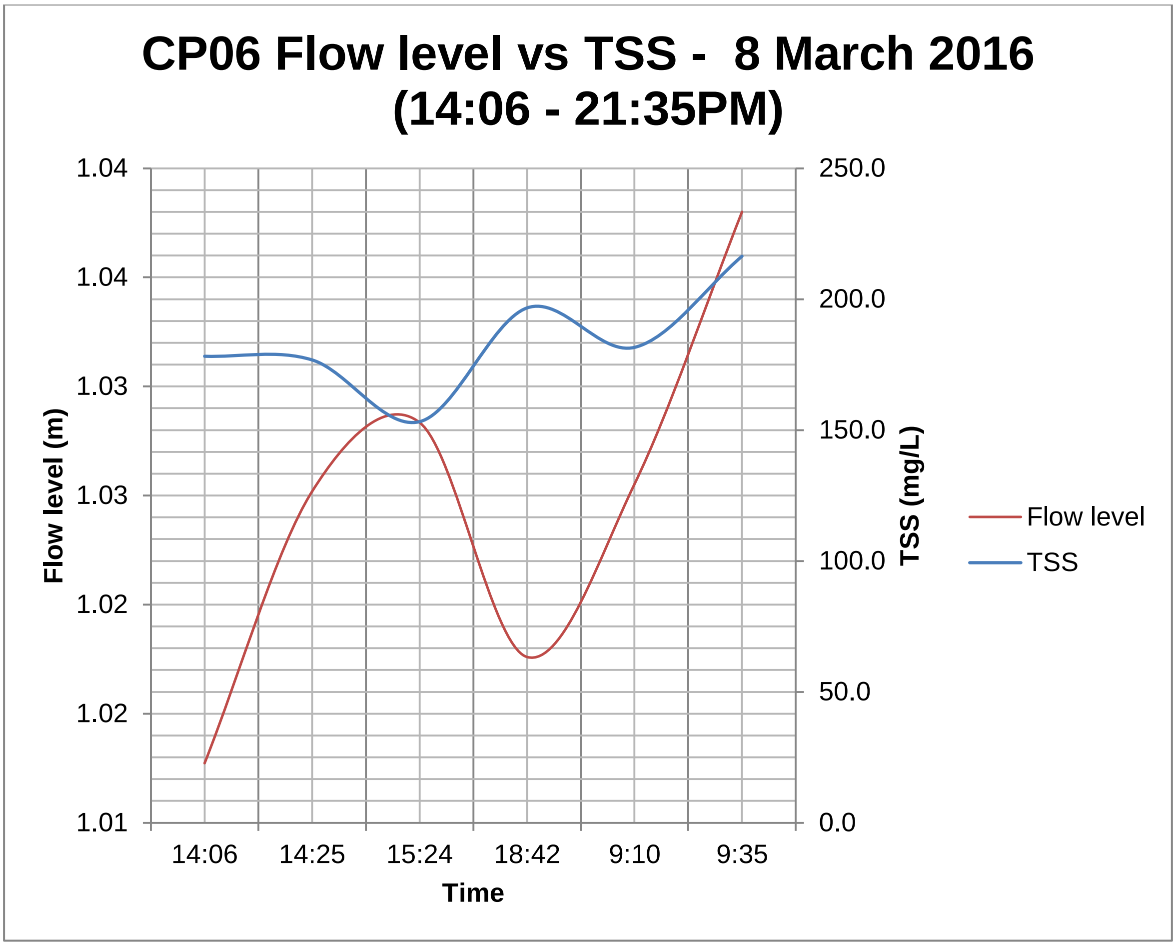

Figure 59 Relationship between TSS and flow level for CP06.

In this case, there is less variability in TSS, the measurements range between 150-220 mg/L. There is a limb of the graph where TSS increases as flow level increases.

There are differences between catchments in terms of the way flow level and TSS interacts. This could be accounted for when considering other factors around the water bodies that could influence these measurements. The steady increase towards the first peak of the CP03 TSS concentration could be due to the rate at which water flows from overland into the stream (could also be linked to the nature of the rainfall event). The total suspended solids concentration increased with increasing flow but then started decreasing with increasing flow level. The times of TSS concentration decrease could be reflective of intermittent times when it had stopped raining but there were changes in the flow level. It could also be linked to the recharge of groundwater.

CP06 showed a more varied flow level. The nature of the decreases in TSS concentration could possibly be linked to groundwater recharge and transport rates from further upstream.

5.4.3 Stormwater quality

Water samples were collected on two occasions to monitor changes in water chemistry during a storm event. In February, samples were collected every hour, manually whilst an automated ISCO sampler was used in CP03 and CP06.

5.4.3.1 Cations

CP03

Figure 60 (data shown in **APPENDIX B24**) and **61** (data shown in **APPENDIX B25**) show the changes in cation concentrations during a storm in February and March 2016, respectively, at CP03.

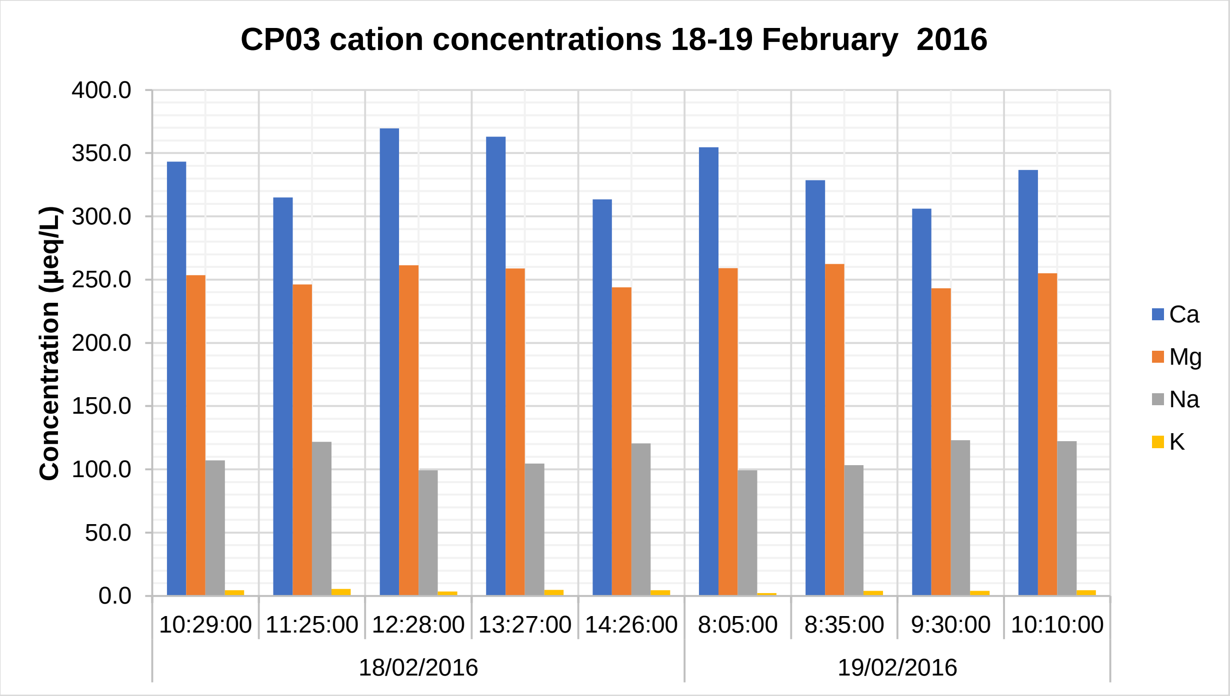

Figure 60 Cation concentrations during CP03 February storm.

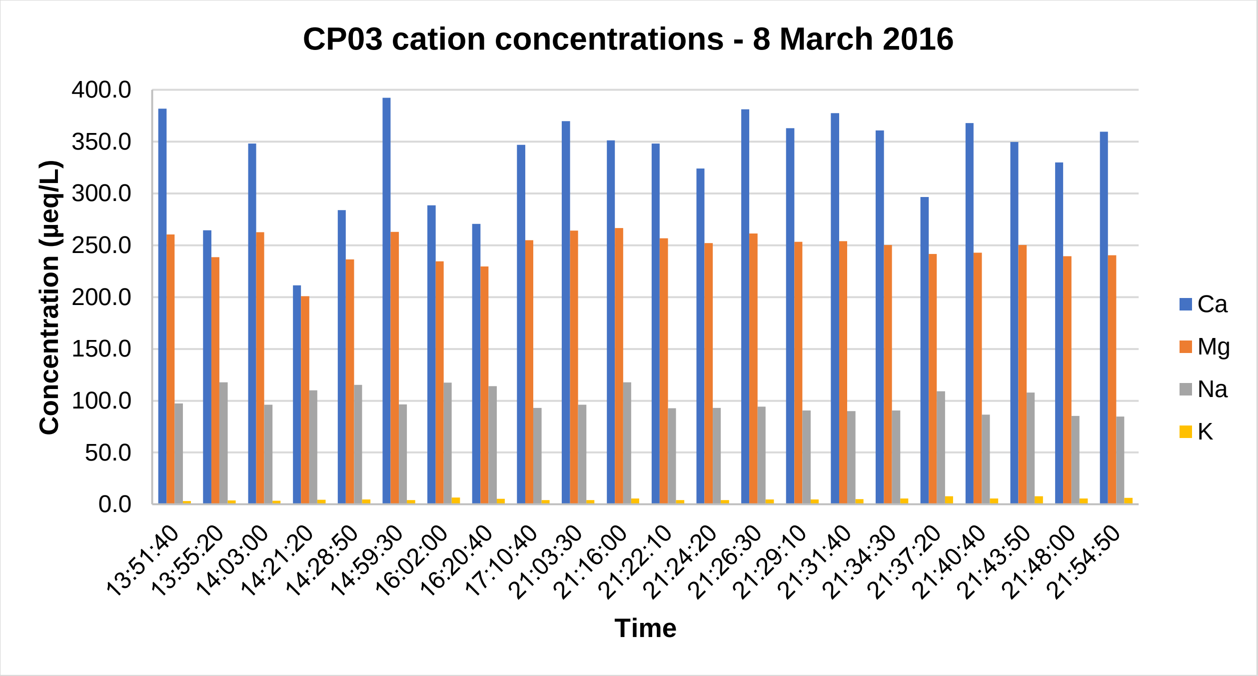

Figure 61 Cation concentrations during CP03 March storm.

As seen in both **Figure 60** and **61**, Ca concentrations were consistently high during the two recorded storms. The highest concentration was reached a couple of hours into the duration of the storm, on both occasions.

The Mg concentration was lower than Ca concentrations in both cases with consistent values in February and March.

The Na concentrations were significantly lower than both Ca and Mg during both storms with similar concentrations in February and March.

CP06

Figure 62 (data shown in **APPENDIX B26**) and **63** (data shown in **APPENDIX B27**) show the changes in cation concentrations during a storm in February and March 2016, respectively, at CP06.

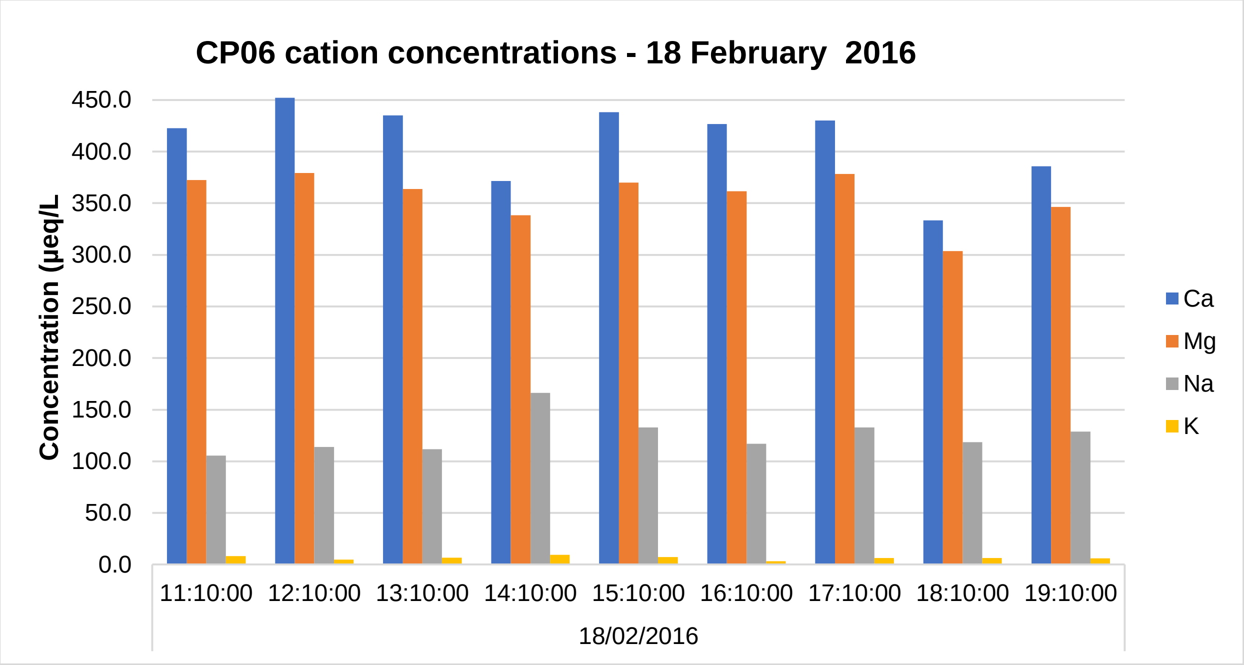

Figure 62 Cation concentrations during CP06 February storm.

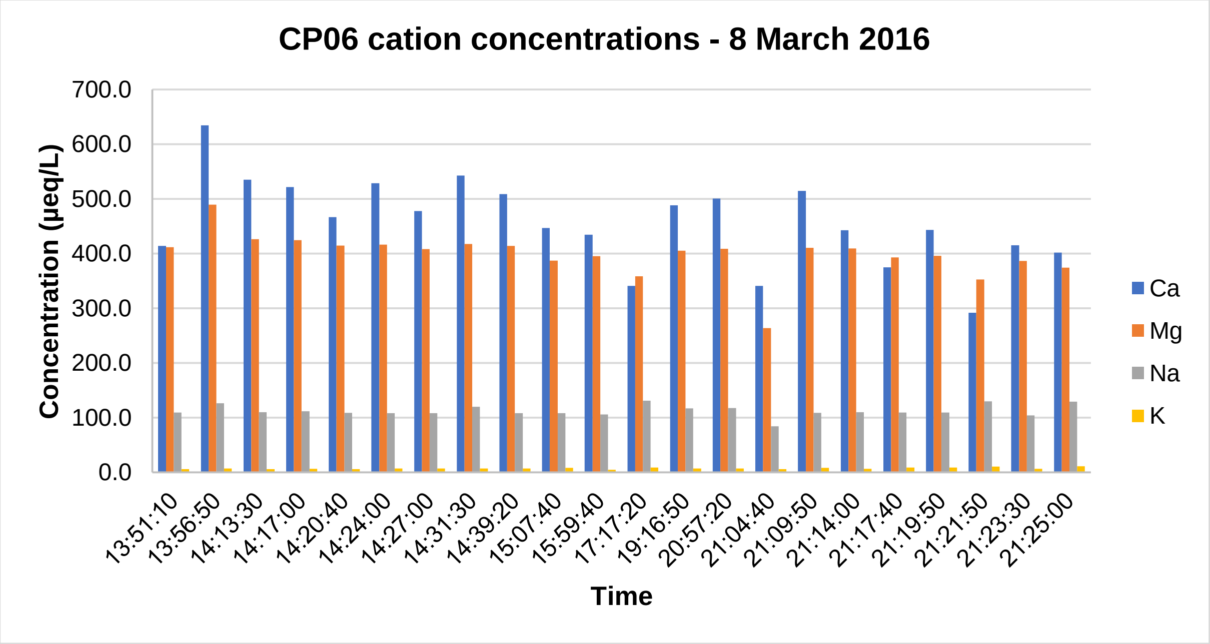

Figure 63 Cation concentrations during CP06 March storm.

The Ca concentrations increased from February to March from 450 – 600+ μeq/L, with the highest concentration occurring between 5 – 60 minutes from the time the storm started. Like CP03, Ca concentrations were always higher than the other cations.

The K concentrations were largely below 10 μeq/L during both storms.

As seen in **Figure 62** and **63**, Mg concentrations also increased from February to March, with the highest concentration occurring within the first 60 minutes of the storm.

The Na concentrations remained consistent from February to March, with the highest concentrations occurring a couple of hours into the storms.

5.4.3.2 Anions

CP03

Figure 64 (data shown in **APPENDIX B28**) and **65** (data shown in **APPENDIX B29**) show the changes in anions concentrations during a storm in February and March 2016, respectively, at CP03.

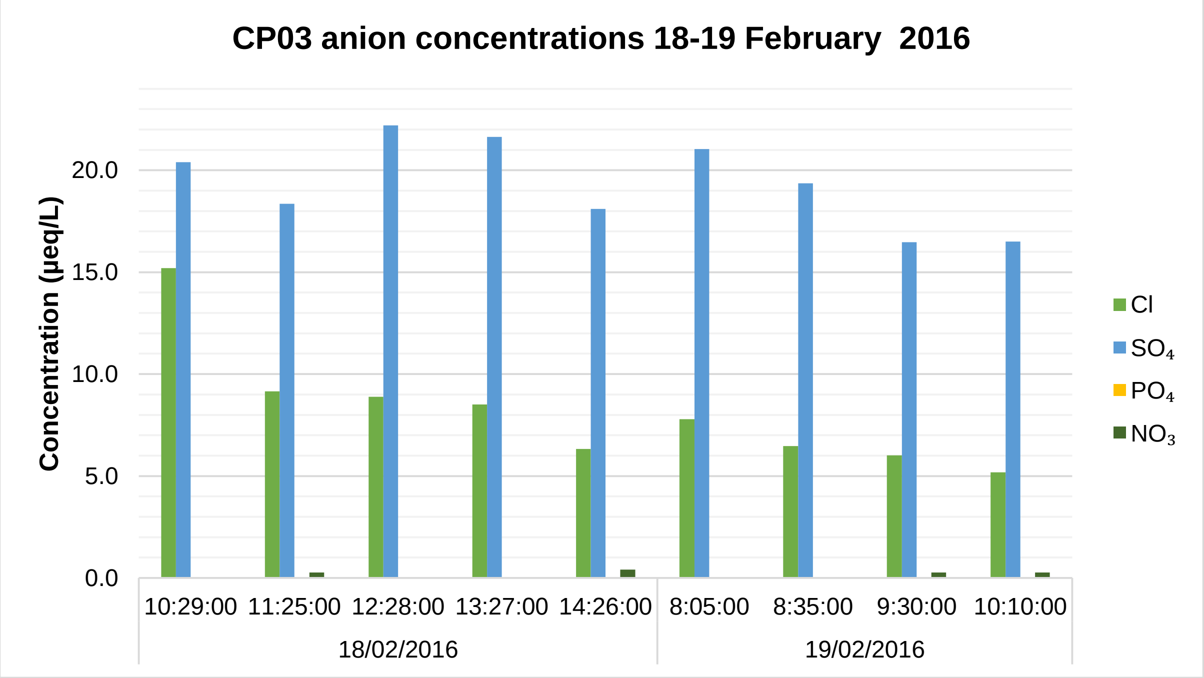

Figure 64 Anion concentrations during CP03 February storm.

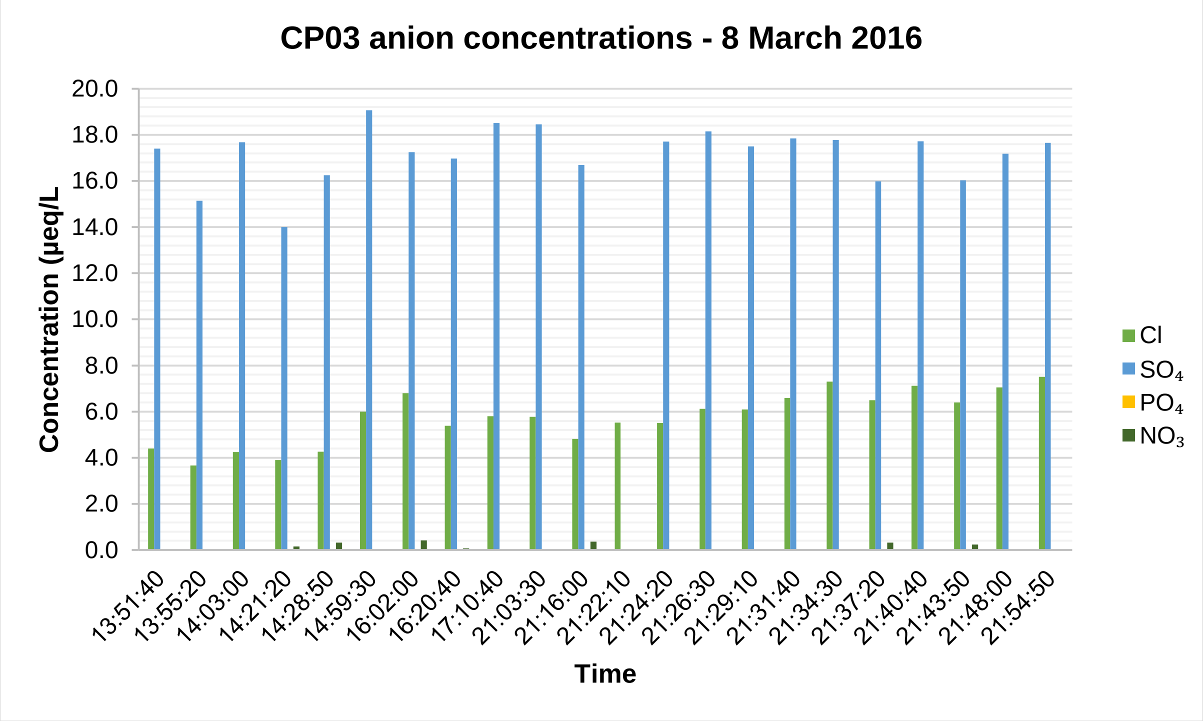

Figure 65 Anion concentrations during CP03 March storm.

The highest Cl concentration was observed at the beginning of the storm in February, whilst it happened four hours into the storm in March. In February, Cl concentrations declined as the storm progressed, whilst there were several peaks and declines in concentrations during the storm in March.

Some of the highest SO_4 concentrations were observed one to two hours into the storm events.

NO_3 and PO_4 had many concentrations that were below detection limits.

CP06

Figure 66 (data shown in **APPENDIX B30**) and **67** (data shown in **APPENDIX B31**) show the changes in cation concentrations during a storm in February and March 2016, respectively, at CP06.

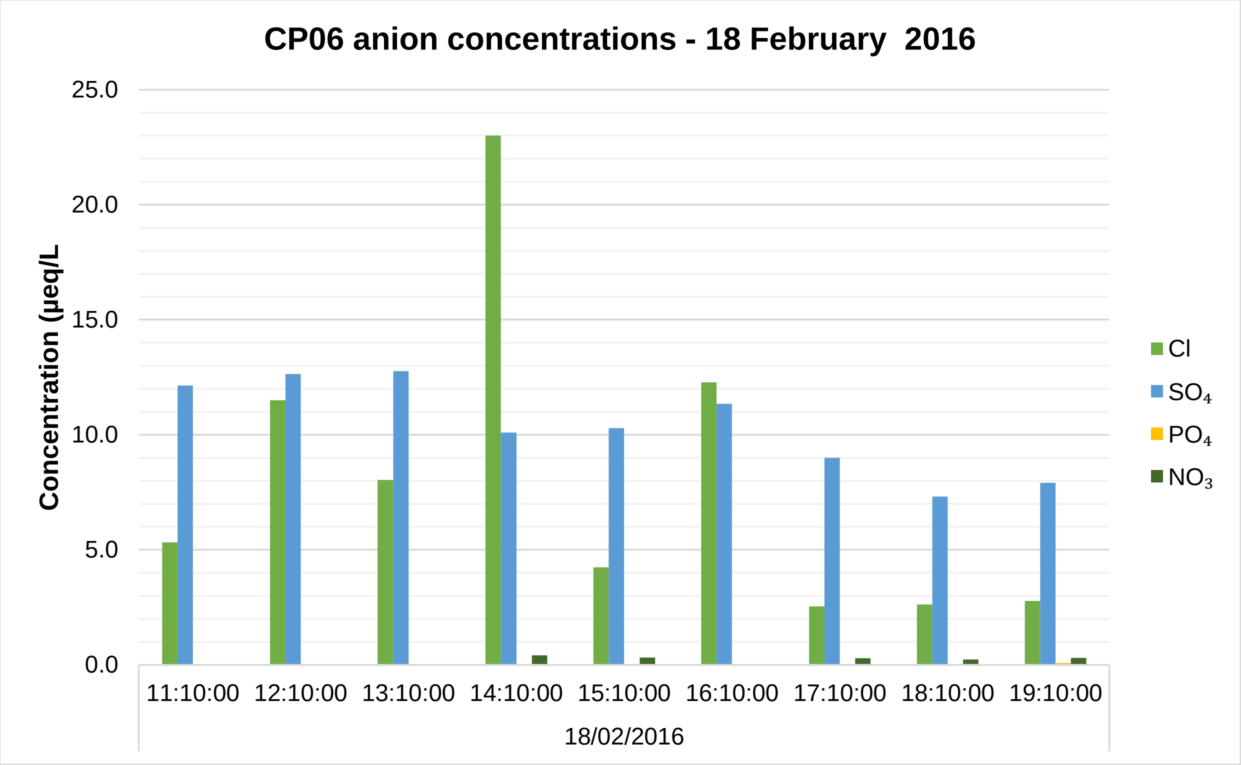

Figure 66 Anion concentrations during CP06 February storm.

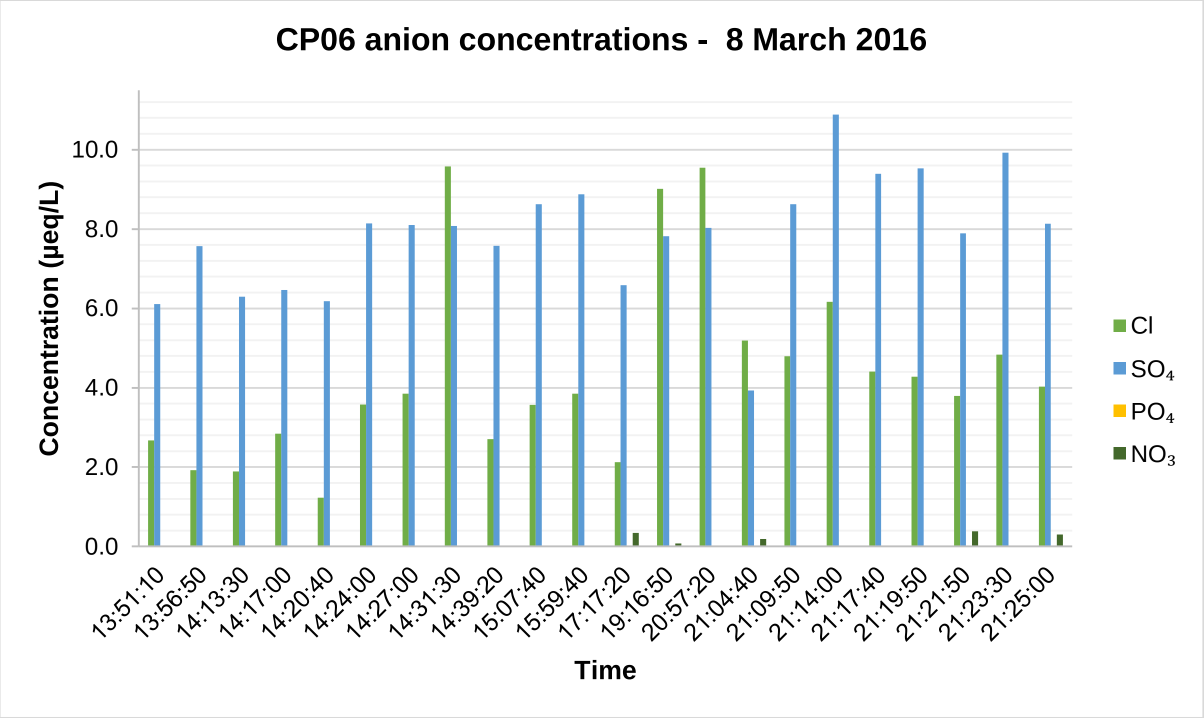

Figure 67 Anion concentrations during CP06 March storm.

The highest Cl concentration is observed 3 hours into the storm in February whilst it happened 1 hour into the storm in March. The February concentrations were higher than those in March.

The SO_4 concentrations observed in February were higher than those in March. The highest concentration occurred 1 hour after the storm had started whilst the highest observed concentration in March occurred near the end of the sampling cycling, 4 hours into the storm.

Although some small NO_3 were visible in **Figure 67**, the PO_4 and NO_3 concentrations were mostly below detection limits.

CP03 SO_4 was almost double those of CP06.

DOC vs SO_4

The relationship between DOC and sulfate is shown in **Figures 68** to **70**.

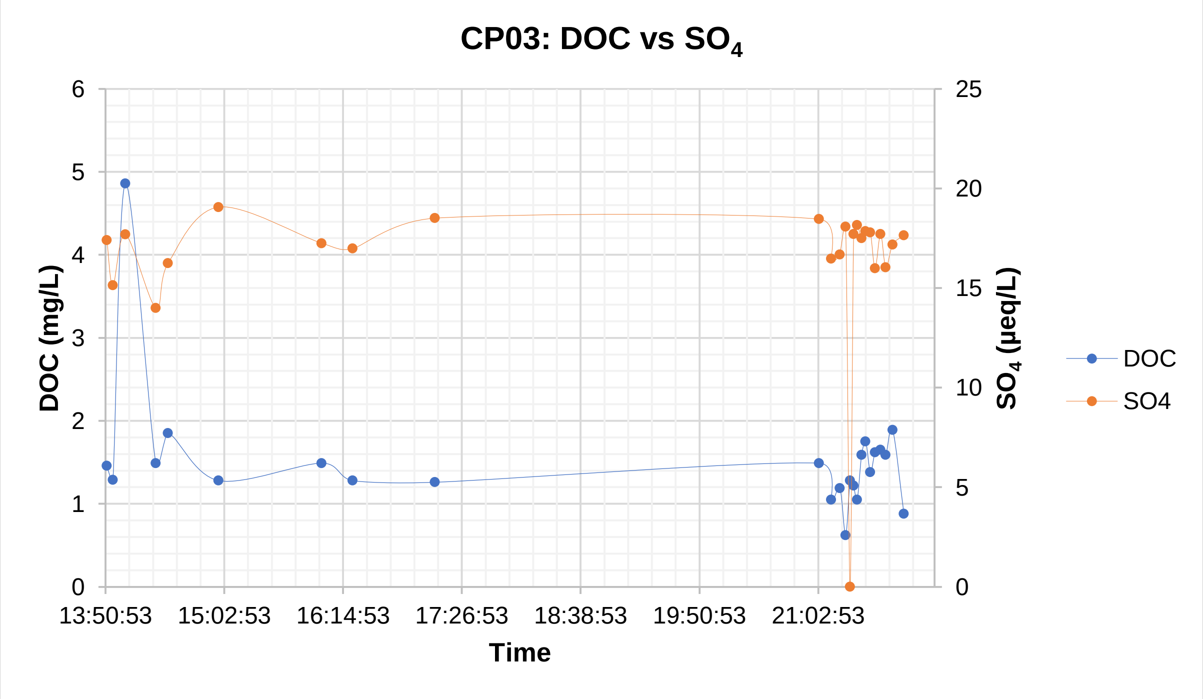

Figure 68 CP03: relationship between DOC and SO_4 08/03/2016.

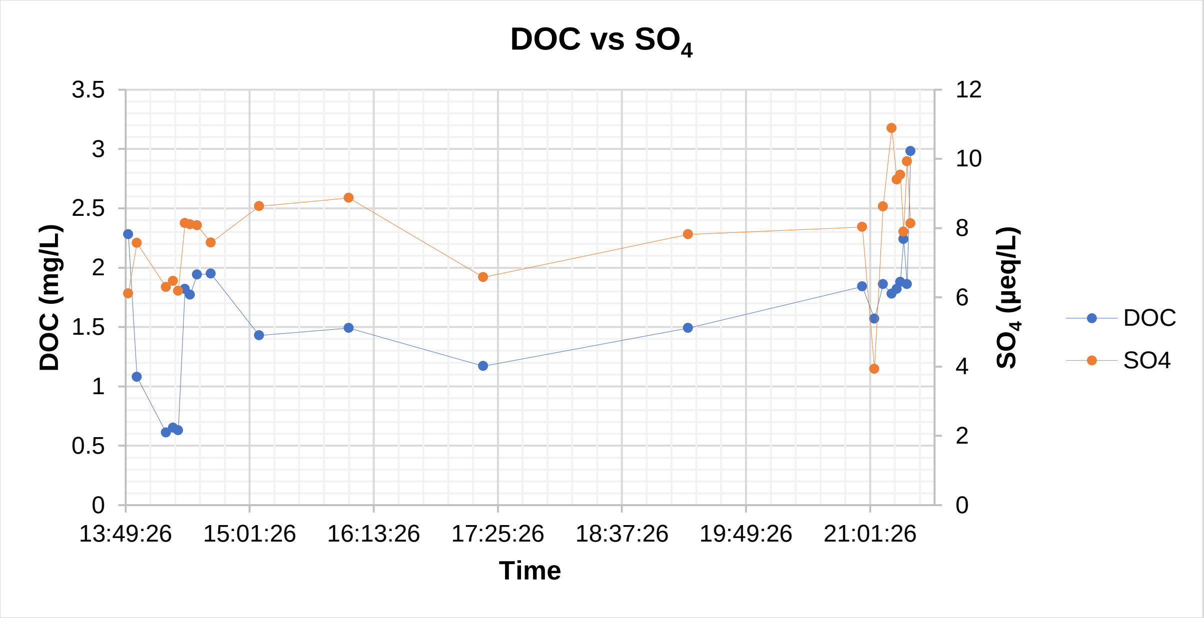

Figure 69 CP06: relationship between DOC and SO_4 on 08/03/2016.

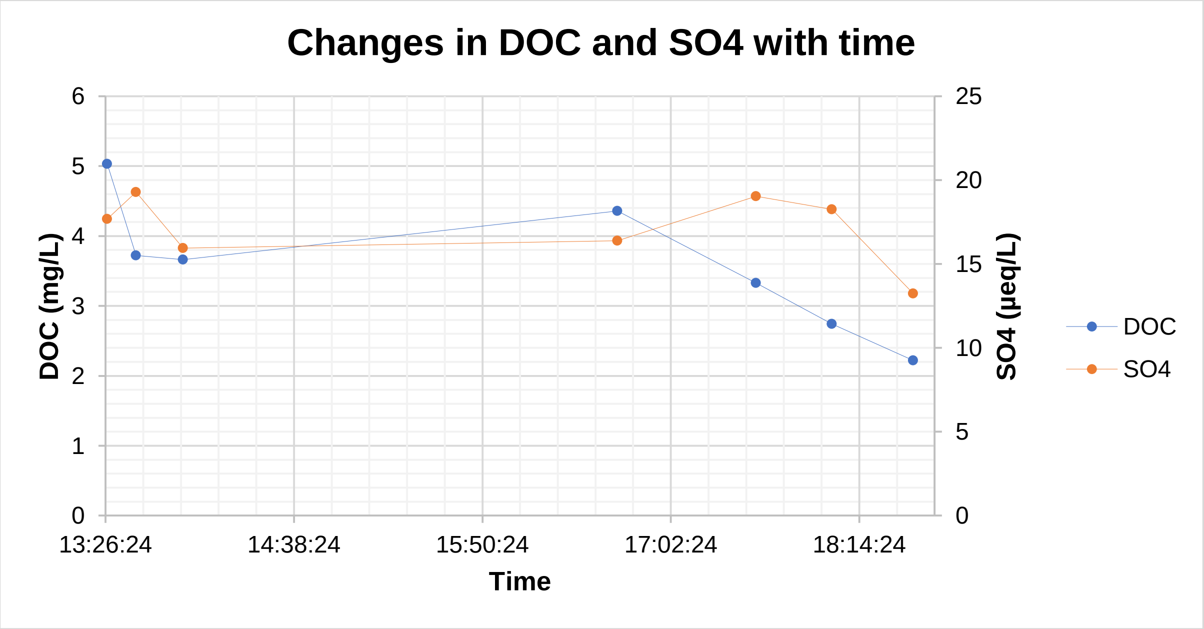

Figure 70 CP06: relationship between DOC and SO_4 on 09/03/2016.

There is an interesting relationship between DOC and SO_4. The sulfates were correlated to the changes in concentration of DOC as seen in the above figures.

The peaks and declines in DOC were very loosely mirrored in SO_4 concentrations for most of the study period. SO_4 > DOC and SO_4 is often double the DOC concentration, the same is reflected in **Figure 69**.

5.6 Spectral absorbance and DOC

5.6.1 CP03

Water samples were collected using an automated ISCO sampler during a week of rainfall in March-2016 and were then analysed for DOC and spectral absorbance.

Figure 71 shows the changes in the concentration of DOC during a storm event on the 08/03/2016 (associated data found in **APPENDIX B32**).

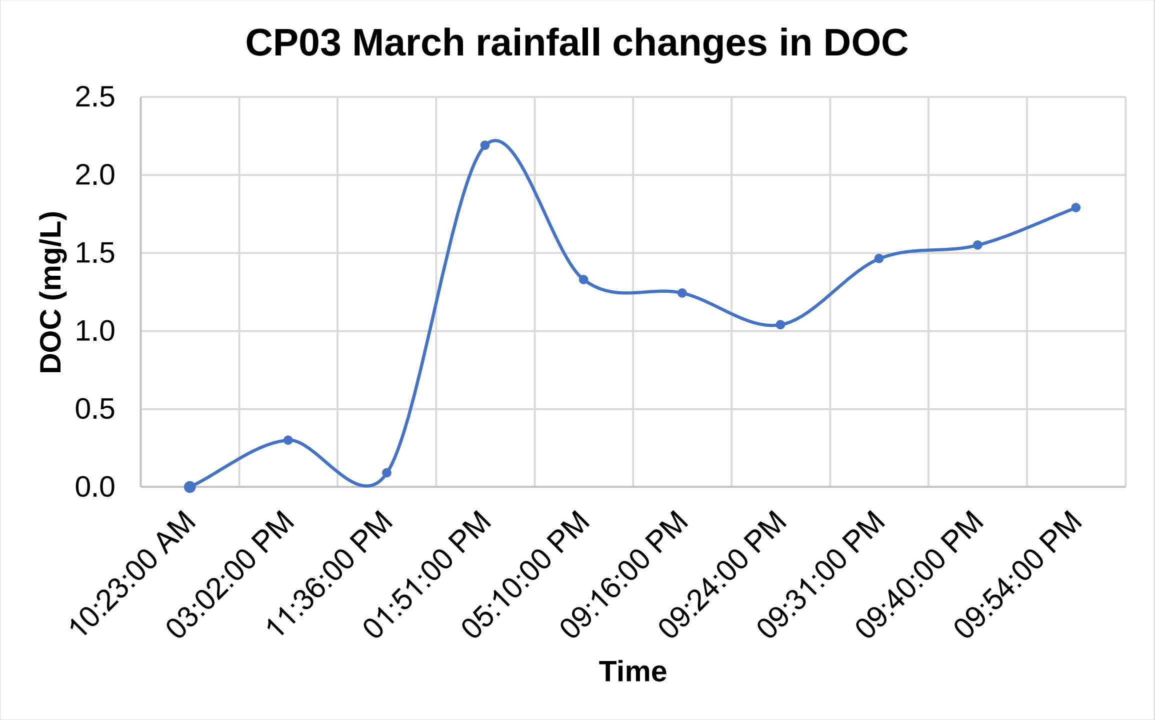

Figure 71 CP03 change in DOC during a storm on March 8, 2016.

There was an initial increase in DOC from the time the first sample was collected before it had started raining. A drop then followed this, by the time it had started raining for a few hours, the concentration of DOC spiked. The concentration of DOC did not maintain the peak but slowly decreased and then started a slow ascent.

The scatterplots shown in **Figure 72** are of DOC against the different wavelengths used for spectral absorbance.

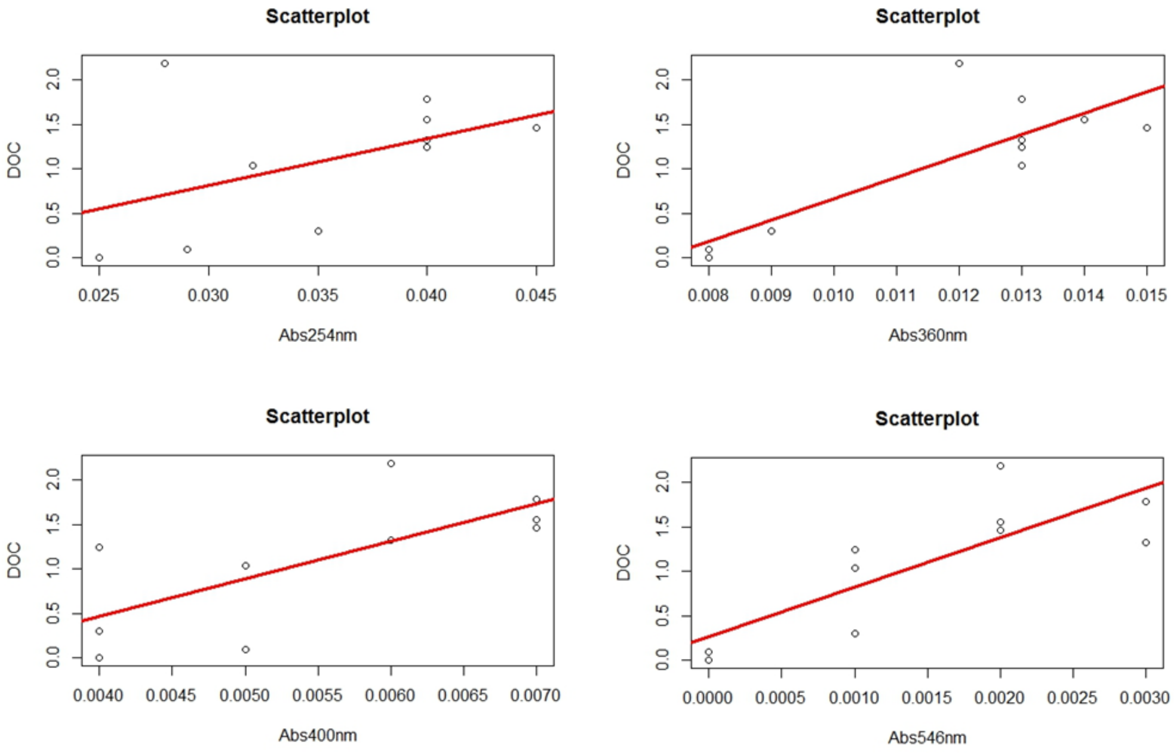

Figure 72 CP03: spectral absorbance vs. DOC

The red lines are trend lines, a simple linear regression were run to get an equation for DOC prediction and the associated R^2. The equations for DOC prediction are shown in **Table 45**.

Table 43 Equations for DOC predictions.

Wavelength (nm)	Eq. for DOC prediction	R²	p-value
254	y = 53.001x - 0.7768	0.2229	0.168
360	y = 240.08x - 1.7336	0.6715	0.004
400	y = 419.59x - 1.2083	0.5163	0.019
546	y = 557.33x + 0.2634	0.6596	0.004

There was a relationship between DOC and spectral absorbance, the R^2 values varied and the ones which was the closest to 1 was at 360 nm. Spectral absorbance explained 67.2% of DOC.

5.6.2 CP06

Water samples were collected using an automated ISCO sampler during a week of rainfall in March-2016 and were then analysed for DOC and spectral absorbance.

The changes that occurred in DOC during the storm were shown in **Figure 73** (associated data found in **APPENDIX B33**).

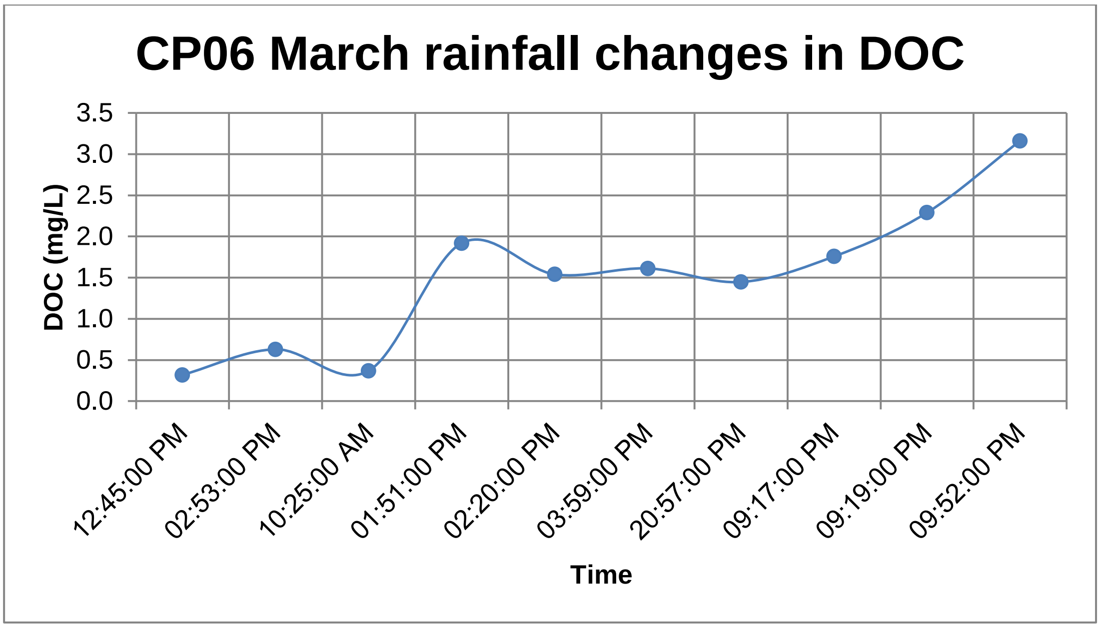

Figure 73 CP06 change in DOC during a storm on March 8, 2016.

Like CP03, there was an initial increase in DOC from the time the first sample was collected before it had started raining. It was then followed by a decrease, and started increasing as it started raining. Unlike CP03, the highest DOC concentration was not reached a couple of hours after it had started raining but rather much later into the storm. There is a steady increase towards the highest DOC concentration.

The scatterplots shown in **Figure 74** are of DOC against the different wavelengths used for spectral absorbance.

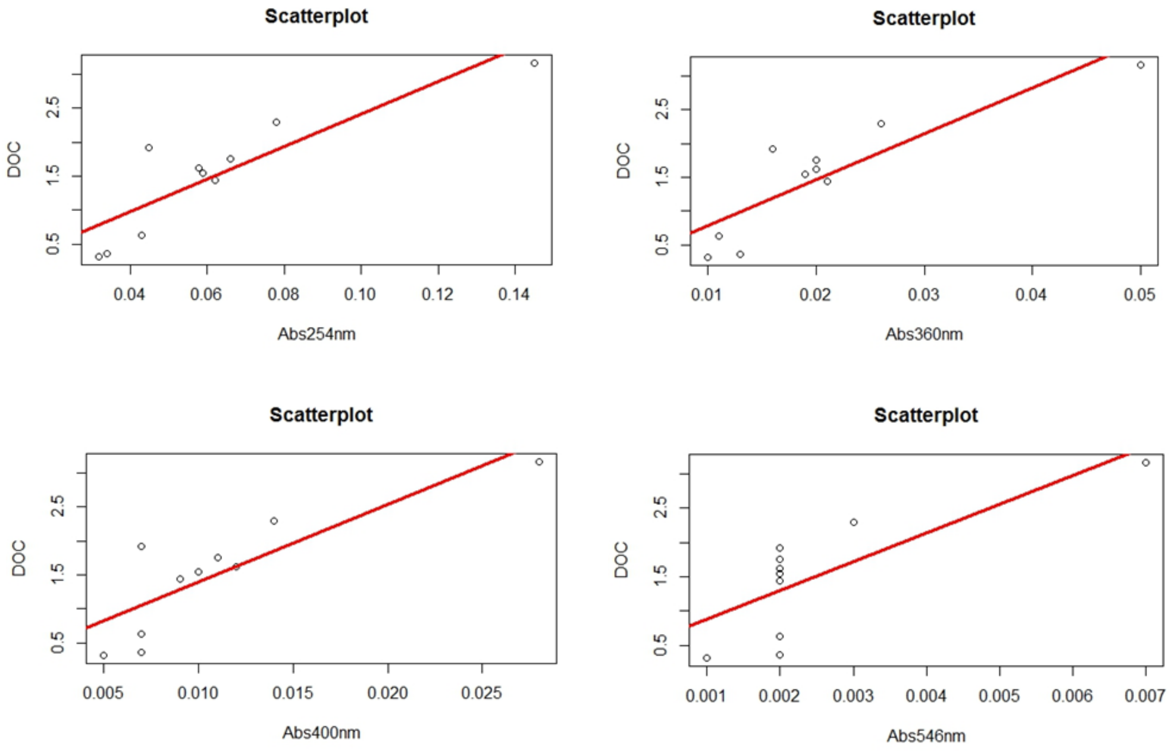

Figure 74 CP06 spectral absorbance vs. DOC

The red lines are trend lines, a simple linear regression was run to get an equation for DOC prediction and the associated R^2. The equations for DOC prediction are shown in **Table 46**.

Table 44 Equations for DOC prediction.

Wavelength (nm)	Eq. for DOC prediction	R²	p-value
254	y = 23.899x + 0.0186	0.7686	0.001
360	y = 68.072x + 0.1029	0.7732	0.001
400	y = 113.94x + 0.2518	0.7121	0.002
546	y = 418.64x + 0.4585	0.607	0.008

As seen in **Table 46**, the closest R^2 value to 1 is at 254 and 360nm.There was a significant relationship between DOC and spectral absorbance at all wavelengths

Overall, CP06 has a higher R^2 values across the wavelengths, indicating a closer relationship between absorbance and DOC at this site.

CHAPTER 6: DISCUSSION

Overview

> *This chapter discusses important patterns from the results chapter and uses literature to support happenings.*

The aim of this study was to investigate the impact of storm events on catchment solute and macronutrient concentrations. In addition, efforts were made to determine whether land-use history and management led to differing responses between catchments. These comparisons were made on the basis that the natural vegetation across these catchments, slope and elevation are very similar.

6.1 Streamwater chemistry across catchments with differing land uses

There were some significant differences between catchments with differing land uses and certain major ions. Some of the factors which affect streamwater chemistry include: geology (which is similar across catchments - normalised) (Mulholland and Hill 1997, Colorado Geological Survey 2000, Chessman and Townsend 2010), topography (Wade 1935, Allan *et al.* 1997, Mulholland 2004, Lewis and Grimm 2007, Fraterrigo and Downing 2008, Andersson and Nyberg 2009, Geen *et al.* 2015) and vegetation (White and Blum 1995, Mulholland and Hill 1997, Merbold *et al.* 2009, Zhang *et al.* 2011). However, geology and topography are assumed to be similar (Gush *et al.* 2002).

The study catchments, to varying degrees, experienced changes in solute concentrations from the historical to recent data. They all experienced decreases in Ca, Mg and Na for which the causes are unknown, but could be linked to the possible impact of decreased application of fire across CP03, CP04 and CP06 along with the change in vegetation in CP03 and CP09-with time. All catchments may be responding to a decrease in catchment disturbance while CP03 is recovering from forest felling and unplanned burn.

At the catchment scale, there was a difference in the vegetation between CP03 and CP09 mainly due to the land management techniques, CP04 and CP06 have similar land use and also receive similar management techniques. Considering the role that geology plays in determining the chemistry of streamwater (Allan *et al.* 1997, Holloway and Dahlgren 2001, Allan 2004, Andersson and Nyberg 2009, Mouri *et al.*

2011), the mechanisms of weathering could have significant influence on the differences between catchments. This means that the rates at which mechanical or chemical weathering occurs at could be different between the catchments, based on the differing vegetation and the historical land management techniques. CP03 was historically ploughed and planted but has been recovering since the 1980s while CP09 has been subject to fire exclusion over this period.

6.1.1 CP03

CP03 in particular experienced decreases in NO_3 with time. Nutrient input concentrations such as NO_3, can be helpful indicators of nutrient cycling in the terrestrial ecosystems that the streams drain (Mulholland 1992, 2004, Mulholland and Hill 1997). This could be linked to the anthropogenic change which was associated with land use, from the afforestation of pine forest. The establishment of such plantations in grasslands can lead to increased inputs of organic matter with input from leaf litter and woody material (Nisbet *et al.* 1995, Principe *et al.* 2015). This increased throughfall and woody input could have been linked to the elevated nitrate concentrations in the catchment. Zhao *et al.* (2017) reported that afforestation caused physical and chemical changes in soil especially in C, N and P.

The forest plantation in the catchment was burnt and the recent data could be reflective of the catchment slowly recovering from the both the devastating fire and afforestation which originally introduced changes into the system. Macdonald *et al.* (2002) showed that throughfall was responsible for more than 60% of variation in leached nitrate. The fire in 1981 increased the input of nitrates through organic matter (leaves and woody material) (Delwiche 2010). The rapid growth of bracken and change with time could possibly be associated to the observed decrease in NO_3 concentrations or the sudden historical increase in NO_3 concentrations and the gap in vegetation (post fire) could have opened up a niche for the bracken to flourish and the scale at which this happened was possibly reflective of the amount of NO_3 and other solute which were available to be taken up in the soil. Niche differentiation is a process through which different species are able to acquire nutrients from portions of the available nutrient pool. Although leaching could possibly decrease with increases in species diversity, this could be a possible cause to the decreased streamwater concentrations (Hooper and Vitousek 1998).

The fire in 1981 was a form of riparian clearing /canopy opening. Allan (2004) reported on the different mechanisms through which land use affected in-stream conditions. Riparian clearing /canopy opening can lead to increases in plant growth and erosion. Increased plant growth occurs because the sun then penetrates levels much lower than when there was a canopy and erosion because of clearing further destabilises the soil. Although plant growth increases, it would take time for the plants to effectively stabilise the soil (Gray 1997). Overall, the changes seed at CP03 may be interpreted as a recovery of the catchment from the major historical disturbances of planting, felling and fire.

6.1.2 CP04 and CP06

These two catchments have similar land uses and have similar land management techniques applied. CP04 and CP06 had similar Ca, Mg, Na and K concentrations in both the historical and recent datasets. These similarities could be attributed to the fore mentioned similar land use and management techniques. Although the historical application of fire was not always as consistent as it has now come to be (there were times when the biennial spring burn catchments were burnt 2 years in a row – CP04 in 1981 and 1982) the general relationship between the two catchments remained.

There were differences observed between the historical and recent NO_3 concentrations. These differences were not particularly due to increased or decreased concentrations but rather that the catchments tended to have low concentrations which were below detection limits. As a consequence the observed historical and recent graphs did not give much information. It is possible that there is a strong nitrogen limitation in these relatively undisturbed control catchments.

6.1.3 CP09

CP09 has had increases in nitrate concentrations. This is a fire exclusion catchment and has experienced increased encroachment by woody vegetation. Since fire is a natural part of this mesic grassland, the absence of this tool can lead to dramatic changes in vegetation - as seen in this system. Aside from the changes in vegetation, in the absence of controlled fire - which generally has short-lived hydrochemical changes in soil water, ground; and surface water, biomass slowly and consistently releases solutes as it decomposes on the catchment floor (Delwiche 2010). While the mechanisms are not clear, it is possible that the changing vegetation either leaks nitrogen more readily than the grassland it is replacing, perhaps through changes in soil mineralisation rates.

6.2 Seasonal streamwater chemistry

The seasonal pattern observed across catchments from the 1980s and 2000s are representative of the different land management techniques. For catchments with the same management techniques, topography and geology, other dominant flow paths come into play. Only the summer historical and recent datasets were compared due to their completeness, relative to other seasons.

The historical data tended to have higher solute concentrations than the recent. Differences between the catchments, for example CP04 and CP06 were similar for both the historical and recent datasets. The observed differences between catchments with different land use could be attributed to those different land uses. In the case of CP04 and CP06, which have similar land uses, other factors such as when fire was applied, the presence of upstream wetlands, groundwater recharge rates and streamflow rates could have been responsible for the differences. i.e. intrinsic differences in catchment hydrology and runoff delivery.

6.3 Streamwater temperature, conductivity, DO and pH

Streamwater temperature is an important property of flowing water and has significant influences on dissolved oxygen, suspended soils, conductivity, pH and the general aquatic ecosystem (Webb *et al.* 2008).

Freshwater usually has conductivity levels < 600 µS/cm, these catchments did not exceed 200 µS/cm. CP03 had consistently low conductivity levels, although it had been expected that this catchment would have had increased conductivity levels due to the historical land use management techniques (previously afforested, now degraded after fire swept through the catchment in 1990); the opposite is true. These low conductivity levels could have been due to current land use management techniques, temperature – warm water has increased conductivity, erosion/weathering and groundwater recharge. Conductivity is temperature dependent, the streamwater temperatures monitored in these mountainous catchments did not exceed 15 ºC during winter of 2015 – except for irregularities in CP03 where temperatures nearly exceeded 20 ºC and dropped below 5 ºC. Considering that the temperatures were generally low, there were overall low conductivity levels across catchments. CP03 and CP09 received more shading from riparian vegetation, which affected the streamwater temperature and conductivity is dependent on temperature, which may further explain why the two catchments had lower conductivity

The level of dissolved oxygen in water is affected by temperature, atmospheric pressure, aquatic vegetation (also excessive organic matter) and the type of water. During the summer of 2014, CP09 had increased conductivity levels and extremely low DO concentrations. A fire had swept through the catchment a couple of months before this happened, which could have mobilised leaching of ions into the stream, increasing conductivity. Dissolved oxygen is sensitive to temperature and excessive organic matter. The decomposition of organic matter uses up DO stock and produces carbon dioxide as a by-product. The burning of riparian vegetation could have reduced shading and increased temperatures, reducing DO.

Streams were approximately circumneutral with differences in soils, vegetation and hydrological pathways determining temporal and spatial differences in pHCP09 had some of the highest DO concentrations, this could be attributed to the topography and the rocky, densely vegetated riparian zone of the catchment (Evans *et al.* 2005, Solheim *et al.* 2010). This was also caused by low temperatures and the shading caused by vegetation along the riparian zone. This fire exclusion catchment has significant differences in vegetation in comparison to the other catchments. Consequently, the historical land management technique has an impact on the DO concentrations.

6.4 Dissolved organic carbon

Differences in the production of DOC across the catchments would be expected when considering the different land use histories (Evans *et al.* 2006, 2008, Clark *et al.* 2010, Moody *et al.* 2013, Finstad *et al.* 2016). However, there were no significant differences in DOC concentrations between catchments, for the monthly sampling trips despite some differences in other chemical measurements. Hence the different land-use histories of these catchments did not produce detectable differences in DOC concentrations.

6.5 Total dissolved solids and total suspended solids

It is important to know all the factors that influence streamwater chemistry and quantify them. The TDS and TSS concentrations calculated for CP03 were higher than those for CP06, this suggested that the rainfall washed a higher concentration of dissolved solids into CP03, along with washing soils into the catchment and disturbing the floor of the stream. The concentrations of TDS and TSS vary from catchment to catchment. This could be attributed to topography, geology, soil generation, vegetation – riparian and otherwise, mechanical weathering forces within each catchment (Mulholland 2004, Lewis and Grimm 2007, Andersson and Nyberg 2009, Hassan *et al.* 2015).

6.6 Storm water quality

Hydrologic processes and geology determine subsurface inputs during a storm. During the March storm, CP06 had quick response times in terms of the concentration of Ca and Mg. Some of the highest concentrations occurred very early during the storm. The change in solute concentrations from February suggests that there was a change in flow paths or soil-geology and water interactions (Mulholland 1993). At the catchment level, both shallow and deep flow paths are important in generating stream stormflow (Christophersen *et al.* 1990, Mulholland 1993).

CP03 had the highest Ca concentrations of all the catchments, this could be attributed to different sources and sinks along different flow paths. These differences can be linked to the different land management techniques. CP03 had much greater disturbance in the past, perhaps leading to greater weathering inputs. Ca dominated the streamwater chemistry. On average, there was a net positive alkalinity, main cations exceeded anions. This could be characteristic of land use or the precipitation chemistry in the region (Avila 1996).

Ca and Mg are weathering products of silicate minerals and their dilution causes a decrease in alkalinity (Ávila *et al.* 1992, Monteith *et al.* 2007). Both cations can be concentrated in the soil through evapotranspiration and make up a large part of the nutrient cycle. The processes that account for observed increases in Ca and Mg in stormflow mostly take place in the early phases of small events.

The flushing of salts that accumulate in or near stream channels can account for these early increases of Ca, Mg, SO_4 and Cl. Patterns of storm solute behaviour are closely linked to hydrological conditions. The amount and intensity of precipitation are major facts which affect the hydrograph, water path ways and solute responses (Hewlett and Hibbert 1967).

6.7 Spectral absorbance as a proxy for DOC

The reliability of using spectral absorbance as a proxy for DOC is constantly questioned (Weishaar *et al.* 2003, Chow *et al.* 2008). Poor correlations between DOC and spectral absorbance have been reported but this is because organic carbon is not always reactive at the same wavelengths from one source to another; and in this case, 254, 360, 400 and 546 nm.

The relationship between DOC and spectral absorbance is commonly investigated at 254 nm (Lewis and Tyburczy 1974, Chow *et al.* 2008, Peacock *et al.* 2014). When correlating DOC with spectral absorbance in this study, the results varied between CP03 and CP06 and furthermore between the wavelengths at which spectral absorbance was read.

Figure 75 shows the intensity of association between absorbance and DOC, in CP03 and CP06.

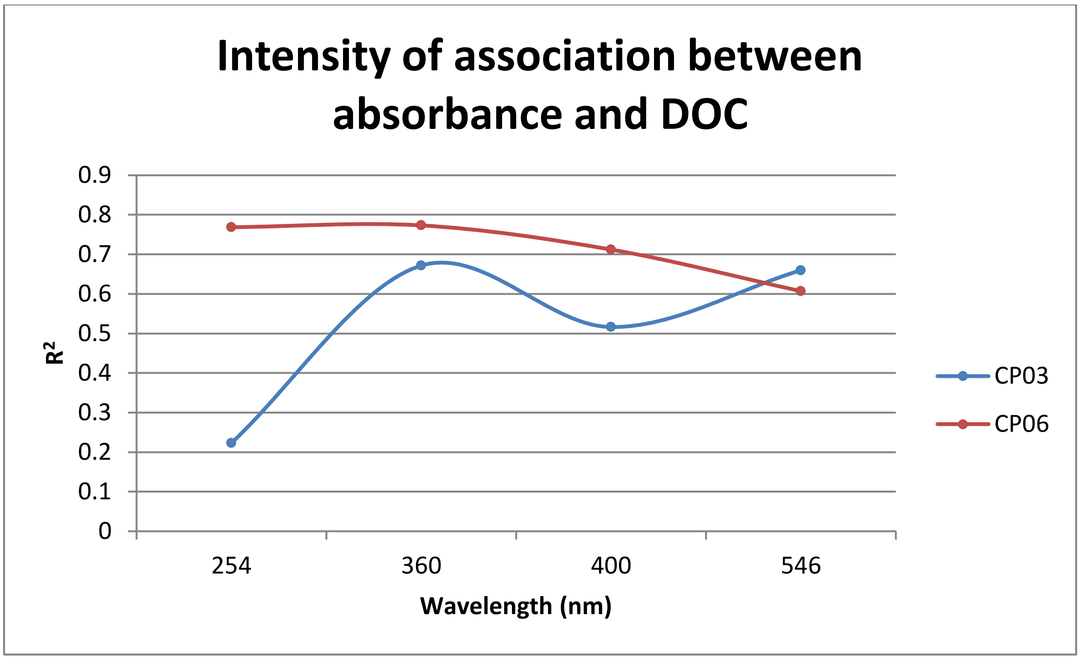

Figure 75 Graph indicating the intensity of association between absorbance and DOC as a function of wavelength.

There is a marked decrease in the association between 400 – 546 nm in CP06. Dissolved organic carbon is most closely related to absorbance at the wavelength range 254 – 360 nm in CP06, about 76.9% of the variance in DOC can be accounted for by variation in absorbance within this range. In CP03, DOC is most closely related to absorbance at 360 nm, about 67.2% of the variance in absorbance can be accounted for by variation in DOC at this wavelength.

Since DOC is a biological product, produced in terrestrial systems (Clark *et al.* 2010), and different catchment with differing land management techniques have different process acting at the catchment scale (Bu *et al.* 2014); different forms of DOC will be produced across the catchments (Moody *et al.* 2013). Consequently, the way in which the DOC interacts will differ when considering the differing vegetation cover between the catchments; thus, the different assemblages of DOC (Peacock *et al.* 2014).

Overall, CP06 had higher R^2 values across the wavelengths, indicating a closer relationship between absorbance and DOC at this site. The presence of a wetland just above the weir could be one of the sources determining the nature of the CP06 DOC or rather, the manner in which the sample attenuates light. The increased microbial activity and slow moving water allows for the decomposition of the abundant organic material found in these systems (Gergel *et al.* 1999).

The use of spectral absorbance as a proxy for DOC has been widely used, this relationship would be better exploited in environments where the water is not as clear as the streams in Cathedral Peak. Another consideration that needs to be made is that more data points make it easier to identify the nature of a relationship such as this, therefore, more data would be required to improve statistical relationships.

CHAPTER 7: CONCLUSION AND RECOMMENDATIONS

Overview

> *This chapter reiterates the purpose of the study, aims and objectives. It provides a summary of the literature review, study site, methods and results: differences that were found between catchments, outlines the changes in chemistry from the historical to recent data, temporal changes that occur during storms, driver(s) of changes in DOC and asserts the use of spectral absorbance as a proxy for DOC. The relevance of the study is summarised and the limitations of the study are also discussed, along with recommendations for future research.*

The purpose of this research was to understand the links between storm events on streamwater chemistry and land use and to further explore the effect of land use on monthly streamwater chemistry. The aims were to identify patterns of seasonal change in solute concentrations and compare results between the catchments, identify the changes to macronutrient concentrations that occur during storm events and compare catchments; and investigate whether there is a correlation between the colour of the sample water and dissolved organic carbon (DOC) and to explore a simpler method of ascertaining DOC concentrations using UV light.

Water is a scarce resource in South Africa and has the potential to limit both the country's development and growth. As a consequence the wise management of water resources and resilience are important (Blignaut and Van Heerden 2009).

Headwater streams are important and their chemistry can be affected by geology, topography, climate, hydrology, mechanical and chemical weathering, rainfall rates, rainfall chemistry, vegetation and climate change (Alexander *et al.* 2007, Andersson and Nyberg 2009). Fire is an important natural part of mesic South African grasslands and consequently the management of this tool can be a factor affecting streamwater chemistry. Other influences on streamwater chemistry include atmospheric deposition, episodic acidification and nitrate leaching (from afforestation). All these factors are of importance and the extent and nature of their impacts are essential to understand.

Carbon cycling in freshwater sources in not sufficiently studied but is an extremely important variable. Dissolved organic carbon is a valuable link between terrestrial and aquatic environments (Yang *et al.* 2017). Concentrations are influenced by organic carbon pools, land use, storm events, land cover and anthropogenic sources (Worrall *et al.* 2004, Clark *et al.* 2010, Dhillon and Inamdar 2014, Kim *et al.* 2014). The use of spectral absorbance as a proxy for DOC has been applied in many studies (Menzel and Vaccaro 1964, Lewis and Tyburczy 1974, Cuthbert and del Giorgio 1992, Kaplan 1992, Gadmar *et al.* 2002, Worrall *et al.* 2004).

The location of the research allowed for the assumption of uniform geology, topography and aspect across all four research catchments. The catchments that were studied include: CP03 (previously afforested – degraded), CP04 (pristine grasslands), CP06 (pristine grasslands) and CP09 (protection from fire).

Monthly grab samples were collected and analysed for major ions and DOC. Other water quality parameters were also collected on the monthly monitoring trips and these included: pH, streamwater temperature, dissolved oxygen and conductivity. A weeklong trip to CPRS was taken for the collection of streamwater samples during storm events for the analysis of major ions, DOC, spectral absorbance, TDS and TSS. All the data were then analysed using a one-way ANOVA (recent data, dissolved oxygen, conductivity, DOC, streamwater temperature), historical data was analysed using linear mixed effects models. This was done because the historical data originally contained a large number of zeros which could have either been actual zeros or missing values. In order to deal with that issue, all the zeros were then replaced with “NA” and tests were run on the data. Comparisons were made between catchments with the stormflow data (major ions, TSS, TDS). The relationship between DOC and spectral absorbance was determined using regression analyses and all the data were further discussed in the results chapter.

CP03 had increased historical NO_3 concentrations, which could have been related to the fire in 1981 and nitrate leaching. CP04 and CP06 had fairly similar concentrations from historical to recent datasets. CP09 experienced increases in the recent NO_3 concentrations which could be caused by the absence of fire.

The catchments had similar monthly DOC, pH, dissolved oxygen and streamwater temperatures. There were differences between months but those showed common patterns across catchments during most months. CP09 had significantly different average streamwater temperatures, and this catchment has trees along the riparian zone of the stream, unlike the other catchments, due to fire exclusion management. The riparian vegetation is a major contributor towards the differences, therefore the land use is a contributing factor.

The DOC concentrations were relatively low across the catchments. Due to the consistently low monthly DOC concentrations, the relatively high concentrations during storms were deemed to be influenced by stormflow path ways and to a lesser extent, the long residence times of water in the weir dam.

There were differences in storm water major ion chemistry between CP03 and CP06 and this could be attributed to the differences in land use. These two catchments also have varying concentration with respect to TDS and TSS. CP06 tended to have higher TDS and TSS concentrations, which could have been attributed to the presence of a wetland upstream of the weir or differences in land use histories.

CP06 spectral absorbance values showed a better relationship with DOC, at all wavelengths, $R^2 = 0.769$ at 245 nm, $R^2 = 0.773$ at 360 nm, $R^2 = 0.712$ at 400 nm and $R^2 = 0.607$ at546 nm as compared to CP03: $R^2 = 0.0.223$ at 245 nm, $R^2 = 0.0.672$ at 360 nm, $R^2 = 0.516$ at 400 nm and $R^2 = 0.659$ at 546 nm. This is presumably due to differences in the quality of the DOC within these catchments. These methods are convenient because the sampling and logging of DOC proxies can be done through time at a low cost. For a catchment, if calibrated specifically absorbance at 360 nm is a reasonable predictor of DOC, but the relationship does not appear to be transferable from one catchment to another if they have different land use histories.

Many factors need to be considered when identifying the nature of the relationship between streamwater chemistry and land use. Land management techniques play a large role in shaping the composition of streamwater chemistry, not only that, but these techniques also have an influence on the mechanical weathering of catchment rocks.

The data collected from this study is valuable because it gives an indication of the quality of important headstreams in Southern Africa. It is essential that such information be continually monitored in order to track changes over time (influence of anthropogenic and natural change). In gaining a better understanding of the quality and quantity of these sources, more informed decisions could be made with regard to their management.

The information about DOC is important because in terms of cleaning water further downstream, it costs more money to remove higher DOC loads. A bigger issue than that is of carbon sources and sinks. In understanding the carbon dynamics of the areas which these streams drain, it would make it easier to make decisions as to how to manage land use and or change. The study has shown that land use and management both strongly influence streamwater chemistry.

Limitations and future studies

One of the main limitations in stormflow chemistry monitoring was the collection of water samples using an ISCO automated sampler. The instrument only has 24 sampling bottles and therefore stops collecting samples after the 24th bottle has been filled, which may not have covered the full storm hydrograph. This means that potential samples that could have been collected, were lost. This could be avoided if proximal distances could be kept to the instruments during storms in order to empty and initiate collection sooner than having to wait the following day.

Another limitation was the single sampling locations across all four catchments. The introduction of multiple sampling points along the stream would also make a difference in the characterisation of the effect of land use on streamwater chemistry. Multiple points make for a better representation of the catchment.

Another limitation was the descriptions associated with the historical data. The data are valuable but the reports omitted important information about the units of anions and could have been annotated better the missing values so that actual zeros could be used in the statistical analyses. This shows how important it is to write clear metadata so that future generations can redo experiments or use data to make comparisons with the present data.

Future studies should include more detailed study of the effect of discharge on the concentrations of major ions in to better identify the changes in concentrations. This would make is possible to further calculate the fluxes of the major ions and identify stormflow path ways. Other possible studies could focus on acid deposition and possibility of acid episodes in catchments. An investigation into the aromatic character of DOC in catchments using specific UV absorbance measurements at 254 nm would give more information about the carbon cycling in these catchments.

REFERENCES

Acocks, J.P.., 1988. Temperate and transitional forest and shrub types. *In*: O.A. Leistner and B.A. Momberg, eds. *Veld Types of South Africa*. Memoirs Botanical Survey of South Africa, 93–122.

Ahearn, D.S., Sheibley, R.W., Dahlgren, R.A., and Keller, K.E., 2004. Temporal dynamics of stream water chemistry in the last free-flowing river draining the western Sierra Nevada, California. *Journal of Hydrology*, 295 (1–4), 47–63.

Alexander, R.B., Boyer, E.W., Smith, R.A., Schwarz, G.E., and Moore, R.B., 2007. The role of headwater streams in downstream water quality. *Journal of the American Water Resources Association*, 43 (1), 41–59.

Allan, J.D., 2004. Landscapes and riverscapes: the influence of land use on stream ecosystems. *Annual Review of Ecology, Evolution, and Systematics*, 35 (1), 257–284.

Allan, J.D., Erickson, D.L., and Fay, J., 1997. The influence of catchment land use on stream integrity across multiple spatial scales. *Freshwater Biology*, 37 (1), 149–161.

Anderson, S.P., Dietrich, W.E., Montgomery, D.R., Torres, R., Conrad, M.E., and Loague, K., 1997. Subsurface flow paths in a steep, unchanneled catchment. *Water Resources Research*, 33 (12), 2637–2653.

Andersson, J.-O. and Nyberg, L., 2009. Using official map data on topography, wetlands and vegetation cover for prediction of stream water chemistry in boreal headwater catchments. *Hydrology and Earth System Sciences*, 13, 537–549.

Augustijn, D., Fares, A., and Tran, D.N., 2011. Temporal and Spatial Variations in Total Suspended and Dissolved Solids in the Upper Part of Manoa Stream, Hawaii. *Journal of Sustainable Watershed Science and Management*, 1 (1), 1–9.

Austnes, K., Evans, C.D., Eliot-Laize, C., Naden, P.S., and Old, G.H., 2010. Effects of storm events on mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment. *Biogeochemistry*, 99 (1–3), 157–173.

Avagyan, A., Runkle, B.R.., and Kutzbach, L., 2014. Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas. *Journal of Hydrology*, 517, 435–446.

Avila, A., 1996. Time trends in the precipitation chemistry at a mountain site in northeastern Spain for the period 1983-1994. *Atmospheric Environment*, 30 (9), 1363–1373.

Ávila, A., Piñol, J., Rodá, F., and Neal, C., 1992. Storm solute behaviour in a montane Mediterranean forested catchment. *Journal of Hydrology*, 140 (1–4), 143–161.

Bates, D., Mächler, M., Bolker, B., and Walker, S., 2015. Fitting Linear Mixed-Effects Models Using lme4. *Journal of Statistical Software*, 67 (1), 1–48.

Beck, K.C., Reuter, J.H., and Perdue, E.M., 1974. Organic and inorganic geochemistry of some coastal plain rivers of the southeastern United States. *Geochimica et Cosmochimica Acta*, 38 (3), 341–364.

Blignaut, J. and Van Heerden, J., 2009. The impact of water scarcity on economic development initiatives. *Water SA*, 35 (4), 415–420.

Bond, H.W., 1979. Nutrient Concentration Patterns in a Stream Draining a Montane Ecosystem in Utah. *Ecological Society of America*, 60 (6), 1184–1196.

Bonjean, M.C., Hutchins, M., and Neal, C., 2007. Acid episodes in the Allt a ' Mharcaidh , Scotland : an investigation based on sub-hourly monitoring data and climatic patterns Acid episodes in the Allt a Mharcaidh , Scotland : an investigation based on sub-hourly monitoring data and climatic patterns. *Hydrology and Earth System Sciences*, 11 (1), 340–355.

Bosch, J.M., 1979. Treatment effects on annual and dry period streamflow at Cathedral Peak. *South African Forestry Journal*, 108 (1), 29–38.

Brandstetter, A., Sletten, R.S., Mentler, A., and Wenzel, W.W., 1996. Estimating dissolved organic carbon in natural waters by UV absorbance (254 nm). *Journal of Plant Nutrition and Soil Science*, 159 (6), 605–607.

Britton, D.L., Day, J.A., and Henshall-Howard, M.P., 1993. Hydrochemical response during storm events in a South African mountain catchment: the influence of antecedent conditions. *Hydrobiologia*, 250 (3), 143–157.

Bu, H., Meng, W., Zhang, Y., and Wan, J., 2014. Relationships between land use patterns and water quality in the Taizi River basin, China. *Ecological Indicators*, 41, 187–197.

Buck, O., Niyogi, D.K., and Townsend, C.R., 2004. Scale-dependence of land use effects on water quality of streams in agricultural catchments. *Environmental Pollution*, 130 (2), 287–299.

Buell, G.R. and Peters, N.E., 1988. Atmospheric deposition effects on the chemistry of a stream in Northeastern Georgia. *Water, Air, and Soil Pollution*, 39 (3–4), 275–291.

Burger, M., 2013. 1:1,000,000 Scale Geology for South Africa [online]. *Council for Geoscience*. Available from: https://www.arcgis.com/home/item.html?id=739c8b22b99b47bb81c2bed660d6c5de [Accessed 8 Aug 2017].

Burns, D.A., 1996. The effects of liming an Adirondack lake watershed on downstream water chemistry. *Biogeochemistry*, 32 (3), 339–362.

Cerro, I., Sanchez-Perez, J.M., Ruiz-Romera, E., and Antigüedad, I., 2014. Variability of particulate (SS, POC) and dissolved (DOC, NO3) matter during storm events in the alegria agricultural watershed. *Hydrological Processes*, 28 (5), 2855–2867.

Chessman, B.C. and Townsend, S.A., 2010. Differing effects of catchment land use on water chemistry explain contrasting behaviour of a diatom index in tropical northern and temperate southern Australia. *Ecological Indicators*, 10 (3), 620–626.

Chow, A.T., Dahlgren, R.A., Zhang, Q., and Wong, P.K., 2008. Relationships between specific ultraviolet absorbance and trihalomethane precursors of different carbon sources. *Journal of Water Supply: Research and Technology—AQUA*, 57 (7), 471.

Christensen, L., Tague, C.L., and Baron, J.S., 2008. Spatial patterns of simulated transpiration response to climate variability in a snow dominated mountain ecosystem. *Hydrological Processes*, 22 (18), 3576–3588.

Christophersen, N., Vogt, R.D., Neal, C., Anderson, H.A., Ferrier, R.C., Miller, J.D., and Seip, H.M., 1990. Controlling mechanisms for stream water chemistry at the Pristine Ingabekken Site in mid-Norway: Some implications for acidification models. *Water Resources Research*, 26 (1), 59–67.

Clark, B. and Ractliffe, G., 2007. *Berg river baseline monitoring programme*. Rondebosch.

Clark, J.M., Bottrell, S.H., Evans, C.D., Monteith, D.T., Bartlett, R., Rose, R., Newton, R.J., and Chapman, P.J., 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of The Total Environment*, 408 (13), 2768–2775.

Collins, B.M., Sobczak, W.V., and Colburn, E.A., 2007. Subsurface flowpaths in a forested headwater stream harbor a diverse macroinvertebrate community. *Wetlands*, 27 (2), 319–325.

Colorado Geological Survey, 2000. Geology and water quality. *Rock Talk*, pp. 1–12.

Correll, D.L., Jordan, T.E., and Weller, D.E., 2001. Effects of Precipitation, Air Temperature, and Land Use on Organic Carbon Discharges from Rhode River Watersheds. *Water, Air, and Soil Pollution*, 128 (1/2), 139–159.

Curtis, C.J., Battabee, R.W., Monteith, D.T., and Shilland, E.M., 2014. The future of upland water ecosystems of the UK in the 21st century: A sythesis. *Ecological Indicators*, 37, 412–430.

Cuthbert, I.D. and del Giorgio, P., 1992. Toward a standard method of measuring color in freshwater. *Limnology and Oceanography*, 37 (6), 1319–1326.

Dale, V.H., 1997. THE RELATIONSHIP BETWEEN LAND-USE CHANGE AND CLIMATE CHANGE. *Ecological Applications*, 7 (3), 753–769.

Davies, C., 2011. *Climate Risk and Vulnerability:A handbook for Southern Africa.*

Day, R.W. and Quinn, G.P., 1989. Comparisons of treatments after an analysis of variance in ecology. *Ecological Monographs*, 59 (4), 433–463.

Delpla, I., Baurès, E., Jung, A.V., and Thomas, O., 2011. Impacts of rainfall events on runoff water quality in an agricultural environment in temperate areas. *Science of the Total Environment*, 409 (9), 1683–1688.

Delwiche, J., 2010. After the fire, follow the nitrogen. *Fire Sciene Brief*, (92).

Dhillon, G.S. and Inamdar, S., 2014. Storm event patterns of particulate organic carbon (POC) for large storms and differences with dissolved organic carbon (DOC). *Biogeochemistry*, 118 (1–3), 61–81.

Dillon, P.J. and Kirchner, W.B., 1975. The effects of geology and land use on the export of phosphorus from watersheds. *Water Research*, 9 (2), 135–148.

Dodds, W.K. and Welch, E.B., 2000. Establishing Nutrient Criteria in Streams. *Journal of the North American Benthological Society*, 19 (1), 186–196.

Donat, M.G., Alexander, L.V., Yang, H., Durre, I., Vose, R., Dunn, R.J.H., Willett, K.M., Aguilar, E., Brunet, M., Caesar, J., Hewitson, B., Jack, C., Klein Tank, A.M.G., Kruger, A.C., Marengo, J., Peterson, T.C., Renom, M., Oria Rojas, C., Rusticucci, M., Salinger, J., Elrayah, A.S., Sekele, S.S., Srivastava, A.K., Trewin, B., Villarroel, C., Vincent, L.A., Zhai, P., Zhang, X., and Kitching, S., 2013. Updated analyses of temperature and precipitation extreme indices since the beginning of the twentieth century: The HadEX2 dataset. *Journal of Geophysical Research: Atmospheres*, 118 (5), 2098–2118.

Dosskey, M.G., Vidon, P., Gurwick, N.P., Allan, C.J., Duval, T.P., and Lowrance, R., 2010. The role of riparian vegetation in protecting and improving chemical water quality in streams. *Journal of the American Water Resources Association*, 46 (2), 261–277.

Edwards, A.M.C., 1973. The variation of dissolved constituents with discharge in some Norfolk rivers. *Journal of Hydrology*, 18 (3–4), 219–242.

Elsenbeer, H., Lack, A., and Cassel, K., 1995. Chemical fingerprints of hydrological compartments and flow paths at La Cuenca, Western Amazonia. *Water*

Resources Research, 31 (12), 3051–3058.

Ensign, S.H. and Doyle, M.W., 2006. Nutrient spiraling in streams and river networks. *Journal of Geophysical Research: Biogeosciences*, 111 (4).

Erlandsson, M., Buffam, I., Fölster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G.A., and Bishop, K., 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. *Global Change Biology*, 14 (5), 1191–1198.

Erol, A. and Randhir, T.O., 2013. Watershed ecosystem modeling of land-use impacts on water quality. *Ecological Modelling*, 270, 54–63.

Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T., and Cressers, M.S., 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology*, 12 (11), 2044–2053.

Evans, C.D., Jones, T.G., Burden, A., Ostle, N., Zieliński, P., Cooper, M.D.., Peacock, M., Clark, J.M., Oulehle, F., Cooper, D., and Freeman, C., 2012. Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology*, 18 (11), 3317–3331.

Evans, C.D., Monteith, D., Wright, D., and Clark, J., 2006. Issues affecting upland water quality : Climate change , acidity , nitrogen and water colour. *Climate change and aquatic ecosystems in the UK: science, policy and management*, 21–25.

Evans, C.D., Monteith, D.T., and Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, 137 (1), 55–71.

Evans, C.D., Monteith, D.T., Wright, D., and Clark, J., 2008. *Issues affecting upland water quality: Climate change, acidity, nitrogen and water colour*.

Fan, M. and Shibata, H., 2015. Simulation of watershed hydrology and stream water quality under land use and climate change scenarios in Teshio River watershed, northern Japan. *Ecological Indicators*, 50, 79–89.

de Fernandes, J.F., de Souza, A.L.T., and Tanaka, M.O., 2014. Can the structure of a riparian forest remnant influence stream water quality? A tropical case study. *Hydrobiologia*, 724, 175–185.

Findlay, S., Quinn, J.M., Hickey, C.W., Burrell, G., and Downes, M., 2001. Effects of land use and riparian flowpath on delivery of dissolved organic carbon to streams. *American Society of Limnology and Oceongraphy*, 46 (2), 345–355.

Finstad, A.G., Andersen, T., Larsen, S., Tominaga, K., and Blumentrath, S., 2016. From greening to browning : Catchment vegetation development and reduced S-deposition promote organic carbon load on decadal time scales in Nordic lakes. *Nature*, (7485), 1–8.

Fraterrigo, J.M. and Downing, J.A., 2008. The influence of land use on lake nutrients varies with watershed transport capacity. *Ecosystems*, 11 (7), 1021–1034.

Gadmar, T.C., Vogt, R.D., and Østerhus, B., 2002. The Merits of the high-temperature combustion method for determining the amount of natural organic carbon in surface freshwater samples. *International Journal of Environmental Analytical Chemistry*, 82 (7), 451–461.

Geen, A.T.., Davis, U.C., and Bianchi, M.L., 2015. Using Wetlands to Remove Microbial Pollutants from Farm Discharge Water. *Agriculture and Natural Resources Publication*, 8512 (January), 1–11.

Gergel, S.E., Turner, M.G., and Kratz, T.K., 1999. Dissolved organic carbon as an indicator of the scale of watershed influences on lakes and rivers. *Ecological Appliations*, 9 (4), 1377–1390.

Goldstein, R.A., Gherini, S.A., Driscoll, C.T., April, R., Schofield, C.L., and Chen, C.W., 1987. Lake-watershed acidification in the North Branch of the Moose River: Introduction. *Biogeochemistry*, 3 (1–3), 5–20.

Gomi, T., Sidle, R.C., and Richardson, J.S., 2002. Understanding processes and downstream linkages of headwater systems. *BioScience*, 52 (10), 905–916.

Gush, M.B., Scott, D.F., Jewitt, G.P.W., Schulze, R.E., and Lumsden, T.G., 2002. *Estimation of Streamflow Reductions Resulting from Commercial Afforestation in South Africa*. Pretoria.

Harriman, R. and Morrison, B.R.S., 1982. Ecology of streams draining forested and non-forested catchments in an area of central Scotland subject to acid precipitation. *Hydrobiologia*, 88 (3), 251–263.

Harvey, J.W. and Bencala, K.E., 1993. The Effect of streambed topography on surface-subsurface water exchange in mountain catchments. *Water Resources Research*, 29 (1), 89–98.

Hassan, Z., Shah, J.A., Kanth, T.A., and Pandit, A.K., 2015. Influence of land use/land cover on the water chemistry of Wular Lake in Kashmir Himalaya (India). *Ecological Processes*, 4 (1), 9.

Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., and Santos, U.D.M., 1986. Compositions and fluxes of particlate organic material in the Amazon River. *Limnology and Oceanography*.

Hewlett, J.D., Fortson, J.C., and Cunningham, G.B., 1977. The effect of rainfall intensity on storm flow and peak discharge from forest land. *Water Resources Research*, 13 (2), 259–266.

Hewlett, J.D. and Hibbert, A.R., 1967. Factors affecting the response of small watersheds to precipitation in humid areas. *International Symposium on Forest Hydrology*, 275–290.

Hirsh, R.M., Slack, J.R., and Smith, R.A., 1982. Techniques of trend analysis for monthly water quality data. *Water Resources Research*, 18 (1), 107–121.

Holloway, J.M. and Dahlgren, R.A., 2001. Seasonal and event-scale variations in solute chemistry for four Sierra Nevada catchments. *Journal of Hydrology*, 250 (1–4), 106–121.

Huntington, T.G., Hooper, R.P., and Aulenbach, B.T., 1994. Hydrologic processes controlling sulfate mobility in. *Water Resources Research*, 30 (2), 283–295.

Iavorivska, L., Boyer, E.W., and Dewalle, D.R., 2016. Atmospheric deposition of organic carbon via precipitation. *Atmospheric Environment*, 146, 153–163.

Inamdar, S.P. and Mitchell, M.J., 2006. Hydrologic and topographic controls on storm-event exports of dissolved organic carbon (DOC) and nitrate across catchment scales. *Water Resources Research*, 42 (3), 1–16.

IPCC, 2014. *Climate change 2014 synthesis report*. Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.

Jaffrain, J., Gérard, F., Meyer, M., and Ranger, J., 2007. Assessing the quality of dissolved organic matter in forest soils using ultraviolet absorption spectrophotometry. *Soil Science Society of America*, 71 (6), 1851.

Jenkins, A., Cosby, I.B.J., Ferrier, R.C., Walker, T.A.B., and Miller, J.D., 1990. Modelling stream acidification in afforested catchment: an assessment of the relative effects of acid deposition and afforestation. *Journal of Hydrology Elsevier Science Publishers B.V*, 120, 163–181.

Johnson, L., Richards, C., Host, G., and Arthur, J., 1997. Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshwater Biology*, 37 (1), 193–208.

Jollymore, A., Johnson, M.S., and Hawthorne, I., 2012. Submersible UV-Vis spectroscopy for quantifying streamwater organic carbon dynamics: Implementation and challenges before and after forest harvest in a headwater stream. *Sensors*, 12 (4), 3798–3813.

Jordan, T.E., Correll, D.L., and Weller, D.E., 1997. Relating nutrient discharges from watersheds to land use and streamflow variability. *Water Resources Research*, 33 (11), 2579–2590.

Jung, K.W., Lee, S.W., Hwang, H.S., and Jang, J.H., 2008. The effects of spatial variability of land use on stream water quality in a costal watershed. *Paddy and Water Environment*, 6 (3), 275–284.

Kalbus, E., Reinstorf, F., and Schirmer, M., 2006. Measuring methods for groundwater - surface water interactions: a review. *Hydrology and Earth System Sciences*, 10 (6), 873–887.

Kaplan, L.A., 1992. Comparison of high-temperature and persulfate oxidation methods for determination of dissolved organic carbon in freshwaters.

Limnology and Oceanography, 37 (5), 1119–1125.

Kim, Y., Ullah, S., Moore, T.R., and Roulet, N.T., 2014. Dissolved organic carbon and total dissolved nitrogen production by boreal soils and litter: The role of flooding, oxygen concentration, and temperature. *Biogeochemistry*, 118 (1–3), 35–48.

Kruger, A.C., 2006. Observed trends in daily precipitation indices in South Africa: 1910–2004. *International Journal of Climatology*, 26 (15), 2275–2285.

Kruger, A.C. and Nxumalo, M., 2017. Surface temperature trends from homogenized time series in South Africa: 1931-2015. *International Journal of Climatology*, 37 (5), 2364–2377.

Lambert, T., Darchambeau, F., Bouillon, S., Alhou, B., Mbega, J.D., Teodoru, C.R., Nyoni, F.C., Massicotte, P., and Borges, A.V., 2015. Landscape Control on the Spatial and Temporal Variability of Chromophoric Dissolved Organic Matter and Dissolved Organic Carbon in Large African Rivers. *Ecosystems*, 18 (7), 1224–1239.

Lambert, T., Pierson-Wickmann, A.C., Gruau, G., Jaffrezic, A., Petitjean, P., Thibault, J.N., and Jeanneau, L., 2014. DOC sources and DOC transport pathways in a small headwater catchment as revealed by carbon isotope fluctuation during storm events. *Biogeosciences*, 11 (11), 3043–3056.

Lawrence, G.B., 2002. Persistent episodic acidification of streams linked to acid rain effects on soil. *Atmospheric Environment*, 36 (10), 1589–1598.

Lee, T.Y., Huang, J.C., Kao, S.J., and Tung, C.P., 2013. Temporal variation of nitrate and phosphate transport in headwater catchments: The hydrological controls and land use alteration. *Biogeosciences*.

Lesch, W., 1992. *Report on the format and status of water quality data in Forestek*.

Lewis, D.B. and Grimm, N.B., 2007. Hierarchical regulation of nitrogen export from urban catchments: Interactions of storms and landscapes. *Ecological Applications*, 17 (8), 2347–2364.

Lewis, W.M. and Tyburczy, J.A., 1974. Amounts and spectral properties of dissolved organic compounds from some freshwaters of the Southeastern U.S. *Archives of Hydrobiology*, 1, 8–17.

Lindell, L., Åström, M., and Öberg, T., 2010. Land-use change versus natural controls on stream water chemistry in the Subandean Amazon, Peru. *Applied Geochemistry*, 25 (3), 485–495.

Lowe, W.H. and Likens, G.E., 2005. Moving Headwater Streams to the Head of the Class. *BioScience*, 55 (3), 196.

Lu, Y., Bauer, J.E., Canuel, E.A., Yamashita, Y., Chambers, R.M., and Jaffé, R., 2013. Photochemical and microbial alteration of dissolved organic matter in temperate headwater streams associated with different land use. *Journal of Geophysical Research: Biogeosciences*, 118 (2), 566–580.

Maher, K., 2011. The role of fluid residence time and topographic scales in determining chemical fluxes from landscapes. *Earth and Planetary Science Letters*, 312 (1–2), 48–58.

Mareschal, L., Laclau, J.-P., Nzila, J.-D.-D., Versini, A., Koutika, L.-S., Mazoumbou, J.-C., Deleporte, P., Bouillet, J.-P., and Ranger, J., 2013. Nutrient leaching and deep drainage under Eucalyptus plantations managed in short rotations after afforestation of an African savanna: Two 7-year time series. *Forest Ecology and Management*, 307, 242–254.

Maserumule, R., 2010. *South African Risk and Vulnerability Atlas*. Science And Technology.

Mast, M.A., Turk, J.T., Clow, D.W., and Campbell, D.D., 2011. Response of lake chemistry to changes in atmospheric deposition and climate in three high-elevation wilderness areas of Colorado. *Biogeochemistry*, 103 (1–3), 27–43.

Mattsson, T., Kortelainen, P., Räike, A., Lepistö, A., and Thomas, D.N., 2015. Spatial and temporal variability of organic C and N concentrations and export from 30 boreal rivers induced by land use and climate. *Science of The Total Environment*, 508, 145–154.

McDiffett, W.F., 1993. Water chemistry dynamics as affected by rainstorms in a high-elevation stream, South Island, New Zealand. *New Zealand Journal of Marine & Freshwater Research*, 27 (3), 373–378.

McDiffett, W.F., Beidler, A.W., Dominick, T.F., and McCrea, K.D., 1989. Nutrient concentration-stream discharge relationships during storm events in a first-order stream. *Hydrobiologia*, 179 (2), 97–102.

Menzel, D.W. and Vaccaro, R.F., 1964. The measurement of dissolved organic and particulate carbon in seawater. *Limnology and Oceanography*, 9 (1), 138–142.

Merbold, L., Ardö, J., Arneth, A., Scholes, R.J., Nouvellon, Y., de Grandcourt, A., Archibald, S., Bonnefond, J.M., Boulain, N., Brueggemann, N., Bruemmer, C., Cappelaere, B., Ceschia, E., El-Khidir, H.A.M., El-Tahir, B.A., Falk, U., Lloyd, J., Kergoat, L., Le Dantec, V., Mougin, E., Muchinda, M., Mukelabai, M.M., Ramier, D., Roupsard, O., Timouk, F., Veenendaal, E.M., and Kutsch, W.L., 2009. Precipitation as driver of carbon fluxes in 11 African ecosystems. *Biogeosciences*, 6 (6), 1027–1041.

Meybeck, M., 1982. Carbon, Nitrogen, and Phosphorus Transport By World Rivers. *American Journal of Science*, 282 (4), 401–450.

Meyer, J.L., Strayer, D.L., Wallace, J.B., Eggert, S.L., Helfman, G.S., and Leonard, N.E., 2007. The Contribution of Headwater Streams to Biodiversity in River Networks1. *JAWRA Journal of the American Water Resources Association*, 43 (1), 86–103.

Mogakabe, D.E. and van Ginkel, C.E., 2008. The water quality of Bospoort Dam. *Department of Water Affairs and Forestry, South Africa*, N/0000/00/, 31.

Mondal, N.C., Singh, V.P., Singh, V.S., and Saxena, V.K., 2010. Determining the interaction between groundwater and saline water through groundwater major ions chemistry. *Journal of Hydrology*, 388, 100–111.

Monteith, D.T., Henrys, P.A., Evans, C.D., Malcolm, I., Shilland, E.M., and Pereira, M.G., 2015. Spatial controls on dissolved organic carbon in upland waters inferred from a simple statistical model. *Biogeochemistry*, 123 (3), 363–377.

Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopácek, J., and Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, 450 (7169), 537–540.

Moody, C.S., Worrall, F., Evans, C.D., and Jones, T.G., 2013. The rate of loss of dissolved organic carbon (DOC) through a catchment. *Journal of Hydrology*, 492, 139–150.

Moore, T.R. and Dalva, M., 2001. Some controns on the release of dissolved organic carbon by plant tissues and soils. *Soil Science*, 166 (1), 38–47.

Moulton, K.L., West, J., and Berner, R.A., 2000. Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *American Journal of Science*.

Mouri, G., Takizawa, S., and Oki, T., 2011. Spatial and temporal variation in nutrient parameters in stream water in a rural-urban catchment, Shikoku, Japan: Effects of land cover and human impact. *Journal of Environmental Management*, 92 (7), 1837–1848.

Mulholland, P.J., 1992. Regulation of nutrient concentrations in a temperate forest stream: Roles of upland, riparian, and instream processes. *American Society of Limnology and Oceanography*, 37 (7), 1512–1526.

Mulholland, P.J., 1993. Hydrometric and stream chemistry evidence of three storm flowpaths in Walker Branch Watershed. *Journal of Hydrology*, 151 (2), 291–316.

Mulholland, P.J., 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: Evidence from long-term chemistry records for Walker Branch Watershed. *Biogeochemistry*, 70 (3), 403–426.

Mulholland, P.J. and Hill, W.R., 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. *Water Resources Research*, 33 (6), 1297.

Mulholland, P.J., Wallace, J.B., and Benfield, E.F., 1997. Dissolved Organic Matter Concentration and Flux in Streams. *Journal of the North American Benthological*

Society, 16 (1), 131–141.

Nänni, U.W., 1956. Forest hydrological research at the Cathedral Peak Research Station. *Journal of the South African Forestry Association*, 27 (1), 2–35.

Nänni, U.W., 1959. Base-flow in Cathedral Peak. *Journal of the South African Forestry Association*, 33 (1), 7–48.

Nel, J., Colvin, C., Le Maitre, D., Smith, J., and Haines, I., 2013. *South Africa's Strategic Water Source Areas*. WWF-South Africa.

Nisbet, T.R., Fowler, D., and Smith, R.I., 1995. An investigation of the impact of afforestation on stream-water chemistry in the Loch Dee catchment, SW Scotland. *Environmental Pollution*, 90 (1), 111–120.

Oliver, B.G., Thurman, E.M., and Malcolm, R.L., 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochimica et Cosmochimica Acta*, 47 (11), 2031–2035.

Ometo, J., Martinelli, L.A., Ballester, M.V., Gessner, A., Krusche, A.V., Victoria, R.L., and Williams, M., 2000. Effects of land use on water chemistry and macroinvertebrates rates in two streams of the Piracicaba river basin, south-east Brazil. *Freshwater Biology*, 44, 327–337.

Park, J.-H., Lee, H.-J., and Shope, C.L., 2011. Effects of Rainfall Variability and Extremes on Stream Water Quality in the Haean Basin, South Korea. *In*: *2011 TERRECO Science Conference*. Garmisch-Partenkirchen, Germany, 243–250.

Peacock, M., Evans, C.D., Fenner, N., Freeman, C., Gough, R., Jones, T.G., and Lebron, I., 2014. UV-visible absorbance spectroscopy as a proxy for peatland dissolved organic carbon (DOC) quantity and quality: considerations on wavelength and absorbance degradation. *Environmental Science: Processes & Impacts*, 16 (6), 1445–1461.

Pinheiro, J.C. and Bates, D.M., 2000. *Mixed-Effects Models in Sand S-PLUS*. New York, NY: Springer New York.

Piñol, J., Ávila, A., and Rodà, F., 1992. The seasonal variation of streamwater chemistry in three forested Mediterranean catchments. *Journal of Hydrology*, 140 (1–4), 119–141.

Pratt, B. and Chang, H., 2012. Effects of land cover, topography, and built structure on seasonal water quality at multiple spatial scales. *Journal of Hazardous Materials*, 209–210, 48–58.

Principe, R.E., Márquez, J.A., Martina, L.C., Jobbágy, E.G., and Albariño, R.J., 2015. Pine afforestation changes more strongly community structure than ecosystem functioning in grassland mountain streams. *Ecological Indicators*, 57, 366–375.

Qualls, R.G. and Haines, B.L., 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution and stream water. *Soil Sciences of America*, 56, 578–586.

Le Quéré, C., Moriarty, R., Andrew, R.M., Peters, G.P., Ciais, P., Friedlingstein, P., Jones, S.D., Sitch, S., Tans, P., Arneth, A., Boden, T.A., Bopp, L., Bozec, Y., Canadell, J.G., Chini, L.P., Chevallier, F., Cosca, C.E., Harris, I., Hoppema, M., Houghton, R.A., House, J.I., Jain, A.K., Johannessen, T., Kato, E., Keeling, R.F., Kitidis, V., Klein Goldewijk, K., Koven, C., Landa, C.S., Landschützer, P., Lenton, A., Lima, I.D., Marland, G., Mathis, J.T., Metzl, N., Nojiri, Y., Olsen, A., Ono, T., Peng, S., Peters, W., Pfeil, B., Poulter, B., Raupach, M.R., Regnier, P., Rödenbeck, C., Saito, S., Salisbury, J.E., Schuster, U., Schwinger, J., Séférian, R., Segschneider, J., Steinhoff, T., Stocker, B.D., Sutton, A.J., Takahashi, T., Tilbrook, B., van der Werf, G.R., Viovy, N., Wang, Y.-P., Wanninkhof, R., Wiltshire, A., and Zeng, N., 2015. Global carbon budget 2014. *Earth System Science Data*, 7 (1), 47–85.

R Development Core Team, 2008. R: A language and environment for statistical computing.

Rees, R.M. and Ribbens, J.C.H., 1995. Relationship between afforestation, water chemistry and fish stocks in an upland catchment in south west Scotland. *Water, Air, and Soil Pollution*, 85 (2), 303–308.

Rice, K.C. and Bricker, O.P., 1995. Seasonal cycles of dissolved constituents in streamwater in two forested catchments in the mid-Atlantic region of the eastern USA. *Journal of Hydrology*, 170 (1–4), 137–158.

Sawicka, K., Monteith, D.T., Vanguelova, E.I., Wade, A.J., and Clark, J.M., 2016. Fine-scale temporal characterization of trends in soil water dissolved organic carbon and potential drivers. *Ecological Indicators*, 68, 36–51.

Schlesinger, W.H. and Melack, J.M., 1981. Transport of organic carbon in the world’s rivers. *Tellus*, 33, 172–187.

Schulze, R.E., 1974. Catchment Evapotranspiration in the Natal Drakensberg. University of Natal.

Scott, D.F., 1993. The hydrological effects of fire in South African mountain catchments. *Journal of Hydrology*, 150 (2–4), 409–432.

Scott, D.F. and Smith, R.E., 1997. Preliminary empirical models to predict reductions in total and low flows resulting from afforestation. *Water SA*, 23 (2), 135–140.

Sebestyen, S.D., Boyer, E.W., and Shanley, J.B., 2009. Responses of stream nitrate and DOC loadings to hydrological forcing and climate change in an upland forest of the northeastern United States. *Journal of Geophysical Research: Biogeosciences*, 114 (G2), 1–11.

Sholkovitz, E.R., 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochimica et Cosmochimica Acta*, 40 (7), 831–845.

Shu, Y. and Villholth, K., 2012. Analysis of flow and baseflow trends in the Usangu Catchment, Tanzania.

Silva, D.M.L., Camargo, P.B., McDowell, W.H., Vieira, I., Salomão, M.S.M.B., and Martinelli, L.A., 2012. Influence of land use changes on water chemistry in streams in the State of São Paulo, southeast Brazil. *Anais da Academia Brasileira de Ciências*, 84 (4), 919–30.

Skjelkvåle, B.L., Stoddard, J.L., Jeffries, D.S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D.T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A., and Worsztynowicz, A., 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution*, 137, 165–176.

Smakhtin, V., 2001. Estimating continuous monthly baseflow time series and their possible applications in the context of the ecological reserve. *Water South Africa*, 27 (2), 213–217.

Sokolova, T.A. and Alekseeva, S.A., 2008. Adsorption of sulfate ions by soils (A Review). *Eurasian Soil Science*, 41 (2), 140–148.

Solheim, A.L., Austnes, K., Eriksen, T.E., Seifert, I., and Holen, S., 2010. *Climate change impacts on water quality and biodiversity ETC Water Technical Report 1 / 2010*. European Environment.

Sophocleous, M., 2002. Interactions between groundwater and surface water: the state of the science. *Hydrogeology Journal*, 10 (10), 52–6752.

van Steenderen, R.A. and van Rossum, P.G., 1985. Seasonal influence on the DOC-UV relationship in water. *Water SA*, 11 (2), 57–60.

Sueker, J.K., Clow, D.W., Ryan, J.N., and Jarrett, R.D., 2001. Effect of basin physical characteristics on solute fluxes in nine alpine/subalpine basins, Colorado, USA. *Hydrological Processes*, 15 (14), 2749–2769.

Süß, E., 2006. Mercury distribution between particulate and dissolved states in wetlands in California , USA. *Freiberg Online Geosciences*, 15, 1–174.

Tong, S.T.Y. and Chen, W., 2002. Modeling the relationship between land use and surface water quality. *Journal of Environmental Management*, 66 (4), 377–393.

La Torre Torres, I.B., Amatya, D.M., Sun, G., and Callahan, T.J., 2011. Seasonal rainfall-runoff relationships in a lowland forested watershed in the southeastern USA. *Hydrological Processes*, 25 (13), 2032–2045.

Toucher, M.L., Clulow, A., van Rensburg, S.J., Morris, F., Gray, B., Majozi, S., Jewitt, G.P.W., Taylor, M.A., Mfeka, S., and Lawrence, K., 2016. *Establishment of and demonstration of the potential of the Cathedral Peak Research Catchments as a living laboratory*.

Tu, J., 2013. Spatial Variations in the Relationships between Land Use and Water Quality across an Urbanization Gradient in the Watersheds of Northern Georgia, USA. *Environmental Management*, 51 (1), 1–17.

Unep/Who, 1996. *Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes*. Military Operations Research. UNEP/WHO.

USDA, 2007. *Sediment laboratory procedures*.

Viviroli, D. and Weingartner, R., 2008. 'Water towers' - A global view of the hydrological importance of mountains. *Mountains: Sources of Water, Sources of Knowledge*, 31, 15–20.

van Vliet, H.R., Kempster, D.P., Satory, P., Gerber, F.A., and Schoonraad, I.J., 1989. *Analytical methods manual*. Pretoria.

van Vliet, M.T.H. and Zwolsman, J.J.G., 2008. Impact of summer droughts on the water quality of the Meuse river. *Journal of Hydrology*, 353 (1), 1–17.

Wade, A., 1935. The Relationship between topography and geology. *Australian Surveyor*, 5 (6), 367–371.

Wang, H. and Han, G., 2011. Chemical composition of rainwater and anthropogenic influences in Chengdu, Southwest China. *Atmospheric Research*, 99 (2), 190–196.

Waters, D. and Jenkins, A., 1992. Impacts of afforestation on water quality trends in two catchments in mid-Wales. *Environmental Pollution*, 77 (2–3), 167–172.

Webb, B.W., Hannah, D.M., Moore, R.D., Brown, L.E., and Nobilis, F., 2008. Recent advances in stream and river temperature research. *Hydrological Processes*, 22 (7), 902–918.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., and Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science and Technology*, 37 (20), 4702–4708.

Wellington, B.I. and Driscoll, C.T., 2004. The episodic acidification of a stream with elevated concentrations of dissolved organic carbon. *Hydrological Processes*, 18 (14), 2663–2680.

Wen, Z.D., Song, K.S., Zhao, Y., Du, J., and Ma, J.H., 2016. Influence of environmental factors on spectral characteristics of chromophoric dissolved organic matter (CDOM) in Inner Mongolia Plateau, China. *Hydrology and Earth System Sciences*, 20, 787–801.

White, A.F. and Blum, A.E., 1995. Effects of climate on chemical weathering in watersheds. *Geochimica et Cosmochimica Acta*, 59 (9), 1729–1747.

Williams, C.A., Hanan, N.P., Neff, J.C., Scholes, R.J., Berry, J.A., Denning, A.S., and Baker, D.F., 2007. Africa and the global carbon cycle. *Carbon Balance Management*, 2 (3), 1–13.

Worrall, F., Harriman, R., Evans, C.D., Watts, C.D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P.S., Nisbet, T., Reynolds, B., and Stevens, P., 2004. Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry*, 70 (3), 369–402.

van Wyk, D.B., 1983. Apparatus for sampling of streams for chemical quality and sediment. *Water SA*, 9 (3), 88–92.

van Wyk, D.B., 1985. The effects of catchment management on sediment and nutrient exports in the Natal Drakensberg. *In*: R.E. Schulze, ed. *Second South African National Hydrology Symposium*. Pietermaritzburg, 266–274.

Yang, Q., Zhang, X., Xu, X., and Asrar, G.R., 2017. An analysis of terrestrial and aquatic environmental controls of riverine dissolved organic carbon in the conterminous United States. *Water*, 9 (383), 1–16.

Yu, S., Xu, Z., Wu, W., and Zuo, D., 2015. Effect of land use on the seasonal variation of streamwater quality in the Wei River Basin, China. *Remote Sensing for Hydrology and Water Resources*, 368, 454–459.

Zanchi, F.B., Waterloo, M.J., Tapia, A.P., Alvarado Barrientos, M.S., Bolson, M.A., Luiz??o, F.J., Manzi, A.O., and Dolman, A.J., 2015. Water balance, nutrient and carbon export from a heath forest catchment in central Amazonia, Brazil. *Hydrological Processes*, 29 (17), 3633–3648.

Zhang, W., An, S., Xu, Z., Cui, J., and Xu, Q., 2011. The impact of vegetation and soil on runoff regulation in headwater streams on the east Qinghai-Tibet Plateau, China. *Catena*, 87 (2), 182–189.

Zhang, Y., Guan, D., Jin, C., Wang, A., Wu, J., and Yuan, F., 2014. Impacts of climate change and land use change on runoff of forest catchment in northeast China. *Hydrological Processes*, 28 (2), 186–196.

Zhang, Y., Su, F., Hao, Z., Xu, C., Yu, Z., Wang, L., and Tong, K., 2015. Impact of projected climate change on the hydrology in the headwaters of the Yellow River basin. *Hydrological Processes*, 29, 4379–4397.

Zhao, F., Zhang, L., Sun, J., Ren, C., Han, X., Yang, G., Pang, G., Bai, H., and Wang, J., 2017. Effect of Soil C, N and P Stoichiometry on Soil Organic C Fractions After Afforestation. *Pedosphere*, 27 (4), 705–713.

APPENDIX

APPENDIX A1

Data collected at across different upper mountain catchments which were a part of a project initiated through SAFRI by van Wyk, 1971. This Table outlines the types of data that was collected at Cathedral Peak, filing codes that were used to store metadata, catchment or samples names, where they were collected and how long the collection lasted, adopted from (Lesch 1992).

CPRS historical data					Running time		
Variable group no.	**Sample category**	**Sample type**	**File code**	**Sample name(s)**	**Start**	**End**	**Data collected**
1	**Grab samples**	pH and	XC11	CAT1-15	1980/10/30	1982/05/26	Date, sample, time, HT, pH, COND,
		conductivity		CAT1, 2, 5, 8, 10, 15	1982/06/03	1982/09/25	ST/FL, R/FLL
				CAT2, 3, 4, 6, 7, 9	1985/10/02	1987/09/23	
				RC, RCD	1987/09/23	1991/06/26	
		Chemical	XC12	CAT3, 4, 6, 7, 9	1981/11/12	1986/09/03	Date, sample, time, HT, Na, K, Ca, Mg,
		analyses		CAT2	1984/01/12	1986/09/03	Cl, SO_4, HCO_3, NO_3, PO_4,
							pH, COND, NH_4, F, Si, KN, TP, ST/FL
		Suspended	XC13	CAT1, 2	1980/09/08	1981/02/19	Date, sample, time, HT, Vol, FLT/EM,
		sediment		CAT3, 4, 6, 7	1980/09/08	1991/05/29	FILT_SLK, OONDDRGS,
				CAT11	1980/10/01	1981/02/04	*TSS, COND, ST/FL
				CAT9	1980/10/01	1990/07/11	
				CAT15	1982/09/29	1985/10/02	
				CAT2	1983/06/02	1991/05/29	
2	**Spate samples**	Chemical	XCA22	CAT3 OP1->4 / AF1->4	1981/11/09	1988/02/18	Date, sample, time, HT, Na, K, Ca, Mg,
		analyses	XCB22	CAT4 OP1->3 / AF1, 4	1981/11/26	1988/07/10	NO_3, PO_4,Cl, SO_4, HCO_3,
			XCC22	CAT6 OP1, 2 / AF1, 4	1981/11/19	1988/04/06	pH, COND, NH_4, F, Si, KN, TP, ST/FL
			XCD22	CAT7 OP1->3 / AF1, 4	1981/12/08	1988/04/06	
			XCE22	CAT9 OP1->3 / AF1	1981/12/08	1988/03/10	
			XCF22	CAT4 OP1->3	1983/11/26	1988/03/10	
		Suspended	XC23	CAT2 OP1->3	1983/12/18	1988/03/10	Date, sample, time, HT, Vol, FLT/EM,
		sediment		CAT3 OP1->3, 5, 6 / AF1->4	1980/09/23	1988/02/21	FILT_SLK, OONDDRGS,
				CAT4 OP1->3 / AF1, 3, 4	1980/09/23	1988/04/06	*TSS, COND, ST/FL
				CAT6 OP1->3 / AF1, 4	1980/09/23	1988/03/16	
				CAT7 OP1->3 / AF1, 4	1980/11/05	1988/04/06	
				CAT9 OP1->2 / AF1 /OP	1982/01/30	1988/03/10	
3	**Precipitation**	Chemical	XC321	RC	1984/10/17	1989/04/05	Date, sample, time, HT, Na, K, Ca, Mg,
		analyses		RCD	1984/10/17	1989/04/05	Cl, SO_4, HCO_3, NO_3, PO_4,
				CD	1984/10/17	1989/04/05	pH, COND, NH_4, F, Si, KN, TP, ST/FL

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refers to any of 2-8 samples of the rising limb of the hydrograph, date – date sample was taken, sample – sample name, time – time the sample was taken, HT – height of the gauging weir, COND – conductivity, KN – total nitrogen, TP – total phosphorus, Vol – volume of sample taken (ml and L), ST/FL – weekly volumes of streamflow, R/FLL – weekly volumes of rainfall, FILT_SLK – mass of filter paper plus sediment sample (g), FILTLG – mass of filter paper before filtration (g), OONDDRGS (g and mg) – oven dried sediment, *calculated TSS (mg/L).

APPENDINX B1

Historical Ca data collected across study catchments.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	**Spring**	26-Nov	377.78	457.13	476.59	351.55
	Summer	31-Dec	534.48	466.86	466.86	321.76
1982		28-Jan	447.25	551.89	474.40	380.39
		25-Feb	491.12	438.12	513.47	375.60
	Autumn	29-Apr	573.24	531.64	498.43	387.42
		27-May	557.63	575.10	512.72	371.76
	Winter	24-Jun	603.20	549.90	621.03	437.93
		29-Jul	545.32	552.06	605.39	337.50
		26-Aug	522.63	515.85	557.60	393.12
	Spring	30-Sep	516.24	501.32	453.87	310.03
		28-Oct	501.59	522.68	244.56	403.72
		25-Nov	541.89	520.39	409.88	390.30
	Summer	30-Dec	689.42	577.67	531.12	499.00
1983		27-Jan	546.39	560.08	491.83	329.12
		24-Feb	482.91	500.17	547.93	361.70
	Autumn	31-Mar	578.84	538.92	489.02	399.20
		28-Apr	600.70	563.13	552.24	274.45
		26-May	557.72	543.61	513.77	386.73
	Winter	30-Jun	538.92	508.98	499.00	359.28
		28-Jul	499.00	374.25	474.05	336.83
		25-Aug	474.05	474.05	461.58	336.83
	Spring	29-Sep	486.53	469.06	436.63	319.36
		27-Oct	499.00	449.10	449.10	324.35
		24-Nov	586.33	449.10	436.63	399.20
	Summer	29-Dec	489.02	419.16	359.28	269.46
1984		26-Jan	532.27	474.05	465.73	324.35
		23-Feb	573.85	482.37	461.58	349.30
	Autumn	29-Mar	518.96	479.04	439.12	309.38
		25-Apr	611.28	573.85	548.90	386.73
		30-May	618.76	528.94	608.78	299.40
	Winter	27-Jun	548.90	486.53	511.48	374.25
		25-Jul	523.95	461.58	511.48	361.78
		29-Aug	538.92	489.02	429.14	389.22
	Spring	26-Sep	523.95	474.05	436.63	349.30
		31-Oct	518.96	459.08	439.12	339.32
		28-Nov	573.85	548.90	511.48	374.25
	Summer	26-Dec	573.85	536.43	511.48	361.78
1985		30-Jan	588.82	489.02	489.02	339.32
		27-Feb	615.43	361.78	499.00	316.03
	Autumn	27-Mar	632.07	411.68	573.85	386.73
		24-Apr	623.75	536.43	523.95	411.68
		29-May	598.80	558.88	528.94	389.22
	Winter	29-Jun	573.85	523.95	548.90	486.53
		31-Jul	568.86	518.96	499.00	349.30
		7-Aug	598.80	548.90	449.10	349.30

Year	Season	DATE	CP03	CP04	CP06	CP09
1985	**Spring**	4-Sep	548.90	499.00	499.00	349.30
		2-Oct	548.90	499.00	449.10	349.30
		6-Nov	499.00	449.10	449.10	299.40
	Summer	4-Dec	499.00	349.30	349.30	249.50
1986		1-Jan	598.80	449.10	449.10	349.30
		5-Feb	598.80	499.00	449.10	299.40
	Autumn	5-Mar	598.80	499.00	548.90	299.40
		2-Apr	449.10	449.10	399.20	349.30
		7-May	698.60	548.90	499.00	349.30
	Winter	4-Jun	648.70	548.90	548.90	399.20
		2-Jul	543.16	455.99	484.58	333.63
		6-Aug	552.19	475.00	465.47	342.96
	Spring	3-Sep	606.68	484.58	475.00	NA

APPENDINX B2

Recent Ca data collected across study catchments.

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	346.90	377.70	446.94	373.08
2015		7-Jan	388.99	540.98	522.51	436.72
		1-Feb	265.45	522.41	466.90	307.12
	Au	14-Apr	315.29	565.77	471.18	244.12
	Sp	4-Nov	355.74	511.77	511.87	408.37
	Su	1-Dec	380.49	540.58	526.28	394.09
2016		28-Feb	363.08	370.24	491.50	379.01
	Au	8-Mar	398.51	372.78	532.96	410.99
		1-Apr	300.53	345.65	354.91	287.92

APPENDINX B3

Historical Mg data.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	Spring	26-Nov	291.75	365.45	389.48	329.41
	Summer	31-Dec	302.58	273.12	253.70	243.99
1982		28-Jan	355.49	355.49	343.15	292.87
		25-Feb	220.70	352.20	230.99	159.56
	Autumn	29-Apr	380.00	381.66	373.94	314.36
		27-May	382.65	392.93	392.93	285.96
	Winter	24-Jun	395.40	367.77	361.60	300.98
		29-Jul	335.40	382.37	388.87	263.05
		26-Aug	370.92	376.01	374.19	283.67
	Spring	30-Sep	393.28	385.36	372.21	306.86
		28-Oct	361.42	350.21	172.29	290.24
		25-Nov	320.93	334.59	265.30	281.24
	Summer	30-Dec	372.07	373.78	348.30	283.90
1983		27-Jan	399.09	392.87	379.87	454.61
		24-Feb	323.52	318.71	363.04	300.09
	Autumn	31-Mar	411.45	362.08	394.99	312.70
		28-Apr	371.75	350.80	383.00	308.59
		26-May	399.46	401.45	418.32	349.73
	Winter	30-Jun	427.91	411.45	411.45	345.62
		28-Jul	370.31	308.59	370.31	329.16
		25-Aug	411.45	432.02	390.88	349.73
	Spring	29-Sep	452.60	394.99	411.45	345.62
		27-Oct	384.02	390.88	411.45	288.02
		24-Nov	390.88	329.16	349.73	329.16
	Summer	29-Dec	394.99	345.62	345.62	263.33
1984		26-Jan	411.45	349.73	384.02	308.59
		23-Feb	411.45	384.02	370.31	329.16
	Autumn	29-Mar	444.37	345.62	394.99	329.16
		25-Apr	452.60	390.88	390.88	349.73
		30-May	427.91	411.45	411.45	329.16
	Winter	27-Jun	432.02	370.31	390.88	308.59
		25-Jul	370.31	308.59	349.73	267.44
		29-Aug	427.91	345.62	329.16	329.16
	Spring	26-Sep	411.45	390.88	370.31	329.16
		31-Oct	411.45	411.45	394.99	329.16
		28-Nov	411.45	411.45	411.45	329.16
	Summer	26-Dec	411.45	411.45	411.45	349.73
1985		30-Jan	411.45	394.99	394.99	279.79
		27-Feb	411.45	246.87	370.31	246.87
	Autumn	27-Mar	438.88	308.59	411.45	308.59

Year	Season	DATE	CP03	CP04	CP06	CP09
1985	Autumn	24-Apr	452.60	411.45	411.45	329.16
	Winter	29-May	452.60	411.45	411.45	329.16
		29-Jun	432.02	411.45	411.45	411.45
	Spring	31-Jul	427.91	427.91	427.91	329.16
		7-Aug	411.45	411.45	329.16	329.16
		4-Sep	411.45	411.45	411.45	329.16
	Summer	2-Oct	329.16	411.45	411.45	329.16
		6-Nov	411.45	246.87	329.16	246.87
		4-Dec	329.16	246.87	246.87	246.87
1986	Autumn	1-Jan	493.74	411.45	329.16	329.16
		5-Feb	411.45	329.16	329.16	246.87
		5-Mar	411.45	329.16	411.45	329.16
	Winter	2-Apr	329.16	329.16	329.16	246.87
		7-May	411.45	329.16	329.16	329.16
		4-Jun	411.45	329.16	411.45	329.16
	Spring	2-Jul	388.98	346.61	356.56	294.60
		6-Aug	388.08	347.26	357.30	294.85
		3-Sep	424.29	347.02	356.81	NA

APPENDIX B4

Recent Mg data.

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	278.33	363.99	409.33	363.13
2015		7-Jan	288.93	421.37	429.79	383.92
		1-Feb	223.90	402.28	395.91	299.36
	Au	14-Apr	255.47	435.37	445.71	233.06
	Sp	4-Nov	280.13	376.28	390.72	374.96
	Su	1-Dec	287.02	426.42	434.22	379.41
2016		28-Feb	268.27	372.35	417.24	355.06
	Au	8-Mar	264.69	368.21	421.49	348.35
		1-Apr	251.99	365.96	408.45	328.72

APPENDIX B5

Historical Na data.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	Spring	26-Nov	227.27	149.16	118.93	118.93
	Summer	31-Dec	130.41	116.32	120.76	100.92
1982		28-Jan	127.67	119.84	129.24	111.58
		25-Feb	138.90	97.44	141.98	146.55
	Autumn	29-Apr	160.81	142.27	134.34	120.53
		27-May	148.99	91.35	100.05	73.95
	Winter	24-Jun	161.92	142.71	165.38	110.02
		29-Jul	151.54	154.89	131.69	132.00
		26-Aug	137.73	148.00	118.77	134.72
	Spring	30-Sep	177.52	148.94	134.99	126.67
		28-Oct	146.06	176.90	58.07	83.65
		25-Nov	181.90	126.99	67.15	49.47
	Summer	30-Dec	149.87	148.10	139.45	91.35
1983		27-Jan	89.37	108.75	122.42	89.28
		24-Feb	163.29	158.93	143.68	135.89
	Autumn	31-Mar	208.80	191.40	165.30	139.20
		28-Apr	192.11	184.22	174.66	108.75
		26-May	186.55	216.00	205.92	141.38
	Winter	30-Jun	165.30	156.60	165.30	147.90
		28-Jul	195.75	141.38	141.38	141.38
		25-Aug	130.50	130.50	108.75	108.75
	Spring	29-Sep	141.38	113.10	119.63	113.10
		27-Oct	130.50	130.50	130.50	97.88
		24-Nov	119.63	141.38	141.38	130.50
	Summer	29-Dec	121.80	130.50	130.50	130.50
1984		26-Jan	174.00	174.00	159.50	97.88
		23-Feb	184.88	130.50	152.25	108.75
	Autumn	29-Mar	139.20	139.20	156.60	139.20
		25-Apr	184.88	130.50	130.50	130.50
		30-May	34.80	17.40	26.10	26.10
	Winter	27-Jun	NA	NA	NA	NA
		25-Jul	NA	NA	NA	32.63
		29-Aug	NA	NA	NA	113.10
	Spring	26-Sep	NA	NA	NA	76.13
		31-Oct	NA	NA	NA	NA
		28-Nov	NA	NA	NA	NA
	Summer	26-Dec	NA	NA	NA	NA
1985		30-Jan	60.90	69.60	69.60	60.90
		27-Feb	58.00	76.13	119.63	58.00
	Autumn	27-Mar	174.00	119.63	141.38	87.00

Year	**Season**	**DATE**	**CP03**	**CP04**	**CP06**	**CP09**
1985	Autumn	24-Apr	206.63	174.00	163.13	87.00
	Winter	29-May	141.38	121.80	147.90	104.40
		29-Jun	130.50	97.88	119.63	163.13
	Spring	31-Jul	104.40	130.50	130.50	130.50
		7-Aug	130.50	130.50	130.50	87.00
		4-Sep	174.00	130.50	130.50	130.50
	Summer	2-Oct	174.00	174.00	174.00	130.50
		6-Nov	130.50	217.50	130.50	130.50
		4-Dec	174.00	87.00	87.00	87.00
1986	Autumn	1-Jan	87.00	87.00	87.00	87.00
		5-Feb	130.50	130.50	174.00	87.00
		5-Mar	130.50	130.50	130.50	130.50
	Winter	2-Apr	43.50	NA	NA	43.50
		7-May	130.50	130.50	130.50	87.00
		4-Jun	130.50	130.50	130.50	43.50
	Spring	2-Jul	49.07	61.55	58.42	21.79
		6-Aug	31.93	59.20	56.07	36.58
		3-Sep	79.52	59.99	57.64	NA

APPENDIX B6

Recent Na data

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	118.90	121.13	131.72	117.04
2015		7-Jan	117.56	122.21	117.06	125.13
		1-Feb	130.85	190.38	130.98	106.74
	Au	14-Apr	128.31	164.46	152.49	98.69
	Sp	4-Nov	134.62	125.57	125.26	115.66
	Su	1-Dec	116.44	128.97	127.50	151.23
2016		28-Feb	118.78	136.76	129.31	112.76
	Au	8-Mar	97.56	110.70	108.82	96.01
		1-Apr	128.31	146.11	143.58	125.84

APPENDIX B7

Historical K data.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	Spring	26-Nov	23.70	13.51	12.25	10.72
	Summer	31-Dec	15.14	6.75	7.96	8.16
1982		28-Jan	15.22	7.75	10.64	10.18
		25-Feb	15.14	5.12	7.09	10.59
	Autumn	29-Apr	16.02	8.83	8.72	7.91
		27-May	11.57	1.91	5.50	2.05
	Winter	24-Jun	9.14	6.66	10.14	6.20
		29-Jul	5.18	7.34	3.53	11.87
		26-Aug	10.08	10.58	8.52	12.43
	Spring	30-Sep	8.19	6.77	6.66	4.49
		28-Oct	5.01	4.19	2.86	1.07
		25-Nov	8.29	3.34	3.23	NA
	Summer	30-Dec	12.07	9.03	8.74	6.33
1983		27-Jan	1.59	NA	2.27	NA
		24-Feb	8.21	8.99	8.48	5.93
	Autumn	31-Mar	11.77	12.28	11.26	11.26
		28-Apr	13.28	15.86	14.17	7.03
		26-May	10.10	12.50	12.00	7.03
	Winter	30-Jun	5.63	5.12	6.14	5.63
		28-Jul	9.59	6.40	8.95	5.76
		25-Aug	5.12	7.03	6.40	5.76
	Spring	29-Sep	4.48	4.60	1.28	3.07
		27-Oct	7.67	8.95	10.23	4.48
		24-Nov	5.76	8.95	7.67	8.31
	Summer	29-Dec	4.60	5.12	9.72	7.16
1984		26-Jan	5.97	4.48	0.85	0.64
		23-Feb	7.67	8.53	3.84	5.12
	Autumn	29-Mar	2.05	3.07	5.63	4.60
		25-Apr	9.59	6.40	5.12	7.03
		30-May	1.53	0.51	1.02	1.53
	Winter	27-Jun	NA	NA	5.76	NA
		25-Jul	NA	NA	NA	1.28
		29-Aug	NA	NA	NA	5.63
	Spring	26-Sep	NA	NA	NA	3.84
		31-Oct	NA	NA	NA	NA
		28-Nov	NA	NA	NA	NA
	Summer	26-Dec	NA	NA	NA	NA
1985		30-Jan	0.51	2.56	NA	3.07
		27-Feb	3.41	1.92	NA	3.41
	Autumn	27-Mar	1.71	0.64	NA	1.92

Year	**Season**	**DATE**	**CP03**	**CP04**	**CP06**	**CP09**
1985	Autumn	24-Apr	2.56	NA	NA	4.48
		29-May	NA	NA	NA	2.05
	Winter	29-Jun	NA	1.92	NA	5.12
		31-Jul	3.58	2.56	NA	5.12
		7-Aug	2.56	NA	NA	NA
	Spring	4-Sep	12.79	7.67	NA	15.35
		2-Oct	10.23	10.23	NA	7.67
		6-Nov	7.67	NA	NA	7.67
	Summer	4-Dec	10.23	12.79	NA	7.67
1986		1-Jan	NA	NA	NA	5.12
		5-Feb	7.67	7.67	NA	7.67
	Autumn	5-Mar	10.23	7.67	NA	10.23
		2-Apr	2.56	NA	NA	2.56
		7-May	7.67	7.67	NA	7.67
	Winter	4-Jun	7.67	7.67	NA	15.35
		2-Jul	5.65	5.24	NA	3.56
		6-Aug	2.81	5.14	NA	6.16
	Spring	3-Sep	8.49	5.17	NA	NA

APPENDIX B8

Recent K data.

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	5.50	5.06	11.71	20.03
2015		7-Jan	7.51	14.22	9.77	9.78
		1-Feb	5.41	8.11	9.74	12.32
	Au	14-Apr	5.33	10.13	11.82	9.00
	Sp	4-Nov	6.24	7.02	3.79	5.94
	Su	1-Dec	5.11	10.72	8.12	7.17
2016		28-Feb	3.89	6.36	5.74	5.93
	Au	8-Mar	3.00	4.29	5.52	5.97
		1-Apr	3.94	5.00	6.88	6.26

APPENDIX B9

Historical Cl data.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	Spring	26-Nov	4.60	5.45	8.46	3.52
	Summer	31-Dec	4.00	4.61	6.77	2.56
1982		28-Jan	6.50	3.89	5.66	2.66
		25-Feb	4.20	4.71	2.06	2.16
	Autumn	29-Apr	4.00	1.23	1.72	1.87
		27-May	2.80	2.50	3.33	2.45
	Winter	24-Jun	2.00	2.07	2.14	2.04
		29-Jul	NA	3.04	1.98	1.78
		26-Aug	NA	2.76	1.62	1.90
	Spring	30-Sep	NA	1.98	3.25	2.62
		28-Oct	NA	1.00	0.71	5.39
		25-Nov	2.25	0.45	0.77	2.19
	Summer	30-Dec	NA	0.80	1.57	1.00
1983		27-Jan	2.40	0.04	0.39	0.25
		24-Feb	2.00	1.63	1.60	1.19
	Autumn	31-Mar	3.00	2.80	3.00	4.20
		28-Apr	3.00	2.79	2.29	1.75
		26-May	2.50	2.86	4.08	4.00
	Winter	30-Jun	2.75	1.80	2.20	2.20
		28-Jul	3.00	1.00	1.25	0.75
		25-Aug	3.00	2.75	2.00	2.50
	Spring	29-Sep	7.00	3.80	3.75	3.40
		27-Oct	3.00	3.25	3.00	4.25
		24-Nov	4.00	4.50	2.00	4.00
	Summer	29-Dec	5.00	2.80	2.40	3.20
1984		26-Jan	NA	3.75	3.33	3.75
		23-Feb	5.00	3.67	3.75	4.00
	Autumn	29-Mar	4.00	3.80	3.40	3.40
		25-Apr	5.00	3.75	4.75	3.75
		30-May	6.00	1.20	0.80	0.60
	Winter	27-Jun	6.00	NA	NA	NA
		25-Jul	4.03	NA	NA	2.75
		29-Aug	3.26	NA	NA	13.20
	Spring	26-Sep	3.77	NA	NA	5.25
		31-Oct	NA	NA	NA	NA
		28-Nov	NA	NA	NA	NA
	Summer	26-Dec	NA	NA	NA	NA
1985		30-Jan	NA	1.60	2.00	2.00
		27-Feb	NA	1.50	3.25	1.33
	Autumn	27-Mar	NA	1.25	2.50	2.50

Year	Season	DATE	CP03	CP04	CP06	CP09
1985	Autumn	24-Apr	NA	1.25	2.25	4.50
1986	Winter	29-May	NA	1.80	1.60	3.20
		29-Jun	NA	2.25	2.25	3.50
	Spring	31-Jul	NA	1.80	2.00	1.80
		7-Aug	NA	1.00	4.00	2.00
		4-Sep	NA	6.00	5.00	6.00
	Summer	2-Oct	NA	3.00	3.00	1.00
		6-Nov	NA	5.00	3.00	5.00
		4-Dec	NA	4.00	4.00	5.00
	Autumn	1-Jan	NA	4.00	5.00	4.00
		5-Feb	NA	3.00	2.00	4.00
		5-Mar	NA	2.00	2.00	3.00
	Winter	2-Apr	NA	4.00	3.00	3.00
		7-May	NA	3.00	6.00	4.00
		4-Jun	NA	4.00	6.00	6.00
	Spring	2-Jul	NA	3.74	3.12	1.92
		6-Aug	NA	2.89	2.53	2.15
		3-Sep	NA	2.91	2.58	NA

APPENDIX B10

Recent Cl data.

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	3.29	1.85	1.11	9.48
2015		7-Jan	16.00	11.25	6.82	24.47
		1-Feb	16.89	42.95	2.56	13.80
	Au	14-Apr	6.48	7.95	4.13	14.77
	Sp	4-Nov	12.96	17.13	12.07	16.55
	Su	1-Dec	13.83	12.58	14.36	14.47
2016		28-Feb	13.91	7.16	9.17	19.34
	Au	8-Mar	4.38	1.93	1.23	10.64
		1-Apr	6.09	3.39	2.26	12.39

APPENDIX B11

Historical SO_4 data.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	Sp	26-Nov	6.06	4.46	9.62	10.67
	Su	31-Dec	5.28	5.06	6.75	7.00
1982		28-Jan	NA	NA	NA	0.68
		25-Feb	4.70	4.84	6.53	NA
	Au	29-Apr	5.11	2.28	1.34	2.29
		27-May	7.18	2.73	2.30	5.05
	W	24-Jun	0.33	NA	NA	0.13
		29-Jul	0.28	0.01	NA	NA
		26-Aug	1.16	2.42	1.02	1.29
	Sp	30-Sep	0.90	0.90	0.54	0.89
		28-Oct	3.06	4.19	2.41	5.79
		25-Nov	6.48	6.16	3.40	5.59
	Su	30-Dec	7.60	6.97	7.26	6.30
1983		27-Jan	6.14	5.77	6.05	6.00
		24-Feb	6.65	6.19	6.27	7.04
	Au	31-Mar	8.00	7.40	7.60	7.00
		28-Apr	9.22	9.12	9.01	9.50
		26-May	9.28	9.81	9.81	9.50
	W	30-Jun	7.80	7.40	7.20	7.80
		28-Jul	7.00	4.75	5.75	6.25
		25-Aug	8.00	8.00	9.00	9.25
	Sp	29-Sep	9.50	11.40	12.00	12.20
		27-Oct	11.33	12.75	6.00	6.75
		24-Nov	5.75	6.25	5.25	6.50
	Su	29-Dec	8.00	7.20	6.80	6.20
1984		26-Jan	8.00	8.25	8.00	7.25
		23-Feb	13.50	9.00	6.75	6.00
	Au	29-Mar	4.80	2.80	3.20	3.20
		25-Apr	5.00	5.50	3.28	5.00
		30-May	6.80	6.40	5.40	5.20
	W	27-Jun	7.75	7.75	6.50	5.50
		25-Jul	7.50	6.75	7.00	7.00
		29-Aug	7.00	6.00	6.00	7.00
	Sp	26-Sep	6.00	5.75	5.75	5.75
		31-Oct	4.80	5.40	5.20	4.20
		28-Nov	3.00	3.75	3.25	3.75
	Su	26-Dec	3.75	3.25	3.50	3.25
1985		30-Jan	4.00	4.20	3.60	3.80
		27-Feb	3.67	2.75	4.00	1.33
	Au	27-Mar	2.67	1.75	2.75	9.50

Year	Season	DATE	CP03	CP04	CP06	CP09
1985	Autumn	24-Apr	2.50	2.50	2.75	9.75
	W	29-May	3.00	3.00	2.80	7.00
		29-Jun	3.75	3.00	2.75	7.00
	Sp	31-Jul	4.20	4.00	4.40	5.40
		7-Aug	5.00	5.00	4.00	5.00
		4-Sep	6.00	6.00	6.00	9.00
	Su	2-Oct	8.00	8.00	7.00	6.00
		6-Nov	8.00	9.00	7.00	7.00
		4-Dec	8.00	8.00	6.00	6.00
1986	Au	1-Jan	2.00	2.00	2.00	5.00
		5-Feb	4.00	5.00	5.00	4.00
		5-Mar	5.00	4.00	4.00	5.00
	W	2-Apr	3.00	2.00	3.00	2.00
		7-May	1.00	2.00	2.00	2.00
		4-Jun	2.00	2.00	1.00	2.00
	Sp	2-Jul	2.58	2.67	2.58	2.12
		6-Aug	2.60	2.90	2.51	1.50
		3-Sep	2.88	2.32	2.86	NA

APPENDIX B12

Recent SO_4 data

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	15.16	10.64	5.49	7.81
2015		7-Jan	19.85	18.70	6.31	8.04
		1-Feb	14.32	13.94	6.79	8.19
	Au	14-Apr	13.69	11.67	5.05	4.64
	Sp	4-Nov	16.13	15.41	5.90	3.75
	Su	1-Dec	18.97	15.60	5.33	4.19
2016		28-Feb	19.33	11.55	8.38	8.76
	Au	8-Mar	17.88	12.07	0.00	8.19
		1-Apr	14.65	8.54	4.87	6.08

APPENDIX B13

Historical PO_4 data.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	Spring	26-Nov	0.025	0.004	0.024	0.014
	Summer	31-Dec	0.003	0.003	NA	0.023
1982		28-Jan	0.012	0.016	0.016	0.022
		25-Feb	0.010	NA	0.020	0.014
	Autumn	29-Apr	0.014	0.008	0.008	0.007
		27-May	0.003	0.008	0.010	0.008
	Winter	24-Jun	0.006	0.013	0.010	0.012
		29-Jul	0.008	0.014	0.015	0.015
		26-Aug	0.014	0.008	0.013	0.014
	Spring	30-Sep	0.008	0.007	0.006	0.004
		28-Oct	0.003	0.006	0.007	0.017
		25-Nov	0.007	0.009	0.014	0.015
	Summer	30-Dec	0.013	0.015	0.011	0.020
1983		27-Jan	0.013	0.016	0.015	0.009
		24-Feb	0.009	0.009	0.008	0.004
	Autumn	31-Mar	0.004	0.004	0.004	0.006
		28-Apr	0.006	0.004	0.005	0.007
		26-May	0.006	0.007	0.006	0.005
	Winter	30-Jun	0.002	0.002	0.004	0.002
		28-Jul	0.001	0.002	0.003	0.001
		25-Aug	0.001	0.002	0.001	0.001
	Spring	29-Sep	NA	NA	NA	NA
		27-Oct	0.001	0.001	0.002	NA
		24-Nov	0.002	0.001	0.001	0.027
	Summer	29-Dec	NA	NA	NA	NA
1984		26-Jan	NA	NA	NA	NA
		23-Feb	0.003	0.003	0.002	0.002
	Autumn	29-Mar	0.001	NA	NA	0.001
		25-Apr	0.003	0.006	0.006	0.006
		30-May	0.013	0.005	0.005	0.009
	Winter	27-Jun	NA	NA	NA	0.005
		25-Jul	NA	NA	NA	NA
		29-Aug	NA	NA	NA	0.002
	Spring	26-Sep	NA	NA	NA	0.001
		31-Oct	NA	NA	NA	NA
		28-Nov	NA	NA	NA	NA
	Summer	26-Dec	NA	NA	NA	NA
1985		30-Jan	NA	NA	0.001	0.001
		27-Feb	0.001	0.001	0.001	0.001
	Autumn	27-Mar	0.001	0.002	0.002	NA

Year	**Season**	**DATE**	**CP03**	**CP04**	**CP06**	**CP09**
1985	**Autumn**	**24-Apr**	**0.002**	**0.001**	**0.004**	**0.012**
	Winter	29-May	0.009	0.003	0.003	NA
		29-Jun	0.004	0.001	0.007	0.006
	Spring	31-Jul	0.001	NA	NA	NA
		7-Aug	NA	NA	NA	NA
		4-Sep	NA	NA	NA	0.001
	Summer	2-Oct	NA	0.001	0.001	0.015
		6-Nov	NA	0.003	NA	NA
		4-Dec	0.002	0.001	0.001	NA
1986	Autumn	1-Jan	0.003	NA	NA	0.006
		5-Feb	0.006	0.004	0.005	0.006
		5-Mar	0.009	0.004	0.006	0.008
	Winter	2-Apr	0.007	0.007	0.005	0.005
		7-May	NA	NA	0.003	NA
		4-Jun	NA	NA	NA	NA
	Spring	2-Jul	0.008	NA	NA	0.004
		6-Aug	0.005	NA	NA	0.004
		3-Sep	0.060	NA	NA	NA

APPENDIX B14

Recent PO_4 data.

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	0.387	0.000	0.000	0.000
2015		7-Jan	0.000	1.617	0.000	0.000
		1-Feb	0.147	0.379	0.000	0.000
	Au	14-Apr	1.119	0.000	0.615	0.000
	Sp	4-Nov	0.000	0.000	0.000	0.000
	Su	1-Dec	0.000	0.000	0.000	0.000
2016		28-Feb	0.000	0.108	0.000	0.000
	Au	8-Mar	0.000	0.000	0.000	0.000
		1-Apr	0.126	0.260	0.000	0.000

APPENDIX B15

Historical NO_3 data.

Year	Season	DATE	CP03	CP04	CP06	CP09
1981	Spring	26-Nov	0.368	0.022	0.028	0.119
	Summer	31-Dec	1.342	0.012	0.035	0.008
1982		28-Jan	1.147	0.014	0.011	0.011
		25-Feb	1.647	0.020	0.016	0.012
	Autumn	29-Apr	2.051	0.027	0.009	0.014
		27-May	1.985	0.005	0.033	0.008
	Winter	24-Jun	2.002	0.012	0.039	0.010
		29-Jul	1.875	0.015	0.008	0.025
		26-Aug	1.347	0.014	0.018	0.009
	Spring	30-Sep	1.680	0.011	0.021	0.017
		28-Oct	1.136	0.005	0.003	0.021
		25-Nov	2.156	NA	0.004	0.021
	Summer	30-Dec	1.846	0.014	0.009	0.005
1983		27-Jan	1.946	NA	0.002	0.004
		24-Feb	2.522	0.016	0.010	0.010
	Autumn	31-Mar	2.344	0.014	0.014	0.008
		28-Apr	0.600	0.012	0.010	NA
		26-May	1.848	0.056	0.022	0.020
	Winter	30-Jun	2.350	0.046	0.006	0.016
		28-Jul	2.103	0.023	0.010	0.013
		25-Aug	1.953	0.023	0.018	0.015
	Spring	29-Sep	1.903	0.024	0.018	0.018
		27-Oct	1.927	0.023	0.010	0.005
		24-Nov	2.020	0.028	0.015	0.645
	Summer	29-Dec	2.822	0.426	0.032	0.020
1984		26-Jan	3.287	0.758	0.023	0.013
		23-Feb	2.845	0.020	0.005	0.008
	Autumn	29-Mar	2.672	0.012	NA	NA
		25-Apr	3.205	0.060	0.010	0.013
		30-May	2.516	0.012	0.008	0.016
	Winter	27-Jun	2.973	0.015	0.018	0.015
		25-Jul	2.130	0.030	0.750	0.013
		29-Aug	2.694	NA	0.016	0.012
	Spring	26-Sep	2.220	0.028	0.030	0.035
		31-Oct	1.750	0.054	0.478	0.050
		28-Nov	2.023	0.023	0.015	0.015
	Summer	26-Dec	1.970	0.018	0.023	0.010
1985		30-Jan	2.168	0.046	0.686	0.022
		27-Feb	4.140	0.015	0.035	0.007
	Autumn	27-Mar	3.363	0.053	0.048	0.025

Year	Season	DATE	CP03	CP04	CP06	CP09
1985	Autumn	24-Apr	3.200	0.048	0.045	0.040
	Winter	29-May	3.090	0.050	0.052	0.032
		29-Jun	2.990	0.040	0.043	0.958
	Spring	31-Jul	2.366	0.056	0.040	0.016
		7-Aug	2.700	0.040	0.030	0.010
		4-Sep	2.640	0.060	0.020	0.030
	Summer	2-Oct	2.270	0.030	NA	0.010
		6-Nov	2.490	0.070	NA	0.120
		4-Dec	2.400	0.010	0.020	0.010
1986	Autumn	1-Jan	3.560	0.050	0.030	0.020
		5-Feb	3.200	0.060	0.020	NA
		5-Mar	2.850	0.010	0.010	NA
	Winter	2-Apr	1.520	0.170	0.200	0.150
		7-May	3.250	0.060	0.020	0.010
		4-Jun	3.090	0.020	0.010	0.010
	Spring	2-Jul	3.182	0.013	0.020	0.018
		6-Aug	3.010	0.068	0.012	0.018
		3-Sep	2.998	0.020	0.013	NA

APPENDIX B16

Recent NO_3 data.

Year	Season	Date	CP03	CP04	CP06	CP09
2014	Su	2-Dec	0.013	0.000	0.000	6.496
2015		7-Jan	0.000	5.309	0.000	0.775
		1-Feb	0.000	0.000	0.000	0.441
	Au	14-Apr	0.000	0.000	0.000	0.389
	Sp	4-Nov	0.063	0.162	0.000	0.549
	Su	1-Dec	0.000	0.000	0.000	0.383
2016		28-Feb	0.201	0.320	0.000	0.000
	Au	8-Mar	0.000	0.000	0.000	0.000
		1-Apr	0.214	0.505	0.277	0.225

APPENDIX B17

Monthly DOC data collected during study.

Season	Date	CP03	CP04	CP06	CP09
Winter	2015/09/06	0.77	0.62	0.86	0.74
	28/08/2015	0.13	0.00	0.27	0.18
Spring	2015/10/09	2.60	1.38	0.30	9.20
Summer	20/12/2015	0.95	0.78	0.10	0.37
	27/01/2016	0.69		1.05	
	25/02/2016	1.38	1.09	0.45	0.76
Autumn	31/03/2016	0.87	0.72	0.91	0.52
	29/04/2016	0.56	0.39	0.29	0.36
	25/05/2016	0.14	0.19	0.35	0.15
Winter	31/07/2016	6.68	11.50	13.10	9.42
	30/08/2016	0.81	1.09	1.45	1.67
Spring	30/09/2016	0.82	0.85	0.62	0.50
	31/10/2016	0.00	0.00	0.00	0.05
	30/11/2016	1.34	1.61	1.50	1.60
Summer	22/12/2016	9.10	11.80	12.80	10.80

APPENDIX B18

Daily average streamwater temperatures (°C).

Date	CP03	CP04	CP06	CP09
15/06/09	9.8	9.9	11.1	7.6
15/06/10	9.1	9.3	10.2	7.0
15/06/11	9.6	9.6	10.5	7.6
15/06/12	10.2	10.3	11.1	8.0
15/06/13	9.6	9.8	10.7	7.3
15/06/14	9.6	9.8	10.7	7.2
15/06/15	9.3	9.6	10.5	7.2
15/06/16	9.0	9.2	10.1	6.7
15/06/17	8.2	8.2	9.4	6.9
15/06/18	8.1	8.2	9.3	6.3
15/06/19	8.4	8.6	9.5	6.4
15/06/20	9.0	9.2	10.0	6.8
15/06/21	9.0	9.3	10.2	6.7
15/06/22	9.1	9.3	14.8	6.7
15/06/23	8.7	9.0	12.0	6.9
15/06/24	8.5	12.3	12.6	6.4
15/06/25	9.3	13.6	12.0	7.2
15/06/26	10.5	10.2	11.7	8.1
15/06/27	9.6	6.9	10.5	7.7
15/06/28	9.5	11.0	10.7	7.3
15/06/29	9.2	10.1	10.4	7.2
15/06/30	9.5	8.6	10.7	7.8
15/07/01	9.0	9.1	10.4	6.9
15/07/02	8.7	8.7	10.0	6.6
15/07/03	8.7	10.7	9.9	6.7
15/07/04	9.1	12.2	10.0	7.1
15/07/05	9.8	14.0	10.6	7.7
15/07/06	10.0	13.5	10.8	7.6
15/07/07	10.7	9.8	11.5	8.5
15/07/08	9.9	13.8	10.9	7.9
15/07/09	10.1	10.1	11.0	7.9
15/07/10	10.5	10.7	11.3	8.1
15/07/11	10.1	10.3	11.0	7.8
15/07/12	10.5	10.8	11.4	8.2
15/07/13	10.3	10.4	11.0	7.9
15/07/14	10.3	10.4	11.1	8.3
15/07/15	10.8	11.0	11.7	8.7
15/07/16	10.6	10.8	11.4	8.4

Date	**CP03**	**CP04**	**CP06**	**CP09**
15/07/17	9.0	9.2	10.1	7.3
15/07/18	9.1	9.0	10.0	7.1
15/07/19	9.1	9.1	10.1	6.9
15/07/20	9.4	9.5	10.3	7.0
15/07/21	9.9	10.0	10.7	7.3
15/07/22	10.7	10.7	11.3	8.6
15/07/23	10.3	10.5	11.1	8.4
15/07/24	10.3	10.5	11.1	8.4
15/07/25	9.6	9.8	10.6	7.5
15/07/26	9.2	9.3	10.1	7.3
15/07/27	9.3	9.4	10.3	7.3
15/07/28	9.0	9.0	10.0	6.9
15/07/29	9.1	9.4	9.8	7.2
15/07/30	9.1	12.4	9.9	7.1
15/07/31	8.1	8.4	9.0	6.4
15/08/01	7.7	7.6	8.7	6.0
15/08/02	8.3	8.3	9.1	6.3
15/08/03	8.5	8.5	9.3	6.8
15/08/04	8.8	8.7	9.5	6.7
15/08/05	9.3	9.4	10.0	7.5
15/08/06	9.1	9.2	9.9	7.1
15/08/07	9.3	9.5	10.1	7.2
15/08/08	9.6	9.8	10.3	7.2
15/08/09	9.5	9.8	10.4	7.7
15/08/10	9.8	9.9	10.6	8.1
15/08/11	10.2	10.4	11.0	8.4
15/08/12	10.5	10.6	11.1	8.5
15/08/13	10.2	10.5	10.9	8.2
15/08/14	10.0	10.1	10.7	8.2
15/08/15	10.3	10.4	10.9	8.4
15/08/16	11.2	11.4	11.7	8.9
15/08/17	11.3	11.5	11.9	9.0
15/08/18	11.4	11.8	10.9	9.3
15/08/19	11.6	12.4	13.5	9.6
15/08/20	12.5	12.9	13.3	10.4
15/08/21	12.0	12.5	12.9	9.8
15/08/22	12.3	12.9	13.1	10.4
15/08/23	12.8	13.1	13.4	10.6
15/08/24	14.6	13.3	13.4	10.8
15/08/25	13.0	12.8	13.1	10.4
15/08/26	18.0	13.0	13.2	10.8

Date	CP03	CP04	CP06	CP09
15/08/27	18.6	13.4	13.5	11.0
15/08/28	18.9	13.9	14.0	11.4
15/08/29	18.7	13.4	13.7	11.0
15/08/30	18.7	13.7	13.9	11.4
15/08/31	18.1	13.9	14.0	11.5
15/09/01	17.3	13.9	14.1	11.7
15/09/02	6.7	12.2	13.0	10.1

APPENDIX B19

Conductivity data (µS/cm).

Season	Date	CP03	CP04	CP06	CP09
Autumn	1-Apr-2014	51	75.1	77.3	55.6
Winter	3-Jun-2014	49.2	66.6	71.6	53
	9-Jul-2014	106.4	109.4	128.4	108.9
	12-Aug-2014	124.8	147.9	158.7	128.4
Spring	11-Sep-2014	72.9	97.6	108.6	89.8
Summer	2-Dec-2014	91.7	109.4	115.1	190.1
	31-Jan-2015	90.4	115.1	118.1	176.3
	24-Feb-2015	96.3	124.2	128.9	113.4
Autumn	14-Apr-2015	77.1	102.5	107.5	84.6
Winter	9-Jun-2015	71.4	97.7	103.7	82
	28-Aug-2015	68	102.4	107.4	97.9
Spring	10-Sep-2015	60.1	87.8	81.2	70.5
	7-Oct-2015	91.2	136.6	129.5	119
Summer	2-Dec-2015	82.8	113	120.2	126.4
	6-Jan-2016	80.6	105	105.8	109
	25-Feb-2016	78.2	100.8	103.8	92
Autumn	31-Mar-2016	95.3	112.2	129.4	104.5
	27-Apr-2016	81	108.4	112.7	92.9
	25-May-2016	79.3	105	110	90.4
Winter	29-Jul-2016	81.9	103.2	112.6	114

APPENDIX B20

Dissolved oxygen data from 2014 – 2016 (mg/L).

Season	**Catchments**	**CP03**	**CP04**	**CP06**	**CP09**
Autumn	1-Apr-2014	8.30	8.03	7.35	8.05
Winter	3-Jun-2014	9.27	9.51	8.99	7.80
	9-Jul-2014	13.92	15.21	11.32	11.93
	12-Aug-2014	9.26	14.09	11.72	10.47
Spring	11-Sep-2014	7.88	8.55	8.12	7.94
Summer	2-Dec-2014	7.07	7.79	7.33	1.57
	31-Jan-2015	6.72	7.10	6.64	1.22
	24-Feb-2015	6.45	7.00	6.88	8.07
Autumn	14-Apr-2015	7.92	8.15	7.46	8.32
Winter	9-Jun-2015	8.75	10.02	9.38	10.34
	28-Aug-2015	8.09	8.13	9.04	7.36
Spring	10-Sep-2015	10.28	9.81	10.97	8.09
	7-Oct-2015	8.12	7.41	7.91	7.33
Summer	2-Dec-2015	7.51	9.36	7.50	7.78
	6-Jan-2016	7.25	6.71	7.89	6.92
	25-Feb-2016	7.50	7.95	7.50	7.31
Autumn	31-Mar-2016	7.99	7.82	7.76	7.61
	27-Apr-2016	8.80	8.36	7.78	7.49
	25-May-2016	8.14	9.34	7.70	7.70
Winter	29-Jul-2016	9.48	9.53	8.91	8.41

APPENDIX B21

pH data.

Season	Date	CP03	CP04	CP06	CP09
Autumn	1-Apr-2014	7.4	7.6	7.2	7.1
Winter	3-Jun-2014	7.8	8.0	7.9	8.1
	9-Jul-2014	7.3	7.9	7.6	7.3
	12-Aug-2014	7.4	8.2	8.1	7.2
Spring	11-Sep-2014	7.4	7.6	7.6	7.2
Summer	2-Dec-2014	7.4	7.5	7.4	6.4
	31-Jan-2015	7.3	7.5	7.2	6.4
	24-Feb-2015	6.6	7.0	6.7	6.7
Autumn	14-Apr-2015	7.5	7.5	7.5	7.3
Winter	9-Jun-2015	7.1	7.8	7.7	7.0
	28-Aug-2015	7.6	7.7	7.7	6.9
Spring	10-Sep-2015	7.8	7.9	7.8	6.9
	7-Oct-2015	7.3	8.2	7.9	7.5
Summer	2-Dec-2015	7.4	8.3	7.8	7.3
	6-Jan-2016	7.3	7.8	7.5	7.6
	25-Feb-2016	7.5	7.5	7.5	6.9
Autumn	31-Mar-2016	7.4	7.7	7.7	7.5
	27-Apr-2016	7.4	7.6	7.6	7.2
	25-May-2016	7.8	8.1	7.8	7.4
Winter	29-Jul-2016	7.9	7.8	7.9	8.2

APPENDIX B22

CP03 TSS, TDS and flow level data.

Sample no.	**Time**	**TSS (mg/L)**	**TDS (mg/L)**	**Flow level (m)**
CP03.1-5	01:51:00 PM - 02:28:00 PM	170.20	6.40	0.4857
CP03.6-9	02:59:00 PM - 05:10:00 PM	173.60	11.40	0.4833
CP03.10-12	09:03:00 PM - 09:16:00 PM	177.60	11.60	0.4859
CP03.13-15	09:19:00 PM - 09:24:00 PM	197.33	14.89	0.5014
CP03.16-18	09:26:00 PM - 09:31:00 PM	176.20	8.80	0.5170
CP03.19-21	09:34:00 PM - 09:40:00 PM	179.20	9.40	0.5327
CP03.22-24	09:43:00 PM - 09:54:00 PM	196.40	14.40	0.5480

APPENDIX B23

CP06 TSS, TDS and flow level data

Sample no.	Time	TSS (mg/L)	TDS (mg/L)	Flow level (m)
CP06.1-4	01:51:00 PM - 02:17:00 PM	178.20	15.20	1.0127
CP06.5-8	02:20:00 PM - 02:31:00 PM	176.80	12.20	1.0252
CP06.9-12	02:39:00 PM - 03:59:00 PM	153.20	16.80	1.0283
CP06.13-16	04:28:00 PM - 20:57:00 PM	196.67	18.67	1.0176
CP06.17-20	09:04:00 PM - 09:17:00 PM	181.60	12.80	1.0255
CP06.21-24	09:19:00 PM - 09:52:00 PM	216.40	17.40	1.0380

APPENDIX B24

CP03 February 2016 major anion concentrations (μeq/L).

Date	**Time**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**PO_4**	**NO_3**
18/02/2016	**10:29:00**	343.4	253.4	107.1	4.5	15.2	20.4	0.0	0.0
	11:25:00	315.0	246.1	121.8	5.5	9.1	18.4	0.0	0.3
	12:28:00	369.5	261.5	99.4	3.5	8.9	22.2	0.0	0.0
	13:27:00	363.1	258.8	104.7	4.6	8.5	21.6	0.0	0.0
	14:26:00	313.6	243.8	120.5	4.4	6.3	18.1	0.0	0.4
19/02/2016	**8:05:00**	354.6	259.0	99.3	2.2	7.8	21.0	0.0	0.0
	8:35:00	328.7	262.3	103.4	4.1	6.5	19.4	0.0	0.0
	9:30:00	306.2	243.1	123.1	4.1	6.0	16.5	0.0	0.3
	10:10:00	336.7	255.1	122.3	4.5	5.2	16.5	0.0	0.3

APPENDIX B25

CP03 8 March 2016 major ion concentrations (µeq/L).

Time	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**PO_4**	**NO_3**
13:51:40	381.7	260.2	97.4	3.2	4.4	17.4	0.0	0.0
13:55:20	264.4	238.3	117.9	4.0	3.7	15.1	0.0	0.0
14:03:00	348.1	262.6	96.1	3.4	4.3	17.7	0.0	0.0
14:21:20	211.2	200.7	110.1	4.4	3.9	14.0	0.0	0.2
14:28:50	283.7	236.4	115.3	4.7	4.3	16.3	0.0	0.3
14:59:30	392.1	263.0	96.6	4.3	6.0	19.1	0.0	0.0
16:02:00	288.5	234.4	117.5	6.7	6.8	17.2	0.0	0.4
16:20:40	270.6	229.6	114.0	5.5	5.4	17.0	0.0	0.1
17:10:40	346.9	254.8	93.1	4.1	5.8	18.5	0.0	0.0
21:03:30	369.6	264.2	96.1	4.0	5.8	18.5	0.0	0.0
21:16:00	351.1	266.6	117.9	5.6	4.8	16.7	0.0	0.4
21:22:10	348.2	256.6	92.7	4.2	5.5	0.0	0.0	0.0
21:24:20	323.9	251.9	93.1	4.2	5.5	17.7	0.0	0.0
21:26:30	381.0	261.4	94.4	4.7	6.1	18.2	0.0	0.0
21:29:10	362.8	253.3	90.5	4.7	6.1	17.5	0.0	0.0
21:31:40	377.3	253.8	90.0	5.2	6.6	17.9	0.0	0.0
21:34:30	360.8	250.3	90.5	5.7	7.3	17.8	0.0	0.0
21:37:20	296.4	241.7	109.2	7.7	6.5	16.0	0.0	0.3
21:40:40	368.0	242.9	86.6	5.8	7.1	17.7	0.0	0.0
21:43:50	349.5	250.3	107.9	8.0	6.4	16.0	0.0	0.2
21:48:00	329.8	239.3	85.3	5.8	7.0	17.2	0.0	0.0
21:54:50	359.4	240.4	84.8	6.2	7.5	17.6	0.0	0.0

APPENDIX B26

CP06 February 2016 major ion concentrations (μeq/L).

Date	Time	Ca	Mg	Na	K	Cl	SO_4	PO_4	NO_3
18/02/2016	**11:10:00**	422.7	372.4	105.5	8.3	5.3	12.1	0.0	0.0
	12:10:00	452.1	379.3	113.7	4.6	11.5	12.6	0.0	0.0
	13:10:00	435.2	363.7	111.6	6.8	8.0	12.8	0.0	0.0
	14:10:00	371.5	338.4	166.2	9.4	23.0	10.1	0.0	0.4
	15:10:00	438.2	370.0	132.9	7.2	4.2	10.3	0.0	0.3
	16:10:00	426.8	361.6	117.1	3.2	12.3	11.3	0.0	0.0
	17:10:00	430.1	378.5	132.8	6.4	2.5	9.0	0.0	0.3
	18:10:00	333.4	303.7	118.5	6.4	2.6	7.3	0.0	0.2
	19:10:00	385.8	346.4	128.6	6.0	2.8	7.9	0.1	0.3

APPENDIX B27

CP06 8 March 2016 major ion concentrations (µeq/L).

Time	Ca	Mg	Na	K	Cl	SO_4	PO_4	NO_3
13:51:10	413.6	411.6	109.2	5.6	2.7	6.1	0.0	0.0
13:56:50	634.1	489.2	126.3	6.8	1.9	7.6	0.0	0.0
14:13:30	534.7	426.4	109.9	5.8	1.9	6.3	0.0	0.0
14:17:00	521.6	424.2	111.6	6.0	2.8	6.5	0.0	0.0
14:20:40	466.8	414.2	108.4	5.5	1.2	6.2	0.0	0.0
14:24:00	528.5	416.0	108.1	6.7	3.6	8.1	0.0	0.0
14:27:00	477.7	408.1	108.0	6.8	3.9	8.1	0.0	0.0
14:31:30	542.5	417.3	120.0	6.6	9.6	8.1	0.0	0.0
14:39:20	508.7	413.8	108.1	6.7	2.7	7.6	0.0	0.0
15:07:40	446.3	387.0	108.2	8.0	3.6	8.6	0.0	0.0
15:59:40	434.5	395.2	105.4	4.7	3.9	8.9	0.0	0.0
17:17:20	341.0	358.0	130.7	8.5	2.1	6.6	0.0	0.3
19:16:50	488.4	405.0	116.6	7.1	9.0	7.8	0.0	0.1
20:57:20	500.7	408.6	117.4	6.8	9.5	8.0	0.0	0.0
21:04:40	340.9	263.4	84.2	5.9	5.2	3.9	0.0	0.2
21:09:50	514.6	410.4	108.6	8.2	4.8	8.6	0.0	0.0
21:14:00	442.8	409.3	109.8	6.1	6.2	10.9	0.0	0.0
21:17:40	374.4	392.7	109.5	8.3	4.4	9.4	0.0	0.0
21:19:50	443.3	395.8	109.2	8.4	4.3	9.5	0.0	0.0
21:21:50	291.4	352.5	129.5	10.3	3.8	7.9	0.0	0.4
21:23:30	414.9	386.2	103.9	6.1	4.8	9.9	0.0	0.0
21:25:00	401.5	373.9	129.2	10.9	4.0	8.1	0.0	0.3

APPENDIX B28

CP03 February 2016 major anion concentrations (µeq/L).

Date	**Time**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**PO_4**	**NO_3**
18/02/2016	**10:29:00**	343.4	253.4	107.1	4.5	15.2	20.4	0.0	0.0
	11:25:00	315.0	246.1	121.8	5.5	9.1	18.4	0.0	0.3
	12:28:00	369.5	261.5	99.4	3.5	8.9	22.2	0.0	0.0
	13:27:00	363.1	258.8	104.7	4.6	8.5	21.6	0.0	0.0
	14:26:00	313.6	243.8	120.5	4.4	6.3	18.1	0.0	0.4
19/02/2016	**8:05:00**	354.6	259.0	99.3	2.2	7.8	21.0	0.0	0.0
	8:35:00	328.7	262.3	103.4	4.1	6.5	19.4	0.0	0.0
	9:30:00	306.2	243.1	123.1	4.1	6.0	16.5	0.0	0.3
	10:10:00	336.7	255.1	122.3	4.5	5.2	16.5	0.0	0.3

APPENDIX B29

CP03 8 March 2016 major ion concentrations (µeq/L).

Time	Ca	Mg	Na	K	Cl	SO_4	PO_4	NO_3
13:51:40	381.7	260.2	97.4	3.2	4.4	17.4	0.0	0.0
13:55:20	264.4	238.3	117.9	4.0	3.7	15.1	0.0	0.0
14:03:00	348.1	262.6	96.1	3.4	4.3	17.7	0.0	0.0
14:21:20	211.2	200.7	110.1	4.4	3.9	14.0	0.0	0.2
14:28:50	283.7	236.4	115.3	4.7	4.3	16.3	0.0	0.3
14:59:30	392.1	263.0	96.6	4.3	6.0	19.1	0.0	0.0
16:02:00	288.5	234.4	117.5	6.7	6.8	17.2	0.0	0.4
16:20:40	270.6	229.6	114.0	5.5	5.4	17.0	0.0	0.1
17:10:40	346.9	254.8	93.1	4.1	5.8	18.5	0.0	0.0
21:03:30	369.6	264.2	96.1	4.0	5.8	18.5	0.0	0.0
21:16:00	351.1	266.6	117.9	5.6	4.8	16.7	0.0	0.4
21:22:10	348.2	256.6	92.7	4.2	5.5	0.0	0.0	0.0
21:24:20	323.9	251.9	93.1	4.2	5.5	17.7	0.0	0.0
21:26:30	381.0	261.4	94.4	4.7	6.1	18.2	0.0	0.0
21:29:10	362.8	253.3	90.5	4.7	6.1	17.5	0.0	0.0
21:31:40	377.3	253.8	90.0	5.2	6.6	17.9	0.0	0.0
21:34:30	360.8	250.3	90.5	5.7	7.3	17.8	0.0	0.0
21:37:20	296.4	241.7	109.2	7.7	6.5	16.0	0.0	0.3
21:40:40	368.0	242.9	86.6	5.8	7.1	17.7	0.0	0.0
21:43:50	349.5	250.3	107.9	8.0	6.4	16.0	0.0	0.2
21:48:00	329.8	239.3	85.3	5.8	7.0	17.2	0.0	0.0
21:54:50	359.4	240.4	84.8	6.2	7.5	17.6	0.0	0.0

APPENDIX B30

CP06 February 2016 major ion concentrations (µeq/L).

Date	Time	Ca	Mg	Na	K	Cl	SO_4	PO_4	NO_3
18/02/2016	**11:10:00**	422.7	372.4	105.5	8.3	5.3	12.1	0.0	0.0
	12:10:00	452.1	379.3	113.7	4.6	11.5	12.6	0.0	0.0
	13:10:00	435.2	363.7	111.6	6.8	8.0	12.8	0.0	0.0
	14:10:00	371.5	338.4	166.2	9.4	23.0	10.1	0.0	0.4
	15:10:00	438.2	370.0	132.9	7.2	4.2	10.3	0.0	0.3
	16:10:00	426.8	361.6	117.1	3.2	12.3	11.3	0.0	0.0
	17:10:00	430.1	378.5	132.8	6.4	2.5	9.0	0.0	0.3
	18:10:00	333.4	303.7	118.5	6.4	2.6	7.3	0.0	0.2
	19:10:00	385.8	346.4	128.6	6.0	2.8	7.9	0.1	0.3

APPENDIX B31

CP06 8 March 2016 major ion concentrations (µeq/L).

Time	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**PO_4**	**NO_3**
13:51:10	413.6	411.6	109.2	5.6	2.7	6.1	0.0	0.0
13:56:50	634.1	489.2	126.3	6.8	1.9	7.6	0.0	0.0
14:13:30	534.7	426.4	109.9	5.8	1.9	6.3	0.0	0.0
14:17:00	521.6	424.2	111.6	6.0	2.8	6.5	0.0	0.0
14:20:40	466.8	414.2	108.4	5.5	1.2	6.2	0.0	0.0
14:24:00	528.5	416.0	108.1	6.7	3.6	8.1	0.0	0.0
14:27:00	477.7	408.1	108.0	6.8	3.9	8.1	0.0	0.0
14:31:30	542.5	417.3	120.0	6.6	9.6	8.1	0.0	0.0
14:39:20	508.7	413.8	108.1	6.7	2.7	7.6	0.0	0.0
15:07:40	446.3	387.0	108.2	8.0	3.6	8.6	0.0	0.0
15:59:40	434.5	395.2	105.4	4.7	3.9	8.9	0.0	0.0
17:17:20	341.0	358.0	130.7	8.5	2.1	6.6	0.0	0.3
19:16:50	488.4	405.0	116.6	7.1	9.0	7.8	0.0	0.1
20:57:20	500.7	408.6	117.4	6.8	9.5	8.0	0.0	0.0
21:04:40	340.9	263.4	84.2	5.9	5.2	3.9	0.0	0.2
21:09:50	514.6	410.4	108.6	8.2	4.8	8.6	0.0	0.0
21:14:00	442.8	409.3	109.8	6.1	6.2	10.9	0.0	0.0
21:17:40	374.4	392.7	109.5	8.3	4.4	9.4	0.0	0.0
21:19:50	443.3	395.8	109.2	8.4	4.3	9.5	0.0	0.0
21:21:50	291.4	352.5	129.5	10.3	3.8	7.9	0.0	0.4
21:23:30	414.9	386.2	103.9	6.1	4.8	9.9	0.0	0.0
21:25:00	401.5	373.9	129.2	10.9	4.0	8.1	0.0	0.3

APPENDIX B32

Spectral absorbance table for CP03.

Date	Time	Sample no.	Abs254nm	Abs360nm	Abs400nm	Abs546nm	DOC
07/03/2016	10:23:00 AM	**CP03**	0.025	0.008	0.004	0.000	0.00
07/03/2016	03:02:00 PM	**CP03 After rainfall**	0.035	0.009	0.004	0.001	0.30
08/03/2016	11:36:00 PM	**CP03**	0.029	0.008	0.005	0.000	0.09
08/03/2016	01:51-02:28 PM	**CP03.1-5**	0.028	0.012	0.006	0.002	2.19
08/03/2016	02:59-05:10 PM	**CP03.6-9**	0.040	0.013	0.006	0.003	1.33
08/03/2016	09:03-09:16 PM	**CP03.10-12**	0.040	0.013	0.004	0.001	1.24
08/03/2016	09:19-21:24 PM	**CP03.13-15**	0.032	0.013	0.005	0.001	1.04
08/03/2016	09:26-09:31 PM	**CP03.16-18**	0.045	0.015	0.007	0.002	1.46
08/03/2016	09:34-09:40 PM	**CP03.19-21**	0.040	0.014	0.007	0.002	1.55
08/03/2016	09:43-09:54 PM	**CP03.22-24**	0.040	0.013	0.007	0.003	1.79

APPENDIX B33

Spectral absorbance Table for CP06.

Date	Time	Sample no.	254 nm	360 nm	400 nm	546 nm	DOC (mg/L)
07/03/2016	12:45:00 PM	**CP06**	0.032	0.010	0.005	0.001	0.32
07/03/2016	2:53:00 PM	**CP06 After rainfall**	0.043	0.011	0.007	0.002	0.63
08/03/2016	10:25:00 AM	**CP06**	0.034	0.013	0.007	0.002	0.37
08/03/2016	01:51-14:17PM	**CP06.1-4**	0.045	0.016	0.007	0.002	1.92
08/03/2016	02:20-02:31PM	**CP06.5-8**	0.059	0.019	0.010	0.002	1.54
08/03/2016	02:39-03:59PM	**CP06.9-12**	0.058	0.020	0.012	0.002	1.61
08/03/2016	04:28-20:57PM	**CP06.13-16**	0.062	0.021	0.009	0.002	1.45
08/03/2016	09:04-09:17PM	**CP06.17-20**	0.066	0.020	0.011	0.002	1.76
08/03/2016	09:19-09:25PM	**CP06.21-24**	0.078	0.026	0.014	0.003	2.29
09/03/2016	12:55:00 PM	**CP06.1-4**	0.145	0.050	0.028	0.007	3.16