Monitoring water quality with riparian trees along the Berg River, Western Cape

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KEYWORDS

Water quality, heavy metals, sediment, riparian vegetation, Berg River, bioindicators, *Salix* sp., *Acacia mearnsii*, *Brabejum stellatifolium*, eutrophication

ABSTRACT

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Heavy metals and nutrients have long been regarded as pollutants to freshwater ecosystems. These elements have a detrimental effect on plants, animals and the water quality of rivers in South Africa. The Berg River flows from the mountains of Franschhoek to the West Coast of the Western Cape. It is an important river in Cape Town, as it is essential for water distribution to town, for agriculture and industry and also supports a rich diversity of organisms in the ecosystem. Along the river, many farms and towns are situated and many tributaries enter the river. The Berg River dam provides for a water supply during the drier periods of the year. Therefore it is crucial to maintain a good water quality. The study was driven by the need to increase the knowledge of water quality in the upper Berg River after the construction of a new major Berg River dam, constructed in 2007.

This study investigated oxygen, water temperature, electrical conductivity, pH, ammonium, nitrate, nitrite in the water and cadmium, copper, lead, iron, zinc, potassium, sodium, calcium, magnesium and phosphorus found in water, sediment and three plant species at ten sites along the upper Berg River, Western Cape.

The results showed that the electrical conductivity, pH and the concentrations of nitrate, calcium and magnesium increased downstream, whereas the water temperature decreased downstream. Nitrate, cadmium, copper, potassium, sodium, calcium and magnesium displayed a general increase towards the colder period in the water. Seasonally, copper and magnesium showed significant winter increase within the sediment. Nitrogen, iron and calcium levels within *Salix* sp., *Acacia mearnsii* and *Brabejum stellatifolium* increased downstream. Nitrogen, cadmium, copper, potassium, calcium, magnesium and phosphorus in the three species were higher in the warmer seasons and decreased in the colder. Sources of pollution stem from the Franschhoek and Dwars tributaries, urban and farm runoff.

DECLARATION

I declare that *Monitoring water quality with riparian trees along the Berg River, Western Cape* is my own work, that it has not been submitted for any degree or examination at any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

Melissa Ruiters Date:

Signed ………………………

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This dissertation is dedicated to my parents, Wilhelmina and Clifford Ruiters.

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LITERATURE REVIEW

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1.1 INTRODUCTION

Clean water is an important resource that is necessary for many purposes such as consumption, irrigation and it also maintains aquatic ecosystems (Carpenter *et al*. 1998). South Africa requires a large amount of freshwater to sustain people and their livelihoods. Davies and Day (1998) state that water extraction from rivers in South Africa is up to approximately two thirds of the standard quantity of accessible surface water per annum. These water bodies have been under increasing threat because of the fast "demographic changes, which have coincided with the establishment of human settlements lacking appropriately sanitary infrastructure" (Fatoki *et al*. 2003).

Rivers are referred to as lotic systems (Jeffries and Mills 1990) because water is continuously moving (Johnson *et al.* 2008). Haslam (1990) explains that rivers flow down the length of a bed on the surface of the earth towards the ocean. As the water moves down the length of the river, it transports dissolved and inorganic material that originates from weathered rocks (Townsend 1980). Jeffries and Mills (1990) state that when the river course alters as the river moves downstream, the type of vegetation and habitats changes. Rivers have been altered by human activities and this has caused serious ecological impacts on these ecosystems (Townsend 1980).

Allan and Flecker (1993) explain factors that contribute to the destruction of rivers. The first way that the authors describe is through habitat loss and degradation. These impacts include farming practices and human dwellings. Farmers often bulldoze certain areas in which many indigenous species are removed from the environment. This causes erosion to be more significant in riparian interfaces.

The second contribution to the destruction of rivers stems from alien species. A huge danger to riparian ecosystem function is caused by invasive species. Invasive woody species increase nutrient cycling as well as decrease the amount of runoff that should occur (Holmes and Richardson 1999). Invasive plants can swiftly dominate a riparian ecosystem because propagules are transferred by the river. The reason why riparian vegetation is sensitive to invasion of exotic species is because of the hydrological character of rivers (Blanchard and Holmes 2008).

The word "riparian" refers to the banks of aquatic systems like rivers, vleis or wetlands and riparian vegetation plays an important role in a catchment (Brown and Magoba 2009). Riparian vegetation offers habitat and migration pathways for a diverse range of animals (Anon. 2004). It is able to control and reuse inputs from upper reaches and also the river (Tabacchi *et al*. 1998). It also decreases the input of matter from land surfaces into the rivers and this then decreases the deterioration of a river's water quality (Kuhar *et al*. 2007).

Water pollution is common in densely populated areas. The water quality deterioration is largely due to the impacts of humans (Struyf *et al.* 2012). The quality of water is not only due to direct human impacts but also through the contribution of interbasin transfers (Luger 1996) which have become more common. Both man made and natural influences decrease the quality of water for various uses such as for drinking, recreation and industry. The quality of water can be assessed by measuring various parameters within the river- which points towards the amount of pollution in the aquatic system (Morrison *et al.* 2001). The changes in the water quality conditions have an impact on the amount and variety of organisms found in the river and also downstream (Camargo *et al.* 2005). Sánchez *et al.* (2007) states that because of the temporal and spatial differences in the chemistry of water, it is important to monitor the water quality.

Biomonitoring is essentially the use of a biological organism to evaluate changes that occur in an area (Wolterbreek 2002). It has become important in research of pollutants in organisms, which shows how much if these pollutants have accumulated over time (Nirmal Kumar *et al*. 2008). Vegetation is the most commonly used biomonitor due to the fact that plants are immobile (Wuytack *et al.* 2010). The use of plant leaves for biomonitoring heavy metals can be dated back since the 1950's (Ataabadie *et al*. 2011). Heavy metals are able to accumulate in plant biomass due to the fact that heavy metals cannot be degraded (Schulze *et al.* 2002). The accumulation of heavy metals within plants provides information on the surrounding environment and therefore one can use plants as biomonitors of an area (Miretzky *et al.* 2004). This is significant for riparian vegetation because the input of a pollutant may be diluted rapidly in the aquatic system, but riparian vegetation can provide accumulated information about the quality of the system (Nirmal Kumar *et al*. 2008).

Rivers are important ecosystems that needed to be protected from degradation and pollution. The Berg River offers a home to a diverse array of organisms- some of which are endemic to the river and this river renders many ecosystem services. Water quality research in the Berg River has been dated back to at least the 1960's (Anon. 2004). The major sources contributing to the deterioration of the Berg River are "agricultural return flow, irrigation releases, urban and industrial runoff and wastewater discharges" (Anon. 2004). It is therefore of utmost importance to investigate the water quality of the Berg River. Monitoring on a continual basis is required, so that there can be more data for long term progress. Key problems that are faced are lack of knowledge and lack of implementation. Many efforts have been attempted such as protection procedures, use of indicator species to gain insight on the quality of rivers, as well as invasive species removal. It is therefore imperative to improve knowledge on these complex ecosystems.

1.2 RIVERINE POLLUTION:

Pollution into rivers has elevated drastically in the past decades and has decreased the water quality tremendously (Carpenter *et al.* 1998). Jeffries and Mills (1990) state that pollutants are able to interact with one another and this often elevates or minimizes the consequences of their toxicity. These pollutants may be transported down a river or may land up on the bottom of the riverbed and build up there (Haslam 1990).

The term pollution is one that is loosely used and has a general meaning. According to Tripathi *et al.* (2006) biologists refer to water pollution as an alteration in the water environment, which results in a decrease in the biodiversity of the habitat and that will consequently degrade the equilibrium of life in lotic ecosystems. Davies and Day (1998) state that pollution can be referred to as the "befouling or contaminating or making offensive to human, animal or plant life". Pollutants may be found in the atmosphere, sediment and water (Gadzala- Kopciuch *et al.* 2004).

Pollution may occur in two ways. Pollution is categorized as point source and non-point source pollution. Point source pollution is defined by being a single source of pollution that can easily be recognized and has a small variability over time (Carpenter *et al.* 1998). This form of pollution includes sources from waste treatment release and storm water runoff (Sliva and Williams 2001). It is frequently examined by determining the release and chemical levels from time to time at a particular area. It can be treated, calculated and regulated at the point where the pollution occurs. Point source pollution has negative effects on the water, but Davies and Day (1998) provide two advantages for this form of pollution. The first one is that one is able to calculate or approximate the amount of pollutants being released. The second advantage is that it is relatively uncomplicated to control.

Non-point source pollution occurs when pollution is released by many sources. Sources include mine seepages, atmospheric pollution and farming runoff (Davis and Day 1998). According to Carpenter *et al.* (1998) non-point discharges are connected to farming activity or events that do not occur often such as a large amount of rainfall or construction activities. It is generally hard to identify as it covers a large surface area of a catchment (Sliva and Williams 2001). Non-point source pollution is generally the largest contributor to water contamination (Carpenter *et al.* 1998).

Water is used to “remove” pollutants or to dilute them. There is generally more than one pollutant in a river (Haslam 1990). The pollutants are then carried downstream or seep into underground water which may be transported to other bodies of water (Carpenter *et al.* 1998). The disadvantage of this is that the pollution moves further away from the individual sources (Jeffries and Mills 1990).

1.3 HEAVY METAL POLLUTION:

According to Dosskey (2001) aquatic pollution results in decreasing water quality for consumption, decreasing the quality of the habitat and consequent sedimentation. Heavy metal output into rivers is of utmost concern globally (Altun *et al.* 2009). By definition, heavy metals “are metallic elements with a density ≥ 5 g/ cm^3” (Schulze *et al.* 2002). These elements include Cd, Cu, Fe, Pb and Zn to name a few. Metals cannot be degraded, as in the case of organic compounds and therefore to remove metal toxicity, it would then need to be “immobilized” (Jadia and Fulekar 2009). Some heavy metals are “essential trace elements” that can occur at higher levels than are required for growth and reproduction (Haslam 1990). Many heavy metals have become familiar contaminants and are indicators of both man-made and natural causes (Kļaviņs *et al*. 2000). Sources of heavy metals in rivers include weathering of rocks, runoff from the river banks and the release of waste from industrial sites (Soares *et al*. 1999).

In particular circumstances, metals may build up to poisonous levels that are ecologically harmful (Altun *et al*. 2009). Heavy metals like Cd and Pb are toxic due to their “strong complexing ability” (Moon and Chae 2007). Lead is very toxic and is accessible to many aquatic organisms such as fish (Fatoki *et al*. 2002). Cadmium is toxic even in small quantities and is often found in aquatic systems at levels that range between 0.1µg/ l and 10 µg /l (Sanders *et al.* 1999). Zinc is more common than Cd. Zn often leads to the release of Cd into the surroundings because Cd is linked with Zn ores (Sanders *et al.* 1999). Zn is needed for metabolic activity in an organism such as fish (Fatoki *et al*. 2002). Zn is unique in the fact that is very toxic to fish but not man (Fatoki *et al*. 2002). Copper is required in small quantities and is important for plant processes such as photosynthesis, seed production and protection against diseases (Jadia and Fulekar 2009).

Pollution of water and sediment by heavy metals is universal (Mowat and Bundy 2001). Heavy metals cannot be broken down and therefore build up in water, sediments, fauna and flora (Miretzky *et al.* 2004). The amount of heavy metals in freshwater affects people who require the water for their daily needs (Miretzky *et al*. 2004). According to Davies and Day (1998) it is hard to determine the definite effects of heavy metals in water due to the toxicity being controlled by various chemical and physical properties. Binning and Baird (2001) state that the heavy metal levels in freshwater (upper, middle and lower reaches of the river) are mostly lower than the levels that occur in the estuary. According to Nicholson *et al.* (2003) sediment is a long-standing “sink” that stores heavy metals. This allows the heavy metals to build up in the sediment over an extended period of time. The consequence of this is that the quality of the sediment and the “maintenance of sediment microbial processes” are greatly decreased. The size of sediment particles can assist in identifying heavy metal sources. According to Sanders *et al.* (1999) when high concentrations of heavy metals are present in finer grained particles of sediment, it is normally linked to pollution, whereas higher levels of heavy metals that occur in coarser particles are mainly from the lithology of the geographical area.

1.4 THE ROLE OF THE SPECIFIC PHYSICO- CHEMICAL PROPERTIES AND ELEMENTS STUDIED IN WATER, SEDIMENT AND PLANTS:

1.4.1 WATER:

1.4.1.1 Physico-chemical variables

Oxygen is a significant property for water quality control (Fatoki *et al.* 2003). It is also essential for all aquatic organisms (Araoye 2009). The lack of oxygen in water reduces growth rate and fecundity of organisms as oxygen is required for metabolic processes (Batuik *et al.* 2009). Oxygen content may be improved during daytime because of photosynthesis, but may decrease at night “with respiratory oxygen demand and may fail to recover the next day” (Madejón *et al.* 2004). According to Harris *et al.* (1992) dissolved oxygen is represented in two ways, namely concentration and as a percentage. In this study concentration as mg/ l was used. The level of dissolved oxygen in rivers that are characterized as unpolluted ranges between 8 to 10 mg/ l (Drolc and Končan 1996, Fatoki *et al.* 2003).

Oxygen and temperature are associated with one another. The ability of a gas to dissolve in water reduces with an elevation in temperature. Therefore if water temperature increases as one moves down a river, it will cause the amount of oxygen to lessen (Townsend 1980). It also affects the “chemical, physical and biological processes in rivers” (Rajele 2004). For instance, the rate of a chemical reaction may increase if the temperature is raised. Not only will the rate of chemical reactions increase, but also the toxicity of heavy metals such as Zn; this in turn causes more organisms and plants to be susceptible to the toxins as temperatures rises (Dallas 2008).

Electrical conductivity (EC) is essentially the measurement of the ability of the water to conduct electricity (Rajele 2004).The more elevated the levels of ions are in the water, the greater the current transported by the water. Ions are direct products of dissolved metals and dissolved matter (Rajele 2004). The EC of water may also be affected by water temperature and also pH. Olias *et al.* (2006) state that if there is an elevation in the pH there is a reduction in the electrical conductivity of the water.

The pH is a physico-chemical characteristic used to determine whether or not the water is acidic or alkaline. According to Morrison *et al*. (2001) pH has a significant affect on lotic systems. If the pH is low it will affect the plants and animals in the river. Acidic pH values (such as 4.5 - 5.8) may cause serious damage to plants (Camargo and Alonso 2006). Low pH values can also lead to the inhibition or change of microbial processes. Heavy metals are generally more soluble at lower OH (Taiz and Zeiger 2010) and therefore the toxicity of the heavy metals can change. Long term monitoring showing changes in pH is an important indicator of modifications in water quality (Harris *et al.* 1992).

1.4.1.2 Elements

Elevated levels of pH (alkaline conditions) causes ammonium to become more poisonous than it would be in acidic conditions (Morrison *et al.* 2001) that cause ammonium to become volatile as ammonia. The presence of ammonium in water systems in their natural state is due to the decomposition of nitrogen containing organic and inorganic waste in sediment and rivers (Facliran and Dube 2009). It may also occur due to gas exchange with the atmosphere and when it is reduced by microbes (nitrogen fixating bacteria). Man made sources of ammonium in the environment include farming practices like the use of fertilizers as well as animal excretions, the food that the animals eat and sewage (Facliran and Dube 2009).

According to de Villiers (2007) inorganic nitrogen in the form of nitrate, nitrite and ammonium ions are nutrients that result in eutrophication when in excess. Nitrate may be derived from farming waste, as well as fertilizers that contain nitrogen (Morrison *et al.* 2001). Nitrate can also originate from waste treatments, as well as groundwater (Naidoo and van Staden 2001). It may also stem from bacterial production, atmospheric deposition (Fenech *et al.* 2012) and irrigation and poor sanitation in densely populated regions (Suthar *et al.* 2009).

The formation of nitrite is due to nitrification of ammonium. This nitrate is then oxidized to nitrate (Jooste and van Leeuwen 1993). The accumulation of nitrite is rare and the reason for this is due to the rapid conversion to nitrate (Jooste and van Leeuwen 1993). Nitrite may be harmful to humans as it is able to come into contact with the blood pigment to create methemoglobinaemia (Legnerova *et al.* 2002), especially in the young and very old.

Cadmium (Cd) is a damaging heavy metal of danger to both plants and animals (Kirkham 2006 and Oste *et al.* 2010). This heavy metal is not required for any biological function within an organism (Pretto *et al.* 2011). It is also a well known ecological contaminant that is commonly dispersed in aquatic ecosystems (Fatoki *et al.* 2004) and is toxic due to the fact that it accumulates in freshwater systems (Pretto *et al.* 2011). Sources of cadmium are from agriculture (Abe 2008), weathering of sediment and rocks, coal burning and runoff from urban areas (Fatoki *et al.* 2004).

Copper (Cu) is a trace element that is beneficial to organisms; however, when found in large quantities, it may be detrimental to the organisms in the environment (Lu and Johnson 1997). Sources of Cu include waste from industrial areas, sewage waste, as well as fertilizers (DWAF 1996, Lu and Johnson 1997). Cu occurs in high amounts in rivers with acidic pH as copper easily dissolves in acidic media (DWAF 1996).

Lead and cadmium are heavy metals that may often hinder the function of necessary nutrients that have similar characteristics to those of zinc and calcium. Lead has a similar charge and shape as calcium and therefore can replace calcium (Nduka and Orisakwe 2011). There is a relationship between pH and Pb; when pH is low the concentration of Pb will be elevated in the system (Fatoki *et al.* 2002). Sewage waste and runoff from both urban and rural settlements are causes of Pb input into rivers

(Fatoki *et al.* 2002). Lead (Pb) is harmful to the majority of living organisms as it affects the nervous- and renal systems and reproductive systems (Jaunakais *et al.* 2010).

Iron is an important nutrient that is required by organisms to grow (Filgueiras and Prego 2007). It comprises 5% of the earth's crust (DWAF 1996) and is commonly found in various rocks and minerals. The availability of this micronutrient is dependant on pH (Vuori 1995). If the pH is high (alkaline) then the iron levels tend to be low and conversely, when the pH is acidic, then iron levels are extremely high (McKnight *et al*. 2001).

Zinc is a necessary element and is required by most living organisms for growth. Anthropogenic sources of zinc include fertilizers and pesticides, as well as degrading tyres (Naito *et al.* 2010). Other sources of zinc include waste water from municipalities and also storm water (Pistelok and Galas 1999). It may also be sourced from mineral weathering, sediment, atmospheric deposition and industrial effluents (DWAF, 1996). The average concentration of zinc in surface water is 3 mg/ l (Fatoki *et al.* 2004).

One of the main sources of potassium (K) is the weathering of silicate rock (Chaudhuri *et al.* 2007). Wastewater also contains K, which comes from a variety of food processing factories, wood processing plants, vineyards, industry and sewage (Arienzo *et al.* 2009). Potassium is required by plants for photosynthesis and protein synthesis (Kanai *et al.* 2011). It is also the primary intracellular cation in organisms and is required in dietary needs (DWAF 1996).

Na together with K are the most significant cations needed for intracellular and extracellular activities of organisms (DWAF 1996). Sources of sodium may come from household products such as soaps, cleaning agents and bleach (Masamba and Mazvimavi 2008). It is commonly found as sodium chloride and is largely found in household waste water because of salt usage in homes. It reacts with water where it produces highly soluble sodium ions (DWAF 1996). Salt in solvent form may change the physical characteristics of rivers by elevating the density (Goodrich *et al.* 2009).

.A large amount of calcium in the water would cause it to be hard, whereas a lower concentration of calcium in water causes the water to be soft (DWAF 1996). Temperature has an affect on calcium (DWAF 1996) and Ca has an influence on the electrical conductivity of water (Ahmed *et al.* 2011). The amount of calcium (and other cations) is the reason why there can be an electrical current within the water.

Magnesium (Mg) is required by both plants and animals. Magnesium influences bacteria adhesion and flocculation of biologically large molecules (de Kerchove and Elimelech 2008). Inputs of Mg are largely in the form of industrial waste (de Kerchove and Elimelech 2008). Magnesium may also be introduced into a system from silicate and carbonate rocks that have weathered (Pogge von Strandmann *et al*. 2008). It is also found in fertilizers, food and pharmaceuticals (Masamba and Mazvimavi 2008).

Phosphorus is generally found in short supply in surface water, but due to urban expansion and rapid agricultural offloading, P has increased dramatically within river systems (Withers and Jarvie 2008). Phosphorus causes the rapid growth of phytoplankton and with nitrogen causes eutrophication (Withers and Jarvie 2008). The result of intensification of P decreases the amount of oxygen in a river, which may cause fish and other species of animals to perish (Cornell 1998, Withers and Jarvie 2008). Sources of P may stem from the atmosphere, from plants found along the river and from sediment material or may be introduced by man through urban and agricultural runoff as well as wastewater effluent and street runoff being released into rivers (Withers and Jarvie 2008).

1.4.2 SEDIMENT

1.4.2.1 Physico-chemical variables

EC is controlled by a variety of factors such as salts, the amount of water in the sediment as well the minerals present within the sediment and the temperature of the sediment (Brevik *et al*. 2006). EC is an indicator of elevated nutrient status and also functions as a way in which one can measure soluble nutrients in soil (it can measure both cations and anions in the soil) (Eigenberg *et al*. 2002). The variations in the river and the sediment EC are proportional to one another (Verma and Saskena 2010).

The pH is a significant property that controls the movement of metals in sediment (Peng *et al*. 2009). Many heavy metals are more mobile in highly acidic environments (Schulz-Zunkel and Krueger 2009). It also has a primary affect on the sediment nutrient condition and that of the surrounding water (Verma and Saskena 2010). According to Peng *et al*. (2009) a reduction of pH in sediment generally leads to the competition for ligands by heavy metals and hydrogen ions. Following this, there is a reduction in adsorption capacity and the bioavailability of heavy metals, causing the metals to become more mobile (Peng *et al*. 2009).

1.4.2.2 Elements

Nitrogen is an important nutrient and contributes to sediment fertility (Verma and Saskena 2010). The number of plants or plant biomass may increase due to an elevation in N amounts (Camargo *et al.* 2005). Nitrogen is commonly known as the most limiting nutrient needed by plants (Spargo *et al*. 2011). This may be due to the complete flushing of nitrogen through the rainy season, as well as the possibility of leaching of N to lower sediment profiles.

Cadmium is highly mobile in sediment (An 2004). A large amount of Cd present in the sediment may be due to zinc ores, where Cd is found naturally in large quantities with Pb (Akkajit and Tongcumpou 2010). Cd normally remains in the sediment solution, however if the pH in the sediment is reduced then the concentration of Cd in a plant rises (Kirkham 2006). Cadmium may remain available to plants in the sediment, due to the adsorption of Pb by soil which is preferred over Cd (Akkajit and Tongcumpou 2010).

Copper is normally found in the sediment surface not exceeding 15 cm down the sediment profile (van Aardt and Erdmann 2004) and is present naturally in sediment (Mouta *et al*. 2008). It is the metal that is the least mobile in sediment (Akkajit and Tongcumpou 2010). Copper that is readily accessible in sediment is influenced by the wetness of the sediment, other elements that are present in the sediment with it and sediment organic matter (Wu *et al.* 2011). Elevated pH of the sediment causes elevated concentrations of accessible copper (Wu *et al.* 2011).

When lead is present in sediment, it becomes less mobile (Brown *et al*. 2008). According to Martínez-Villegas *et al*. (2004) lead is able to replace calcium and potassium and it can interact with sediment components. Lead is present in sediments at levels that range between 1 mg kg^{-1} to 200 mg kg^{-1} (Chirenje *et al*. 2004).

Iron is one of the common metals (Karlsson *et al*. 2008). Iron availability and the various ways in which it can exist in ion form is dependant on pH and redox potential (Veado *et al*. 2000). Acidic pH is known to encourage the solution of iron. Alkaline pH of the sediment enhances the production of iron oxides (Khan *et al*. 2010).

Zinc is closely associated with cadmium in the sediment (Kirkham 2006). When concentrations of zinc are low, plants absorb more cadmium from the sediment (Kirkham 2006). Zinc and cadmium contend for adsorption on sediment components (Lambert *et al*. 2007).

Potassium is abundant in many types of sediment, but only a small portion is accessible to crops (Ghosh and Singh 2001). The amount of potassium in the sediment ranges from 0.04 % to 3.00 % (Ashley *et al.* 2006). The exchange of potassium in various kinds of sediment is influenced by other macronutrients that occur in the sediment (Ghosh and Singh 2001).

A buildup of salts occurs in sediment, when plants only take up small quantities of Na (Berthrong *et al*. 2009) and the buildup of Na specifically causes the exchangeable sodium percentage in the sediment to decrease, in regards to water penetrating the sediment and water retention in sediment (Walker and Bernal 2008). The amount of sodium in the sediment is associated with the amounts calcium and magnesium (Sarah 2004).

Calcium is known to enhance activity of bacteria present in sediment that are responsible for the fixation of nitrogen and or the production of nitrate (Verma and Saskena 2010). A lack of Ca is normally related to acidic conditions, which in turn results in the buildup of poisonous salts of iron in the sediment.

A shortage of Mg often occurs in low pH sediments and coarse textured sediments (Senthurpandian *et al*. 2009).The amount of Mg in sediment is often lower than the concentration of Ca in the sediment.

The quantity of phosphorus lost to the water above sediment rises with the phosphorus content of the sediment (Carpenter *et al.* 1998). According to Kulhánek *et al*. (2009) the amount of phosphorus in sediment is generally lowest in sediment solution. Soil that contains a large amount of P may be due to a continuous application of fertilizers and manure onto the land (Verma and Saskena 2010).

1.4.3 PLANTS

1.4.3.1 Elements

According to Hultine *et al*. (2008) the quantity of plant accumulated nitrogen may be associated with the level of N in surface and groundwater, as well as mineralization in sediments. Nitrate is the most significant source of N for plants (Chen *et al*. 2008) and plants that are found in sediments with an acidic pH normally take up N in this form (Maathuis 2009). Buskiene and Uselis (2008) state that N promotes the growth of plants and N may influence plant characteristics like the quality, production and the number of leaves, as well as roots, and the rate of decay of senesced leaves (Drake *et al*. 2008).

Cadmium in plants is able to build up to high concentrations, which are poisonous to animal life, yet may cause little harm to the plants (Pinto *et al*. 2004). When cadmium concentration does reach toxic levels for the plants, it results in stunting and chlorosis (Stout *et al*. 2010) and it is also able to deactivate enzymes in plants, which leads to slowing down processes such as photosynthesis (Pinto *et al*. 2004). Other elements such as iron are able to minimize the amount of Cd uptake by plants (Peralta-Videa *et al*. 2009).

Copper is an important element that is necessary for plant metabolism (Shi *et al*. 2011), and pigment substances within a plant (Olette *et al*. 2008). Its concentration in plants can be promoted if there is a lack of iron and zinc uptake, whereas a large amount of Cu may inhibit Fe and Zn uptake into the plant (Shi *et al*. 2011). A toxic concentration of Cu leads to chlorosis, as well as inhibition of cell division. Copper toxicity also leads to the reduction of electron flow in the oxygen-evolving complex and slows down the photosynthetic ability of vegetation (Olette *et al*. 2008).

Lead is regarded as having a low solubility and accessibility for plant absorption as it is able to precipitate (Peralta- Videa *et al*. 2009). Lead toxicity may cause inhibition of germination in seeds, plant growth and chlorophyll production (Peralta- Videa *et al*. 2009). It is also able to inhibit mitosis and may cause wilting (John *et al*. 2008). A large amount of Pb in a plant may cause a disruption in mineral nourishment (Pb has the ability to inhibit the uptake of Ca and Fe) (Sharma and Dubey 2005).

Iron is a nutrient required by plants for processes such as respiration and photosynthesis (Kim and Guerinot 2009). Another important role of iron is that it is a cofactor for some enzymes and it is required for chlorophyll production (Jeong and Connolly 2009). A large amount of Fe is found within sediment, but many times, plants lack Fe, as it has a low solubility (Ma and Ling 2009). The amount of iron that is unacceptable for crops is if it reaches a level of more than 20 mg/ kg^{-1} in the sediment (Majerus *et al*. 2007). The symptoms of iron toxicity include stunting and an excess manufacture of ethylene in crops and it may also cause a decrease in Ca, Mg and P (Majerus *et al*. 2007).

Zinc is a micronutrient that is necessary for plant metabolism (Durand *et al*. 2010). It is needed in some enzymes and has a significant role in DNA transcription (Jadia and Fulekar 2009). If levels of Zn are low within the sediment it causes plants (such as the tomato plant for instance) to have stem growth problems (Broadley *et al*. 2006) as well as chlorosis in leaves (Jadia and Fulekar 2009). An overload of zinc causes heavy metals to be moved from active sites on proteins, minimizes the tissue water content and alters the P and Mg content in plants (Sagardoy *et al*. 2008).

Potassium is one of the most common elements found abundantly in the cells of plants (Britto and Kronzucker 2008). It is needed for maintaining electrical potential gradients across the cell membranes, production of turgor and enzyme activation (Britto and Kronzucker 2008). The addition of K significantly raises the N and P absorption by plants (Rani and Jose 2009). The functions of potassium in vegetation include moving photosynthates into the sink organs and decreasing excess absorption of Na and Fe in inundated soils (Cakmak 2005).

The presence of sodium in large concentrations within plants causes a reduction in growth, the leaves become damaged, and normally this is evident in more mature leaves (Blumwald *et al*. 2000) and it is the leading cause of ion-specific harm (Zhang *et al*. 2010). Sodium and potassium ions contend for entrance into the plant, as they are alike in ionic structure (Zhang *et al*. 2010). Plants normally prefer the uptake of K over Na (generally the concentrations of K are higher than Na within a plant). The concentration of calcium ions in the sediment has the ability to adjust the amount of sodium ions taken up by a plant and is able to prohibit a toxic buildup of sodium within a plant (Melgar *et al*. 2006).

Calcium is important for plants and is involved in many aspects of a plant's growth. It is needed in large concentrations and calcium ions are able to help a plant to respond to light, temperature, salt and plant hormones (Kudla *et al*. 2010). The lack of calcium within a plant may be due to large concentrations of potassium and magnesium (Chaney *et al*. 2008). High amounts of calcium stop seeds from germinating and minimize the development of the plant (White and Broadley 2003). The optimal level of calcium in the leaves of vegetation is about 5 g kg^{-1} (Chaney *et al*. 2008).

Plants need magnesium for photosynthesis (Hermans *et al*. 2010). It aids in the activation of approximately 300 enzymes and is needed for synthesis of organic molecules that are necessary for plants to grow (Bolou- Bi *et al*. 2010). One of the key roles of magnesium is coupled to its function in chlorophyll, where it is the central point (Bolou- Bi *et al*. 2010). A lack of Mg within a plant may lead to chlorosis in leaves (Cakmak and Kirkby 2008), chlorophyll decay between veins (Hermans *et al*. 2010) and a decrease in stomatal conductance (Cakmak and Kirkby 2008). Toxic levels of Mg in plants may damage photosynthesis by slowing down K transport (Cakmak and Kirkby 2008).

Phosphorus is a large contributor in aiding the establishment and production of alien species (Fisher *et al.* 2006). Alien vegetation normally has higher concentrations of P than indigenous species (Fisher *et al.* 2006). The growth of herbaceous species occurs rapidly when compared to that of woody species (Fisher *et al.* 2006). Mainstone and Parr (2002) discuss four possible ways in which increased P levels can influence riparian vegetation. The first way that the authors describe is by an elevation in the growth rate of vegetation. The second way is by the promotion of vegetation species that rely on larger nutrient concentrations and this in turn modifies “species composition or balance”. It can also affect riparian vegetation by promoting algal growth and therefore decreasing the amount of solar radiation that penetrates the water. Algae hinder seed germination and growth of seedlings. Lastly, P can also affect riparian vegetation by decreasing the penetration of the roots (into the sediment) and this causes the plants to be easily removed when the velocity of the river is high. Toxic levels of P in a plant may cause necrosis of leaves and death (Lambers *et al*. 2008).

1.5 NUTRIENT AVAILABILITY AND EUTROPHICATION:

The amount of nutrients that occur in river ecosystems has increased due to farming activities and also because of domestic waste (de Villiers 2007). Gregory *et al.* (1991) explain that these nutrients are moved from land ecosystems into the rivers or into streams and pass through riparian vegetation rooting areas. The “sediment solution” first moves into the rooting zone before it passes into the river. Vegetation along river banks provides seasonal leachates into rivers. Gregory *et al.* (1991) states that because of seasonal leachates, the river bank community greatly alters the quantity and timing of nutrient export.

Inorganic nitrogen (N) and phosphorus (P) amounts in rivers arise from natural and man-made causes. Nutrient enrichment in the form of N and P are in part due to farms (de Villiers *et al.* 2007). Fertilizers contain large amounts of N and P that build up in the sediment. “The amount of P lost to surface waters increases with the P content of the sediment” (Carpenter *et al.* 1998). Jeffries and Mills (1990) explain that N and P are used to increase crop production. The applications of N and P to crops are often mismanaged and the fertilizers cause the excessive amounts to land up in the water and not the crops. The number of plants or plant biomass may increase due to an elevation in N amounts (Camargo and Alonso 2006). Large amounts of nutrients are discharged from sewage management plants constructed to remove organic effluents (Jeffries and Mills 1990).

Eutrophication results from an increased input of P and N into rivers (Carpenter *et al.* 1998). This process develops when the habitat is no longer able to “buffer” against an extreme amount of nutrients that enter the system, particularly that of P (Jeffries and Mills 1990). This has negative impacts on freshwater systems. It causes an elevation in the growth of algae and invasive plants that in turn has an impact on the water in terms of increase in eutrophication. Carpenter *et al.* (1998) state that cyanobacteria are well-known indicators that eutrophication is occurring. Smith (2003) states that cyanobacteria can decrease the quality of water. When cyanobacteria prevail in big rivers, it is predicted in most cases to be due to an increase in P (Smith 2003). This also has an effect on deep water oxygen, which becomes exhausted when eutrophication occurs (Smith 2003) and ultimately this decreases the water quality of rivers.

1.6 RIPARIAN VEGETATION AND ITS ROLE IN FRESHWATER ECOSYSTEMS:

Riparian plant life plays a significant role in maintaining ecosystem function. It decreases the possibility of erosion, promotes nutrient storage and provides an environment in which organisms can live and reproduce (Castelli *et al*. 2000). It also reduces the velocity of floods and is important for its role in bank steadiness, particularly when alien plants are removed (Sieben and Reinecke 2008). Riparian vegetation is able to retain water and this therefore raises evapotranspiration and groundwater recharge (Esler *et al.* 2008). It also serves as natural fire breaks and supplies corridors for distribution and mobility of fauna and flora.

Riparian vegetation also provides oxygen, regulates organic material flow, as well as the equilibrium of the sediment and sediment that falls onto the river bed (Gadzala-Kopciuch *et al.* 2004). These plants are “sensitive indicators” of the surroundings in which they occur. Haslam (1978) states that the vegetation found in an area where pollution occurs can provide a substantial amount of information about that area. The amount of metals and toxins that the plants take up are considerably higher than that amount found in the water (Miretzky *et al.* 2004).

Jadia and Fulekar (2009) state that plants have adapted three ways that enable them to tolerate heavy metal toxicity. Exclusion is the process by which the movement of metals is limited and steady metal levels are maintained in the shoots. Inclusion occurs when the shoot metal levels mirror the metal levels in the sediment in a “linear relationship”.

The last process is known as bioaccumulation. This process occurs when metals build up in the roots and the aerial parts of the plants at both elevated and minimized levels. Plants take up metals from the water and sediment into the roots (Haslam 1990). A lot of plants accumulate metals and trace elements in the upper parts of the plant, especially the leaves and the absorption of the concentration of the trace elements and heavy metals is dependent on the species of plant and the particular metal being taken up (Madejón *et al.* 2004).

When pollutants accumulate in plants, the toxicity of these pollutants are reduced. The presence of "microflora" on roots allows various metals to be absorbed and changed in the plant (Haslam 1990). These metals are then accumulated in various organs of the plant and the accumulated pollutants are degraded during the process of oxidation (Haslam 1990). Miretzky *et al.* (2004) state that the degree to which metals are adsorbed and where they are found in the plant has a significant influence on the ability and speed of the elimination of the metal. The plants are essentially filters and purifiers of both water and sediment (Haslam 1990).

1.7 THE RELATIONSHIP BETWEEN WATER, SEDIMENT AND PLANTS:

Land found adjacent to a river that has an interaction with the river and connects water pathways with runoff are known as riparian zones (Dosskey *et al.* 2010). This boundary between land and water is sensitive to changes in the environment (Naiman and Décamps 1997). Riparian zones are known by the well developed floodplains, a wide variety of vegetation and wet soils (Naiman and Décamps 1997). These riparian zones have a significant role in controlling the water and chemical exchange between the terrestrial and aquatic systems.

There is a significant link between water nutrient content and sediment and riparian vegetation (Castelli *et al.* 2000). Sediment characteristics, such as the physical, chemical and morphological ones, are strongly associated with both plant distribution and hydrological regimes. Sediment determines the chemical properties of plants and surface water. Topsoil characteristics direct water motion and the ability to retain water and manage the amount of water that the riparian communities receive (Nilsson and Svedmark 2002). Soil is able to retain water and this also affects the distribution of riparian plants (Naiman and Décamps 1997).

Rivers receive particulate and dissolved material from sediment (Townsend 1980). Arrays of elements are found in freshwater and this influences the kind of vegetation that occurs there. Plants also change many characteristics of the river body, like temperature and by sediment trapping (Jeffries and Mills 1990). The motion of water has a great influence on plants (Haslam 1978). The movement of water replenishes the plant with necessary oxygen (for respiration) and carbon dioxide (for photosynthesis) required for the plants biological processes (Haslam 1978).

The water chemistry can be influenced by riparian plants. This may be due to the chemical absorption and nutrient cycling by the plants or by providing detritus to soil (Dosskey *et al.* 2010). Aquatic plants change the river system through their development and metabolic activity (Madsen *et al*. 2001). When plants are able to colonize an area they can often reduce the velocity of the current. The plant roots are found within soil and young soil is made by decomposing plants or roots, which ultimately influence the chemical quality of soil water (Dosskey *et al.* 2010).

According to Dosskey *et al.* (2010) in river systems where soil is wet, the decay of plant detritus uses up the oxygen supply found within soil that is required by roots of the vegetation. The absorption of nutrients by plants influences the amount of nutrients within the river (Dosskey *et al.* 2010). The hydrology of an ecosystem is the main reason for the types of vegetation found in an area. The way in which vegetation, the roots of the vegetation and plant debris is distributed within the riparian zone and the river is what drives the relationship between riparian plants and water (Dosskey *et al.* 2010).

1.8 DAMS AND ENVIRONMENTAL IMPACTS ON RIVERS:

Dams are often built to lessen water shortages. It is thought that there are approximately 42 000 large dams and 800 000 small dams across the world (Freeman 2003). Dams are valuable structures for the management, as well as storage of water. The bigger dams are important for economic value and social development and offer significant functions like electricity production and flood management (Wei *et al*. 2009). Although dams provide economic and social advantages, the construction and structure of dams causes negative impacts on the river ecosystems.

Negative impacts caused by dams:

Nutrients, heavy metals and water temperature changes:

Dams are able to change the nutrient and heavy metal content, as well as water temperature. Richardson *et al.* (2007) provide an example of a dam that catches fine sediments and nutrients that are carried by floods, causing modifications in the lower areas of the river. This is due to the buildup of elements in the dammed water, which has a longer standing period than that of flowing water (Wei *et al*. 2009). It further disrupts the movement of organic materials and heavy metals (Wei *et al*. 2009). Nutrient overload in the dammed area not only reaches the river by flooding but also by decomposition. When a dam is constructed, the amount of water increases and floods the land and riparian zones (Nilsson and Berggren 2000). This causes the vegetation that is not adapted to such a disturbance to decompose. The chemistry of rivers is altered and becomes more acidic because of the decay of plants (Allan and Flecker 1993). Animals may also perish with the large volume of water, also decomposing and releasing nutrients (Nilsson and Berggren 2000). Organic matter in soils that have been inundated with water may also decompose, liberating P and N, which may increase eutrophication. The water temperature is increased by dams, as a variation is normally present between the water found above the dam and the water that is released from the dam (Hancock 2002). The changes in temperature cause changes in the kinds of vegetation found in the ecosystem, impacting the exchanges that are required between leaves and root areas (Hancock 2002).

Hydrology:

Many rivers are altered by damming in terms of modified flow. A dam changes the rivers arrangement and flow (Wei *et al*. 2009). The amount of water flowing and speed of the water are affected by dams and these factors are then limited in terms of its role in water cleansing. The amount of water released downstream is reduced. In some instances large decreases in flow influences the water temperature by minimizing the capacity for retaining heat (Poole and Berman 2001).The amount of water released changes the morphology and geomorphology of the area (Poole and Berman 2001). Dams alter geomorphology through altering sediment cycling (Nilsson and Berggren 2000). The dam lake accumulates large amounts of sediments that were formerly carried to lower reaches of the river. When water is discharged, the river below the dam is more prone to erosion. This causes channels to be simplified and alters geomorphology in the river bed (Nilsson and Berggren 2000).

Riparian communities:

The changes caused by dams (nutrients and heavy metal status and hydrology) have serious implications for plants. Many species are adapted to rivers and may become locally extinct as the flow of the river changes. The first sign of stress to plants subjected to inundation occurs in the roots (Nilsson and Berggren 2000). The soil is saturated with water and therefore becomes oxygen depleted, which causes the plant to undergo oxygen stress (Nilsson and Berggren 2000). Mantel *et al*. (2010) state that species of riparian plants experience changes in habitat structure due to sediment that accumulates. Sediment is trapped within the dam, causing sediment depletion downstream. The lack of sediment causes difficulty in root systems of plants to establish themselves in the soil. This and flow also have a negative impact on the ability of seeds to germinate, especially seeds that are not adapted to dispersal by floating in the water.

1.9 AIMS AND OBJECTIVES

The aim of this study was to investigate water quality, including heavy metal pollution in the water and riparian vegetation of the Berg River.

1.9.1 Research objectives:

The main objectives of the study were:

- To determine water quality of the Berg River in terms of nutrients and heavy metals, as well as selected physico- chemical properties of the river,
- To assess the heavy metal accumulation of *Salix* sp., A*cacia mearnsii* and *Brabejum stellatifolium* for possible use as indicator species.

1.9.2 Research Questions:

- What are the main sources of pollution in the river?
- Are there heavy metals present in the Berg River that are significantly high in both water and plants?
- Which of the above plant species accumulates the highest concentrations of heavy metals in its leaves?

CHAPTER 2

Monitoring water quality and pollution in the upper Berg River

2.1 THE BERG RIVER LOCATION AND CHARACTERISTICS:

The Berg River occurs in the Western Cape, South Africa. It originates in the mountains above Franschhoek, at 1500 masl and declines to 180 masl at the convergence with the Franschhoek River (Luger 1996). It extends for a length of 285 km and includes at least sixteen tributaries. The river drains an area of about 8980 km^2 (Anon. 2004). The river flows northwards, through the towns of Paarl and Wellington as well as passing near Gouda, Piketberg and Hopefield (Luger 1996) (Figure 2.1). The largest modification that occurred to the river from the 1930's up until now is that the “braided systems” that flowed near Franschhoek and Paarl cannot be found there anymore (Anon 2007). This is due to the isolation that weirs and levees cause, which prohibits flooding of the land away from the main system. This area is currently farmland, which channeled the river into a single system.

This catchment provides much of Cape Town’s water and also provides irrigation along the length of the river (de Villiers 2007). At least half of the catchment is used for farming (de Villiers 2007). The drainage area lies within the winter precipitation portion of the south-western Cape (Anon. 2004). The amount of evaporation is far higher than the amount of rainfall, across the catchment, but despite this, the catchments “water budget” is dominated by runoff (de Villiers 2007). The geology of the upper region is largely Table Mountain Sandstone and here the river is fast flowing. This type of geology is “well weathered” and the rocks are dated to the Ordovician age (between 488- 443 million years ago) (Anon 2005) and this is the reason as to why these rocks leach very few ions (Anon 2007). The river flows slowly through shale in the middle reaches and there is an extensive estuary. According to Davies and Day (1998) the Berg River has been exposed to degradation by a variety of causes since the 1950's. This includes the input of excessive amounts of nutrients from farming runoff, return flows from effluent stemming from waste water treatment plants, from industries and from vineyards. The Berg River has also been exposed to degradation by alien species of both aquatic and riparian fauna and flora and also largely due to informal settlements found near or on the banks of the river and the input of pollution it brings (Davies and Day 1998).

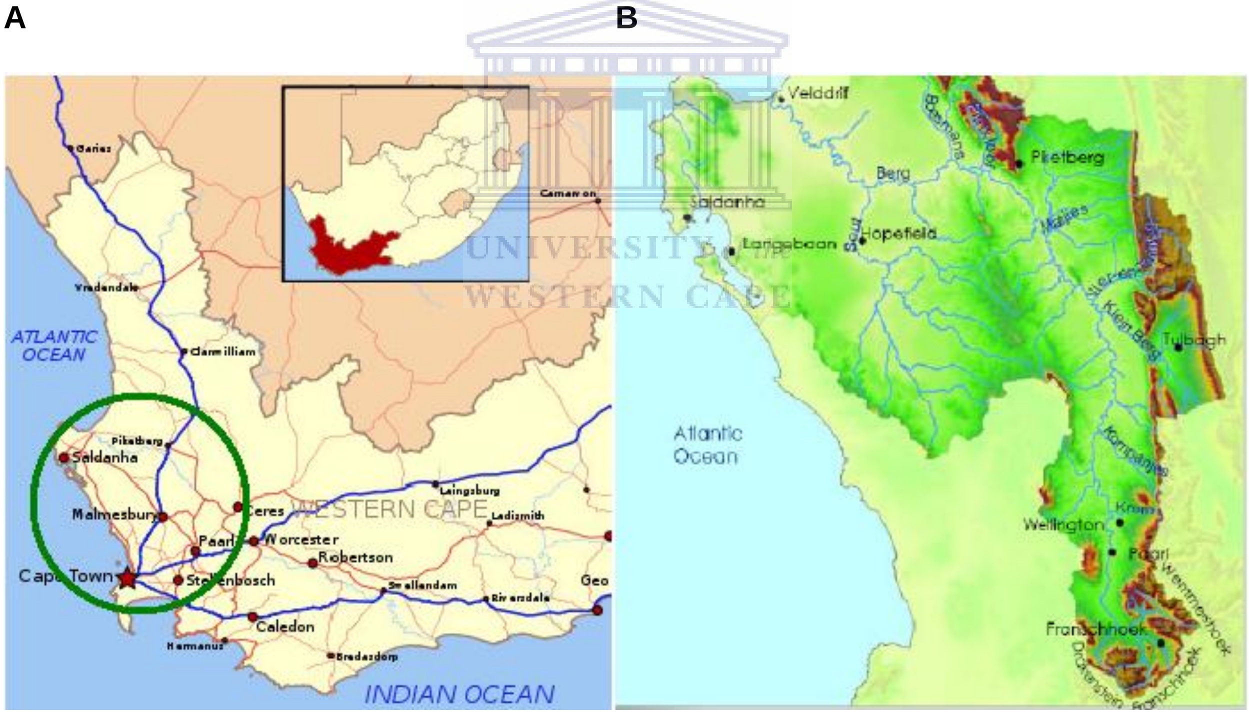


Figure 2.1. A: A map of the Western Cape, indicating the Berg River location in the green circle. B: The Berg River drainage area (DWAF 2004).

2.2 CHARACTERISTICS OF THE STUDY AREA:

Ten sites were chosen along the upper reaches of the Berg River for the purposes of this study (Figure 2.2 and Table 2.1).

Figure 2.2. The locality of the Berg River sampling sites (Google Earth).

The study area was determined by taking sampling areas along the river over a 30 km stretch. Ten locations were sampled from the source of the river to the Paarl area. The first two (B 1 and B 2) and second last (B 9) sampling sites correspond with the Berg River dam baseline research monitoring sites. In this study the sites are called B 1, B 2 etc.

2.2.1 Berg River 1 (B 1):

The Berg River Baseline Monitoring Programme (BMP) has aimed to describe the status of the Berg River prior to the construction of the Berg River Dam. Berg River 1 (B 1) site is one of the official monitoring sites (termed Berg River Monitoring Site 1- BRM 1). The river bank has been stabilised where the fynbos vegetation is found. Alien vegetation has been cut and burnt extensively and therefore riparian fynbos has been able to cover the banks of the river again. The mountains have also been cleared of alien vegetation, which has been cut and burnt. Remains of pine trees are still evident. This site was chosen as it is above most human activity, and is one of the BMP official sites.

2.2.2 B 2:

It is situated just below the Berg River Dam. It contains many herbaceous and woody species of fynbos. The water at this site is fast flowing due to the release of water from the dam. The alien vegetation has been removed and the fynbos is returning. This site is also an official monitoring site i.e. BRM 2.

2.2.3 B 3:

The site below the Franschhoek tributary shows signs of human activities or remnants thereof. Not many fynbos species occur on the site, but many *Acacia* plants are present and *Brabejum stellatifolium* is clumped on the riverbank. The Waste Water Treatment Works (WWTW) in Franschhoek (treats 73 000 cubic metres per year) releases treated effluent water into the Franschhoek River (Anon 2004). The Berg River and the polluted Franschhoek River have converged and are joined at this site.

2.2.4 B 4:

The fourth site is found below the Wemmershoek tributary. The sampling site is a farm known as La Chanelle farm. Clearing of all vegetation along the riverbank has occurred, as well as burning of vegetation along the banks of the river. Large, dense masses of *Myriophyllum heterophyllum* occur along the banks of the river. Compared to many of the other sites, few fynbos species occur here. The alien vegetation has been removed from the site. On the adjacent side of the river a pipe outlet releases water into the river. The WWTW in Wemmershoek (treats 36 500 cubic metres per year) releases treated effluent water into the Wemmershoek River (Anon 2004).

2.2.5 B 5:

Site five occurs below the Dwars tributary and is known as Bieun Donne farm. This site lies adjacent to an experimental agricultural farm. Most of the vegetation, both indigenous and alien has been removed. There is a concrete drift across the river. The water flows over this when the river is full. The area contains lush vegetation. The

Dwars Tributary produces 28 % of the runoff for the Berg River (Anon 2004). There are WWTW that discharge effluent into this tributary.

2.2.6 B 6:

Site six is Simondium which is a large arable farm. There is much alien vegetation such as *Acacia mearnsii*, *Typha capensis* and *Phragmites australis* along the river. The water contains rusted metal and some litter. The water is fast flowing, the bed sandy and has dense vegetation. The riverbank has been altered by bulldozing, destroying parts of the banks, causing erosion and destroying many of the plants that occurred there.

2.2.7 B 7, B 8 and B 9:

Site seven is at a horse ranch (Dieu farm), where the water is fast flowing and dense masses of alien vegetation occur along the river bank. In between site seven and site eight, there is a resort and camping site where sewage could possibly be illegally discharged into the river. The eighth - and ninth - sites are both deciduous fruit farms, where alien vegetation was considered a large problem and was removed by “Working for Water”. Lindenhof farm is the eighth site and Firwoods farm is site nine. A golf course is adjacent to site nine, where surface runoff from fertilizers and pesticides flow into the river system increasing water pollution.

2.2.8 B 10:

Site ten is at a recreational park in Paarl (Paarl Arboretum). It occurs adjacent to a road and next to it is a vineyard. The river has been channelized. All alien vegetation has been removed. The WWTW situated in Paarl releases treated effluent water (16 million cubic metres per year) into the Berg River (Anon 2004) but it is located below this site.

2.3 MATERIALS AND METHODS:

Sampling commenced in February 2009 and was conducted at the ten sites described above (Figure 2.2). The Berg River sampling sites stretched over an approximate 30 kilometres from above Franschhoek to Paarl.

Table 2.1. List of sampling sites across the Berg River.

Sites	Description	Coordinates	
B 1	Above the dam	S33.95646	E19.07270
B 2	Below the dam	S33.89977	E19.05296
B 3	Below Franschhoek tributary	S33.87805	E19.03524
B 4	La Chanelle Farm	S33.87577	E19.01863
B 5	Bieun Donne Farm	S33.83994	E18.98460
B 6	Simondium	S33.82481	E18.96481
B 7	Dieu Farm	S33.80527	E18.95595
B 8	Lindenhof Farm	S33.79082	E18.96880
B 9	Firwoods	S33.76944	E18.97669
B 10	Paarl Park	S33.74803	E18.96789

2.3.1 FIELD PROCEDURES:

Samples were taken during the months depicted in Table 2.2. The seasons in which the months occur are important, as seasonal changes of the weather have an effect on inorganic pollution in the river.

Table 2.2. The months of data sampling, as well as the season in which sampling occurred along the river during 2009 and 2010.

Month	Year	Season	Day of Sampling
February	2009	Summer	0
March	2009	Autumn	31
April	2009	Autumn	59
June	2009	Winter	120
June	2009	Winter	141
August	2009	Winter	175
September	2009	Spring	218
October	2009	Spring	252
December	2009	Summer	295
January	2010	Summer	352
February	2010	Summer	378
April	2010	Autumn	415

2.3.1.1 WATER SAMPLING:

The oxygen content and temperature of the water were determined *in situ* using a YSI Model 55 Oxygen and Temperature Meter. The temperature of rivers differs due to response to the different temperatures of the sediment and of the air (Townsend 1980). A Metrohm Conductivity Meter was used to determine the electrical conductivity of the water. Electrical conductivity is an “indicator” of the salt concentration of the water (Morrison *et al*. 2001). A large amount of salts causes high salinity and causes water to become “brackish” (Morrison *et al*. 2001). Water samples were collected in 300 ml plastic bottles. The water samples were filtered using Whatman number 42 filter paper and were preserved by placing them in a refrigerator in the dark at 4 ºC to prevent algal growth. The samples were analyzed after the very last month of sampling.

2.3.1.2 SEDIMENT SAMPLING:

The sediment was sampled during the wet and dry seasons, near the river bank at each site. This occurred during the wet season (August 2009) and dry season (April 2010). The sediment was collected using a garden trowel and placed in a zip lock bag, then dried and stored in a cool area until all other samples were collected in the twelve month period. The sediment was dried at ambient temperature (air dried) and sieved (through a 2 mm sieve) to remove larger plant and sediment particles.

2.3.1.3 PLANT SAMPLING:

Leaf samples from alien and indigenous species (*Salix* sp: Figure 2.3., *Acacia mearnsii*: Figure 2.4 and *Brabejum stellatifolium*: Figure 2.5) were taken, once a month at the ten sites adjacent to the river. Large, mature leaves from various branches were placed into brown paper bags. Mature leaves were preferred over young leaves, as the leaves contain more nutrients and show which nutrients may have accumulated in the plants for a longer period of time and this may be due to water relations within a plant that corresponds to the age of leaves (Tomašević *et al*. 2008). Some 20 to 25 leaves were collected from each site. Table 2.3 indicates which species occurred at each site. The indigenous species *Brabejum stellatifolium* has sclerophyllous leaves (Marschner 1995).

Table 2.3. The Berg River sites and the plant species found along the river.

Description	***Salix* sp.**	***A.mearnsii***	***B.stellatifolium***
Above the dam		√	√
Below the dam		√	√
Below Franschhoek tributary		√	√
La Chanelle Farm		√	√
Bieun Donne Farm	√	√	√
Simondium	√	√	
Dieu Farm	√	√	
Lindenhof Farm	√	√	
Firwoods	√	√	
Paarl Park	√	√	

Figure 2.3. ***Salix*** **sp. a common riparian species found along rivers.**

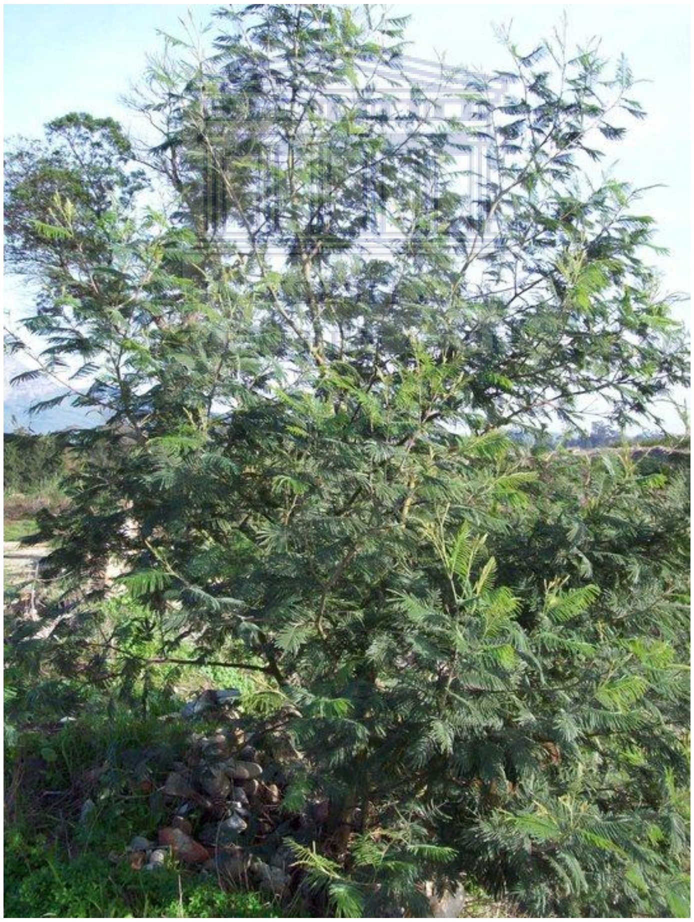


Figure 2.4. ***Acacia mearnsii*** **an invasive species.**

Figure 2.5. Indigenous species *Brabejum stellatifolium,* endemic to the Western Cape found here along the bank of the Berg River.

2.4 LABORATORY PROCEDURES:

2.4.1 WATER:

The filtered water samples were tested for ammonium, nitrate and nitrite, using Aquamerck reagent kits (with a resolution of 1.0%). The pH was determined using a Radiometer PHM 64 Research pH Meter. Reduced pH has an influence “on the dissolving or sedimentation of heavy metals” (Levkov and Krstic 2002). Analysis of cadmium, copper and lead, as well as iron, zinc, potassium, sodium, calcium and magnesium present in the water was carried out with a Unicam Solaar M Series Atomic Absorption Spectrophotometer (AAS). Phosphorus concentrations were obtained by using an ICP Spectrometer (Thermo, iCAP 6000 series) at Elsenburg: Institute for Plant Production Laboratory.

2.4.2 SEDIMENT:

The sediment pH was determined using the sticky point method (Tan 1996). It is known as the sticky point method because a small amount of water is added to the sediment until it reaches a point where it will stick to a surface. The sticky point method required 100 g of dried sediment that was weighed, distilled water was added and stirred to make it into a paste consistency. After 10 minutes, measurements were taken with a Radiometer PHM 64 research pH meter. The conductivity of the sediment was also determined by using the sticky point method with a YSI Model 35 Conductance Meter.

Sediment digestion took place by utilizing the aqua regis solution, 3:1 HCL: HNO_3. One gram of dried sediment was inserted into a digestion tube, which contained 12 ml of the 3: 1 HCL: HNO_3 digestion solution. The sediment samples were placed in a heating block for three hours at 110 °C. When the solution was evaporated to near dryness, the tubes were left to cool and were diluted by using 20 ml of 2 % (v/v with H_2O) nitric acid. The solution was then filtered using Whatman number 42 filter paper and made up to 100 ml with distilled water in a volumetric flask.

Total nitrogen was determined by using the Kjeldahl distillation and titration method (Bremner and Mulvaney 1982). Five ml of the digested samples were used. The distillate was titrated with 0.01 N HCL, where N is the normality. The nitrogen percentage present was calculated as follows:

$$\%N = (\text{Vol. ml HCl} - \text{blanks average ml HCL}) * \text{NHCl} * 14007 / \text{sample mass (mg)}$$

(Moore and Chapman 1986)

2.4.3 PLANTS:

Leaves were rinsed in distilled water and oven dried at 70 ºC. The plants were milled (using a Wiley Mill), 0.4 g was weighed into cigarette paper and digested using 4.4 ml of a sulphuric-peroxide solution (Allen *et al*. 1986). Using the digestion method from Allen *et al.* (1986), the sulphuric peroxide was prepared.The sulphuric- peroxide solution was made up of 14 g lithium, 0.42 g of selenium powder and 350 ml of hydrogen peroxide. Sulphuric acid (420 ml) was slowly added to the mixture, which was placed on ice to keep it cool (Grimshaw 1987). The mixture was stored at 2 ºC in a refrigerator and covered in foil to prevent sunlight from penetrating. The samples were placed in digestion heat blocks with a starting temperature of 150 ºC, thereafter the temperature was increased by 50 ºC every hour up until a maximum temperature of 350 ºC was reached. As soon as the solution reached a colourless or light milk colour, it was removed from the digestion block and left to cool. The clear solution was filtered through Whatmans number 42 filter paper and made up to 100 ml. Blanks were prepared in the same way but contained only the cigarette paper and the digestion mixture. The same elements were analysed in plants as in water and sediment.

2.5 STATISTICAL ANALYSIS:

A statistical programme (SAS 9.2) was used to analyse the results of the chemical analyses. The statistical analysis used in the analyses is that of ANOVA’s. In order to compare means of samples, T - tests were used in the form of student T - tests.

CHAPTER 3

RESULTS

Site specific and seasonal accumulation of heavy metals and physico-chemical properties

RESULTS

3.1 WATER

Many of the parameters for water displayed similar trends and can be divided accordingly into: no pattern, constant pattern, increase in variables and decrease in variables over space and also: no pattern, constant pattern, a wet season high and a wet season low over time.

The amount of rainfall (mm) that occurred over the sampling period is given in Figure 3.1. Rainfall has an effect on the input of inorganic pollution into the river. The seasonal differences in precipitation cause variations in the river's water quality. This can be seen in Figure 3.2.1 (a and c) and Figure 3.2.3 (a, b and g).

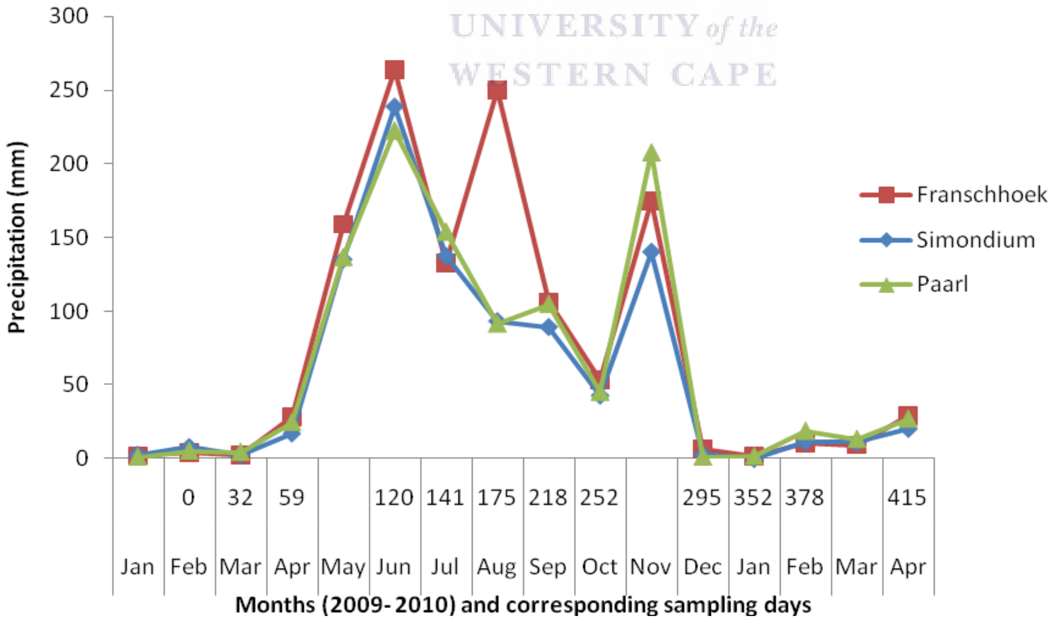


Figure 3.1. The mean monthly rainfall, which occurred along the Berg River from Franschhoek to Paarl during 2009 and 2010.

3.1 (A) No pattern across the sites:

Figure 3.1.1 shows that some of the chemical parameters showed no discernable pattern within the water samples over the ten sites. The mean values for oxygen (mg/ l) ranged between 6.38 mg/ l and 7.88 mg/ l (Figure 3.1.1. (a)). The lowest mean value for dissolved oxygen occurred at site 10 and the highest at sites 5 and 8. Copper concentrations ranged between 0.0007 mg/ l and 0.0016 mg/ l across the sampling sites. The lowest mean concentration occurred at site 9 and the highest value occurs at site 7 (Figure 3.1.1. (b)). Significant differences between means were seen for iron concentrations across the sampling sites (Figure 3.1.1. (c)). The mean values for iron across the sites ranged between 0.02 mg/ l and 0.08 mg/ l with the lowest values at sites 2 and 3 and the highest at sites 5 and 6.

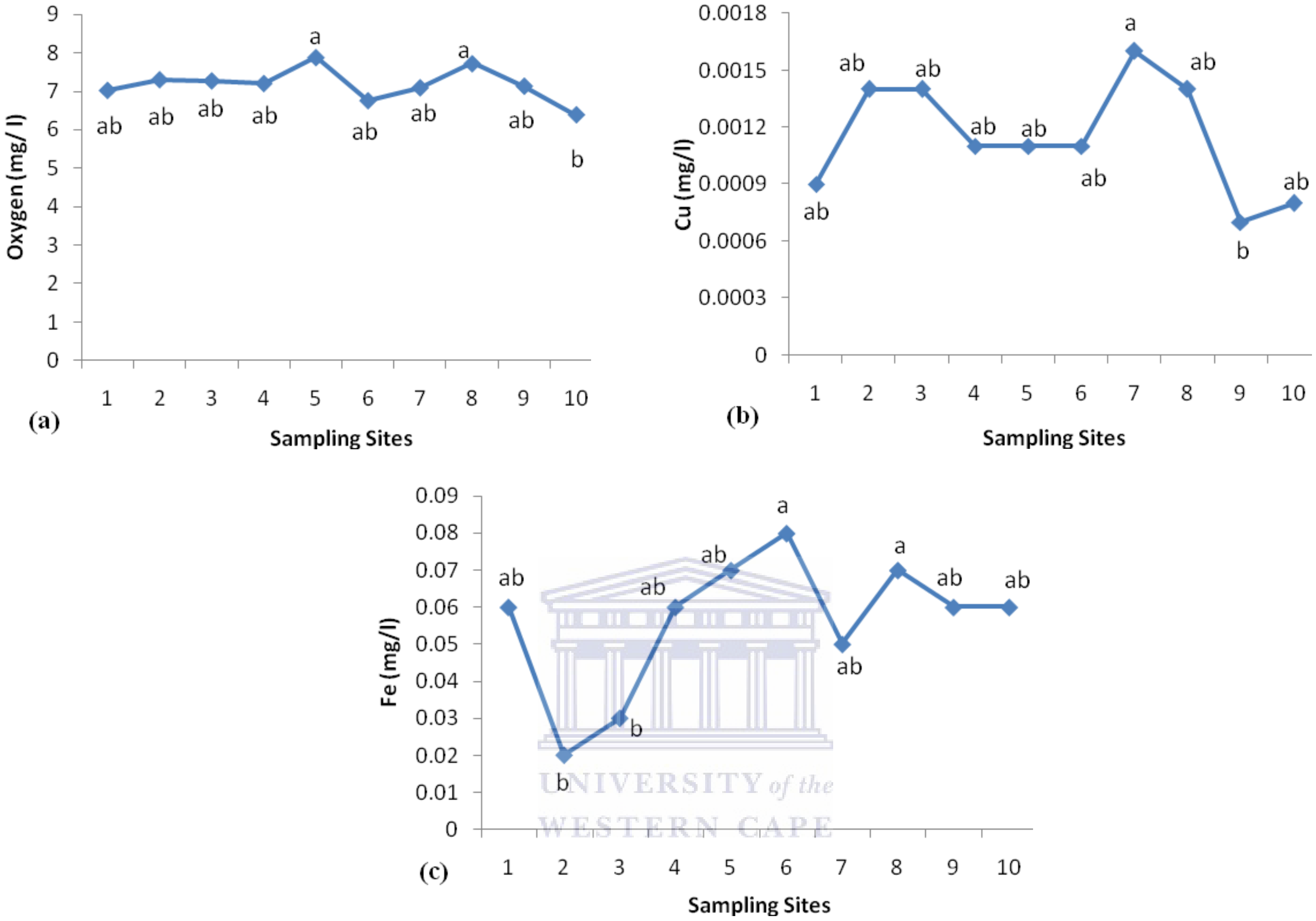


Figure 3.1.1. (a): Mean oxygen concentration (mg/ l), (b) mean copper concentration (mg/ l) and (c) mean iron concentration (mg/ l) at the ten sampling sites along the upper Berg River over the 2009- 2010 study period. Means with the same letter are not significantly different ($p \leq 0.05$).

3.1 (B) Constant pattern across the sites:

The following chemical parameters in Table 3.1.1 showed no significant changes across the ten sites over the study period. The mean and standard deviation values for the parameters are representatives of the concentrations that were present at the sites. Ammonium levels ranged between 0.1 mg/ l and 0.25 mg/ l. Mean nitrite levels were very low throughout as they ranged between 0.09 mg NO_2^-/ l and 0.11 mg NO_2^-/ l. The mean cadmium concentrations along the sites also remained low with a range between 0.005 mg/ l and 0.078 mg/ l. The mean concentrations for zinc ranged between 0.0014 mg/ l and 0.0025 mg/ l and for phosphorus it ranged between 1.00 mg/ l and 1.08 mg/ l.

Table 3.1.1 The averages and standard deviations of ammonium, nitrite, cadmium, zinc and phosphorus at the ten sampling sites along the Berg River over 2009- 2010 study period.

Parameter	Units	Mean	StDev
NH_4^+	mg/ l NH_4^+	0.146	0.040
NO_2^-	mg/ l NO_2^-	0.098	0.008
Cd	mg/ l	0.024	0.027
Zn	mg/ l	0.002	0.000
P	mg/ l	1.040	0.042

3.1 (C) Increase in parameters and concentrations downstream:

Almost half of the parameters that were tested increased downstream. The levels of the various parameters were lowest at the first two sites and increased from site 3 onwards (Figure 3.1.2). Electrical conductivity mean values across the sites ranged from 32.92 µS cm^{-1} to 103.92 µS cm^{-1} (Figure 3.1.2. (a)). The highest EC mean was experienced at site 7. The mean pH values ranged between 5.59 and 6.61 across the sampling sites. As seen in Figure 3.1.2. (b), the lowest pH value was found at site 1 and the highest at site 8. In Figure 3.1.2. (c) site 1 had the lowest mean nitrate value (0.17 mg NO_3^- l) of the ten sites. No differences were evident from site 3 to site 10. The sampling sites had mean nitrate levels ranging between 0.17 mg NO_3^- l and 1.50 mg NO_3^- l. The potassium concentration ranged between 0.79 mg/ l and 2.11 mg/ l. The lowest mean concentration of potassium occurred at site 1 and the highest occurred at site 8 (Figure 3.1.2. (d)). The mean concentrations of sodium ranged between 0.42 mg/ l and 0.92 mg/ l, for calcium it ranged between 0.05 mg/ l and 0.27 mg/ l and both of these elements were highest at site 10 (Figure 3.1.2. (e and f)). Site 3 had the highest mean concentration of magnesium as seen in Figure 3.1.2. (g) and it was caused by input from the Franschhoek River. The values ranged between 0.04 mg/ l and 0.89 mg/ l.

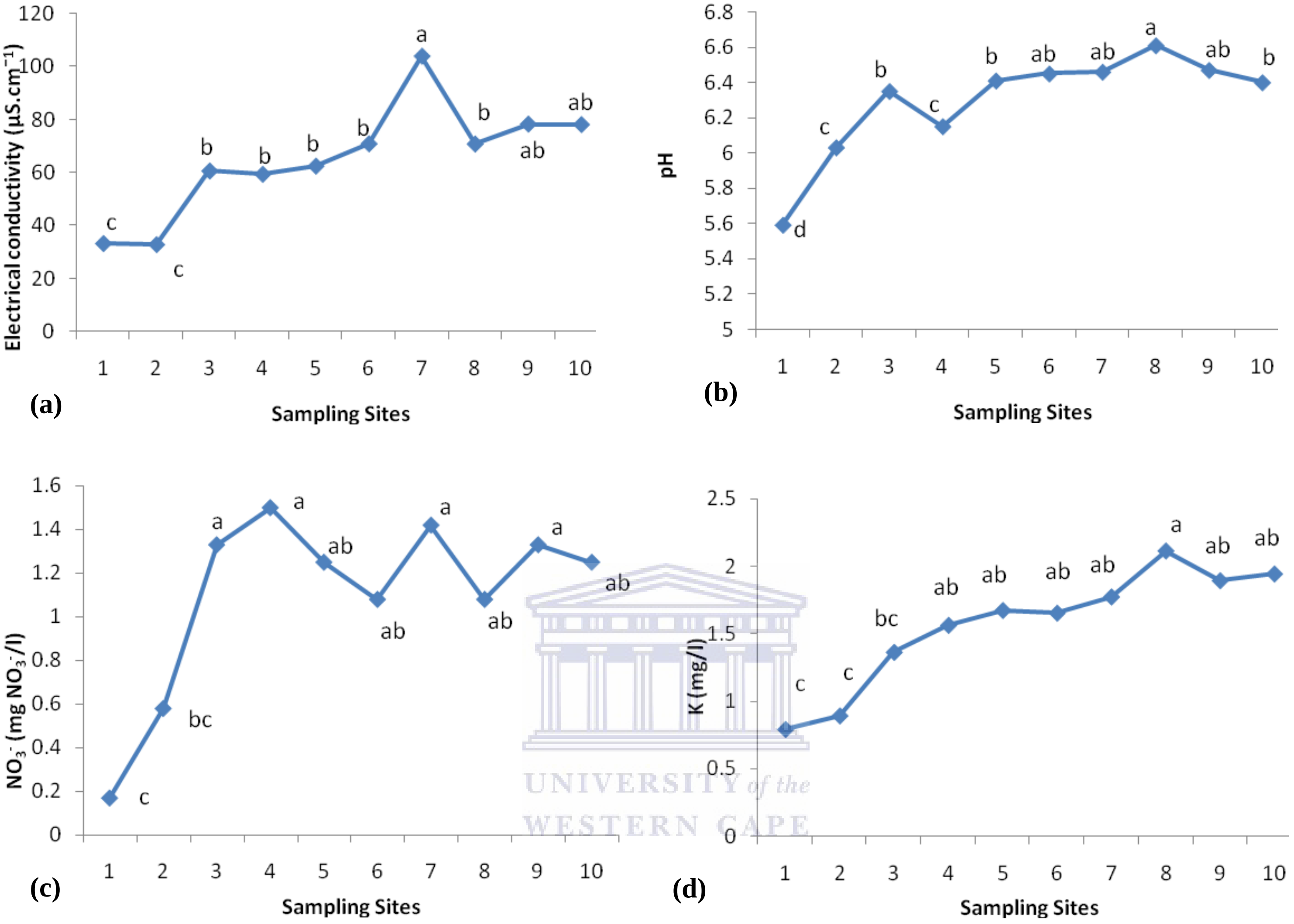


Figure 3.1.2. (a): Mean electrical conductivity (µS cm^{-1}), (b) mean pH, (c) mean nitrate concentration (mg/ l), (d) mean potassium concentration (mg/ l) in the upper Berg River. Means with the same letter are not significantly different ($p \leq 0.05$).

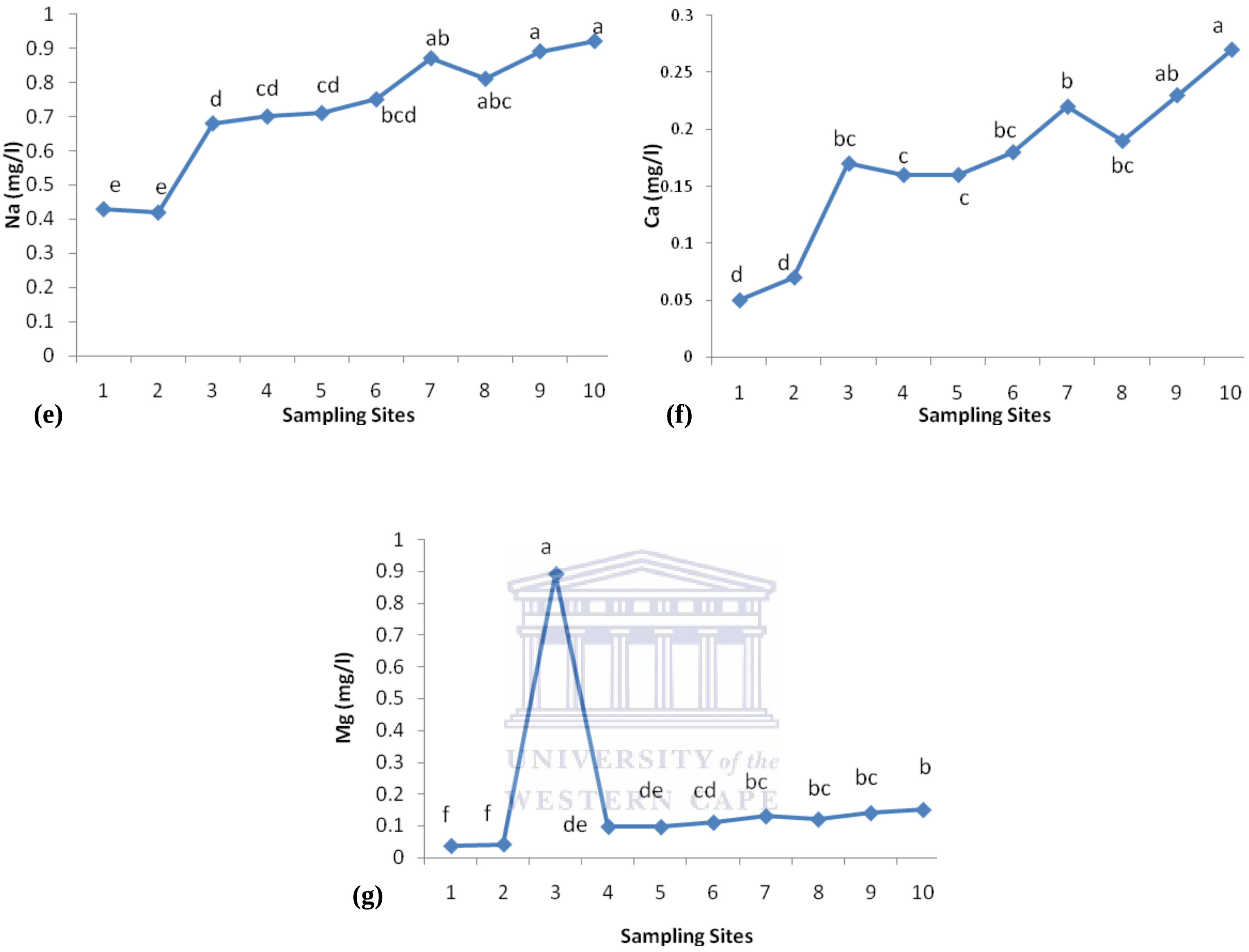


Figure 3.1.2.continued (e): Mean sodium concentration (mg/ l), (f) mean calcium concentration (mg/ l) and (g) mean magnesium concentration (mg/ l) at the ten sampling sites along the upper Berg River over the 2009- 2010 study period. Means with the same letter are not significantly different ($p \leq 0.05$).

3.1 (D) Decrease in parameters downstream:

The mean water temperature and mean lead concentrations displayed a trend of decreasing in the downstream direction. The mean surface water temperature ranged between 18.19 °C and19.63 °C (Figure 3.1.3. (a)) across the ten sites sampled. The lowest mean temperature was experienced at site 5 and the highest mean temperature across the ten sites occurred at site 2. The mean lead concentrations ranged between 0.006 mg/ l and 0.070 mg/ l. In Figure 3.1.3. (b) the lowest reading was observed at site 4 and the highest reading was observed at site 1. The higher level of Pb at site 1 is attributed to the fact that the pH of site 1 was low (Figure 3.1.2. (b)) and also due to the geology of the catchment.

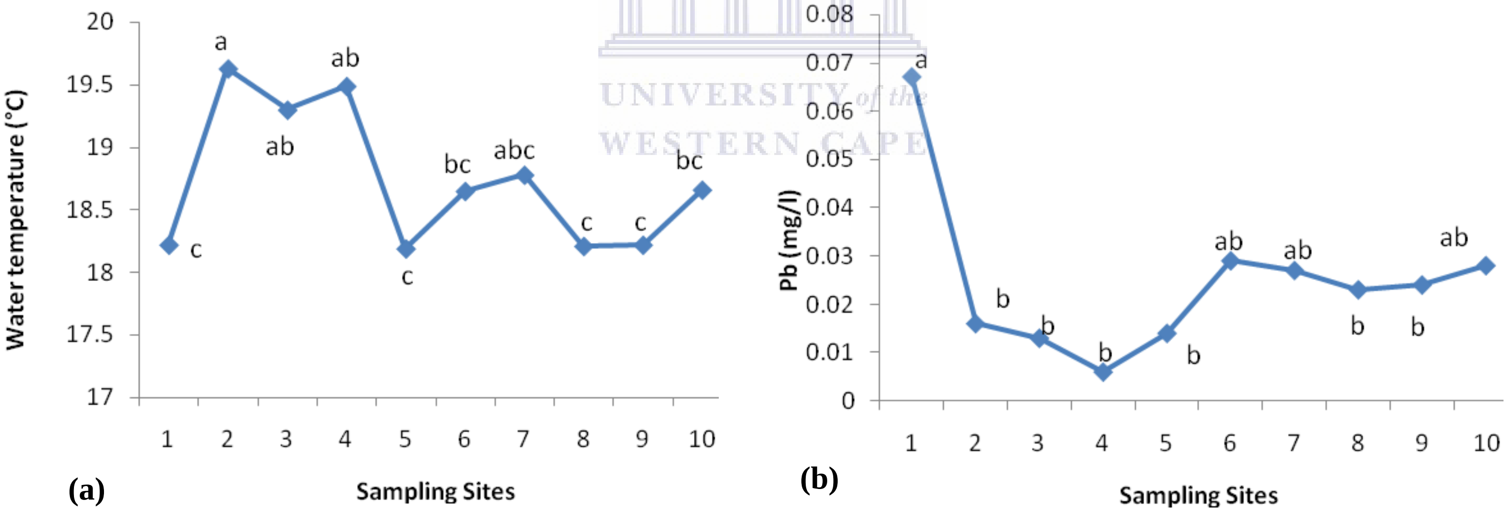
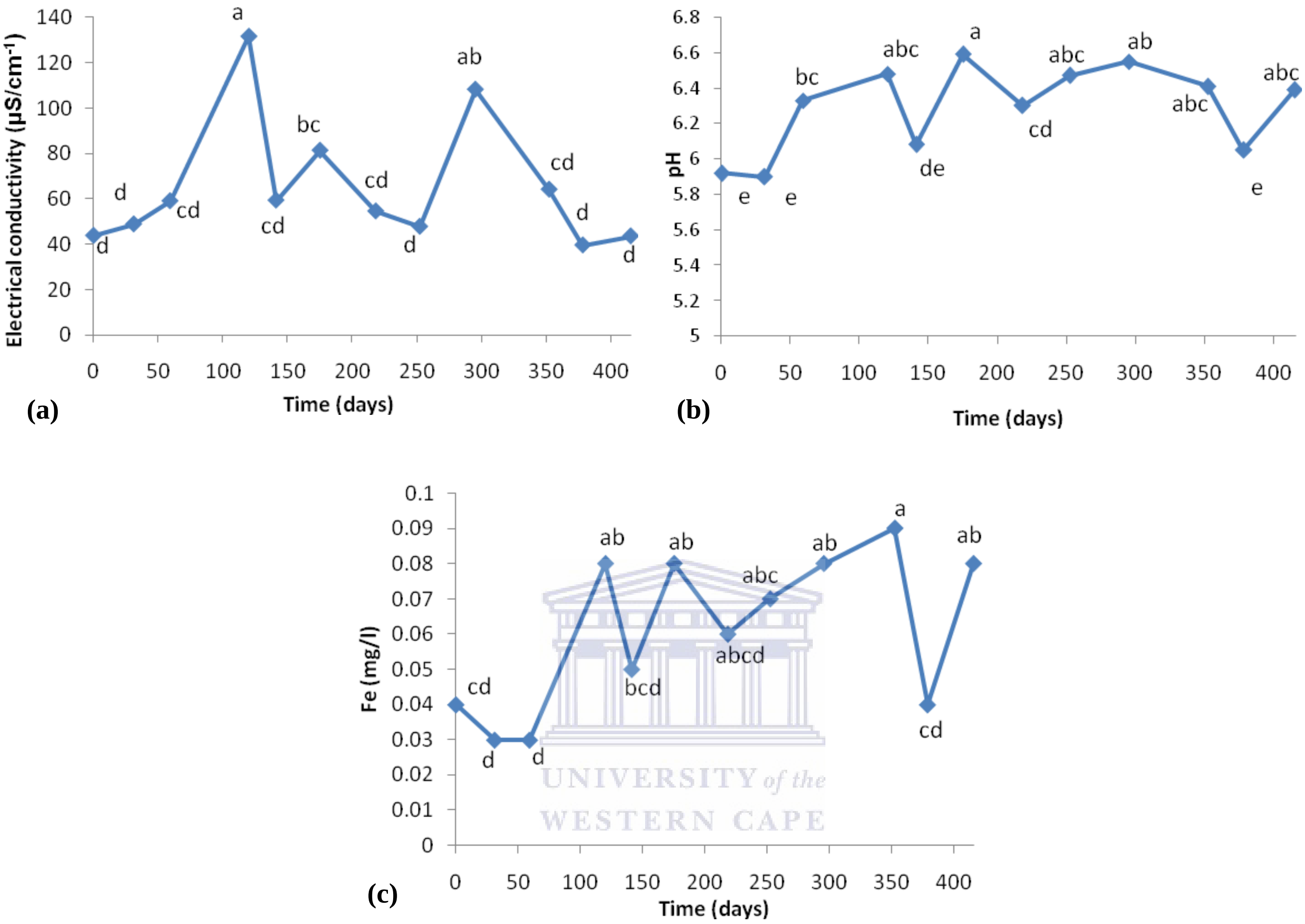


Figure 3.1.3. (a): Mean water temperature (°C) and (b) mean lead concentration (mg/ l) at the ten sampling sites along the upper Berg River over the 2009- 2010 study period. Means with the same letter are not significantly different ($p \leq 0.05$).

Water results over the sampling period:

3.2 (A) No pattern over the sampling period:

Electrical conductivity, pH and iron displayed no evident seasonal trends. The three variables showed many fluctuations over the year of study (Figure 3.2.1). Seasonal fluctuations in mean EC values ranged between 39.5 µS/ cm^{-1} and 131.6 µS/ cm^{-1} over the study period. Electrical conductivity was the lowest during summer (day 378) of 2010 and peaked during the winter month (day 120) of 2009 (Figure 3.2.1. (a)). Seasonal variation of mean pH values was low and ranged from 5.90 and 6.59 (Figure 3.2.1. (b)). The lowest pH (5.90) was experienced on day 31 during autumn and the highest pH (6.59) was measured on day 175 during winter. The mean iron concentrations were low during the end of autumn and the beginning of winter of 2009, with a sharp increase to day 120 and steadily increased over the spring and summer months. The results show that iron concentrations were lowest in autumn (days 31 and 59) and highest in summer (day 352) (Figure 3.2.1. (c)). Seasonal mean concentrations of Fe varied between 0.03 mg/ l and 0.09 mg/ l.



(a) (b) (c)

Figure 3.2.1. (a): Seasonal variation of mean electrical conductivity (µS cm^{-1}), (b) mean pH and (c) mean iron concentration (mg/ l) in the upper Berg River. Means with the same letter are not significantly different (p ≤ 0.05).

3.2 (B) A constant pattern over the sampling period:

Nitrite and phosphorus remained constant throughout most of the year. A significant variation of both nitrite and phosphorus concentrations occurred in the first three months after which the levels stayed constant. In Figure 3.2.2. (a and b) it is evident that on day 31 the highest level of mean nitrite concentration (0.65 mg NO_2^-/ l) occurred and on day 59 for mean phosphorus concentration (1.50 mg/ l).

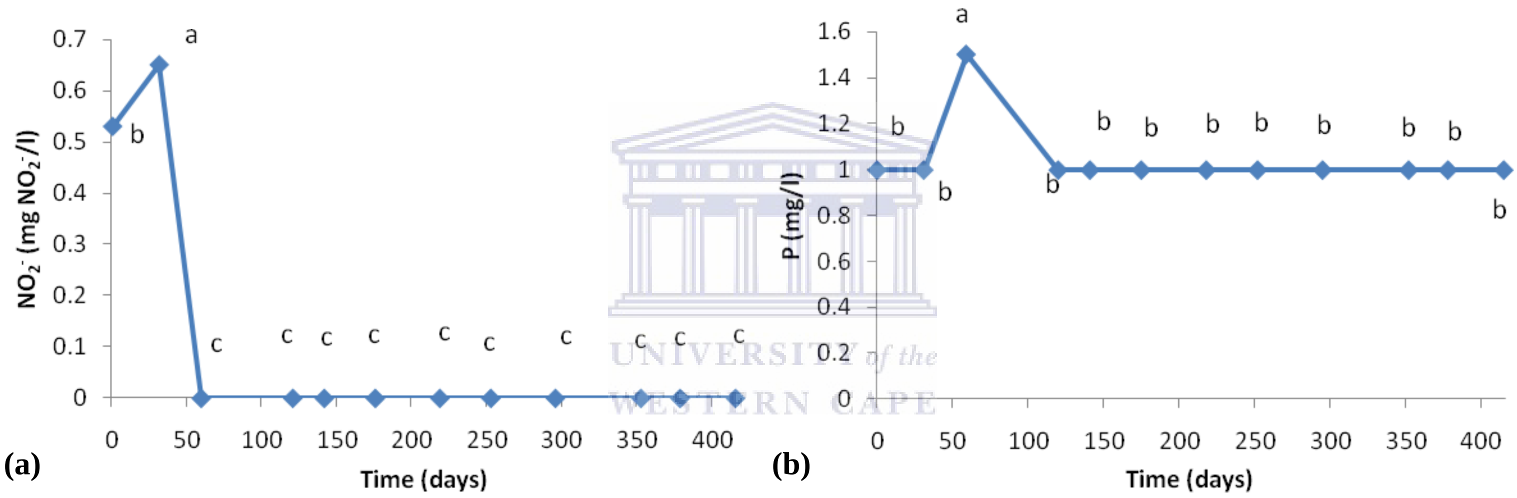


Figure 3.2.2. (a): Seasonal variation of mean nitrite concentration (mg/ l) and (b) mean phosphorus concentration (mg/ l) in the upper Berg River. Means with the same letter are not significantly different (p ≤ 0.05).

3.2 (C) A wet season high:

A general increase in some of the variables occurred towards the colder period. The levels of the variables (nitrate, cadmium, copper, zinc, potassium, sodium, calcium and magnesium) remained fairly high compared to the summer and autumn months. During the study period there was a significant change in the mean nitrate concentration which ranged between 0.0 mg NO_3^-/ l and 3.7 mg NO_3^-/ l (Figure 3.2.3. (a)). On day 120 (winter) the highest nitrate concentration was reached. In Figure 3.2.3. (b), the mean cadmium concentrations were fairy low during the winter and autumn months but the mean cadmium concentration was highest during the spring (day 218). The mean values throughout the year ranged between 0.002 mg/ l and 0.100 mg/ l. The mean concentrations of copper decreased during the autumn and winter months and increased in the early spring months and decreased in autumn again. The lowest concentration occurred during the winter months and highest during spring, and ranged between 0.0003 mg/ l and 0.0020 mg/ l (Figure 3.2.3. (c)). The mean concentrations of zinc over the study period ranged from 0.0003 mg/ l to 0.0032 mg/ l. Figure 3.2.3. (d) showed seasonal variation, as concentrations are lower during the winter months and higher during the summer months. Zinc was completely washed out during the last two months of winter (days 141 and 175). Potassium levels increased abruptly during June (winter). The mean concentration ranged between 0.51 mg/ l and 4.93 mg/ l as seen in Figure 3.2.3. (e). Sodium levels increased for the first three months and peaked in winter and gradually decreased during the summer months. There was a significant change in the mean sodium concentration of the surface water on the onset of winter rainfall. Levels of sodium were very low during autumn (Figure 3.2.3. (f)) and the values for sodium ranged between 0.29 mg/ l and 1.16 mg/ l. There was a significant difference by day 120 (winter) and then a steady decrease of calcium concentrations during the summer months (Figure 3.2.3. (g)). The calcium concentrations that occurred over the year ranged between 0.05 mg/ l and 0.39 mg/ l. Concentrations of magnesium remained low during the autumn months with a peak occurring on day 120 (Figure 3.2.3. (h)) and decreased at the end of summer and the beginning of the autumn (Figure 3.1.16. B). Magnesium levels over the year ranged between 0.05 mg/ l and 0.17 mg/ l. As with many of the other metals, there was a significant difference in the mean concentrations of Mg by day 120.

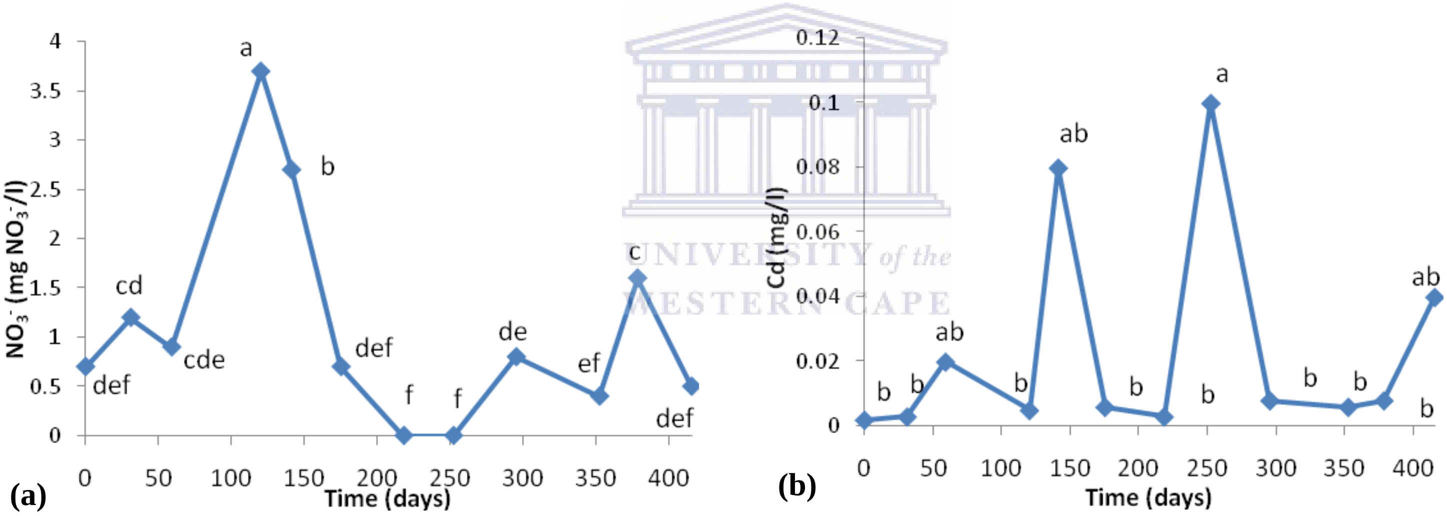


Figure 3.2.3. (a): Seasonal variation of mean nitrate concentration (mg/ l) and (b) mean cadmium concentration (mg/ l) in the upper Berg River. Means with the same letter are not significantly different ($p \leq 0.05$).

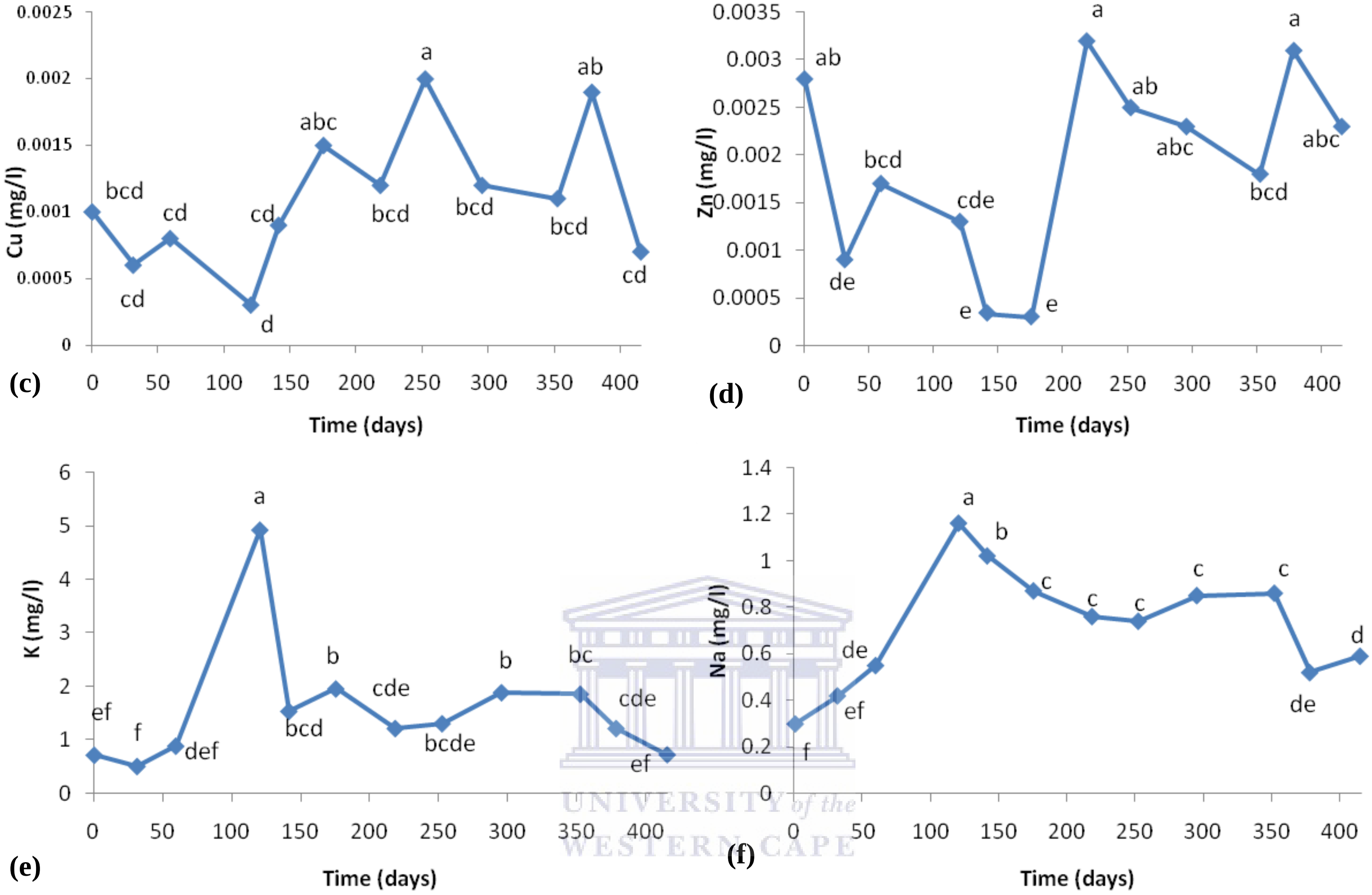


Figure 3.2.3.continued: Seasonal variation of (c) mean copper concentration (mg/ l), (d) mean zinc concentration (mg/ l), (e) mean potassium concentration (mg/ l) and (f) mean sodium concentration (mg/ l) in the upper Berg River. Means with the same letter are not significantly different (p ≤ 0.05).

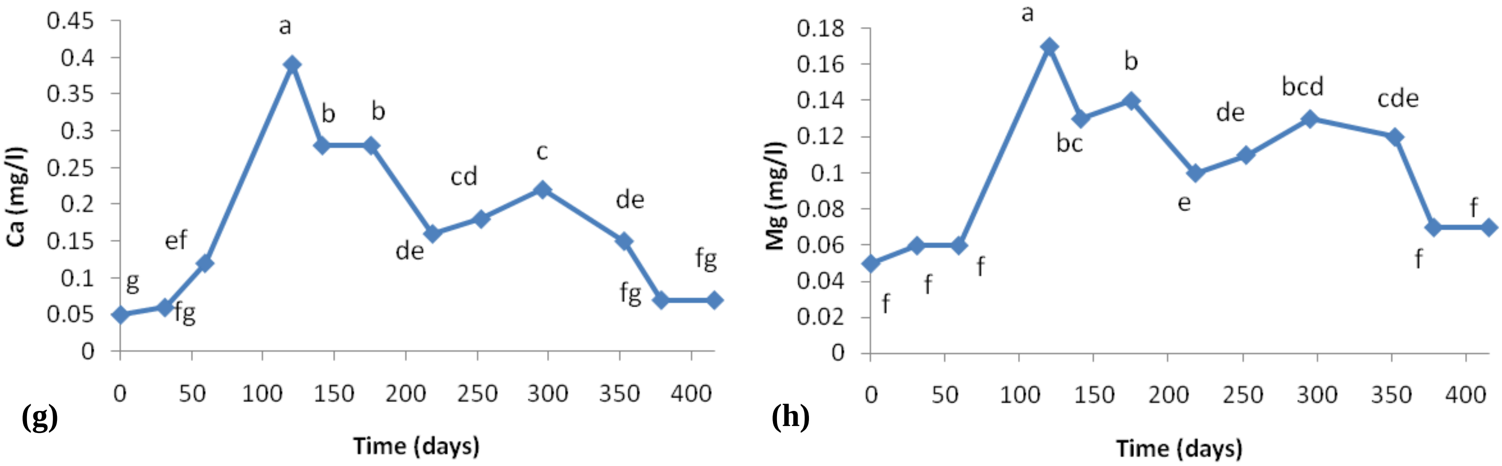


Figure 3.2.3. continued: Seasonal variation of (g) mean calcium concentration (mg/ l) and (h) mean magnesium concentration (mg/ l) in the upper Berg River. Means with the same letter are not significantly different ($p \leq 0.05$).

3.2 (D) A wet season low:

Oxygen (mg/ l) as well as ammonium and lead showed an increase in concentrations at the onset of spring. The levels of each variable remained fairly low in the first six months of sampling after which there was a significant increase. As the late summer and early autumn months arrived, the concentrations of the various variables began to decrease. In Figure 3.2.4. (a), the mean levels of dissolved oxygen ranged between 2.04 mg/ l and 9.49 mg/ l. Oxygen levels were steady during the last summer month and autumn months of 2009 then decreased in the winter months of 2009. There was a peak in the first month of spring due to heavy rainfall during the spring months of 2009 and then oxygen levels declined in the months of summer and early autumn. The mean levels of ammonium (Figure 3.2.4 (b)) remained low throughout the autumn and winter months (days 0 - 175) (these months are associated with rainfall) and sharply increased in mid spring (days 218 - 295) where it remained high during the summer months over the study period. Ammonium concentrations for the duration of the year ranged between 0.00 mg/ l and 0.37 mg/ l. The mean lead concentration was highest during the summer month (day 295) and lowest during the first month of sampling. The mean values for lead during the year of study ranged between 0.000 mg/ l and 0.070 mg/ l (Figure 3.2.4. (c)).

There was also a clear seasonal trend in terms of water temperature. Temperatures were high in the summer months, gradually decreasing over the cooler period and increasing again in late spring. Seasonal fluctuations in mean temperatures as given in Figure 3.2.4. (d) varied between 13.41 °C and 25.15 °C. The lowest mean temperature occurred during the winter of 2009 and the highest mean temperature during the summer of 2010.

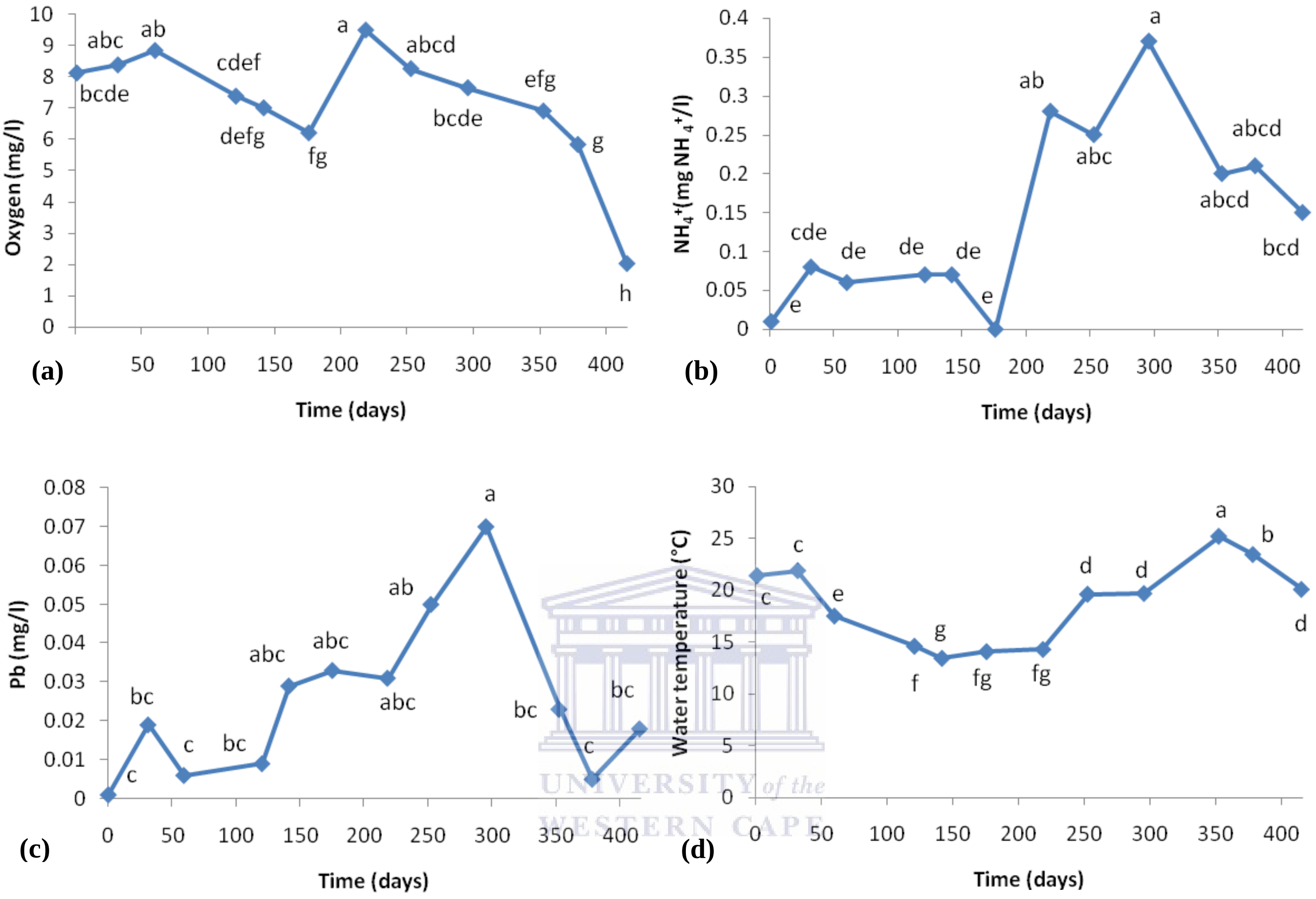


Figure 3.2.4. (a): Seasonal variation of mean oxygen concentration (mg/ l), (b) mean ammonium concentration (mg/ l), (c) mean lead concentration (mg/ l), and (d) mean water temperature (°C) in the upper Berg River. Means with the same letter are not significantly different ($p \leq 0.05$).

3.3 SEDIMENT

Table 3.3.1 indicates the seasonal concentration the various elements, electrical conductivity and pH of the sediment that was sampled in the wet and in the dry season. Results showed that there was no significant difference ($p > 0.05$) between the wet and dry season sampling for the physico–chemical properties and metals excluding copper and magnesium. This was because the variation between sites was greater in general than that between seasons.

Table 3.3.1. Comparisons of the sediment chemical characteristics occurring over the wet and dry seasons at ten sites on the upper Berg River. Means followed by the same letter are not significantly different $p \leq 0.05$.

Parameters	Units	Dry season (day 175)	Wet season (day 415)
EC	**µS cm^{-1}**	71.23 (a)	264.07 (a)
pH		5.75 (a)	5.65 (a)
N	**mg kg^{-1}**	0 (a)	0 (a)
Cd	**mg kg^{-1}**	0.10 (a)	0.01 (a)
Cu	**mg kg^{-1}**	0.40 (b)	0.86 (a)
Pb	**mg kg^{-1}**	0.01 (a)	0.02 (a)
Fe	**mg kg^{-1}**	10.84 (a)	21.30 (a)
Zn	**mg kg^{-1}**	6.87 (a)	6.69 (a)
K	**mg kg^{-1}**	0.00 (a)	0.73 (a)
Na	**mg kg^{-1}**	29.62 (a)	31.32 (a)
Ca	**mg kg^{-1}**	47.56 (a)	37.19 (a)
Mg	**mg kg^{-1}**	11.84(b)	17.19 (a)
P	**mg kg^{-1}**	1 (a)	1 (a)

In Table 3.3.1 it can be seen that the sediment pH was slightly acidic. Nitrogen was below the detection limits in the sediment samples during the dry and wet season. The mean copper and magnesium concentrations were significantly higher in the wet season. The mean phosphorus levels remained constant in both the dry and the wet season (Table 3.3.1).

3.4 PLANTS

During the course of the sampling period, many of the acacias were removed by the "Working for Water" project as these are alien species. Leaves of *Salix* sp. were absent during some of the winter and the spring months, as it is a deciduous species. This species was initially found at the last 6 sites, but over the sampling period trees were removed at certain sites. *Brabejum stellatifolium*, on the other hand, was only found at the first five sites and was also removed at one site. This has implications for the relative values of the three species, as some missing data occurred for monthly samples. Many of the elements present within *Salix* sp., *Acacia mearnsii* and *Brabejum stellatifolium* displayed similar trends and can be divided accordingly into different categories over space and time.

3.4 [A] Overall, no significant differences across the sites:

The results for cadmium, lead, zinc and sodium showed no significant variations across the sites within the three species (Figure 3.4.1). Mean cadmium levels (Figure 3.4.1. (a)) ranged between 0.0 mg kg^{-1} and 0.3 mg kg^{-1} for *Salix* sp., for *Acacia mearnsii* it ranged between 0.0 mg kg^{-1} and 0.6 mg kg^{-1} and for *Brabejum stellatifolium* it ranged between 0.00 mg kg^{-1} and 0.07 mg kg^{-1}. In Figure 3.4.1. (b) the mean levels of Pb in *B. stellatifolium* displayed a sharp spike in Pb concentration that occurred at site 2. The mean Pb concentrations in *Salix* sp. leaves were in the range of 0.000 mg kg^{-1} and 0.001 mg kg^{-1} and in *Acacia mearnsii*, between 0.001 mg kg^{-1} and 0.008 mg kg^{-1}. The mean concentration of Pb ranged between 0.000 mg kg^{-1} and 0.003 mg kg^{-1} for *B. stellatifoilum*. *Salix* sp. displayed mean concentrations of zinc (Figure 3.4.1. (c)) between 111.18 mg kg^{-1} and 180. 00 mg kg^{-1}, *Acacia mearnsii* between 38 mg kg^{-1} and 77.65 mg kg^{-1} and *B. stellatifoilum* ranging between 38.18 mg kg^{-1} and 57.21 mg kg^{-1} . There was no significant difference over the study area for the three species other than the increase of Na levels at site 10 in *Acacia mearnsii*. Sodium levels ranged between 177.14 mg kg^{-1} and 298.00 mg kg^{-1} in *Salix* sp. Mean levels of Na in *Acacia mearnsii* ranged between 293.60 mg kg^{-1} and 5281.00 mg kg^{-1} and the mean levels of Na in *Brabejum stellatifolium* ranged between 121.08 mg kg^{-1} and 145.19 mg kg^{-1} (Figure 3.4.1. (d)).

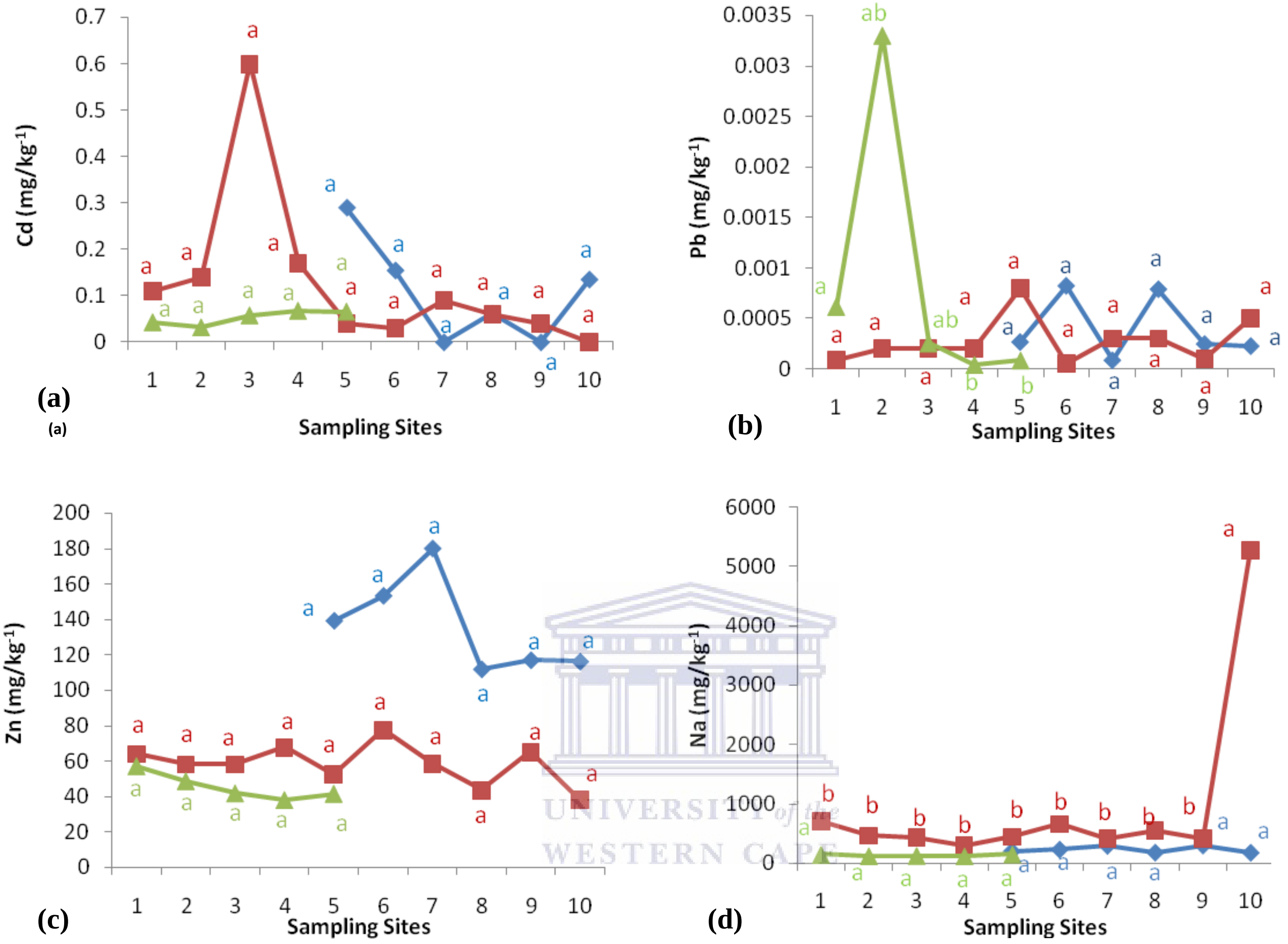


Figure 3.4.1. (a): Mean cadmium (mg kg^{-1}) concentration, (b) mean lead (mg kg^{-1}) concentration, (c) mean zinc (mg kg^{-1}) concentration and (d) mean sodium (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green), at the ten sampling sites along the upper Berg River over the 2009- 2010 study period. Means with the same letter are not significantly different ($p \leq 0.05$).

3.4 [B] A random pattern across the sites:

The four variables (copper, potassium, magnesium and phosphorus) showed no clear pattern and showed increases in concentrations at random sites. In some of these variables, within the species there were no significant variations (Figure 3.4.2.(a and d)), whereas in other species no common trend was clear between the species. Copper levels in the three species showed little differences between the sites. *Salix* sp. however showed a peak at site 5 and *Acacia mearnsii* at site 9 (Figure 3.4.2.(a)). The mean Cu levels for *Salix* sp. ranged between 3.00 mg kg^{-1} and 14.98 mg kg^{-1}. Mean Cu concentrations in *Acacia mearnsii* ranged between 8.70 mg kg^{-1} and 12.38 mg kg^{-1}. *Brabejum stellatifolium* had mean Cu concentrations ranged between 4.90 mg kg^{-1} and 5.74 mg kg^{-1}. *Acacia mearnsii* and *Brabejum stellatifolium* followed a similar trend in potassium across the first five sites, both peaked at site 4 and then decreased again. The mean K concentrations in *Salix* sp. decreased at sites 7 and 9 and increased significantly at site 10. Overall, K appears to increase downstream. The mean K concentrations ranged between 860.0 mg kg^{-1} and 8095.0 mg kg^{-1} in *Salix* sp. The mean levels of K within the leaves of *Acacia mearnsii* ranged between 230.0 mg kg^{-1} and 6009.4 mg kg^{-1}. *Brabejum stellatifolium* contained mean K concentrations that ranged between 153.2 mg kg^{-1} and 3534.6 mg kg^{-1} (Figure 3.4.2. (b)). In Figure 3.4.2.(c), little variation between sites can be seen. The levels of Mg remained fairly constant throughout for both *Acacia mearnsii* and *Brabejum stellatifolium*, with site 1 which contained a high level and decreased again at site 2. In both *Acacia mearnsii* and *Salix* sp. the Mg levels were low at the downstream site (site 10). The mean levels of Mg in *Salix* sp. ranged between 275.75 mg kg^{-1} and 1040.00 mg kg^{-1}. *Acacia mearnsii* displayed mean concentrations of Mg that ranged between 140 mg kg^{-1} and

210 mg kg^{-1}. The mean concentration of Mg in *Brabejum stellatifolium* ranged between 111.43 mg kg^{-1} and 168.94 mg kg^{-1}. Phosphorus tended to be higher downstream in *Brabejum stellatifolium*, as shown in Figure 3.4.2.(d). *Salix* sp. contained higher levels of P at site 9 (Figure 3.4.2. (d)). In *Salix* sp., mean levels of P ranged between 10.25 mg kg^{-1} and 27.00 mg kg^{-1} and the mean concentrations of P in *Acacia mearnsii* ranged between 5.17 mg kg^{-1} and 8.00 mg kg^{-1}. Mean levels of P in *Brabejum stellatifolium* over the sites varied between 2.58 mg kg^{-1} and 3.50 mg kg^{-1}.

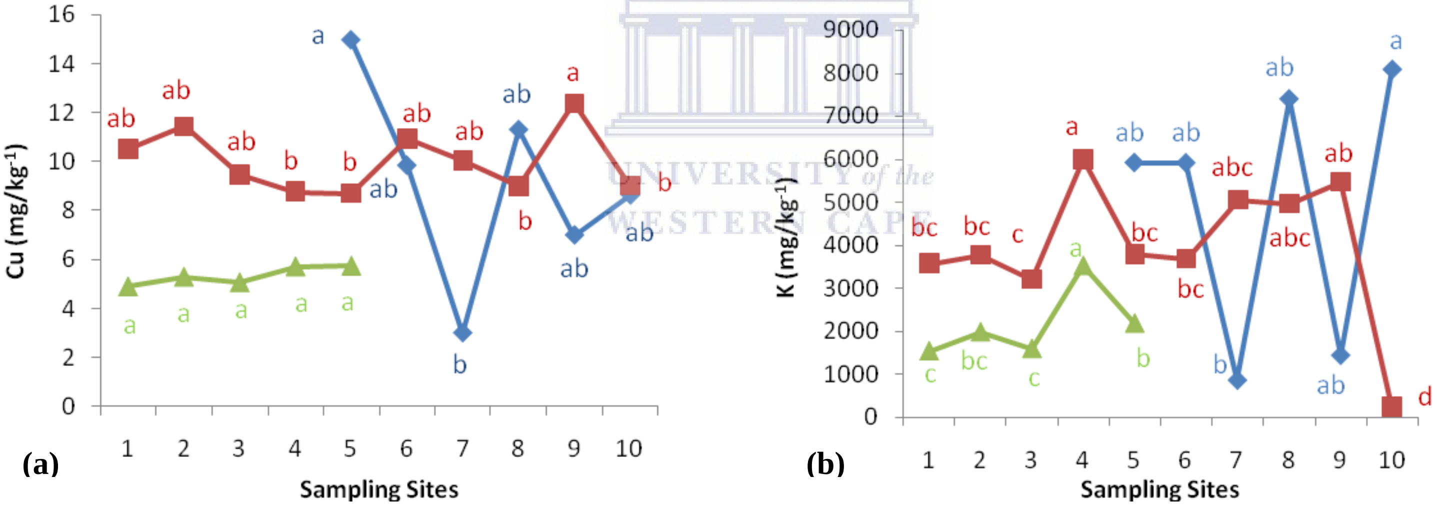


Figure 3.4.2. (a): Mean copper (mg kg^{-1}) concentration, (b) mean potassium (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green), at the ten sampling sites along the upper Berg River over the 2009- 2010 study period. Means with the same letter are not significantly different (p ≤ 0.05).

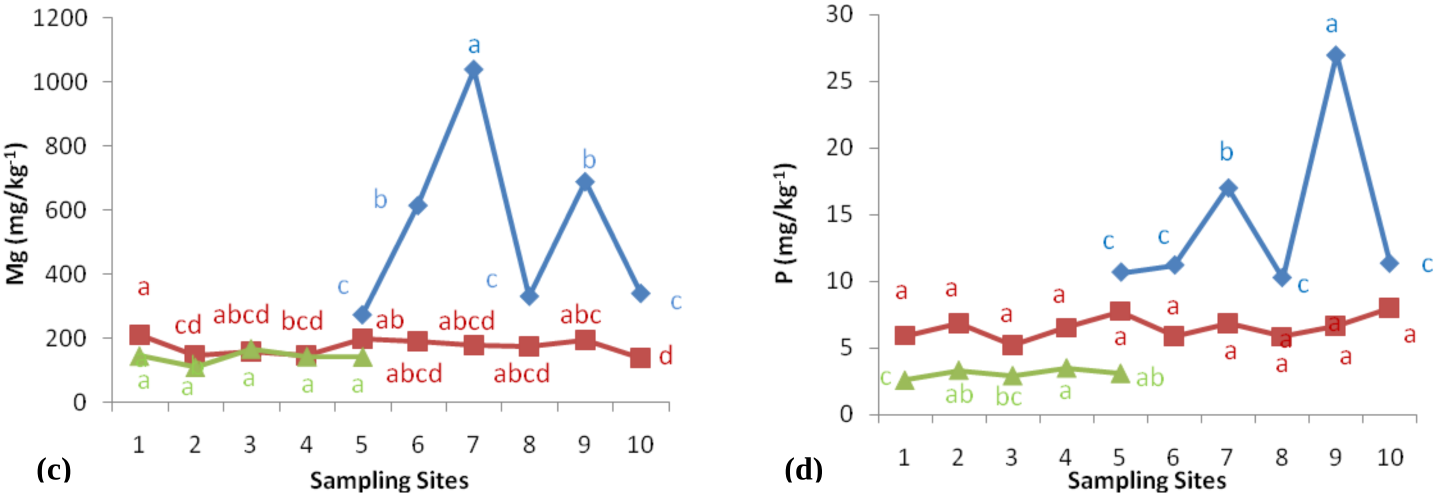


Figure 3.4.2. continued: (c) Mean magnesium (mg kg^{-1}) concentration and (d) mean phosphorus (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green), at the ten sampling sites along the upper Berg River over the 2009- 2010 study period. Means with the same letter are not significantly different (p ≤ 0.05).

3.4 [C] Increase in concentrations downstream:

In Figure 3.4.3 the levels of nitrogen, iron and calcium within the three species showed an increase in the downstream direction. The concentrations of nitrogen and iron remained low at the first 6 sites. An increase in nitrogen levels occurred from site 7 onwards. It is apparent that there were no clear differences across the sites for the three species, although *Salix* sp. and *Acacia mearnsii* seem to have peaked at the downstream sampling sites, 9 and 10 (Figure 3.4.3. (a)). No significant change occurred in the N levels of the leaves of *Brabejum stellatifolium* whereas the mean N concentrations across the sites showed significant variation in *Salix* sp. and *Acacia mearnsii*. Nitrogen means ranged between 19680 mg kg^{-1} and 33700 mg kg^{-1} for *Salix* sp., for *Acacia mearnsii* it ranged between 13731 mg kg^{-1} and 27400 mg kg^{-1} and lastly for *Brabejum*, it ranged between 3241 mg kg^{-1} and 10886 mg kg^{-1}. The mean Fe concentration displayed very little significant difference over the study area (Figure 3.4.3(b)). The levels of Fe remained very low in the first six sites and showed some significant increases further downstream. The mean concentrations of Fe in *Salix* sp. across the sites ranged between 19.11 mg kg^{-1} and 606.00 mg kg^{-1}. *Acacia mearnsii* leaves contained levels of Fe that ranged between 10.43 mg kg^{-1} and 202.00 mg kg^{-1}. The mean values for *Brabejum stellatifolium* ranged between 4.93 mg kg^{-1} and 10.70 mg kg^{-1}. Figure 3.4.3.(c) shows that the calcium levels, displayed variation in *Salix* sp. and *Acacia mearnsii* with spikes occurring at sites 5 and 9. The mean Ca concentration in *Salix* sp. ranged between 688.70 mg kg^{-1} and 1658.70 mg kg^{-1}. *Acacia mearnsii* mean Ca concentrations ranged between 470.50 mg kg^{-1} and 1031.60 mg kg^{-1}and for *Brabejum stellatifolium*, it ranged between 721.09 mg kg^{-1} and 941.04 mg kg^{-1}.

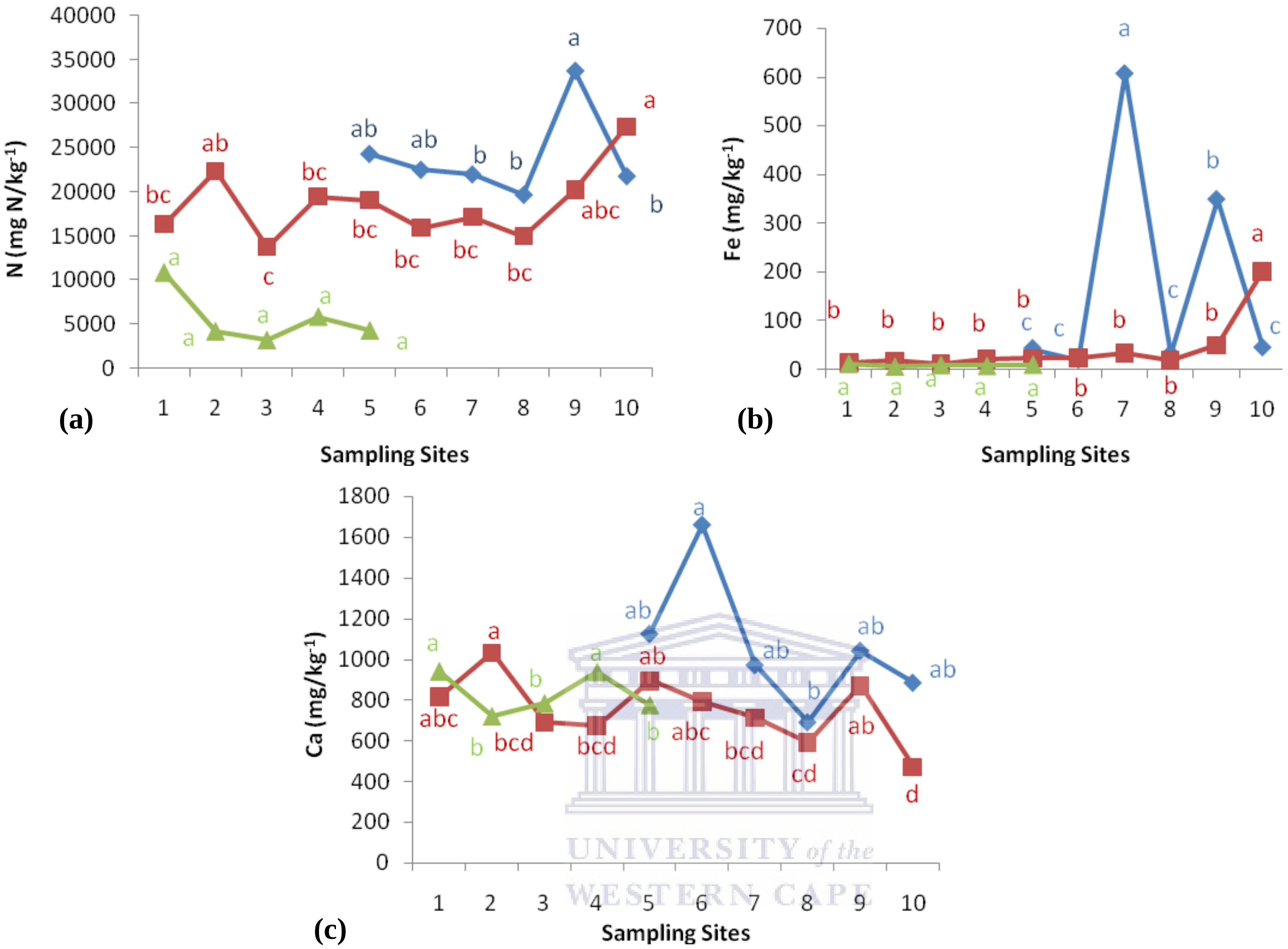


Figure 3.4.3. (a): Mean nitrogen (mg kg^{-1}) concentration, (b) mean iron (mg kg^{-1}) concentration and (c) mean calcium (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green), at the ten sampling sites along the upper Berg River over the 2009- 2010 study period. Means with the same letter are not significantly different ($p \leq 0.05$).

Plant results over the sampling period:

3.4 [D] No significant differences over the sampling period:

Iron levels displayed no evident seasonal trends within the leaves of the three species. The iron levels remained constant throughout the period of sampling. The mean Fe concentration displayed very little significant difference over the study area (Figure 3.4.4). The levels of Fe were highest in the first month of sampling and remained very low for the rest of the sampling period. The mean concentrations of Fe in *Salix* sp. across the sites ranged between 0.98 mg kg^{-1} and 280.33 mg kg^{-1}. *Acacia mearnsii* leaves contained levels of Fe that ranged between 1 mg kg^{-1} and 203 mg kg^{-1}. The mean values for *Brabejum stellatifolium* ranged between 0.15 mg kg^{-1} and 88.40 mg kg^{-1}.

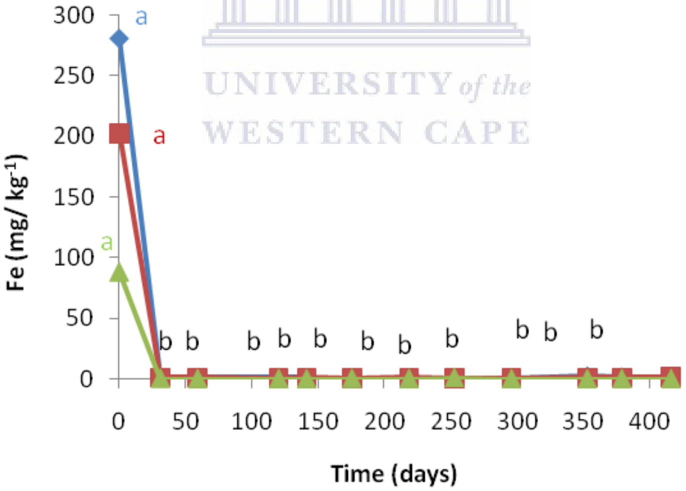


Figure 3.4.4. Seasonal variation of mean iron (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green) found along the upper Berg River. Means with the same letter are not significantly different ($p \leq 0.05$).

3.4 [E] A random pattern over the sampling period:

During the study period, Pb concentrations showed no clear trend (Figure 3.4.5. (a)). Lead levels peaked in the late autumn and then dropped for the most part of the remaining sampling time. The mean Pb concentration in *Salix* sp. ranged between 0.000 mg kg^{-1} and 0.001 mg kg^{-1}. The mean levels of Pb in *Acacia mearnsii* ranged between 0.0000 mg kg^{-1} and 0.0007 mg kg^{-1}. The mean Pb levels in *Brabejum stellatifolium* ranged between 0.000 mg kg^{-1} and 0.001 mg kg^{-1}. The levels of Zn were higher during the first four months of sampling, during the late summer towards early winter for all three species. Zinc levels decreased over the late winter and late spring months and tended to increase again in the summer months as the sampling period came to an end (Figure 3.4.5 (b)). The mean Zn levels ranged between 24.55 mg kg^{-1} and 173.15 mg kg^{-1} in *Salix* sp. The mean levels ranged from 13.21 mg kg^{-1} and 153.04 mg kg^{-1} for Zn in *Acacia mearnsii* and *Brabejum stellatifolium* ranged between 3.46 mg kg^{-1} and 1433.92 mg kg^{-1}. In the early months of sampling mean Na concentrations were higher compared to the rest of the year. Sodium levels hardly fluctuated over the year and seasonally mean levels of sodium were higher in the autumn and late winter months. The mean concentration for *Salix* sp. ranged between 32.89 mg kg^{-1} and 290.17 mg kg^{-1} (Figure 3.4.5.(c)). Mean Na concentrations of *Acacia mearnsii* ranged between 146.40 mg kg^{-1} and 2820.40 mg kg^{-1} and in *Brabejum stellatifolium* ranged between 45.96 mg kg^{-1} and 366.00 mg kg^{-1}.

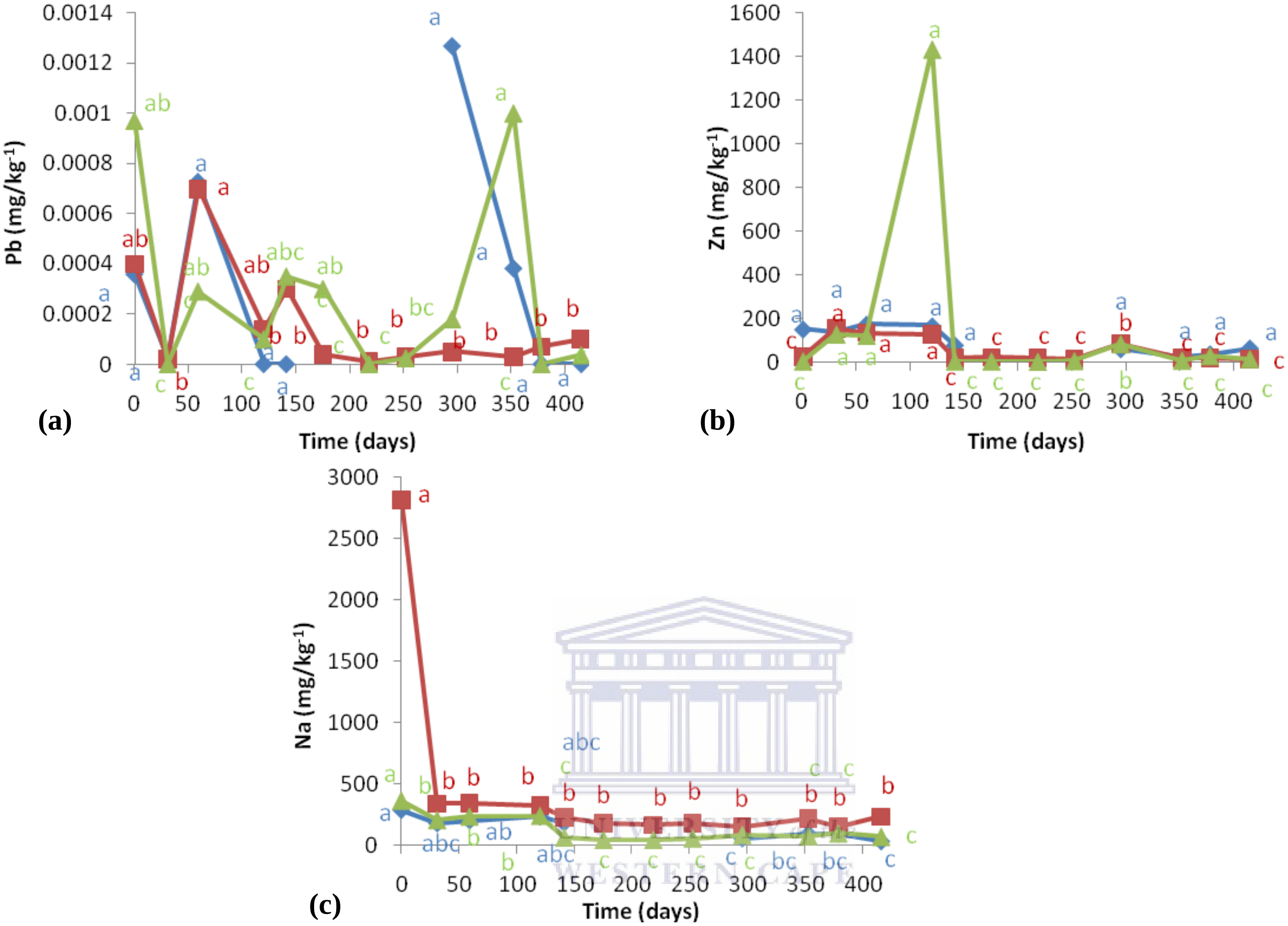


Figure 3.4.5. (a): Seasonal variation of mean lead (mg kg^{-1}) concentration, (b) mean zinc (mg kg^{-1}) concentration and (c) mean sodium (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green) found along the upper Berg River. Means with the same letter are not significantly different ($p \le 0.05$).

3.4 [F] A cool season trough:

Salix sp., *Acacia mearnsii* and *Brabejum stellatifolium* showed similar trends for nitrogen, cadmium, copper, potassium, calcium, magnesium and phosphorus as seen in Figure 3.4.6. The levels were generally high in the warmer seasons. The levels then decreased during the colder months. As summer approached, the levels of the elements increased again within the species. There was a distinct change in leaf nitrogen levels from late winter to early summer. In each species it appeared that levels of N remained fairly high for the first six months (the autumn and winter months), after which there was a decrease in the spring and early summer months. The levels of N then increased in the late summer months and early autumn (Figure 3.4.6. (a)). Seasonally there were significant variations in each species, with mean levels of N that ranged between 2099 mg kg^{-1} and 28540 mg kg^{-1} for *Salix* sp., 3001 mg kg^{-1} and 31090 mg kg^{-1} for *A*. *mearnsii* and 15 mg kg^{-1} and 28370 mg kg^{-1} for *B*. *stellatifolium*. There was no significant difference of the mean concentration of cadmium (Figure 3.4.6. (b)) over the study period in *Salix* sp., whereas there were significant differences that occurred in *Acacia mearnsii* and *Brabejum stellatifolium*. Over the duration of sampling, mean levels of Cd for *Salix* sp. ranged between 0 mg kg^{-1} to 0.35 mg kg^{-1}, for *Acacia* it ranged between 0 mg kg^{-1} and 0.34 mg kg^{-1} and for *Brabejum* it ranged between 0 mg kg^{-1} and 0.27 mg kg^{-1}. The three species displayed similar seasonal trends in Cu concentrations. A general increase in mean Cu levels occurred in the late summer and autumn months, followed by a decrease in levels during the winter and spring months. The levels of Cu increased again in the late summer months. The mean Cu concentration for *Salix* sp. ranged between 1.94 mg kg^{-1} and 24.43 mg kg^{-1}, in *Acacia* *mearnsii* it ranged between 3.79 mg kg^{-1} and 27.02 mg kg^{-1} and in *Brabejum stellatifolium* it ranged between 1.33 mg kg^{-1} and 22.64 mg kg^{-1} (Figure 3.4.6. (c)). Seasonally, mean K levels remained fairly constant in *Acacia mearnsii* and *Brabejum stellatifolium* (Figure 3.4.6. (d)). The mean K levels hardly fluctuated in the winter and spring months of sampling, thereafter a dip occurred in summer for the three species. Levels of K in *Salix* sp. ranged between 1143.0 mg kg^{-1} and 13987.0 mg kg^{-1}, in *Acacia measrnsii* it ranged between 612.0 mg kg^{-1} and 5886.8 mg kg^{-1} and for *Brabejum* it ranged between 1344.0 mg kg^{-1} and 2932.5 mg kg^{-1}. Calcium levels decreased from day 141, in mid winter up until the beginning of summer. In the summer months the level of Ca increased significantly, peaking at the last month of sampling in early autumn (Figure 3.4.6. (e)). The mean Ca levels for *Salix* sp. ranged between 203.1 mg kg^{-1} and 1376.9 mg kg^{-1}. The mean Ca levels for *Acacia mearnsii* ranged between 594.4 mg kg^{-1} and 1254.0 mg kg^{-1}. In *Brabejum stellatifolium* mean levels of Ca ranged between 588.8 mg kg^{-1} and 1113.4 mg kg^{-1}. The Mg concentrations remained high up until day 141 within the leaves of the three riparian trees (Figure 3.4.6. (f)). The levels of Mg remained fairly constant through the winter and spring months but as the summer months arrived the Mg concentrations decreased even more. The last four months showed a trend of increased levels of Mg with the arrival of late summer and early autumn. Seasonally the mean Mg levels for *Salix* sp. ranged between 97.00 mg kg^{-1} and 632.80 mg kg^{-1}. The mean Mg concentrations for *Acacia mearnsii* ranged between 59.86 mg kg^{-1} and 228.93 mg kg^{-1}. In *B. stellatifolium*, means for Mg ranged between 66.12 mg kg^{-1} and 207.29 mg kg^{-1}. The first month of the sampling period showed a significantly higher level of P (during summer) as shown in

Figure 3.4.6. (g). Over the autumn, winter and spring months the levels of P remained fairly constant, with a further dip that was evident on day 295, the P levels increased again over the late summer months. In *Salix* sp., mean levels of P ranged between 2.50 mg kg^{-1} and 19.34 mg kg^{-1}. *Acacia mearnsii* mean P concentrations ranged between 2.50 mg kg^{-1} and 11.60 mg kg^{-1}. *Brabejum stellatifolium*'s P levels ranged between 1.80 mg kg^{-1} and 4.25 mg kg^{-1}.

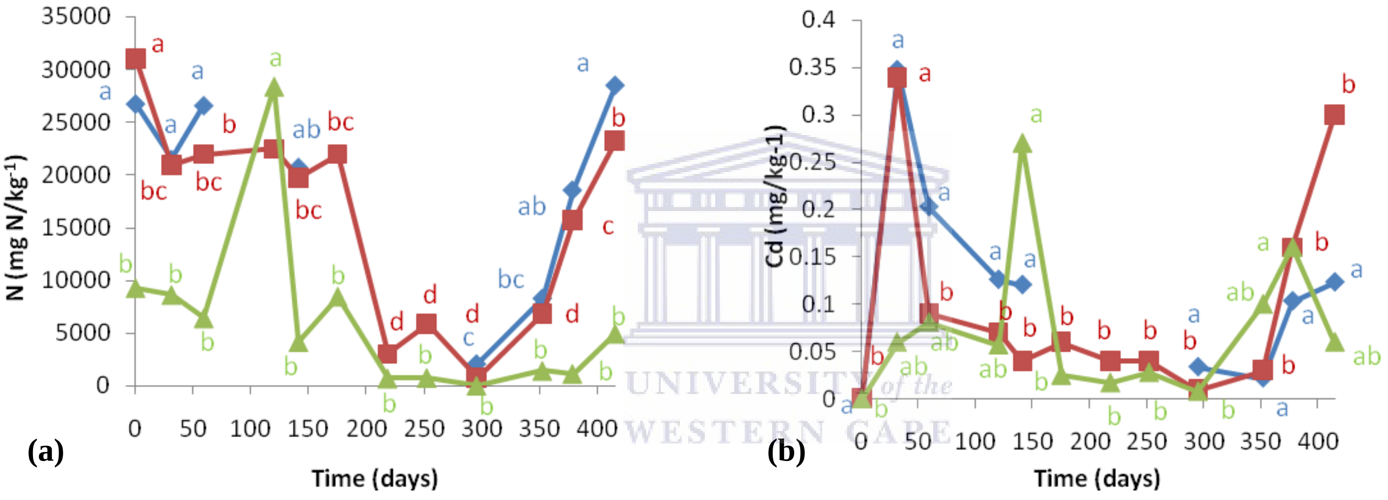


Figure 3.4.6. (a): Seasonal variation of mean nitrogen (mg kg^{-1}) concentration and (b) mean cadmium (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green) found along the upper Berg River. Means with the same letter are not significantly different (p ≤ 0.05).

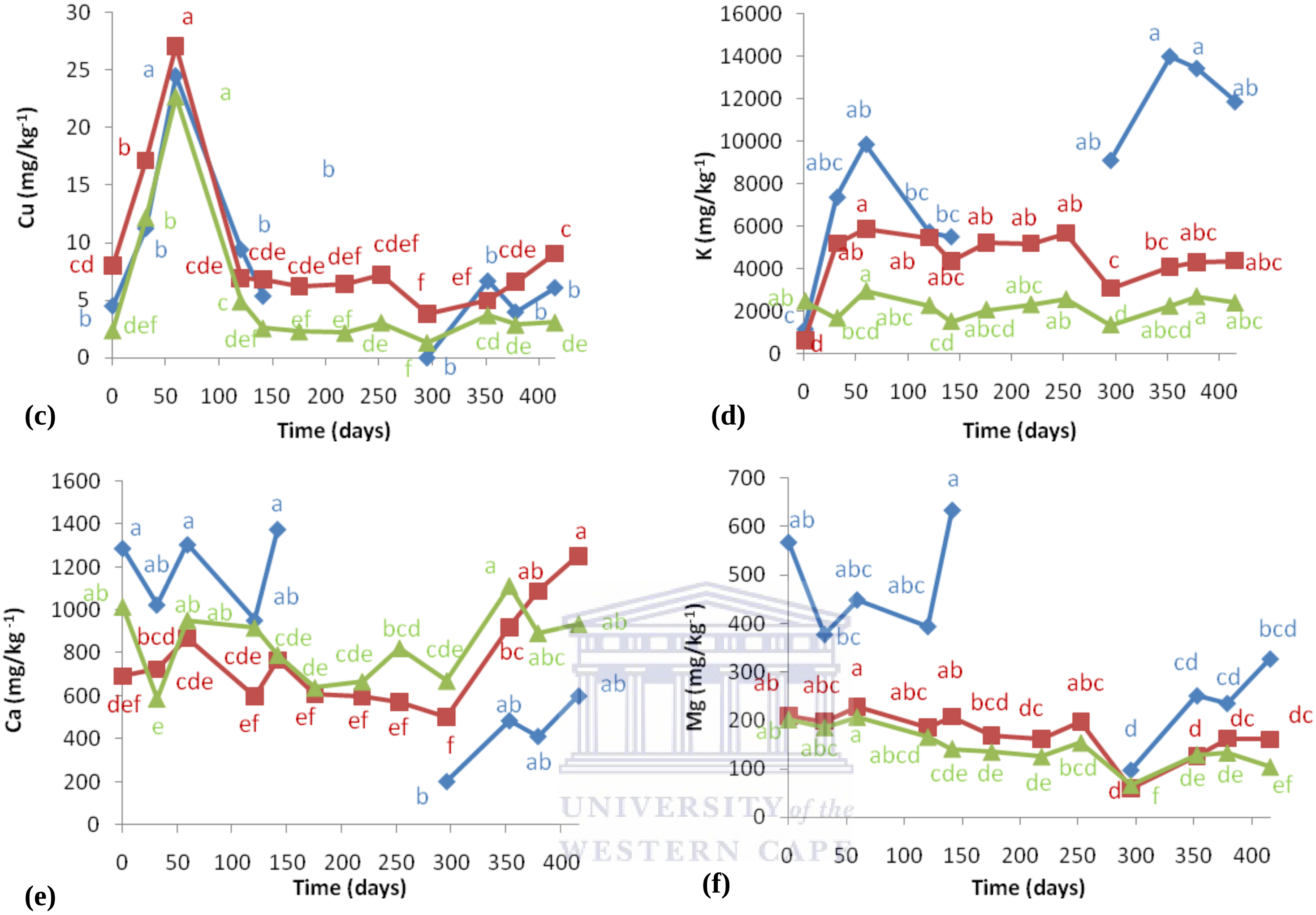
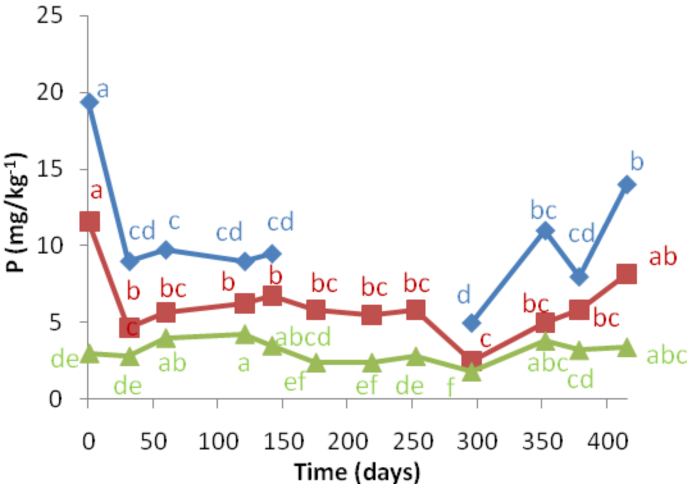


Figure 3.4.6. continued: Seasonal variation of (c) mean copper (mg kg^{-1}) concentration, (d) mean potassium (mg kg^{-1}) concentration, (e) mean calcium (mg kg^{-1}) concentration, (f) mean magnesium (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green) found along the upper Berg River. Means with the same letter are not significantly different (p ≤ 0.05).



(g)

Figure 3.4.6. continued: Seasonal variation of (g) mean phosphorus (mg kg^{-1}) concentration within the leaves of *Salix* sp. (highlighted in blue), *Acacia mearnsii* (highlighted in red) and *Brabejum stellatifolium* (highlighted in green) found along the upper Berg River. Means with the same letter are not significantly different ($p \leq 0.05$).

CHAPTER 4

Discussion

4.1 WATER

4.1 (A) No pattern across the sites:

The low mean dissolved oxygen value at site 10 (Figure 3.1.1. (a)) may be due to decomposition of organic material and reduced turbulence (Vega *et al*. 1998). This site has a density of macrophytes and the water is generally slow flowing. Izonfuo and Bariweni (2001) state that an elevation in temperature results in a lower solubility of oxygen and therefore a reduction in temperature results in an elevation of oxygen solubility. This corresponds with the results from sites 5 and 8, which have the highest dissolved oxygen and as seen in Figure 3.1.3. (a), the low temperatures were experienced at sites 5 and 8.

Iron concentrations are affected by pH, if the pH is low then concentrations of Fe will increase (DWAF 1996). The pH shown in Figure 3.1.2. (b) remained low throughout the sampling sites and tended to be lower upstream, although Fe concentrations in this study (Figure 3.1.1. (c)) were also lower there.

4.1 (B) Constant across the sites:

It is possible that variations over the year at sites masked differences along the river. The constant ammonium, nitrite and phosphorus concentrations across the sites (Table 3.1.1) can be explained by the fact that sites, further downstream may have nutrient concentrations similar to that of upstream reaches because of algae and vegetation that use the nutrients within the river (de Villiers 2007). In the upper areas of a river, forest and land runoff occur as well as dams, which increase the residence time of headwaters (Camargo *et al.* 2005). These factors result in addition of these nutrients into the river and when dam water is released, these nutrients travel downstream. Nitrite may have remained constant (Table 3.1.1) and in low concentrations across the sites because of the rapid conversion to nitrate (Jooste and van Leeuwen 1993). The nitrate levels increased as seen in Figure 3.1.2. (c) and this could be attributed in part to the oxidation process that occurred. It was surprising to find P constant when in previous studies; it increased downstream (Ruiters 2008) and subsequently (Struyf *et al*. 2012) showed an increase.

Cd and Zn are chemically similar and often interact with one another in an aquatic ecosystem (Nawrot *et al.* 2010). The Zn:Cd ratio in nature is usually 300:1 (DWAF 1996) but in Table 3.1.1 the opposite trend occurred, where the concentration of Cd was higher than that of Zn. In a study conducted by Guay *et al.* (2010) levels of Cd were also higher than that of Zn and were attributed to the geology having an enriched amount of Cd relative to Zn by an approximate constant amount or also due to human input of Cd.

Zn is also affected by pH and if pH is of acidic nature then Zn leaching will occur, which increases Zn concentration in the water (DWAF 1996). The levels of Zn measured were low, although the pH remained acidic throughout the sampling sites and according to DWAF (1996) this is the general standard in water.

4.1 (C) Increase in parameters and concentrations downstream:

The general trend for the parameters, as expected was that the first two sites would have lower values and tended to increase from the site where the Berg River and Franschhoek River confluence (site 3) as evident in Figure 3.1.2. Anon. (2004) states that interbasin transfer of water to the Berg River may occur as a result of irrigation demand. However, increased human activity (Struyf *et al*. 2012) can account for these increases.

The EC of water shows the occurrence of ions within the water like that of nitrate, sodium, calcium and magnesium (DWAF 1996). Begum *et al.* (2009) observed that high EC values are predominant with Na ions. EC in this study (Figure 3.1.2. (a)) is a reflection of the amount of ions in the river, as all of the parameters in this section had increased downstream just as EC increased.

The natural pH condition of the upper Berg River can be classified as acidic due to leached humic acids from the fynbos vegetation (Ractliffe 2007). This acidic nature of the river is affected by sewage inflow and runoff from both industry and agriculture (Ractliffe 2007). The increased pH following site 4 (Figure 3.1.2. (b)) may arise from agriculture as Ractliffe (2007) stated and also from the diluted effluent flowing into the river from the tributaries. A rise in pH changes the “toxicity of other pollutants in the river” (Morrison *et al*. 2001). This pattern can be seen in the various concentrations in Figure 3.1.2. where there was an increase of the various parameters.

The Franschhoek River’s waste water treatment works’ effluent water runs into the Berg River. Morrison *et al*. (2001) states that high levels of nitrate are commonly found in treated waste water because ammonium is oxidized to nitrate. In Figure 3.1.2. (c) levels of nitrate increased significantly at sites 3 and 4- where the Franschhoek and Wemmershoek tributaries enter the Berg River system.

It may be possible that cation competition could have occurred (Orzepowski and Pulikowski 2008). K and Na concentrations were higher than that of Ca and the higher level of these cations could have decreased the availability of Ca as shown in Figure 3.1.2. (d, e and f). Potassium is highly soluble in water, resulting in high concentrations of K in aquatic systems (Griffioen 2001). Generally, with the increase of pH downstream, there was an increase of Ca and as pH dropped at site 4, so did Ca. According to Fernández-Aláez and Fernández-Aláez (2010) significant reductions in calcium levels can be related to elevated H^+ concentrations.

Calcium is used as a primary flocculant to treat effluent water (Parker 1971) and the increase of Ca from site 3 onwards (Figure 3.1.2. (f)) may be due to the various inputs from the Franschhoek, Wemmershoek and Dwars tributaries. In Figure 4.1 one can see the Franschhoek River joining the Berg River, where the colour of the Franschhoek River is darker in colour and can have a higher salinity and poor water quality (Anon. 2004, Adams 2011). The treated effluent flows into the Franschhoek River and is further diluted when the two rivers merge. The Ca levels can also be due to the acidic pH levels, as acidic pH often decreases the concentration of Ca of a river (Adams 2011). This is also evident in Figure 3.1.2. (b and f).

Figure 4.1. The confluence where the Franschhoek River (on the left) and Berg River (right) join.

Mg levels remained low before the river converged with the Franschhoek River, where it increased significantly (Figure 3.1.2. (g)). This shows that the input from the tributary increased the amount of Mg dramatically at site 3. Inputs of Mg can also come from agricultural wastes and tributaries (de Kerchove and Elimelech 2008). Sites 4- 10 are largely cultivated areas and had gradual increases in Mg concentrations downstream and it is thought that it was due to agricultural waste.

(D) Decrease in parameters downstream:

Water temperature depicted in Figure 3.1.3. (a) decreasing downstream may have been caused by the time at which sampling commenced. The time of day and the weather may also have had an influence on the temperature decreasing downstream. Low temperatures may also be caused by dams or by the transport of water from one river basin to the next, or may be caused by changes in the kinds of plant life on the riverbanks (Davies and Day 1998). In this study it could be that the three main tributaries that enter the Berg River may have decreased the water temperatures as well. The plant life of the upper reaches include more smaller shrubs, but as one moves downstream there are much larger trees (such as *Salix* spp. which was found from site 6 onwards). These trees provide shading and therefore decrease the surface water temperature. Johnson (2004) reviewed other literature and has suggested that a decrease in surface water temperature may occur within reaches downstream.

The Pb decrease downstream may be influenced by the pH results found in the study. As stated before, there is a relationship between pH and Pb; when pH is low the concentration of Pb will be elevated in the system (Fatoki *et al.* 2002). Conversely, as seen in Figure 3.1.2. (b) the pH increased downstream and with that Pb levels decreased downstream (Figure 3.1.3. (b)). The geology of the system can also be an input of Pb into rivers (Fatoki *et al.* 2002). At site 1 the river is surrounded by the Drakenstein Mountain and it could be due to runoff from the mountains that the levels of Pb were highest at this site. The higher lead levels at site 1 are unexpected.

Water results over the sampling period:

4.2 (A) No pattern over the sampling period:

Electrical conductivity is usually a reflection of discharge of water which displays the dilution effect (Müller *et al.* 2012). In the first 7 months (about 200 days) of sampling this pattern can be seen (Figure 3.1 and Figure 3.2.1. (a)). Much of the rainfall in the catchment area occurred during the first 8 months of the sampling period, especially on day120, where there was a significant increase in EC due to runoff.

The pH range (Figure 3.2.1. (b)) that the river displayed falls with the range of the pH (6.5- 8.5) of the lotic systems where pollution is not prevalent (Harris *et al.* 1992). According to Reza and Singh (2010) pH values higher than 6 generally shows that carbonates of Ca and Mg are present in water. This can be seen in the seasonal variations of Ca and Mg in Figure 3.2.3 (g and h).

The low pH raises the solubility of Fe (Morrison *et al*. 2001). pH and Fe follow a similar trend in variations as indicated in Figure 3.2.1. (b and c). Filgueiras and Prego (2007) state that high iron values may be due to mineralization of organic material that occurs in the river. Another reason why Fe levels could have been variable is due to the soil-water interaction that occurs in the wet winter months (Reza and Singh 2010).

4.2 (B) A constant pattern over the sampling period:

With the exception of day 32, no significant variation in concentrations was observed for nitrite and phosphorus (Figure 3.2.2 (a and b)). The strange sudden increase in those concentrations may possibly be attributed to the low flow rate of the summer months. According to Bowes *et al.* (2009) the concentration of P decreases as the flow rate of the river increases and causes the dilution of P. Dilution of nitrite may have occurred to such an extent, that it was below detection level. The pattern of no seasonality differences in P was also observed from 1985-1994 (de Villiers 2007). The constant values experienced over time and across seasons suggest a constant input throughout the year.

(C) A wet season high:

The concentrations of the parameters nitrate, Cd, Cu, Zn, K, Na, Ca and Mg increased during winter as shown in Figure 3.2.3. (a- h). The high concentrations may be due to runoff entering the system. In a study conducted on the Berg River by de Villiers (2007) it was deduced that in previous years (from 1985- 2004) runoff increases during the wet season, which is consistent with the winter precipitation of this catchment area (de Villers 2007). When surface runoff reaches the river, it may bring with it nutrients, sediments and heavy metals (Tong and Chen 2002).

The seasonal [NO_x] profile used in de Villiers' (2007) study increased during winter, where runoff was high and it was concluded that this was as a result of non point source enrichment from agricultural runoff. There was also an increase of the use of nitrate based fertilizer that could have caused NO_x to have increased during that sampling period. The nitrate concentrations in this study also increased during the winter months and significantly on day 120 (Figure 3.2.3. (a)) where rainfall was also highest during the year of sampling (Figure 3.1).

In a study conducted by Reza and Singh (2010) Cu increased with heavy rainfall because of runoff from farmed areas and domestic sewage waste from these areas. The heavy rainfall occurred during the early spring months. Similar to the above study, the Cu concentrations (Figure 3.2.3. (c)) increased in the early months of spring in the Berg River, where there was heavy rainfall (Figure 3.1).

Zinc concentration in water largely depends on water inflow (Pistelok and Galas 1999) and therefore the concentration of zinc increased dramatically during the spring month (day 252) (Figure 3.2.3.(d)). In a study by Jackson *et al.* (2007) on metal contamination of the Berg River it was found that the increase in Zn concentrations could be a result of pesticides that contain Zn.

The results of K, Na, Ca and Mg all had a peak on day 120 (June 2009) and Cd on day 252 (Figure 3.2.3. (b- h)). Müller *et al.* (2012) state that these ions determine the ionic strength of the water. Jeffries and Mills (1990) state that rivers with great acidity bring with them a larger metal output and often these metals increase with acidic pH. The acidity of the Berg River over the sampling period ranged between 5.90 and 6.59 (Figure 3.2.1. (b)) which is acidic. The increase of the concentrations may have occurred because of the acidic pH and heavy rainfall.

4.2 (D) A wet season low:

Various literature conclude that dissolved oxygen is the result of high temperatures, as temperature lowers the solubility of oxygen (Dragun *et al*. 2009, Townsend 1980). In the results (Figure 3.2.4. (a and d)) however, the two parameters follow a similar trend. The dissolved oxygen decreased in the winter months of 2009, which results in the release of metals found in solution (Dragun *et al*. 2009).

Dissolved oxygen, ammonium, lead and water temperature showed lower values in winter than in summer (Figure 3.2.4). In Reza and Singh’s (2010) research, it was found that many heavy metals displayed an increase in concentration in the summer period of sampling. The plausible reason these authors give is due to metal accumulation in times where river flow is low.

Reza and Singh (2010) also state that high levels of metals may be due to high evaporation rates of the river followed by higher temperatures. Increased temperature and low flow rates can have the same affect on ammonium. Water levels were lower in summer and more organic matter may have decomposed during the summer months, which may have caused an increase in ammonium Figure 3.2.4 (b)). Dragun *et al.* (2009) had similar findings, as Pb was highest during the summer months due to high water temperatures. The temperature in the Berg River displayed seasonal changes, as temperatures were lower during the late autumn and winter months and increased during late spring and summer (Figure 3.2.4 (d)). According to Dallas (2008) seasonal patterns of temperature displays a sinusoidal pattern; where temperatures are highest in summer and lowest in winter.

CONCLUSION

The present study aimed to determine water quality with respect to nutrients, heavy metals and physico-chemical properties within the river system.

The spatial results revealed that there was an increase in parameters downstream. In a study conducted by Ruiters (2008) results shown that nutrient enrichment had occurred in the upper lower portion of the Berg River. Many of the parameters (such as EC, pH, Na, Ca and Mg) of this current study mirrored the results of the 2008 study. However, there was an increase in the concentrations of nitrate and potassium. Compared to the results obtained from Ruiters (2008) and from the research of Struyf *et al*. (2012) it can be concluded that an increase in pollution has occurred and that the water quality has decreased.

Seasonal trends of nitrate, Cd, Cu, Zn, K, Na Ca and Mg displayed higher concentrations during the wet season than in the dry season. de Villiers (2007) states that “a worst case scenario for the nutrient status of the Berg River” would be a mixture of more farming runoff and direct pollution. Due to the heavy rainfall, runoff may account for much of the increase in parameters during the wet season. It can be estimated that nutrient levels will increase if discharges of runoff from various sources do not decrease (de Villiers 2007).

4.3 SEDIMENT

Cu and Mg were the only two parameters to show significant differences over the wet and dry season (Table 3.3.1). The seasonal metal concentration of the analysed sediment is shown in Table 3.3.1.

The electrical conductivity was very variable across the sites down the river and therefore showed no significant difference between the wet and dry season (Table 3.3.1). Variability of EC was explained by Thirumala *et al.* (2011) as being caused by greater ionic concentration of the river during the flooding time.

The pH remained fairly low and was of an acidic nature (Table 3.3.1). The soil pH is a significant parameter that controls the transfer behaviour in sediment (Peng *et al*. 2009). The lower pH values cause an increase in the competition between H^+ dissolved metals for ligands, which results in increased mobility of the heavy metals (Schulz- Zunkel and Krueger 2009, Peng *et al*. 2009). This may be the case in this study as pH was low. The pH of the soil was lower than that of the river (Figure 3.2.1. (b)). The low pH values (below 7) may be attributed to the leaching of humic acids from the fynbos found at the sites (Ractliffe 2007).

N remained the same in the sediment during the dry and the wet season. Struyf *et al*. (2012) observed N increases downstream within the sediment of the upper Berg River. The results for N (Table 3.3.1) are very surprising, as in previous studies (de Villiers

2007, Ruiters 2008) N was detected within the sediment. The absence of N within the sediment may be due to an error in methodology.

The highest seasonal concentration of Cd was exactly the same in both the water and sediment (Figure 3.2.3. (b) and Table 3.3.1). When concentrations of Zn were low, plants absorb more cadmium from the sediment (Kirkham 2006). The Zn levels are low (they were lower than the average level of 90 mg kg given by Larcher (2001)) for soil (Table 3.3.1).

The average content of Pb in soil is 30 mg kg (Larcher 2001). The average Pb level in the river water over the sampling period (Figure 3.2.4. (c) and Table 3.3.1) was higher than that of the sediment. In sediment however, Pb concentration was lower than the average content value as expressed by Larcher (2001). Kalavrouziotis *et al*. (2009) states that Pb is generally an immobile element, therefore it could have accumulated in the sediment.

Fe generally is found at an average concentration of 40000 mg kg in the soil (Larcher 2001). The level of Fe in the river was much less than that found in the sediment (Figure 3.2.1. (c) and Table 3.3.1). The sediment Fe levels were much lower than the average given by Larcher (2001). Na in the river was also less than that found in the sediment (Figure 3.2.3. (f) and Table 3.3.1). Generally Na content found in the soil is 5000 mg kg (Larcher 2001) and the Berg River sediment's levels were well below this.

The levels of K were higher in the river water compared to that of the sediment (Figure 3.2.3. (e) and Table 3.3.1). The seasonal levels of K in the river are much higher than that of the sediment, which is lower than the average soil content (14000 mg kg) given by Larcher (2001). The release of K is usually slower than the rate by which it is taken up by plants (Ashley *et al*. 2006) and this may possibly be the reason why the amount of K was higher in water than in the sediment.

Ca as stated in Larcher (2001) resides in the soil on average as 15000 mg kg. The level of Ca in the Berg River sediment was lower than this (Table 3.3.1). Sediment Ca was higher than the Ca concentrations in the water. As explained in the section before, Ca is used as an ingredient in flocullants and these ions may have accumulated in the sediment. When looking at the levels of Ca compared to the levels of Mg in the sediment, one can see that the levels of Ca are also higher than Mg. Sediment generally contains a lower amount of Mg than Ca due to the fact that Mg^{2+} ions are not absorbed as strongly as Ca^{2+} ions (Senthurpandian *et al.* 2009) and are thus more prone to leaching compared to Ca ions (Senthurpandian *et al.* 2009) and therefore Mg levels are less than Ca within the sediment.

Copper and magnesium displayed significant variations over the wet and dry seasons within the sediment. Both concentrations were higher in the wet season than in the dry season. The seasonal Cu concentration in the river was much lower than in the sediment (Figure 3.2.3. (c) and Table 3.3.1). The Cu concentration within the sediment was much lower than the average Cu content (30 mg kg) in soils (Larcher 2001). The input of Cu may be due to the fact that Cu can easily complex with organic material and thus a large amount of organic-Cu compounds are formed in the sediment (Fagbote and Olanipekun 2010). The organic-Cu compounds make Cu more readily available in the residue fraction (Fagbote and Olanipekun 2010). A low pH causes an increased availability in Cu in sediments for the plants to absorb (Henning *et al*. 2001).

Mg input also displayed significant variation within the sediment over the dry and wet seasons. The average value for Mg in the soil (5000 mg kg- Larcher 2001) was higher than that of the Berg River sediment as seen in Table 3.3.1. Similar to Cu, the river water's concentration of Mg was much lower than in the sediment. Mg is mainly present in inorganic compounds and also significant amounts are found with organic material in humus (Wu *et al.* 2002).

According to Kulhánek *et al*. (2009) the amount of phosphorus in sediment is generally lowest in sediment solution, and the amount of sediment in the study remained low during the two seasons (Table 3.3.1). The P of the sediment is mirrored by the P of the water, which was also constant for the most part. The average content of P in sediment is 800 mg kg (Larcher 2001) and the amount of P in the sediment was well below this value.

CONCLUSION

When the seasonal concentrations of the sediment are compared to that of water, it can be observed that overall; the concentrations of the parameters in sediment are much higher than that of the water. This suggests that the sediment is a significant sink of elements in the river, where they accumulate (Kesavan *et al.* 2010). Coetzee (1993) explains that it is usually accepted that the elements found in the top layers of the sediment mirror the present water quality of a natural water body and this applies to the results of the Berg River, as it is evident that there was a larger amount of elements accumulated in the sediment. The significant increases in Cu and Mg in the wet season within the sediment are reflected by the seasonal Cu and Mg concentrations in the water- therefore displaying an input of pollution in the sediment and thus the river.

When the seasonal sediment concentrations of the elements are compared to that of the average content of mineral elements in soil (Larcher 2001), it can be seen that all of the elements are much lower than the average content values. These values can be used to compare with the vegetation as vegetation reflects the chemical nature of the soil on which plants grow (Larcher 2001).

4.4 PLANTS

Analyses were carried out to check for differences down the course of the river and over time (seasonal effects). The elements with similar patterns were then grouped together.

4.4 (A) Overall, no significant differences across the sites:

Critical Cd concentrations in plants range between 5 mg kg and 30 mg kg (Vandecasteele *et al.* 2002) and the Cd concentrations within the leaves of the three species were much lower than this (Figure 3.4.1. (a)). According to Doğanlar and Atmaca (2011) trees that accumulate large concentrations of Zn do not accumulate Cd. In Figure 3.4.1. (a) and Figure 3.4.1. (c) it is evident that all three species accumulated Cd, but the Cd concentrations within the leaves are much lower than the Zn concentrations found across the sites. Doğanlar and Atmaca (2011) also state that *Salix caprae* (used in their study) accumulated a higher concentration of Cd than the other shrub species used in the study. This was confirmed by Vandescasteele *et al*. (2002) who stated that Cd accumulation in willow species is high, even if the plants are growing in unpolluted soils. However, *Acacia mearnsii* in this study accumulated a higher concentration across the sampling sites than both *Salix* sp. and *Brabejum stellatifolium* (Figure 3.4.1. (a)).

The Pb concentration in leaves of the three species remained fairly constant throughout the sites. What was surprising was the peak of Pb in *Brabejum stellatifolium*, at site 2 as it was the least viable bioaccumulator of the three species (Figure 3.4.1 (b)). The normal limit of Pb within a plant is 3 mg kg (Doğanlar and Atmaca 2011) and therefore Pb pollution did not pose a threat to the health of the three species. Larcher (2001) lists the normal range as up to 20 mg kg.

Similarly to the results of the water, Zn concentrations within the plant species were not significantly different (Table 3.1.1 and Figure 3.4.1 (c)). The pattern of no significant differences in the accumulation of Pb in the leaves of the plants across the sites was also seen by Doğanlar and Atmaca (2011), showing relatively pristine sites and polluted sites reflecting these results. *Salix* sp. accumulated the highest concentration of Pb, but the concentrations of Pb were well below toxic amounts (between 300 mg kg- 400 mg kg) given by Doğanlar and Atmaca (2011).

Na concentrations along the length of the Berg River also displayed minimal trends within the three species (Figure 3.4.1 (d)). In the study conducted by Ruiters (2008) this pattern was also observed across the sites. However in the present study there was a significant difference at site 10. The Na concentration at site 10 within the leaves of the plants is reflected by the increase in the Na concentration that was present at site 10 in the water (Figure 3.1.2. (e)). It can be assumed that there was a Na input in the river where the plants accumulated Na as well.

4.4 (B) A random pattern across the sites:

The Cu concentration in water of the last three sites (Figure 3.2.3. (c)) corresponds with the Cu concentration within the leaves of *Salix* sp. at sites 8-10 (Figure 3.4.2. (a)). Since there was variability within the Cu concentration within the sediment (Table 3.3.1) during the sampling period, one can assume that Cu may have accumulated in the sediment and have been taken up in plants (Cardwell *et al*. 2002).

Acacia mearnsii and *Brabejum stellatifolium* both displayed the same pattern in K concentrations within the leaves of the plants across the sites, increasing from site 4 onwards (Figure 3.4.2. (b)). The increase in K concentrations downstream reflects the increase of K levels downstream in the water (Figure 3.1.2. (d)). However, the results for *Salix* sp. are more erratic, with many fluctuations that occurred across the sites. The K concentration for site 9, when compared to the Ruiters (2008) study, shows that K concentrations within the plants were in the same range and remained constant at this site.

Larcher (2001) states that the plant requirement for Mg ranges between 1000-3000 mg kg. Mg concentrations within the leaves of *Salix* sp. fell within this range and it accumulated the highest concentration of Mg (Figure 3.4.2. (c)). The Mg concentrations in the leaves of *Acacia mearnsii* and *Brabejum stellatifolium* were much lower than Larcher's required levels. The increase in Mg concentrations in *Salix* sp. also parallels the increase downstream of Mg concentration in the water (Figure 3.1.2. (g)). This trend was also seen in the study by Ruiters (2008).

According to Zhang and Lu (2011) aquatic vegetation species may differ in their means to accumulate nutrients from the surrounding area. This can clearly be seen in Figure 3.4.2 (d), where the P concentrations were significantly higher in *Salix* sp. and *Brabejum stellatifolium* but not *Acacia mearnsii*. *Acacia mearnsii* reflects the constant trend that was seen in the water and sediment. This also correlates with the study done by Ruiters (2008).

4.4 (C) Increase in concentrations downstream:

N, Fe and Ca concentrations within the leaves of the three species increased downstream. As mentioned before, plant N is largely obtained from nitrate in water and sediment. The levels of N in the plant surpassed the nitrate concentration within the water (Figure 3.1.2. (c)). *Salix* sp. accumulated the largest amount of N and *Brabejum stellatifolium* the lowest (Figure 3.4.3. (a)). Struyf *et al.* (2012) explains that the riparian habitats withholds N inputs into the aquatic system and thus the potential for larger inputs of riparian nutrients is high with increasing anthropogenic use of land. The mineralisation of N increases downstream in the presence of anthropogenic intrusion (Struyf *et al*. 2012). The authors also noted a strong increase in N downstream at a 35 km distance and concluded that N increased due to nutrient increases by human practices. The results of this study show similar findings to Struyf *et al.* (2012) in terms of N.

Plants require 100 mg kg of Fe (Larcher 2001). The levels of Fe within the leaves of *Salix* sp. and *Acacia mearnsii* increased to well above the requirement level, particularly at the last four sites. In Figure 3.4.3. (b) site 7 displayed an increase that is six times higher than the required amount, showing that a significant input of Fe occurred. In the study conducted by Demirezen and Askoy (2006), the authors compared Fe concentrations in water, sediment and plants and concluded that plants accumulated more Fe than found in the water and sediment. This correlates with the Berg River results as shown in Figure 3.2.1. (c), Table 3.3.1 and Figure 3.4.3 (b).
When comparing the Fe concentrations of the leaves of the three species it can be seen that *Salix* sp. accumulated more Fe than the other two species.

Calcium is required in large quantities by plants. The concentrations of Ca found within the leaves of the three species are lower than what plants normally require (between 3000-15000 mg kg- Larcher 2001) and are generally in the same range of concentrations (Figure 3.4.3. (b)). The downstream increase of Ca also occurred in the water (Figure 3.2.3. (g)). The concentrations of Ca were higher in *Salix* sp. than *Acacia mearnsii* and *Brabejum stellatifolium*.

Plant results over the sampling period:

4.4 (D) No significant differences over the sampling period:

The Fe concentrations showed minimal variation, where maximum concentrations within the leaves were highest during the first month of sampling and then decreased (Figure 3.4.4.). Plants require 100 mg kg of Fe and in the first month of sampling the Fe concentrations within the leaves exceeded this in *Salix* sp. and *Acacia mearnsii*. The concentrations of Fe were acceptable in *Brabejum stellatifolium*. In the study done by Adams (2011), the same pattern was seen within the leaves of the three species along the Franschhoek River.

4.4 (E) A random pattern over the sampling period:

According to Peralta-Videa *et al*. (2009) Pb is known to have a low solubility and availability for plant absorption due to the fact that it can precipitate as phosphates. This may be the reason as to why Pb concentrations were low within the plants over the sampling period (Figure 3.4.5. (a)). In a study conducted by Bidar *et al.* (2009) the authors found that low concentrations of metals were found during spring months within the leaves where most of the metals were found within the roots of the plants. As the months passed, the metal concentration increased within the leaves, which corresponded with the decrease of metal concentration in the roots. Although root metal concentration was not analysed during this study, Pb within the leaves displayed similar increases and decreases during the autumn and spring months respectively.

Zn and Na show a similar pattern over the year with one random increase occurring within *Brabejum stellatifolium* and *Acacia mearnsii* (Figure 3.4.5. (b and c)). Zn is required in small quantities ranging between 10 – 50 mg kg (Larcher 2001) and the levels within the plants exceeded these values. The higher levels within the plants show an influx of Zn for most part of the year (Figure 3.4.5. (b)).

4.4 (F) A cool season trough:

Most of the elements (N, Cd, Cu, K, Ca, Mg and P) were generally higher in the warmer seasons (Figure 3.4.6.). Bidar *et al.* (2009) state that many other studies have shown a decrease of element concentrations in the growing season compared with autumn. The inverse pattern can be seen in this study. The increase in N, Cd, Cu, K, Ca, Mg and P concentrations during the growing season corresponds with work done by Richardson and Marshall (1986) where highest accumulation of P occurred during the growing season. In a study done by Fife *et al.* (2008) the concentrations of N, P and K in older leaves decreased steadily from August to April months and found that *Acacia mearnsii* showed much more variation than other species anaylsed. *A. mearnsii w*as also the highest accumulator of N in this study (Figure 3.4.6. (a)).

Decreases in concentrations of elements occurred at the time of plant senescence (Fife *et al.* 2008). Kabata- Pendias (2010) states that during the winter season, vegetation may have low concentrations of various trace elements. The elements in Figure 3.4.6 all portray similar patterns of being lower during the winter season. According to Dosskey *et al.* (2010) the vegetation demand for P, K, Ca and Mg is smaller than that of N. Therefore when plants take up nutrients, their uptake highest during the growing season. When the plants mature the growth of leaves slows down and the uptake of elements decreases (Dosskey *et al.* 2010).

When looking at the water results in Figure 3.2.3 the concentrations of the elements increased significantly during the winter time. It is speculated that the plants accumulated these high levels of elements during their growing season. The results for Figure 3.2.3 correspond with the increase of concentrations seen in the plants in Figure 3.4.6.

CONCLUSION

The spatial results revealed that there was an increase in several parameters downstream. The concentrations of the N, Fe and Ca tested within the leaves of the three species displayed significant variation and the Ca concentrations correlates with the Ca levels that increased in the water.

Seasonal trends of N, Cd, Cu, Zn, K, Na Ca and Mg displayed higher concentrations during the plants growing season. When comparing this to the water data, it is evident that these same parameters were much higher during the wet season as discussed before. The plants show an increase in concentrations just after the wet season. Plants tend to accumulate more elements during the growing season (Dosskey *et al.* 2010).

When comparing the three species to one another in terms of bioaccumulation, it is evident that, overall, *Salix* sp. was the better accumulator of the three species. However, *Acacia mearnsii* also displayed higher accumulation of some elements at times. *Brabejum stellatifolium* generally displayed much lower element concentrations.

CHAPTER 5

Summary and Recommendations

5.1 SUMMARY

Riparian trees were used as bioindicators to provide knowledge about the pollution status of the upper Berg River system. This study was undertaken in part because of the new Berg River dam. The river's health was determined by using both biotic (riparian vegetation) and abiotic factors (water and sediment).

5.1.1 Water

Surface water results revealed that spatially, site 1 in the headwaters had the lowest values for EC, pH, nitrate, K, Ca and Mg. It was expected that the outcome for many of the factors examined would be that the least impacted site would show the lowest concentrations. Ammonium, nitrite, Cd, Zn and P showed no significant differences across the sampling sites. Electrical conductivity, pH and concentrations of nitrate, K, Na, Ca and Mg increased downstream, possibly due to input of pollution by the rivers' tributaries, whereas water temperature and lead decreased downstream. The major sources of pollution that occur along the Berg River that may have contributed to the deterioration of water quality are agricultural runoff and urban runoff as well as inputs from tributaries.

Seasonally, the colder season (winter) displayed the highest concentrations of elements over the study period. These high concentrations of water quality factors experienced in the colder seasons were probably due to the initial runoff caused by the high rainfall experienced (Adams 2011, Struyf *et al*. 2012) during the sampling period. Other variables such as water temperature, ammonium and lead decreased during the colder months. Lower temperatures obviously occur in the colder months and dilution or flushing out of concentrations of the elements within the river appeared to occur after the initial increase.

5.1.2 Sediment

Copper and magnesium concentrations in the sediment were both higher in the wet season, showing that the levels of Cu and Mg increased with the amount of rainfall that entered the system. Nitrogen was absent in sediment and this suggests that an error in the methodology may have occurred. Phosphorus concentrations remained constant at 1 mg kg $^{-1}$ in both the dry and wet season. All other elements, as well as physico-chemical properties showed no significant differences in seasonality.

5.1.3 Plants

The trees showed no visible differences between the sampling sites. Cadmium, lead and zinc showed no significant variation between sites. Spatially, some elements (copper, sodium, magnesium and phosphorus) showed a random pattern across the sites. The levels of nitrogen and iron in the leaves of the trees increased towards the downstream area of the river.

Seasonally, only iron remained constant within the three species and displayed no significant differences over the duration of the sampling period. Lead, zinc and sodium had random patterns that occurred throughout the year. There was a distinct increase in the levels of many of the elements in the leaves during the warmer seasons over the year of sampling. The summer months are the growing season for the plants and the leaves tended to accumulate higher concentrations of elements.

Of the three riparian species analyzed, *Salix* sp. displayed the highest accumulation of heavy metals over the sampling period. According to Ladislas *et al.* (2012) an ideal bioindicator is expected to show certain traits. These include the fact that the organism must be able to accumulate high concentrations of heavy metals without dying and to be sessile- therefore representing the pollution within the surrounding environment. The organism must also be widely distributed in the sampling area, for scientific repetition and to survive for a long period of time. Although *Salix* sp. was not found at all the sampling sites, it did accumulate the highest concentrations of metals and also showed more variation than the other two species. If one takes the traits given by Ladislas *et al.* (2012) into regard, then *Acacia mearnsii* and *Salix* sp. are the better two species for bioaccumulation. Due to the fact that *Brabejum stellatifolium* has sclerophyllous leaves, it generally accumulates lower concentrations of elements (Marschner 1995) than the other two species and therefore would not be as effective for riverine pollution biomonitoring. However, if the vegetation along the river is well managed, it may become the species with the evident distribution.

5.2 RECOMMENDATIONS

Two of the three species of plants investigated in this study can be used as viable indicators of pollution; however, they are invasive species. *Acacia mearnsii* grows rapidly and absorbs much more water and nutrients from the system, causing indigenous species to suffer. Although management of these species has been put into place, it was evident during the period of investigation that mismanagement of the removal of the alien species was occurring. Many of the indigenous species were removed together with the alien species, therefore it is recommended that proper management and education must be extended to all parties involved in removing alien species.

If this study were to be repeated, the species used in this study may not be present along the river in the future due to their removal. It would be ideal to use a species that is found across all the sites, however no such plants presently occur, as many of the Acacia's were being removed by Working for Water.

Many farms are found adjacent to the river and use the river as a source of irrigation. Conversely, it may be in part because of agricultural runoff that water quality has deteriorated. Agricultural inputs have caused heavy metal accumulation elsewhere in the Berg River Management area (Meerkotter 2012). Thus monitoring of not only surface water and water-interface sediment of rivers, but also crop soils and crops is recommended.

As runoff is a source of pollution, it may be reduced by the use of wetlands both artificial and natural. Areas that produce higher runoff input may possibly use restricted areas into which the runoff can be drained, or riparian vegetation can be encouraged to help filter excessive nutrients.

This study provided seasonal information of sediment analysis. Monthly sampling of river sediment may offer more insight into the accumulation of nutrients and heavy metals into the sediment from the rivers, which in turn may provide more information into the accumulation of these nutrients and heavy metals in the plants at specific sites.

The Berg River has many tributaries that contribute to the pollution of the river. Future studies could quantify the amount of pollution that is released via these tributaries.

5.3 CONCLUSION

This study adds to the body of evidence (de Villiers 2007, Ruiters 2008, Struyf *et al.* 2012) for deteriorating water quality downstream in the upper Berg River. It did not indicate any lasting negative effects (that were investigated in this study) due to the construction of the Berg River dam.

Monitoring with trees has been shown to be an option, but the alien species will hopefully continue to be removed, allowing for re-establishment of indigenous species.

There is a need to watch the pollution from the tributaries (Knight 2009, Adams 2011) and other sources, especially during low flow (de Villiers 2007). This points to the requirement for continued research into the effects of pollution caused by smaller tributaries in to the Berg River.

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