UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

Investigating the relationship between coal usage and the change in cations and sulphate fluxes in three rivers in the Waterberg, South Africa.

By

LENKE BRUYNS

(442549)

Supervised by Prof. M. C. Scholes

School of Animal, Plant and Environmental Sciences

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements of the degree of Master of Science.

DECLARATION

I declare that this Dissertation is my own, unaided work. It is being submitted for the degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

(Signature of candidate)

23rd day of May 20 16 .

ABSTRACT

The Matimba and soon to be completed Medupi power stations located in close proximity to the town of Lephalale are a cause for environmental concern due to the known effects that coal combustion has on air, soil and water quality. The Medupi power station is currently being constructed, while the Matimba power station may have already negatively altered the water quality of the rivers especially those downwind of the power stations. The Lephalala (perennial river, upwind), the Mokolo (perennial river, upwind) and Matlabas (seasonal river, downwind) Rivers were selected due to the locations relative to the power stations. The concentrations and flux of cations and sulphate ions within the rivers in the Waterberg District Municipality were investigated for any seasonal or annual patterns using monthly data from a single sampling station along each river. Data for the concentrations of sodium, potassium, magnesium, calcium, ammonium and sulphate were analysed in conjunction with river discharge, rainfall and ambient temperature data available for each hydrological year from 1999 to 2010. The data were converted to seasonal and annual values in order to determine the influence of the quality and quantity of coal combusted as well as climatic variables (rainfall, temperature and discharge) on ion fluxes measured. Sodium was the dominant cation in all rivers, reaching a maximum concentration of 0.0015 mol.ℓ^{-1} (in 2007), 0.0007 mol.ℓ^{-1} (in 2007) and 0.0006 mol.ℓ^{-1} (in 2001) in the Lephalala, Mokolo and Matlabas Rivers, respectively. Other cation concentrations were four times lower in the Lephalala and Mokolo Rivers, while they were eight times lower in the Matlabas Rivers. Sulphate concentrations were approximately nine, five and 15 times lower than the cation concentrations measured within the Lephalala, Mokolo and Matlabas Rivers, respectively. The mean summed cation flux was highest in the Lephalala River (0.0015 ± 0.0010 Eq.ℓ^{-1}), which was approximately 1.7 and 2.1 times higher than summed cation fluxes measured in the Mokolo (0.0009 ± 0.0002 Eq.ℓ^{-1}) and Matlabas (0.0007 ± 0.0006 Eq.ℓ^{-1}) Rivers. Cation fluxes were highest during the rainfall season (summer and spring) in the river closest to the Matimba power station (Mokolo Rivers) while summed cation flux in the Lephalala and Mokolo Rivers (located further away from the power station) showed no specific seasonality. It was, however, noted that the cation fluxes during spring and winter were elevated for both rivers, possibly indicating

that the cations are deposited onto the catchment during winter causing an increase in flux after the rains return in spring. Sulphate flux was highest during the dry season (winter and autumn) in the Lephalala River, while sulphate fluxes in the Mokolo and Matlabas Rivers were highest during spring. The fluxes measured in all three rivers were more often significantly altered by river discharge, when compared to ambient temperature. No significant relationship between rainfall and ion fluxes were found, possibly indicating the presence of a longer lag time that spans over months and possibly even years. The effect of the rainfall in one season might only be seen in the flux measured in another season. The sulphate fluxes within the Lephalala River were found to be significantly related to the amount of coal burned at the Matimba power station, which is located beyond the existing modelled deposition footprint. This is possibly due to the north easterly wind direction becoming less predominant during the dry winter months of May and June, allowing the sulphate ions to travel further along the south westerly axis. The water quality, defined as the magnitude of the cation and sulphate fluxes measured, of the rivers upwind of the power stations is worse than the Matlabas River which is directly within the projected area of deposition, possibly indicating that other sources of ions could be responsible for the greater input of ions into the river system. The Lephalala and Mokolo River Catchments are highly developed catchments, with a continual influx of people seeking employment at the mines and power stations. The current population size already exceeds the capacity of the existing sewerage, housing and power supply infrastructure as many households do not have access to these basic services. Leaching of ions from sewerage, waste water and household and agricultural chemicals may be the principal driver of water quality degradation within these rivers. This highlights the need for improved basic sanitation and industrial effluent systems within the rapidly developing Lephalale and surrounding informal villages.

ACKNOWLEDGEMENTS

My sincerest gratitude goes to my supervisor, Professor M.C. Scholes, for her constant guidance, hard words and motivation to improve this study, the outcomes and myself as a person. Thank you to ESKOM and the South African Weather Services for providing the data used in this study. Thank you to the University of the Witwatersrand and the National Research Foundation for funding my degree and to the rest of the School of Animal, Plant and Environmental Sciences for being such a supportive group of people.

To my parents I will be ever grateful for providing me with the opportunity to further my studies and for supporting and encouraging me to improve myself since I was young. To David, my fiancé, thank you so much for dealing with my moods, stress and challenges throughout the course of this degree. Your little gestures of motivation and care never went unnoticed.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER 1: GENERAL INTRODUCTION AND RATIONALE

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: METHODS AND MATERIALS

CHAPTER 4: RESULTS

CHAPTER 5: DISCUSSION

LIST OF TABLES

CHAPTER 1: GENERAL INTRODUCTION AND RATIONALE

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: METHODS AND MATERIALS

CHAPTER 4: RESULTS

CHAPTER 5: DISCUSSION

CHAPTER 1: GENERAL INTRODUCTION AND RATIONALE

The Waterberg District Municipality within the Limpopo Province of South Africa (Figure 1.1) is very rich in coal deposits occurring along an intracratonic rift (Cairncross 2001). Widespread availability of coal and the continual increase in electricity demand in South Africa (having doubled since 1980; Eskom 2013) has led to the area being developed into one of South Africa's energy-producing hubs – with various active coal mines and electricity generating coal-fired power stations located within the basin.

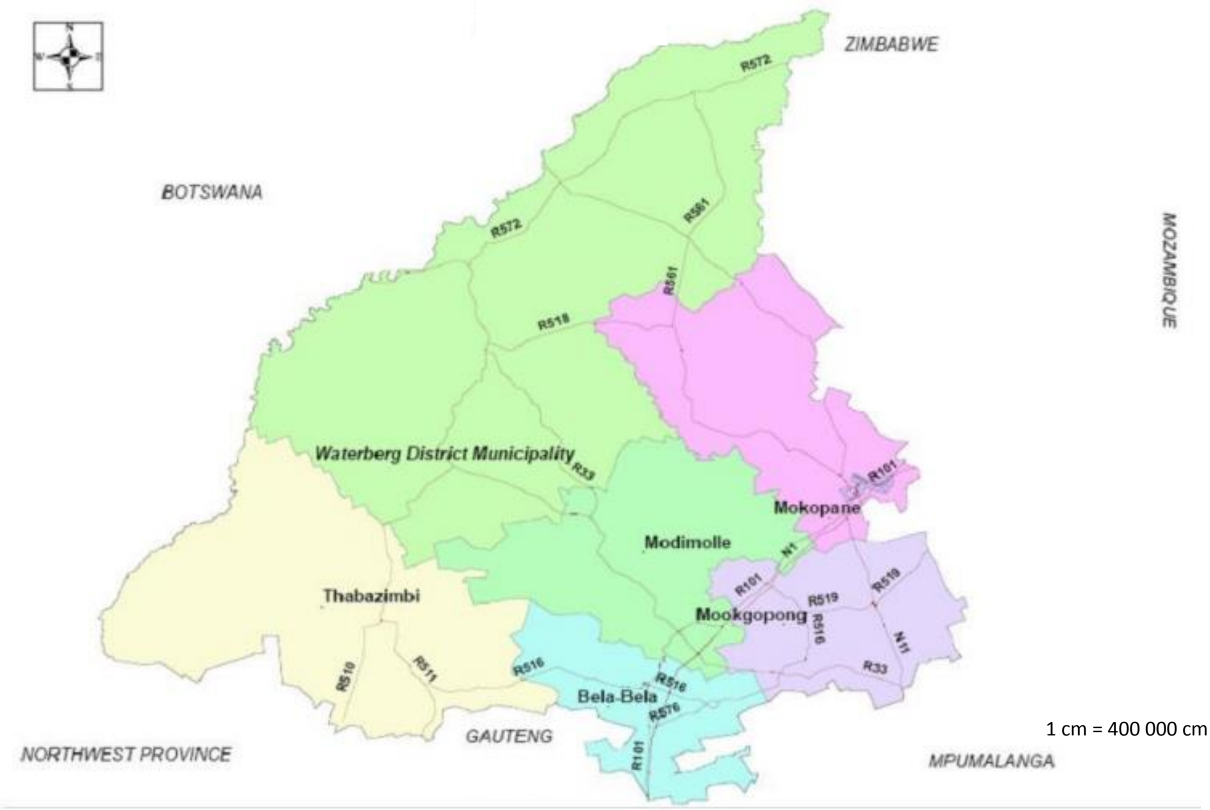


Figure 1.1. The distribution of local municipalities within the Waterberg region of the Limpopo Province, South Africa (Source: IDP 2014). Colours are used simply to distinguish between municipalities.

The Matimba coal-fired power station, fully operational since 1990, has six 665MW units that produce a mean of 23 789 GWh of electricity per year. The station's sole source of coal is the Grootegeluk Colliery, with Matimba burning approximately 14.8 million tons of coal per annum (Ryan 2014). The high amounts of coal burned at power stations across South Africa, and the subsequent high carbon, sulphur and nitrogen emissions, have led to widespread pollution in

Mpumalanga Province and the Vaal Triangle such as the exceedences of SO_2, NO_2 and fine particulate atmospheric concentration maximum limits set by the World Health Organisation (Thomas and Scorgie 2006; Josipovic *et al*. 2011). Future exceedences of the WHO limits set for the atmospheric concentrations of SO_2, NO_2 and fine particulate are now also feared in Limpopo Province.

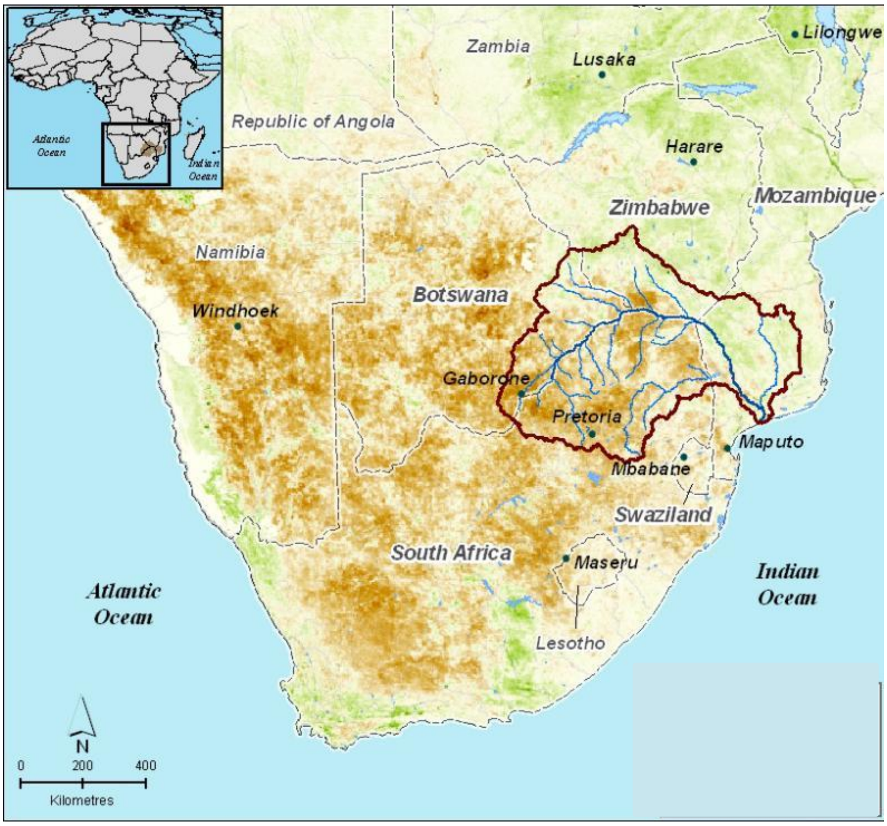
The 4800 MW Medupi coal-fired power station will be the 7th largest coal-fired power station in the world once construction is completed, burning 14.6 million tons of coal on an annual basis. The first of six units officially came online on the 30th of August 2015, contributing 800 MW of power to the national power grid. Once Medupi power station is fully operational, a total amount of 29.4 million tons of coal will burned in the Waterberg District Municipality on an annual basis if both power stations are functioning at full capacity. The doubling of the amount of coal burned within the Waterberg District Municipality is expected to negatively alter the ecosystem processes within the system, with knock-on effects on the requirements for healthcare systems, ecosystem supply in basic human needs and economic performance within the Municipality.

The Waterberg is important for its biodiversity with the Waterberg Biosphere Reserve receiving international status under UNESCO’s Man and Biosphere program in 2001. The reserve stretches over 150 000 hectares, consisting of many conservation areas and conserves a high diversity of species (Henning 2006), including the endangered Waterberg cycad (*Encephalartos eugene-maraisii*; Donaldson 2010) and the near-threatened fish species, the endemic Waterberg shortfin barb (*Barbus sp. nov. ‘Waterberg’*; Engelbrecht and Bills 2007). A total of 21 threatened bird species (critical, endangered and vulnerable species according to the IUCN Redlist) are also believed to occur within the area (DEA 2010). The reserve is located in the southern part of the Waterberg District Municipality and downwind (southwest) of the major polluting parties within the region.

Some studies have started to determine the impacts that the power station has on the reserve and the surrounding natural, communal and commercial areas. Power station fallout has been linked to a change in the distribution of predominantly pollution-resistant crustose lichen populations (Itzkin

2012), increased soil acidity (Itzkin 2012) and decreased populations of already threatened faunal and floral species (DEA 2010). As a whole these studies, although limited, suggest the effects are occurring at an ecosystem scale. This has certainly been the case in other areas affected by industrial pollution (e.g. Gordon and Gorham 1963, Ali 1993 and Tilt 2006). Acidified surface waters are commonly associated with industrial emissions but are only beginning to receive attention in the Waterberg. This highlights the need for deeper understanding and quantification of the effects of deposition within the area.

The river network within the Limpopo Province is broadly referred to as the Limpopo River Basin (Figure 1.2), spanning 408 000km^2 in four countries – South Africa (184 150km^2; 45%), Botswana (81 400km^2; 20%), Mozambique (79 800km^2; 20%) and Zimbabwe (62 900km^2; 15%). The Limpopo River is 1 770km long, flowing from its origin in the Limpopo Province, South Africa, along the borders between South Africa and its neighbouring countries into the Indian Ocean at Xai Xai in Mozambique.



<u>Figure 1.2</u>. The Limpopo River Basin, located in Southern Africa, drains catchments from South Africa, Botswana, Zimbabwe and Mozambique (Source: www.limpoporak.com).

The main South African tributaries of the Limpopo River are (from origin to mouth) the Crocodile (West), Matlabas, Mokolo, Lephalala, Mogalakwena, Sand, Nzhelele, Levhuvu, Letaba and Olifants Rivers. The Lephalala, Mokolo and Matlabas Rivers are located close to the origin of the Limpopo River and drain the catchments in which Lephalale town, the Grootegeluk coal mine and Eskom's Matimba power station are located. Any pollution of these headwaters would thus affect not only the surrounding communities but also the rest of the Limpopo River and all industries and communities from neighbouring countries dependant on the use of its water.

The expected deposition footprint of the Matimba power station does not include the Lephalala and Mokolo Rivers sampled (Figure 1.3). The available footprint of SO_2 around the Matimba power station initially seems to not include the Matlabas River, yet an extension of the footprint image is expected to include the Matlabas River. The footprint is fully discussed in the literature review.

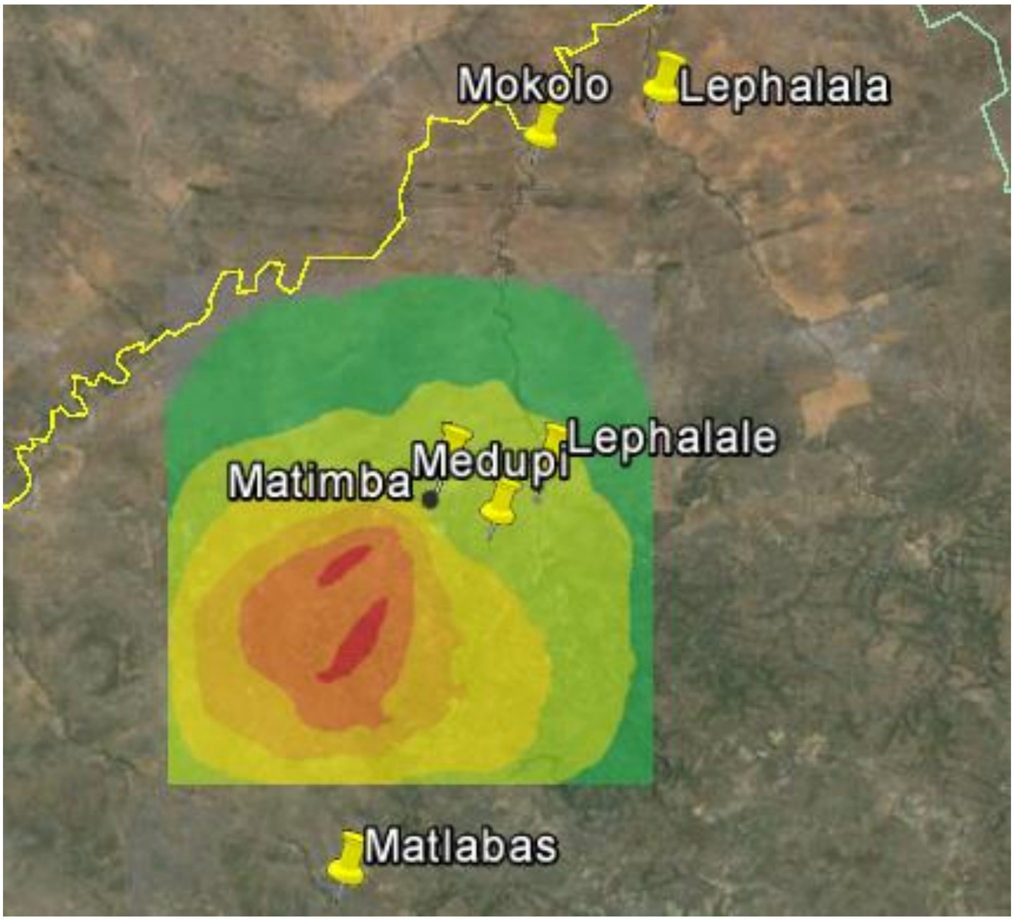


Figure 1.3. A generalised map showing the location of the Matimba and Medupi power stations, the sampling stations along the Lephalala, Mokolo and Matlabas Rivers as well as the modelled distribution of SO_2 concentrations eminating from the Matimba power station.

1.1 The use of individual cation, summed cation and sulphate fluxes in measuring water quality changes

Base cations like calcium, magnesium, potassium and sodium have various natural and anthropogenic sources, including dust from soils, unpaved roads, agricultural tillage and industrial emissions (Scorgie and Kornelius 2009). Additionally, the combustion of coal in power stations emits these cations into the atmosphere, from where they are deposited onto the terrestrial and aquatic systems. Investigating the change in the flux of individual cations provides an understanding of the most probable cation sources and which cations could be a cause for ecosystem and human health concerns if thresholds set by the South African Water Quality Guidelines of 1996 are exceeded.

The use of summed cation flux provides an understanding of the total change in the alkalinity of the river system in order to interpret elevated pH values or to identify if it masks the deposition of acidic anions that could negatively impact ecosystem functioning and human health. Summed cations are useful when used in conjunction with other anions, such as sulphate, as the measured pH is the nett result of the deposition of both alkaline and acidic species.

Patterns in the change in pH of both soils and rivers can mimic SO_2 emissions and consequently sulphur concentration changes, indicating the strong influence that sulphuric acid has on the pH of precipitation (Vet et al. 2014). Sulphate ions are commonly dominating acidified mine waters (Singh 1988) and are commonly used to assess if water sources have been impacted by mining operations. Sulphate concentrations are suitable proxies to assess the effects that coal combustion has on water quality in the rivers surrounding the coal-fired power stations due to the widespread availability of data. Elevated sulphate concentrations can occur in waters with alkaline pH values even if base cation deposition exceeds the deposition of sulphate, emphasising the importance of investigating the summed cation and sulphate fluxes together as done in this study.

For the purpose of this study, “water quality” is defined as the magnitude of the cations and sulphate fluxes measured within the Lephalala, Mokolo and Matlabas Rivers. These values are compared to threshold values set by the South African Water Quality Guidelines (SAWQG 1996) in order to determine whether the river water is clean (good quality) or polluted (bad quality). Clean water is water in which the fluxes of the cations and sulphate are within the target water quality range (TWQR) limits stipulated by the SAWQG for each individual ion. Polluted water has ion fluxes that exceed these limits set, while fluxes lower than the TWQR are considered to be of no concern within this study. When two rivers are compared, “worse water quality” indicates that higher cation or sulphate fluxes were measured in the one river compared to another river. It is, however, possible that fluxes for both rivers are still within the TWQR and of no direct concern.

1.2 Conceptual framework of the study

All ecosystems, including the Waterberg system, are highly interlinked with various processes acting at the same time (Tansley 1935). Pools of nutrients (e.g. calcium, potassium, sodium, magnesium and ammonium) exist within the system, while fluxes between the pools drive the chemical processes that occur. Conclusions on the importance of the relative magnitude of the pools and fluxes can only be made once all the natural and anthropogenic factors of the system are understood.

Three rivers within the Waterberg District Municipality were studied: the Lephalala River (perennial, upwind), the Mokolo River (perennial, upwind) and the Matlabas River (seasonal, downwind). These rivers were chosen due to the location relative to the Matimba power station, with the Matlabas River located within the predicted footprint of the power station plumes. Data available for the selected river sampling stations included cation (sodium, potassium, magnesium, calcium and ammonium) and sulphate concentrations as well as river discharge which were used to calculate seasonal and annual ion fluxes from 1999 to 2011. Concentrations of cations and sulphate continually fluctuate within the rivers, with the measured fluxes only indicating the resultant changes. The rainfall and ambient temperature data available for the town of Lephalale were used to investigate the influence of climatic variables on measured fluxes.

For the purposes of this study, the factors driving the change in chemical ion flux across the soil-water and air-water interfaces within the Waterberg District Municipality are limited to the quality and use of coal at the Matimba power station, changes in land cover and land use, area-specific soil characteristics and changes in wind direction, wind speed, rainfall, temperature, river discharge and human population size (Figure 1.4).

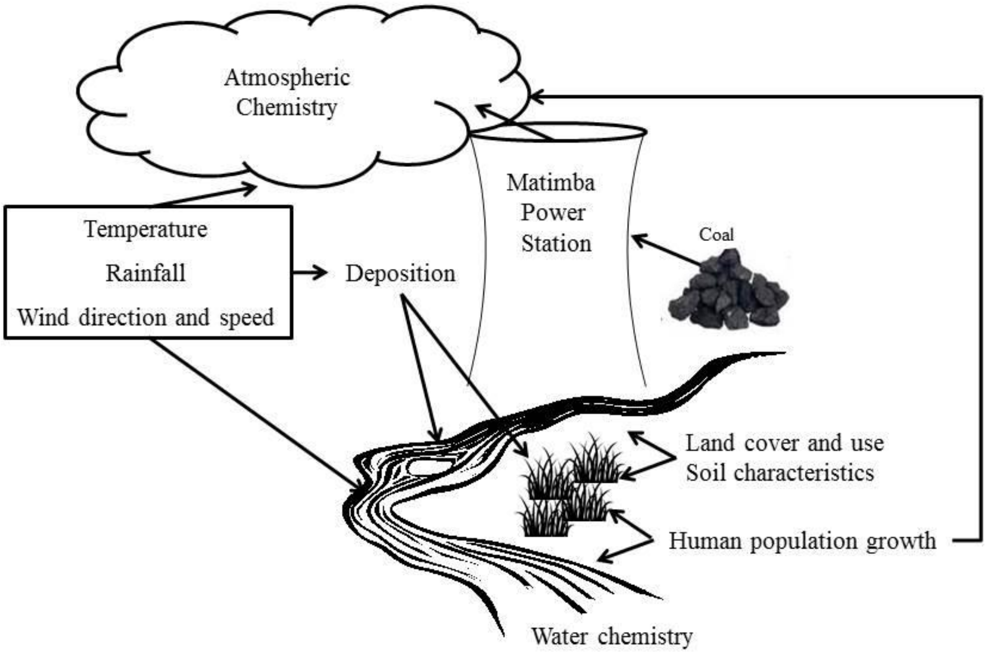


Figure 1.4. A simplified representation of the various natural and anthropogenic factors driving changes in chemical ion pool and flux magnitude within the Waterberg rivers.

An understanding of how these parameters are interlinked is necessary in order to determine the relative size and direction of the influence that one parameter has on another (Figure 1.5). Smaller boxes indicate primary factors while the secondary factors are shown in larger boxes. The size of the arrow gives an indication of the relative impact that each factor has on another, with the impacts of river discharge and river ion concentrations on river ion flux expected to be the largest. Rainfall, atmospheric chemistry, wind, ambient temperature, human population size, land characteristics and coal usage can be considered to be the primary factors driving the changes in ion fluxes measured within the river systems. These parameters also directly impact changes in other primary factors such as atmospheric chemistry which is altered by changes in rainfall, wind, ambient temperature, human population size and coal usage at the Matimba power station. Atmospheric chemistry thus needs to be well understood in order to determine how it is changed by the various natural and anthropogenic drivers.

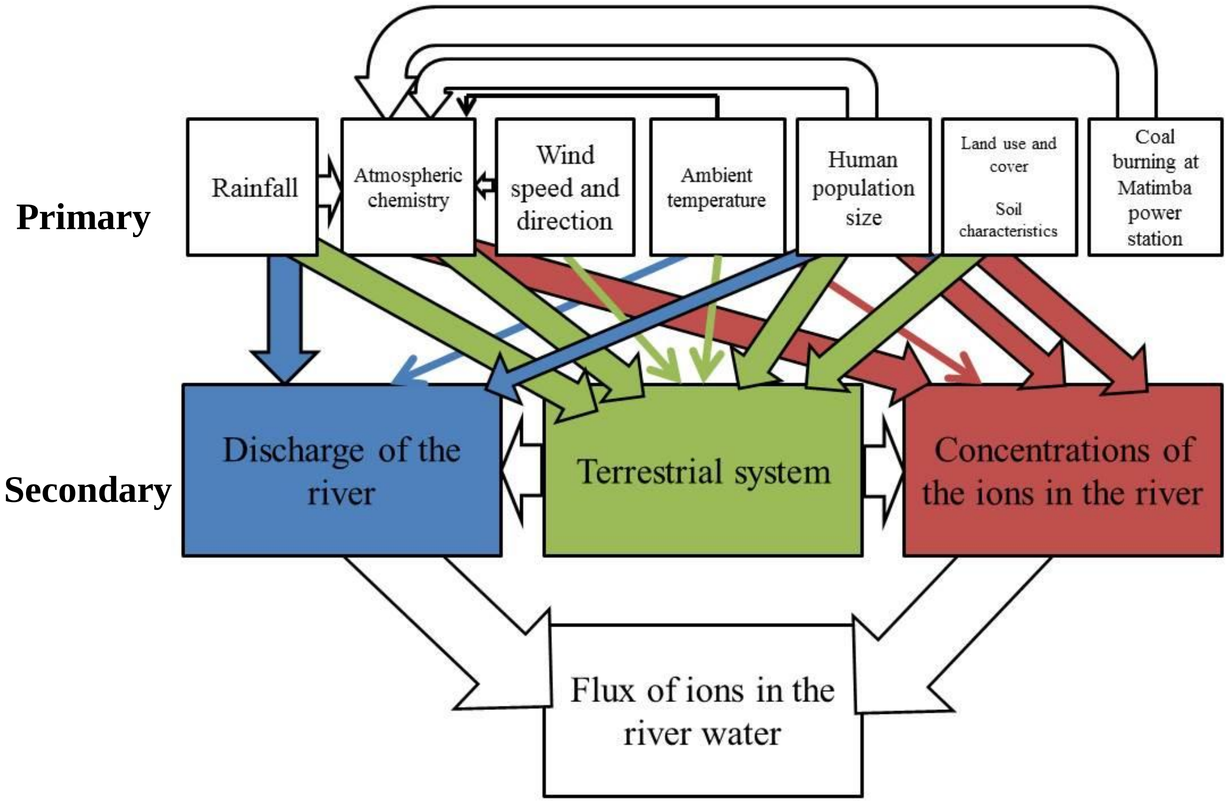


Figure 1.5. The factors driving the changes in ion fluxes measured in a river within the Waterberg District Municipality can broadly be divided into primary and secondary factors that are highly interlinked.

The secondary factors driving changes in ion fluxes measured are discharge of the river, the ability of the terrestrial system to buffer ion inputs and the concentrations of the ions in the rivers. These secondary factors are continually altered by changes in the primary factors. The characteristics of the terrestrial system, including porosity, resistance to erosion and vegetation cover, also drives changes in river discharge and ion concentrations. Ultimately, the resultant river discharge and ion concentrations are the only two factors used to determine the flux of ions within the river.

A total of 31 different scenarios are possible with different combinations of the four natural factors considered (rainfall, ambient temperature, river discharge and ion concentration) when calculating the flux of cations and sulphate within the rivers. These factors were chosen as they are easily measured with extensive data sets already available for the rivers in the Waterberg District Municipality. Sixteen of these scenarios are listed in table 1.1 while the other 15 scenarios are the inverses of scenarios 2 to 16. Scenario 1 is the base to which all other scenarios are compared. These scenarios can act as guidelines to the possible biological, physical or chemical mechanisms driving changes in ion fluxes when interpreting the results.

Table 1.1. The possible scenarios and outcomes when considering different combinations of the four primary natural factors that can drive changes in measured cation and sulphate fluxes within river water.

Scenario	Rainfall	Ambient Temperature	River Discharge	Ion Concentration		Flux
1	Initial State	Initial State	Initial State	Initial State		Initial State
2	Initial State	Initial State	Decrease	Initial State		Increase
3	Initial State	Decrease	Initial State	Initial State		Initial State
4	Initial State	Decrease	Decrease	Initial State		Increase
5	Decrease	Initial State	Initial State	Initial State		Initial State
6	Decrease	Initial State	Decrease	Initial State		Increase
7	Decrease	Decrease	Initial State	Initial State		Initial State
8	Decrease	Decrease	Decrease	Initial State		Increase
9	Initial State	Initial State	Initial State	Decrease		Decrease
10	Initial State	Initial State	Decrease	Decrease		Initial State
11	Initial State	Decrease	Initial State	Decrease		Decrease
12	Initial State	Decrease	Decrease	Decrease		Initial State
13	Decrease	Initial State	Initial State	Decrease		Decrease
14	Decrease	Initial State	Decrease	Decrease		Initial State
15	Decrease	Decrease	Initial State	Decrease		Decrease
16	Decrease	Decrease	Decrease	Decrease		Decrease

If only river discharge decreases while all other parameters remain at the initial state (scenario 2), it is expected that the measured flux would increase. If only ambient temperature decreases while all other parameters remain at the initial state (scenario 3), no change in measured fluxes is expected. These scenarios can also be interpreted for increased river discharge or ambient temperature values.

Decreases in river discharge are expected to directly increase ion fluxes as these two factors are inversely related. Decreased river discharge can occur even though rainfall remains the same (scenario 2 and 4) due to various reasons including run-off into groundwater, uptake of water by extensive vegetation cover or by rapid evaporation of rainfall due to very high ambient and thus surface temperatures. Decreased river discharge in scenario 6 is most probably associated with decreased rainfall and thus decreased surface run-off from the catchment. Decreased rainfall does not, however, always directly translate into significantly decreased river discharge as the river can be recharged by groundwater. It is therefore possible that the river discharge remains the same even when decreased rainfall is measured (scenarios 5 and 7). The ion flux will remain the same as flux is directly influenced by discharge and not rainfall.

In scenario 8, the decrease in all factors but ion concentration will translate into a decrease in ion flux due to the inverse proportionality of flux and discharge. Ion concentrations can be maintained in the absence of rainfall (scenarios 5 to 8) if the contribution of dry deposition is large enough to compensate for the decrease in wet deposition. Although rainfall and temperature does not directly change the flux of ions measured in the river, decreased rainfall possibly decreases river discharge while decreased ambient temperature to some extent alters atmospheric chemistry, decreases river discharge and increases ion concentration due to increased surface evaporation.

Decreases in ion concentration while river discharge remains the same (scenarios 9, 11, 13 and 15) translates into decreased ion fluxes measured as ion concentration and ion flux are directly proportional. If both ion concentration and discharge decreases (scenarios 10, 12, 14 and 16), the ion flux measured is assumed to stay the same if the magnitudes of change in these two parameters are similar. The system in which these factors are measured is highly interlinked and complex indicating that each scenario needs to be understood in its entirety in order to make useful conclusion with regards to the possible reasons why the measured changes in ion fluxes occurred. The biological, physical and chemical mechanisms most likely influencing each scenario is summarized in table 1.2.

Table 1.2. The physical, biological and chemical mechanisms most likely to explain how rainfall (R), ambient temperature (T), river discharge (RD) and ion concentration (IC) ultimately alters ion flux within a river in the Waterberg District Municipality.

	R	**AT**	**RD**	**IC**	**Physical mechanisms**	**Biological mechanisms**	**Chemical mechanisms**
2	=	=	↓	=	Delay in change in river discharge after rainfall.	Extensive vegetation takes up water, decreasing runoff.	
3	=	↓	=	=	Changes in temperatures alter evaporation rates and river discharge.	Denser vegetation cover acts as buffer against effects of temperature.	
4	=	↓	↓	=	Delay in change in river discharge after rainfall. Changes in ambient temperatures alter river discharge.	Extensive vegetation takes up water, decreasing runoff.	
5	↓	=	=	=	River discharge is maintained by groundwater flow during decreased rainfall.		Decreased wet deposition during decreased rainfall. Unchanged ion concentrations possibly due to other sources.
6	↓	=	↓	=	Decreased river discharge due to decreased rainfall, yet some delay can be expected.	Closer relationship between rainfall and discharge in residential areas due to impenetrability of the land’s surface.	No change in ion concentration due to less dilution and decreased wet deposition
7	↓	↓	=	=	River discharge is maintained by groundwater flow during decreased rainfall.		Decreased wet deposition during decreased rainfall. Unchanged ion concentrations possibly due to other sources.
8	↓	↓	↓	=	Decreased river discharge due to decreased rainfall, yet some delay can be expected.	Closer relationship between rainfall and discharge in residential areas due to impenetrability of the land’s surface.	No change in ion concentration due to less dilution and decreased wet deposition.
9	=	=	=	↓	Most likely due to decreased atmospheric ion concentration as rainfall remains the same.	Decreased ion concentration possibly due to increased uptake of ions by vegetation.	Decreased leaching of ions from soils due to adsorption of the ions by plants.
10	=	=	↓	↓	Delay in change in river discharge after rainfall. Decreased ion concentrations due to decreased leaching due to decreased water flow.	Extensive vegetation takes up water, decreasing runoff.	
11	=	↓	=	↓	Decreased temperatures decrease total evaporation, increasing river discharge and thus decreasing ion concentrations.		Decreased ion concentrations likely due to decreased atmospheric concentrations or decreased reaction rates in cooler temperatures.
12	=	↓	↓	↓	Delay in change in river discharge after rainfall. Increased ion concentrations likely due to decreased dilution or decreased leaching with decreased water flow.	Extensive vegetation takes up water, decreasing runoff.	
13	↓	=	=	↓	Decreased wet deposition of atmospheric ions with decreased rainfall.		Ions suspended in the atmosphere in the form of other chemical species in absence of rainfall.
14	↓	=	↓	↓	Decreased river discharge due to decreased rainfall, yet some delay can be expected. Decreased ion concentrations due to decreased wet deposition.		
15	↓	↓	=	↓	River discharge is maintained by groundwater flow during decreased rainfall. Decreased ion concentrations due to decreased wet deposition.		
16	↓	↓	↓	↓	Decreased rainfall during cooler months. Decreased ion concentrations due to decreased wet deposition.		

Changes measured within the rivers are the nett effects of the fluxes of ions, indicating that the input-output balances are not equal to zero. The interaction between river acidification due to sulphate deposition and alkalinisation due to cation deposition often neutralizes the effects of the individual ion fluxes to a certain extent. It can be assumed that the concentrations of cations and sulphate continually fluctuate within the river water, with the measured changes in water chemistry only indicating the resultant changes. Understanding the chemistry of the cations and sulphate from its release to its deposition is important as it gives an indication of how the ions change throughout the deposition process.

The dissertation is structured in order to present the study aim, objectives and key questions first. The second chapter is the literature review, which describes the context of the study as well as the important coal quality and ion chemistry processes that underline the study. The third chapter describes the methods and materials, including field sites descriptions, data collection and processing. The results are presented in the fourth chapter, presenting the analyses of the temporal and spatial trends in pH, ion concentrations, ion fluxes and its relation to rainfall, temperature, discharge and the amount of coal combusted at the Matimba Power Station. The fifth and final chapter is the discussion in which the objectives are answered individually. A final conclusive discussion is presented, summarizing the findings made throughout the dissertation.

1.3 Aim

The study aimed to investigate the relationship between water quality changes measured in the Lephalala, Mokolo and Matlabas Rivers and the changes in local climatic variables, amount of coal burned and quality of coal burned at the Matimba power station.

1.4 Objectives

Objective 1

To describe the changes in pH, individual and summed cation and sulphate concentrations measured for the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2011.

Key questions:

1. What are the temporal trends in pH values measured for the Lephalala, Mokolo and Matlabas Rivers? Why do the rivers show these specific trends?
2. What cations are the major contributors to the summed cation trends found from 1999 to 2011? What are the possible explanations of these changes?
3. Are the trends in summed cation and sulphate concentrations in the Lephalala, Mokolo and Matlabas Rivers the same?
4. Why do concentrations increase and decrease during specific seasons and years?

Objective 2

To determine the annual and seasonal flux of individual cations, summed cations (using equivalent charges) and sulphate ions at a single sampling station along each of the Lephalala, Mokolo and Matlabas Rivers using long term river discharge and water quality data. This is to be done for each hyr\drological year from 1999 to 2010.

Key questions:

1. During which year, over the period of record, is the flux of individual cations, summed cations and sulphate ions across the soil-water interface the greatest for each of the selected rivers and what are the possible reasons for this?
2. What is the seasonal flux of individual cations, summed cations and sulphate ions from 1999 to 2010?
3. Does the river southwest (downwind) of the power station show different flux patterns from the rivers located to the northeast (upwind)?

Objective 3

Investigate the relationship between the amount and quality of coal burned at the Matimba power station and the flux of summed cations and sulphate ions in the Lephalala, Mokolo and Matlabas rivers at an annual resolution.

Key questions:

1. What relationship exists between the amount of coal burned and the measured changes in summed cation and sulphate ion flux?
2. How has the quality of coal burned at Matimba power station changed since its commissioning in 1991?
3. How is this relationship expected to change after Medupi power station comes online?

CHAPTER 2: LITERATURE REVIEW

Coal quality and use in South African coal-fired power stations

Emissions from coal-fired power stations are made up of flue gases, aerosols, fly ash and particulate matter. The ionic composition of the emissions is dependent on the quality of coal combusted and the combustion efficiency of the specific coal-fired power station. Lignite is the lowest quality coal and is commonly used as the combustion fuel in steam-electric power generation stations (Gaffney and Marley 2009). Other coal types generally used in coal-fired power stations across the world include sub-bituminous and bituminous coal (Table 2.1). Bituminous coal, characterised by its deep black colour, is a relatively soft coal with a quality intermediate of lignite and anthracite. Sub-bituminous coal has a grey to brown colour, with a quality intermediate of lignite and bituminous coal. The chemical composition of coal in South Africa indicates that coal produced in the country is sub-bituminous to bituminous and of high quality.

Table 2.1. General description, use and chemical composition after combustion of three common coal types used in power generation in Texas, USA, compared to values found for South African coal samples (Compiled from Meyers *et al*. 1976; McKerall *et al*. 1982; Gaffney and Marley 2009, Van der Merwe *et al*. 2014^{A} and Mainganye *et al*. 2013^{B}).

		Bituminous	Sub-bituminous	Lignite	South Africa	
Description		Dense black or brown coal	Variable properties ranging from those of lignite to those of bituminous coal	Lowest rank of coal		
Uses		Power generation, heat generation and power applications in manufacturing	Used primarily as fuel for power generation	Used primarily as fuel for power generation		
					Author A	Author B
Chemical composition after combustion (% by weight)	SiO_2	20 – 60	40 – 60	15 – 45	49.30	55.66
	Al_2O_3	5 – 35	20 – 30	10 – 25	34.00	27.95
	Fe_2O_3	10 – 40	4 – 10	4 – 15	5.78	3.22
	CaO	1 – 12	5 – 30	15 – 40	5.06	4.38
	MgO	0 – 5	1 – 6	3 – 10	0.99	1.91
	SO_3	0 – 4	0 – 2	0 – 10	0.24	0.03
	Na_2O	0 – 4	0 – 2	0 – 6	<0.01	0.31
	K_2O	0 – 3	0 – 4	0 – 4	0.87	0.45

When comparing South African coal to coal used across the world, South African coal can be considered as low sulphur coal with a mean concentration of 0.87 x 10^4 mg $S.kg^{-1}$ (Kalenga *et al.*

2011) and a certified concentration range of 0.40 – 1.29 x 10^4 mg $S.kg^{-1}$ (Wagner and Hlatshwayo 2005). Coal sample analyses from around the world have reported measured sulphur concentrations of 0.59 – 9.45 x 10^4 mg $S.kg^{-1}$ (United States of America; Hsieh and Wert 1985, Calkins 1994) and 5.40 – 15.10 x 10^4 mg $S.kg^{-1}$ (Spain; Olivella *et al.* 2002). The average individual metal concentrations within South African coal have also been found to show a decreasing trend as follows: Na > Ca > Fe > Mg > K > Ba > Mn > Cr > Pb > Zn > Cu > As > Co > Sb > Hg, with sodium and mercury concentrations measured at 25 294 mg $Na.kg^{-1}$ and 0.21 mg $Hg.kg^{-1}$ respectively (Kalenga *et al.* 2011).

South Africa is the 6th largest coal producing country in the world, producing approximately 247 million tons of coal per annum. Approximately 27% (67 million tons per annum) of the coal produced is exported (Table 2.2). The quality of the coal exported is measured to be much better than that of the domestically used coal (Table 2.3), leaving the lowest quality coal to be burned within the local coal-fired power stations. Gross critical values of coal combusted at power stations indicated the energy content and quality of coal and are often given in conjunction with volatile matter and ash content values, both increasing with decreased coal quality.

South Africa is the 4th largest coal consuming country in the world (Table 2.2) and both the supply and demand of coal (for direct use, conversion to fuels and combustion for electricity generation) has exponentially increased from 1950 to 2006 (Figure 2.1). The total usage of coal per annum within the country is still small when compared to other mega coal consumers such as China, USA and India, yet the increasing trend is expected to continue due to a continual increase in the demand for electricity associated with rapid population growth and economic development without sufficient alternatives of renewable energy sources.

Table 2.2. The global amount of hard coal produced, exported and used in major coal producing countries in 2009. Countries are ranked according to domestic consumption. Compiled from information in Eberhard (2011).

Country	Produced (Mtce*/annum)	Exported (Mtce/annum)	Consumed (Mtce/annum)
China	2 971	23	2 948
USA	919	53	866
India	526	Negligible (estimated at 1.5 in 2005) – imported 77 million tons**	603
South Africa	247	67	180
Russia	229	116	113
Australia	335	262	73
Indonesia	263	230	33

* Million tons of coal equivalents

** Sourced from the USA EIA, August 2010

Table 2.3. The calorific value of coal reserves located across South Africa as provided by Anglo American Thermal Coal (Anglo 2013).

	Calorific value* (kcal.kg^{-1})	
Coal Deposit	**Thermal Export Coal**	**Thermal Domestic Coal**
Kleinkopje	6 190	4 580
Landau	6 210	4 170
Mafube	6 260	5 010
Zibulo	6 100	4 900

*The total potential energy that the coal has that can be converted into heating energy, measured in kilocalories per kilogram of coal.

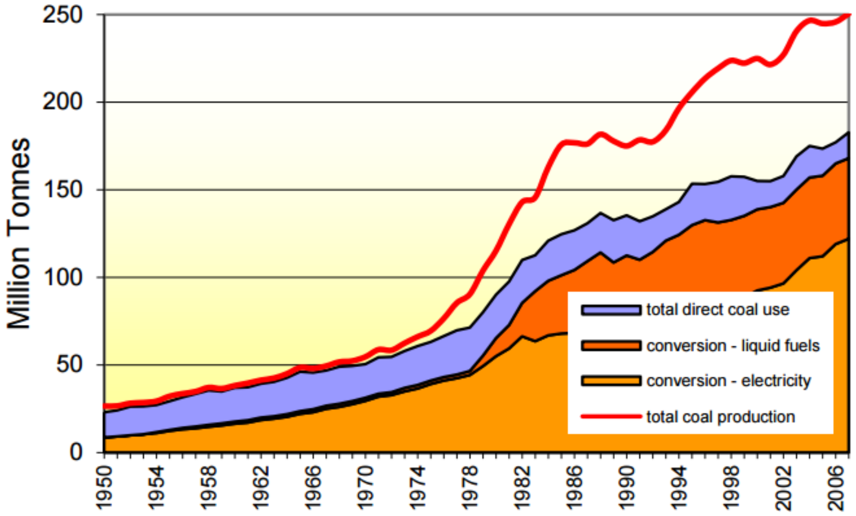


Figure 2.1. South African coal production, consumption and exports: 1950 to 2006 (Marquard 2007).

The emissions, from combusted coal, serve as reactants for many atmospheric chemical processes. The link between coal combustion emissions and changes in ion concentrations in surrounding rivers can only be understood once the atmospheric chemistry of the emissions is considered.

2.1 Atmospheric chemistry of emissions

The emissions of oxides of sulphur compounds (including SO_2) lead to several chemical and physical changes resulting in the formation of secondary particulate matter and aerosols due to oxidation. Oxidation can occur as either gas-phase oxidation (in the absence of water) or aqueous phase oxidation (during which water is essential).

The reaction of SO_2 with OH to form SO_3 is extremely slow (Cox and Penkett 1972). When SO_3 reacts with water vapour (H_2O), sulphuric acid (H_2SO_4) is formed which then dissolves into H^+ and SO_4^{2-} ions. Sulphur dioxide dissolved in water droplets occurs as three different species depending on how far along the reaction chain the specific constituent is. These three species are hydrated SO_2, bisulphite ion (HSO_3^-) and the sulphite ion (SO_3^{2-}). The sulphite ions can then be oxidized by ozone to form sulphate ions, which is a common chemical measure of water quality.

Nitrogen is also deposited from the emissions of coal fired power stations, at a ratio of 1 nitrogen ion for every 2 sulphate ions. The most important contributors to N dry deposition are ammonia (NH_3), nitrogen dioxide (NO_2) and nitric acid (HNO_3; Trebs *et al*. 2006). Muthige (2013) found that power stations were not the only source of nitrogen oxides within the areas surrounding the Matimba power station. Nitrogen oxide concentrations were found to be closer related to low-level sources and had no relationship with the sulphur oxides present. Sulphur oxides were selected to investigate the impact of power station plumes on water quality as it was found to be more closely related to coal combustion emissions than low-level sources. There were also no N data available for the rivers other than NH_4.

2.1.1 Abiotic factors influencing reaction rates

The nature and rate of change of primary to secondary particulates depends on several factors, including the availability of oxygen, the humidity of the air as well as temperature (Hewitt 2001).

Changes in the concentrations of measured secondary compounds can thus be expected to change with a change in the distance of the particulates from the plume, a change in the humidity, the availability of water in the air and a change in ambient temperatures.

Within the plume of a coal-fired power station, the oxidation rates of SO_2 are limited and likely to be lower than in background air due to oxidant limitation (Richards *et al.* 1981; Hewitt 2001). Ozone (O_3) acts as the main source of oxygen within the reactions and is quickly depleted by the rapid reaction with the oxides of nitrogen (~10 times faster than with S; Hewitt 2001), limiting or halting the gas-phase oxidation of SO_2 within the power station plume. Once the plume has moved further away from the source, sufficient mixing with background air replenishes the availability of oxygen allowing for the oxidation of SO_2 to proceed. Clark *et al*. (1984) estimated the oxidation rate of SO_2 at 1%.hr^{-1} within the plume while the rate was estimated to increase to 4.3%.hr^{-1} when diluted with background air.

When coal-fired power station plumes interact with urban plumes close to the source an increased rate of oxidation of SO_2 within the plume is observed, increasing from 2.2%.hr^{-1} to 4.1%.hr^{-1} (Luria *et al.* 1983). Meagher and Luria (1982) found that this occurrence was due to the high background concentration of hydrocarbons, HO_2 and RO_2, in urban plumes. RO_2 is the general term referring to oxidized free radicals. SO_2 oxidation by the OH radical only occurred once the hydrocarbons were depleted.

In areas that are considered to be warm and dry, such as the area surrounding the Matimba and Medupi power stations, the absence of humidity most of the time indicates that SO_2 reaction rates are generally slower than in areas with increased humidity (Meagher and Luria 1982; Liebsch and De Pena 1982). The only driver of aqueous phase reactions in dry areas is the occurrence of sporadic rainfall events. When the plume comes into contact with either water droplets or clouds, the rate of oxidation has been found to increase significantly (5.5%.hr^{-1} to 10%.hr^{-1}: Gillani *et al*. 1981; 1%.hr^{-1} to 6%.hr^{-1}: Dittenhoefer and De Pena 1980).

The combination of no rainfall and low temperatures during winter months slows the oxidation rates and thus deposition of SO_2, as suggested by increased ambient sulphur dioxide concentrations during the colder months (Scorgie and Kornelius 2009). Ambient SO_2 concentrations accumulate during the dry winter months, with highest SO_4^{2-} deposition rates found with the first rainfall during spring/summer (Held and Mphepya 2000).

2.2 Deposition of emissions

Bulk deposition is the total deposition of emissions, when both dry and wet depositions for all chemical species present are considered. Chemical species present include the primary emission of SO_2 and its secondary products, H_2SO_4 and SO_4^{2-}, as well as cations species such as sodium, magnesium, calcium, potassium and ammonium. These species are subject to continual production from a variety of sources and removal from the earth's atmosphere through both dry and wet deposition (Hewitt 2001).

Previous South African studies have found that the dry deposition of SO_2 has the greatest contribution to total deposition of sulphur in the Highveld region (60 – 70%) while wet deposition is relatively limited (30 – 40%) due to limited rainfall (Rorich and Turner 1994, Skoroszewski 1999). Dry and wet depositions vary temporally and spatially, with wet deposition being more predominant at specific times. Although wet deposition is less predominant overall, its contribution could be considered more important as large amounts of ions are deposited in a very short period of time, increasing the instantaneous flux of ions across the air-water interface. Higher rainfall years have been found to correspond with years of increased total sulphur deposition, increasing the deposition by up to two times (Scorgie and Kornelius 2009). The mean flux ($\mu g.m^{-2}.hr^{-1}$) of sulphur was also found to be highest during summer in areas close to sources (Zunckel 1999), most probably due to the deposition of ions in close proximity during rainfall events. In areas further from the source, sulphur deposition was higher during the winter months when the particulates travelled further before being deposited.

2.2.1 *Existing trajectories for the Waterberg District Municipality*

Winds within the Waterberg area are predominantly northeasterly and reach speeds of 0.1 - 8.0 m.s^{-1} (Figure 2.2). The annual atmospheric SO_2 concentrations originating from the Matimba power station have been projected to be highest downwind of the power stations at > 6 µg·m^{-3} and concentrations of 1 - 5 µg.m^{-3} further away (Figure 2.3; Zunckel and Raghunandan 2013). The areas directly surrounding the power stations have annual atmospheric SO_2 concentrations of 2 to 3 µg.m^{-3}, less than half of the concentration measured downwind. The concentration of SO_2 across the area is still significantly less than the limit of 50 µg.m^{-3} set by the national ambient air quality standards (DEA 2009). Kuylenstierna *et al*. (2001) estimated the base cation deposition in the Waterberg to be in the range of 25 – 50 meq.m^{-2}.yr^{-1}. When the sulphate deposition values are converted from µg.m^{-2} to meq.m^{-2} (Table 2.4), it is clear that the deposition of base cations will not neutralise the deposition of sulphate species within the Waterberg area.

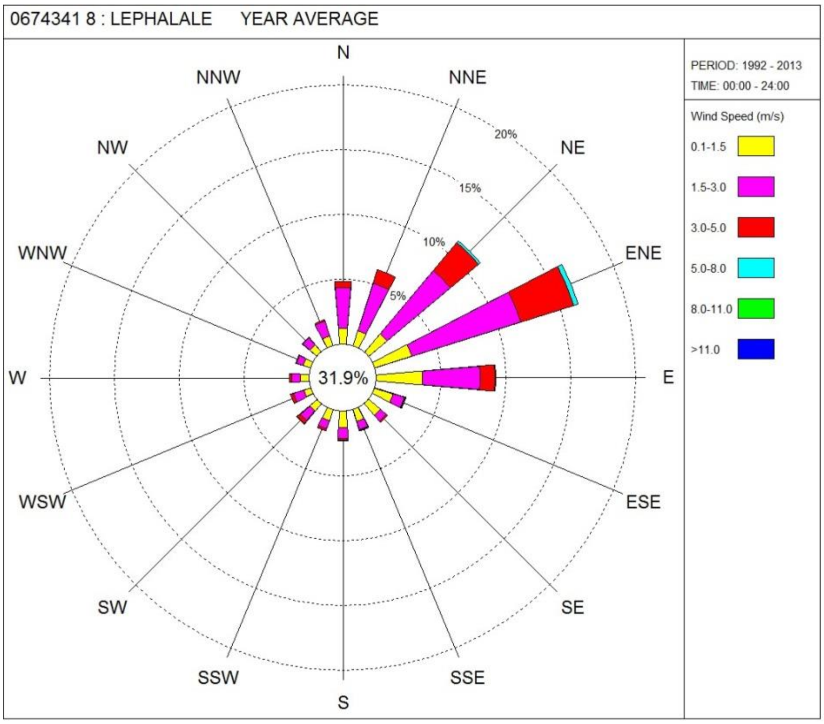


Figure 2.2. The proportion of time that the wind blew from each of the marked directions for the period of 1992 to 2013. Figure was supplied by the South African Weather Service for the town of Lephalale.

Table 2.4. The expected resultant deposition in the area surrounding the Matimba power station using estimated sulphate and base cation deposition data.

Sulphate deposition in µg.m^{-3}	**Sulphate deposition in meq.m^{-3}**	**Mean base cation deposition in meq.m^{-2} ***	**Resultant deposition in meq.m^{-2}**	**pH more acidic or basic?**
1	21	37.5	-16.5	Basic
2	42	37.5	4.5	Acidic
3	62	37.5	24.5	Acidic
4	84	37.5	46.5	Acidic
5	104	37.5	66.5	Acidic
6	125	37.5	87.5	Acidic

* Only a mean base cation deposition concentration is available in Zunckel and Raghunandan (2013). Used as the deposition concentration across the entire area surrounding the Matimba power station.

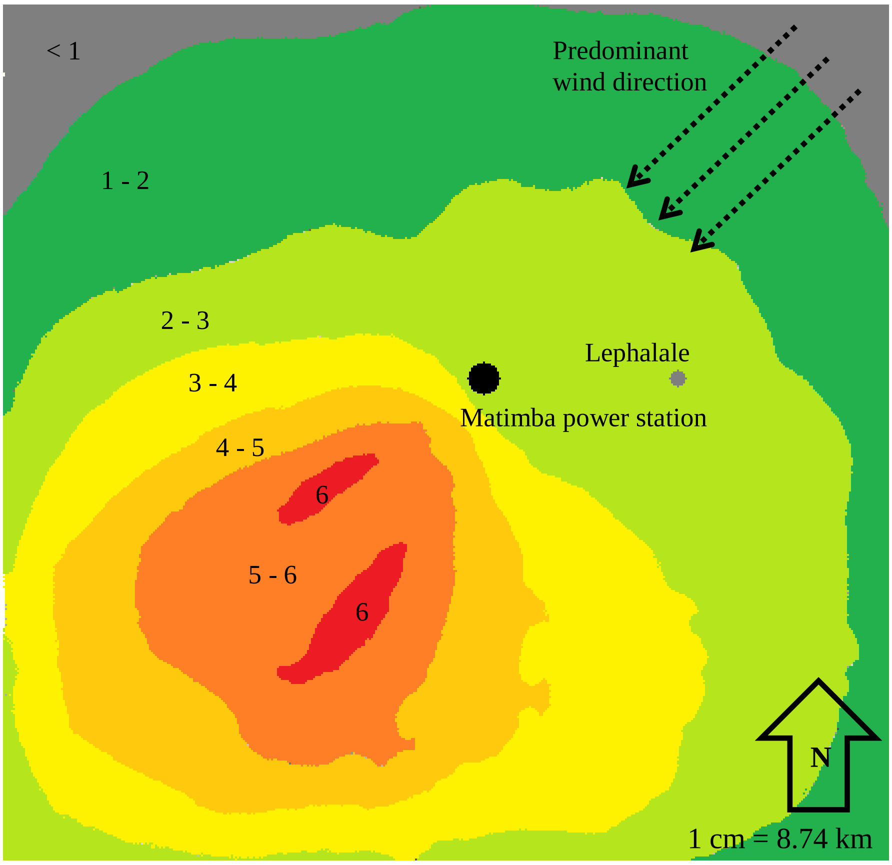


Figure 2.3. The modelled annual average SO_2 concentrations (µg.m^{-3}) resulting from emissions at Matimba Power Station (Adapted from Zunckel and Raghunandan 2013).

The annual average SO_2 concentrations projected for the areas most affected (5 – 6 and >6 µg.m^{-3}) are higher than the concentrations already measured in areas assumed to be highly impacted by the combustion of coal at coal-fired power stations. These areas include Middelburg, Carolina and Brits

(3.6 – 4 µg.m^{-3}); Witbank, Kriel and Komati (4 – 4.6 µg.m^{-3}), Elandsfontein (4.44 µg.m^{-3}) and Slangheuwel (4.77 µg.m^{-3}). The city of Johannesburg has an atmospheric SO_2 concentration of 5 µg.m^{-3} (Scheifinger and Held 1997). The areas and rivers downwind of the Matimba power station are thus at great risk of acidifying as SO_2 is deposited onto the terrestrial and aquatic systems.

2.2.2 Terrestrial deposition of ions and the resulting soil chemistry

The Waterberg District Municipality is predominantly terrestrial, with less than 1% of the total surface area covered with rivers and wetlands (IDP 2014). The deposition of the emissions from the coal-fired power stations is thus mostly onto the terrestrial system, from which it may be leached into the rivers draining the various catchments. In order to understand how the deposition affects the terrestrial and eventually the aquatic systems, an understanding of the specific soil characteristics, land cover and soil chemistry in the Waterberg District Municipality is necessary.

2.2.3 Soil characteristics of the Waterberg District Municipality

The Waterberg District Municipality (WDM) is located within the Limpopo River Basin, south of the town of Lephalale. The lithology of the area shows that there are 26 dominant rock types (DEA 2010), mostly sandstone (De Klerk 2003). Sandstone is a highly porous rock type, allowing for sufficient drainage of the top soils and seepage of water into various water bodies.

The WDM is covered by various soil types (Figure 2.4; Table 2.5). The type of soil indicates the drainage efficiency, buffering capacity as well as cation exchange capacity of a specific piece of land. Different soils thus differ in their capacity to buffer the effects of ions deposited on the surface of the soil.

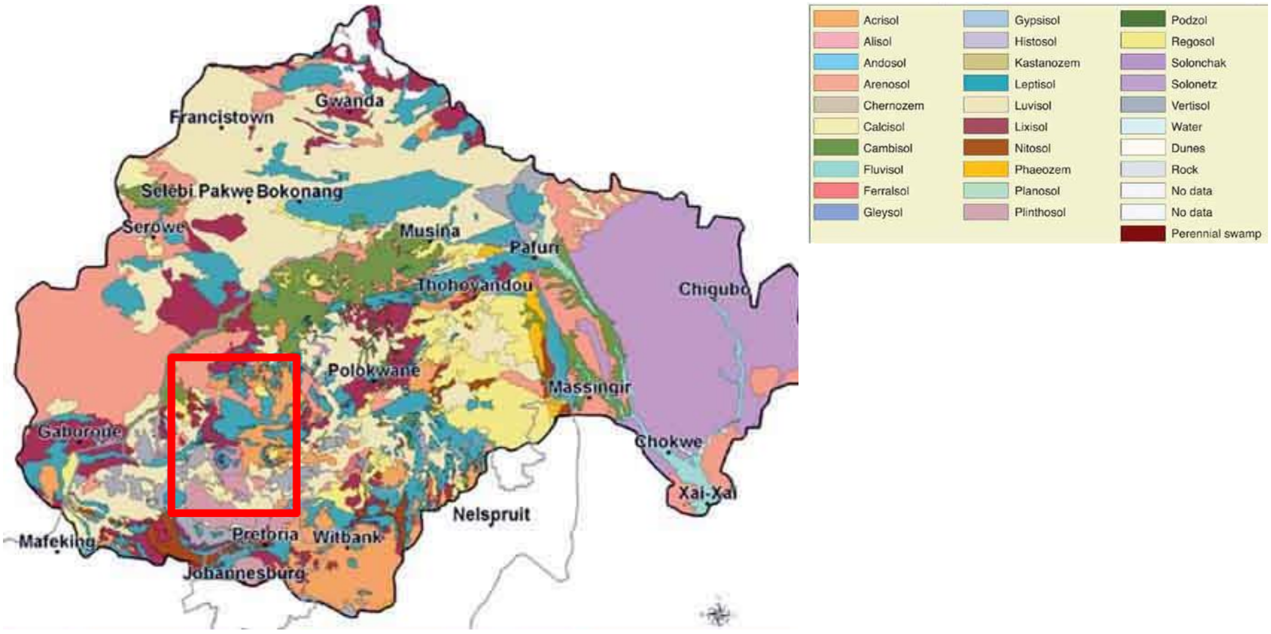


Figure 2.4. The lithology of the Limpopo River Basin. The Waterberg District Municipality is highlighted. (Source: www.limpoporak.com).

Table 2.5. Soil types occurring within the Waterberg District Municipality, ranked from most common to least common.

Soil type	Drainage	Important characteristics
Leptisol	Free draining soils with low water holding capacity	Associated with mountainous areas
Acrisol	Clay-rich, thus dense with low draining capacity	Toxic concentrations of aluminium
Plinthosol	Non-porous	Iron-rich soils
Luvisol	Good internal drainage	High base saturation
Arenosol	Coarse, thus good drainage	Rich in bases in dry areas
Histosol	Poor drainage	Confined to poorly drained basins or areas with high precipitation / evaporation ratio. Often suffer nutrient deficiency
Lixisol	Free draining	Low cation exchange capacity, base saturation > 50%, high pH, low nutrient availability
Regosol	Fine soil, weak drainage	Common in dry and mountainous areas

The sensitivity of the soil indicates the likelihood of the soil being acidified by acid deposition, which is inversely proportional to the critical threshold of the soil. The critical threshold is site specific and is determined using soil cation exchange capacity and base saturation. The soils within the Waterberg District Municipality are predominantly of class 5 (least sensitive) soil sensitivity (Table 2.6) with only a small area of Regosol soil just south of Vaalwater having a soil sensitivity rating of 1 (most sensitive; Josipovic *et al*. 2011). The finer soils have higher organic matter contents due to less oxygen being available for decomposition processes, ultimately indicating an increased cation exchange capacity. These soils retain most of the ions deposited from the atmosphere, but also leach very few of the cations naturally occurring within the soil.

Table 2.6. Allocated soil sensitivity classes against critical loads of acidity (Josipovic *et al*. 2011).

Sensitivity class	Critical load range (meq.m^{-2}.yr^{-1})
1[a]	0 – 25
2	25 – 50
3	50 – 75
4	75 – 100
5[b]	> 100[c]

a: Most sensitive b: Least sensitive c: No critical load

The non-sensitivity of the soils within the Waterberg District Municipality generally indicates high cation exchange capacity and high base saturation soil characteristics. Cations are thus readily available within the soils. Sulphate / sulphur deposition mobilizes the cations, which are either used by the vegetation or leached through the catchment into the water bodies. Understanding the land cover and use of the area is thus important in order to understand the most likely destination of any cations leached from the soils.

2.2.4 Land use and cover within the Waterberg District Municipality

The geographical size of the Waterberg District Municipality is 1.4 million hectares and the major land uses are linked to rural development and mining activities (IDP 2014). A very large portion of the area (~94%) is covered by ‘natural’ vegetation while farmlands are ~5% (Table 2.7). The relative proportion of irrigated land is small and limited to the areas along the Mokolo, Lephalala and Limpopo Rivers, indicating that the growth of crops is highly dependent on precipitation in the rest of the district. Mining activities within the Municipality borders are economically important, yet only cover a mere ~0.3% of the area. This does not, however, imply that the ecological effects of the mining activities are trivial.

Table 2.7. Land use and cover within the Waterberg District Municipality. Table was compiled from the information given in the Waterberg IDP 2014 - 2016.

Land use / cover	Area (ha)	% cover
Degraded forest, woodland, bush clumps and thicket	1 297 184.7	94.1
Cultivated commercial dryland	39 624.4	2.9
Cultivated subsistence dryland	17 244.7	1.3
Industrial area (including residence)	9 916.9	0.7
Cultivated commercial irrigated land	8 488.2	0.6
Mines and quarries	3 609.3	0.3
Rivers	1 532.2	0.1
Wetlands	828.7	0.1
Total	**1 378 429.2**	**100.000**

With the rapid human population and economic growth expected to continue within the Waterberg District Municipality, one can expect that the percentage area covered by farmlands, industrial areas and mining areas will increase significantly while the area of 'natural vegetation' is expected to become smaller. This change in land cover and use will affect the input of both anions and cations into the natural systems, altering both soil and water chemistry. Although the rivers cover only a very small area, the effects of increased human habitation in each river catchment will be reflected in the water quality of the Waterberg Rivers draining into the Limpopo River.

2.2.5 Soil chemistry and the effect of deposition

The effect that anion and cation deposition has on soils depends on the difference in rate of deposition of the precipitation and the rate of acid neutralizing capacity (ANC) generation (Driscoll *et al*. 2001) and is thus dependant on the soil type. ANC is the ability of soils to neutralize acid inputs by increasing the alkalinity of the soil and is the result of terrestrial processes such as mineral weathering, cation exchange, immobilization of SO_4^{2-} (Charles 1991) and atmospheric deposition of cations (Kuylenstierna *et al*. 2001). Anion deposition affects the ecosystem functioning when the soils are not basic enough to buffer the input of anions through precipitation (McGonigle *et al*. 2004).

The ANC processes occur in solution phase and are closely linked to rate of water flow through the terrestrial system (Driscoll *et al*. 2001). With increased precipitation, the ANC of the soil decreases due to rapid water flow and elevation of the water table into the upper soil horizon where acid neutralising processes are less effective. Water draining from the surface soils (during the rainy season) is thus more acidic, while water draining from the sub soils (predominant during the dry season) is less acidic due to the leaching of cations mobilised by the acid neutralising processes (Likens *et al*. 1996).

Although anthropogenic acidification is considered to be the most important input of anions into the terrestrial system, natural acidification processes also contribute to the mobilisation and leaching of cations from the terrestrial system. Natural acidification processes include the production and transport of organic acids formed by decomposing plant matter as well as the organic acids formed by the oxidation of natural nitrogen and sulphur pools (Driscoll *et al*. 2001). With approximately 94% of the Waterberg District Municipality area covered with degraded forest, woodland, bush clumps and thicket, the input of organic acids from decomposing plant material is an important process within the system.

Josipovic *et al*. (2011) compared current deposition rates of anions and cations to the critical load of the soils and found that the current mean acidic deposition rate of 20 - 40 $meq.m^{-2}.yr^{-1}$ in the Waterberg District Municipality is still well within the critical load range of 100 $meq.m^{-2}.yr^{-1}$ found for the soils within the area. Consequently, no exceedances of critical load values within the area have been measured thus far.

The most common soil cations are sodium (Na^+), potassium (K^+), calcium (Ca^{++}), magnesium (Mg^{++}), hydrogen (H^+) and ammonium (NH_4^+). The cations are leached from the terrestrial system when H^+ from deposited acids displaces the cations from the negatively charged soil particles and into the soil solution. The cations within the soil solution are either utilized by the vegetation or the microbial biomass (predominantly Na^+, Ca^{++} and Mg^{++}) for growth (Kirchman 2012) or move laterally and then horizontally into the surrounding water bodies (Figure 2.5). In the figure, only H_2SO_3 and H_2SO_4 inputs are represented as data for only sulphate ions were used while nitrogenous sources and concentrations were not included in this study.

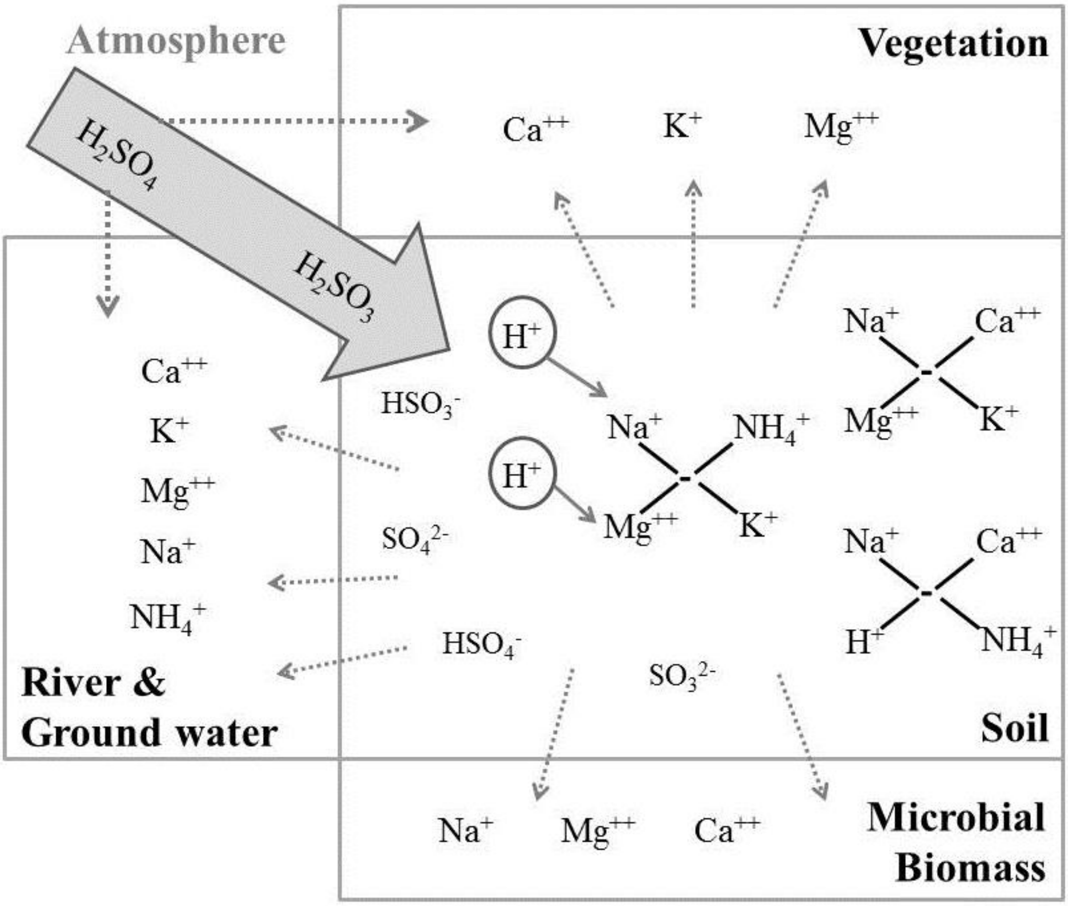


Figure 2.5. A diagrammatic representation of the cations attracted by negatively charged soil particles and the displacement thereof by the hydrogen ions from deposited acids.

2.2.6 Deposition into the aquatic system and the resulting water chemistry

The emissions of the Matimba power station are continuously directly deposited onto the aquatic system within the Waterberg District Municipality. The emissions are deposited from the atmosphere as acids (anions) or oxides (cations), initiating chemical changes when dissolved in the river water.

2.2.6.1 Sulphate ions

Anion precipitation, commonly known as "acid rain", is a well-known consequence of increased SO_2 emissions. Secondary products formed in the atmosphere are HSO_3^-, SO_3^{2-} and SO_4^{2-} (Hewitt 2001). These products are then deposited in the form of H_2SO_4 (sulphuric acid) and H_2SO_3 (sulphurous acid) after reacting with free-floating or precipitation bound H^+ ions. Once the acids are deposited they then dissociate back into the ionic form as they dissolve within the river water (Figure 2.6). The H_3O^+ ions formed during the dissociation of sulphurous acid are then dissociated into water and H^+ ions.

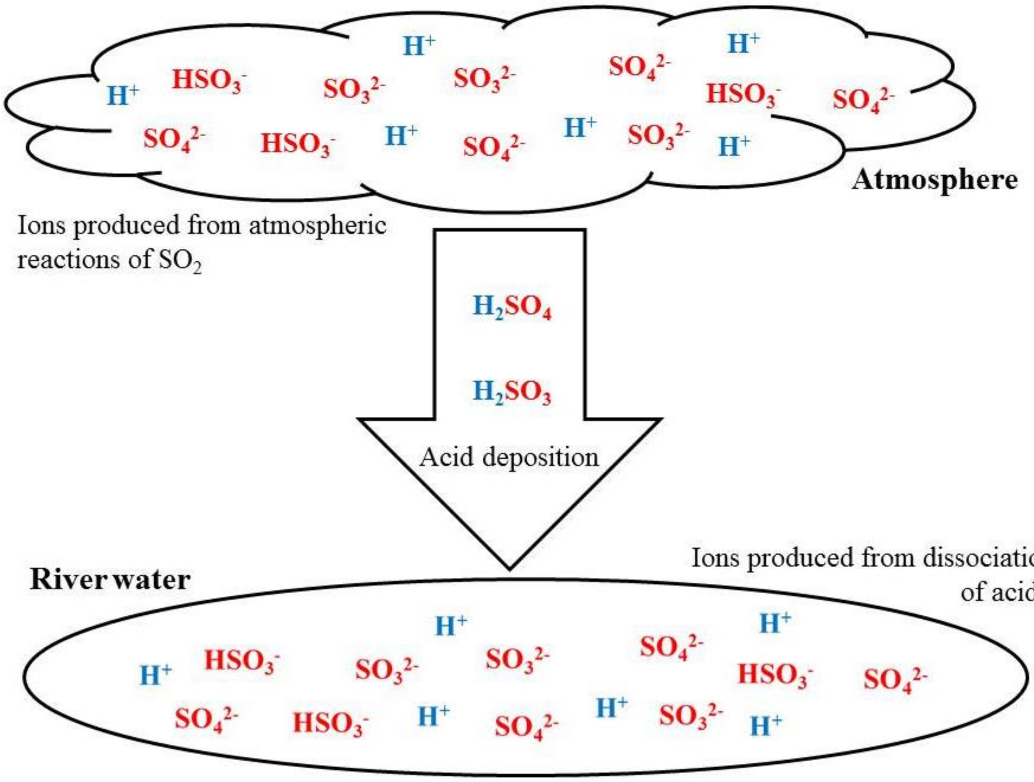


Figure 2.6. Transfer of sulphur containing anions from the atmosphere into water during the river acidification process as a result of SO_2 emissions.

2.2.6.2 Cations

The concentration of cations within river water is the result of total cation input from both direct deposition as well as cations leaching from soils due to soil acidification. Common cations deposited (as oxides) include Na^+, Mg^{++}, Ca^{++} and K^+. In the river these cations react with HSO_3^-, SO_3^{2-} and SO_4^{2-} anions already present in the water to form salts (see Table 2.8) which are dissolved. The removal of anions increases the pH of the water. Any net deposition of cations as oxides will increase the pH due to decreased concentrations of H^+ and increased concentrations of OH^- ($O^{2-} + H^+$), increasing alkalinity.

Table 2.8. Reactions of commonly deposited oxides and anions originating from coal-fired power station emissions.

Oxide	**Anion**	**Reaction**
NaO	HSO_3^-	$NaO + 2HSO_3^- \rightarrow 2NaHSO_3 + O^{2-}$
	SO_3^{2-}	$NaO + SO_3^{2-} \rightarrow NaSO_3 + O^{2-}$
	SO_4^{2-}	$NaO + SO_4^{2-} \rightarrow NaSO_4 + O^{2-}$
MgO	HSO_3^-	$MgO + HSO_3^- \rightarrow Mg(HSO_3)_2 + O^{2-}$
	SO_3^{2-}	$MgO + SO_3^{2-} \rightarrow MgSO_3 + O^{2-}$
	SO_4^{2-}	$MgO + SO_4^{2-} \rightarrow MgSO_4 + O^{2-}$
CaO	HSO_3^-	$CaO + HSO_3^- \rightarrow Ca(HSO_3)_2 + O^{2-}$
	SO_3^{2-}	$CaO + SO_3^{2-} \rightarrow CaSO_3 + O^{2-}$
	SO_4^{2-}	$CaO + SO_4^{2-} \rightarrow CaSO_4 + O^{2-}$
K_2O	HSO_3^-	$K_2O + HSO_3^- \rightarrow KHSO_3 + O^{2-}$
	SO_3^{2-}	$K_2O + SO_3^{2-} \rightarrow K_2SO_3 + O^{2-}$
	SO_4^{2-}	$K_2O + SO_4^{2-} \rightarrow K_2SO_4 + O^{2-}$

Ammonium (NH_4^+), regardless of whether it has come from decomposition or fertiliser inputs, is not often leached into the rivers (Hooda *et al*. 2000). Although it is a cation, the presence of NH_4^+ eventually decreases the pH of water due to either oxidation to produce H^+ ions (Equation 1) or the use of OH^- ions to produce water (Equation 2).

$$2NH_4^+ + 4O_2 \rightarrow 2NO_3^- + 4H^+ + 2H_2O \quad \text{… Equation 1}$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \quad \text{… Equation 2}$$

The pH measured for a specific river is thus the nett result of all these reactions. The pH of the groundwater in the Waterberg has been found to be near-neutral (ranging between 6 and 8; Bester and Vermeulen 2010), and any pH values outside of this range would thus highlight any net changes.

2.2.7 pH of South African Rivers

Mountain catchment waters typically have a pH of 4.0 to 7.0 (Mackintosh *et al*. 2002) which is normal due to the chemical reactions with carbon dioxide (Galloway *et* al. 1982). The mean pH for the Limpopo subcatchment waters is elevated (8.2 ± 0.2; Chilundo *et al.* 2008) when compared to these catchments waters, yet is of no specific concern as values of up to 8.5 is considered acceptable for drinking water (WHO 2003). The waters of the Olifants and Changane subcatchments have mean pH values of 7.8 ± 0.4 and 8.2 ± 0.2, respectively (Chilundo *et al*. 2008) while the pH in the Chunies River ranges from 8.1 to 8.6 units (Germs *et al*. 2004).

The mean pH of rivers across South Africa is 8.4 ± 0.02 (Van Niekerk 2004), a value that is within the target range for aquacultural and irrigation purposes (Table 2.9). The pH is, however, elevated when compared to the target range for industrial processes and ecosystem functioning in surface waters as identified by the South African Water Quality Guidelines of 1996.

Table 2.9. The pH target range values set for different water use types as determined by the South African Water Quality Guidelines of 1996.

Water Use	Target Range
Aquaculture	6.5 – 9.0
Ecosystem functioning (surface waters)	6.0 – 8.0
Industrial processes	7.0 – 8.0
Irrigation	6.5 – 8.4

Slightly alkaline pH conditions have not yet been associated with serious consequences (SAWQG 1996) and would be less of a concern than more acidic conditions in which acid resistant species replace the species naturally occurring within the system. The diel and seasonal variations in pH indicates that most systems are resilient to the change in water acidity, yet a variation of more than 0.5 units from the background pH value can be a cause for concern (SAWQG 1996).

The pH of water can be defined as the logarithm of the reciprocal of the concentration of hydrogen ions (H^+) present. Changes in pH are often misunderstood due to it being on a logarithmic scale, while a change of just 0.1 units means that the water is 1.3 times more acidic or alkaline (Table 2.10). If the threshold of 0.5 units variation is surpassed, it indicates that the water is more than 3.2 times more acidic or alkaline, a change that many species or processes cannot adapt to.

Table 2.10. The relative change in water acidity or alkalinity with every 0.1 unit change in pH (Murrell 2011).

pH difference	Times more acidic / alkaline	pH difference	Times more acidic / alkaline	pH difference	Times more acidic / alkaline
0.1	1.3	1.1	13	2.1	126
0.2	1.6	1.2	16	2.2	158
0.3	2.0	1.3	20	2.3	200
0.4	2.5	1.4	25	2.4	251
0.5	3.2	1.5	32	2.5	316
0.6	4.0	1.6	40	2.6	398
0.7	5.0	1.7	50	2.7	501
0.8	6.3	1.8	63	2.8	631
0.9	7.9	1.9	79	2.9	794
1.0	10.0	2.0	100	3.0	1000

Measuring the pH of water is the initial step in determining the quality, yet many other parameters are also used. The parameters specifically identified for the purposes of this study (sodium, magnesium, potassium, ammonium, calcium and sulphate concentrations) also have target water quality ranges set by the South African Water Quality Guidelines of 1996 and are especially important when considering the feasibility of water for human and livestock consumption.

2.2.8 Target water quality ranges of other standard water quality parameters in South Africa

The Department of Water Affairs and Forestry (DWAF), as it was known in 1996, developed the South African Water Quality Guidelines to serve as a primary source of decision-support when the feasibility of water for domestic and agricultural use needed to be determined. Different water uses have different target water quality ranges, yet the most important uses in the Waterberg District Municipality include domestic use, water for livestock, irrigation and industrial use (Table 2.11). Functioning of aquatic ecosystems is also integral to the area, while aquaculture is not of particular importance.

Table 2.11. The cation and sulphate target water quality ranges (mg·ℓ$^{-1}$) set for different water use types as determined by the South African Water Quality Guidelines of South Africa of 1996.

	Domestic	**Livestock**	**Irrigation**	**Industrial**	**Aquatic ecosystems**	**Aquaculture**
Ammonium	0 – 1.0	-	-	-	< 7	0 – 0.3
Calcium	0 – 32	1 – 1000	-	0 – 50	-	20 – 100
Magnesium	0 – 30	0 – 500	-	-	-	-
Potassium	0 – 50	-	-	-	-	-
Sodium	0 – 100	0 – 2000	< 70	-	-	-
Sulphate	0 – 200	0 – 1000	-	0 – 30	-	-

* - = no guideline values available

Degradation of water quality due to widespread use in various sectors is often associated with large scale changes in water quality parameters, yet changes can also occur due to changes in climatic variables such as the amount of rainfall, minimum and maximum daily temperatures and river discharge. These changes are measured on an hourly, daily, monthly and sometimes yearly resolution while the measured effects do not often exceed this timeframe. These climatic variables are not mutually exclusive and their interaction can either reduce or exaggerate the effects measured.

The exceedance of these target water quality ranges would be interpreted as pollution of the water source for the specific use. Polluted water in terms of domestic use would thus not directly translate in water being too polluted to be used in livestock farming. For the purposes of this study, polluted water is water with cation and sulphate concentrations exceeding the ranges set for domestic use (Table 2.11). “Decreased water quality” is a relative term and would indicate the quality of a river’s water when compared to a river in which lower cation and sulphate concentrations were measured.

2.3 Environmentally initiated changes in water quality

2.3.1 Rainfall

The effect that increased rainfall has on water quality is site specific, depending on the size and seasonality of the stretch of river. Generally, the effects are divided between two outcomes – either increasing or decreasing water quality. The more commonly known effect of increased rainfall is the increase in water quality due to the dilution of excess nutrients, chemicals and other materials in the water (Sipaúba-Tavares *et al.* 2007). This effect is associated with heavy, sudden rainfall events during which the volume of rain is more than the run-off of a particular pollutant, nutrient, chemical or eroded material (Cánovas *et al*. 2008). This view is more strongly held in areas with seasonal rivers, with flow of the river restored by heavy rainfall events early in the rainfall season. The deposition accumulated on the riverbed and catchment is expected to initially decrease the quality of the water, yet the large volume of rain dilutes the ions often masking these changes from measurements made at a monthly resolution.

The second possible outcome explains that increased run-off washes any pollutants, nutrients, chemicals or eroded materials on surface soils into the rivers while increased discharge has been found to decrease the natural acid neutralizing capacity (Driscoll *et al*. 2001). Water quality is thus expected to decrease due to increased concentration of the various constituents, which is aggravated by the water's decreased capability of naturally reducing the acidifying effects thereof. Merolla (2011) found that sulphate concentrations increased during flooding events on the Highveld of South Africa, supporting the general finding that acidity increases with increased rainfall. This finding is even more pronounced in areas closer to power stations.

Semi-arid areas, such as the Lephalala, Matlabas and Mokolo River Catchments in the Waterberg, have low annual rainfall (450-500, 550-600 and 500-550 mm per annum, respectively) with rainfall patterns that are periodic, unpredictable and seasonal. Rainfall events after a long dry season have been found to accelerate water quality degradation due to pollutants being accumulated on surface areas during the dry season (Bae 2013). These accumulated particles are either washed off from the surrounding areas into the rivers, or particles on the dry river bottoms are re-suspended. A peak in concentrations of the various ions is thus expected to be measured soon after a rainfall event occurring after a dry period.

The expected changes in discharge, ion concentration and ion flux is generalised in Figure 2.7. The changes measured are expected to have some lag time after the rainfall occurs, with ion concentration changing the quickest due to direct deposition into the river and rapid runoff from the river catchment. Discharge is expected to have a longer lag time as some water travels over the soil surface while large amounts of water seep through the soil, filling the rivers as groundwater. The latter is a much longer process, with the flow of groundwater usually one order of magnitude smaller than the flow of stream water depending on soil specific characteristics such as porosity, permeability, specific yield and specific retention (Schoeneberger *et al*. 1998). Ion flux is a function of ion concentration and discharge and is thus expected to be the intermediate of these two parameters.

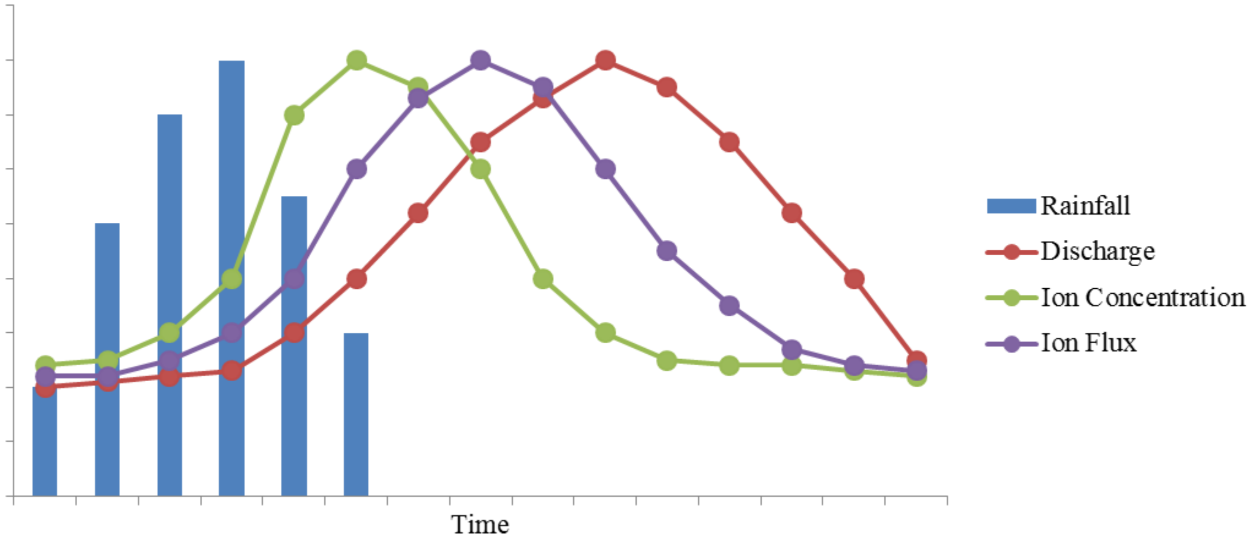


Figure 2.7. A generalised representation of the expected changes in discharge, ion concentration and ion flux due to rainfall. Time is expected to be in months, yet shorter periods of time can be expected in extreme weather scenarios.

Rainfall is not the only climatic variable that affects water quality. Increased rainfall together with increased temperature has been found to increase the concentrations of most water pollutants (Delpha *et al*. 2009). It is thus important to also understand the effect that ambient temperature has on water quality parameters.

2.3.2 Temperature

The effect that ambient temperature has on water temperature and thus the various measured water quality parameters is determined by different factors such as the amount of solar radiation, heat intensity, wind speed, total surface area exposed and the depth of the river water. Shallow, wide streams are much more susceptible to changes in water temperature with change in air temperature than a deep, narrow river would be. Various changes within a water body occur when the air

Table 2.12. Changes occurring within rivers and other water bodies due to increased air, and thus water, temperature.

Parameter	Change	Effects	Description
Evaporation rates	Increased	Negative (positive for N)	With increased evaporation rates the dilution effect of the river water is decreased and increased concentrations of all major elements (except N; See van Vliet and Zwolsman 2008) are measured. Larger rivers are less sensitive to increased evaporation rates as a smaller percentage of the total volume of water is lost (Hamilton 2010). The larger surface areas of dams make it more susceptible to increased water loss due to evaporation.
Decomposition rates	Increased	Negative	Organic acids are produced from the decomposition of plant matter. Increased temperatures increase decomposition rates (Conant *et al*. 2011), thus increasing rates at which natural acidification processes occur.
Chemical reaction rates	Increased	Negative / positive	Various chemical reactions occur within the water body after both natural and anthropogenic inputs of the major elements considered in water quality measures. The increase in reaction rates can thus yield a negative (increased rate of acid dissociation) or positive (increased rate of salt formation) outcome. These effects are, however, expected to counteract one another with only the net result thereof being measured.
Oxygen diffusion rates	Decreased	Negative	The availability of oxygen in water is an important mechanism to counter act any increase in H^+ concentration and thus acidity. The O^{2-} ions produced from the reaction of an oxide and an anion to form a salt usually reacts with the free H^+ ions to produce OH^-. If the rate of oxygen diffusion across the water surface is decreased, the O^{2-} will no longer neutralize the occurrence of the H^+ ions but will instead react to form O_2 to support aquatic life. During times of increased temperature, the pH of the water is thus expected to increase.
Occurrence of macrophytes and epiphytes	Decreased	Negative	Macrophytes and epiphytes occurring on top of the river, on the river bottom and along the river bank absorb chemical elements that occur within the water, acting as a sink (Carpenter and Lodge 1986). The decreased growth and increased death of these water plants increases the concentration of chemical elements in the water in two major ways: 1. The uptake of chemical elements is decreased 2. The release of already absorbed chemical elements from dying plants is increased.

temperature increases, often negatively affecting water quality. These effects are, however, reduced with increased wind speed which decreases air temperature and solar radiation effects.

Changes in air temperatures and consequently surface water temperatures, initiate changes in evaporation, decomposition (Van Vliet and Zwolsman 2008), chemical reaction and oxygen diffusion (Ducharne 2008) rates as well as the occurrence of macrophytes and epiphytes (Whitehead *et al*. 2000; see Table 2.12). The effect of increased temperatures can therefore be both negative and positive, depending on the result being measured. When interpreting the results obtained from this study, these parameters can only be used as possible explanations for any temperature related changes in cation and sulphate flux, with definite outcomes only possible when the individual rates are scientifically measured and compared.

Temperatures within the Limpopo River basin are high, with high evapotranspiration rates estimated across the basin (Figure 2.8). High evapotranspiration rates of 2 001 to 2 500 mm per year are generally estimated for the Limpopo River basin, with only the tributaries within the Waterberg Mountains experiencing a decreased evaporation rate of 1 001 to 1 500 mm per year due to increased elevation. The water quality of the rivers is thus expected to be highly dependent on temperature, with dependence increasing with distance from the mountainous source areas.

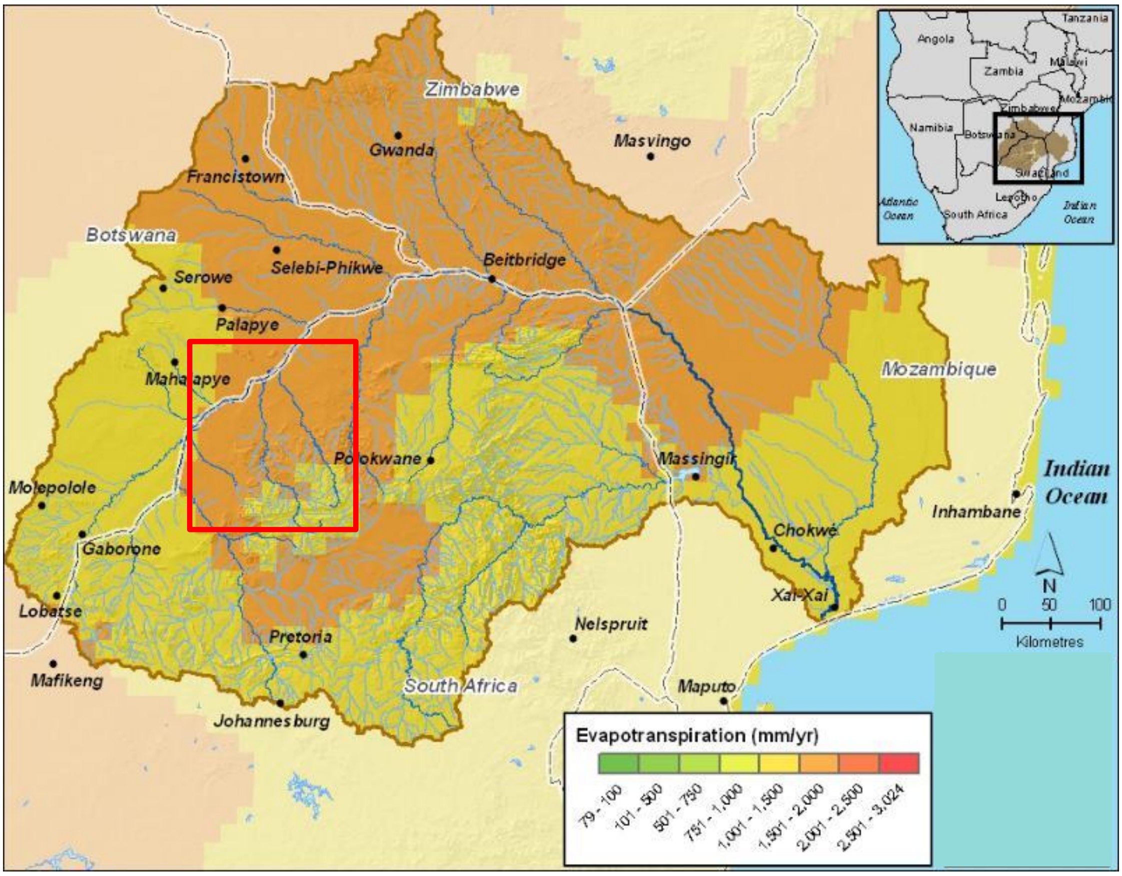


Figure 2.8. Evaporation rates estimated for the Limpopo River basin. Rates are high across the basin, with an increase in evaporation from south to north. The Lephalala, Mokolo and Matlabas River catchments are highlighted (Source: www.limpoporak.com).

2.4 Human population growth impacts on water quality

Human activities widely affect the distribution, quantity and quality of water resources due to their daily needs for food, water, sanitation, shelter, energy, transport and recreation. Ironically, the development made possible by the availability of water also hinders further development once unmanaged water systems become too polluted to be exploited. Although vast parts of the catchments within the Waterberg District Municipality have very low population densities, the majority of the human population within the Municipality are living around the town of Lephalale and its surrounding industrial operations.

The human footprint on the landscape within a catchment can be used to understand how humans are altering the quality of water resources. A high human footprint index of 41 to 60 units (out of a possible 100) is found for the town of Lephalale and the area directly surrounding it. This scored indicated that the grid cell in which the area occurs is within the 41 to 60% least influenced part of the biome and is thus an intermediate score. The rest of the Waterberg District Municipality has an intermediate human footprint index (11 to 30 units), with only conservation areas being the exception (2 to 10 units; www.limpoporak.com). Based on these scores, the Mokolo River (located in close proximity to Lephalale) is expected to be most affected by human impacts while the Matlabas River (located in an area associated with conservation) is expected to be least affected.

The human population in the Lephalale Municipality increased from 96 102 people in 2001, to 115 768 people during the 2011 census showing an increase of 20.5% in 10 years (IDP 2014). This is expected to indirectly alter the water quality of the Mokolo River which flows through the town. With 27% of the youth being unemployed and 38% of the population living below the breadline (less than R14 600 per annum) it is estimated that approximately 12 234 households depend on free basic services. With an average household size of 3.9 people, it can thus be estimated that at least 47 713 people would use the water they can directly access from the river.

2.4.1 *Direct impacts*

Common direct uses of water from the river would include drinking water, bathing, washing and small scale irrigation of crops grown within informal communities. Uses that directly negatively affect water quality are limited to bathing and washing, during which soaps (rich in nitrate) and cleaning detergents (regularly containing ammonia, chlorine and sodium hydroxide) are washed into the stream. These uses can occur either in the stream itself or in an area located within the catchment from which the pollutants are then washed into the rivers. High nitrate values have previously been found to occur in waters downstream of Alexandra Township located along the banks of the Jukskei River in Gauteng, South Africa (Matowanyika 2010). The effect that the direct use of the water by a single person would have on the quality of the water in a river is negligible, yet with the rapidly increasing population size in the area the summed effect is escalated to one that could negatively affect water quality. These effects, however, still are minimal when compared to the negative effects of secondary human impacts on water quality such as sewage effluent from surrounding villages.

2.4.2 Indirect impacts

The source of water contaminants can be either a point or non-point source, with various processes occurring once the contaminant is released into the environment. Point source contaminants of water resources include discharge from sewage-treatment plants and storm water drains, chemical spills, seepage from landfill sites and agriculturally applied fertilizers and chemicals. In the Lephalale Municipality alone, more than 6 300 households do not have access to basic sanitation (IDP 2014), with sewage most probably discharged directly into the rivers or onto the surrounding catchments. Increased nitrate concentrations are measured in water systems as a result of sewage effluent (Wade et al. 2008) often corresponding with areas with inefficient waste water treatment works and large human settlements (Verheul 2012). Urban sewage is also rich in trace metals and nutrients which usually are positively charged cations.

The area is commonly used for livestock (cattle, sheep, piggery and poultry) farming, but also produces crops such as sorghum, wheat, maize and sunflowers (IDP 2014). The addition of nitrogen rich fertilizers to improve the yield of crops is expected. Agricultural runoff is especially rich in nutrients and pesticides / herbicides (Bartram and Balance 1996). An increase in availability of cations would increase the pH to very alkaline conditions which could kill or harm fish by damaging their outer surfaces, preventing them from excreting metabolic wastes and increasing the uptake of salts due to osmoregulation (Evans *et al*. 2005). Inorganic pesticides and herbicides contain copper, copper sulphate, ferrous sulphate and sulphur (Zacharia 2011) that would either acidify or increase the pH of the water resources depending on the ratio of anions to cations present in the chemical. Point source pollution of water resources is a much more intensive and common process, yet is often short-lived and easier to control and rehabilitate.

Non-point sources are predominantly deposition from the atmosphere in the form of either precipitation (wet deposition) or fallout (dry deposition). Non-point sources are more diffuse and less intensive. These sources are, however, impossible to control once the contaminants are airborne and often lead to unforeseen water pollution problems over a longer period of time.

Large scale power generating stations emit high concentrations of gases and particulate matter into the air, yet domestic plumes originating from the suburban areas are important contributors. These plumes are predominantly due to the widespread use of automotive vehicles as well as the burning of various fuel types for cooking, heating and lighting especially in areas that lack the infrastructure to support all the people living within the settlements. With 15% of all households in the Waterberg District Municipality not having access to electrical connections, gas, paraffin, wood, coal and even animal dung are important fuel sources in their day to day living (IDP 2014). Pollutants released by the burning of these fuels include CO, NO_2, SO_2, inhalable particulates and polycyclic aromatic hydrocarbons (Walton and Ngcukana 2009). The use of gas, paraffin and wood has increased while the use of use of coal and animal dung has decreased since 2001 (Table 2.13). The SO_2 emission factors of paraffin ($0.1 g \cdot kg^{-1}$) and wood ($0.2 g \cdot kg^{-1}$) are ~116 and ~58 times smaller than the SO_2 emission factor of coal ($11.6 g \cdot kg^{-1}$; Liebenberg-Enslin *et al*. 2007), yet still have a greater contribution to total domestic SO_2 emissions due to the widespread use of these more affordable and easily accessible fuel sources. When domestic SO_2 emissions are compared to emissions from other sources within the district, it only contributes 0.01% of the total amount of SO_2 emitted (Walton and Ngcukana 2009; Figure 2.9).

Table 2.13. The number of households within the Waterberg District Municipality using the various sources of energy and fuel for cooking, heating and lighting (IDP 2014).

	2001 (20 277 households)			**2011** (29 880 households)		
	Cooking	**Heating**	**Lighting**	**Cooking**	**Heating**	**Lighting**
Electricity	9 174	10 515	16 904	18 046	18 059	25 398
Gas	369	195	67	927	262	34
Paraffin	1 598	1 139	525	2 202	1 401	164
Candles	-	-	6 683	-	-	4 143
Wood	12 929	11 837	-	8 600	6 258	-
Coal	114	137	-	18	20	-
Animal dung	49	40	-	11	15	-
Solar	71	43	46	17	142	77
Other	79	477	159	25	1	-
4482 households (15%) have no electrical connections						

* - = no data available

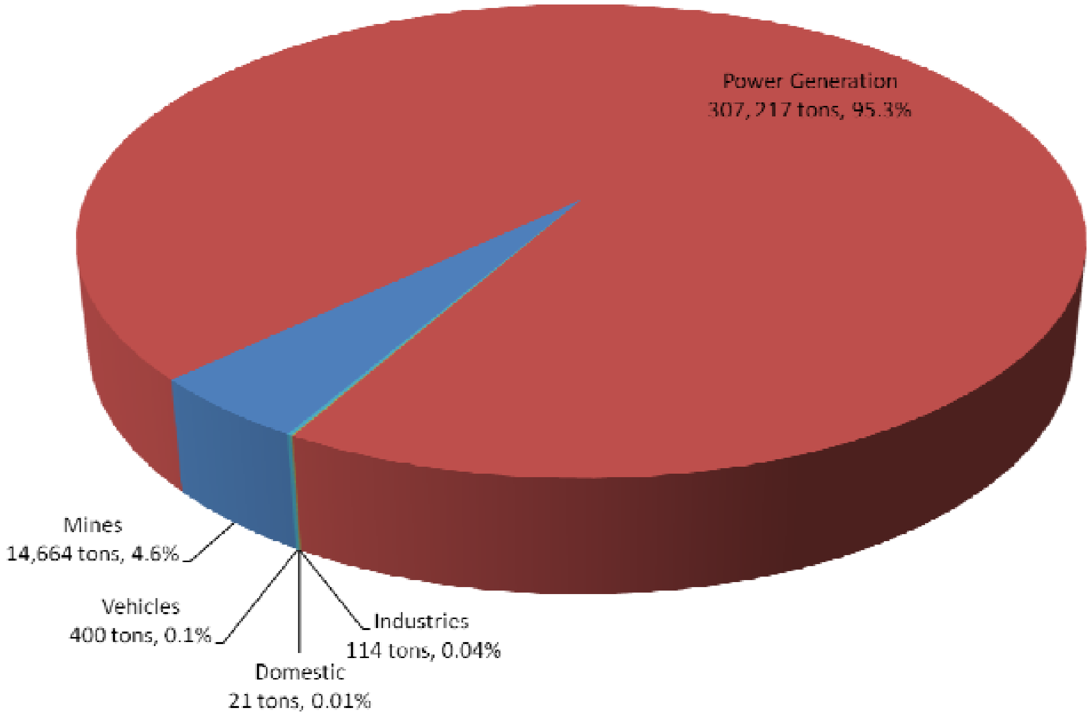


Figure 2.9. Total SO_2 emissions from each of the quantifiable sources identified within the Waterberg District (Walton and Ngcukana 2009).

The plumes generated from household use of fuel are expected to be deposited over shorter distances than emissions from power generating stations, yet still negatively affecting water quality parameters such as the concentrations of anions and cations measured. Hourly ambient SO_2 concentrations measured at the Marapong monitoring station (Lephalale), located upwind of the Matimba power station, mostly ranged between 180 to 210 ppb which is similar to the concentrations measured downwind of the Matimba power station (210 to 240 ppb; Muthige 2013).

The interaction of coal combustion, atmospheric chemistry, ion deposition, soil chemistry and water chemistry with external drivers such as wind, rainfall, temperature and human population size results in the changes in pH, cation and sulphate concentrations and thus fluxes measured within a river system. By investigating each of the components individually, a better understanding of the temporal and spatial trends of these changes is gained. The extent to which the identified external drivers influence the chemical changes measured is explored allowing an informed decision on whether the combustion of coal at the Matimba power station is of human and ecosystem health concern.

CHAPTER 3: METHODS AND MATERIALS

3.1 Study Site

3.1.1 Geographic location of the power stations and selected river basins

The Matimba (23°40'6"S 27°36'38"E) and Medupi (23°43'21.72"S 27°40'45.19"E) power stations are located approximately 20 kilometres west of Lephalale within the Waterberg Water Management Area (WMA) in the Limpopo River basin, Limpopo Province, South Africa. Matimba power station, which was commissioned between 1988 and 1993, has a chimney height of 250 meters expelling plumes high into the atmosphere. Medupi power station is still being constructed, with its chimneys reaching 220 meters. The Matimba power station is located only 12 kilometres northwest of the Medupi power station and the depositional areas are expected to overlap.

The major sub-catchments within the Limpopo River basin include the Nzhelele, Sand, Mogalakwena, Lephalala, Mokolo and Matlabas River basins (Figure 3.1). The Waterberg Water Management Area (WMA) comprises of the Lephalala, Mokolo and Matlabas River basins located towards the western half of the Limpopo River basin.

For the purposes of this study, the water quality data for the Lephalala, Mokolo and Matlabas Rivers, from a single sampling station along each river, were used. These rivers and specific sampling stations were chosen based on their location relative to the Matimba power station (Table 3.1), with the Lephalala and Mokolo Rivers located upwind (northeast) of the power station and the Matlabas River located downwind (southwest). The Matlabas River was expected to be most impacted by the effects of coal combustion at Matimba power station.

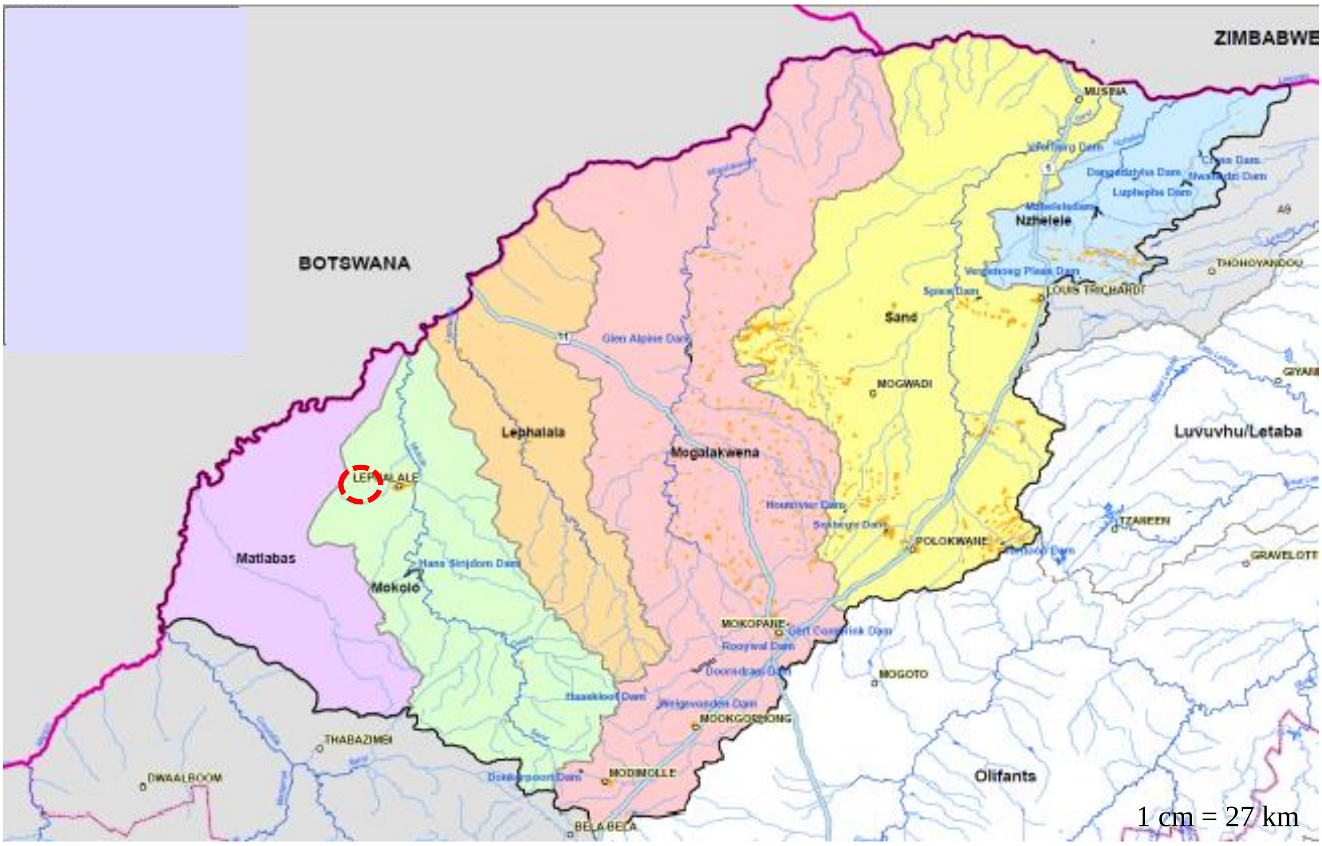


Figure 3.1. The major sub-catchments within the Limpopo Water Management Area in the Limpopo Province, South Africa. The location of the power stations is indicated in red (Source: www.dwa.gov.za)

Table 3.1. Location and description of the sampling station selected for each of the Lephalala, Mokolo and Matlabas Rivers in relation to the Matimba power station.

River	**Location of sampling station along each river**		**Description of location of sampling station**	**Direction of sampling station from power station**	**Distance of sampling station from power station**
	Latitude	**Longitude**			
Lephalala	23°13'1.00"S	27°53'30.00"E	Ga-Seleka Village Bossche Diesch, R572 Bridge on Lephalala River.	Northeast	57.9 km
Mokolo	23°35'57.00"S	27°44'31.00"E	Mokolo River at Moorddrift / Vught	Northeast	16.3 km
Matlabas	24° 9'34.00"S	27°28'47.00"E	Matlabas River at Haarlem East	Southwest	55.7 km

3.1.2 *The Lephalala River Catchment*

The Lephalala River has a catchment area of 4 868km^2 (Boroto 2001; Figure 3.2) and the land is used predominantly for agriculture and game farming (Oberholster *et al*. 2010) with no industries or mines occurring within its boundaries. The river is perennial, originating in the Waterberg mountains where rainfall is high. It then flows north into the Limpopo River. The main tributaries of the Lephalala River are the Klip, Goud, Melk and Boklandspruit Rivers (Busari 2008).

Figure 3.2. The Lephalala River Catchment, Limpopo, South Africa (Source: www.limpoporak.com). The position of the Lephalala River sampling station is indicated in red and Lephalale town in orange.

The Lephalala River sampling station selected is located along the lower reaches of the river, close to its confluence with the Limpopo River. This site was selected as it is located upwind (northeast) of the Matimba power station. It is located in close proximity to a large informal settlement and is used as a water source for livestock and domestic use. During a site visit in late August of 2015 the river was non-continuous with minimal surface flow observed, most probably due to low rainfall occurring during the dry winter season. The impact of human settlement on the river is evident by the widespread occurrence of refuse and unwanted objects scattered in and around this section of river (Figure 3.3).

Figure 3.3. The stretch of the Lephalala River along which the selected river sampling station is located. (Photos taken by Lenke Bruyns on 22 August 2015).

The upper parts of the catchment are predominantly used for irrigation purposes through surface water extraction and there are many small farm dams located along the river tributaries for this purpose. The middle reaches of the river are surrounded by ‘pristine’ wilderness and play a vital role in the tourism industry within the area. The concern, however, is that there is a rapid increase in the number of hotels and lodges along the middle and upper reaches of the river, which could pose water quality threats if the effluent from these holdings is not properly managed.

The lower, drier reaches of the river support rural subsistence as well as commercially irrigated cultivation with many farms located along the river banks (DWA 2013). A large number of people reside in rural villages within the Lephalala River Catchment (HDA 2013) along the lower reaches of the river and are dependent on the river for drinking and washing purposes.

The Lephalala River Basin has a naturalized mean annual runoff (MAR) of 150 million m^3 (GOSA-DWAF 2003), a denaturalized MAR of 99 million m^3 (Görgens and Boroto 1999) and an ecological reserve of 17 million m^3 (GOSA-DWAF 2003). Naturalized run-off is defined as the run-off resulting from natural processes, such as precipitation. Denaturalized run-off is the run-off resulting from anthropogenic activities.

The ratio of denaturalized to naturalized runoff is 0.66 and is considered to be an intermediate value indicating that the basin is in the transition of undeveloped to developed. During the months of May to August, precipitation is often absent. During these months the ecological reserve is maintained by the denaturalized MAR assumed to be supplied by the agricultural activities and discharge from the high density of towns (villages) located along the river (Figure 3.4).

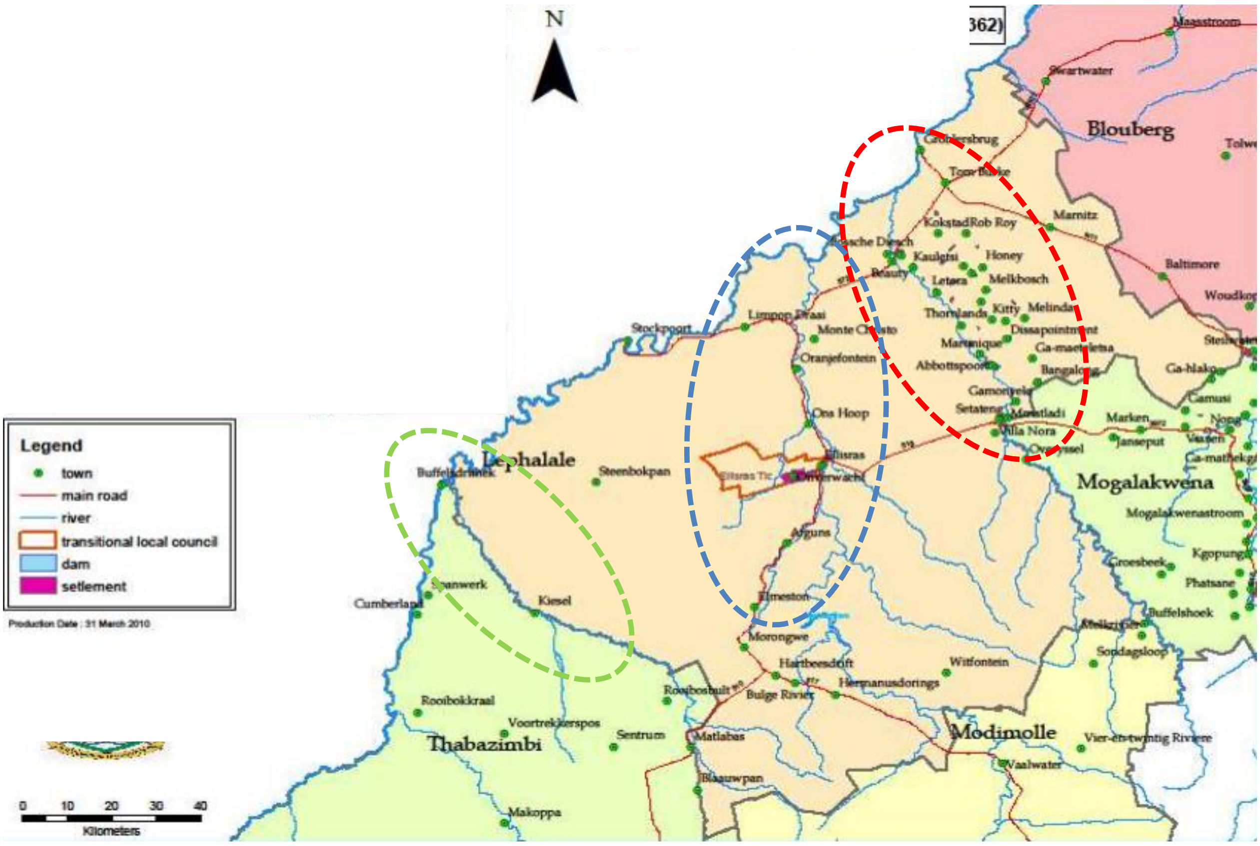


Figure 3.4. The location of towns and informal settlements around the Lephalala (red), Mokolo (blue) and Matlabas (green) Rivers within the Lephalale District Municipality (Source: mfma.treasury.gov.za).

3.1.3 The Mokolo River Catchment

The Mokolo River Catchment drains an area of 8 387km^2 with the perennial river originating in the flattish hills (koppies) just north of the town of Alma and flowing north to its confluence with the Limpopo River at the South Africa / Botswana border (Figure 3.5). The main tributaries are Grootspruit, Klein Sandspruit, Heuningspruit, Malmanies, Poer-se-Loop and Rietspruit Rivers (Busari 2008). The Mokolo Dam was built along the lower reaches of the river to supply water to Lephalale Municipality, Matimba power station and the Grootegeluk coal mine (DWA 2013). The dam also supplies water for the ongoing construction of the Medupi power station (Dhemba 2013).

<u>Figure 3.5</u>. The Mokolo River Catchment, Limpopo, South Africa (Source: www.limpoporak.com). The position of the Mokolo River sampling station is indicated in red and Lephalale town in orange.

Figure 3.6. The stretch of the Mokolo River along which the river sampling station is located. Arrows indicate the location of the pipelines and suspected water pump (Photos taken by Lenke Bruyns on 22 August 2015).

The Mokolo River sampling station is located in close proximity to the town of Lephalale and the surrounding mines and power stations along the lower reaches of the river. This station was selected as it is located directly upwind (northeast) and in close proximity to the Matimba power station and Lephalale town. The Mokolo River is located in closer proximity to the Matimba power station than the Lephalala River. The section of river where the sampling station is located is wide and shallow. Signboards around the area indicate that it is marked as a mining area, with no indication of the type and size of mining operations. Pipelines and a pump on the river bank could indicate direct use of water from the river while the destination of this water is unknown (Figure 3.6).

The catchment is well developed with industries, mines and extensive agricultural activities located within its borders. Three large towns (Lephalale, Vaalwater and Alma) occur within the catchment with the centres of each town located along the banks of the river. Mining activities within the catchment are expected to expand as the Mokolo River Catchment, together with the Lephalale River Catchment, have approximately 40% of South Africa’s remaining coal reserves (DWA 2013). The development of more mines and power stations within these catchments is inevitable, and already planned, as the coal reserves in the Highveld are nearing depletion. The ground water within the catchment is already not suitable for human consumption and use due to high salt content (Bester and Vermeulen 2010), and is believed to be due to the leaching of salts from the salt rich geology found in the study area (Bester 2009). Surface soils (5 – 15m) are expected to have decreased salt content and thus leaching due to leachable salts in this zone being washed away from the system over many years (Bester 2009). The deeper soils (>15m) are expected to still be rich in salts and could explain the high salt content of the ground water flowing through these soils. Further concerns of ground as well as surface water pollution are emphasized by the extensive coal mining activities and rapid, uncontrolled growth of informal villages within the catchment (Figure 3.4).

Extensive irrigation of crops from the Mokolo Dam occurs within the catchment (full supply capacity of 146 million $m^3.yr^{-1}$; DWA 2013) with 87% of all water use within the catchment allocated to agricultural activities. Denaturalized MAR is 117 million m^3 (Görgens and Boroto 1999), while only the combined naturalised MAR and ecological reserve for the Mokolo / Matlabas River basins are available as 382 and 76 million m^3, respectively (GOSA-DWAF 2003). The increased flow of water, especially as denaturalised surface run-off but also seepage, through the terrestrial system decreases the natural acid neutralising capacity of the soils as it has been found to be inversely proportional to the rate of water flow through the system.

3.1.4 The Matlabas River Catchment

The Matlabas River Catchment (Figure 3.7), draining an area of 6 014km^2, is largely undeveloped due to limited water resources and thus limited economic growth potential. The river runs through predominantly flat area, originating in the Waterberg mountain range, with no particularly significant tributary (Busari 2008), flowing west towards its confluence with the Limpopo River.

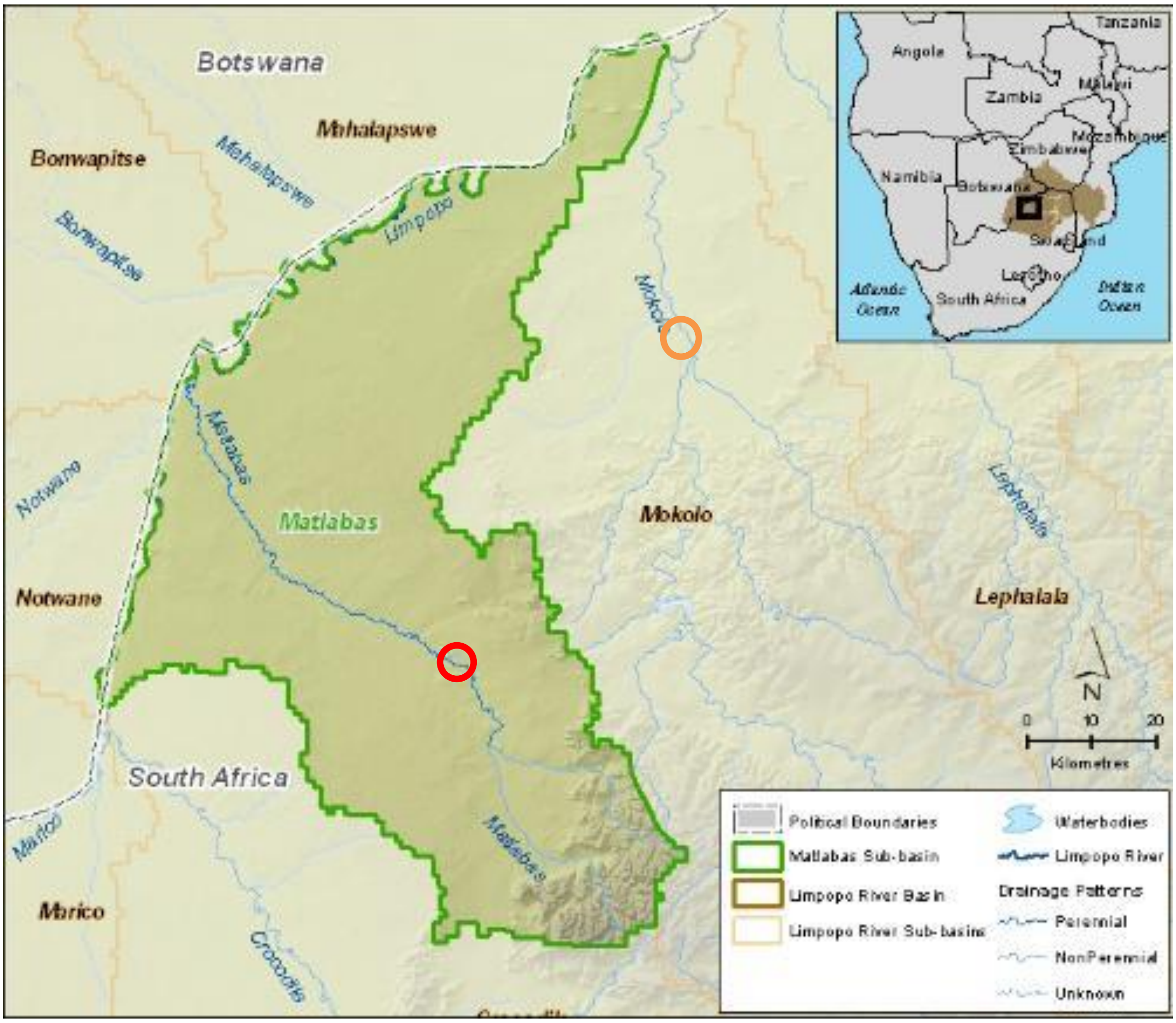


Figure 3.7. The Matlabas River Catchment, Limpopo, South Africa (Source: www.limpoporak.com). The position of the Matlabas River sampling station is indicated in red and Lephalale in orange.

The Matlabas River sampling station is located along the middle to upper reaches of the river and was selected as it is located directly downwind (southwest) of the Matimba power station. Direct access to the location of the sampling station was not possible as it is located on private farmland. During a visit in August 2015 it was evident that construction was occurring on the property, with no indication of the nature or timespan of the operations. The Matlabas River can be assumed to be more pristine than the Lephalala and Mokolo Rivers, yet water quality degradation due to development may occur in the future.

Although the mean annual run-off of the catchment is estimated at 49 million m^3 per year, the Matlabas River is seasonal, filling during the summer rainfall season and flowing up to April/May each year (DWA 2013). The Matlabas River is the main water source of the Marakele National Park located within the catchment, providing water to the park in order to fill its three separately positioned man-made dams during the rainy season (Pienaar 2006). Other activities, such as irrigation of farms in the catchment, rely on groundwater usage due to low surface water yields (Maré 2013) and no dams are constructed along the flow path of the river (DWA 2013).

No water quality problems have been reported for the Matlabas River which can be expected due to little development within the catchment, with land use largely limited to conservation and game farming. The low water availability in the catchment also does not allow for any large developments in the near future, yielding no direct concern regarding water quality problems within the catchment until this challenge is overcome through intensive planning and intervention. The Steenbokpan area, a quaternary catchment within the Matlabas River Catchment, is, however, part of the Lephalale coalfield and has already been earmarked to be mined once the water supply problems are addressed. According to a census in 2011, 5 723 people live within the catchment. This number is expected to increase exponentially once mining is initialised further limiting both water supply and water quality within the catchment.

3.2 Data collection methodology

3.2.1 Inorganic Chemistry data for the Lephalala, Mokolo and Matlabas Rivers

The dataset for the inorganic chemical water quality parameters for all surface waters (rivers, lakes and dams) in South Africa is available online from the Water Sciences and Management Department at the North West University, Potchefstroom Campus (http://www.waterscience.co.za/waterchemistry/data.html). This national dataset was compiled by Professor Jan Marten Huizenga and consists of more than 500 000 samples collected across the country from 1972 to 2011.

This dataset has been used for previous preliminary analyses and investigations of change over time within the Waterberg Rivers (e.g. Burne 2015) and was thus the most suitable dataset to use in this study. The measurements of pH and the concentrations (mmol.ℓ^{-1}) of sodium (Na^+), magnesium (Mg^{++}), calcium (Ca^{++}), potassium (K^+), ammonium (NH_4^+) and sulphate (SO_4^{2-}) for the Lephalala, Mokolo and Matlabas Rivers were extracted for 1999 to 2011. The concentrations were converted to mol.ℓ^{-1} by dividing the concentrations by 1000.

The data were available at a monthly resolution but inconsistency in both collection of samples and quality of lab techniques were expected to have caused the difference in the number of observations available for each station (Table 3.2). Although all monthly pH values were available, no cation and sulphate concentration values were available for specific months during the period of 1999 to 2011 in each of the rivers. This is thought to be due to inconsistent sampling by the designated technicians. The averaging of monthly values to determine annual means often masked the absence of values for certain months. For specific years, no values were recorded for any of the months of that year. Values are thus missing for specific years for each of the rivers. Years with no values were excluded from the analysis of water quality change patterns in the Lephalala (2003, 2006, 2008, 2009 and 2010), Mokolo (2007, 2008 and 2011) and Matlabas (2007 and 2008) Rivers.

Table 3.2. The number of sampling events recorded for each month for the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2011.

River	**Year**	**January**	**February**	**March**	**April**	**May**	**June**	**July**	**August**	**September**	**October**	**November**	**December**	**Total**
Lephalala	1999	1	1	3	1	-	-	-	-	-	-	-	-	6
	2000	1	-	3	2	2	-	-	2	1	3	2	1	17
	2001	1	1	1	2	2	1	1	-	-	-	2	2	13
	2002	2	1	1	2	1	2	2	-	2	-	-	-	13
	2003	-	-	-	-	-	-	-	-	-	-	-	-	0
	2004	1	-	-	1	2	2	2	1	-	-	-	-	9
	2005	-	-	2	-	-	-	-	-	-	-	-	-	2
	2006	-	-	-	-	-	-	-	-	-	-	-	-	0
	2007	1	1	-	-	-	-	-	-	-	-	-	-	2
	2008	-	-	-	-	-	-	-	-	-	-	-	-	0
	2009	-	-	-	-	-	-	-	-	-	-	-	-	0
	2010	-	-	-	-	-	-	-	-	-	-	-	-	0
	2011	-	1	-	-	-	-	-	-	-	-	-	-	1
	TOTAL													**63**
Mokolo	1999	2	3	5	3	3	5	4	1	-	-	-	1	27
	2000	1	2	2	1	2	2	-	2	2	1	3	1	19
	2001	2	2	2	2	2	2	1	3	2	2	1	2	23
	2002	2	1	1	2	1	1	1	1	1	1	1	-	13
	2003	1	1	-	-	-	1	1	-	-	-	-	-	4
	2004	-	-	-	2	1	1	2	1	1	-	-	-	8
	2005	-	-	1	-	-	-	1	-	-	-	1	-	3
	2006	2	1	-	1	1	-	1	1	-	-	1	-	8
	2007	-	-	-	-	-	-	-	-	-	-	1	-	1
	2008	-	-	-	-	-	-	-	1	-	-	-	-	1
	2009	-	1	-	-	1	-	-	1	-	-	1	-	4
	2010	1	-	1	1	-	1	1	-	-	-	-	-	5
	2011	-	-	-	-	-	-	-	-	-	-	-	-	0
	TOTAL													**116**
Matlabas	1999	1	1	1	1	1	1	-	-	-	-	-	-	6
	2000	-	-	1	1	1	1	-	2	-	-	-	-	6
	2001	-	1	1	1	1	1	1	2	-	-	1	1	10
	2002	1	1	1	-	-	-	1	-	-	-	-	-	4
	2003	-	1	1	-	-	-	-	-	-	-	-	-	2
	2004	-	-	-	-	-	1	-	-	-	-	-	-	1
	2005	-	-	1	-	-	-	-	-	-	-	-	-	1
	2006	-	1	-	1	1	-	1	1	-	-	-	-	5
	2007	-	-	-	-	-	-	-	-	-	-	-	-	0
	2008	-	-	-	-	-	-	-	-	-	-	-	-	0
	2009	-	-	-	-	-	-	-	-	1	-	-	-	1
	2010	1	1	1	1	-	-	1	-	-	1	-	-	6
	2011	1	1	-	-	-	-	-	-	-	-	-	-	2
	TOTAL													**44**

* - = no samples / data available

Data are most regularly available for the months during 1999 to 2002, while data become more sporadic from 2003. There are multiple possible reasons for this, including insufficient funding to maintain the planned sampling frequency or problems with the analysis of the samples in the laboratory.

No outliers in the organic chemistry data were identified and excluded. Some values were very high or low, but needed to be investigated with other data used in order to determine whether it was in fact an outlier or if significant changes in water quality occurred during that specific month or year.

3.2.2 Discharge data

The discharge data for the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2011 were accessed online from the Department of Water Affairs database (http://www.dwa.gov.za/hydrology/hymain.aspx). Discharge data ($m^3\ s^{-1}$) were available at a monthly resolution, which were then converted to mean daily discharge ($m^3\ s^{-1}$) by dividing the discharge value by the number of days in each of the corresponding months. This was necessary in order to calculate flux data at various resolutions.

All monthly discharge values from January 1999 to December 2011 were cross-checked and outliers were validated or rejected based on the rainfall data available for the same period. Very few high values were not substantiated by the rainfall recorded for the same period and were excluded from the discharge data available for the Lephalala (3 values) and Matlabas (7 values) Rivers. Monitoring of discharge in the Mokolo River was found to be very inconsistent with data missing for long periods of time including January 2000 to June 2000, and September 2008 to October 2009. This is thought to be due to faulty or unmaintained meters as these values are believed to be received from stationary automated meters at the gauging stations. A total of 28 measurements were excluded, including measurements labelled as “faulty” in the original dataset for 1999 to 2011 (Table 3.3).

Table 3.3. The description of the discharge data provided and used for the Lephalala, Mokolo and Matlabas Rivers.

River	Period of data collection	Number of observations provided	Number of observations used	Original data resolution
Lephalala	January 1999 – December 2011	153	150	Monthly
Mokolo	January 1999 – December 2011	135	107	Monthly
Matlabas	January 1999 – December 2011	155	148	Monthly

The exclusions of faulty and invalidated values given at a monthly resolution for the Lephalala, Mokolo and Matlabas Rivers were often masked by averaging the monthly values for each year. No discharge values were available for the Mokolo River during 2009: data were unavailable from January to October and "faulty" measurements were recorded in November and December of the same year. The absence of discharge data meant that no flux data would be available for the Mokolo River for 2009.

3.2.3 Climatic data

Daily rainfall (mm.d^{-1}), maximum daily temperature (˚C), wind direction and wind speed (m.s^{-1}) data for the town of Lephalale from 1992 to 2013 were obtained from the South African Weather Service (SAWS) Data Bank.

The total monthly rainfall during the period of 1999 to 2011 was calculated by adding all daily rainfall measurements across each month (mm.month^{-1}). These values were used to cross-validate any outliers in the discharge data for the same period as well as to investigate the relationship between rainfall and the flux of cations and sulphate ions at a monthly resolution. Annual total rainfall was calculated by adding all rainfall records for each month (mm.yr^{-1}). These values were compared to the flux of cations and sulphate ions at a monthly and annual resolution.

The dataset has only been updated to include data collected until the end of 2012, with no values available for 2013 onwards. Analysis of data available to the present would provide an understanding of how the first phase of power generation at the Medupi power station could already be contributing to changes in cation and sulphate fluxes within the Waterberg Rivers. The completed unit 6 of the power station has a full potential of 794MW and has been utilised since May of 2015 due to electricity supply shortages across South Africa. The analysis of the effect of Medupi power station could be compromised if data collection stopped in 2011, as no data have been made available yet.

The maximum daily temperatures (˚C) for the period of 1999 to 2011 were calculated for both an average monthly and average annual resolution. Monthly mean values were calculated by averaging the daily temperatures recorded during the month. Annual mean temperature was calculated by averaging the daily temperatures recorded and not the monthly averages already calculated. These values were respectively used to investigate the relationship between temperature and cation and sulphate ion flux at a monthly and an annual resolution.

The average wind direction and speeds across the period of 1992 to 2013 were provided as rose diagrams for each month – all values for the same month from different years were pooled into one figure (e.g. January 1992 – 2013, February 1992 – 2013, etc.). Values recorded before 1999 and after 2011 were originally included into the figures by the SAWS Data Bank. No raw data were available and thus the figures could not be altered to include only the period of interest. Wind data could not be used to investigate the relationships between ion flux and wind direction or speed, respectively, yet did provide an understanding of how the depositional areas around the Matimba power station are expected to change between seasons.

3.2.4 Data on the quality and quantity of coal burned at the Matimba power station

The data for the quantity and quality of coal burned at the Matimba power station from 1991 to 2013 were requested from the Air Quality, Climate Change and Ecosystem Management Centre of Excellence at ESKOM’s Megawatt Park, Johannesburg. The amount of coal burned (in tonnes) was available at an annual resolution from 1991 to 2004 and at a monthly resolution from January 2005 to December 2013. The monthly data were used to compile annual amounts of coal burned at the Matimba power station from 1999 to 2011. This period corresponds with the period of the inorganic chemistry data that are available for the Lephalala, Mokolo and Matlabas Rivers. Data indicating coal quality (gross critical value in MJ.kg^{-1}, volatile matter content in % and ash content in %, as fired) were supplied at a monthly resolution from January 2005 to December 2011, but were converted to annual mean values for analysis purposes. No coal quality data were available from January 1999 to December 2004.

3.3 Data processing methodology

The methods of data processing are presented according to the different sets of data analysed. Data analysed included pH, cation and sulphate concentrations, cation and sulphate fluxes, temperature, rainfall, river discharge and coal quantity and quality data.

3.3.1 Calculating summed cation concentrations using equivalent charges

An equivalent (symbol: Eq) is the amount of a substance multiplied by its valence charge. The monthly equivalent concentration of each individual cation (Na, Mg, Ca, K and NH_4) was calculated by multiplying the concentration of the cation ($mol.\ell^{-1}$) for each month with its valence charge. Monthly summed cation concentrations were calculated by adding the equivalent charges of all cations across each year. The annual concentrations of summed cations (using equivalent charges) could then be calculated by adding all monthly equivalent concentrations for each specific year (Table 3.4). This was done for each year from 1999 to 2011 in the Lephalala, Mokolo and Matlabas Rivers, respectively.

Table 3.4. A simplified representation of the use of monthly concentrations of individual cations to calculate monthly and annual summed cation concentrations using equivalent charges.

Month	**Cation**	**Valency**	**Equivalent concentration**	**Cation**	**Valency**	**Equivalent concentration**	**Cation**	**Valency**	**Equivalent concentration**	**Cation**	**Valency**	**Equivalent concentration**	**Cation**	**Valency**	**Equivalent concentration**	**Summed cation concentration using equivalent charges**
January	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
February	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
March	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
April	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
May	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
June	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
July	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
August	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
September	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
October	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
November	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
December	Na	1	1 x [Na$^+$]	Mg	2	2 x [Mg^{++}]	Ca	2	2 x [Ca^{++}]	K	1	1 x [K$^+$]	NH$_4$	1	1 x [NH$_4^+$]	[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]
Year	**∑(Na)**	**1**	**1 x [Na$^+$]**	**∑(Mg)**	**2**	**2 x [Mg^{++}]**	**∑(Ca)**	**2**	**2 x [Ca^{++}]**	**∑(K)**	**1**	**1 x [K$^+$]**	**∑(NH$_4$)**	**1**	**1 x [NH$_4^+$]**	**[Na$^+$ (eq)] + [Mg^{++} (eq)] + [Ca^{++} (eq)] + [K$^+$ (eq)] + [NH$_4^+$ (eq)]**

3.3.2 Calculating the flux of individual cations, summed cations and sulphate ions

A flux is defined as the instantaneous rate at which pollutants are passing a point of reference on a river (Richards 1998), like a sampling station, and is usually expressed in units of micro-moles per area per time, yet mass rather that molar units can also be used (e.g. mg/m^2/d; Jenkins 2005). The estimation of riverine fluxes is used in the determination of erosion rates, the sedimentation rates in reservoirs, water and soil conservation planning and water quality modelling (Raymond *et al*. 2013).

The calculations of the summed cation and sulphate fluxes across the soil-water interface were done using the formula

$$\frac{Q_r \sum_{i=1}^{n} (C_i \, Q_i)}{\sum_{i=1}^{n} (Q_i)}$$

where C_i is the instantaneous concentration measured in sample *i* (mol.ℓ^{-1}), Q_i is the mean daily discharge (m^3.s^{-1}) associated with C_i, Q_r is the mean discharge for each sampling period, and *n* is the number of (C,Q) data pairs per sampling period (OSPAR 1998) The final flux values were thus given in equivalents per litre (Eq.ℓ^{-1}) per season and per year.

Flux values were calculated at annual and seasonal resolutions for each hydrological year from 1999 to 2010. A hydrological year is defined as the period from the 1st of June of the current year until the 31st of May of the following year. The hydrological year of 1999 is thus the period of June 1999 to May 2000, etc. Seasonal data were divided into summer (December – February), autumn (March – May), winter (June – August) and spring (September – November). Seasonal data were important to determine the relationships between ion fluxes and climatic variables such as temperature and rainfall.

3.3.3 Statistical investigation of the changes in summed cation and sulphate ion fluxes calculated for each river

The fluxes of summed cations and sulphate ions in the Lephalala, Mokolo and Matlabas Rivers were statistically compared in the following ways:

1. A direct comparison of the absolute values of the summed cation and sulphate fluxes calculated only for 1999 and 2010 using ANOVAs;
2. A comparison of the trend in ion fluxes annually measured in the three rivers from 1999 to 2010 using non-linear regressions;
3. A comparison of the annual mean summed cation and annual mean sulphate fluxes between the three rivers from 1999 to 2010 using blocked ANOVAs. Blocked ANOVAs were blocked by river; and
4. A comparison of the seasonal mean summed cation and sulphate fluxes across the period of 1999 to 2010 in each of the rivers using ANOVA. If a significant difference was found, a Tukey Honestly Significant Differences (HSD) test was used to determine where the significant difference(s) occurred.

All data were tested for a normal distribution before using the ANOVA analyses as it is a parametric test. The Shapiro-Wilk normality test was used in R. Data were assumed to be normally distributed if t a p-value of less than 0.05 was presented.

Mean summed cation and sulphate flux values were also compared to threshold values given in the South African Water Quality Guidelines (SAWQG 1996). These values were provided in milligrams per litre (mg.ℓ^{-1}), but were converted to equivalents per litre (Equation 3; Eq.ℓ^{-1}) to allow for comparisons.

$$\text{Eq} = \frac{\text{mg} \cdot 1000 \cdot \text{valency}}{\text{atomic weight}} \qquad \text{... Equation 3}$$

3.3.4 Investigating the changes in coal quantity and quality from 1999 to 2011

The quantity of coal burned at the Matimba power station from 1999 to 2011 was provided in tonnes. Data for the years prior to 2005 were only available at an annual resolution while data from 2005 to 2011 were available at a monthly resolution. The absence of coal quality data prior to 2005 limited analyses investigating the significance of the change in gross critical value (MJ.kg^{-1}), volatile matter content (%) and ash content (%) to the period of 2005 to 2011.

CHAPTER 4: RESULTS

The changes in summed cation and sulphate concentrations from 1999 to 2011 and fluxes using daily river discharge between 1999 and 2010 were investigated for the Lephalala, Mokolo and Matlabas Rivers located in close proximity to the Matimba power station in the Limpopo Province in South Africa. All data relating to cations are presented first, which is then followed by all data relating to sulphate. This was done to improve the understanding of the relationships between the changes in fluxes and the climatic and anthropogenic variables known for the Lephalala area.

Climatic variables considered were average maximum daily temperature and total rainfall for each hydrological year and month from 1999 to 2010. The anthropogenic variables were restricted to the quantity and quality of coal burned at the Matimba power station over the same time period. The changes were compared as absolute values at specific points in time as well as over the entire period. The changes in ion fluxes are presented first followed by the relationships with climatic and coal variables.

4.1 Changes in pH values measured for the rivers from 1999 to 2011

Analyses performed by Craig Burne (Burne 2015) revealed that the pH values of the rivers in the Waterberg Water Management Area generally increased by an average of one unit after the commissioning of the Matimba Power Station (1988 – 1991; Table 4.1).

Table 4.1. Changes in pH values of the Lephalala, Mokolo and Matlabas Rivers after the commissioning of the Matimba power station (1988 - 1991) as found by Burne (2015).

	Before 1988	After 1991	Difference
Lephalala River	6.3	7.1	+ 0.8
Mokolo River	6.6	7.6	+ 1.0
Matlabas River	6.2	7.6	+ 1.4

The mean pH values from 1999 to 2011 for the Lephalala, Matlabas and Mokolo Rivers were 7.86 ± 0.18, 7.28 ± 0.24 and 7.51 ± 0.19, respectively (Figure 4.1). A comparison of the mean pH values measured from 1999 to 2011 to the mean pH values calculated for "after 1991" by Burne (2015) revealed that the pH of the Lephalala River further increased by 0.76 units. The pH of the Mokolo and Matlabas Rivers decreased by 0.09 and 0.32 units, respectively. Using pH change equivalents (Murrell 2011) it was found that the Lephalala River was 5.0 to 6.3 times less acidic during the period of 1999 to 2011, while the Mokolo and Matlabas Rivers were ~1.3 and ~2.0 times more acidic when compared to the values found by Burne (2015).

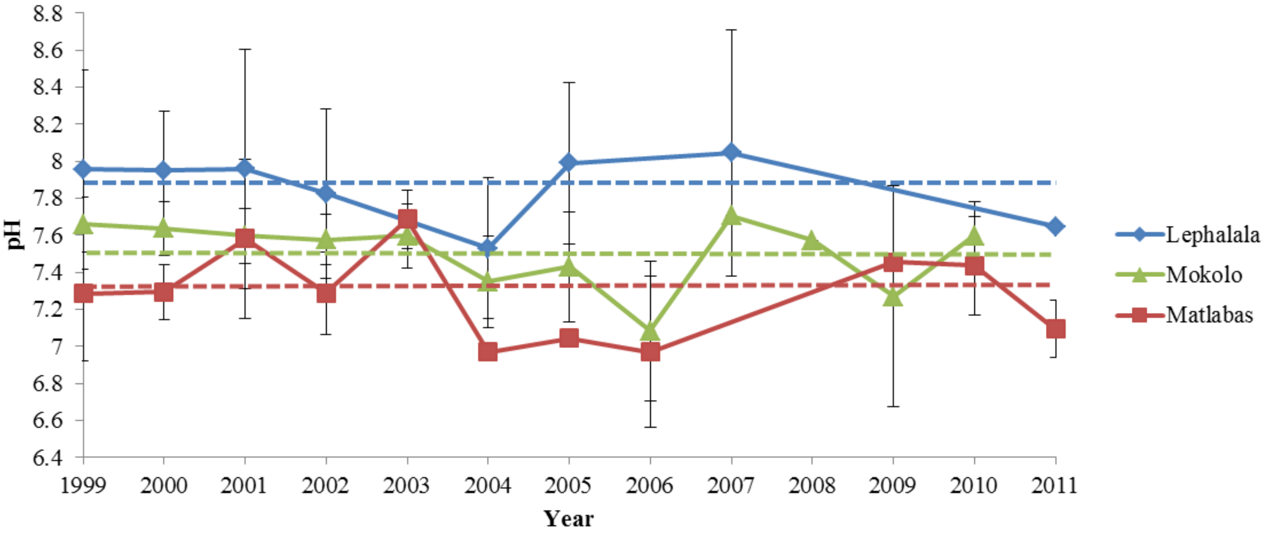


Figure 4.1. The annual and overall mean pH values of the Lephalala, Mokolo and Matlabas Rivers measured from 1999 to 2011. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The mean pH values across the three rivers are highly significantly different (ANOVA, d.f. = 8.644 x 10^{-6}). A Tukey Honest Significant Differences (HSD) test revealed that the mean pH values measured significantly differed for all rivers: Lephalala / Matlabas ($p \approx 0.000$), Matlabas / Mokolo ($p = 0.039$) and Lephalala / Mokolo ($p = 0.002$).

The pH of the Lephalala River did not significantly decrease from 2001 to 2004 (0.43 units; ANOVA, d.f. = 20, $p = 0.0850$) or from 2007 to 2011 (0.40 units; ANOVA, d.f. = 2, $p = 0.5648$). The latter is possibly due to very few data points being available for the years of 2007 and 2011 and no data being available for 2008 to 2010. The decreases in pH of the Mokolo River was found to be statistically not significant for 2003 to 2006 (0.51 units; ANOVA, d.f. = 10, $p = 0.0886$) and 2007 to 2009 (0.43 units;

ANOVA, d.f. = 4, p = 0.4874). The largest decrease in the pH of the Matlabas River was from 2003 to 2004 and was found to be significantly different (0.72 units; ANOVA, d.f. = 2, p = 0.0162) most likely due to very few yet similar data points being available for 2004.

The distributions of the pH values measured for the Lephalala and Mokolo Rivers were negatively skewed (Figure 4.2) – most of the values are greater than the mean values, with the mean value decreased by shorter periods of lower pH values. This indicates that the pH values are predominantly greater than ~7.95 and 7.6 in the Lephalala and Mokolo Rivers, respectively. The distribution of the pH values measured in the Matlabas River indicates that the data points are more evenly distributed over a larger range of values (6.9 to 7.7). The average pH of the Matlabas River is the result of continual deviations above and below the calculated average, while the pH never stabilizes at a certain value for longer than a year.

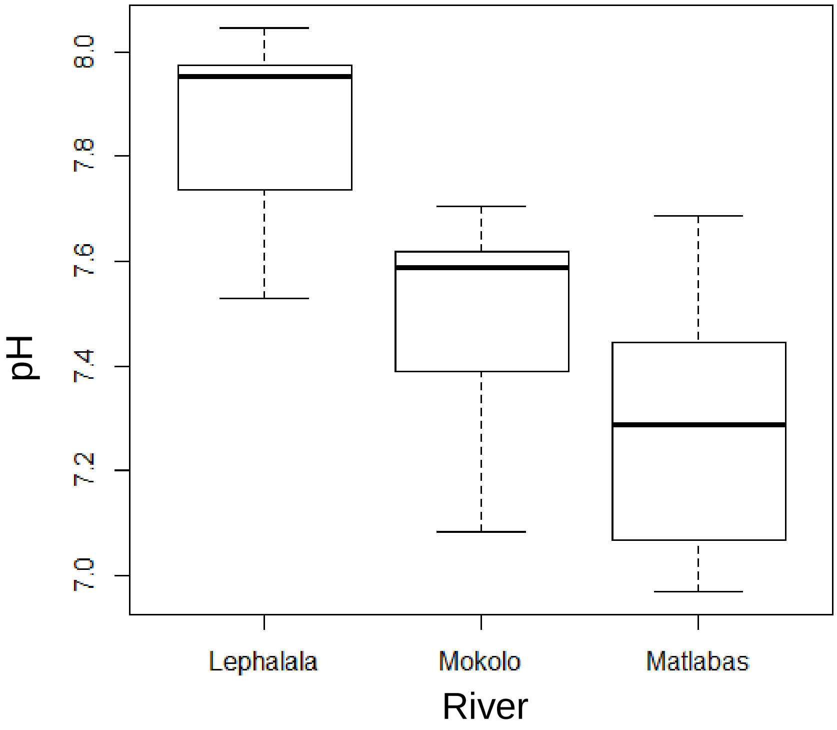


Figure 4.2. The statistical distribution of the pH values measured for the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2011.

A decrease in average pH and increase in variability was found from northeast to southwest. The Lephalala River had the highest and least variable pH, while the Matlabas River had the lowest and most variable pH of the rivers measured.

4.2 Investigating the change in individual and summed cation concentrations measured in each of the rivers from 1999 to 2011

Cation concentrations measured from 1999 to 2011 were sodium, magnesium, calcium, potassium and ammonium. Understanding which cation drives the overall fluctuations in summed cation concentrations is important as cations are deposited or leached from anthropogenic sources such as coal burning and town effluent but also by natural processes such as soil weathering and vegetation decomposition. The measured concentrations of individual cations were compared to the concentration of summed cations (using equivalent charges) for the Lephalala, Mokolo and Matlabas Rivers over the period of 1999 to 2011 (Figure 4.3). Summed cation concentrations measured for each river showed sodium to be the dominant ion, while ammonium ion concentrations are negligible.

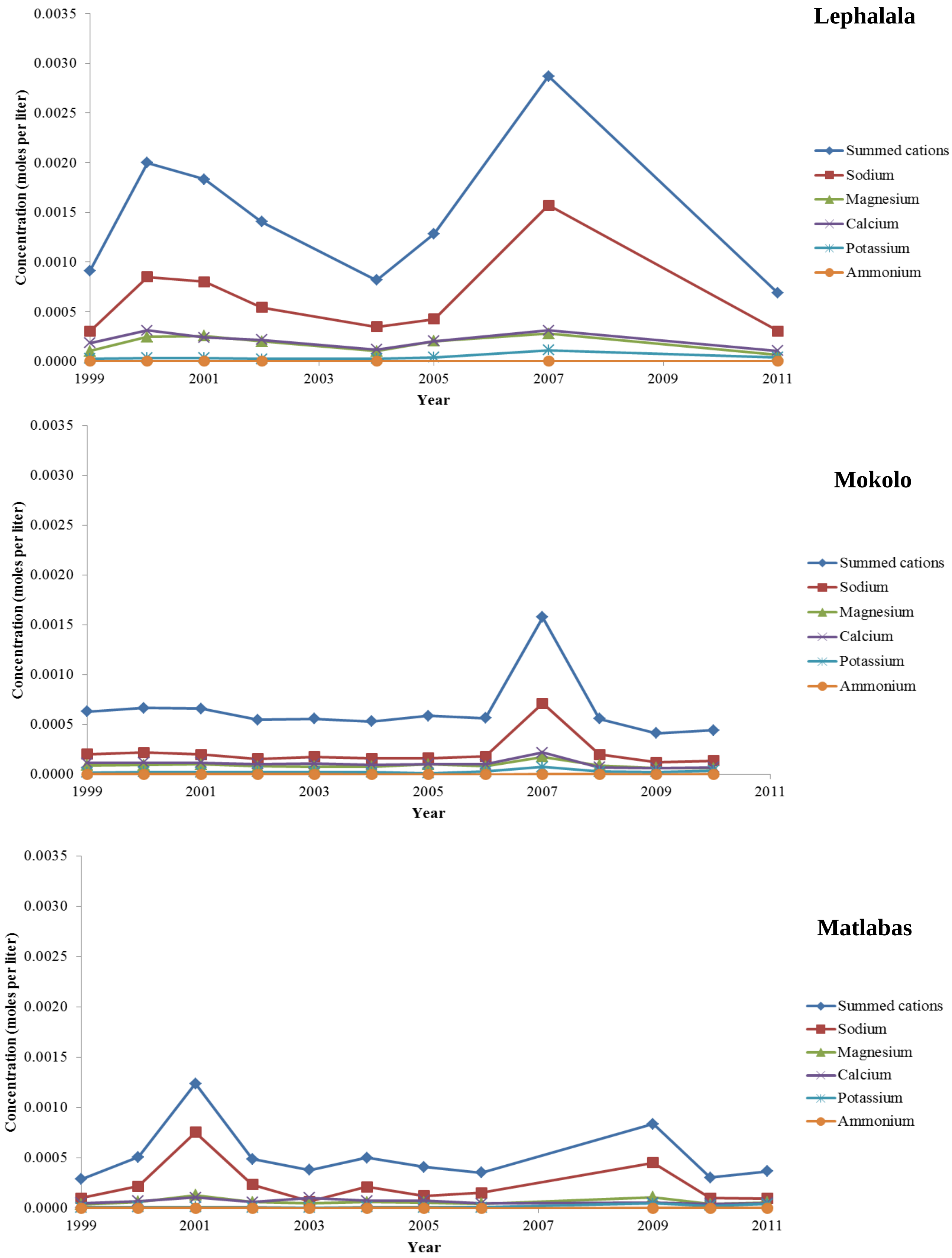


Figure 4.3. Concentrations of summed cations and each individual cation measured in the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2011.

Table 4.2. The statistical results indicating the strength and significance of the relationship (using non-linear regression) between summed cation and sodium concentrations measured in the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2011.

River	Relationship strength (R^2)	Relationship significance (p)	Degrees of freedom
Lephalala	0.9484	4.387×10^{-5}	6
Mokolo	0.9867	1.042×10^{-10}	10
Matlabas	0.9761	1.318×10^{-8}	9

The relationship between the change in summed cations and sodium concentrations is very strong and significant in all three of the rivers (Table 4.2), indicating that sodium is the major contributor to the summed cation concentrations measured. The sodium concentrations within the Lephalala, Mokolo and Matlabas Rivers ranged from 0.0003 to 0.0016, 0.0002 to 0.0007, and 0.0001 to 0.0008 moles per litre, respectively. The highest sodium concentrations in both the Lephalala and Mokolo Rivers occurred in 2007, respectively increasing by 300% and 250% from 2006. Summed cation concentrations in the Matlabas River were highest in 2001 and 2009, respectively increasing by 300% and 150% from the previous year.

Sodium values measured in 2007 were ~2.3 and ~6.4 times higher in the Lephalala River when compared to the Mokolo and Matlabas Rivers, respectively. Decreased concentrations were measured from northeast to southwest, with the Mokolo River located in closest proximity to the town of Lephalale. By 2009, the measured cation concentrations in the Lephalala and Mokolo Rivers had decreased by ~ 38% and 75%, to 0.0018 and 0.0004 moles per litre, respectively when compared to values measured in 2007. The cation concentrations in the Matlabas River had increased by 100% reaching concentrations of 0.0008 moles per litre in 2009, still ~2.3 times lower than the concentration values measured for the Lephalala River in the same year.

Concentrations of all other cations ranged from zero to 0.0003, zero to 0.0002, and zero to 0.0001 moles per litre, for the Lephalala, Mokolo and Matlabas Rivers, respectively. This range is below the range of the sodium concentrations, with no overlap in range values. The increases in concentrations of the other cations from the year preceding the year with the highest concentration measured (Table

4.3) were not as high as the increases in sodium concentrations. The concentration of all cations (excluding sodium) increased the most in the Mokolo River, with the highest concentrations measured in 2007.

Table 4.3. Percentage increase from year preceding maximum cation concentrations measured in the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2011.

	Lephalala River	**Mokolo River**	**Matlabas River**
Sodium	300%	250%	300%
Magnesium	50%	100%	0%
Calcium	50%	100%	0%
Potassium	100%	100%	0%
Ammonium	~ 0%	~ 0%	0%

The concentrations of cations in the Lephalala and Matlabas Rivers are more variable than for the Mokolo River. The concentrations of summed cations in the Lephalala and Matlabas Rivers continuously varied between 0.0008 and 0.0029, and 0.0003 and 0.0012 moles per litre, respectively. Cation concentrations in the Lephalala River significantly increased from 2004 to 2007 (ANOVA, d.f. = 9, $p = 0.0234$) but the increase from 1999 to 2000 was found to be not significant (ANOVA, d.f. = 21, $p = 0.0559$). The increases in cation concentrations in the Matlabas River from 2000 to 2001 (ANOVA, d.f. = 14, $p = 0.2576$) and from 2006 to 2009 (ANOVA, d.f. = 5, $p = 0.5441$) were respectively found to be not significant. Further analysis also indicated that the highest cation concentration measured for the Lephalala River (in 2007; $0.0029 \pm 0.0022\ \text{mol}\cdot\ell^{-1}$) did not significantly differ from the lowest cation concentration (in 2004; $0.0008 \pm 0.0006\ \text{mol}\cdot\ell^{-1}$) measured in the same river (ANOVA, d.f. = 14, $p = 0.1505$).

Concentrations in the Mokolo River remained at approximately 0.0006 moles per litre, with a single sharp significant increase (ANOVA, d.f. = 8, $p = 0.0005$) to 0.0016 moles per litre in 2007. Statistically, the mean concentrations of cations after 2007 ($0.0005 \pm 0.0005\ \text{mol}\cdot\ell^{-1}$) are not significantly lower than the mean cation concentration before 2007 ($0.0006 \pm 0.0007\ \text{mol}\cdot\ell^{-1}$; Wilcox Test, $p = 0.25$). A Wilcox Test was used as data for before 2007 (Shapiro-Wilk Normality Test, $p = 0.2584$) and after 2007 (Shapiro-Wilk Normality Test, $p = 0.4087$) were not normally distributed. The input and output of cations in the Mokolo catchment can thus be assumed to be more consistent, while the Lephalala and Matlabas catchments are more vulnerable to the change in natural and anthropogenic cation inputs.

4.3 Rainfall intensity and seasonality within the Waterberg District Municipality

The rainfall recorded for the Lephalale town is highly variable due to the sporadic nature of the rainfall events occurring within this relatively dry area. During the period of 1999 to 2010, the wettest hydrological year recorded was 2007 (June 2007 – May 2008) with a mean monthly precipitation of 43.78 ±50.96 mm and the driest hydrological year recorded was 2002 (June 2002 – May 2003) with a mean monthly rainfall of 19.90 ± 28.29 mm (Figure 4.4). The average monthly amount of rain for the wettest year was found to be not significantly higher than the average monthly amount of rain measured for the driest year (Paired T-test, p = 0.0584). A paired T-test was used as both the 2002 (Shapiro-Wilk Normality Test, p = 0.0027) and 2007 (Shapiro-Wilk Normality Test, p = 0.0245) data were found to be normally distributed. The significance value for the comparison between the wettest and driest years is very close to 0.05 indicating that the difference is large even though it is not statistically significant.

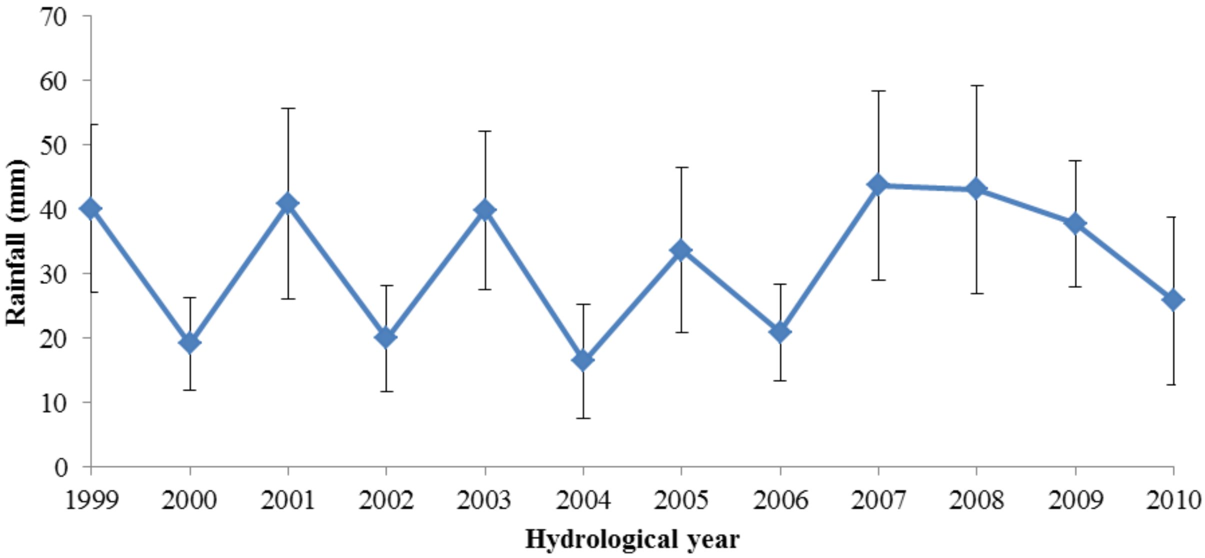


Figure 4.4. Mean monthly rainfall recorded for each hydrological year for Lephalale town from 1999 to 2010. Variation is indicated with standard error bars.

The rainfall values in 2004 and 2005 are positively skewed (Figure 4.5) and this is expected to be true for the other years from 1999 to 2010 too.

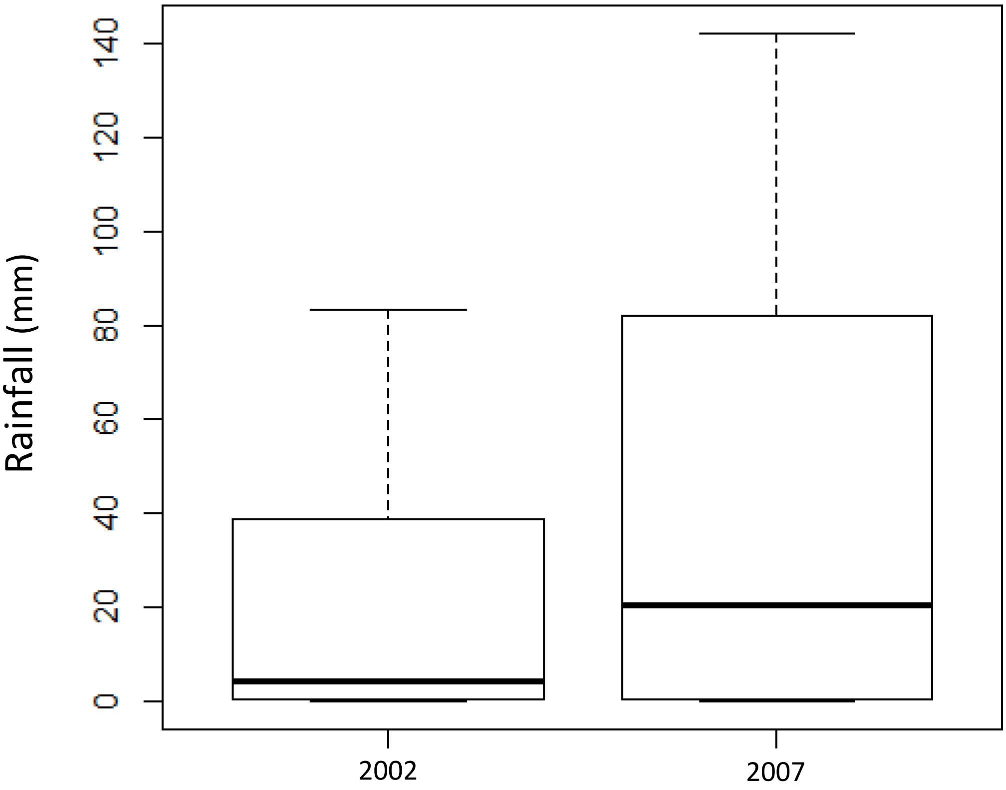
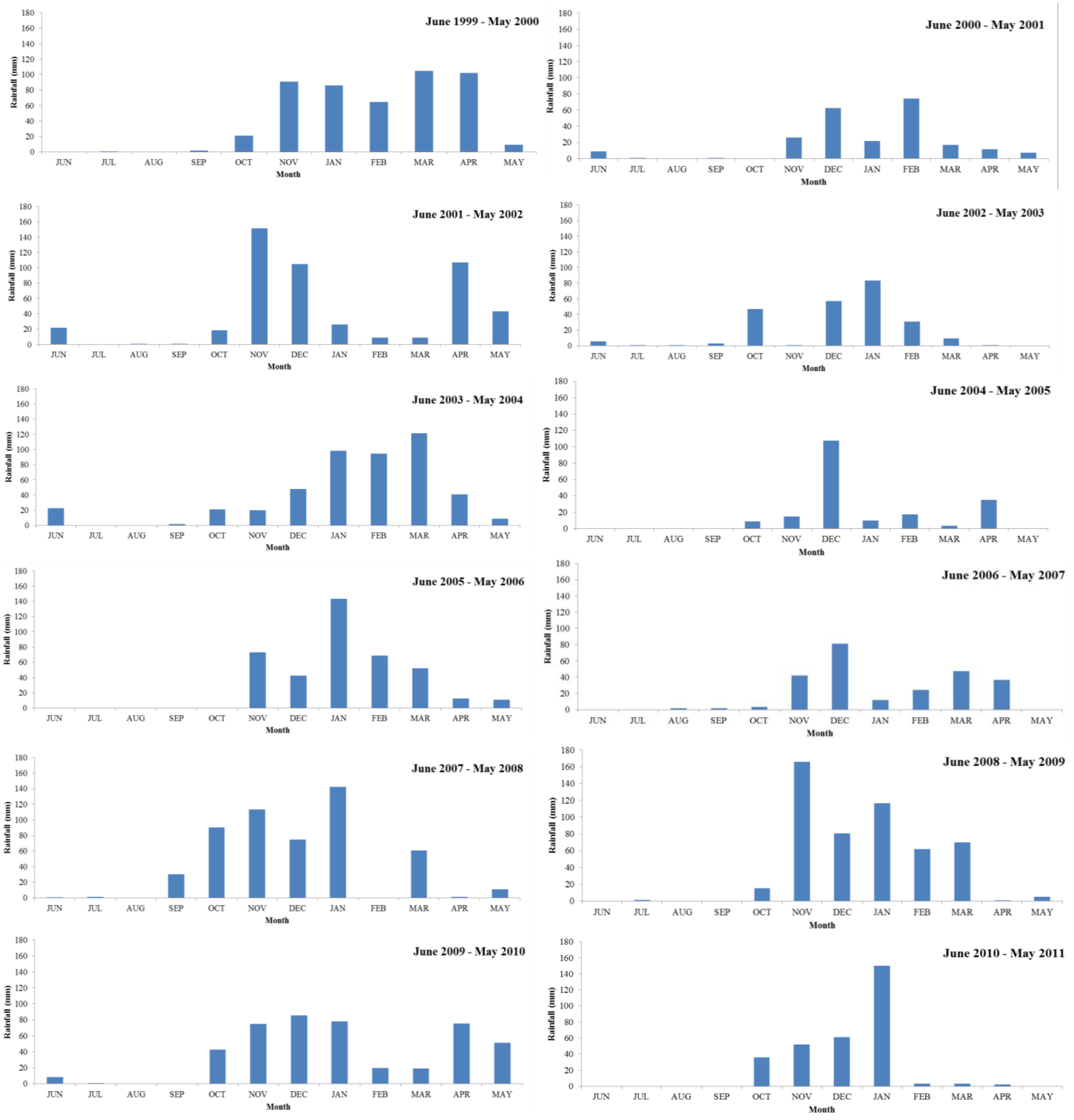


Figure 4.5. Mean monthly rainfall recorded for Lephalala in the driest (2002) and wettest (2007) hydrological years.

The distribution of the data indicates that the mean and the variability of the rainfall values calculated are increased by the sporadic occurrences of heavy rainfall events. In 2007 hydrological year, heavy rainfall events occurred in November 2007 (113.4mm) and January 2008 (142.4mm), while no rainfall occurred during June to August 2007 and February 2008. The heaviest rainfall event during the 2002 hydrological year occurred in January 2003 (83.6mm). Very low rainfall was recorded from June to September 2002 and from April to May 2003. Generally, heavier rainfall events occur during the warmer months of October to March (Figure 4.6) indicating a summer rainfall region and the high seasonality of the rainfall events.



June 1999 - May 2000

June 2000 - May 2001

June 2001 - May 2002

June 2002 - May 2003

June 2003 - May 2004

June 2004 - May 2005

June 2005 - May 2006

June 2006 - May 2007

June 2007 - May 2008

June 2008 - May 2009

June 2009 - May 2010

June 2010 - May 2011

Figure 4.6. The monthly rainfall recorded for the Lephalale area for each hydrological year from 1999 to 2010.

4.4 Investigating the change in flux of the individual cations in the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2010

Ion fluxes for the Lephalala, Mokolo and Matlabas Rivers were calculated for the hydrological years of 1999 to 2010 from the ion concentrations and river discharge data available for these rivers. Flux values were calculated for individual cations and summed cations at a seasonal and annual resolution.

4.4.1 Sodium flux within the Lephalala, Mokolo and Matlabas Rivers

Sodium fluxes within the Lephalala, Mokolo and Matlabas Rivers ranged from 0.0002 to 0.0012 $Eq{\cdot}\ell^{-1}$, 0.0002 to 0.0007 $Eq{\cdot}\ell^{-1}$, and 0.0001 to 0.0006 $Eq{\cdot}\ell^{-1}$, respectively (Figure 4.7). Sodium flux within the Lephalala River increased by 300% from 1999 to 2000 and by 140% from 2004 to 2006, reaching its highest value is 2006 (0.0012 $Eq{\cdot}\ell^{-1}$). Sodium flux within the Mokolo River was relatively constant, with a single sharp increase of 133% from 2006 to 2007, reaching a value of 0.0007 $Eq{\cdot}\ell^{-1}$. Sodium flux within the Matlabas River also showed sharp increases with the flux values increasing by 200% over a two year period from 2000 to 2002. The highest sodium flux value for the Matlabas River during the period of 1999 to 2010 was measured in 2002, with a value of 0.0006 $Eq{\cdot}\ell^{-1}$.

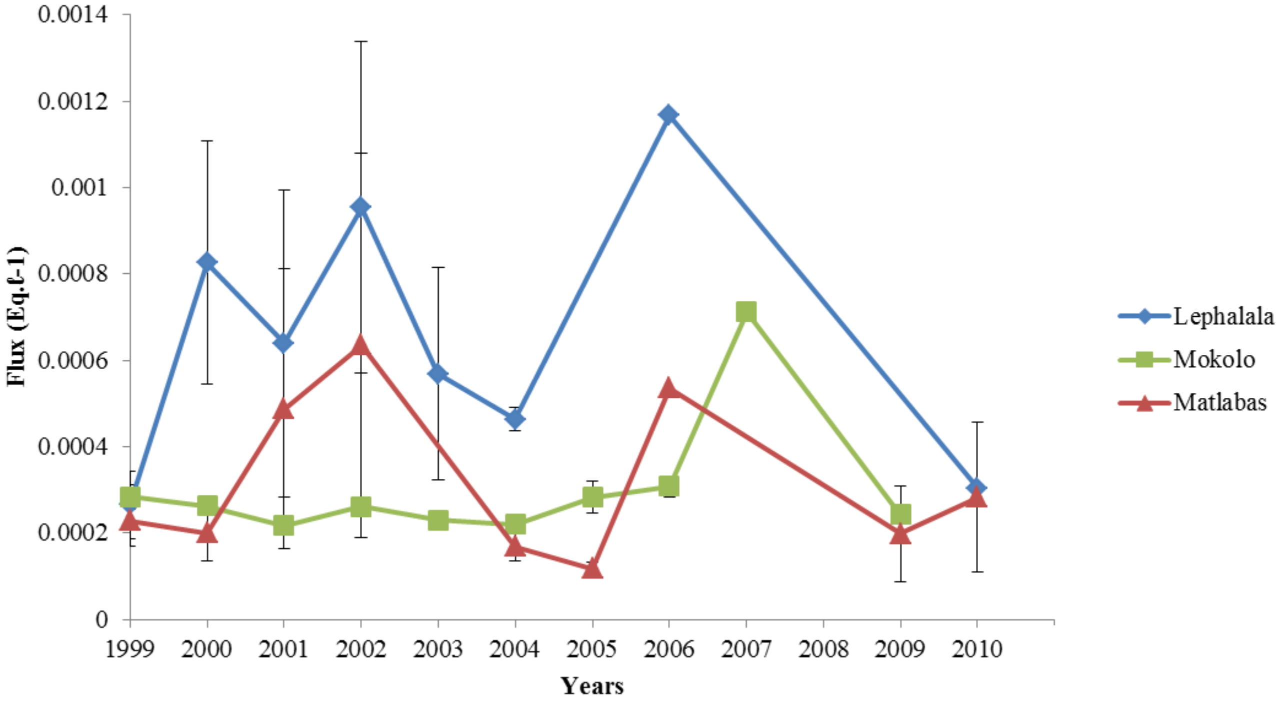


Figure 4.7. Annual mean flux in sodium cations measured in the Lephalala, Mokolo and Matlabas Rivers during each hydrological year from 1999 to 2010. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The mean sodium flux values for the Lephalala (0.0007 ± 0.0005 Eq·ℓ^{-1}), Mokolo (0.0003 ± 0.0001 Eq·ℓ^{-1}) and Matlabas (0.0003 ± 0.0004 Eq·ℓ^{-1}) Rivers were found to be significantly different (ANOVA, d.f. = 64, p = 0.003). A Tukey HSD test revealed that the Mokolo and Matlabas Rivers did not significantly differ (p=0.874) due to mean sodium flux values being the same while large standard deviations were found. Significant differences did, however, exist when the Lephalala River was compared to the Mokolo (p = 0.003) and Matlabas (p = 0.014) Rivers, respectively. The sodium fluxes within the Lephalala River are thus significantly elevated when compared to the fluxes within the Mokolo and Matlabas Rivers.

The mean sodium flux in the Lephalala River for each season (Figure 4.8) showed that high values occurred during spring of 2000 and 2002 as well as the winter of 2001. Summer and autumn sodium fluxes were lower, with the exception of a high sodium flux value recorded for the summer of 2007. The mean sodium flux value across the period of 1999 to 2010 was highest for spring (0.0011 ± 0.0008 Eq·ℓ^{-1}), followed by winter (0.0009 ± 0.0006 Eq·ℓ^{-1}), summer (0.0005 ± 0.0004 Eq·ℓ^{-1}) and autumn (0.0004 ± 0.0002 Eq·ℓ^{-1}). These values were found to be not significantly different (ANOVA,

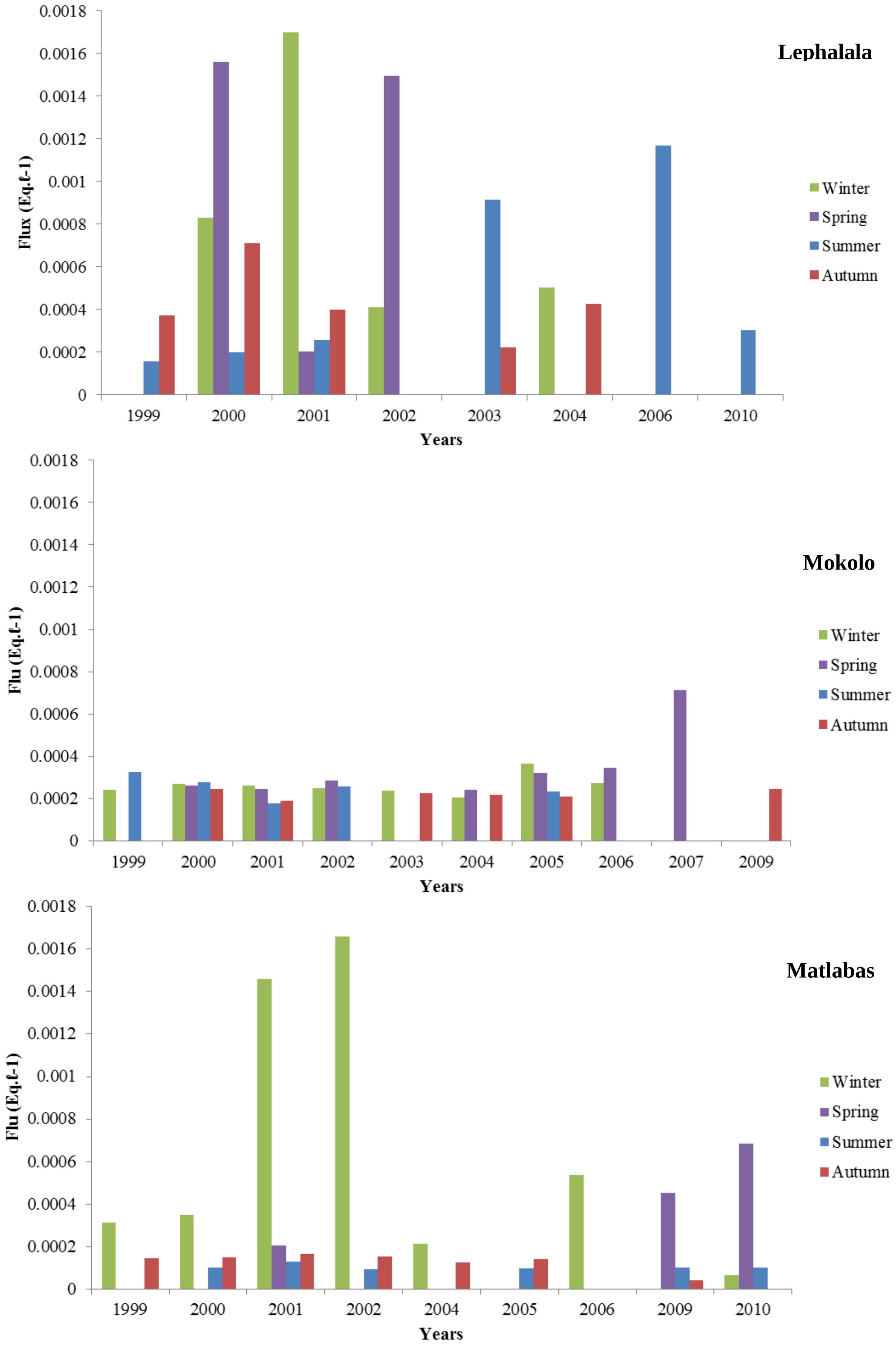


Figure 4.8. Mean flux in sodium cations measured in the Lephalala, Mokolo and Matlabas Rivers during summer, autumn, winter and spring from 1999 to 2010.

d.f. = 14, p = 0.227), most probably due to the high variance calculated. No significant seasonal differences were found within the Lephalala River, possibly indicating that the sodium fluxes within the river are not dependent on seasonal parameters such as rainfall and temperature. Increased flux values that are measured in the Lephalala River are most probably due to decreased river discharge or increased sodium concentrations.

The mean sodium flux in the Mokolo River for each season (Figure 4.8) showed that the values remained relatively consistent across the period of 1999 to 2010, with a single increased flux measured during the spring of 2007. The mean flux value for each season showed the same pattern as the Lephalala River, with the flux being highest during spring (0.00034 ± 0.00017 $\mathrm{Eq}\cdot\ell^{-1}$) followed by winter (0.00026 ± 0.00005 $\mathrm{Eq}\cdot\ell^{-1}$), summer (0.00025 ± 0.00005 $\mathrm{Eq}\cdot\ell^{-1}$) and autumn (0.00022 ± 0.00002 $\mathrm{Eq}\cdot\ell^{-1}$). These values were found to be not significantly different (ANOVA, d.f. = 22, p = 0.145), indicating that no significant seasonal changes in sodium fluxes occur. This could possibly indicate that the flux of sodium within the Mokolo River is not dependent on rainfall, river discharge and temperature changes between seasons. Differences in sodium concentrations are thus the most likely reason for significant changes in sodium fluxes within the Mokolo River.

The mean sodium flux in the Matlabas River for each season (Figure 4.8) indicated that sodium flux was elevated during the winter months. Summer and autumn flux values remained low, while two increased flux values were measured during the spring of 2009 and 2010.

The mean flux values for each season did not show the same pattern as the other two rivers, with the highest values recorded during winter (0.00066 ± 0.00064 $\mathrm{Eq}\cdot\ell^{-1}$). Spring, autumn and summer had mean flux values of 0.00045 ± 0.00024 $\mathrm{Eq}\cdot\ell^{-1}$, 0.00013 ± 0.00004 $\mathrm{Eq}\cdot\ell^{-1}$ and 0.00010 ± 0.00001 $\mathrm{Eq}\cdot\ell^{-1}$, respectively. The sodium values across seasons were found to be significantly different (ANOVA, d.f. = 19, p = 0.038). A Tukey HSD test revealed that the significant differences occurred between winter and autumn (p = 0.006) and between winter and summer (p = 0.007). All other pairs were not significantly different, indicating that sodium fluxes within the Matlabas River are consistent throughout most of the year with significant increases recorded during the winter months.

Winter months within the Waterberg District Municipality are dry and cool and the Matlabas River has a significantly lower discharge during this season. The increased fluxes during the winter are likely due to the decrease in these parameters while sodium concentrations remain relatively constant. Consistency of sodium concentrations in the absence of rain could also indicate that the sodium ions are not predominantly deposited from the atmosphere, but is likely due to input of sodium from the sodium rich soils surrounding and underlying the river.

The sodium flux threshold implemented to ensure that the health of the humans dependant on the water is not compromised is set at ~ 4350 $Eq.\ell^{-1}$ (SAWQG 1996). This threshold is never surpassed at an annual or seasonal resolution in the Lephalala, Mokolo and Matlabas Rivers during any of the hydrological years from 1999 to 2010. The highest flux recorded over this period (~0.0017 $Eq.\ell^{-1}$; winter 2001 in the Lephalala River) is ~2.5 x 10^6 times lower than the threshold value, indicating that sodium fluxes were of no concern for the considered period.

Sodium fluxes in both the rivers upwind of the Matimba power station (Lephalala and Mokolo Rivers) show no dependence on seasonal difference in rainfall and temperature, while the river located downwind of the station (Matlabas River) showed elevated sodium concentrations during the dry, cooler winter months. The most likely explanation for this increase is the seasonal nature of the river, with the decreased discharge expected during winter increasing the concentration of sodium ions and thus flux.

4.4.2 Magnesium flux within the Lephalala, Mokolo and Matlabas Rivers

Magnesium fluxes ranged from 0.00006 to 0.00032 $Eq\cdot\ell^{-1}$, 0.00010 to 0.00018 $Eq\cdot\ell^{-1}$, and 0.00005 to 0.00013 $Eq\cdot\ell^{-1}$ in the Lephalala, Mokolo and Matlabas Rivers, respectively (Figure 4.9). Magnesium fluxes reached a maximum value that is ~7 times smaller than the maximum sodium flux recorded over the same period. Magnesium fluxes within the Lephalala Rivers increased by 150% and 233% from 1999 to 2000 and from 2003 to 2004, respectively. The highest flux value recorded in the Lephalala River from 1999 to 2010 was 0.000032 $Eq\cdot\ell^{-1}$ in 2001. Mean magnesium fluxes within the Mokolo River showed a gradual increase of 60% from 2003 to 2005, with a decrease of 20 % from

2005 to 2006. The magnesium flux recovered to the previous value by 2007, reaching a value of 0.00018 Eq·ℓ$^{-1}$. No sharp changes in magnesium flux occurred within the Matlabas River, yet the highest flux value (0.00013 Eq·ℓ$^{-1}$) was measured in 2002 after increasing by 63% from 1999.

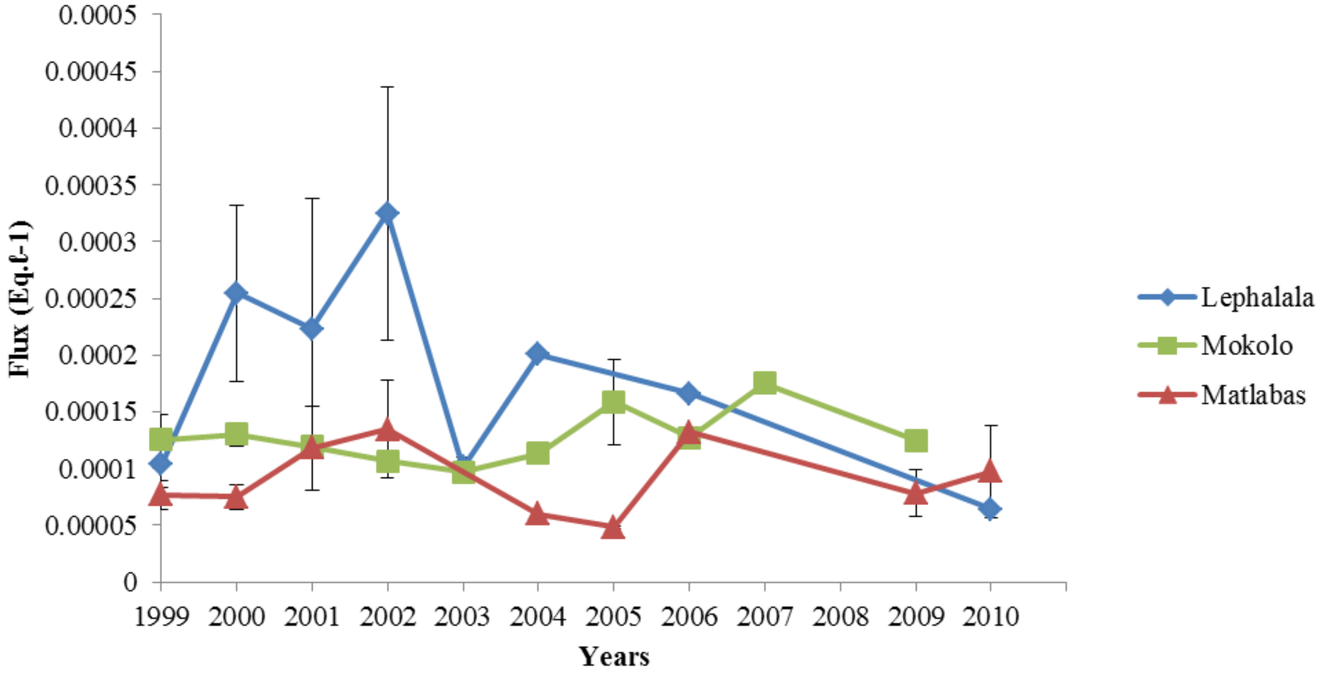


Figure 4.9. Annual mean flux in magnesium cations measured in the Lephalala, Mokolo and Matlabas Rivers during each hydrological year from 1999 to 2010. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The mean magnesium fluxes recorded from 1999 to 2010 in the Lephalala (0.00020 ± 0.00015 Eq·ℓ$^{-1}$), Mokolo (0.00013 ± 0.00004 Eq·ℓ$^{-1}$) and Matlabas (0.00009 ± 0.00006 Eq·ℓ$^{-1}$) were found to be significantly different (ANOVA, d.f. = 64, p = 0.001). A Tukey HSD test revealed that the significant differences occurred between the Lephalala and Matlabas Rivers (p = 0.0006) and the Lephalala and Mokolo Rivers (p = 0.0204) while the Mokolo and Matlabas Rivers were not significantly different (p = 0.3644). The mean magnesium flux in the Lephalala River for each season (Figure 4.10) showed that magnesium fluxes were very high during spring of 2000 and 2002 and the winter of 2001. The timing corresponds with the increased flux of sodium cations measured in the same river, indicating that the increased flux of sodium and magnesium was probably caused by the same factor. Magnesium flux within the Lephalala River is highest during spring (0.000338 ± 0.000228 Eq·ℓ$^{-1}$), followed by winter (0.000295 ± 0.000182 Eq·ℓ$^{-1}$), autumn (0.000162 ± 0.000055 Eq·ℓ$^{-1}$) and summer (0.000100 ± 0.000041 Eq·ℓ$^{-1}$). These values significantly differ (ANOVA, d.f. = 14, p = 0.0493), with the significant difference occurring between the flux in summer and spring (Tukey HSD, p = 0.0076). A significant decrease in magnesium flux within the Lephalala River occurs with the change from magnesium cations within the Mokolo River is not significantly influenced by the change in seasonal parameters such as temperature, rainfall and river discharge.

The mean magnesium flux within the Matlabas River for each season (Figure 4.10) indicates that the flux during summer and autumn is less variable from year to year, while large increases were found during the winter of 2001 (0.000228 Eq·ℓ^{-1}) and 2002 (0.000233 Eq·ℓ^{-1}), and the spring of 2010 (0.000187 Eq·ℓ^{-1}). The overall mean magnesium flux was ~2 times greater during spring (0.000128 ± 0.000053 Eq·ℓ^{-1}) and winter (0.000125 ± 0.000079 Eq·ℓ^{-1}) than during autumn (0.000066 ±0.000023 Eq·ℓ^{-1}) and summer (0.000068 ± 0.000019 Eq·ℓ^{-1}). Statistically, these values were found to be not significantly different (ANOVA, d.f. = 19, p = 0.0808) due to large variances, indicating that seasonality does not significantly influence the flux of magnesium cations within the Mokolo River.

The threshold value used to determine whether the amount of magnesium flux in a river is dangerous to human health is set to ~ 2470 Eq.ℓ^{-1} (SAWQG 1996). The magnesium fluxes measured in the Lephalala, Mokolo and Matlabas Rivers at both an annual and seasonal resolution from 1999 to 2010 remained well below this threshold value, with the highest magnesium flux value recorded over this period (0.000563 Eq.ℓ^{-1}; winter 2001 in the Lephalala River) being ~4.5 x 10^6 times smaller than the set threshold. This indicates that the fluxes of magnesium in these rivers were of no particular concern to human health over the period investigated.

The fluxes of magnesium cations within the Mokolo and Matlabas Rivers are not significantly different from one season to the next, possibly indicating that the input of magnesium into the catchment is consistent throughout the year. Magnesium flux within the Lephalala River is consistent throughout most of the year, yet significantly lower flux values are found during the summer months.

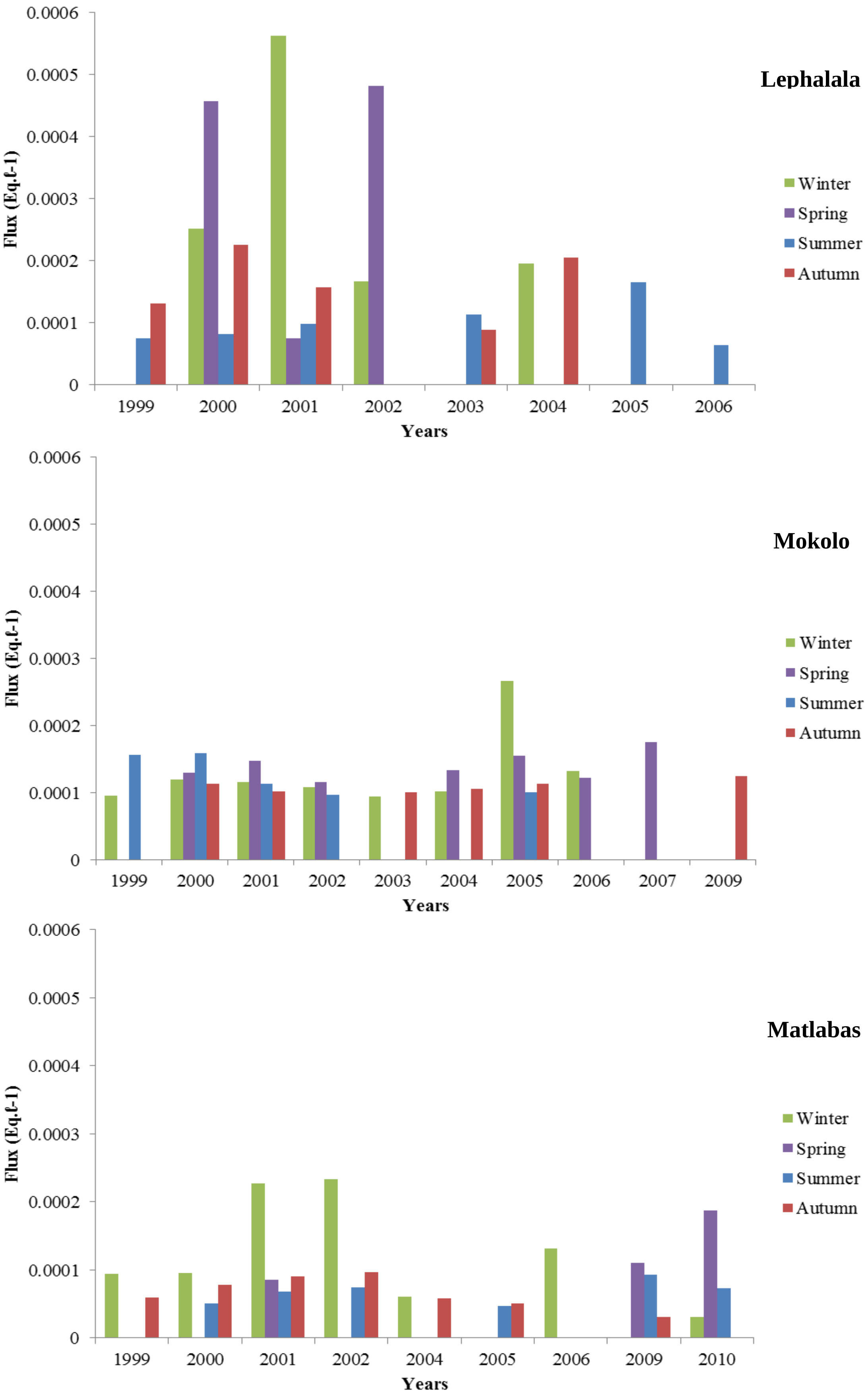


Figure 4.10. Mean flux in magnesium cations measured in the Lephalala, Mokolo and Matlabas Rivers during summer, autumn, winter and spring from 1999 to 2010.

4.4.3 Calcium flux within the Lephalala, Mokolo and Matlabas Rivers

Calcium fluxes within the Lephalala, Mokolo and Matlabas Rivers ranged from 131 to 305 Eq·ℓ^{-1}, 121 to 221 Eq·ℓ^{-1}, and 52 to 172 Eq·ℓ^{-1}, respectively (Figure 4.11). Calcium fluxes within the Lephalala River increased by 72.71% from 1999 to 2000, decreased by 46.32% from 2002 to 2004, and again increased by 54.21% from 2004 to 2005. The change in calcium flux in the Mokolo River from 1999 to 2010 mirrors the change in magnesium flux over the same period, which could possibly indicate that the change in both the ions is driven by the same factor. Calcium flux within the Matlabas River increased by 124.90% from 1999 to 2003. It decreased by the same margin from 2003 to 2004 after which it consistently fluctuated between 56 and 76 Eq·ℓ^{-1}.

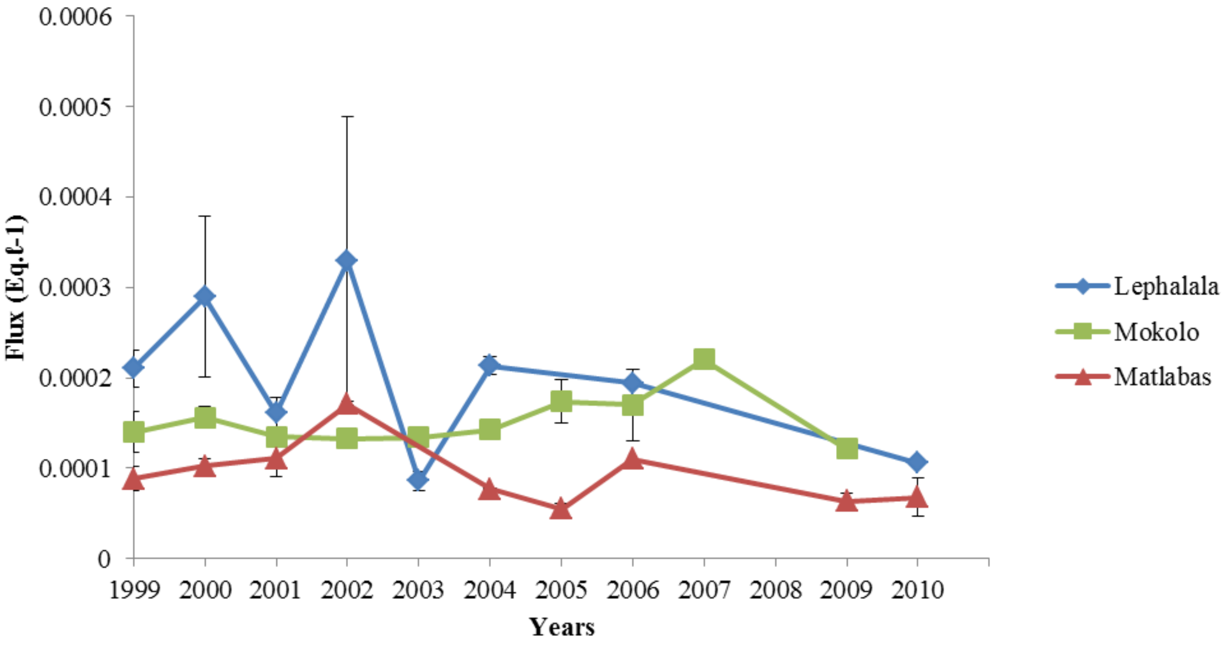


Figure 4.11. Annual flux in calcium cations measured in the Lephalala, Mokolo and Matlabas Rivers from during each hydrological year from 1999 to 2010. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The mean calcium flux recorded from 1999 to 2010 in the Lephalala (0.000210 ± 0.000123 Eq·ℓ^{-1}), Mokolo (0.000151 ± 0.000032 Eq·ℓ^{-1}) and Matlabas (0.000096 ± 0.000041 Eq·ℓ^{-1}) Rivers were found to be highly significantly different (ANOVA, d.f. = 64, p = 1.608 x 10^{-5}). A Tukey HSD test revealed that the significant differences were between all the rivers: the Lephalala and Mokolo (p = 0.0214), Lephalala and Matlabas (p = 0.00001) and the Mokolo and Matlabas (p = 0.0236) Rivers. The calcium fluxes in the rivers located upwind of the power station are thus not significantly elevated when compared to the Matlabas River.

The mean calcium flux in the Lephalala River for each season (Figure 4.12) showed elevated flux values during spring of 2000 and 2002. These increased calcium fluxes occurred at the same time as the increased sodium and magnesium fluxes were recorded. This could indicate that the elevated fluxes are probably due to change in the same parameters driving the changes in individual cation concentrations. The most likely explanatory parameter is river discharge as it is the only common parameter while the amount of cations deposited would differ between the different cations depending on the source.

Calcium flux was highest during spring (0.000378 ± 0.000223 Eq·ℓ$^{-1}$), followed by winter (0.000216 ± 0.000044 Eq·ℓ$^{-1}$), autumn (0.000188 ± 0.000062 Eq·ℓ$^{-1}$) and summer (0.000140 ± 0.000061 Eq·ℓ$^{-1}$). Calcium flux significantly differed between seasons (ANOVA, d.f. = 14, 0.0321), with the significant difference occurring between summer and spring (Tukey HSD, p = 0.0209). All other pairs were found to be not significantly different indicating that the flux of calcium in the Lephalala River remained consistent throughout the year, yet significantly decreased with the change from spring to summer. The same pattern was found for the flux of magnesium within the Lephalala River, possibly indicating a common factor influencing the flux of these cations in the rivers.

The mean calcium flux in the Mokolo River for each season (Figure 4.12) indicates that the flux remained relatively consistent across the entire period of 1999 to 2010. Although no predominant increases in calcium flux are seen, elevated fluxes are recorded for the winter of 2005 and the spring of 2006 and 2007. Calcium flux was higher during spring (0.000174 ± 0.000033 Eq·ℓ$^{-1}$) and summer (0.000155 ± 0.000010 Eq·ℓ$^{-1}$) when compared to winter (0.000140 ± 0.000042 Eq·ℓ$^{-1}$) and autumn (0.000134 ± 0.000009 Eq·ℓ$^{-1}$). These values are not significantly different (ANOVA, d.f. = 22, p = 0.0972), indicating that change in rainfall and temperature with a change in season does not significantly affect the flux of calcium within the Mokolo River. When the rainy season (summer and spring) is broadly compared to the dry season (winter and autumn), the flux of calcium in the Mokolo

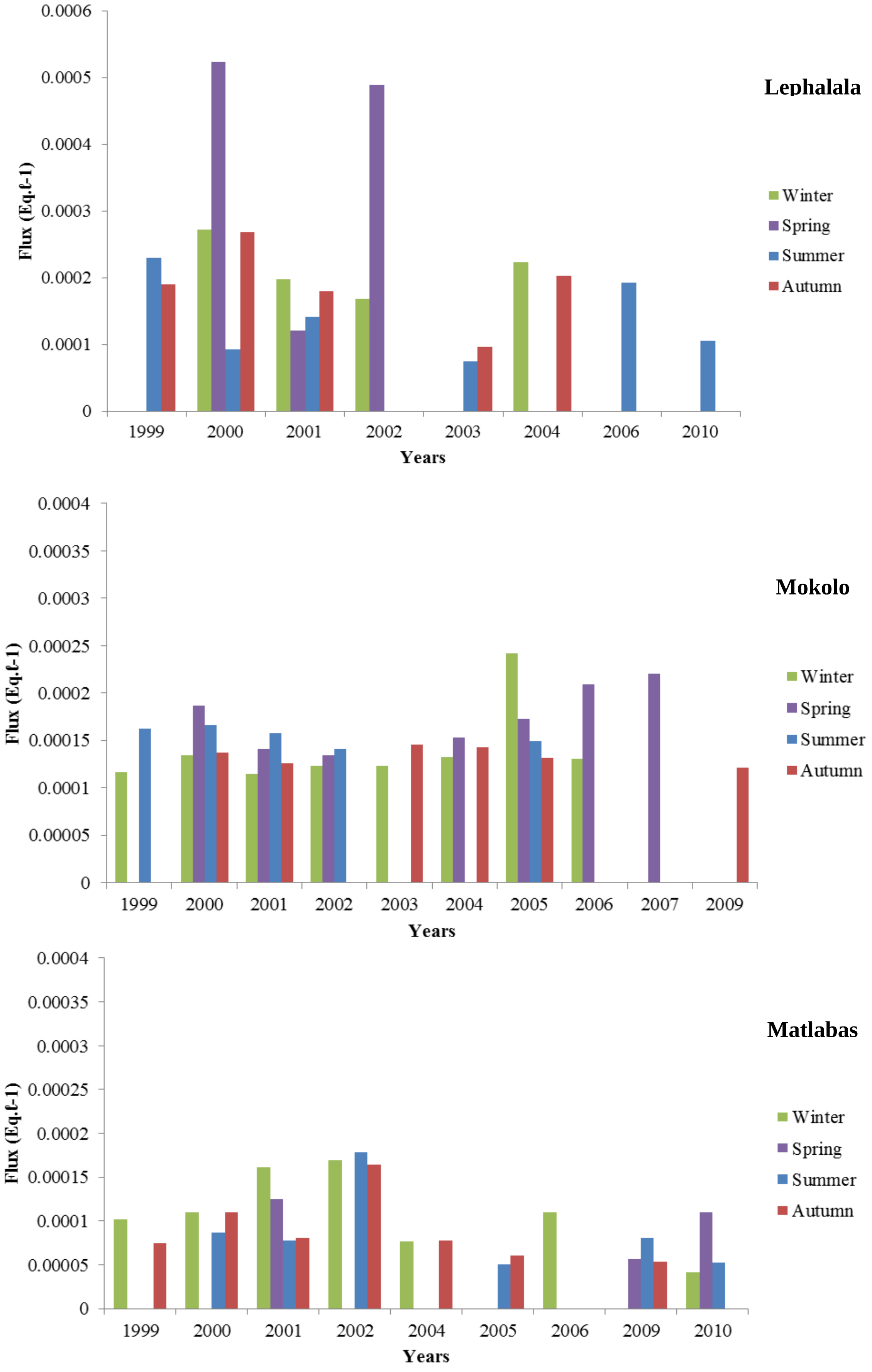


Figure 4.12. Mean flux in calcium cations measured in the Lephalala, Mokolo and Matlabas Rivers during summer, autumn, winter and spring from 1999 to 2010.

River is lower during the latter, indicating some (although not significant) effect of rainfall on the flux of calcium. An increase in flux with an increase of rainfall only occurs when discharge does not directly increase as well. Higher calcium fluxes are most probably due to increased ion deposition while river discharge remains relatively unchanged.

The mean calcium flux in the Matlabas River for each season (Figure 4.12) indicates that flux remained low during all seasons for the entire period of 1999 to 2010, with one noticeable increase measured during the winter of 2006. The consistency of the flux of calcium was confirmed when no significant differences were found to exist between the overall season means (ANOVA, d.f. = 19, p =0.7519): winter (0.000110 ± 0.000045 $\text{Eq}\cdot\ell^{-1}$), spring (0.000097 ± 0.000036 $\text{Eq}\cdot\ell^{-1}$), autumn (0.000089 ± 0.000038 $\text{Eq}\cdot\ell^{-1}$) and summer (0.000087 ± 0.000047 $\text{Eq}\cdot\ell^{-1}$).

The South African Water Quality Guidelines (1996) indicates that human health is only of concern once calcium fluxes surpass ~ 1600 $\text{Eq.}\ell^{-1}$. No annual or seasonal fluxes measured in the Lephalala, Mokolo and Matlabas Rivers exceeded this threshold value. The highest value recorded from 1999 to 2010 (0.000524 $\text{Eq.}\ell^{-1}$; spring 2000 in the Lephalala River) is approximately 3×10^6 times smaller than the threshold value, indicating that calcium fluxes in these rivers are of no concern to human health yet.

No common patterns in calcium flux within the Lephalala, Mokolo and Matlabas Rivers were found. Calcium flux significantly decreased during summer in the Lephalala River while flux in the Mokolo River was elevated during summer (0.000155 ± 0.000010 $\text{Eq}\cdot\ell^{-1}$) when compared to the mean calculated for all calcium fluxes within the river (0.000151 ± 0.000032 $\text{Eq}\cdot\ell^{-1}$). Fluxes within the Matlabas River did not change between seasons. The changes in the flux of calcium in the river upwind of the Matimba power station (Lephalala and Mokolo Rivers) could indicate that flux is influenced by the change in deposition intensity and distance from the source with change in rainfall.

4.4.4 Potassium flux within the Lephalala, Mokolo and Matlabas Rivers

Potassium fluxes ranged from 0.000029 to 0.000080 Eq·ℓ$^{-1}$, 0.000024 to 0.000074 Eq·ℓ$^{-1}$ and 0.000011 to 0.000047 Eq·ℓ$^{-1}$ in the Lephalala, Mokolo and Matlabas Rivers, respectively (Figure 4.13). These flux values are ~ 3 to 4 times smaller than the corresponding values for sodium, magnesium and calcium fluxes. Potassium flux within the Lephalala River gradually increased from 1999 to 2003, with a single decrease of 24% from 2003 to 2004. A sharp increase in flux occurred from 2004 to 2006 (135%) after which it decreased again by 46% to a flux value of 0.000043 Eq·ℓ$^{-1}$ in 2010. The potassium flux within the Mokolo River increased by 58% from 2001 to 2002, and by 130% from 2006 to 2007, reaching its maximum value in 2007 (0.000074 Eq·ℓ$^{-1}$). Changes in fluxes within the Matlabas River showed a similar pattern to the changes within the Lephalala and Mokolo Rivers, yet only indicated a single sharp increase of 290% from 2006 to 2009 reaching its maximum value (0.000047 Eq·ℓ$^{-1}$). Both the Lephalala and Mokolo Rivers reached maximum potassium flux values in 2007, while the maximum flux value in the Matlabas River was recorded in 2009. Potassium flux in the Matlabas River was possibly also highest in 2007, yet cannot be determined due to missing data.

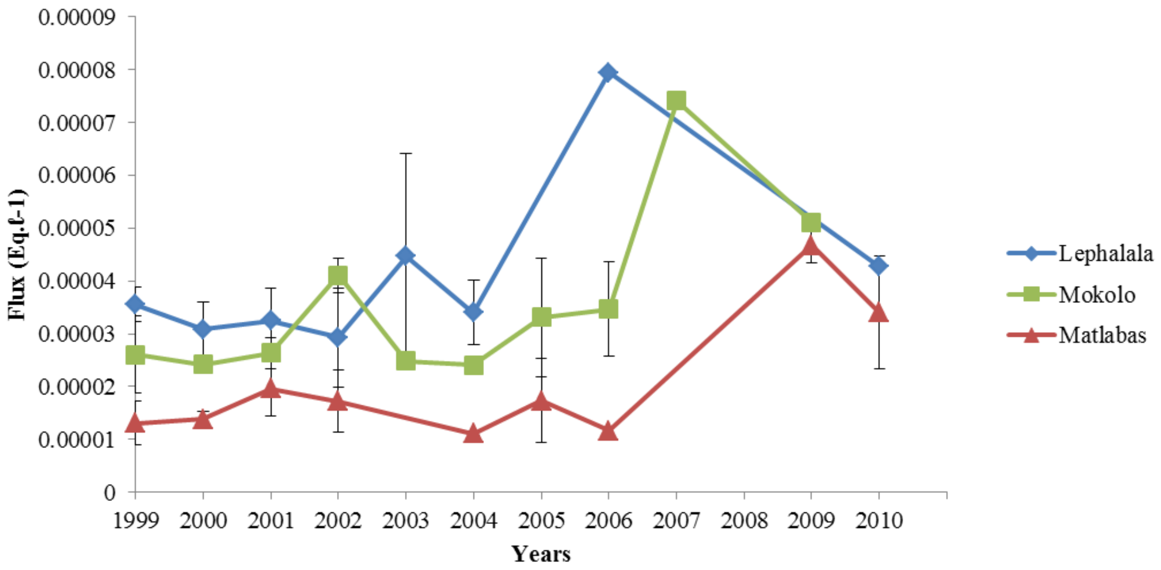


Figure 4.13. Annual mean flux in potassium cations measured in the Lephalala, Mokolo and Matlabas Rivers during each hydrological year from 1999 to 2010. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The mean potassium flux recorded from 1999 to 2010 in the Lephalala (0.000037 ± 0.000016 $Eq{\cdot}\ell^{-1}$), Mokolo (0.000032 ± 0.000014 $Eq{\cdot}\ell^{-1}$) and Matlabas (0.000022 ± 0.000014 $Eq{\cdot}\ell^{-1}$) Rivers was found to be significantly different between rivers (ANOVA, d.f. = 64, p = 0.0066). A Tukey HSD test showed that the Lephalala and Matlabas Rivers significantly differed (p = 0.0064), while the Mokolo River did not significantly differ from the Lephalala (p = 0.5106) or Matlabas (p = 0.0627) Rivers. The Mokolo River is located in the middle between the Lephalala and Matlabas Rivers along the NE to SW axis from the Matimba power station, and shares commonality with both the other rivers.

The mean potassium flux in the Lephalala River for each season (Figure 4.14) indicated that potassium flux predominates within the summer season, with especially high values recorded in 2003, 2006 and 2010. Potassium flux with the Lephalala River was higher during summer (0.000046 ± 0.000022 $Eq{\cdot}\ell^{-1}$) and spring (0.000041 ± 0.000004 $Eq{\cdot}\ell^{-1}$) than in winter (0.000029 ± 0.000013 $Eq{\cdot}\ell^{-1}$) and autumn (0.000030 ± 0.000007 $Eq{\cdot}\ell^{-1}$). Although these values are statistically not significantly different (ANOVA, d.f. = 14, p = 0.2572), it is clear that flux values are elevated during the rainy season (summer and spring). This could indicate that rainfall has some influence on the flux measured within the river even if it is statistically considered to be not significant.

The mean potassium flux in the Mokolo River for each season (Figure 4.14) revealed that the flux was once again elevated during the summer and spring seasons. Elevated potassium flux values are recorded during summer 2005, spring 2006 and 2007 and autumn of 2010. Potassium flux within the Mokolo River was highest during spring (0.000038 ± 0.000019 $Eq{\cdot}\ell^{-1}$), followed by summer (0.000038 ± 0.000017 $Eq{\cdot}\ell^{-1}$), autumn (0.000030 ± 0.000012 $Eq{\cdot}\ell^{-1}$) and winter (0.000025 ± 0.000005 $Eq{\cdot}\ell^{-1}$). These values were found to be not significantly different (ANOVA, d.f. = 22, p = 0.2461) most probably due to large variance. It is, however, seen that the potassium fluxes are elevated in the rainy season (spring and summer) when compared to the dry season (autumn and winter) possibly showing some relationship between rainfall and the flux of potassium within the Mokolo River.

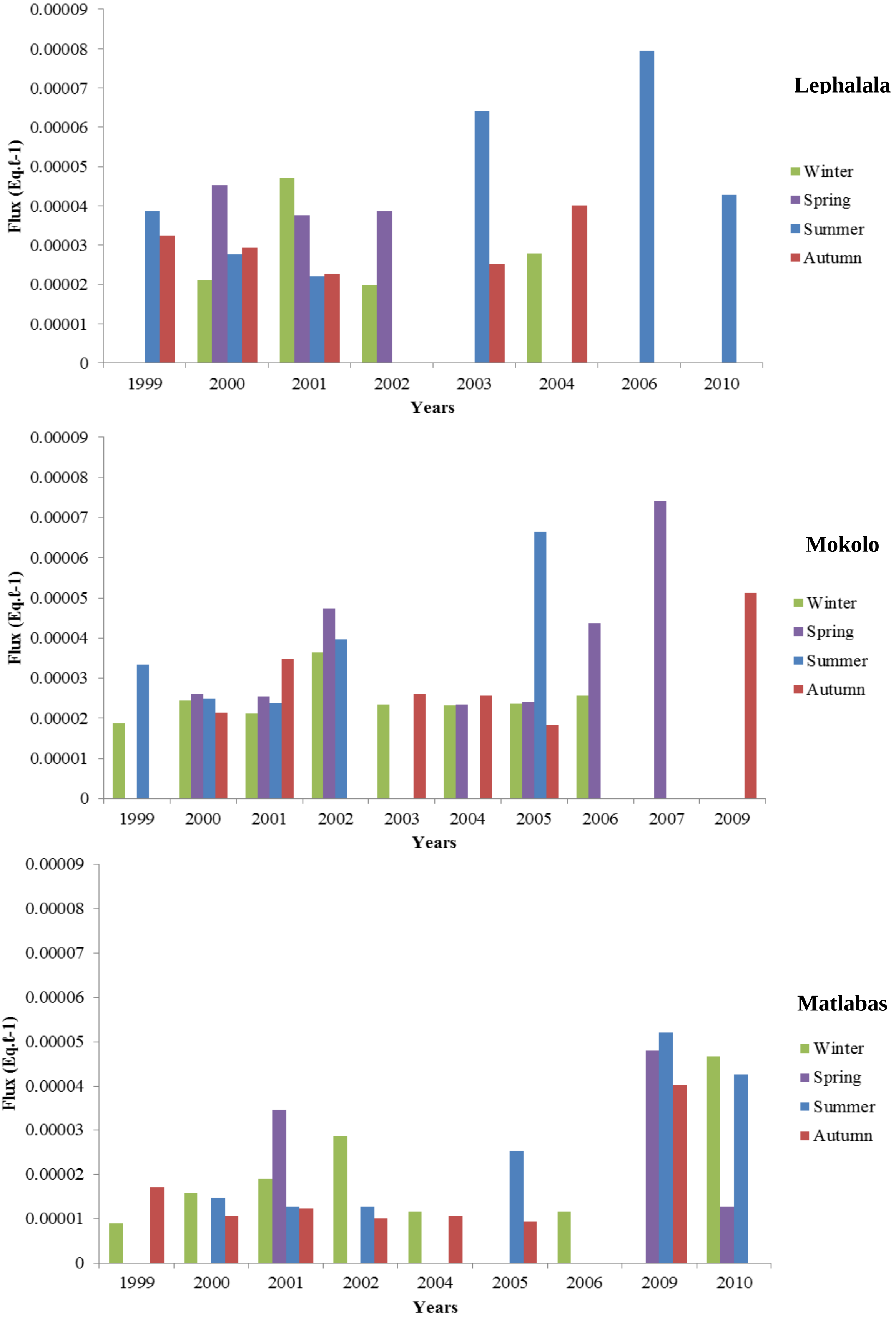


Figure 4.14. Mean flux in potassium cations measured in the Lephalala, Mokolo and Matlabas Rivers during summer, autumn, winter and spring from 1999 to 2010.

The mean potassium flux in the Matlabas River for each season (Figure 4.14) showed elevated flux values during spring of 2001 and winter of 2002. No preliminary reasons for these values could be presented. Elevated values across all seasons were recorded for 2009 to 2010, indicating that a longer term change in potassium input into the Matlabas River occurred. The highest potassium flux values in the Matlabas River were recorded in spring (0.000032 ± 0.000018 Eq·ℓ^{-1}), followed by summer (0.000027 ± 0.000017 Eq·ℓ^{-1}), winter (0.000020 ± 0.000013 Eq·ℓ^{-1}) and autumn (0.000016 ± 0.000011 Eq·ℓ^{-1}). These values were found to be not significantly different (ANOVA, d.f. = 19, p = 0.3521) but also showed elevated flux values during the rainy season as also found for the Lephalala and Mokolo Rivers.

The human health threshold set for potassium flux is ~1280 Eq.ℓ^{-1} (SAWQG 1996), a value approximately 3 x 10^7 times greater than the highest potassium flux recorded for the Lephalala, Mokolo and Matlabas Rivers at both an annual and seasonal resolution from 1999 to 2010 (~0.000037 Eq.ℓ^{-1}; Lephalala 2007) . Potassium flux in these rivers is of no concern and is expected to remain below the threshold in the near future as the fluxes will have to increase significantly in order to exceed the threshold set.

The elevated potassium fluxes during the rainy season (spring and summer) in the Lephalala, Mokolo and Matlabas Rivers could indicate that the flux of the cation is not significantly influenced by the direct wet deposition of the cation from the atmosphere. If this were to be true, potassium flux in the Mokolo River would predominate during the rainy season due to its close proximity to the assumed source, while flux in the Lephalala and Matlabas Rivers would predominate during the dry season as these rivers are located further away from the point of source. The increase of potassium flux during the rainy season in all three rivers is most likely to be due to the increase leaching of the cation from the surrounding surfaces and soils, indicating that the potassium is most probably from natural sources.

4.4.5 Ammonium flux within the Lephalala, Mokolo and Matlabas Rivers

Ammonium flux values measured within the Lephalala, Mokolo and Matlabas Rivers are lower than the fluxes measured for sodium, magnesium, calcium and potassium. Ammonium fluxes ranged from 0.000001 to 0.000003 Eq·ℓ$^{-1}$, 0.000001 to 0.000005 Eq·ℓ$^{-1}$, and 0.000001 to 0.000002 Eq·ℓ$^{-1}$ in the Lephalala, Mokolo and Matlabas Rivers, respectively (Figure 4.15). Ammonium flux values in the Lephalala River continuously fluctuated across the entire period of 1999 to 2010, with the maximum value recorded in 2003. A sharp decline of 67% occurred from 2003 to 2004, followed by a sharp increase of 200% from 2004 to 2006. Ammonium flux values recorded for the Mokolo River remained relatively consistent from 1999 to 2007, followed by an increase of 400% from 2007 to its maximum value in 2009. The largest change in ammonium flux within the Matlabas River occurred from 2004 to 2005 (decrease; 50%). From 2005 to 2010, the flux of ammonium ions remained relatively consistent.

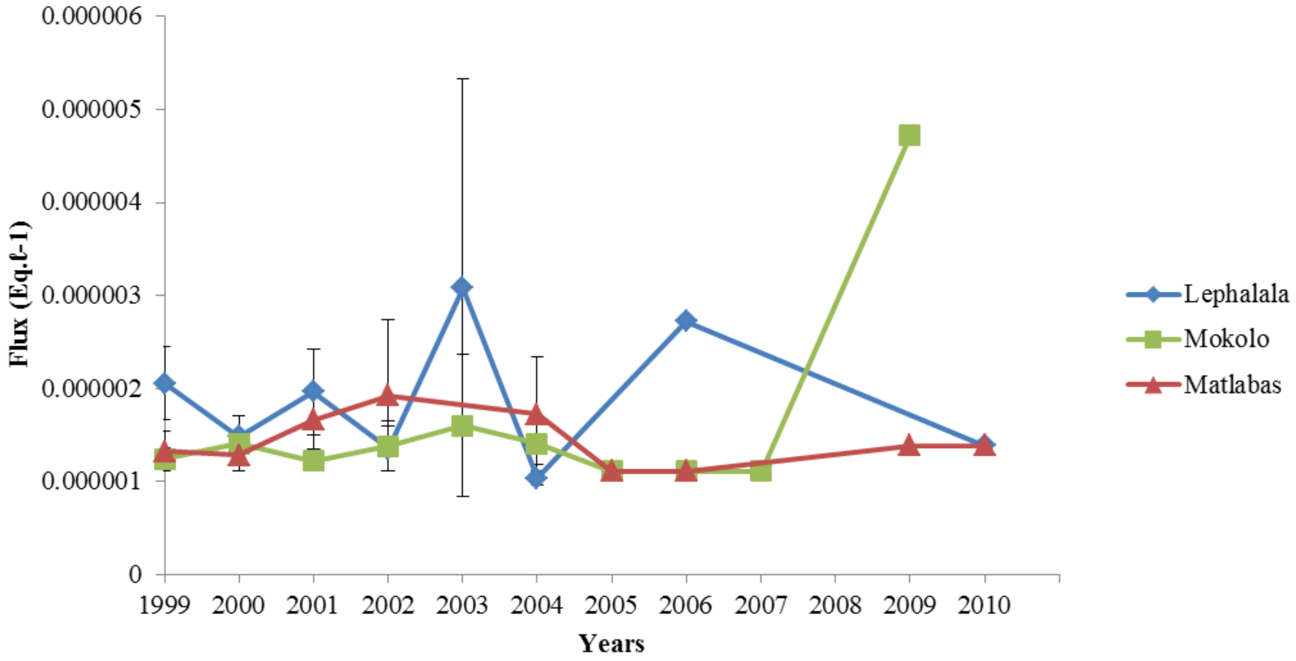


Figure 4.15. Annual mean flux in ammonium cations measured in the Lephalala, Mokolo and Matlabas Rivers during each hydrological year from 1999 to 2010. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The mean ammonium flux values recorded from 1999 to 2010 for the Lephalala (0.000002 ± 0.000001 Eq·ℓ$^{-1}$), Mokolo (0.000001 ± 0.000001 Eq·ℓ$^{-1}$) and Matlabas (0.000001 ± 0.000001 Eq·ℓ$^{-1}$)

Rivers were found to be not significantly different (ANOVA, d.f. = 64, p = 0.2436). This is probably due to the relatively large variances, indicating that ammonium flux can be considered to be the same in all three rivers. The flux of ammonium is thus not dependent on the direction and distance of the geographical location of the river monitoring site in relation to the possible source (Matimba power station).

The mean ammonium flux in the Lephalala River for each season (Figure 4.16) showed that increased flux values occurred predominantly during the summer months, with an especially increased value recorded for the summer of 2003. Flux values recorded during spring were low, unlike the results found for the other cations discussed. Ammonium flux values in the Lephalala River were highest during summer (0.000003 ± 0.000001 $\text{Eq}\cdot\ell^{-1}$) with lower fluxes recorded for winter (0.000002 ± 0.000001 $\text{Eq}\cdot\ell^{-1}$), autumn (0.000002 ± 0.0000005 $\text{Eq}\cdot\ell^{-1}$) and spring (0.000001 ± 0 $\text{Eq}\cdot\ell^{-1}$). The flux values were found to be not significantly different between seasons (ANOVA, d.f. = 14, p = 0.2005), possibly due to large variances calculated for the flux during summer and winter.

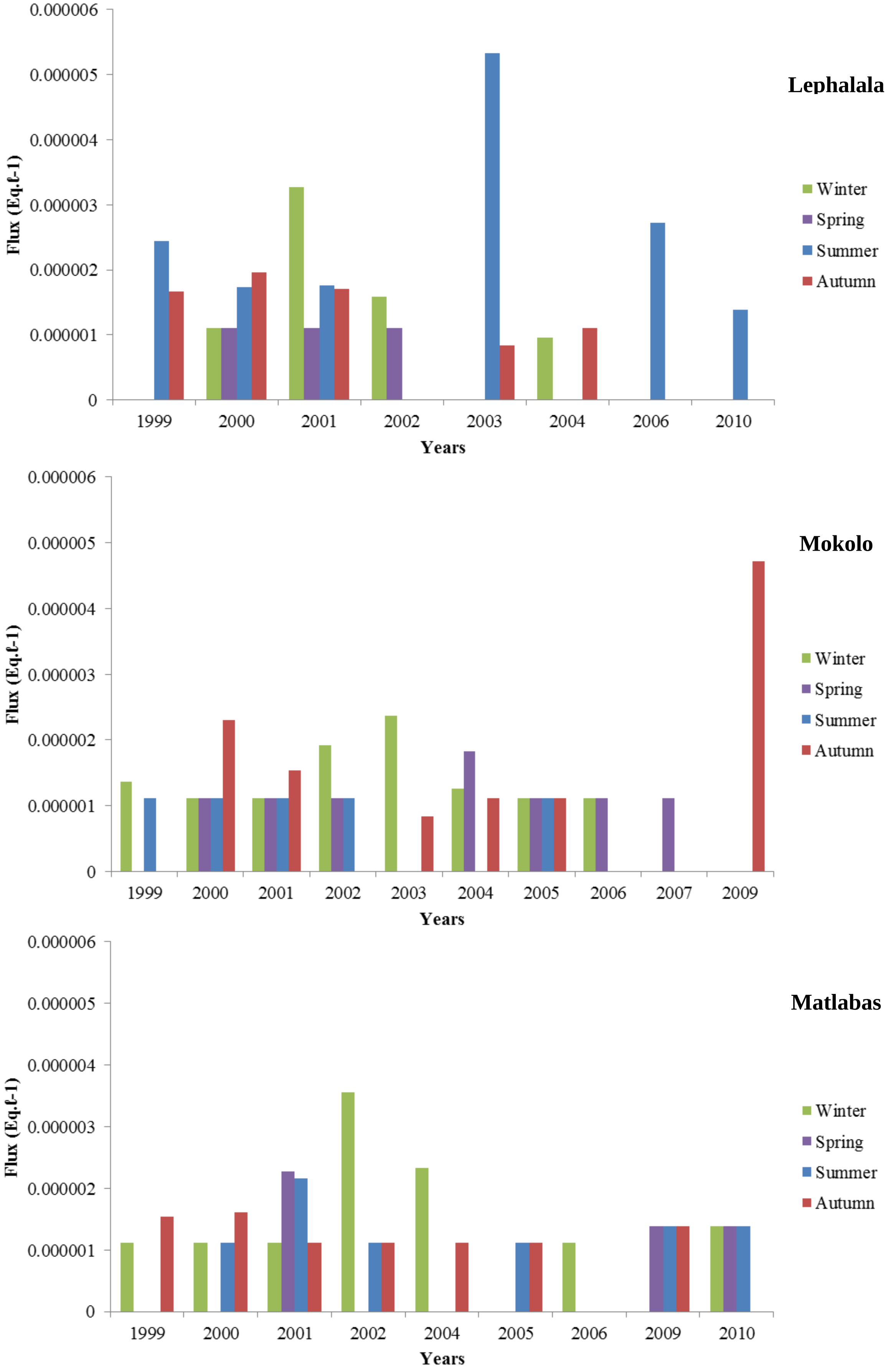


Figure 4.16. Mean flux in ammonium cations measured in the Lephalala, Mokolo and Matlabas Rivers during summer, autumn, winter and spring from 1999 to 2010.

This could possibly be due to a delayed increase in river discharge after rainfall commenced in spring. Delays can be expected as the Lephalala River Catchment is a developed catchment with various water uses that could intercept the water before reaching the river.

The mean ammonium flux in the Mokolo River for each season (Figure 4.16) clearly showed that the flux remained at 0.000001 Eq·ℓ^{-1} for most of the period of 1999 to 2010. Isolated increases in flux were measured in especially the autumn of 2000 and 2009 as well as the winter of 2003. Ammonium flux within the Mokolo River was higher during autumn (0.000002 ± 0.000002 Eq·ℓ^{-1}) and winter (0.000001 ± 0.0000005 Eq·ℓ^{-1}) than in summer (0.000001 ± 0 Eq·ℓ^{-1}) and spring (0.000001 ± 0.0.0000003 Eq·ℓ^{-1}). Statistically, the flux values were not significantly different between seasons (ANOVA, d.f. = 22, p = 0.2751) yet fluxes were elevated during the dry season (autumn and winter) when compared to the rainy season (summer and spring).

The mean ammonium flux in the Matlabas River for each season (Figure 4.16) again showed a relatively consistent flux value throughout the period of 1999 to 2010. Elevated ammonium flux values were recorded during the summer of 2001, the spring of 2001 and the winters of 2002 and 2004. Ammonium flux was more predominant in spring (0.000002 ± 0.0.0000005 Eq·ℓ^{-1}) and winter (0.0.000002 ± 0.0.0000009 Eq·ℓ^{-1}) and less predominant in summer (0.000001 ± 0.0000004 Eq·ℓ^{-1}) and autumn (0.000001 ± 0.0000002 Eq·ℓ^{-1}). No significant differences in flux values between seasons were found (ANOVA, d.f. = 19, p = 0.5879), indicating no seasonal differences in the flux of ammonium within the Matlabas River.

The highest ammonium flux recorded both annually and seasonally (0.000005 Eq.ℓ^{-1}; summer of 2003 in the Lephalala River) was approximately 1.2 x 10^{7} times smaller than the human health threshold flux value set by the South African Water Quality Guidelines of 1996 (~60 Eq.ℓ^{-1}). Ammonium fluxes are relatively low in the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2010, with no concern of the threshold being surpassed in the near future.

No significant differences in ammonium flux values were found between seasons in the Lephalala, Mokolo or Matlabas Rivers. The flux of ammonium within these rivers is thus not significantly changed by any expected seasonal changes in rainfall, temperature and river discharge. Increased flux values were recorded in months of sporadic high rainfall or temperature events, and is most likely due to the sharp increase of ion concentrations in the river in a relatively short time. Understanding the flux of summed cations within the Lephalala, Mokolo and Matlabas Rivers could provide further understanding of the seasonality of cations changes and how this would affect overall water quality.

4.5 Investigating the change in summed cation fluxes measured in each of the rivers from 1999 to 2010

Summed cation flux data were compared in two ways: by only considering two points in time (1999 and 2010), and by comparing the response surface of the graphs indicating change in cation flux in the Lephalala, Mokolo and Matlabas Rivers. No threshold values for summed cations are available in guidelines such as the South African Water Quality Guidelines (SAWQG), yet the thresholds for the individual cations have already been discussed.

No significant difference in the absolute flux of summed cations in 1999 and 2010 was found within the Lephalala (ANOVA, d.f. = 2, p = 0.1851), Mokolo (ANOVA, d.f. = 2, p = 0.7811) and Matlabas (ANOVA, d.f. = 3, p = 0.8750) Rivers. The Mokolo River had no flux values available for the 2010 hydrological year, and values from 2009 were used instead. Changes in flux occur between these two static points in all rivers, with fluxes increasing and decreasing over the 12 year period (Figure 4.17).

No significant relationships were found to exist between the rivers in terms of the cation concentrations measured (Non-linear regression, d.f. = 3, p = 0.7666). Neither the increase in cation flux in the Lephalala River from 2001 to 2002 (ANOVA, d.f. = 4, p = 0.5102) nor the increase from 2003 to 2006 (ANOVA, d.f. = 2, p = 0.1183) were found to be significant. The increase in cation flux measured in the Mokolo River from 2006 to 2007 was found to be significant (ANOVA, d.f. = 2, p = 0.0295). The increases in cation flux in the Matlabas River were found to be not significant for 2000 to 2002 (ANOVA, d.f. = 4, p = 0.3295) yet the flux significantly increases from 2005 to 2006 (ANOVA, d.f. = 2, p = 0.0017).

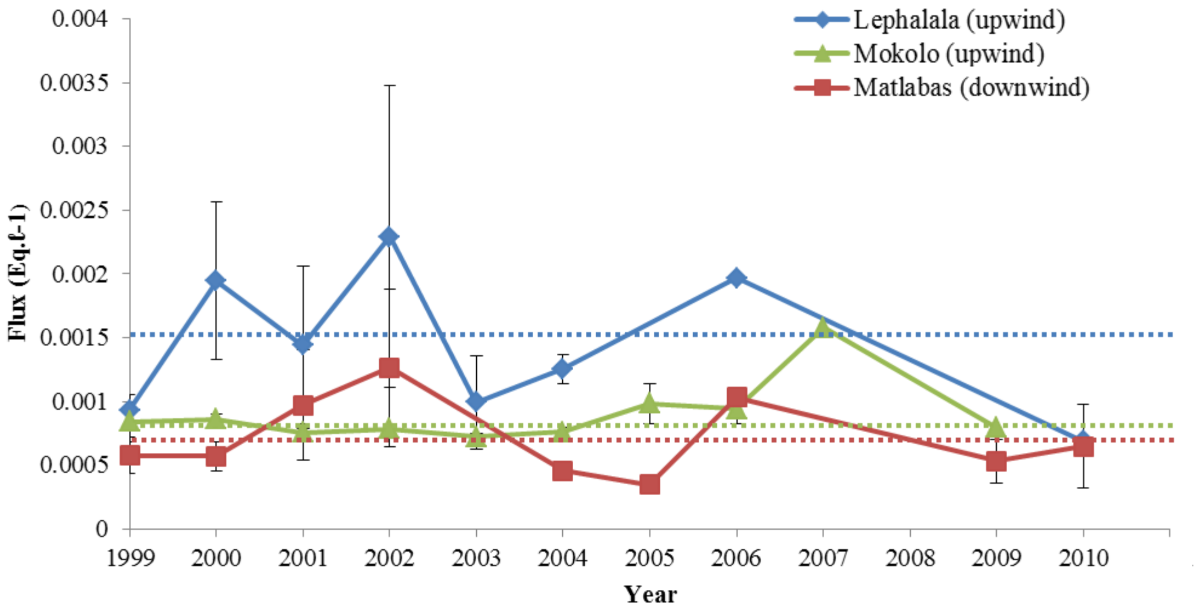


Figure 4.17. Flux of summed cations in the Lephalala, Mokolo and Matlabas Rivers during each hydrological year from 1999 to 2010. The average flux of cations over the 12 year period is indicated by the dotted line for each river. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The changes in fluxes are the net results of the various anthropogenic, natural and climatic factors influencing the concentrations of ions measured at any given point, temporally and spatially. Possible reasons for the pattern of cation flux measured in each of the rivers are explored in later sections by studying the relationship between the fluxes measured and the anthropogenic and climatic variables known for the Lephalale area.

The mean cation flux value measured across the period of 1999 to 2010 for each river is also indicated in Figure 4.17. The Lephalala River had the highest mean cation flux value of 0.001508 ± 0.000986 Eq.ℓ^{-1}. The Mokolo and Matlabas Rivers had mean cation flux values of 0.000861 ± 0.000213 and 0.000726 ± 0.000578 Eq.ℓ^{-1}, respectively. No significant differences (Blocked ANOVA, d.f. = 10, p = 0.0802) exists between the yearly concentrations measured within each river, also indicated by the very large standard deviation values calculated. Very significant differences (Blocked ANOVA, d.f. = 2, p = 0.0009 with Lephalala having the highest cation flux values, This finding is contradicted by the largely overlapping standard deviations calculated for the rivers (Figure 4.18).

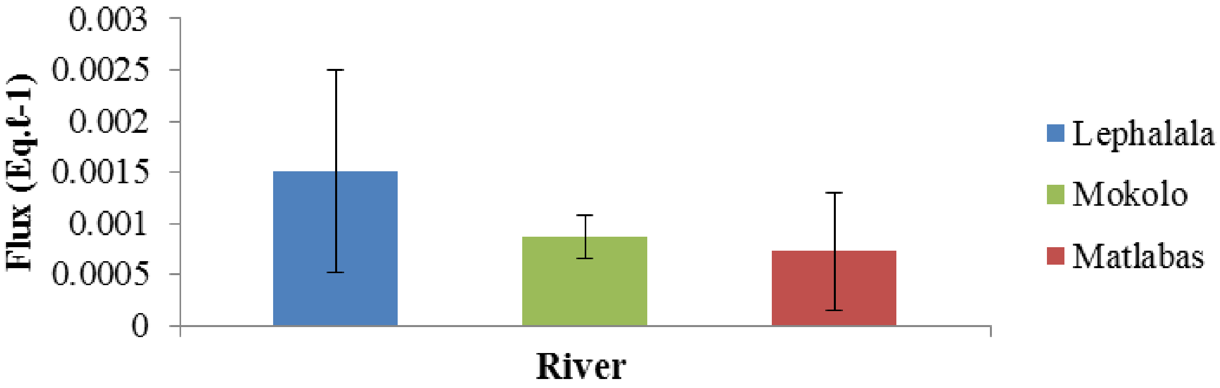


Figure 4.18. Mean cation flux values calculated for the Lephalala, Matlabas and Mokolo Rivers from 1999 to 2010.

The mean summed cation fluxes in the Lephalala River for each season (Figure 4.19) showed that especially high flux values were recorded in spring of 2000 and 2002 as well as the winter of 2001. The same peaks were found for sodium, magnesium and calcium fluxes indicating that these cations are the main contributors to the flux of summed cations. Summed cation flux within the Lephalala River was highest during spring (0.002562 ± 0.001669 Eq·ℓ^{-1}), followed by winter (0.001913 ± 0.000965 Eq·ℓ^{-1}), autumn (0.001129 ± 0.000397 Eq·ℓ^{-1}) and summer (0.001029 ± 0.000535 Eq·ℓ^{-1}). The flux values were found to be not significantly different between seasons (ANOVA, d.f. = 14, p = 0.0838).

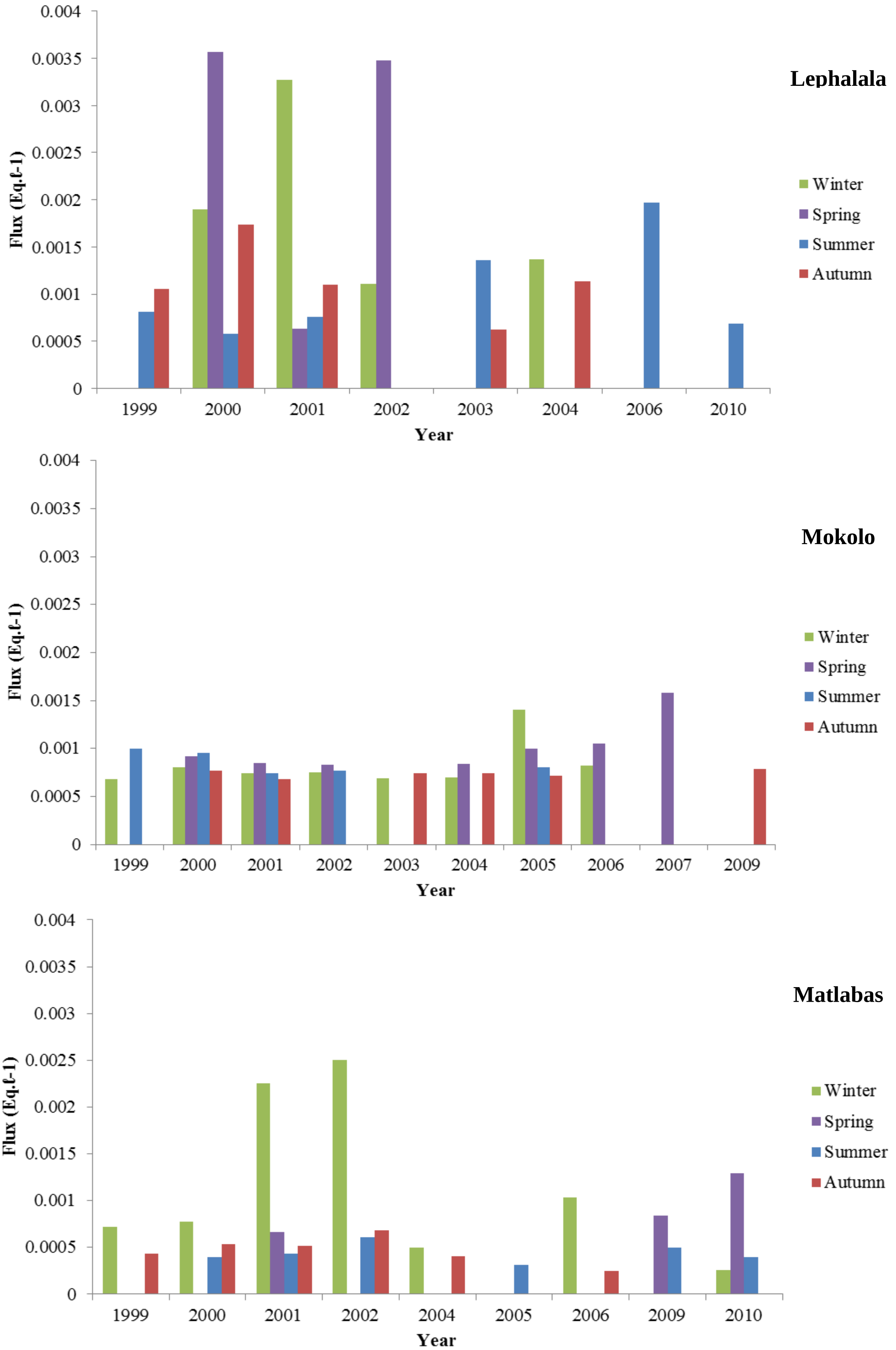


Figure 4.19. Mean fluxes in summed cations measured in the Lephalala, Mokolo and Matlabas Rivers during summer, autumn, winter and spring from 1999 to 2010.

The mean summed cation fluxes in the Mokolo River for each season (Figure 4.19) was ~ 2 times less than the flux of cations in the Lephalala River over the same period. The flux of cations remained relatively constant from 1999 to 2010, with elevated fluxes found for the winter of 2005 and the spring of 2007. Summed cation flux in the Mokolo River was higher during spring (0.001010 ± 0.000265 Eq·ℓ^{-1}) and summer (0.000853 ± 0.000114 Eq·ℓ^{-1}) than during winter (0.000826 ± 0.000240 Eq·ℓ^{-1}) and autumn (0.000740 ± 0.000039 Eq·ℓ^{-1}). The flux values were found to be not significantly different between seasons (ANOVA, d.f. = 22, $p = 0.1302$) most probably due to the high variance in flux values. Flux values were, however, elevated in the rainy season (spring and summer) when compared to the dry season (winter and autumn).

The mean summed cation flux in the Matlabas River for each season (Figure 4.19) was ~ 4 and 2 times lower than cation flux within the Lephalala and Mokolo Rivers, respectively. The cation flux remained relatively constant from 1999 to 2010, with increased flux values measured during the winter of 2001, 2002 and 2006 as well as the spring of 2009 and 2010. The flux of summed cations in the Matlabas River was highest during winter (0.001149 ± 0.000876 Eq·ℓ^{-1}), followed by spring (0.000931 ± 0.000325 Eq·ℓ^{-1}), autumn (0.000459 ± 0.000139 Eq·ℓ^{-1}) and summer (0.000442 ± 0.000102 Eq·ℓ^{-1}). Summed cation flux values were not significantly different between seasons (ANOVA, d.f. = 19, $p = 0.0562$), yet a p-value of close to 0.05 indicates that the differences are large regardless of the lack of statiscal difference.

The flux of summed cations within the Lephalala River is much greater than in the Mokolo and Matlabas Rivers, indicating that the input of cations into the Lephalala River Catchment most likely has the largest contribution of non-atmospheric cation inputs into the system. Cation flux values were highest during spring in the Lephalala and Mokolo Rivers, both located upwind of the Matimba power station. Cation flux in the Matlabas River is highest during winter, the dry season during which cations are able to disperse over longer distances before being deposited. Cations do have various natural and anthropogenic sources and cannot alone explain the influence that coal combustion has on atmospheric and aquatic ion concentrations. Sulphate is predominantly released by the combustion of coal and can provide a better proxy for the impacts of coal burning at coal-fired power stations on water quality.

4.6 Investigating the change in sulphate concentrations measured in each of the rivers from 1999 to 2011

Sulphate concentrations for the Lephalala, Mokolo and Matlabas Rivers were measured from 1999 to 2011. The trends of sulphate concentrations (Figure 4.20) were found to be not significantly different (Non-linear regression, d.f. = 3, p = 0.0677) between rivers across the period of measurement. No significant differences were found between the absolute sulphate concentrations measured in 1999 and 2011 in the Lephalala (ANOVA, d.f. = 6, p = 0.3738), Mokolo (ANOVA, d.f. = 30, p = 0.1702) and Matlabas (ANOVA, d.f. = 6, p = 0.2696) Rivers.

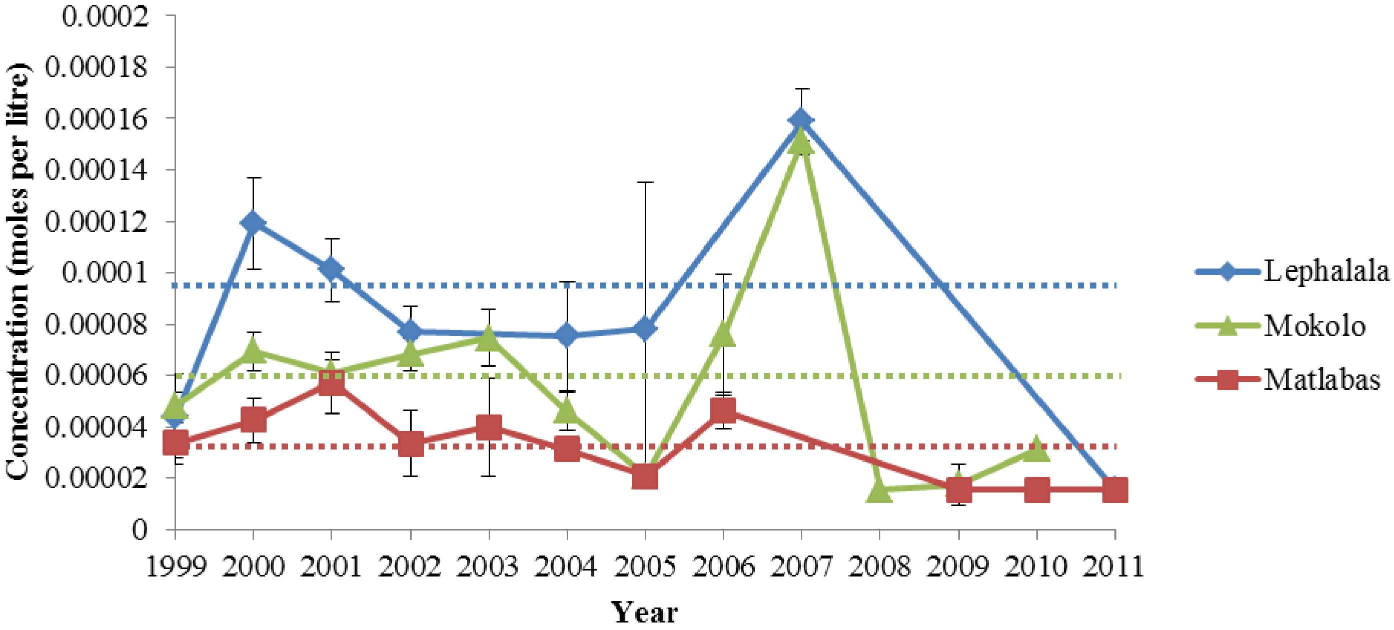


Figure 4.20. Concentrations of sulphate measured in the Lephalala, Mokolo and Matlabas Rivers during each calendar year from 1999 to 2011. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

The increase in sulphate concentration measured in the Lephalala River from 1999 to 2000 was significant (ANOVA, d.f. = 21, p = 0.0301) yet the increase from 2005 to 2007 was not significant (ANOVA, d.f. = 2, p = 0.3021). The sulphate concentrations measured for the Mokolo River significantly changed from 1999 to 2000 (increased; ANOVA, d.f. = 44, p = 0.0370), 2003 to 2005 (decreased; ANOVA, d.f. = 5, p = 0.0089), 2005 to 2007 (increased; ANOVA, d.f. = 3, $p < 2.2 \times 10^{-16}$), 2007 to 2008 (decreased; ANOVA, d.f. = 2, $p < 2.2 \times 10^{-16}$). The process driving the changes in sulphate concentrations significantly alters the concentrations.

The sulphate concentration in the Matlabas River did not significantly increase from 1999 to 2001 (ANOVA, d.f. = 14, p = 0.1395) and from 2005 to 2006 (ANOVA, d.f. = 5, p = 0.0836). Thus, sulphate concentrations in the Matlabas River did not significantly change at any time over the period of 1999 to 2011.

The Lephalala, Mokolo and Matlabas Rivers had mean sulphate concentrations of 0.000084 ± 0.000044 $mol \cdot \ell^{-1}$, 0.000057 ± 0.000037 $mol \cdot \ell^{-1}$ and 0.000032 ± 0.000014 $mol \cdot \ell^{-1}$, respectively (Figure 4.32). Mean sulphate concentrations significantly differed from year to year (Blocked ANOVA, d.f. = 12, $p = 5.475 \times 10^{-6}$) and between rivers (Blocked ANOVA, d.f. = 2, p = 0.003). Mean sulphate concentrations decrease from geographical northeast to southwest, the same direction in which winds predominantly blow.

4.7 Investigating the change in sulphate flux measured in each of the rivers during each hydrological year from 1999 to 2010

Changes in sulphate fluxes in the Lephalala, Mokolo and Matlabas Rivers between 1999 and 2010 were also analysed in three ways: a direct comparison between 1999 and 2010, comparing the response surfaces indicating the changes in flux in each river over the entire period and by comparing the mean sulphate flux values calculated for each river to the other rivers and to the guideline values given in the South African Water Quality Guidelines (SAWQG 1996).

A significant change in the absolute value of the sulphate flux in 1999 and 2010 was found for the Lephalala (increase; ANOVA, d.f. = 2, p = 0.0002) and Mokolo (decrease; ANOVA, d.f. = 2, p = 0.000009) Rivers. No significant difference between the sulphate flux values in 1999 and 2010 was found for the Matlabas River (ANOVA, d.f. = 3, p = 0.6093). Sulphate flux values were ~10 times smaller than the corresponding summed cation values measured, fluctuating from zero to 0.000007, zero to 0.000119, and zero to 0.000005 Eq.ℓ$^{-1}$ in the Lephalala, Matlabas and Mokolo Rivers, respectively (Figure 4.21). Sulphate fluxes in the Lephalala River increased by 185% from 1999 to 2002, after which it remains relatively consistent. Sulphate flux in the Mokolo River increased by 275% from 2001 to 2004, reaching the highest sulphate flux value measured across all three rivers (0.000119 Eq.ℓ$^{-1}$).

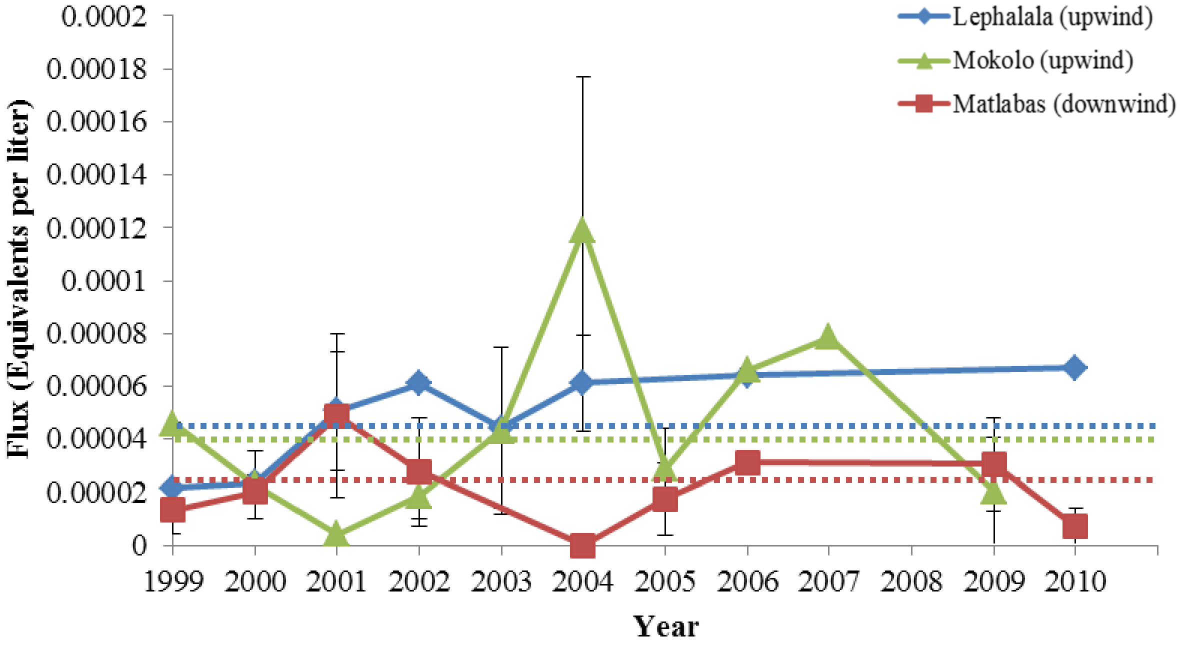


Figure 4.21. Flux of sulphate ions in the Lephalala, Mokolo and Matlabas Rivers during each hydrological year from 1999 to 2010. The average flux of sulphate over the 12 year period is indicated by the dotted line for each river. Standard errors are indicated, with the absence of bars indicating that a single value was recorded during the specific year.

No significant relationship exists between the response surfaces of the sulphate fluxes measured in the rivers from 1999 to 2010 (Non-linear regression, d.f. = 2, p = 0.0830). The Lephalala, Matlabas and Mokolo Rivers had mean sulphate flux values of 0.000045 ± 0.000028, 0.000040 ± 0.000048 and 0.000024 ± 0.000031 Eq.ℓ$^{-1}$, respectively (Figure 4.21). Sulphate concentrations did not significantly differ from year to year in each of the specific rivers (Blocked ANOVA, d.f. = 10, p = 0.1245). No significant differences in mean sulphate concentrations were found between rivers (Blocked ANOVA, d.f. = 2, p = 0.4150), supported by the completely overlapping standard deviation values (Figure 4.22).

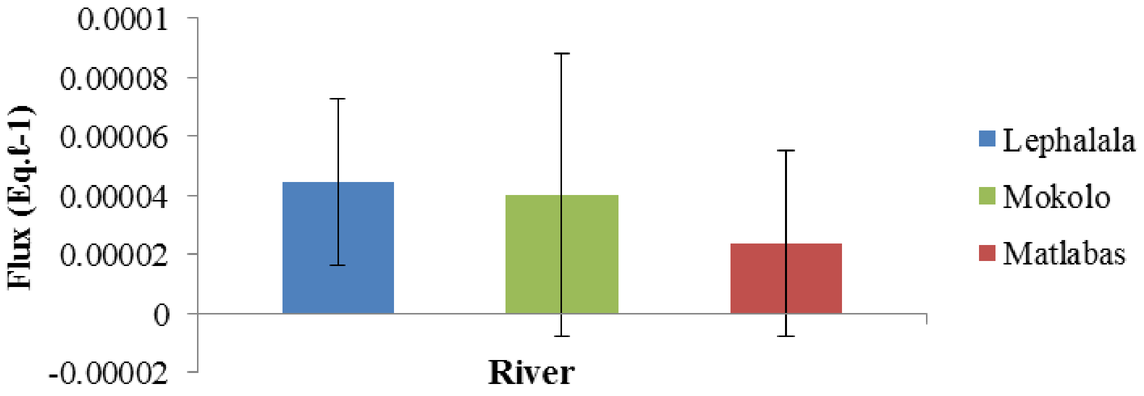


Figure 4.22. Mean sulphate flux values calculated for the Lephalala, Matlabas and Mokolo Rivers from 1999 to 2010.

When the mean sulphate flux values calculated for the Lephalala, Mokolo and Matlabas Rivers were compared to threshold values given in the South African Water Quality Guidelines (SAWQG 1996) it is clear that no human health effects are expected as the threshold for these effects is set at ~4200 Eq.ℓ^{-1}, which is approximately 3.5 x 10^7 times higher than the highest mean sulphate flux value calculated. Surface waters in South Africa usually have flux values of around 105 Eq.ℓ^{-1} with elevated values of up to 2100 Eq.ℓ^{-1} in areas highly impacted by mining activities (SAWQG 1996). Although the catchments of the Lephalala and Mokolo Rivers are highly developed mining areas, the mean sulphate flux values of 0.000045 ± 0.000028 and 0.000040 ± 0.000048 Eq.ℓ^{-1} are well below the expected range.

The mean sulphate flux in the Lephalala River for each season (Figure 4.23) showed no usually high cation flux values during any of the seasons. Sulphate flux values were lower in autumn (0.000004 ± 0.000003 Eq·ℓ^{-1}) and winter (0.000003 ± 0.000002 Eq·ℓ^{-1}) than in spring (0.000006 ± 0.000004 Eq·ℓ^{-1}) and summer (0.000005 ± 0.000003 Eq·ℓ^{-1}). Sulphate flux values did not significantly differ between seasons (ANOVA, d.f. = 14, p = 0.7166), indicating that seasonal changes in rainfall, temperature and river discharge did not significantly change the measured sulphate flux within the Lephalala River.

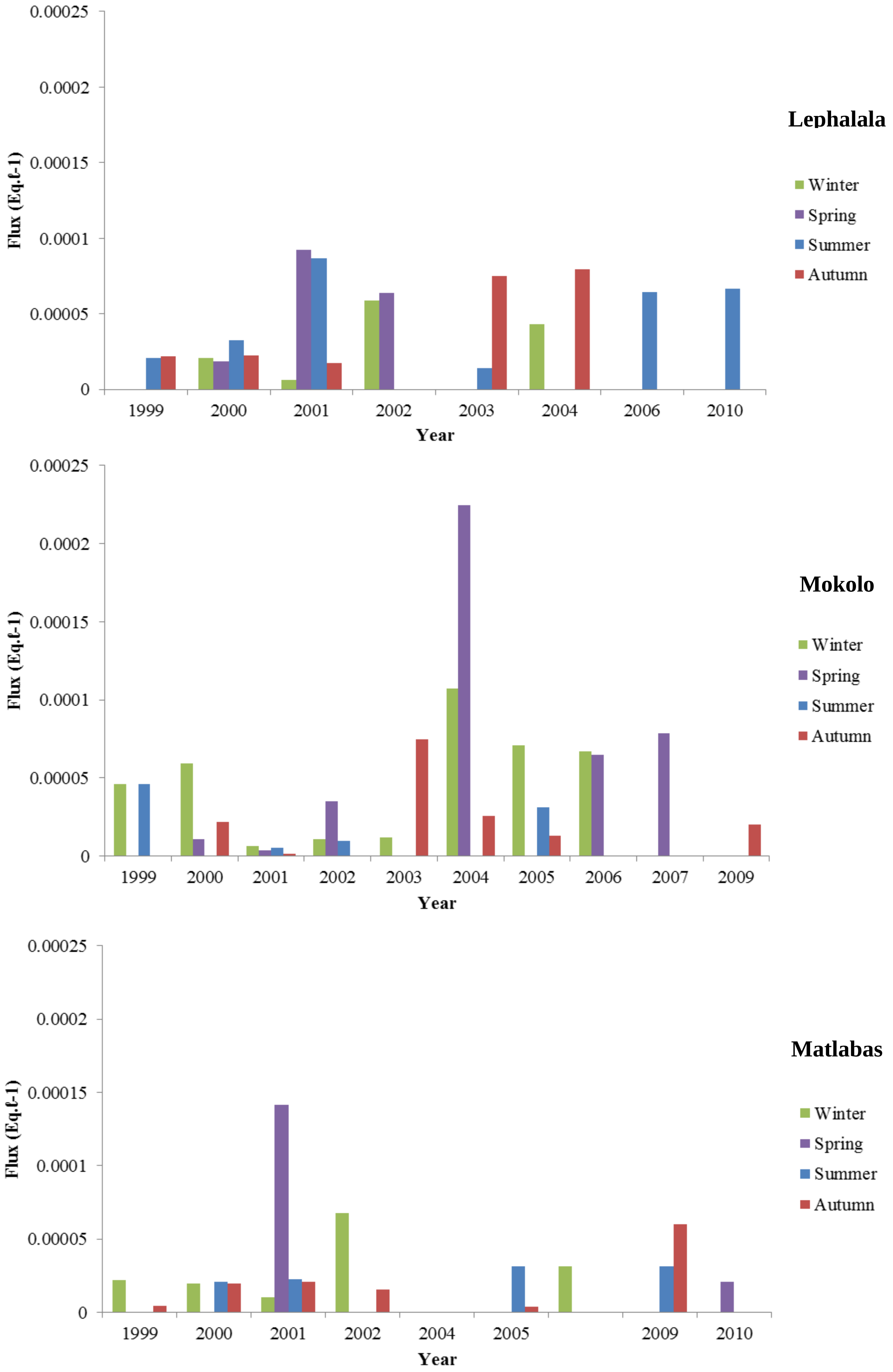


Figure 4.23. Mean flux in sulphate measured in the Lephalala, Mokolo and Matlabas Rivers during summer, autumn, winter and spring from 1999 to 2010.

The mean sulphate flux in the Mokolo River for each season was similar to the sulphate flux values measured for the Lephalala River (Figure 4.23). Elevated flux values were recorded during the spring of 2004 (0.000220 $Eq\cdot\ell^{-1}$). Mean sulphate flux was highest during spring (0.000006 ± 0.000008 $Eq\cdot\ell^{-1}$), followed by winter (0.000005 ± 0.000004 $Eq\cdot\ell^{-1}$) and autumn (0.000003 ± 0.000003 $Eq\cdot\ell^{-1}$) and summer (0.000002 ± 0.000002 $Eq\cdot\ell^{-1}$). Although the values are statistically not significantly different between seasons (ANOVA, d.f. = 22, p = 0.4336), flux values are elevated during the cooler months of spring, winter and autumn.

The mean sulphate flux in the Matlabas River for each season (Figure 4.23) was ~2 times smaller than the flux values recorded for the Lephalala and Mokolo Rivers. Increased sulphate flux values were recorded during the spring of 2001. Sulphate flux within the Matlabas River was highest during spring (0.000005 ± 0.000008 $Eq\cdot\ell^{-1}$), followed by summer (0.000002 ± 0.000001 $Eq\cdot\ell^{-1}$), autumn (0.000002 ± 0.000002 $Eq\cdot\ell^{-1}$) and winter (0.000002 ± 0.000002 $Eq\cdot\ell^{-1}$). The sulphate flux values did not significantly differ between seasons (ANOVA, d.f. = 19, p = 0.3645) and was not specifically elevated during the rainy or dry season indicating that seasonal changes in rainfall, temperature and river discharge did not change the flux of sulphate within the Matlabas River.

The increased cation flux during rainy season (spring and summer) in the Lephalala River and during the cooler seasons in the Mokolo River could indicate the influence that seasonal patterns in rainfall has on the deposition of the atmospheric cations. The most likely explanation for this pattern is that cations are able to disperse over longer distances in the absence of rain, but are deposited close to the source in the event of rainfall. To further explore the possible explanation for differences in cation and sulphate flux with change in seasons, it is important to understand how changes in climatic variables such as rainfall, temperature and river discharge affect the ion fluxes measured in each of the rivers.

4.8 Investigating the impact of climatic variables on measured cation and sulphate flux

Various climatic variables influence the water quality parameters measured by altering the concentration of ions within the water body. Changes in cation and sulphate flux are due to changes in ion concentrations, rainfall, temperature and river discharge. These data were available for each season (summer, autumn, winter and spring) and years from 1999 to 2011 for the Lephalala, Mokolo and Matlabas Rivers. These data are summarised for quick reference purposes (Table 4.4, 4.5 and 4.6).

4.8.1 Investigating the impact of ambient temperature on measured cation and sulphate flux

During the period of 1999 to 2010, the hottest hydrological year recorded for the Lephalale area was 2002 with an average maximum temperature of 31.3˚C while 1999 was the coolest year recorded, with an average maximum temperature of 27.8˚C (Figure 4.24). The temperatures recorded for these two years were found to be significantly different (ANOVA, d.f. = 21, p = 0.0477).

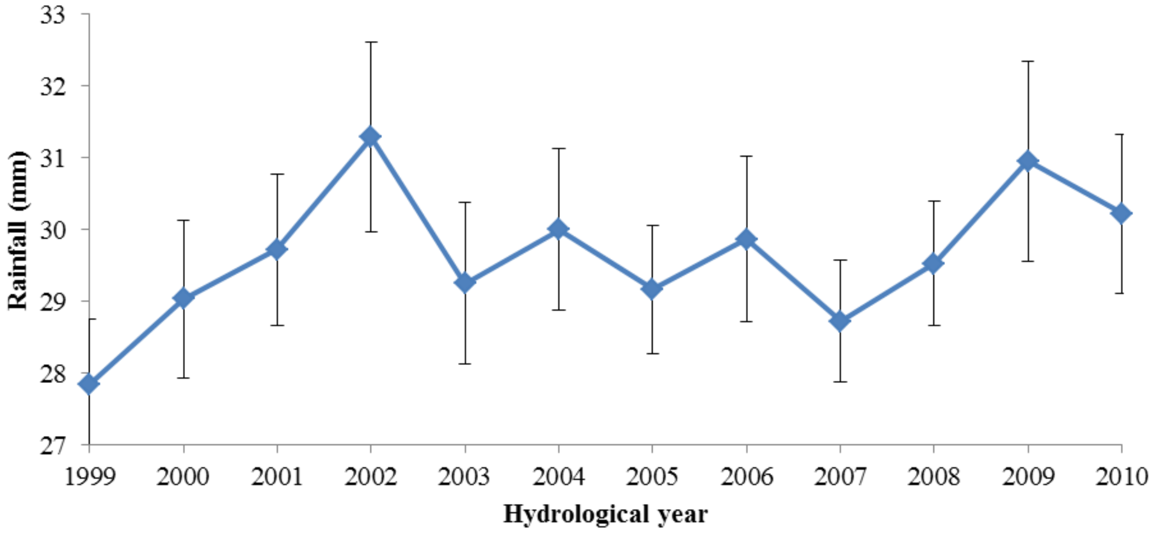


Figure 4.24. Mean daily maximum ambient temperatures recorded for Lephalale town during each hydrological year from 1999 to 2010. Variation is indicated with standard error bars.

Table 4.4. The ambient temperature, total rainfall, daily discharge, mean ion concentrations, ion flux and resultant flux values for the Lephalala River.

Year	**Season**	**Temperature (˚C)**		**Rainfall (mm)**		**Mean daily discharge (cumecs)**		**Summed cation Concentration (mol.ℓ$^{-1}$)**		**Sulphate Concentration (x 10^{-5} mol.ℓ$^{-1}$)**		**Summed cation Flux (Eq.ℓ$^{-1}$)**		**Sulphate ion Flux (x 10^{-5} Eq.ℓ$^{-1}$)**		**Resultant Flux * (Eq.ℓ$^{-1}$)**	
		Season mean	Annual mean	Season total	Annual total	Season mean	Annual mean	Season mean	Annual mean	Season mean	Annual mean	Season	Year	Season	Year	Season	Year
1999	**Winter**	25.15 ± 2.84	27.84 ± 3.01	0.6	543.6	0.0100 ± 0.0000	1.1200 ± 1.2900		0.0011 ± 0.0001		7.59 ± 4.84		0.0009 ± 0.0002		2.14 ± 0.09		0.0005
	Spring	30.07 ± 4.41		113.4		0.0100 ± 0.0200											
	Summer	31.70 ± 3.74		213.0		2.3300 ± 3.3400		0.0011 ± 0.0004		8.07 ± 1.43		0.0008		2.08		0.0004	
	Autumn	25.76 ± 2.88		216.6		2.1300 ± 0.8800		0.0010 ± 0.0005		7.46 ± 5.55		0.0011		2.21		0.0006	
2000	**Winter**	24.08 ± 2.95	29.03 ± 3.82	9.2	270.8	0.1200 ± 0.0800	0.5500 ± 0.9500	0.0019 ± 0.0004	0.0022 ± 0.0007	11.36 ± 7.94	13.55 ± 6.78	0.0019	0.0019 ± 0.0012	2.08	2.36 ± 0.62	0.0010	0.0010
	Spring	30.88 ± 4.12		26.0		0.0400 ± 0.0100		0.0035 ± 0.0008		18.59 ± 6.34		0.0036		1.86		0.0018	
	Summer	32.38 ± 3.80		200.4		1.9800 ± 3.2200		0.0018 ± 0.0015		13.22 ± 5.65		0.0006		3.26		0.0003	
	Autumn	28.11 ± 3.28		35.2		0.0800 ± 0.0800		0.0017 ± 0.0002		8.58 ± 4.34		0.0017		2.25		0.0009	
2001	**Winter**	25.33 ± 3.65	29.72 ± 3.63	21.6	442.6	0.0100 ± 0.0000	0.2300 ± 0.2300	0.0033 ± 0.0003	0.0014 ± 0.0011	13.39 ± 1.84	7.95 ± 2.99	0.0033	0.0014 ± 0.0012	6.42	5.07 ± 4.50	0.0017	0.0007
	Spring	29.37 ± 4.96		170.0		0.5500 ± 0.9500		0.0006 ± 0.0001		7.32 ± 1.02		0.0006		9.23		0.0003	
	Summer	34.61 ± 3.39		92.2		0.1700 ± 0.1100		0.0008 ± 0.0001		6.28 ± 0.99		0.0008		8.65		0.0004	
	Autumn	30.85 ± 3.66		158.8		0.1800 ± 0.1500		0.0010 ± 0.0004		6.95 ± 2.44		0.0011		1.75		0.0006	
2002	**Winter**	25.50 ± 3.51	31.28 ± 4.59	7.0	229.6	0.0500 ± 0.0500	0.0400 ± 0.0200	0.0012 ± 0.0002	0.0024 ± 0.0012	6.82 ± 3.72	8.88 ± 4.79	0.0011	0.0023 ± 0.0017	5.87	6.11 ± 0.35	0.0006	0.0012
	Spring	32.16 ± 4.71		50.4		0.0600 ± 0.0300		0.0035 ± 0.0013		13.02 ± 4.66		0.0035		6.36		0.0018	
	Summer	36.08 ± 3.17		162.6		0.0300 ± 0.0200											
	Autumn	31.61 ± 4.10		9.6		0.0100 ± 0.0100											

2003	**Winter**	24.64 ± 3.39	29.25 ± 3.90	22.8	537.6		0.7500 ± 0.9900		0.0011 ± 0.0004		10.00 ± 9.25		0.0010 ± 0.0005		4.42 ± 4.31		0.0005
	Spring	32.36 ± 4.77		42.8		0.0000 ± 0.0000											
	Summer	31.49 ± 3.66		300.6		0.3800 ± 0.4400		0.0014 ± 0.0000		23.66 ± 0.00		0.0014		1.38		0.0007	
	Autumn	27.25 ± 2.80		171.4		1.8700 ± 1.8400		0.0007 ± 0.0001		5.45 ± 2.03		0.0006		7.47		0.0003	
2004	**Winter**	25.04 ± 3.76	30.00 ± 3.91	0.0	131.4	0.0400 ± 0.0100	0.0500 ± 0.0300	0.0013 ± 0.0003	0.0013 ± 0.0002	5.60 ± 2.31	6.23 ± 3.96	0.0014	0.0013 ± 0.0002	4.31	6.12 ± 2.58	0.0007	0.0007
	Spring	32.23 ± 3.84		23.4		0.0100 ± 0.0200											
	Summer	32.85 ± 3.65		69.6		0.0700 ± 0.0600											
	Autumn	29.59 ± 3.60		38.4		0.0700 ± 0.0400		0.0013 ± 0.0002		7.80 ± 8.09		0.0011		7.95		0.0006	
2005	**Winter**	26.50 ± 3.28	29.17 ± 3.09	0.0	442.8	0.0100 ± 0.0000	0.4900 ± 0.6700										
	Spring	32.88 ± 3.93		73.4		0.0000 ± 0.0000											
	Summer	32.08 ± 3.24		293.8		1.4200 ± 2.1900											
	Autumn	26.43 ± 3.29		75.6		0.5200 ± 0.6600											
2006	**Winter**	24.88 ± 2.69	29.87 ± 3.99	2.0	243.4	0.0300 ± 0.0100	0.1600 ± 0.2700		0.0029 ± 0.0022		15.88 ± 1.79		0.0020 ± 0.0000		6.41 ± 0.00		0.0010
	Spring	31.45 ± 3.64		46.8		0.0300 ± 0.0300											
	Summer	32.18 ± 3.79		110.6		0.5600 ± 0.8200		0.0029 ± 0.0022		15.88 ± 1.79		0.0020 ± 0.0000		6.41		0.0010	
	Autumn	29.26 ± 4.55		84.0		0.0100 ± 0.0100											
2007	**Winter**	24.80 ± 3.49	28.72 ± 2.95	1.6	531.6	0.0000 ± 0.0000	0.6500 ± 0.7100										
	Spring	30.29 ± 4.93		233.8		1.0000 ± 1.7300											
	Summer	31.78 ± 3.56		223.2		1.4800 ± 1.1300											
	Autumn	29.06		73.0		0.1000											

		± 3.40				± 0.0500		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
2008	**Winter**	25.88 ± 3.38	29.53 ± 3.00	1.0	521.8	0.0200 ± 0.0100	0.9300 ± 0.7600	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	Spring	32.28 ± 4.39		181.4		0.9100 ± 1.5800		▨		▨		▨		▨		▨	
	Summer	32.81 ± 2.82		264.2		1.8800 ± 0.8100		▨		▨		▨		▨		▨	
	Autumn	28.26 ± 2.99		75.2		0.8900 ± 1.3100		▨		▨		▨		▨		▨	
2009	**Winter**	24.39 ± 3.48	30.96 ± 4.84	8.6	429.6	0.0500 ± 0.0200	0.1000 ± 0.0500	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	Spring	32.15 ± 4.49		117.2		0.0600 ± 0.0700		▨		▨		▨		▨		▨	
	Summer	35.09 ± 3.29		158.8		0.1600 ± 0.0400		▨		▨		▨		▨		▨	
	Autumn	31.38 ± 4.89		145.0		0.1300 ± 0.0400		▨		▨		▨		▨		▨	
2010	**Winter**	25.14 ± 3.35	30.22 ± 3.83	0.0	331.0	0.0900 ± 0.0200	0.5300 ± 0.8100	▨	0.0007 ± 0.0000	▨	1.56 ± 0.00	▨	0.0007 ± 0.0000	▨	6.68 ± 0.00	▨	0.0004
	Spring	33.47 ± 4.05		88.4		0.0700 ± 0.0200		▨		▨		▨		▨		▨	
	Summer	31.59 ± 3.05		236.6		1.7400 ± 2.3300		0.0007 ± 0.0000		1.56 ± 0.00		0.0007		6.68		0.0004	
	Autumn	30.11 ± 4.09		6.0		0.2200 ± 0.0500		▨		▨		▨		▨		▨	

* Resultant flux = (cation flux + sulphate flux) / 2

▨ No data available

Table 4.5. The ambient temperature, total rainfall, daily discharge, mean ion concentrations, ion flux and resultant flux values for the Mokolo River.

Year	**Season**	**Temperature (˚C)**		**Rainfall (mm)**		**Mean daily discharge (cumecs)**		**Summed cation Concentration (mol·ℓ^{-1})**		**Sulphate Concentration (x 10^{-5} mol·ℓ^{-1})**		**Summed cation Flux (Eq.ℓ^{-1})**		**Sulphate ion Flux (x 10^{-5} Eq.ℓ^{-1})**		**Resultant Flux * (Eq.ℓ^{-1})**	
		Season mean	Annual mean	Season total	Annual total	Season mean	Annual mean	Season mean	Annual mean	Season mean	Annual mean	Season	Year	Season	Year	Season	Year
1999	**Winter**	25.15 ± 2.84	27.84 ± 3.01	0.6	543.6	0.0236 ± 0.0050	0.0259 ± 0.0254	0.0007 ± 0.0001	0.0007 ± 0.0001	3.65 ± 2.56	5.04 ± 3.45	0.0007	0.0008 ± 0.0002	4.60	4.60 ± 0.00	0.0004	0.0004
	Spring	30.07 ± 4.41		113.4		0.0018 ± 0.0031											
	Summer	31.70 ± 3.74		213.0		0.0523 ± 0.0907		0.0009 ± 0.0002		10.02 ± 2.48		0.0010		4.61		0.0005	
	Autumn	25.76 ± 2.88		216.6				0.0007 ± 0.0000		3.85 ± 1.71							
2000	**Winter**	24.08 ± 2.95	29.03 ± 3.82	9.2	270.8	0.0790 ± 0.0726	0.018 ± 0.0430	0.0008 ± 0.0000	0.0008 ± 0.0001	4.90 ± 2.12	7.03 ± 2.28	0.0008	0.0009 ± 0.0001	5.91	2.30 ± 2.57	0.0004	0.0005
	Spring	30.88 ± 4.12		26.0		0.0718 ± 0.0191		0.0009 ± 0.0001		8.54 ± 2.54		0.0009		1.10		0.0005	
	Summer	32.38 ± 3.80		200.4		0.0159 ± 0.0275		0.0009 ± 0.0001		8.05 ± 1.22		0.0010		0.00		0.0005	
	Autumn	28.11 ± 3.28		35.2		0.1204 ± 0.1043		0.0008 ± 0.0000		5.67 ± 0.76		0.0008		2.20		0.0004	
2001	**Winter**	25.33 ± 3.65	29.72 ± 3.63	21.6	442.6	0.0495 ± 0.0123	0.0608 ± 0.0425	0.0007 ± 0.0001	0.0008 ± 0.0001	4.62 ± 3.37	5.60 ± 2.76	0.0007	0.0008 ± 0.0001	0.62	0.42	0.0004	0.0004
	Spring	29.37 ± 4.96		170.0		0.0128 ± 0.011		0.0008 ± 0.0001		6.04 ± 2.96		0.0008		0.36		0.0004	
	Summer	34.61 ± 3.39		92.2		0.1151 ± 0.0356		0.0007 ± 0.0001		5.01 ± 0.70		0.0007		0.53		0.0004	
	Autumn	30.85 ± 3.66		158.8		0.0657 ± 0.0337		0.0007 ± 0.0001		6.97 ± 2.64		0.0007		0.17		0.0004	
2002	**Winter**	25.50 ± 3.51	31.28 ± 4.59	7.0	229.6	0.0621 ± 0.0578	0.0345 ± 0.0251	0.0007 ± 0.0000	0.0008 ± 0.0001	7.32 ± 3.12	7.75 ± 1.97	0.0007	0.0008 ± 0.0000	1.08	1.86 ± 1.44	0.0004	0.0004
	Spring	32.16 ± 4.71		50.4		0.0375 ± 0.0132		0.0008 ± 0.0001		7.91 ± 1.42		0.0008		3.52		0.0004	
	Summer	36.08 ± 3.17		162.6		0.0375 ± 0.0519		0.0008 ± 0.0000		8.15 ± 1.69		0.0008		0.98		0.0004	
	Autumn	31.61 ± 4.10		9.6		0.0011 ± 0.0018											

2003	**Winter**	24.64 ± 3.39	29.25 ± 3.90	22.8	537.6	0.0143 ± 0.0118	0.0249 ± 0.0250	0.0007 ± 0.0002	0.0007 ± 0.0001	6.76 ± 3.09	6.99 ± 1.63	0.0007	0.0007 ± 0.0000	1.18	4.32 ± 4.44	0.0004	0.0004
	Spring	32.36 ± 4.77		42.8													
	Summer	31.49 ± 3.66		300.6		0.0068 ± 0.0118											
	Autumn	27.25 ± 2.80		171.4		0.0534 ± 0.0925		0.0007 ± 0.0001		7.15 ± 0.67		0.0007		7.46		00004	
2004	**Winter**	25.04 ± 3.76	30.00 ± 3.91	0.0	131.4	0.0613 ± 0.0203	0.0340 ± 0.0228	0.0007 ± 0.0001	0.0007 ± 0.0001	3.12 ± 0.00	2.95 ± 0.42	0.0007	0.0008 ± 0.0001	10.70	11.90 ± 9.98	0.0004	0.0004
	Spring	32.23 ± 3.84		23.4		0.0056 ± 0.0088		0.0008 ± 0.0000		3.12 ± 0.00		0.0008		22.40		0.0004	
	Summer	32.85 ± 3.65		69.6		0.0351 ± 0.0274											
	Autumn	29.59 ± 3.60		38.4		0.0341 ± 0.0115		0.0007 ± 0.0000		2.08 ± 0.00		0.0007		2.59		0.0004	
2005	**Winter**	26.50 ± 3.28	29.17 ± 3.09	0.0	442.8	0.0063 ± 0.0020	0.0401 ± 0.0502	0.0014 ± 0.0000	0.0009 ± 0.0003	2.08 ± 0.00	7.74 ± 7.18	0.0014	0.0010 ± 0.0003	7.07	2.88 ± 3.08	0.0007	0.0005
	Spring	32.88 ± 3.93		73.4		0.0017 ± 0.0025		0.0010 ± 0.0000		2.08 ± 0.00		0.0010		0.00		0.0005	
	Summer	32.08 ± 3.24		293.8		0.0421 ± 0.0499		0.0010 ± 0.0000		14.16 ± 6.50		0.0008		3.14		0.0004	
	Autumn	26.43 ± 3.29		75.6		0.1104 ± 0.1244		0.0007 ± 0.0000		3.77 ± 2.39		0.0007		1.30		0.0004	
2006	**Winter**	24.88 ± 2.69	29.87 ± 3.99	2.0	243.4	0.0516 ± 0.0068	0.0421 ± 0.0428	0.0008 ± 0.0002	0.0009 ± 0.0002	2.08 ± 0.00	3.64 ± 2.70	0.0008	0.0009 ± 0.0002	6.71	6.61 ± 0.14	0.0004	0.0005
	Spring	31.45 ± 3.64		46.8		0.0174 ± 0.0120		0.0011 ± 0.0000		6.76 ± 0.00		0.0011		6.50		0.0006	
	Summer	32.18 ± 3.79		110.6		0.0981 ± 0.1627											
	Autumn	29.26 ± 4.55		84.0		0.0014 ± 0.0024											
2007	**Winter**	24.80 ± 3.49	28.72 ± 2.95	1.6	531.6				0.0016 ± 0.0000		15.16 ± 0.00		0.0016 ± 0.0000		7.85 ± 0.00		0.0008
	Spring	30.29 ± 4.93		233.8		0.0008 ± 0.0013		0.00016 ± 0.0000		15.16 ± 0.00		0.0016		7.85		0.0008	
	Summer	31.78 ± 3.56		223.2		0.0863 ± 0.1495											
	Autumn	29.06		73.0		0.0664											

		± 3.40				± 0.0540		▨		▨		▨		▨		▨	
2008	**Winter**	25.88 ± 3.38	29.53 ± 3.00	1.0	521.8	0.0238 ± 0.0075	0.0238 ± 0.0075	0.0006 ± 0.0000	0.0006 ± 0.0001	1.56 ± 0.00	1.69 ± 1.37	▨	▨	▨	▨	▨	▨
	Spring	32.28 ± 4.39		181.4		▨		▨		▨		▨		▨		▨	
	Summer	32.81 ± 2.82		264.2		▨		0.0006 ± 0.0000		3.12 ± 0.00		▨		▨		▨	
	Autumn	28.26 ± 2.99		75.2		▨		0.0007 ± 0.0000		3.90 ± 0.00		▨		▨		▨	
2009	**Winter**	24.39 ± 3.48	30.96 ± 4.84	8.6	429.6	▨	0.0239 ± 0.0299	0.0008 ± 0.0000	0.0008 ± 0.0001	3.12 ± 0.00	2.58 ± 1.22	▨	0.0008 ± 0.0000	▨	2.03 ± 0.00	▨	0.0004
	Spring	32.15 ± 4.49		117.2		▨		0.0009 ± 0.0000		0.39 ± 0.00		▨		▨		▨	
	Summer	35.09 ± 3.29		158.8		0.0027 ± 0.0047		0.0007 ± 0.0000		3.12 ± 0.00		▨		▨		▨	
	Autumn	31.38 ± 4.89		145.0		0.0451 ± 0.0781		0.0007 ± 0.0002		3.12 ± 0.00		0.0008		2.03		0.0004	
2010	**Winter**	25.14 ± 3.35	30.22 ± 3.83	0.0	331.0	0.1591 ± 0.1390	0.1147 ± 0.0925	0.0006 ± 0.0001	0.0006 ± 0.0001	3.12 ± 0.00	3.12 ± 0.00	▨	▨	▨	▨	▨	▨
	Spring	33.47 ± 4.05		88.4		0.0084 ± 0.0101		▨		▨		▨		▨		▨	
	Summer	31.59 ± 3.05		236.6		▨		▨		▨		▨		▨		▨	
	Autumn	30.11 ± 4.09		6.0		0.1766 ± 0.1539		▨		▨		▨		▨		▨	

* Resultant flux = (cation flux + sulphate flux) / 2

▨ No data available

Table 4.6. The ambient temperature, total rainfall, daily discharge, mean ion concentrations, ion flux and resultant flux values for the Matlabas River.

Year	Season	Temperature (˚C)		Rainfall (mm)		Mean daily discharge (cumecs)		Summed cation Concentration (mol·ℓ$^{-1}$)		Sulphate Concentration (x 10^{-5} mol·ℓ$^{-1}$)		Summed cation Flux (Eq.ℓ$^{-1}$)		Sulphate ion Flux (x 10^{-5} Eq.ℓ$^{-1}$)		Resultant Flux * (Eq.ℓ$^{-1}$)	
		Season mean	Annual mean	Season total	Annual total	Season mean	Annual mean	Season mean	Annual mean	Season mean	Annual mean	Season mean	Annual mean	Season mean	Annual mean	Season mean	Annual mean
1999	**Winter**	25.15 ± 2.84	27.84 ± 3.01	0.6	543.6	0.0003 ± 0.0004	0.3987 ± 0.6478	0.0007 ± 0.0000	0.0005 ± 0.0001	2.08 ± 0.00	3.47 ± 1.70	0.0007	0.0006 ± 0.0002	2.20	1.30 ± 1.22	0.0004	0.0003
	Spring	30.07 ± 4.41		113.4		0.0000 ± 0.0000		▨		▨		▨		▨		▨	
	Summer	31.70 ± 3.74		213.0		1.1735 ± 0.9677		▨		▨		▨		▨		▨	
	Autumn	25.76 ± 2.88		216.6		0.3232 ± 0.2052		0.0004 ± 0.0001		3.94 ± 1.74		0.0004		0.46		0.0002	
2000	**Winter**	24.08 ± 2.95	29.03 ± 3.82	9.2	270.8	0.0246 ± 0.0154	0.0228 ± 0.0252	0.0009 ± 0.0003	0.0007 ± 0.0001	4.59 ± 2.74	4.35 ± 2.36	0.0008	0.0006 ± 0.0002	2.00	2.00 ± 0.06	0.0004	0.0003
	Spring	30.88 ± 4.12		26.0		0.0041 ± 0.0014		▨		▨		▨		▨		▨	
	Summer	32.38 ± 3.80		200.4		0.0696 ± 0.0970		0.0006 ± 0.0003		2.08 ± 0.00		0.0004		2.10		0.0002	
	Autumn	28.11 ± 3.28		35.2		0.0329 ± 0.0407		0.0006 ± 0.0001		4.87 ± 2.47		0.0005		2.00		0.0003	
2001	**Winter**	25.33 ± 3.65	29.72 ± 3.63	21.6	442.6	0.0016 ± 0.0011	0.0329 ± 0.0623	0.0030 ± 0.0022	0.0018 ± 0.0020	6.85 ± 4.85	5.76 ± 3.91	0.0023	0.0010 ± 0.0009	1.10	4.90 ± 6.20	0.0012	0.0005
	Spring	29.37 ± 4.96		170.0		0.1082 ± 0.0955		0.0007 ± 0.0000		7.33 ± 0.00		0.0007		14.00		0.0004	
	Summer	34.61 ± 3.39		92.2		0.0181 ± 0.0232		0.0004 ± 0.0000		4.61 ± 7.14		0.0004		2.30		0.0002	
	Autumn	30.85 ± 3.66		158.8		0.0033 ± 0.0026		0.0005 ± 0.0000		2.08 ± 0.00		0.0005		2.10		0.0003	
2002	**Winter**	25.50 ± 3.51	31.28 ± 4.59	7.0	229.6	0.0006 ± 0.0007	0.0049 ± 0.0133	0.0025 ± 0.0000	0.0013 ± 0.0020	2.08 ± 0.00	3.36 ± 2.21	0.0025	0.0013 ± 0.0011	6.80	2.77 ± 3.54	0.0013	0.0007
	Spring	32.16 ± 4.71		50.4		0.0000 ± 0.0000		▨		▨		▨		▨		▨	
	Summer	36.08 ± 3.17		162.6		0.0184 ± 0.0245		0.0006 ± 0.0000		5.91 ± 0.00		0.0006		0.00		0.0003	
	Autumn	31.61 ± 4.10		9.6		0.0006 ± 0.0001		0.0007 ± 0.0000		2.08 ± 0.00		0.0007		1.60		0.0004	

2003	**Winter**	24.64 ± 3.39	29.25 ± 3.90	22.8	537.6	0.0000 ± 0.0000	0.0656 ± 0.1319										
	Spring	32.36 ± 4.77		42.8		0.0000 ± 0.0000											
	Summer	31.49 ± 3.66		300.6		0.1067 ± 0.0225											
	Autumn	27.25 ± 2.80		171.4		0.1866 ± 0.2367											
2004	**Winter**	25.04 ± 3.76	30.00 ± 3.91	0.0	131.4	0.0134 ± 0.0042	0.0340 ± 0.0440	0.0005 ± 0.0000	0.0005 ± 0.0001	3.12 ± 0.00	2.60 ± 0.74	0.0005	0.0005 ± 0.0001	0.00	0/00	0.0003	0.0003
	Spring	32.23 ± 3.84		23.4		0.0042 ± 0.0005											
	Summer	32.85 ± 3.65		69.6		0.0744 ± 0.0652											
	Autumn	29.59 ± 3.60		38.4		0.0130 ± 0.0091		0.0004 ± 0.0000		2.08 ± 0.00		0.0004		0.00		0.0002	
2005	**Winter**	26.50 ± 3.28	29.17 ± 3.09	0.0	442.8	0.0018 ± 0.0002	0.2385 ± 0.5205		0.0004 ± 0.0001		4.06 ± 1.85		0.0003 ± 0.0000		1.76 ± 1.93		0.0002
	Spring	32.88 ± 3.93		73.4		0.0008 ± 0.0007											
	Summer	32.08 ± 3.24		293.8		0.4030 ± 0.6171		0.0003 ± 0.0000		5.75 ± 0.00		0.0003		3.12		0.0002	
	Autumn	26.43 ± 3.29		75.6		0.6270 ± 0.8839		0.0004 ± 0.0000		3.21 ± 1.60		0.0004		0.39		0.0002	
2006	**Winter**	24.88 ± 2.69	29.87 ± 3.99	2.0	243.4	0.0053 ± 0.0028	0.0026 ± 0.0019	0.0010 ± 0.0004	0.0010 ± 0.0004	5.48 ± 8.20	5.48 ± 8.20	0.0010	0.0010 ± 0.0000	3.12	3.12 ± 0.00	0.0005	0.0005
	Spring	31.45 ± 3.64		46.8		0.0028 ± 0.0003											
	Summer	32.18 ± 3.79		110.6		0.3614 ± 0.6191											
	Autumn	29.26 ± 4.55		84.0		0.0000 ± 0.0000											
2007	**Winter**	24.80 ± 3.49	28.72 ± 2.95	1.6	531.6	0.0000 ± 0.0000	0.2787 ± 0.5277										
	Spring	30.29 ± 4.93		233.8		0.0012 ± 0.0021											
	Summer	31.78 ± 3.56		223.2		0.7340 ± 0.7878											
	Autumn	29.06		73.0		0.0981											

		± 3.40				± 0.0451		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
2008	**Winter**	25.88 ± 3.38	29.53 ± 3.00	1.0	521.8	0.0110 ± 0.0111	0.3484 ± 0.6534	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
	Spring	32.28 ± 4.39		181.4		0.0073 ± 0.0086		▨		▨		▨		▨		▨	
	Summer	32.81 ± 2.82		264.2		1.1707 ± 0.9724		▨		▨		▨		▨		▨	
	Autumn	28.26 ± 2.99		75.2		0.1450 ± 0.1314		▨		▨		▨		▨		▨	
2009	**Winter**	24.39 ± 3.48	30.96 ± 4.84	8.6	429.6	0.0233 ± 0.0178	0.2388 ± 0.4984	▨	0.0005 ± 0.0003	▨	1.56 ± 0.00	▨	0.0005 ± 0.0003	▨	3.05 ± 3.02	▨	0.0003
	Spring	32.15 ± 4.49		117.2		0.0128 ± 0.0075		0.0008 ± 0.0000		1.56 ± 0.00		0.0008		0.00		0.0004	
	Summer	35.09 ± 3.29		158.8		0.0843 ± 0.0635		0.0005 ± 0.0003		1.56 ± 0.00		0.0005		3.12		0.0003	
	Autumn	31.38 ± 4.89		145.0		0.8209 ± 0.8246		0.0003 ± 0.0000		1.56 ± 0.00		0.0003		6.04		0.0002	
2010	**Winter**	25.14 ± 3.35	30.22 ± 3.83	0.0	331.0	0.0414 ± 0.0330	0.1108 ± 0.1971	0.0003 ± 0.0000	0.0006 ± 0.0005	1.56 ± 0.00	1.56 ± 0.00	0.0003	0.0006 ± 0.0006	0.00	0.70 ± 1.20	0.0002	0.0003
	Spring	33.47 ± 4.05		88.4		0.0113 ± 0.0045		0.0013 ± 0.0000		1.56 ± 0.00		0.0013		2.08		0.0007	
	Summer	31.59 ± 3.05		236.6		0.3836 ± 0.2758		0.0004 ± 0.0001		1.56 ± 0.00		0.0004		0.00		0.0002	
	Autumn	30.11 ± 4.09		6.0		0.0735 ± 0.0273		▨		▨		▨		▨		▨	

* Resultant flux = (cation flux + sulphate flux) / 2

▨ No data available

The mean daily maximum temperatures calculated for each month from January 1999 to December 2011 indicated that temperatures are highest at the start and end of each year, with colder temperatures recorded during the months of May to August (Figure 4.25). Statistically, the mean temperature for December across all years is significantly higher than the mean temperature recorded for June across all years (ANOVA, d.f. = 755, p = 2.2 x 10^{-16}) indicating a significant change in temperature from winter to summer. Cation and sulphate flux values are expected to be higher during summer months due to increased rainfall increasing the concentration of ions deposited from the atmosphere.

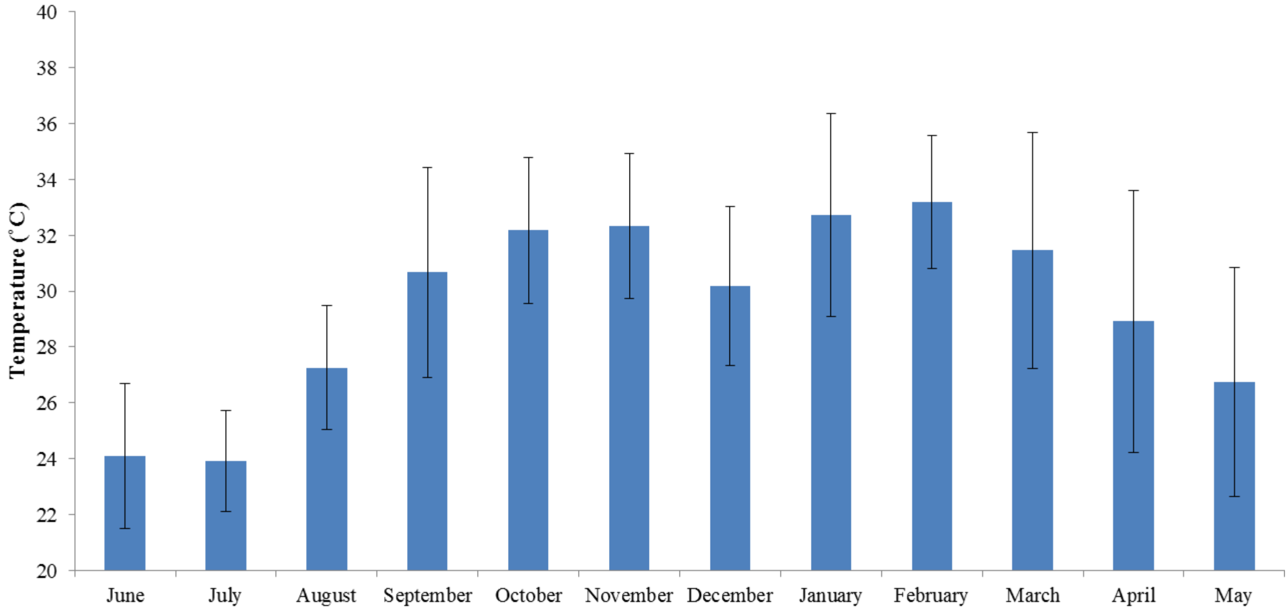


Figure 4.25. Mean maximum temperatures measured for Lephalale for each hydrological year from 1999 to 2010. Variation is indicated with standard error bars.

Analyses of the changes in parameters across the entire period of 1999 to 2010, indicated that no statistical relationship exists between temperature and the change in summed cation flux in the Lephalala (Non-linear regression, d.f. = 5, p = 0.2914), Mokolo (Non-linear regression, d.f. = 7, p = 0.3803) or Matlabas (Non-linear regression, d.f. = 6, p = 0.9516) Rivers at an annual resolution. Graphical representation of the changes in temperature and cation flux over time (Figure 4.26) confirms that there is no relationship, as temperature remains relatively constant (between 28 and 31˚C) while large changes in cation fluxes were measured.

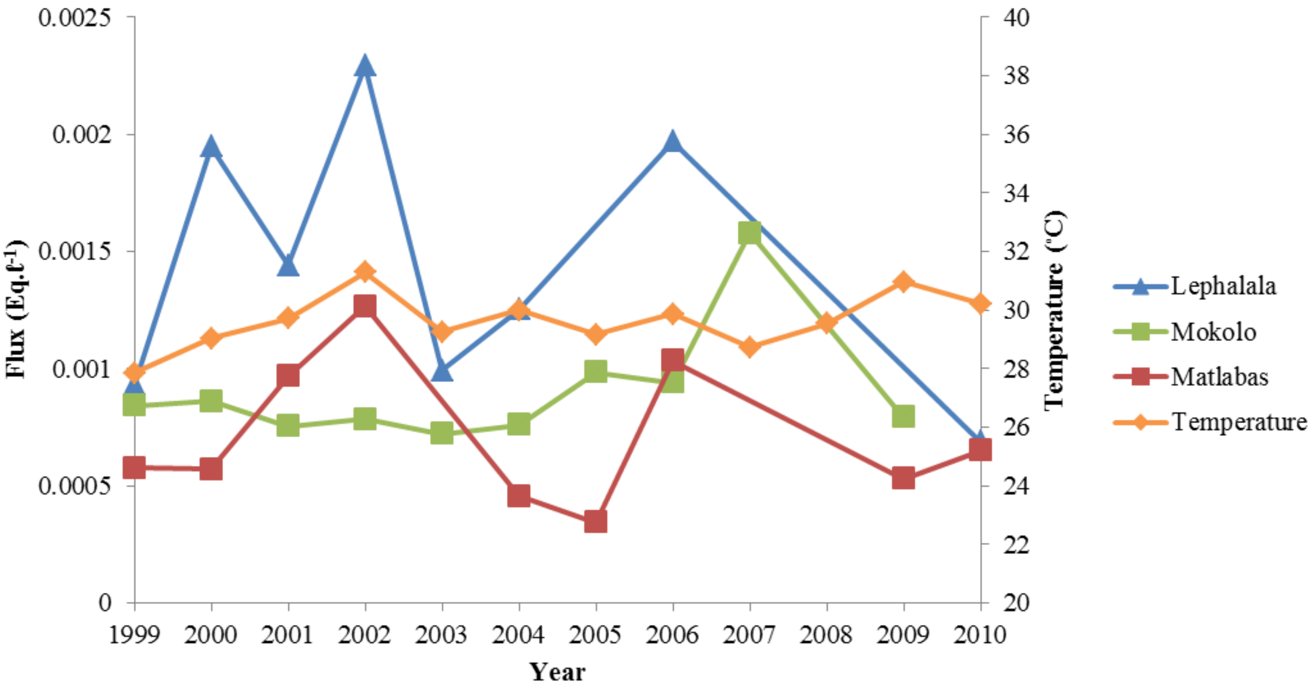


Figure 4.26. The graphical representation of the relationship between mean daily maximum temperature and the flux of summed cations as calculated for every year from 1999 to 2010.

Investigation also revealed no significant relationship between temperature and sulphate concentrations in the Mokolo (Non-linear regression, d.f. = 7, p = 0.5807) and Matlabas (Non-linear regression, d.f. = 5, p = 0.2795). A significant relationship was found in the Lephalala River (Non-linear regression, d.f. = 5, p = 0.0195), A graphical representation of the changes in temperature and sulphate flux over time does not indicate the presence of a significant relationship (Figure 4.27). The relatively lower p-value calculated for the Matlabas River compared to the Mokolo Rivers indicates that the relationship between temperature and sulphate flux is, however, stronger. The higher p-value calculated for the cation and temperature relationship indicates that the relationship is weaker than the relationship between temperature and sulphate flux in the Lephalala and Matlabas Rivers. The opposite is true in the Mokolo Rivers which could indicate that the leaching of cations from the catchment is increased with increased rainfall occurring during the summer months. It could also be due to the relatively smaller sulphate flux values calculated for the rivers, often masking the relationship between the two parameters.

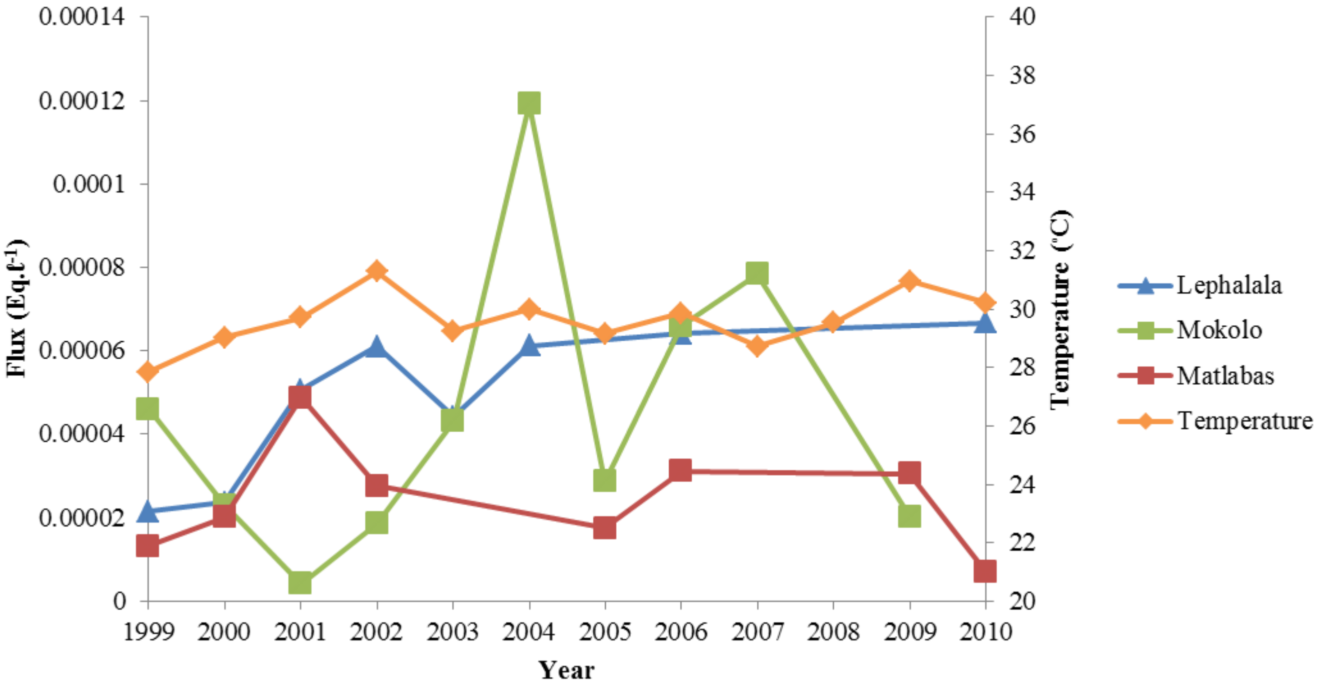


Figure 4.27. The graphical representation of the relationship between mean daily maximum temperature and the flux of sulphate ions as calculated for every year from 1999 to 2010.

The statistical significance between ambient temperature and summed cation and sulphate flux at a monthly resolution was determined for the Lephalala, Mokolo and Matlabas Rivers and indicated that no significant relationship exists between these two parameters for most of the time (Table 4.7). A significant relationship between ambient temperature and summed cation flux was found for the Matlabas River in 2000, yet this period does not correspond with any large changes in fluxes or ambient temperatures measured. A significant relationship between ambient temperature and sulphate flux was found in the Mokolo River during 2000, yet again occurring in a year during which no maximum or minimum values for the 1999 to 2010 period were measured.

Table 4.7. The significance of the relationship between ambient temperature and summed cation and sulphate flux (using non-linear regression) in the Lephalala, Mokolo and Matlabas Rivers for each hydrological year from 1999 to 2010.

Year	Lephalala River				Mokolo River				Matlabas River			
	Cation Flux		Sulphate Flux		Cation Flux		Sulphate Flux		Cation Flux		Sulphate Flux	
	Sig	p	Sig	p	Sig	p	Sig	p	Sig	p	Sig	p
1999	*	*	*	*	*	*	*	*	*	*	*	*
2000	NSR	0.68	NSR	0.53	NSR	0.22	SR	0.03	SR	0.01	NSR	0.47
2001	NSR	0.21	NSR	0.26	NSR	0.86	NSR	0.74	NSR	0.06	NSR	0.78
2002	*	*	*	*	NSR	0.70	NSR	0.92	NSR	0.26	*	*
2003	*	*	*	*	*	*	*	*	*	*	*	*
2004	*	*	*	*	NSR	0.25	NSR	0.90	*	*	*	*
2005	*	*	*	*	NSR	0.81	NSR	0.98	*	*	*	*
2006	*	*	*	*	*	*	*	*	*	*	*	*
2007	*	*	*	*	*	*	*	*	*	*	*	*
2008	*	*	*	*	*	*	*	*	*	*	*	*
2009	*	*	*	*	*	*	*	*	*	*	*	*
2010	*	*	*	*	*	*	*	*	*	*	*	*

Sig = significant relationship
p = p-value calculated using non-linear regression analysis
SR = significant relationship
NSR = no significant relationship
* = no or too few data points available

Increased ambient temperatures are expected to increase the flux of ions within the rivers due to increased evaporation, decreased river volume and discharge, and thus increased ion concentrations. This effect was not seen within the Lephalala, Mokolo and Matlabas Rivers most probably due to the warmer months being the rainfall season within the area. The effects that temperature would have on changes in ion fluxes is likely masked by the increased rainfall, cooling the air and water temperatures and replenishing river volume lost due to evaporation.

4.8.2 Investigating the impact of rainfall on measured cation and sulphate flux

Heavy rainfall events after dry periods often coincide with initially increased cation and sulphate concentrations measured in rivers within the same month due to the accumulation of ions on the land surface when no precipitation occurs. This often corresponds with periods of increased fluxes too as increased concentrations increase flux values. The correspondence between rainfall events and increased cation and sulphate fluxes in the Lephalala, Mokolo and Matlabas Rivers is investigated at an annual and then a monthly resolution.

Graphical analysis of the changes in rainfall and the flux of summed cations over the entire period of 1999 to 2010 showed that there was no relationship between rainfall and cation flux in any of the rivers (Figure 4.28). Statistical analysis showed that the relationship between rainfall and cation flux is not significant in the Lephalala (Non-linear regression, d.f. = 6, p = 0.2063), Mokolo River (Non-linear regression, d.f. = 8, p = 0.4519) and Matlabas (Non-linear regression, d.f. = 7, p = 0.6861) Rivers. The cation flux values were highest when the rainfall was lowest, indicating that the cation flux is more directly influenced by the ion concentration deposited than discharge.

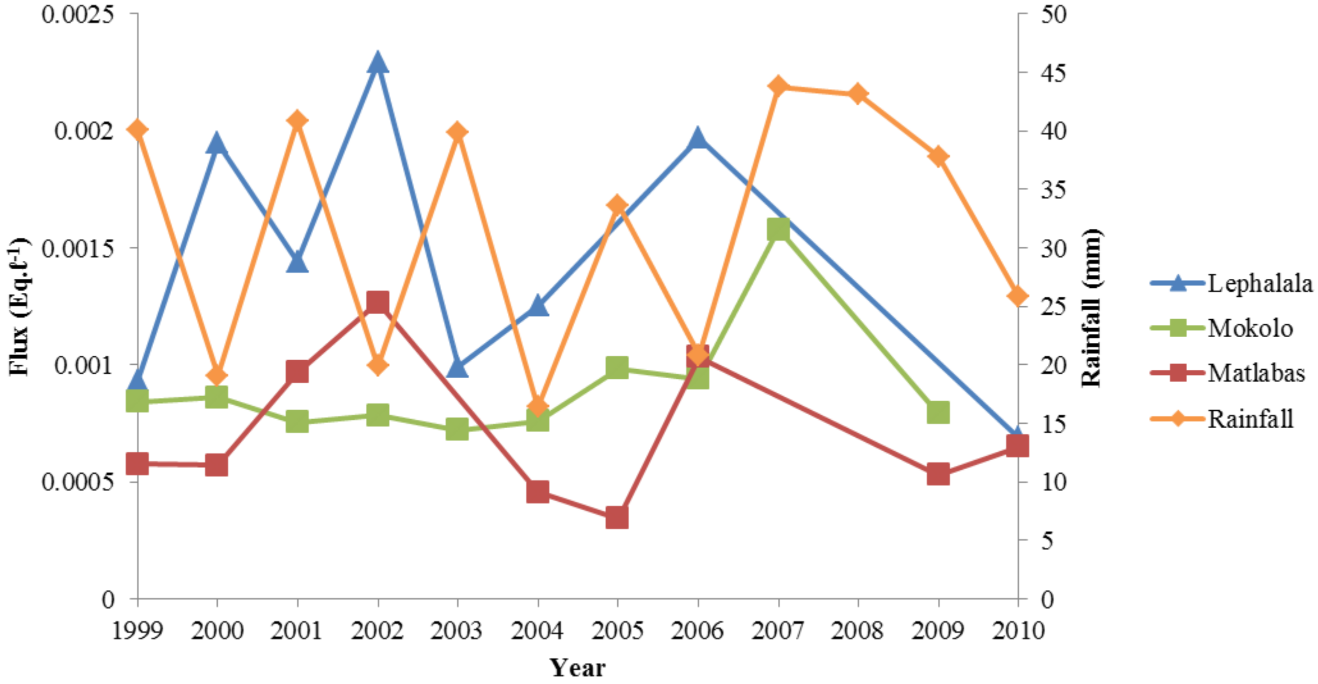


Figure 4.28. The graphical representation of the relationship between mean monthly rainfall per year and the flux of cations as calculated for every year from 1999 to 2010.

Graphical analysis of the relationship between rainfall and sulphate concentration indicated there is no relationship between these two parameters (Figure 4.29). Additional statistical investigation revealed that there is no significant relationship between rainfall and flux of sulphate in the Lephalala (Non-linear regression, d.f. = 6, p = 0.4456), Mokolo (Non-linear regression, d.f. = 8, p = 0.4433) or Matlabas (Non-linear regression, d.f. = 6, p = 0.8298) Rivers. The relationship between rainfall and change in sulphate flux is however strongest for the Mokolo River which is located just upwind of the power station, being the river located closest to the Matimba power station. This could possibly indicate that the amount of sulphate deposition in close proximity of the power station is determined by the occurrence of rainfall events.

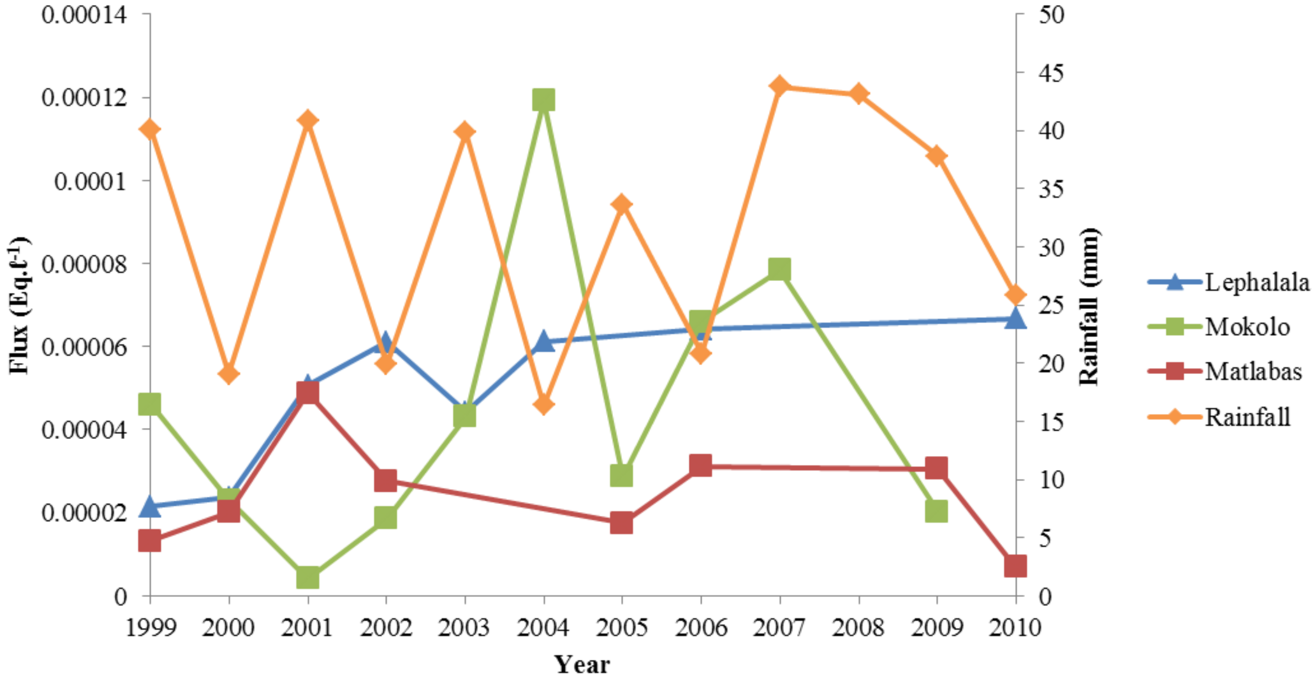


Figure 4.29. The graphical representation of the relationship between mean annual rainfall using total monthly rainfall and the flux of sulphate as calculated for every year from 1999 to 2010.

At a monthly resolution, the statistical analysis of the relationship between ion flux and rainfall indicated that changes in total monthly rainfall did not significantly alter the flux of cations and sulphate in any of the hydrological years from 1999 to 2010 (Table 4.8). It is also clear that rainfall has a greater effect on ion flux when compared to temperature, as very few years showed a significant relationship between ion flux and ambient temperature.

Table 4.8. The significance of the relationship between rainfall and summed cation and sulphate flux (using non-linear regression) in the Lephalala, Mokolo and Matlabas Rivers for each hydrological year from 1999 to 2010.

Year	**Lephalala River**				**Mokolo River**				**Matlabas River**			
	Cation Flux		**Sulphate Flux**		**Cation Flux**		**Sulphate Flux**		**Cation Flux**		**Sulphate Flux**	
	Sig	p	Sig	p	Sig	p	Sig	p	Sig	p	Sig	p
1999	*	*	*	*	*	*	*	*	*	*	*	*
2000	NSR	0.12	NSR	0.23	NSR	0.41	NSR	0.41	NSR	0.40	NSR	0.40
2001	NSR	0.29	NSR	0.10	NSR	0.28	NSR	0.28	NSR	0.29	NSR	0.29
2002	*	*	*	*	NSR	0.95	NSR	0.95	*	*	*	*
2003	*	*	*	*	*	*	*	*	*	*	*	*
2004	*	*	*	*	NSR	0.84	NSR	0.84	*	*	*	*
2005	*	*	*	*	NSR	0.45	NSR	0.45	*	*	*	*
2006	*	*	*	*	*	*	*	*	*	*	*	*
2007	*	*	*	*	*	*	*	*	*	*	*	*
2008	*	*	*	*	*	*	*	*	*	*	*	*
2009	*	*	*	*	*	*	*	*	*	*	*	*
2010	*	*	*	*	*	*	*	*	*	*	*	*

Sig = significant relationship ($p<0.05$)
p = p-value calculated using non-linear regression analysis
SR = significant relationship
NSR = no significant relationship
* = no or too few data points available

Temperature and rainfall are not the only factors that affect the flux of ions within rivers. The changes seen are often delayed as a result of the accumulated effects of different climatic variables and the variation in river discharge.

4.8.3 Investigating the impact of discharge on measured cation and sulphate flux

The mean daily discharge of the Lephalala, Mokolo and Matlabas Rivers for each season (Figure 4.30) indicates that the discharge of the Mokolo River has no specific seasonality, most probably due to the large size of the river. The river is not seasonal and is recharged by the water received from groundwater. The Lephalala and Matlabas Rivers have higher daily discharge during summer and autumn, following rainfall events predominantly occurring during spring and summer.

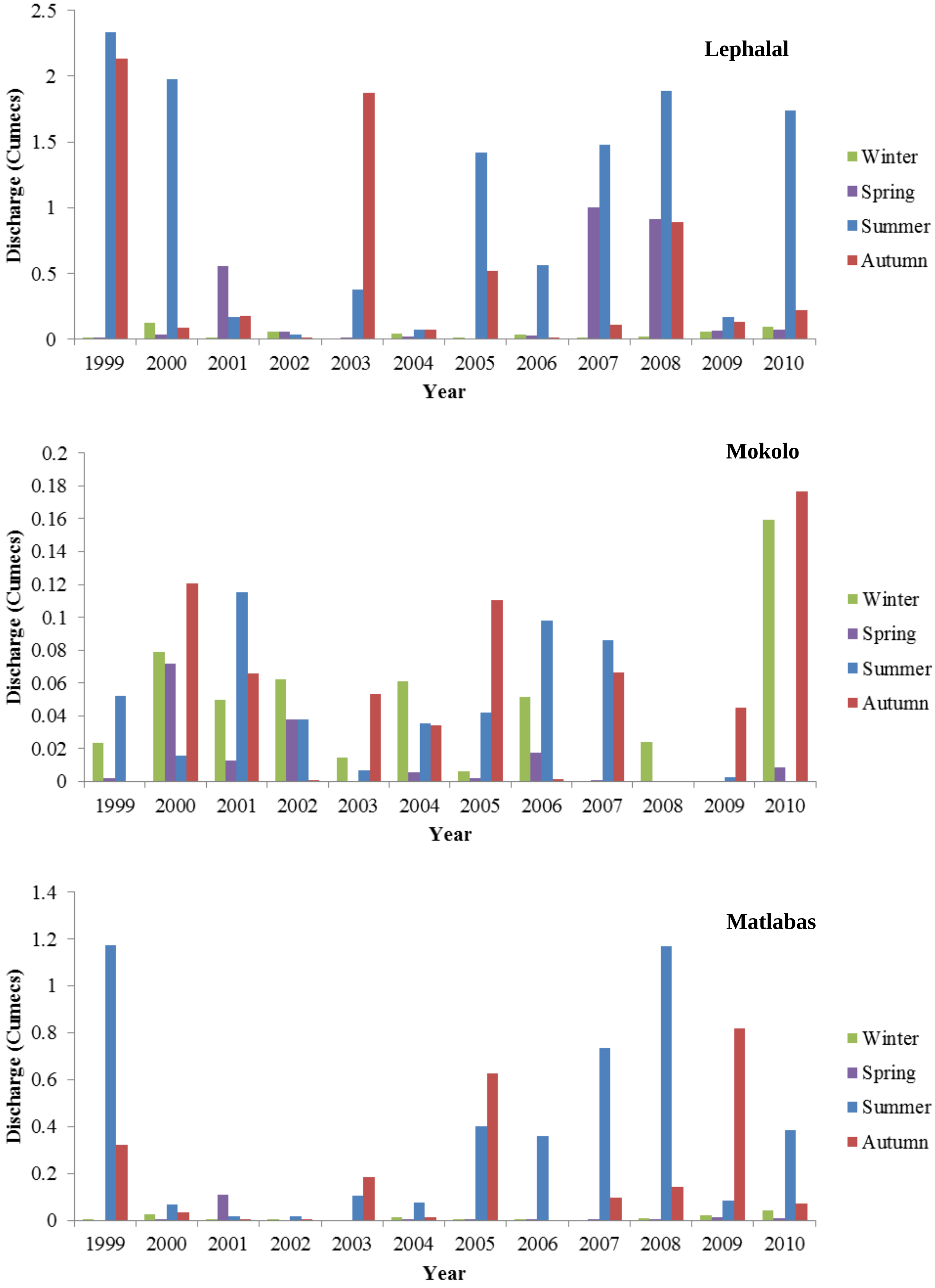


Figure 4.30. The seasonal mean discharge values measured for the Lephalala, Mokolo and Matlabas Rivers during each hydrological year from 1999 to 2010.

When the significance of the relationships between discharge and ion flux is statistically investigated (Table 4.9), it is clear that ion flux changes are marginally more significantly related to changes in river discharge than to temperature and rainfall, respectively. Discharge can thus be assumed to be the main driver of ion flux changes within the Lephalala, Mokolo and Matlabas Rivers.

Table 4.9. The significance of the relationship between daily river discharge and summed cation and sulphate flux (using non-linear regression) in the Lephalala, Mokolo and Matlabas Rivers for each hydrological year from 1999 to 2010.

Year	**Lephalala River**				**Mokolo River**				**Matlabas River**			
	Cation Flux		**Sulphate Flux**		**Cation Flux**		**Sulphate Flux**		**Cation Flux**		**Sulphate Flux**	
	Sig	p	Sig	p	Sig	p	Sig	p	Sig	p	Sig	p
1999	*	*	*	*	*	*	*	*	*	*	*	*
2000	SR	0.02	SR	0.03	NSR	0.20	NSR	0.95	NSR	0.19	NSR	0.30
2001	SR	0.03	NSR	0.15	NSR	0.22	NSR	0.93	NSR	0.47	NSR	0.07
2002	*	*	*	*	NSR	0.49	NSR	0.71	NSR	0.60	*	*
2003	*	*	*	*	*	*	*	*	*	*	*	*
2004	*	*	*	*	SR	0.05	SR	0.60	*	*	*	*
2005	*	*	*	*	NSR	0.29	NSR	0.13	*	*	*	*
2006	*	*	*	*	*	*	*	*	*	*	*	*
2007	*	*	*	*	*	*	*	*	*	*	*	*
2008	*	*	*	*	*	*	*	*	*	*	*	*
2009	*	*	*	*	*	*	*	*	*	*	*	*
2010	*	*	*	*	*	*	*	*	*	*	*	*

Sig = significant relationship ($p<0.05$)
p = p-value calculated using non-linear regression analysis
SR = significant relationship
NSR = no significant relationship
* = no or too few data points available

Years in which the relationship between discharge and ion flux is not significant, other external drivers (natural or anthropogenic) can be assumed to be of greater significance. These years do not correspond with unusually high or low flux values. The use of the data is also limited due to many years having missing or insufficient data points.

4.8.4 A summary of the relationship between ion flux and change in climatic parameters within the Lephalala, Mokolo and Matlabas Rivers

When the seasonal changes in ion concentrations, rainfall, temperature, discharge and the ion flux were compared to the outcomes expected (Table 1.1) some seasons had followed the expected outcomes, while other seasons did not. The expected outcome was met more frequently for cation flux than for sulphate flux in all three rivers (Table 4.10). Ion fluxes within the Matlabas River followed the expected outcomes for a much greater proportion of the time when compared to the Lephalala and Mokolo Rivers.

Table 4.10. The proportion (%) of seasons that followed the expected flux changes as described for each combination of ion concentration, rainfall, ambient temperature and river discharge.

River	Cation flux	Sulphate flux	Position relative to power station
Lephalala River	61%	44%	Upwind
Mokolo River	88%	58%	Downwind (close)
Matlabas River	100%	78%	Downwind (far)

The Mokolo River is located closest to the Matimba power station and Lephalale town and showed deviation from the expected cation flux outcomes for the intermdiate proportion of the time. The low proportion of expected outcomes found for the Lephalala River could indicate that a significant amount of the measure cations within the water is due to anthropogenic activities on the ground, and not the addition of cations through atmospheric deposition. The high proportion of expected outcomes found for the Matlabas River could infdicate that the flux of ions within this river is determined by the climatic variables considered.

The statistical significant relationships are summarized in Table 4.11 in which the three variables of temperature, rainfall and discharge are summarized to show their influence in each river in each year. Statistically, the relationship between the flux of cations and sulphate ions within the Lephalala, Mokolo and Matlabas Rivers and the change in at least one climatic variable is not significant in most years for which data are available. The years in which no significant relationships between ion flux and a climatic variable was found (indicated by an “!”), possibly indicate other external drivers that are not accounted for in this study. These drivers could include changes in the amount of fossil fuels burned, fires and other anthropogenic changes.

Table 4.11. A summary of the significance of the relationships between changes in climatic variables and ion flux within the Lephalala, Mokolo and Matlabas Rivers.

Year	Lephalala River		Mokolo River		Matlabas River	
	Cation Flux	Sulphate Flux	Cation Flux	Sulphate Flux	Cation Flux	Sulphate Flux
1999	*	*	*	*	*	*
2000	D	!	!	T	T	!
2001	D	!	!	!	!	!
2002	*	*	!	!	!	*
2003	*	*	*	*	*	*
2004	*	*	D	D	*	*
2005	*	*	!	!	*	*
2006	*	*	*	*	*	*
2010	*	*	*	*	*	*

T = temperature
R = rainfall
D = discharge
! = other possible drivers of ion flux changes
* = no data available

Increased cation fluxes were measured in the Lephalala River in 2002 and 2006 while no unusually high sulphate flux values were found. The increase in 2002 is most probably due to a significant change in rainfall and river discharge. The increase in 2006 is most probably due to the incompleteness of the data set as only a single value was recorded for this specific year. If more values were available, a different pattern might have been observed.

Increased cation fluxes in the Mokolo River were measured for 2007, while sulphate fluxes were elevated during 2004 and 2007. A significant relationship between ion flux and discharge was found for the year of 2004, indicating that the change is possibly due to change in river discharge. As the Mokolo River Catchment is highy developed, other possible drivers include direct dumping into the river or the run-off of sewage and washing water from the surrounding catchment.

The Matlabas River had maximum cation flux values in 2002 and 2006, while sulphate flux values were high in 2001.No significant relationship between ion fluxes and the climatic variables were found during 2002, yet insufficient data for 2006 made it impossible to determine the probable drivers in change of flux. It is, however, most probably due to only single values being available for each year. These values could be sporadic, high values changing the pattern in ion flux observed. The increased cation flux is most likely due to changes in rainfall and daily river discharge, while the increase in sulphate flux cannot be explained by the considered climatic variables.

4.9 Change in coal quality over time

Three parameters indicating coal quality were investigated – gross critical value ($MJ.kg^{-1}$), volatile matter content (%) and ash content (%). These values are only available from 2005; therefore comparisons between the mean measurements for 2005 and 2011 were made (Table 4.12).

Table 4.12. A direct comparison of the mean gross critical value, volatile matter and ash content of coal burned at the Matimba power station in 2005 and 2011.

	2005	**2011**
Gross Critical Value ($MJ.kg^{-1}$)	19.11 ± 0.1977	18.78 ± 0.1899
Volatile Matter (%)	37.00 ± 0.7476	24.48 ± 0.4301
Ash content (%)	30.32 ± 0.6143	31.78 ± 0.7161

The gross critical value data were found to be normally distributed for 2005 (Shapiro-Wilk Normality Test, $p = 0.2748$) and 2011 (Shapiro-Wilk Normality Test, $p = 0.7608$) and can be compared using a parametric test. The gross critical value significantly decreased (Paired T-test, d.f. = 11, $p = 0.0055$) from 2005 to 2011, indicating that the quality of coal burned within the Matimba power station decreased. A weak negative linear trend was found for the gross critical value of coal burned from 2005 to 2011 (Figure 4.31), thus a further increase in quantity of coal burned is expected in the future in order to compensate for the decreased energy value per unit coal burned.

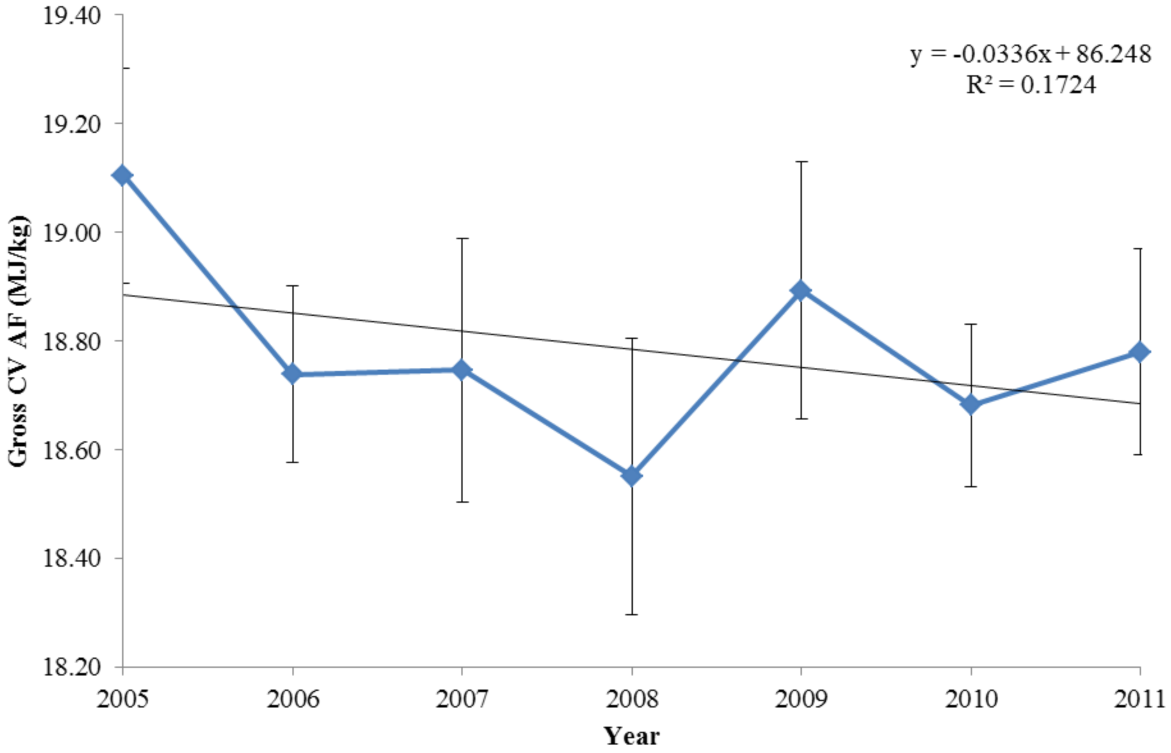


Figure 4.31. Annual mean gross critical values (as fired) of the coal burned at Matimba Power Station from 2005 to 2011. Variation is indicated with standard error bars.

The volatile matter content data were found to be not normally distributed for both 2005 (Shapiro-Wilk Normality Test, p = 0.0252) and 2011 (Shapiro-Wilk Normality Test, p = 0.0175) and has to compared using a non-parametric test. The volatile matter content of the coal significantly decreased (Mann-Whitney-U-Test, $p = 7.395 \times 10^{-7}$) between 2005 and 2011, translating into a significant decrease in the amount of matter released into the atmosphere per unit coal burned. This does not, however, directly translate into a decreased total amount of volatile matter released into the atmosphere if the total amount of coal burned has significantly increased.

A strong negative linear trend was found for the changes in volatile matter content from 2005 to 2011 (Figure 4.32), the volatile matter remained relatively consistent from 2005 to 2008 and from 2009 to 2011. A very sharp decrease in volatile matter content from 2008 (37.04 ± 0.55%) to 2009 (24.56 ± 0.43%) was found.

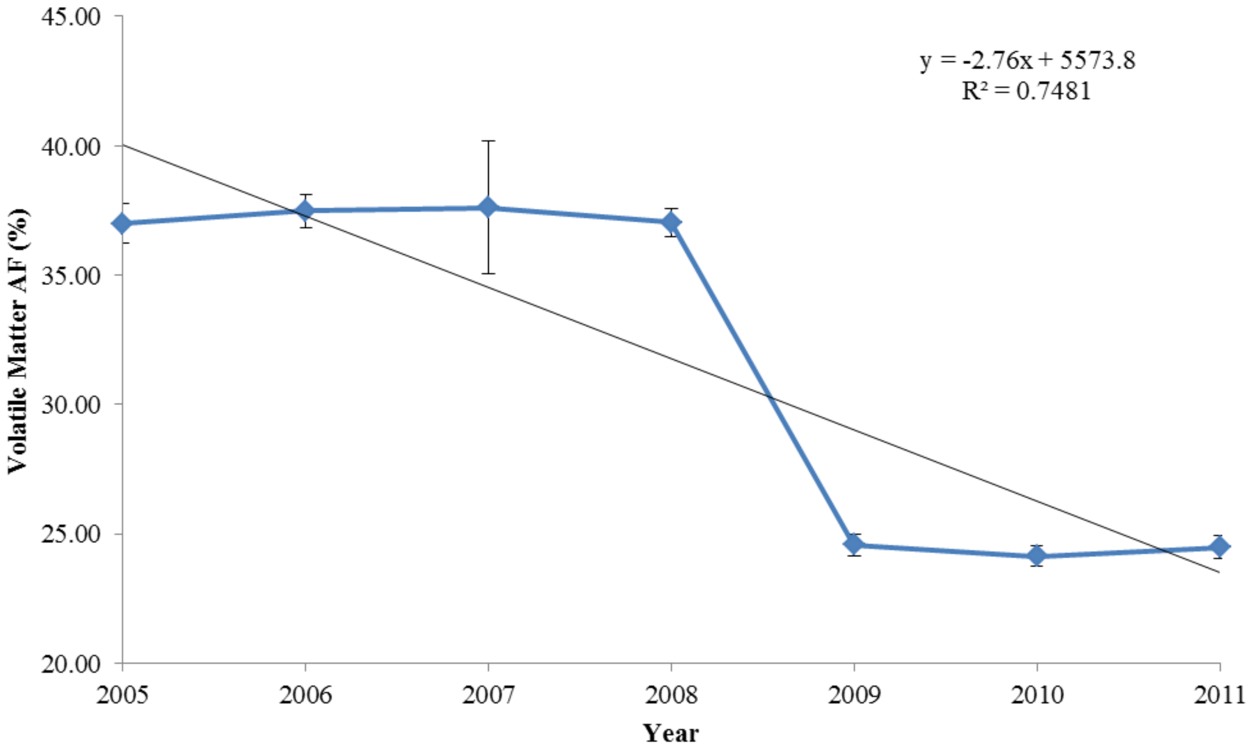


Figure 4.32. Annual mean volatile matter content of the coal burned at Matimba Power Station from 2005 to 2011. Variation is indicated with standard error bars.

The mean monthly amount of volatile matter (in tonnes) released into the atmosphere during each year from 2005 to 2011 showed a strong negative linear trend (Figure 4.33). The total amounts of volatile matter released in 2005 and 2011 were statistically compared to test the significance of the change. A Shapiro-Wilk Normality test showed that the data were normally distributed for 2005 ($p = 0.2127$) and 2011 ($p = 0.2963$). The amount of volatile matter released in 2011 was significantly lower than the amount of volatile matter released in 2005 (ANOVA, d.f. = 22, $p = 6.801 \times 10^{-10}$), indicating that the decrease in volatile matter (%) was not masked by any increase in the total amount of coal burned at the Matimba power station.

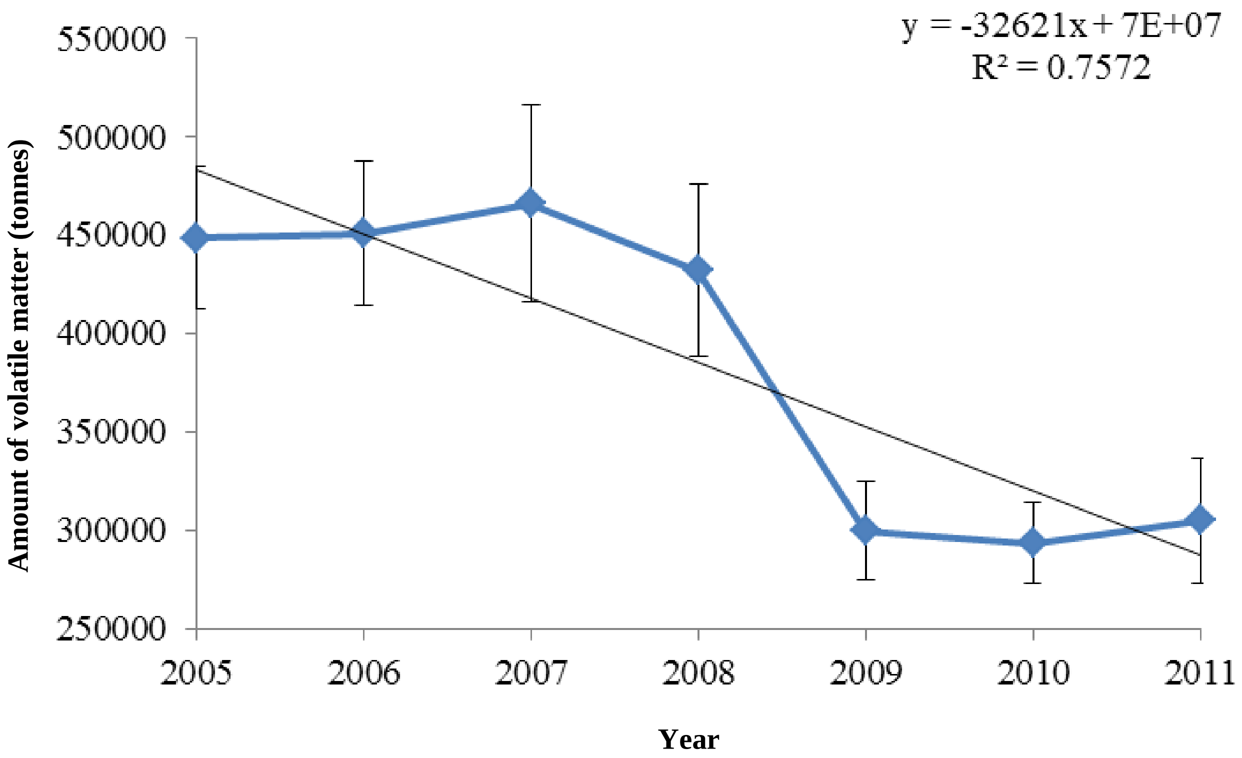


Figure 4.33. Mean monthly amount of volatile matter (in tonnes) released into the atmosphere from Matimba power station during each year from 2005 to 2011. Variation is indicated with standard error bars.

The ash content data for 2005 (Shapiro-Wilk Normality Test, p = 0.3612) and 2011 (Shapiro-Wilk Normality Test, p = 0.6708) were found to have a normal distribution, and were compared using a parametric test. The mean ash content of the coal as fired significantly increased from 30.32% in 2005 to 31.78% in 2011 (Paired T-test, d.f. = 11, p = 0.0004). The general linear trend in the change of ash content was found to be a weak positive trend (Figure 4.34), with no abrupt change in ash content between 2008 and 2009, as was found for the volatile matter content of the coal (Figure 4.32).

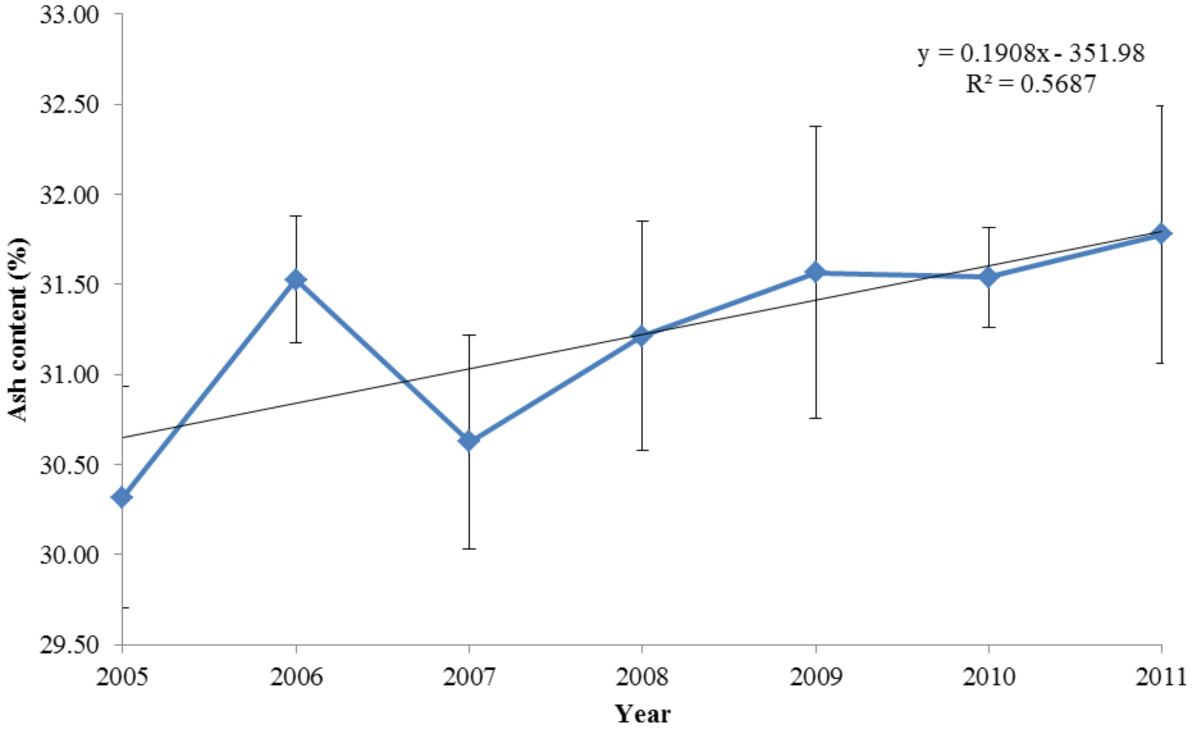


Figure 4.34. Annual mean ash content of the coal burned at Matimba Power Station from 2005 to 2011. Variation is indicated with standard error bars.

The total impact of the changes in coal quality on the deposition of ions and changes in water quality is dependent on the change in the amount of coal burned. Understanding how the amount of coal burned at the Matimba power station has changed from 1999 to 2011 is thus vital in understanding the overall impact of burning coal within the Waterberg District Municipality.

4.10 The relationship between coal usage and flux of ions measured

4.10.1 Changes in the annual amount of coal combusted at the Matimba power station

The annual amount of coal burned at Matimba power station increased from 10 263 700 tonnes in 1991 to 14 549 860 and 14 593 397 tonnes in 2005 and 2011, respectively (Figure 4.35). A line of best fit indicated a strong positive linear relationship ($R^2 = 0.8668$), with the amount of coal increasing by an average of 219 570 tonnes per year. This trend is expected to continue at an increased rate once Medupi power station is commissioned, with the amount of coal burned increasing until the maximum capacities of both the power stations are reached.

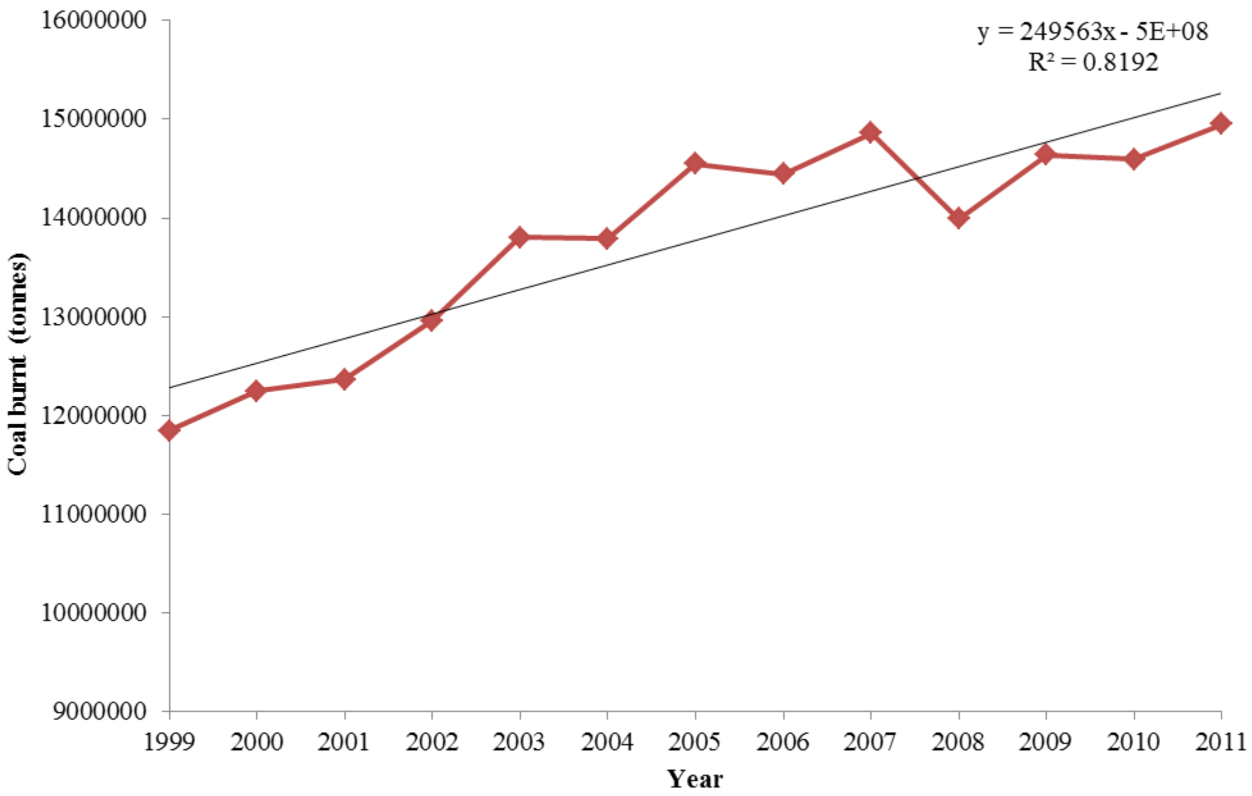


Figure 4.35. Annual quantity of coal burnt at the Matimba power station from 1991 to 2011, as recorded by ESKOM.

The amount of coal burned from 1999 to 2004 was available only at an annual resolution, limiting its usefulness in statistically comparing individual years. All annual coal usage values were divided into two groups: "Before 2005" and "2005 onwards". A comparison of the average annual amount of coal burned before 2005 (12 157 854.0 ± 1 072 003.3 tonnes) and 2005 onwards (14 576 426.0 ± 313 188.8 tonnes) indicated that there has been a very significant increase in the amount of coal burned at the station (ANOVA, d.f. = 19, $p = 1.439 \times 10^{-5}$). Increased usage is expected due to increased demand for electricity while the decreased calorific value of the coal burned decreases the amount of energy produced per unit coal burned.

4.10.2 Investigating the relationship between the quantity of coal burned and the changes in cation and sulphate fluxes within the Lephalala River.

The flux of cations (Figure 4.36; Non-linear regression, d.f.= 6, p = 0.6020) and sulphate ions (Figure 4.37; Non-linear regression, d.f.= 6, p = 0.0199) in the Lephalala River from 1999 to 2010 showed a significant relationship with the use of coal at the Matimba power station and sulphate flux from 1999 to 2010. Large variations in cation fluxes indicated no specific trend in flux values while the usage of coal showed a positive trend over this specific period. The significance of the relationship between sulphate flux and coal usage is graphically confirmed in Figure 4.37.

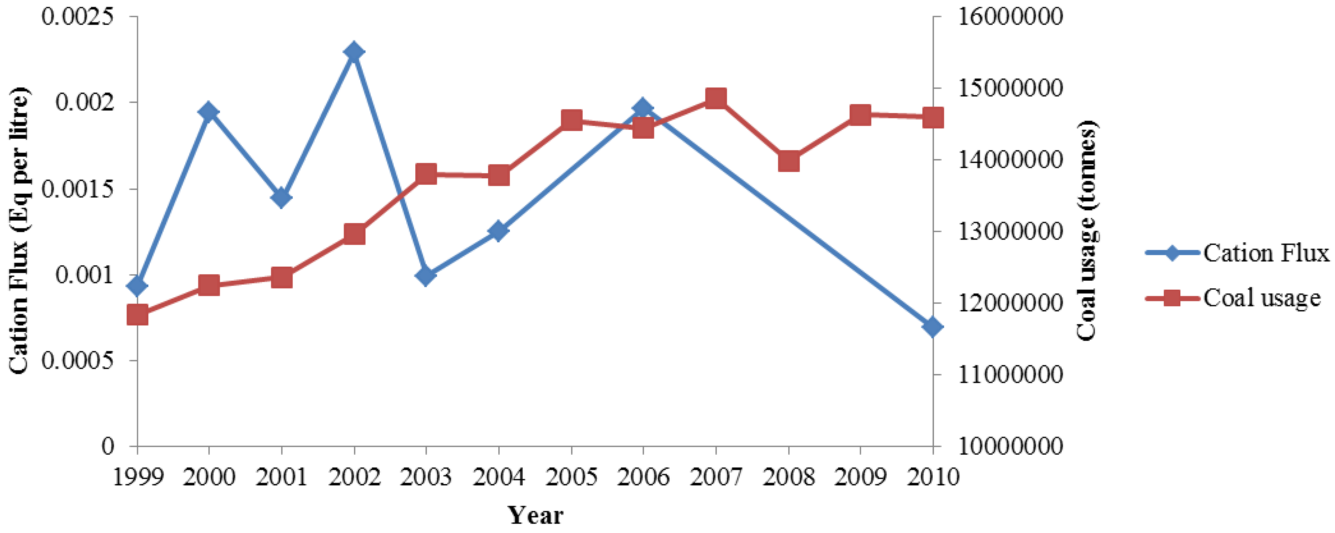


Figure 4.36. Summed cation flux within the Lephalala River and the coal usage at the Matimba power station from 1999 to 2010.

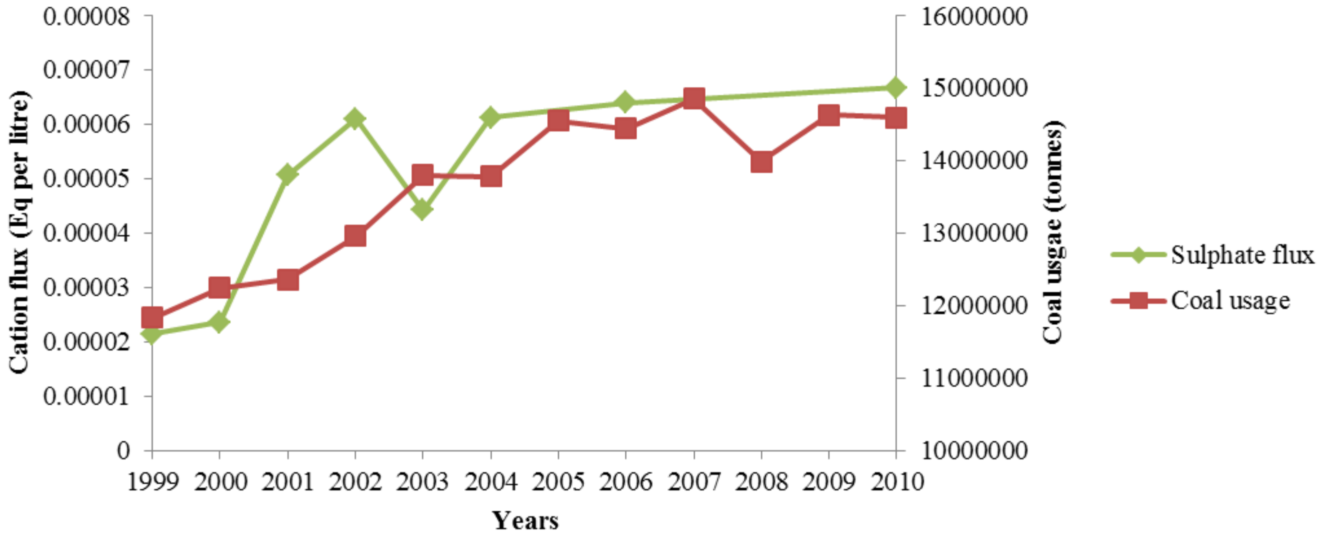


Figure 4.37. Sulphate flux within the Lephalala River and the coal usage at the Matimba power station from 1999 to 2010.

No significant relationship was expected as the river is located upwind of the Matimba power station, outside of the projected area of ion deposition. Wind roses for Lephalale supplied by the South African Weather Services do indicate that the northeasterly wind direction becomes less predominant during the months of May to August, with the month of June being the windiest (wind blowing 48%

of the time) with wind speeds of up to 5m.s^{-1} blowing from a north-easterly direction for approximately 4% of the time (Figure 4.38). This is higher than the proportion of time the wind blows in the same direction during the month of January (<1%). During the winter months, the deposition zone around the Matimba power station can thus be expected to be further along the north-easterly axis towards the Lephalala River when compared to the general projections presented, possibly increasing the amount of ions deposited in and around the river during this period. This is also supported by the earlier evidence presented as flux increases in the Lephalala and Matlabas Rivers during the drier, winter months (Figures 4.19 and 4.23). This effect can either be immediate after direct deposition into the river or delayed as rainfall is often limited during winter months, limiting the leaching of ions deposited onto the terrestrial system.

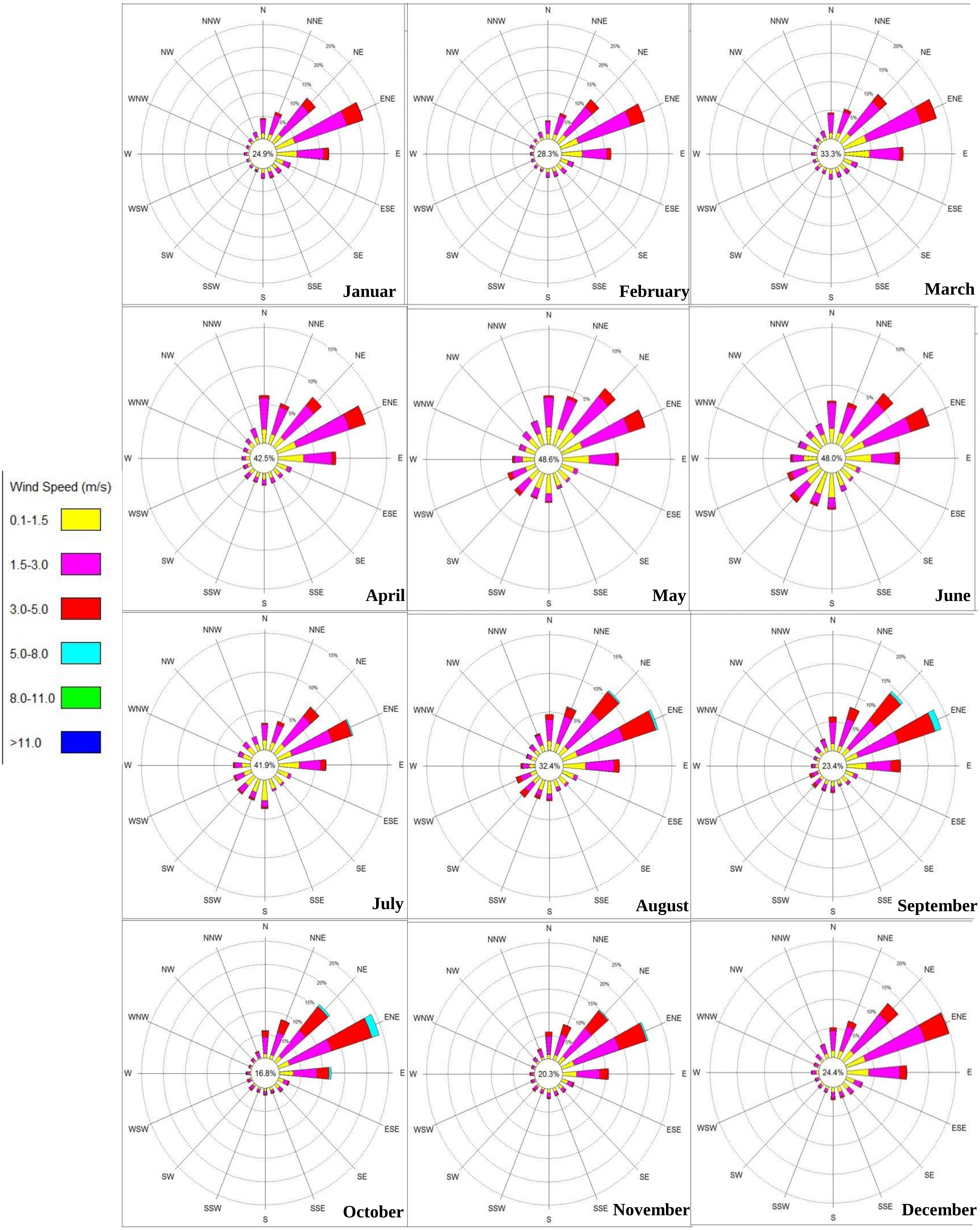


Figure 4.38. Wind direction and speed measured for Lephalale during every month of the year averaged over the period of 1991 to 2013.

4.10.3 Investigating the relationship between the quantity of coal burned and the changes in cation and sulphate fluxes within the Mokolo and Matlabas Rivers.

A comparison of coal usage with cation and sulphate fluxes in the Mokolo and Matlabas Rivers indicated no similarity in the trends. Statistically, all relationships were found to be not significant: coal usage vs cation (Non-linear regression, d.f. = 8, p = 0.1812) and sulphate (Non-linear regression, d.f. = 8, p = 0.2077) in the Mokolo River and coal usage vs cation (Non-linear regression, d.f. = 7, p = 0.5121) and sulphate (Non-linear regression, d.f. = 6, p = 0.7023) in the Matlabas River.

The significance of the relationship between cation flux and the river located in close proximity to the Matimba power station (Mokolo) was found to be stronger. The relationship between sulphate flux and the rivers located upwind from the power station (Lephalala and Mokolo) was strongest.

Cation deposition is thus predominant in the area surrounding the power station, while sulphate deposition predominates in areas outside of the predicted area of deposition. It is possible that the deposition of cations and sulphate from the Matimba power station is more significantly determined by the distance of the site from the source rather than its direction from the source. The distance at which ions are deposited is also influenced by the occurrence of rainfall events, as wet deposition decreases the distance at which the ions are deposited by rapidly removing the ions from the atmosphere.

CHAPTER 5: DISCUSSION

The following discussion is based on the changes in cation and sulphate concentrations (1999 to 2011 by calendar year) and fluxes (1999 to 2010 by hydrological year) measured within the Lephalala, Mokolo and Matlabas Rivers. The relationships with climatic variables are also investigated. These changes are also discussed in relation to the change in coal quality and quantity burned at the Matimba Power Station in Lephalale. Each objective previously stated is discussed individually before all aspects are discussed in an integrated format.

All interpretation of results and discussion points is done knowing the limitations of the data presented. Data from a single sampling station along each of the three predominant rivers within the Waterberg District Municipality (WDM) were used. The selection was based on its location relative to the Matimba Power Station. It is possible that certain trends specific to a single river continuum were missed as the data of only a single sampling station along wach river were used. The extrapolation of the data was done knowing that many data are missing from the available data set. The results presented and discussed are, however, correct for the data that are currently available for the river water quality within the WDM.

5.1 Trends in pH, cation and sulphate concentrations measured in the Lephalala, Mokolo and Matlabas Rivers

When compared to the pH values found by Burne (2015), it was evident that the pH of the Lephalala River has increased (5.0 to 6.3 times less acidic) while the pH of the Mokolo and Matlabas Rivers has decreased (~1.3 and 2.0 times more acidic, respectively). The differences in the changes can be due to a difference in the ratio of cations and sulphate ions deposited or due to different natural acid neutralising capacities (ANC) of the river catchments (Driscoll *et al*. 2001). The Matlabas River Catchment is expected to have the highest natural ANC due to slower movement of water through the catchment, the seasonality of the river and the decreased discharge measured for this river. Slower movement of water is expected due to the lower degree of development within this catchment, while large residential and industrial areas within the Lephalala and Mokolo catchments are expected to have higher surface to ground water ratio. The Lephalala and Mokolo Rivers are larger rivers with increased denaturalised run-off decreasing the natural ANC and thus increasing the likelihood of acidifying effects. This does not support the changes found in the pH of the rivers, indicating that the input of ions into the system far exceeds the effects of the natural remediating processes.

Sodium is a major contributor to summed cation concentrations within the Lephalala, Mokolo and Matlabas Rivers. In the majority of the Waterberg Rivers, including thermal springs, the dominant cation is sodium with calcium also occurring in high concentrations. These cations are followed by potassium and magnesium (Olivier *et al*. 2008). Similar trends were found in this study, with the exception of magnesium occurring at higher concentrations than potassium, possibly indicating increased magnesium into the river system.

There are at least three possible major sources of sodium, other cations and sulphate ions within the Waterberg District Municipality: ions within soils, emissions of coal-fired power stations and other industrial, agricultural and household anthropogenic sources.

The Waterberg is part of the Karoo Super Group (north of Lephalale) and the Waterberg Group (south of Lephalale; Figure 5.1). Ground water within the Karoo Super Group is expected to be rich in sodium, calcium and potassium (Bothma 1998) which are the three predominant cations measured within the Lephalala, Mokolo and Matlabas Rivers.

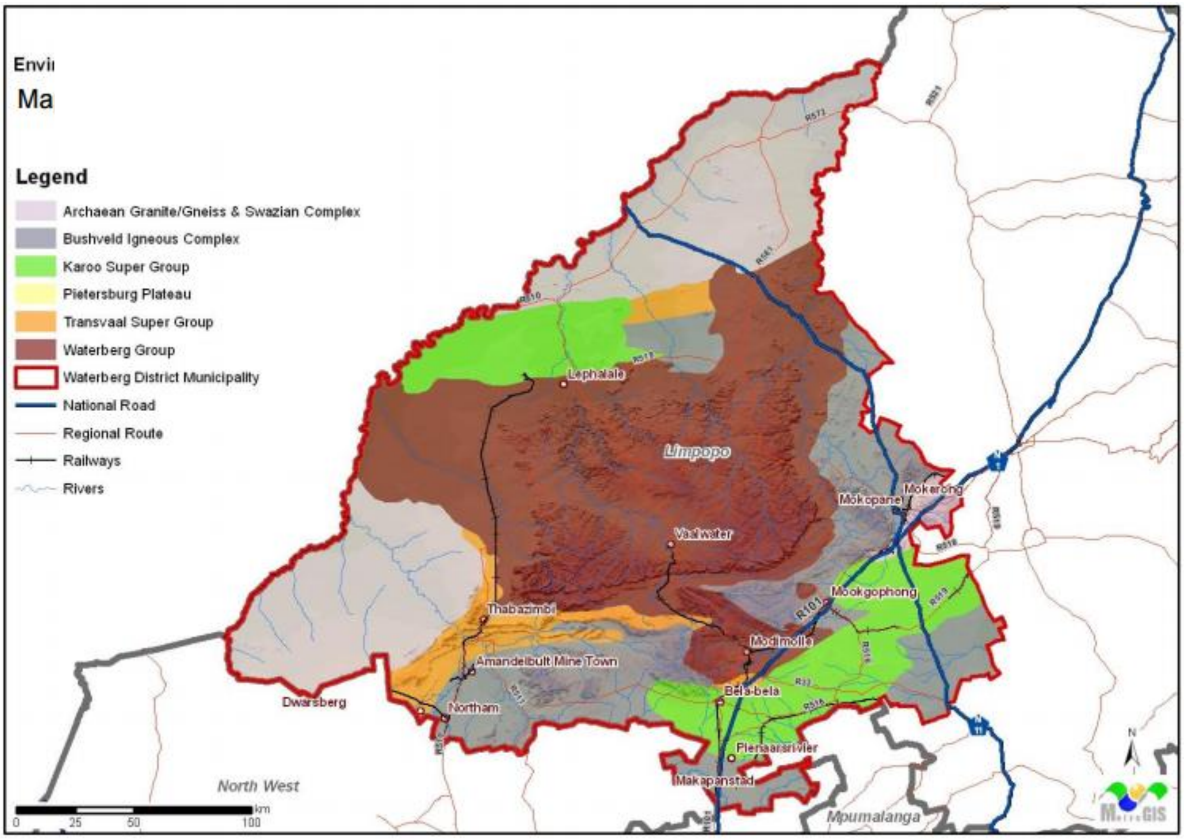


Figure 5.1. A simplified representation of the geological systems within the Waterberg District Municipality (DEA 2010).

Water discharged from mining operations in the Waterberg area has always been found to be rich in $NaHCO_3$ (Annandale 2009), indicating that the water sources across the Waterberg District Municipality can be expected to have high concentrations of sodium naturally occurring due to weathering and ground water movement. Most water samples collected throughout the Waterberg District Municipality are sodium chloride dominant which is associated with slow moving to stagnant ground water with little to no recharge (DWA 2010). Increased sodium concentrations in the Lephalala, Mokolo and Matlabas Rivers can be assumed to be due to naturally weathering and leaching processes, yet anthropogenic processes are expected to be responsible for large differences in sodium (and other cation) concentrations between the three rivers.

Sulphate ions are naturally abundant in the environment generally occurring within many soils. Sulphate ions are, however, not highly mobile (EPA 2003) indicating that the leaching of sulphate ions from the soils is minimal. Leaching is expected to increase with increased ion mobility in the presence of other anions. Sulphates are commonly used in the mining and metal industries, water and sewage treatment and the manufacturing of numerous chemicals, fungicides and insecticides (Greenwood *et al*. 1984). Ammonium sulphate is used in the fertilizer industry (EPA 2003).

Anthropogenic inputs of cations and sulphates due to effluent from septic systems, leachate from landfills and household as well as agricultural chemicals are very likely within the Lephalala and Mokolo River Catchments. Sanitation within the Waterberg District Municipality is poor to absent as only 45.4% of all households have access to hygienic toilets: flush toilets that are connected to the sewer system or septic tanks (Table 5.1; IDP 2014). The hygienic toilets are expected to predominantly occur within the larger towns and not within the rural villages occurring along the rivers. The majority (94%) of these waterborne sanitation systems are older than 20 years, while 15% of the sanitation network is in very poor condition and may be experiencing impairment in functionality (IDP 2014). A total of 1 589 households (5.3%) do not have access to any form of toilet, discharging human wastes directly onto the terrestrial system from where it is leached into the groundwater and rivers during rainfall events.

Table 5.1. The number of households within the Waterberg District Municipality that have access to each of the sanitation types (IDP 2014).

Sanitation type	**Number of households**	**Proportion of population (%)**	
No toilet	1 589	5.4	Number of households with hygienic toilets *13 434* (45.4%)
Flush toilet connected to sewer system	11 803	39.9	
Ventilation Improved Pit (VIP)	7 198	24.3	
Pit toilet without ventilation	6 785	22.9	Number of households without hygienic toilets *16 142* (54.6%)
Chemical toilet	385	1.4	
Flush toilet with septic tank	1 631	5.5	
Bucket toilet	185	0.6	
Total	**29 576**	**100.0**	

The trends in cation and sulphate concentration changes are not the same in any of the rivers, yet both the Lephalala and Matlabas Rivers show a sharp increase in concentrations during 2000 – 2001. These rivers are located in two different river catchments, making an environmental parameter the most probable driver of change. Elevated amounts of rainfall were recorded during 1999 (544 mm) and 2001 (443 mm) when compared to the average rainfall of 350 – 400 mm per annum (IDP 2014). Following a year of low rainfall in 2000 (271 mm), the increased rains in 2001 probably led to the depositing and leaching of high amounts of cations and sulphate into these rivers. The high concentrations measured in 2000 most probably is due to the relatively dry winter and spring preceding the 200mm of rain measured during the summer of 2000. The concentrations of cations and sulphate within the Mokolo River remained relatively consistent and this is probably due to the more consistent run-off of water in this highly developed catchment as decreased natural run-off is supplemented by denaturalized run-off. This is a result of the on-going use of water supplied by the municipalities within the developed areas while sewerage and other effluents are better managed.

The Matlabas River, the only river located downwind from the Matimba Power Station, did not show the expected increased cation and sulphate concentrations relative to the Lephalala and Mokolo Rivers which are both located upwind. The upwind rivers clearly had increased concentrations of especially sulphate, with the Lephalala River having the highest mean cation and sulphate concentrations between 1999 and 2011. Concentrations decreased from northeast to southwest with the Lephalala River having the highest and the Matlabas River having the lowest mean values. This pattern is seen with all ions throughout the entire period of 1999 to 2011 (Table 5.2).

South African coal composition indicates only 0.00 to 0.31% Na_2O and 0.03 to 0.24% SO_3 (Van der Merwe *et al*. 2014 and Mainganye *et al*. 2013). With a mean of 12 964 044 ± 1 463 312 tonnes of coal burned each year from 1999 to 2011, this translates to 0 – 40 200 tonnes of Na_2O and 3 900 – 31 100 tonnes of SO_3 released into the atmosphere per annum. A small proportion of these atmospheric ions are rapidly deposited when it rains (wet deposition) yet some are also deposited as dry deposition. The Matlabas River is seasonal, only flowing during the rainfall season. Any ions deposited by dry deposition will accumulate on the dry river basin, contributing to increased concentrations measured when the river flow recuperates. The input of cations and sulphate ions into the system due to the combustion of coal at the Matimba Power Station is still less concerning when compared to the other immediate anthropogenic sources mentioned.

Table 5.2. A summary of the location, description, concentration trends and possible drivers in the Lephalala, Mokolo and Matlabas Rivers.

	Lephalala River	**Mokolo River**	**Matlabas River**
Location from Matimba Power Station	Upwind	Upwind	Downwind
General description of river catchment	Large number of informal settlements, rural livelihoods. Poor or no sanitation systems.	Well developed, industrial area. Existing sewerage systems are in poor condition.	Undeveloped, agricultural area. Low population density.
Seasonality and discharge of the river	Perennial river. Mean discharge of 13.46 ± 31.24 cumecs and a range of 0.01 to 176.34 cumecs during 1999 to 2010.	Perennial river. Mean discharge of 2.10 ± 2.23 cumecs and a range of 0.02 to 8.86 cumecs during 1999 to 2010.	Seasonal river. Mean discharge of 4.38 ± 11.32 cumecs and a range of 0.00 to 50.90 cumecs during 1999 to 2010.
Ion concentration trends	Consistently high ion concentrations. Outside of the projected area of deposition.	Ion concentrations remain relatively constant at values intermediate of concentrations recorded in Lephalala and Matlabas Rivers. A single elevated suplate concentration measured during 2004.	Ion concentrations fluctuate a lot, but remains at lower values than the concentrations recorded for the Lephalala and Mokolo Rivers.
Most likely driver of changes in ion concentrations	Periodic leaching of sewerage and / or other anthropogenic wastes or incomplete understanding of deposition footprint of power station.	Consistent input of ions into system, most likely due to effluent and chemical run-off.	Ion input is most likely related to the burning of coal at the Matimba Power Station.

The interaction of cation and sulphate concentrations with the discharge of each of the rivers resulted in annual and seasonal flux patterns that differ between the cations and sulphate ions measured. No single pattern or trend was found to be common throughout all ion species, indicating the dynamic nature of the system.

5.2 Annual and seasonal fluxes of cations and sulphate ions within the Lephalala, Mokolo and Matlabas Rivers

The flux of an ion is directly determined by the concentration of the ion as well as the discharge of the specific river. Flux is proportional to ion concentration and inversely proportional to discharge. The ion concentration patterns and trends within the Lephalala, Mokolo and Matlabas Rivers have already been discussed. Discharge is not directly discussed, but is related to the changes in ion fluxes measured within the rivers.

Seasonal changes in individual cation, summed cation and sulphate fluxes within the three rivers were predominantly not significant (Table 5.3).The significant changes did however indicate a weak relationship between flux and rainfall or discharge, with fluxes increasing during winter and decreasing during summer in the rivers located further away from the Matimba Power Station.

Table 5.3. The seasonality and direction of changes in individual cation, summed cation and sulphate fluxes in the Lephalala, Mokolo and Matlabas Rivers from 1999 to 2010.

Ion	Lephalala River	Mokolo River	Matlabas River
Sodium	X	X	↑ (winter)
Magnesium	↓ (summer)	X	X
Calcium	↓ (summer)	X	X
Potassium	X	X	X
Ammonium	X	X	X
Summed cations	X	X	X
Sulphate	X	X	X

X = no seasonality shown

The increase in sodium flux in the Matlabas River during winter is most probably due to an increase in the concentration of ions for two reasons: an increase in the deposition footprint of ions from the Matimba Power Station plumes when rain is absent or due to a decrease in discharge of the seasonal river during the dry season. The latter is expected to be the most probable explanation as no significant relationships between ion fluxes and rainfall were found. The greater significance of the relationship between ion fluxes and river discharge possibly indicates that there is a lag period between rainfall events and changes in ion fluxes measured. A lag period is defined as the time delay between maximum rainfall amount and the peak discharge measured, usually presented in a hydrograph (Yu et al. 2000).

The data were all analysed by hydrological year, which commences with the start of the winter season. A hydrological year thus runs from one dry season to the next, with rainfall being highest in the middle of the hydrological year. The hydrological year within the Lephalale area runs from June to May with rainfall being highest from November to February. The fluxes of especially sodium, magnesium, summed cations and sulphate ions were increased in winter and early spring. These increased fluxes are expected to be due to the increased rainfall measured during the rainfall season, four to seven months before.

The discharge of the Mokolo River follows a similar pattern, with discharge being highest during late autumn and during winter. Discharge within the Lephalala and Matlabas also indicated increased values during autumn. In both rivers the discharge then decreases during winter and spring and increases again during summer. This could indicate a shorter lag period between rainfall and discharge as the rainfall measured during spring and summer is seen in the increased discharge in summer and autumn (one to three months later).

Lag time is not a constant value, yet varies inversely with the flow rate of water through the river catchment (Pilgrim 1987). Greater amplitude on a hydrograph is thus expected to be accompanied by a decreased time lag as it indicates the increased rate of water movement from the catchment into the river. The flow rate and thus magnitude of this lag period is determined by various factors, including catchment characteristics such as catchment size, land cover and climate (Verstraeten and Poesen 2001 and Zhou *et al*. 2002) as well as deposition rates of ions into the waterbodies (Verstraeten *et al*. 2003; Table 5.4).

Table 5.4. The climatic and topographic factors that influence the flow rate of water and thus the lag time between maximum rainfall and peak discharge within a river catchment.

Factor	**Flow rate of water through catchment**	**Lag time**
Increased rainfall intensity	↑	↓
Wider rainfall distribution	↓	↑
Catchment size	↓	↑
Elongated catchment shape	↓	↑
Increased slope of catchment	↑	↓
Increased natural or artificial water storage capacity	↓	↑
Increased soil permeability*	↓	↓
Increased urbanization	↑	↓

* Increased soil permeability indicates the absence of an inverse relationship between flow rate and lag time. Increased permeability increases the amount of water that seeps into the groundwater reservoirs, increasing the time it takes for the water to reach the river.

The magnitude of the lag effect within each of the river catchments within the Waterberg District Municipality is unknown, yet it is expected that the Matlabas River Catchment will have the shortest lag time between the peak rainfall event and the peak flux event due to its intermediate size (6 014km^2) and more rounded shape (Figure 5.2) when compared to the Lephalala (very elongated; 4 868km^2) and Mokolo (less elongated; 8 387km^2). The latter two river catchments also have increased artificial water storage capacities, further increasing the expected time lag. Using small "natural" plots of 108km^2, Yu *et al*. (2000) found that the average lag time ranged from 2.04 to 5.96 minutes. The plots used in their study are ~ 4.5 x 10^5, 7.8 x 10^5 and 5.6 x 10^5 times smaller than the Lephalala, Mokolo and Matlabas River Catchments, respectively. Lag times in the order of months can be expected to be found within these river catchments, as increased catchment size and increased lag time are proportional.

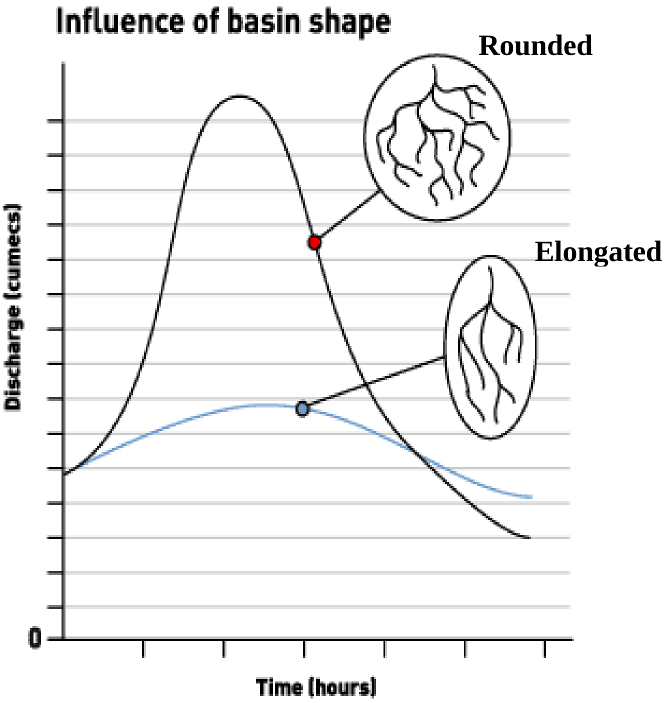


Figure 5.2. The influence that a rounded and elongated river catchment shape has on the curve of a hydrograph.

The Lephalala and Mokolo River Catchments are more developed catchments, with most of the Waterberg District Municipality's population living within the boundaries of these two catchments (HDA 2013). When considering the extent of urbanisation within the different catchments in isolation from all other factors influencing time lag, one would expect the Lephalala and especially Mokolo River Catchments to have a very short lag time as water rapidly runs off across the concrete covered catchment surfaces (Figure 5.3). Although the urbanised area within the catchment is minimal when compared to the area not developed, the area directly surrounding the Mokolo River sampling station is best represented by the scenario in the bottom left box. Other factors, such as catchment size and shape and the presence of artificial water storage systems and agricultural land use practices regularly outweigh the effects of urbanization as urban areas only represent a smaller portion of the complete catchment.

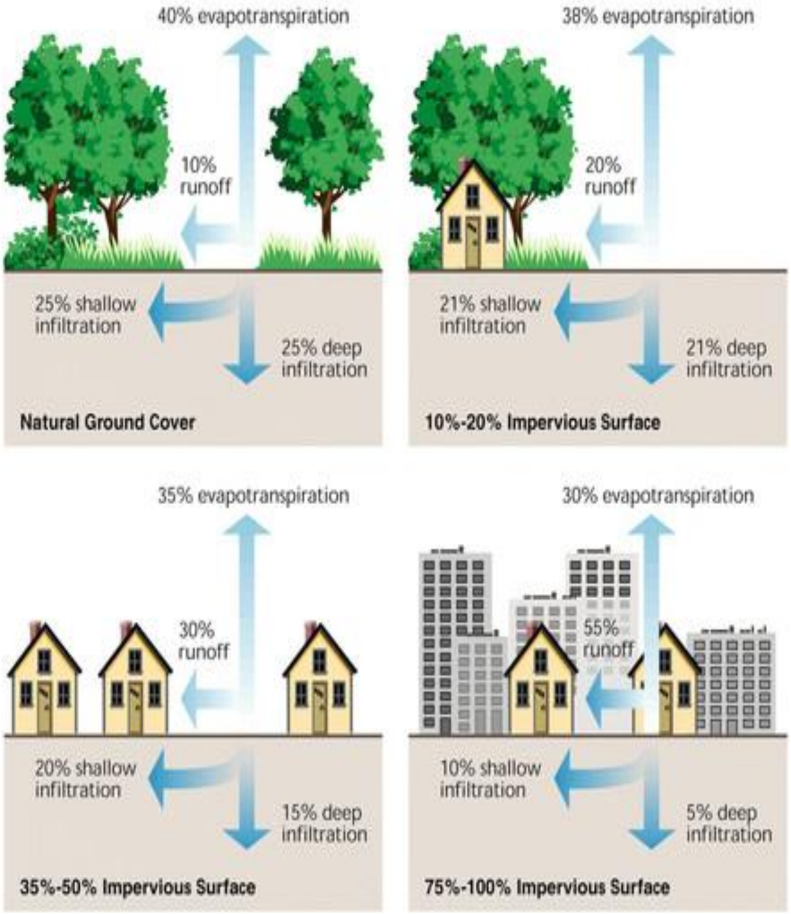


Figure 5.3. A diagrammatic representation of the changes in surface permeability and runoff with different degrees of urbanization.

As of 2014, a total of 13 526.2 ha (1%) of the Waterberg District Municipality was classified as urbanized, yet this area is expected to keep on expanding due to the various potential development highlighted for the area. The Spatial Development Framework compiled for the Waterberg District Municipality identified seven functional precincts for the area, namely mineral potential areas, coal fields, potential agriculture fields, nature conservation areas, hunting lodges, biospheres and development clusters (PlanPractice 2004). The Mokerong area and the Lephalale/Onverwacht area are the two development clusters already identified within the proximity of Lephalale town (PlanPractice 2004).

The estimated expansion rate of developments within the Lephalale area (Table 5.5; IDP 2008) is relatively low when considering that the Waterberg District Municipality spans across 1.4 million hectares. This does, however, only include three of the many developments expected to occur within the area. With the developed and industrialised areas estimated to only cover ~13 500 ha at present, a single development is expected to increase this area by ~0.1% per annum. The intensive nature of the pollutant sources within the Waterberg District Municipality has led to the degradation of water quality regardless of the limited geographic extent and is expected to continue altering water quality within the area if the rapid development is not properly managed.

Table 5.5. The expected rate of the expansion of business, industrial, mixed and educational land use within the Lephalala area for three major developments planned. The table is compiled from information given in the Lephalale Intergrated Development Plan for 2008/2009 (IDP 2008).

	Medupi power station and associated expansion of Grootegeluk coal mine	**A future power station and its associated coal mining activities**
Expected timeframe	2007 – 2016	2017 – 2023
Business areas	5 ha/annum	5 ha/annum
Commercial and industrial areas	5 ha/annum	5 ha/annum
Mixed land use areas	2 ha/annum	2 ha/annum
Educational areas	6 ha/annum	6 ha/annum
Total	18 ha/annum	18 ha/annum
Additional notes	Expansion of area used for all developments expected to continue increasing at 2.5% per annum after completing of initial estimated timeframe.	

More recent Integrated Development Plans available for the Lephalale Local Municipality do not address the rate at which different land uses are expected to grow. It is also important to note that the Sasol establishment was listed within the Lephalale Integrated Development Plan of 2008/2009 (IDP 2008), yet never occurred.

5.3 Quality and quantity of coal burned at the Matimba coal-fired power station, and its relation to the changes in cation and sulphate concentrations measured

Various parameters are used to determine the quality of coal used for different purposes. Gross critical value (CV), volatile matter and ash content are the most common measurements used and are discussed in terms of the coal combustion at the Matimba Power Station from 2005 to 2011.

Gross critical or calorific value is defined as “the heat produced by combustion of a unit quantity of a solid or liquid fuel when burned at constant volume… under specific conditions…” (ASTM International). The gross CV of the coal burned at Matimba Power Station was highly variable, yet the general decrease in value indicates that the energy value per unit coal is decreasing, increasing the amount of coal needed to supply South Africa with electricity. With the amount of coal burned at the station already increasing at a rate of 249 563 tonnes per annum, it can be expected to continue with this trend due to the interaction between lower energy value of coal and the increasing demand for electricity in especially the development hubs in the northern parts of the country.

A decrease in volatile matter, defined as “substances, other than moisture, that are given off as gas and vapour during combustion”, in the coal combusted at the Matimba Power Station was so pronounced that the amount of volatile matter released (in tonnes) also decreased regardless of the sharp increase in the amount of coal burned over the same period. Volatile matter is usually a mixture of short- and long-chain hydrocarbons and some sulphur, indicating that a significant decrease in the amount of sulphur within the power station plume can be expected from after 2008.

The amount of coal burned at the Matimba Power Station did not significantly alter the ion fluxes measured in the Mokolo and Matlabas Rivers as well as the cation fluxes measured within the Lephalala River. These fluxes are expected to be determined by the rapidly increasing human population within the catchments, with the indirect effects often being detrimental to river health and functioning. Sulphate fluxes within the Lephalala River were, however, significantly related to the amount of coal burned, a finding that does not match the deposition footprint modelled for the area surrounding the Matimba Power Station (Zunckel and Raghunandan 2013).

It is possible that the importance of the dry deposition of sulphate ions during the dry winter months is underestimated. This can be especially important during the months of May and June when the north-easterly wind direction is less predominant and deposition further along the south-westerly axis is possible. This is supported by the increased sulphate concentrations measured in the Lephalala River during spring and even summer, possibly due to the commencement of the rainfall season washing the deposited ions from the catchment. The slow reaction rates of SO_2 within saturated power station plumes due to oxidant limitations allow the ions to travel further before being deposited (Hewitt 2001). Increased coal combustion is expected to decrease the availability of oxidants even more, allowing SO_2 ions to travel even further from the source. When interacting with urban plumes expected over the Mokolo and Lephalala River Catchments, increased rates of SO_4^{2-} ion formation is expected. These sulphate ions are then deposited across these river catchments (Luria *et al*. 1983).

Once Medupi Power Station is fully operational, the amount of coal burned within the Waterberg District Municipality will increase from 14.8 million tonnes per annum to a total of 29.4 million tonnes per annum (Ryan 2014). The increase of 99% in the amount of coal burned is expected to have various negative consequences, including increased cation and sulphate depositions especially in all of the studied river catchments. Deposition of ions can, however, be expected to occur at further distances with increased release of ions from coal combustion, increasing the deposition footprint around the Matimba Power Station. Currently, the amount of cations and sulphate ions released due to the combustion of coal at the Matimba Power Station is still within a range that allows for the ecosystem to continue functioning. It is, however, likely that the doubling of the amount of coal burned within the area will cause exceedances of ion concentrations acceptable to ecosystem functioning, regardless of the significant decrease in volatile matter already discussed.

5.4 An overview of the water quality of the Lephalala, Mokolo and Matlabas Rivers and the potential threats within the Waterberg District Municipality

The Waterberg District Municipality is a rapidly developing metropolis within the Limpopo Province of South Africa. With an increase of 20.5% in the population size (IDP 2014) from 2001 (96 102) to 2011 (115 768) the area is expected to be home to 156 785 people by 2020 and 213 682 people by 2030 (LDPR 2013). This translates into the number of households within the Waterberg District Municipality increasing to approximately 5 times the current number of households. Only 40% of the current population resides within the urban areas while 45% lives within the 34 tribal communities mostly scattered along the Lephalala River (HDA 2013). The remaining 15% is not specified, but it expected to be residing in small informal settlements close to the major employment entities: Exxaro's Grootegeluk mine and ESKOM's Matimba and Medupi power stations.

The water quality within the Waterberg District Municipality is still relatively good when compared to other coal-burning hubs such as the Highveld areas surrounding Witbank and Middelburg in the Mpumalanga Province of South Africa (see McCarthy and Pretorius 2009). The results showing that the rivers upwind of the Matimba Power Station (Lephalala and Mokolo Rivers) showed higher cation and sulphate concentrations and fluxes than the Matlabas River, located downwind of the power station, challenge the knowledge of the micro and meso scale circulation patterns in the area together with the predicted footprint. To date the predicted footprint is generated from modelling studies with little ground based validation.

The difference in cation deposition footprints is possibly due to the rapid ion transformation chemistry in turbulent boundary layers within the plume. A boundary layer is the first one to two kilometres of the atmosphere and its turbulence is determined by the wind speed, temperature and humidity within the layer (Van Ulden and Holtslag 1985). The surface layer (100 to 500 meters) experiences the sharpest gradients in these parameters and is usually the most turbulent. The Matimba power station is approximately 130 meters high with stacks reaching heights of approximately 220 meters (Bohlweki 2006). These are well within the turbulent layer, indicating that turbulence could be responsible for the deposition of cations in close proximity of the power station. The effects thereof can be expected to be measured in the Mokolo River, located only 16.3 kilometers northeast of the power station (Figure 5.4). The small variance in cation flux values measured within the Mokolo River could indicate the consistent input of cations due to deposition from power station plumes. The combustion of coal at the Matimba power station is thus expected to be a contributor to the cation fluxes measured within the Mokolo and Matlabas Rivers, yet is not the significant driver of cation fluxes seen within these rivers. Anthropogenic input are also expected to contribute to the cation fluxes measured within the Mokolo River. Although turbulence is expected to also contribute to the fluxes measured within the Lephalala River, the contribution is expected to less significant due to the river's location and distance from the power station.

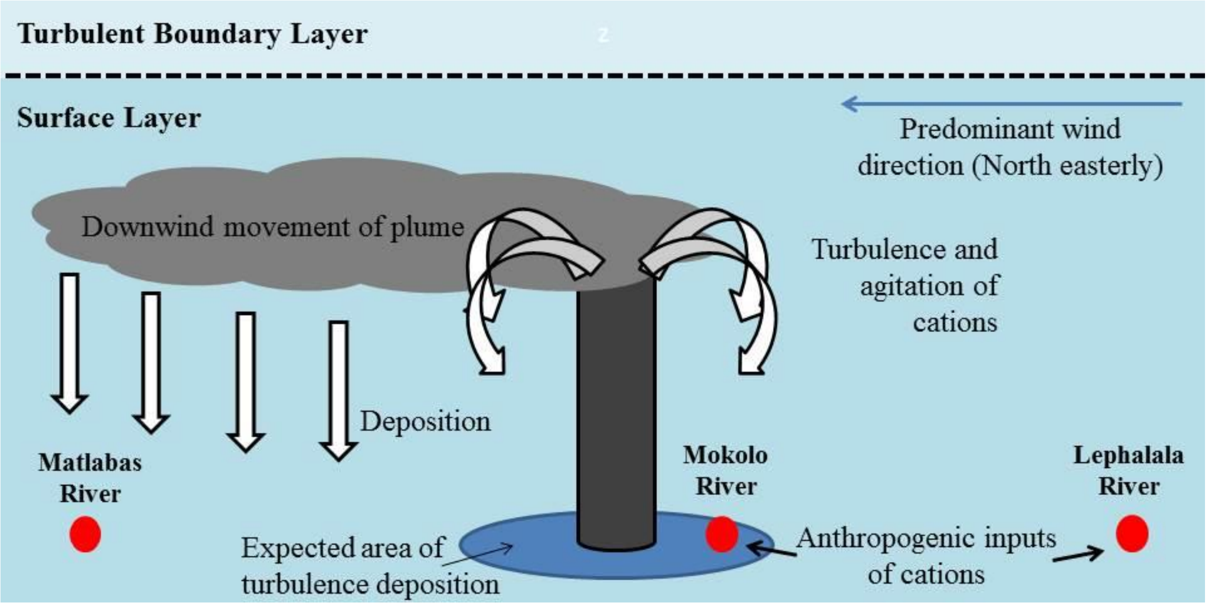
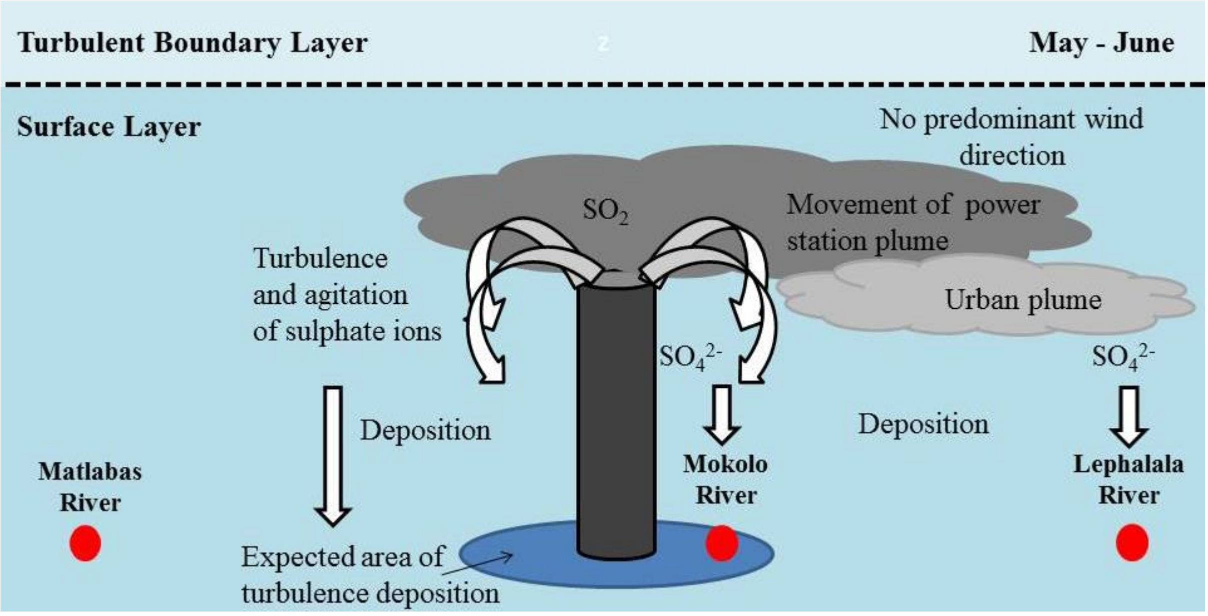


Figure 5.4. A diagrammatic representation of the effect of turbulence on the deposition of cations in close proximity of the Matimba power station. Diagram is not to scale.

Within the Lephalala River Catchment, the indirect effects (increased population size, failing infrastructure) of electricity production are believed to currently far outweigh the direct effects which include the deposition of cations from the station plumes. Although the effects of coal combustion is expected to increase enormously when Medupi Power Station is fully operational, the continual growth of the human population and the increasing backlog in infrastructure is expected to remain the main water quality concern within the larger part of the Waterberg District Municipality.

The drivers of the sulphate deposition footprints for the Mokolo and Matlabas Rivers are expected to be the same as the turbulent processes explained for the cation deposition footprints. The same generalised concept is expected to apply to the Lephalala River for most of the year (July – April), yet a deviation from the model is expected during the months of May and June (Figure 5.5). The north-easterly wind direction is less predominant during these months, with sulphate ions expected to be deposited at further distances “upwind” of the Matimba Power Station during this period.



<u>Figure 5.5</u>. A diagrammatic representation of the relationship between coal usage at the Matimba Power Station and the sulphate fluxes measured in the Lephalala River. This is expected to occur during May and June when the north-easterly wind direction is less predominant. Diagram is not to scale.

Sulphate ions from anthropogenic sources are expected to still contribute to the sulphate concentrations and fluxes measured within the Lephalala River. Other sources of sulphate ions within the Lephalala, Mokolo and Matlabas River Catchments include mining processes, industrial processes, vehicular emissions and residential burning of fossil fuels (Walton and Ngcukana 2009). With the increase in power generation capacity through the construction of the Medupi Power Station, these sources are also expected to increase as development and human population density increases.

The Lephalale Integrated Development Plan for 2015 to 2016 (IDP 2015) indicates that the Municipality has clear goals of how they want to achieve the balance between economic development and sustainable development. While direct attention has been given to the expected consequences of large scale combustion of coal within the area it is even more important to improve the basic livelihoods of those moving into the area in search of employment. Delivering basic sanitation services as well as the improvement of the existing sewerage and waste water networks, transport networks and electricity supply to rural communities has to be prioritised to ensure that development can continue moving forward.

CHAPTER 6: REFERENCES

Ali, E. A. 1993. Damage to plants due to industrial pollution and their use as bioindicators in Egypt. *Environmental Pollution* 81(3): 251 – 255.

Anglo. 2013. *Anglo American Fact Book 2012 / 2013*. Accessed from www.angloamerican.com/~/media/Files/A/Anglo-American-PLC-V2/investors,a-reports/2013rep/AA-Factbook-2012-2013.pdf.

Annandale, J. G., Beletse, Y. G., Stirzaker, R. J., Bristow, K. L. and Aken, M. E. 2009. *Is irrigation with coal-mine water sustainable?* Abstracts of the International Mine Closure Conference, 19th – 23rd October 2009, Pretoria, South Africa.

Bae, H. 2013. Changes of River's Water Quality Responded to Rainfall Events. *Environment and Ecology Research* 1(1): 21 – 25.

Bartram, J. and Balance, R. 1996. (eds.). *Water Quality Monitoring: A practical Guide to the Design of Freshwater Quality Studies and Monitoring Programme.* Published on behalf of UNDP and WHO, Chapman and Hall, London. 383 pp.

Bester, M. 2009. *Groundwater resource assessment of the Waterberg coal reserves.* Master of Science Dissertation, University of the Free State, Bloemfontein, South Africa.

Bester, M. and Vermeulen, P. D. 2010. Investigation of potential water quality and quantity impacts associated with mining of the shallow Waterberg coal reserves, west of the Daarby Fault, Limpopo Province, South Africa. *Water SA* 36(5): 531 – 542.

Bohlweki. 2006. *Environmental Impact Assessment Report for the Proposed Establishment of a New Coal-Fired Power Station in the Lephalale Area, Limpopo Province.* Bohlweki Environmental (Pty) Ltd, Final Report, Ref no: 12/12/20/695.

Boroto, R. A. J. 2001. Limpopo River: Steps towards sustainable and integrated water resource management. *Regional Management of Water Resources*, Proceedings of a Symposium held during the 6th IAHS Scientific Assembly at Maastricht, The Netherlands, July 2001.

Bothma, A. 1998. *A generic environmental management plan for coal-fired power stations*. Masters of Science, Rand Afrikaans University, Johannesburg.

Burne, C. 2015. *Macro-nutrient and hydrological trends in some streams of the Waterberg, Limpopo: investigating the effects of land use change in catchment water quality*. Master of Science Dissertation, University of the Witwatersrand, Johannesburg, South Africa.

Busari, O. 2008. Groundwater in the Limpopo Basin: occurrence, use and impact. *Environment, Development and Sustainability* 10(6): 943 – 957.

Cairncross, B. 2001. An overview of the Permian (Karoo) coal deposits of southern Africa. *African Earth Sciences* 33(3-4): 529 – 562.

Calkins, W. H. 1994. The chemical forms of sulphur in coal: a review. *Fuel* 73(4): 475 – 484.

Cánovas, C. R., Hubbard, C. G., Olias, M., Nieto, J. M., Black, S. and Coleman, M. L. 2008. Hydrochemical variations and contaminant load in the Rio Tinto (Spain) during flood events. *Journal of Hydrology* 350(1-2): 24 – 40.

Carpenter, S. R. and Lodge, D. M. 1986. Effects of submerge macrophytes on ecosystem processes. *Aquatic Botany* 26(3-4): 341 – 370.

Charles, D. F. (ed.). 1991. *Acidic Deposition and Aquatic Ecosystems. Regional Case Studies*. New York: Springer-Verlag.

Chilundo, M., Kelderman, P. and O'Keeffe, J. H. O. 2008. Design of a water quality monitoring network for the Limpopo River Basin in Mozambique. *Physics and Chemistry of the Earth* 33(8-13): 655 – 665.

Clark, P. A., Fletcher. I. S., Kallend, A. S., McElroy, W. J., Marsh, A. R. W. and Webb, A. H. 1984. Observations of cloud chemistry during long-range transport of power plant plumes. *Atmospheric Environment* 18(9): 1849 – 1858.

Conant, R. T., Ryan, M. G., Agren, G. I., Birge, H. E., Davidson, E. A., Eliasson, P. E., Evans, S. E., Frey, S. D., Giardina, C. P., Hopkins, F. M., Hyvonen, R., Miko, U., Kirschbaum, F., Lavallee, J. M., Leifeld, J., Parton, W. J., Steinweg, J. M., Wallenstein, M. D., Wetterstedt, J. A. M. and Bradford, M. A. 2011. Temperature and soil organic matter decomposition rates – synthesis of current knowledge and a way forward. *Global Change Biology* 17(11): 3392 – 3404.

Cox, R. A. and Penkett, S. A. 1972. Aerosol formation from sulphur dioxide in the presence of ozone and olefinic hydrocarbons. *Journal of the Chemical Society, Faraday Transactions 1* 68: 1735 – 1753.

DEA. 2009. *National Environmental Management: Air Quality Act, 2004 (Act No. 39 of 2004): National Ambient Air Quality Standards*. Department of Environmental Affairs. Government Gazette, 24 December 2009.

DEA. 2010. Department of Environmental Affairs: Environmental Management Framework for the

Waterberg District, Status Quo Report. 281 pp.

De Klerk, A. 2003. *The Waterberg Biosphere Reserve: A land use model for ecotourism development.* Master of Science Dissertation, University of Pretoria.

Delpha, I., Jung, A-V., Baures, E., Clement, M. and Thomas, O. 2009. Impacts of climate change on surface water quality in relation to drinking water production. *Environment International* 35(8): 1225 – 1233.

Dhemba, N. 2013. *Compilation of an application for exemption from minimum emission standards and extension of the minimum emission standard timeframes for ESKOM's power stations: Water Resources Assessment*. ILISO Consulting (Pty)Ltd, October 2013, ESKOM Project number PO 4501425553.

Dittenhoefer, A. C. and De Pena, R. G. 1980. Sulphate aerosol production and growth in coal-operated power plant plumes. *Journal of Geophysical Research* 85(C8): 4499 – 4506.

Donaldson, J.S. 2010. *Encephalartos eugene-maraisii*. The IUCN Red List of Threatened Species 2010: e.T41904A10587250. http://dx.doi.org/10.2305/IUCN.UK.20103.RLTS.T41904A10587250.en. Downloaded on **18 February 2016**.

Driscoll, C. T., Lawrence, G. B., Bulger, A. J., Butler, T. J., Cronan, C. S., Eager, C., Lambert, K. F., Likens, G. E., Stoddard, J. L. and Weathers, K. C. 2001. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. *BioScience* 51(3): 180 – 198.

Ducharne, A. 2008. Importance of stream temperature to climate change impact on water quality. *Hydrology and Earth System Sciences* 12(3): 797 – 810.

DWA. 2010. *Hydrogeological Assessment and Aquifer Recharge Potential within the Lephalale (Ellisras) Local Municipality Area*. Department of Water Affairs, Republic of South Africa.

DWA. 2013. *Joint Water Quality Baseline Report: Limpopo Basin between the Republic of Botswana and South Africa*. Departments of Water Affairs of Botswana and South Africa, August 2013.

Eberhard, A. 2011. *The Future of South African Coal: Market, Investment, and Policy Challenges*. Program on Energy and Sustainable Development, Working Paper #100, January 2011.

Engelbrecht, J. and Bills, R. 2007. *Barbus sp. nov. 'Waterberg'*. *In*: IUCN 2013. IUCN Red List of Threatened Species. Version 2013.2. www.iucnredlist.org. Downloaded on 5 May 2014.

EPA. 2003. *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Sulfate*. United States Environmental Protection Agency, EPA 822-R-03-007, February 2003.

EPA. 2013. National Ambient Air Quality Standards for Particulate Matter. *Federal Register* 78: 3086 – 3287.

Eskom. 2013. *Interim Integrated Report for the six months ended 30 September 2013*. Eskom Holdings SOC Limited.

Evans, D. H., Piermarini, P. M. and Choe, K. P. 2005. The multifunctional fish gill: dominant site of gas exchange, osmoregulation, acid-base regulation, and excretion of nitrogenous waste. *Physiological Review* 85(1): 97 – 177.

Gaffney, J. and Marley, N. 2009. The Impacts of Combustion Emissions on Air Quality and Climate – From Coal to Biofuels and Beyond. *Atmospheric Environment* 43(1): 23 – 36.

Galloway, J. N., Likens, G. E., Keene, W. C. and Miller, J. M. 1982. The composition of precipitation in remote areas of the world. *Journal of Geophysical Research* 87(C11): 8771 – 8786.

Germs, W., Coetzee, M. S., Van Resnburg, L. and Maboeta, M. S. 2004. A preliminary assessment of the chemical and microbial water quality of the Chunies River – Limpopo. *Water SA* 30(2): 267 – 272.

Gillani, N. V., Kohli, S. and Wilson, W. E. 1981. Gas-to-particle conversion of sulphur in power plant plumes – 1. Parameterization of the conversion rate for dry, moderately polluted ambient conditions. *Atmospheric Environment* 15(10-11): 2293 – 2313.

Gordon, A. G. and Gorham, E. 1963. Ecological Aspects of Air Pollution from an Iron-Sintering Plant at Wawa, Ontario. *Canadian Journal of Botany* 41(7): 1063 – 1078.

Görgens, A. H. M. and Boroto, R. A. J. 1999. Limpopo River: hydrological investigations to prepare for integrated water resources planning. *Proceedings of the 9th SA National Hydrological Symposium*, SANCIAHS, Cape Town, South Africa.

GOSA-DWAF. 2003. *Limpopo Water Management Area Overview of water resources availability and utilization*. Government of South Africa – Department of Water Affairs and Forestry.

Greenwood, N. N. and Earnshaw, A. 1984. *Chemistry of the Elements*. Pergamon Press, Oxford, England.

Hamilton, S. K. 2010. Biogeochemical implications of climate change for tropical rivers and floodplains. *Hydrobiologia* 657(1): 19 – 35.

HDA. 2013. *Lephalale Local Municipality Municipal Profile*. Housing Development Agency, South

Africa.

Held, G. and Mphepya, J. 2000. Wet and dry deposition in South Africa. XI Congresso Brasiliero de Meteorologia, Rio de Janeiro, 16 – 20 October 2002, Paper QA00002, 2824 – 2833.

Henning, B. J. 2006. The relevance of ecosystems to ecotourism in the Waterberg Biosphere Reserve. PhD Thesis, University of Pretoria, Pretoria.

Hewitt, C. N. 2001. The Atmospheric Chemistry of Sulphur and Nitrogen in Power Station Plumes. *Atmospheric Environment* 35(7): 1155 – 1170.

Hooda, P. S., Rendell, A. R., Edwards, A.C., Withers, P. J. A., Aitken, M.N. and Truesdale, V.W. 2000. Relating Soil Phosphorus Indices to Potential Phosphorus Release to Water. *Journal of Environmental Quality* 29: 1166 – 1171.

Hsieh, K. C. and Wert, C. A. 1985. Direct measurement of organic sulphur in coal. *Fuel* 64(2): 256 – 262.

IDP. 2008. *Lephalale Municipality: Integrated Development Plan Review 2008 – 2009.* Lephalale Municipality, South Africa.

IDP. 2014. *Lephalale Municipality: Integrated Development Plan 2014 – 2016.* Lephalale Municipality, South Africa.

IDP. 2015. *Waterberg District Municipality Integrated Development Plan 2015 – 2016.* Waterberg District Municipality, South Africa.

Itzkin, A. 2012. Baseline data (soils, lichens and EIAs) needed to measure impacts of Eskom’s Medupi Power Station in the Waterberg Priority Area. BSc Honours Research Report, School of Animal, Plant and Environmental Sciences, University of the Witwatersrand, Johannesburg.

Jenkins, C. 2005. *Nutrient flux assessment in Port Waterways*. Environmental Protection Authority. Adelaide, South Australia.

Josipovic, M., Anegarn, H. J., Kneen, M. A., Pienaar, J. J. and Piketh, S. J. 2011. Atmospheric dry and wet deposition of sulphur and nitrogen species and assessment of critical loads of acidic deposition exceedance in South Africa. *South African Journal of Science* 107: 1 – 10.

Kalenga, P. M., Cukrowska, E., Tutu, H. and Chimuka, L. 2011. Characterization of South African coal for metals, inorganic and organic sulphur compounds. *South African Journal of Chemistry* 64: 254 – 262.

Kirchman, D. L. 2012. *Processes in Microbial Ecology*. New York: Oxford University Press.

Kuylenstierna, J. C. I., Rodhe, H., Cinderby, S., Hicks, K. 2001. Acidification in developing countries: Ecosystem sensitivity and the critical load approach on a global scale. *Ambio* 30(1): 20 – 28.

LDPR. 2013. *Lephalale CBD Development Plan*. Lephalala Municipality, South Africa.

Liebenberg-Enslin, H., Thomas, R., Walton, N. and van Nierop, M. 2007. *Vall Triangle Priority Area Air Quality Management Plan – Baseline Characterisation*. Project completed in May 2007 by Airshed Planning Professionals (Pty) Ltd, Gondwana Environmental Solutions (Pty) Ltd and Zitholele Consulting on behalf of the Department of Environmental Affairs and Tourism, Pretoria.

Liebsch, E. J. and De Pena, R. G. 1982. Sulphate aerosol production in coal-fired power plant plumes. *Atmospheric Environment* 16(6): 1323 – 1331.

Likens, G. E., Driscoll, C. T. and Buso, D. C. 1996. Long-Term Effects of Acid Rain: Response and Recovery of a Forest Ecosystem. *Science* 272(5259): 244 – 246.

Luria, M., Olszyna, K. J. and Meagher, J. F. 1983. The atmospheric oxidation of flue gases from a coal-fired power plant: a comparison between smog chamber and airborne plume sampling. *Journal of the Air Pollution Control Association* 483 – 487.

Mackintosh, G. S., De Souza, P. F. and De Villiers, H. A. 2002. *Design and operation guideline for municipal sized surface water limestone contactors*. Paper presented at the Biennial Conference of the Water Institute of Southern Africa (WISA), 19 – 23 May 2002, Durban, South Africa.

Mainganye, D., Ojumu, T. V. and Petrik, L. 2013. Synthesis of Zeolites Na-P1 from South African Coal Fly Ash: Effect of Impeller Design and Agitation. *Materials* 6(5): 2074 – 2089.

Maré, J. 2013. *Environmental Impact Assessment Report for the Proposed Thabametsi Coal-Fired Power Station in a Site near Lephalale, Limpopo Province*. Savannah Environmental (Pty) Ltd, 12 June 2013, Report no. 2013/06/IPP/SW/01/R1.

Marquard, A. 2007. The development of energy policy in South Africa, PhD Thesis, University of Cape Town, South Africa.

Matowanyika, W. *Impact of Alexandra Township on the Water Quality of the Jukskei River.* Master of Science Dissertation, University of the Witwatersrand, Johannesburg, South Africa.

McCarthy, T. S. and Pretorius, K. 2009. *Coal mining on the Highveld and its implications for future water quality in the Vaal River System.* Abstracts of the International Mine Water Conference, 19th – 23rd October 2009, Pretoria, South Africa.

McGonigle, A. J. S., Delmelle, P., Oppenheimer, C., Tsanev, V. I., Delfosse, T., Williams-Jones, G., Horton, K. and Mather, T. A. 2004. SO_2 depletion in tropospheric volcanic plumes. *Geophysical Research Letters* 31: L13201, 4 pgs.

McKerall, W. C., Ledbetter, W. B. and Teague, D. J. 1982. *Analysis of Fly Ashes Produced in Texas.* Texas Transportation Institute, Report No. 240-1, Texas A&M University, College Station, Texas.

Meagher, J. F. and Luria, M. 1982. Model calculations of the chemical processes occurring in the plume of a coal-fired power plant. *Atmospheric Environment* 16(2): 183 – 195.

Merolla, S. 2011. *The effects of floods and high rainfall in the water quality in the selected sub-areas of the Upper Vaal Catchment.* Master of Science Dissertation, University of Johannesburg, South Africa.

Meyers, J. F., Pichumani, R. and Kapples, B. S. 1976. *Fly ash. A Highway Construction Material.* Federal Highway Administration, Report No. FHWA-IP-76-16, Washington, DC.

Murrell, S. 2011. How does one pH compare to another? *Better Crops* 95: 27.

Muthige, M. S. 2013. *Ambient air quality impacts of a coal-fired power station in Lephalale area.* Master of Science Dissertation, University of the Witwatersrand, Johannesburg, South Africa.

Oberholster, P. J., Ashton, P. J., Fritz, G. B. and Botha, A-M. 2010. First report on the colony-forming freshwater ciliate *Ophrydiumversatile* in an African river. *Water SA* 36: 315 – 322.

Olivella, M. A., Palacios, J. M., Vairavamurthy, A., del Rio, J. C. and De las Heras, F. X. C. 2002. The study of sulphur functionalities in fossil fuels using destructive- (ASTM and Py – GC – MS) and non-destructive- (SEM – EDX, XANES and XPS) techniques. *Fuel* 81(4): 405 – 411.

Olivier, J., Van Nieker, H. J. and Van der Walt, I. J. 2008. Physical and chemical characteristics of thermal springs in the Waterberg area in Limpopo Province, South Africa. *Water SA* 34(2): 163 – 174.

OSPAR. 1998. *Principles of the Comprehensive Study in Riverine Inputs and Direct Discharges (RID).* OSPAR Report 1998-5. 17pp.

Pienaar, F. C. 2006. *A plant ecological evaluation of mechanical bush thinning in Marakele Park, Limpopo Province*. Master of Science Dissertation, University of the Free State, Bloemfontein, South Africa.

Pilgrim, D. H. 1987. (ed.) *Australian Rainfall and Runoff: A Guide to Flood Estimation.* Institution of Engineers, Canberra, Australia.

PlanPractice 2004. *Environmental Impact Assessment for the Proposed Matimba-Witkop No. 2400 kV Transmission Line, Limpopo Province: Specialist Study – Land Use Implications*. PlanPractice Town Planners, Menlo Park, Pretoria, South Africa.

Raymond, S., Moatar, F., Meybeck, M. and Bustillo, V. 2013. Choosing methods for estimating dissolved and particulate riverine fluxes from monthly sampling. *Hydrological Sciences Journal* 58(6): 1326 – 1339.

Richards, L. W., Anderson, J. A., Bulmenthal, D. L., Brandt, A. A., McDonald, J. A., Watus, N., Macias, E. S. and Bhardwaja, P.S. 1981. The chemistry, aerosol physics, and optical properties of a western coal-fired power plant plume. *Atmospheric Environment* 15(10-11): 2111 – 2134.

Richards, R. P. 1998. *Estimation of Pollutant Loads in Rivers and Streams: A Guidance Document for NPS Programs*. US Environmental Protection Agency, Region VIII.

Rorich, R. P. and Turner, C. R. 1994. *Ambient monitoring network annual data report for 1993 and regional long-term trend analysis.* Eskom report no. TRR/S94/059.

Ryan, B. 2014. New coal report raises strategic questions. Available online: http://www.bdlive.co.za/business/mining/2014/04/23/new-coal-report-raises-strategic-questions.

SAWQG. 1996. *South African Water Quality Guidelines (1st Edition).* Edited by S Holmes, CSIR Environmental Services, Pretoria, South Africa.

Scheifinger, H. and Held, G. 1997. Aerosol behaviour on the South African Highveld. *Atmopsheric Environment* 31(21): 3497 – 3509.

Schoeneberger, P. J., Wysocki, D. A., Benham, E. C. and Broderson, W. D. 1998. *Field Book for Describing and Sampling Soils: Version 1.1*. National Soil Survey Center, Natural Resources Conservation Service, US Department of Agriculture, Lincoln, Nebraska.

Scorgie, Y. and Kornelius, G. 2009. Modelling of acid deposition over the South African Highveld. Paper presented at the annual South African National Association for Clean Air Conference, 14 – 16 October 2009, Vanderbijlpark, South Africa.

Singh, G. 1988. Impact of Coal Mining on Mine Water Quality. *International Journal of Mine Water* 7(3): 49 – 59.

Sipauba-Tavares, L. H., Guariglia, C. S. T. and Braga, F. M. S. 2007. Effects of rainfall on water quality in six sequentially disposed fishponds with continuous water flow. *Brazilian Journal of Biology* 67(4): 643 – 649.

Skoroszewski, R. 1999. *Specialist Report: Water quality.* Lesotho Highlands Development Authority Report no LHDA 648-F-15. Metsi Consultants / Southern Waters Ecological Research and Consulting, Freshwater Research Unit, University of Cape Town.

Tansley, A. G. 1935. The Use and Abuse of Vegetational Concepts and Terms. *Ecology* 16(3): 284 – 307.

Thomas, R. and Scorgie, Y. 2006. Air Quality Impact Assessment for the Proposed New Coal-Fired Power Station (Kendal North) in the Witbank Area. *Ninham Shand Consulting Services*, Report No.: APP/06/NMS-01 Rev 0.3.

Tilt, B. 2006. Perceptions of Risk from Industrial Pollution in China: A Comparison of Occupational Groups. *Human Organization* 65(2): 115 – 127.

Trebs, I., Lara, L. L., Zeri, L. M. M., Gati, L. V., Artaxo, P., Dlugi, R., Slanina, J., Andreae, M. O. and Meixner, F. X. 2006. Dry and wet deposition of inorganic nitrogen compounds to a tropical pasture site (Rondonia, Brazil). *Atmospheric Chemistry and Physics* 6(2): 447 – 469.

Van Der Merwe, E. M., Prinsloo, L. C., Mathebula, C. L., Swart, H. C., Coetsee, E. and Doucet, F. J. 2014. *Surface and bulk characterization of an ultrafine South African coal fly ash with reference to polymer applications*. University of Pretoria, South Africa.

Van Niekerk, H. 2004. *South African-UNEP GEMS/Water: Monitoring Programme Design.* DWAF-RQS Report Number: N/0000/00/REQ0604. Pretoria, South Africa.

Van Ulden, A. P. and Holtslag, A. A. M. 1985. Estimation of Atmospheric Boundary Layer Parameters for Diffusion Applications. *Journal of Climate and Applied Meteorology* 24: 1196 – 1207.

Van Vliet, M. T. H. and Zwolsman, J. J. G. 2008. Impact of summer droughts on the water quality of the Meuse River. *Journal of Hydrology* 353(1-2): 1 – 17.

Verheul. J. K. 2012. *Assessing the effects of different land uses on water quality in the Upper Wilge River Catchment*. Master of Science Dissertation, University of Johannesburg, South Africa.

Verstraeten, G. and Poesen, J. 2001. Factors controlling sediment yield from small intensively cultivated catchments in a temperate humid climate. *Geomorphology* 40(1-2): 123 – 144.

Verstraeten, G., Poesen, J., de Vente, J. and Koninck, X. 2003. Sediment yield variability in Spain: a quantitative and semiqualitative analysis using reservoir sedimentation rates. *Geomorphology* 50(4): 327 – 348.

Vet, R., Artz, R. S., Carou, S., Shaw, M., Ro, C., Aas, W., Baker, A., Bowersox, V., Dentener, F., Galy-Lacaux, C., Hou, A., Pienaar, J. J., Gillett, R., Forti, M. C., Gromov, S., Hara, H., Khodzher, T., Mahowald, M. N., Nickovic, S., Rao, P. S. P. and Reid, N. W. 2014. A Global Assessment of Precipitation Chemistry and Deposition of Sulfur, Nitrogen, Sea Salt, Base Cations, Organic Acids, Acidity and pH, and Phosphorous. *Atmospheric Environment* 93: 3 – 100.

Wade, T. J., Calderon, R. L., Brenner, K. P., Sams, E., Beach, M., Haugland, R., Wymer, L., Dufour, A. P. 2008. High sensitivity of children to swimming-associated gastrointestinal illness: results using a rapid assay of recreational water quality. *Epidemiology* 19(3): 375 – 383.

Wagner, N. J. and Hlatshwayo, B. 2005. The occurrence of potentially hazardous trace elements in the five Highveld coals, South Africa. *Coal Geology* 63(3-4): 228 – 246.

Walton, N. and Ngcukana, N. 2009. *Waterberg District Municipality Air Quality Management Plan*. Gondwana Environmental Solutions, June 2009.

Whitehead, P. G., Wilby, R. I., Battarbee, R. W., Kernan, M., Wade, A. J. 2009. A review of the potential impacts of climate change on surface water quality. *Hydrological Sciences Journal* 54(1): 101 – 123.

WHO. 2003. *pH in Drinking-wate: Background document for development of the WHO Guidelines for Drinking-water Quality*. World Health Organisation, Report No. WHO/SDE/WHO/03.04/12.

Yu, B., Rose, C. W., Ciesiolka, C. C. A. and Cakurs, U. 2000. The relationship between runoff rate and lag time and the effects of surface treatments at the plot scale. *Hydrological Sciences Journal* 45(5): 709 – 726.

Zacharia, J. T. 2011. Identity, Physical and Chemical Properties of Pesticides, *in* Stoytcheva, M. (ed.) *Pesticides in the Modern World – Trends in Pesticides Analysis*. InTech, 388 pp.

Zhou, G., Goel, N. K. and Bhatt, V. K. 2002. Stochastic modelling of the sediment flux of the Upper Yangtze River (China). *Hydrological Sciences Journal* 47: S93 – S105.

Zunckel, M. 1999. Dry deposition of sulphur over eastern South Africa. *Atmospheric Environment* 33(21): 3515 – 3529.

Zunckel, M. and Raghunandan, A. 2013. *Atmospheric Impact Report: In support of Eskom's* *application for postponement of the Minimum Emission Standards compliance timeframes for the Duvha Power Station*. Report No. uMN043-2013, December 2013, U-Moya-NILU Consulting (Pty) Ltd.