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LINKING STREAMWATER QUALITY OF THE UPPER VAAL RIVER CATCHMENT AREA TO ACID DEPOSITION

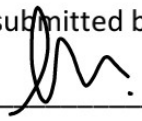
Isabel Mbewe

A Research Report submitted to the Faculty of Science, University of Witwatersrand, Johannesburg, in partial fulfilment for the degree of Master of Science (Course work and research report)

Johannesburg, 2017

DECLARATION

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



_____

(Isabel Mbewe)

_21st_ day of _September_ 20 _17_ in _Johannesburg_

ABSTRACT

Acid deposition is the conveyance of acidic compounds predominantly oxides of nitrogen and sulphur, acids, and salts from the atmosphere to the earth's surface. It has detrimental effects on both terrestrial and aquatic ecosystems. The concentration of industrial structure over the Highveld region of South Africa makes it a prominent air pollution area accounting for approximately 90% of South Africa's scheduled emissions of industrial dust, sulphur dioxide and nitrogen oxides. The high pollution levels mean the Highveld region is an acid deposition hotspot. This paper investigated the link between stream water quality and acid deposition by precluding the influence of land use and catchment geology on water quality in the Upper Vaal. The study catchments within the Upper Vaal Water Management Area were delineated using digital elevation model data in ArcGIS. A total of 3970 polygons were derived from the delineation with each polygon representing a distinct catchment drained by a distinct stream which is part of a larger network of streams draining the Upper Vaal Water Management Area. The derived catchment polygons were characterised with land cover and geology using GIS tools. Spatial analysis was conducted to identify headwater catchments drained by first order streams with at least 95% natural landcover. 148 catchments meet this criterion, representing 4.51% of total catchment area in the Upper Vaal. Forty-two (42) study sites representing 1.22% of total catchment area were selected from among the 148 catchments with < 5% human activity by increasing linear distance of sample catchments from Majuba power station, assumed to represent a deposition gradient. All catchments with > 5% human activities or whose upper polygons include such activities were excluded. In situ measurements of pH, conductivity and dissolved oxygen were made at study sites while collected stream water samples were analysed for nitrate, sulphate and chloride ions in the laboratory. A multivariate general linear model used to predict the significance, magnitude and direction of relationships among the variables revealed that modelled wet sulphur deposition, fine grained sandstone and siltstone, as well as red and greenish grey mudstone with sandstone generally have no substantial impact on stream water quality in the studied headwater catchments of the Upper Vaal. Dolerite geology shows a significant effect on conductivity and sulphate concentrations. It accounts for approximately 16% and 17% of multivariate variance of conductivity and sulphate concentrations respectively observed in the studied catchments. An important link exists between distance from Majuba power

station and stream water quality. Distance from the power station is markedly associated with stream water conductivity, pH, SO_4^{2-} and Cl^- but not NO_3^- . It accounts for approximately 14% of multivariate variance of conductivity, 13.3% of pH, 35% of Sulphate concentration and 15% of chloride concentration. The trend of better stream water quality as one moves away from Majuba power station which is assumed to be a proxy for total deposition (including S and N but also base cations which contribute to salinity), and because distance accounts for the larger portion of variance observed in water quality, strongly suggests that proximity to emission sources has a more significant influence on stream water quality than other factors in the Upper Vaal. An important relationship between water quality and acid deposition may therefore exist.

DEDICATION

In memory of my father

Orton Tony Mbewe

1949 – 2008

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The completion of this study could not have been possible without the constant guidance, support and suggestions of Prof. Christopher Curtis in the School of Geography, Archaeology and Environmental Studies at the University of Witwatersrand throughout the project. Thank you for also taking time off your busy schedule to do long hours of sampling campaigns with me in very remote places.

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LIST OF SYMBOLS

˚C	degrees Celsius
Keq H^+ $km^{-2}yr^{-1}$	Acid deposition flux (Kilo equivalents of hydrogen ions flux per square kilometre per year)
Kg ha^{-1} yr^{-1}	kilograms per hectare per year
m	Metres
mgl^{-1}	milligrams per litre
ml	Millilitres
mm	Millimetres
nm	nanometres
pH	Potential of hydrogen
ppb	Parts per billion
α	alpha
µl	microlitre
μScm^{-1}	micro Siemens per centimetre

NOMENCLATURE

Cl^-	Chloride ion
DEM	Digital Elevation Model
DVs	Dependent variables
GIS	Geographical information system
HCl	Hydrogen chloride / hydrochloric acid
HNO_3	Nitric acid
H_2O_2	hydrogen peroxide
HSO_3	Hydrogen thiosulphite
InSAR or IfSAR	Interferometric Synthetic Aperture Radar
IVs	Independent variables
LIDAR	Light Detection and Ranging
LULC	Landuse Landcover
NO_2	Nitrogen dioxide
NO_3^-	Nitrate ion
NO_X	Oxides of nitrogen
O_3	Ozone
OH	Hydroxyl ion
SO_2	Sulphur dioxide
SO_4^{2-}	Sulphate ion
SRTM	Shuttle Radar Topography Mission
SPSS	Statistical Package for the Social Sciences
VOC	Volatile Organic Compound

CHAPTER ONE – INTRODUCTION

1.1 GENERAL INTRODUCTION

The occurrence of acids in precipitation is linked to increasing levels of anthropogenic gaseous atmospheric pollutants specifically sulphur and nitrogen oxides (Andersson and Rodhe, 1982; Cowling and Linthurst, 1981, 1981; Gorham, 1982). Sulphur dioxide can be converted chemically in the atmosphere to sulphuric acid, while nitrogen oxides formed primarily during the combustion of fossil fuels, can be converted to nitric acid. Consequent to being formed in the atmosphere, the acids fall to the earth in the form of wet and dry deposition, commonly referred to as acid precipitation (Adams, 2012; Gilliam, 1987; Graedel and Crutzen, 1989; Rogora et al., 2001; Smith, 1872). While natural rain water is slightly acidic with a pH of 5 to 6 mainly because of dissolved carbon dioxide which produces carbonic acid, pH of precipitation in industrialised regions is usually less than 5 due to emissions of sulphur dioxide and oxides of nitrogen into the atmosphere (Bybee, 1983). Large quantities of sulphur dioxide and nitrogen oxide emissions emanate from industrialized regions covering less than five percent of the earth's surface: China; Eastern North America; Japan; and Europe. Southern Africa is also a significant source region of atmospheric pollutants (Martins et al., 2007; Venter et al., 2012). Factors such as distribution of anthropogenic sources, contribution of natural sources and meteorology influence acid deposition (Adams, 2012).

Various authors suggest that acid precipitation is responsible for substantial adverse effects - the wet and dry deposition of acidic precursors and oxidants may lead to acidifying reactions in the terrestrial and aquatic ecosystems (Cowling and Linthurst, 1981; Eriksson, 1989; Galloway, 1996; Gorham, 1998; Greaver et al., 2012; Lars Emmelin, 1976; Likens et al., 1979; Reuss and Johnson, 2012; Schindler, 1988). Some of the environmental consequences of acid deposition which can be quantified on the basis of extensive studies include:

- deterioration of statues and monuments, stone facings on buildings, metal structures, and painted surfaces on homes and automobiles (Cowling, 1982);
- possible reductions in forest productivity, damage to agricultural crops, and increased stress on other vegetation systems (Abrahamsen and Miller, 1984);

- acidification and demineralization of soils and consequent reductions in soil fertility and possibly irreversible changes in soil geochemistry (Adams, 2012; Andersson and Rodhe, 1982; Asano and Uchida, 2005);
- mobilization and leaching of toxic heavy metals and other cations from the soils into ground and surface waters leading to contamination of drinking water supplies;
- acidification of fresh water lakes and reservoirs and damage to fish and other aquatic organisms (Adams, 2012; Baker et al., 1991; Driscoll et al., 2001; Nikolaidis et al., 1989).

1.2 PROBLEM STATEMENT

South Africa has the largest industrialised economy in Africa and one of the largest industrialised economies in the southern hemisphere. It is also the only industrialised regional energy producer on the African continent (Held, 1996; Josipovic et al., 2011; Venter et al., 2012). A large portion of its industrial structure is concentrated on the Highveld plateau, and accounts for approximately 90% of South Africa's scheduled emissions of industrial dust, sulphur dioxide and nitrogen oxides and has thus been identified and declared a national air pollution priority area. Global maps of nitrogen dioxide (NO_2) satellite retrievals show the South African Highveld as a notable $N0_2$ hotspot, and 1990 statistics indicate that globally South Africa was the ninth highest atmospheric sulphur emitting country (Venter et al., 2012). Areas that are located downwind from these major emission sources have been shown to be acid sensitive (Hallowes and Groundwork, 2014; Held, 1996; Kuylenstierna et al., 2001; Josipovic et al., 2011; Lloyd, 2011; Lourens et al., 2012; Scorgie and Kornelius, 2009; Venter et al., 2012). Acid deposition is therefore a major concern in the region given high emission levels of acidic precursors.

This study investigated the link between acid deposition and stream water quality in selected natural headwater catchments (i.e. headwater catchments which preclude cultivation, plantations, mines, and urban build-up) within the Upper Vaal Water Management Area. The selection of natural headwater catchments as sample sites and exclusion from the study of all catchments which include anthropogenic activities guaranteed that the water chemistry of streams that were sampled could have only been influenced by either catchment geology, acid deposition or a combination of catchment geology and acid deposition. In pristine

catchments nitrates, sulphates and chlorides are largely cycled and retained within these systems with marginal discharge to ground and surface water unless they are exposed to pollution (Curtis et al., 1998; Evans et al., 2011; Helliwell et al., 2001). The pH and salinity of stream waters are mainly determined by geology and soil characteristics in natural catchments (Langan and Wilson, 1992).

1.3 RESEARCH QUESTIONS

I. What influence does geology of natural catchments (i.e. catchments that exclude cultivation, plantations, mines, and urban build-up) within the Upper Vaal have on stream water quality with respect to pH, conductivity, as well as loadings of sulphate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-) ions?

II. How does modelled acid deposition influence stream water quality in natural headwater catchments across the Upper Vaal?

III. Is there a link between stream water quality of natural catchments and their distance from Majuba power station assumed to be a proxy for total deposition (including S and N but also base cations which contribute to salinity).

1.4 AIMS

I. To link stream water quality in Upper Vaal to acid deposition by precluding the influence of catchment geology and land use and land cover (LULC) on water quality.

II. To determine whether there is a link between stream water quality of natural headwater catchments and their distance from Majuba power station.

1.5 OBJECTIVES

I. To identify natural headwater catchments across the Upper Vaal using GIS techniques and analyse their stream waters for pH, conductivity, as well as loadings of SO_4^{2-}, NO_3^- and Cl^-.

II. To use a multivariate general linear model to examine linkages between geology, acid deposition, distance from Majuba power station and stream water pH,

conductivity, as well as loadings of SO_4^{2-}, NO_3^- and Cl^- and to quantify the significance, magnitude and direction of relationships among the variables.

1.6 STRUCTURE OF THE REPORT

This report is organized in six distinct chapters. Chapter one gives a general introduction of the study: it briefly discusses the problem of acid deposition; and summarizes goals as well as objectives of the study. Chapter two reviews literature on acid deposition – it defines the acid deposition issue, outlines a historic perspective of the problem and also reviews the chemistry of acid precipitation. It further deliberates on the limitations of the data as well as instruments of measure used in the study. Chapter three provides a general description of the study area including its location, geology, topography and main economic activities. Chapter four discusses the research methods engaged. It summarizes: data and GIS methods employed in identifying sample sites; the water sampling strategy; as well as laboratory methods for stream water sample analysis. Chapter five is a presentation of the results of the GIS and water analyses as well as the statistical modelling. Chapter six discusses the findings and interprets the outcomes of the statistical model, it also makes conclusions based on the results of the statistical analyses.

CHAPTER TWO – LITERATURE REVIEW

This literature review defines acid deposition and provides an overview of the historic perspective of the acid deposition problem. It discusses: the chemistry of acid precipitation; the characteristics of acid sensitive areas; how soil, geology, vegetation as well as LULC influence stream water quality; and the main effects of acid deposition. It further summaries literature on the data and instruments of measure utilised in the study.

2.1 DEFINING ACID DEPOSITION

Acid deposition is the conveyance of acidic elements predominantly oxides of nitrogen and sulphur, acids as well as salts from the atmosphere to the earth's surface (Adams, 2012; Ellerman, 2000; Schwartz, 1989). Though these compounds can be introduced into the atmosphere through natural processes such as volcanic eruptions and decomposition of organic matter, in industrialized areas where coal containing sulphur is extensively used in power generation they are released at rates that substantially overshoot natural emission (Graedel and Crutzen, 1989; Schindler, 1988; Schwartz, 1989; Whelpdale et al., 1997). It is now well established that globally natural sources of sulphur emissions i.e. volcanoes, bogs, marshes, tide flats, other soils and vegetation are insignificant relative to emissions from anthropogenic activities (Adams, 2012).

Acid deposition comprises the settling of these released materials and the products of their reactions in the atmosphere. It can be either wet or dry. Wet deposition of substances involves processes associated with in-cloud droplet formation and scavenging. Aerosol particles act as nuclei for water condensation. These small and wet particles then grow by condensation and merge to form droplets. Gases such as SO_2 and small particles may be incorporated during this process as the droplets scavenge materials within the cloud. Below the cloud, falling droplets (or snowflakes) may also take up pollutants by interception and impaction processes (Adams, 2012; Lovett et al., 1982). Dry deposition takes place in the absence of hail, rainfall or snowstorms when acids that have been converted chemically into salts and gases settle to the ground by eddy transport, adsorption, absorption and adhesion (Lovett et al., 1982; Schwartz, 1989). While wet deposition is a quick process with the largest quantities of wet deposited pollutants settling to the ground during major hail, rainfall or

snowstorms events, dry deposition is slower, more steady and incessant. Seasonal factors influence dry deposition and it is of greater importance or has more influence and impact in areas close to major emission points than at sites remote from emissions (Adams, 2012).

2.2 HISTORIC PERSPECTIVE OF ACID DEPOSITION

In his 1852 findings on the chemical composition of rain within Manchester city in England and its immediate surrounding areas, English chemist Robert Angus Smith highlighted differences in the quality of precipitation in the middle of the polluted city in comparison to its unpolluted countryside. He pointed out that sulphuric acid in the atmosphere of industrialised Manchester was the root cause of fading fabrics as well as damage to stone, brick, mortar, iron, galvanised iron and brass. Smith conceived the phrase acid rain in his 1872 publication entitled 'Air and Rain: The Beginnings of a Chemical Climatology' (Bricker and Rice, 1993; Cowling, 1982; Gorham, 1982, 1998). Smith (1872) articulates the principle concepts that after years of research are acknowledged as the root causes of acid precipitation. On the foundation of studies he carried out in Germany, England, and Scotland, he showed that the chemical composition and quality of precipitation an area receives is determined by numerous factors: sulphur and ammonia emissions into the atmosphere through anthropogenic processes that burn coal; decomposition of organic matter; topography; direction of air currents; path of smoke plume; shelter by obstacles to wind currents; distance to sea; and the quantity as well as prevalence of precipitation. He suggested comprehensive methods of collecting and analysing precipitation, highlighted damage caused by acid rain to plants such as bleaching of chlorophyll, and proposed that the probability of atmospheric deposition of metals such as copper and arsenic was higher for industrialised areas than non-industrialised ones (Cowling, 1982; National Research Council, 1900; Smith, 1872).

What we know today about acid precipitation and how it affects the environment originated from studies in agriculture, limnology, and chemistry of the earth's atmosphere (Cowling, 1982). Crowther and Ruston (1911) demonstrated that the degree of acidity in precipitation decreased from the centre of Leeds in England and was associated with combustion of coal. Through a series of experiments they were able to demonstrate how natural rain and dilute sulphuric acid could both prevent healthy plant growth and germination of seeds because

they affected soil processes of nitrification, nitrogen fixation, and ammonification. Egnér (1955) started a network of collecting and analysing precipitation in Europe. The network which provided information on changes in chemical composition of precipitation proved valuable for the agriculture and forestry activities (Cowling, 1982; Egnér and Eriksson, 1955; Rossby and Egnér, 1955). Eriksson (1952, 1960) came up with the theory of biogeochemical circulation of matter in the atmosphere, stating that all elements are recycled over and over again. Using information gathered through the precipitation network set up by Egnér (1955) - Eriksson (1955, 1960); Rossby and Egner (1955) tested a number of theories relating to atmospheric processes through which air pollutants get distributed such as: deposition, scavenging, trajectory and dispersal processes. Findings indicated that the distribution and chemical conversion of many pollutant substances in the atmosphere was mostly accomplished through atmospheric conveyance and deposition (Eriksson, 1955, 1960; Rossby and Egner, 1955).

Gorham (1989) built the underlying principles for our current knowledge of the reasons we experience acid deposition including its effects on water ecosystems. Using research carried out in Canada as well as England, Gorham and others established that acid precipitation distinctly influenced the breakdown of bedrock, soil processes, and water chemistry (Gorham 1989, 1998). Odén (1968) proved that acid deposition is a regional and transboundary problem. His studies of routes of air masses showed that sulphur dioxide emitted in England and central Europe, resulted in acid precipitation in Scandinavia (Cowling, 1982; Odén, 1968).

A case study carried out by Sweden for the United Nations Conference on the Human Environment raised major concern throughout the international community about acid rain as a serious widespread pollution problem with severe ecological consequences following its publication (Bolin, 1971; Cowling, 1982; Cowling and Linthurst, 1981). In North America concern around acid deposition and its effects on ecology first developed in Canada and then later in the United States (Cowling, 1982). Likens and colleagues (1979) initiated the discourse on the spread of acid precipitation in the region and its implication for both water and land ecosystems in North America. They pointed out that atmospheric alteration of oxides of nitrogen resulted in the formation of nitric acid contributing to the phenomenon of acid precipitation in the eastern U.S (Driscoll et al., 2001; Galloway et al., 1976; Galloway and Likens, 1981; Likens, 1976; Likens et al., 1979). Likens and colleagues later published maps to

show the distribution of acid precipitation in the eastern United States. In the early 1980's a system of controlled acidification of whole lakes was established in the United States to help investigate impacts of acid deposition (Schindler, 1980).

2.3 THE CHEMISTRY OF ACID PRECIPITATION (SO_2 AND NO_X)

Atmospheric acidification results from the oxidation of sulphur, nitrogen and organic compounds to form their equivalent acids. The gas and aqueous phase pathways depend on the production of oxidising free radicals particularly hydroxyls (OH) that react directly with these compounds or produce molecular oxidants. The most important molecular oxidants are H_2O_2, organic peroxides and O_3. These oxidants are not reactive in the gas phase, but are highly reactive in the aqueous phase with dissolved SO_2 and HNO_2. Thus oxidants may be produced in a photochemically active region and conveyed long distances before reacting with dissolved SO_2 and HNO_2 in the aqueous phase such as fogs, clouds, and rain (Pandis and Seinfeld, 1989).

PHOTOCHEMICAL OXIDATION CYCLE

Free radicals are activated by sunlight to attack volatile organic compounds (VOCs) in the atmosphere. The VOCs decompose to produce oxidising free radicals such as OH and other partly oxidised products which may also produce further radicals in the presence of sunlight. The complex mixture of carbon-based compounds that exist in polluted air react with initiator radicals at rates that are reliant upon the structure of their molecules. These reactions produce varying yields of free radical species of O_3, NO_2, H_2O_2, and other partly oxidised organic products depending on the concentrations of VOCs and oxides of nitrogen (Liang and Jacobson, 1999; Pandis and Seinfeld, 1989; Seigneur and Saxena, 1984).

GAS PHASE REACTIONS

SULPHUR DIOXIDE

OH radical reactions are the dominant gas phase mechanisms by which nitrogen dioxide and sulphur dioxide are consumed in the atmosphere (Calvert et al., 1978; Stockwell and Calvert, 1983).

Sulphur dioxide-, is an inorganic anhydride of a weak acid which has a high rate of dry deposition of about one to three days to plants and damp faces. It does not nonetheless dissolve completely in clouds or precipitation. Due to it only being partially soluble in water, precipitation does not remove it from the atmosphere in considerable amounts unless it is oxidised to other forms of sulphate that are more soluble (Pandis and Seinfeld, 1989). This oxidation normally takes place in the gas phase set off by OH free radicals in a series of three reactions as follows (Eq 1-3):

$$SO_2 + OH + M \rightarrow HOSO_2 \qquad \text{Eq 1}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \qquad \text{Eq 2}$$

$$SO_3 + H_2O(g) \rightarrow H_2SO_4 + M \qquad \text{Eq 3}$$

M is the catalyst in the reaction

NITROGEN DIOXIDE

Nitrogen dioxide possibly through oxidation can be deposited to vegetation in its dry form. It can be further oxidised in the gas phase reactions by OH to form nitric acid (Eq 4). The rate of reaction of NO_2 and OH is much faster than the SO_2 and OH reaction (Eq 1) (Adams, 2012).

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad \text{Eq 4}$$

AQUEOUS PHASE REACTIONS

SULPHUR DIOXIDE

SO_2 is moderately soluble and in the aqueous phase it is converted to sulphur in oxidation state 4 (S (IV)) (Eq 5 – Eq 7) which is made up of SO_2 (g), SO_2 (aq), HSO_3^- (bisulphite ion) and SO_3^{2-} (sulphite ion). S (IV) is oxidised to oxidation state 6 which includes sulphate (SO_4^{2-}) by either H_2O_2 or O_3 (Hewitt, 2001; Liang and Jacobson, 1999; Pandis and Seinfeld, 1989; Seigneur and Saxena, 1984).

$$SO_2(g) + H_2O \rightarrow SO_2.H_2O \qquad \text{Eq 5}$$

$$SO_2.H_2O \rightarrow H^+ + HSO_3^- \qquad \text{Eq 6}$$

$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \quad \text{Eq 7}$$

$$S(IV) + H_2O_2 \rightarrow S(VI) + H_2O \quad \text{Eq 8}$$

$$S(IV) + O_3 \rightarrow S(VI) + O_2 \quad \text{Eq 9}$$

Sulphuric acid occurring in the atmosphere may be partially neutralized by ammonia and other basic substances like carbonates. H_2SO_4 and SO_4^{2-} salts are present in the atmosphere commonly as aerosol particles due to low vapour pressure. They have low diffusion coefficients and their dry deposition rates are therefore very slow. The particles are however readily absorbed into rain clouds and are therefore deposited mostly through precipitation. (Adams, 2012).

NITROGEN DIOXIDE

NO_2 does not readily dissolve in water and is mostly unreactive in the aqueous phase at the concentrations that it typically occurs at in the atmosphere. It reacts as follows with OH in the aqueous phase (Eq 10-12):

$$NO_2 + OH + M \rightarrow HNO_3 \quad \text{Eq 10}$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \quad \text{Eq 11}$$

$$N_2O_5 + H_2O(aq) \rightarrow 2HNO_3(aq) \quad \text{Eq 12}$$

Nitric acid unlike sulphuric acid is fairly unstable and dissolves readily in rainclouds and precipitation (Pandis and Seinfeld, 1989). It easily adheres, permeates and dissolves onto surfaces. Nitric acid is usually conveyed to the earth's surface through dry deposition at rapid rates. When the atmosphere has no water vapour, aerosol particles may take up nitric acid as long as there are appropriate amounts of basic substances available to neutralize the acid. Nitric acid in its aerosol state is less susceptible to dry deposition in comparison to its vapour equivalent. Organic nitrates are usually formed from atmospheric reactions of nitrogen dioxide, they act as reserve species that can add to long range conveyance of atmospheric nitrogen compounds (Pandis and Seinfeld, 1989; Seigneur and Saxena, 1984).

2.4 HYDROGEN CHLORIDE GAS EMISSIONS AND ACID DEPOSITION

After SO_2 and NO_x, Hydrogen chloride (HCl) gas emissions are possibly the single main source of anthropogenic atmospheric acidity and adversely affect natural ecosystems. In comparison to other anions of acids such as NO_3^- and SO_4^{2-}, Cl^- is not affected by reduction-oxidation reactions and anion adsorption. Additionally while it can be cycled within soil organic matter, its net biological uptake is negligible particularly in regions of high marine Cl^- deposition. Owing to the high mobility of Cl^-, HCl readily acidifies both terrestrial and aquatic ecosystems (Evans et al., 2011). A greater portion of the world's HCl emissions come from burning coal and oil which contain trace amounts of chloride (Evans et al., 2011; Iapalucci et al., 1969). In the UK for instance, coal is the principal source of HCl emissions. Iapalucci and colleagues (1969) estimate that at least 94% of chloride content in coal is possibly emitted as HCl in flue gases during combustion.

HCl is a very reactive gas and is speedily removed from the atmosphere by most surfaces especially if they are moist. The rates of dry deposition to vegetation of HCl gas are very similar to those for HNO_3 gas. Huebert (1983) proposes that atmospheric turbulence rather than condition of surfaces mostly determines the rate of dry deposition of HCl gas. The gas is more speedily removed from the atmosphere relative to gases such as SO_2 and NO_2 and is deposited close to sources. It is greatly soluble and rapidly dissolves in cloud or rain if present (Lightowlers and Cape, 1988). Similar to dry deposition, wet deposition is likely to remove HCl quickly from the air and deposition usually occurs close to emission sources. Several investigations reveal large concentrations of HCl close to sources of emission. Patrinos and colleagues (1983) evaluated wet deposition from a large coal-fired power station and estimated that nearly all chloride released was wet deposited within 15Km of the source during rain. Further, Stevenson (1968) discovered very high concentrations of non-sea chloride concentrations in precipitation linked to HCl emissions in central England adjacent to major sources. Gorham (1958) also notes a significant relationship between acidity and chloride ion concentration in rain water samples collected in some urban areas.

The long distance conveyance of HCl is nonetheless a probability when HCl dissolves in clouds that are not precipitating. Studies show that HCl is a noteworthy acidifying agent of cloud

waters. Marsh (1983) estimates that HCl contributes at least 57% of the acidity measured in clouds which have combined with power station emissions. Cocks and Mcelroy (1984) postulated that the uptake of HCl by inert particles in the atmosphere is not substantial except at humidities > 90% and HCl concentrations > 100 ppb. Under the conditions existing in a power station or an incinerator plume, HCl may be adsorbed onto fly ash particles. As the plume scatters, the temperature, concentration and humidity changes and HCl is desorbed from the particles at a rate which depends strongly on the ambient relative humidity (Lightowlers and Cape, 1988). All HCl is projected to be desorbed after about 30 minutes for a relative humidity of 95%. In typical atmospheric conditions where humidity is lower, the desorption rate is significantly quicker than this (Cocks and Mcelroy, 1984). The reaction with alkali present in the ash has little influence on this process. HCl emitted from a stack is therefore likely to be in gaseous form and unattached to particles when it reaches the ground in the absence of cloud or rain (Lightowlers and Cape, 1988).

Clarke and Radojevic (1983) propose that at concentrations of about 10^{-3}M, chloride ions speed up the oxidation of sulphite to sulphate. This effect is therefore significant in marine aerosols or in emissions containing HCl. Consequently, SO_2 in precipitation is oxidized more speedily if chloride ions are present. This leads to reductions in gaseous SO_2 concentrations (and subsequently reductions in dry deposition of SO_2) close to emission points, but increases acidity of precipitation due to the production of sulphuric acid. The acidity of HCl in solution may limit the catalytic effect of chloride ions in which case the SO_2 concentrations close to emission points as well as the production of sulphuric acid in precipitation is not significantly dissimilar from those in atmospheres where HCl is not present (Lightowlers and Cape, 1988).

Due to its high solubility in water HCl is more effectively removed by precipitation than the main acid pollutants SO_2 and NO_x. Furthermore, HCl is a strong acid in solution and reacts instantaneously to yield hydrogen ions whereas the acidity of SO_2 and NO_x can only be realised after oxidation to their corresponding acids. This process may take a few hours to a number of days dependent on the oxidising capability of the atmosphere. The acidity of precipitation in the proximity of a power station plume may be almost exclusively due to the solution of HCl despite the concentration of HCl in the plume being smaller than that of SO_2. Conversely, the contribution of HCl to acidity in precipitation at a distance from the emission

source may be several times lower than contributions from S and N oxides (Lightowlers and Cape, 1988).

2.5 CHARACTERISTICS OF ACID SENSITIVE AREAS

An area's sensitivity to acid deposition is governed by geology, topography and interactions between drainage water and soil. Vulnerable and affected areas result from intrinsic ecosystem sensitivity and exposure to acid deposition (Greaver et al., 2012). Other factors contributing to sensitivity include landscape position, vegetation, soil characteristics, land use and hydrology flow path (Sullivan et al., 2011).

Acidification takes place when the rate at which acids supplied to waters flowing through a watershed into a water body plus those falling directly on its surface is higher than the rate at which alkalinity can be supplied by the watershed and that stored within the water body (Adams, 2012). Generally waters with low alkalinity values (below 200 µeq l^{-1}) are sensitive to acidification. This is because alkalinity provides buffering to acidic components in unacidified waters. The connection between acid deposition and water acidification was first discovered in Scandinavia in 1959. Widespread extinctions of fish populations in southern Norway linked to water acidification have also been extensively documented (Andersson and Rodhe, 1982; Cowling, 1982; Gorham, 1989; Ulrich, 1984).

The maximum load that will not result in chemical alterations in soils and waters and lead to long-term detrimental effects on the most sensitive ecosystems is known as the critical load (Nilsson, 1988). Critical loads incorporate the concept of a catchment's ability to generate acid neutralising capacity. Nilsson (1988) reports that most soils and waters in regions with low quantities of base cations are not likely to be considerably altered by loads of 10-20 keq H^+ km^{-2} yr^{-1} in the deposition. Southwestern Scandinavia for instance receives hydrogen ions loads of approximately 100 keq km^{-2} yr^{-1} in deposition. Further, many forest ecosystems can withstand maximum nitrogen loads of 10-20 kg N ha^{-1} yr^{-1}. In highly productive locations such as southern Sweden and central Europe the critical load for nitrogen is as high as 30-40 kg ha^{-1} yr^{-1} (Nilsson, 1988).

Acid deposition occurs primarily in the eastern United States but has been observed in the west as well. Fog with a pH of 2.2 has been observed in California. Over much of eastern North

America all forms of precipitation on average are quite acidic. pH of precipitation ranges from 5 to 4.1 in this region. Individual rain episodes with pH values of 3.0 are observed in the north-eastern United States. Within these regions anthropogenic sulphur emissions exceed the natural emissions by at least a factor of five (Adams, 2012). In eastern North America over 90% of precipitation acidity may be the result of human activities (Adams, 2012; Andersson and Rodhe, 1982).

Through numerous studies of soils, bedrock-geology and surface waters, large portions of the United States have been identified to be acid sensitive (Driscoll et al., 2001; Galloway et al., 1976; Likens et al., 1979; McFee, 1980). Extensive acid sensitive areas exist in Wisconsin, Minnesota, upper Michigan, the Yukon, a number of south-eastern states, the north-western regions as well as numerous areas of the west apart from the renowned north-eastern region of the country (Adams, 2012; Schindler, 1988; Schwartz, 1989). In Europe, Scandinavia and the United Kingdom are important areas that are known to be sensitive to acid deposition. The Netherlands, Denmark, Belgium, Switzerland, West Germany, Italy, and Ireland have also been included on the list of susceptible areas. Forest damage in central Europe has been related to the direct effects of gaseous pollutants. In contrast in southern Scandinavia which has smaller total depositions of sulphur and nitrogen, adverse effects on tree growth have not yet been demonstrated (Abrahamsen and Miller, 1984; Andersson and Rodhe, 1982). Vast areas in southern and eastern Asia, southern Africa, and South America are also acid sensitive (Adams, 2012; Hicks et al., 2008; Kuylenstierna et al., 2001).

2.6 INFLUENCE OF CATCHMENT SOILS AND GEOLOGY ON STREAM WATER QUALITY

Although soil and water acidification is a natural phenomenon, the process has been augmented by acid deposition in a number of developed regions such as North America and continental Europe including the UK. The rate and degree to which catchments are acidified vary depending on their physical as well as biological structures (Langan and Wilson, 1992). Geology and soil characteristics of catchments to a large extent determine the acidity of waters that drain them as well as their susceptibility to further acidification in the presence of pollution. This is because the amount of precipitation that falls directly on to water bodies is insignificant in comparison to that which is directed through the flora, soils as well as

underlying bedrock of any given catchment before reaching surface waters. The quality of water permeating soils and bedrocks of catchments is highly influenced by their mineral compositions as it comes into contact with them (Langan and Wilson, 1992).

The neutralization of acidic substances in both the soil and bedrock of a watershed plays a critical part in the neutralization of a catchment discharge. Complex geochemical processes in soils play a major role in determining the quality of percolate which infiltrates down to surface waters. Catchment soils are important in controlling surface water alkalinity. Alkalinity of the soil is linked to the weathering of cations and other nutrients as well as the solubilisation of organic substances which together provide the basic chemical constituents important to freshwater biota (Abrahamsen and Miller, 1984; Adams, 2012; Greaver et al., 2012; McFee, 1980). Research carried out in areas in the eastern region of North America and in Europe that are sensitive to acid deposition has shown that acidification of stream waters is determined by characteristics of watershed soils such as thickness, base cation content, and SO_4^{2-} adsorption capacity (Cosby et al., 1985; Driscoll et al., 2001; Johnson et al., 1984; Reuss and Johnson, 1985, 2012).

Geochemical investigations of stream headwaters in the Oregon Range and the Rocky mountains have revealed that the weathering processes in the bedrock of a watershed are the main source of solutes in streams providing evidence that bedrock processes and rock types impact on the extent to which a stream is acidified (Asano and Uchida, 2005). Cations produced through weathering processes in bedrocks are naturally continuously leached from the soil. The rate of leaching in tropical humid areas is usually higher than in cooler climate areas. Increased acidity of precipitation increases cation leaching. This produces an acidification and aluminium toxicity effect because some of the hydrogen ions linked to acid precipitation are retained in soils, resulting in soil acidification and an increase in aluminium mobilization (Abrahamsen and Miller, 1984; Adams, 2012).

Asano and Uchida (2005) propose that the ability of watershed soils to neutralize acids is the principal factor that controls the susceptibility of surface waters to acidification. They further suggest that if base cations have leaked out of the soil, its acid neutralization capacity is reduced, and surface waters are likely to be acidified especially if the bedrock is impervious and does not weather easily. For instance, where catchments are underlain by carbonate

bedrock, the dissolution of the carbonate results in the leakage of calcium together with bicarbonate anions from the soil. If base-rich silicate minerals that disintegrate easily underlie the catchment, hydrolysis dominates bedrock chemical processes resulting in the loss of base cations along with bicarbonate in fairly natural areas, and strong acid anions in regions of substantial pollution. If leached base cations and bicarbonate anions are replaced through weathering processes at rates that roughly equal their loss, then the rate of acidification in the absence of acidifying pollutants proceeds gradually. Generally, the presence of carbonate or weatherable silicate materials significantly reduces the susceptibility of waters to acidification (Langan and Wilson, 1992).

Since catchment bedrocks and soils that are calcareous in nature such as limestones are readily soluble, streams in such catchments usually have high amounts of calcium bicarbonate and other basic substances which deliver buffering capacity. This is true for much of central Europe, where despite the acidity of the precipitation, the waters are not acidified (Tollan, 1981). The low calcium content of sandstone bedrocks on the other hand implies that the waters that drain them are acidic (Ahearn et al., 2005). Areas with shallow acid soils overlying granite rocks or highly weathered sandy soils are the most susceptible to water acidification (Andersson and Rodhe, 1982). Acid sensitive regions are largely underlain by silica or quartz-rich bedrock with scant or thin top soils. Studies have however shown that there are areas that lie outside this type of geology which can also be acidified (Tollan, 1981).

Langan and Wilson (1992) propose that when determining the susceptibility of waters to acidification at individual catchment scale, the spatial distribution of different soil types should be an essential consideration. For regional assessments, the supposition is that if water flow is low, surface water quality generally reflects the chemical properties of the bedrock materials with which the water has been in contact over an extended period. Conversely, during periods of high flow, surface waters are supplied by diffusion through the soil column rather than through the bedrock. The chemistry of such waters therefore largely reflect the capability of the soils to buffer incoming acidity, mainly by means of cation exchange. However, in areas where soils are maintained for agriculture, through flow waters are highly unlikely to be acidified and the enhancing effects of such soils on water quality must be taken into consideration. Additionally, catchments of similar sensitivity acidify at dissimilar rates which are dependent on their proximity to pollution sources. Catchment

systems which are therefore greatly prone to acidification but positioned in a low pollution region will acidify at a much lower rate compared to similar catchments exposed to significant inputs of acid deposition. Table 1 explains the classification of geology depending on their susceptibility to acidification after Edmunds and Kinniburgh (1986)

Category	Rock type
High	Granite, acid igneous rocks most metasediments, grits, quartz sandstones, decalcified sandstones, some quaternary sands
Medium	Intermediate igneous rocks, metasediments free of carbonates, impure sandstones and shales, coal measure sediments
Low	Basic and ultrabasic igneous rocks, calcareous sandstones, mudstones and marls, most drift and alluvial deposits
None	Limestones, chalk, dolomitic limestone and related sediments

Table 1 Classification of geology depending susceptibility to acidification

2.7 INFLUENCE OF LANDUSE/LANDCOVER ON STREAM WATER QUALITY

In pristine ecosystems atmospheric deposition is the key source of nitrogen. Nitrogen is largely cycled and retained within these systems with marginal discharge to ground and surface water (Helliwell et al., 2001). Reynolds and Edwards (1995) however call attention to the fact that escalating atmospheric nitrogen inputs as a result of pollution may possibly go beyond the capacity of biota and soils to retain nitrogen causing disruptions in the nitrogen cycle leading to nitrogen saturation. Inorganic nitrogen is mainly leached as NO_3^- as contributions of ammonium (NH_4^+) to overall inorganic N losses are usually insignificant in pristine ecosystems.

Long-term and seasonal variations of stream and lake water NO_3^- concentrations in afforested catchments show changes in N saturation that occur through distinguishable phases (Aber et al., 1989; Stoddard, 1994). The NO_3^- variations reveal fluctuations in rates as well as the comparative significance of nitrogen conversions as the afforested catchments become more nitrogen enriched. Initial phases of N saturation exhibit low inputs and efficient retention of nitrogen as well as an obvious surge in the intensity and rate of recurrence of NO_3^- episodes. Later stages show consistently high surface water NO_3^- concentrations because the rate at which N is supplied is higher than uptake by microbes and vegetation. Gundersen and others

(1998a, b) demonstrate that carbon to nitrogen ratios of forest floors are equally useful in evaluating the risk of NO_3^- saturation as well as consequent leaching. They advise that the carbon to nitrogen ratio of forest floors is negatively related to nitrate leaching and nitrification and add that if this ratio is below critical point which is 25, NO_3^- concentrations of surface waters are likely to be higher than normal.

Several studies show that that streams draining mature coniferous forests contain more NO_3^- in comparison to those draining neighbouring catchments without conifers resulting in possible acidification of such stream waters (Harriman and Morrison, 1982; Reynolds and Edwards, 1995; Tollan, 1981). More recent investigations indicate that the age of conifer plantations as well as the flux of enhanced nitrogen deposition partially determine the amount of NO_3^- leaching from conifer forests. There are indications that NO_3^- concentrations and fluxes from streams draining conifer plantations which are less than 15 years may be lower than those of streams in neighbouring catchments with older plantations because the rate of nitrogen uptake in such young forest surpasses the rate at which it is supplied from deposition, mineralisation and nitrification (Reynolds et al., 1994).

The degree and timing of NO_3^- leaching as well as the exact factors that regulate nitrogen breakthrough in natural catchments are not well understood because the process interactions controlling these ecosystem responses to nitrogen deposition are complex. Generally there is no net removal of nitrogen in vegetation in natural catchments. Biological processes of immobilisation, volatilisation, fixation, mineralisation and denitrification enhance the retention of nitrogen within natural ecosystems. However, inputs of inorganic nitrogen from cloud-water as a result of pollution increase wet inorganic inputs of nitrogen to natural catchments. The acidifying and nutrient effects of N (and S) have the capacity to upset the nitrogen equilibrium of catchments in the long term causing it to break through to surface waters leading in due course to a declining ANC (Curtis et al., 1998; Helliwell et al., 2001). Several studies have observed high levels of NO_3^- in upland regions in Britain where nitrogen deposition is high, indicating that elevated surface water NO_3^- is due to atmospheric pollution (Allott et al., 1995; Curtis et al., 1998; Helliwell et al., 2001).

Hornbeck (1992) suggests that decreasing the intensity of harvest for forested catchments can diminish long-term effects of H^+ from acid deposition on the acidification of soils and

stream waters. In his investigations of annual H^+ budgets for a catchment with a 65 year old spruce fir forest, as well as an adjacent one three years after a whole tree harvest, Hornbeck observes that catchment sinks for H^+ as a result of weathering and mineralisation processes were 85% higher in the harvested catchment whereas H^+ sources owing to biomass uptake were 60% higher for the untouched catchment. He estimates a net consumption of 550 $H^+ ha^{-1} yr^{-1}$ three years subsequent to the harvest in comparison to a net production of 520 $H^+ ha^{-1} yr^{-1}$ for the 65 year old forest. While soil pH increases by 0.2-0.4 units right after harvest, minimal change is observed in stream water pH from the harvested catchment. He approximates that a total of 30 000 $H^+ ha^{-1}$ are produced as a result of biomass removal over a three year period in contrast to 50 000 $H^+ ha^{-1}$ that could be added due to acid deposition (at rates observed during the study) over a 65 year period before a subsequent harvest.

Annual grasslands are naturally constantly losing nitrates (Ahearn et al., 2005). This is because the nitrogen feedback between aging vegetation, their soils and fresh growth is constantly being interrupted. Nitrates build up in the soil during dry months when uptake by plants and leaching is low. With the onset of rains, the accumulated nitrate is flushed out of the soil at rates higher than uptake by new plant growth (Holloway and Dahlgren, 2001). This implies streams with grassland watershed will have varying loads of nitrates depending on season.

Andersson and Rodhe (1982) advise that while land use may increase or decrease soil acidity and therefore affect water quality, land use changes do not seem to offer an adequate explanation of regional water acidification in regions receiving precipitation of pH less than 4.5. Studies of landuse changes linked to crop cultivation and forest plantations in acid sensitive areas of Norway have shown no logical, orderly and regular relationship between land use and the acidification of lakes or mortality rate of fish. For much of Norway, acid deposition is more important than land use in determining water quality, but in areas of low deposition, land use can be an important determining factor. Adam (2012) suggests that for land that is mostly used for agricultural purposes, techniques of ploughing, fertilization as well as liming of soils are more significant determinants of soil chemistry and therefore stream chemistry than acid deposition. Ahearn and colleagues (2005) and; Johnson and colleagues (1997) however propose that crop cultivation greatly alters and influences the nitrogen, phosphorous, and sediment content of stream waters. Catchments that are dominated by row crop agriculture have been observed to have streams with high concentrations of nitrates

and total dissolved solids, as well as high pH values. Most streams show different concentrations of nitrogen depending on season and no noticeable differences for the amounts of phosphorous or suspended solids. The seasonal changes in nitrogen concentrations can be accounted for by landscape structures such as gradient and density of vegetation cover (Johnson et al., 1997).

In their investigations of the impacts of urban landuse in Alabama and Ontario, Basnyat and colleagues (2000) concluded that urban landuse was the major determinant of the concentration of soluble reactive phosphorous while cultivation only had a minor impact on both nitrogen and phosphorous concentrations. Determining the influence of urban cover on stream quality is however not so easy and usually gives inaccurate results. This is because much of the cover in built-up regions is impermeable and runoff is mostly directed through storm water drains to wastewater treatment plants (which may be in the same river basin or a different one), before it is released into streams as a localized or stationary pollution source (Ahearn et al., 2005).

2.8 REVIEW OF THE DATA AND INSTRUMENTS OF MEASURE UTILISED IN THE STUDY

THE NATURE OF DIGITAL ELEVATION MODELS AND THEIR APPLICATIONS

Digital elevation models (DEM) are digital images depicting elevations of complete or portions of planetary surfaces with respect to their geographic positions. They are raster or vector representations of uninterrupted terrain surfaces used as inputs to quantify features of landscapes (Toppe, 1987). DEMs are generated through various techniques such as Light Detection and Ranging (LIDAR), Interferometric synthetic aperture radar (InSAR or IfSAR), photogrammetry and land surveying among others. Remote sensing is the most commonly used method among mappers (Li et al., 2004). DEMs are generally useful for deriving topographic features and landscape data. In combination with other spatial data DEMs are an important database for mapping as well as landscape analyses (Edwards and Lowell, 1996).

Remotely sensed DEM data- may, however, contain ambiguity and error related to the sensor (hardware) systems or with the image preprocessing such geometric rectification, data

conversion, classification and data generalization (Congalton, 1991). Mark (1988) suggests that although DEM resolution is the principal determinant of its precision, the nature of the DEM (floating point or integer) as well as the actual sampling of the terrain during production of the original DEM also affects its correctness. He argues that coarser-resolution DEMs generally have a greater number of errors than DEMs with a finer-resolution. He estimates that about 1% of cells in a 30m resolution DEM are flaws, increasing to as much as 5% for a 3-arc-second DEM. Additionally, DEM data stored in integer form commonly contains more errors than DEM stored in floating point format. Systematic sampling errors when generating DEMs create visible striping artifacts in the data which are particularly noticeable in integer format. DEM errors are especially troublesome in areas of low elevation (Mark, 1988; Tarboton, 1997; Tarboton et al., 1991).

These inaccuracies in DEMs are categorized as either sinks or peaks. Sinks, also known as pits or depressions constitute areas encircled by higher elevation values. They are zones of internal drainage which inhibit the downslope flow channeling of water. While some sinks may be natural, especially in karst or glacial regions, most are flaws in the DEM (Mark 1988). Similarly peaks or spikes are zones encircled by cells of lower elevation value. Unlike sinks, peaks are usually natural features and are comparatively less disadvantageous to the evaluation of flow direction. Such DEM errors, particularly sinks, have to be removed before deriving any surface information from DEM data (Mark, 1988; Rae et al., 2007; Tarboton, 1997; Tarboton et al., 1991).

ERRORS AND UNCERTAINTIES IN SPATIAL DATA AND IMPLICATIONS FOR GENERATED OUTPUTS

Progressively more and more natural resource managers depend on spatially explicit data that is stored, evaluated and presented with Geographic information systems (GIS)(Crosetto et al., 2002; Crosetto and Tarantola, 2001; Edwards and Lowell, 1996). Crosetto and colleagues 2002 point out that a growing number of complex decisions are being made on the basis of information derived from digital spatial models. Lanter and Veregin (1992) caution that while GIS visual outputs are convincing, there is no mitigation against inaccuracies. Hwang and others (1998) also emphasize that GIS information usually includes some measure of uncertainties in outputs. Foody and Atkinson (2002); Norton and Williams

(1992) add that ultimately, uncertainties and errors in GIS outputs result in misrepresentations as well as inappropriately high confidence levels for specific management decisions that can be extremely costly due to their irreversibility.

GIS researchers advise that several areas including cartographic, locational and feature, spatial databases, as well as spatial analysis all add to overall uncertainty in GIS (Altman, 1994; Burrough et al., 1992; Chrisman, 1982). Primary introduction of ambiguity and inaccuracy can occur due to imprecise and inaccurate measurement during the original collection of spatial data. For instance digitizing attributes such as contour lines and cadastral boundaries symbolized on paper maps by outlining their shapes with an indicator encoding their coordinates is a common method of generating digital spatial data. Errors are commonly introduced during such initial traces or processes of joining the coordinates and generalizing the resulting features (Burrough and McDonnell, 1998; Rae et al., 2007). Secondary introduction of uncertainty and error occurs in succeeding data processing such as conversion between vector and raster formats of spatial data. The quality of the transformation as well as accuracy of boundary representation rely greatly on the cell size of the resultant raster map. Large cell size results in loss of features particularly narrow features like rivers (Congalton, 1997, 1991). Morris (2003) further suggests that querying of existing digital spatial data to create new data layers can be challenging if some features display partial fuzzy membership to one or more classes. Querying information from data layers and buffering features also introduces errors (Congalton, 1997; Morris, 2003).

THE DERIVATION OF STREAM NETWORKS FROM DIGITAL ELEVATION DATA IN GIS – MERITS AND DETRIMENTS OF EXISTING APPROACHES

Drainage networks are the basis for outlining drainage basins, a vital constituent in hydrological models as well as planning the management of resources (O'Callaghan and Mark, 1984). Such drainage networks and their associated watersheds form complicated functional entities for hydrological processes and geomorphological processes generally. Several factors such as industrial development, population growth and intensified cultivation exert tremendous pressure on water resources making it necessary to monitor drainage networks for both water quality and quantity (Vogt et al., 2003).

GIS tools can be used to derive stream networks and their flow pathways from DEMs - a process referred to as delineation. They permit the joint examination of DEM data and environmental factors in order to extract information on location and characteristics of drainage networks and their catchments in order to evaluate the impacts of anthropogenic pressures on water resources (Jenson and Domingue, 1988; Seemuller, 1989). The algorithms in the raster processing system in GIS uses neighborhood operations to estimate attribute information such as slope, aspect and shaded relief, as well as point of inflection. While catchments and overland flow routes are all closely related to these morphological features and properties, they also present non-neighborhood complications like determining flow direction in the interior of flat areas. To overcome such limitations, neighborhood techniques in GIS tools allow for the extraction of topographic depressions and flow directions that may be further processed to delineate catchments as well as overland flow paths (Jenson and Domingue, 1988). Mark, 1984; O'Callaghan and Mark (1984) have made an attempt to eliminate depressions by smoothing the DEM data. Though this smoothing approach gets rid of shallow depressions, deeper depressions remain. Jenson and Domingue, 1988; Jenson and Trautwein, 1987; Mark et al., 1984 propose a second method of filling depressions by increasing values of cells with the lowest values on a depression's boundary. Collins, (1973) recommends an algorithm for filling depressions which however fails to fully accommodate flat areas as demonstrated by Douglas (1986).

The automatic extraction of catchment data from DEMs has the advantage of being less biased and generating more reproducible dimensions than the traditional labor-intensive methods applied to topographic maps. Delineation in GIS is generally quicker and analysis time is greatly reduced as the tools are computer intensive and require very little analyst intervention. Digital data generated by this approach also have the benefit of being readily imported and explored further in GIS. In addition, delineation outputs have the benefit of precise registration with the DEM. Though the processes are mainly raster based, the catchment polygons, drainage networks and tabular attribute information defining catchment linkages generated can be readily converted into vector format.

LIMITATIONS OF USING GIS AND TOOLS TO ASCRIBE STREAM WATER QUALITY

GIS and multivariate statistics tools are commonly utilized in the analysis of spatial data and complex interactions so as to inform watershed management decisions. These tools can be used to effectively determine significance of relationships between LULC, soils, or geology of catchment areas and streamwater quality. Sliva and Williams (2001) however argue that ascribing the quality of streamwaters to point and non-point sources such as agriculture, air pollution, and landcover is however difficult as complications of scale always arise. They add that the effectiveness of GIS and multivariate tools relies on both data quantity and data quality and data collected for such studies are typically insufficient especially when dealing with entire catchments.

Seasonality also produces varying outcomes for analyses of the influence of LULC on streamwater quality. While some authors argue for carrying out investigations in storm season, as maximum connection between the landscape and local watercourses occurs during this time, others propose analyzing stream water quality in various seasons and linking water quality for each season with LULC (Ahearn et al., 2005; Basnyat et al., 2000; Johnson et al., 1997). Although the issue of varying water quality due to changes in seasons has been addressed by many authors, few if any investigations have linked dry and wet year streamwater quality with LULC gradients. Ahearn and colleagues (2005) add that quantifying urban cover influences on streamwater quality with GIS methods and multivariate statistics is complicated.

MULTIVARIATE STATISTICAL TECHNIQUES

2.8.5.1 PRINCIPAL COMPONENT ANALYSIS

Principal component analysis (PCA) is a multivariate statistical technique for scaling down data and defining patterns within large data sets. It is wholly founded on Eigen scrutiny of the covariance or correlation matrix and hence restrictions of multivariate normality are not imposed on the data (Tabachnick et al., 2001). If there are huge dissimilarities in standard deviations of variables, PCA outcomes differ substantially depending on whether the correlation or the covariance matrix is used. For variables with widely differing variances, the first few principal components describe the variables with the greatest variance. Each variable

is standardized to unit variance and contributes equally when the correlation matrix is used (Farnham et al., 2003; Tabachnick et al., 2001).

2.8.5.2 MULTIVARIATE MULTIPLE REGRESSION

OVERALL PURPOSE

Multivariate regression is a generalization of variance to a situation in which there are two or more independent variables (IVs) and multiple dependent variables (DVs). It assesses whether differences in means among groups in an arrangement of DVs are likely to have occurred by coincidence. Hypotheses about means are tested by comparing inconsistencies (Bray and Maxwell, 1985; Haase and Ellis, 1987). A number of multivariate statistics exist in multivariate analysis programs which assess the significance, magnitude and direction of main effects and interactions among groups: Hotelling's trace, Wilks' Lambda, Roy's greatest characteristic root (gcr) and pillai's criteria. When an effect has only two levels (i.e. one degree of freedom), F tests for Hotelling's trace, Wilks' Lambda and Pillai's criteria are equal. When an effect has more than two levels, F values are usually dissimilar but all three statistics are either significant or all are insignificant. In rare instances however, some of the statistics may be significant while others are not (Bray and Maxwell, 1985; Tacq, 1997).

By evaluating several dependent variables concurrently, multivariate analyses improve the chance of determining dependent variables that change due to variations in independent variables as well as the direction and magnitude of the interactions. Furthermore, it protects against inflated type I errors that arise as a result of carrying out a series of tests on possibly interrelated dependent variables. Additionally, under particular conditions, it may possibly reveal differences not exhibited when separate tests are carried out on dependent variables (Chamberlain, 1982; Haase and Ellis, 1987).

LIMITATIONS OF MULTIVARIATE MULTIPLE REGRESSION

Multivariate data analyses are complex analyses which require several assumptions to be taken into consideration and met (Osborne and Waters, 2002). They are also often characterized by indistinctness in interpretation of the effects of independent variables on any particular dependent variable.

THEORETICAL CONSIDERATIONS

The ascription of causality to independent variables in multivariate data analyses are in no way assured by the statistical test. The inference that significant changes in dependent variables are triggered by associated variations in independent variables is therefore a common-sense exercise and not a statistical one. Care needs to be therefore exercised when inferring causation from a significant independent variable-dependent variable relationship. The choice of variables is more a question of judgement and research design than statistics. Skill is vital in picking dependent variables that have a possibility of revealing effects of independent variables. The degree of association among dependent variables must also be taken into consideration. Dependent variables that are uncorrelated are the optimal choice as they quantify separate aspects of the influence of independent variables (Tabachnick et al., 2001).

PRACTICAL CONSIDERATIONS

MULTIVARIATE NORMALITY

Statistical tests for multivariate multiple regression analyses are reliant on even distribution of multivariate data, the sampling distributions of means of dependent variables in all cells and their linear combinations have to be normally distributed. Mardia (1971) however demonstrates that multivariate analyses are robust to minor violations of normality provided the violations are due to skewness rather than outliers. He shows that even with an uneven distribution and only a small number of dependent variables, a sample size of about 20 in the smallest cell should warrant robustness. With small, uneven samples, an evaluation of whether dependent variables are likely to be fairly evenly distributed in the population determines normality. Conversions to normality executed on uneven samples can also produce normality (Chamberlain, 1982; Mardia, 1971; Osborne and Waters, 2002, 2002).

SENSITIVITY TO OUTLIERS

Multivariate analysis is sensitive to outliers and if any are present within multivariate data, they typically give rise to either Type I or Type II errors in the analysis with no indication as to which is occurring. Tests for outliers are therefore suggested to accompany multivariate analyses (Osborne and Waters, 2002; Tabachnick et al., 2001).

HOMOGENEITY OF VARIANCES

Multivariate analysis necessitates that dependent variables have equivalent levels of variance across the range of independent variables.

HOMOGENEITY OF VARIANCE-COVARIANCE MATRICES

Homogeneity of variance for individual dependent variables is generalized to homogeneity of variance-covariance matrices in multivariate analysis. The supposition is that the variance-covariance matrices within each cell of a model are sampled from the equivalent population variance-covariance matrix and can be combined to generate a single estimation of error. The combined matrix is ambiguous as an approximation of error variance if the within-cell error matrices are varied (Chamberlain, 1982; Haase and Ellis, 1987; Osborne and Waters, 2002; Tabachnick et al., 2001).

Tests for the assumption of homogeneity of variance-covariance matrices in multivariate analysis are founded on a generality of the Monte Carlo test of robustness which predicts robustness of significance tests as long as sample sizes are the same; the result of the Box's *M* test which is a very sensitive test of homogeneity of variance-covariance can be overlooked. If sample sizes are however uneven and Box's *M* test is significant at $p < 0.001$, then robustness is not assured. The higher the number of dependent variables and the bigger the difference in cell sample sizes, the larger the probable misrepresentation of α levels. On condition that cells with larger samples yield larger variances and covariances, the alpha level is conservative and the null hypotheses can be precluded with confidence. If cells with smaller samples yield larger variances and covariances however, the significance test is too liberal. Null hypotheses may be accepted with confidence but indications of mean inconsistencies are uncertain. Pillai's criterion and not Wilks' Lambda should be applied in the evaluation of multivariate significance in this case (Olson, 1979). If not, sample sizes may be equalized by random removal of cases so as to maintain power at reasonable levels (Chamberlain, 1982; Haase and Ellis, 1987; Osborne and Waters, 2002; Tabachnick et al., 2001).

LINEARITY

Multivariate analysis presumes linear associations among all sets of dependent variables and all sets of covariates in every cell. Nonconformities to linearity diminish the power of

statistical tests for several reasons: linear combinations of dependent variables do not capitalize on the separation of groups for the independent variables; and covariates do not capitalize on correction for error (Bray and Maxwell, 1985; Tabachnick et al., 2001).

MULTICOLLINEARITY AND SINGULARITY

When correlations amongst dependent variables are high, one of them is usually a near-linear amalgamation of the others. Such a dependent variable provides data that makes the information of one or more of the other dependent variables redundant. In such instances, it is logically and statistically questionable to take into account all dependent variables in analysis. The typical solution is the exclusion of the redundant dependent variable from the assessment. If however important theoretical motives to keep all dependent variables exist, a principle components analysis on the collective within-cell correlation matrix is suggested. Component scores are entered as a substitute set of dependent variables in this case (Tabachnick et al., 2001).

CHAPTER THREE – GENERAL DESCRIPTION OF STUDY AREA

3.1 LOCATION

The Vaal River catchment occupies the central north eastern area of South Africa. It extends from Ermelo in KwaZulu-Natal, just West of Swaziland in the east, across to Kuruman in the Northern Cape in the West. To the North West, the catchment area borders Botswana as well as the Crocodile (West) and Olifants catchments. Johannesburg sits on the boundary of the catchment area. It is bounded by Lesotho in the South East and by the Upper Orange and Lower Orange catchments in the South West (DWAF, 2004). The Vaal River Catchment is separated into three water management areas: the Upper, Middle, and Lower Vaal water management areas.

The Upper Vaal Water Management Area stretches over an expanse of approximately 55 565 km^2. It is positioned near the central region of the country covering: the Free State to the convergence of the Mooi and Vaal Rivers; the south east of Mpumalanga; the south west of Gauteng; and borders Lesotho in the south. It comprises the Vaal, Klip, Liebensbergvlei, Wilge, and Mooi Rivers and spreads to the confluence of the Vaal and Mooi Rivers. The area also includes key dams: the Sterkfontein, Vaal and Grootdraai Dams (DWAF, 2004). Figure 1 shows the location of the Upper Vaal with respect to Eskom power stations and main cities and towns.

3.2 TOPOGRAPHY

The Upper Vaal is positioned on the Central South African plateau. It generally has undulating topography with a maximum altitude of around 3276m and minimum of roughly 1293m (Figure 2). Key landscape structures in the region are the Witwatersrand in the north, the Drakensberg escarpment in the east and the slopes of the Maluti Mountains in the south.

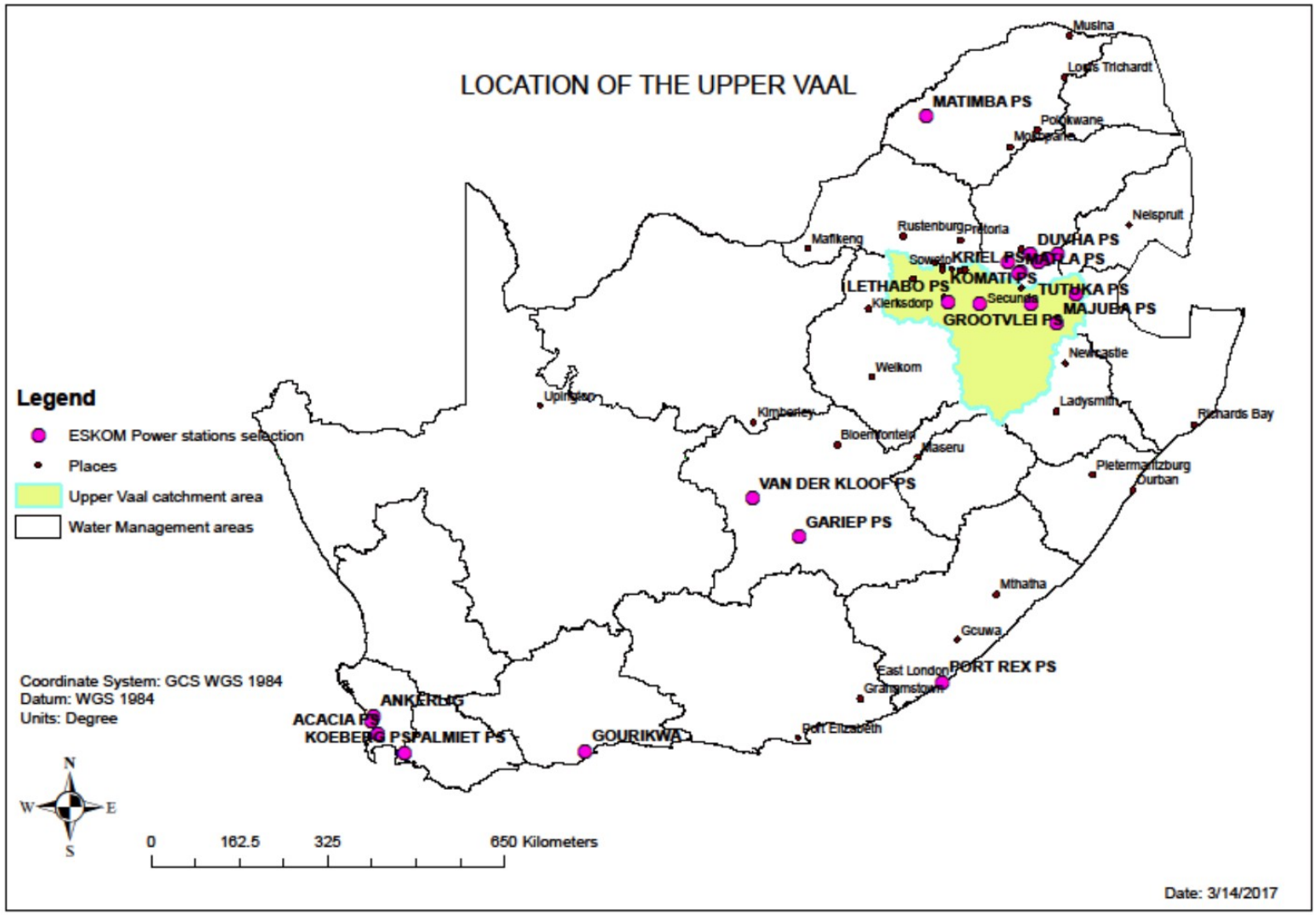


Figure 1 Location of the Upper Vaal with respect to main places and power stations

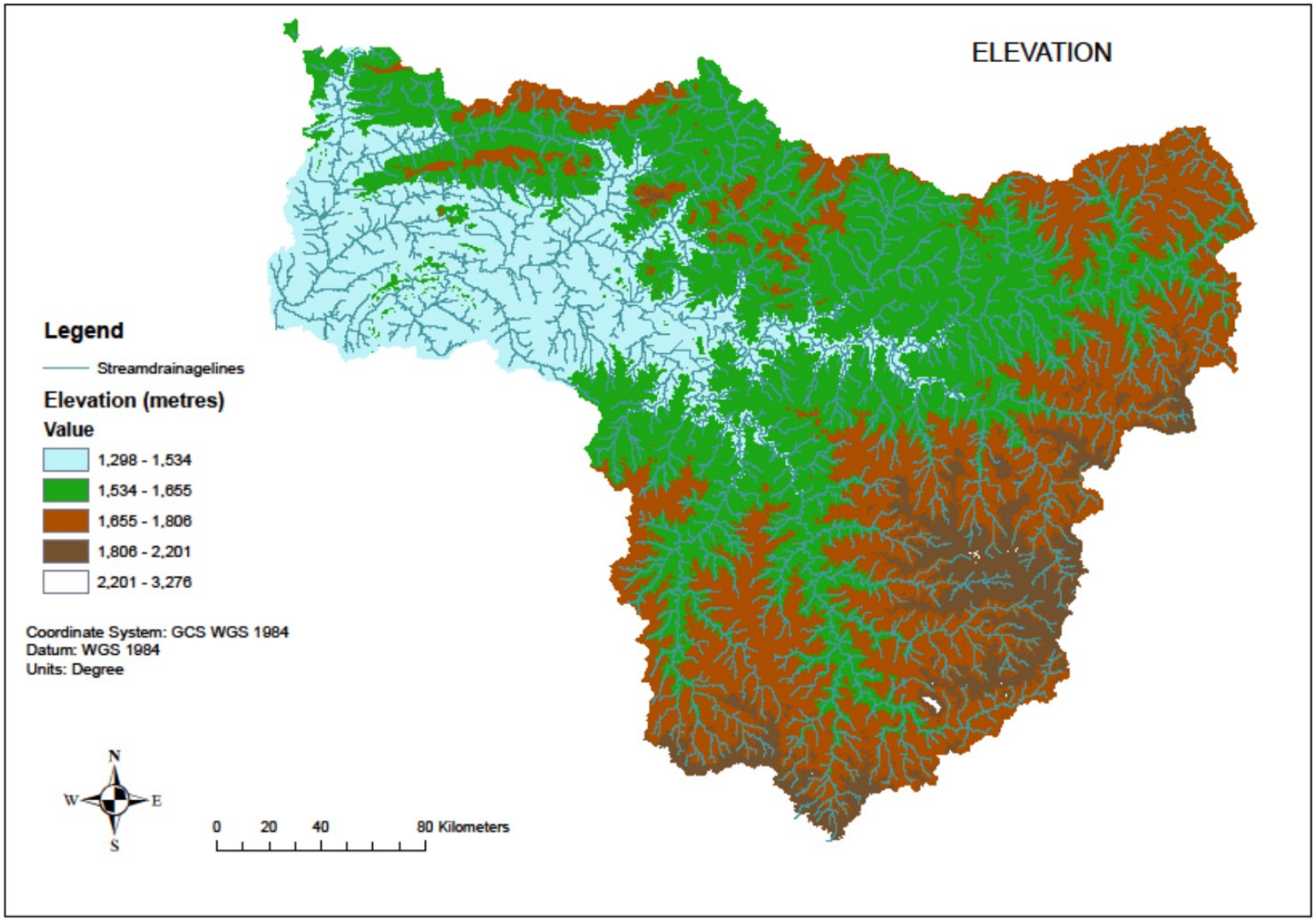


Figure 2 Elevation of the Upper Vaal

3.3 GEOLOGY

Fine sedimentary rocks underlie approximately 80% of the Upper Vaal area. Igneous and metamorphic rocks dominate the area north of the Vaal River and west of longitude 28°E. The central zones which are largely in the Mooi River tributary catchment area do however have extensive dolomite exposures (DWAF, 2004). Figure 3 is a geology map for the Upper Vaal.

3.4 SOILS

Soil depths in the Upper Vaal area are mostly moderate to deep upstream of the Vaal Barrage around Vereeniging. Three significant soil categories dominate the area: sandy loam covering the upper areas of the Wilge and Vaal catchments as well as north of the Vaal River along around its central sections; clay loam in the Klip River catchment area around Gauteng, plus the Suikerbosrand River catchments in addition to the central zones south of the Vaal River; and clay soil in the central and lower regions of the Vaal and Wilge River catchments (DWAF, 2004).

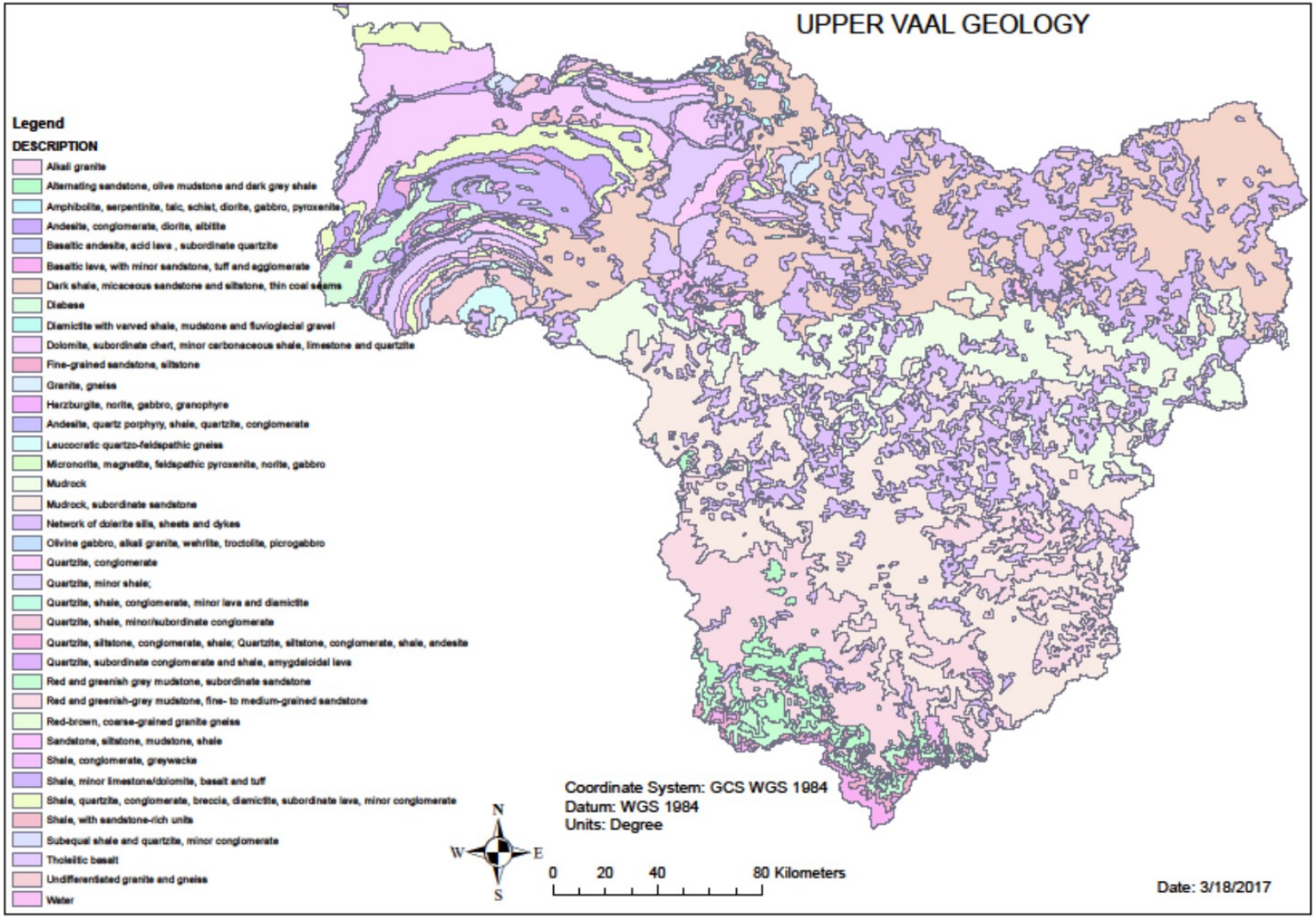


Figure 3 Geology of the Upper Vaal

3.5 VEGETATION AND ECOLOGY

Upper Vaal vegetation is generally savannah grassland with scant bushveld in places where climatic conditions permit. The region has important biodiversity zones. Some ecologically sensitive areas in the region include: the Blesbokspruit wetland; wetlands around Wakkerstroom; and wetlands in the Klip river catchment. The Upper Vaal is rich in bird species, reptiles as well as several small and large mammals (du Plessis, 2017). The Golden Gate National Park situated in the extreme south is a significant conservation area. Several other smaller conservation areas are dispersed throughout the catchment (DWAF, 2004).

3.6 CLIMATE

Average annual temperatures in the Upper Vaal area vary from 12°C in the east to 16°C in the west with a mean of approximately 15°C for the whole catchment. The Vaal River catchment area experiences its highest temperatures in January while minimum temperatures typically occur in July (DWAF, 2004).

Rainfall is highly seasonal with most fall taking place in summer between October and April. December and January are the peak rainfall months. Rainfall is largely in the form of convectional thunderstorms with hail. Frost occurs during the winter period - from around May to the end August. The declines in average annual rainfall westwards from the eastern escarpment sections across the central plateau are steady and consistent with mean yearly precipitation of approximately 1000mm in the east to about 500mm in the west and an average of roughly 700mm (DWAF, 2004).

3.7 LANDUSE

Notable land uses in the Upper Vaal are: nature conservation and recreation; agricultural; industrial; and mining. Figure 4 is a detailed landuse and landcover map for the area.

3.7.1 NATURE CONSERVATION

The main nature conservation areas are the Golden Gate National Park, the Allemanskraal Game Reserve; and Bloemhof Dam Nature Reserve as well as several smaller conservation areas distributed throughout the catchment area (DWAF, 2004).

3.7.2 AGRICULTURE

Cultivated dry land is prevalent across the Upper Vaal with areas around the Wilge, Vaal Dam and Vaal Barrage being the most cultivated. Wheat and maize are the key crops cultivated (DWAF, 2004).

3.7.3 INDUSTRY

Extensive urban and industrial areas historically built around the mining activities cover the northern and western portions of the Upper Vaal area. The most important industries include petro-chemical, iron and steel, and paper. Three coal fired power stations are operational in the area: the Tutuka, Lethabo and Majuba power stations. The Upper Vaal is located downwind of major pollution emitting power stations in the country (DWAF, 2004).

3.7.4 MINING

Mining activities in the Upper Vaal area include mining for base metals, coal, precious metals, semi-precious stones and industrial minerals.

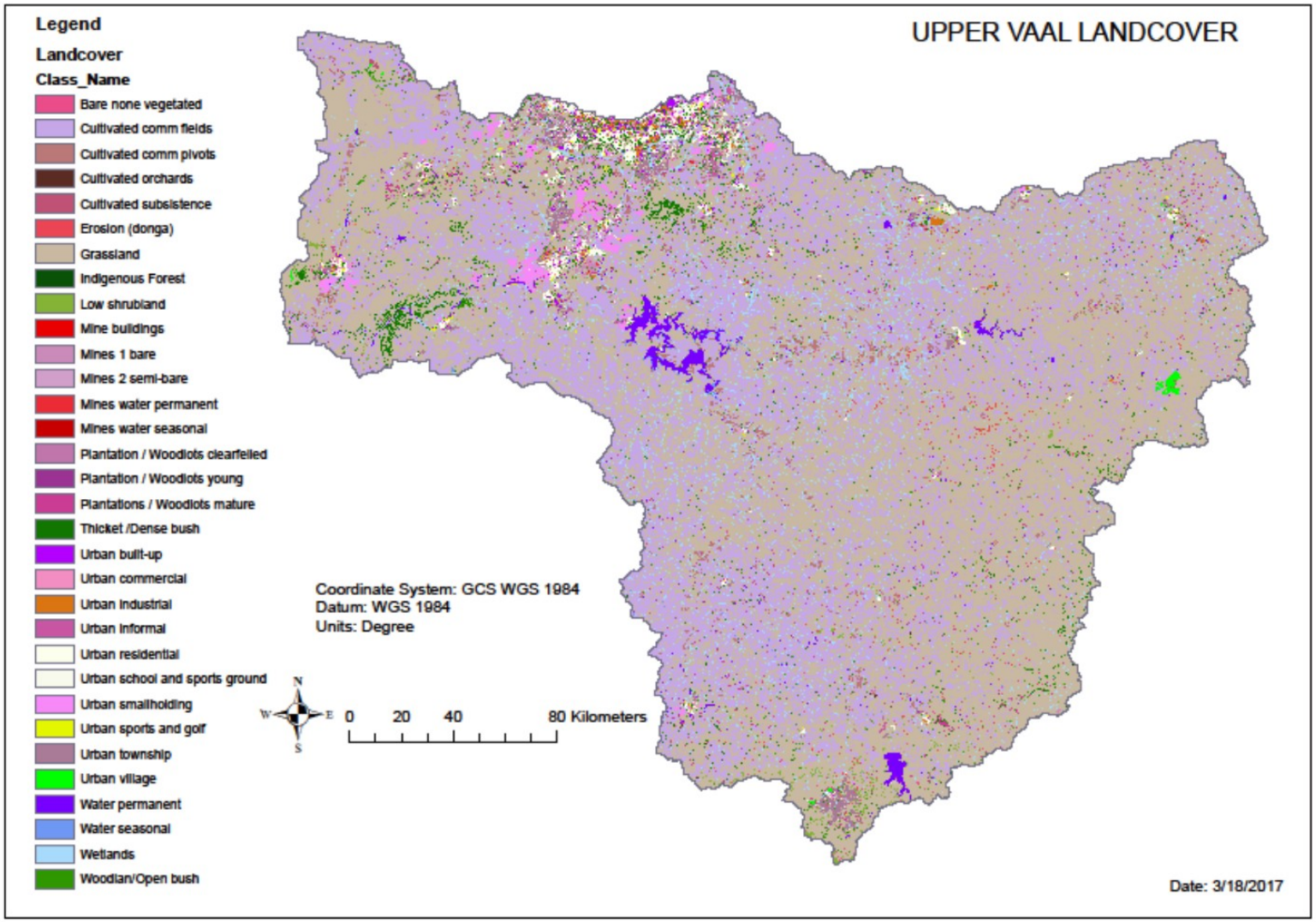


Figure 4 Landcover of the Upper Vaal

CHAPTER FOUR – RESEARCH DESIGN AND METHODS

4.1 DATA SETS

Data to delineate the Upper Vaal area and to determine the percentage of landcover and geology feature classes for all catchment polygons derived were acquired from various publicly accessible sites, the school of Animal Plant and Environmental Science (APES) and school of Geography, Archaeology and Environmental Studies (GAES). Modelled wet sulphur deposition data were obtained from eScience who use the WRFChem model to predict deposition rates. The WRFChem is an atmospheric chemistry model fully coupled with the WRF (Weather Research and Forecasting model) that is used for forecasting and modelling weather as well as research on dispersion, air quality, atmospheric chemistry and regional climate. It takes into consideration emission of gases and particulates to the atmosphere, their chemical transformation and interaction with weather, and their dry and wet deposition. Only modelled wet sulphur deposition was supplied for this project.

4.1.1 SATELLITE IMAGERY

Fifteen STRM 30m DEM images were downloaded from the United States Geological Survey website.

Table 2 DEM images

DEM ID	Publication date	Resolution	Co-ordinates
STRM IS27EO29V3	23 Sept 2014	1-Arc	-27, 29
STRM IS26EO29V3	23 Sept 2014	1-Arc	-26, 29
STRM IS27EO30V3	23 Sept 2014	1-Arc	-27, 30
STRM IS28EO29V3	23 Sept 2014	1-Arc	-28, 29
STRM IS28EO30V3	23 Sept 2014	1-Arc	-28, 30
STRM IS26EO30V3	23 Sept 2014	1-Arc	-26, 30
STRM IS29EO28V3	23 Sept 2014	1-Arc	-29, 28
STRM IS29EO29V3	23 Sept 2014	1-Arc	-29, 29
STRM IS27EO29V3	23 Sept 2014	1-Arc	-27, 26
STRM IS26EO26V3	23 Sept 2014	1-Arc	-26, 26
STRM IS27EO25V3	23 Sept 2014	1-Arc	-27, 25
STRM IS27EO28V3	23 Sept 2014	1-Arc	-27, 28

STRM IS27EO27V3	23 Sept 2014	1-Arc	-27, 27
STRM IS28EO27V3	23 Sept 2014	1-Arc	-28, 27
STRM IS28EO28V3	23 Sept 2014	1-Arc	-28, 28

4.1.2 GEOGRAPHICAL DATA

GIS vector files of geology, landuse, Eskom power stations, main places, and rivers were obtained from various public sites, GAES, APES and eScience.

Table 3 Vector files

Vector file	File name	Publication	scale	Access
National Landcover	NLC 2013/2014	Dec 2014	1:1 250 000	http://egis.environment.gov.za
Geology	saGEOLWGS84	April 2008	1:1 880 000	http://sageoscience.maps.arcgis.com
Water Management areas	Water_ManagementAreas_2004KZM	2004	1:6 000 000	http://www.dwaf.gov.za
ESKOM power stations	ESKOM_Powerstations	Nov 2014	1:6 000 000	GAES
Main rivers	Rivers_WGS84	Jul 2009	1:1 880 000	APES
Modelled wet sulphur deposition	Wet_sulphur_deposition	2014	1:1 745 000	eScience
Main Towns	Places	2004	1:6 000 000	APES

4.2 GIS ANALYSIS

4.2.1 GIS DATA PREPROCESSING

To ensure high quality map products were produced and accurate data analysis was performed, a series of tools in ArcGIS Data Reviewer that support both automated and visual analysis of GIS data were used for quality control purposes. These tools were used to detect anomalies with features, attributes and relationships in the data. Spatial checks analysed the spatial relationships of features; attribute checks scrutinized the attribute values of features and tables; feature integrity checks evaluated the properties of the attributes; metadata checks examined the metadata of the feature datasets and feature classes; and managed data review was valuable in understanding the integrity of the entire dataset.

Accuracy for all GIS analyses was set at a confidence level of 95%. Therefore, 95% of the positions in the dataset and on the maps have an error with respect to true ground position

that is equal to or lesser than the accuracy value. The accuracy value reflects all uncertainties including those introduced by map production, data conversion and data manipulation.

4.2.2 CATCHMENT DELINEATION

Boundaries of catchments in the Upper Vaal were defined in order to identify headwater catchments that are drained by first order streams and have < 5% human activity. The DEM datasets were merged into one entity using the Mosaic – Data Management tool in ArcGIS 10.3 in order to reduce discontinuities along boundaries of the intersecting rasters. STRM IS27EO29V3 was designated as the target raster and the rest of the DEM data sets were fused into it. The Clip – Data Management tool was then used to clip the target raster using the Upper Vaal vector layer as the clip extent.

An initial conditioning phase to hydrologically correct the DEM was then conducted. The conditioning generated three data sets that were utilized in subsequent stages of the delineation. The data sets that were generated are: a DEM with filled depressions; a flow direction raster; and a flow accumulation raster.

The Fill tool in the Hydrology toolbox was used to eliminate any imperfections (sinks) in the DEM. The DEM grid derived from the clip was set as the input raster in the Fill tool dialogue box. The output was a depression free DEM in which the cells contained in sinks were elevated to the lowest elevation value on the edge of the sink so that every cell in the depressionless DEM was connected to a minimum of one declining path leading to the edge of the data set.

The Flow Direction raster defined the course of flow from each cell in the raster as well as the final destination of the water flowing across the catchment. The depressionless DEM derived from running the original DEM grid through the Fill tool was set as the input raster in the Flow Direction dialogue box. An output raster displaying the maximum variation in elevation between cell centres was created.

The flow direction raster was input into the Flow Accumulation tool. The output was a raster of accrued flow to every downslope cell determined by the cumulative weightiness of cells flowing into them. Symbology of the flow accumulation raster was altered to allow easy visualization of areas with high flow build-up. The number of classes was fixed at two and the first break value was set at a starting point of 10 000. All cells with less than 10 000 upstream

cells flowing into them, were symbolised differently from those with more than 10 000 upstream cells. The Raster Calculator was used to generate a new raster layer of stream network by setting a condition such that for all flow accumulation pixels greater or equal to 10 000 the output was a stream which was a part of a bigger network of streams and no data for anything less than 10 000.

The stream raster generated was then set as the input in the Stream to Feature tool and the output was a vector layer with features representing the linear network. The stream raster was also run through the Stream Link tool and distinct values were allocated to all links between connections. Stream links and the flow direction raster were then processed through the Watershed tool. This delineated catchments upstream of all links in the stream network. The resultant catchment grid had a distinct value for each catchment area drained by a distinct link. The conversion tool was then used to convert the catchment raster to polygon. A total of 3970 polygons were derived from the delineation with each polygon representing a distinct catchment drained by a distinct stream which is part of a larger network of streams draining the Upper Vaal Water Management area. Figure 5 is a schematic presentation of the steps in delineation.

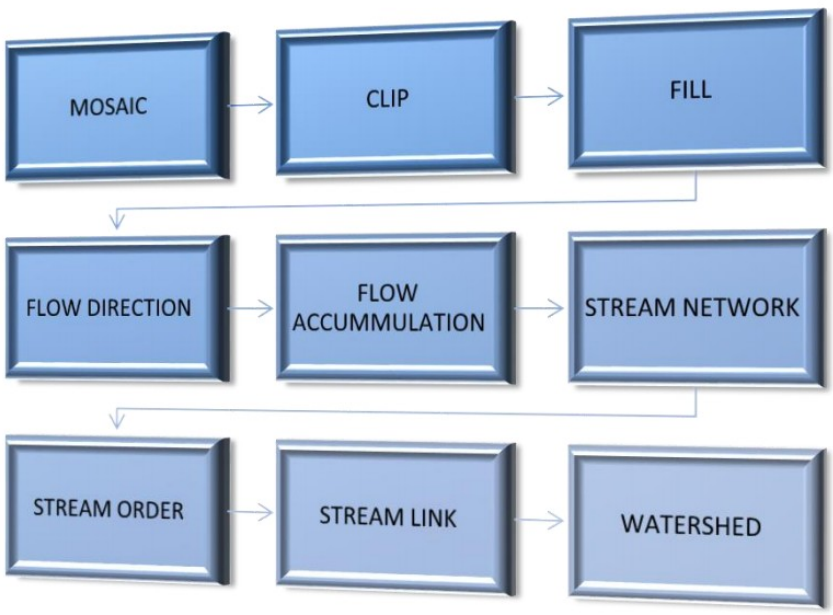


Figure 5 Delineation process

4.2.3 NATURAL CATCHMENT IDENTIFICATION

The mosaic landcover map consisting of seven land cover classes i.e. cultivation, degraded, mines, natural, plantations, urban build up and waterbodies, was clipped using catchment polygons derived from the delineation as the extent. The resultant landcover clip was converted into polygon. The intersection between the landcover and the polygons was then calculated and its area cross tabulated using the Tabulate Intersection tool. The catchment polygons layer was set as the input zone feature that identified the zones with the Object ID attribute field for the layer defining the zones. The land cover polygon layer was set as the input feature that identified the classes with the description attribute field for this layer defining the classes. The output was a table showing the areas and percentage of each landcover class within each zone. The table helped in identifying headwater catchment polygons whose combined natural and waterbodies cover consisted of at least 95% of the total catchment area. A total of 148 catchments in the Upper Vaal were identified to be natural headwater catchments drained by first order streams. Forty-two (42) study sites were selected from among the 148 catchments with < 95% human activity with each study site being positioned along a first order stream draining a headwater catchment with < 5% non-natural cover. All catchments with > 5% human activities or whose upper polygons include such activities were excluded. Catchments were selected to follow a roughly linear pattern of increasing distance from Majuba power station which was assumed to represent a gradient of decreasing acid deposition.

4.2.4 DETERMINATION OF CATCHMENT GEOLOGY COMPOSITIONS

The geology map was clipped with the catchment polygons set as the output extent. The resultant clip was converted into polygon. The intersection between the geology and the polygons was then calculated and its area cross tabulated using the Tabulate Intersection tool. The catchment polygons layer was set as the input zone feature that identified the zones with the Object ID attribute field for the layer defining the zones. The geology polygon layer was set as the input feature that identified the classes with the description attribute field for this layer defining the classes. The output was a table showing the areas and percentage of each geology class within each zone.

4.3 ASSESSMENT OF STREAM WATER QUALITY TO DETECT ACID DEPOSITION

The stream water quality study focused on assessing the physical and chemical characteristics of the stream waters in a sample of 42 catchments that were determined using GIS analysis to be headwater catchments in which combined natural and waterbodies cover consisted of at least 95% of total catchment area. pH, conductivity as well as estimates of levels of Cl^-, NO_3^- and SO_4^{2-} of collected samples based on laboratory measurements were used as indicators of an acid deposition signal in sampled catchments.

4.3.1 CALIBRATION OF THE YSI PROFESSIONAL PLUS MULTI METER

The YSI professional plus multi meter was used to measure pH, conductivity, temperature and DO of the water in situ at each sample site. Before each sampling campaign, the meter was calibrated to ensure the accuracy and precision of measurements that were taken.

Laboratory glassware was used in place of the transport cup, to perform pH and conductivity calibrations. Between standardizations, ambient temperature tap water was used to rinse the probe module before a second rinse in deionized water. Excess water was shaken off the probe module and absorbent paper towels were used to dry off the outside of the probe module in order to minimise carry over contamination of calibration solutions and improve accuracy of the adjustments. To further enhance accuracy, small amounts of previously used calibration solutions were also used to pre-rinse the probe module before calibration readings were taken. Calibration values were taken while sensors were completely submersed in calibration solutions.

4.3.1.1 pH CALIBRATION

The pH sensor of the YSI was calibrated with the 2-point option on the pH menu of the instrument using two buffer solutions with pH 7 and 4. pH was highlighted in the calibrate menu of the YSI. A sufficient amount of buffer 7 allowing total immersion of the pH probe in the solution was poured into a clean and pre-rinsed beaker. The pH sensor was then completely submerged in the calibration solution and the calibration value of the buffer at the present temperature was entered using the keypad of the YSI. The pH reading was observed and after showing no significant change for approximately 30 seconds the enter key

was pressed to accept the calibration value. This returned the YSI pH calibration screen. The probe module was then rinsed in tap water and distilled water before being dried and pre-rinsed in buffer 4 solution before the calibration procedure was repeated for pH 4 calibration. When the pH reading for the buffer stabilised, the calibrate button was entered to complete the pH calibration process.

4.3.1.2 CONDUCTIVITY CALIBRATION

Specific conductance was selected from the calibration menu of the YSI. A sufficient amount of 1413µS cm^{-1} conductivity standard was placed in a clean and pre-rinsed beaker so that total immersion of the conductivity probe was possible. The conductivity sensor was completely immersed into standard solution and using the YSI keypad, the calibration value of the standard solution that was used was entered in µS cm^{-1} at 25°C. The conductivity reading was accepted after approximately 30 seconds of showing stable values.

4.3.2 STREAM WATER SAMPLING STRATEGY AND SAMPLE COLLECTION

A total of 42 stream water samples were collected from catchments that were determined using GIS analysis to be headwater catchments in which combined natural and waterbodies cover consisted of at least 95% of total catchment area. At each study site the YSI probe was completely immersed in the stream allowing a few minutes for the instrument to stabilize before noting readings of time, temperature, pH, conductivity, and DO (mgl^{-1} and % saturation) while the probe was still submerged. A GPS was used to determine precise GPS co-ordinates at each sample site. Grab samples were collected at all 42 study sites. A clean 500 ml plastic sample container was rinsed three times with water from the stream before being directly dipped into the water without stirring up the stream bottom to collect a sample. A cap was then screwed on the container and it was kept on ice in a cooler box while being transported back to the laboratory for analysis.

4.3.3 LABORATORY METHODS FOR ANALYSIS OF STREAM WATER SAMPLES

Collected stream water samples were all filtered through Whatman GF/C 40 1.2µm filters before being analysed to determine concentrations of SO_4^{2-}, NO_3^- and Cl^- using a Hach DR2800 spectrophotometer.

4.3.3.1 MERCURIC THIOCYANATE METHOD FOR CHLORIDE DETERMINATION

APPARATUS

- Hach DR 2800 spectrophotometer
- Sample cells
- 0.1 to 1 ml pipette
- Pipette tips

REAGENTS AND SOLUTIONS

- Ferric ion solution
- Mercuric thiocyanate solution
- Deionized water

METHOD

The Mercuric Thiocyanate Method (0.1 to 25mgl^{-1} Cl^-) for the assessment of chloride ions content was selected from the programmed tests menu of the Hach DR 2800. A sample cell was filled with 10 ml of sample. A blank sample was also prepared using 10 ml of deionized water. 0.8 ml of mercuric thiocyanate solution was then transferred into each sample cell using a pipette. The cells were then swirled to ensure thorough mixing. 0.4 ml of ferric ion solution was then transferred into each cell using a pipette. The cells were swirled again to mix. The timer on the Hach was started allowing a two minute reaction to take place. Within five minutes of the timer expiring, the blank was wiped and inserted into the cell holder of the spectrophotometer with the fill line facing right and instrument zeroed. The prepared sample was also wiped, inserted into the cell holder and the instrument read. The results in mgl^{-1} Cl^- were noted

4.3.3.2 CADMIUM REDUCTION METHOD FOR POWDER PILLOWS TO DETERMINE NITRATE

APPARATUS

- Hach DR 2800 spectrophotometer
- Sample cells
- 25 ml graduated mixing cylinder

REAGENTS AND SOLUTIONS

- NitraVer 6 Nitrate reagent powder pillows
- NitriVer 3 Nitrite reagent powder pillows

METHOD

The Cadmium Reduction Method low range for the determination of nitrates was selected from the programmed tests menu of the Hach DR 2800. A 25 ml graduated mixing cylinder was filled with 15 ml of sample. Contents of one NitraVer 6 reagent powder pillow were then added to the cylinder and a stopper inserted. The timer on the spectrophotometer was started and the reaction allowed to take place for three minutes shaking the cylinder vigorously during this time. After three minutes, the timer was set for a further two minutes reaction period. Once the two minutes had expired, 10 ml of the sample was transferred into a clean sample cell, care being taken so that no cadmium particles were transferred. Contents of one NitriVer 3 Nitrite reagent powder pillow were then added to the sample cell. The timer was started allowing a 30 second reaction period, gently shaking the cell during this period. The timer was started again allowing a 15 minute reaction. After 15 minutes a second sample cell was filled with 10 ml of the original sample to be used as the sample blank, wiped and inserted in the cell holder of the Hach with the fill line facing right. The instrument was then zeroed. The prepared sample was wiped and inserted into the cell holder and the instrument read. The results in mgl^{-1} NO_3^-N (NB 1mg NO_3^-N = 62/14 or 4.43 mg nitrate) were noted.

4.3.3.3 SULFAVER 4 POWDER PILLOW PROCEDURE FOR THE DETERMINATION OF SULPHATE

APPARATUS

- Hach DR 2800 spectrophotometer
- sample cells

REAGENTS AND STANDARDS

- SulfaVer 4 regent powder pillows

METHOD

The two to 70 mgl^{-1} SulfaVer 4 Method for determining sulphate was selected from the programmed tests menu of the Hach DR 2800. 10 ml of sample was placed in a sample cell and contents of one SulfaVer 4 reagent powder pillow were added, swirling briskly to dissolve the powder. The Hach timer was started and a five minute reaction allowed to take place. A second sample cell was filled with 10 ml of sample. After the timer expired, the blank was wiped and inserted in the cell holder with the fill line facing right. The instrument was then zeroed. Within five minutes of the timer expiring, the cell with the sample was wiped and inserted in the cell holder of the Hatch and the instrument read. The results in mgl^{-1} sulphate were noted.

4.4 STATISTICAL ANALYSES

4.4.1 TESTING THE ASSUMPTION THAT ACID DEPOSITION HAS A SIGNIFICANT EFFECT ON STREAM WATER QUALITY IN THE UPPER VAAL

PCA was first conducted on geology data. The purpose of the PCA was to identify the key geology composites and compute composite geology scores for all the 42 study sites. A multivariate general linear model in SPSS was then used to analyse the significance, direction and magnitude of relationships between geology, wet sulphur deposition, distance from Majuba power station and stream water quality of natural headwater catchments in the Upper Vaal. The model helped to determine whether changes in geology, wet sulphur deposition and distance from Majuba power station have significant effects on stream water pH, conductivity, as well as loading of sulphate, nitrate and chloride ions. Further, the regression allowed for the determination of overall fit (variance explained) of the model and explained the relative contribution of geology, acid deposition and distance of study sites from Majuba power station to the total variance.

4.4.2 TESTING STATISTICAL ASSUMPTIONS

4.4.2.1 SHAPIRO-WILK TEST FOR NORMALITY

Multivariate normality is unfortunately a particularly problematic supposition to test for and cannot be directly tested in SPSS. The distribution of dependent variables for the various

combinations with groups of independent variables was instead used to test for multivariate normality. This was assessed using the Shapiro-Wilk test for normality. All variables that did not show a normal distribution were transformed by square root transformation.

4.4.2.2 LEVENE'S TEST OF HOMOGENEITY OF VARIANCES

The variance of dependent variables across groups was determined using Levene's test.

4.4.3 CRITERIA FOR SIGNIFICANCE TESTING

Pillai's criterion was the preferred measure of testing significance and determining, direction and magnitude of relationships between geology, acid deposition and pH, conductivity as well as concentrations of sulphate, nitrate and chloride of stream waters considering that some assumptions of multivariate analysis had not been met. The test determined the overall fit of the model and elucidated the relative contribution of geology, wet sulphur deposition and distance from Majuba power station to the total variance.

CHAPTER FIVE – RESULTS

This study investigated the link between acid deposition and stream water quality in selected natural headwater catchments (i.e. headwater catchments which preclude cultivation, plantations, mines, and urban build-up) within the Upper Vaal Water Management Area. The selection of natural headwater catchments as sample sites and exclusion from the study of all catchments which include anthropogenic activities guaranteed that the water chemistry of streams that were sampled could have only been influenced by either catchment geology, acid deposition or a combination of the two. In pristine catchments nitrates, sulphates and chlorides are largely cycled and retained within these systems with marginal discharge to ground and surface water unless they are exposed to pollution (Curtis et al., 1998; Evans et al., 2011; Helliwell et al., 2001). The pH and salinity of stream waters are mainly determined by geology and soil characteristics in natural catchments (Langan and Wilson, 1992).

This chapter summarises collected data, its statistical treatment, as well as the process of the analyses. The results are presented in three distinct sections, each linked to a particular objective of the study and supporting the assumptions that were made:

- Outputs of the GIS analysis help identify natural headwater catchments; determine their geology compositions; as well as their annual rates of modelled wet sulphur deposition in sampled catchments
- Stream water quality assessment outcomes give an indication of pH, conductivity, sulphate, nitrate and chloride of sampled streams denoting the occurrence of acid deposition in the sampled catchments;
- Statistical outcomes quantify the significance, magnitude and direction of relationships between geology, annual rates of modelled wet sulphur deposition, distance from Majuba and pH, conductivity, sulphate, nitrate and chloride of sampled catchments.

5.1 OUTPUTS OF THE GIS ANALYSIS

The GIS analysis outputs helped identify natural headwater catchments; determine their geology compositions; as well as the annual rates of modelled wet sulphur deposition. Figures 6-9 below are the products of the various stages of the delineation that was conducted so as to determine the boundaries of the catchments in the Upper Vaal and to derive the drainage network. A total of 3970 polygons representing a total catchment area of 55 565 km^2 were derived from the delineation. Each polygon derived represents a distinct catchment drained by a distinct stream which is part of a larger network of streams draining the Upper Vaal Water Management area. Spatial analysis conducted to identify headwater catchments drained by first order streams with at least 95% natural landcover revealed that 148 catchments meet this criterion, representing 4.51% of total catchment area in the Upper Vaal. Forty-two (42) study sites representing 1.22% of total catchment area were selected from among the 148 catchments with < 5% human activity. All catchments with > 5% human activities or whose upper polygons include such activities were excluded. Figure 10 highlights catchments across the Upper Vaal that were identified as natural. Figure 11 is a map showing the 42 natural catchments that were used as study sites. The GPS coordinates, elevation as well as a general description of the vegetation and streams in catchments used as study sites are given in Appendix I (Table I). Table 4 highlights the percentages of natural cover, waterbodies, cultivation, degraded land, mines, plantations and urban cover in each study catchment.

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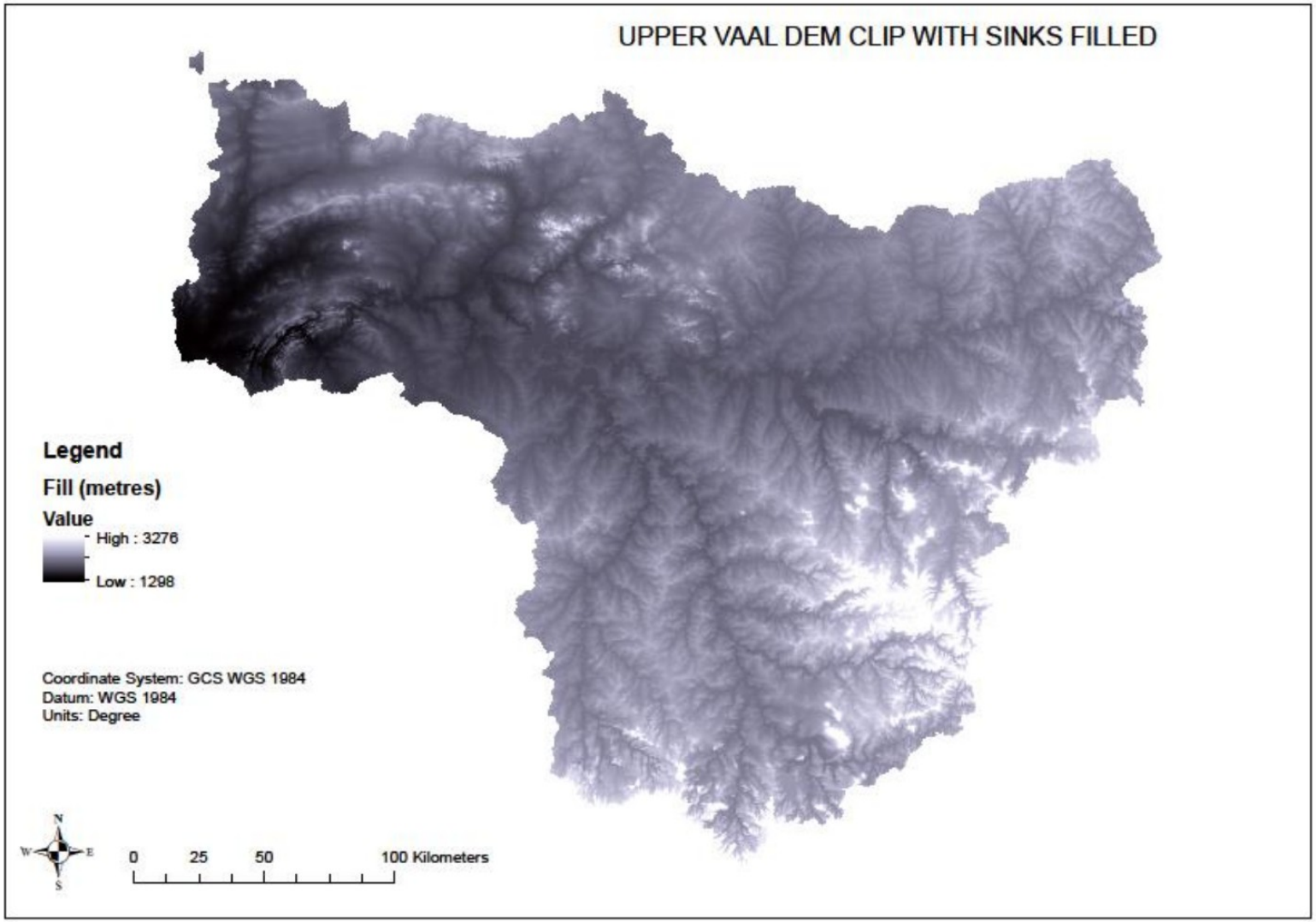


Figure 6 Fill output – DEM after sinks have been filled

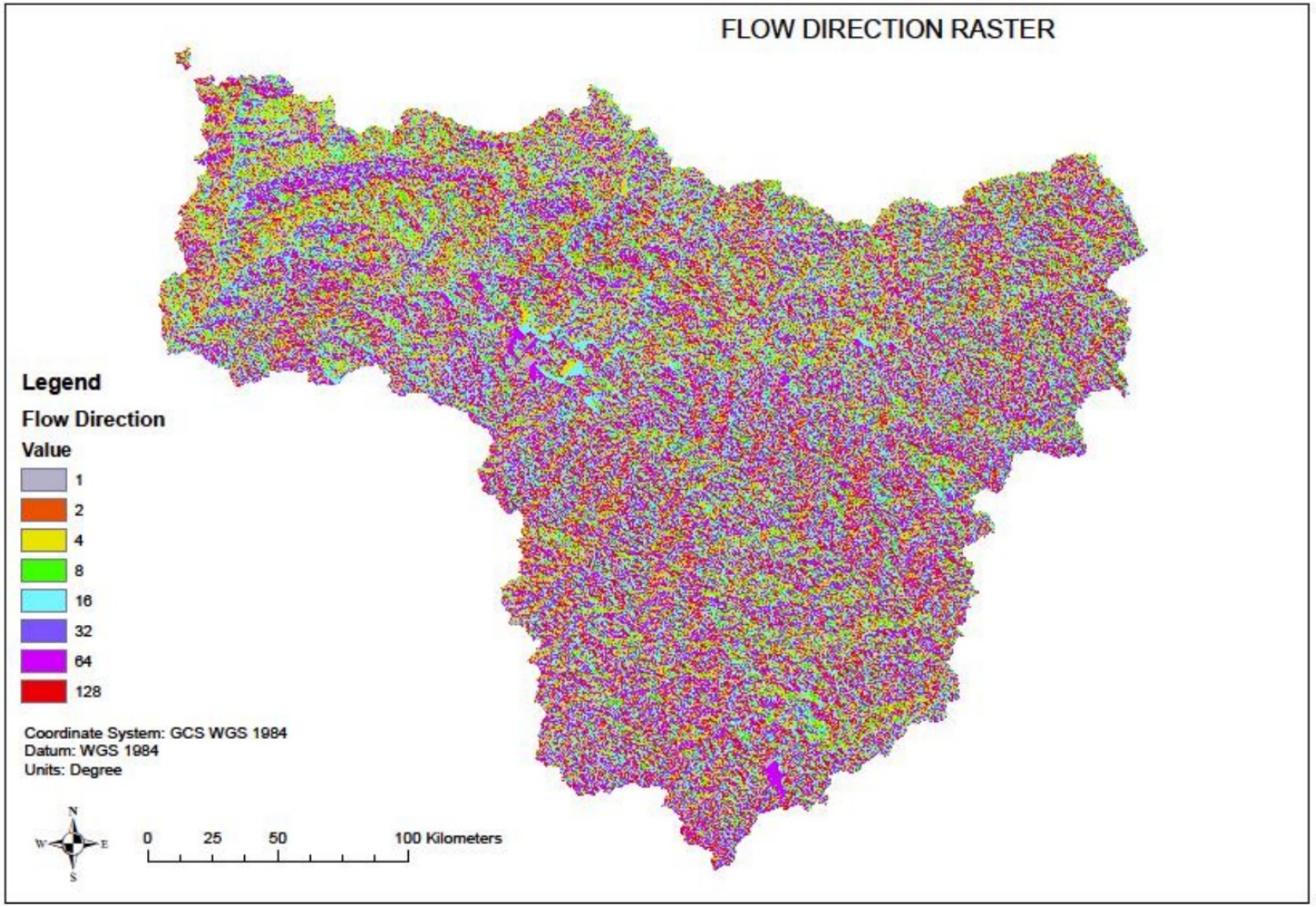


Figure 7 Flow direction output with values indicating the eight valid output directions relating to the eight adjacent cells into which flow could travel

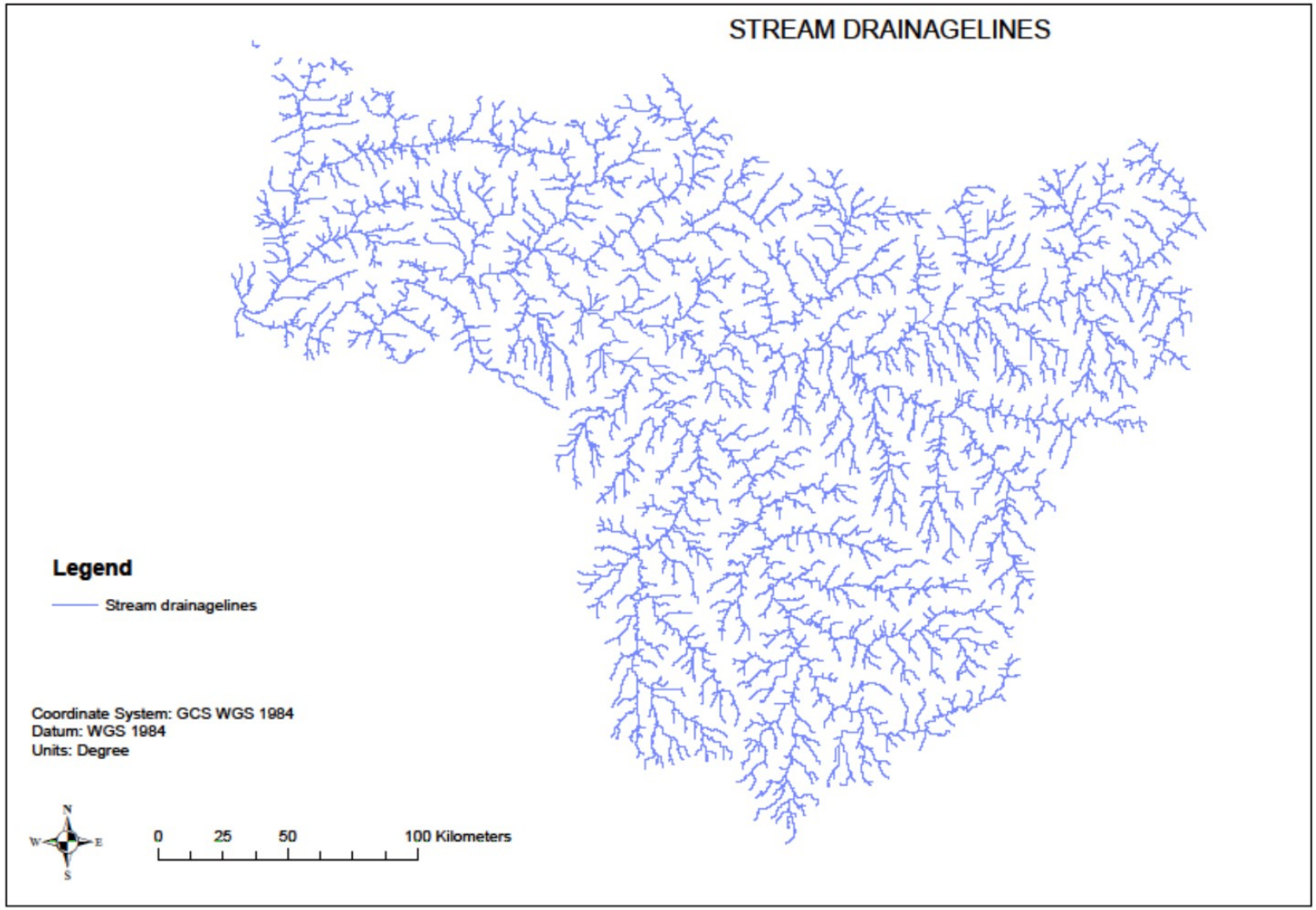


Figure 8 Network of streams in the Upper Vaal derived from the delineation

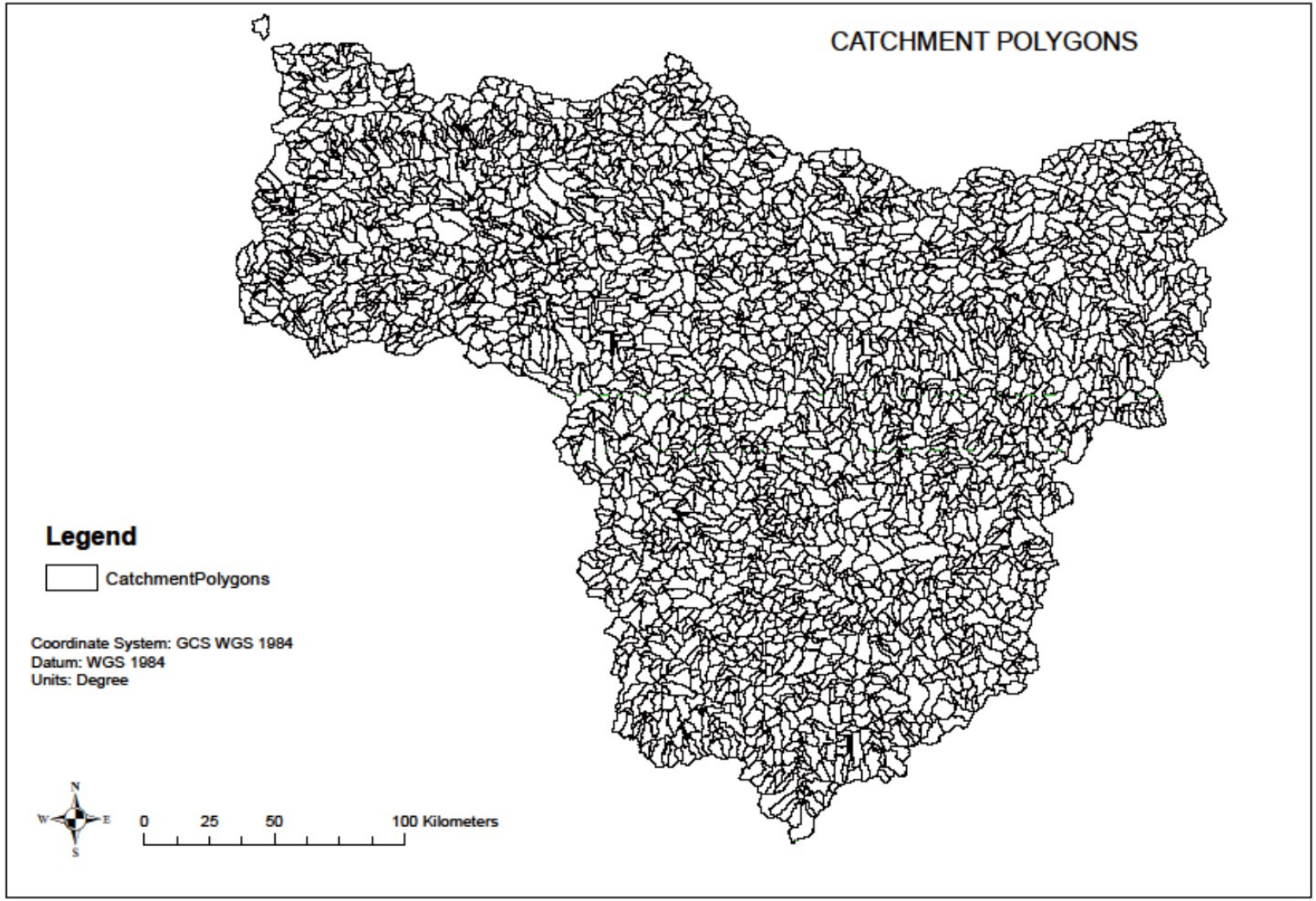


Figure 9 The 3970 catchment polygons derived through delineation. Each catchment polygon represents a distinct catchment drained by a distinct stream which is part of a larger network.

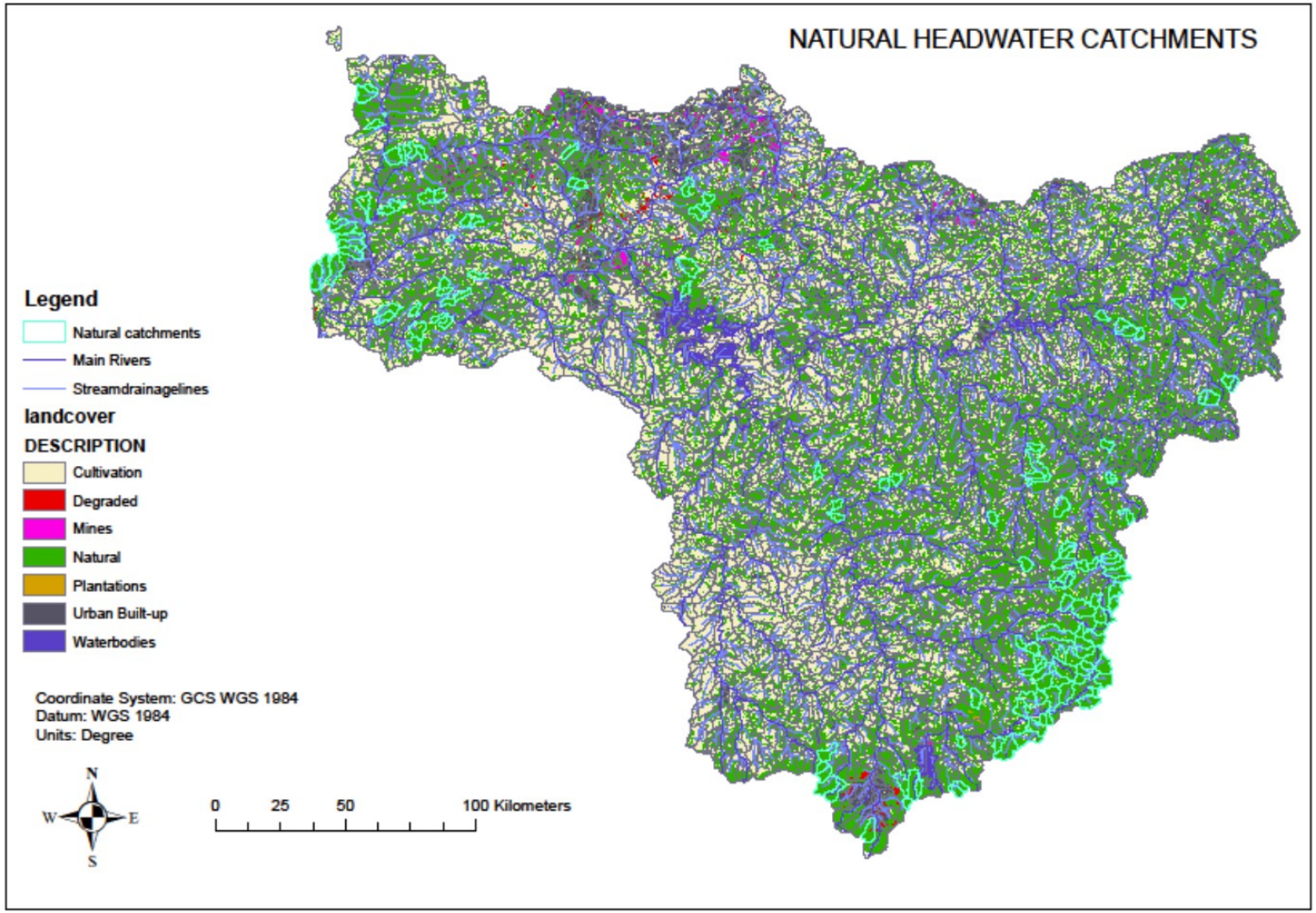


Figure 10 Distribution of 148 headwater catchments with < 5% of non- natural cover representing 4.51% of total catchment area in the Upper Vaal.

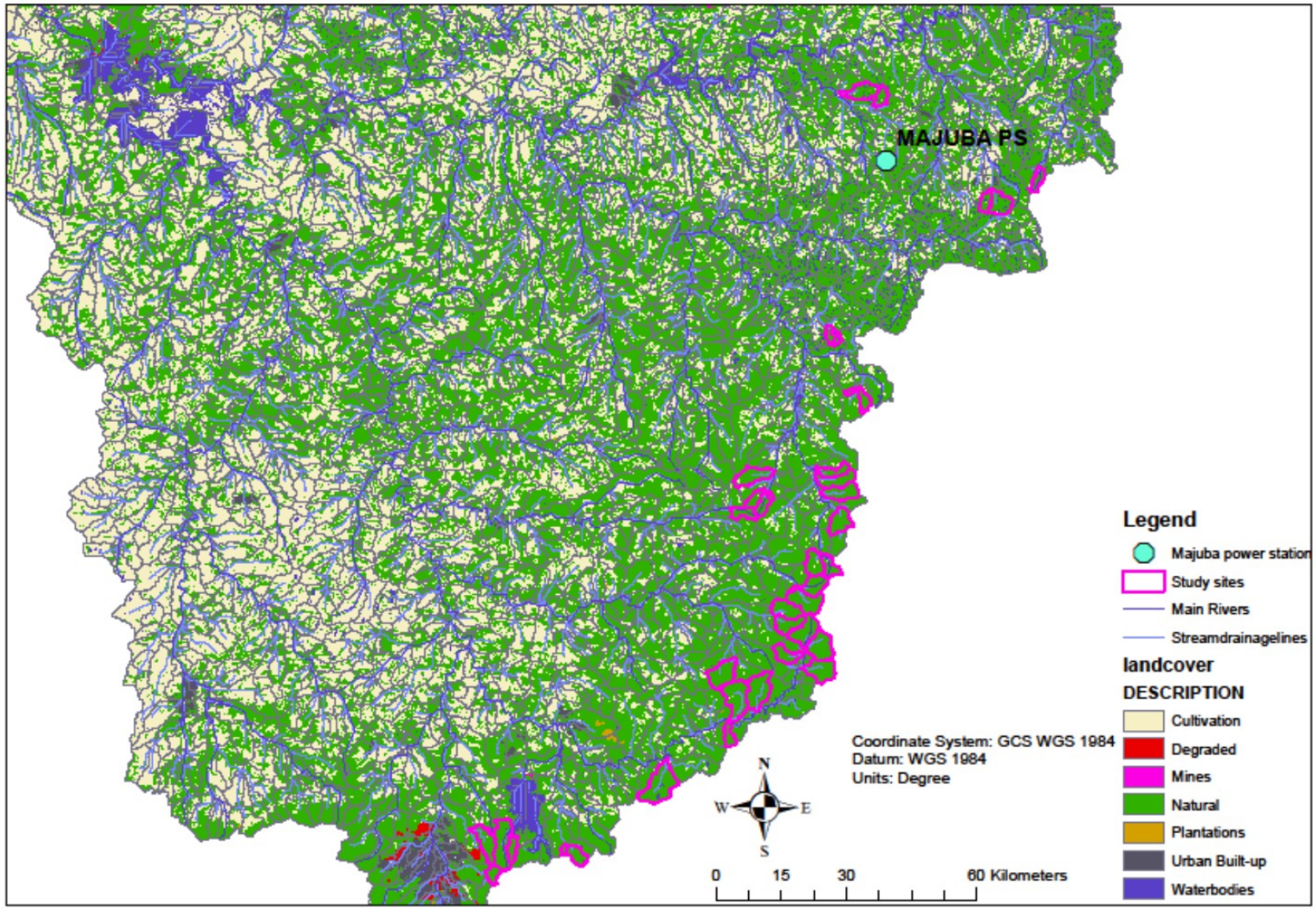


Figure 11 Location and distribution of the forty-two (42) catchments used as study sites.

Table 4 Landcover composition of the 42 study sites highlighting the percentages of natural cover, waterbodies, cultivation, degraded land, mines, plantations and urban cover in each study catchment.

SITE ID	NATURAL (%)	WATERBODIES (%)	CULTIVATION (%)	DEGRADED (%)	MINES (%)	PLANTATIONS (%)	URBAN (%)
IS3955	99.545	0.029	-	-	-	-	-
IS3939	98.165	-	1.826	-	-	-	-
IS3945	95.114	4.486	0.371	-	-	-	-
IS3937	97.698	-	2.302	-	-	-	-
IS3941	97.085	0.100	1.119	-	-	-	0.076
IS3941B	99.662	-	-	-	-	-	-
IS3863	94.663	3.138	0.944	-	-	-	-
IS3760	99.368	0.074	0.356	-	-	-	-
IS3715	98.698	-	1.302	-	-	-	-
IS3639	98.371	-	1.459	-	-	-	-
IS3693	98.105	1.895	-	-	-	-	-
IS3582	100	-	-	-	-	-	-
IS3549	99.938	-	-	-	-	-	-
IS3627	99.733	-	-	-	-	-	-
IS3577	99.188	0.483	-	0.095	-	-	-
IS3523	99.459	-	0.363	-	-	-	-
IS3480	98.596	0.014	1.390	-	-	-	-
IS3467	99.842	-	-	-	-	-	-
IS3467B	100	-	-	-	-	-	-
IS3416	99.853	0.005	-	-	-	-	-
IS3366	95.419	-	4.581	-	-	-	-
IS3369	98.036	-	1.453	-	-	-	-

IS3275	99.758	-	-	-	-	-	-
IS3184	98.654	-	1.239	-	-	-	-
IS3157	95.919	0.037	4.926	-	-	-	-
IS3131	96.146	0.059	3.794	-	-	-	-
IS3237	98.233	0.008	1.759	-	-	-	-
IS3225A	95.450	-	4.550	-	-	-	-
IS3225B	94.935	2.568	5.065	-	-	-	-
IS3203	96.202	-	3.798	-	-	-	-
IS3155	95.677	-	4.323	-	-	-	-
IS2972	96.470	-	3.313	-	-	-	-
IS2972B	100	-	-	-	-	-	-
IS2792	91.518	7.488	0.903	-	-	0.091	-
SPRING	91.675	8.325	-	-	-	-	-
IS2792A	90.328	9.3669	0.305	-	-	-	-
IS2792B	87.326	7.675	4.999	-	-	-	-
IS2360	91.341	4.716	3.942	-	-	-	-
IS2370	90.344	5.694	3.962	-	-	-	-
IS1946	91.553	4.778	3.668	-	-	-	-
IS1891	91.973	6.932	0.948	-	-	0.148	-
IS2303	90.272	9.226	0.169	-	-	-	-

Figure 12 is a map showing the distribution of rock types across the study sites. There are 11 different rock classes and 15 different combinations across the 42 catchments sampled in the study. 28.57 % of the study sites are underlain by÷ red and greenish-grey mudstone with fine- to medium-grained sandstone and sandstone, siltstone, mudstone and shale. 16.67 % are underlain by÷ red and greenish-grey mudstone with fine- to medium-grained sandstone; sandstone, siltstone, mudstone and shale; and network of dolerite sills, sheets and dykes. 14.28 % are underlain by sandstone, siltstone, mudstone and shale. 7.14% are underlain by÷ red and greenish-grey mudstone with fine- to medium-grained sandstone; sandstone, siltstone, mudstone and shale; and mudrock. 4.76% are underlain by÷ mudrock and subordinate sandstone; sandstone, siltstone, mudstone and shale; and mudrock. 4.76% are underlain by÷ mudrock and dark shale, micaceous sandstone and siltstone, and thin coal seams. 2.38 % are underlain by mudrock. 4.76 % are underlain by÷ basaltic lava; fine-grained sandstone; alternating sandstone; red and greenish grey mudstone with subordinate sandstone; and water. 2.38 % are underlain by sandstone, siltstone, mudstone and shale; and dark shale, micaceous sandstone and siltstone, and thin coal seams. 2.38 % are underlain by÷ red and greenish-grey mudstone with fine- to medium-grained sandstone and sandstone; sandstone, siltstone, mudstone and shale; network of dolerite sills, sheets and dykes; and mudrock. 2.38 % are underlain by basaltic lava and fine-grained sandstone. 2.38 % are underlain by: basaltic lava; fine-grained sandstone; alternating sandstone; red and greenish-grey mudstone with fine- to medium-grained sandstone; as well as red and greenish grey mudstone with subordinate sandstone. 2.38 % are underlain by÷ basaltic lava; red and greenish-grey mudstone with fine- to medium-grained sandstone; as well as red and greenish grey mudstone with subordinate sandstone. 2.38 % are underlain by÷ alternating sandstone; and red and greenish-grey mudstone with fine- to medium-grained sandstone. 2.38 % are underlain by÷ red and greenish-grey mudstone with fine- to medium-grained sandstone; sandstone, siltstone, mudstone and shale; and network of dolerite sills, sheets and dykes. Table 5 highlights the geology compositions of the individual study catchments determined in GIS.

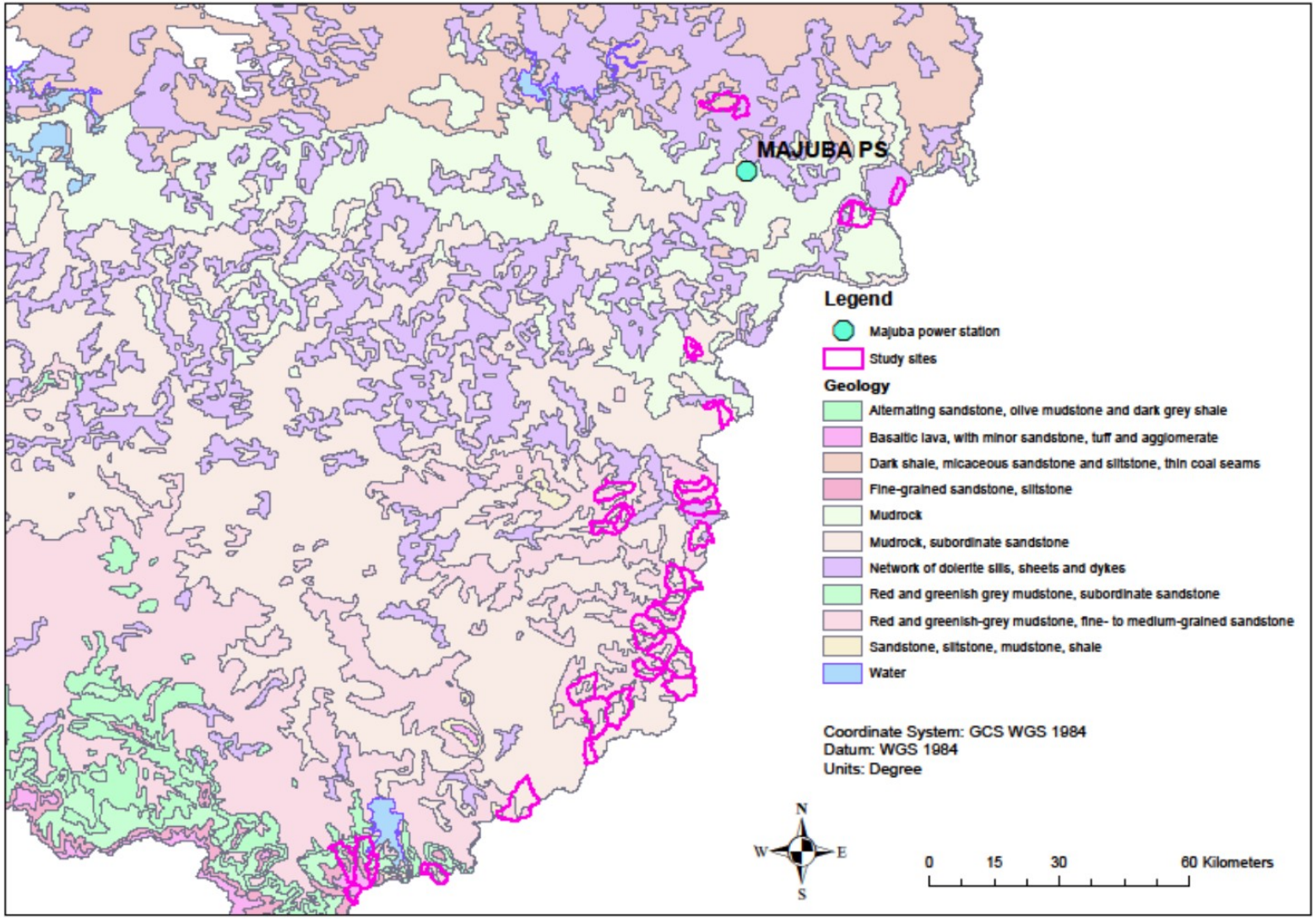


Figure 12 Distribution of various rock types in the 42 study catchments

Table 5 Geology highlighting percentages of the various rock types that occur in each of the 42 study catchments.

SITE ID	BASALTIC LAVA (%)	FINE GRAINED SANDSTONE , SILTSTONE (%)	ALTERNATING SANDSTONE (%)	RED AND GREENISH GREY MUDSTONE, FINE TO MEDIUM GRAINED SANDSTONE (%)	RED AND GREENISH GREY MUDSTONE, SUBORDINATE SANDSTONE (%)	WATER (%)	MUDROCK (%)	MUDROCK, SUBORDINATE SANDSTONE (%)	SANDSTONE , SILTSTONE, MUDSTONE, SHALE (%)	NETWORK OF DOLERITE SILLS, SHEETS AND DYKES (%)	DARK SHALE, MICACEOUS SANDSTONE, COAL SEAMS (%)
IS3955	72.057	27.943	-	-	-	-	-	-	-	-	-
IS3939	39.787	29.503	12.640	3.140	14.930	-	-	-	-	-	-
IS3945	40.060	19.002	19.427	-	18.156	3.354	-	-	-	-	-
IS3937	20.238	19.411	20.427	-	37.612	2.312	-	-	-	-	-
IS3941	45.736	-	-	51.885	2.379	-	-	-	-	-	-
IS3941B	-	-	8.995	-	91.004	-	-	-	-	-	-
IS3863	-	-	-	-	37.112	-	-	60.311	2.577	-	-
IS3760	-	-	-	-	-	-	-	100.00			-
IS3715	-	-	-	67.587	-	-	-	30.099	2.314	-	-
IS3639	-	-	-	60.035	-	-	-	35.283	4.681	-	-
IS3693	-	-	-	46.885	-	-	-	51.477	1.6384	-	-
IS3582	-	-	-	63.985	-	-	-	34.468	1.5470	-	-
IS3549	-	-	-	64.692	-	-	-	33.042	2.2652	-	-
IS3627	-	-	-	10.604	-	-	-	89.396	-	-	-
IS3577	-	-	-	54.155	-	-	-	45.845	-	-	-
IS3523	-	-	-	65.523	-	-	-	27.151	7.326	-	-

IS3480	-	-	-	69.703	-	-	-	30.297	-	-	-
IS3467	-	-	-	68.949	-	-	-	31.051	-	--	-
IS3467B		-	-	70.326	-	-	-	29.674	-	-	-
IS3416	-	-	-	68.844	-	-	-	31.157	-	-	-
IS3366	-	-	-	54.566	-	-	-	45.434	-	-	-
IS3369	-	-	-	32.913	-	-	-	67.087	-	-	-
IS3275	-	-	-	10.240	-	-	-	66.886	-	22.874	-
IS3184	-	-	-	39.713	-	-	-	2.4395	-	57.848	-
IS3157	-	-	-	84.259	-	-	-	11.671	-	4.069	-
IS3131	-	-	-	80.930	-	-	-	19.070	-	-	-
IS3237	-	-	-	69.387	-	-	-	30.613	-	-	-
IS3225A	-	-	-	57.894	-	-	-	42.106	-	-	-
IS3225B	-	-	-	50.613	-	-	-	49.387	-	-	-
IS3203	-	-	-	43.478	-	-	-	56.522	-	-	-
IS3155	-	-	-	59.168	-	-	-	23.005	2.673	15.154	-
IS2972	-	-	-	-	-	-	-	100	-	-	-
IS2972B	-	-	-	-	-	-	-	99.999	-	-	-
IS2792	-	-	-	-	-	-	-	100	-	-	-
SPRING	-	-	-	-	-	-	-	99.999	-	-	-
IS2792A	-	-	-	-	-	-	-	99.999	-	-	-
IS2792B	-	-	-	-	-	-	-	73.864	-	26.136	-
IS2360	-	-	-	-	-	-	28.239	4.076	-	67.686	-
IS2370	-	-	-	-	-	-	73.951	4.438	-	21.610	-
IS1946	-	-	-	-	-	-	-	-	-	94.821	5.179
IS1891	-	-	-	-	-	-	-	-	-	27.429	72.571
IS2303	-	-	-	-	-	-	-	-	-	100	-

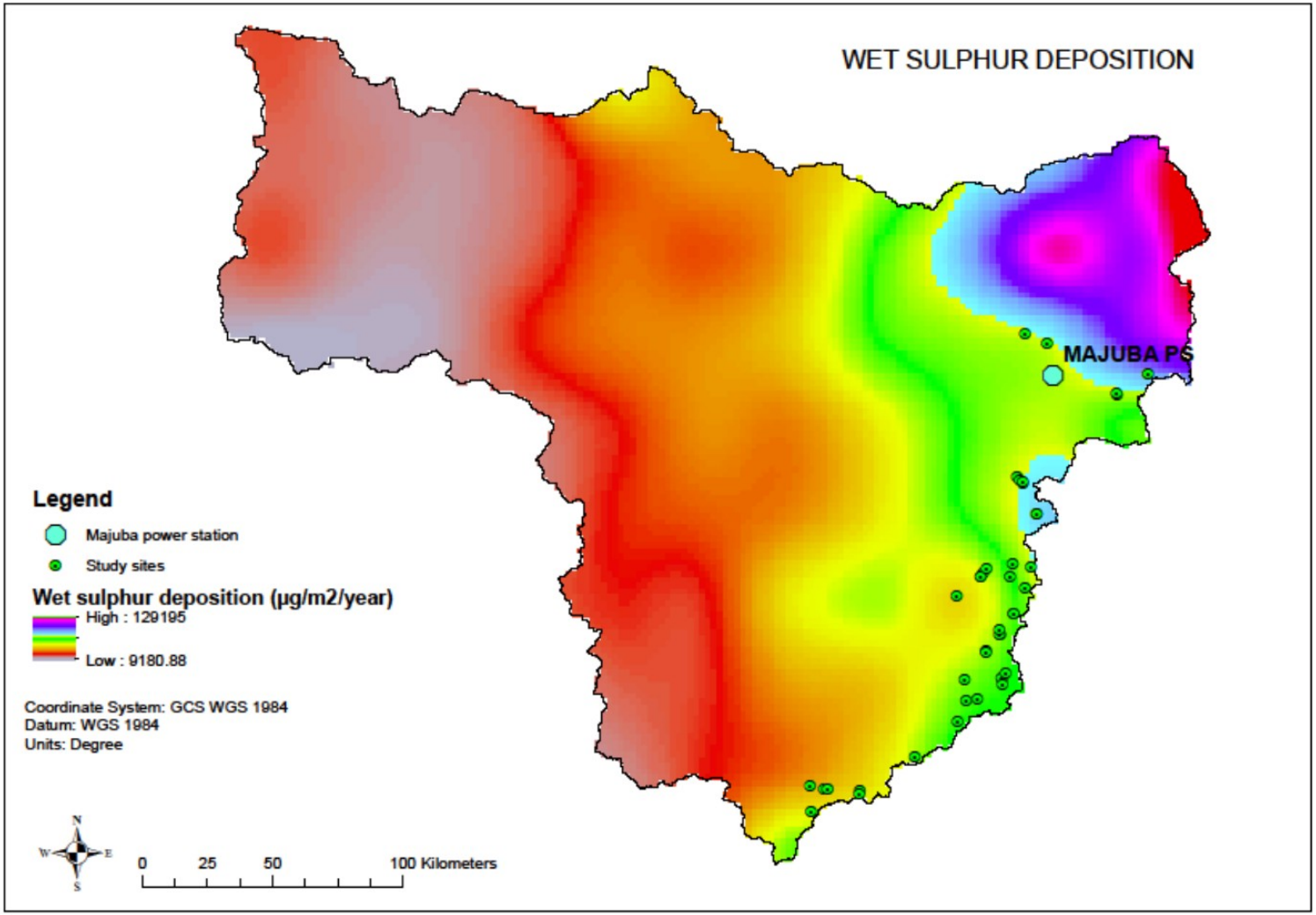


Figure 13 modelled annual wet sulphur deposition rates for 2014, with location of study sites.

5.2 WATER QUALITY ASSESSMENT OUTCOMES

Table 6 summaries results for wet sulphur deposition rates, conductivity, pH, as well as sulphate, nitrate and chloride concentrations of stream water sampled from the 42 catchments studied. The values are an indication of salinity levels of stream waters in the study catchments and therefore acid deposition rates.

Table 6 Water quality and modelled wet sulphur deposition data for study sites

SITE ID	DISTANCE FROM MAJUBA POWER STATION (m)	MODELLED WET SULPHUR DEPOSITION (µg/m²/year)	CONDUCTIVITY (µS cm⁻¹)	pH	SO_4^{2-} (mg l⁻¹)	NO_3^- (mg l⁻¹)	Cl^- (mg l⁻¹)
IS3955	185 701	42145	25.0	6.88	0	0.02	0.8
IS3939	177 144	31744	347.7	7.72	0	0.02	4.6
IS3945	176 910	34945	116.0	7.94	3	0.01	0.5
IS3937	175 933	35749	105.4	7.59	7	0.01	0.8
IS3941	172 190	38325	149.5	7.20	0	0.02	8.1
IS3941B	172 479	39174	138.9	7.18	0	0.02	2.3
IS3863	154 038	48722	119.3	7.35	0	0.02	5.3
IS3760	135 963	53769	59.0	6.11	0	0.00	5.6
IS3715	128 308	53738	130.5	6.73	0	0.00	9.6
IS3639	120 010	50066	146.7	7.22	1	0.01	9.5
IS3693	126 257	53907	108.4	6.75	0	0.01	8.2
IS3582	117 387	54822	89.9	7.41	1	0.01	3.1
IS3549	118 019	54822	76.1	8.99	3	0.01	1.9
IS3627	119 787	55039	42.8	7.15	1	0.01	20.4
IS3577	115 055	54615	50.7	7.03	0	0.01	2.2
IS3523	119 788	48917	59.8	6.89	7	0.01	9.2
IS3480	115 055	48917	59.0	7.28	3	0.01	5.2
IS3467	108 844	48698	41.3	7.25	1	0.01	3.6
IS3467B	108 723	48698	37.0	6.86	0	0.01	2.8
IS3416	101 105	48698	65.9	7.3	7	0.01	4.1
IS3366	101 548	54008	58.7	6.74	3	0.01	5.7
IS3369	99 717	54008	51.3	7.26	1	0.01	2.5
IS3275	93 598	61035	29.8	6.50	0	0.01	2.0
IS3184	94 9023	54412	195.4	6.78	7	0.01	21.6
IS3157	82 263	65945	46.2	6.74	11	0.01	2.5
IS3131	79 360	59012	55.7	6.82	1	0.01	5.5
IS3237	72 920	38035	93.6	6.87	0	0.00	13.9
IS3225A	72 882	46084	133.6	7.51	8	0.01	12.5

IS3225B	93 155	46084	186.9	8.02	13	0.01	15.7
IS3203	83 775	46084	184.4	7.96	18	0.01	31.1
IS3155	77 005	48472	53.0	7.22	0	0.00	5.7
IS2972	80 460	70817	82.7	6.93	8	0.01	12.6
IS2972B	80 210	70817	248.9	7.10	0	0.00	41.3
IS2792	83 776	65407	362.0	7.95	37	0.00	42.6
SPRING	77 005	67192	224.4	6.83	32	0.07	9.3
IS2792A	42 225	67192	155.7	7.27	8	0.00	15.0
IS2792B	53 176	67192	172.1	7.40	13	0.01	14.8
IS2360	53 232	63098	461.0	8.02	59	0.01	11.1
IS2370	40 715	63098	365.2	8.17	52	0.01	1.8
IS1946	41 395	65484	468.8	8.09	54	0.00	34.7
IS1891	42 225	65666	506.0	8.47	51	0.01	15.1
IS2303	42 214	74938	172.1	7.57	10	0.00	3.2

Table 7 gives a descriptive statistical summary of the five water quality parameters analyzed in the study. The conductivity range was 481 µS cm^{-1} with a minimum of 25 µs cm^{-1} and a maximum of 506 µS cm^{-1}. Average conductivity was 149.4 µS cm^{-1} with a standard deviation of 126.4 µS cm^{-1}. pH values ranged from a minimum of 6.11 to a maximum of 8.99, a range of 2.88. Average pH was 7.31 with a standard deviation of 0.57. Sulphate loadings ranged from a minimum 0 mg l^{-1} to a maximum 59 mg l^{-1}, a range of 59 mg l^{-1}. The average sulphate concentration was 10.00 mg l^{-1} with a standard deviation of 16.53 mg l^{-1}. Nitrate concentrations ranged from a minimum 0 mg l^{-1} to a maximum 0.07 mg l^{-1}, a range of 0.07 mg l^{-1}. The average nitrate concentration was 0.01 mg l^{-1} with a standard deviation of 0.01 mg l^{-1}. Chloride concentrations ranged from a minimum 0.5 mg l^{-1} to a maximum 42.6 mg l^{-1}, a range of 42.1 mg l^{-1}. The average chloride concentration was 10.19 mg l^{-1} with a standard deviation of 10.53 mg l^{-1}.

Table 7 Descriptive summary of the water quality data collected for the study

Statistics						
		CONDUCTIVITY (µScm1)	pH	SULPHATE (mgl-1)	NITRATE (mgl-1)	CHLORIDE (mgl-1)
N	Valid	42	42	42	42	42
	Missing	0	0	0	0	0
Mean		149.4	7.311	10.3	.225	10.19
Std. Error of Mean		19.5	.088	2.52	.063	1.63
Median		112.2	7.235	3.00	.010	5.70
Std. Deviation		126.4	.571	16.33	.410	10.53
Variance		15967.5	.326	266.76	.168	110.85
Skewness		1.5	.715	2.06	1.443	1.81
Std. Error of Skewness		.4	.365	.37	.365	.365
Kurtosis		1.6	.751	3.07	.086	2.952
Std. Error of Kurtosis		.8	.717	.72	.717	.717
Range		481.0	2.880	58.00	.060	42.100
Minimum		25.0	6.110	0.00	.010	.500
Maximum		506.0	8.990	59.00	0.070	42.600

5.3 STATISTICAL ANALYSIS

This section describes the outcomes of the statistical analyses conducted in order to examine linkages between geology, acid deposition, distance from Majuba power station and stream water pH, conductivity, as well as concentrations of sulphate, nitrate and chloride ions and to quantify the significance, magnitude and direction of relationships among the variables. The data used in the statistical analyses were derived from: water quality analyses of samples collected from 42 catchments that were determined to be natural; modelled wet sulphur deposition rates for the study catchments derived in GIS from the modelled deposition data provided by eScience; distance of the study sites from Majuba power station as determined using GIS; as well as the catchment geology compositions of the sites.

5.3.1 COMPONENT ANALYSIS (PCA) OF GEOLOGY DATA

In order to derive a smaller number of representative and uncorrelated geology categories, so as to be able to carry out analyses that would yield meaningful results, the factorability of the 11 geology classes was investigated. A number of well-recognised criteria for the factorability of a correlation were used. Nine classes correlated at 0.3 with at least two other classes, while two classes correlated with at least one class signifying reasonable factorability (Table 8). Secondly, the Kaiser-Meyer-Olkin measure of sampling adequacy was 0.361, below the suggested value of 0.6 indicating that the sample size was not quite adequate. The Bartlett's test of sphericity tested the null hypothesis that the correlation matrix for the geology classes is an identity matrix i.e. a matrix in which all diagonal elements are 1 and all off diagonal elements are zero. The test was significant ($p < 0.05$), the null hypothesis was therefore rejected (Table 9). Additionally, communalities which show the proportion of each variable's variance that can be explained by the principal components were all above 0.3 (Table 10) further confirming that each geology class shared some common variance with other geology classes. Given these overall indications, PCA was conducted with all 11 geology classes.

The PCA was used to identify the key geology composites and compute geology regression score factors for all the 42 sampled catchments. The initial Eigenvalues (Table11) indicated that the first component explained 33.98% of the variance, the second 17.45%, the third 11.38% and the fourth 9.43%. The rest of the components had Eigenvalues below 1 and were

therefore ruled out on that basis. Four, three and two component solutions were examined using varimax rotations of the rotated component matrix (Tables II and III, Appendix I). The three factor solution, which explained 62.80% of the variance, was selected because it verifies the theory of 'leveling off' of Eigenvalues on the scree plot after three components (Figure 14). In addition, the inadequate number of primary loadings as well as complications of interpreting subsequent components supported the decision to exclude the fourth component and to retain the first three.

During subsequent stages of the analysis, two geology classes were excluded because they loaded on more than one component, did not contribute to the three components retained or failed to meet a minimum condition of having a primary factor loading of 0.3 and above (Tables II and III, Appendix I). Mudrock, subordinate sandstone; and red and greenish grey mudstone with subordinate sandstone had loadings on more than one component and were therefore excluded. The geology categories fine grained sandstone, siltstone; alternating sandstone; basaltic lava; and water had loadings between 0.6 and 0.9 on the first principal component. Network of dolerite sills, sheets and dykes; mudrock; and dark shale, micaceous sandstone, coal seams: had loadings between 0.5 and 0.8 on the second principal component. Red and greenish grey mudstone with fine to medium grained sandstone; and sandstone, siltstone, mudstone, shale had loadings between 0.6 and 0.9 on the third principal component (Table III). The first principal component was labelled fine grained sandstones and siltstone, the second dolerite sills, sheets and dykes and the third red greenish grey mudstone with sandstone. A Pearson's r test for the principal components gives a significance value of $P > 0.05$, showing there are statistically no significant correlations between our principal components (Table 12). Regression factor scores assigned to the principal components for each study site were used in subsequent analyses.

Table 8 Correlation matrix.

Nine classes correlated at 0.3 with at least two other classes, while two classes correlated with at least one class signifying reasonable factorability

Correlation Matrix												
		BASALTIC	FINE GRAINED	ALTERNATING SANDSTONE	REDGREENFINETOMEDIUM	REDGREENSUBORDSANDSTONE	WATER	MUDROCK	MUDROCKSUBSANDSTONE	SANDSTONE	NETWORK	DARKSHALE
Correlation	BASALTIC	1.000	.856	.551	-.236	.302	.473	-.077	-.505	-.140	-.132	-.065
	FINEGRAINED	.856	1.000	.733	-.331	.409	.571	-.069	-.455	-.126	-.119	-.058
	ALTERNATING	.551	.733	1.000	-.190	.504	.800	-.068	-.447	-.124	-.117	-.057
	REDGREENFINETOMEDIUM	-.236	-.331	-.190	1.000	-.364	-.239	-.236	-.046	.292	-.306	-.198
	REDGREENSUBORDSANDSTONE	.302	.409	.504	-.364	1.000	.454	-.076	-.186	-.008	-.131	-.064
	WATER	.473	.571	.800	-.239	.454	1.000	-.047	-.308	-.086	-.081	-.039
	MUDROCK	-.077	-.069	-.068	-.236	-.076	-.047	1.000	-.230	-.085	.322	-.039
	MUDROCKSUBSANDSTONE	-.505	-.455	-.447	-.046	-.186	-.308	-.230	1.000	.048	-.479	-.256
	SANDSTONE	-.140	-.126	-.124	.292	-.008	-.086	-.085	.048	1.000	-.098	-.071
	NETWORK	-.132	-.119	-.117	-.306	-.131	-.081	.322	-.479	-.098	1.000	.267
	DARKSHALE	-.065	-.058	-.057	-.198	-.064	-.039	-.039	-.256	-.071	.267	1.000
Sig. (1-tailed)	BASALTIC		.000	.000	.066	.026	.001	.314	.000	.188	.202	.342
	FINEGRAINED	.000		.000	.016	.004	.000	.332	.001	.213	.226	.357
	ALTERNATING	.000	.000		.114	.000	.000	.334	.001	.216	.230	.360

	REDGREENFINETOMEDIUM	.066	.016	.114		.009	.064	.066	.387	.030	.024	.104
	REDGREENSUBORDSANDSTONE	.026	.004	.000	.009		.001	.316	.119	.480	.203	.344
	WATER	.001	.000	.000	.064	.001		.384	.024	.295	.306	.402
	MUDROCK	.314	.332	.334	.066	.316	.384		.071	.297	.019	.403
	MUDROCKSUNSANDSTONE	.000	.001	.001	.387	.119	.024	.071		.381	.001	.051
	SANDSTONE	.188	.213	.216	.030	.480	.295	.297	.381		.269	.327
	NETWORK	.202	.226	.230	.024	.203	.306	.019	.001	.269		.044
	DARKSHALE	.342	.357	.360	.104	.344	.402	.403	.051	.327	.044	

Table 9 KMO and Bartlett's Test.

Kaiser-Meyer-Olkin measure of sampling adequacy was 0.361, below the suggested value of 0.6 indicating that the sample size was not quite adequate. The Bartlett's test of sphericity tested the null hypothesis that the correlation matrix for the geology classes is an identity matrix i.e. a matrix in which all diagonal elements are 1 and all off diagonal elements are zero. The test was significant ($p < 0.05$), the null hypothesis was therefore rejected.

KMO and Bartlett's Test		
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.361
Bartlett's Test of Sphericity	Approx. Chi-Square	252.642
	Df	55
	Sig.	.000

Table 10 Communalities

Communalities which show the proportion of each variable's variance that can be explained by the principal components were all above 0.3 further confirming that each geology class shared some common variance with other geology classes.

Communalities		
	Initial	Extraction
BASALTIC	1.000	.686
FINEGRAINED	1.000	.816
ALTERNATING	1.000	.793
REDGREENFINETOMEDIUM	1.000	.822
REDGREENSUBORDSANDSTONE	1.000	.475
WATER	1.000	.641
MUDROCK	1.000	.346
MUDROCKSUNSANDSTONE	1.000	.924
SANDSTONE	1.000	.376
NETWORK	1.000	.755
DARKSHALE	1.000	.273
Extraction Method: Principal Component Analysis.		

Table 11 Total variance explained.

The initial Eigenvalues indicate that the first component explained 33.98% of the variance, the second 17.45%, the third 11.38% and the fourth 9.43%. The rest of the components had Eigenvalues below 1 and were therefore ruled out on that basis

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.737	33.975	33.975	3.737	33.975	33.975	3.631	33.009	33.009
2	1.919	17.446	51.421	1.919	17.446	51.421	1.855	16.861	49.870
3	1.252	11.382	62.803	1.252	11.382	62.803	1.423	12.933	62.803
4	1.037	9.426	72.229						
5	.941	8.556	80.784						
6	.701	6.375	87.159						
7	.573	5.210	92.369						
8	.516	4.692	97.061						
9	.210	1.905	98.966						
10	.082	.748	99.714						
11	.031	.286	100.000						
Extraction Method: Principal Component Analysis.									

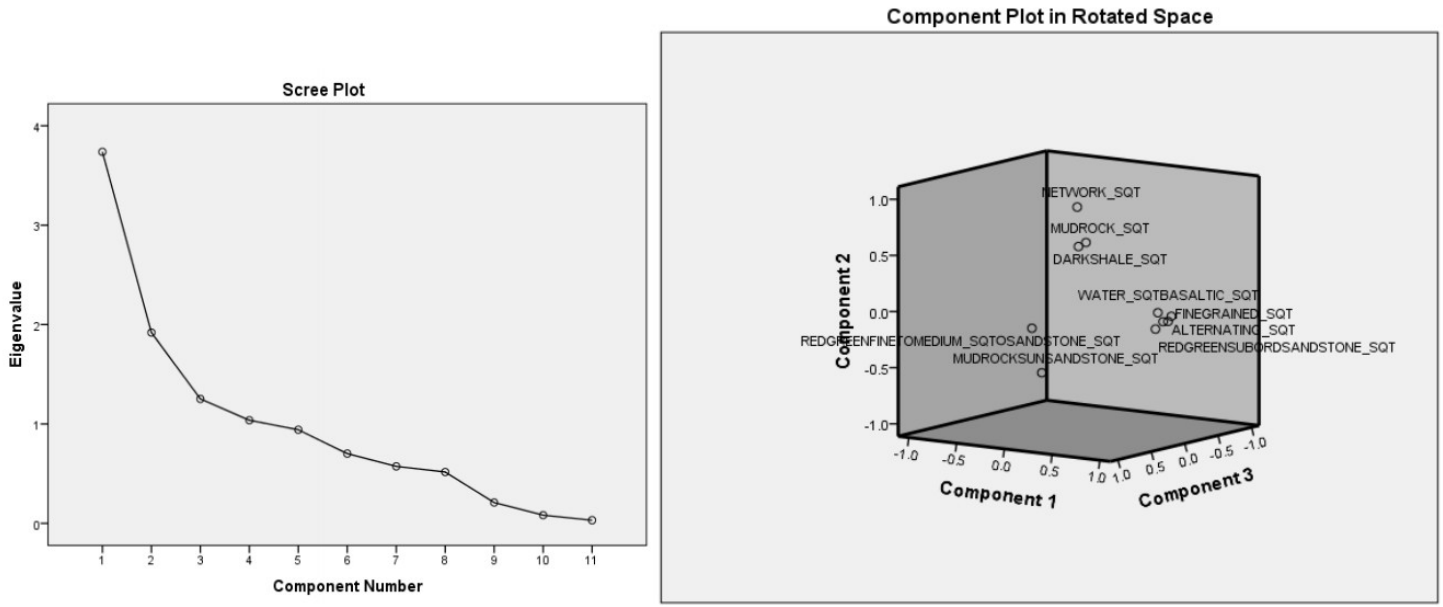


Figure 14 Scree plot of plot of components

The three factor solution, which explained 62.80% of the variance, was selected because it verifies the theory of 'leveling off' of Eigenvalues on the scree plot after three components

Table 12 Correlations among principal components

A Pearson's r test for the principal components gives a significance value of P> 0.05, showing there are statistically no significant correlations between our principal components

Correlations				
		FINEGRAINEDSANDSTONEANDSILTSTONE_COMPONENT	DOLERITESILLSSHEETSDYKES_COMPONENT	REDGREENISHGREYMUDSTONEWITHSANDSTONE_COMPONENT
FINEGRAINEDSANDSTONEANDSILTSTONE_COMPONENT	Pearson Correlation	1	.000	.000
	Sig. (2-tailed)		1.000	1.000
	N	42	42	42
DOLERITESILLSSHEETSDYKES_COMPONENT	Pearson Correlation	.000	1	.000
	Sig. (2-tailed)	1.000		1.000
	N	42	42	42
REDGREENISHGREYMUDSTONEWITHSANDSTONE_COMPONENT	Pearson Correlation	.000	.000	1
	Sig. (2-tailed)	1.000	1.000	
	N	42	42	42

5.3.2 EXPLORING LINKAGES BETWEEN ACID DEPOSITION, GEOLOGY, DISTANCE FROM MAJUBA POWER STATION AND STREAM WATER QUALITY USING SCATTERPLOTS

Several scatterplots were generated in SPSS in order to examine whether meaningful relationships exist between modelled wet sulphur deposition, geology, distance from Majuba and pH, conductivity and concentrations of sulphate, nitrate and chloride in the stream waters of study catchments.

Plots of fine grained sandstone and siltstone; and red greenish grey mudstone with sandstone with the water quality parameters measured in the study show no strong linear relationships (Figures 15 and 16). Dolerite geology on the other hand shows a significant effect on conductivity and sulphate ions concentrations (Figure 17). Plots of wet sulphur deposition against conductivity, sulphate, nitrate and chloride show a distinct trend though it is not quite adequate to reach a satisfactory significance level (Figure 17). There are positive linear relationships between modelled wet sulphur deposition and conductivity, sulphate and chloride concentrations of stream waters in study catchments. Distance from Majuba power station is markedly associated with stream water conductivity, pH, sulphate and chloride but not nitrate (Figure 19).

5.3.2.1 FINE GRAINED SANDSTONE AND SILTSTONE Vs WATER QUALITY

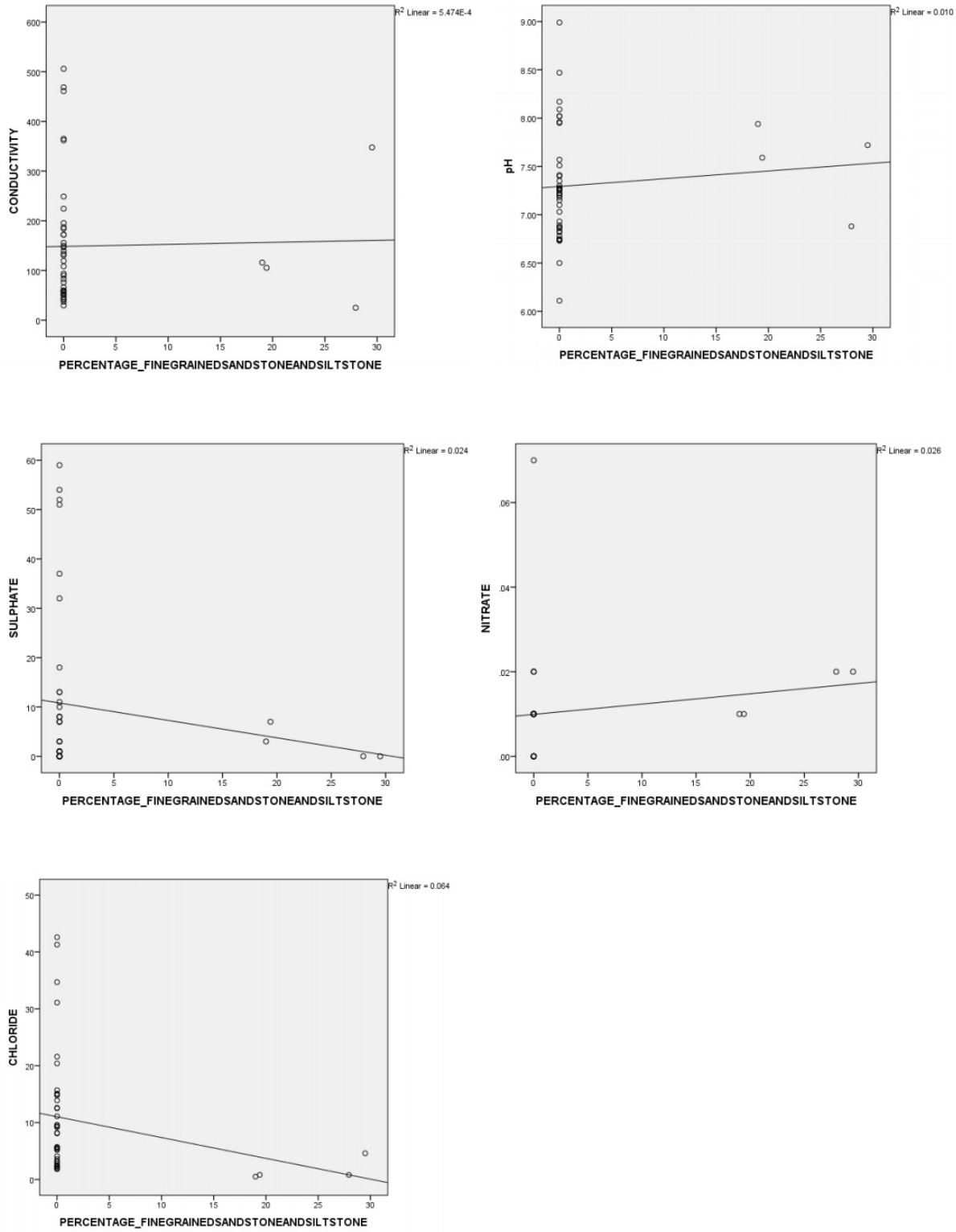


Figure 15 Scatterplots of fine grained sandstone geology with conductivity (µS cm^{-1}), pH, sulphate (mg l^{-1}), nitrate (mg l^{-1}) and chloride (mg l^{-1}).

5.3.2.2 RED GREENISH GREY MUDSTONE WITH SANDSTONE Vs WATER QUALITY

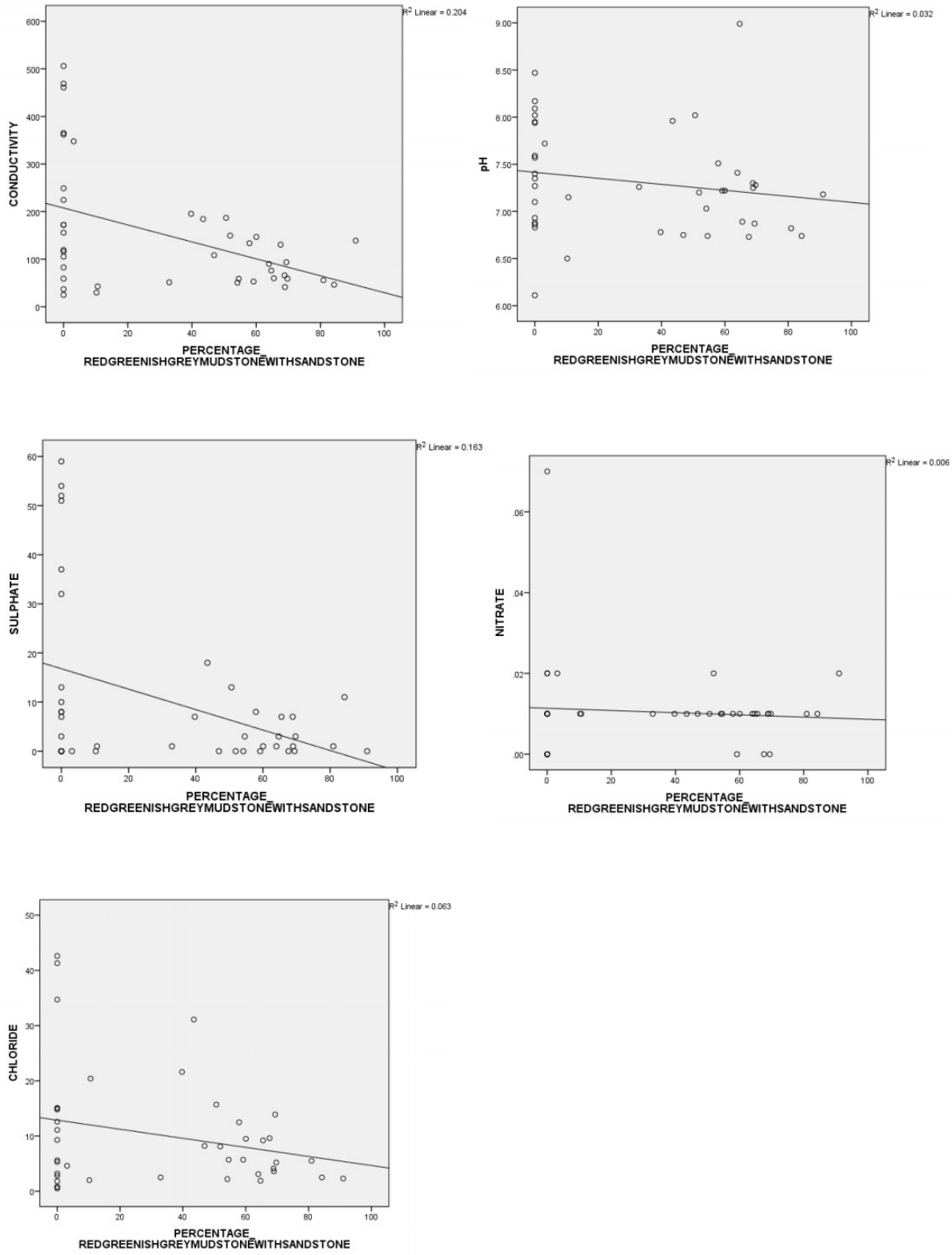


Figure 16 Scatterplots of red greenish grey mudstone with sandstone geology with conductivity (µS cm^{-1}), pH, sulphate (mg l^{-1}), nitrate (mg l^{-1}) and chloride (mg l^{-1}).

5.3.2.3 DOLERITE Vs WATER QUALITY

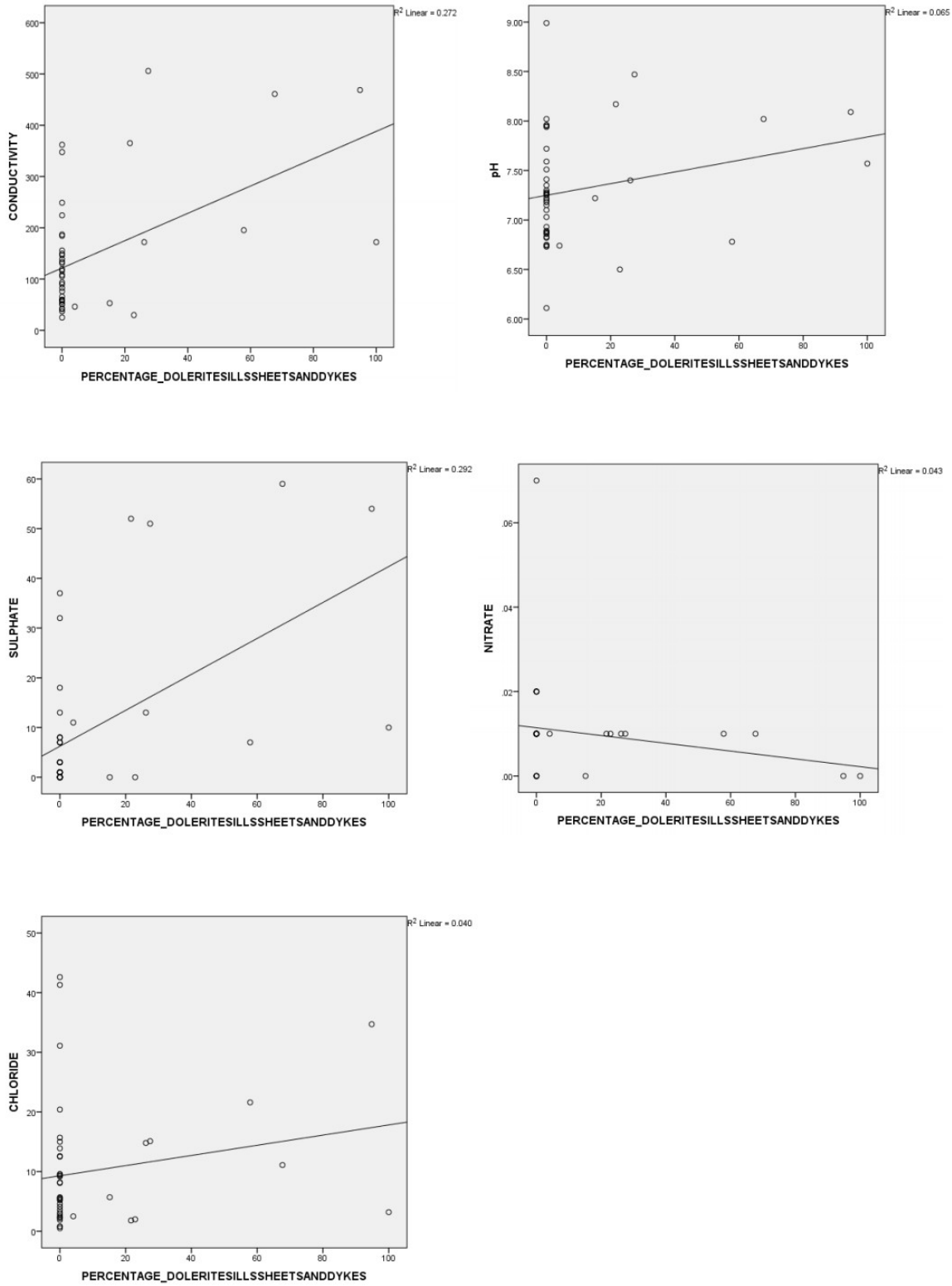


Figure 17 Scatterplots of dolerite geology with conductivity (µS cm^{-1}), pH, sulphate (mg l^{-1}), nitrate (mg l^{-1}) and chloride (mg l^{-1}).

5.3.2.4 DEPOSITION Vs WATER QUALITY

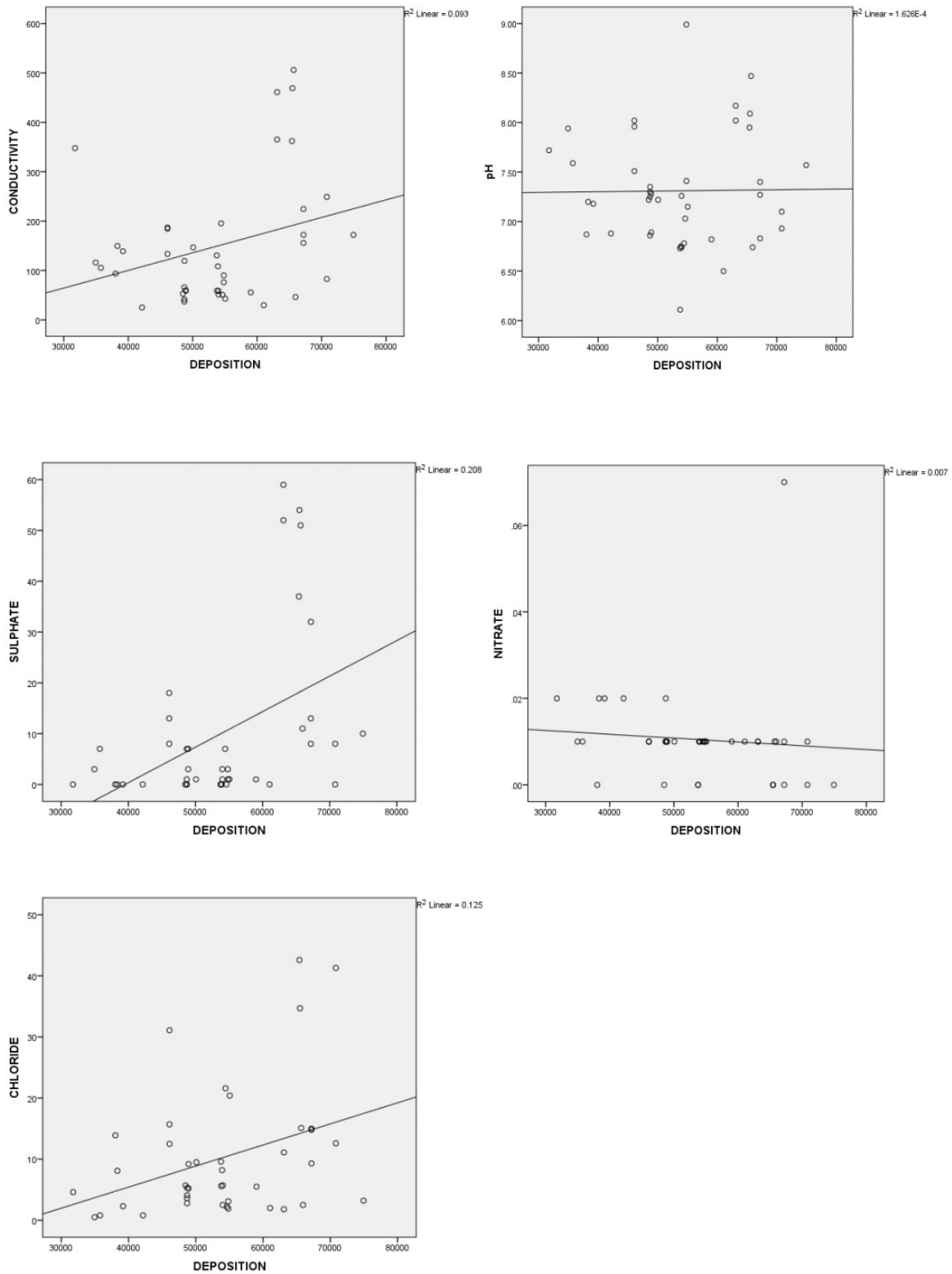


Figure 18 Scatterplots of modelled wet sulphur deposition rates (µg m^{-2} $year^{-1}$) with conductivity (µS cm^{-1}), pH, sulphate (mg l^{-1}), nitrate (mg l^{-1}) and chloride (mg l^{-1}).

5.3.2.5 DISTANCE OF CATCHMENTS FROM MAJUBA POWER STATION Vs WATER QUALITY

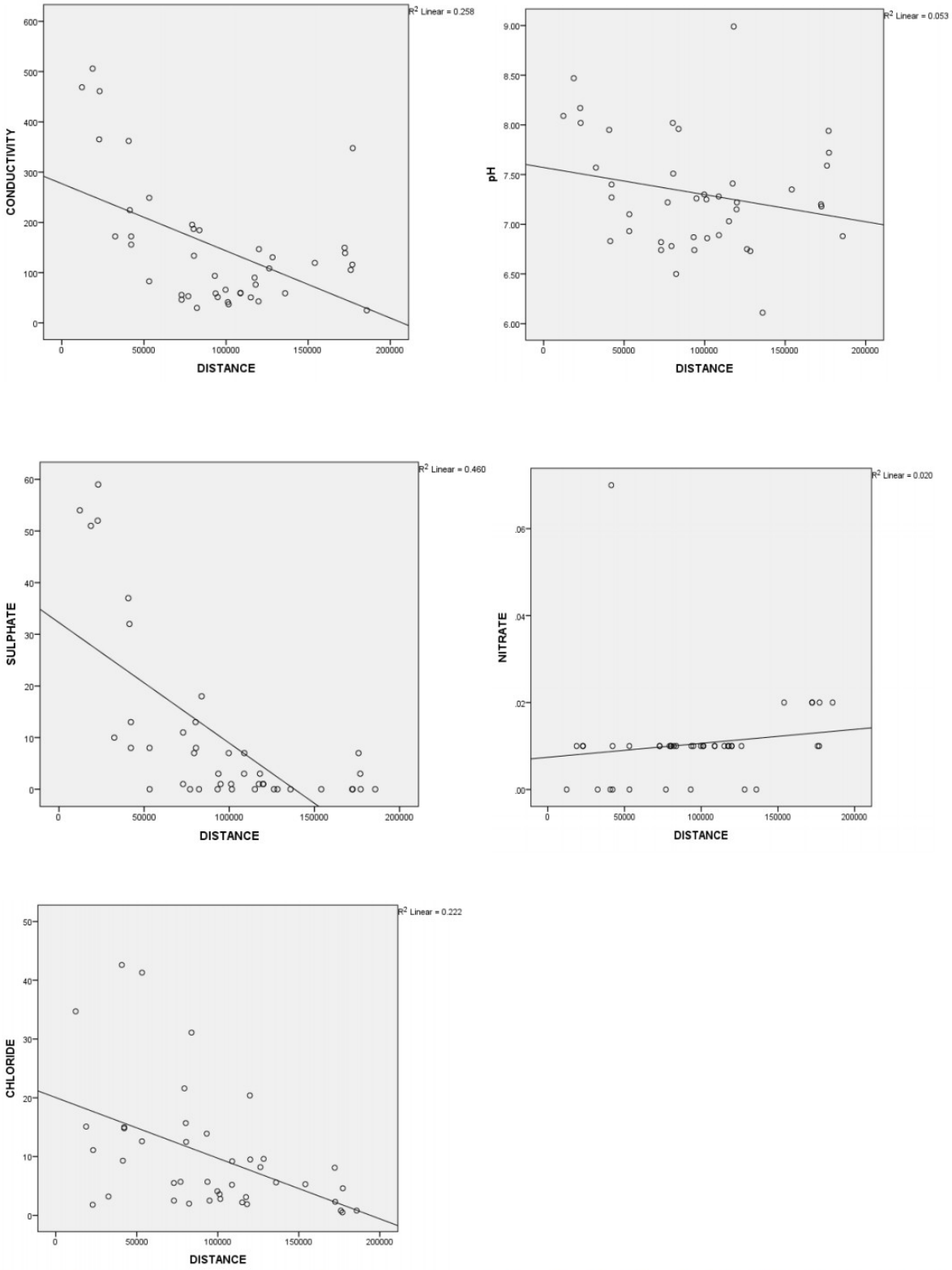


Figure 19 Scatterplots of linear distance (m) of study catchments from Majuba with conductivity (µS cm^{-1}), pH, sulphate (mg l^{-1}), nitrate (mg l^{-1}) and chloride (mg l^{-1}).

5.3.3 EXPLORING LINKAGES BETWEEN ACID DEPOSITION, GEOLOGY, DISTANCE FROM MAJUBA AND STREAM WATER QUALITY USING A MULTIVARIATE GENERAL LINEAR MODEL

A multivariate general linear model in SPSS was used to evaluate the assumption that acid deposition has a substantial effect on stream water quality in the Upper Vaal. Before analyzing the linkages between wet sulphur deposition, distance from Majuba power station, geology and stream water quality in the Upper Vaal using the model, a sequence of Pearson correlations were conducted between dependent variables to assess the assumption that they were associated with each other in the moderate range 0.20 - 0.60 (Meyers et al., 2006). A significant pattern of relationships among most of the dependent variables was observed as seen in table 13, signifying the suitability of multivariate analysis of variance as a method of statistical analysis. The Pearson's r showed that statistically significant correlations exist between conductivity and pH, sulphate and chloride loadings with sig. (2-tailed) value < 0.05. pH correlated to sulphate loadings and conductivity; nitrate loadings are uncorrelated to any of the variables; and chloride loadings showed significant correlations with conductivity, sulphate loadings and nitrate loadings. To examine the diagonals of the covariance matrices a Levene's test was conducted. The test gave p values greater than 0.05 (Table 14) for all variables indicating that were are approximately equal variances among the variables. The covariance matrices between the variables were therefore presumed to be equal for the purposes of the multivariate general linear model.

Table 15 summarizes the outcomes of the multivariate tests. Pillai's criterion was preferred over Wilk's lambda, Hotelling's Trace and Roy's Largest Root because it is considered the most powerful and robust statistic for general use even when there are departures from general assumptions. F values for deposition; fine grained sandstones with siltstone; and red greenish grey mudstone and sandstone are not significant with p values > 0.05 for all three variables. Statistically significant effects were obtained for the variable distance: Pillai's' Trace = 0.42, F (5, 32) = 4.81, p = 0.002, η^2 = 0.43; and dolerite sills, sheets and dykes: Pillai's' Trace = 0.41, F (5, 32) = 4.48, p = 0.003, η^2 = 0.41

An examination of between subject effects (Table 16) verifies the outcomes of the multivariate tests. The effects assessed at alpha level 0.05 show wet sulphur deposition; fine

grained sandstones with siltstone; as well as red greenish grey mudstone and sandstone had no statistically significant effect on conductivity, pH, concentrations of sulphate, nitrate and chloride concentrations with p values > 0.05. Tests between distance from Majuba power station and water quality were significant for conductivity ($p = 0.02$), pH ($p = 0.02$), sulphate ($p < 0.001$), and chloride ($p = 0.01$) but show no effect on nitrate ($p > 0.05$). Dolerite sills, sheets and dykes show a statistically significant effect on conductivity ($p = 0.01$) and sulphate ($p = 0.01$) but show no statistically significant effect on pH, nitrate and chloride.

Table 13 Correlations among the dependent variables

A significant pattern of relationships among most of the dependent variables was observed signifying the suitability of multivariate analysis of variance as a method of statistical analysis. The Pearson's r showed that statistically significant correlations exist between conductivity and pH, sulphate and chloride loadings with sig. (2-tailed) value < 0.05.

Correlations						
		CONDUCTIVITY	pH	SULPHATE	NITRATE	CHLORIDE
CONDUCTIVITY	Pearson Correlation	1	.592**	.770**	.216	.668**
	Sig. (2-tailed)		.000	.000	.170	.000
	N	42	42	42	42	42
pH	Pearson Correlation	.592**	1	.548**	-.105	.248
	Sig. (2-tailed)	.000		.000	.510	.113
	N	42	42	42	42	42
SULPHATE	Pearson Correlation	.770**	.548**	1	.062	.559**
	Sig. (2-tailed)	.000	.000		.696	.000
	N	42	42	42	42	42
NITRATE	Pearson Correlation	.216	-.105	.062	1	.469**
	Sig. (2-tailed)	.170	.510	.696		.002
	N	42	42	42	42	42
CHLORIDE	Pearson Correlation	.668**	.248	.559**	.469**	1
	Sig. (2-tailed)	.000	.113	.000	.002	
	N	42	42	42	42	42
**. Correlation is significant at the 0.01 level (2-tailed).						

Table 14 Levene's test.

The test gave p values greater than 0.05 for all variables indicating that there are approximately equal variances among the variables.

Levene's Test of Equality of Error Variances[a]				
	F	df1	df2	Sig.
CONDUCTIVITY	1.699	11	30	.122
pH	.609	11	30	.807
SULPHATE	1.904	11	30	.080
NITRATE	1.633	11	30	.140
CHLORIDE	1.304	11	30	.270
Tests the null hypothesis that the error variance of the dependent variable is equal across groups.				
a. Design: Intercept + DEPOSITION + DISTANCE + GEOLOGY				

Table 15 Multivariate tests

Pillai's criterion was preferred over Wilk's lambda Hotelling's Trace and Roy's Largest Root because it is considered the most powerful and robust statistic for general use even when there are departures from general assumptions. F values for deposition; fine grained sandstones with siltstone; and red greenish grey mudstone and sandstone are not significant with p values > 0.05 for all three variables.

Multivariate Tests[a]									
Effect		Value	F	Hypothesis df	Error df	Sig.	Partial Eta Squared	Noncent. Parameter	Observed Power[c]
Intercept	Pillai's Trace	.903	59.820[b]	5.000	32.000	.000	.903	299.099	1.000
	Wilks' Lambda	.097	59.820[b]	5.000	32.000	.000	.903	299.099	1.000
	Hotelling's Trace	9.347	59.820[b]	5.000	32.000	.000	.903	299.099	1.000
	Roy's Largest Root	9.347	59.820[b]	5.000	32.000	.000	.903	299.099	1.000
DEPOSITION (µg/m²/year)	Pillai's Trace	.092	.646[b]	5.000	32.000	.666	.092	3.230	.205
	Wilks' Lambda	.908	.646[b]	5.000	32.000	.666	.092	3.230	.205
	Hotelling's Trace	.101	.646[b]	5.000	32.000	.666	.092	3.230	.205
	Roy's Largest Root	.101	.646[b]	5.000	32.000	.666	.092	3.230	.205
DISTANCE (m)	Pillai's Trace	.429	4.806[b]	5.000	32.000	.002	.429	24.030	.955
	Wilks' Lambda	.571	4.806[b]	5.000	32.000	.002	.429	24.030	.955
	Hotelling's Trace	.751	4.806[b]	5.000	32.000	.002	.429	24.030	.955
	Roy's Largest Root	.751	4.806[b]	5.000	32.000	.002	.429	24.030	.955
	Pillai's Trace	.156	1.179[b]	5.000	32.000	.341	.156	5.896	.362

FINE GRAINED SANDSTONE AND SILTSTONE	Wilks' Lambda	.844	1.179[b]	5.000	32.000	.341	.156	5.896	.362
	Hotelling's Trace	.184	1.179[b]	5.000	32.000	.341	.156	5.896	.362
	Roy's Largest Root	.184	1.179[b]	5.000	32.000	.341	.156	5.896	.362
DOLERITE SILLS SHEETS DYKES	Pillai's Trace	.411	4.472[b]	5.000	32.000	.003	.411	22.362	.939
	Wilks' Lambda	.589	4.472[b]	5.000	32.000	.003	.411	22.362	.939
	Hotelling's Trace	.699	4.472[b]	5.000	32.000	.003	.411	22.362	.939
	Roy's Largest Root	.699	4.472[b]	5.000	32.000	.003	.411	22.362	.939
RED GREENISH GREY MUDSTONE WITH SANDSTONE	Pillai's Trace	.093	.658[b]	5.000	32.000	.658	.093	3.291	.208
	Wilks' Lambda	.907	.658[b]	5.000	32.000	.658	.093	3.291	.208
	Hotelling's Trace	.103	.658[b]	5.000	32.000	.658	.093	3.291	.208
	Roy's Largest Root	.103	.658[b]	5.000	32.000	.658	.093	3.291	.208

a. Design: Intercept + DEPOSITIONµgm2year + DISTANCE (m) + FINEGRAINEDSANDSTONEANDSILTSTONE + DOLERITE SILLS SHEETS DYKES + RED GREENISH GREY MUDSTONE WITH SANDSTONE

b. Exact statistic

c. Computed using alpha = .05

Table 16 Tests of between subjects effects

An examination of between subject effects verifies the outcomes of the multivariate tests. Effects are assessed at alpha level 0.05

Tests of Between-Subjects Effects									
Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.	Partial Eta Squared	Noncent. Parameter	Observed Power[f]
Corrected Model	CONDUCTIVITY	439.442[a]	5	87.888	7.067	.000	.495	35.336	.996
	pH	.136[b]	5	.027	3.124	.019	.303	15.621	.821
	SULPHATE	120.109[c]	5	24.022	16.911	.000	.701	84.556	1.000
	NITRATE	.601[d]	5	.120	.863	.515	.107	4.314	.272
	CHLORIDE	30.539[e]	5	6.108	3.798	.007	.345	18.990	.897
Intercept	CONDUCTIVITY	143.663	1	143.663	11.552	.002	.243	11.552	.911
	pH	2.502	1	2.502	288.366	.000	.889	288.366	1.000
	SULPHATE	18.699	1	18.699	13.164	.001	.268	13.164	.942
	NITRATE	.014	1	.014	.101	.752	.003	.101	.061
	CHLORIDE	13.810	1	13.810	8.587	.006	.193	8.587	.814
DEPOSITION (µg/m²/year)	CONDUCTIVITY	16.688	1	16.688	1.342	.254	.036	1.342	.204
	pH	.018	1	.018	2.073	.159	.054	2.073	.289
	SULPHATE	2.348	1	2.348	1.653	.207	.044	1.653	.240
	NITRATE	.030	1	.030	.216	.645	.006	.216	.074
	CHLORIDE	2.074	1	2.074	1.290	.264	.035	1.290	.198
DISTANCE (m)	CONDUCTIVITY	72.966	1	72.966	5.867	.021	.140	5.867	.654
	pH	.048	1	.048	5.546	.024	.133	5.546	.630
	SULPHATE	28.657	1	28.657	20.175	.000	.359	20.175	.992
	NITRATE	.081	1	.081	.584	.450	.016	.584	.115
	CHLORIDE	10.677	1	10.677	6.639	.014	.156	6.639	.708

FINE GRAINED SANDSTONE AND SILTSTONE	CONDUCTIVITY	14.243	1	14.243	1.145	.292	.031	1.145	.181
	pH	.022	1	.022	2.534	.120	.066	2.534	.341
	SULPHATE	3.330	1	3.330	2.345	.134	.061	2.345	.320
	NITRATE	.005	1	.005	.038	.846	.001	.038	.054
	CHLORIDE	.686	1	.686	.427	.518	.012	.427	.097
DOLERITE SILLS SHEETS DYKES	CONDUCTIVITY	85.288	1	85.288	6.858	.013	.160	6.858	.722
	pH	.013	1	.013	1.534	.224	.041	1.534	.226
	SULPHATE	10.395	1	10.395	7.318	.010	.169	7.318	.749
	NITRATE	.064	1	.064	.460	.502	.013	.460	.101
	CHLORIDE	3.083	1	3.083	1.917	.175	.051	1.917	.271
RED GREENISH GREY MUDSTONE WITH SANDSTONE	CONDUCTIVITY	23.506	1	23.506	1.890	.178	.050	1.890	.268
	pH	1.374E-5	1	1.374E-5	.002	.968	.000	.002	.050
	SULPHATE	2.471	1	2.471	1.739	.196	.046	1.739	.250
	NITRATE	.001	1	.001	.010	.920	.000	.010	.051
	CHLORIDE	.143	1	.143	.089	.767	.002	.089	.060
Error	CONDUCTIVITY	447.705	36	12.436					
	pH	.312	36	.009					
	SULPHATE	51.137	36	1.420					
	NITRATE	5.016	36	.139					
	CHLORIDE	57.895	36	1.608					
Total	CONDUCTIVITY	6276.400	42						
	pH	307.050	42						
	SULPHATE	434.000	42						
	NITRATE	9.440	42						
	CHLORIDE	428.000	42						
Corrected Total	CONDUCTIVITY	887.148	41						
	pH	.448	41						

	SULPHATE	171.245	41						
	NITRATE	5.617	41						
	CHLORIDE	88.435	41						
a. R Squared = .495 (Adjusted R Squared = .425)									
b. R Squared = .303 (Adjusted R Squared = .206)									
c. R Squared = .701 (Adjusted R Squared = .660)									
d. R Squared = .107 (Adjusted R Squared = -.017)									
e. R Squared = .345 (Adjusted R Squared = .254)									
f. Computed using alpha = .05									

CHAPTER SIX – DISCUSSION AND CONCLUSIONS

6.1 RELATIONSHIPS BETWEEN GEOLOGY, WET SULPHUR DEPOSITION, DISTANCE FROM MAJUBA POWER STATION AND STREAM WATER QUALITY

6.1.1 GEOLOGY

Geology of sites studied consists of three main categories: fine grained sandstone and siltstone; dolerite sills, sheets and dykes; and red greenish grey mudstone with sandstone. Fine grained sandstone and siltstone; and red greenish grey mudstone with sandstone show no statistically significant effect on conductivity, pH, sulphate, nitrate and chloride concentrations of stream waters across the study sites. Fine grained sandstone and siltstone occurs in only four of the sites studied. It was therefore not adequately represented in the sample to give an accurate signal of its influence on water quality. The average conductivity value for the four sites in which it occurs is 148.42 μScm^{-1} just slightly below the 149.44 μScm^{-1} average observed for all the total sites studied suggesting it could probably be correlated to conductivity. Scatterplots of fine grained sandstone and siltstone; and red greenish grey mudstone with sandstone with water quality variables show no strong linear relationships (Figures 15 and 16). Dolerite geology shows a significant effect on conductivity and sulphate concentrations - It accounts for approximately 16% and 17% of multivariate variance of conductivity and sulphate concentrations respectively observed in the studied catchments. Figure 17 shows plots of the relationships between dolerite and the water quality parameters measured in the study.

Dolerite rocks are subvolcanic and are comparable to volcanic basalt or plutonic gabbro, comprising mostly of feldspar and pyroxene. They are rich in magnesium and calcium oxide but have low quantities of silicon dioxide and alkali oxides such as sodium and potassium oxides. Since dolerite is rich in iron it oxidises readily in air and water. Chemical weathering of dolerite rocks readily releases water-soluble cations such as magnesium, calcium and sodium. This accounts for why dolerite shows a significant effect on conductivity. Cations released in the catchments during the weathering process increase salinity of the waters impacting on conductivity. Catchments underlain by dolerite have a high buffer capacity against acidification. Edmunds and Kinniburgh (1986) classify catchments underlain by this

type of geology as having low susceptibility to acidification. It is therefore unlikely that stream waters in catchments with dolerite would be acidified unless acids supplied to the waters flowing through the catchments into streams plus those falling directly on the surface of the streams exceed critical loads resulting in chemical alterations of the waters (Curtis et al., 1998; Helliwell et al., 2001).

While the breakdown of complex organic matter by enzymes into simpler compounds in catchments can release sulphate, studies show that mobilization rates do not exceed organic sulphate formation and retention. Further, because dolerite rocks have high contents of iron oxides, their sulphate adsorption capacity is quite high. Sulphate ions become associated with iron oxide and their mobility is reduced. The indication of a significant relationship between dolerite and sulphate concentration suggests that there are factors external to catchment characteristics that supply sulphate to the catchments at rates that are higher than their adsorption and buffer capacities.

6.1.2 WET SULPHUR DEPOSITION

This study found no link between modelled wet sulphur deposition and stream water conductivity, pH, as well as nitrate, sulphate and chloride concentrations. The deposition data used in the statistical analyses were incomplete and did not include dry S as well as wet and dry N deposition data as initially intended. A complete acid deposition dataset could have possibly returned different outcomes for acid deposition effects on water quality. Studies show that dry deposition can be much higher close to sources. Therefore total S and N deposition may have shown stronger linkages with water quality. Also, the wet sulphur deposition data are modelled and may not be an accurate representation of deposition rates for the study area. Distance from Majuba power station may therefore be a better proxy for total deposition than the modelled wet sulphur deposition data used in the study. Plots of wet sulphur deposition with conductivity, sulphate, nitrate and chloride show a distinct trend though it is not quite adequate to reach a satisfactory significance level (Figure 18). While there is a deposition signal, it is not detectable in the model perhaps because the gradient in deposition is not large enough or the sample size is inadequate. Modelled wet sulphur deposition shows positive linear relationships with conductivity, sulphate and chloride. This inclination is in good agreement with literature on the influence of acid deposition on stream

water chemistry. Eriksson (1989); Gorham (1998); and Morgan (1984) suggest that acid deposition has adverse effects on aquatic ecosystems. Lahermo and others (1994) demonstrate a clear correlation between anthropogenic sulphur deposition and sulphate concentrations in Finnish stream waters. Evans et al (2011); and Gorham (1958) argue that HCl emissions from burning of coal can adversely impact natural ecosystems. They contend that while Cl^- can be cycled within soil organic matter, its net biological uptake is negligible in regions of high deposition.

6.1.3 DISTANCE OF STUDY SITES FROM MAJUBA POWER STATION

There is an important link between distance from Majuba power station and stream water quality. Distance from the power station is markedly associated with stream water conductivity, pH, sulphate and chloride but not nitrate. It accounts for approximately 14% of multivariate variance of conductivity, 13.3% of pH, 35% of sulphate concentration and 15% of chloride concentration. Generally, natural headwater catchments that are further from the power station, present better stream water quality with low conductivity, sulphate and chloride (Figure 19).

Patrinos and colleagues (1983) evaluated wet deposition from a large coal-fired power station and estimated that nearly all chloride released was wet deposited within 15 km of the source during rain. Stevenson (1968) discovered very high concentrations of non-sea chloride concentrations in precipitation linked to HCl emissions in central England adjacent to major sources. Gorham (1958) also notes a significant relationship between acidity and chloride ion concentration in rain water samples collected in some urban areas. The correlations observed from the scatterplots of distance with water quality correspond with the 1852 findings of English chemist Robert Angus Smith on the chemical composition of rain within Manchester city in England and its immediate surrounding areas, where he highlighted differences in the quality of precipitation in the middle of the polluted city in comparison to its unpolluted countryside (Smith, 1872). Crowther and Ruston (1911) similarly established that there were variations in rainfall acidity declining from the centre of Leeds in England and associated the acidity with coal combustion. Analyses of SO_4^{2-} and Cl^- from the deposit gauges introduced in later years showed a similar trend with SO_4^{2-} and Cl^- declining away from polluted centres.

The trend of better stream water quality as one moves away from Majuba power station strongly suggests that proximity to emission sources has a more significant influence on stream water quality than other factors in the Upper Vaal and an important relationship between water quality and acid deposition may exist. The low nitrate concentrations observed support the choice of study catchments and suggests minimal impacts on water quality from cultivation which is the predominant land cover in the Upper Vaal. Although catchments closest to the power station are underlain by dolerite geology which the model indicates has a significant effect on conductivity and sulphate, distance accounts for a larger portion of multivariate variance observed in water quality. Also, while the bulk of the catchments consist of red greenish grey mudstone with sandstone geology which is classified as having low susceptibility to acid deposition just like dolerite they seem to acidify at a lower rate in comparison suggesting that proximity to emission sources is the more significant factor in determining water quality than geology. Langan and Wilson (1992) elucidate that catchments of similar sensitivity acidify at different rates which are dependent on their proximity to pollution sources (i.e. deposition load), therefore a catchment system which is not susceptible to acidification but positioned in a high pollution region will acidify at a much higher rate than a similar catchment that is exposed to insignificant inputs of acidifying pollution.

6.2 LIMITATIONS OF THE STUDY

Human activity particularly cultivation is predominant across large portions of the Upper Vaal. There are therefore very few headwater catchments within the study area that are 100% natural. This narrowed the number of catchments that could be used in the study impacting on the sample size and possibly results obtained. Furthermore, sites identified as natural using GIS analyses were mostly remote and far apart in terrain that is generally hilly which was rather problematic for the sampling campaign as very few samples could be collected on any specific day. Some sites identified could not be accessed either because the terrain posed a challenge or they were situated on private property and required permission to collect samples from them. Additionally, due to the ongoing drought a number of streams had very low water levels, with some sites being found to be completely dry, stagnant, or with very little water flowing through channels. This may have had an impact on conductivity as well as SO_4^{2-}, NO_3^- and Cl^- concentrations of stream water samples due to high evaporation rates. Due

to time constraints, this study was only conducted during the mid to late summer months and therefore the varying outcomes of landcover influence on stream water quality that seasonality produces could not be accounted for.

Very few catchments have uniform geology, it was therefore difficult to come up with adequate sample sites that met the criteria of 100% natural cover and uniform geology that was initially intended. The geology data set of the 42 sites studied comprised a total of 11 geology classes and 14 different combinations complicating statistical analyses. PCA had to be conducted in order to scale down the data set as well as define patterns to carry out subsequent analyses that would yield meaningful results. Additionally, since only 42 sites were studied, some of the data obtained was not normally distributed, a requirement for multivariate statistics and had to be transformed before being used in statistical analyses. Finally, the deposition data provided was incomplete and was not an accurate reflection of annual acid deposition rates in the Upper Vaal. Studies show that that dry deposition can be much higher close to sources. Therefore total S and N deposition may have shown stronger linkages with water quality. Also, the wet sulphur deposition data are modelled and may not be an accurate representation of deposition rates for the study area.

6.3 CONCLUSIONS

Only 4.51% of the total area of 55 565 km^2 of the Upper Vaal represents first order headwater catchments which are primarily natural with >95% natural landcover. Therefore, the majority of stream and river lengths drain catchments with >5% human modified landcover which may impact water quality and had to be excluded from the study on that basis. This study found that modelled wet sulphur deposition, fine grained sandstone and siltstone, as well as red and greenish grey mudstone with sandstone generally have no substantial impact on stream water quality in the studied headwater catchments of the Upper Vaal. Dolerite geology shows a significant effect on conductivity and sulphate concentrations. It accounts for approximately 16% and 17% of multivariate variance of conductivity and sulphate concentrations respectively observed in the studied catchments. Modelled wet sulphur deposition shows no significant influence on stream water conductivity, pH, as well as nitrate, sulphate and chloride concentrations. However, an important link exists between distance from Majuba power station and stream water quality. Distance from the power station is markedly

associated with stream water conductivity, pH, sulphate and chloride but not nitrate - It accounts for approximately 14% of multivariate variance of conductivity, 13.3% of pH, 35% of sulphate concentration and 15% of chloride concentration. Generally, natural headwater catchments that are further from the power station, present better stream water quality with lower conductivity, sulphate and chloride. The trend of better stream water quality as one moves away from Majuba power station strongly suggests that proximity to emission sources has a more significant influence on stream water quality than other factors in the Upper Vaal and an important relationship between water quality and acid deposition may exist. Although catchments closest to the power station are underlain by dolerite geology which the model indicates has a significant effect on conductivity and sulphate, distance accounts for a larger portion of multivariate variance observed in water quality. Catchments with mudstone geology which also has similar susceptibility to acidification as dolerite show lower conductivity, sulphate, nitrate and chloride concentrations in stream waters because they are further away from emission sources as indicated by distance from the power station.

Very few sites of low pH sites were observed even though the study was conducted in a region well known for high acid deposition levels due to the fact that the dolerite geology of most of the catchments has a high buffer capacity against acidification. Catchments therefore have low susceptibility to acidification. Further, only natural catchments were studied thereby eliminating the potential influence of land use (mining, cultivation, plantations and urban build-up) on stream water pH. Increased salinity observed even in the most natural first order catchments of the Upper Vaal as a result of high acid deposition levels has several negative repercussions further downstream. Despite the fact that agriculture and acid mine drainage are the main contributors to salinity in downstream catchments, increased salt concentrations as a result of acid deposition impact on the Vaal river system and ecosystem services (Bird and Scholes, 2012). High salt concentrations are associated with problems of eutrophication and reduced irrigated crop production in downstream catchments. Further, the economic cost of purification of salt enriched water to domestic and industrial standards is a major concern. Mitigation measures to reduce the threat of acid deposition associated with power generation facilities could include: use of alternative fuels, use of low sulphur fuels and flue gas desulphurization.

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