



Some impacts of sulfur and nitrogen deposition on the soils and surface waters of the Highveld grasslands, South Africa.

Theresa Leigh Bird

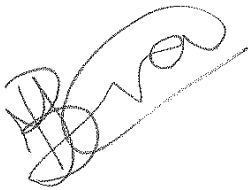
9505067D

2011

A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy

DECLARATION

I declare that this thesis, submitted for the Degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg, is my own unaided work, unless acknowledged to the contrary in the text. It has not been submitted before for any degree or examination at any other University.



Theresa Leigh Bird

7th day of OCTOBER 2011.

ABSTRACT

Atmospheric deposition of sulfur (S) and nitrogen (N) as a result of fossil fuel combustion is known to impact ecosystem structure and function. Potential impact includes acidification of soil and surface water and mobilisation of metal ions, with the resultant loss of plant productivity, changes in plant species diversity and changes in biotic communities in aquatic ecosystems. Rates of S ($\sim 8 \text{ kg S ha}^{-1} \text{ year}^{-1}$) and N ($> 6 \text{ kg S ha}^{-1} \text{ year}^{-1}$) deposition to the grasslands of the South African Highveld are comparable to other industrialised areas where ecosystem impacts have been observed. As part of a larger project, this work investigated four aspects of ecosystem impact: changes in soil and river water chemistry as well as S and N mineralisation rates.

Reassessment of the soil chemistry at 18 sites on the South African Highveld after a 16-year period showed increases in both acidic and basic ion concentrations for individual sites and when the values for these sites were averaged to represent the study region. Grouping the soils by clay content showed that all sites with less than 25% clay (16 of 18 sites) showed significantly reduced $\text{pH}(\text{H}_2\text{O})$ values. Sites with less than 4% clay showed increased exchangeable acidity and decreased acid neutralising capacity. Spatial scaling and mapping from site to soil form and land type, showed that across 92% of the study area the $\text{pH}(\text{H}_2\text{O})$ values had been reduced. This method identified the sandier soils, near the southern and eastern boundaries of the study area where rainfall is higher, as sensitive to additional acidic inputs via atmospheric deposition. Clay-rich soils occur in the drier central part of the study area, close to emission sources. It is suggested that this proximity to emission sources results in the co-deposition of basic and acidic ions, adding to the buffering capacity of the soils, resulting in small but significant increases in soil acidity status over the 16 years.

Sulfur and N mineralisation rates, using the *in situ* incubation method at 11 sites, were found to range between -0.66 and $1.09 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$ and -0.97 and $1.21 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. This translated into an annual flux of between -40 and 9.9 kg S ha^{-1} and between 27 and 81 kg N ha^{-1} from the soil organic pools. The use of the *in situ* incubation technique to determine S mineralisation is a new development and is proposed for in-field studies where S and N cycling are of

interest as the method allows for concurrent mineralisation rate determination. It was found that from a biogeochemical perspective the Highveld grasslands are under researched with respect to S and N and complete assessments of the S and N cycles are proposed. The S budget proposes accretion of S in the soil organic pool due to continued inputs via deposition and low losses to the atmosphere or deeper soil horizons. Nitrogen, however, appears to limit productivity in these grasslands because atmospheric inputs and mineralisation rates are approximately equal to plant uptake.

In the assessment of river water quality it was hypothesised that between 1991 and 2008 concentrations of dissolved salts, sulfate, nitrate and ammonium would increase in surface waters at five sites draining the Highveld grasslands. The Department of Water Affairs water quality monitoring database was accessed to assess for spatial and temporal differences in water quality. Significant spatial differences were found; however, over time few significant increases were found to support the hypothesis: sulfate, nitrate-plus-nitrite, and ammonium were observed to increase at one site each. In addition, the export of nitrogen, as mass load, from natural grasslands was found to be negligible at $<2 \text{ kg N ha}^{-1}\text{year}^{-1}$.

A conceptual framework proposes that soil texture, distance from emissions and land use are key drivers in the response of the grassland soils and surface waters to atmospheric S and N deposition. Although the study identified the soils most sensitive to deposition, it is proposed that processes in the Highveld grasslands are not yet negatively affected by the additional sulfur and nitrogen inputs. Continued monitoring for impacts on ecosystem structure and function is advocated.

The highest function of ecology is the understanding of consequences.

Pardot Kynes

Muad'Dib - Book 2 in the Dune series

by Frank Herbert

ACKNOWLEDGEMENTS

It is a humbling experience to acknowledge those people who have, mostly out of kindness, helped along the journey of my PhD. I am indebted to so many for encouragement and support.

My sincerest thanks are extended to my project supervisor and mentor, Professor Mary Scholes, for her encouragement and guidance. Eskom and SASOL are acknowledged for their bursary and investment in the research. The National Research Foundation, Andrew Mellon Foundation and the University of the Witwatersrand are thanked for their post-graduate bursary support. The Eskom-SASOL Impacts Working group is acknowledged for their direction and feedback.

My research committee in the School of Animal, Plant and Environmental Sciences, Professors Graham Alexander and David Mycock (as chairmen), Dr Barend Erasmus, Dr Chris Herold and Dr Kristy Ross (as committee members), are thanked for their interest and valuable comments on the research. The reviewers of the three manuscripts submitted to journals are thanked for the constructive advice improving the quality of the manuscripts and this thesis.

Several people helped with: the collection of samples, analyses in the laboratory, the preparation of maps, providing advice for statistical analyses and they are all thanked for their contributions. Special mention goes to the support staff of the School of APES, Allison, Chris, Ewa, James, Jason, Kim, Lawrence, Leanne, Lydia, Rori, Ryan, Rob and Stephen C. for help in the field and lab, Stephen W. for assistance with some of the images, Cristy for proof-reading a draft of the thesis. Thanks also to Mr Joseph Mathai for statistical analyses, Prof Edward Witkowski for statistical advice and Ms Jolene Fisher for GIS and statistical advice. Dr Adri Kotze and team at BEM Labs (Pty) Ltd are thanked for their efficient service and prompt response to queries. My heart-felt thanks to Dr Nina Snyman for the private, hands-on tutorials in using ArcGIS. I am grateful to Super Group Limited for assistance with printing copies of the thesis.

To my many friends and family, you should know that your support and encouragement was worth more than I can express on paper.

Thank you Jenny and Meg for breakfasts, tea-breaks and advice – you were always there with a word of encouragement or listening ear.

To Carl - thank you for your enthusiasm, pride and curiosity to share my map of the world.

Mom and Bridget, you knew it would be a long and sometimes bumpy road, but encouraged and supported me along the way. Thank you.

To dad who was often in my thoughts on this journey – you are missed.

TABLE OF CONTENTS

DECLARATION.....	ii
ABSTRACT	iii
ACKNOWLEDGEMENTS	vi
TABLE OF CONTENTS	vii
LIST OF FIGURES.....	xii
LIST OF TABLES.....	xvi
CHAPTER 1: INTRODUCTION.....	1
1.1 Aims	4
1.2 Hypotheses	4
1.3 Key Questions	5
1.4 Thesis structure.....	6
1.5 Contribution to science	7
1.6 Policy relevance of potential impacts on the study area.....	10
CHAPTER 2: LITERATURE REVIEW	11
2.1 Ecosystem services.....	11
2.1.1 What are ecosystem services?	11
2.1.2 The Sulfur cycle	13
2.1.3 The Nitrogen cycle	15
2.1.4 Human alteration of nutrient cycles.....	17
2.2 Atmospheric transformations and deposition	21
2.2.1 Atmospheric chemical reactions	21
2.2.2 Deposition events	22
2.2.3 Deposition across South Africa.....	23
2.3 Impacts of sulfur and nitrogen deposition.....	25
2.3.1 Impacts on soils	28

2.3.2 Impacts on vegetation.....	30
2.3.3 Impacts on freshwater systems	33
2.4 Ecological heterogeneity	34
CHAPTER 3: STUDY AREA AND SAMPLING SITES	36
3.1 The Highveld	36
3.1.1 Deposition to the Highveld grasslands.....	40
3.2 Location of soil sampling sites.....	49
3.3 The Vaal Dam Catchment	52
3.3.1 Location of water quality sampling sites	52
CHAPTER 4: THE ACIDITY STATUS OF SOILS OF THE HIGHVELD GRASSLANDS, SOUTH AFRICA	54
4.1 Introduction	55
4.2 Materials and Methods	58
4.2.1 Area description.....	58
4.2.2 Soil sampling	58
4.2.3 Laboratory methods.....	59
4.2.4 Statistical analyses	60
4.3 Results	61
4.3.1 Site-by-site comparison across sampling years.....	61
4.3.2 Regional soil acidity status based on means across sites	62
4.3.3 Site grouping based on soil texture.....	65
4.3.4 Using soil form and land type to calculate areal extent of increased soil acidity	67
4.4 Discussion.....	72
4.4.1 pH and base status.....	72
4.4.2 Soil Texture.....	74
4.4.3 Acidity status at soil form and regional scale	75
4.4.4 Conclusion.....	76

4.4.5 Thesis linkage	77
CHAPTER 5: SULFUR AND NITROGEN CYCLING IN GRASSLANDS OF THE MPUMALANGA HIGHVELD, SOUTH AFRICA	78
5.1 Introduction	79
5.2 Materials and Methods	81
5.2.1 Area and site description	81
5.2.2 Laboratory methods	83
5.2.3 Calculation of net mineralisation rates	83
5.2.4 Data analysis	84
5.2.5 Meteorological records	85
5.3 Results	86
5.3.1 Net SO_4^{2-} mineralisation rate	86
5.3.2 Net inorganic N mineralisation rate	87
5.3.3 Variation between land types	88
5.3.4 Total annual SO_4^{2-} and N mineralised based on land type	90
5.3.5 Controls of mineralisation rates	91
5.3.6 Sulfur and Nitrogen cycles	92
5.4 Discussion	96
5.4.1 Seasonality and controls of net SO_4^{2-} and N mineralisation	96
5.4.2 Annual amounts of SO_4^{2-} and N released	99
5.4.3 S and N cycling in grasslands	100
5.4.4 Thesis linkage	102
CHAPTER 6: CHANGES IN WATER CHEMISTRY IN THE VAAL DAM CATCHMENT BETWEEN 1991 AND 2008	103
6.1 Introduction	104
6.2 Materials and methods	106
6.3 Results	108
6.4 Discussion	113

6.4.1 Thesis linkage	115
CHAPTER 7: ECOSYSTEM SERVICES IN THE GRASSLANDS OF SOUTH AFRICA AFFECTED BY N DEPOSITION AND LAND-USE CHANGE	117
7.1 Introduction	118
7.2 Materials and Methods	121
7.2.1 Domain description	123
7.2.2 Nitrogen deposition modelling.....	123
7.2.3 Soil chemical dynamics	125
7.2.4 Hydrological studies.....	126
7.3 Results	128
7.3.1 Total (wet + dry) N deposition:.....	128
7.3.2 Re-assessment of soils near Arnot Power Station.....	131
7.3.3 Re-assessment of soils of the Highveld grasslands.....	132
7.3.4 Stream export of nitrogen	132
7.4 Discussion.....	134
7.4.1 Modelled N deposition	134
7.4.2 Ecosystem services affected by N deposition.....	136
7.4.3 Ecosystem services affected land-use change	136
7.4.4 Conclusion.....	137
7.4.5 Thesis linkage.....	137
CHAPTER 8: DISCUSSION	139
8.1 Initial concern about the Highveld grasslands	139
8.1.1 Key quantitative findings as they relate to the current state	139
8.2 Cause-effect relationships.....	140
8.2.1 Cation exchange capacity and the capacity to retain anions	143
8.2.2 Atmospheric deposition of S and N.....	143
8.2.3 Fire	144

8.2.4 Climate	144
8.2.5 Land use.....	145
8.2.6 Temporal scale	145
8.2.7 Spatial scale	146
8.3 Key research questions - answered	150
<i>Key question 1: How have the rates of wet and dry deposition changed since 1991?</i>	150
<i>Key question 2: How have the top- and sub-soil chemical properties, as measured by Fey and Guy (1993) changed in the Vaal Dam catchment, between 1991 and 2007?</i>	151
<i>Key question 3: Do any of the soils studied (18 soil sample sites – 13 soil types), show exceedance of S retention capacities, if so, why?</i>	151
<i>Key question 4: How has the Acid Neutralising Capacity of the soils in the catchment changed between 1991 and 2007?</i>	152
<i>Key question 5: What are the rates of soil S and N mineralisation in the top-soils of the Highveld grasslands?</i>	152
<i>Key question 6: How has water quality, in terms of dissolved salts, SO_4^{2-} and NO_3^- changed between 1991 and 2008?</i>	153
8.4 Recommendations	154
8.4.1 Conclusion	155
CHAPTER 9: REFERENCES.....	156

LIST OF FIGURES

Figure 1.1: A representation of the structure of the thesis (chapter number in parentheses). The manuscript title and key research questions (KQ - detailed in Section 1.3 on page 5) are detailed for each results chapter.	6
Figure 2.1: Global sulfur reservoirs, fluxes, and turnover times (in the mid-1980's). Major reservoirs are underlined; pool sizes and fluxes are given in Tg S and Tg S year ⁻¹ respectively. Turnover times (reservoir divided by largest flux to or from reservoir) are in parentheses (reproduced from Reeburgh, 1997).	14
Figure 2.2: Global nitrogen reservoirs, fluxes and turnover times. Major reservoirs are underlined; pool sizes and fluxes are given in Tg N and Tg N year ⁻¹ respectively. Turnover times (reservoir divided by largest flux to or from reservoir) are in parentheses (reproduced from Reeburgh, 1997).	16
Figure 2.3: A conceptual framework illustrating human alteration of Earth's ecosystems (Vitousek <i>et al.</i> 1997).....	18
Figure 2.4: A schematic representation of the mechanisms resulting in ecosystem impacts as a result of deposition of S and N (modified from Aerts and Bobbink, 1999).	27
Figure 3.1: a) Map of South Africa, where the red frame indicates the study area in the Highveld grasslands. (b) Detailed map of the Highveld grasslands indicating the location of the 2007 soil sampling sites and the DWA water quality monitoring points used in the investigation of the impacts of S and N deposition on the soils and surface waters of the area. Deposition receptor sites and the land types are also indicated.	39
Figure 3.2: Predicted spatial variations in total S deposition for break-point years 1948 to 2007 (kg S ha ⁻¹ year ⁻¹). The projections for break-point years were based on the meteorology for 2000/1 – considered an average rainfall year for the area (Blight <i>et al.</i> , 2009).	43
Figure 3.3: Predicted spatial variations in total N deposition for break-point years 1948 to 2007 (kg N ha ⁻¹ year ⁻¹). The projections for break-point years were based on the meteorology for 2000/1 – considered an average rainfall year for the area (Blight <i>et al.</i> , 2009).	45
Figure 3.4: Interpolated (a) S and (b) N deposition (kg ha ⁻¹) at receptor points in the main study area. Receptor point name abbreviations: V = Verkykkop; E =	

Elandsfontein; K2 = Kendal 2; L = Leandra; M1 = Majuba 1; M3 = Majuba 3; Mak = Makalu; C = Camden; Am = Amersfoort; SandC = Sandspruit head-water catchment.

..... 47

Figure 4.1: (a) Mean ($\pm$ standard error) pH(H₂O), (b) acid neutralising capacity (cmol_c kg⁻¹) and (c) exchangeable acidity (cmol₍₊₎ kg⁻¹) in 1991 and 2007, represented by groups of sites based on similar clay content (%). Groups are described in Table 4.4. * indicates statistically significant differences between sampling years, 1991 and 2007, at alpha=0.05..... 66

Figure 4.2: Maps showing the acidity status of the soils of the Highveld grasslands by a) acid neutralising capacity in 2007 (cmol_c kg⁻¹), b) exchangeable acidity in 2007 (cmol₍₊₎ kg⁻¹) and c) change in pH(H₂O) between 2007 and 1991. Sampling sites were considered representative of specific soil forms in which they occurred and where more than one site occurred on the same soil form, a mean of the site values was used to represent the soil form. The grey areas are soil forms that were not sampled and the soil acidity status is unknown..... 68

Figure 4.3: Maps showing the acidity status of the soils of the Highveld grasslands by a) acid neutralising capacity in 2007 (cmol_c kg⁻¹), b) exchangeable acidity in 2007 (cmol₍₊₎ kg⁻¹) and c) change in pH(H₂O) between 2007 and 1991. Sampling sites were considered representative of land type in which they occurred and where more than one site occurred on the same land type, a mean of the site values was used to represent the land type..... 70

Figure 5.1: Location of sites used to investigate net SO₄²⁻ and N mineralisation in an area of the grassland biome of South Africa. Weather data from the South African Weather Service stations at Secunda, Standerton and Ermelo were used to describe weather patterns over the area sampled. 82

Figure 5.2: Mean ($\pm$ standard deviation) monthly minimum and maximum air temperatures and mean monthly rainfall for the three weather stations in the region of the mineralisation sampling sites. Total rainfall from January 2008 to January 2009 was 734 mm. 85

Figure 5.3: Mean ($\pm$ standard error) net sulfate mineralisation rate (μ g SO₄²⁻ g⁻¹ soil day⁻¹) from February 2008 to January 2009 (for 11 sites; n=44). Where rates or slope of the graph between two sampling points is positive, SO₄²⁻ is

mineralised. In contrast, where rates or slope of the graph are negative, SO_4^{2-} was immobilised. 86

Figure 5.4: Mean net N mineralisation, ammonification and nitrification ($\mu\text{g N g}^{-1} \text{ soil day}^{-1}$) for February 2008 to January 2009 (for 11 sites; $n=44$). Standard error presented for net N mineralisation at each monthly sampling. 87

Figure 5.5: Monthly mean ($\pm$ standard error) net SO_4^{2-} mineralisation rates ($\mu\text{g g}^{-1} \text{ day}^{-1}$) sorted by land type over the period January 2008 to January 2009. Series represent the 3 land types – identifier code (e.g. Ba) followed by the relevant sampling site numbers. 89

Figure 5.6: Monthly mean ($\pm$ standard error) net N mineralisation rates ($\mu\text{g g}^{-1} \text{ day}^{-1}$) sorted by land type over the period January 2008 to January 2009. .. 90

Figure 5.7: Annual mean ($\pm$ standard error) net inorganic SO_4^{2-} and N mineralised ($\text{kg ha}^{-1} \text{ year}^{-1}$) between January 2008 and January 2009, sorted by land type (with relevant sampling site numbers). 91

Figure 5.8: The sulfur cycle in Highveld grasslands of South Africa. The units for pools are kg ha^{-1} and the units for fluxes (in italic text) are $\text{kg ha}^{-1} \text{ year}^{-1}$ 94

Figure 5.9: The nitrogen cycle in Highveld grasslands of South Africa. The units for pools are kg ha^{-1} and the units for fluxes (in italic text) are $\text{kg ha}^{-1} \text{ year}^{-1}$ 96

Figure 6.1: Time series plots of water chemical variables at five sites in the Vaal Dam catchment between 1991 and 2008. Monthly median concentrations (mg l^{-1}) are presented for (a) SO_4^{2-} (b) NO_3+NO_2 (c) NH_4^+ (d) ANC (meq l^{-1}) and (e) DMS. The dashed 'Target' line is the National Drinking Water quality guideline (Department of Water Affairs and Forestry, 1996). 112

Figure 7.1(a): The biomes of South Africa with the modelling and study domain indicated in red. (b) The domain over the Highveld grasslands of South Africa used for N deposition modelling. The sampling sites of the Arnot and Highveld soil chemistry studies are indicated by the filled circles. The quaternary catchments investigated in the hydrological study are also indicated; in the text quaternaries C1 are referred to as the Klip catchment, B1 is referred to as the Olifants catchment and X3 is referred to as the Sabie catchment. The coloured background areas are the grassland and savanna biomes covering the domain. 122

Figure 7.2: Total N deposition model output ($\text{kg ha}^{-1} \text{ year}^{-1}$) over the Mpumalanga Highveld modelling domain under 3 different rainfall scenarios (a)

Average rainfall scenario (690mm MAP); (b) Above average rainfall scenario (1014mm MAP); (c) Below average rainfall scenario (480mm MAP).	129
Figure 7.3: Projected N and S deposition across the Highveld modelling domain, in the year 2020 (to support Figure 3.3).	130
Figure 7.4: Total (wet + dry) N deposition (modelled as in Section 7.3.1) and export (as $\text{NO}_3^- + \text{NH}_4^+$) from three catchments within the modelling domain.	133
Figure 8.1: A conceptual framework of the cause-effect relationships in the Highveld grasslands resulting in spatial and temporal heterogeneity in responses to S and N deposition. Increases in cause resulting in increases in effect are marked by lowercase s; lowercase o indicates an increase in cause which results in a decrease in effect. Arrow colour denotes temporal scale: black – long-term; blue – short-term and red arrows mark influences over short- and long-term.	142
Figure 8.2: Spatial differences in evaporation, rainfall, deposition, clay rich soils and sand rich soils across the Highveld grassland study area. The direction of the arrow shows the gradient of increase: Evaporation increases northerly and westerly; Rainfall increases to the south and east; Deposition increases northerly and westerly, with a maximum in the central region of the study area.	148

LIST OF TABLES

Table 2.1: Nitrogen compounds typically found in wet and dry deposition. Chemical species tabulated are not equal contributors to atmospheric N at any particular site (Hanson and Lindberg, 1991; Lovett, 1992; Hesterberg <i>et al.</i> , 1996; Fowler <i>et al.</i> , 1999).....	23
Table 2.2: Soil processes producing (sources) and consuming (sinks) H ⁺ ions (De Vries and Breeuwsma, 1987).	28
Table 3.1: Projected SO ₂ and NO _x emissions break-point years of S and N deposition to the Highveld modelling domain (from Blight <i>et al.</i> , 2009).	41
Table 3.2: Coordinates of discrete receptor points selected for model outputs (modified from Blight <i>et al.</i> 2009). AQ station refers to an existing air quality monitoring station.	49
Table 3.3: Details for the 19 sites re-sampled in the Highveld grasslands in 2007 including site altitude (m above sea level) and mean annual rainfall (mm) of the land type (Land Type Survey Staff, 1985; 2002). Land types are areas of uniform terrain type, soil pattern and climate and the areal extent (in km ²) of the land type within the study area of the Highveld grasslands is given. The depth of top- and sub-soil is the average depth (in mm) of sites sampled in 2007. In some cases if compaction limited sampling the sub-soil, then no sub-soil depth is given.....	51
Table 3.4: Location of the DWA water quality monitoring points in the Vaal Dam catchment used to assess the impact of S and N deposition on water.....	53
Table 4.1: Methods used to analyse Highveld grassland soils collected in 2007. Procedures followed by numeric superscripts were different to those used by Fey and Guy (1993). In 1991: 1. Extractable base cations were quantified by AAS; 2. Texture was determined by the pipette method and sand class screening; 3. Adsorbed sulfate was quantified by reduction-distillation using the methylene blue procedure of Tabatabai (1982); 4. Nitrate and Chloride concentrations were not quantified by Fey & Guy (1993).....	60
Table 4.2: Site-by-site comparison across sampling years 1991 and 2007 where the differences are reported as number of soils sampled, either in the top-soil or sub-soil horizons meeting the criteria listed. The number of sites where changes were statistically significant is indicated in parentheses ($\alpha=0.05$). *Indicates sites where pH was below the pH 4.2 Al-buffer limit in 2007 but not in 1991.....	62

Table 4.3: Chemical properties of top-soils and sub-soils of Highveld grasslands between 1991 and 2007 (top-soils: n=17; sub-soils: n=12). The mean is calculated from 18 sampling sites with the minimum and maximum concentrations in each sampling year also presented. Significant differences between 1991 and 2007 are marked as: * $p < 0.05$ and ** $p < 0.01$. Changes in pH the difference between 2007 and 1991 values and are referred to as the absolute difference. The change in all other properties is expressed as the difference between 2007 and 1991 values as a percentage of the 1991 value. ***Exchangeable Na was not measured in 1991; these values have been calculated based on the 2007 percentage contribution of Na to total exchangeable bases..... 64

Table 4.4: Correlation coefficients (r) between soil chemical properties and particle size distribution for Highveld grassland soils in 2007. * $p < 0.05$ (n=261)..... 65

Table 4.5: Statistically similar Highveld grassland sites based on percentage clay content of incremental depth samples from 2007. 65

Table 4.6: Areal extent of areas indicating increased soil acidity, based on fine scale soil form and land type pattern. Areas are presented for where ANC in 2007 is less than $0 \text{ cmol}_c \text{ kg}^{-1}$, exchangeable acidity, in 2007, is greater than $0.5 \text{ cmol}_{(+) } \text{ kg}^{-1}$ and where the difference in $\text{pH}(\text{H}_2\text{O})$ between the two sampling years (1991 and 2007) was negative. Known areas are those where the chemical properties are inferred from the soil chemical analyses conducted at the 18 sampling sites. 71

Table 5.1: Variable contributions to Principle Components Analysis. 92

Table 5.2: Details of pools and fluxes, in terms of sizes and literature sources, used in compiling the S and N cycles of the Highveld grasslands. Units for pool sizes are kg ha^{-1} and units for fluxes (in italics) are $\text{kg ha}^{-1} \text{ year}^{-1}$ 93

Table 6.1: Wet and dry season monthly discharge ($\text{m}^3 \times 10^6$) and mean chemical variable concentrations (mg l^{-1} , except for ANC – meq l^{-1}) at five river sites in the Vaal Dam catchment between 1991 and 2008. All sites were statistically significantly different ($\alpha < 0.05$) unless marked (grey filled cells)..... 109

Table 6.2: Statistically significant trends in the change of chemical variables at five sites in the Vaal Dam catchment. Where the trends confirmed the hypotheses, p-values are in black; where trends confirmed the inverse hypothesis, p-values are in blue. Trend analysis conducted on median monthly concentrations (mg l^{-1}) for all variables except ANC which is based on median monthly charge balance (meq l^{-1}). 110

Table 7.1: Estimated total base case emissions for anthropogenic sources on the Highveld.	125
Table 7.2: Change in mean (n=15) soil chemical properties in the vicinity of the Arnot Power Station between 1996 and 2006, for top- and sub-soil horizons (n=15). All changes reported in table are significant ($\alpha=0.05$ using paired t-tests).	131
Table 7.3: Comparison of measured ($\text{kg N ha}^{-1} \text{ year}^{-1}$) and predicted annual Total N deposition ($\text{kg N ha}^{-1} \text{ year}^{-1}$).	135

CHAPTER 1: INTRODUCTION

Large scale human mobilisation of reactive forms of sulfur (S) and nitrogen (N) into the atmosphere primarily occurs through the combustion of fossil and bio-fuels and the volatilisation of agricultural fertiliser products (Vitousek *et al.*, 1997a; Dentener *et al.*, 2006). Increases in emissions, since the beginning of the industrial revolution, have been driven by increasing populations and hence increased energy demands (Galloway, 1995). Fossil fuel combustion and other anthropogenic emissions result in increased concentrations of aerosol particles, and S and N in cloud water and precipitation (Rodhe *et al.*, 1995) that become inputs of S and N to the recipient ecosystems. The impacts of deposition of these reactive forms of S and N include the acidification of soils and associated freshwater systems, soil nutrient depletion as a result of the loss of basic cations, fertilisation of naturally N-limited ecosystems and increased availability of metal ions (for example aluminium); many of these impacts then cause disrupted ecosystem functioning (Rodhe *et al.*, 1995) and changes in plant or freshwater species diversity (Stevens *et al.*, 2004). Investigations into the links between elevated emissions, deposition and ecosystem functioning began in response to declining fish populations in European lakes as a result of increased acidity (1960's) and subsequently declining productivity in forests in the (Schindler, 1988; Cowling and Nilsson, 1995). Most of the research in the field has been focussed around the highly industrialised areas of Europe and North America and many studies were based near local source and recipient sites. The research was directed by the observed effects on sensitive ecosystems especially forests (Mitchell *et al.*, 1992; Matzner and Murach, 1995; Falkengren-Grerup *et al.*, 1998; Fowler *et al.*, 1999) and poorly buffered freshwater systems (Fowler *et al.*, 2005).

International policy changes, for example the Convention of Long-range Transboundary Air Pollution in Europe (Berge *et al.*, 1999; Reinds *et al.*, 2008) and the Clean Air Act and amendments in the United States (Butler *et al.*, 2001; Driscoll *et al.*, 2001; Likens *et al.*, 2001), were implemented in response to the impacts on forested ecosystems of Europe and North America as a consequence of decades of atmospheric deposition of S and N compounds. These policies have resulted in dramatically reduced S emissions and deposition such that, some local areas where

anthropogenic deposition is less than $10 \text{ kg S ha}^{-1}\text{year}^{-1}$, crop S deficiencies have been observed because inputs are lower than crop S demand (Scherer, 2009). Targets to reduce N deposition, in contrast, have been more modest (Aber *et al.*, 1998) and the impacts of N deposition to ecosystems continues to be a concern (Bowman *et al.*, 2008; Bobbink *et al.*, 2010).

With these reductions in S deposition, the recent focus of international research has been on N deposition. Required as a macronutrient for plant productivity N deposition has a dual role in ecosystems; it can act as a fertiliser where N limitations restrict carbon (C) fixation. In excess, through the processes of acidification and eutrophication, N deposition has been linked to reduced biodiversity in grasslands of Europe (Bobbink, 1991; Wedin and Tilman, 1996; Stevens *et al.*, 2004; Bobbink *et al.*, 2010; Stevens *et al.*, 2010; Van den Berg *et al.*, 2010) and North America (Clark and Tilman, 2008).

South Africa is reliant on coal-fired power stations for the majority of its base-load electricity supply. Due to the proximity to coal beds, nine coal-fired power stations are clustered on the Mpumalanga Highveld. The prevailing air circulation over the Highveld is in the form of anti-cyclonic high pressure systems and westerly waves (Preston-Whyte and Tyson, 1993; Tyson *et al.*, 1996). These atmospheric conditions prevent the dispersal of atmospheric pollutants emitted by power stations and other energy demanding industrial activities (Tyson *et al.*, 1988; Held *et al.*, 1994; Zunckel *et al.*, 2000). In winter, anti-cyclonic subsidence prevails and deposition of reactive S and N occurs close to the source (Collett *et al.*, 2010), decreasing further away from the major source region (Zunckel *et al.*, 2000). Combined wet and dry S deposition to the Mpumalanga Highveld has recently been modelled to be $\geq 35 \text{ kg S ha}^{-1}\text{year}^{-1}$ near large point sources and approximately $8 \text{ kg S ha}^{-1}\text{year}^{-1}$ over the Highveld more regionally (Blight *et al.*, 2009). In contrast remote background sites in South Africa receive $\sim 1 \text{ kg S ha}^{-1}\text{year}^{-1}$ (Blight *et al.*, 2009). These modelled estimates for S deposition are higher than estimates from regional modelling studies (Zunckel *et al.*, 1996) and field-monitored deposition (Mphepya *et al.*, 2004) over the Highveld region. The differences in total S deposition are possibly related to the models, input data used (including rainfall), the inherent model assumptions and the scale of modelling. Zunckel *et al.* (1996) report the findings of a pilot study using an inferential deposition model based on two-week

field experiments in winter and summer at one air quality monitoring station (Elandsfontein) on the Highveld. Wet deposition (quantified from rainwater concentrations) and ambient air concentrations (to infer dry deposition) of Mphepya *et al.* (2004) was monitored at two field sites over a period of 13 years.

Modelling estimates for N deposition to the South African Highveld range between $6.7 \text{ kg N ha}^{-1}\text{year}^{-1}$ (Collett *et al.*, 2010) and $>15.0 \text{ kg N ha}^{-1}\text{year}^{-1}$ (Blight *et al.*, 2009). These modelled N deposition estimates (Lowman, 2003; Blight *et al.*, 2009; Collett *et al.*, 2010) correspond to field-monitored deposition (calculated from S and N concentrations in the atmosphere and in precipitation) over the same region (Mphepya *et al.*, 2001; Mphepya, 2002; Galy-Lacaux *et al.*, 2003) and are comparable to those in developed countries where impacts on ecosystems have previously been recorded. Modelled S deposition rates (from atmospheric concentrations) from 1997 to 2000 for CASTNet sites across the USA ranged between 0.4 and $16.5 \text{ kg S ha}^{-1} \text{ year}^{-1}$. Nitrogen deposition over the same period ranged between 1.1 and $10.4 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Baumgardner *et al.*, 2002). Between 2004 and 2006, the highest S and N deposition rates ($21 \text{ kg S ha}^{-1} \text{ year}^{-1}$ and $>9 \text{ kg N ha}^{-1} \text{ year}^{-1}$) from a USA national monitoring network were recorded in the Ohio River Valley (EPA, 2008). In comparison to monitored deposition rates, some modelled projections overestimated deposition in the Adirondak mountains of New York state (total N deposition of $20 \text{ kg N ha}^{-1} \text{ year}^{-1}$) and some parts of southern California ($32 \text{ kg N ha}^{-1} \text{ year}^{-1}$) (EPA, 2008). Across Europe modelled deposition estimates for the year 2000 ranged between 1.3 and $15.5 \text{ kg S ha}^{-1} \text{ year}^{-1}$ and between 1.8 and $27.4 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Pieterse *et al.*, 2007; Duprè *et al.*, 2010).

Atmospheric circulation, air quality and deposition quantities are well researched over the central South African Highveld due to the clustering of emission sources. Impacts of atmospheric deposition on ecosystem functioning have been researched in the afforested areas of the Mpumalanga eastern escarpment and the adjacent high-altitude grasslands (Lowman, 2003; Mamatsharaga, 2004; Ndala *et al.*, 2006). However, the impacts of S and N deposition on the soil chemistry and nutrient cycling processes of the central Highveld grasslands have, in contrast, received much less research focus. The catchment for the Vaal Dam which is the main source of fresh water to Gauteng, South Africa's most populated administrative province, extends over the Highveld grasslands of the Mpumalanga and Free State

provinces. Knowing that this region receives large quantities of S deposition, Fey and Guy (1993) investigated the capacity of the soils of the Vaal Dam catchment to retain sulfate (SO_4^{2-}) from atmospheric S deposition. It was found that in 1991 many of the soils were nearing the limit of the capacity to retain SO_4^{2-} (Fey and Guy, 1993).

In order to improve the understanding of the impacts of S and N deposition on the grassland ecosystems of the Highveld region, this research investigated the changes in soil chemistry of the Highveld grasslands since the work of Fey and Guy (1993) and to examine the processes of S and N mineralisation in these grassland soils. Changes in water chemistry at five river sites between 1991 and 2008 were also investigated.

1.1 Aims

The project aimed,

- to use modelled wet and dry S and N deposition rates to the Highveld grasslands, between 1991 and 2008, to quantify inputs to the elemental cycles,
- to quantify change in concentrations of S and N in the soils of the Vaal Dam catchment since 1991,
- to quantify the rates of S and N mineralisation,
- to estimate S and N budgets for the grasslands, and
- to relate these changes to changing water quality in terms of dissolved salts, SO_4^{2-} and NO_3^- .

1.2 Hypotheses

The following hypotheses were proposed at the beginning of the project.

1. Wet and dry deposition of S and N increased over the Vaal Dam catchment between 1991 and 2008.
2. Sulfur retention capacity has been exceeded in at least 75% of the areal extent of soils in the Vaal Dam catchment (in 12 of 18 soil sampling points and 12 of the 13 soil types).

3. All top-soils of the northern half of the Vaal Dam catchment are N saturated, due to their proximity to the atmospheric pollutant source (11 soil sampling sites).
4. Elevated soil S and N concentrations have resulted in poorer water quality evidenced by elevated levels of dissolved salts, SO_4^{2-} and NO_3^- in the catchment rivers.

1.3 Key Questions

The following key questions (KQ) directed the research by addressing the hypothesis(es) mentioned below each question.

1. How have the rates of wet and dry deposition changed since 1991?
 - 1.1. Hypothesis 1
2. How have the top- and sub-soil chemical properties, as measured by Fey and Guy (1993) changed in the Vaal Dam catchment between 1991 and 2007?
 - 2.1. Hypotheses 2 and 3
3. Do any of the soils studied (18 soil sample sites), show exceedance of S retention capacities, if so, why?
 - 3.1. Hypothesis 2
4. How has the acid neutralising capacity of the soils in the catchment changed between 1991 and 2007?
 - 4.1. Hypotheses 2 and 3
5. What are the rates of soil S and N mineralisation in the top-soils of the Highveld grasslands?
 - 5.1. Hypothesis 3
6. How has water quality, in terms of dissolved salts, SO_4^{2-} and NO_3^- changed between 1991 and 2008?
 - 6.1. Hypothesis 3 and 4

1.4 Thesis structure

The thesis will be structured as outlined in Figure 1.1.

(1) Introduction including Contribution to science			
(2) Literature Review			
(3) Study area and sampling sites			
(4) The acidity of soils of the Highveld grasslands, South Africa KQ 2, KQ 4, (KQ3) In preparation for Environmental Monitoring and Assessment	(5) Sulfur and nitrogen cycling in the grasslands of the Mpumalanga Highveld, South Africa KQ 5, (KQ3) Under revision for Oecologia	(6) Changes in water chemistry in the Vaal Dam catchment between 1991 and 2008 KQ 6, (KQ3) In preparation for Water SA	(7) Ecosystem services in the grasslands of South Africa affected by nitrogen deposition KQ 1 and an integrated view of the modelling domain Under revision for AMBIO
(8) Discussion of research findings within a conceptual framework			
(9) References			

Figure 1.1: A representation of the structure of the thesis (chapter number in parentheses). The manuscript title and key research questions (KQ - detailed in Section 1.3 on page 5) are detailed for each results chapter.

The introductory chapter is followed by a synthesis of the literature and identification of the knowledge gaps in the field of study (Chapter 2). A general description of the study area and the sampling sites is provided in Chapter 3, including the findings that address key question 1 regarding the amount of S and N deposited on these grasslands between 1991 and 2007. Detailed sample collection and analytical methods are described in the specific results chapters. Chapters 4 to

7 are included as copies of manuscripts either under review for publication in journals or, in the case of Chapter 6, in preparation for journal publication. Each results chapter includes specific research goals, methods, results and discussion. Due to the stand-alone nature of these manuscripts, it is noted that there is some repetition of content. Figures and tables have been cross-referenced to avoid duplication.

Chapter 4 reports the changes in soil chemistry between 1991 and 2007 at multiple spatial scales and identifies the soil types in the study area that are most sensitive to S and N inputs using a spatial scaling approach. These S and N inputs are placed in context with internal cycling processes in Chapter 5, where S and N mineralisation patterns are presented over an annual cycle. In Chapter 6 the changes in water chemistry in rivers draining the Highveld grasslands between 1991 and 2008 are reported. Nitrogen deposition effects on the Highveld grassland ecosystems are considered from an integrated perspective in Chapter 7, starting with the amount of deposition received, then considering soil chemical changes and finally the effects on water chemistry.

An integrated discussion of the key findings is provided in Chapter 8 within a conceptual framework. The discussion includes a response to the key questions posed (Section 1.3 on page 5). References are included as the final chapter (Chapter 9).

1.5 Contribution to science

South Africa has S and N deposition levels comparable to those in high deposition areas in the northern Hemisphere (Blight *et al.*, 2009) and studies of air quality, air circulation and deposition started in the early 1980's (Tyson *et al.*, 1988) and are currently ongoing. Factors that motivated the assessment of the impact of S and N deposition within the Highveld grasslands and Vaal Dam catchment areas include,

- the high density of power and petrochemical plants in a relatively small area,
- the unique atmospheric circulation conditions promoting deposition of pollutants, within a short distance from the source and

- the proximity between pollution source and the catchment which forms the main water source for Gauteng.

These factors suggest that the ecosystem processes are likely to be influenced by the deposition loads and that older research findings needed updating. The research by Fey and Guy (1993) was used as a basis to measure the changes in soil chemical components over a 16 year period.

The research approach considered a temporal scale of 16 years for soils and 17 years for water quality impacts. The spatial scale of the study included comparisons by sites, between sites, across the study area more generally and then up-scaling to the soil form and land type scales, in order to comment on the changes at a regional scale of the Highveld grasslands.

From the investigation the following findings are considered to be noteworthy contributions to science.

1. This research serves as a new point in time against which further impacts of S and N deposition to the Highveld grasslands can be assessed.
2. The evidence of increased acidity status of soils of the Highveld grasslands, together with the capacity to predict soil sensitivity based on soil clay content, has identified sensitive soils that can be monitored for future impacts. The most sensitive soils are sandy, with less than 4% clay and occur near the southern and eastern boundaries of the study site. Rainfall is also higher along these boundaries than to the northern, central and western sections of the study area. Although more distant from emission sources, it is proposed that these sandy soils receiving higher rainfall relative to the rest of the study area, are receiving deposition in amounts that are approaching critical loads. In the central and northern parts of the study area the soils have higher clay content. These soils are also closer to emission sources and it is speculated that they receive co-deposition of acidic and neutralising compounds. It is proposed that the balancing effect of the acidic and neutralising compounds, together with the high clay content, has provided sufficient buffering capacity to these soils to restrict increases in soil acidity status. Further research should address co-deposition in relation to the capacity of soils to neutralise continued acidic inputs.

3. The identification of soils sensitive to atmospheric S and N deposition was by means of a spatial mapping and scaling method. Results were first compared by site and then, as an average of all sites, across the study area more generally. Sites were then grouped by similar clay contents and these data were then used to interpret differences between years according to soil texture. The site differences were then mapped at the soil form and land type scales to allow for the calculation of the areas where soil acidity status had decreased the most. The interpretation of these results, in conjunction with rainfall and distance from emissions allowed for the identification of the soils most sensitive to atmospheric S and N deposition.
4. The use of acid neutralising capacity (ANC) has assisted in categorising the soils and waters with respect to S and N inputs; either via atmospheric deposition or other sources. This could become a useful indicator in continued monitoring programmes.
5. Although commonly used to determine net N mineralisation, the use of the *in situ* mineralisation method to quantify sulfate (SO_4^{2-}) turnover rates is, as far as the author is aware, the first application of the method to quantify S mineralisation. This method provides a field-based quantification of S mineralisation and can be used to plot seasonal and annual trends which can contribute to ecosystem S budgets.
6. Comprehensive nutrient budgets for the South African grasslands were not available in the literature. Thus the estimation of the S and N nutrient cycles is a first attempt at quantifying the pool sizes and flux rates of these two macro-nutrients in these grasslands. These budgets extend the understanding of nutrient cycling processes in these grasslands. From these budgets it is proposed that the grasslands are accreting in S through storage in the soil organic S pool. Because there is no accretion of N in the soils, it is suggested that in spite of atmospheric N inputs, these natural grasslands remain N limited. However further investigation into the impacts of N on species abundance and diversity in these grasslands is recommended.
7. Water quality in the Vaal Dam catchment was not found to show impacts of atmospheric S and N deposition as hypothesised. In a similar way to soils, increased concentrations of both acidic and neutralising ions in surface waters were found. Spatial differences between ion concentrations suggest that land use

and water use – prior to discharge into streams – are stronger influences of water quality in this catchment.

8. The broader perspective of N deposition and its impacts to ecosystems of the Highveld, synthesised in Chapter 7, positions South African ecosystems and impacts within the current dominance of N deposition in the international literature. The Highveld grasslands receive comparable levels of N deposition to other impacted ecosystems internationally. The findings of this study show that the natural grasslands of the South African Highveld are not yet measurably impacted by N deposition. This study adds to the body of knowledge about sensitive areas receiving N deposition. The results also demonstrate that a long-term programme to monitor for impacts on these grasslands would be valuable.

1.6 Policy relevance of potential impacts on the study area

The findings from this study are likely to be of interest to several interested and affected parties. The production activities of Eskom and SASOL are among the largest S and N emission sources in the region. By funding the research the companies have shown concern about the impacts on ecosystems where these emissions are eventually deposited. Other industrial emitters may also be interested in the findings of the research. Stock farmers reliant on the fertility of soils to maintain grass productivity as forage for livestock could be affected by the long-term implications of S and N deposition. Organisations involved in conservation of species diversity in these grasslands could be affected by the findings. Similar organisations involved in water provisioning, management and treatment could use the findings in developing new management strategies for the Vaal Dam catchment. National and local government may use the data to support new policy with regards to S and N emissions as a result of the impacts reported.

CHAPTER 2: LITERATURE REVIEW

In order to consider the key research questions identified in Chapter 1, the current state of the literature is expanded in this chapter. The chapter begins with a description of ecosystem services highlighting S and N cycling and the processes within each elemental cycle. Human alteration of these nutrient cycles is then considered with specific reference to anthropogenic emissions of S and N through fossil fuel combustion, the atmospheric reactions and the impacts of deposition, after transformation and transport. Ecological heterogeneity and the use of conceptual frameworks are introduced as frameworks for exploring the diversity of impacts and ecosystem responses in heterogeneous systems.

2.1 Ecosystem services

2.1.1 What are ecosystem services?

The Millennium Ecosystem Assessment was an integrated assessment of the consequences of ecosystem change on human well-being and involved governments, private sector organisations, non-governmental organisations and scientists, undertaken between 2001 and 2005 (Millennium Ecosystem Assessment, 2005a). The outcome presented a new framework for making connections between social and ecological systems (Carpenter *et al.*, 2009). Carpenter *et al.* (2009) commented that sustainability science, within which the concept of ecosystem services developed, is unique in that research findings direct policy and feedbacks from policy implement further direct research and experimentation. Ecosystem services are naturally anthropocentric and defined as the flows or processes that benefit human needs (Dominati *et al.*, 2010). Although mention of ecosystem services occurs as early as the mid-1960's it was de Groot *et al.* (2002) that first proposed a classification framework including regulating, habitat, production and information functions which, when ecological, socio-cultural and economic values were applied became the goods and services delivered by ecosystems. The categories accepted by sustainability scientists now, are those mentioned in the Millennium Ecosystem Assessment (2005c) and include provisioning, regulating, supporting and cultural services.

The capital assets of ecosystems are composed of the biotic and abiotic components (Daily *et al.*, 2000). Dominati *et al.* (2010) emphasise soils as natural

capital of ecosystems and point out that soils are, however, rarely explicitly mentioned in ecosystem service frameworks and they propose a framework for the provision of ecosystem services delivered by soils. The role of soils in ecosystem services covers provisioning, regulating and cultural services meeting human needs at multiple levels (including physiological, safety and security, social and self-actualisation needs) (Dominati *et al.*, 2010). The specific services delivered include soil fertility through nutrient cycling and delivery of nutrients to plants, as a filter of water and reservoir of nutrients assisting in the provisioning of nutrients for plants and flood mitigation, and soil also has a structural role by providing physical support to plants, animals and human infrastructure as well as being a source of raw materials.

Nutrient cycling is the movement of elements through biotic and abiotic compartments of an ecosystem and within soils it is a provisioning service supplying nutrients to organisms and thus underpins all other ecosystem services (Millennium Ecosystem Assessment, 2005b; Dominati *et al.*, 2010) such as the provisioning services of food, fibre and fresh water or climate regulation through the sequestration of C in soil organic matter. According to Dominati *et al.* (2010) the inherent (difficult to change without great cost) and manageable properties of soils will influence the processes and ecosystem services. The drivers of these soil properties are either natural – for example, climate, geology, geomorphology and biodiversity which usually affect inherent properties over long time scales – or anthropogenic – such as land use, farming practices and technology which can be manipulated over short time scales to optimise ecosystem services. Human activities have had important positive and negative impacts on the cycling of several key nutrients – S, N, C, phosphorus (P), and possibly iron (Fe) and silicon (Si). Over the past two centuries this has mostly been through transformation of the land surface and intensification of agricultural and industrial practices (Vitousek *et al.*, 1997b; Millennium Ecosystem Assessment, 2005b; Steffen, 2010). Reports of declining regulating services (disease, pest, erosion, pollination, water regulation and purification) are mainly a result of increased human population (Steffen, 2010) and forewarn declines in the other service categories (Carpenter *et al.*, 2009). Daily *et al.* (2000) suggest that degradation of ecosystems usually precedes the valuation of the services delivered

and in many cases capital assets in degrading ecosystems are poorly understood and/or monitored.

Soil nutrient cycling processes are conservative, according to the literature, by two definitions. If inputs of an element, for example S, to soil pools are equal to outputs the soil processes can be considered conservative (Mitchell and Fuller, 1988). An alternative definition, and the one used throughout this thesis, is when losses of an element from soil pools are minimal and there is net accumulation (Davidson *et al.*, 2007). By this definition inputs of an element, for example N, are conserved in the soil pools by efficient retention of physical, chemical and biological processes. This conservation can be observed where the conserved element limits biological productivity (Asner *et al.*, 1997). Because N availability often limits plant production, and is therefore usually conserved in soil pools, Aber *et al.* (1989) described 'N saturation' as the state when ecosystems dispose of N in excess of biotic demand to drainage water.

This thesis intends to extend the understanding of impacts to the ecosystem services of the South African Highveld grasslands as a result of changes to the S and N cycles through human activities. The following sections describe the general patterns of S and N cycling, the human alteration of these cycles and the potential impacts based on evidence from ecosystems worldwide.

2.1.2 The Sulfur cycle

Sulfur (S) is released into the atmosphere (Figure 2.1) through volcanic activity ($10 \text{ Tg S year}^{-1}$), terrestrial dust ($20 \text{ Tg S year}^{-1}$), biogenic processes ($2.5 \text{ Tg S year}^{-1}$) and via anthropogenic emissions usually associated with fossil fuel combustion ($93 \text{ Tg S year}^{-1}$) (Reeburgh, 1997). These gaseous and particulate S compounds undergo rapid chemical transformation to sulfate (SO_4^{2-}) in aerosols and cloud water, with subsequent deposition to land and water surfaces via precipitation and dry deposition (Reeburgh, 1997).

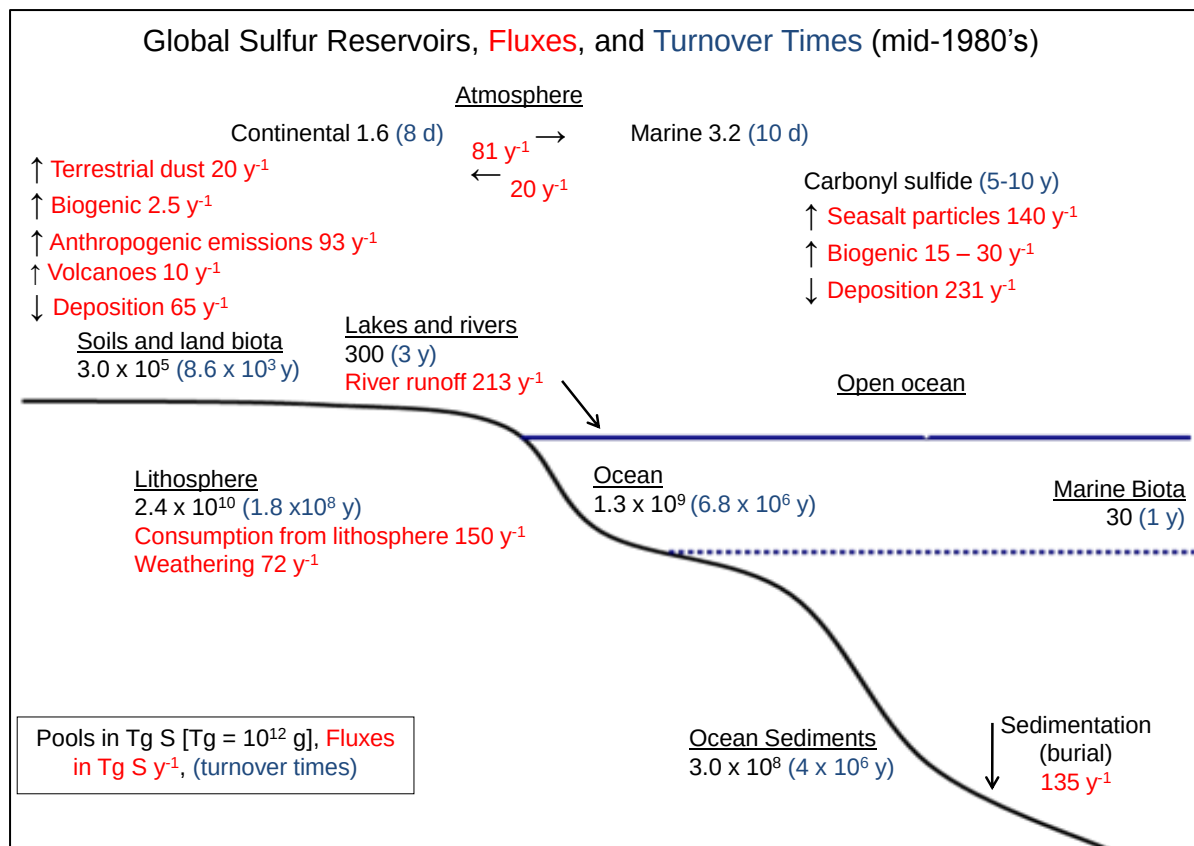


Figure 2.1: Global sulfur reservoirs, fluxes, and turnover times (in the mid-1980's). Major reservoirs are underlined; pool sizes and fluxes are given in Tg S and Tg S year^{-1} respectively. Turnover times (reservoir divided by largest flux to or from reservoir) are in parentheses (reproduced from Reeburgh, 1997).

Sulfur is a macro-nutrient where optimal plant growth requires (dry weight) concentrations between 0.2 and 0.5% (Marschner, 1986). Although some uptake of sulfur dioxide (SO_2) via leaf surfaces can occur, higher plants predominately take up S as SO_4^{2-} ions from the soil via the roots (Marschner, 1986). As a constituent of the amino acids cysteine and methionine, S can be part of the structural components or as a functional group of coenzymes and secondary plant products (Marschner, 1986). The storage of organic S compounds is then as standing biomass or as necromass in the surface soil from where it is released, under aerobic conditions, through decomposition processes either as smaller organic molecules or eventually as inorganic SO_4^{2-} . The dynamic flux from organic to inorganic S pools is referred to as mineralisation (Edwards, 1998). In some agricultural areas, the limitations of anthropogenic S inputs have resulted in S deficiencies and renewed interest in organic storage and mineralisation processes resulting in S availability for crops (Bloem *et al.*, 2001; Riffaldi *et al.*, 2006; Boye *et al.*, 2009; Scherer, 2009). Immobilisation opposes the process of mineralisation by the incorporation of

inorganic S into the soil microbial biomass which then becomes unavailable for higher plant uptake. The inorganic ions, predominantly SO_4^{2-} , if not assimilated into soil microbial or above-ground plant biomass, become susceptible to leaching into ground water and subsequently surface water. Mineralisation and immobilisation occur simultaneously and their relative rates are controlled by those factors that control microbial activity (temperature, soil moisture, available substrate) (Edwards, 1998); however, land-use practice can also influence the relative dominance of the two processes (Knights *et al.*, 2001; Boye *et al.*, 2009).

Sulfate anions can be retained on soil particle surfaces over varying time scales by the process of adsorption. Non-specific adsorption of SO_4^{2-} occurs in association with the positively charged surfaces of amphoteric (positive, negative or neutrally charged) surfaces on the soil particles. The sites available for association of SO_4^{2-} anions is pH dependent and when hydrogen ions (H^+) become more available at lower pH values, more adsorption sites are created. In contrast, SO_4^{2-} anions are held more tightly at specific adsorption sites which are more common in soils with high free-iron and aluminium hydroxide and oxide levels. These associations result in the displacement of water (H_2O) or hydroxide (OH^-) molecules when the SO_4^{2-} bonds with the metal ions (reviewed by Edwards, 1998). The adsorption of SO_4^{2-} is affected by the availability of phosphate (PO_4^{2-}) and nitrate (NO_3^-) anions (Scherer, 2009).

Both organic and inorganic S compounds become part of lake and ocean sediments via surface runoff and ground water leaching. These pools have slow turn-over rates in the order of 4×10^6 years (Reeburgh, 1997). Biological processes under anaerobic conditions can result in the release of S as hydrogen sulphide (H_2S) from swamps, lakes and surface ocean water. The H_2S is then oxidised (by oxygen and water vapour) in the atmosphere to SO_2 gas and SO_4^{2-} aerosols and 'acid rain' as sulphuric acid ($\text{H}_2\text{SO}_4^{2-}$) (Kellogg *et al.*, 1972).

2.1.3 The Nitrogen cycle

The N and S cycles are similar except that the S cycle includes a source through volcanic activity; however, it excludes the fixation of atmospheric gas into reactive compounds that occurs in the N cycle. The largest N pool (Figure 2.2) is in

the inert form of dinitrogen (N_2) in the atmosphere ($\sim 4.0 \times 10^9$ Tg N). The transformation into bio-available forms of N occurs through lightening (5 Tg N year^{-1} - (Schlesinger, 2009) and through biological N fixation ($120 \text{ Tg N year}^{-1}$ (Schlesinger, 2009) by free-living cyanobacteria and through plant-bacteria mutualistic associations. Many estimates for N cycle pool and flux sizes, such as those in Figure 2.2, are based on values from the mid-1990's (Reeburgh, 1997; Gruber and Galloway, 2008; Schlesinger, 2009). More recent values are available to illustrate the magnitude of human impact on the N cycle (expanded in section 2.1.4 Human alteration of nutrient cycles).

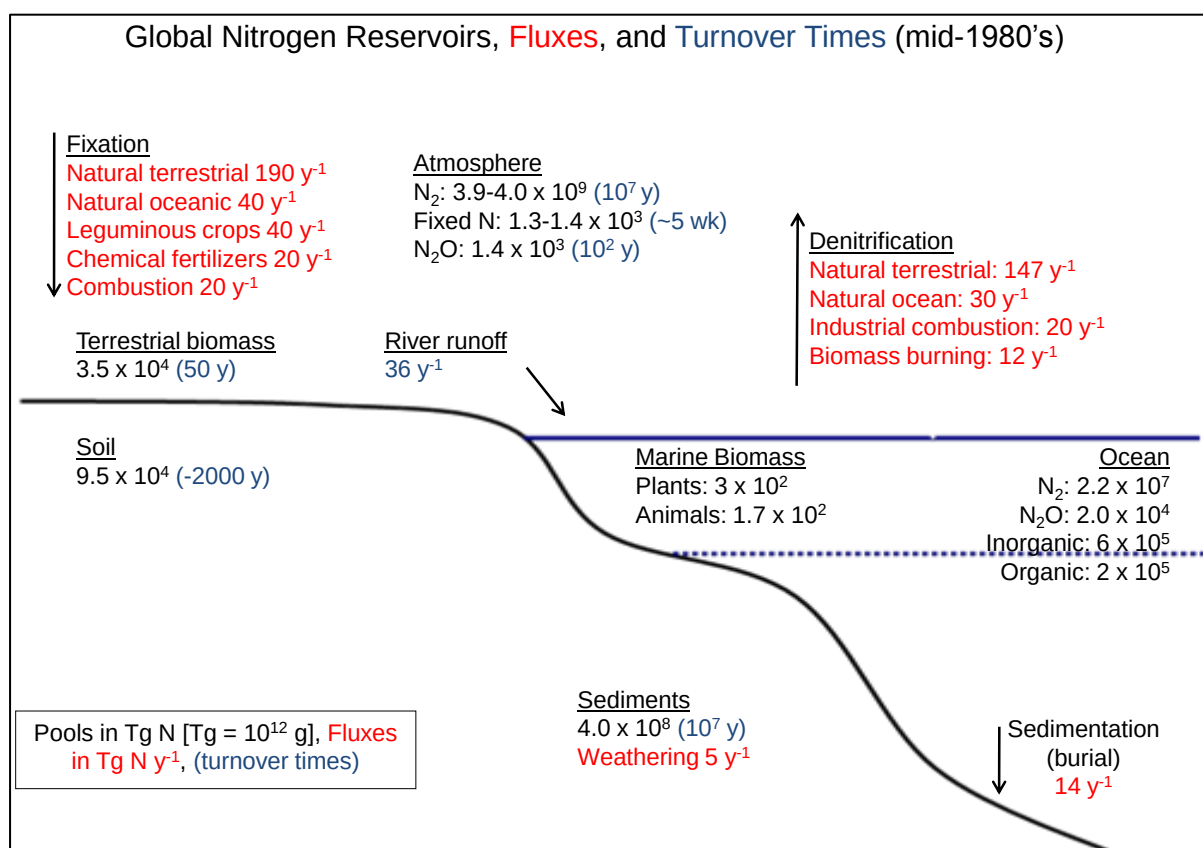


Figure 2.2: Global nitrogen reservoirs, fluxes and turnover times. Major reservoirs are underlined; pool sizes and fluxes are given in Tg N and Tg N year⁻¹ respectively. Turnover times (reservoir divided by largest flux to or from reservoir) are in parentheses (reproduced from Reeburgh, 1997).

Higher plants take up nitrogen in the form of ammonium (NH_4^+) and NO_3^- . Ammonium uptake includes the assimilation of NH_4^+ in organic compounds in the roots due to the potential toxicity of ammonia (NH_3) – the solution equilibrium partner. Nitrate, however, is mobile in the xylem and can be stored in the vacuoles of cells in the roots and shoots without detrimental effect (Marschner, 1986). Nitrogen is also a macronutrient where (plant dry weight) N concentrations between 2 and 5%

are required for optimal plant growth and is used in all amino acids and other N containing organic compounds (Marschner, 1986). When plants or animals die the organic N contents, via decomposition, are returned to the inorganic soil pool through the process of mineralisation resulting in the release of NH_4^+ . The transformation process of nitrification is a rapid 2-step oxidative process facilitated by bacteria where NH_4^+ is converted into NO_3^- (Singer and Munns, 1996; Brasseur *et al.*, 1999). Both inorganic NH_4^+ and NO_3^- are soluble in soil water and are therefore susceptible to leaching, however NO_3^- is more mobile than NH_4^+ due to its negative charge. The enrichment of surface waters by N, especially NO_3^- , can remove N productivity limitations of macrophytes, algae and bacteria and result in anoxic conditions as decomposition of plant material removes oxygen from river, lake and, more commonly, coastal waters (Schindler, 1971; Vitousek *et al.*, 1997a; Smith *et al.*, 1999). This process of eutrophication has substantial knock-on effects on the populations of aquatic animals and is mainly a result of the overuse of inorganic fertilisers in agriculture (Vitousek *et al.*, 1997a; Galloway *et al.*, 2004).

Nitrogen can be returned to the atmosphere from inorganic terrestrial and aquatic pools through the processes of volatilisation (end product NH_3), and denitrification (end products dinitrogen gas, N_2 and nitrogen dioxide, NO_2). Nitrogen dioxide is involved in the formation of tropospheric ozone (O_3) and photochemical smog (Galloway *et al.*, 2004; Gruber and Galloway, 2008).

2.1.4 Human alteration of nutrient cycles

Vitousek *et al.* (1997b, p494) begin their article about the human dominance of Earth's ecosystems by stating that "all organisms modify their environment and humans are no exception" and they present a conceptual framework for human alterations of ecosystems (Figure 2.3). Most of these human ecosystem modifications have occurred in the last 200 years, since the beginning of the Industrial Revolution and as a result of increasing human populations and resource demands including food and energy (Vitousek *et al.*, 1997b; Steffen, 2010). The capacity to produce enough food to sustain an increase in human population was through the use of N fertilisers generated via the Haber-Bosch process (commercialised in 1910) (Gruber and Galloway, 2008). Land use changes associated with large scale commercial crop and meat production have also resulted

in alteration of natural biogeochemical cycles, including N, C, P and S (Gruber and Galloway, 2008; Steffen, 2010).

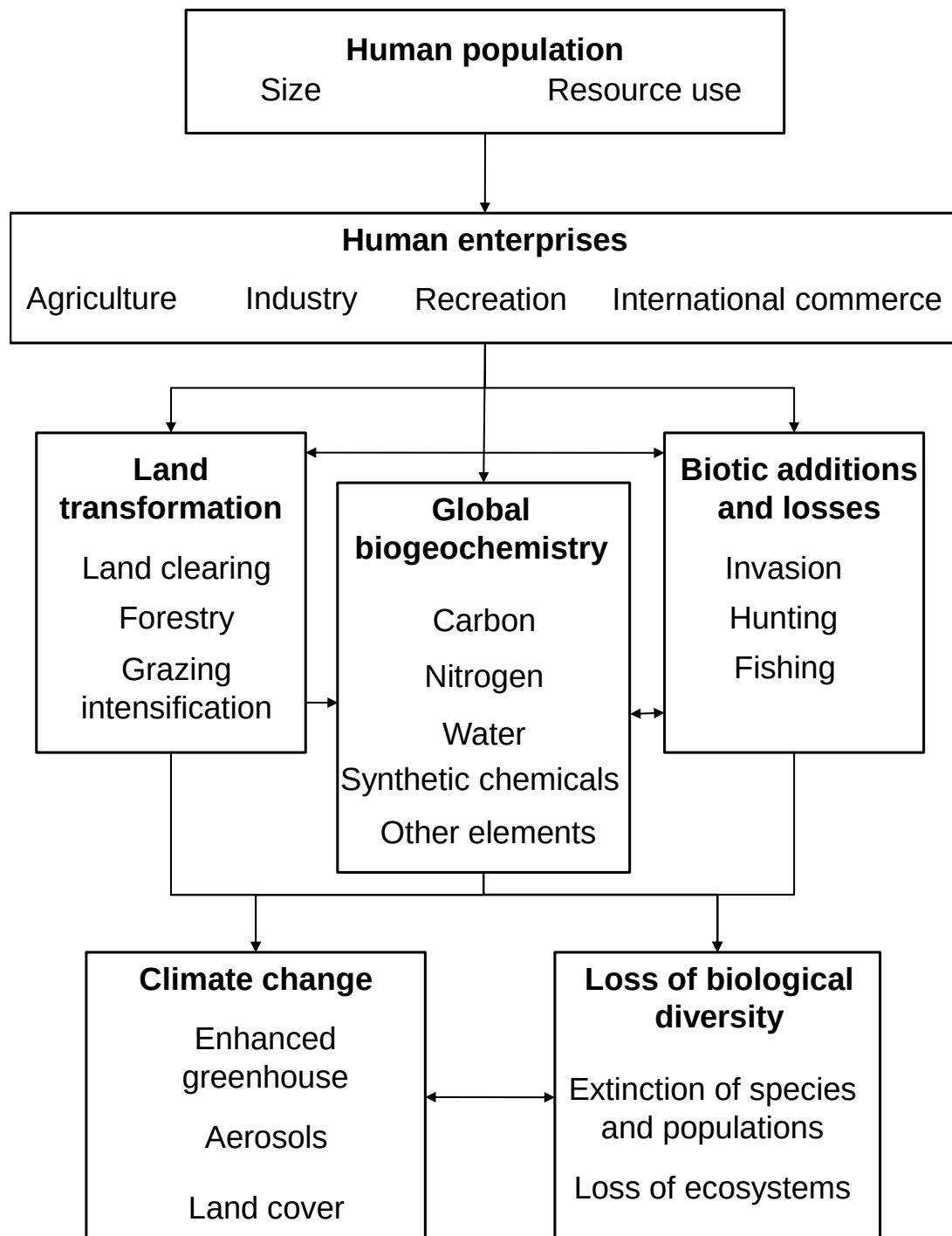


Figure 2.3: A conceptual framework illustrating human alteration of Earth's ecosystems (Vitousek *et al.* 1997).

For the most part increased energy (electricity) demands have been met by the combustion of fossil fuels (Steffen, 2010). Sulfur and N are essential nutrients incorporated into biological material and cycled via metabolic processes. It is not

surprising therefore, that the utilisation of fossilised biological material such as oil, coal and natural gas has affected the mobility and availability of these elements at a global scale (Kennedy, 1986). Recently mobilised S and N are found in reactive forms and actively cycle, by bacterial mediation, between oxidised and reduced forms until stabilised into a long-term storage sink (Galloway, 1996). Anthropogenic emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x) are most often associated with the combustion of fossil fuels. Anthropogenic release of S peaked in the 1960's (Steffen, 2010) and have decreased in many industrialised centres worldwide as a result of legislative restrictions (as reviewed by Berge *et al.*, 1999; Butler *et al.*, 2001; Driscoll *et al.*, 2001; Likens *et al.*, 2001; Reinds *et al.*, 2008). One exception is the recent industrial growth in Asia that has resulted in increased emissions regionally (Hicks *et al.*, 2008; Steffen, 2010). Even with legislative control, global anthropogenic emissions continue to exceed natural emissions to the atmosphere by a factor of two (Steffen, 2010).

Global N cycle pool sizes (in 2005) are given by Galloway *et al.* (2008) with specific reference to the anthropogenic modification of the N cycle. Inorganic fertiliser production via the Haber-Bosch process amounted to $121 \text{ Tg N year}^{-1}$ in 2005 – a 20% increase from 1995. The commercial use of biological nitrogen fixation (C-BNF) through cropping of leguminous plants increased from 31.5 to $40 \text{ Tg N year}^{-1}$ between 1995 and 2005. In the same period combustion of fossil fuels increased by 24%; however globally the emission of NO_x remained roughly constant at $\sim 25 \text{ Tg N year}^{-1}$ (Galloway *et al.*, 2008). Human N additions to terrestrial ecosystems, based on estimates from the mid-1990's, exceed natural emission processes (Schlesinger, 2009; Steffen, 2010) and are projected to increase further to match human population growth and food requirements (Gruber and Galloway, 2008). The emission of N species from fossil fuel combustion is expected to reach $200 \text{ Tg N year}^{-1}$ in 2050 (Galloway *et al.*, 2004) resulting in deposition of reactive N compounds, NO_x and NH_y (reduced nitrogen compounds), of approximately $50 \text{ kg ha}^{-1} \text{ year}^{-1}$ to parts of developing Asia (Galloway *et al.*, 2004). In 2005, a multi-model (23 models) study at regional ($1^\circ \times 1^\circ$) and global ($23.5^\circ \times 10^\circ$) scales suggested that areas with little anthropogenic N deposition received $0.5 \text{ kg ha}^{-1} \text{ year}^{-1}$ or less and maximum N deposition was approximately $10 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Dentener *et al.*, 2006). Enhanced emissions result in enhanced deposition and hence affect

ecosystem functioning (Kennedy, 1986; Cole, 1992; Vitousek *et al.*, 1997a). At least two reviews of the scientific evidence (Vitousek *et al.*, 1997a; Schlesinger, 2009) have summarised the effects of human alteration of the N cycle as follows,

- approximately doubled rate of N input into the terrestrial N cycle,
- increased global atmospheric concentrations of nitrous oxide (N₂O) which is a effective greenhouse gas and is linked to other N oxides that result in photochemical smog,
- accelerated loss of basic soil nutrients (calcium - Ca and potassium - K) with long-term effects on soil fertility,
- N compounds have contributed to acidification of soils, streams and lakes in several regions,
- increased transfer of N through rivers into estuaries and coastal oceans,
- increased organic carbon storage in terrestrial ecosystems,
- accelerated loss of biological diversity especially of plants using efficient N pathways and the animals that rely on them, and
- altered composition and functioning in marine and coastal ecosystems including coastal marine fishery declines (Vitousek *et al.*, 1997a; Schlesinger, 2009).

The dominance of the N cycle in the recent literature, with respect to human alteration, is two-fold. Firstly, legislative control reducing S emissions has lead to reduced deposition of S in many areas. In addition, N has a dual role in ecosystems as a fertiliser and pollutant (when in excess of biotic requirements) and each N molecule can be involved in a cascade of effects as it moves through the ecosystem compartments (Galloway *et al.*, 2003; Galloway *et al.*, 2008) thus resulting in a wider variety of ecosystem impacts. Reactive forms of S and N have both immediate and delayed impacts (Galloway, 1996). Immediate impacts include changes in atmospheric radiation, human health impacts, photochemical smog, infrastructural material and ecosystem damages, such as vegetation mortality. Delayed impacts are as a result of the roles of S and N in biogeochemical processes and the rapid conversion between different reactive forms, accumulating in these reactive forms in ecosystems and because stabilisation rates do not keep pace with mobilisation rates (Galloway, 1996).

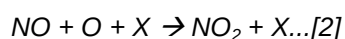
2.2 Atmospheric transformations and deposition

2.2.1 Atmospheric chemical reactions

Gaseous emissions of S and N are transformed via oxidative processes soon after emission, where multiple oxidation steps can occur before deposition of reactive compounds occurs on vegetation and soil surfaces. Primary chemical species of concern from emissions include SO₂, nitrous oxide (N₂O), nitric oxide (NO), nitrogen dioxide (NO₂) and NH₃ (Lindberg, 1992; Hewitt, 2001).

Sulfur undergoes several reactions whilst airborne and the most predominant gas-phase reaction is with the hydroxyl (OH) radical to form sulfuric acid (H₂SO₄). Subsequent to formation, H₂SO₄ can remain in solution and react with various compounds to form sulfate salts or it can form fine-aerosol acid sulfate during cloud evaporation (Lindberg, 1992; Brasseur *et al.*, 1999).

Nitrous oxide, NO and NH₃ are highly reactive in the atmosphere (Brasseur *et al.*, 1999; Hewitt, 2001). Nitric oxide (NO) can be rapidly reduced in polluted air where particulates function as reaction centres. The reactions that occur are complex and may be catalysed by ozone (Equations 1 and 2):



where X is a catalytic surface, such as water vapour. The product NO₂ is fairly reactive and can stimulate the production of O₃ (Kennedy, 1986). In the presence of high NO concentrations the oxidation of carbon monoxide (CO), methane (CH₄) and non-methane hydrocarbons, results in net production of tropospheric O₃. In contrast, when NO concentrations are low, the oxidation processes for these compounds become a sink for O₃ (Kennedy, 1986). It is through the influence of NO on the concentrations of the hydroxyl (OH) radical - the main oxidising agent in the atmosphere - that the concentration of O₃ is affected (Vitousek *et al.*, 1997a). In both scenarios, nitric acid, the end product of NO oxidation, becomes the main component of acid rain. In the 1990's it was estimated that > 80% of atmosphere NO was due to human activities (Vitousek *et al.*, 1997a). Ammonia is a primary acid neutralising agent in the atmosphere, influencing the pH of aerosols, cloud-water and

rainfall. Anthropogenic sources account for approximately 70% of all NH_3 emissions (Schlesinger and Hartley, 1992). While SO_x and NO_x have been the focus of years of research, actual versus potential acidification has been given comparatively little attention (Draaijers *et al.*, 1997). In some cases acidic emissions are accompanied by emissions of basic cations (for example from slag furnaces, smelters, limestone quarries and concrete factories and some agricultural activities) where the net acidification is zero (Rodhe *et al.*, 1995; Draaijers *et al.*, 1997). Gaseous NH_3 is also basic and may neutralise some atmospheric acidity, however, once deposited especially onto soil surfaces, it is subject to rapid conversion to NO_3^- .

2.2.2 Deposition events

Deposition of the oxidised and reduced forms of S and N occurs through a variety of processes. When species remain in solution, it is possible that deposition takes place during precipitation events, referred to as wet deposition, or through cloud or fog deposition, depending on the prevailing climate (Baumgardner *et al.*, 2002). Closer to emission sources, however, S and N forms may be directly deposited as dry compounds (Brasseur *et al.*, 1999; Hewitt, 2001). In some cases direct gas absorption to surfaces, especially of plants, may occur. Generally dry deposition is the major pathway of deposition in drier climates (Lindberg, 1992; Padgett *et al.*, 1999) and close to source sites (Kennedy, 1986; Zunckel *et al.*, 2000). In wetter climates, however, fog and wet deposition predominate (Lovett, 1992; Olbrich, 1993; Zunckel *et al.*, 2000; Brasseur and Roeckner, 2005). Many studies have shown that site elevation, climatic circulation, land-use type and vegetation will impact on the proportional contributions by depositional pathways (for example: Lovett, 1992; Olbrich, 1993; Zunckel *et al.*, 2000; Tyson and Gatebe, 2001). Typically N compounds can be sorted by the most common type of deposition observed (Table 2.1).

Table 2.1: Nitrogen compounds typically found in wet and dry deposition. Chemical species tabulated are not equal contributors to atmospheric N at any particular site (Hanson and Lindberg, 1991; Lovett, 1992; Hesterberg *et al.*, 1996; Fowler *et al.*, 1999).

Wet Deposition		Dry Deposition	
<i>Compound</i>	<i>State</i>	<i>Compound</i>	<i>State</i>
NO (nitric oxide)	gas	NO ₃ (nitrate)	particulate
NO ₂ (nitrogen dioxide)	gas	NH ₄ ⁺ (ammonium)	particulate
NH ₃ (ammonia)	gas	dissolved organic N	
HNO ₃ (nitric acid)	gas or vapour		
NO ₃ (nitrate)	particulate		
NH ₄ ⁺ (ammonium)	particulate		

In many ecosystems atmospheric deposition is not continuous. Episodic acidification events, as a measurable difference in pH between high and base flow in streams and rivers, are most common during seasons of high precipitation. In temperate zones, episodic acidification often occurs during spring snow melt (Lawrence, 2002). By nature these events usually take the form of wet deposition. As snow melts, acidic compounds deposited during snow-fall events or as dry deposition onto snow surface, become available and contribute to soil acidity by percolation and nitrification and to stream, river and lake acidity by runoff. The slow recovery of ecosystems in areas where S emissions have been reduced can, in some cases, be attributed to episodic events (Lawrence, 2002; Kowalik *et al.*, 2007).

In areas where there is little or no precipitation in a particular season, dry deposition will dominate. When spring or winter rains commence these deposits are then washed through the ecosystem in a similar manner as in snow-melt events (Lawrence, 2002). In these areas, there is concern that episodic inputs of acidic compounds are linked to drastic changes in surface waters and the resultant effects on biota in the surface water body (Laudon and Bishop, 1999). This can primarily be attributed to the fact that in these episodic events, contact with soil is limited thus reducing the capacity for neutralisation (Laudon and Bishop, 1999). The complexity of measuring chemistry of high-flow water, which is by nature transient, has resulted in limited information regarding changes in watershed chemistry indicating recovery from acidification (Lawrence, 2002).

2.2.3 Deposition across South Africa

South Africa is reliant on coal-fired power stations for the majority of its base-load electricity supply. Due to the proximity to coal beds, nine coal-fired power

stations are clustered on the Mpumalanga Highveld. The prevailing air circulation prevents the dispersal of atmospheric pollutants emitted by power stations and other energy demanding industrial activities (Tyson *et al.*, 1988; Held *et al.*, 1994; Zunckel *et al.*, 2000). The atmospheric conditions of the Mpumalanga Highveld have been monitored since the late 1980's (Tyson *et al.*, 1988) to estimate the spatial extent of deposition as a result of the dominant atmospheric circulation patterns (Tyson *et al.*, 1996; Piketh *et al.*, 1999a). Anthropogenic sources of SO_4^{2-} have been found at sites remote from industrial sources (Galpin and Turner, 1999b; Piketh *et al.*, 1999a; Piketh *et al.*, 1999b) at levels comparable with those in the north-eastern USA and central Europe (Mphepya *et al.*, 2004). At sites closer to the clustered industrial activities the anthropogenic influence is stronger with biomass burning and dust sources dominating at remote sites (Mphepya *et al.*, 2004; Mphepya *et al.*, 2006). Marine inputs contribute relatively minor amounts of acidic ions in precipitation and dry deposition inputs across the South African interior (Galpin and Turner, 1999b; Piketh *et al.*, 1999b; Mphepya *et al.*, 2004).

Combined wet and dry S deposition to the Mpumalanga Highveld has recently been modelled to be $\geq 35 \text{ kg S ha}^{-1}\text{year}^{-1}$ near large point sources and approximately $8 \text{ kg S ha}^{-1}\text{year}^{-1}$ over the Highveld more generally (Blight *et al.*, 2009). In contrast remote background sites in South Africa receive $\sim 1 \text{ kg S ha}^{-1}\text{year}^{-1}$ (Blight *et al.*, 2009). Regional-scale modelling estimates for N deposition to the South African Highveld range between $6.7 \text{ kg N ha}^{-1}\text{year}^{-1}$ (Collett *et al.*, 2010) and $>15 \text{ kg N ha}^{-1}\text{year}^{-1}$ (Blight *et al.*, 2009). A local-scale modelling study, using the inferential method, investigated N deposition to afforested areas and natural grassland areas showed that commercial forest plantations on the South African Highveld received approximately $70 \text{ kg N ha}^{-1}\text{year}^{-1}$ and neighbouring montane grassland only $25 \text{ kg N ha}^{-1}\text{year}^{-1}$ (Lowman, 2003). These differences were explained to be a consequence of surface roughness of the forested areas increasing dry deposition by interception of wind and by increased exposure to fog and mist as wet deposition (Lowman, 2003).

Monitoring and modelling of air quality and deposition over the South African interior is extensive compared with the scarcity of research investigating the impacts of the deposition on the ecosystems of the area. The next section (Section 2.3) of

this review expands on the ecosystem impacts that have been recorded elsewhere as well as those investigations that have been undertaken in South Africa.

2.3 Impacts of sulfur and nitrogen deposition

Policy changes regarding emissions of SO_x and NO_x in Europe and North America in the 1970's and 1980's (Rodhe *et al.*, 1995; Berge *et al.*, 1999; Butler *et al.*, 2001; Likens *et al.*, 2001; Reinds *et al.*, 2008) were driven by increased acidity of streams and lakes (1960's) as a result of both immediate and delayed consequences of acid deposition resulting impacts on aquatic communities sensitive to acidity. These freshwater observations were supported by increased soil acidity in forested catchments (1980's) and in severe cases forest tree mortality was observed (Rodhe *et al.*, 1995). Since policy revisions have restricted SO_x emissions, the concern in developed countries has shifted to NO_x and O₃ and the potential impacts on soils, vegetation and freshwater systems. In developing countries, as a result of rapid economic growth, SO_x is still the dominant pollutant of concern (Embersson, 2003; Hicks *et al.*, 2008; Steffen, 2010).

In complex ecosystem studies it is often difficult to establish clear cause-effect relationships for productivity declines. This has been observed in many studies investigating the impacts of atmospheric pollutants on ecosystems, especially where the extent of visible damage is large and local emissions are low (Matzner and Murach, 1995). Matzner and Murach (1995) expand possible reasons for this difficulty:

- the lag time between stressor (high concentration of atmospheric pollutants) and visible symptomatic response of biota;
- many interacting factors, either natural (climate, soil and pests) or as a result of human activities, such as management, site history and air pollution;
- problems inherent in testing hypotheses on the effects of air pollution where the dynamics and responses occur on decadal scales;
- local uniqueness of ecosystems and management increase the difficulty for extrapolation of case study results to countrywide or regional scales, or

- certain symptomatic responses, for example defoliation in vegetation studies, can be unspecific with respect to the cause therefore increase experimental design complexity (Matzner and Murach, 1995).

Emberson (2003) remarked on the synergistic effect that pollutant 'cocktails' can have on biota, especially SO₂ and NO₂ or NO_x and O₃, adding complications to causative pollutants for observed impacts. Several hypotheses have been proposed to explain the response of biota to atmospheric pollution, of which none can be considered mutually exclusive (Pearson and Soares, 1995). Direct injury mechanisms affect biotic components of ecosystems as a result of interactions with the gaseous emissions themselves or the associated transformed chemical species. Indirectly, emissions and transformed products can result in changes in the abiotic components of an ecosystem in turn affecting the productivity of the biotic components, for example soil chemical changes affecting pathways of plant nutrition and physiology (Matzner and Murach, 1995).

The next three sections focus on the impacts of deposition products to soils, vegetation and freshwater systems as reported in the literature. A generalised model of the mechanisms resulting in potential impacts is presented in Figure 2.4.

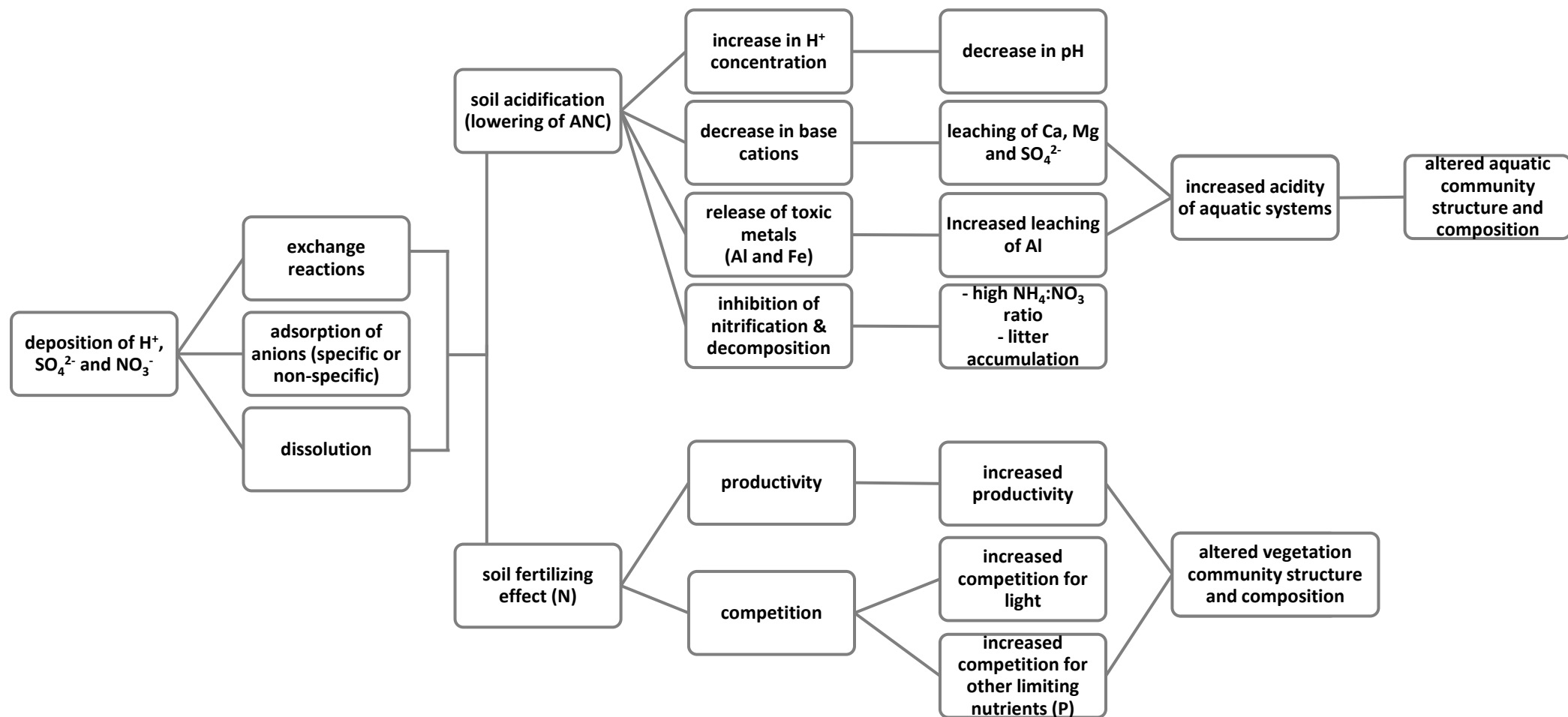


Figure 2.4: A schematic representation of the mechanisms resulting in ecosystem impacts as a result of deposition of S and N (modified from Aerts and Bobbink, 1999).

2.3.1 Impacts on soils

The acidification of soil is a natural process when acid (H^+) producing processes become uncoupled from H^+ consuming reactions (Table 2.2) (De Vries and Breeuwsma, 1987). A major concern about acid deposition of anthropogenic origin relates to how it affects the rate of acidification of soils and, through runoff and percolation, other components of ecosystems (Kennedy, 1986). Increased soil hydrogen (H^+) ion concentrations can be accelerated by atmospheric deposition processes by the H^+ ions that accompany SO_4^{2-} (as H_2SO_4) and NO_3^- (as HNO_3) in wet deposition and after dissolution of dry deposition compounds.

Table 2.2: Soil processes producing (sources) and consuming (sinks) H^+ ions (De Vries and Breeuwsma, 1987).

H^+ sources	H^+ sinks
Uptake of cations	Uptake of anions
Mineralisation of anions	Mineralisation of cations
Oxidation reactions	Reduction reactions
Dissociation of weak acid (CO_2 , organic acids)	Association of weak acids (CO_2 , organic acids)
Weathering, desorption of anions	Weathering, desorption of cations
Precipitation, adsorption of cations	Precipitation, adsorption of anions

Hydrogen ions (H^+) compete with base cations (Ca, Mg, K and Na) on soil colloid cation exchange sites. These displaced base cations become available for leaching, reducing the capacity of soils to neutralise further incoming acid deposition. In natural acidification processes, leached base cations are usually associated with bicarbonate (HCO_3^-) and organic acids. However, under large S and N deposition loads, base cations are more often associated with SO_4^{2-} and NO_3^- in soil leachate solutions (De Vries and Breeuwsma, 1987). Soil solution pH regulates several ecological reactions including the solubility of nutrient elements (De Vries and Breeuwsma, 1987). Low soil pH (high H^+ concentrations) can result in the release of aluminium (Al^{3+}) ions into the soil solution in the process of buffering hydrogen (H^+) ions. Aluminium is potentially toxic to plant roots and soil organisms as well as aquatic biota in rivers and lakes downstream (Matzner and Murach, 1995).

Most soils have buffering mechanisms (Figure 2.4) to resist changes in acidity including cation exchange on the charged surfaces of soil and organic matter colloids (replacement of basic cations with H^+), buffering (exchange reactions

between bicarbonate and Al ions) and neutralisation (salt formation of acid inputs and bases in the soil solution). The relative contribution of these processes depends on the soil composition, temperature and pH buffer range. Some of these mechanisms are rate limited, such as the release of base cations from parent material via weathering processes. In some cases, persistent acid inputs can increase the weathering rate of soil parent material, leading to release of neutralising bases, such as Ca and magnesium (Mg) (Wellburn, 1994). Other buffering mechanisms are limited by the capacity of the neutralising agent, for example cation (or anion) exchange sites on soil colloids. The capacity of soils to retain acid and base cations for exchange to and from the soil solution is referred to as the cation exchange capacity (CEC). This property is closely related to the base saturation of a soil that describes the proportion of exchangeable cations that are basic (Ca, Mg, Na and K). These soil properties can be used to assess the capacity of soils to buffer against acidic imbalances. A related concept is the acid neutralising capacity (ANC) of a soil. Soil ANC is calculated as the difference between strong base cations and strong acid anions (SO_4^{2-} , NO_3^- and Cl^-) and describes the capacity of a soil to neutralise acid inputs.

Soil sensitivity to acid deposition can be mapped based on soil, geological, climate and land cover properties or a combination of multiple characteristics using global databases and global information system (GIS) mapping tools (Kuylensstierna *et al.*, 1995; Kuylensstierna *et al.*, 2001; Phoenix *et al.*, 2006; Hicks *et al.*, 2008). Soil sensitivity classes can be compared with deposition of S and N ions and critical load exceedance estimated (Kuylensstierna *et al.*, 1995; Kuylensstierna *et al.*, 2001; Phoenix *et al.*, 2006). Critical loads are 'quantitative estimates of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson and Grennfelt, 1988) and can be used to identify areas where soils are likely to acidify as a result of S and N deposition and where impacts on ecosystem function may become evident when critical loads are exceeded. Critical loads are calculated from deposition rates, for both acidic and basic ions, and compared with the base saturation status of soil for an area of interest and presented as annual rates ($\text{meq m}^{-2} \text{ year}^{-1}$) usually as sensitivity classes (Kuylensstierna *et al.*, 1995). Exceedance of critical loads is when the soil base saturation and base cation input

via deposition are insufficient to neutralise incoming acidity via deposition, being a rate limited buffering mechanism. The concept of critical loads is often used in conjunction ANC (Draaijers *et al.*, 1997) of soils and has been applied to both developed (Baron, 2006; Ouimet *et al.*, 2006; Reinds *et al.*, 2008) and developing countries (Kuylensstierna *et al.*, 1995; Van Tienhoven *et al.*, 1995; Kuylensstierna *et al.*, 2001; Bouwman *et al.*, 2002; Zhao *et al.*, 2007; Hicks *et al.*, 2008) for the protection and management of ecosystems (Burns *et al.*, 2008).

Soil sensitivity can be useful in interpreting if biotic ecosystem components are likely to be impacted by atmospheric deposition. The sensitivity of ecosystems to atmospheric deposition needs to include the sensitivity of the biota in and above the soils. Plant species that are weaker competitors for light and limiting nutrients (Figure 2.4) are likely to be outcompeted by quick-growing tall species that are tolerant of acidic soils (Bobbink *et al.*, 1998).

In order to understand how soils in the Vaal Dam catchment, on the South African Highveld, respond to atmospheric deposition of S and in turn affect salt load in runoff, Fey and Guy (1993) collected 19 representative soils from the catchment, many of which showed negligible capacity to retain SO_4^{2-} . These findings supported earlier concern that atmospheric deposition would result in increased salt concentrations in surface waters of the area with a large domestic and industrial supply-base (Taviv and Herold, 1989; Herold and Gorgens, 1991). In contrast, a study investigating the critical loads of soils of the Mpumalanga Highveld (of which the Vaal Dam catchment is part) showed that the incoming acidity via deposition was balanced by the soils natural weathering rate (Van Tienhoven *et al.*, 1995).

2.3.2 Impacts on vegetation

The investigation presented in this thesis did not include the study of either direct or indirect impacts to vegetation; however a description of the potential impacts, both direct and indirect, is included here for completeness.

Sulfur and N as atmospheric pollutants, prior to deposition, can result in direct leaf injury, usually by SO_2 . Leaf injury appears to be dosage dependent (Ashmore, 2003; Murray, 2003; Shen and Liu, 2003) and is a factor of the concentration of a

particular pollutant and the contact time, which is affected by light intensity, air temperature, relative humidity, wind speed, surface wettability and leaf morphology (Wellburn, 1994). These environmental conditions influence the opening of leaf stomatal guard cells and thus influence the amount of gaseous pollutants that enter while the stomata are open for exchange of carbon dioxide (CO₂) and H₂O. In all cases visible injury, including discolouration, is indicative of internal cellular damage and usually results in reduced growth and yield (Embersson, 2003) and resistance to other stressors, such as pests and pathogens, drought and frost (Wellburn, 1994; Burkhardt, 1995; Ashmore, 2003), as well as reducing the market value of crops.

Galloway (1996) distinguished between immediate and delayed consequences of the mobilisation of S and N. Many of the delayed consequences within ecosystems are a result of indirect effects of the atmospheric pollutants deposited on the vegetative and soil surfaces. Primary indirect effects on vegetation are as a result of accelerated soil acidification (Matzner and Murach, 1995; Galloway, 1996) affecting plant physiology through nutritional supply (Wellburn, 1994; Matzner and Murach, 1995).

Natural vegetation is affected by accelerated acidification by the restriction of species distribution patterns owing to low tolerance of acidity or adaptation to low nutrient conditions usually by competitive exclusion by more tolerant species (Falkengren-Grerup *et al.*, 1995; Sanders *et al.*, 1995; Bobbink *et al.*, 2010; Stevens *et al.*, 2010). These species shifts can result in the loss of genetic diversity (Sanders *et al.*, 1995) and reduced ecosystem resilience to further system disturbances (Holling, 1973; Chapin *et al.*, 2000; Steffen, 2010).

Many studies have reported a positive growth response of vegetation during early stages of high NO_x deposition (Matzner and Murach, 1995; Persson and Majdi, 1995; Emberson, 2003). Some authors have suggested that the growth response could be as a result of changes in carbon allocation in trees under high N loads, reducing fine root biomass in favour of shoot biomass and mycorrhizal activity (Persson and Majdi, 1995). Some central European forests were found to have increased growth in spite of large deposition loads, but the lower acidification potentials, high soil water availability and the early stage of exposure to pollutants explained the positive response to the surplus N (Matzner and Murach, 1995).

Soil acidity (Figure 2.4) as a result of atmospheric deposition, usually associated with S compounds, most commonly affects plant root development, especially of fine roots, through changes in chemical composition and mycorrhizae dysfunction (Matzner and Murach, 1995; Persson and Majdi, 1995). Matzner and Murach (1995) cite studies that have observed increases in shallow and lateral root development in response to increasing acidity and propose that this is a result of the plant accessing other soil compartments that would not be affected by reduced pH and increased concentrations of H^+ and Al^{n+} ions (Falkengren-Grerup *et al.*, 1995). The extent of fine root damage is more strongly related to Ca:Al molar ratios than to Al concentrations alone (Ulrich, 1986; Persson and Majdi, 1995; Horswill *et al.*, 2008). These changes in root development are thought to exacerbate the effects of plant stressors such as drought and frost (Matzner and Murach, 1995) by compromising plant access to water and nutrient supplies. Sites of damage as a result of direct impacts are susceptible to pest and pathogen attack- (Lorenzini *et al.*, 1995; Ashmore, 2003; Emberson, 2003). Percy (2003) suggested that in some cases there is no direct link between injury and productivity loss but that the injuries reduce carbon stores which are used in responding to stress. Plant nutritional pathways, under acidified conditions, are also likely to be affected by the efficacy of the soil microorganisms. The metabolic processes of these organisms are pH specific and if the soil solution pH is outside the effective range, the release of nutrients from decomposing organic matter can be reduced (Wright and Schindler, 1995; Emberson, 2003). For example, nitrification is inhibited at low pH and as such most soil N available in acidified soils is NH_4^+ (Falkengren-Grerup *et al.*, 1995).

Compared with S, deposition of N has a relatively small role in increasing the acidity of soils contributing to plant species shifts as a result of acid tolerance. Accumulated N, as a result of deposition, has important impacts on the competitive relationships between plant species, where nitrophilic species can out-compete species that are adapted to low N conditions. These nitrophilic species then produce at accelerated rates leading to increased competition for light. Wedin and Tilman (1996) found that C3 grasses replaced native C4 and short forb species through competitive exclusion under elevated N deposition over a 12-year period in Minnesota grasslands. Rapid plant growth due to removal of N limitations also increases the susceptibility to secondary disturbance (Aerts and Bobbink, 1999).

Elevated N contents in plant cells may lead to increased herbivory and potential pathogenic invasions. In addition, as a result of compromised physiology, plants may become less tolerant of frost and drought conditions (Bobbink *et al.*, 1998), resulting in lowered competitive advantage for individuals and species. There is potential that these impacts could be observed prior to N saturation as described by Aber *et al.* (1989).

2.3.3 Impacts on freshwater systems

Woodmansee (1978) referred to water as a “vector” in the N cycle by linking the atmosphere, biosphere and geosphere through transformations and translocations of N. Water is involved in elemental cycles as rain, infiltrated soil water, soil moisture used in metabolism of biota and the geological processes of erosion and chemical weathering. Inputs of elements into soil pools can, at some later stage, be removed to freshwater pools by erosion of sediments, as part of the runoff solution or via leaching beyond the rooting zone.

Acidification of streams, dams and lakes is mostly indirect through runoff and drainage through acidified soils, although direct deposition of S and N compounds on the surface water bodies does occur. Catchments are considered to be saturated when S and N concentrations in the water increase consistently and significantly (Aber *et al.*, 1989; Galloway, 1996). Variation in acid runoff concentrations in neighbouring catchments affected by similar deposition levels is strongly influenced by the underlying geology (Wellburn, 1994). However, seasonal variations are often evident within catchments and linked to weather and climate, where episodic events show high concentrations of acid ions (Laudon and Bishop, 1999; Lawrence, 2002).

Aquatic fauna resist acidity changes in fresh water systems mainly through the neutralisation of acid ions by bicarbonate (HCO_3^-); however, at pH values less than 5.4, HCO_3^- is almost absent (Wellburn, 1994). Aquatic species are variable in their sensitivity to acidification of fresh water which can affect different life-stages within a species with differing effects. Fish death, in most species, occurs at a pH between 3 and 3.4 through loss of critical ions (for example, sodium - Na and chloride - Cl) across the gill surface membranes (Wellburn, 1994). Freshwater invertebrate groups are affected by pH values lower than 5.5 through imbalances of Ca and Al, affecting internal pH control and osmoregulation. The decline of these populations can affect

the stability of food webs through bioaccumulation of Al and heavy metals in the invertebrates and the birds and other vertebrates that feed on invertebrates (Wellburn, 1994).

Many northern Hemisphere studies investigating impacts of S and N deposition on surface waters were concerned with concentrations and fluxes of S, N, Al, alkalinity, base cations, and pH changes (Baron *et al.*, 2000; Evans *et al.*, 2001; Kernan and Helliwell, 2001; Wright *et al.*, 2001; Cooper, 2005; Kowalik *et al.*, 2007; Baron *et al.*, 2009). In South Africa, the concern with regards to surface waters near emission source areas has been directed to the concentration of salts, rather than acidification of surface waters (Taviv and Herold, 1989; Herold and Gorgens, 1991; Herold *et al.*, 2001). The salts (for example potassium sulfate - K_2SO_4) are associations of cations and anions (including SO_4^{2-} and NO_3^-) that have leached or runoff into the river and open-water systems. The salt content of water is a concern in industrial processes, for example in cooling towers at coal-fired power stations, and in irrigated agriculture where increased soil salinity can reduce crop productivity. Modelling exercises have suggested that total dissolved salt (TDS) concentrations in the Vaal Dam catchment will increase by 1.8-times over background levels depending on S and N emissions and deposition quantities (Herold *et al.*, 2001). In addition to the impacts on biota of these systems, the cost of treating water with increased salt loads to meet the requirements of water users; agricultural, domestic and industrial, was the basis for concern regarding elevated salt concentrations (Roos and Pieterse, 1995; van Niekerk *et al.*, 2009). These concerns are similar to water quality concerns in regards to eutrophication and appropriateness of use, addressed by Singh *et al.* (2004), Shrestha and Kazama (2007) and Taylor *et al.* (2007).

2.4 Ecological heterogeneity

Ecological heterogeneity refers to the differences between ecosystem patches with reference to a particular organism or process (Kotliar and Wiens, 1990; Pickett *et al.*, 2003) usually observed as system resources and constraints that are spatially explicit (Pickett, 1988). The concept is used within the field of landscape ecology to understand how organisms or processes functionally respond to differences in the abiotic environment (Kotliar and Wiens, 1990; Pickett *et al.*, 1997). An understanding

of ecological heterogeneity, with respect to the abiotic template and the biotic pattern, is useful when investigating the response of complex adaptive systems where the response to perturbations is often non-linear (Levin, 1998), as is the case with ecosystem response to human alteration of the biogeochemical processes (Steffen, 2010). If species diversity within the biotic and abiotic components of a system confer resilience (Holling, 1973; Chapin *et al.*, 2000; Steffen, 2010), then understanding the drivers of change and heterogeneity – usually represented in a graphical conceptual framework – can be useful in building management and conservation protocols for the system (Rogers, 2003; Cavana and Mares, 2004). Holling (2001, p403) stated that “functional diversity [in complex systems] builds resilience”. An impoverished state as a result of reduced diversity would therefore result in low resilience and increased vulnerability of the system to unexpected perturbation (Holling, 2001). Ecosystem services are derived from the functional processes and ecosystem structure, as the biotic communities and abiotic components. It is therefore possible to consider that ecosystem heterogeneity, with respect to structure and function, confers resilience to the ecosystem services by reducing vulnerability to external perturbations to the system.

The heterogeneity of the Highveld grasslands is explored in the integrated discussion of this thesis (Chapter 8) with particular reference to the responses of soil patches to atmospheric deposition within a framework of the causal relationships between patches and sensitivity to continued atmospheric inputs of S and N.

CHAPTER 3: STUDY AREA AND SAMPLING SITES

3.1 The Highveld

The Highveld region is an elevated plateau in the central interior of South Africa where the topography is flat or gently undulating at an altitude between 1000 and 1800 m above sea level (masl) (Huntley, 1984). The region receives mostly summer rainfall, between 600 and 700 mm of rainfall annually near the escarpment in the east and as little as 300 mm year⁻¹ in the west (Middleton and Bailey, 2009). Precipitation is normally in the form of thundershowers. The evaporative demand across the grassland biome of South Africa ranges between 1400 mm year⁻¹ in the east and 2000 mm year⁻¹ in the west (Middleton and Bailey, 2009).

The vegetative cover of the Highveld is dominated by grassland with isolated patches of shrub and tree cover, normally restricted to occasional rocky outcrops (O'Connor and Bredenkamp, 2003; Mucina and Rutherford, 2006). The dominance of anti-cyclonic conditions in winter lead to conditions suitable to the development of frost (O'Connor and Bredenkamp, 2003). The occurrence of frost across the Highveld grasslands is one of the mechanisms debated in the literature to exclude woody growth from the region (Bond and Midgley, 2000; Bond *et al.*, 2003b; Mills *et al.*, 2006). These grasslands are known to have high species diversity (Zunckel, 2003) including threatened plant (Cowling and Hilton-Taylor, 1994), fish (Skelton *et al.*, 1995), mammal (Lombard, 1995) and bird (Collar *et al.*, 1994) species many of which are endemic to the region. Although there is conservation interest with respect to the threatened species, the area is under protected in formal reserves (Lombard, 1995; O'Connor, 2005; Mucina and Rutherford, 2006) when compared with other biomes within South Africa. The Highveld grasslands are used as grazing for low density stock farming, less than 1 animal unit (AU) ha⁻¹ (O'Connor, 2005), and are considered natural as they are not fertilised or modified to enhance the quality or quantity of the grazing for cattle. These grasslands have supported herbivores since the middle to late Triassic (Bredenkamp *et al.*, 2002) although commercial and communal cattle stocking rates have increased by between 6 and 35-times the pre-settlement densities (O'Connor, 2005).

The Mpumalanga Highveld lies to the east of the Vereeniging - Johannesburg – Pretoria urban complex at a mean altitude of 1700 masl with approximately 70% of the areas accounted for by grasslands and stock farming. The remainder is used for crop cultivation and commercial forestry (Tyson *et al.*, 1988). The location of the Highveld in the subtropical latitudes implies that the subcontinent is climatologically exposed to the descending limb of the Hadley cell of general circulation. These semi-permanent anti-cyclonic conditions (Preston-Whyte and Tyson, 1993) result in dispersion climatology of the area is some of the most unfavourable in the world (Tyson *et al.*, 1988). Pollutants, from fossil fuel power stations and other energy demanding industries, become trapped below stable layers that are resident in the order of tens of days (Tyson *et al.*, 1996; Zunckel *et al.*, 2000; Tyson and Gatebe, 2001). In addition models suggest that 71% of air over the Highveld plateau is recycled over an average of 8 days (Tyson *et al.*, 1996). Held *et al.* (1994) summarised the understanding of atmospheric pollutant recirculation and accumulation as follows.

- Sulfate concentrations ($[\text{SO}_4^{2-}]$) are determined by air mass type, the pressure system influencing the intensity and direction of air mass flow, the depth of mixing layer and the oxidation chemistry of the air mass.
- Pollutant removal processes, for example easterly ventilation, westerly ventilation, washout and the rare occurrence of tropical cyclones, result in low $[\text{SO}_4^{2-}]$ periods, approximately 17 times per year, and persist for only a couple of days at each occasion.
- In contrast, periods with relatively high ground-level $[\text{SO}_4^{2-}]$ occur when warm, moist air masses predominate with small pressure gradients. These processes include: regional-scale recirculation, local conversions and accumulation and down-mixing from pollutant pools aloft. These episodes occur on average 19 times per year and persist for up to a few days (Held *et al.*, 1994).

Due to the nature of atmospheric circulation over the Highveld, Zunckel *et al.* (2000) estimated that the dry-to-wet deposition ratio for the region is 60:40 in drier parts of the Highveld, with greater wet deposition contributions to the wetter eastern and southern parts of the Highveld. At the time of the report, wet deposition rates over South Africa ranged between $6 \text{ kg S ha}^{-1} \text{ year}^{-1}$ close to sources and

1 kg S ha⁻¹ year⁻¹ at sites distant from sources (Zunckel *et al.*, 2000). The emissions from activities on the Highveld contribute significantly to the atmospheric pollution of the southern Africa region. South of the equator 40% of emissions from Africa, originate in the area and 80% of the total deposition in South Africa has its origin on the Highveld (excluding the western, south-western and southern region – Zunckel *et al.*, 2000). While the majority of these emissions are from industrial processing and power stations, biogenic sources (bushfires and burning of bio-fuels) have a noteworthy background effect on rainfall acidity (Zunckel *et al.*, 2000; Otter *et al.*, 2001). Otter *et al.* (2001) calculated that bushfire emissions amounted to 16.3 Gg N yr⁻¹ (0.015 Tg N yr⁻¹ as NO_x and 3.71 Gg N yr⁻¹ as NO₂) and more than 5.6 Gg C yr⁻¹ as organic acids.

Throughout the thesis the general location of sites or soil forms are referred to by geographical location within the study area. These are described below (Figure 3.1).

- The central part of the study area is in the vicinity of Standerton. The dominant land type in this section is 'Ea' (soils with one or more of vertic, melanic, red structured diagnostic horizons).
- The northern section of the study area is north of Standerton. The 'Bb' (soils with plinthic catena dystrophic and or mestrophic, red soils) and 'Ea' land types are co-dominant in this region.
- The eastern section of the study area extends east of Ermelo. The 'Bb' land type is dominant in this section.
- The southern section is from site 12, south to the boundary of the study area. The 'Bb' land type is also dominant in this section.
- The western section extends from sites 11 and 13 west. 'Ea' and 'Ca' (soils with plinthic catena upland duplex and or margalitic soils) land types dominate this region.

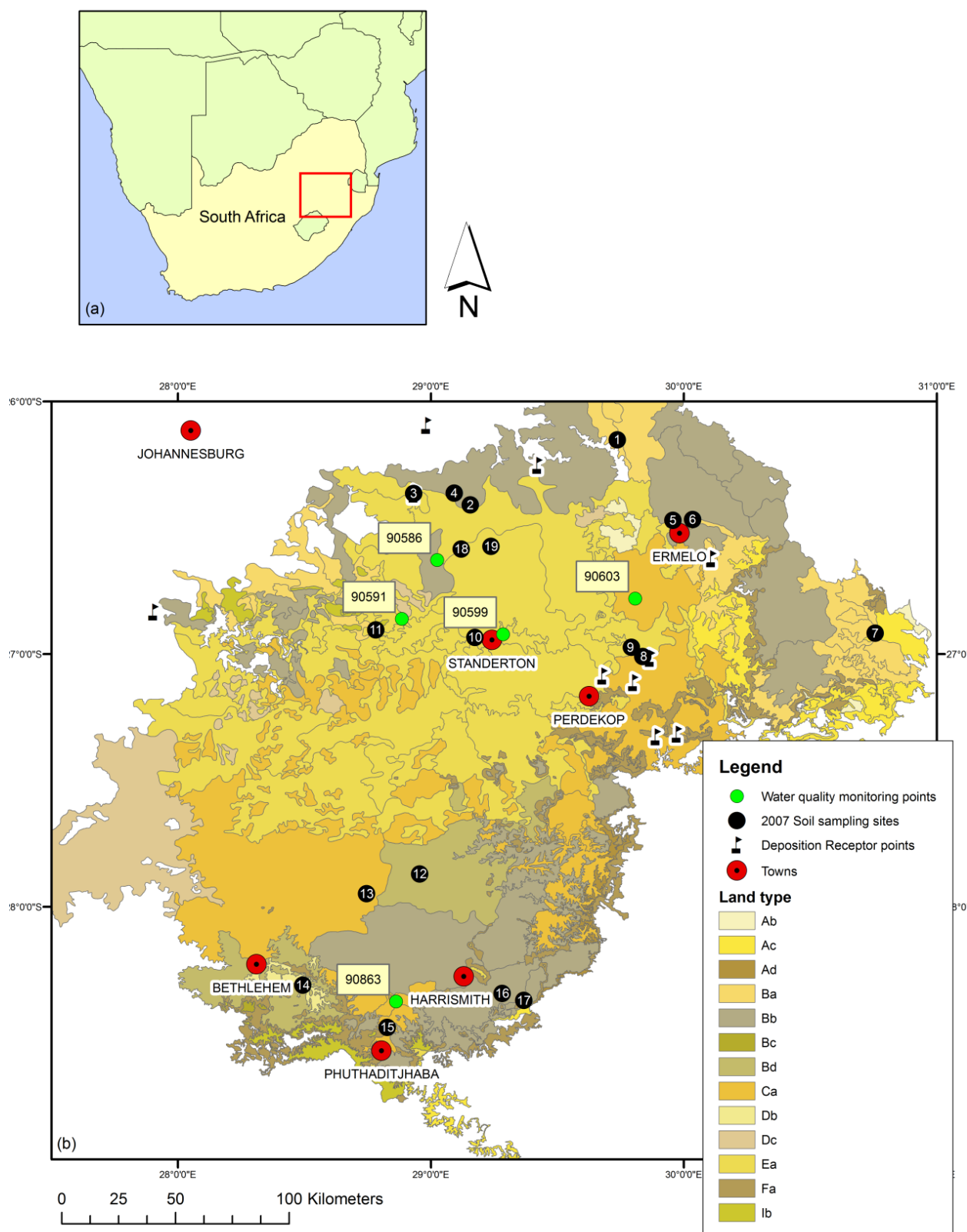


Figure 3.1: a) Map of South Africa, where the red frame indicates the study area in the Highveld grasslands. (b) Detailed map of the Highveld grasslands indicating the location of the 2007 soil sampling sites and the DWA water quality monitoring points used in the investigation of the impacts of S and N deposition on the soils and surface waters of the area. Deposition receptor sites and the land types are also indicated.

3.1.1 Deposition to the Highveld grasslands

Sulfur and N deposition was modelled by Airshed Planning Professionals as part of the Eskom-SASOL project: “Investigation into the effects of atmospheric pollutants on the soil-water-ecosystem continuum, Phase 0”. The modelling domain extended an area of 380 km (east-west) by 430 km (north-south) covering the Highveld region of South Africa and included the main study area of this thesis (Figure 3.1). The deposition rates and amounts summarised below are from the project report submitted to the sponsors in 2009 (Blight *et al.*, 2009).

Part of the modelling investigation was to estimate deposition over time at break-point emission years and using an average climatic year, which was the rainfall received in the 2000/2001 hydrological year. The break-point years were identified as those where emissions showed substantial changes due to new power station commissions, new large-scale industrial plants, increased motor vehicle numbers and decommissioning of power plants (Table 3.1). Deposition rates were plotted over the domain as isopleths for 8 break-point years (S deposition rates in Figure 3.2 and N deposition rates in Figure 3.3). The maximum levels of modelled S deposition, according to the isopleths plots in Figure 3.2, have increased from 5 kg S ha⁻¹ year⁻¹ in 1948 to >35 kg S ha⁻¹ year⁻¹ in 2007. Similarly the maximum rates of N deposition have increased from 0.5 kg N ha⁻¹ year⁻¹ in 1948 to >15 kg N ha⁻¹ year⁻¹ in 2007. It is valuable to note that there are sites, close to emission sources, within the maximum isopleths band that receive >35 kg S ha⁻¹ year⁻¹ and >15 kg N ha⁻¹ year⁻¹, respectively. For the Highveld grassland area studied in this thesis, both the minimum and maximum rates mentioned are valid as the northern boundary of the study area is close to the main emission source area where maximum rates apply and the southern boundary of the study area is at the southern edge of the domain where minimum rates apply.

Table 3.1: Projected SO₂ and NO_x emissions break-point years of S and N deposition to the Highveld modelling domain (from Blight *et al.*, 2009).

Break-point Year	SO ₂ Emissions (kt year ⁻¹)			NO _x Emissions (kt year ⁻¹)(as NO)		
	Power Generation	Major Industry	Other Sources	Power Generation	Major Industry	Other Sources
1948	9	-	14	3	-	61
1951	49	-	15	17	-	61
1961	108	38	16	37	11	62
1965	161	38	17	53	11	62
1974	460	67	21	131	12	73
1979	645	141	24	213	31	84
1984	930	350	29	304	173	101
2000	1,126	292	45	340	179	158
2006	1,534	300	51	554	170	195
2020	1,897	296	62	644	178	295

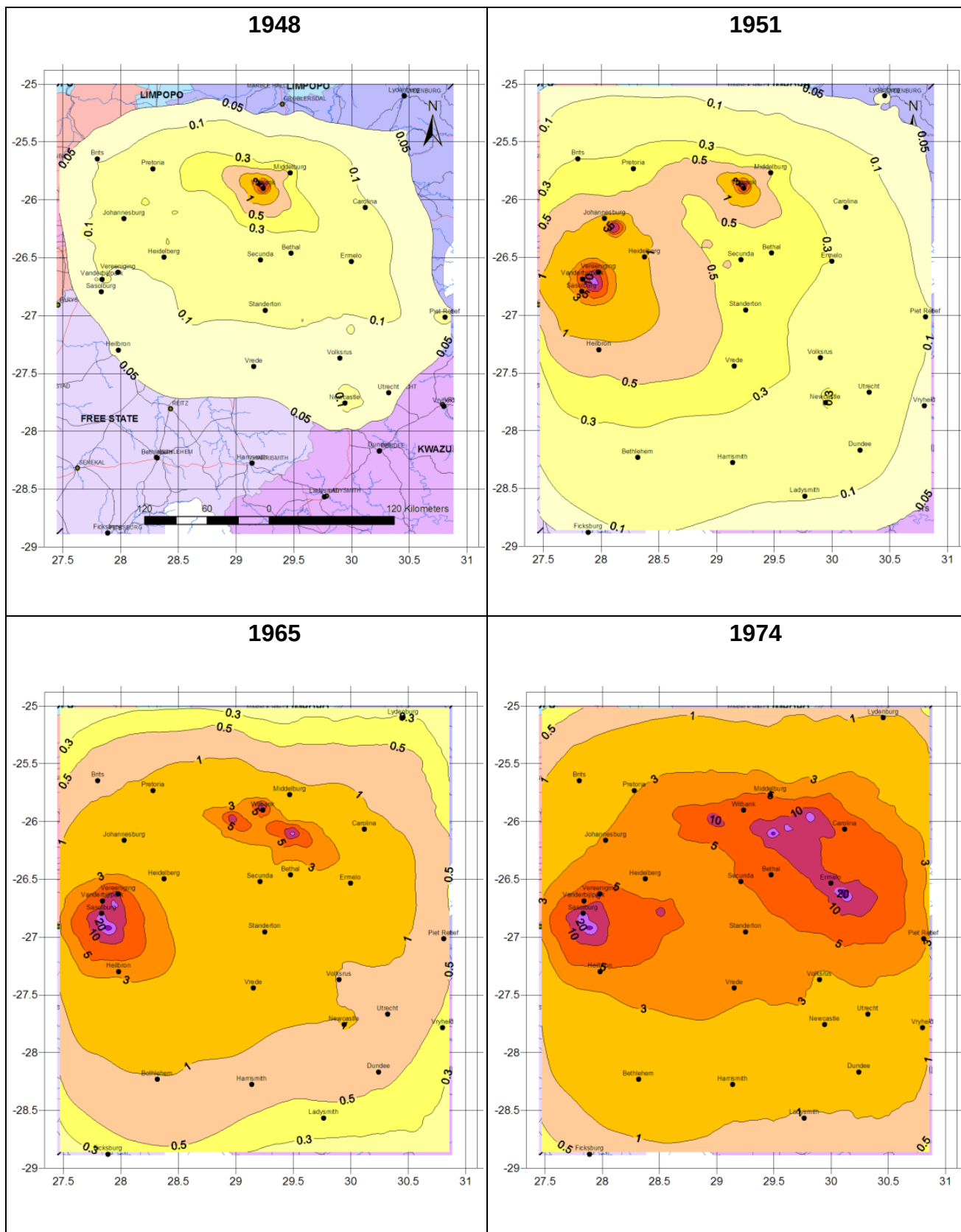


Figure 3.2: continues overleaf

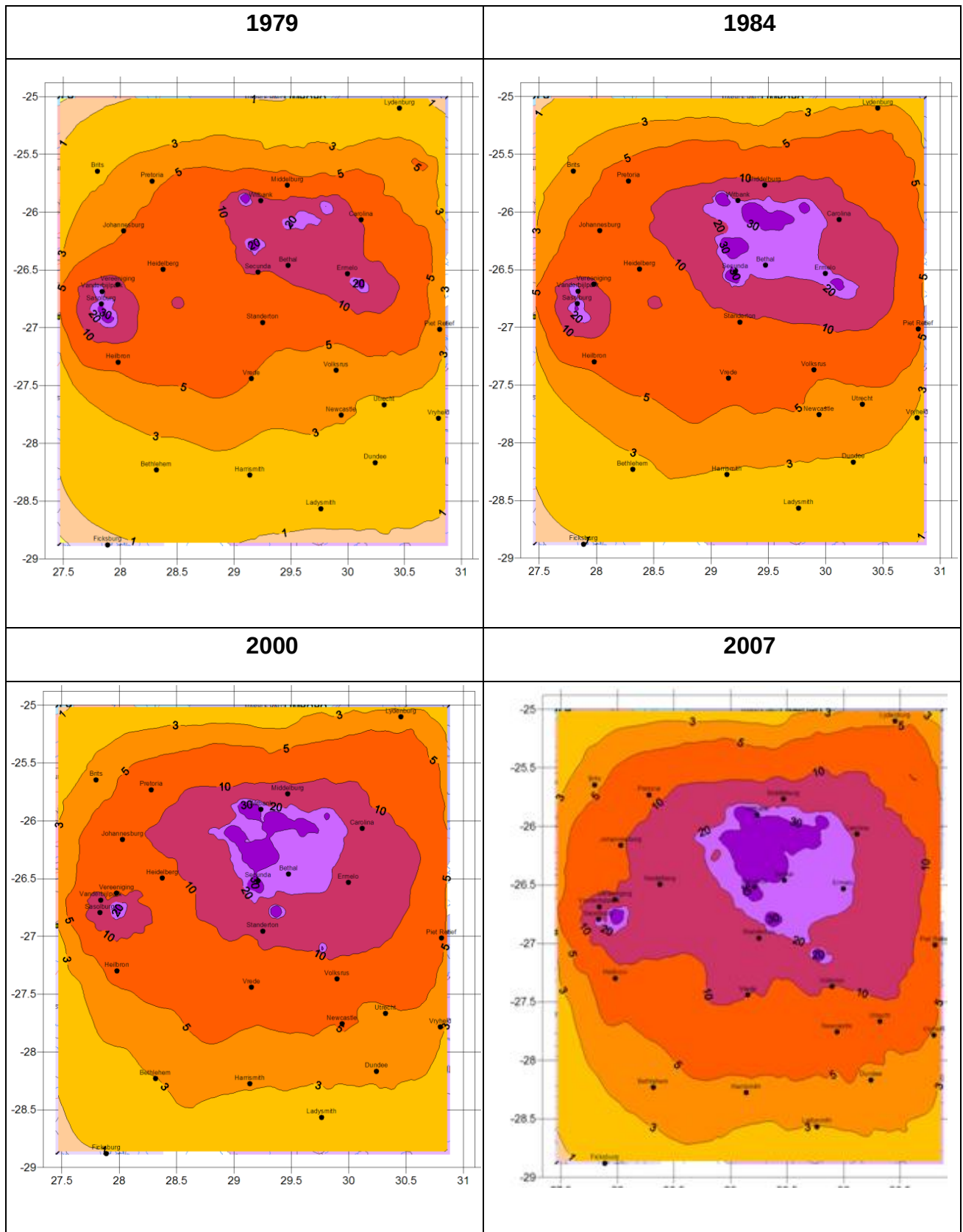


Figure 3.2: Predicted spatial variations in total S deposition for break-point years 1948 to 2007 ($\text{kg S ha}^{-1} \text{ year}^{-1}$). The projections for break-point years were based on the meteorology for 2000/1 – considered an average rainfall year for the area (Blight *et al.*, 2009).

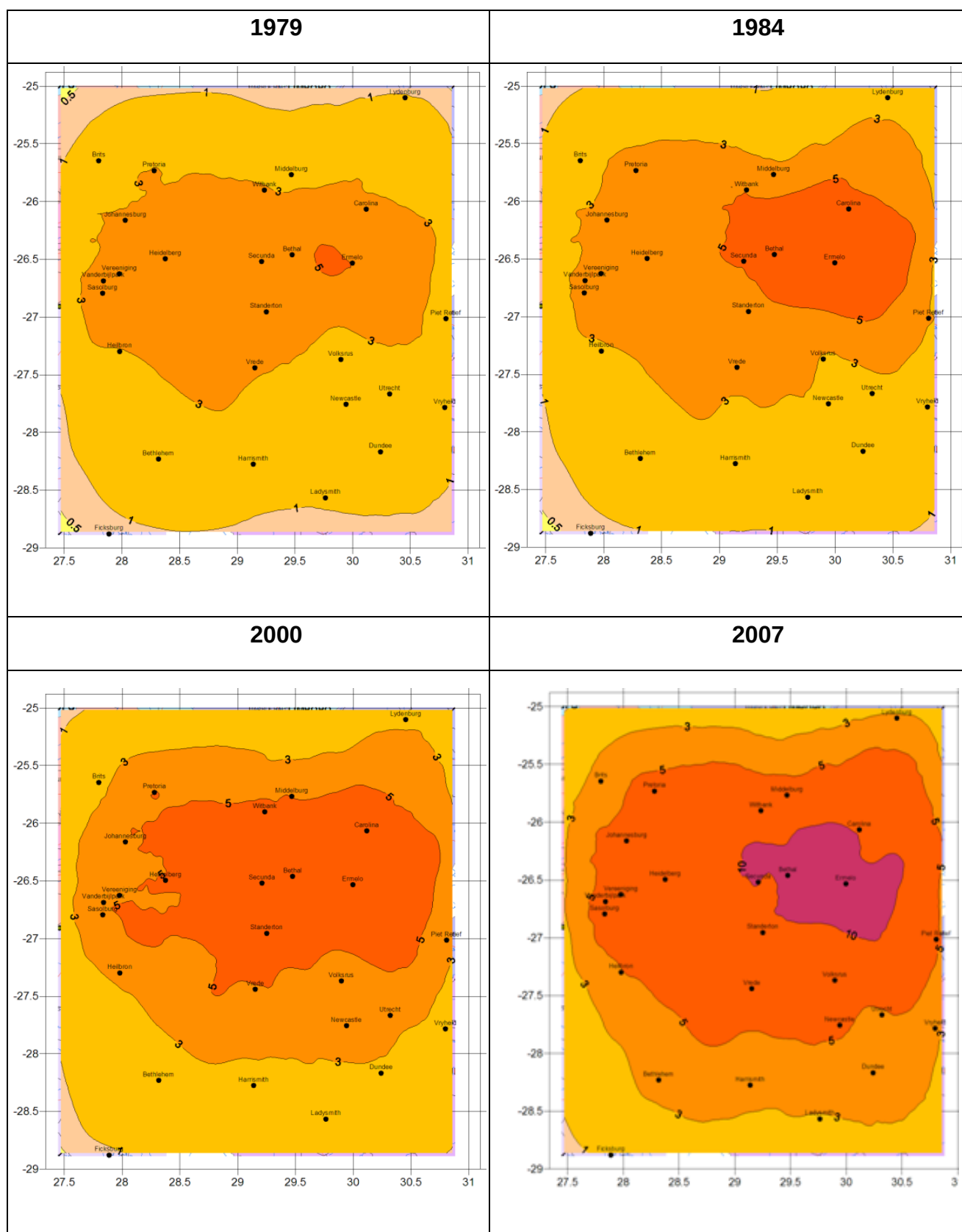


Figure 3.3: Predicted spatial variations in total N deposition for break-point years 1948 to 2007 (kg N ha⁻¹ year⁻¹). The projections for break-point years were based on the meteorology for 2000/1 – considered an average rainfall year for the area (Blight *et al.*, 2009).

For the verification of the CALPUFF model outputs, receptor points were used to compare modelled values with values measured at the receptor points (Blight *et al.*, 2009). The S and N deposition to the Highveld grasslands study area was then calculated, by the author of this thesis, from deposition rates at 10 modelling domain receptor points (Figure 3.4) located within the main Highveld grassland study area or close to the northern and western boundaries of the study area. Deposition rates at the receptor points at the break-point years of interest (1984, 2000 and 2007) were used to calculate the deposition of S and N to the Highveld study area between 1991 and 2007 – the soil sampling years. Linear interpolation was used to calculate annual increases for S and N, by determining the change in deposition between two break-point years and dividing by the number of years in the interval to calculate an annual change in deposition. Annual deposition amounts were then summed between 1991 and 2007 and plotted S for each receptor point (Figure 3.4). All calculations were performed for wet, dry and total (wet + dry) deposition for S and N.

Kendal air quality monitoring point (K2) received the most S deposition between 1991 and 2007; more than double than that of the other receptor points at a predicted rate of $>80 \text{ kg S ha}^{-1} \text{ year}^{-1}$. Compared with measured deposition at Kendal, it was found that the model overestimated by a factor of two, within the range (-0.5 to +2) recommended by the US-EPA for dispersion models (cited in Blight *et al.*, 2009). This difference was in part a result of higher rainfall used in the model, from the 2000/01 hydrological year, which was higher than mean rainfall over the 8 years (1985 to 1992) during which deposition had been measured near Kendal (755mm against 663mm) (Blight *et al.*, 2009). Other receptor points near power stations (Elandsfontein, Leandra, Majuba 1 and Camden) received approximately 400 kg ha^{-1} of S of modelled deposition in the 16 years.

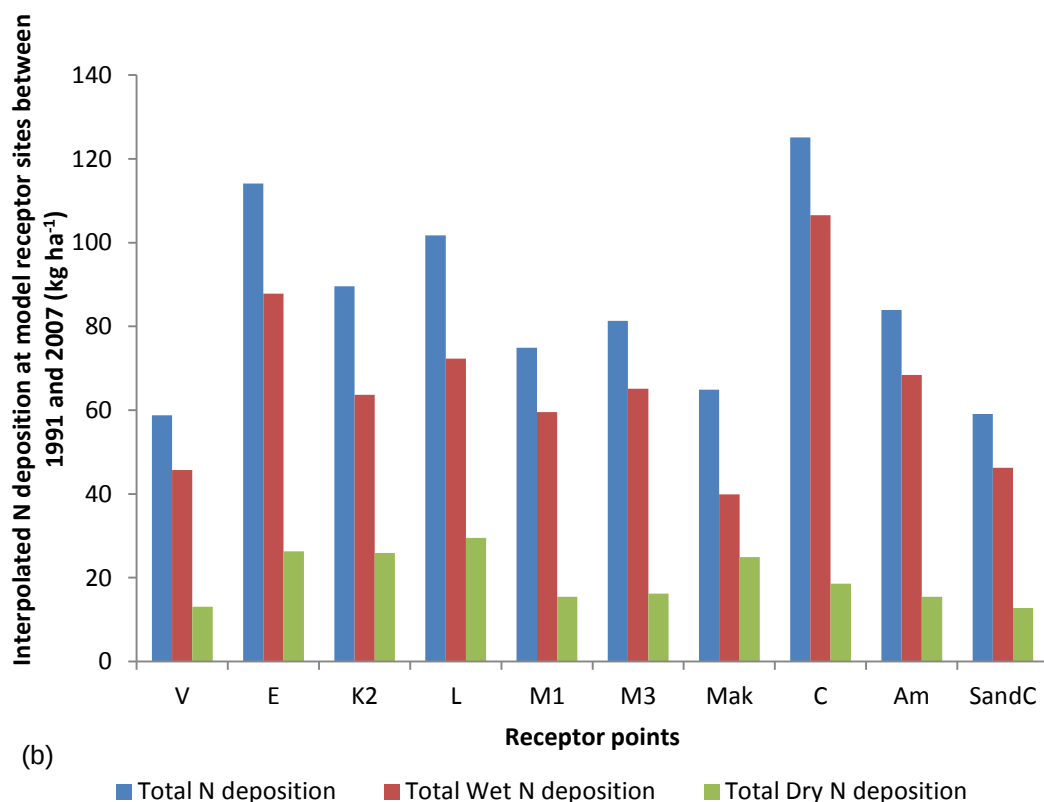
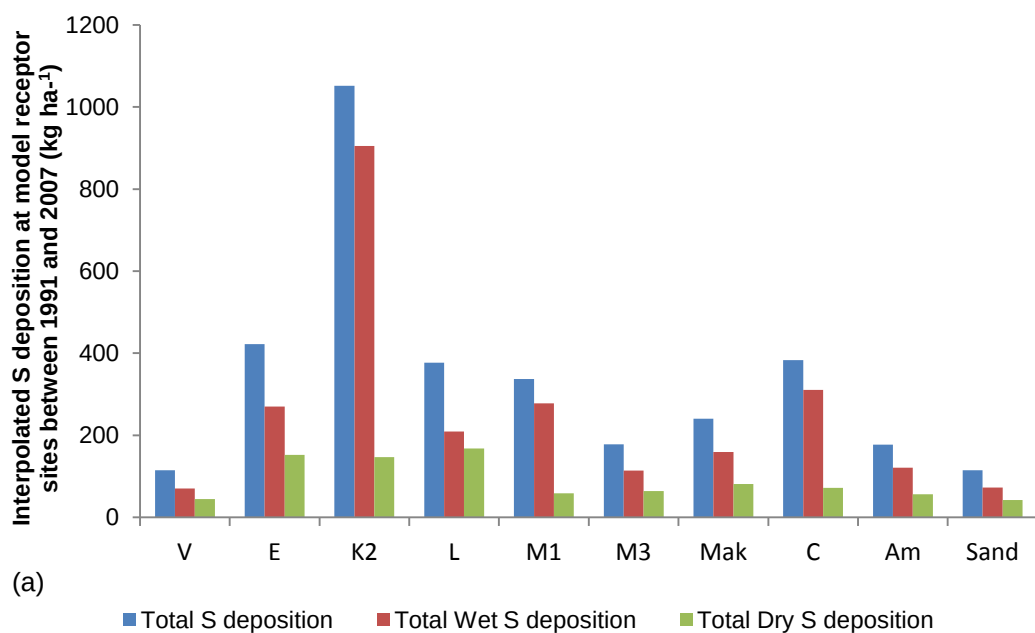


Figure 3.4: Interpolated (a) S and (b) N deposition (kg ha⁻¹) at receptor points in the main study area. Receptor point name abbreviations: V = Verkykkop; E = Elandsfontein; K2 = Kendal 2; L = Leandra; M1 = Majuba 1; M3 = Majuba 3; Mak = Makalu; C = Camden; Am = Amersfoort; SandC = Sandspruit head-water catchment.

The mean ($\pm$ standard error) amount of S deposited between 1991 and 2007, across all receptor points was $339 \pm 87 \text{ kg S ha}^{-1}$. In contrast, Camden and Elandsfontein showed the highest amounts of N deposition ($\sim 120 \text{ kg ha}^{-1}$) between 1991 and 2007. The mean ($\pm$ standard error) amount of N deposited between 1991 and 2007, across all receptor points was $85 \pm 7 \text{ kg N ha}^{-1}$. For both S and N a greater proportion of the inputs were deposited as wet deposition; at all sites dry deposition amounted to less than 200 kg ha^{-1} for S and 20 kg ha^{-1} for N. The higher proportion of wet-to-dry deposition could be because of the higher rainfall in 2000/01 relative to rainfall reported in published reports of measured air quality and deposition, as well as the slight over prediction of wet deposition for both S and N by the model (Blight *et al.*, 2009). The discrepancies in the contribution of dry S deposition to total deposition is apparent in the literature and Blight *et al.* (2009) explain that this is related to the difficulty of measuring dry deposition (relative to wet deposition) and that it is more commonly modelled using the inferential method. It was also noted that wet and dry deposition rates vary independently, both spatially and temporally, and thus a cautious approach should be taken when comparing sites and over different periods (Blight *et al.*, 2009). Base cation deposition is under represented in the literature for the Highveld grasslands. Some field monitored values are presented by Mphepya *et al.* (2004) where Ca (47%) and Mg (17%) were the largest contributors to the wet deposition of base cations ($39.4 \mu\text{eq l}^{-1}$) over the period 1986 to 1999 at the Amersfoort.

Table 3.2: Coordinates of discrete receptor points selected for model outputs (modified from Blight *et al.* 2009). AQ station refers to an existing air quality monitoring station.

Latitude	Longitude	Receptor Type	Receptor name	Receptor abbreviation
27°19'40.08"S	29°53'22.56"E	AQ Station	Verkykkop(Eskom)	V
26°15'9.00"S	29°25'17.04"E	AQ Station	Elandsfontein	E
26°05'40.20"S	28°58'55.19"E	AQ Station	Kendal 2	K2
26°22'01.20"S	28.°55'58.79"E	AQ Station	Leandra	L
27°06'46.08"S	29°48'00.00"E	AQ Station	Majuba 1	M1
27°05'12.84"S	29°40'42.96"E	AQ Station	Majuba 3	M3
26°50'00.24"S	27°54'10.80"E	AQ Station	Makalu	Mak
26°37'21.36"S	30°06'32.40"E	AQ Station	Camden	C
27°01'00.12"S	29°52'00.12"E	AQ Station	Amersfoort	Am
27°19'00.12"S	29°58'23.16"E	Catchment headwater	Sandspruit head-water catchment	SandC

3.2 Location of soil sampling sites

In order to assess how the soils had responded to incoming S and N deposition over time (Chapter 4), the 19 sites used in the Fey and Guy (1993) study were re-sampled (Figure 3.1). These sites were selected by Fey and Guy (1993) because they represent the dominant land types in the catchment. As no location co-ordinates were available from the Fey and Guy (1993) study, the sites were relocated using the information available, which included a published map (1:1 400 000), soil form and land type descriptions. Thus the 2007 sampling locations may differ from the 1991 (Fey and Guy, 1993) by as much as 10 km. Before sampling was initiated it was confirmed that the sites were located on the same land type as described in the Fey and Guy (1993) report to confirm that sampling in 1991 and 2007 are comparable. The response of soils sampled within the major land types became a useful method for grouping the individual sampling sites to establish patterns of change in soil characteristics over time. Data screening of the chemical results showed that values from Site 10 in 2007 were considerably higher, relative to values reported for the 1991 sampling (Fey and Guy, 1993) and from all other sites in 2007. It was decided not to include the site in further analyses of the results.

Sulfur and N mineralisation (Chapter 5) was monitored at 11 of the 18 sampling sites (site numbers 1 to 6, 8, 9, 11, 18 and 19) were sampled monthly from January 2008 to January 2009 due to their proximity to each other and the laboratory. The intent was to minimise the time when the soils were exposed to changing temperature and water content as this could affect microbiological activity and therefore the amount of SO_4^{2-} , NO_3^- and NH_4^+ in the soils. All samples were collected from natural grasslands at least 200 m from the nearest access road and away from patches of disturbed vegetation. Recently grazed patches were avoided during sampling. The details of the soil sampling methods are described in each chapter. The 11 sampling sites were representative of the major land types of the study area.

Table 3.3: Details for the 19 sites re-sampled in the Highveld grasslands in 2007 including site altitude (m above sea level) and mean annual rainfall (mm) of the land type (Land Type Survey Staff, 1985; 2002). Land types are areas of uniform terrain type, soil pattern and climate and the areal extent (in km²) of the land type within the study area of the Highveld grasslands is given. The depth of top- and sub-soil is the average depth (in mm) of sites sampled in 2007. In some cases if compaction limited sampling the sub-soil, then no sub-soil depth is given.

Site	Land type identifier and description	Altitude at site (masl)	Mean annual rainfall (mm)	Areal extent (km ²)	Depth of top-soil (mm)	Depth of sub-soil (mm)
1	Ba – plinthic catena, dystrophic and or mesotrophic red soils.	1627	680	190	300	>500
2	Bb – plinthic catena dystrophic and or mestrophic, red soils	1635	680	2159	300	-
3	Ea – One or more of vertic, melanic, red structured diagnostic horizons	1647	680	3461	200	-
4	Bb - plinthic catena dystrophic and or mestrophic, red soils	1586	680	2159	300	500
5	Bb - plinthic catena dystrophic and or mestrophic, red soils	1676	720	1212	300	>500
6	Ba - plinthic catena, dystrophic and or mesotrophic red soils.	1691	720	56	300	>500
7	Ac – Red and yellow, dystrophic and or mesotrophic apedal freely drained	1135	842	264	200	-
8	Ea – One or more of vertic, melanic, red structured diagnostic horizons	1640	680	419	200	500
9	Ea– One or more of vertic, melanic, red structured diagnostic horizons	1632	720	419	200	400
10*	Ea– One or more of vertic, melanic, red structured diagnostic horizons	1696	680	2385	300	-
11	Ea– One or more of vertic, melanic, red structured diagnostic horizons	1588	638	336	200	>500
12	Bd – Plinthic catena eutrophic, red soils	1659	646	1549	200	400
13	Ca – Plinthic catena upland duplex and or marginalitic soils	1625	640	4133	200	-
14	Db– Prismaeutanic and or pedocutanic diagnostic horizons, B horizon not red	1679	617	246	300	-
15	Ca - Plinthic catena upland duplex and or marginalitic soils	1650	656	422	300	500
16	Bb - plinthic catena dystrophic and or mestrophic, red soils	1563	706	687	300	>500
17	Bb - plinthic catena dystrophic and or mestrophic, red soils	1510	960	340	300	-
18	Ea - One or more of vertic, melanic, red structured diagnostic horizons	1586	680	2385	200	>500
19	Ea One or more of vertic, melanic, red structured diagnostic horizons	1630	680	2385	300	-

* results of chemical analyses in 2007 were considerably higher relative to values reported for the 1991 sampling and from all other sites in 2007. It was decided not to include this site in further analyses of the results.

3.3 The Vaal Dam Catchment

The Vaal River is the main tributary of the Orange River and is situated in the interior of South Africa draining from the eastern escarpment, westward towards the Atlantic Ocean. The Vaal Dam is located approximately 56 km south of Johannesburg, near the town of Vereeniging. The dam drains a catchment area of approximately 38 500 km² falling mostly within the provincial boundaries of the Free State and Mpumalanga. The catchment receives an annual average precipitation of 700 mm; however, the average potential evaporation is in the order of 1 500 mm per year (Midgley *et al.*, 1994; Middleton and Bailey, 2009).

The Vaal Dam was constructed in the 1930's as a water source for nearby irrigated agricultural initiatives. The major user is now Rand Water to supply the growing needs of potable water for industrial and domestic activities over an area of 17 000 km² including most of the Gauteng province and the town of Rustenburg in the North West province. Due to these growing demands, three inter-basin transfer schemes have been established where water is transferred into the Vaal Dam catchment from the Tugela and Usutu rivers (Kwa-Zulu Natal province), as well as from the Katse Dam via the Lesotho Highlands Water Project (Midgley *et al.*, 1994; Middleton and Bailey, 2009).

3.3.1 Location of water quality sampling sites

The South African Department of Water Affairs (DWA) water quality and flow monitoring network was used to investigate changes in the river water quality of the Vaal Dam catchment. Five sampling sites were selected in the primary catchment; split between the C1 (90586, 90591, 90599 and 90603) and C8 (90863) secondary catchments (Figure 3.1; Table 3.4). Those DWA water quality monitoring points closely associated with soil sampling sites were selected. These sites were required to have records of selected water quality variables from 1991 to 2008. The list of variables used to investigate the impacts of S and N deposition on fresh water quality is detailed in Chapter 6. While weekly or bi-monthly records were preferable, occasional monthly records were considered adequate; from which monthly medians for each variable were calculated. Monthly discharge (m³) for the sites was also acquired from DWA for the matching period that water quality variables were available.

Table 3.4: Location of the DWA water quality monitoring points in the Vaal Dam catchment used to assess the impact of S and N deposition on water.

DWA Site number	DWA Station number	Location	Latitude	Longitude	Analysis start date	Analysis end date
90586	C1H004	Branddrift Roodebank on Waterval River	26° 37' 40.58"S	29° 1' 28.09"E	1991-01	2008-06
90591	C1H008	Elandslaagte on Waterval River	26° 51' 39.99"S	28° 53' 4.99"E	1991-01	2008-04
90599	C1H019	Grootdraai Dam on Vaal River; downstream weir	26° 55' 18.99"S	29° 17' 4.99"E	1995-11	2008-06
90603	C1H027	Tweefontein spruit	26° 46' 49.00"S	29° 48' 24.99"E	1995-01	2008-04
90863	C8H005	Elands river below Qwa Qwa	28° 22' 32.00"S	28° 51' 42.00"E	1991-01	2008-06

CHAPTER 4: THE ACIDITY STATUS OF SOILS OF THE HIGHVELD GRASSLANDS, SOUTH AFRICA

Due to the rates of S and N deposition there is concern that ecosystem services derived from the Highveld grasslands may be affected. This chapter investigates the changes in chemical properties in top- and sub-soil of the Highveld grasslands originally assessed by Fey and Guy (1993) and again in 2007. By re-sampling at 18 sites on the Highveld grasslands it was found that soil acidity status had increased to some extent across the study area. A spatial scaling approach was used to identify the soils with the largest increase in soil acidity and therefore most sensitive to atmospheric S and N inputs. The supporting ecosystem service of nutrient cycling was the focus of this section as changes in the acidity status of soils will influence nutrient cycling processes. The ability of soil to provide supporting services will in turn impact the provisioning and regulatory services provided by a particular ecosystem.

The manuscript below is under review for *Geoderma*, with the title, authors and affiliations given below. Where possible figures and tables and been cross-referenced to prior chapters to reduce duplication. My involvement in the manuscript included the field and laboratory preparative work as well as the initial interpretation of the data and manuscript drafts. The textural and chemical analyses were contracted to BEM Labs, as credited in the manuscript text. My project supervisor, Prof. Mary Scholes, assisted with the further data interpretation, commented on drafts of the manuscript and assisted implementing the changes suggested by the first-round reviewers of the journal submission.

The acidity status of soils of the Highveld grasslands, South Africa.

T.L. Bird and M.C. Scholes

School of Animal, Plant and Environmental Sciences, University of the Witwatersrand, Johannesburg. Private Bag x3, Wits, 2050, South Africa

ABSTRACT

This study investigates the acidity status of the soils of the Highveld grasslands, South Africa, which is an area known to be under pressure from high levels of acidic deposition. Re-assessment of the soil chemistry after 16 years showed increases of both acidic and basic ion concentrations for individual sites and when the values for sites were averaged to represent the study region. This could be due to the co-deposition of acidic substances (e.g. sulphuric and nitric acids) and basic substances (e.g. fly-ash). However when clustering the sampling sites by clay content, all sites with less than 25% clay (16 of 18 sites) showed significantly reduced pH(H₂O) values and 7 (of 18) sites showed increased exchangeable acidity and acid neutralising capacity below 0 cmol_c kg⁻¹ between sampling years. When these sampling sites were used to represent the soil form, pH(H₂O) values were reduced in 92% of the study area. Mapping of the pH values, exchangeable acidity and acid neutralising capacity, allowed for the identification of soils sensitive to additional acidic inputs. The areas of sensitive soils co-occurred with areas of higher rainfall. It is suggested that the critical loads for these areas have not yet been exceeded.

4.1 Introduction

In the 1960's European and North American scientists were investigating declines in forest productivity and the link between local air pollution and ecosystem impacts was first proposed by Oden in 1968 (Galloway, 1989). Fossil fuel emissions, from electricity production and industrial activities, are the source of the reactive sulfur (S) and nitrogen (N) species deposited on soil and vegetation surfaces. These chemical species accelerate soil acidification and can result in changes in ecosystem structure and function within decades (Johnson *et al.*, 1984). Through co-ordinated policy

implementation and management, developed countries affected by acidic deposition have managed to reduce the impacts to ecosystems, primarily by implementing emission controls (Galloway, 1995). However, recovery from acidic deposition may take decades, especially in the case of sulfur. This recovery lag time is a result of the deposited S being adsorbed to soil iron (Fe) or aluminium (Al)-hydrated oxides with the lag time being positively correlated with Fe and Al oxide content, and negatively correlated with pH and organic matter content (Mitchell *et al.*, 1992). Once the retention capacity through adsorption is saturated, cations will accompany sulfate (SO_4^{2-}) in leachate as sulfate-salts, exerting a long-term effect on cation removal from the soils (Johnson *et al.*, 1984). Through the adsorption and leaching processes, soil pH will decrease as a result of the increased proton concentration.

Developing countries, through economic development, urban expansion and population growth, were identified by Galloway (1989) and Kuylenstierna *et al.* (1995) to be the next regions of focus for impacts as a result of acid deposition from industrial emissions. Soils sensitive to acid deposition were identified for the developing world in a modelling exercise by Kuylenstierna *et al.* (1995) based on soil type, land cover and soil moisture as a function of annual precipitation and potential evapotranspiration. South African Highveld grasslands (grasslands found in the interior of the country at an altitude of between 1400-1700 masl) were shown to be moderately sensitive to acid deposition. Kuylenstierna *et al.* (2001) used these sensitivity maps to model critical load exceedance. In spite of the high deposition loads calculated for 1990 from fossil fuel power stations and industrial development, the model suggested that critical loads were not yet exceeded in these grasslands. Evidence of increased soil acidity status may, however, be evident at a scale finer than the $5^\circ \times 5^\circ$ resolution used in the modelling study by Kuylenstierna *et al.* (2001).

The Highveld grasslands are underlain by large coal beds that support several coal-fired power stations, a petrochemical refinery and other energy-demanding industries. The emissions from these activities are comparable with those in the developed world (Tyson *et al.*, 1988). Climatically the Highveld region is affected by the anti-cyclonic subsiding air circulation patterns that are characteristic of the descending

limb of the Hadley cell of general circulation (Preston-Whyte and Tyson, 1993). In winter this subsidence leads to high- and surface level inversions unfavourable for the dispersion of pollution (Tyson *et al.*, 1988).

Over a two year cycle (September 2005 to August 2007) passive samplers were used at a $1^\circ \times 1^\circ$ scale to quantify the monthly mean concentrations of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) over the Highveld and beyond (Josipovic *et al.*, 2010). Josipovic *et al.* (2010) report that ambient air concentrations of SO_2 close to emission sources exceeded the UNECE CLRTAP (United Nations Economic Commission for Europe - Convention on Long-range Transboundary Air Pollution) (UNECE-CLRTAP, : www.unece.org/env/lrtap) 2004 critical level, of $20 \mu\text{g m}^{-3}$ for sensitive lichen and semi-natural and forest vegetation. By contrast, mean monthly NO_x concentrations ($<10 \mu\text{g m}^{-3}$) were below the most conservative critical levels ($40 \mu\text{g m}^{-3}$) (Josipovic *et al.*, 2010). Combined wet and dry S deposition to the Highveld has were recently modelled to be $\geq 35 \text{ kg S ha}^{-1}\text{year}^{-1}$ near large point sources and approximately $8 \text{ kg S ha}^{-1}\text{year}^{-1}$ over the Highveld more generally (Blight *et al.*, 2009). In contrast remote background sites in South Africa receive $\sim 1 \text{ kg S ha}^{-1}\text{year}^{-1}$ (Blight *et al.*, 2009). Modelled estimates for N deposition to the South African Highveld range from $6.7 \text{ kg N ha}^{-1}\text{year}^{-1}$ (Collett *et al.*, 2010) to $>15 \text{ kg N ha}^{-1}\text{year}^{-1}$ (Blight *et al.*, 2009). These modelled S and N deposition estimates (Lowman, 2003; Blight *et al.*, 2009; Collett *et al.*, 2010) are similar to field-monitored deposition over the same region (Mphepya *et al.*, 2001; Mphepya, 2002; Galy-Lacaux *et al.*, 2003) and are comparable to those in developed countries where impacts on ecosystems have been recorded.

Impacts of the accumulated acid species on soils and ecosystems in the area are poorly understood. Fey and Guy (1993) investigated the potential of the soils in the Vaal Dam Catchment to adsorb SO_4^{2-} and found that the overall SO_4^{2-} retention capacity was low. This prompted concern about the biodiversity of the grassland species, the potential for acidification of stream waters, negative impacts on the aquatic invertebrate biodiversity and the ability of the system to provide potable water for the region (Braune and Rogers, 1987; Herold *et al.*, 2001; Mucina and Rutherford, 2006). The Fey and Guy report remains the definitive study on soil properties of the region.

Here we investigate the acid-base status of Highveld grassland soils at multiple spatial scales from site-specific changes to soil form and regional changes.

4.2 Materials and Methods

4.2.1 Area description

The area of Highveld grasslands studied (Figure 3.1) lies in the interior of South Africa located in the Mpumalanga and Free State administrative provinces. The study area has a mean annual precipitation of approximately 700 mm with a corresponding annual potential evaporation in the order of 1500 mm (Midgley *et al.*, 1994; Middleton and Bailey, 2009). South Africa is divided into seven vegetation biomes (Mucina and Rutherford, 2006), one which is the Grasslands, these areas are underlain by a range of soils. Within each biome land types classified by a broad soil pattern, topography and climate (Land Type Survey Staff, 1985;2002). The South African soil classification system defines the broad soil pattern as a combination of soil forms and series (MacVicar *et al.*, 1977). Each broad soil pattern can be represented by a number of soil forms with the vegetation remaining constant (i.e. grassland) across the soil pattern (Land Type Survey Staff, 1985;2002). Grasslands support high species diversity and the most common land use practice is free-range cattle ranching (Mucina and Rutherford, 2006).

4.2.2 Soil sampling

Soils were collected in June 2007 from the 19 sites identified and sampled by Fey and Guy (1993) as they represent the dominant land types of the study area (Table 3.3). All samples were collected from natural grasslands at least 200 m from the nearest access road and away from patches of disturbed vegetation. Although fires occur frequently, sometimes annually, in these grasslands, none of the sites were sampled after a recent burn. Three replicate samples, within 1 m of each other, were collected at each site from the points of an equilateral triangle with a base of 15 m. The three replicates at each point were bulked, in order to collect enough soil for analyses. Collection was via hand auger of 100 mm diameter in 100 mm depth increments to 500 mm depth or until compaction limited the sampling. Where compaction was not

reached before 500 mm, a bulked sample from 500 mm to the limiting depth was collected. Soils were air dried, crushed if necessary, and sieved to 2 mm before analysis.

Sampling by Fey and Guy (1993) took place by horizon but the horizon depths were not given and were simply referred to as A and B horizons. Using the South African Land Type Memoirs (Land Type Survey Staff, 1985;2002) and Fey (2010), horizon depths were assigned to each of the sites. In 2007, because horizon break points were not easily visible in the field, the 100 mm incremental depths were analysed separately. In order to compare chemical properties between 1991 and 2007 by horizon, the data from the incremental samples in 2007 were averaged across depths using the South African Land type Memoirs (Land Type Survey Staff, 1985;2002) and Fey (2010). In this manuscript, the A horizon is referred to as the top-soil and the B horizon as the sub-soil. Data screening of the chemical results showed that values from Site 10 in 2007 were considerably higher relative to values reported for the 1991 sampling (Fey and Guy 1993) and from all other sites in 2007. It was decided not to include the site in further analyses of the results. Top-soil data for site 16 was missing in the Fey and Guy (1993) report and only the subsoil values were given.

4.2.3 Laboratory methods

The analyses of soils were conducted¹ according to standard methods (Table 4.1). All extraction methods in 2007 were matched to those used by Fey and Guy (1993) but detection methods varied in some cases. Soil acid neutralising capacity (ANC) was calculated using the charge balance equation, in molar concentrations (equation 3), as per Reuss (1991). Because exchangeable nitrate (NO_3^-) and chloride (Cl^-), were not determined in 1991, the proportional contribution to ANC in 2007 was used to estimate ANC in 1991.

$$\text{ANC (cmol}_c \text{ kg}^{-1}) = 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] - [\text{NO}_3^-] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] \dots [3]$$

¹ Conducted by BEM Labs (Pty) Ltd; +27218531490

Table 4.1: Methods used to analyse Highveld grassland soils collected in 2007. Procedures followed by numeric superscripts were different to those used by Fey and Guy (1993). In 1991: 1. Extractable base cations were quantified by AAS; 2. Texture was determined by the pipette method and sand class screening; 3. Adsorbed sulfate was quantified by reduction-distillation using the methylene blue procedure of Tabatabai (1982); 4. Nitrate and Chloride concentrations were not quantified by Fey & Guy (1993).

Analysis	Reagent	Procedure	Reference
Soil pH	1:2.5 (m/v) extraction ratio Distilled water 1 M KCl (potassium chloride) 1 M K ₂ SO ₄ (potassium sulfate)	pH meter	For all extractants: McLean (1982) and Soil and Plant Analysis Council (1998)
Exchangeable acidity	1 M KCl	Titration with 0.1N NaOH	Soil and Plant Analysis Council (1999b)
Exchangeable Al	1 M KCl	Titration with 0.1N HCl	Soil and Plant Analysis Council, (1999b)
Extractable base cations	1 M CH ₃ COONH ₄ (ammonium acetate)	ICP-OES ¹	Chapman (1965) Soil and Plant Analysis Council (1998)
Soil texture		Hydrometer ²	Day (1956)
Adsorbed sulfate	0.01 M Ca(H ₂ PO ₄) ₂ (calcium phosphate) (pH 4)	ICP-OES ³	Soil and Plant Analysis Council (1999b)
Nitrate	2 M KCl	Auto-analyser with Cd column ⁴	Soil and Plant Analysis Council (1999a)
Chloride	1 M KNO ₃	Titrate with AgNO ₃ ⁴	Soil and Plant Analysis Council (1991)

4.2.4 Statistical analyses

Statistica® 6.0 was used for the statistical analysis of all data. Student t-tests (n=3 per year) were used to test for differences between years. The Basic Statistics module was used to produce correlation matrices. The 2007 soil data (chemical analyses and soil texture values) were analysed using the General Linear Model ANOVA to test for site differences, where differences were evident, a post-hoc Tukey test was performed and the output requested by homogenous groups. The alpha value of 0.05 was used in all cases where p-values are less than the alpha value (0.05), are reported.

ESRI (Environmental Systems Research Institute, Redlands, California) ArcGIS version 9.3 was used to construct maps and to calculate the area of soil acidity in the study area. Each soil sampling site was mapped according to soil form and land type using GIS which allowed a visual representation of ANC in 2007, exchangeable acidity

in 2007 and the difference in pH(H₂O) between the two sampling years at the soil form level. Where more than one site occurred on the same soil form, the values for the sites were averaged.

4.3 Results

4.3.1 Site-by-site comparison across sampling years

The soil chemical properties that contribute to soil acidity status - pH, exchangeable acidity, exchangeable Al and base cations - were compared at each sampling site between the two sampling years. The number of sites where these properties changed, either by increasing or decreasing, relative to 1991 values, was noted (Table 4.2).

A site-by-site comparison of pH(H₂O) showed that 12 out of 18 top-soils and 7 out of 12 sub-soils had decreased by at least 0.5 pH units relative to 1991; the majority of these decreases were statistically significant (Table 4.2). However, the values for pH (KCl), pH (K₂SO₄), exchangeable Al and adsorbed SO₄²⁻ showed only a few significant decreases or increases over time. Base cation concentrations mostly increased significantly over time and ANC showed significant increases and decreases in equal proportions.

Table 4.2: Site-by-site comparison across sampling years 1991 and 2007 where the differences are reported as number of soils sampled, either in the top-soil or sub-soil horizons meeting the criteria listed. The number of sites where changes were statistically significant is indicated in parentheses ($\alpha=0.05$). *Indicates sites where pH was below the pH 4.2 Al-buffer limit in 2007 but not in 1991.

	Criteria	Top-soils	Sub-soils
Total number of samples	Number of soils sampled	18	12
pH(H₂O)	Decrease by 0.5 pH units or more	12 (12)	7 (6)
	pH <4.2 (Al-buffer limit)*	3(3)	2(2)
pH(KCl)	Decrease by 0.5 pH units or more	3(2)	1(0)
	pH <4.2 (Al-buffer limit)*	2(2)	0
pH(K₂SO₄)	Decrease by 0.5 pH units or more	4(4)	2(2)
	pH <4.2 (Al-buffer limit)*	0	0
Exchangeable Al³⁺	Decreased Al ³⁺ concentration	3	2
	Increased Al ³⁺ concentration	15 (4)	10 (3)
Adsorbed SO₄²⁻	Increased SO ₄ ²⁻ concentration	11 (1)	7
Base cations	Increased Na concentration	11 (5)	6 (4)
	Increased K concentration	13 (8)	9 (7)
	Increased Ca concentration	12 (10)	8 (7)
	Increased Mg concentration	14 (10)	9 (7)
ANC	Increased ANC	9(7)	5(3)
	Decreased ANC	9(7)	7(5)
Exchangeable acidity	Increased exchangeable acidity	8(4)	6(3)
	Decreased exchangeable acidity	10(2)	6(1)

The pH(H₂O) data provide some evidence for increased acidity status over time whereas the other soil chemistry data (Table 4.2) do not support this observation. To further investigate the changes in soil acidity status, data were explored at a regional scale.

4.3.2 Regional soil acidity status based on means across sites

The acid-base status of the soils, across all sites, was examined. The results were averaged for the top- and sub-soils across all 18 sites and compared between sampling

years (Table 4.3). Only the pH(H₂O) and the K (potassium) concentrations in the top-soils and exchangeable Al³⁺ in the sub-soils were statistically significantly different between 1991 and 2007. The pH(H₂O) in 2007 was found to be significantly lower, by 1 pH unit, compared with the 1991 top-soil mean. In contrast the K concentrations increased over time and the exchangeable Al³⁺ increased by 5-fold in the sub-soils. The regional comparison (as a mean of the 18 sampling sites to represent the region) also offered some weak evidence of increased soil acidity status as described the in the following section.

Table 4.3: Chemical properties of top-soils and sub-soils of Highveld grasslands between 1991 and 2007 (top-soils: n=17; sub-soils: n=12). The mean is calculated from 18 sampling sites with the minimum and maximum concentrations in each sampling year also presented. Significant differences between 1991 and 2007 are marked as: * p<0.05 and ** p<0.01. Changes in pH the difference between 2007 and 1991 values and are referred to as the absolute difference. The change in all other properties is expressed as the difference between 2007 and 1991 values as a percentage of the 1991 value. *Exchangeable Na was not measured in 1991; these values have been calculated based on the 2007 percentage contribution of Na to total exchangeable bases.**

		pH(water)			pH(KCl)			pH(K ₂ SO ₄)			Adsorbed SO ₄ ²⁻ (cmol ₍₊₎ kg ⁻¹)			Exchangeable Al (cmol ₍₊₎ kg ⁻¹)		
		1991	2007	Absolute difference	1991	2007	Absolute difference	1991	2007	Absolute difference	1991	2007	Difference (%)	1991	2007	Difference (%)
Top-soils	Mean	5.79	4.79	** -1.00	4.74	4.79	0.05	5.28	5.27	-0.01	0.03	0.04	32	0.30	0.17	-44
	Min	4.60	3.64	-0.96	3.88	3.82	-0.06	4.49	4.31	-0.18	0.00	0.01	100	0.02	0.01	-57
	Maximum	7.42	5.63	-1.79	6.01	5.67	-0.34	6.57	6.02	-0.55	0.13	0.11	-17	2.63	1.05	-60
	SE	0.18	0.15		0.15	0.13		0.15	0.13		0.01	0.01		0.15	0.08	
Sub-soils	Mean	5.80	5.05	-0.76	4.80	5.04	0.24	5.43	5.50	0.07	0.05	0.05	-8	0.02	0.13	*498
	Min	4.80	3.60	-1.20	3.80	3.92	0.12	4.41	4.47	0.06	0.01	0.01	-40	0.01	0.01	-24
	Maximum	6.92	7.06	0.14	5.94	6.48	0.54	6.54	6.84	0.30	0.14	0.09	-34	0.04	0.65	1367
	SE	0.23	0.32		0.20	0.24		0.20	0.22		0.01	0.01		0.00	0.04	
		Na (cmol ₍₊₎ kg ⁻¹)			K (cmol ₍₊₎ kg ⁻¹)			Ca (cmol ₍₊₎ kg ⁻¹)			Mg (cmol ₍₊₎ kg ⁻¹)			Exchangeable acidity (cmol ₍₊₎ kg ⁻¹)		
		1991***	2007	Difference (%)	1991	2007	Difference (%)	1991	2007	Difference (%)	1991	2007	Difference (%)	1991	2007	Difference (%)
Top-soils	Mean	0.09	0.16	70	0.30	0.46	*55	3.81	7.58	99	2.69	5.25	96	0.46	0.22	-52
	Min	0.00	0.00	16	0.08	0.07	-13	0.34	0.47	39	0.26	0.32	23	0.00	0.05	5290
	Maximum	0.46	0.82	79	0.78	1.07	37	11.03	20.17	83	13.69	15.17	11	3.32	1.05	-68
	SE	0.01	0.05		0.05	0.06		0.81	1.67		0.83	1.37		0.19	0.08	
Sub-soils	Mean	0.21	0.32	50	0.19	0.30	59	4.08	6.88	69	3.25	5.28	62	0.89	0.18	-80
	Min	0.00	0.00	27	0.05	0.06	33	0.22	0.09	-57	0.33	0.20	-40	0.02	0.05	195
	Maximum	0.96	1.65	71	0.44	0.57	28	12.74	21.63	70	9.72	19.18	97	7.65	0.66	-91
	SE	0.05	0.14		0.03	0.05		1.23	2.22		0.99	1.86		0.52	0.04	

4.3.3 Site grouping based on soil texture

Further investigation of the 2007 results was undertaken to understand the links between soil texture and contributors of soil acidity. Soil particle size classes were significantly correlated with pH (in all extractant solutions), base cations and ANC (Table 4.4). The relationships between chemical properties and clay content were selected for further analyses as the negative charge on clay particles is more likely to be involved in chemical processes that would affect soil acidity status. Clay content varied between 0.2 and 43% with the Tukey test assigning the 18 sites to 9 groups based on the similarity of soil clay content (Table 4.5). Significant differences were detected in pH(H₂O), ANC and exchangeable acidity between 2007 and 1991 Figure 4.1a-c. Significant decreases in pH(H₂O) were detected at sites with low clay content (Figure 4.1a).

Table 4.4: Correlation coefficients (r) between soil chemical properties and particle size distribution for Highveld grassland soils in 2007. * p<0.05 (n=261).

Particle size class (%)	pH(H ₂ O)	pH(KCl)	pH(K ₂ SO ₄)	Adsorbed SO ₄ ²⁻ (cmol _(c) kg ⁻¹)	ANC (cmol _(c) kg ⁻¹)	Exchangeable Al (cmol ₍₊₎ kg ⁻¹)	Exchangeable acidity (cmol ₍₊₎ kg ⁻¹)
Clay	*0.52	*0.52	*0.55	0.02	*0.61	*-0.34	*-0.38
Silt	*0.50	*0.46	*0.41	-0.10	*0.63	*-0.35	*-0.39
Sand	*-0.56	*-0.55	*-0.55	0.02	*-0.67	*0.37	*0.41

Table 4.5: Statistically similar Highveld grassland sites based on percentage clay content of incremental depth samples from 2007.

Site numbers	4, 18 (n=30)	2, 9, 13 (n=37)	11 (n=18)	14 (n=11)	19 (n=9)	8 (n=13)	3, 15 (n=28)	1, 5, 6, 7, 12, 16 (n=97)	17 (n=18)
Mean clay content (%)	25.4	19.5	15.3	14.8	11.5	10.4	9.7	4.3	1.1
Clay % range	9.8 - 39.6	3.8 - 43.0	1.2 - 40.8	4.8 - 22.4	7.8 - 13.8	2.4 - 18.0	0.2 - 28.8	0.2 - 17.6	0.2 - 5.2

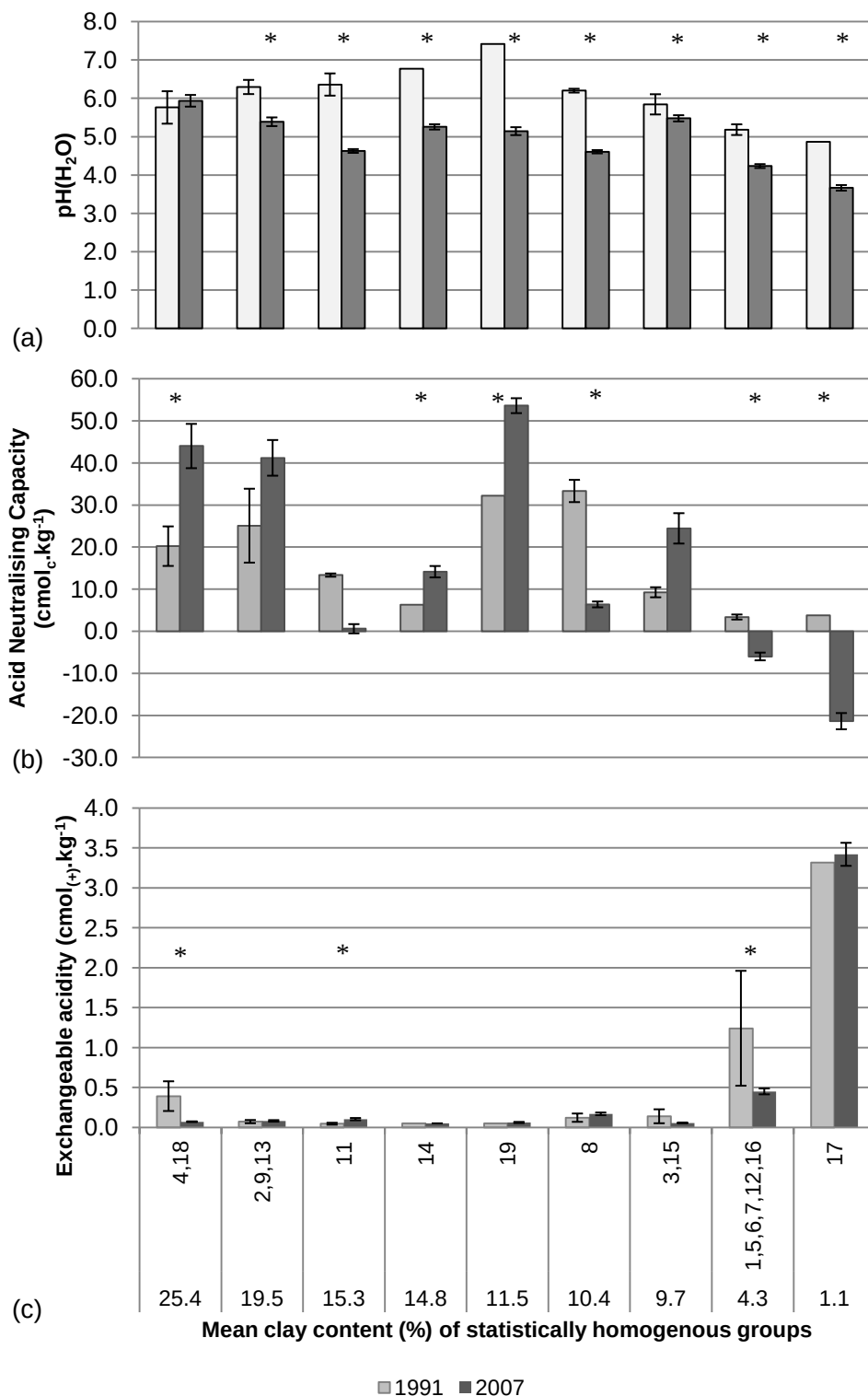


Figure 4.1: (a) Mean ($\pm$ standard error) pH(H₂O), (b) acid neutralising capacity (cmol_c kg⁻¹) and (c) exchangeable acidity (cmol₍₊₎ kg⁻¹) in 1991 and 2007, represented by groups of sites based on similar clay content (%). Groups are described in Table 4.4. * indicates statistically significant differences between sampling years, 1991 and 2007, at $\alpha=0.05$.

4.3.4 Using soil form and land type to calculate areal extent of increased soil acidity

Since acidity status of the Highveld grassland soils increased with clay content, spatial grouping of ANC, exchangeable acidity and pH was applied to the study area at the scale of soil form (Figure 4.2). In small areas close to the periphery of the study area ANC is negative (Figure 4.2a). Central to the study area are areas where acidic inputs are buffered by available ANC. Exchangeable acidity (Figure 4.2b) displays a similar pattern to ANC where the highest acidity levels are close to those where ANC is negative. However, some areas that have available ANC do show increased exchangeable acidity. The difference in pH(H₂O) between 1991 and 2007 (Figure 4.2c) shows that the central study area, where buffering capacity is available as ANC, is the only area where pH has increased. Similarly, those areas where ANC is negative show the largest decreases in pH over the 16 years.

Expanding this analysis to the land types (Table 3.3 and Figure 3.1) would allow for interpolation of the unknown areas. Using the soil forms to represent the land type it was possible to map soil acidity at a scale which leads to an understanding at the landscape level (Figure 4.3a-c). Where two or more soil forms occurred on the same land type, the ranges were calculated and presented in the maps. From Figure 4.3a, it is apparent that the areas where ANC is negative are limited to the study area periphery where the soils are sandier. The clay-rich soils of the central study area still have capacity to neutralise incoming acidity. However these areas can also have high exchangeable acid values (Figure 4.3b). The areas with the highest exchangeable acidity do correspond with those areas where ANC is negative. The pH(H₂O) values have decreased across nearly all of the study area.

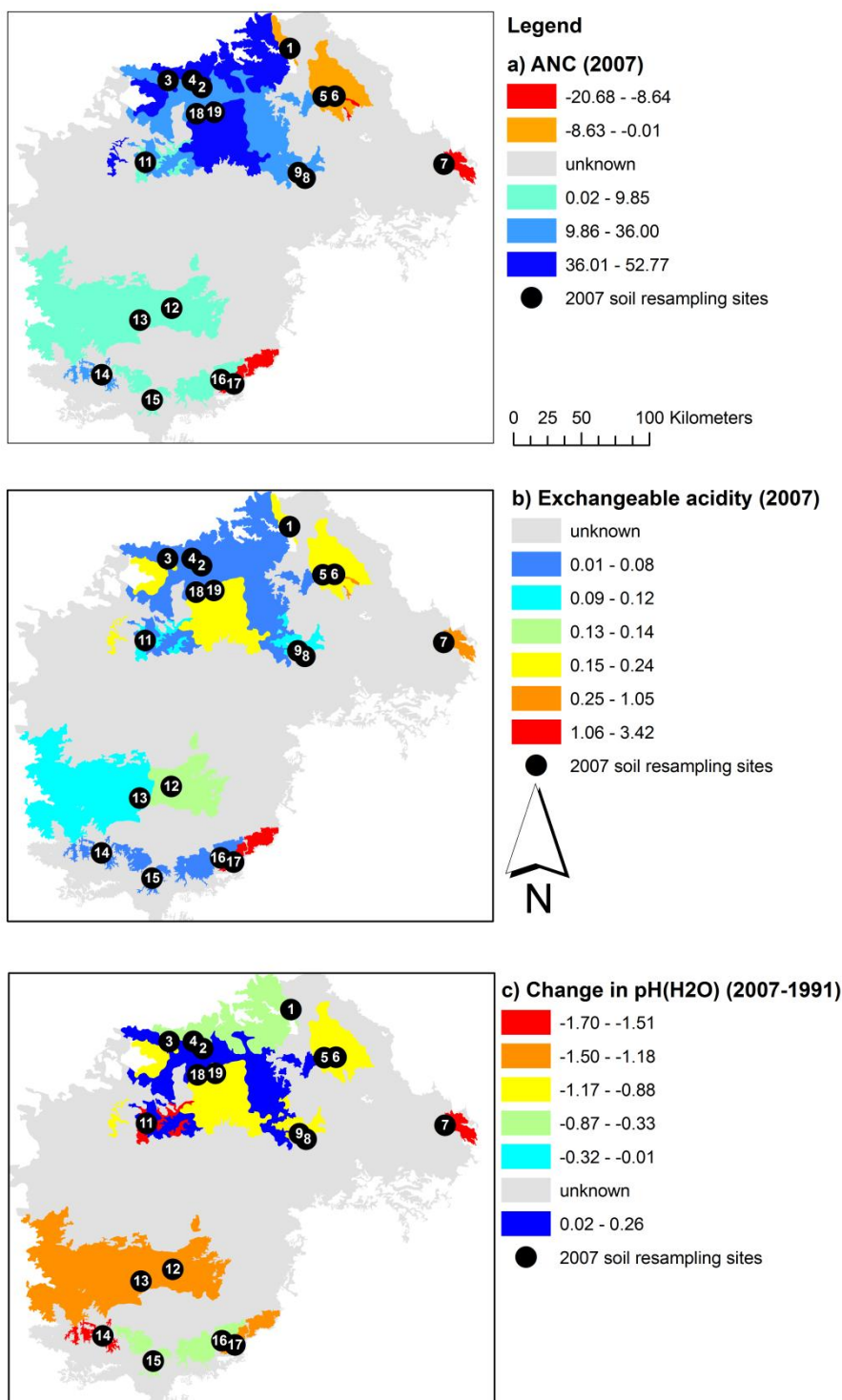


Figure 4.2: Maps showing the acidity status of the soils of the Highveld grasslands by a) acid neutralising capacity in 2007 ($\text{cmol}_c \text{kg}^{-1}$), b) exchangeable acidity in 2007 ($\text{cmol}_{(+)} \text{kg}^{-1}$) and c) change in $\text{pH}(\text{H}_2\text{O})$ between 2007 and 1991. Sampling sites were considered representative of specific soil forms in which they occurred and where more than one site occurred on the same soil form, a mean of the site values was used to represent the soil form. The grey areas are soil forms that were not sampled and the soil acidity status is unknown.

The areal extent of the soil acidity status is summarised at the two scales of soil form and land type in Table 4.6. The sum of the areas, at the soil form scale and the land types scale, is calculated where ANC, in 2007, was less than $0 \text{ cmol}_c \text{ kg}^{-1}$; exchangeable acidity, in 2007, was greater than $0.5 \text{ cmol}_{(+)} \text{ kg}^{-1}$ and the difference in $\text{pH}(\text{H}_2\text{O})$ between 2007 and 1991 was negative. The values are presented as the percentage of the sampled areas and the percentage of the total study area. The exchangeable acidity threshold of $0.5 \text{ cmol}_{(+)} \text{ kg}^{-1}$ was considered valid as nearly all sites and soils fell below this threshold and those that are higher than this value are considered, in this environment, to show increased acidity status using a reduction in $\text{pH}(\text{H}_2\text{O})$ and negative ANC values. The comparison in Table 4.6 between the soil form and land type shows that the area of known acidity status increases by 0.4% for ANC, 8.3% for exchangeable acidity and 19.4% for $\text{pH}(\text{H}_2\text{O})$. When ANC and exchangeable acidity are used as acidity indicators, only 11.9% of the total area can be considered to have increased acidity status in 2007. However, when $\text{pH}(\text{H}_2\text{O})$ is used as an indicator, 91.5% of the study area has increased acidity status.

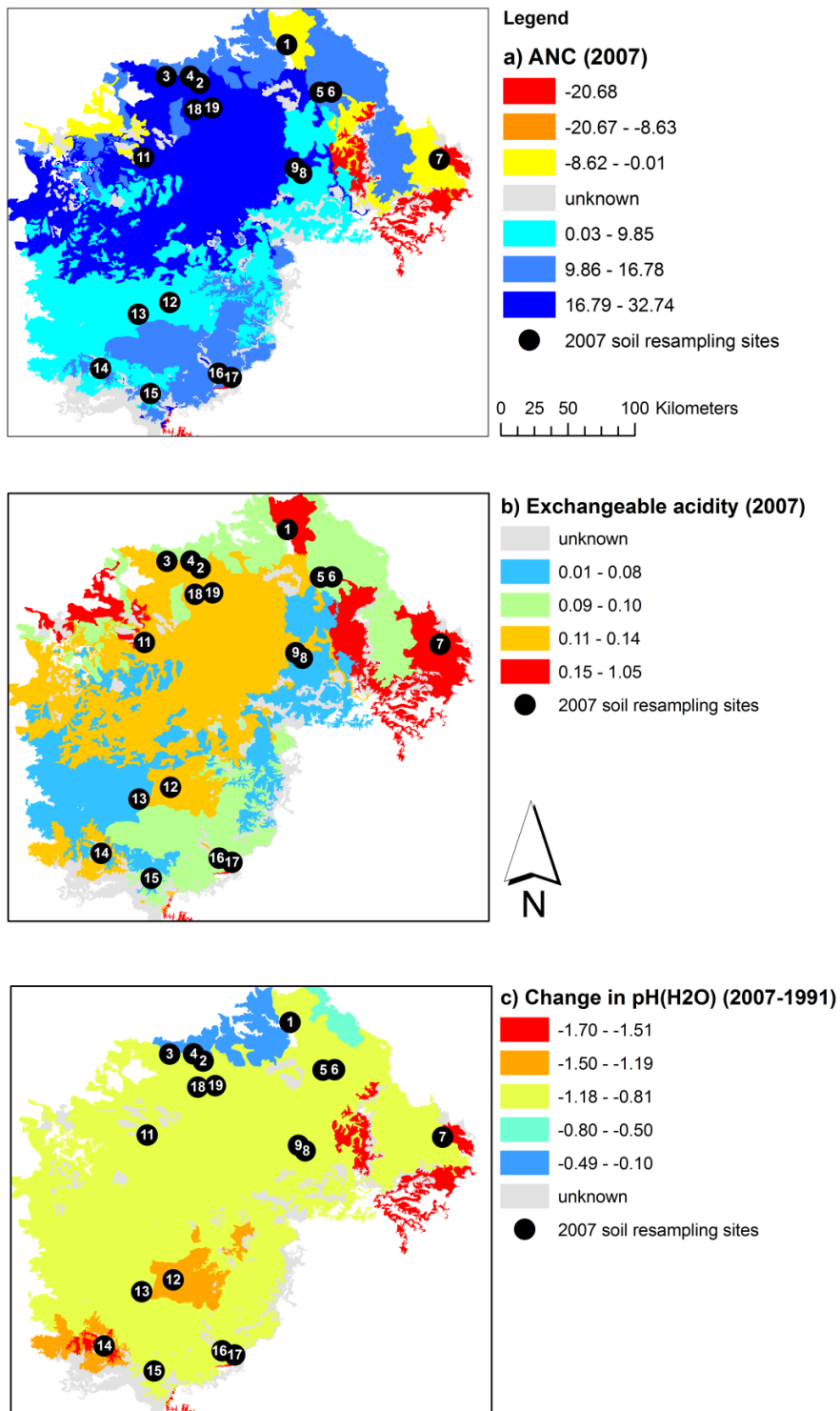


Figure 4.3: Maps showing the acidity status of the soils of the Highveld grasslands by a) acid neutralising capacity in 2007 ($\text{cmol}_c \text{ kg}^{-1}$), b) exchangeable acidity in 2007 ($\text{cmol}_{(+)}. \text{kg}^{-1}$) and c) change in $\text{pH}(\text{H}_2\text{O})$ between 2007 and 1991. Sampling sites were considered representative of land type in which they occurred and where more than one site occurred on the same land type, a mean of the site values was used to represent the land type.

Table 4.6: Areal extent of areas indicating increased soil acidity, based on fine scale soil form and land type pattern. Areas are presented for where ANC in 2007 is less than 0 cmol_c kg⁻¹, exchangeable acidity, in 2007, is greater than 0.5 cmol₍₊₎ kg⁻¹ and where the difference in pH(H₂O) between the two sampling years (1991 and 2007) was negative. Known areas are those where the chemical properties are inferred from the soil chemical analyses conducted at the 18 sampling sites.

	Total study area (km ²)	Total sampled area (km ²)	Sampled area as percentage of total study area (%)	ANC < 0 cmol _c kg ⁻¹ (2007)			Exchangeable Acidity > 0.5 cmol ₍₊₎ kg ⁻¹			pH(H ₂ O)(2007-1991) < 0 pH units		
				Area (km ²)	Area as a % of sampled area	Area as a % of total area	Area (km ²)	Area as a % of sampled area	Area as a % of total area	Area (km ²)	Area as a % of sampled area	Area as a % of total area
Soil form	53 940	17 847	33.1%	2 052	11.5	3.8	650	3.6	1.2	14 386	80.6	26.7
Land type		49 341	91.5%	5 892	11.9	10.9	5 892	11.9	10.9	49 341	100.0	91.5

4.4 Discussion

The emphasis of this research was on soil properties, linking soil function to exchanges with the atmosphere. The deposition data indicate the potential concern for increased soil acidity, where potential down-stream effects could include long-term changes in biodiversity both terrestrial and aquatic (Muniz, 1990; Fenn *et al.*, 2003a; Stevens *et al.*, 2004; Phoenix *et al.*, 2006; Bobbink *et al.*, 2010). The question was therefore: are the soils of the Highveld grassland region sensitive to acidic deposition? After the sensitivity of the soils was determined, known deposition values were used to speculate on the decrease of the ANC, the usefulness of the concept of critical loads in this context and impacts on biodiversity and ecosystem services, specifically the supply of potable water.

4.4.1 pH and base status

The pH(H₂O) values (Table 4.3) measured in 2007 were significantly lower than in 1991 across the sites. This pattern was not observed for the values measured using KCl and K₂SO₄, where no significant differences were observed (Table 4.3). The ionic strength of water is lower than the salt solutions and is therefore likely to displace only the weakly exchanged cations, including H⁺ and base cations. It is suggested that the pH measured in water reflects the difference between the proton concentration in the soil solution and the base cations that are easily removed from the soil surfaces and serves as a valuable indicator (Kennedy, 1986). This value indicates what is happening *in situ*, in that the soils are receiving a combination of both acidic and basic ions via deposition and weathering. The stronger extractants of KCl and K₂SO₄ may be masking the small differences between the basic and the acidic cations in the solution. The rates of turnover of cations and anions from solubilisation-precipitation, uptake-mineralisation processes as well as desorption and adsorption dominate soil processes in the short term but weathering rates need to be considered in the longer term.

The exchangeable acidity levels reported for the Highveld grassland soils are well below those reported in forested and grassland ecosystems elsewhere in the world. For example southern Appalachian watersheds (Knoepp and Swank, 1994), Chinese forests (Dai *et al.*, 1998), New Zealand grasslands (Alfredsson *et al.*, 1998) and even afforested *Eucalyptus grandis* plantations on acidic soils in the South

African Natal-midlands (du Toit, 2003). The exchangeable acidity in the Highveld grassland soils reported here was similar to those also in the South African Highveld grasslands near the Arnot power station where values ranged between 0.69 and 2.36 $\text{cmol}_{(+)} \text{kg}^{-1}$ in top-soils and 0.59 and 1.20 $\text{cmol}_{(+)} \text{kg}^{-1}$ in sub-soils (Reid, 2007), therefore, the 0.5 $\text{cmol}_{(+)} \text{kg}^{-1}$ exchangeable acidity threshold was considered to be a realistic one to use for sites showing increased soil acidity in these grasslands over the 16 year period.

In this study, Ca, Mg and K increased significantly at most of the study sites in both top- and sub soils (Table 4.2). Increased base cation concentrations at most sampling sites implied that the pattern would persist in a regional comparison. Calcium, Mg and K concentrations increased on average across the study area from 1991 (Table 4.3). The source of the cations may be fly-ash from ash-dumps close to the power stations (Mphepya, 2002; Mphepya *et al.*, 2004). Inputs of base cations in wet deposition totalled 39.4 $\mu\text{eq l}^{-1}$ over the period 1986 to 1999 at the Amersfoort deposition monitoring station where 47% and 17% were Ca and Mg ions respectively (Mphepya *et al.*, 2004). These base cations inputs were higher compared to the inputs at less industrialised sites of Louis Trichart, by 10.2 $\mu\text{eq l}^{-1}$ (Limpopo province in the north of South Africa) and Skukuza (in the Kruger National Park in the low lying areas of the Mpumalanga province), by 16 $\mu\text{eq l}^{-1}$ (Mphepya, 2002; Mphepya *et al.*, 2004; Mphepya *et al.*, 2006). Evidence also exists for considerable inputs (29 to 69% of aerosol loading depending on season and distance from source) of cations from soil dust (Piketh *et al.*, 1999a; Piketh *et al.*, 1999b; Mphepya *et al.*, 2004). The grasslands of the Mpumalanga Highveld are also regularly burnt through accidental and intentional ignition. The intentional ignition is usually to reduce fuel loads or to improve forage quality for livestock (Bond, 2003). These frequent (annual or biennial) fires could be a source of base cations to the top-soils of these grassland areas. Maenhaut *et al.* (1996) found that pyrogenic emissions enriched atmospheric amounts of K and Ca on the Mpumalanga Highveld where pyrogenic apportionment (modelled via absolute principle components analysis) amounted to 86% and 36% for K and Ca respectively. These alkaline inputs replenish the buffering capacity of the soils, including ANC, which offsets the acidic deposition inputs. These findings in the Highveld grasslands are in contrast to soil acidification studies that show decreasing base cation concentrations (for example Binkley *et al.*, 1989). The

different responses are likely to be due to the different uptake of base cations by different vegetation types and various input pathways, indicating the importance of the land use and above-ground biotic ecosystem components in acidification processes.

4.4.2 Soil Texture

Clay surfaces play an essential role in maintaining cations in the systems; the standard assumption is that with increasing clay content the cation exchange capacity of the soil increases, thereby enhancing the buffering capacity of the soil. Statistical grouping of the sites in this study by clay content showed a relationship between clay content and acidity status. As the mean clay content increases above 25%, there was an increase in $\text{pH}(\text{H}_2\text{O})$ values over time; at any value below 25%, significant decreases in $\text{pH}(\text{H}_2\text{O})$ values were observed (Figure 4.1). Clay content was also related to ANC and exchangeable acidity. The ANC is a measure of the soil capacity to neutralise acids (Ulrich, 1986; Reuss, 1991). One would expect that as the number of cations exchange surface increases the ANC would increase. This was found to be the case, where the ANC values (in 2007) were positive when the clay content was above 4.3% and become negative below this clay content value (Figure 4.1).

The literature refers to ANC exceedance and the linked concept of critical loads (for example, Draaijers *et al.*, 1997). ANC is used as an indicator to monitor change in the acid-base status of soils which may be changing as a result of land practice, aerial deposition, weathering rates and other soil chemical processes. In many studies, soils have been defined as being sensitive based on the relative ability of the soil to buffer acidic inputs and basic losses (Kuylenstierna *et al.*, 1995; Kuylenstierna *et al.*, 2001; Bouwman *et al.*, 2002). In this study, soils with clay content in the region of 5% and below are considered to be sensitive because of the low pH values, negative ANC and high exchangeable acidity (Figure 4.1). These negative ANC values indicate that the rate of incoming acid anions is occurring faster than either the release from geologic sources or via deposition of base cations and these soils will continue to acidify under deposition levels. From Figure 4.1 site 17 showed a decrease in $\text{pH}(\text{H}_2\text{O})$ of 1.2 pH units, had the lowest ANC value and the highest concentration of exchangeable acidity in 2007 (greater than $1 \text{ cmol}_{(+)} \text{ kg}^{-1}$).

4.4.3 Acidity status at soil form and regional scale

Scaling the site data to soil form and land type allowed for the spatial representation of the soil acidity status. Areas of potential soil sensitivity were identified (sites 5, 6, 7, 16 and 17) and are located near the periphery of the study area where the rainfall is higher. The increased acidity status is most likely attributable to leaching (Ca concentrations decreased significantly in the top-soils of 2 of the 5 sensitive sites, with significant increases in the sub-soils; similar patterns were observed for Mg concentrations) on these sandy soils. Some areas (for example, site 5) when grouped by land type instead of soil form, show reduced sensitivity. Thus the smaller scale of soil form highlights sensitivity of smaller soil patches while the larger land type scale allows for an estimate of soil acidity status across areas within the region.

Wet deposition processes dominate total (wet + dry) deposition across the Highveld region by contributing between 60 and 90% of S and more than 80% of N deposition (Blight *et al.*, 2009). Modelled total S deposition across the Highveld region was more than 8 kg ha⁻¹ year⁻¹ with maximum deposition rates near emission sources to be 35 kg ha⁻¹ year⁻¹ or more for an average rainfall year (Blight *et al.*, 2009). Modelled total deposition of N species across the majority of the Highveld region was between 2 and 6 kg ha⁻¹ year⁻¹ with a maximum of more than 8 kg ha⁻¹ year⁻¹ for an average rainfall year. In below-average rainfall years deposition rates, for S and N, were lower than in average rainfall years. In above-average rainfall years maximum total N deposition increased to more than 15 kg ha⁻¹ year⁻¹ and the area receiving maximum S deposition increased although not the maximum rate of deposition (35 kg ha⁻¹ year⁻¹) (Blight *et al.*, 2009). The deposition rates of S modelled in the study by Blight *et al.* (2009) were comparable to field-monitored deposition (maximum wet deposition between 1 and 5 kg S ha⁻¹ year⁻¹ and maximum dry deposition 10 kg S ha⁻¹ year⁻¹ – Zunckel *et al.*, 2000; wet deposition in remote areas of 5.9 kg S ha⁻¹ year⁻¹ and 2.8 kg N ha⁻¹ year⁻¹ – Mphepya *et al.*, 2006) within the Highveld grassland region. When comparing field-monitored and modelled depositions the US-EPA accuracy guidelines for dispersion models suggest variation between -50% to +200%. Nitrogen deposition was underestimated by the model relative to measured values, varying between -30 to -70% of measured values (Blight *et al.*, 2009).

Critical loads are defined as 'a quantitative estimate of an exposure to one or more pollutants, below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson and Grennfelt, 1988). It is proposed that soils around the periphery of the study area are sensitive to additional acidic inputs. But calculations of critical loads for the potential acidic species were not conducted in this study. Previous studies have calculated critical loads for the southern African region (critical input limit of upwards of 50 meq acidity $\text{m}^{-2} \text{year}^{-1}$ – Kuylenstierna *et al.*, 2001) and for the Highveld and escarpment of South Africa (critical S deposition loads of between 39 and 86 meq $\text{m}^{-2} \text{year}^{-1}$ – van Tienhoven *et al.*, 1995). The most sensitive soils are on the escarpment, likely a result of high rainfall, land use and soil properties. This study provides further evidence to support this pattern. The critical load modelling studies that identified this area of South Africa to be at moderate risk of acidification are based on large scale (input data with resolutions between $1^{\circ} \times 1^{\circ}$ to $10^{\circ} \times 10^{\circ}$) mapping of deposition fluxes and soil properties (Kuylenstierna *et al.*, 1995; Kuylenstierna *et al.*, 2001; Bouwman *et al.*, 2002). Bouwman *et al.* (2002) projected that, in 1992, 6% of (semi-)natural ecosystem area in southern Africa had deposition fluxes exceeding the critical load by a ratio greater than 1 at a moderate level of buffering capacity. This area increased to 9% of (semi-)natural ecosystems by projections of 2015 at a moderate level of buffering capacity (Bouwman *et al.*, 2002). Kuylenstierna *et al.* (2001), however, found no evidence for critical load exceedance for southern Africa. Allowing for potential errors in modelling at the scale of a degree or more, and comparing the results with the sampling and site based study reported here, the percentage of areas exceeding the buffering capacity are similar to Bouwman *et al.* (2002). This supports the use of sampled sites to represent soil forms and land types and the interpretation of 18 sampled sites as representative of the whole study area.

4.4.4 Conclusion

This study has shown that soil acidity has increased marginally across the entire study area, with only very limited areas showing more marked increases in acidity over the 16 years. Mapping of soil acidity status allowed the southern and eastern boundary soils to be identified as sensitive to acid deposition. From the soil texture, soil chemistry (increases in components of acidity in some cases of base cation concentrations), climate amounts and deposition rates to deduce that it is

unlikely that critical loads have been exceeded. Confounding factors such as changing land use, fire frequencies as well as the lack of baseline biodiversity analyses along deposition gradients prevents commentary on the impact on plant and invertebrate species diversity changes in these grasslands. Modelling studies suggest that as a result of acid deposition, even well-buffered soils could result in increased salt content in surface waters within the next 40 years (Herold *et al.*, 2001); however, measured values to support modelled forecasts are lacking. We suggest that the implementation of species diversity surveys and investigation of long-term data sets for increases in surface water salt concentrations to corroborate modelling work. Monitoring of soil chemistry and atmospheric deposition of acidic and basic ions should continue in conjunction with assessment of species diversity and water quality.

4.4.5 Thesis linkage

Chapter 4 has shown that soil acidity status has generally increased across the Highveld grasslands. However increased concentrations of base cations at sites in the centre of the study area were also recorded and co-deposition of basic cations with acidic ions may be adding to the buffering capacity of these soils. Sandier soils, closer to the periphery of the study area, were identified as the soils most sensitive to acidic inputs. Soil acidity status can influence nutrient cycling by affecting the size and structure of microbiological communities involved in the mineralisation process leading to decreased rates of release of inorganic S and N from soil organic pools. This, in turn, could reduce the provisioning services delivered by these grassland ecosystems. To assess if nutrient cycling has been affected by atmospheric deposition, SO_4^{2-} and N mineralisation rates were quantified using the *in situ* incubation method. The results of this investigation are presented in Chapter 5, together with proposed S and N cycles for the Highveld grasslands.

CHAPTER 5: SULFUR AND NITROGEN CYCLING IN GRASSLANDS OF THE MPUMALANGA HIGHVELD, SOUTH AFRICA

In Chapter 4 it was shown that the soil acidity status had increased generally across the Highveld grasslands, with sandier soils showing the largest increases in acidity status and most sensitivity to further acidic inputs via atmospheric deposition. This increased acidity status could already have impacted the nutrient cycling processes, particularly mineralisation as increased soil acidity can decrease microbial activity. The ecosystem supporting service of nutrient cycling processes, pools and fluxes in natural grasslands of South Africa have been poorly studied compared with neighbouring savannas. This chapter investigates the cycling of S and N in selected grasslands of the Highveld by investigating the net mineralisation rates of the top-soils. In addition, S and N cycles, as storage pools and process fluxes, are proposed for these grasslands using literature values and the measured mineralisation rates.

The manuscript below is under revision for *Oecologia*. The title, authors and affiliations are as given below. As for the manuscript presented in Chapter 4, my involvement was the field and laboratory work, initial interpretation of the data and the preparation of the graphics and manuscript drafts. Prof. Scholes contributed through further data interpretation and changes to the manuscript text and figures.

Dynamics of S and N in grasslands of the Mpumalanga Highveld, South Africa

Theresa L. Bird* and Mary C. Scholes

School of Animal, Plant and Environmental Sciences, University of the Witwatersrand,
Johannesburg. Private Bag x3, Wits, 2050, South Africa

ABSTRACT

The dynamics of S and N were investigated in the Highveld grasslands of South Africa as a result of questions being raised related to changing land use and potentially adverse impacts of atmospheric deposition. This study investigated SO_4^{2-} and N mineralisation rates using the *in situ* incubation technique and found a seasonal range of -0.66 to $1.09 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$ and -0.97 and $1.21 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. Over an annual cycle -40 to 9.9 kg ha^{-1} of S and $27 -$

81 kg ha⁻¹ of N were mineralised from the organic matter pool of grassland soils. Nutrient budgets showed that 83% of the S and 97% of the N were held in the soil organic pools with extremely small amounts of N and S being present in the above-ground biomass. Biomass production is probably limited by the interaction of low rainfall and cold winter night-time temperatures. There was no evidence of negative impacts of atmospheric S and N deposition on soil processes and some evidence for potential S accretion in the soils. N appears to limit primary productivity in the Highveld grasslands. The findings extend the understanding of S and N cycling in species-diverse and economically important Highveld grasslands.

5.1 Introduction

South African grasslands extend over an area of 349 174 km² (O'Connor and Bredenkamp, 2003) across the central plateau (average altitude of 1700 m above sea level). These grasslands are bordered by moist warm savannas on the north and east; dry warm savannas on the northwest and dry cool semi-desert to the south (Bredenkamp *et al.*, 2002) and are commonly referred to as the Highveld grasslands. While climatic factors limit the extent of the grassland biome (Bredenkamp *et al.*, 2002), frost, fire, and in some micro-sites, soil clay-content have been postulated to exclude woody plants (Bredenkamp *et al.*, 2002; O'Connor and Bredenkamp, 2003). The high central plateau is exposed to high pressure weather systems that lead to clear conditions (Preston-Whyte and Tyson, 1993) favourable to the development of frost and under windy conditions, fires. Bredenkamp and colleagues (2002) proposed that since the fire regime is similar in grasslands and neighbouring savannas, it is frost that excludes indigenous trees that are adapted to dry conditions and fire. Huntley (1984) made the distinction between “true” grasslands that are the climatic climax community and “false” grasslands where climate would allow succession to shrubland, savanna, woodland or forest but the grassland state is maintained by factors such as grazing, fire or edaphic factors such as seasonal water-logging. The Highveld grasslands are true climatic climax grassland communities mostly underlain by Karoo Supergroup sedimentary rock of the Carboniferous and Permian epochs, with occasional dolerite intrusions and extrusive basalt and rhyolites (Huntley, 1984). Due to the biogeographic history (Bredenkamp *et al.*, 2002), greater climate variability and reduced nutrient status compared with northern temperate grasslands (Knapp *et al.*, 2006), the Highveld grasslands have

rich biodiversity and are of conservation interest (Zunckel, 2003; Mucina and Rutherford, 2006). The impact of crop agriculture, stock grazing, mining and high levels of S and N deposition on grassland biodiversity are of concern in areas that are not protected by conservation efforts.

Located within the grassland biome is the urban complex of Johannesburg-Pretoria-Vereeniging and extensive coal beds that support industry, coal-to-liquid fuel plants and coal-fired power stations. Poor pollutant (aerosols and trace gases) dispersal conditions (Zunckel *et al.*, 2000) are established by the predominantly anti-cyclonic air circulation (Tyson *et al.*, 1996). This leads to higher concentrations of atmospheric pollutants near emission sources (Mphepya *et al.*, 2004; Josipovic *et al.*, 2010). The burning of accumulated biomass in grasslands can be a substantial source of rainwater acidity, although the contribution of this source affects remote-site rainfall more than sites near industrial sources (Galpin and Turner, 1999b). The combination of clustered emission sources and atmospheric circulation patterns result in high levels of S and N deposition on the grasslands of the Highveld of South Africa, especially those east of the Johannesburg-Pretoria-Vereeniging complex.

Elsewhere in the world S and N deposition have had significant impacts on ecosystem processes and products, for example those associated with nutrient cycling (as reviewed by Galloway, 1996) as well as the impacts on crops and forests described by Emberson *et al.* (2003). Although rainwater quality (since 1983), ambient air quality (since 1978) (Held *et al.*, 1996) as well as both wet and dry deposition (since 1995 – Mphepya *et al.*, 2004) have been studied in these South African grasslands, little is known about the impact of deposition on the ecosystem processes in this region. Recent findings in a study investigating the impacts of S and N deposition on soil chemistry of the Highveld grasslands, suggest that there has been some degree of soil acidification over relatively short periods (Reid, 2007 – 10 years; Chapter 4 (this thesis) – 16 years). Soils with higher clay content appear to remain buffered where co-deposition of acidic and basic cations enhances the buffering capacity of the soils (Reid, 2007; Chapter 4).

In order to further understand S and N cycling in the Highveld grasslands, a year-long *in situ* mineralisation study was conducted. The sequential core *in situ* technique (developed by Raison *et al.* (1987) was used to determine changes in

inorganic N concentrations over time. Below-ground processes dominate nutrient cycling in grassland ecosystems (Stewart *et al.*, 1983) and the instrumental role of microbial processes in redistribution and accumulation of organic S compounds is described by Parton *et al.* (1988). Sulfate is the dominant form of inorganic S in soils (Edwards, 1998) and the main form of S available for plant uptake (Anderson, 1978; Riffaldi *et al.*, 2006), where SO_4^{2-} can be released biochemically or microbially from soil organic matter (Riffaldi *et al.*, 2006). Inorganic N (as NH_4^+ and NO_3^-) is released from organic matter via microbial processes. Nitrogen mineralisation has been extensively studied however S mineralisation in South African soils is limited to a laboratory incubation to compare the impact of cultivation on S dynamics in grasslands (du Toit and du Preez, 1995).

In western Europe, crop S deficiencies are now evident because inputs from anthropogenic S emissions are generally less than $10 \text{ kg ha}^{-1} \text{ year}^{-1}$ and lower than crop-plant demand (Riffaldi *et al.*, 2006) (Boye *et al.*, 2009; Niknahad Gharmakher *et al.*, 2009; Scherer, 2009). In contrast, modelled S deposition on the Highveld grasslands of South Africa amounts to approximately $8 \text{ kg S ha}^{-1} \text{ year}^{-1}$ and modelled N deposition is $6 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Blight *et al.*, 2009). These large inputs from anthropogenic activities could impact nutrient cycling. The purpose of this research was to explore the patterns of net SO_4^{2-} and inorganic N mineralisation over 1 year in the Highveld grassland ecosystem exposed to S and N atmospheric deposition. The data were also used, together with published literature, to compile S and N nutrient budgets for these grasslands.

5.2 Materials and Methods

5.2.1 Area and site description

The mineralisation study was undertaken as part of an investigation into the impact of atmospheric S and N deposition on the South African Highveld grasslands (Chapter 4). Based on monthly frequency of sampling, the requirement to analyze soils as soon as possible after collection, and the size of the original study area, only 11 of the original 18 sites (described in Chapters 3 and 4) were included in this study due to their proximity to each other and the laboratory (Figure 5.1). These 11 sites represented the major land types of the region as areas of similar broad soil pattern,

climate and terrain (Land Type Survey Staff, 1985;2002). All sites are situated within the grassland biome (Mucina and Rutherford, 2006).

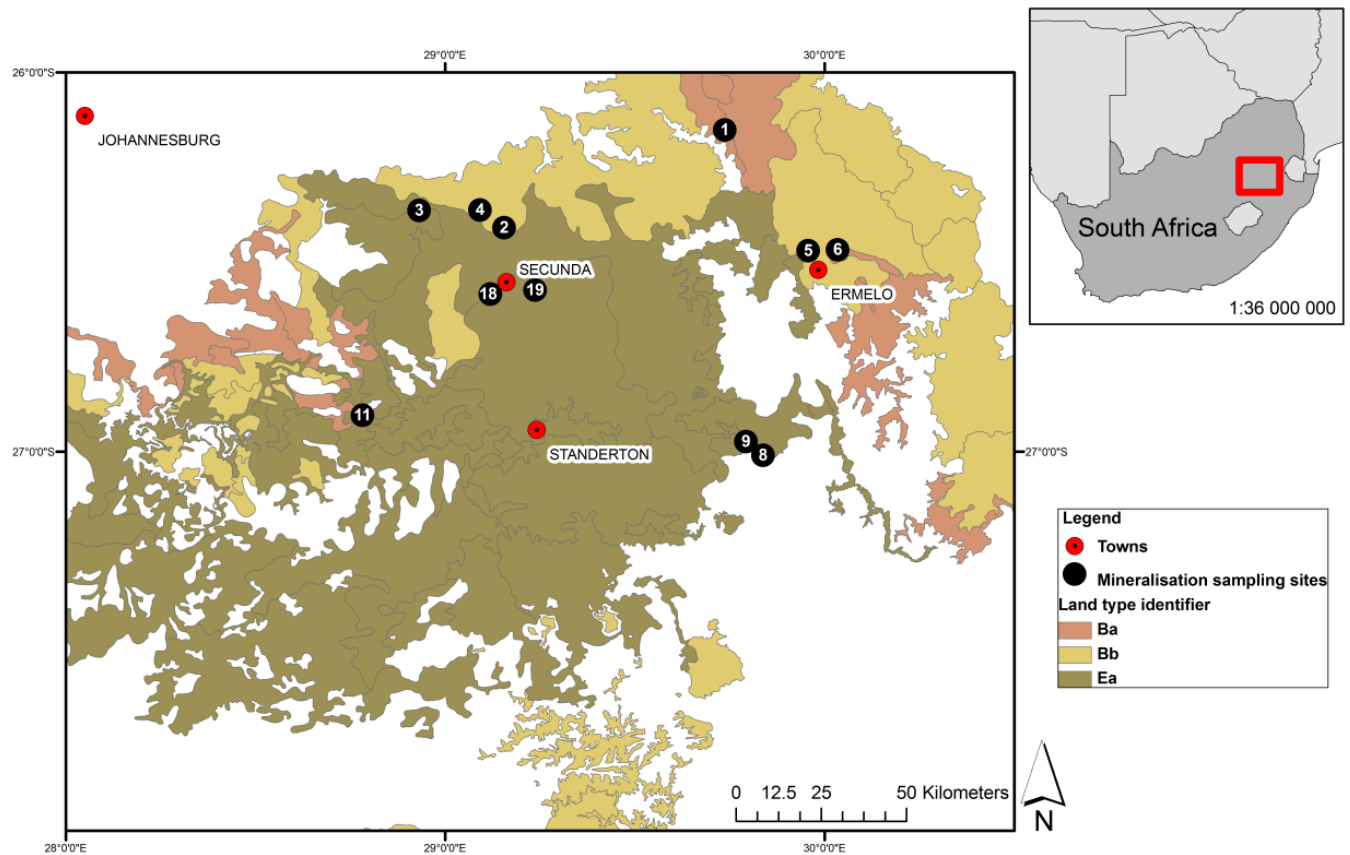


Figure 5.1: Location of sites used to investigate net SO_4^{2-} and N mineralisation in an area of the grassland biome of South Africa. Weather data from the South African Weather Service stations at Secunda, Standerton and Ermelo were used to describe weather patterns over the area sampled.

The sequential core *in situ* mineralisation technique (Raison *et al.*, 1987) was used to quantify net S and N mineralisation rates over an annual cycle and to identify potential controls on the rates of nutrient cycling. At each site 4 pairs of stainless steel tubes (internal diameter: 50 mm; length: 250 mm) were inserted to a depth of 200 mm. Three pairs of tubes were at the apexes of a triangle with a base of approximately 10 m; the fourth set was placed at the centre of the triangle. The sampling was conducted monthly from January 2008 to November 2008 in the last week of the calendar month and again in the second week of January 2009 with a total of 11 sampling periods over an annual cycle. At each sampling, one tube of the pair was removed and marked as the initial (T0) soil. The remaining tube was covered with low density polyethylene (plastic wrap) and secured to prevent leaching of accumulated inorganic S and N by rainfall. The incubated tube (T1) was collected at the following month's sampling. All collected soils were stored in paper bags in

cooler boxes during sampling and stored at 4°C until analysis, which usually occurred less than 48 hours after collection. Fires occurred in 3 of the 11 sites during the sampling period: Sites 1 and 3 were burnt in June 2008 and Site 9 burnt in August 2009.

5.2.2 Laboratory methods

Before sub-sampling, gravel and large roots were removed from the soils. Soils were not sieved due to the high clay content of some of the soils, but were manually mixed before sub-sampling. Extraction of inorganic N involved shaking a 10 g (± 0.1 g) soil subsample in 25 ml of 0.5 M K_2SO_4 extractant for 30 minutes at 60 rpm. The samples were then centrifuged at 3000rpm for 10 minutes. The clear supernatant was used to determine the ammonium (NH_4^+) and nitrate (NO_3^-) concentrations by colourimetric procedures described in Anderson and Ingram (1993). Sulfate concentrations were determined by ICP-OES after extraction in 0.01 M calcium phosphate at pH 4 according to the methods detailed by the Soil and Plant Analysis Council (1998). In order to account for soil water content, 10 g sub-samples were dried at 100°C for 48 hours. Total N was determined on the samples collected in January 2008 using the Kjeldahl digestion method followed by colourimetric analysis (Anderson and Ingram, 1993).

5.2.3 Calculation of net mineralisation rates

Since mineralisation and immobilisation occur simultaneously it is only possible, using the *in situ* incubation methodology, to determine the net effect of the opposing processes (Smith *et al.*, 1994; Edwards, 1998). The net rates of inorganic N production were calculated as the differences in mineral N concentrations, as the sum of NH_4^+ and NO_3^- , between the field incubated core (Time 1) and the initial core (Time 0), divided by the number of days of incubation. The net production (release / immobilisation) of NH_4^+ and NO_3^- individually, was also calculated on a monthly basis in a similar manner as for total inorganic N. Sulfate mineralisation was also calculated as the difference between the concentrations of SO_4^{2-} in the Time 1 (incubated) core and the Time 0 (initial) core, accounting for the number of days of incubation.

Annual net N and SO_4^{2-} mineralised were calculated as the sum of the net monthly concentrations multiplied by the soil bulk density (1.3 ton m^{-3}) to a depth of 150 mm, as detailed in equation 4.

$$\text{Annual amount mineralised (kg ha}^{-1}\text{)} = [(T1-T0)_{s1} + (T1-T0)_{s2} + \dots + (T1-T0)_{s11}] * (BD * \text{depth} * \text{area}) \dots [4]$$

where T1 is the concentration (g kg^{-1} soil) of the inorganic N or SO_4^{2-} at sampling time after incubation and T0 is the corresponding initial concentration in that sampling month; s indicates the respective sampling period from 1 to 11; BD is the bulk density of 1.3 ton m^{-3} converted to kg ha^{-1} by multiplying by the depth (0.15 m) and the area (10000 m^2). The mean and standard error of annual SO_4^{2-} and N mineralised was calculated from the replicate sampling points representing each land type.

5.2.4 Data analysis

Mean substitution of monthly mean mineralisation rates irrespective of sampling site was used to estimate missing values accounting for 4% of the data set. Normality testing revealed that some months for both N and S mineralisation were not normally distributed. Transforming the raw data resulted in further deviation from a normal distribution. However, General Linear Model (GLM) analyses with repeated measures design were used to investigate for differences between sites and between months for all net mineralisation rates, as the residuals were normally distributed. The Fisher LSD post-hoc test was used as a multiple comparison test for significance. Principal component analysis (PCA) was used to explore the relationships between soil properties, monthly mean meteorological conditions and N and S mineralisation rates. Soil water content, particle size distribution, as well as the following chemical properties were included in the PCA: pH (in distilled water), Bray II phosphorus, organic carbon (%), total N (%) and total S (ppm). These additional soil characteristics were part of the re-assessment of the soils of the Highveld grasslands detailed in Chapter 4. Mean monthly maximum and minimum temperature, rainfall in the previous month and rainfall in the current month were included in the PCA analysis as indicators of climate. Statistica 6.0 from Statsoft Inc. (<http://www.statsoft.com/>) was used for all analyses.

5.2.5 Meteorological records

Since the rate of release of SO_4^{2-} and inorganic N are often related to the soil water content and temperatures, meteorological records from the South African Weather Service for the weather stations at Secunda, Ermelo and Standerton from January 2008 to January 2009 were obtained for comparison SO_4^{2-} and N mineralisation rate patterns and weather conditions. These three stations had the most complete meteorological data sets for the sampling period within the region covered by the sampling sites (Figure 5.1). The daily minimum and maximum temperatures from all three stations were used to calculate mean monthly minimum and maximum temperatures for the region. The daily rainfall for each station was summed for the monthly total and the mean monthly rainfall for the region calculated from the three stations (Figure 5.2).

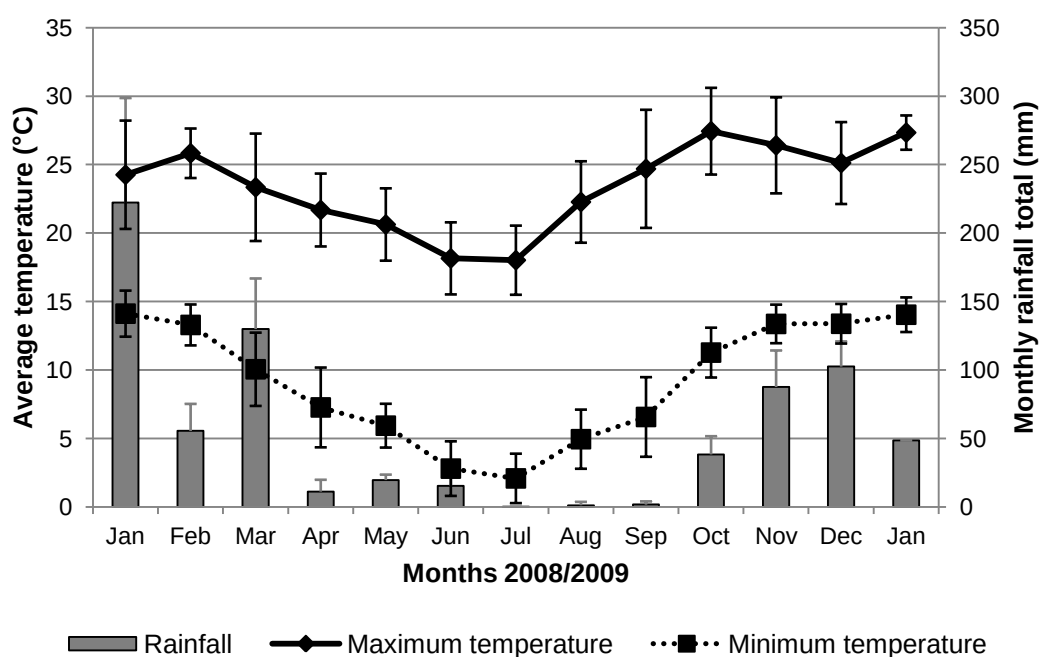


Figure 5.2: Mean ($\pm$ standard deviation) monthly minimum and maximum air temperatures and mean monthly rainfall for the three weather stations in the region of the mineralisation sampling sites. Total rainfall from January 2008 to January 2009 was 734 mm.

5.3 Results

5.3.1 Net SO_4^{2-} mineralisation rate

Mean net SO_4^{2-} mineralisation rate (Figure 5.3) was positive for 4 of the 12 months investigated. The SO_4^{2-} mineralisation rate varied between $-2.38 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$ and $0.32 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$ (Figure 5.3). The overall pattern showed maximum immobilisation in August and the peak mineralisation in November 2008. The largest variation (as standard error) was recorded in June ($0.09 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$) and the smallest in September and January ($0.02 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$). The sustained increase of sulfate released from May through to July was likely a result of rainfall a few days prior to the April sampling. After which the cold air temperatures and drier conditions would have resulted in the striking immobilisation pattern seen in August. Rising temperatures from August into spring may have resulted in the release of sulfate, even prior to the spring rains, which arrived in October 2008. The arrival of spring rains and warmer temperatures in October would have provided optimal conditions for the microbial communities involved in mineralisation of SO_4^{2-} leading to the peak release of SO_4^{2-} in November.

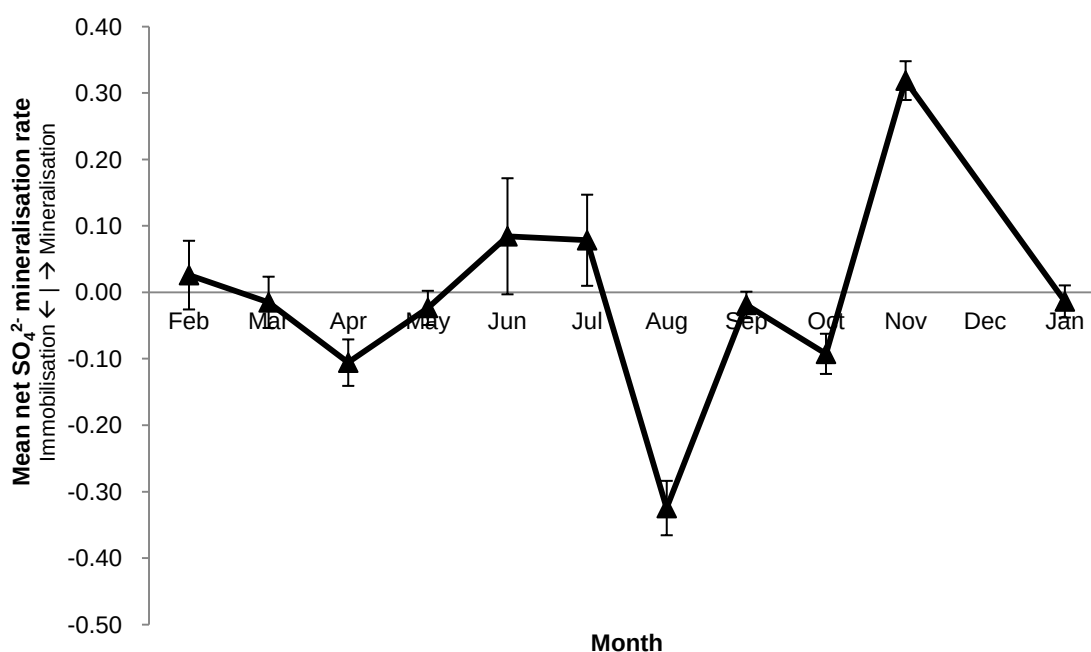


Figure 5.3: Mean ($\pm$ standard error) net sulfate mineralisation rate ($\mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$) from February 2008 to January 2009 (for 11 sites; $n=44$). Where rates or slope of the graph between two sampling points is positive, SO_4^{2-} is mineralised. In contrast, where rates or slope of the graph are negative, SO_4^{2-} was immobilised.

Sulfate mineralisation rate varied significantly between months ($F=17.712$; $p=0.0000$) where August was shown to be significantly lower than all other months ($p<<0.01$ in all cases). The November peak in mineralisation rate was significantly higher than all other months ($p<<0.01$).

5.3.2 Net inorganic N mineralisation rate

Mean net N mineralisation rate (Figure 5.4) ranged between $-0.60 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ and $0.52 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. Inorganic N was immobilised in three of the 12 months sampled. Net N mineralisation rate varied significantly between months ($F=28.8948$; $p=0.0000$) where May was found to have significantly higher N mineralisation rates than all other months ($p<0.01$ in all cases). Conversely, June was found to have mineralisation rates lower than all other months ($p=0.0000$ at all sites). This is likely to have been related to the net mineralisation spike measured in May. Generally the warmer wetter months showed net N mineralisation such that, from September to January, the overall pattern was the release of N.

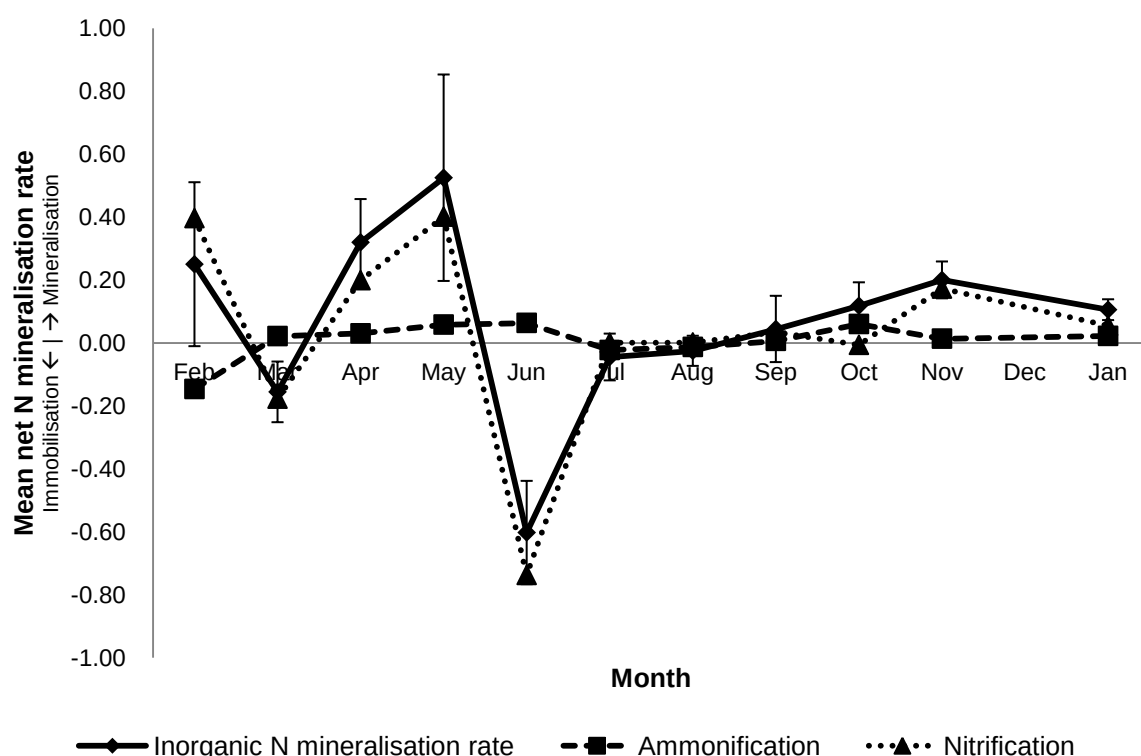


Figure 5.4: Mean net N mineralisation, ammonification and nitrification ($\mu\text{g N g}^{-1} \text{ soil day}^{-1}$) for February 2008 to January 2009 (for 11 sites; $n=44$). Standard error presented for net N mineralisation at each monthly sampling.

The availability of NO_3^- - released via nitrification - contributed more than the availability of NH_4^+ - released via ammonification – to the overall net N mineralisation (Figure 5.4) and can thus be considered as the dominant process in these grassland sites. The net release of NH_4^+ was close to zero in most months. Nitrification in contrast was more variable and closely matched the overall rate of net N mineralisation.

5.3.3 Variation between land types

It was reported in Chapter 4, that interpreting the indicators of soil acid-base status acidity - change in pH, exchangeable acidity and acid neutralising capacity – showed that soil acidity increased across the study area, over a 16-year period. This increased acidity was observed at the land type scale (Land Type Survey Staff, 1985;2002). Net SO_4^{2-} mineralisation rates (Figure 5.5) differed significantly ($F=3.9634$; $p=0.0266$) between the land type categories, however, land type was not related to net N mineralisation rates ($p=0.2423$). Mineralisation of SO_4^{2-} in June and July (Figure 5.3) was higher in sites of the Ba (plinthic catena, dystrophic and or mesotrophic red soils) and Ea (one or more of vertic, melanic, red structured diagnostic horizons) land types, respectively. The statistically significant decrease in SO_4^{2-} mineralisation rate during August was similar in all three land types – Ba, Ea and Bb. Sampling sites within the Bb land type (plinthic catena, dystrophic and or mesotrophic red soils) had significantly lower net SO_4^{2-} mineralisation rates than sampling sites on either Ba ($p=0.0146$) and Ea ($p=0.0242$) soils. The decrease in mineralisation rate, and switch to immobilisation, as a result of drying and cooling in July-August is also more rapid than in the more water-retentive clay soils in the Ea and Bb soils.

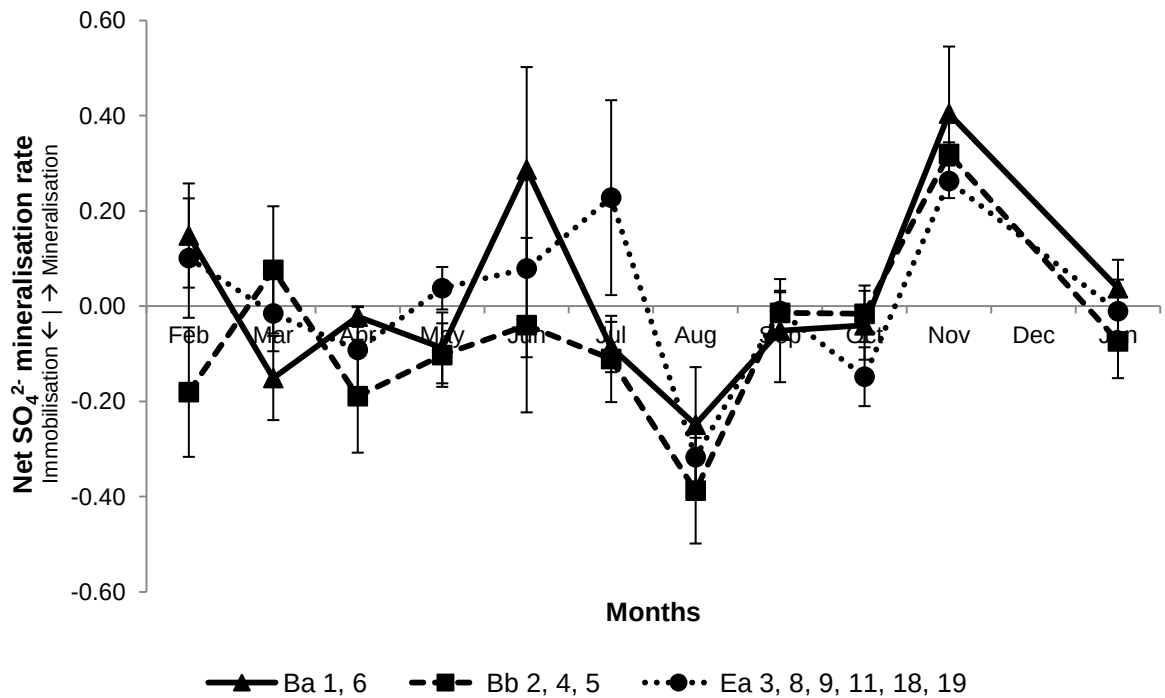


Figure 5.5: Monthly mean ($\pm$ standard error) net SO_4^{2-} mineralisation rates ($\mu\text{g g}^{-1} \text{ day}^{-1}$) sorted by land type over the period January 2008 to January 2009. Series represent the 3 land types – identifier code (e.g. Ba) followed by the relevant sampling site numbers.

The similarity of net N mineralisation rates (Figure 5.6) across the land type is only deviated from in the Ba soil-pattern in May where these soils again show rapid and more positive response to the rainfall received in April – more so than the Bb and Ea soils. While statistical differences between mineralisation rates would be expected for N, as was found for SO_4^{2-} , the variation between rates for land types is less than in for SO_4^{2-} . There is an exception to the explanation to positive response of Ba soils to rainfall and warm ambient temperatures evident in November where these soils showed a release of SO_4^{2-} (Figure 5.5). The tendency for these soils to immobilise N between October and November may have been related to plant demand of N at the beginning of the growing season leading to net N limitation over this period.

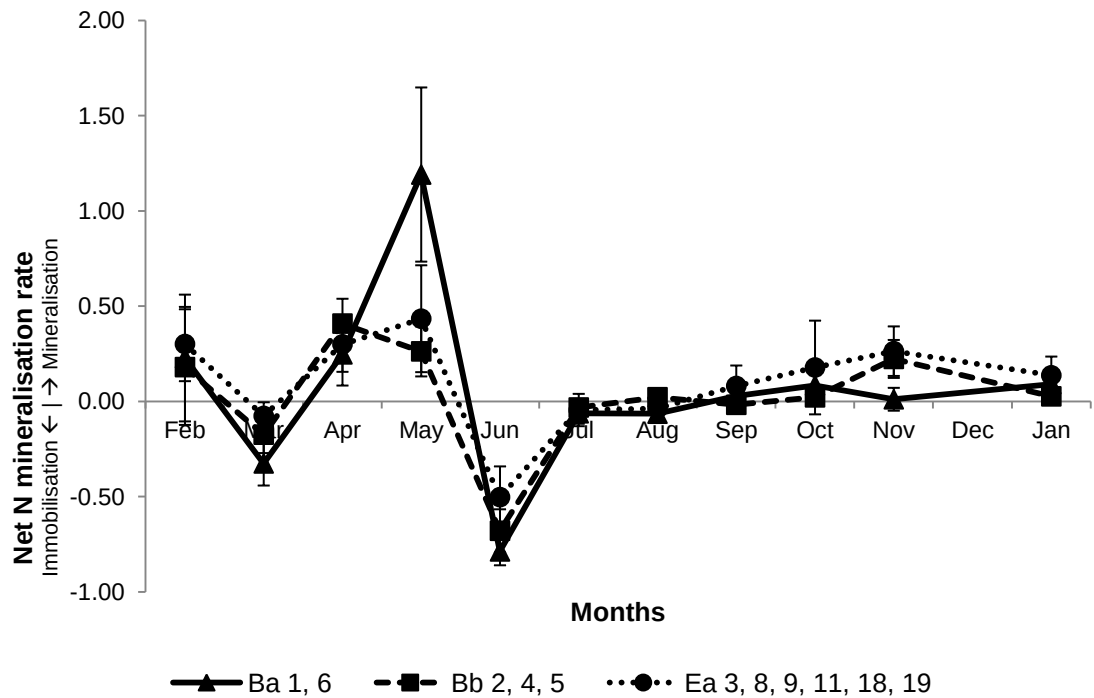


Figure 5.6: Monthly mean ($\pm$ standard error) net N mineralisation rates ($\mu\text{g g}^{-1} \text{ day}^{-1}$) sorted by land type over the period January 2008 to January 2009.

5.3.4 Total annual SO_4^{2-} and N mineralised based on land type

Soils of the Ba and Ea land types differed only slightly in the amount of SO_4^{2-} (5.7 and 9.9 $\text{kg ha}^{-1} \text{ year}^{-1}$ for Ba and Ea respectively) and inorganic N mineralised (80.3 and 81.1 $\text{kg ha}^{-1} \text{ year}^{-1}$ for Ba and Ea respectively) (Figure 5.7). In the Bb land type only 27.7 $\text{kg ha}^{-1} \text{ year}^{-1}$ inorganic N was mineralised and 40.5 $\text{kg ha}^{-1} \text{ year}^{-1}$ SO_4^{2-} was immobilised. While the amount of SO_4^{2-} mineralised by the soils of the Bb land type was significantly lower than the Ba and Ea land types ($F=6.0569$; $p=0.0049$), the differences between N mineralised by the different land type were not statistically significant ($F=1.7599$; $p=0.1848$). The soils of the Bb land type had the highest mean clay (16%) and silt (11%) contents and thus with slow drainage, on the rare occasion (<20 days during 2008) that rain events exceeded of 20 mm per event, may have developed anaerobic microsites leading to reduced mineralisation of SO_4^{2-} and inorganic N.

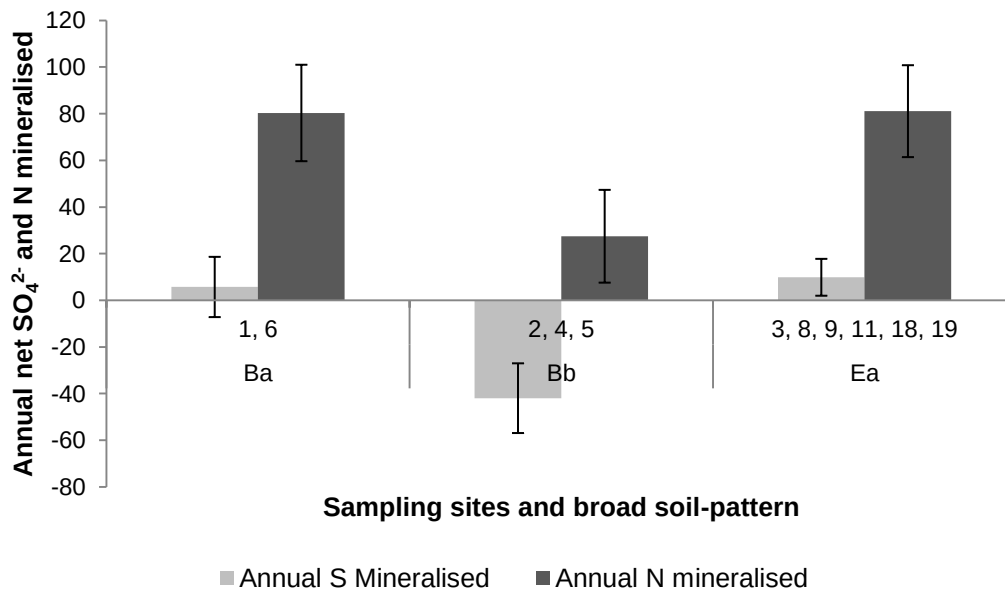


Figure 5.7: Annual mean ($\pm$ standard error) net inorganic SO_4^{2-} and N mineralised ($\text{kg ha}^{-1} \text{ year}^{-1}$) between January 2008 and January 2009, sorted by land type (with relevant sampling site numbers).

5.3.5 Controls of mineralisation rates

The principal components analysis (PCA) suggested that soil physical and chemical properties had the strongest influence on mineralisation rates. The first five factors explained 78.7% of the total variance in the data set, where the first factor explained 33.9% of total variance (Table 5.1) and factors 6 through 15 together explained only 20.2% of the total variance (data not shown due to smaller contribution to the variance in the data set). Factor 1 was primarily a function of soil physical (particle size distribution) and chemical properties (organic C, total N and total S); while factor 2 was mainly a function of the climatic conditions. The soil properties contributing to Factor 1 are likely to have been a result of site differences. A multiple regression analysis (output not shown), with SO_4^{2-} and N mineralisation rates as the dependent variables, based on the correlation matrix from the PCA analysis indicated that net SO_4^{2-} and N mineralisation rates were significantly affected by maximum temperature ($p < 0.01$ for both S and N), minimum temperature ($p < 0.01$ for both S and N), and rainfall in previous month ($p < 0.5$ for both S and N). Net N mineralisation rate was also significantly affected by rainfall in the current month ($p = 0.000$). Although the contribution of the previously mentioned

variables (temperature and rainfall) to the multiple regression were significant, the overall regression equations only explained 6.8% and 16.6% of the variation in the net SO_4^{2-} and net N mineralisation rates respectively. In the PCA Factor 2, mostly composed of climatic variables, explained only 19.3% of the variance of the data set. Most of the variance was explained by the differences in sites (Factors 1 and 3). The site differences are expected as the sampling site placement was intended to cover the dominant land types of the area sampled by Fey and Guy (1993).

Table 5.1: Variable contributions to Principle Components Analysis.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Percentage of total variance explained by factor	34%	19%	11%	8%	7%
Eigenvalue	5.098	2.898	1.594	1.173	1.041
Maximum temperature		0.23		0.17	
Minimum temperature		0.32		0.04	
Rainfall previous month		0.14		0.35	0.04
Rainfall current month		0.21		0.01	0.10
Soil water content	0.06	0.05		0.36	
Phosphorus (Bray II)	0.03		0.36		0.01
Clay content	0.14		0.05		
Silt content	0.13		0.02		
Sand content	0.14		0.02		
pH(water)	0.02		0.49		0.01
Organic C	0.15		0.02		
Total N	0.15		0.03	0.01	
Total S	0.17		0.01	0.01	
N Mineralisation rate		0.02	0.01	0.05	0.46
S Mineralisation rate		0.01			0.38

5.3.6 Sulfur and Nitrogen cycles

The S and N cycles of the Highveld grasslands were compiled using current findings in published literature. Surface soils to a depth of 200 mm were used to calculate the elemental cycles as biological processes are dominant in this layer (Raison *et al.*, 1987). The minimum and maximum values for pool and flux sizes are presented (Table 5.2), while the elemental cycles have been compiled using the maximum

values (from Table 5.2) for the pools and fluxes. In these semi-arid grasslands, where evaporative potential exceeds precipitation, occurrences of anaerobic conditions resulting in losses to the atmosphere are rare. Similarly losses of SO_4^{2-} and NO_3^- through leaching are minimal.

Table 5.2: Details of pools and fluxes, in terms of sizes and literature sources, used in compiling the S and N cycles of the Highveld grasslands. Units for pool sizes are kg ha^{-1} and units for fluxes (in italics) are $\text{kg ha}^{-1} \text{ year}^{-1}$.

Pool / flux (kg ha^{-1}) / ($\text{kg ha}^{-1} \text{ year}^{-1}$)	Pool / flux size		Source
	Minimum	Maximum	
Standing biomass	598	2000	O'Connor and Bredenkamp (2003) Snyman (2005)
Sulfur			
Above-ground biomass	0.5	1.8	Du Preez <i>et al.</i> (1983)
Above-ground necromass (litter)	0.1	0.6	Du Preez <i>et al.</i> (1983)
Below-ground – living	0.6	1.6	Du Preez <i>et al.</i> (1983)
Total S – soil	62.4	555.8	Du Toit and Du Preez (1995)
Inorganic S (SO_4^{2-}) – soil	7.1	88.6	This study
Microbial S – soil		23.4	Edwards (1998)
<i>Mineralisation</i>	0.6	29.7	This study
<i>Immobilisation</i>	-5.4	-80.0	This study
<i>Plant uptake</i>		9.0	Scholes and Walker (1993)
<i>Losses through burning</i>	0.3	1.2	Assume 50% loss in annual burns
<i>Deposition</i>	7.4	35.0	Blight <i>et al.</i> (2009)
Nitrogen			
Above-ground biomass	2.2	7.3	Snyman (2005)
Above-ground necromass (litter)	0.7	4.3	Scholes and Walker (1993) Fynn <i>et al.</i> (2003)
Below-ground – living	1.2	3.4	Snyman (2005) Scholes and Walker (1993)
Total N – soil	195.0	6630.0	This study
Inorganic NH_4^+ – soil	0.2	120.7	This study
Inorganic NO_3^- – soil	0.6	68.5	This study
Microbial N – soil	12.5	250.0	Parton <i>et al.</i> (1988) Scholes & Walker (1993)
<i>Mineralisation</i>	3.29	161.5	This study
<i>Ammonification</i>	-34.5	47.5	This study
<i>Nitrification</i>	-10.0	80.5	This study
<i>Immobilisation</i>	-5.1	-99.0	This study
<i>Plant uptake</i>		41.1	Scholes <i>et al.</i> (2003a)
<i>Losses through burning</i>		8.7	Tainton and Mentis (1984) Scholes <i>et al.</i> (2003a)
<i>Deposition</i>	3.90	8.50	Blight <i>et al.</i> (2009)

In the S cycle (Figure 5.8), the two above-ground pools, standing biomass (0.09% S in leaf tissue, 0.05% S in root tissue) and litter (0.09% S), contain 1.8 and 0.6 kg S ha⁻¹ respectively and the S pool stored below ground in grass roots was as much as 1.6 kg S ha⁻¹. Grass roots had a turnover time of 20 months in semi-arid grasslands near Bloemfontein, South Africa (Snyman and du Preez, 2005), becoming incorporated into the largest pool in the sulfur cycle; the soil organic S pool (467 kg S ha⁻¹). As decomposition progresses 29.7 kg S ha⁻¹ year⁻¹ is mineralised as SO₄²⁻. Estimated microbial biomass S was 5% of the soil organic S pool, approximately 23.4 kg S ha⁻¹ (Maynard *et al.*, 1983; Edwards, 1998). Estimated plant uptake from the inorganic S pool was 9 kg S ha⁻¹ year⁻¹ in a grass-dominated savanna ecosystem (du Preez *et al.*, 1983) and was used to represent plant uptake in the Highveld grasslands considered in the present study.

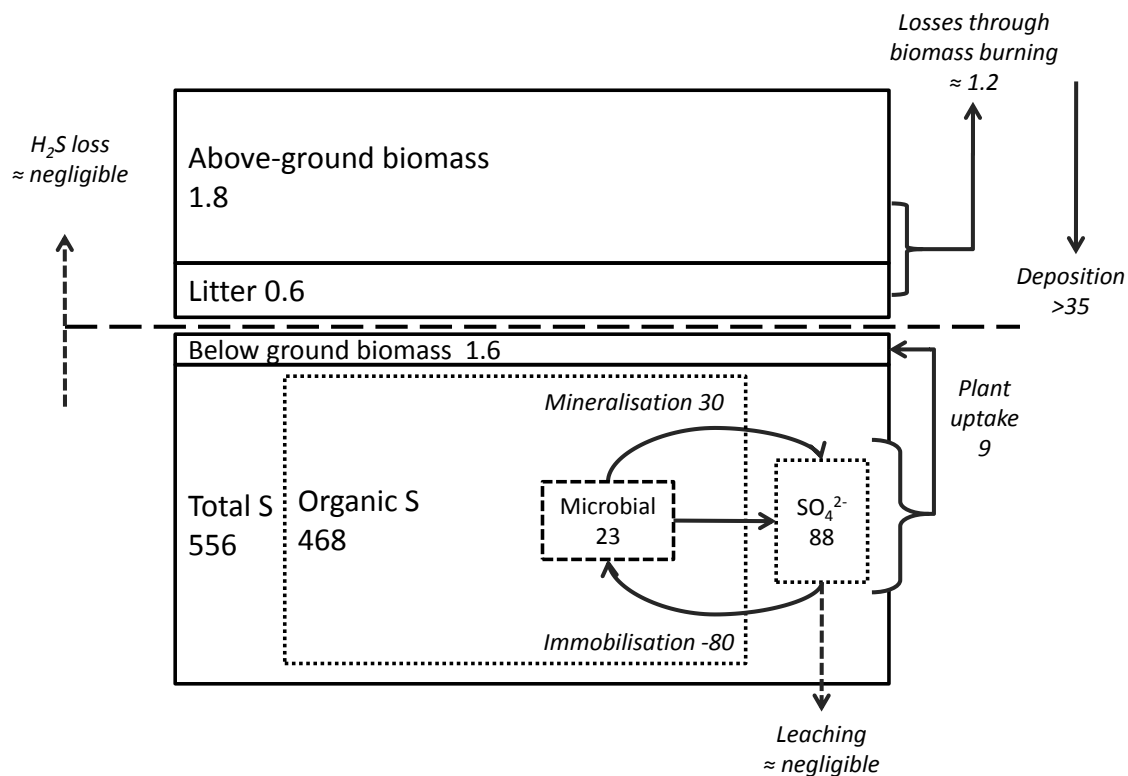


Figure 5.8: The sulfur cycle in Highveld grasslands of South Africa. The units for pools are kg ha⁻¹ and the units for fluxes (in italic text) are kg ha⁻¹ year⁻¹.

Plant uptake has perhaps been overestimated for this ecosystem as the above-ground pools are smaller than those in savanna ecosystems (Scholes and Walker, 1993). Approximately half of the S stored in above-ground biomass pools is released into the atmosphere during grassland fires which occur at a frequency varying between annual and triennial. Maximum modelled S deposition, released via

biomass burning as well as fossil fuel combustion, was modelled to be a maximum of $>35 \text{ kg S ha}^{-1} \text{ year}^{-1}$ (Blight *et al.*, 2009). Sulfur deposition, as SO_4^{2-} , would contribute to the inorganic pool in the surface soil.

Nitrogen in these grasslands is predominantly stored in organic form in the surface soils where microbial biomass constitutes approximately 4% of the organic N pool (Figure 5.9). Up to $47.5 \text{ kg N ha}^{-1}$ is mineralised from this organic pool annually as NH_4^+ and $80.5 \text{ kg NH}_4^+ \text{ ha}^{-1} \text{ year}^{-1}$ of the ammonium pool is oxidised to nitrate. Even though the nitrification rate is higher than that ammonification rate, the ammonium pool ($120 \text{ kg NH}_4^+ \text{ ha}^{-1}$) remains larger than the nitrate pool ($68.5 \text{ kg NO}_3^- \text{ ha}^{-1}$). Mineralisation exceeds immobilisation by a maximum of 1.6-times. Plant uptake from both inorganic N pools (estimated by Scholes *et al.*, 2003a to be $41 \text{ kg ha}^{-1} \text{ year}^{-1}$) is incorporated into the above-ground biomass pools (0.363% N in leaf tissue, 0.103% N in root tissue and 0.660% N in litter), where the living biomass (7.3 kg N ha^{-1}) is larger than the litter pool (4.3 kg N ha^{-1}). Losses of N through fire in these grasslands are large ($8.7 \text{ kg N ha}^{-1} \text{ year}^{-1}$) relative to the small biomass pool. This estimation of loss is based on the loss of 75% of N stored in the above-ground pools calculated for savanna ecosystems where 80% of the fuel loads are grasses (Scholes *et al.*, 2003a). Deposition of N through wet and dry deposition processes, where the sources of atmospheric N include fossil fuel combustion and biomass burning, returns approximately all the N lost during fires ($9 \text{ kg N ha}^{-1} \text{ year}^{-1}$), some of which is returned to the inorganic pools, predominantly NO_3^- through deposition processes.

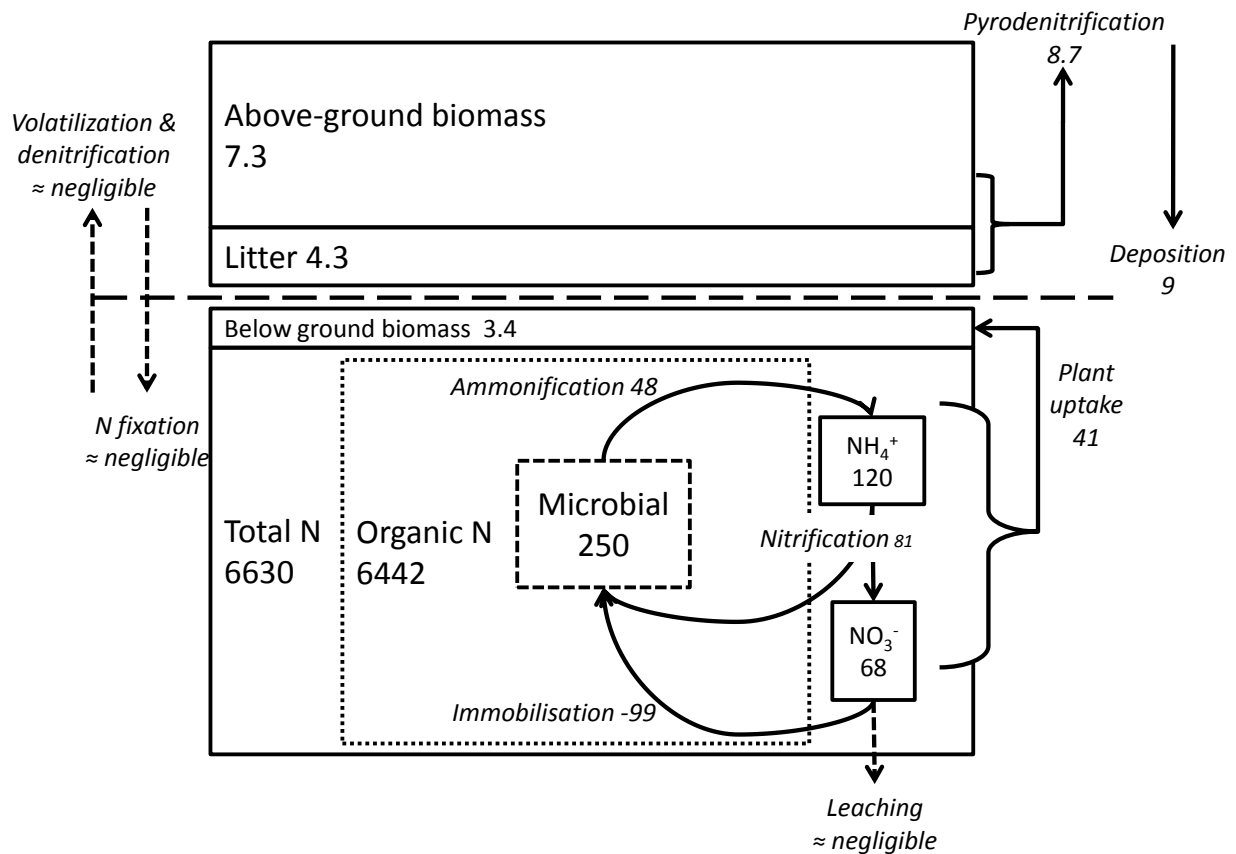


Figure 5.9: The nitrogen cycle in Highveld grasslands of South Africa. The units for pools are kg ha⁻¹ and the units for fluxes (in *italic text*) are kg ha⁻¹ year⁻¹.

5.4 Discussion

The study of SO₄²⁻ and N mineralisation in the Highveld grasslands has allowed interpretation of the data set at various levels. Firstly, the data provided some understanding of seasonal variations and controls of mineralisation rates. Since soil physical characteristics were found to be important controllers, it was possible to scale up the data to an annual flux categorised by the land type allowing interpretation at a larger spatial scale. These annual fluxes were then placed in context of the pools and fluxes of S and N within the grassland ecosystems.

5.4.1 Seasonality and controls of net SO₄²⁻ and N mineralisation

While the *in situ* incubation technique is commonly used to determine net N mineralisation rates, the current study is, as far as the authors are aware, the first use of the technique for SO₄²⁻ mineralisation. An additional advantage of the method is that net SO₄²⁻ and N mineralisation can be determined simultaneously. Since immobilisation, mobilisation (as depolymerisation) and mineralisation occur

simultaneously with offset peaks (Edwards, 1998); the *in situ* core technique allows the measurement of the net effect of these processes. The use of laboratory incubations of soil is the common method used for assessing potential SO_4^{2-} mineralisation (Pirela and Tabatabai, 1988; Ghani *et al.*, 1991; Knights *et al.*, 2001; Riffaldi *et al.*, 2006). Pamidi *et al.* (2001) compared an open incubation method and a plant uptake experiment to quantify S mineralisation and found that the open incubation method did not accurately simulate plant uptake as postulated in earlier studies. This suggests that the laboratory studies possibly under estimate field mineralisation rates and improvements could be made using the *in situ* incubation technique.

The pattern of net SO_4^{2-} mineralisation rates in the perennial Highveld grasslands showed similar seasonal patterns to the net N mineralisation rates as found in annual grasslands by Jones and Woodmansee (1979). Seasonal change in mineralisation rates can be especially useful to understand S and N availability in semi-arid ecosystems where decomposition, and therefore mineralisation are linked to climate resulting in pulses of nutrient release during wet periods (Scholes and Walker, 1993; Snyman and du Preez, 2005).

The range of net SO_4^{2-} mineralisation rates recorded for these Highveld grasslands was broader than those in other studies (ranges from -0.66 to $1.09 \mu\text{g SO}_4^{2-} \text{g}^{-1} \text{soil day}^{-1}$) with peaks in the warmer summer months. Laboratory incubation studies of S mineralisation in grassland soils from Iowa (USA) (Pirela and Tabatabai, 1988), New Zealand (Ghani *et al.*, 1991) and Italy (Riffaldi *et al.*, 2006) showed a similar range of S mineralisation (between 0.04 and $1.63 \mu\text{g SO}_4^{2-} \text{g}^{-1} \text{soil day}^{-1}$). Apart from the influence of incubation temperature and moisture, Riffaldi *et al.* (2006) found that soils with high clay-plus-silt content had lower S mineralisation rates. However, Highveld grassland soils with the highest clay-plus-silt contents, the Ea soil pattern (22.9%), showed the highest mean annual mineralisation rates (Figure 5.6). Sulfate mineralisation rates between 0.010 and $0.057 \mu\text{g SO}_4^{2-} \text{g}^{-1} \text{soil day}^{-1}$ (du Toit and du Preez, 1995) were higher in cultivated relative to undisturbed soils, of South African grasslands. In contrast, potential mineralisable N was lower in the cultivated soils compared with the matched undisturbed soils (du Toit and du Preez, 1995).

Nitrogen mineralisation is well studied in grasslands of the world using both laboratory incubation studies to calculate potential N mineralisation (Abbasi *et al.*, 2001; Gleeson *et al.*, 2008) as well as the *in situ* core incubation technique to calculate net N mineralisation (Blair, 1997; Yahdjian and Sala, 2008; Zhang *et al.*, 2008; Stock *et al.*, 2010) and $^{15/14}\text{N}$ isotope studies to measure gross mineralisation (Holst *et al.*, 2007). The daily net N mineralisation rates measured in the Highveld grasslands were similar to N mineralisation rates determined by laboratory incubations of Pakistani grassland soils (0.15 to $1.50 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ Abbasi *et al.* (2001) and South African grassland and savanna soils (0.08 to $0.46 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ – du Preez and du Toit, 1995). Maximum net N mineralisation rates (-0.01 to $1.10 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$) measured by *in situ* core method in Mongolian grasslands (Zhang *et al.*, 2008) were also comparable to the rates in the Highveld grasslands. However, Highveld grassland mineralisation rates are higher than those (-0.03 to $0.04 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$) from Patagonian grasslands (Yahdjian and Sala, 2008).

The potential N mineralisation rates determined by Fynn *et al.* (2003) were almost four-times higher than those measured in the current study in the Highveld grasslands; these differences are likely related to the location of the grasslands studied by Fynn *et al.* (2003) that receive higher annual precipitation (790 mm year^{-1}) and that the potential mineralisation rates were measured in the top 100 mm of the soil which has been shown to have more active microbial populations.

The seasonal patterns found in the mineralisation of SO_4^{2-} and N in the Highveld grasslands have highlighted the impact of soil water on microbial activity. While N release was more rapid – within days of increased soil water content – and persisted as elevated rates for approximately two months, the SO_4^{2-} release was slower. Increased ambient temperatures, prior to the spring rain, also resulted in increased mineralisation rates. In many of the studies cited above, the *in situ* core method for assessing net N mineralisation rates was only used during the active growing season and so an annual pattern is difficult to predict. The pattern of increased mineralisation rates in the warmer summers, or growing season, was comparable between the published studies and the Highveld grasslands, usually showing higher rates near the beginning of summer. The influence of fire on the increased rates of mineralisation at specific sites (sites 1, 3 and 9) in the Highveld

grasslands cannot be discounted and may explain the site and month differences at highlighted by the post-hoc LSD analyses. The release of nutrients from the standing litter laying and enhanced conditions for mineralisation as a result of fire causing soil temperatures to increase due to decreased cover, were proposed as mechanisms for peak mineralisation rates after fires in South African grassland fires (Tainton and Mentis, 1984). The productivity of structurally similar grasslands in South Africa (Kwa-Zulu Natal) and North America (Kansas) was compared in a study by Knapp *et al.* (2006) and it was found that productivity in North American grasslands was largely controlled by temperature, while soil moisture mainly controlled productivity in the South African grasslands. Stewart *et al.* (1983) proposed that in a similar pattern, nutrient cycling in temperate grasslands was controlled by temperature and in semi-arid and sub-tropical grasslands by moisture. Similar responses have been found for nutrient cycling in South African savannas (Scholes and Walker, 1993; Scholes *et al.*, 2003a; Scholes *et al.*, 2003b).

5.4.2 Annual amounts of SO_4^{2-} and N released

The maximum net sulfate mineralised in Highveld grassland soils accounted for 5.4% of the total S and 6.4% of the organic S pools, which is within the range of rates of other S mineralisation studies; in Australian grasslands (Nguyen and Goh, 1994) and Iowan grassland soils (Pirela and Tabatabai, 1988) and other South African grassland soils (du Toit and du Preez, 1995). Laboratory incubation studies use SO_4^{2-} mineralised during the incubation period to calculate the annual potential SO_4^{2-} mineralised. It is proposed that using the *in situ* incubation technique minimizes the assumptions when scaling short-term laboratory incubations to annual mineralisation.

The range of N mineralised annually in the Highveld grasslands of South Africa, between 1.7 and 161.6 kg N ha⁻¹ year⁻¹, is similar to those in many grassland systems around the world; for example in Kansas (Blair, 1997), a grassland steppe ecosystem in Inner Mongolia, China (Zhang *et al.*, 2008) and for Yellowstone National Park (Frank *et al.*, 2000). The wide range of N mineralisation rates in Highveld grassland soils can be explained by the intentional selection of the sampling sites to capture the major land types by Fey and Guy (1993). Site effects were not statistically significant, for individual sites across the sampling months, for

either S or N. However statistically significant differences were evident, for SO_4^{2-} , when monthly mineralisation rates were converted to an annual amount mineralised and grouped by land type. This suggests that, in the Highveld grasslands, with similar topography, climate and vegetation, mineralisation of SO_4^{2-} and N is controlled on a monthly basis by prevailing climatic conditions. However over an annual cycle the soil physical and chemical properties are controllers of the amount of SO_4^{2-} and N released. In other studies the influence of soil properties on mineralisation rates is mixed. In a 10-week incubation study soil properties such as texture and pH were not found to influence S mineralisation in Tuscan soils; however, initial organic C and N contents were influential (Riffaldi *et al.*, 2006). du Toit and du Preez (du Toit and du Preez, 1995) found that in addition to organic C, total N and the fine-silt-plus-clay content influenced S mineralisation rates in South African grassland soils. An investigation of S mineralisation in relation to N and C in French soils found, after a stepwise multiple regression, that organic C, pH, initial SO_4^{2-} and clay content could be used in an equation to predict S mineralisation with good accuracy ($R^2=0.84$) (Niknahad Gharmakher *et al.*, 2009). The influence of organic C on the rate of mineralisation is common across most mineralisation studies with local differences in the relative importance of other soil properties and climate.

5.4.3 S and N cycling in grasslands

Nitrogen budgets exist for other South African biomes, notably savannas (Scholes and Walker, 1993; Scholes *et al.*, 2003a) and the fynbos (Stock and Allsopp, 1992). The N budget proposed in Figure 5.9 appears to be the first attempt for the grassland biome. The S cycle, which also appears to be novel for the biome, highlights the accretion of S in the total soil pool because inorganic inputs are higher than plant demand and minor losses to deep soil horizons by leaching are likely as seasonal flushes. Losses of SO_4^{2-} via leaching in Californian soils only occurred where mean annual precipitation exceeded 630 mm year^{-1} (Jones and Woodmansee, 1979). The Highveld grasslands receive, on average, between 600 and 700 mm of rainfall annually near the escarpment in the east and as little as 300 mm year^{-1} in the west (Middleton and Bailey, 2009). However, the evaporative demand across the grassland biome of South Africa ranges between $1400 \text{ mm year}^{-1}$ in the east and $2000 \text{ mm year}^{-1}$ in the west (Middleton and Bailey, 2009). Under these conditions of water deficit, it is likely that leaching of sulfate

would only occur during short periods of heavy rain especially early in the growing season when plant demand is low. The release of S in gaseous form to the atmosphere via anaerobic processes is expected to be minimal because of the water deficit; however, there may be occasions of temporary saturation of the surface soils and anaerobic conditions suitable for SO_4^{2-} reduction. Jones and Woodmansee (1979) suggested that S losses as H_2S are unlikely even from water-logged rangeland soils and that more often SO_4^{2-} is reduced to insoluble sulfides, such as iron sulfide (FeS), under anaerobic conditions.

Because plant uptake is less than 20% of the deposited and mineralised SO_4^{2-} and because leaching of SO_4^{2-} is limited to short periods, it appears as though these grasslands are not S limited. The accretion of S in the soil pools which could have long-term implications on the anion-cation balance of the soils. The soils of the area that are rich in clay have available capacity to neutralise increased anion concentrations. The accretion of SO_4^{2-} through association with base cations or through adsorption chemistry will reduce the capacity of the soil to neutralise other acidic inputs. This is cause for concern especially in the sandier soils that have lower buffering capacity and are at risk of further acidification and subsequent consequences such as altered plant community structure. In contrast, it is evident that the Highveld grasslands are N limited because the pool of inorganic N (available through atmospheric deposition and mineralisation processes, $170.0 \text{ kg ha}^{-1} \text{ year}^{-1}$) is approximately equal to the sum of plant uptake, immobilisation by microbial communities and losses of plant and litter material in fires. Due to the small sizes of the above- and below-ground biomass pools, the uptake rate may be an overestimate. These grasslands have larger total ecosystem N stocks relative to neighbouring savannas (Scholes and Walker, 1993; Scholes *et al.*, 2003a). The differences in total ecosystem N stocks are mainly due to the grassland organic N pool that is nearly double the size of the savanna pool, although the above-ground biomass pools are larger in savannas because of the woody plant component storing up to 190 kg N ha^{-1} (Scholes and Walker, 1993). In compiling the S and N cycles of the Highveld grasslands, it was necessary to consult published results for the savanna biome. This highlights the lack of adequate biogeochemical characterisation of the Highveld grasslands. The large differences in the total ecosystem S and N stocks between the two biomes also suggests that the plant community differences

as well as differences in functional drivers such as climate (for example heavy frost in winter) and more frequent fires, are likely to affect the biogeochemical functioning of these grasslands in very different ways to savannas. While there is value in the S and N cycles proposed in this report, a need exists for more detailed research in these under protected and diverse grasslands. A large proportion of the Highveld grasslands are impacted by increased urbanisation, agriculture, mining as well as deposition of S and N compounds associated with these activities. There is already enough evidence to suggest that S deposition to these grasslands is resulting in accretion of S in the soils. However, in spite of N deposition, these grasslands are still N limited.

5.4.4 Thesis linkage

The S and N cycles presented in this chapter further the understanding of the functioning of South African Highveld grasslands, especially those receiving atmospheric S and N deposition. From these cycles it is suggested that the natural grasslands are conservative with regards to S and N because losses are assumed to be negligible. While the conservation of S and N in the soils and vegetation of the Highveld grasslands is proposed, modelling studies, in contrast, suggest that atmospheric S deposition would increase the concentration of dissolved salts in surface waters draining Highveld grasslands (Taviv and Herold, 1989; Herold and Gorgens, 1991; Herold *et al.*, 2001). Therefore investigating the change of water quality over a period of time would help understand how the soil processes and water are coupled. Chapter 6 investigates water quality in rivers draining the Highveld grasslands between 1991 and 2008 in order to comment on the influence that deposition of S and N has on water quality and if the soils of the Highveld grasslands are conservative with respect to S and N inputs.

CHAPTER 6: CHANGES IN WATER CHEMISTRY IN THE VAAL DAM CATCHMENT BETWEEN 1991 AND 2008

In Chapter 4 it was demonstrated that pH and ANC of sandier soils, especially those with clay content less than 4% near the eastern and southern boundaries of the study area, have decreased over a 16-year time frame. Although soil acidity has increased, net SO_4^{2-} and N mineralisation rates were within the range exhibited by grasslands globally (Chapter 5). The inorganic products of mineralisation – SO_4^{2-} , NO_3^- and NH_4^+ - could be susceptible to leaching when soil moisture conditions are suitable. Leaching losses of S and N were assumed to be negligible based on available evidence (Chapter 5). Leaching of S and N compounds of into fresh water systems, after high levels of atmospheric deposition, has been of global interest because of acidification and subsequent ecosystem impacts. In South African fresh water systems, authors have raised concerns that deteriorating water quality, as increased dissolved salt, SO_4^{2-} and NO_3^- concentrations, in surface waters of the Vaal Dam catchment (38 500 km² of Highveld grassland) may be a result of atmospheric S and N deposition (Taviv and Herold, 1989; Fey and Guy, 1993; Herold *et al.*, 2001). In this next chapter, the concentrations of ten water quality variables at five sites in the Vaal Dam catchment were assessed using multivariate statistical methods. The time frame analysed matched the time frame of soil sampling; from the original assessment by Fey and Guy (1993) in 1991 until the re-assessment in 2007 and the mineralisation study in 2008. Water purification (regulatory) and the provision of fresh water are the ecosystem services of concern in this chapter. This chapter is in preparation for submission to Water SA, with the title, authors and affiliations as described below. In the preparation of this manuscript, I was responsible for the collation and preparation of data, the canonical correspondence analysis (CCA) analysis, the initial data interpretation and the draft versions of the text and graphics. The ANCOVA and trend analyses were contracted out to Mr Joseph Mathai of DMSA and his contribution will be acknowledged in the manuscript submitted to the journal. Further data interpretation and comments on manuscript drafts was provided by Prof. Scholes.

Using multivariate statistical analysis to assess changes in water chemistry in the Vaal Dam catchment between 1991 and 2008.

Theresa L. Bird* and Mary C. Scholes

School of Animal, Plant and Environmental Sciences, University of the Witwatersrand,
Johannesburg. Private Bag x3, Wits, 2050, South Africa

ABSTRACT

Multivariate statistical analysis was used to investigate change in water chemistry at five river sites in the Vaal Dam catchment, draining the Highveld grasslands. These grasslands receive more than $8 \text{ kg S ha}^{-1} \text{ year}^{-1}$ and $6 \text{ kg N ha}^{-1} \text{ year}^{-1}$ via atmospheric deposition. It was hypothesised that between 1991 and 2008 concentrations of dissolved mineral salts, sulfate, nitrate and ammonium would increase as a result of the S and N deposition received. Significant spatial differences were found, by analysis of covariance, between sites within the catchment. Canonical correspondence analysis (CCA) showed that the environmental variables used in the analysis, discharge and month of sampling, explained a small proportion of the total variance in the data set - <10% at each site. However, the total data set variance, explained by the four hypothetical axes generated by the CCA was >93% for all five sites. Sulfate, nitrate-plus-nitrite, ammonium and phosphate concentrations increased at one site each, between 1991 and 2008. Over the same time frame, acid neutralising capacity was decreased significantly at one of the five river sites. The concentrations of the ions analysed, with rare exception, were within the national guidelines between 1991 and 2008. The N and S concentrations of the five selected river sites within the Vaal Dam catchment have not increased over time.

6.1 Introduction

The Vaal Dam and barrage supply Gauteng, and beyond, with water for domestic and industrial use, where the catchment for these reservoirs covers the Highveld grasslands. Sulfur and N are deposited in the catchment as a result of the clustering of coal-fired power stations and other industrial activities. Atmospheric deposition ranges between 1 and $>35 \text{ kg S ha}^{-1} \text{ year}^{-1}$ and 1 and $>15 \text{ kg N ha}^{-1} \text{ year}^{-1}$ over the Highveld generally, with sites near stationary point sources receiving more than double these amounts (Blight *et al.*, 2009; Collett *et al.*,

2010). These quantities are comparable with industrialised sites elsewhere in the world (Dovland and Pederson, 1996: 5 to 15 kg N ha⁻¹ year⁻¹; and more recently by Dentener *et al.*, 2006: 10 to 70 kg S ha⁻¹ year⁻¹) where the impacts have resulted in disturbed ecosystem services (for example the review of the eastern USA by Lovett *et al.*, 2009). Disturbances to ecosystem functioning occur after deposition of S and N compounds and include acidification of soils and waters affecting the chemical cycling processes and can be harmful to biota within these ecosystems (Wellburn, 1994). International studies with regards to impacts on aquatic systems have investigated changes in concentrations of S, N, Al, alkalinity, base cations, and changes in pH (Baron *et al.*, 2000; Evans *et al.*, 2001; Kernan and Helliwell, 2001; Wright *et al.*, 2001; Cooper, 2005; Kowalik *et al.*, 2007; Baron *et al.*, 2009).

The levels of deposition to the Highveld generally, and the Vaal Dam catchment specifically, prompted concern that the catchment would show elevated salt concentrations as a result of S deposition and inputs of S and other ions transferred from soil storage pools into rivers via runoff (Taviv and Herold, 1989). Elevated salt concentrations, have the potential to reduce irrigated crop production (van Rensburg *et al.*, 2008) and cause eutrophication (Roos and Pieterse, 1995). The economic cost of purification of salt-enriched water to industrial requirements is an additional concern (Econ., 2000). As a result of abstraction for domestic, industrial and irrigation use, salt concentrations are already problematic in the middle and lower Vaal River system (below the Vaal Dam) where water is abstracted for irrigated crop agriculture (Braune and Rogers, 1987; Roos and Pieterse, 1995; van Rensburg *et al.*, 2008). Increased salt concentrations as a result of atmospheric S and N deposition may be impacting the Vaal River system and ecosystem services further downstream than where the deposition is received.

Subsequent to the concern raised by the modelling study of Taviv and Herold (1989), Fey and Guy (1993) investigated the capacity of the major soil types of the Vaal Dam catchment to retain SO₄²⁻. Their methods included the textural and chemical characterisation of the soils, as well as three methods for assessing SO₄²⁻ adsorption. They found that the retention capacity over most of the catchment was low (Fey and Guy, 1993). More recent assessment showed that the soils of the central Highveld grasslands, which also form the central region of the Vaal Dam catchment, are well buffered against deposition inputs, however, soils on the eastern

and southern boundaries of the Highveld grasslands may be more sensitive (Chapter 4).

This study quantified the changes of water quality variables at five sites in the Vaal Dam catchment between 1991 (when Fey and Guy sampled) and 2008, using multivariate statistics to assess the impact of S and N deposition on water chemistry.

6.2 Materials and methods

The South African Department of Water Affairs (DWA) water quality network and database was accessed for the long-term record of the regularly measured major chemical compounds. Results of the analysis of water samples are accessible via the Water Management System (WMS) (<http://www.dwaf.gov.za/Hydrology/CGI-BIN/HIS/CGIHis.exe/Station> and <http://www.dwa.gov.za/iwqs/wms/data/000key.asp>). Five river water quality monitoring points in the Upper Vaal Management Area were selected for the current investigation. Four of the five sites were located in the C1 secondary catchment (90586, 90591, 90599 and 90603) and one site in the C8 secondary catchment (90863) (Figure 3.1).

The criteria for selection of water quality monitoring points in this study were sampling frequency, duration and location. The sites were required to have regular sampling frequency during the period January 1991 to early 2008. Although weekly or fortnightly sampling was preferred, monthly sampling records were considered sufficient over short time periods of less than one year. Two sites (90599 and 90603) had shorter records as the sampling points were only installed in 1995. However, sampling frequency met the selection criteria and the two sites were included in the study. Water quality monitoring points were selected based on to their proximity to sites where soil sampling occurred (in 1991 and 2007) to examine the impact of S and N deposition on soil chemistry (Chapter 4). Dissolved major salts (DMS; used as a surrogate of total dissolved salts), phosphate (PO_4^{2-}), sulfate (SO_4^{2-}), nitrate-plus-nitrite ($\text{NO}_3^- + \text{NO}_2^-$), ammonium (NH_4^+) and base cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) were analysed for changes at each of the five sites using statistical analyses. For chemical variables, monthly median concentrations were calculated. Monthly discharge volumes were used as a covariate to the chemical variables to account for seasonal differences in concentrations. Wet season months were October to March and dry season months were April to September every year. Because monthly discharge is

not normally distributed, the natural logarithm (ln(discharge)) was used in all statistical procedures. The use of monthly median concentrations and monthly discharge was recommended by Malan *et al.* (2003) for integrating water quality and quantity in modelling in-stream flow requirements to meet biological community demands.

Acid neutralising capacity (ANC) of water was calculated according to the charge-balance equation (using molar concentrations) of Reuss (1991) (equation 5). ANC is an indicator of the capacity of water to buffer against incoming acidity and is frequently used to assess for the impact of acidic deposition on soils and fresh water. Chloride (Cl⁻) concentrations were accessed from the database to calculate ANC.

$$ANC \text{ (meq l}^{-1}\text{)} = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^{+}] + [K^{+}] - [NO_3^{-}] - [Cl^{-}] - 2[SO_4^{2-}] \dots [5]$$

Statistical analysis was used to examine the water quality at the five sites for changes over a 17-year period. During this period the mean ($\pm$ standard error) quantities of S and N deposited to the catchment were $339 \pm 87 \text{ kg S ha}^{-1}$ and $85 \pm 7 \text{ kg N ha}^{-1}$ (Chapter 3). An analysis of covariance (ANCOVA) was used to test for site (spatial) differences in water quality. To assess for differences between sites, the ANCOVA compares the regression line that describes the relationship between the covariate (ln(discharge)) and a chemical variable of interest at two different sites in a pair-wise comparison. The analyses were conducted using SAS version 9.1 (<http://www.sas.com/technologies/analytics/statistics/stat/index.html>).

The relationship between independent (environmental) variables (calendar year of sampling, month of sampling, wet (October to March) or dry season (April to September) and ln(discharge)) and the water quality (chemical) variables were also investigated using the constrained ordination technique of canonical correspondence analysis (CCA) (Lepš and Šmilauer, 2003). The CCA generates hypothetical axes from the environmental variables to represent theoretical environmental gradients along which the water chemical variables are plotted. In the CCA procedure, cases of rare concentration values were down-weighted and the analysis was evaluated using a Monte-Carlo permutation test (9999 permutations). The CCA procedure was conducted using Canoco for Windows 4.55 (ter Braak and Šmilauer, 2002).

Trend analyses were conducted for all sites to test for significant changes in concentrations (temporal). Trend analysis is based on the sign test, where the data set is split in half and each sample in the first half of the data set is compared with the matching sample in the second half of the data set. The number of occasions where the second sample was larger than the first sample were summed and a probability score for the trend was calculated (Cox and Stuart, 1955). Trend analyses were conducted using SAS version 9.1.

6.3 Results

Testing for differences between sites using an ANCOVA procedure, with the natural log of mean monthly discharge ($\ln(\text{discharge})$) as the covariate to the median monthly concentrations of chemical variables of interest, showed that nearly all sites varied significantly from all others for most variables (Table 6.1). Sites 90586 and 90591 were statistically similar for ANC and Na; and sites 90591, 90599 and 90603 were statistically similar for NH_4^+ . Because the ANCOVA showed a high degree of spatial difference, the sites were considered independent in further analyses.

The largest mean monthly discharge, irrespective of season, was measured at site 90599 (Table 6.1). This site also showed the largest variance between monthly discharge in the wet and dry months. Site 90603 showed the smallest mean monthly discharge irrespective of season as well as smallest variance between wet and dry season flow. The concentration of chemical variables was higher in the dry season months at all sites, except site 90599 where wet season concentrations were higher. Concentrations of SO_4^{2-} , $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ and the base cations (Na^+ , Ca^{2+} , K^+) were highest at site 90586 during the dry season months (Table 6.1). The ANC was lowest at site 90863 during wet months and at site 90599 during dry months.

Sulfate and Na^+ contributed the most to the overall salt balance (Table 6.1) with concentrations greater than 10 mg l^{-1} . Ammonium and $\text{NO}_3^- + \text{NO}_2^-$ were found in concentrations lower than 5 mg l^{-1} . Dissolved major salt concentrations range between 150 and 500 mg l^{-1} where the chemical variables examined contributed approximately 40% of the salt balance. The salts contributing to DMS (Cl^- , CaCO_3 (calcium carbonate), and F^- (fluoride) were not investigated in this study.

Table 6.1: Wet and dry season monthly discharge ($\text{m}^3 \times 10^6$) and mean chemical variable concentrations (mg l^{-1} , except for ANC – meq l^{-1}) at five river sites in the Vaal Dam catchment between 1991 and 2008. All sites were statistically significantly different ($\alpha < 0.05$) unless marked (grey filled cells).

Site	90586		90591		90599		90603		90863	
Season	WET	DRY	WET	DRY	WET	DRY	WET	DRY	WET	DRY
Monthly discharge	12.92 ± 2.21	1.78 ± 0.22	19.13 ± 3.70	3.55 ± 0.92	83.50 ± 20.13	8.19 ± 2.20	6.16 ± 0.75	1.36 ± 0.28	15.63 ± 1.87	3.05 ± 0.34
SO₄²⁻	69.66 ± 2.24	82.70 ± 4.90	56.23 ± 2.26	77.32 ± 3.73	27.25 ± 0.81	25.73 ± 0.47	49.04 ± 1.96	67.49 ± 2.84	12.01 ± 0.42	13.90 ± 1.07
NO₃+NO₂	2.53 ± 0.17	3.23 ± 0.13	0.97 ± 0.12	0.49 ± 0.08	0.22 ± 0.05	0.15 ± 0.01	0.22 ± 0.05	0.38 ± 0.07	0.90 ± 0.06	2.71 ± 0.15
NH₄⁺	0.46 ± 0.09	1.15 ± 0.16	0.05 ± 0.01	0.04 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	0.06 ± 0.03	0.05 ± 0.01	0.17 ± 0.03	0.29 ± 0.04
ANC	4.85 ± 0.16	5.73 ± 0.10	4.21 ± 0.17	5.84 ± 0.12	2.74 ± 0.08	2.75 ± 0.05	5.42 ± 0.17	6.92 ± 0.14	2.03 ± 0.78	3.31 ± 0.08
DMS	405.89 ± 9.01	500.53 ± 9.49	345.87 ± 12.25	475.27 ± 9.47	185.32 ± 5.47	178.61 ± 2.38	359.85 ± 11.98	470.50 ± 10.51	128.20 ± 4.33	197.57 ± 4.89
Mg	19.39 ± 0.37	22.27 ± 0.41	16.65 ± 0.56	22.73 ± 0.40	11.23 ± 0.25	10.97 ± 0.19	21.00 ± 0.62	27.42 ± 0.63	5.46 ± 0.18	8.68 ± 0.22
Na	46.27 ± 1.44	61.17 ± 1.80	39.34 ± 2.05	57.72 ± 1.75	13.36 ± 0.75	12.24 ± 0.27	31.45 ± 2.17	46.16 ± 1.97	9.15 ± 0.47	15.51 ± 0.59
Ca	35.36 ± 0.71	42.24 ± 0.74	29.57 ± 0.99	41.07 ± 0.74	16.92 ± 0.47	16.59 ± 0.23	32.64 ± 0.77	41.45 ± 0.76	14.25 ± 0.46	21.58 ± 0.53
K	7.56 ± 0.19	9.50 ± 0.26	6.79 ± 0.19	7.93 ± 0.19	3.29 ± 0.10	3.09 ± 0.03	5.68 ± 0.26	6.68 ± 0.25	2.46 ± 0.13	3.58 ± 0.16
PO₄²⁻	0.77 ± 0.06	1.38 ± 0.06	0.37 ± 0.04	0.36 ± 0.03	0.05 ± 0.01	0.03 ± 0.00	0.26 ± 0.04	0.33 ± 0.04	0.21 ± 0.03	0.52 ± 0.04

The ordination biplots generated by CCA, to investigate the influence of the season and $\ln(\text{discharge})$ on the concentration of chemical species, showed no distinct patterns for the five river sampling sites (biplots not shown). Eigenvalues, from the CCA, explain how much of the variance is accounted for by the data set used and suggest that the environmental variables used, only account for a small proportion of variance in the data set (6.3% at site 90586; 4.2% at site 90591; 1.1% at site 90599; 3.1% at site 90603; and 2.7% at site 90863). However, the cumulative variance of the first two (of four) synthetic axes exceeded 93.0% at all five sites. Thus, environmental variables and chemical variables not analysed (such as pH, water temperature and hardness) may have also influenced water chemistry. In spite of the exclusion of these variables in this analysis, the synthetic axes generated in the CCA, suitably account for the variance in this data set (chemical species and independent variables).

Changes in water quality over time were tested using trend analysis (Table 6.2). The hypotheses tested were that, if the catchments drained by the monitoring points were impacted by S and N deposition, the SO_4^{2-} , $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ and DMS concentrations would show an increasing trend over time. Conversely, the base cation concentrations and ANC values would show a decreasing trend. However, NH_4^+ , $\text{NO}_3^- + \text{NO}_2^-$ and SO_4^{2-} concentrations increased at only one monitoring site each (three different sites). Decreasing concentration trends for Mg^{2+} , Ca^{2+} and Na^+ were found at one site each where Mg^{2+} and Ca^{2+} both decreased at the same site (90603). The hypotheses were contradicted at some sites; for example NH_4^+ , $\text{NO}_3^- + \text{NO}_2^-$ and SO_4^{2-} concentrations decreased at two sites. Potassium concentrations increased at 3 of the 5 sites and none of the sites show the hypothesised decrease in K^+ concentrations. No significant trends in DMS concentrations were detected.

Table 6.2: Statistically significant trends in the change of chemical variables at five sites in the Vaal Dam catchment. Where the trends confirmed the hypotheses, p-values are in black; where trends confirmed the inverse hypothesis, p-values are in blue. Trend analysis conducted on median monthly concentrations (mg l^{-1}) for all variables except ANC which is based on median monthly charge balance (meq l^{-1}).

Chemical variable	90586 (n=105)	90591 (n=104)	90599 (n=76)	90603 (n=78)	90863 (n=108)
SO_4^{2-}	p=0.039		p=0.007	p<0.001	
$\text{NO}_3^- + \text{NO}_2^-$			p=0.040	p=0.001	
NH_4^+	p<0.001	p=0.004	p<0.001		
ANC	p=0.009			p=0.015	
DMS					
Mg^{2+}	p=0.004			p=0.008	p=0.020
Na^+			p=0.003		
Ca^{2+}				p=0.004	p=0.003
K^+	p=0.025		p<0.001	p<0.001	
PO_4^{2-}	p=0.025	p<0.001		p<0.001	

Seasonal fluctuations in chemical concentrations are evident in time-series plots (Figure 6.1), where the concentration peaks occur during the dry months. Time-series plots for the water quality variables were compared with South African drinking water quality guidelines (Department of Water Affairs and Forestry, 1996). Sulfate at all sites has remained consistently below the conservative 200 mg l⁻¹ guideline since 1997 with one recent exceedance of target at site 90586 (Figure 6.1a). Concentrations of SO₄²⁻ for site 90599 always fell below 40 mg l⁻¹ and at site 90863 always below 120 mg l⁻¹. Nitrogen species (Figure 6.1b and c) rarely peaked above the respective target concentrations (6 mg l⁻¹ for NO₃⁻+NO₂⁻ and 1 mg l⁻¹ for NH₄⁺). Site 90586 showed the most number of peaks above the target level for both N species with increasing frequency of peaks above the NH₄⁺ target guidelines from 2002. Concentrations of NH₄⁺ for Sites 90591, 90599 and 90603 mostly fell below 0.2 mg l⁻¹ and always below 2 mg l⁻¹.

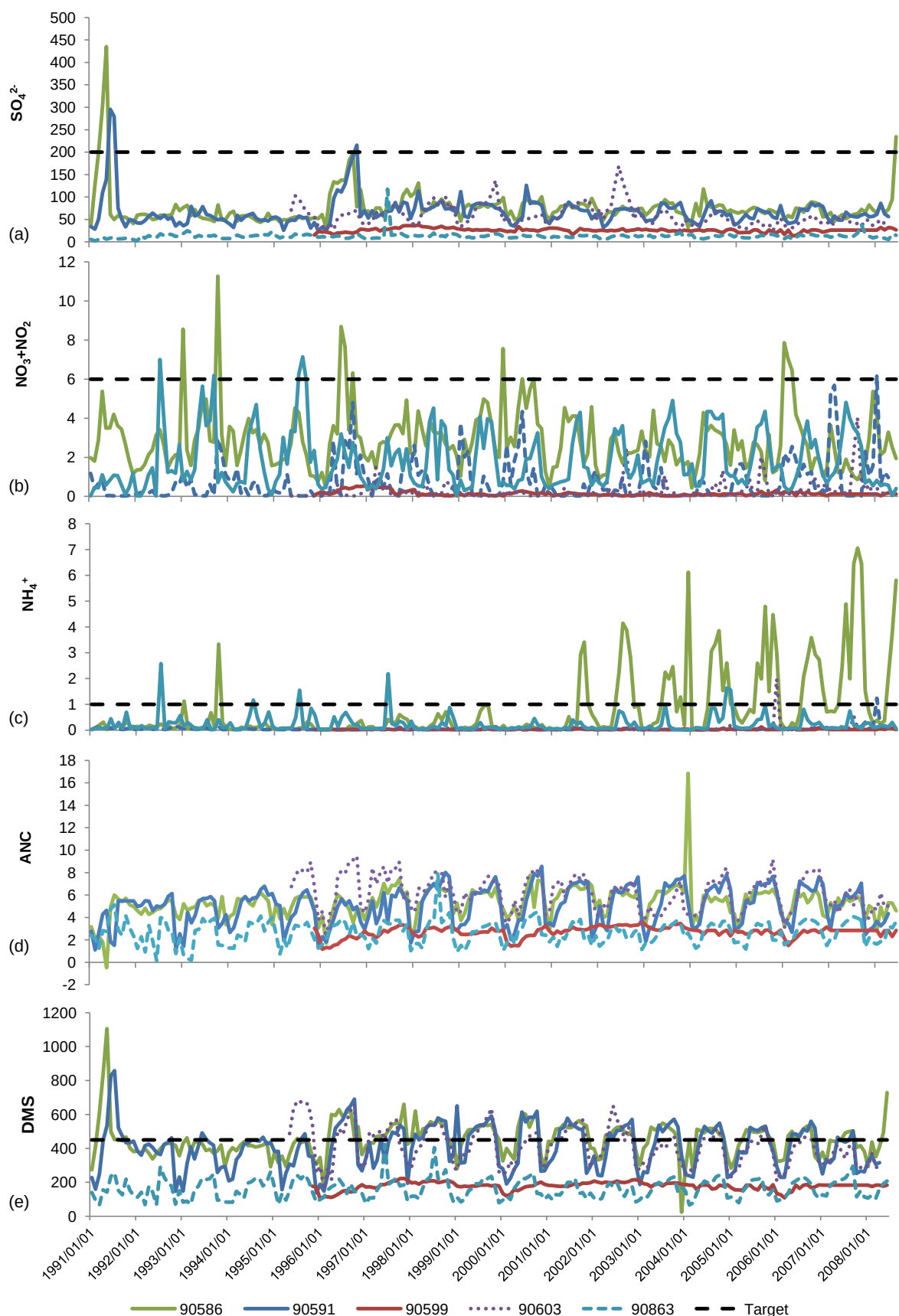


Figure 6.1: Time series plots of water chemical variables at five sites in the Vaal Dam catchment between 1991 and 2008. Monthly median concentrations (mg l⁻¹) are presented for (a) SO_4^{2-} (b) $\text{NO}_3 + \text{NO}_2$ (c) NH_4^+ (d) ANC (meq l⁻¹) and (e) DMS. The dashed 'Target' line is the National Drinking Water quality guideline (Department of Water Affairs and Forestry, 1996).

6.4 Discussion

It was expected that if the soils in the Vaal Dam catchment were showing signs of impact as a result of S and N deposition it would be evident by increases in the inorganic S and N concentrations of water. This was only found at two sites (90596 for NH_4^+ and SO_4^{2-} and 90599 for $\text{NO}_3^- + \text{NO}_2^-$) over the 17-year sampling period (1991 to 2008). Site 90586 and 90599 are downstream from mining and industrial operations. In addition, site 90599 is downstream of an urban centre and an inter-basin transfer input (Usutu river transfer from the Heyshope Dam) (Dr. Chris Herold, *pers. comm.*). Due to the acidifying nature of S and N inorganic species, a reduction in basic cations and ANC charge balance was expected; however, this was rarely found at these five locations. The most recent analyses show that soils of the Highveld grasslands, especially those central to the Vaal Dam catchment, have the capacity to neutralise some acid inputs via atmospheric deposition and many soils showed increased concentrations of basic cations (Chapter 4). The mechanisms proposed for increased soil basic cation concentrations were via fly-ash, soil dust and ash deposition from biomass burning. The same sources could contribute, in part, to the increases in cation concentrations at the five sites investigated.

The spatial differences between the sites, highlighted by the output from the ANCOVA analysis, confirm the variability between rivers within the catchment (Day *et al.*, 1998) and together with the CCA suggest that additional environmental variables, including land use, point-source pollution and diffuse inputs from agricultural sources, are stronger influences on the quality of water in the Vaal Dam catchment when compared with S and N deposition. Inclusion of more sites and more environmental variables could be used with CCA analysis to explain more of the variation in the data set than was found in this investigation. The inclusion of PO_4^{2-} was to examine if increases in S and N were associated with increases in PO_4^{2-} which could be linked to agricultural sources as opposed to S and N deposition. However, the increases in PO_4^{2-} at three sites may be linked to the geology as Grobler and Silberbauer (1985) found that the sedimentary geology of the Vaal River catchment (below the Vaal Dam) significantly increased the concentrations of soluble reactive PO_4^{2-} when compared with the igneous geology of the Limpopo catchment. More than 85% of the Vaal Dam catchment is underlain by sedimentary geology (Vorster, 2003; Middleton and Bailey, 2009). Elevated Ca^{2+}

concentrations were found to reduce the solubility of PO_4^{2-} and decrease its availability for phytoplankton in the Vaal River (at Balkfontein) in the Free State province (Roos and Pieterse, 1995), thus reducing the potential for eutrophication of the aquatic system as a result of high levels of PO_4^{2-} .

The range of the absolute concentration values of the 10 water quality variables at these five sites was generally higher than those recorded in other surface waters receiving atmospheric deposition. For alpine systems in the Rocky Mountains of Colorado, USA, Baron *et al.* (2009) found stream water NO_3^- , SO_4^{2-} and Ca^{2+} concentrations 74%, 94% and 93% lower than the mean values for the Vaal Dam catchment sites. Streams in the United Kingdom, had mean concentrations of SO_4^{2-} , NO_3^- , and Na^+ within a similar range of the Vaal Dam catchment sites, however, the UK streams showed much less variance between minimum and maximum values (Evans *et al.*, 2001). Acid neutralising capacity of UK streams fell within the range of those calculated for the Vaal Dam catchment, however, the median values in UK streams were lower (Kernan and Helliwell, 2001; Kowalik *et al.*, 2007). The ranges for NH_4^+ , NO_3^- , SO_4^{2-} and dissolved salts was broader in the Vaal Dam catchment than those recorded in Japan (Shrestha and Kazama, 2007), India (Singh *et al.*, 2004) and UK streams (Cooper, 2005), although the mean values in these studies were similar. Compared with the study by Roos and Pieterse (1995), the Vaal Dam catchment rivers had lower SO_4^{2-} , Ca^{2+} , Mg^{2+} , K^+ and Na^+ concentrations. Salinity in the Vaal River, downstream from the Vaal Dam, was similar to those in South African rivers (Crocodile, Komati and Olifants) impacted by similar land uses, including mining and irrigated agriculture (van Niekerk *et al.*, 2009). South African rivers less affected by mining and irrigated agriculture (Berg, Thukela and lower Orange) had comparatively lower salinity (van Niekerk *et al.*, 2009). The investigation by Roos and Pieterse was further downstream on the Vaal River, after substantial industrial and domestic effluent inputs as well as use for irrigated crop farming and could be the reason for dramatically increased concentrations (more than 200% increase in SO_4^{2-} concentrations) of these ions further downstream.

At the five Vaal Dam catchment sites, the SO_4^{2-} concentrations were consistently below drinking water quality targets but inorganic N concentrations have been more problematic especially at site 90586. The eutrophication potential of inorganic N could be offset by the turbid nature of the Vaal tributaries in general

(Davies *et al.*, 1992), which retards the growth of algae due to reduced light availability. For eutrophication to occur in surface waters the supply of the (previously) primary limiting nutrient – usually N or P – is increased and the limitation of plant production is removed (Smith *et al.*, 1999). Although surface waters productivity are usually more limited by P, consistently high N concentrations may place the surface waters of the catchment at higher risk of the effects of eutrophication, including degradation of the water source through decreased clarity and shifts in biological communities and food webs (Smith *et al.*, 1999).

The salinity of the Vaal River system has been modelled to increase as a result of S and N deposition (for example, Taviv and Herold, 1989; Herold and Gorgens, 1991; Herold *et al.*, 2001; van Niekerk *et al.*, 2009) and therefore it is surprising that DMS showed no significant changes in concentrations over the 17-years of this study. The results from the three statistical analyses performed suggest that the Vaal Dam catchment, although impacted by land use for example mining and urbanisation, is not yet showing signs of impact as a result of S and N deposition and that the water quality, with few exceptions, remains within the target range of drinking water quality standards.

6.4.1 Thesis linkage

The interpretation of statistical analyses suggests that water quality at five sites in the Vaal Dam catchment is spatially, due to site differences revealed by the ANCOVA analysis, and temporally variable, from the findings of the trend analysis showing increases and decreases in chemical variables over the 17-year period analysed. The concentrations of the selected water quality variables differed, with rare exception, significantly at all five sites, suggesting that land type and, perhaps, water-use above the monitoring site was more influential on water quality than soils and S and N deposition. Increases in S and N were only found at one and two sites respectively. ANC was found to decrease at only site over the 17 years. The multivariate analysis approach, the variables and the sites selected did not show convincing evidence that surface waters are affected by atmospheric S and N deposition or did not show signs of quality degradation.

The thesis has thus far focussed on both S and N deposition and the impacts on the soil processes and water quality. The international literature recently focussed

on N deposition and its impacts, as a result of reduced S emissions and deposition with continued or increased N emissions and deposition. The next chapter focuses on the impacts of N deposition on ecosystem services of the Highveld grasslands from a regional perspective.

CHAPTER 7: ECOSYSTEM SERVICES IN THE GRASSLANDS OF SOUTH AFRICA AFFECTED BY N DEPOSITION AND LAND-USE CHANGE.

This chapter addresses N deposition at the regional scale of the South African Highveld from an integrated perspective, establishing the regional perspective by reporting modelled atmospheric N deposition (inputs), soil chemistry (internal cycling and acid buffering processes) and water N export from headwater catchments (outputs). The impacts of N deposition on ecosystem services are discussed with particular reference to the role of land-use change in the response of ecosystems to N deposition.

The manuscript below, modified only to reduce repetition, presents results from the studies conducted by research partners for the ESKOM-SASOL project: “Investigation into the effects of atmospheric pollutants on the soil-water-ecosystem continuum, Phase 0” (Blight *et al.*, 2009). An early draft of this manuscript was presented at the International Nitrogen Initiative (INI) Workshop on Nitrogen Deposition, Critical Loads and Biodiversity during 16-18th November, 2009 in Edinburgh, UK. The manuscript is currently under review for AMBIO (title, authors and author affiliations are included below). My contribution to the manuscript was the re-assessment of the soils across the Highveld grasslands as based on the earlier work by Fey and Guy (1993). In addition, I collated the data from co-authors and constructed the manuscript for the presentation at the INI workshop and made revisions for submission to AMBIO. The co-authors provided access to their research findings and commented on drafts of the manuscript before submission.

Ecosystem services in the grasslands of South Africa affected by N deposition.

Theresa Bird¹, Mary Scholes², Yvonne Scorgie³, Gerrit Cornelius⁴, Joanne-Lynne Reid⁵, Nina-Marie Snyman⁶, Jennifer Blight⁷, Simon Lorentz⁸.

1. PhD candidate, School of Animal, Plant and Environmental Sciences, University of the Witwatersrand, Johannesburg. Private bag X3, WITS, 2050, South Africa.

2. Professor, School of Animal, Plant and Environmental Sciences, University of the Witwatersrand, Johannesburg. Private bag X3, WITS, 2050, South Africa.

3. ENVIRON Australia PTY Ltd. and Department of Geography, Environmental Management and Energy Studies, University of Johannesburg. PO Box 560, North Sydney, 2060, Australia.

4. Airshed Planning Professionals (Pty) Ltd and Department of Chemical Engineering, University of Pretoria. PO Box 5260, Halfway House, 1685, South Africa.

5. MSc graduate, School of Animal, Plant and Environmental Sciences, University of the Witwatersrand, Johannesburg. Private bag X3, WITS, 2050, South Africa. Current address: AEA, New Street Square, London, EC4A 3BF

6. Post-doctoral fellow, School of Bioresources Engineering and Environmental Hydrology, University of KwaZulu-Natal. Private bag X01 Scottsville, 3209, South Africa.

7. Lecturer, School of Civil Engineering Surveying and Construction, University of KwaZulu-Natal. Private bag X01 Scottsville, 3209, South Africa.

8. Associate Professor, School of Bioresources Engineering and Environmental Hydrology, University of KwaZulu-Natal. Private bag X01 Scottsville, 3209, South Africa.

ABSTRACT

In an integrated investigation on the effects of acidic deposition on South African grassland ecosystems, N deposition was modelled within a domain 380 km (east-west) by 430 km (north-south) and under three rainfall scenarios (average, above-average and below-average). Wet deposition was projected to contribute 80% to total N deposition (maximum total deposition of 15 kg N ha⁻¹year⁻¹) in the above-average rainfall scenario, decreasing to a 60% (maximum 8 kg N ha⁻¹year⁻¹) contribution in the below-average year simulation. Within the modelling domain a soil process study found some evidence of soil acidification, most evident in soils closer to source and in soils with less than 25% clay content. Nitrogen export into water bodies was negligible (<2 kg N ha⁻¹ year⁻¹) in untransformed grasslands. An afforested catchment showed larger (by 16-times) export of N compared with natural grasslands. It is suggested that ecosystem services in natural grasslands are presently more threatened by land-use and biodiversity changes than N deposition.

7.1 Introduction

Nitrogen is a limiting nutrient in many ecosystems globally (Vitousek and Howarth, 1991). This limitation can be removed from unmanaged ecosystems to a greater or lesser extent by reactive, oxidised and reduced, N forms deposited via wet and dry atmospheric processes. Nitrogen emissions and subsequent deposition in developing countries were expected to show the largest increases globally

(Galloway, 1995). More recent modelling suggests that 11% of natural vegetation globally receives in excess of the $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$ critical load, with expected increases in N deposition above critical loads in 2030, in parts of Europe, Asia and Africa (Dentener *et al.*, 2006). Removing N limitations to productivity can lead to N saturation; a situation where available N is in excess to the combined plant and microbial demands (Aber *et al.*, 1989). Under N saturated conditions, mobile inorganic N species can potentially be lost through leaching and denitrification. The impacts of excess N deposition are mainly related to nutrient imbalances as other resources limit ecosystem productivity once any N limitation is removed (Aber *et al.*, 1998). Fertilisation experiments have shown that productivity in South African grasslands is limited by N and P (reviewed by O'Connor and Bredenkamp, 2003). Recently Stevens *et al.* (2004) showed that plant species richness in the grasslands of Great Britain decreases by 1 species per 4 m^2 for every $2.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$ of chronic N deposition, where species adapted to higher N levels out-compete those species better suited to low N conditions. South African grasslands have a high level of biodiversity and yet only a small percentage of these grasslands are protected in conservation areas (Mucina and Rutherford, 2006). In addition to the potential impact by mining and agriculture on this diversity, the impact of atmospherically deposited N, known from other published studies to affect biodiversity in grasslands, is not well understood in the South African system. It is suspected that N deposition to these Highveld grasslands may already be affecting ecosystem processes as these areas receive reactive N (NO_x and NH_y) amounts comparable with those of other industrialised regions. The ammonium and nitrate content of precipitation at Amersfoort ($22.3 \mu\text{eq l}^{-1}$ of NH_4^+ and $25.0 \mu\text{eq l}^{-1}$ of NO_3^-) - a town within the grassland biome affected by emissions from industrial activities - is comparable to industrialised regions in Europe (15 to $50 \mu\text{eq l}^{-1}$ of NH_4^+ and 15 to $35 \mu\text{eq l}^{-1}$ of NO_3^-) and is higher than at Louis Trichart ($9.7 \mu\text{eq l}^{-1}$ of NH_4^+ and $8.0 \mu\text{eq l}^{-1}$ of NO_3^-) - a remote rural town in the Limpopo Province of South Africa, outside of the main emissions plume where the measured rainwater concentrations can be regarded as typical background levels for the area (Dovland and Pederson, 1996; Galy-Lacaux *et al.*, 2003; Mphepya *et al.*, 2004). Industrial sources are the primary contributor (Galpin and Turner, 1999b) to elevated levels of N species in the rainwater at Amersfoort, due to access to rich coal supplies underlying the Highveld grasslands.

Species diversity of the South African grasslands is threatened by afforestation, crop agriculture, commercial and communal grazing, mining and urban development (Neke and Du Plessis, 2004; O'Connor, 2005). The influence of human activities on ecosystem structure, diversity and function can persist for decades and centuries after the activity has ceased (Foster *et al.*, 2003). The impacts of land use on the N cycle are widely reported in the literature, for example: afforestation (Bruland *et al.*, 2008; Farley *et al.*, 2008), crop agriculture (Neke and Du Plessis, 2004; Brodowski *et al.*, 2005; O'Connor, 2005) and grazing (O'Connor, 2005; Zhang *et al.*, 2008). Prior land use in North American forests influenced the ecosystem response to N deposition more strongly than forest species composition or the amount of deposition received (Goodale and Aber, 2001). In addition, the growth of intact North American old-growth forests were relatively unaffected by N deposition and other changes to the physical and chemical environment by elevated CO₂ and troposphere O₃ when compared to forests with a land-use history of agriculture or timber harvesting (Ollinger *et al.*, 2002).

As a result of the exposure to S and N emissions and subsequent deposition, there is a concern that the ecosystem services provided by the affected grasslands could be compromised. Ecosystem services, according to the Millennium Ecosystem Assessment (Millennium Ecosystem Assessment, 2005c), can be categorised into 4 groups: supporting, provisioning, regulating and cultural. In this synthesis paper, we consider how the supporting, provisioning and regulating services, including nutrient cycling, food provisioning and water purification, provided by the grasslands of the South African Highveld, may be compromised by N deposition. We document research through an integrated study covering the N inputs through deposition, mainly oxidised forms, over an area 380 km by 430 km, the acid-base status of soils in the vicinity of a coal-fired power station and over a large (53 940 km²) grassland study area and oxidised N stream export from three small headwater catchments, on the affected Mpumalanga Highveld. The outcome from these findings will inform the establishment of long-term monitoring sites to monitor the impacts of N (and sulfur) deposition on ecosystem services, including biodiversity.

7.2 Materials and Methods

Integrated study in the Highveld grasslands

The grassland biome covers the high central plateau of South Africa at a mean altitude of 1700 masl covering 29% of the country's surface area and is so called because woody plants are absent or rare (Figure 7.1a). The Highveld grasslands are dominated by summer rainfall mainly in the form of thunderstorms. Mean annual precipitation (MAP) ranges from 400 mm to >1200 mm (O'Connor and Bredenkamp, 2003), however, mean evaporative potential usually exceeds MAP (Schulze, 2003). The airflow across this part of the country is predominately easterly with extended periods of subsidence due to the descending limb of the Hadley cell of general circulation (Preston-Whyte and Tyson, 1993). In winter, clear skies with associated inversions create conditions suitable for frost. These climatic conditions together with annual fires and grazing, limit woody species to patches that provide protection from fire and where water retention is higher. These patches include gullies, steep slopes and rocky outcrops (O'Connor and Bredenkamp, 2003; Mucina and Rutherford, 2006). Some 3700 plant species have been recorded in these grasslands, where only 1 in 6 is a graminoid species and other species are forbs and small shrubs. However, only 2.2% of the biome is protected in small reserves (Mucina and Rutherford, 2006).

The approach to understanding how grasslands are impacted by N deposition included modelling N deposition over a region (domain) where the impacts were highest near to the highest density of sources. In addition, the soil chemistry of sites that had been investigated in the 1990's was re-assessed in 2006 and 2007. The hydrology of small upland catchments of concern were also investigated for indicators of impacts of N deposition. These investigations were carried out within the grasslands of the Mpumalanga Highveld; an elevated plateau east of the Johannesburg-Pretoria-Vereeniging urban complex. The Mpumalanga Highveld is approximately 30 000 km² in size where ~70% is grassland mostly used in low density stock farming (Tyson *et al.*, 1988). The specific approach for each component of the integrated study is detailed below.

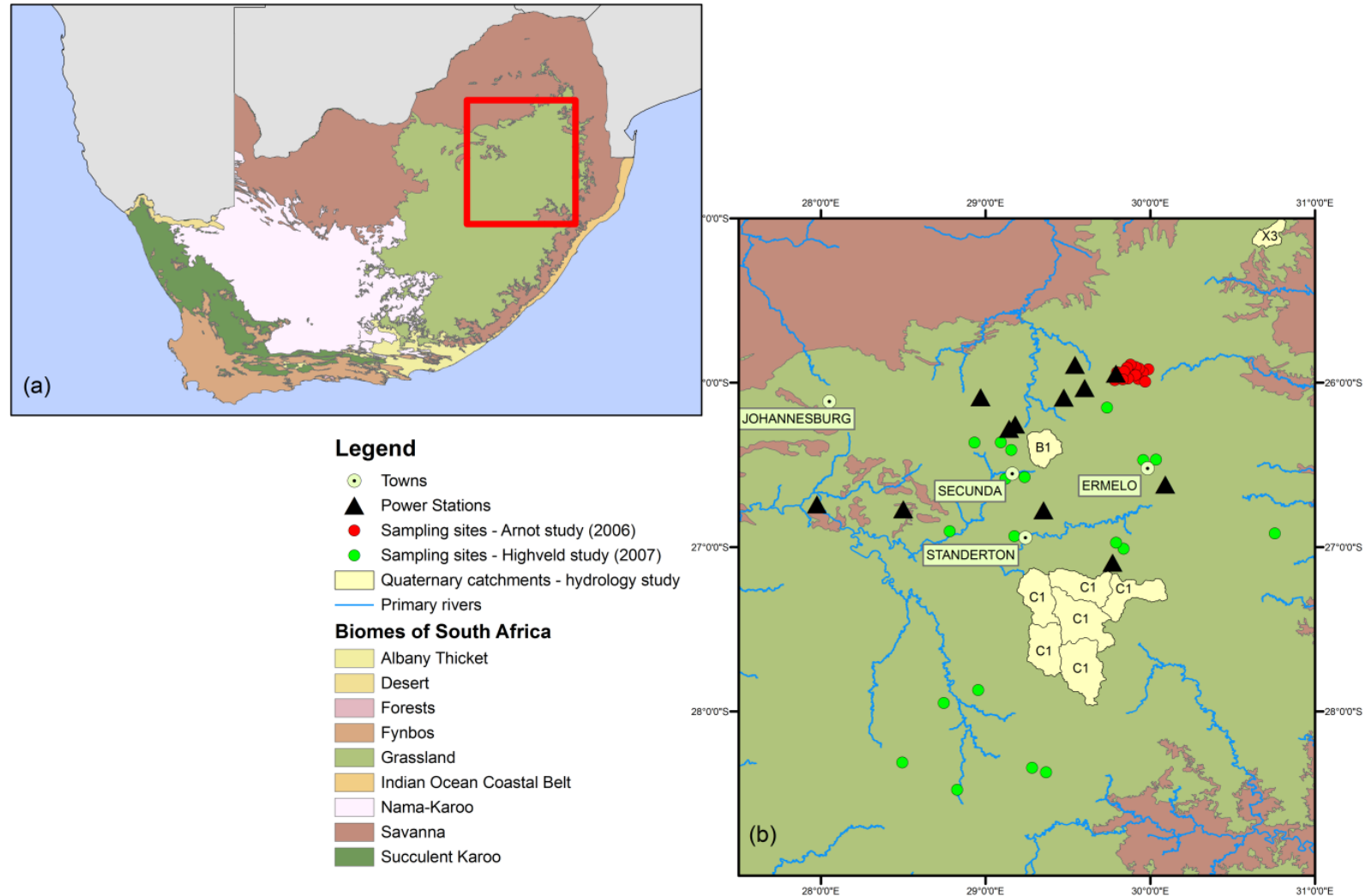


Figure 7.1(a): The biomes of South Africa with the modelling and study domain indicated in red. (b) The domain over the Highveld grasslands of South Africa used for N deposition modelling. The sampling sites of the Arnot and Highveld soil chemistry studies are indicated by the filled circles. The quaternary catchments investigated in the hydrological study are also indicated; in the text quaternaries C1 are referred to as the Klip catchment, B1 is referred to as the Olifants catchment and X3 is referred to as the Sabie catchment. The coloured background areas are the grassland and savanna biomes covering the domain.

7.2.1 Domain description

The domain (Figure 7.1b) for deposition modelling covers the area of 380 km (east-west) by 430 km (north-south) with the south west corner at 28°53'4.56" south and 27°26'54.99" east and falls within the grassland biome (Figure 7.1a and b). Areas where ecosystem services were potentially affected by N deposition, within the modelling domain, were identified for soil and hydrological investigations (Figure 7.1b).

7.2.2 Nitrogen deposition modelling

The US Environmental Protection Agency approved, CALPUFF modelling suite, was chosen for N deposition modelling and comprises the CALMET (CALifornia METeorological model) meteorological model, the CALPUFF (CALifornia PUFF model) dispersion model and the CALPOST result-processing module (US-EPA, 1995; Scire *et al.*, 2000). The main reasons for the selection of the CALPUFF modelling suite were that the model is applicable to large modelling domains; the model is able to characterise spatial variations in meteorological conditions and is therefore applicable for use in complex terrain, urban and coastal environments; CALPUFF is able to undertake first-order chemical transformation calculations and is therefore suited to the prediction of secondary pollutants (e.g. quantified conversion of sulfur oxides and nitrogen oxides to sulfate and nitrate which contribute significantly to ambient fine particulate concentrations); the model incorporates a resistance deposition model to predict spatially and temporally varying gas and particle dry deposition rates and determines wet deposition through the use of pollutant-specific scavenging coefficients. CALPUFF is also appropriate for various source configurations including point, volume, area and line sources and has been demonstrated in previous studies to perform relatively well in the simulation of ambient sulfur dioxide and nitrogen dioxide concentrations on the Highveld (Scorgie; Scorgie and Thomas, 2006) and use could be made of certain of the CALPUFF input data from previous studies thus reducing the resources required for modelling. CALPUFF has been satisfactorily used to model deposition in several contexts internationally. For example, dry and wet N deposition on the de la Plata River, as a result of emissions from the city of Buenos Aires (Pineda Rojas and Venegas, 2008

670) and deposition of heavy metals in the vicinity of a zinc smelter (MacIntosh *et al.*, 2010).

South African rainfall is highly seasonal with large inter-annual variability, in addition, potential rainfall acidity trends have been measured to follow trends in regional rainfall, with a downward trend apparent during periods of reduced rainfall (Galpin and Turner, 1999b;a). To account for the variability in rainfall and potential differences in deposition as a result, three climate scenarios were used in the model: an average rainfall scenario based on the 2000/ 2001 meteorological year; a below-average rainfall scenario based on the 2006/2007 meteorological year and an above-average rainfall scenario based on the 1995/1996 meteorological year. Accurate upper-air data for the below-average rainfall year (2006/2007) were unavailable and poorer quality radiosonde station data had to be used to provide the upper-air meteorological data for CALMET modelling. The upper-air data required by CALMET includes pressure, geopotential height, temperature, wind direction and wind speed for various levels. Surface data requirements include wind speed, wind direction, mixing depth, cloud cover, temperature, relative humidity, pressure and precipitation. These variables were used from at least 10 surface stations within the modelling domain while the ETA-model stations (from South African Weather Service) and two radiosonde stations were used. Ninety-two rainfall stations within the modelling domain provided the hourly rainfall data.

A single emission scenario was used in all three meteorological scenarios for deposition of mainly oxidised forms of both N and S, although the focus of this report is N deposition. The emission scenario was based on sources of atmospheric emissions in the base emissions year, October 2000 to September 2001, where the following source emissions were collated (Table 7.1):

- power generation - primarily coal-fired power generation for the national grid;
- industrial sources – combustion and process emissions from industries holding permits under the Atmospheric Pollution Prevention Act of 1965 or licenses under the 2004 Air Quality Act;
- household fuel burning – including coal, wood, LPG and paraffin burning;
- vehicle tailpipe emissions – including petrol- and diesel-driven vehicles;
- biomass burning (agricultural and wild fires), and

- institutional and commercial fuel burning – including heavy fuel oil (HFO), coal, wood and gas combustion at schools, hospitals and businesses (where available).

Table 7.1: Estimated total base case emissions for anthropogenic sources on the Highveld.

Source group	Annual Emissions (tons year ⁻¹)	
	NO _x	SO ₂
Major sources(a)	526 345	1 417 934
Other industrial sources	4 099	11 866
Household fuel burning	3 449	9 123
Vehicle exhaust emissions	147 577	23 221
Biomass burning (wild fires)	3 204	620
Total	684 674	1 462 764

(a) Includes large scale coal-fired power stations and major industrial sources.

Reduced N deposition, as ammonia (NH₃) gas, was not included in the model. Atmospheric and ground-based measurements of ammonia emissions and depositions are lacking globally (Clarisse *et al.*, 2009) and as a result, the accuracy of NH₃ inventories is uncertain in part because this is an unregulated pollutant (Fenn *et al.*, 2003b). The main sources of NH₃ gas are via livestock wastes, fertilisers and biogenic emissions from soils and vegetation (Fenn *et al.*, 2003a; Fenn *et al.*, 2003b; Galloway *et al.*, 2004). Agricultural inputs, as livestock wastes and fertilisers, were not included in the model due to the research focus of impacts on the natural, unimproved grasslands of the Highveld region. These grasslands are grazed and therefore will produce NH₃ via volatilization. The petro-chemical plant in the vicinity of Secunda, is another source of NH₃ in South Africa (Van der Walt *et al.*, 1998). It is therefore expected that total – oxidised and reduced – N deposition would be underestimated (by approximately 30%) and wet deposition contributions overestimated (by approximately 20%) in the model output.

7.2.3 Soil chemical dynamics

Soils can buffer incoming acid compounds and thereby slow the impact of acid deposition on vegetation and ground- and surface waters. Examination of the soil chemistry can thus give clues to the overall state of the ecosystem with respect to acidification processes. Two regions within the Mpumalanga Highveld were investigated for indications of changes in soil chemistry over time. The first region (studied by Reid 2007), lies within 20 km of the Arnot coal-fired Power Station

(Figure 7.1b) (approximately 50 km east of Middelburg in Mpumalanga). Of the 11 base-load coal-fired power stations in South Africa owned and operated by Eskom (Electricity Supply Commission), eight of them are situated in the Mpumalanga province. Arnot is the most easterly of these power stations and is the furthest from the industrial hubs of Gauteng, Witbank and Middelburg and background pollution levels were therefore assumed to be low. The Arnot power station was fully operational by 1975, making it one of the oldest power stations in South Africa and this relatively long history of air pollution and deposition on the soil surface, coupled with the low background pollution levels, makes the Arnot power station an ideal location to monitor the long-term impacts of air pollution on soil properties. Sample points were located from 1.3 km to 19.9 km downwind of the power station. The plume was found (Pretorius *et al.*, 1986) to strike the ground most frequently in the direction south-east to east-south-east (van Tienhoven, 1997) and sampling was conducted in an arc ranging from south-east to east-south-east as the wind blows in this direction with a 37.4 % frequency. The study carried out near Arnot compared soil chemical properties of the top- (0 – 100 mm) and sub-soils (200 – 400 mm) between 1996 and 2006. Soils were collected from natural grasslands at 15 sampling sites where three replicate samples were collected by 100 mm hand-auger at each sampling site. The soils were oven dried at 60°C for 48 hours and sieved to 2 mm prior to physical and chemical analyses. Analyses included soil texture, pH – in distilled water, K₂SO₄ and KCl, acid neutralising capacity, extractable cations, extractable acidity, organic carbon, extractable Fe, Mn, and Al, soluble cations, electrical conductivity, total S, extractable sulfate (0.01 M calcium phosphate extraction at pH 4) and total N. The methodological procedures for these analyses are described in Reid (2007).

Soil chemical properties were also re-assessed in 2007 in the Highveld grasslands by revisiting sites from an investigation undertaken in 1991 (Fey and Guy, 1993). The methodology and full set of results are presented in Chapter 4 of this thesis.

7.2.4 Hydrological studies

Water quality variables, from the national Department of Water Affairs water quality network database, were examined in the three headwater catchments; the

Sabie (X31A, 172 km²), in the north-east corner of the domain; the Klip (C13A-F, 4 150 km²) in the central south-east section of the domain and the Olifants (B11C, 412 km²) central to the modelling domain (Figure 7.1). The Klip and Olifants headwater catchments are dominated by grassland and anthropogenic activities are limited to grazing (stocking densities of <1 animal unit (AU) ha⁻¹ – O'Connor, 2005) and maize production (fertilisation with inorganic nitrogen-phosphorus-potassium (NPK) fertilisers with N inputs of 100 to 290 kg ha⁻¹ year⁻¹ – O'Connor, 2005). Some mining occurs in the Olifants catchment, but the headwater catchments were selected on the basis of minimal mining extent observed during site visits. In the Sabie catchment land use is predominantly afforestation of the native grassland. This catchment is afforested with exotic pine and eucalypt plantations that are fertilised at planting and in some cases at mid-rotation (usually at canopy closure or after thinning operations) and as a result, some of these export sources may not be atmospheric. No formal towns exist in any of the catchments. Small settlements (each comprising a few families) occur in the Klip and Olifants catchment. The selection of these catchments was performed by selection of stakeholders and experts (Lorentz *et al.*, 2008) because these catchments are minimally impacted by other pollution sources and because flow and water quality are routinely recorded at discharge weirs in each catchment. Water quality records for the Klip catchment have been collected from 1974; in the Olifants catchment from 1990 and in the Sabie catchment since 1976. All records up to 2006 were used for all three catchments. Observed times series are either weekly or monthly observations. The frequency and duration of water sampling as well as the treatment of outliers is described in detail in Lorentz *et al.* (2008). Constituents analysed includes sodium (Na⁺), potassium (K⁺), magnesium (Mg⁺), calcium (Ca⁺), pH (in water), electrical conductivity (EC), chloride (Cl⁻), sulfate (SO₄²⁻), total alkalinity, fluoride (F⁻), phosphate (PO₄²⁻), ammonium (NH₄⁺), nitrate (NO₃⁻), silica (Si), Kjeldahl total nitrogen (TN), total phosphates (TP) and total dissolved solids (TDS). Laboratory analyses were conducted at the laboratories of the Institute for Water Quality Studies, made accessible via the Water Management System according to the methods described in Department of Water Affairs and Forestry (1992). The results for nitrate are presented here and trends over time for the other chemical species are discussed elsewhere (Lorentz *et al.*, 2008).

7.3 Results

7.3.1 Total (wet + dry) N deposition:

Modelled total N deposition based on average rainfall (Figure 7.2a) suggests that the highest amount of annual deposition received annually is $>8 \text{ kg N ha}^{-1} \text{ year}^{-1}$ and occurs in the area between 26 and 27°S and 29.5 and 30.5°E . The area where modelled N deposition is the highest is close to an area where stationary source of N emissions are concentrated, although ground level dispersed vehicle exhaust emissions do contribute to the spatial extent of N deposition. In Figure 7.2a the coloured bands represent a decrease of $2 \text{ kg N ha}^{-1} \text{ year}^{-1}$ in modelled deposition outwards from the central dark areas to the domain edges further away from stationary emission sources. Under this scenario wet deposition contributes 60% of the total. In the above-average rainfall scenario, with 45% more than average rainfall, maximum N deposition increases to $>15 \text{ kg N ha}^{-1} \text{ year}^{-1}$ and heavier deposition is predicted throughout the modelling domain (Figure 7.2b), where 80% of total deposition is via the more effective wet deposition processes.

The final scenario was the below-average rainfall year (Figure 7.2c), where the proportion of wet to dry deposition is similar to the average rainfall year (Figure 7.2a). The maximum deposition rate is again $>8 \text{ kg N.ha}^{-1}\text{year}^{-1}$ with a distinct southerly and easterly shift in distribution of deposition under this scenario. It is cautioned that this distribution shift could be a result of poorer quality radiosonde data that were used. In spite of efforts to construct and check the upper-air files and ensure the accuracy of the CALMET runs, it is apparent from the plots (Figure 7.2c) that the wind fields were not adequately characterised. The ‘bulls-eye’ patterns in Figure 7.2a-c is a result of the concentration of primary emission sources on the Mpumalanga Highveld and stable meteorological conditions that limit dispersal of atmospheric pollutants.

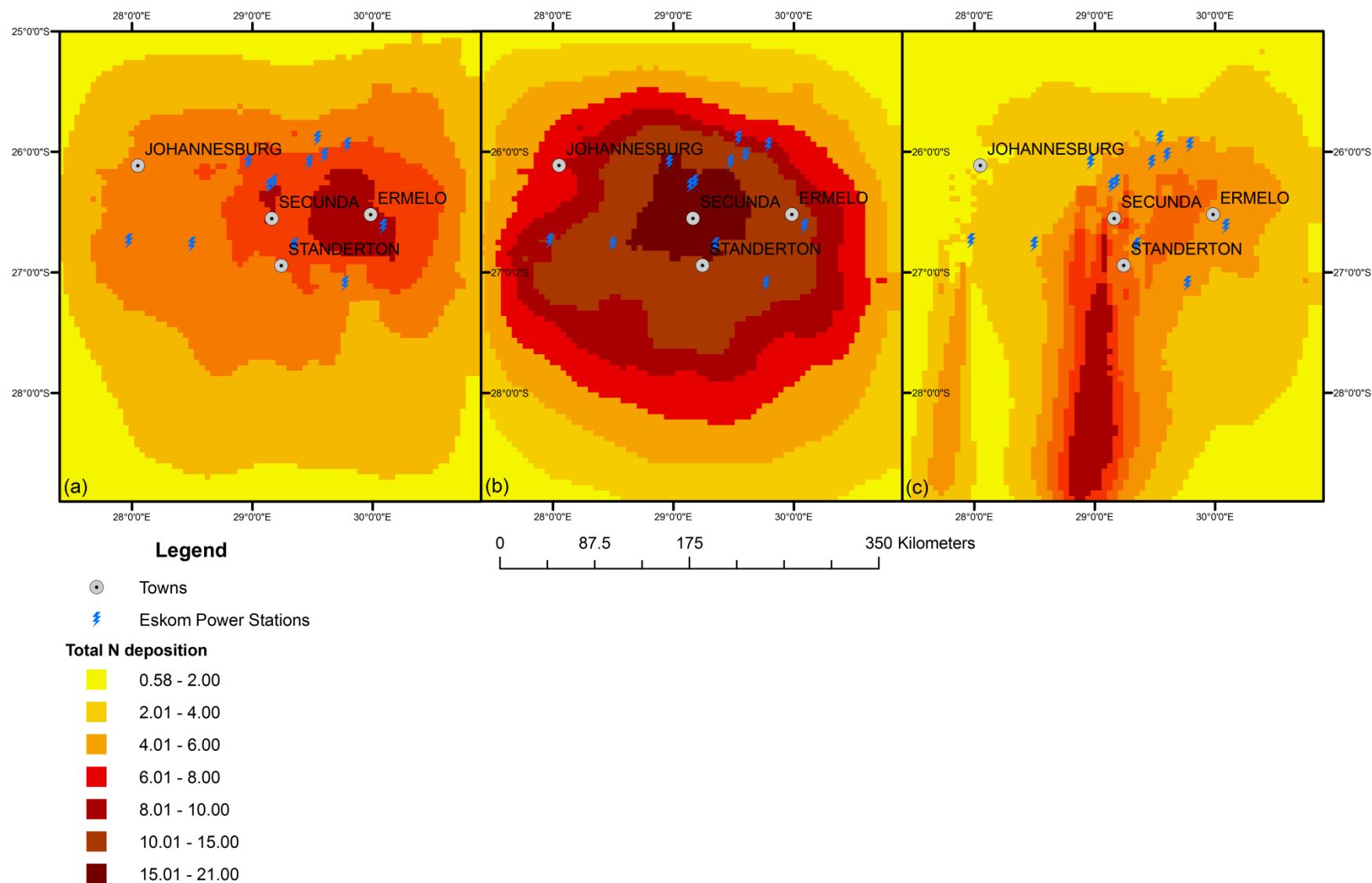


Figure 7.2: Total N deposition model output ($\text{kg ha}^{-1} \text{ year}^{-1}$) over the Mpumalanga Highveld modelling domain under 3 different rainfall scenarios (a) Average rainfall scenario (690mm MAP); (b) Above average rainfall scenario (1014mm MAP); (c) Below average rainfall scenario (480mm MAP).

Projected long-term trends in N deposition

Nitrogen deposition across the modelling domain was modelled for eight break-point years between 1948 and 2020 (Figure 3.3 and Figure 7.3). A twenty-fold increase in maximum levels of N deposition occurred between 1948 ($0.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$) and 2007 ($10 \text{ kg N ha}^{-1} \text{ year}^{-1}$) (Figure 3.3). In 2007 the areas on the periphery of the modelling domain receive between 1 and $3 \text{ kg N ha}^{-1} \text{ year}^{-1}$; more than double the 1948 maximum deposition levels. In addition to modelling past deposition, a prediction of N deposition for the year 2020 was modelled. The maximum N deposition remains at $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$ as in 2007, however, a larger area will be affected by the maximum deposition rates.

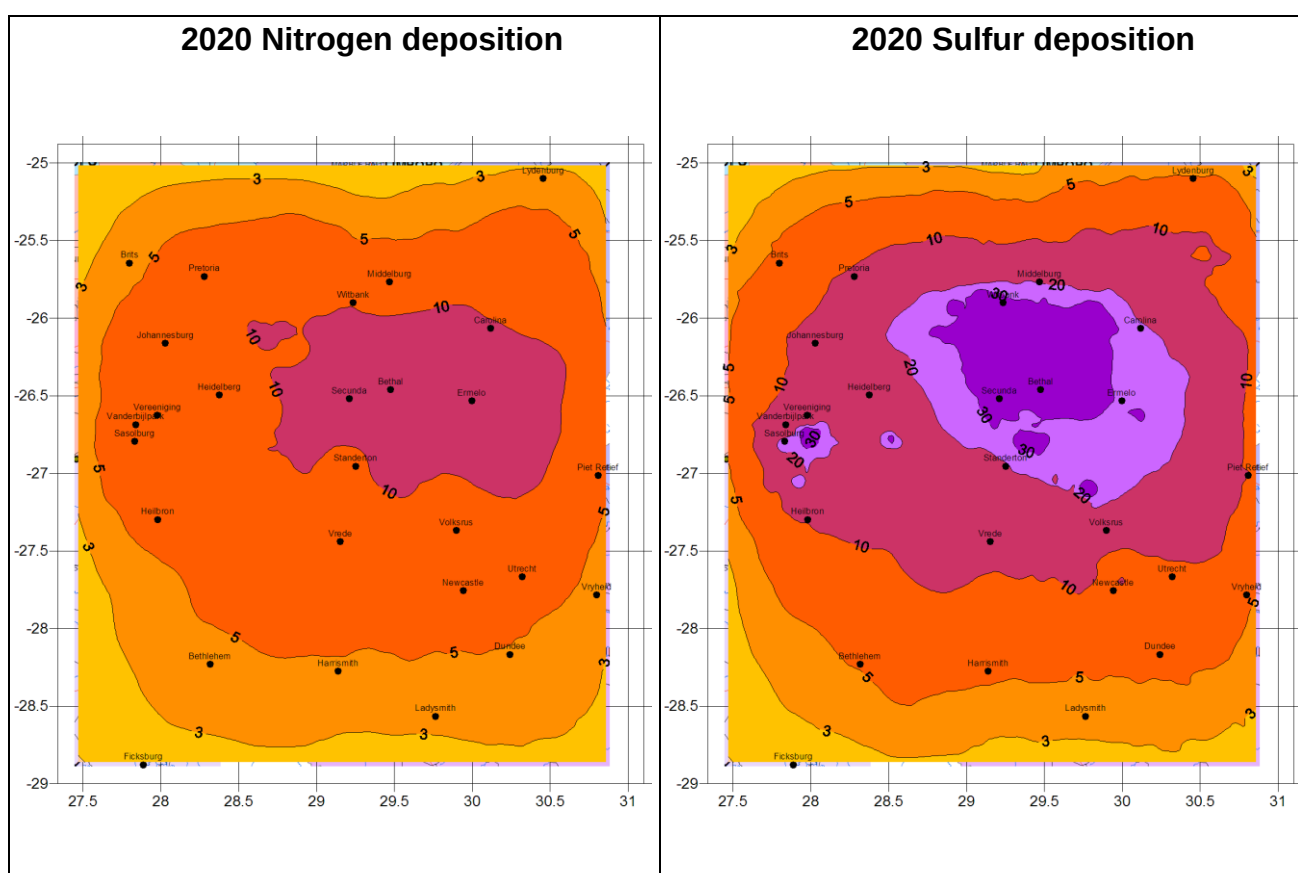


Figure 7.3: Projected N and S deposition across the Highveld modelling domain, in the year 2020 (to support Figure 3.3).

7.3.2 Re-assessment of soils near Arnot Power Station

In the vicinity of the Arnot Power Station, the concentrations of calcium and magnesium in the top-soils and the sub-soils as well as the effective cation exchange capacity (ECEC) in the sub-soils increased significantly since 1996 (Table 7.2). However, pH(K₂SO₄), the concentration of exchangeable hydrogen and aluminium, total sulfur in the top-soils and the sub-soils showed that the soils have become more acidic over the ten years (Table 7.2). Extractable sulfate in the top-soils and soluble sulfate in the sub-soils also indicated acidification of the soils in the vicinity of the Power Station.

The soils near Arnot were also analyzed for spatial differences in soil chemical properties. While there were no significant spatial trends in N species, acid neutralizing capacity (ANC) and soluble SO₄²⁻ showed significant correlations with distance from the source (Arnot Power Station). Soluble sulfate decreased linearly with distance ($R^2=0.7$; $p=0.04$) while ANC increased with distance from the power station according to a logarithmic relationship ($R^2=0.9$).

Table 7.2: Change in mean (n=15) soil chemical properties in the vicinity of the Arnot Power Station between 1996 and 2006, for top- and sub-soil horizons (n=15). All changes reported in table are significant ($\alpha=0.05$ using paired t-tests).

Reduced impact on acidity				Increased impact on acidity			
Property	Affected horizon	1996	2006	Property	Affected horizon	1996	2006
Ca (mmol _c kg ⁻¹)	Top-soil	10.9	13.8	pH(K ₂ SO ₄)*	Top-soil	5.0	4.9
	Sub-soil	3.9	5.3		Sub-soil	5.0	4.8
Mg (mmol _c kg ⁻¹)	Top-soil	5.8	7.5	Exchangeable H ⁺ (mmol _c kg ⁻¹)	Top-soil	3.8	13.1
	Sub-soil	2.9	4.4		Sub-soil	5.0	12.0
ECEC (mmol _c kg ⁻¹)	Sub-soil	51.8	88.7	Exchangeable Al ³⁺ (mmol _c kg ⁻¹)	Top-soil	25.0	53.2
					Sub-soil	40.1	67.0
				Total S (mg kg ⁻¹)	Top-soil	15.6	104.4
					Sub-soil	16.1	60.0
				Sulfate (extractable) (mg kg ⁻¹)	Top-soil	13.7	16.6
				Sulfate (soluble) (mg l ⁻¹)	Sub-soil	9.5	10.9
				Total N (%)	Top-soil	0.1	0.2

* % change in pH meaningless (pH is a logarithm) so the mean difference in pH(K₂SO₄) between the sampling years is presented.

7.3.3 Re-assessment of soils of the Highveld grasslands

Chapter 4 describes the re-assessment of the Highveld grassland soils in detail; this section summarises some of the findings with respect to soil acidity status at the study-area scale. Mean pH(H₂O) of the 18 sites between 1991 and 2007 decreased significantly in top-soils by almost 1 pH unit (Table 4.3). Exchangeable Al³⁺ concentrations in sub-soils increased significantly between sampling years to a mean 0.13 cmol kg⁻¹. Top-soil exchangeable Al³⁺ decreased slightly (but not significantly) between 1991 and 2007. Statistically significant relationships were found between soil particle size distributions and many of the soil chemical properties analysed. When soils were grouped by clay percentage, the mean pH(H₂O) in soils with clay content less than 25% had decreased significantly between 1996 and 2007 (Figure 4.1a). Similarly, the group of soils with only 1% clay content was found to contain the largest concentration of exchangeable acidity (Figure 4.1b). Clay particles have a negative charge and thus increased clay content should increase the capacity to retain positively charged base cations, thus increasing the capacity of the soils to neutralise acidic inputs. Sandier soils, in contrast, would have fewer exchange sites to retain base cations and quicker through-flow rates and thus potentially, the incoming acidic ions could leach out neutralizing base cations quicker than in soils with higher clay content.

7.3.4 Stream export of nitrogen

Comparison of modelled total N deposition rates and measured mean stream water N (as NH₄⁺ and NO₃⁻) export rates showed differences between the three catchments in the modelling domain (Figure 7.4). In spite of the rapid rates of nitrification in the grassland catchments (Chapter 5), very little (less than 0.1 kg N ha⁻¹ year⁻¹) N is exported to stream water in the Olifants (0.08 kg N ha⁻¹ year⁻¹; 75% NO₃⁻) and Klip (0.09 kg N ha⁻¹ year⁻¹; 70% NO₃⁻) catchments. The Sabie catchment shows a much larger export of N (1.6 kg N ha⁻¹ year⁻¹; 88% NO₃⁻).

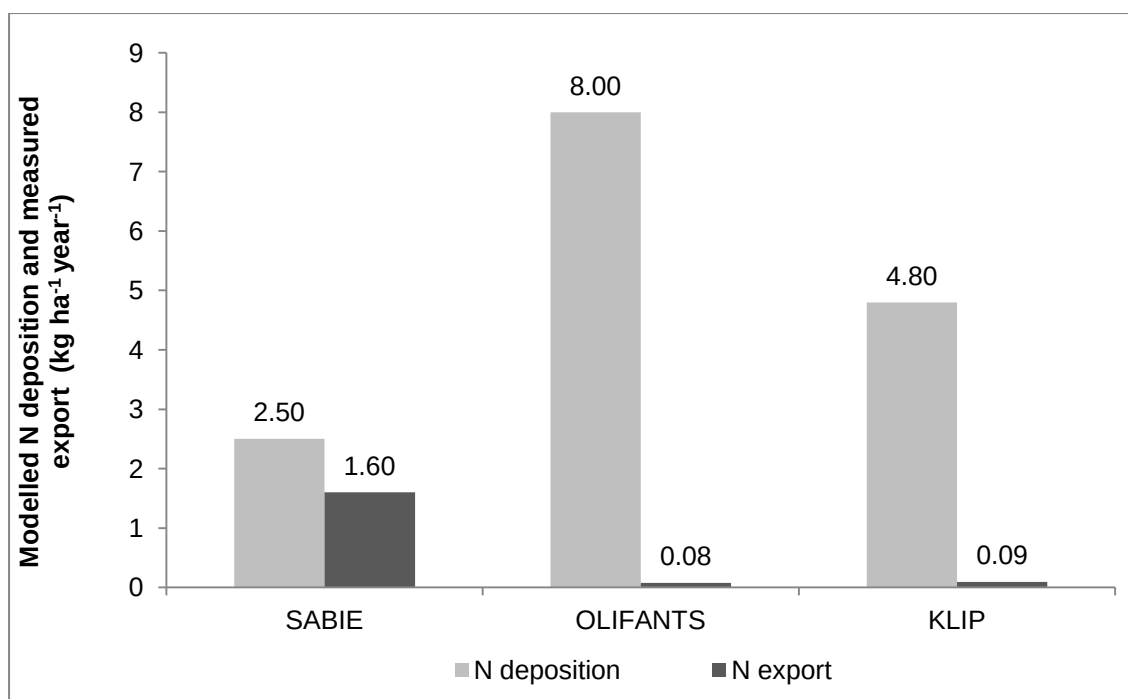


Figure 7.4: Total (wet + dry) N deposition (modelled as in Section 7.3.1) and export (as $\text{NO}_3^- + \text{NH}_4^+$) from three catchments within the modelling domain.

Although the natural state of the Sabie catchment is high-altitude grassland, the catchment is afforested with exotic pine and eucalypt plantations, some of the export sources may thus not be atmospheric as a result of fertilisation. The difference between export from the afforested catchment and the grassland catchments suggests that this change in land use and plant species diversity has had important impacts on the plant-soil dynamics allowing for increased exports of NO_3^- relative to the less modified grassland catchments of the Olifants and Klip. Similar results were found in the Sabie catchments under paired experiments between afforested areas and neighbouring grassland (Mamatsharaga, 2004). Ndala *et al.* (2006) showed that nitrification was the dominant process in the mineralisation of N from organic sources in afforested catchments, while in neighbouring grasslands ammonification was the major contributor (88.1%) to net N mineralisation. This is in contrast to the grasslands in the Highveld grasslands, where nitrification was the larger contributor to the net N mineralisation rate and ammonification the minor contributor (Chapter 5). In addition, the water-soluble NO_3^- concentration was considerably lower (up to 0.9 mmol l^{-1}) in the grassland soils than in forested areas (Ndala *et al.*, 2006). Grasslands were shown consistently to lead to greater conservation of base cations, NO_3^- and Cl^- , and to a lesser extent SO_4^{2-} , than the neighbouring afforested catchments, where NO_3^- losses into stream water (Mamatsharaga, 2004) were a

cause for concern that these ecosystems were showing signs of impact of atmospheric N deposition.

7.4 Discussion

7.4.1 Modelled N deposition

The modelled deposition values fall within the range of those measured in grasslands in Great Britain – 5 to 35 kg ha⁻¹ year⁻¹ (Stevens *et al.*, 2004) and eastern Europe – 11 to 20 kg ha⁻¹ year⁻¹ (Bowman *et al.*, 2008) although they are lower than bulk deposition levels (27 to 39 kg ha⁻¹ year⁻¹) recorded on Chinese agro-ecosystems (Liu *et al.*, 2006). Although South African ecosystems have been receiving reactive N species for a shorter period (late 1908 first unit online; since the late 1940's) than those in industrialised areas in the northern hemisphere, the levels are now comparative to those under which other ecosystems have been impacted, thus warranting further understanding of how ecosystem services are affected.

Modelled total N deposition was largely composed of wet deposition of NO₃⁻ and ammonium-nitrate (NH₄-NO₃). The time taken for the formation of these products from emissions and spatial variations in rainfall, account for the area of maximum deposition being located some distance away from significant NO_x source areas. Dry N deposition of the gases NO, NO₂ and nitric acid (HNO₃), is predicted to peak over the central Highveld coincident with the widespread elevated NO₂ concentrations (Blight *et al.*, 2009). Over the entire modelling domain contributions to dry N deposition were predicted as follows: NO (~20%), NO₂ (~40%) and HNO₃ (~40%); excluding gaseous ammonia deposition and biogenic emissions which were not modelled. The unavailability of a complete and time-resolved ammonia emissions data set for anthropogenic and natural sources hindered the inclusion of ammonia releases in the modelling. Results from the current study provide an initial indication of the significance of such emissions. The contribution of wet to total N deposition is likely to be significantly overstated due to the omission of gaseous ammonia. Gaseous ammonia is estimated to contribute over 30% of the total N deposition (Galy-Lacaux *et al.*, 2003).

Predicted total N deposition at Amersfoort was lower than the total 'measured' N deposition published rates (Galy-Lacaux *et al.* (2003) and Mphepya *et al.* (2001) –

Table 7.3). Some of this difference is due to dry deposition of ammonia gas not having been accounted for in the model predictions. Dry deposition of gaseous ammonia is given as accounting for 33% of the total N deposition at Amersfoort, approximately $5.55 \text{ kg N ha}^{-1} \text{ year}^{-1}$. Excluding gaseous ammonia, predicted N deposition comprised 50% of that measured at Amersfoort.

Table 7.3: Comparison of measured ($\text{kg N ha}^{-1} \text{ year}^{-1}$) and predicted annual Total N deposition ($\text{kg N ha}^{-1} \text{ year}^{-1}$).

		Predicted Deposition	Previously Measured Deposition (a)	Ratio of Predicted to Measured
NO, NO ₂ , HNO ₃ (gas)	dry	0.96	1.30	0.7
NO ₃ (particle)	dry	0.05	0.12	0.4
NH ₃ (gas)	dry	NM	5.55	NA
NO ₃ (particle)	wet	2.93	5.50	0.5
HNO ₃ (gas) ; (NH ₄) ₂ SO ₄ (particle)	wet	1.67	4.00	0.4
TOTAL (all constituents)		5.61	16.47	0.3
TOTAL (excluding NH ₃ gas dry deposition)		5.61	10.92(b)	0.5

NM – not modelled; NA – not applicable.

(a) Galy-Lacaux *et al.* (2003) present modified measurements of N deposition for Amersfoort for the 1996-8 period, as earlier published by Mphepya *et al.* (2001).

(b) Total measured N deposition excluding gaseous ammonia.

By the early 1980s, South African power generation primarily occurred over the Mpumalanga Highveld. Throughout the 1980s emissions intensified over this region with two new power stations being commissioned and operated at full capacity and a facility to produce liquid fuels from coal at Secunda becoming fully operational (Blight *et al.*, 2009). The significance of the Mpumalanga Highveld region as the dominant source of emissions in South Africa, persisted throughout the 1990's and 2000's and is projected to become even more significant by 2020 as existing power stations increase their output and further power stations are commissioned, with the projected maximum deposition in an average rainfall year increasing to $14 \text{ kg N.ha}^{-1}.\text{year}^{-1}$ by 2020. Although no trends for N deposition are available for the Highveld, increased quantities of SO_4^{2-} (9.38% per annum at Warden) and NO_3^- (9.34% per annum at Ladysmith and 7.82% per annum at Warden) were detected in rainwater at two stations on the edge of the main deposition plume between 1985 and 1995 (Galpin and Turner, 1999b). The increases were linked to industrial

activities as either the primary (Warden) or secondary (Ladysmith) contributor to rainwater chemistry (Galpin and Turner, 1999a).

7.4.2 Ecosystem services affected by N deposition

The Highveld grasslands of South Africa affected by N deposition appear to be showing signs of increased acidity (Table 7.1; Figure 4.1) although this increase is difficult to attribute solely to N deposition. Total sulfur (wet + dry) deposited over the Highveld grassland, between 1991 and 2007, was approximately $339 \pm 87 \text{ kg ha}^{-1}$ (Chapter 3, Figure 3.4). Increased soil acidity can compromise the supporting service of nutrient cycling, which provides the basis of food provisioning services in these ecosystems. However, the co-deposition of base cations (Chapter 4) may offset the effects of acid deposition on nutrient cycling. For example, maintaining a soil moisture pH suitable for microorganisms involved in the decomposition of organic matter and the release of inorganic N through mineralisation. Plant nutrient imbalances have been used as indicators of N saturation in other ecosystems (Aber *et al.*, 1989). At this stage, however, there is no substantive evidence that nutrient imbalances exist in the area of interest. There is potential that changes in grassland plant species abundance may occur prior to N saturation and nutrient imbalances. Many ecosystems in South Africa, grasslands included, have developed on ancient geologic surfaces that are naturally acidic. The biota that occur in these regions may therefore be well adapted to acidic conditions and be more tolerant of acidic deposition. It also appears that the grasslands conserve NO_3^- and SO_4^{2-} , as evident from the stream export data, by preventing the leaching these compounds into the water systems, unless land-use modification has occurred. This is in part because of the aridity, where mean evaporative potential exceeds mean annual precipitation, or by losses to atmosphere through biogenic emissions, plant or microbial uptake or losses to the atmospheric pool through the N emissions from annual fires over large areas.

7.4.3 Ecosystem services affected land-use change

According to land cover surveys, 30% of the grassland biome in South Africa has already been transformed by commercial activities including cultivation (23%), plantation forestry (4%), urbanisation (2%) and mining (1%) (Fairbanks *et al.*, 2000). The inclusion of the Sabie catchment in the current report illustrates the influence of

land use on the ecosystem response to N deposition. The Sabie catchment has been impacted by land-use change through the afforestation with exotic timber plantations. Prior to afforestation the catchment was high-altitude grassland. Disturbance of soil organic matter pools during site preparation for planting, increases in the C:N ratio of organic matter inputs after afforestation, and plant N demands (grasses to trees) have altered the availability of N. Changes in the vegetation structure have also affected the atmospheric processes involved in N deposition resulting in larger quantities of N deposition (Lowman, 2003). Land-use change may accelerate N losses from soil stores. The Sabie catchment was the only catchment in the study that showed substantial losses of N in stream export. This puts the catchment at risk for larger N losses if N deposition should increase as projected by the modelling exercise, where water purification as a regulating ecosystem service could become less effective. The high plant N demand in exotic plantations may retard the rate of progression towards N saturation but the soils may acidify further resulting in nutrient imbalances, requiring management response.

7.4.4 Conclusion

Measureable impacts on the Highveld grassland ecosystems would be expected given the amount of N deposition received annually, which is comparable to industrialised sites elsewhere. However, from soil chemical analyses the evidence is less convincing, suggesting that increased soil acidity can be offset by base cation inputs that buffer against incoming N and accompanying S deposition. Stream-flow export of N is also low from unmodified grasslands. Some areas further from the main sources of N emissions with low soil clay content may well be impacted by N and S deposition. These should be the areas of primary concern for in-depth investigations, including the impacts on species diversity.

7.4.5 Thesis linkage

In this chapter the regional impacts of N deposition are discussed in terms of ecosystem services and land use. Based on the results thus far, untransformed natural grasslands show a more conservative response to N deposition inputs – as low levels of N have been exported into surface waters – than the ecosystem with a land-use change history where soil and vegetation structure are dramatically altered, as observed in the Sabie catchment where N exported amounted to

1.6 kg N ha⁻¹ year⁻¹. The limitations of the atmospheric deposition model with respect to the NH_x are noted and it is expected that N deposition might be underestimated by approximately one third. It is also noted that the N deposition is co-occurring with S and base cation deposition. As a result of this co-deposition, it is difficult to separate the role of N deposition on soil chemistry from other inputs, especially S which has a stronger influence on soil acidity. The impact of land-use change and N deposition in the Sabie catchment on water quality highlights the conservative nature of untransformed grasslands with respect to N (and S) inputs.

These findings are discussed in the next chapter (Chapter 8) along with those reported in Chapters 4, 5 and 6. In Chapter 8, conclusions about some of the impacts of S and N deposition on the Highveld grasslands are drawn and recommendations for further investigation in the area are made.

CHAPTER 8: DISCUSSION

8.1 Initial concern about the Highveld grasslands

The work of Fey and Guy (1993), upon which some of the work in this thesis is based, is a definitive study of the Highveld grassland soils against which the current state was compared. Concerns had been raised that S and N deposition would lead to an increase in salt loads in the surface waters of the Vaal Dam catchment, resulting in elevated economic costs associated with the purification processes required to meet domestic, agricultural, and industrial needs (Taviv and Herold, 1989; Herold and Gorgens, 1991). Soil processes and water quality are coupled through the processes of infiltration, leaching and water storage. Fey and Guy (1993) investigated the SO_4^{2-} retention capacity of soils over a large geographical area (approximately 40 000km²) showing that there was limited capacity to retain SO_4^{2-} . Their findings supported earlier modelling studies suggesting that increased salt loads would become evident in the surface waters after the retention capacity was exhausted.

One of the aims of this thesis was to assess the current (2007) state of the soil chemistry compared with that in 1991 (Fey and Guy, 1993) and to investigate changes in water chemistry, in order to explore the coupling of the soil and water processes. This final chapter synthesises the findings of this thesis into a conceptual framework of cause and effect relationships for the Highveld grasslands receiving atmospheric S and N deposition. Responses are then provided for the key research questions posed in Section 1.3: Key Questions (page 5).

8.1.1 Key quantitative findings as they relate to the current state

Soil pH(H₂O) values had significantly decreased at most study sites and at both soil depths between the 1991 and 2007 assessments suggesting that this increased acidity is unlikely to have been a result of only natural processes (weathering, leaching, nitrification and plant uptake) which occur over longer periods. In most cases, the increased acidity appeared to be

buffered by high cation concentrations – either due to the textural and chemical properties of the soil or as a result of deposition of cations through dust (Piketh *et al.*, 1999a), fire (Maenhaut *et al.*, 1996) or fly-ash (Mphepya *et al.*, 2004). pH and cation concentrations (as ANC) decreased more over time on sandier and wetter soils, that are mainly found near the eastern and southern study area boundaries. Because these areas have higher annual rainfall, (200 and 400 mm more than the northern and central parts of the study area) and due to their sandy texture, these soils are more sensitive to S and N deposition than the rest of the study area. The sandier soils have fewer cation exchange sites where incoming H^+ will more easily remove base cations in more rapidly infiltrating water, accelerating base cation loss to lower horizons. It is also suggested that, with higher rainfall leading to a dominance of wet deposition in the area (Zunckel *et al.*, 2000), these soils are receiving deposition levels approaching critical loads. This finding is based on the evidence that the inputs of anions and H^+ exceed the rate at which exchange surfaces and neutralising base cations are deposited or released via weathering. Water quality in the Vaal Dam catchment did not consistently show elevated salt loads or elevated SO_4^{2-} and NO_3^- concentrations at the five sites investigated, suggesting that the grasslands are conservative with respect to these anions through the soil-water coupled processes. The use of the S and N mineralisation study to construct S and N budgets for these grasslands suggested that S is accreting in the soils, probably in the organic pools. Nitrogen, however, likely limits productivity as atmospheric inputs and mineralisation are balanced by plant uptake, losses by fire and immobilisation by microbial communities.

8.2 Cause-effect relationships

A conceptual framework of the causes resulting in the different soil and surface water responses to S and N deposition is proposed for the Highveld grasslands (Figure 8.1). Frameworks are useful in proposing a common conceptual system across different research approaches, perspectives and or study sites, so that causal factors, scales and interactions within ecosystems can identified (Pickett *et al.*, 2003). The conceptual framework presented here

(Figure 8.1) is a causal-loop diagram. The premise of a causal-loop diagram is to present cause-effects relationships, such that any cause can at some stage become an effect and vice-versa. These relationships are represented by an annotated arrow. An increase in the cause that results in an increase in the effect is annotated with a plus sign (+); an increase in the cause that leads to a decrease in the effect is annotated with a minus sign (-) (Cavana and Mares, 2004).

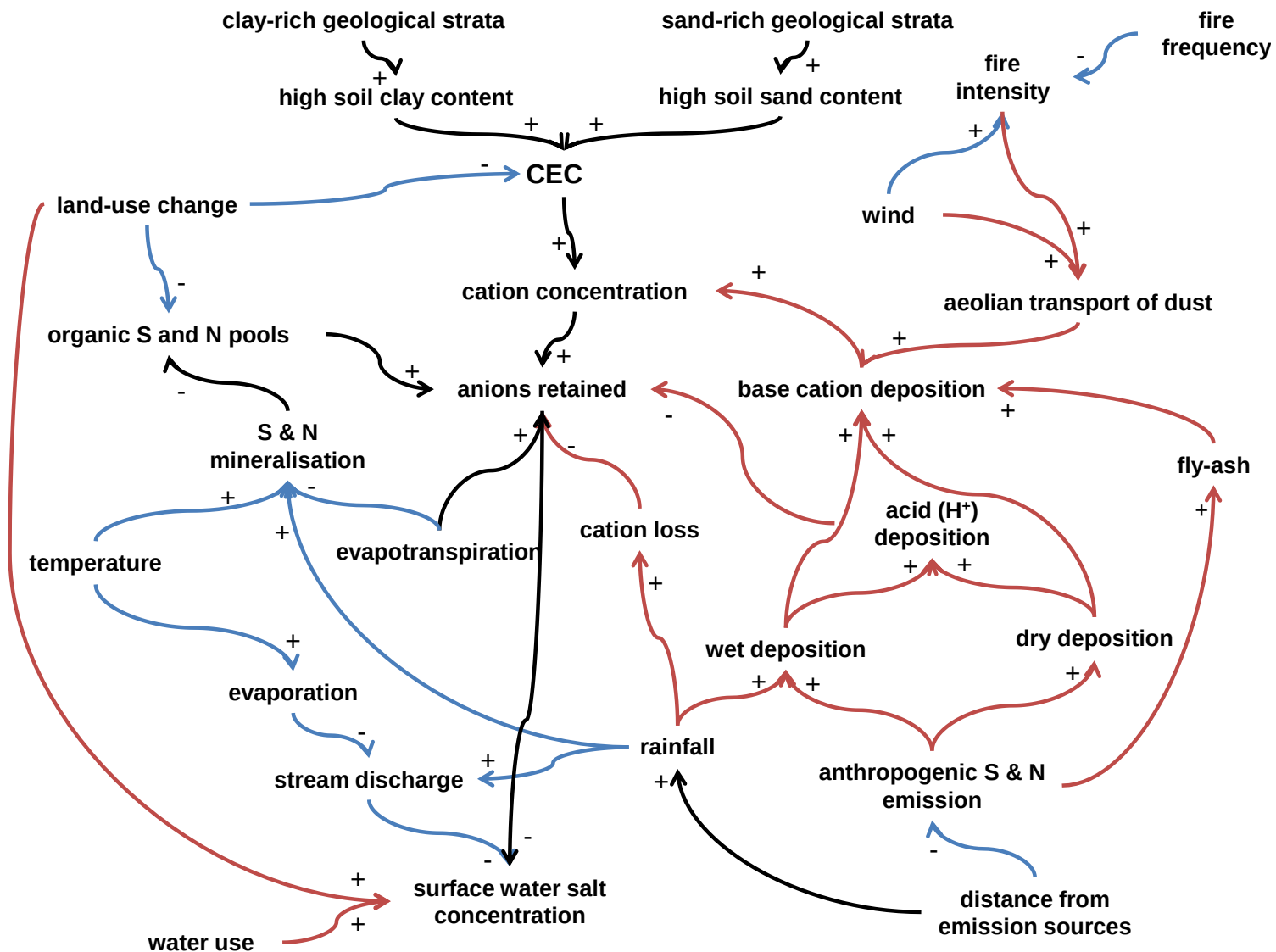


Figure 8.1: A conceptual framework of the cause-effect relationships in the Highveld grasslands resulting in spatial and temporal heterogeneity in responses to S and N deposition. Increases in cause resulting in increases in effect are marked by lowercase s; lowercase o indicates an increase in cause which results in a decrease in effect. Arrow colour denotes temporal scale: black – long-term; blue – short-term and red arrows mark influences over short- and long-term.

8.2.1 Cation exchange capacity and the capacity to retain anions

The geology of the Highveld grasslands is mainly sedimentary strata formed during the late Palaeozoic and early Mesozoic eras between 250 and 60 Ma before present (Vorster, 2003). Clay-rich soils are derived from clay-rich geological strata and similarly sand-rich soils are derived from sand-rich strata. Soil texture influences cation exchange capacity (CEC) where clay soils have, by their more-or-less permanent negative charge, a higher capacity to exchange positively charged cations. Sandier soils, by contrast, will have lower CEC (Figure 8.1). As a result of higher CEC, clay soils are able to retain more cations at exchange sites. More anions can be retained in soils with higher CEC through exchange and adsorption chemistry. Soil organic matter content can improve CEC in a soil and it is proposed that reduced organic pools as a result of land-use change will decrease the CEC of these grassland soils and therefore reduce the potential to retain anions in soil pools. Increased amounts of anions retained in the soils will reduce the salt load in surface waters; however, salt loads in surface waters show no patterns at present.

8.2.2 Atmospheric deposition of S and N

In an average rainfall year, modelled total S deposition varies from 1 to >35 kg ha⁻¹ year⁻¹ and N deposition between 1 and >15 kg ha⁻¹ year⁻¹ across a 380 km (east-west) by 430 km (north-south) area (Blight *et al.*, 2009). Sulfur and N deposition to the Highveld grasslands is a persistent source of acidity over the long-term (modelled until 2020) and is likely to increase as energy demands increase, new power stations are commissioned and old power stations are re-commissioned (Blight *et al.*, 2009). These inputs can therefore be considered chronic and areas closer to emission sources receive the highest deposition than more remote areas (Figure 8.1). As anthropogenic S and N emissions increase, wet and dry deposition of both acid anions and base cations will also increase. Acid anion deposition will decrease anion retention capacity, as the soil exchange and adsorption sites are occupied. This will to some extent, be balanced by the increase in the base cation deposition. Base cation deposition is affected positively by fly-ash inputs, which are related to amount of fuel combusted and emissions generated, as well as through aeolian transportation, where the source of the entrained dust particles is from soil and ash from grassland fires.

8.2.3 Fire

Fire is a frequent (annual to triennial) occurrence in the Highveld grasslands (Bond, 2003). The role of fire in recycling of nutrients should therefore be considered in grassland nutrient dynamics. Because the effect of fire was not included in the current study, only general trends, and not quantitative figures, are included here.

Slow post-fire recovery of trees under low CO₂ conditions in the late Tertiary period has been postulated to result in the expansion of grassland into paleo-savannas (Bond *et al.*, 2003a). Grasses with the tussock growth-form that are dominant over southern Africa provide an excellent fuel source by having large surface area to volume ratio and by having been cured by frost or winter drought, resulting in surface fires (Bond, 2003). The management objectives for prescribed burning include the improvement of the quality and quantity of the grass sward for livestock, conserving biodiversity, control of invasive alien plant species and reduction of the fire hazard of large fuel loads (Bond, 2003). In addition to removing moribund material, which can result in self-shading and reduced production in some species (Bond, 2003), fire also affects nutrient release through volatilisation of C, N and S (Fynn *et al.*, 2003), through deposition of ash (Snyman, 2003) and increased mineralisation by altered surface soil properties (Tainton and Mentis, 1984). Biomass burning can be an important source of cations (Figure 8.1) in the fine aerosol fraction (Maenhaut *et al.*, 1996); however, these inputs are likely to be seasonal as land managers tend to burn grassland fires in late winter and early spring (August – October). Fire intensity will influence the completeness of combustion and therefore the amount of ash and biomass residue available for wind transport. Similarly, fire frequency will affect the intensity of fires because more frequent fires can reduce fuel loads, in turn reducing fire intensity. The frequency of fire in grasslands ranges between 1 and 8 years depending on production rates which are related to rainfall (Bond, 2003).

8.2.4 Climate

Rainfall can affect the capacity of soils to retain anions. Rainfall varies inter-annually and spatially across South Africa. The eastern and southern boundaries of the Highveld grasslands receive higher rainfall (between 200 and 400 mm higher) than the central and western regions (Midgley *et al.*, 1994; Middleton and Bailey,

2009). In a situation of water-deficit, where potential evapotranspiration exceeds rainfall, anion retention, via adsorption, exchange and salt formation mechanisms, will increase as leaching and erosive losses of base cations will decrease (Figure 8.1). Reduced runoff (and therefore stream flow) will result in increased salt loads due to the concentrating effect of evaporation. Under water deficit conditions, S and N mineralisation rates will also reduce as the microbial communities compete for soil moisture, and where conditions are too dry for metabolic processes, immobilisation of S and N will occur. Under these conditions, accretion of S and N in the soils is likely to result.

Increased rainfall, and thus runoff, will temporarily increase S and N mineralisation and increase the loss of anions and base cations through leaching or through erosive runoff, thereby decreasing the anion retention capacity of soils and increasing the concentration of cations and anions in surface waters.

8.2.5 Land use

Reduced organic pools will occur under land-use change conditions, where mechanical disturbance of the vegetation and soil surface would reduce both organic pools and remove the replenishing source of organic material. Erosion of disturbed surface soils by land-use change, will remove base cations and CEC.

Current land-use threats to the grassland biomes include mining, urban expansion, conversion to crop farming and afforestation with exotic tree species for paper and pulp (O'Connor and Bredenkamp, 2003; Mucina and Rutherford, 2006). Under the grassland condition, a large proportion of S (84%) and N (97%) are stored in organic pools (Chapter 5) in the top soils. Should these organic storage pools be disturbed through land use, accelerated breakdown or losses via erosion (wind and water) of the remaining organic pools will result. Erosion by surface runoff will result in losses of anions from soil pools and thus will increase the salt loads in surface waters (Figure 8.1).

8.2.6 Temporal scale

Causal loop diagrams have been criticised in the literature for not adequately capturing the magnitude of the influences or the scale(s) at which the influences occur (Forrester, 1994). To address this, the links in the causal loop framework

(Figure 8.1) have been highlighted to group the relationships by similarity in temporal scale. For example, the influence of evapotranspiration on anion retention capacity is likely to occur in the long-term (black arrow) as a result of extended periods of reduced rainfall and an increase in warm, clear days. However, the influences of rainfall and temperature on mineralisation are more likely to occur in the short-term (blue arrow) of days, weeks or perhaps months. The aeolian transport of base cations is marked to occur in both the long- and short-term (red arrow). Fire and cation input occur seasonally and as such affect soil chemistry on short-time scales with regular inputs, because both fires (Bond, 2003) and aeolian transport (Garstang *et al.*, 1997) have been occurring across the subcontinent for more than 30 000 years, these seasonal influences would have long-term impacts on the soils of the subcontinent as these cation inputs neutralise the acidic inputs slowing potential down-stream effects. The processes that occur over both long- and short-term are those that are a result of the strongly seasonal climate of the region, but have changed little in their seasonality over geologic time. Anthropogenic emissions and deposition are considered to have only been active for a short-term (± 70 years) but may have long-term impacts.

8.2.7 Spatial scale

The study area covers a large portion of the Highveld grasslands and the soils were all sampled in natural, unimproved grasslands. Low-density free-range grazing for stock-farming does occur (usually less than 1 animal unit ha⁻¹). At this scale, climate is similar across all sites; however, minor differences in geology result in heterogeneity of soils. This spatial scale is addressed in the causal loop framework, by including the influence of geology and distance from emission sources. Although the geology is predominantly sedimentary, over the spatial scale of the Highveld grasslands, the type of sedimentary strata varies and occasional igneous intrusions occur (Vorster, 2003). These parent material differences have influenced the soil type and texture over geologic time resulting in spatial heterogeneity of soils while the above-ground vegetation remains roughly homogenous grassland. In addition to the heterogeneous soil template, the spatial scale of anthropogenic emission sources and deposition patterns will also influence the causes that enhance or dampen soil CEC and anion retention capacity; sites closer to the clustered emission sources of coal-fired power stations, industrial and vehicular emissions receive

higher rates of deposition than more remote sites (Figures 3.2 and 3.3). Those sites that are able to retain more anions, especially excess acid anions, will provide sustainable ecosystem services for a longer time than those where anion retention is limited.

The influence of climatology, deposition and soil texture overlap spatially across the study area Figure 8.2. In the figure, the direction of the arrow shows the gradient of increase such that evaporation increases northerly and westerly; rainfall increases to the south and east; deposition increases northerly and westerly, with a maximum in the central region of the study area. The clay soils are also located more centrally to the study area and sandier soils on the eastern and southern boundaries. Because of the overlap of these factors at this spatial scale there are likely to be some confounding issues. Response of a soil patch to atmospheric deposition of S and N is therefore a function of the deposition of acidic and basic ions received, the balance between rainfall received and evaporative demand, and the soil texture. In spite of these confounding issues, the soil texture was seen as a good predictor of response with respect to soil acidity status, where pH decreased significantly in soils with less than 25% clay. At 4% clay and below, ANC decreased significantly and exchangeable acidity increased significantly. It is these areas that are proposed as the most sensitive to acidic inputs via atmospheric deposition.

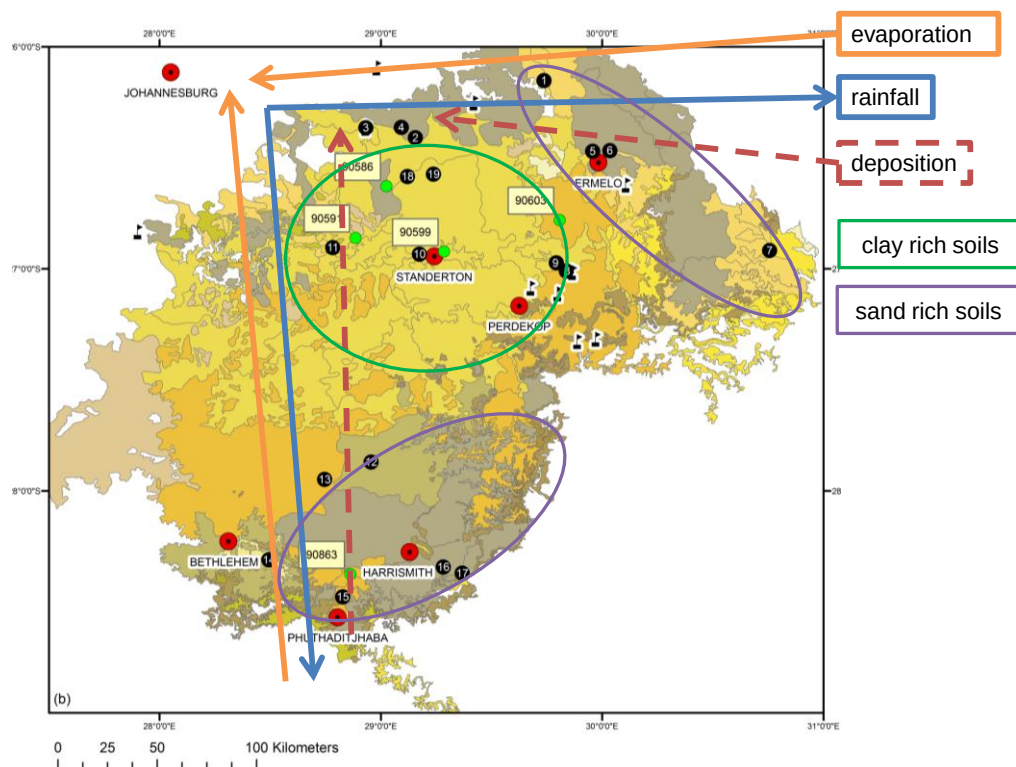


Figure 8.2: Spatial differences in evaporation, rainfall, deposition, clay rich soils and sand rich soils across the Highveld grassland study area. The direction of the arrow shows the gradient of increase: Evaporation increases northerly and westerly; Rainfall increases to the south and east; Deposition increases northerly and westerly, with a maximum in the central region of the study area.

Application of the conceptual framework

The conceptual framework presented in Figure 8.1 is focussed on soil texture and chemistry and their influence on the heterogeneity of response to atmospheric S and N deposition. With respect to the ecosystem service of nutrient cycling (a provisioning service), the amount of S stored in the large soil organic pool and the net immobilisation of SO_4^{2-} on an annual basis suggests that S cycling and release to plants is still tightly coupled and minimal amounts of S leach out of these soils.

The conceptual framework does not link deposition, especially N, to changes in biodiversity. The eutrophying effect of N on grassland species diversity is well researched in areas of Europe and North America impacted by large N deposition loads. The N cycle proposed in this thesis suggests that these grasslands are still N-limited; however the even gradual removal of this limitation could initiate changes in species abundance and competition which could in time result in lowered species diversity.

The soils of the central Highveld grasslands are sufficiently well buffered against incoming acidity to continue to adequately provide the ecosystem services of water storage (a provisioning service) and water filtration (a regulating service). Water quality is more likely to be affected by land-use change in the short-term or by continued anthropogenic S and N deposition in the long-term. Runoff, during storm events, may remove dry deposition directly into surface waters and could result in episodic input events that may have different influences on water quality and aquatic biota than slower continuous inputs from ground water infiltration. These changes are not considered by the conceptual framework directly. Similarly, the changes in plant species diversity of the Highveld grasslands is not yet known in relation to atmospheric S and N deposition and the conceptual framework does not make links between soil chemistry and diversity. The lack of species diversity data are considered to be an important knowledge gap to address in further research in this area.

In addition, the framework only considered increases in anthropogenic emissions. If reduced emissions due to improved technology or changes in location of fossil fuel combustion were to occur, the conceptual model does not account for the lag effects that could affect ecosystem services in this study area.

The cause-effect relationships in the conceptual model are based on key principles in soil science and therefore would make the model suitable to all ecosystems. There are however, many differences to the soils of this area and soil of areas where impacts to atmospheric deposition have been observed. The processes occurring in these old soils may not translate well to more recently derived soils. Much of the study area also experiences a water deficit for at least part of the year such that evaporation exceeds precipitation, limiting the amount of soil moisture that can infiltrate past the rooting zone. For this reason the model may not be appropriate in areas where precipitation exceeds evaporation potential. Under these conditions moisture moves through the soil below the rooting depth where there is sufficient contact between water and cation-anion exchange sites to remove the ions out of the rooting zone and eventually to recharge streams and other surface water bodies, with accompanying ions.

Many other atmospheric deposition impact studies have occurred in forested areas. It is speculated that the difference in dominant vegetation type is likely to change the cause-effect relationships by different plant nutrient demands, atmospheric deposition received - because the surface area of trees increase deposition – and because the organic matter inputs from forested areas are expected to be different to those from frequently burned perennial grasslands. For this reason, cautionary application of the conceptual model is advised in areas where the natural vegetation is not grassland.

8.3 Key research questions - answered

Baron *et al.* (2000) refer to identifying the subtle changes in ecosystems as a result of continuous, but low rates, of S and N deposition. The research findings in the Highveld grasslands could be considered evidence that subtle changes are occurring and so support the establishment of a programme to monitor ecosystem changes in the long-term, especially on the identified sensitive soil patches. Using the main findings from this thesis, the key questions will be specifically addressed below.

Key question 1: How have the rates of wet and dry deposition changed since 1991?

Modelled S and N deposition rates to the Highveld grasslands are summarised in Chapter 3. Maximum levels of modelled S deposition have increased from 5 kg S ha⁻¹ year⁻¹ in 1948 to >35 kg S ha⁻¹ year⁻¹ in 2007. Similarly the maximum rates of N deposition have increased from 0.5 kg N ha⁻¹ year⁻¹ in 1948 to >15 kg N ha⁻¹ year⁻¹ in 2007. Although modelled S and N deposition rates increased generally over the study area between 1948 and 2007, deposition at the specific receptor sites showed decreases in modelled deposition between 1991 and 2007. Mean S deposition (for 10 receptor sites) decreased from 19.8 to 15.4 kg S ha⁻¹ year⁻¹. Similarly mean N deposition (for 10 receptor sites) decreased from 5.0 to 3.5 kg N ha⁻¹ year⁻¹. Linear projections based on deposition at specific receptor sites show that between 1991 and 2007 the study area received an average ($\pm$ standard error) of 339 $\pm$ 87 kg S ha⁻¹ and 85 $\pm$ 7 kg N ha⁻¹. There were no receptor points in the model for the southern portion of the study area, however, from the other model output (isopleths figures) it is expected that these areas would receive less deposition than the northern part of the study area.

Key question 2: How have the top- and sub-soil chemical properties, as measured by Fey and Guy (1993) changed in the Vaal Dam catchment, between 1991 and 2007?

Re-assessment of soil chemical properties, in 2007, revealed increases of both acidic and basic ion concentrations in the soils of the Highveld grasslands (Chapter 4). In the site-by-site comparison, assessment of all the sites and in the analysis of soil acidity status by soil texture, it was found the pH(H₂O), exchangeable acidity and acid neutralising capacity could be used to indicate increased soil acidity across the study area. This allowed the identification of the sandier soil types near the eastern and southern study area boundaries to be the most sensitive to S and N deposition. Higher soil clay contents and increases in base cations suggest that the soils in the central Highveld are able to buffer acid anion inputs from atmospheric S and N deposition.

Key question 3: Do any of the soils studied (18 soil sample sites – 13 soil types), show exceedance of S retention capacities, if so, why?

No soils showed exceedance of S retention capacities as the change in SO₄²⁻ was not significant in either top- or sub-soils. However, the decrease in ANC in soils with low clay content is a concern that S retention capacities maybe close to exceedance in these soils. Sites located closer to the potential sources of fly-ash with potentially neutralising base cations, appear to receive co-deposition of base cations and acidic S and N compounds, adding to the inherent buffering capacity of these soils. The anion retention in these central soils appears to be capacity limited as the clay colloid surfaces are supplemented by base cation inputs from fly-ash. The sandier sites nearer the escarpment may not receive the base cations which fall out of the air column closer to the source as heavier particulate matter. The structure of sandy soil limits the association with base cations and therefore the number of exchange sites for SO₄²⁻ and NO₃⁻, implying in these peripheral soils capacity of the soils to retain anions is limited by the number of colloidal exchange surfaces.

Additional evidence that S retention capacity had not been exceeded is from the S mineralisation study and from surface water S concentrations. Sulfur cycling from the mineralisation study shows that immobilisation of S is common and that the soil organic S pool is larger than the inorganic SO₄²⁻ pool. With reference to water quality, the SO₄²⁻ concentration was found to increase over time at only one of the

five water quality monitoring points. The other salt concentrations and ANC values at that site did not support the possibility that the increasing trend of SO_4^{2-} concentrations was related to the soil S retention capacity being exceeded.

Key question 4: How has the Acid Neutralising Capacity of the soils in the catchment changed between 1991 and 2007?

Although NO_3^- and Cl^- were not reported by Fey and Guy (1993), ANC for soils in 1991 was estimated based on the proportional contribution of NO_3^- and Cl^- in 2007. When comparing ANC values on a site-by-site basis, almost equal (significant) increases and decreases were found in the top- and sub-soils. However, when analysing the ANC values for soils by their clay content, it was found that soils with low clay content (4% or less) had shown a significant decrease in ANC between 1991 and 2007 and that ANC values in these soils was less than $0 \text{ cmol}_c \text{ kg}^{-1}$. The ANC values corroborated the findings for $\text{pH}(\text{H}_2\text{O})$ and exchangeable acidity and identified the soils of the periphery of the study area as being sensitive to atmospheric S and N inputs.

Key question 5: What are the rates of soil S and N mineralisation in the top-soils of the Highveld grasslands?

The SO_4^{2-} mineralisation rate in the Highveld grasslands varied between $-0.66 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$ and $1.09 \mu\text{g SO}_4^{2-} \text{ g}^{-1} \text{ soil day}^{-1}$. The overall pattern showed an immobilisation depression in winter and the peak mineralisation in late spring. The positive influence of soil moisture was observed for net SO_4^{2-} and N mineralisation. Across all 11 sites net N mineralisation rate ranged between $-0.97 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ and $1.21 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. Statistically significant differences between sampling months were found for both SO_4^{2-} and N mineralisation rates. When grouped by land type – which has been used in the re-assessment of soil chemistry in 2007 – it was found that mineralisation in the Ba and Ea land types were similar for both SO_4^{2-} and N, while the Bb land type showed much lower annual net N mineralisation rates and annual immobilisation of SO_4^{2-} . Sulfur mineralisation has traditionally been determined in laboratory-based experiments that involve the disturbance of the soil through removal and transport, as well as some preparatory steps such as drying and sieving. This disturbance can affect the activity of microbes involved in the mineralisation process. The incubation

of the soils in the laboratory then occurs under ideal temperature and moisture conditions resulting in potential S mineralisation. These values are then scaled up to annual quantities. The *in situ* incubation method limits disturbance to the insertion and removal of the incubation column which isolates the soil from the surrounding column to limit the plant uptake and potential leaching losses. Transport of the soils is at cool temperatures, sieving and drying are avoided and chemical analysis of S and N occurs as soon as possible after collection, usually within 2 days. The SO_4^{2-} mineralisation rates determined for the Highveld grasslands using the *in situ* incubation method were comparable with S mineralisation measured in other grasslands globally. The monitoring of mineralisation and pool sizes in the long-term will enable the identification of when S deposition exceeds soil retention capacities and plant demand and when ecosystem services may be impacted more seriously. Lowered S and N mineralisation rates could indicate that the soil pH has become unsuitable for the microorganisms involved in the decomposition of organic material. The need for mineralisation may also be suppressed by plant uptake needs being met by deposition of inorganic S and N compound. Additionally in ecosystems impacted by both S and N deposition, mineralisation of both S and N can be monitored simultaneously using the *in situ* incubation technique, developed for N mineralisation studies and tested for S mineralisation studies.

Key question 6: How has water quality, in terms of dissolved salts, SO_4^{2-} and NO_3^- changed between 1991 and 2008?

The coupling of soil and water processes was highlighted as an initial concern for the Highveld grasslands earlier in the chapter. The findings from the investigation of water quality in some respects mirror those of the soil chemical reassessment; at some sites increased concentrations of SO_4^{2-} (1 site; 90586), NO_3^- (1 site; 90603) and NH_4^+ (1 site: 90586) occurred. However, at other sites concentrations of these water quality variables were found to decrease over the timeframe of investigation: SO_4^{2-} decreased at sites 90599 and 90603; NO_3^- decreased at site 90599 and NH_4^+ decreased at sites 90591 and 90599. No significant changes in dissolved salt concentrations were detected over the period investigated. Many hydrologists correct surface water ion and salt concentrations by using concentration-flow curves. Due to the fact that the five sites selected had poor regression coefficients for concentration-flow curves, multivariate statistics were used to analyse for changes in

concentrations overtime. The variability in the water quality data sets is related to the complexity of the Vaal Dam catchment from inputs from inter-basin transfers, mining activities, water treatment plants and urban development. Monthly discharge and the hydrological season (wet or dry) were both found to influence water chemistry such that lower concentrations of dissolved salts, SO_4^{2-} and NO_3^- were recorded in the wetter months due to dilution by rainwater and runoff. The chemical variables expected to show the effect of atmospheric S and N deposition (as proposed in the literature) provided no evidence that, at any of the five sites investigated, S and N deposition had resulted in changes in water chemistry. The complexity of water quality in the Vaal Dam catchment, due to water use, land use, inter-basin transfers and the inter-annual rainfall variability, is well known. Isolating a single chronic input source, such as atmospheric S and N deposition, to this catchment will be difficult. Many of the mining activities, waste water works and urban development occurs near the major S and N emission sources thus obscuring the influence of deposition in these areas. The use of multivariate analysis and median monthly concentration values, in contrast to the concentration-flow curves that are commonly used, did not provide convincing evidence of impact or non-impact. Careful site selection and inclusion of more environmental variables may strengthen this technique in further studies.

8.4 Recommendations

The Highveld grasslands are well researched with respect to atmospheric quality (for example the early research from Tyson *et al.*, 1988; Held *et al.*, 1996). More recently wet and dry deposition networks have been extended (Mphepya *et al.*, 2004; Mphepya *et al.*, 2006; Josipovic *et al.*, 2010). In contrast, the terrestrial and aquatic systems are less well monitored with specific reference to monitoring for impacts of atmospheric S and N deposition. It is recommended that soil chemistry continued to be monitored and that water quality in the central and peripheral regions of the Highveld grasslands be monitored. It is also suggested that deposition of both base cations and acid anions be monitored near the areas identified as sensitive to deposition, so that finer-scale cause-effect relationships can be established.

The importance of diverse biological communities is discussed in the literature (for example, Chapin *et al.*, 2000; Sala *et al.*, 2000) as the source of ecosystem

resilience to disturbance (Holling, 2001). It is therefore recommended that, in order to understand ecosystem services in the Highveld grassland more fully, the diversity be inventoried and monitored. Recent studies have focussed on plant diversity along depositional gradients (Stevens *et al.*, 2004; Stevens *et al.*, 2009; Stevens *et al.*, 2010), such as is evident across the Highveld.

Comprehensive S and N budgets for these grasslands were identified as a knowledge gap. The findings from comprehensive biogeochemical studies in these grasslands could, for example, inform crop farmers about the need for inorganic fertilisers and the appropriate timing for applications. The management recommendations are linked to more comprehensive biogeochemical budgets. It is recommended that the grassland state be preserved, with compensatory incentives to landowners if necessary. These grasslands are able to retain acid anions and limit down-stream impacts. Maintaining the unimproved, natural state is likely to be the most effective method of limiting short-term impacts of S and N deposition on ecosystem services. Management of water use and S and N emissions is also advocated to limit inputs of acid anions but specific recommendations are outside of the scope of this thesis.

8.4.1 Conclusion

The grasslands of the South African Highveld receive S and N deposition comparable to other industrialised regions globally. Soil chemistry has shown that soil acidity increased between 1991 and 2007 and that the periphery of the study area is more sensitive to deposition because the soils are sandier and have limited capacity to buffer incoming acidity. Water quality and biological processes do not yet appear to be impacted in the patterns described in the literature. Preservation of the grassland state is recommended to limit any further impacts that could occur.

CHAPTER 9: REFERENCES

- Abbasi, M.K., Shah, Z., and Adams, W.A., 2001. Mineralization and nitrification potentials of grassland soils at shallow depth during laboratory incubation. *Journal of Plant Nutrition and Soil Science* **164**(5), 497-502.
- Aber, J.D., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., McNulty, S., Rustad, L., and Fernandez, I., 1998. Nitrogen saturation in temperate forest ecosystems. *BioScience* **48**(11), 921-934.
- Aber, J.D., Nadelhoffer, K.J., Steudler, P., and Melillo, J.M., 1989. Nitrogen saturation in Northern forest ecosystems. *BioScience* **39**(6), 378-386.
- Aerts, R., and Bobbink, R., 1999. The impact of atmospheric nitrogen deposition on vegetation processes in terrestrial, non-forest ecosystems. In: Langan, S. (Ed.), *The impact of nitrogen deposition on natural and semi-natural ecosystems*. Kluwer Academic Publications, Dordrecht, The Netherlands.
- Alfredsson, H., Condon, L.M., Clarholm, M., and Davis, M.R., 1998. Changes in soil acidity and organic matter following the establishment of conifers on former grassland in New Zealand. *Forest Ecology and Management* **112**(3), 245-252.
- Anderson, J.M., and Ingram, J.S.I., 1993. *Tropical soil biology and fertility: Handbook of methods*. 2nd Edition ed. CAB International, Wallingford, Oxon. 221 pp.
- Anderson, J.W., 1978. *Sulfur in biology*. The Institute of Biology's Studies in Biology No. 101. Edward Arnold, London. 59 pp.
- Ashmore, M.R., 2003. Air pollution impacts on vegetation in Europe. In: Emberson, L., Ashmore, M.R., Murray, F. (Eds.), *Air pollution impacts on crops and forests*. Imperial College Press, London, pp. 59-88.
- Asner, G.P., Seastedt, T.R., and Townsend, A.R., 1997. The decoupling of terrestrial carbon and nitrogen cycles. *BioScience* **47**(4), 226-234.
- Baron, J.S., 2006. Hindcasting nitrogen deposition to determine an ecological critical load. *Ecological Applications* **16**(2), 433-439.
- Baron, J.S., Rueth, H.M., Wolfe, A.M., Nydick, K.R., Allstott, E.J., Minear, J.T., and Moraska, B., 2000. Ecosystem responses to nitrogen deposition in the Colorado Front Range. *Ecosystems* **3**(4), 352-368.

- Baron, J.S., Schmidt, T.M., and Hartman, M.D., 2009. Climate-induced changes in high elevation stream nitrate dynamics. *Global Change Biology* **15**(7), 1777-1789.
- Baumgardner, R.E., Lavery, T.F., Rogers, C.M., and Isil, S.S., 2002. Estimates of the atmospheric deposition of sulfur and nitrogen species: Clean Air Status and Trends Network, 1990-2000. *Environmental Science & Technology* **36**(12), 2614-2629.
- Berge, E., Bartnicki, J., Olendrzynski, K., and Tsyro, S.G., 1999. Long-term trends in emissions and transboundary transport of acidifying air pollution in Europe. *Journal of Environmental Management* **57**(1), 31-50.
- Binkley, D., Valentine, D., Wells, C., and Valentine, U., 1989. An empirical analysis of the factors contributing to 20-year decrease in soil pH in an old-field plantation of loblolly pine. *Biogeochemistry* **8**(1), 39-54.
- Blair, J.M., 1997. Fire, N availability, and plant response in grasslands: A test of the Transient Maxima hypothesis. *Ecology* **78**(8), 2359-2368.
- Blight, J., Cornelius, G., Herold, C., Lorentz, S., and Scholes, M., 2009. *An investigation into the effects of atmospheric pollution on the soil-water-ecosystem continuum in the eastern regions of South Africa - Phase 0 research report*. Report number: RES/RR/09/30350, Eskom Holdings Limited, Rosherville, South Africa.
- Bloem, E., Haneklaus, S., Sparovek, G., and Schnug, E., 2001. Spatial and temporal variability of sulphate concentration in soils. *Communications in Soil Science and Plant Analysis* **32**(9-10), 1391-1403.
- Bobbink, R., 1991. Effects of Nutrient Enrichment in Dutch Chalk Grassland. *Journal of Applied Ecology* **28**(1), 28.
- Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinderby, S., Davidson, E., Dentener, F., Emmett, B., Erisman, J.W., Fenn, M., Gilliam, F., Nordin, A., Pardo, L., and De Vries, W., 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecological Applications* **20**(1), 30-59.
- Bobbink, R., Hornung, M., and Roelofs, J.G.M., 1998. The Effects of Air-Borne Nitrogen Pollutants on Species Diversity in Natural and Semi-Natural European Vegetation. *Journal of Ecology* **86**(5), 717-738.

- Bond, W.J., 2003. Fire. In: Cowling, R.M., Richardson, D.M., Pierce, S.M. (Eds.), *Vegetation of southern Africa*. Cambridge University Press, Cambridge, pp. 421-446.
- Bond, W.J., and Midgley, G.F., 2000. A proposed CO₂-controlled mechanism of woody plant invasion in grasslands and savannas. *Global Change Biology* **6**(8), 865-869.
- Bond, W.J., Midgley, G.F., and Woodward, F.I., 2003a. The importance of low atmospheric CO₂ and fire in promoting the spread of grasslands and savannas. *Global Change Biology* **9**(7), 973-982.
- Bond, W.J., Midgley, G.F., and Woodward, F.I., 2003b. What controls South Africa vegetation - climate or fire? *South African Journal of Botany* **69**(1), 79-91.
- Bouwman, A., Van Vuuren, D., Derwent, R., and Posch, M., 2002. A global analysis of acidification and eutrophication of terrestrial ecosystems. *Water, Air, & Soil Pollution* **141**(1), 349-382.
- Bowman, W.D., Cleveland, C.C., Halada, L., Hresko, J., and Baron, J.S., 2008. Negative impact of nitrogen deposition on soil buffering capacity. *Nature Geoscience* **1**(11), 767-770.
- Boye, K., Nilsson, S., and Eriksen, J., 2009. Net sulfur mineralization potential in Swedish arable soils in relation to long-term treatment history and soil properties. *Biology and Fertility of Soils* **45**(7), 743-751.
- Brasseur, G.P., Orlando, J.J., and Tyndall, G.S. (Eds.), 1999. Atmospheric chemistry and global change. Oxford University Press, Oxford, 654 pp.
- Brasseur, G.P., and Roeckner, E., 2005. Impact of improved air quality on the future evolution of climate. *Geophysical Research Letters* **32**(23), L23704 (23704 pages).
- Braune, E., and Rogers, K.H., 1987. *The Vaal River catchment: problems and research needs*. Report number: 143, South African National Scientific Programmes, Pretoria.
- Bredenkamp, G.J., Spada, F., and Kazmierczak, E., 2002. On the origin of northern and southern hemisphere grasslands. *Plant Ecology* **163**(2), 209-229.
- Brodowski, S., Amelung, W., Lobe, I., and Du Preez, C., 2005. Losses and biogeochemical cycling of soil organic nitrogen with prolonged arable cropping in the South African Highveld - evidence from d- and l-amino acids. *Biogeochemistry* **71**(1), 17-42.

- Bruland, G.L., Bliss, C.M., Grunwald, S., Comerford, N.B., and Graetz, D.A., 2008. Soil nitrate-nitrogen in forested versus non-forested ecosystems in a mixed-use watershed. *Geoderma* **148**(2), 220-231.
- Burkhardt, J., 1995. Hygroscopic salts on the leaf surface as a possible cause of forest decline symptoms. *Water, Air, & Soil Pollution* **85**(3), 1245-1250.
- Burns, D.A., Blett, T., Haeuber, R., and Pardo, L.H., 2008. Critical loads as a policy tool for protecting ecosystems from the effects of air pollutants. *Frontiers in Ecology and the Environment* **6**(3), 156-159.
- Butler, T.J., Likens, G.E., and Stunder, B.J.B., 2001. Regional-scale impacts of Phase I of the Clean Air Act Amendments in the USA: the relation between emissions and concentrations, both wet and dry. *Atmospheric Environment* **35**(6), 1015-1028.
- Carpenter, S.R., Mooney, H.A., Agard, J., Capistrano, D., DeFries, R.S., Díaz, S., Dietz, T., Duraiappah, A.K., Oteng-Yeboah, A., Pereira, H.M., Perrings, C., Reid, W.V., Sarukhan, J., Scholes, R.J., and Whyte, A., 2009. Science for managing ecosystem services: Beyond the Millennium Ecosystem Assessment. *Proceedings of the National Academy of Sciences* **106**(5), 1305-1312.
- Cavana, R.Y., and Mares, E.D., 2004. Integrating critical thinking and systems thinking: from premises to causal loops. *System Dynamics Review (Wiley)* **20**(3), 223-235.
- Chapin, F.S., Zavaleta, E.S., Eviner, V.T., Naylor, R.L., Vitousek, P.M., Reynolds, H.L., Hooper, D.U., Lavorel, S., Sala, O.E., Hobbie, S.E., Mack, M.C., and Diaz, S., 2000. Consequences of changing biodiversity. *Nature* **405**(6783), 234.
- Chapman, H.D., 1965. Total exchangeable bases. In: Black, C.A., Evans, D.D., White, J.L., Ermenger, L.E., Clark, F.E. (Eds.), *Methods of soil analysis, Part 2*. American Society of Agronomy, Wisconsin.
- Clarisse, L., Clerbaux, C., Dentener, F., Hurtmans, D., and Coheur, P.F., 2009. Global ammonia distribution derived from infrared satellite observations. *Nature Geoscience* **2**(7), 479-483.
- Clark, C.M., and Tilman, D., 2008. Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands. *Nature* **451**(7179), 712-715.
- Cole, D.W., 1992. Nitrogen chemistry, deposition and cycling in forests - Overview. In: Johnson, D.W., Lindberg, S.E. (Eds.), *Atmospheric deposition and forest nutrient cycling*. Ecological Studies. Springer-Verlag, New York, pp. 150-152.

- Collar, N.J., Crosby, M.J., and Stattersfield, A.J., 1994. *Birds to watch 2: the World list of threatened birds*. BirdLife International (BirdLife Conservation Series 4), Cambridge, United Kingdom. 407 pp.
- Collett, K.S., Piketh, S.J., and Ross, K.E., 2010. An assessment of the atmospheric nitrogen budget on the South African Highveld. *South African Journal of Science* **106**(5/6), DOI: 10.4102/sajs.v4106i4105/4106.4220 (4109 pages).
- Cooper, D.M., 2005. Evidence of sulphur and nitrogen deposition signals at the United Kingdom Acid Waters Monitoring Network sites. *Environmental Pollution* **137**(1), 41-54.
- Cowling, E., and Nilsson, J., 1995. Acidification research: Lessons from history and visions of environmental futures. *Water, Air and Soil Pollution* **85**(1), 279-292.
- Cowling, R.M., and Hilton-Taylor, C., 1994. Patterns of plant diversity and endemism in southern Africa: an overview. *Stelitzia* **1**, 31-52.
- Cox, D.R., and Stuart, A., 1955. Some Quick Sign Tests for Trend in Location and Dispersion. *Biometrika* **42**(1), 80-95.
- Dai, Z., Liu, Y., Wang, X., and Zhao, D., 1998. Changes in pH, CEC and exchangeable acidity of some forest soils in southern China during the Last 32-35 Years. *Water, Air, & Soil Pollution* **108**(3), 377-390.
- Daily, G.C., Söderqvist, T., Aniyar, S., Arrow, K., Dasgupta, P., Ehrlich, P.R., Folke, C., Jansson, A., Jansson, B.-O., Kautsky, N., Levin, S., Lubchenco, J., Mäler, K.-G., Simpson, D., Starrett, D., Tilman, D., and Walker, B., 2000. The value of nature and the nature of value. *Science* **289**(5478), 395-396.
- Davidson, E.A., de Carvalho, C.J.R., Figueira, A.M., Ishida, F.Y., Ometto, J.P.H.B., Nardoto, G.B., Sabá, R.T., Hayashi, S.N., Leal, E.C., Vieira, I.C.G., and Martinelli, L.A., 2007. Recuperation of nitrogen cycling in Amazonian forests following agricultural abandonment. *Nature* **447**(7147), 995-998.
- Davies, B.R., Thoms, M., and Meador, M., 1992. An assessment of the ecological impacts of inter-basin water transfers, and their threats to river basin integrity and conservation. *Aquatic Conservation: Marine and Freshwater Ecosystems* **2**(4), 325-349.
- Day, J.A., Dallas, H.F., and Wackernagel, A., 1998. Delineation of management regions for South African rivers based on water chemistry. *Aquatic Ecosystem Health and Management* **1**(2), 183-197.

- Day, P.R., 1956. Report of the committee on physical analyses, 1954–1955. *Proceedings of the Soil Science Society of America* **20**, 267-269.
- de Groot, R.S., Wilson, M.A., and Boumans, R.M.J., 2002. A typology for the classification, description and valuation of ecosystem functions, goods and services. *Ecological Economics* **41**(3), 393-408.
- De Vries, W., and Breeuwsma, A., 1987. The relation between soil acidification and element cycling. *Water, Air, & Soil Pollution* **35**(3), 293-310.
- Dentener, F., Drevet, J., Lamarque, J.F., Bey, I., Eickhout, B., Fiore, A.M., Hauglustaine, D., Horowitz, L.W., Krol, M., Kulshrestha, U.C., Lawrence, M., Galy-Lacaux, C., Rast, S., Shindell, D., Stevenson, D., Van Noije, T., Atherton, C., Bell, N., Bergman, D., Butler, T., Cofala, J., Collins, B., Doherty, R., Ellingsen, K., Galloway, J., Gauss, M., Montanaro, V., Müller, J.F., Pitari, G., Rodriguez, J., Sanderson, M., Solomon, F., Strahan, S., Schultz, M., Sudo, K., Szopa, S., and Wild, O., 2006. Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation. *Global Biogeochemical Cycles* **20**(4), GB4003 (4021 pages).
- Department of Water Affairs and Forestry, 1992. *Analytical methods manual*. Report number: Technical report TR 151, Department of Water Affairs and Forestry, Pretoria, South Africa.
- Department of Water Affairs and Forestry, 1996. *South African Water Quality Guidelines (second edition). Volume 1: Domestic Use*. Report number, Department of Water Affairs and Forestry, Pretoria, South Africa.
- Dominati, E., Patterson, M., and Mackay, A., 2010. A framework for classifying and quantifying the natural capital and ecosystem services of soils. *Ecological Economics* **69**(9), 1858-1868.
- Dovland, H., and Pederson, U., 1996. Acid deposition in Europe. In: Whelpdale, D.M., Kaiser, M.S. (Eds.), *Global acid deposition assessment*. World Meteorological Organization, pp. 53-67.
- Draaijers, G.P.J., Van Leeuwen, E.P., De Jong, P.G.H., and Erisman, J.W., 1997. Base-cation deposition in Europe - Part II. Acid neutralization capacity and contribution to forest nutrition. *Atmospheric Environment* **31**(24), 4159-4168.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., and Weathers, K.C., 2001. Acidic

- deposition in the north-eastern United States: Sources and inputs, ecosystem effects, and management strategies. *BioScience* **51**(3), 180-198.
- du Preez, D.R., Gunton, C., and Bate, G.C., 1983. The distribution of macronutrients in a broad leaf woody savanna. *South African Journal of Botany* **2**, 236-242.
- du Toit, B., 2003. Effects of site management operations on the nutrient capital of a eucalypt plantation system in South Africa: scientific paper. *Southern African Forestry Journal* **199**, 15-26.
- du Toit, M.E., and du Preez, C.C., 1995. Swawelfraksies, -verhoudings en -verwantskappe in geselekteerde onversteurde en bewerkte Suid-Afrikaanse gronde (in Afrikaans). *South African Journal of Plant and Soil* **12**(1), 11-19.
- Duprè, C., Stevens, C.J., Ranke, T., Bleeker, A., Peppler-Lisbach, C., Gowing, D.J.G., Dise, N.B., Dorland, E., Bobbink, R., and Diekmann, M., 2010. Changes in species richness and composition in European acidic grasslands over the past 70 years: the contribution of cumulative atmospheric nitrogen deposition. *Global Change Biology* **16**(1), 344.
- Edwards, P.J., 1998. *Sulfur cycling, retention, and mobility in soils: a review*. Report number: General Technical Report NE-250, USDA Forest Service, USDA Forest Service.
- Embersson, L., 2003. Air pollution impacts on crops and forests: An introduction. In: Embersson, L., Ashmore, M.R., Murray, F. (Eds.), *Air pollution impacts on crops and forests*. Imperial College Press, London, pp. 3.
- EPA, 2008. *Integrated science assessment for oxides of nitrogen and sulfur - ecological criteria*. EPA - United States Environmental Protection Agency EPA/600/R-08/082F, North Carolina. 898 pp.
- Evans, C.D., Harriman, R., Monteith, D.T., and Jenkins, A., 2001. Assessing the suitability of acid neutralising capacity as a measure of long-term trends in acidic waters based on two parallel datasets. *Water, Air and Soil Pollution* **130**, 1541-1546.
- Falkengren-Grerup, U., Brunet, J., and Diekmann, M., 1998. Nitrogen mineralisation in deciduous forest soils in south Sweden in gradients of soil acidity and deposition. *Environmental Pollution* **102**(1, Supplement 1), 415-420.
- Falkengren-Grerup, U., Brunet, J., and Quist, M.E., 1995. Sensitivity of plants to acidic soils exemplified by the forest grass *Bromus benekenii*. *Water, Air, & Soil Pollution* **85**(3), 1233-1238.

- Farley, K.A., Piñeiro, G., Palmer, S.M., Jobbágy, E.G., and Jackson, R.B., 2008. Stream acidification and base cation losses with grassland afforestation. *Water Resources Research* **44**(7), W00A03 (11pages).
- Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W., and Neitlich, P., 2003a. Ecological effects of nitrogen deposition in the western United States. *BioScience* **53**(4), 404-420.
- Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., and Sickman, J.O., 2003b. Nitrogen emissions, deposition, and monitoring in the western United States. *BioScience* **53**(4), 391-403.
- Fey, M., 2010. *Soils of South Africa*. Cambridge University Press, Cambridge. 288 pp.
- Fey, M.V., and Guy, S.A., 1993. *The capacity of soils in the Vaal Dam Catchment to retain sulphate from atmospheric pollution*. Report number: WRC report 414/1/93, Water Research Commission, Pretoria.
- Forrester, J.W., 1994. System dynamics, systems thinking, and soft OR. *System Dynamics Review* **10**(2), 245-256.
- Foster, D., Swanson, F., Aber, J.B.I., Brokaw, N., Tilman, D., and Knapp, A., 2003. The importance of land-use legacies to ecology and conservation. *BioScience* **53**(1), 77-88.
- Fowler, D., Cape, J.N., Coyle, M., Fletchard, C., Kuylensteirna, J., Hicks, K., Derwent, D., Johnson, C., and Stevenson, D., 1999. The global exposure of forests to pollutants. *Water, Air and Soil Pollution* **116**, 5-32.
- Fowler, D., Smith, R.I., Muller, J.B.A., Hayman, G., and Vincent, K.J., 2005. Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. *Environmental Pollution* **137**, 15-25.
- Frank, D.A., Groffman, P.M., Evans, R.D., and Tracy, B.F., 2000. Ungulate stimulation of nitrogen cycling and retention in Yellowstone Park grasslands. *Oecologia* **123**(1), 116.
- Fynn, R.W.S., Haynes, R.J., and O'Connor, T.G., 2003. Burning causes long-term changes in soil organic matter content of a South African grassland. *Soil Biology and Biochemistry* **35**(5), 677-687.

- Galloway, J.N., 1989. Atmospheric acidification: Projections for the future. *Ambio* **18**(3), 161-166.
- Galloway, J.N., 1995. Acid deposition: Perspectives in time and space. *Water, Air, & Soil Pollution* **85**(1), 15-24.
- Galloway, J.N., 1996. Anthropogenic mobilization of sulphur and nitrogen: Immediate and delayed consequences. *Annual Review of Energy & the Environment* **21**(1), 261-292.
- Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., and Cosby, B.J., 2003. The nitrogen cascade. *BioScience* **53**(4), 341-356.
- Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., and Vöörsmarty, C.J., 2004. Nitrogen cycles: Past, present, and future. *Biogeochemistry* **70**(2), 153-226.
- Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., and Sutton, M.A., 2008. Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* **320**(5878), 889-892.
- Galpin, J.S., and Turner, C.R., 1999a. Trends in composition of rain quality data from the South African interior. *South African Journal of Science* **95**(5), 225-228.
- Galpin, J.S., and Turner, C.R., 1999b. Trends in rain quality data from the South African interior. *South African Journal of Science* **95**(5), 223-225.
- Galy-Lacaux, C., Al Ourabi, H., Galloway, J., Lacaux, J.P., Mphepya, J., Pienaar, K., Pont, V., Sighe, L., and Yoboué, V., 2003. *Dry and wet atmospheric nitrogen deposition in Africa*. DEBITS Special Issue no. 27. pp.
- Garstang, M., Tyson, P.D., Cachier, H., and Radke, L., 1997. Atmospheric transports of particulate and gaseous products by fire. In: Clark, J.S., Cachier, H., Goldammer, J.G., Stocks, B. (Eds.), *Sediment records of biomass burning and global change*. NATO ASI Series 1: Global Environmental Change Vol. 51, Springer-Verlag, Berlin, pp. 207-252.
- Ghani, A., McLaren, R.G., and Swift, R.S., 1991. Sulphur mineralisation in some New Zealand soils. *Biology and Fertility of Soils* **11**(1), 68-74.

- Gleeson, D.B., Herrmann, A.M., Livesley, S.J., and Murphy, D.V., 2008. Influence of water potential on nitrification and structure of nitrifying bacterial communities in semiarid soils. *Applied Soil Ecology* **40**(1), 189-194.
- Goodale, C.L., and Aber, J.D., 2001. The Long-Term Effects of Land-Use History on Nitrogen Cycling in Northern Hardwood Forests. *Ecological Applications* **11**(1), 253-267.
- Grobler, D.C., and Silberbauer, M.J., 1985. The combined effect of geology, phosphate sources and runoff on phosphate export from drainage basins. *Water research* **19**(8), 975-981.
- Gruber, N., and Galloway, J.N., 2008. An Earth-system perspective of the global nitrogen cycle. *Nature* **451**(7176), 293-296.
- Hanson, P.J., and Lindberg, S.E., 1991. Dry deposition of reactive N compounds: A review of leaf, canopy and non-foliar measurements. *Atmospheric Environment* **25**, 1615-1634.
- Held, G., Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R., and Walmsley, R.D., 1996. *Air pollution and its impacts on the South African Highveld*. Environmental Scientific Association, Cleveland, South Africa. 144 pp.
- Held, G., Scheifinger, H., and Snyman, G.M., 1994. Recirculation of pollutants in the atmosphere of the South African Highveld. *South African Journal of Science* **90**, 91-97.
- Herold, C.E., and Gorgens, A., 1991. *Vaal Dam salinity assessment with particular reference to atmospheric deposition*. Report number: NC120/12/DEQ0391, Department of Water Affairs Hydrological Research Institute, Pretoria, South Africa.
- Herold, C.E., Taviv, I., and Pitman, W.V., 2001. *Modelling of long-term effect of atmospheric deposition on the salinity of runoff from the Klip River catchment*. Report number: 697/1/01, Water Research Commission, Pretoria, South Africa.
- Hesterberg, R., Blatter, A., Fahrni, M., Rosset, M., Neftel, A., Eugster, W., and Wanner, H., 1996. Deposition of nitrogen-containing compounds to an extensively managed grassland in central Switzerland. *Environmental Pollution* **91**(1), 21-34.
- Hewitt, C.N., 2001. The atmospheric chemistry of sulphur and nitrogen in power station plumes. *Atmospheric Environment* **35**(7), 1155-1170.

- Hicks, W.K., Kuylensstierna, J.C.I., Owen, A., Dentener, F., Seip, H.-M., and Rodhe, H., 2008. Soil sensitivity to acidification in Asia: Status and prospects. *AMBIO: A Journal of the Human Environment* **37**(4), 295-303.
- Holling, C.S., 1973. Resilience and stability of ecological systems. *Annual Review of Ecology and Systematics* **4**, 1-23.
- Holling, C.S., 2001. Understanding the complexity of economic, ecological, and social systems. *Ecosystems* **4**(5), 390-405.
- Holst, J., Liu, C., Brüggemann, N., Butterbach-Bahl, K., Zheng, X., Wang, Y., Han, S., Yao, Z., Yue, J., and Han, X., 2007. Microbial N turnover and N-oxide (N₂O/NO/NO₂) fluxes in semi-arid grassland of Inner Mongolia. *Ecosystems* **10**(4), 623-634.
- Horswill, P., O'Sullivan, O., Phoenix, G.K., Lee, J.A., and Leake, J.R., 2008. Base cation depletion, eutrophication and acidification of species-rich grasslands in response to long-term simulated nitrogen deposition. *Environmental Pollution* **155**(2), 336.
- Huntley, B.J., 1984. Chapter 1: Characteristics of South African biomes. In: Booysen, P.d.V., Tainton, N.M. (Eds.), *Ecological effects of fire in South African Ecosystems*. Springer-Verlag, Berlin, pp. 1-17.
- Johnson, D.W., Reuss, J.O., Brown, K.A., Crawford, D.V., and Beament, J., 1984. Soil-mediated effects of atmospherically deposited sulphur and nitrogen [and discussion]. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences* **305**(1124, Ecological Effects of Deposited Sulphur and Nitrogen Compounds), 383-392.
- Jones, M., and Woodmansee, R., 1979. Biogeochemical cycling in annual grassland ecosystems. *The Botanical Review* **45**(2), 111-144.
- Josipovic, M., Annegarn, H., Kneen, M., Pienaar, J., and Piketh, S., 2010. Concentrations, distributions and critical level exceedance assessment of SO₂, NO₂ and O₃ in South Africa. *Environmental monitoring and assessment* **171**(1), 181-196.
- Kellogg, W.W., Cadle, R.D., Allen, E.R., Lazrus, A.L., and Martell, E.A., 1972. The sulfur cycle. *Science* **175**(4022), 587-596.
- Kennedy, I.R., 1986. *Acid soil and acid rain: The impact on the environment of nitrogen and sulfur cycling*. Research Studies Press Limited, England. 234 pp.

- Kernan, M.R., and Helliwell, R.C., 2001. Partitioning the variation within the acid neutralizing capacity of surface waters in Scotland in relation to land cover, soil and atmospheric depositional factors. *The Science of the total environment* **265**(1-3), 39-49.
- Knapp, A., Burns, C., Fynn, R., Kirkman, K., Morris, C., and Smith, M., 2006. Convergence and contingency in production-precipitation relationships in North American and South African C4 grasslands. *Oecologia* **149**(3), 456-464.
- Knights, J.S., Zhao, F.J., McGrath, S.P., and Magan, N., 2001. Long-term effects of land use and fertiliser treatments on sulphur transformations in soils from the Broadbalk experiment. *Soil Biology and Biochemistry* **33**(12-13), 1797-1804.
- Kotliar, N.B., and Wiens, J.A., 1990. Multiple scales of patchiness and patch structure: A hierarchical framework for the study of heterogeneity. *Oikos* **59**(2), 253-260.
- Kowalik, R.A., Cooper, D.M., Evans, C.D., and Ormerod, S.J., 2007. Acidic episodes retard the biological recovery of upland British streams from chronic acidification. *Global Change Biology* **13**(11), 2439-2452.
- Kuylenstierna, J.C., Rodhe, H., Cinderby, S., and Hicks, K., 2001. Acidification in developing countries: Ecosystem sensitivity and the Critical Load Approach on a global scale. *AMBIO: A Journal of the Human Environment*: **30**(1), 20-28.
- Kuylenstierna, J.C.I., Cambridge, H., Cinderby, S., and Chadwick, M.J., 1995. Terrestrial ecosystem sensitivity to acidic deposition in developing countries. *Water, Air, & Soil Pollution* **85**(4), 2319-2324.
- Land Type Survey Staff, 1985. *Land types of the maps 2628 East Rand, 2630 Mbabane*. Report number: Memoirs of Agricultural and Natural Resources, South Africa, No. 5, ARC - Institute for Soil Climate & Water, Pretoria, South Africa.
- Land Type Survey Staff, 2002. *Land types of the maps 2728 Frankfort & 2828 Harrismith*. Report number: Memoirs of Agricultural and Natural Resources, South Africa, No. 28, ARC - Institute for Soil Climate & Water, Pretoria, South Africa.
- Laudon, H., and Bishop, K.H., 1999. Quantifying sources of acid neutralisation capacity depression during spring flood episodes in Northern Sweden. *Environmental Pollution* **105**, 427-435.

- Lawrence, G.B., 2002. Persistent episodic acidification of stream linked to acid rain effects on soil. *Atmospheric Environment* **36**, 1589-1598.
- Lepš, J., and Šmilauer, P., 2003. *Multivariate analysis of ecological data using CANOCO*. Cambridge University Press, Cambridge. 284 pp.
- Levin, S.A., 1998. Ecosystems and the biosphere as Complex Adaptive Systems. *Ecosystems* **1**(5), 431-436.
- Likens, G.E., Butler, T.J., and Buso, D.C., 2001. Long- and short-term changes in sulfate deposition: Effects of the 1990 Clean Air Act Amendments. *Biogeochemistry* **52**(1), 1-11.
- Lindberg, S.E., 1992. Atmospheric deposition and canopy interactions of sulfur. In: Johnson, D.W., Lindberg, S.E. (Eds.), *Atmospheric depositions and forest nutrient cycling*. Ecological Studies. Springer-Verlag, New York, pp. 74-90.
- Liu, X., Ju, X., Zhang, Y., He, C., Kopsch, J., and Fusuo, Z., 2006. Nitrogen deposition in agroecosystems in the Beijing area. *Agriculture, Ecosystems & Environment* **113**(1-4), 370-377.
- Lombard, A.T., 1995. The problems with multi-species conservation: do hotspots, ideal reserves and existing reserves coincide? *South African Journal of Zoology* **30**(3), 145-163.
- Lorentz, S.A., Blight, J., Snyman, N., and Titshall, L., 2008. *An investigation into the effects of atmospheric pollutants on the surface water quality in the eastern regions of South Africa: Preliminary results of water quality monitoring*. Report number: WRC Project K5/1697; Deliverable 7., Water Research Commission, Pretoria, South Africa.
- Lorenzini, G., Panicucci, A., and Nali, C., 1995. A gas-exchange study of the differential response of *Quercus* species to long-term fumigations with a gradient of sulphur dioxide. *Water, Air, & Soil Pollution* **85**(3), 1257-1262.
- Lovett, G.M., 1992. Atmospheric deposition and canopy interactions of nitrogen. In: Johnson, D.W., Lindberg, S.E. (Eds.), *Atmospheric deposition and forest nutrient cycling*. Ecological Studies. Springer-Verlag, New York, pp. 152-165.
- Lovett, G.M., Tear, T.H., Evers, D.C., Findlay, S.E.G., Cosby, B.J., Dunscomb, J.K., Driscoll, C.T., and Weathers, K.C., 2009. Effects of air pollution on ecosystems and biological diversity in the eastern United States. *Annals of the New York Academy of Sciences* **1162**(1), 99-135.

- Lowman, G.R.P., 2003. *Deposition of nitrogen to grassland versus forested areas in the vicinity of Sabie, Mpumalanga, South Africa*. Master of Science Thesis, School of Animal Plant and Environmental Sciences University of the Witwatersrand, Johannesburg, 119 pp.
- MacIntosh, D.L., Stewart, J.H., Myatt, T.A., Sabato, J.E., Flowers, G.C., Brown, K.W., Hlinka, D.J., and Sullivan, D.A., 2010. Use of CALPUFF for exposure assessment in a near-field, complex terrain setting. *Atmospheric Environment* **44**(2), 262-270.
- MacVicar, C.N., de Villers, J.M., Loxton, R.F., Verster, E., Lambrechts, J.J.N., Merryweather, E.R., Le Roux, J.V.R.T.H., and Harmse, H.J.v.M., 1977. *Soil classification: a binomial system for South Africa*. Science Bulletin 390 Department of Agricultural Development, Pretoria, South Africa. 150 pp.
- Maenhaut, W., Salma, I., Cafmeyer, J., Annegarn, H.J., and Andreae, M.O., 1996. Regional atmospheric aerosol composition and sources in the eastern Transvaal, South Africa, and impact of biomass burning. **101**, 23631-23650.
- Malan, H.L., Bath, A., Day, J.A., and Joubert, A., 2003. A simple flow-concentration modelling method for integrating water quality and water quantity in rivers. *Water SA* **29**(3), 305-311.
- Mamatsharaga, A.L., 2004. *Water quality and soil nutrient mobility in afforested and grassland catchments of Mpumalanga Province, South Africa*. Master of Science Thesis, University of the Witwatersrand, Johannesburg, 94 pp.
- Marschner, H., 1986. *Mineral nutrition of higher plants*. Academic Press, London. 674 pp.
- Matzner, E., and Murach, D., 1995. Soil changes induced by air pollutant deposition and their implication for forests in central Europe. *Water, Air, & Soil Pollution* **85**(1), 63-76.
- Maynard, D.G., Stewart, J.W.B., and Bettany, J.R., 1983. Sulfur and nitrogen mineralization in soils compared using two incubation techniques. *Soil Biology and Biochemistry* **15**(3), 251-256.
- McLean, E.O., 1982. Chapter 12 - Soil pH and lime requirement. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), *Methods of soil analysis, Part 2*. American Society of Agronomy, Wisconsin.

- Middleton, B.J., and Bailey, A.K., 2009. *Water Resources of South Africa (WR2005)*. Report number: TT 380/08, Water Research Commission, Pretoria, South Africa.
- Midgley, D.C., Pitman, W.V., and Middleton, B.J., 1994. *Surface water resources of South Africa 1990. Volume II. Appendices*. Report number: 298/2.1/94, Water Research Commission, Pretoria, South Africa.
- Millennium Ecosystem Assessment, 2005a. Chapter 1: MA conceptual framework. In: Hassan, R., Scholes, R.J., Ash, N. (Eds.), *Millennium Ecosystem Assessment. Ecosystems and human well-being: Current state and trends. Volume 1*. Island Press, Washington, DC., pp. 25-36.
- Millennium Ecosystem Assessment, 2005b. Chapter 12: Nutrient cycling. In: Hassan, R., Scholes, R.J., Ash, N. (Eds.), *Millennium Ecosystem Assessment. Ecosystems and Human Well-being: Current State and Trends. Volume 1*. Island Press, Washington, DC., pp. 331-353.
- Millennium Ecosystem Assessment, 2005c. *Ecosystems and human well-being: Synthesis*. Island Press, Washington, DC. 137 pp.
- Mills, A.J., Rogers, K.H., Stalmans, M., and Witkowski, E.T.F., 2006. A Framework for Exploring the Determinants of Savanna and Grassland Distribution. *BioScience* **56**(7), 579-589.
- Mitchell, M.J., and Fuller, R.D., 1988. Models of sulfur dynamics in forest and grassland ecosystems with emphasis on soil processes. *Biogeochemistry* **5**(1), 133-163.
- Mitchell, M.J., Harrison, R.B., Fitzgerald, J.W., Johnson, D.W., Lindberg, S.E., Zhang, Y., and Autry, A., 1992. Chapter 5: Sulfur chemistry, deposition and cycling in forests. In: Johnson, D.W., Lindberg, S.E. (Eds.), *Atmospheric deposition and forest nutrient cycling: A synthesis of the Integrated Forest Study*. Springer-Verlag, New York, pp. 72-74.
- Mphepya, J.N., 2002. *Atmospheric deposition characteristics of sulphur and nitrogen compounds in South Africa*. PhD thesis Thesis, Potchefstroomse Universiteit vir Christelike Hoer Onderwys, Potchefstroom.
- Mphepya, J.N., Galy-Lacaux, C., Lacaux, J.P., Held, G., and Pienaar, J.J., 2006. Precipitation chemistry and wet deposition in Kruger National Park, South Africa. *Journal of Atmospheric Chemistry* **53**-, 169-183.

- Mphepya, J.N., Pienaar, J.J., Galy-Lacaux, C., Held, G., and Turner, C.R., 2001. Precipitation chemistry at a rural and an industrial site in South Africa. National Association Clean Air Conference, 10-12 October 2001., Port Elizabeth, South Africa.
- Mphepya, J.N., Pienaar, J.J., Galy-Lacaux, C., Held, G., and Turner, C.R., 2004. Precipitation chemistry in semi-arid areas of southern Africa: A case study of a rural and an industrial site. *Journal of Atmospheric Chemistry* **47**, 1-24.
- Mucina, L., and Rutherford, M.C., 2006. *The vegetation of South Africa, Lesotho and Swaziland*. Strelitzia 19. South African National Biodiversity Institute, Pretoria, South Africa. 807 pp.
- Muniz, I.P., 1990. Fresh-water acidification – its effects on species and communities of fresh-water microbes, plants and animals. *Proceedings of the Royal Society of Edinburgh Section B – Biological Sciences* **97**, 227-254.
- Murray, F., 2003. Air pollution impacts on vegetation in Australia. In: Emberson, L., Ashmore, M.R., Murray, F. (Eds.), *Air pollution impacts on crops and forests*. Imperial College Press, London, pp. 103-118.
- Ndala, S.M., Scholes, M.C., and Fey, M.V., 2006. Soil properties and processes driving the leaching of nitrate in the forested catchments of the eastern escarpment of South Africa. *Forest Ecology and Management* **236**(2-3), 142-152.
- Neke, K.S., and Du Plessis, M.A., 2004. The threat of transformation: Quantifying the vulnerability of grasslands in South Africa. *Conservation Biology* **18**(2), 466-477.
- Nguyen, M.L., and Goh, K.M., 1994. Sulphur cycling and its implications on sulphur fertilizer requirements of grazed grassland ecosystems. *Agriculture, Ecosystems & Environment* **49**(2), 173-206.
- Niknahad Gharmakher, H., Machet, J., Beaudoin, N., and Recous, S., 2009. Estimation of sulfur mineralization and relationships with nitrogen and carbon in soils. *Biology and Fertility of Soils* **45**(3), 297-304.
- Nilsson, J., and Grennfelt, P. (Eds.), 1988. Critical Loads for sulphur and nitrogen. Nord: 97. Nordic Council of Ministers, Copenhagen, 418 pp.
- O'Connor, T.G., 2005. Influence of land use on plant community composition and diversity in Highland Sourveld grassland in the southern Drakensberg, South Africa. *Journal of Applied Ecology* **42**(5), 975-988.

- O'Connor, T.G., and Bredenkamp, G.J., 2003. Grassland. In: Cowling, R.M., Richardson, D.M., Pierce, S.M. (Eds.), *Vegetation of southern Africa*. Cambridge University Press, Cambridge, pp. 215-257.
- Olbrich, K.A., 1993. *The chemistry and frequency of mist events on the Eastern Transvaal escarpment*. Report number: 18-90325-5-0 to the Department of Water Affairs., Council for Scientific and Industrial Research, Pretoria, South Africa.
- Ollinger, S.V., Aber, J.D., Reich, P.B., and Freuder, R.J., 2002. Interactive effects of nitrogen deposition, tropospheric ozone, elevated CO₂ and land use history on the carbon dynamics of northern hardwood forests. *Global Change Biology* **8**(6), 545-562.
- Otter, L.B., Marufu, L., and Scholes, M.C., 2001. Biogenic, biomass and biofuel sources of trace gases in southern Africa. *South African Journal of Science* **97**, 131-138.
- Ouimet, R., Arp, P., Watmough, S., Aherne, J., and DeMerchant, I., 2006. Determination and mapping critical loads of acidity and exceedances for upland forest soils in eastern Canada. *Water, Air, & Soil Pollution* **172**(1), 57-66.
- Padgett, P.E., Allen, E.B., Bytnerowicz, A., and Minich, R.A., 1999. Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California. *Atmospheric Environment* **33**, 760-781.
- Pamidi, J., Goh, K., and McLaren, R., 2001. Comparison of three different methods of determining soil sulphur mineralization in relation to plant sulphur availability in soils. *Biology and Fertility of Soils* **34**(3), 131-139.
- Parton, W., Stewart, J., and Cole, C., 1988. Dynamics of C, N, P and S in grassland soils: a model. *Biogeochemistry* **5**(1), 109-131.
- Pearson, J., and Soares, A., 1995. A hypothesis of plant susceptibility to atmospheric pollution based on intrinsic nitrogen metabolism: Why acidity really is the problem. *Water, Air, & Soil Pollution* **85**(3), 1227-1232.
- Percy, K., 2003. Air pollution impacts in North America. In: Emberson, L., Ashmore, M.R., Murray, F. (Eds.), *Air pollution impacts on crops and forests*. Imperial College Press, London, pp. 35-57.
- Persson, H., and Majdi, H., 1995. Effects of acid deposition on tree roots in Swedish forest stands. *Water, Air, & Soil Pollution* **85**(3), 1287-1292.

- Phoenix, G.K., Hicks, W.K., Cinderby, S., Kuylensstierna, J.C.I., Stock, W.D., Dentener, F.J., Giller, K.E., Austin, A.T., Lefroy, R.D.B., Gimeno, B.S., Ashmore, M.R., and Ineson, P., 2006. Atmospheric nitrogen deposition in world biodiversity hotspots: the need for a greater global perspective in assessing N deposition impacts. *Global Change Biology* **12**(3), 470-476.
- Pickett, S.T.A., 1988. Natural processes. In: Mac, M.J. (Ed.), *Status and trends of the nation's biological resources*. U.S. Department of Interior U.S. Geological Survey, Reston, Virginia, pp. 11-19.
- Pickett, S.T.A., Burch, W.R., Dalton, S.E., Foresman, T.W., Grove, J.M., and Rowntree, R., 1997. A conceptual framework for the study of human ecosystems in urban areas. *Urban Ecosystems* **1**(4), 185-199.
- Pickett, S.T.A., Cadenasso, M.L., and Benning, T.L., 2003. Biotic and abiotic variability as key determinants of savanna heterogeneity at multiple spatiotemporal scales. In: du Toit, J.T., Roger, K.H., Biggs, H.C. (Eds.), *The Kruger experience: ecology and management of savanna heterogeneity*. Island Press, Washington DC, pp. 22-40.
- Pieterse, G., Bleeker, A., Vermeulen, A.T., Wu, Y., and Erisman, J.W., 2007. High resolution modelling of atmosphere-canopy exchange of acidifying and eutrophying components and carbon dioxide for European forests. *Tellus: Series B* **59**(3), 412-424.
- Piketh, S.J., Annegarn, H.J., and Tyson, P.D., 1999a. Lower tropospheric aerosol loadings over South Africa: The relative contribution of aeolian dust, industrial emissions, and biomass burning. **104**, 1597-1607.
- Piketh, S.J., Formenti, P., Annegarn, H.J., and Tyson, P.D., 1999b. Industrial aerosol characterisation at a remote site in South Africa. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **150**(1-4), 350-355.
- Pineda Rojas, A., and Venegas, L., 2008. Dry and Wet Deposition of Nitrogen Emitted in Buenos Aires City to Waters of de la Plata River. *Water, Air, & Soil Pollution* **193**(1), 175-188.
- Pirela, H.J., and Tabatabai, M.A., 1988. Sulfur mineralization rates and potentials of soils. *Biology and Fertility of Soils* **6**(1), 26-32.
- Preston-Whyte, R.A., and Tyson, P.D., 1993. *The atmosphere and weather of southern Africa*. Oxford University Press, Oxford. 374 pp.

- Raison, R.J., Connell, M.J., and Khanna, P.K., 1987. Methodology for studying fluxes of soil mineral-N *in situ*. *Soil Biology and Biochemistry* **19**(5), 521-530.
- Reeburgh, W.S., 1997. Figures summarizing the global cycles of biogeochemically important elements. *Bulletin of the Ecological Society of America* **78**(4), 260-267.
- Reid, J.L., 2007. *Investigating the long-term effects of air pollution on soil properties in the vicinity of the Arnot power station*. Master of Science Thesis, School of Animal Plant and Environmental Sciences University of the Witwatersrand, Johannesburg, 81 pp.
- Reinds, G., Posch, M., de Vries, W., Slootweg, J., and Hettelingh, J.P., 2008. Critical Loads of sulphur and nitrogen for terrestrial ecosystems in Europe and Northern Asia using different soil chemical criteria. *Water, Air, & Soil Pollution* **193**(1), 269-287.
- Reuss, J.O., 1991. The transfer of acidity from soils to surface waters. In: Ulrich, B., Sumner, M.E. (Eds.), *Soil Acidity*. Springer-Verlag, New York, pp. 203-218.
- Riffaldi, R., Saviozzi, A., Cardelli, R., Cipolli, S., and Levi-Minzi, R., 2006. Sulphur mineralization kinetics as influenced by soil properties. *Biology and Fertility of Soils* **43**(2), 209-214.
- Rodhe, H., Grennfelt, P., Wisniewski, J., Agren, C., Bengtsson, G., Johansson, K., Kauppi, P., V, K., Rasmussen, L., Rasseland, B., Scholte, L., and Sellden, G., 1995. Acid Reign '95? - Conference Summary Statement. *Water, Air and Soil Pollution* **85**(1), 1-14.
- Rogers, K.H., 2003. Adopting a heterogeneity paradigm: Implications for management of protected savannas. In: du Toit, J.T., Roger, K.H., Biggs, H.C. (Eds.), *The Kruger experience: ecology and management of savanna heterogeneity*. Island Press, Washington DC, pp. 41-58.
- Roos, J.C., and Pieterse, A.J.H., 1995. Salinity and dissolved substances in the Vaal River at Balkfontein, South Africa. *Hydrobiologia* **306**, 41-51.
- Sala, O.E., Chapin, F.S., III, Armesto, J.J., Berlow, E., Bloomfield, J., Dirzo, R., Huber-Sanwald, E., Huenneke, L.F., Jackson, R.B., Kinzig, A., Leemans, R., Lodge, D.M., Mooney, H.A., Oesterheld, M., Poff, N.L., Sykes, M.T., Walker, B.H., Walker, M., and Wall, D.H., 2000. Global biodiversity scenarios for the year 2100. *Science* **287**(5459), 1770-1774.

- Sanders, G.E., Skarby, L., Ashmore, M.R., and Fuhrer, J., 1995. Establishing critical levels for the effects of air pollution on vegetation. *Water, Air, & Soil Pollution* **85**(1), 189-200.
- Scherer, H.W., 2009. Sulfur in soils. *Journal of Plant Nutrition and Soil Science* **172**(3), 326-335.
- Schindler, D.W., 1971. Carbon, nitrogen, and phosphorus and the eutrophication of freshwater lakes. *Journal of Phycology* **7**(4), 321-329.
- Schindler, D.W., 1988. Effects of Acid Rain on Freshwater Ecosystems. *Science* **239**(4836), 149-157.
- Schlesinger, W.H., 2009. On the fate of anthropogenic nitrogen. *Proceedings of the National Academy of Sciences* **106**(1), 203-208.
- Schlesinger, W.H., and Hartley, A.E., 1992. A global budget for atmospheric NH₃. *Biogeochemistry* **15**(3), 191-211.
- Scholes, M.C., Scholes, R.J., Otter, L.B., and Woghiren, A.J., 2003a. Biogeochemistry: The cycling of nutrients. In: du Toit, J.T., Roger, K.H., Biggs, H.C. (Eds.), *The Kruger experience: ecology and management of savanna heterogeneity*. Island Press, Washington DC, pp. 130-148.
- Scholes, R.J., Bond, W.J., and Eckhardt, H.C., 2003b. Vegetation dynamics in the Kruger ecosystem. In: du Toit, J.T., Roger, K.H., Biggs, H.C. (Eds.), *The Kruger experience: ecology and management of savanna heterogeneity*. Island Press, Washington DC, pp. 242-262.
- Scholes, R.J., and Walker, B.H., 1993. *An African Savanna: Synthesis of the Nylsvley study*. Cambridge University Press, Cambridge. 306 pp.
- Schulze, R.E., 2003. Climate. In: Cowling, R.M., Richardson, D.M., Pierce, S.M. (Eds.), *Vegetation of southern Africa*. Cambridge University Press, Cambridge, pp. 21-42.
- Scire, J.S., Strimaitis, D.G., and Yamartino, R.J., 2000. *A user's guide for the CALPUFF dispersion model (Version 5)*. Earth Tech Inc. pp.
- Scorgie, Y., *Urban Air Quality Management and Planning in South Africa (in preparation)*. PhD Thesis, University of Johannesburg, Johannesburg.
- Scorgie, Y., and Thomas, R., 2006. *Eskom Mpumalanga Highveld Cumulative Scenario Planning Study, Air Pollution Compliance Assessment and Health Risk Analysis of Cumulative Operations of Current, Return to Service and*

- Proposed Eskom Power Stations Located within the Mpumalanga and Gauteng Provinces*. Eskom Holdings Ltd, Rosherville, South Africa.
- Shen, B.H., and Liu, C.P., 2003. Air pollution impacts on vegetation in Taiwan. In: Emberson, L., Ashmore, M.R., Murray, F. (Eds.), *Air pollution impacts on crops and forests*. Imperial College Press, London, pp. 145-163.
- Shrestha, S., and Kazama, F., 2007. Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji River basin, Japan. *Environmental Modelling & Software* **22**(4), 464-475.
- Singer, M.J., and Munns, D.N., 1996. *Soils: An introduction*. 3rd ed. Prentice-Hall, Inc., New Jersey. 480 pp.
- Singh, K.P., Malik, A., Mohan, D., and Sinha, S., 2004. Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India)—a case study. *Water research* **38**(18), 3980-3992.
- Skelton, P.H., Cambray, J.A., Lombard, A., and Benn, G.A., 1995. Patterns of distribution and conservation status of freshwater fishes in South Africa. *South African Journal of Zoology* **30**(3), 71-81.
- Smith, C.J., Chalk, P.M., Crawford, D.M., and Wood, J.T., 1994. Estimating gross nitrogen mineralization and immobilization rates in anaerobic and aerobic soil suspensions. *Soil Science Society of America Journal* **58**(6), 1652-1660.
- Smith, V.H., Tilman, G.D., and Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental Pollution* **100**(1-3), 179-196.
- Snyman, H.A., 2003. Short-term response of rangeland following an unplanned fire in terms of soil characteristics in a semi-arid climate of South Africa. *Journal of Arid Environments* **55**(1), 160-180.
- Snyman, H.A., and du Preez, C.C., 2005. Rangeland degradation in a semi-arid South Africa—II: influence on soil quality. *Journal of Arid Environments* **60**(3), 483-507.
- Soil Plant Analysis Council, 1991. Chloride, *Soil analysis: Handbook of reference methods*. CRC Press, Boca Raton, pp. 165-173.
- Soil Plant Analysis Council, 1998. *Handbook of Reference Methods for Plant Analysis*. CRC Press, Boca Raton. pp.
- Soil Plant Analysis Council, 1999a. Ammonium and nitrate, *Soil analysis: Handbook of reference methods*. CRC Press, Boca Raton, pp. 149-157.

- Soil Plant Analysis Council, 1999b. Soil pH and exchangeable acidity and aluminium, *Soil analysis: Handbook of reference methods*. CRC Press, Boca Raton, pp. 27-39.
- Steffen, W., 2010. Observed trends in Earth System behavior. *Wiley Interdisciplinary Reviews: Climate Change* **1**(3), 428-449.
- Stevens, C.J., Dise, N.B., and Gowing, D.J., 2009. Regional trends in soil acidification and exchangeable metal concentrations in relation to acid deposition rates. *Environmental Pollution* **157**(1), 313-319.
- Stevens, C.J., Dise, N.B., Mountford, J.O., and Gowing, D.J., 2004. Impact of nitrogen deposition on the species richness of grasslands. *Science* **303**(5665), 1876-1879.
- Stevens, C.J., Duprè, C., Dorland, E., Gaudnik, C., Gowing, D.J.G., Bleeker, A., Diekmann, M., Alard, D., Bobbink, R., Fowler, D., Corcket, E., Mountford, J.O., Vandvik, V., Aarrestad, P.A., Muller, S., and Dise, N.B., 2010. Nitrogen deposition threatens species richness of grasslands across Europe. *Environmental Pollution* **158**(9), 2940-2945.
- Stewart, J.W.B., Cole, C.V., and Maynard, D.G., 1983. Chapter 8: Interactions of biogeochemical cycles in grassland ecosystems. Scope 21 - The Major Biogeochemical Cycles and their interactions. <http://www.icsu-scope.org/downloadpubs/scope21/contents.html>. Access date: June 28, 2010.
- Stock, W., Bond, W., and van de Vijver, C., 2010. Herbivore and nutrient control of lawn and bunch grass distributions in a southern African savanna. *Plant Ecology* **206**(1), 15-27.
- Stock, W.D., and Allsopp, N., 1992. Functional perspective of ecosystems. In: Cowling, R.M. (Ed.), *The ecology of fynbos: Nutrients, fire and diversity*. Oxford University Press, Cape Town, pp. 241-259.
- Tabatabai, M.A., 1982. Chapter 28: Sulphur. In: Page, A.L. (Ed.), *Methods of soil analysis, Part 2 - Chemical and microbiological properties*. American Society of Agronomy and Soil Science Society of America, Madison, Wisconsin, pp. 501-538.
- Tainton, N.M., and Mentis, M.T., 1984. Chapter 6: Fire in grassland. In: Booysen, P.d.V., Tainton, N.M. (Eds.), *Ecological effects of fire in South African ecosystems*. Springer-Verlag, Berlin, pp. 115-147.

- Taviv, I., and Herold, C.E., 1989. *Preliminary estimation of the impact of air pollution on water quality in the Vaal Dam*. Report number: 697/1/01, Water Research Commission, Pretoria, South Africa.
- Taylor, J.C., Janse van Vuuren, M.S., and Pieterse, A.J.H., 2007. The application and testing of diatom-based indices in the Vaal and Wilge Rivers, South Africa. *Water SA* **33**(1), 51-59.
- ter Braak, C.J.F., and Šmilauer, P., 2002. *CANOCO Reference manual and CanoDraw for Windows user's guide: Software for canonical community ordination (version 4.5)*. Microcomputer Power, Ithaca, New York. pp.
- Tyson, P.D., Garstang, M., and Swap, R., 1996. Large-scale recirculation of air over Southern Africa. *Journal of Applied Meteorology* **35**, 2218-2236.
- Tyson, P.D., and Gatebe, C.K., 2001. The atmosphere, aerosols, trace gases and biogeochemical change in southern Africa: a regional integration. *South African Journal of Science* **97**, 106-118.
- Tyson, P.D., Kruger, F.J., and Louw, C.W., 1988. *Atmospheric pollution and its implications in the Eastern Transvaal Highveld*. Report number: 150, CSIR, South African National Scientific Programmes, Pretoria, South Africa.
- Ulrich, B., 1986. Natural and anthropogenic components of soil acidification. *Zeitschrift für Pflanzenernährung und Bodenkunde* **149**(6), 702-717.
- UNECE-CLRTAP, Convention on Long-Range Transboundary Air Pollution. www.unece.org/env/lrtap. Access date: 04 February, 2011.
- Urban Econ, 2000. *The economic cost effects of salinity. Volume 1: Integrated Report*. Report number TT 123/00, Water Research Commission, Pretoria.
- US-EPA, 1995. *A user's guide for the CALPUFF dispersion model*. Report number: EPA-454/B-95-006, US-Environmental Protection Agency, Research Triangle Park, North Carolina.
- Van den Berg, L.J.L., Vergeer, P., Rich, T.C.G., Smart, S.M., Guest, D., and Ashmore, M.R., 2010. Direct and indirect effects of nitrogen deposition on species composition change in calcareous grasslands. *Global Change Biology* **10.1111/j.1365-2486.2010.02345.x**.
- Van der Walt, H., du Toit, P., Pienaar, J.J., and Julies, A., 1998. Integration of passive sampler monitoring in non-electrified residential areas into a modern ambient air quality monitoring network. 11th World Clean Air and Environment Congress, Durban.

- van Niekerk, H., Silberbauer, M., and Hohls, B., 2009. Monitoring programme revision highlights long-term salinity changes in selected South African rivers and the value of comprehensive long-term data sets. *Environmental monitoring and assessment* **154**(1), 401-411.
- van Rensburg, L.D., Strydom, M.D., du Preez, C.C., Bennie, A.T.P., le Roux, P.A.L., and Pretorius, J.P., 2008. Prediction of salt balances in irrigated soils along the lower Vaal River, South Africa. *Water SA* **34**(1), 1117.
- van Tienhoven, A.M., 1997. *Assessment of long-term pollution impacts on soil properties in the vicinity of the Arnot power station on the South African Highveld*. Master of Science Thesis, Department of Geological Sciences, University of Cape Town, Cape Town.
- Van Tienhoven, A.M., Olbrich, K.A., Skoroszewski, R., Taljaard, J., and Zunckel, M., 1995. Application of the critical loads approach in South Africa. *Water, Air and Soil Pollution* **85**, 2577-2582.
- Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., and Tilman, D.G., 1997a. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* **7**(3), 737-750.
- Vitousek, P.M., and Howarth, R.W., 1991. Nitrogen limitation on land and in the sea - how it can occur. *Biogeochemistry* **13**(2), 87-115.
- Vitousek, P.M., Mooney, H.A., Lubchenco, J., and Melillo, J.M., 1997b. Human domination of earth's ecosystems. *Science* **277**(5325), 494-499.
- Vorster, C.J., 2003. *Simplified geology: South Africa, Lesotho and Swaziland*. Council for Geoscience, Pretoria, South Africa.
- Wedin, D.A., and Tilman, D., 1996. Influence of Nitrogen Loading and Species Composition on the Carbon Balance of Grasslands. *Science* **274**(5293), 1720.
- Wellburn, A., 1994. *Air pollution and climate change: the biological impact*. 2nd ed. Longman Scientific & Technical, Essex, England. 268 pp.
- Woodmansee, R.G., 1978. Additions and losses of nitrogen in grassland ecosystems. *BioScience* **28**(7), 448-453.
- Wright, R.F., Alewell, C., Cullen, J.M., Evans, C.D., Marchetto, A., Moldan, F., Prechtel, A., and Rogora, M., 2001. Trends in nitrogen deposition and leaching in acid-sensitive streams in Europe. *Hydrology and Earth System Sciences* **5**(3), 299-301.

- Wright, R.F., and Schindler, D.W., 1995. Interaction of acid rain and global changes: Effects on terrestrial and aquatic ecosystems. *Water, Air, & Soil Pollution* **85**(1), 89-99.
- Yahdjian, L., and Sala, O.E., 2008. Do litter decomposition and nitrogen mineralization show the same trend in the response to dry and wet years in the Patagonian steppe? *Journal of Arid Environments* **72**(5), 687-695.
- Zhang, X., Wang, Q., Li, L., and Han, X., 2008. Seasonal variations in nitrogen mineralization under three land use types in a grassland landscape. *Acta Oecologica* **34**(3), 322-330.
- Zhao, Y., Duan, L., Larssen, T., Hu, L., and Hao, J., 2007. Simultaneous assessment of deposition effects of base cations, sulfur, and nitrogen using an extended Critical Load function for acidification. *Environmental Science & Technology* **41**(6), 1815-1820.
- Zunckel, K., 2003. Managing and conserving southern African grasslands with high endemism. *Mountain Research and Development* **23**(2), 113-118.
- Zunckel, M., Robertson, S., Tyson, P.D., and Rodhe, H., 2000. Modelled transport and deposition of sulphur over southern Africa. *Atmospheric Environment* **34**, 2797-2808.
- Zunckel, M., Turner, C.R., and Wells, R.B., 1996. Dry deposition of sulphur on the Mpumalanga highveld: a pilot study using the interential method. *South African Journal of Science* **92**(October), 485-491.