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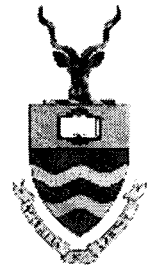

UNIVERSITY OF THE WITWATERSRAND
JOHANNESBURG

DEPOSITION OF NITROGEN TO GRASSLAND VERSUS FORESTED AREAS IN THE VICINITY OF SABIE, MPUMALANGA, SOUTH AFRICA

Guy Russell Pollock Lowman

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, in fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Johannesburg, March, 2003

DECLARATION

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

GP Lawson

(Signature of candidate)

28 TH day of OCTOBER 2003

ABSTRACT

Nitrogen deposition to adjacent grassland and forested areas in the vicinity of Sabie, Mpumalanga, South Africa was studied. Total deposition amounts to the forested area are calculated to be 71.2 kg N ha^{-1} yr^{-1} and to the grassland area, 25 kg N ha^{-1} yr^{-1}. The average deposition amounts are similar to or at least approach nitrogen mineralisation amounts at nearby sites of 50-70 kg N ha^{-1} yr^{-1}. The deposition amounts are made up of 21.4 kg N ha^{-1} yr^{-1} dry deposition, 7.8 kg N ha^{-1} yr^{-1} wet deposition and 42 kg N ha^{-1} yr^{-1} cloud droplet deposition for the forest. For the grassland, the amounts are 7 kg N ha^{-1} yr^{-1} dry deposition, 7.8 kg N ha^{-1} yr^{-1} wet deposition and 10.5 kg N ha^{-1} yr^{-1} cloud droplet deposition. For both wet and cloud droplet deposition, the amount attributable to nitrate was greater than that attributable to ammonium. For wet deposition, nitrate contributed 4.1 kg N ha^{-1} yr^{-1} and ammonium contributed 3.7 kg N ha^{-1} yr^{-1} to both forests and grasslands. For cloud droplet deposition to forests, the amounts were 28 kg N ha^{-1} yr^{-1} attributable to nitrate and 14 kg N ha^{-1} yr^{-1} attributable to ammonium. For grasslands the amounts were 7 and 3.5 kg N ha^{-1} yr^{-1}. In both forests and grasslands, the component of dry deposition contributing the most to deposition was ammonia gas, the amounts being 14.2 and 4.3 kg N ha^{-1} yr^{-1} respectively. Nitric acid contributes 3.7 and 1.9 kg N ha^{-1} yr^{-1} respectively and is followed by the nitrogen dioxide component that contributes 1.6 and 0.5 kg N ha^{-1} yr^{-1}. Ammonium and nitrate particles contribute the least to deposition. For the forests the amounts are 1 and 0.9 kg N ha^{-1} yr^{-1} and for the grasslands they are 0.2 and 0.1 kg N ha^{-1} yr^{-1}. A strong seasonal variance in deposition amounts is apparent with maximum deposition amounts occurring in Summer and minimum amounts in Winter. Intermediate amounts are deposited in Autumn and Spring, with the latter season having slightly larger deposition amounts. The seasonal variance is strongly linked to the seasonal rainfall and cloud droplet deposition patterns. Biomass burning is indicated as a possible important factor in influencing the chemical composition of rainfall during Spring. Of the deposition amounts obtained in this study, the deposition from cloud droplets is high compared to other studies and is probably overestimated. Further research into this area is needed.

DEDICATION

To my wife, for everything.

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A number of people have contributed their support and knowledge towards the completion of this thesis. Fore-mostly, my supervisor, Professor Mary Scholes, is thanked for providing an inspirational, informative and structured environment that steered this task to completion. The members of my research committee, Professors R. Pienaar and J. D. Mycock, who chaired the research committee at various stages, and Professor H. J. Annegarn are also thanked for their contributions. In particular, Professor Annegarn contributed much guidance and insight for my venture into the field of atmospheric related science.

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CHAPTER 1 - INTRODUCTION

1.1 General Introduction

The influence of anthropogenic activity on the earth system is topical, with issues such as 'global warming' and 'ozone holes' being at the forefront of popular debate and interest. Continuing scientific activity has expanded the range of issues, and the anthropogenic influences on nitrogen cycling have become important in recent years (Galloway *et al.,* 1995; Vitousek *et al.,* 1997). Galloway *et al.* (1995) describe a more than doubling in the quantity of nitrogen fixed in terrestrial ecosystems as a result of anthropogenic influences. The relevant anthropogenic activities include fossil fuel combustion, biomass burning and other industrial activities. The impacts of these activities are facilitated through the atmospheric related processes of emission, transport and deposition of substances. The southern African region is subject to a combination of natural and anthropogenic factors that exacerbate these atmospheric related factors. In terms of emissions, electricity generation from the combustion of coal is a major contributor. Forty seven percent of the electricity in Africa is generated in an area approximately 250 km south west of the study area (Eskom 1994) known as the Eastern Transvaal Highveld (ETH) (Tyson *et al.,* 1988) (Figure 1). After 1994,

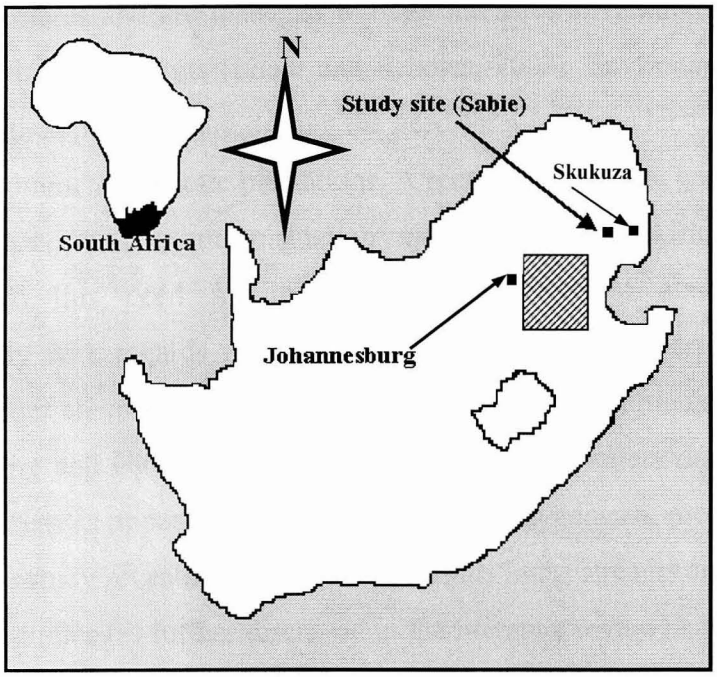

Figure 1 – Regional position of the study site (ETH region shaded)

with the election of the new government, the ETH became mostly incorporated into a new province called Mpumalanga. Also contributing towards high emission levels are a number of mining and smelting operations in the mineral rich Southern African region. The ETH area is again a major emitter, although emissions from these processes from as far afield as the Zambian copper belt may affect the study area. Another major contributor to emissions sources relevant to the study area, biomass burning, is also sourced from local as well as more distant areas. This kind of long distance influence of emission sources relates to the transportation characteristics of the atmosphere of the Southern African region. The meteorology of the area, which is dealt with in more detail later, is characterised by a combination of long range transport, re-circulation and stagnation of air masses that to a degree exacerbate the emission processes in terms of pollution effects. Under these emission and transport conditions, inputs from the atmosphere to ecosystems are likely to be of significance and should be considered when performing nutrient cycling, environmental and ecological studies.

Forests ecosystems in particular are sensitive to atmospheric related processes and the large commercial, exotic forest plantations present in South Africa are prime candidates for consideration in any investigation into the effects of pollution on ecosystems in southern Africa. The forest plantations occupy approximately 1.52 million hectares and are managed through intensive silviculture, primarily for sawn timber and fibre markets (Louw and Scholes, 2002). Environmental, economic and socio-political pressures are driving the need for a better understanding of the ecology of these commercial exotic plantations. A recent study on the geo-chemical impact of afforestation, with exotic plantation species in South Africa (Nowicki, 1997), highlighted this need for understanding the role of atmospheric deposition, particularly with regards nitrogen, in southern Africa. As part of Nowicki's study, stream-water chemistry in the area was investigated. In particular, attention was paid to sampling and comparing the chemistry of stream-waters draining predominantly forested areas as opposed to stream waters draining adjacent predominantly grassland areas. The study revealed elevated nitrate levels in the streams draining forested areas. Previous studies (as further discussed in the literature review) have indicated a variety of possible contributors towards the leaching of nitrate from ecosystems, one being deposition of nitrogen from the atmosphere.

This study is designed to obtain a quantification of the annual nitrogen deposition to adjacent grassland and forested areas in one of the areas studied by Nowicki (1997) on the eastern escarpment of Mpumalanga near the town of Sabie (Figure 1). Technical, financial and time constraints did not allow for the exact on-site measurement of deposition and deposition amounts have been calculated using a number of methods and information sources. The details are discussed in the methods section, but a summary is given below for introductory purposes. For wet deposition, on-site rainfall amounts have been combined with rainfall chemistry measured approximately 30 km from the study site. Dry deposition has been calculated using ambient concentrations and deposition velocities. For some of the relevant nitrogen species, concentrations have been estimated using measurements from a number of sites around southern Africa, the closest being approximately 90 km from the study site. Deposition velocities have been calculated using an inferential model using meteorological information measured 20 km from the study site. The model is not suited to some of the nitrogen species and deposition velocities have been estimated from literature in these cases. A previous study (Olbrich, 1993), has measured deposition from mist (cloud droplet deposition) using a mist collector 20 km from the study site and the information is used in this study to complete the deposition calculations.

1.2 Aims, Objectives, Hypotheses and Key Questions

Aims

- The aim of the project is to quantify the deposition of nitrogen from the atmosphere to a predominantly grassland area as opposed to a predominantly forested area.

Objectives

- To quantify and interpret wet deposition patterns for the period 1995 -1999 for the study areas.
- To quantify dry deposition for the period 1999 –2000 for the study areas.
- To better understand the role of nitrogen deposition and nitrogen loss on nutrient cycling in the selected sites.

Hypotheses

- Dry deposition of nitrogen from the atmosphere to a predominantly forested area is larger than that to a predominantly grassland area.
- Wet deposition of nitrogen to the study sites is larger than dry deposition.

Key Questions

- What chemical forms/species of nitrogen are deposited in the greatest amounts?
- How has wet deposition changed over time?
- What are the factors controlling the amount of deposition?

1.3 Study Site

The area investigated corresponds to the catchment areas of two streams sampled by Nowicki (1997), draining a forested area and a grassland area in the vicinity of the Mac-Mac pools near the town of Sabie, Mpumalanga, South Africa. Figure 1 shows the regional position of the study site.

Figure 2 shows the area in more detail in relation to the Arnot power station and the Palmer monitoring station. The relevance of the above sites is described in more detail in the literature review and methods section.

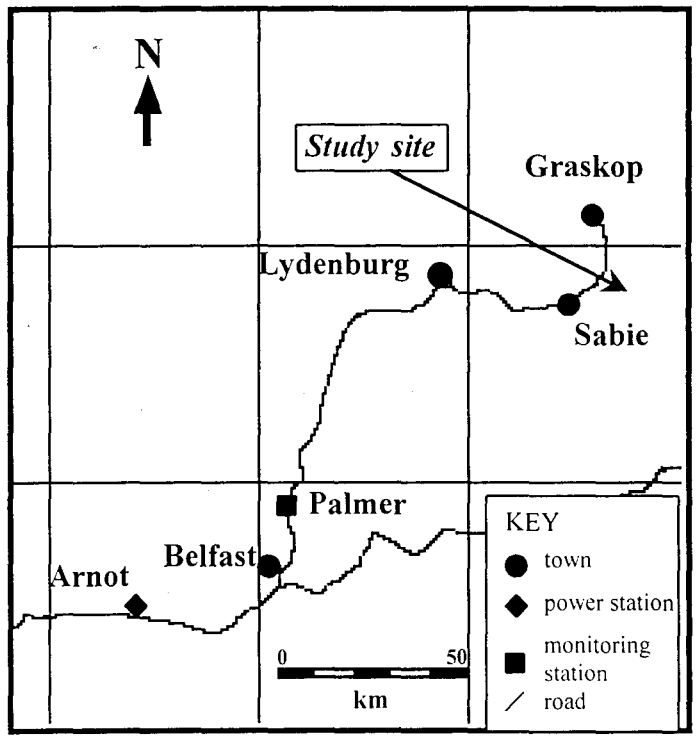

Figure 2 – Study site in relation to Arnot power station and Palmer monitoring station

Figure 3 shows the more exact location of the study area and the following details:

- rivers sampled by Nowicki (1997)
- proposed areas of influence of nitrogen deposition from the atmosphere on the the two rivers sampled by Nowicki (1997) to be used in the study

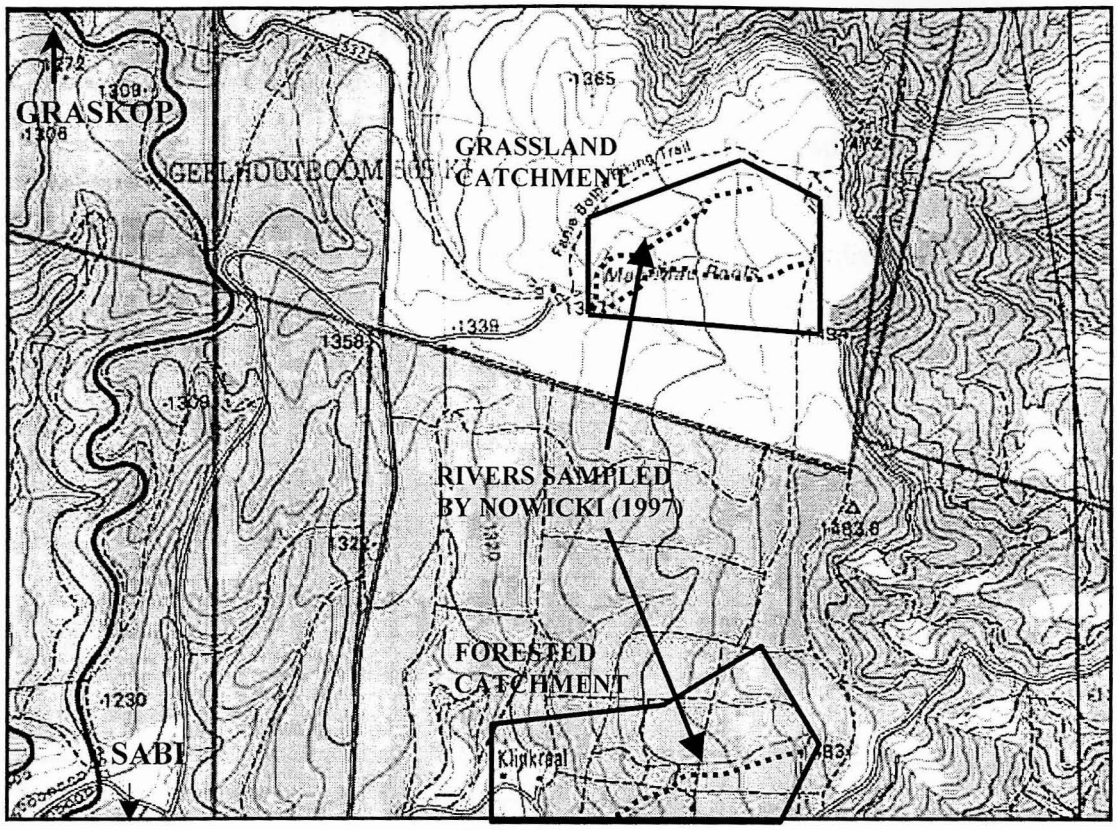

Figure 3 – Location of the study area and position of rivers sampled by Nowicki (1997)

A general description of the study area is given by Nowicki (1997) and the following relevant facts have been obtained from this.

The eastern escarpment area is developed on land previously covered by montane grasslands (White, 1978). The forested vegetation in the area is mostly exotic *Pinus* species – *P. patula, P. elliottii, P. taeda.* The rain falls predominantly in summer months and the mean annual rainfall ranges from 1050 – 1650 mm. Summer temperatures range from an average daily minimum of 13.1°C to an average daily maximum of 22.3°C.

CHAPTER 2 – LITERATURE REVIEW

The literature review is dealt with under the following sub-headings:

Nitrogen in the environment - A general description of the sources and movement of nitrogen through the atmosphere, biosphere, pedosphere and hydrosphere.

Nitrogen in the atmosphere - a more detailed description of nitrogen in the atmosphere including aspects of emission, transport and deposition and relevant nitrogen chemistry.

2.1. Nitrogen in the environment

Figure 4 below illustrates the occurrence of nitrogen in various pools in the environment viz. the atmosphere, biosphere, pedosphere and hydrosphere.

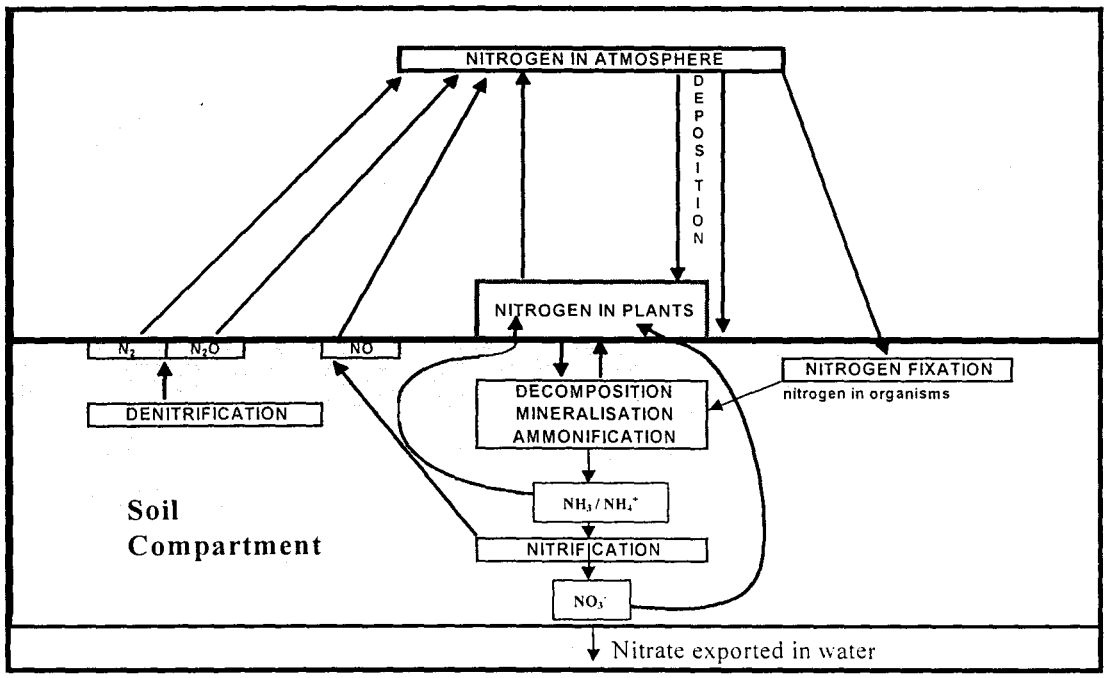

Figure 4 – Nitrogen cycling through the atmosphere, pedosphere, biosphere and hydrosphere.

As illustrated in Figure 4 each of the spheres has the ability to receive / take-up, store and expel nitrogen in one form or another. The atmosphere receives nitrogen in gaseous and aerosol forms from emissions from both biogenic and anthropogenic origins / activities. These are transported, transformed and deposited / taken up by terrestrial and oceanic systems to varying degrees dependant on the form of nitrogen.

Nitrogen is transformed within the pedosphere by various processes viz. nitrogen fixation, ammonification, immobilisation and de-nitrification. Losses of nitrogen may occur from the pedosphere, of which nitrate leaching is one.

The ability to store and the expulsion of nitrate from the pedosphere has been described in terms of the concept of saturation (Aber *et al.*, 1989; Agren & Bosatta 1988; Cole, 1992; Dempster *et al.*, 1988). "N saturation can be defined as that forest soil condition whereby N flux density (i.e. N input from N mineralisation plus atmospheric N input) exceeds the systems retention capacity and NO_3^- starts leaching out of the system" (Cole, 1992). The exceedance of the soils retention capacity and resultant nitrate leaching has been ascribed to a number of influences including soil properties (Van Miegroet *et al.*, 1992), harvesting (Iseman *et al.*, 1999), forest health (Durka *et al.*, 1994), the degree of de-nitrification (Montgomery *et al.*, 1997) and atmospheric deposition of nitrogen (Dise and Wright, 1995). The latter forms the focus of this study and is dealt with in more detail below.

2.2. Nitrogen in the atmosphere

General Aspects

Deposition of gases and particulates from the atmosphere to the earth's surface can be viewed as a step in a cycle that comprises three elements:

- *emission* of gases and particulates from various sources into the atmosphere
- *transport and transformation* of the gases and particulates within the atmosphere
- *deposition* of the gases and particulates from the atmosphere.

These processes are schematically represented in Figure 5, which also illustrates the possibility of a link between regions of emissions (e.g. the ETH) and areas of deposition, as discussed in more detail later. Deposition may be considered to occur via three pathways viz. wet and dry deposition and deposition from mist (cloud droplet interception) (Turner *et al.*, 1996). 'Dry deposition is the removal of particles or gases from the atmosphere through the delivery of mass to the surface by non-precipitation atmospheric processes and the subsequent chemical reaction with or physical attachment to vegetation, soil or the built environment' (Dolske and Gatz, 1985).

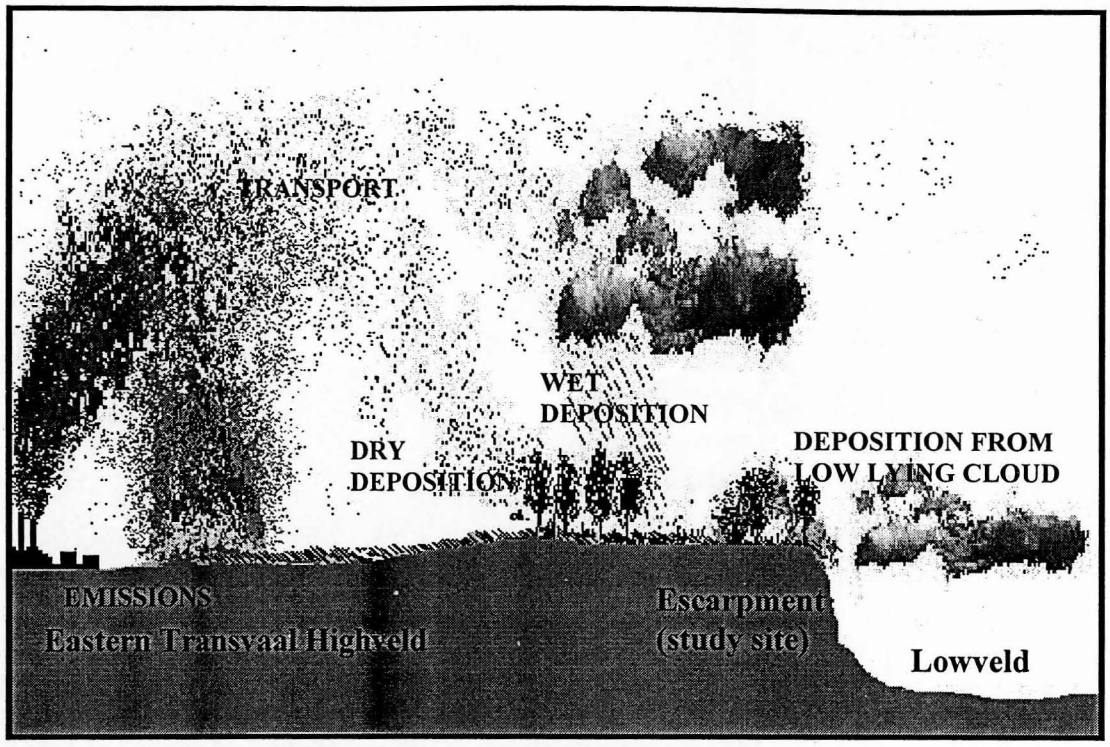

Figure 5 - A schematic cross-section looking northwest, from the Johannesburg area to the study site on the edge of the Mpumalanga escarpment. The schematic shows the general processes of emission , transport and transformation and deposition of nitrogen compounds in the atmosphere in context to the regional position of the study area.

Wet deposition is that occurring via precipitation. Deposition via mist or cloud can be considered as a pathway between wet and dry deposition (Turner *et al.*, 1996). Nitrogen occurs in a number of different forms in the atmosphere. Figure 6 illustrates the various major forms and the transformations and reactions they may undergo. Appendix 1 details these reactions and transformations. Not all of the forms shown in Figure six are reactive enough in the troposphere to warrant considerable attention in a deposition study. The main reactive nitrogenous compounds relevant to deposition to landscapes / forests are listed below under the types of deposition they undergo (Fowler *et al.*, 1999; Hanson and Lindberg, 1991; Lovett, 1992; Stulen *et al.*, 1998):

Dry Deposition

- nitric oxide gas (NO);
- nitrogen dioxide gas (NO_2);
- ammonia gas (NH_3);
- nitric acid vapour/gas (HNO_3);
- particulate nitrate (NO_3^-); and
- ammonium (NH_4^+)

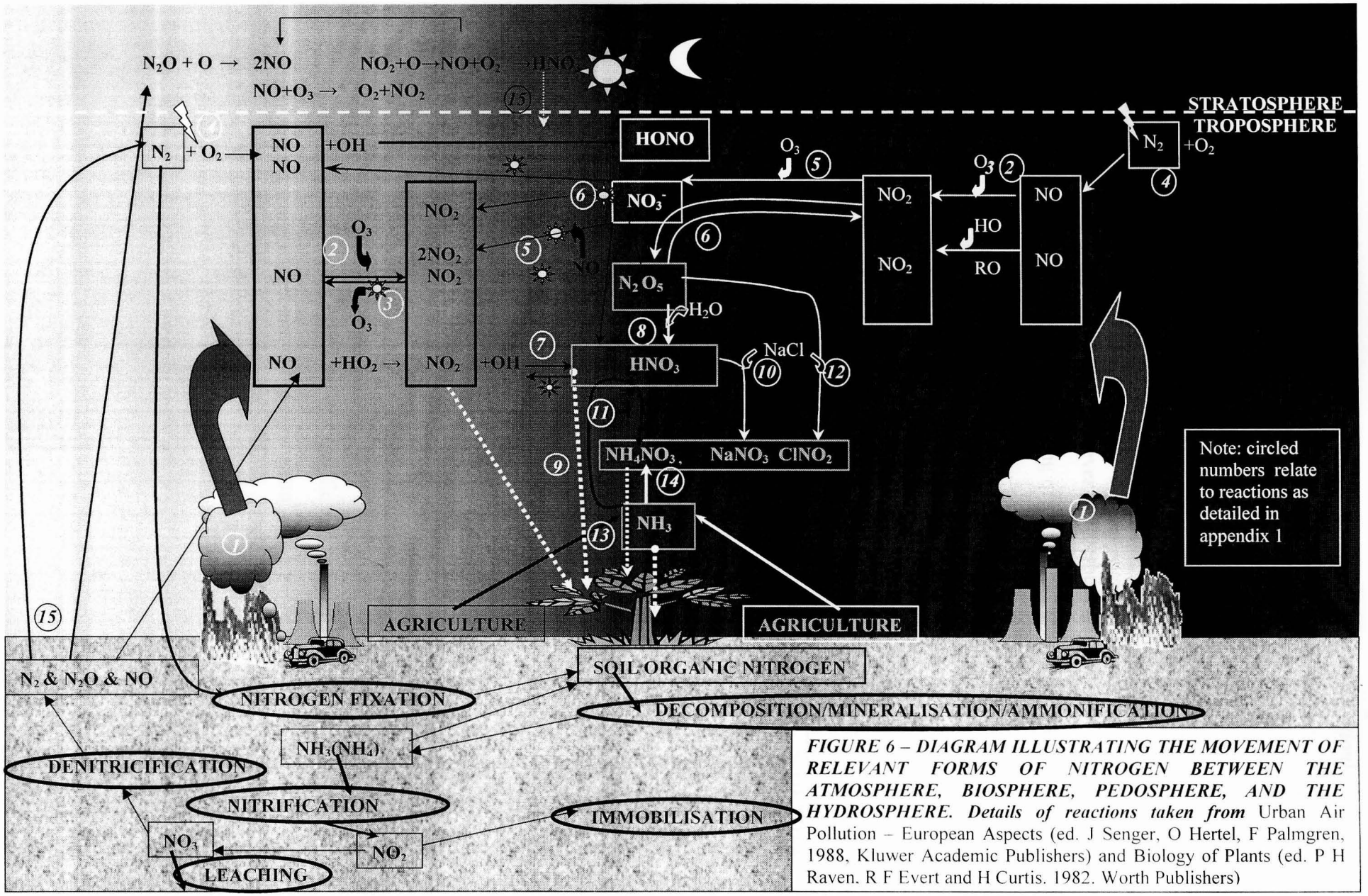

FIGURE 6 – DIAGRAM ILLUSTRATING THE MOVEMENT OF RELEVANT FORMS OF NITROGEN BETWEEN THE ATMOSPHERE, BIOSPHERE, PEDOSPHERE, AND THE HYDROSPHERE. Details of reactions taken from Urban Air Pollution – European Aspects (ed. J Senger, O Hertel, F Palmgren, 1988, Kluwer Academic Publishers) and Biology of Plants (ed. P H Raven, R F Evert and H Curtis. 1982. Worth Publishers)

Wet deposition (rain) and deposition from mist (cloud droplet interception)

- particulate nitrate (NO_3^-)
- particulate ammonium (NH_4^+)
- dissolved organic nitrogen

The nitrogen compounds listed above do not contribute equally to the atmospheric nitrogen loading at a particular site. Many of the studies reviewed for this discussion concentrated on only one of the forms of nitrogen being deposited. However, Hesterburg *et al.* (1996) completed a relatively comprehensive study in Switzerland showing quantitatively the relative importance of a number of forms of nitrogen to deposition in the particular area of their study (see Table 1 below). Another relatively comprehensive study - Miller and Friedland (1999) – is also included in the table for comparison.

Table 1- Forms of nitrogen and the percentage contribution to deposition from Hesterburg *et al.* (1996) and Miller and Friedland (1999).

FORM OF NITROGEN	**% OF TOTAL DEPOSITION (wet and dry) Hesterburg *et al.* (1996)**	**% OF TOTAL DEPOSITION (wet and dry) Miller & Friedland (1999)**	**% OF TOTAL DEPOSITION (wet, dry & occult) Miller & Friedland. (1999)**
NH_3 dry	46.6%	Not evaluated	Not evaluated
NH_4^+ wet	20.1%	29.3%	15.3%
NO_3^- wet	12.2%	46.0%	24.0%
NO_2 dry	10 %	Not evaluated	Not evaluated
$HNO_3 + NO_3^-$ dry	5%	23.9%	12.5%
NH_4^+ dry	3.9%	0.7%	0.4%
NO, N_2O_5, HONO, NO_2, PAN	2.2%	Not evaluated	Not evaluated
NH_4^+ occult		See next column	21.7%
NO_3^- occult		See next column	26.1%

The above studies are useful as guidelines to highlight the generally important forms of nitrogen to deposition. However, the factors controlling amounts of nitrogen deposited as well as the relative proportions of the various forms are site specific and variances occur. For example in the Swiss study there is a significant amount of agricultural activity – hence the necessity to evaluate NH_3 gas and the resultant high contribution it makes. In the North American study, the site is not influenced by agricultural activity and NH_3 was not evaluated. Furthermore, occult deposition was important in the high elevation North American study whereas it was not evaluated in the Swiss study. This site-specific variability is particularly relevant to the present study because of the difficulty in obtaining data that would allow for a comprehensive analysis of nitrogen deposition.

If the study site can be described in terms of factors influencing nitrogen deposition, any available quantitative data from other studies could be placed in context with this information. The important factors controlling nitrogen deposition can be highlighted by referring to the calculations used to obtain quantities of wet, dry and occult deposition. These calculations are discussed below and the controlling factors are then highlighted and discussed further.

Calculations for deriving amounts of wet, mist/cloud and dry deposition

In calculating wet deposition the amount of chemical compounds received per unit area of the surface is equal to the amount of precipitation per unit area of the sample multiplied by the measured concentration of the pollutant in the sample (Zunckel, 1998). For calculating the amount of nitrogen deposited via mist or cloud droplet interception, the amount of water deposited to the surface and the concentration of nitrogen in that water needs to be known (i.e. similar to the calculation for deposition via precipitation). The difficulty lies in measuring the amount of water deposited. A method of inferring this from other variables may be used. It has been shown that the rates of deposition of water from mist events are similar to the rates of momentum transfer for the droplet size 4 - 20μm radius (Beswick *et al.*, 1991). This size range contains the bulk of the cloud /mist water, and the relationship to momentum transfer may therefore be used to estimate cloud/mist droplet deposition from a knowledge of the roughness length (z_o) and wind velocity (Fowler *et al.*, 1991). This deposition needs to be combined with the duration of mist / cloud events for the particular period under investigation as well as the measured concentration of the pollutant in the mist/cloud to obtain the amount of nitrogen received per unit area of the surface for the given time period. It is a noteworthy point that the concentration of atmospheric pollutants in cloud water at an elevated site was shown to be much greater than that in rainwater at the same site by Fowler *et al.* (1988). Further studies in the U.K. and elsewhere have corroborated this general trend (Fowler *et al.*, 1996; Lovett, 1992). Olbrich (1993) has shown a similar trend in measurements made on the Eastern Escarpment. These elevated concentrations and the more intimate interaction of mist events with vegetation emphasises the importance of accounting for nitrogen deposition via mist/cloud droplet interception in the study.

For **dry deposition** the calculation commonly used and referred to as the inferential method (Hicks *et al.*, 1987) is:

$$-F = V_d \cdot C$$

F = dry deposition rate (negative sign is convention and indicates downward flux)
C = atmospheric concentration, V_d = deposition velocity

The above calculation is used in place of more direct measurements of dry deposition in light of the difficulty in executing the latter. A more detailed explanation of the concept of deposition velocity is appropriate so as to facilitate further discussion. The above equation is often viewed in terms of a resistance analogy where a resistance component is used to account for the chemical and biological processes that control pollutant adsorption and capture at natural surfaces (fig.7). These resistances are the inverse of the deposition velocity and for trace gases are resolvable into three components:

$$V_d = 1 / (R_a + R_b + R_c)$$

R_a = the aerodynamic resistance
R_b = the boundary layer resistance (resistance of the layer in contact with the surface)
R_c = canopy resistance (the resistance of a single leaf is extrapolated to an entire canopy)
(R_c can be broken down into various resistances e.g. cuticular and stomatal)

The above resistances reflect the division of the uptake of a gas by a plant into three steps (Cape and Unsworth 1987):

1) Gas brought to the leaf (essentially by turbulence in the atmosphere);
2) Gas diffuses through non-turbulent boundary layer (the thin layer directly above the leaf surface in which there is no turbulence and movement is by diffusion);
3) Gas absorbed through stomata / deposited onto surface

The strengths of the above resistances (and therefore the value of V_d) are dependent on a number of factors, including the more important ones outlined below:

R_a – wind speed and canopy roughness

R_b – morphology of leaf, micro roughness

R_s - stomatal control, type of gas, chemistry of the leaf surface

The crux of the above is that atmospheric conditions, vegetative features and the type of gas all combine to determine an appropriate site/situation specific V_d. Measurement of these factors and input into a model such as that developed by Hicks *et al.* (1987) allow for the determination of a relevant V_d. Inherent in the combination of atmospheric and vegetative factors is a difference in the degree of deposition to short vegetation (e.g. grassland) and tall vegetation (e.g. forests) which is relevant to the present study. This is emphasised by Fowler *et al.* (1999) "...the turbulence generated within the surface layer of the atmosphere occurs as a consequence of the frictional drag at the earth's surface and forests, among all natural land cover classes, generate the greatest frictional drag at the surface. Forests are therefore aerodynamically rough surfaces with rates of turbulent exchange between the atmosphere and forests larger by an order of magnitude or more than those over grassland...".

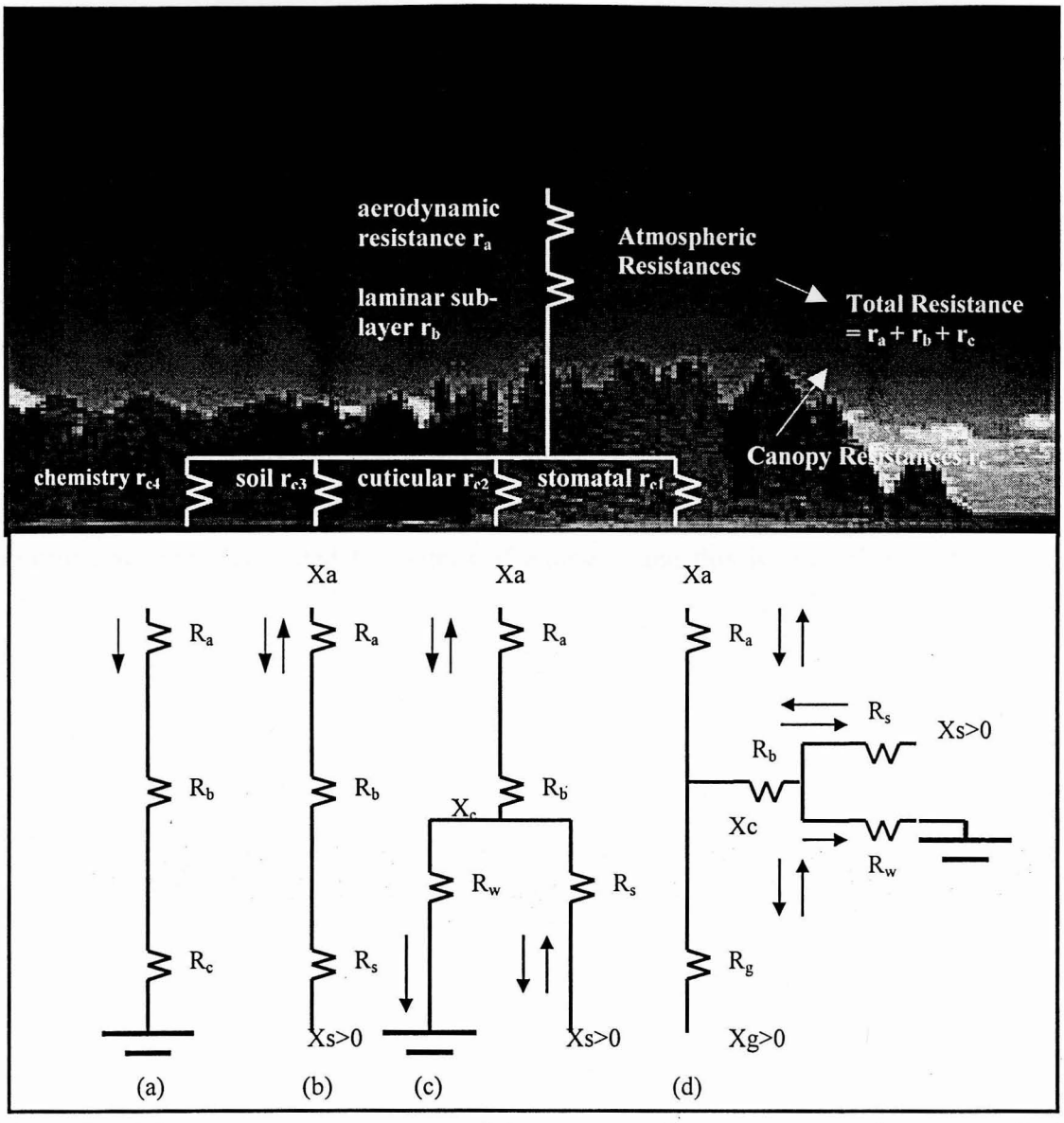

Figure 7 – Schematic representations of the concept of a resistance analogy as applied to dry deposition. The diagram at the top is modified from Fowler et al. (1999) and the diagram at the bottom is reproduced from Asman et al. (1998). For the lower diagram the following explanations apply:

(a) – canopy resistance model – assumes concentration of gas of interest at the surface is zero. X_a= concentration in air, R_a= atmospheric resistance, R_b = boundary layer resistance

(b) The stomatal compensation point model allows bi-directional exchange via stomata (R_s = stomatal resistance)

(c) The canopy compensation point model calculates the canopy concentration X_c as a result of competing stomatal exchange and deposition to leaf cuticles (R_w).

(d) A more complex canopy-exchange model accounting for exchange with a ground concentration (X_g) and diffusion through the canopy air space (R_g).

The calculations described above for wet, cloud/mist and dry deposition indicate rainfall amount, 'mistfall' amount, concentration (in air, precipitation and mist) and deposition velocity as being the important controlling parameters to allow quantification of nitrogen deposition. Factors such as rainfall, 'mistfall' and concentrations may be influenced by regional considerations such as 'pollutant' emissions and dispersion climatology. These considerations are discussed below. This is followed by a discussion highlighting details of deposition pertaining to specific nitrogen species. This discussion is aimed in particular at detailing concentration and deposition velocity parameters. This is in light of the fact that for dry deposition, actual measurements of concentrations and fluxes are not available for the study site and estimates from data at other sites will have to be made (as discussed in the methods section). Deposition velocities will also have to be inferred. Concentrations are closely related to sources of emission and this is also discussed below along with dry deposition parameters.

Regional emission and dispersion characteristics having a possible influence on the study site.

The possible link between areas of emission and areas of deposition has been illustrated in Figure 5. This phenomenon may be illustrated as being relevant to the proposed study site by reference to discussions in Tyson and Preston-Whyte (2000). Their discussion describes the linking of areas of emission and deposition by two phenomena – synoptic scale transport and local/meso-scale transport of material in the atmosphere. Figure 8 illustrates the local meso-scale transport possibilities relevant to this study. The Mpumalanga escarpment region is shown as being influenced by air coming from the 'Highveld Plateau' to the west as well as the 'Lowveld' to the east during the day.

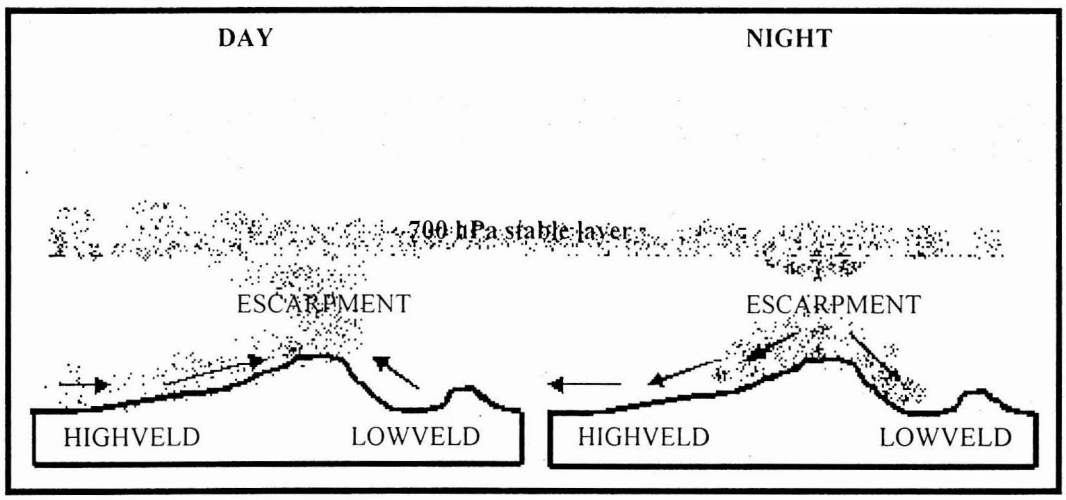

Figure 8 - Schematic illustration of mountain-plain and plain-mountain winds and their possible effect on pollution transport on the escarpment region (reproduced from figure 15.2 in Tyson and Preston-Whyte, 2000)

The flow from the west is particularly relevant because it may bring air from a region termed the 'Eastern Transvaal Highveld' (Tyson *et al.*, 1988). The area has been referred to as the powerhouse of South Africa and contains a number of pollution sources, notably the electrical power stations using coal combustion in the power generation process.

The closest power station to the study site - Arnot power station - is approximately 135 km southwest of the study site (Figure 2). As discussed previously in Figure 6 and in more detail below, combustion processes result in increased nitrogen emissions. The transport of such emissions to the study site may impact on the amount of nitrogen deposition to the study site by way of affecting concentration levels of pollutants at the site. These levels will exist at some dynamic equilibrium level resulting from the air movement towards the study site from the Highveld during the day (bringing pollution) and the reverse flow during the night (removing the pollution). The flow from the east is not necessarily as likely to affect pollution concentrations to the same degree, but it is noteworthy that the air coming from this area will be associated with the formation of mist as a result of up-slope fog formation. Thus these mist events and their associated deposition may have a chemistry differing to that associated with the dry and wet precipitation events.

The above discussion has focussed on a relatively simple concept involving only localised ground airflow considerations. The area of southern Africa is also subject to relatively complex regional synoptic air-flows that may have an effect on background pollution concentrations (Tyson and Preston-Whyte, 2000). These background pollution concentrations express themselves as a haze layer. ' Over much of the year, aerosols are trapped in a dust pall beneath the ~500 hPa stable discontinuity to form a pronounced haze layer. The primary constituents of the haze layer are surface derived dust, urban-industrial pollution, biomass burning products and marine aerosols.' (Tyson and Preston-Whyte, 2000).

Figure 9 provides a useful summation of the impact of these various sources of pollution on the general area in which the study site falls. The Misty Mountain site is approximately 20 km's southwest of the study site. Aeolian dust is a consistently high contributor to background aerosol loading, followed by industrial sulphur. Industrial sulphur contributions to the Misty Mountain site are relatively high. Biomass burning seems to be a generally low contributor. However, the burn period is restricted to a few months in late Winter / Spring and its contribution during these months may be significantly more noticeable. This possibility will be addressed further below.

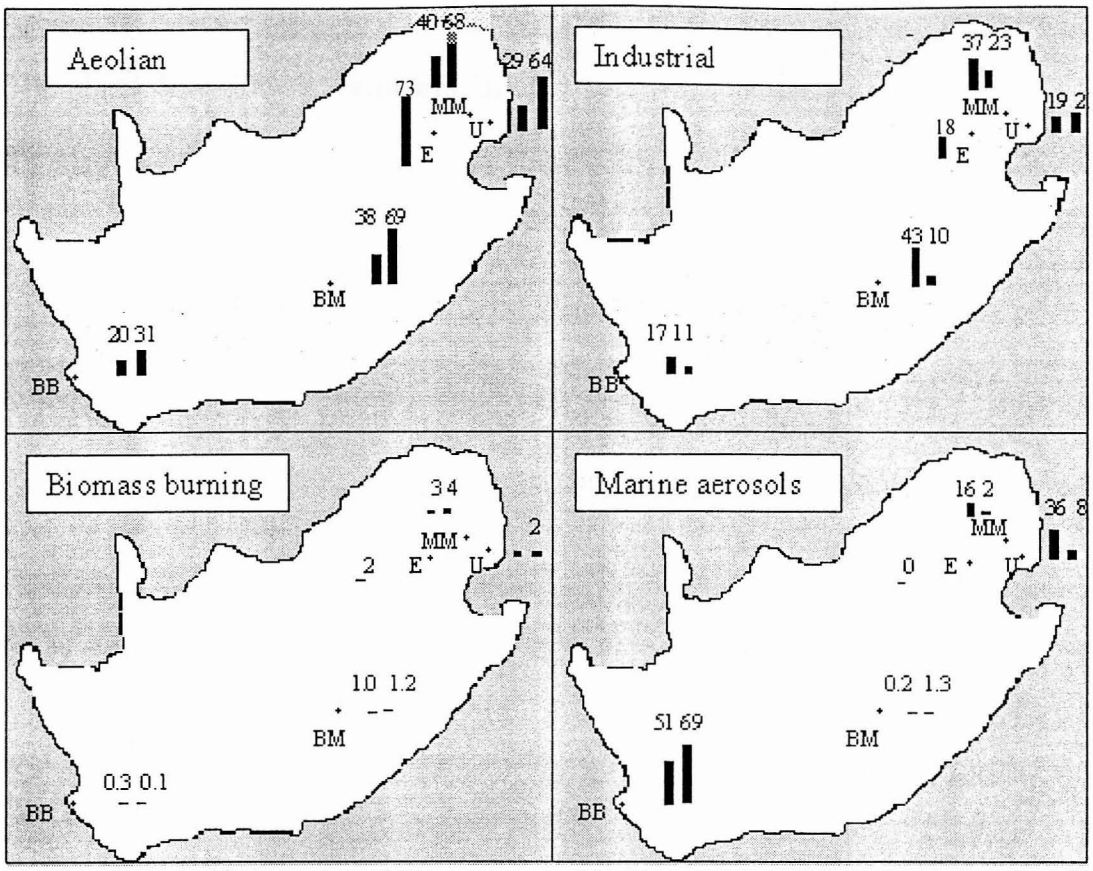

Figure 9 – Summer(first bar) and Winter(second bar) percentage contributions of aeolian dust, industrial sulphur, biomass burning and marine aerosols to the total detected background aerosol loading over South Africa. MM-Misty Mountain, E-Elandsfontein, U-Ulusaba, BM-Ben McDhui. BB-Brandbaai. Note that Elandsfontein has only Winter values.(adapted from figure 15.10 in Tyson and Preston-Whyte, 2000)

Regarding the more complex regional synoptic airflows for the region, the following points are relevant. One of the more relevant airflow systems to the present study is that of the southern African plume to the Indian Ocean and re-circulation pathways associated with it. It appears that the relatively high industrial sulphur signature at Misty Mountain arises from a circulation pattern that pushes polluted air from the 'Eastern Transvaal Highveld" south eastwards to the Indian Ocean. The plume then partially recirculates back over Mocambique towards the eastern escarpment region (in which the study site is located). Besides this re-circulation of industrial pollution from the ETH, recent work with satellite images, show a distinct plume arising from biomass burning in central/ southern Africa being pushed south eastwards. again to the Indian Ocean. The plume pathway crosses over the study site and indicates biomass burning to be a possible significant contributor to nitrogen concentrations during the Winter/Spring months. A point with regarding nitrogen fixation by lightning is appropriate at this point to conclude the regional characterisation of the proposed study site. The escarpment region in which the study site falls has one of the highest incidences of lightning occurrences in the world (pers. com. Prof. H. Annegarn, 2001). Figure 6 illustrates the conversion of unreactive N_2 to the more reactive NO and the high incidence of lightning may well have an influence on amounts of nitrogen being deposited.

Details of deposition parameters for specific nitrogen species

Nitric oxide (NO)

NO by itself is usually ignored in deposition studies due to its low deposition velocity of < 0.1 cm s^{-1} (Böttger *et al.,* 1978). Its rapid conversion to NO_2 and generally low concentrations away from emission sources (Warneck, 1988) accentuates its low importance in deposition studies. Nitric oxide reacts with ozone to form nitrogen dioxide in a few seconds. The reverse reaction by photolysis occurs at a slower rate. This results in an equilibrium concentration, with nitrogen dioxide in the region of two to five times the concentration of nitrogen oxide in sunlit conditions depending on ozone concentrations.

Despite its relatively low importance with regards deposition, NO is by far the most important nitrogen-containing species emitted into the atmosphere on a mass basis from human activities, this due mostly to fossil fuel combustion in power stations and motor vehicles (point 1, Figure 6) (Metcalfe *et al.*, 1999). NO also has natural sources such as lightning and soils (Fowler *et al.*, 1998). A further source that may be natural or anthropogenically related is NO emitted during biomass burning. As discussed previously, the study site is situated in an area that is affected by fossil fuel combustion, biomass burning and a high level of lightning occurrence. Elevated NO concentrations resulting from these emissions will translate into elevated concentrations of NO_2 (and other nitrogen compounds) downwind from the sources. (i.e. this study site). This indirect effect on deposition levels at the study site needs to be considered, especially when making inferences.

Emissions of NO not only have an effect on NO_2 concentrations but also have a bearing on NO_2 deposition. To explain this, the flux of NO needs to be detailed first. Nitric oxide differs from many other gasses in that natural environments may not only act as depositionary surfaces for nitric oxide, but may to varying degrees also emit nitric oxide. The soil, for instance, may be a source or a sink for NO. Generally if atmospheric concentrations of NO are high the soil is a sink and vice versa.

This issue of bi-directional flux may be represented by an alteration to the resistance analogy formulae:

$$NO\ flux = C_{soil} - C_{air} / (r_a + r_b + r_c)$$

C_{soil} = nitrogen concentration in soil
C_{air} = ambient nitrogen concentration
r_a = canopy aerodynamic resistance
r_b = boundary layer resistance
r_c = diffusion resistance of the soil

Fowler *et al.* (1998) indicate that for atmospheric NO concentrations < 10 μg N m^{-3} the soil is a source, whereas for >20 μg N m^{-3} it is a sink and the maximum flux might approach 20 μg N m^{-2} s^{-1} (Fowler *et al.*, 1998). The ambient concentration leading to no net soil atmosphere exchange is the compensation point and is in the range of 0.1–5 nl L^{-1} (0.1 – 5 ppb) (0.058 – 2.9 μg N m^{-3}) for unmanaged soils (Johansson, 1987). Thus under certain conditions, there may essentially be a negative flux from the atmosphere to the soil.

NO emitted from soil converts rapidly to NO_2. Thus emitted NO can be practically viewed as emitted NO_2 and this makes the evaluation of nitrogen dioxide flux in natural systems a bi-directional issue as well, with the same problems regarding inferences (Fowler *et al.*, 1998). The complications will be discussed further below.

Nitrogen dioxide (NO_2)

At emission sources, the ratio of NO to NO_2 is relatively high, but decreases away from the source with NO_2 becoming the dominant component (Warneck, 1988). Table 2 lists NO_2 concentrations quoted in literature. Urban polluted type areas are listed first followed by sub-urban and rural type areas. The following general inferences may be made with regards NO_2 concentrations from Table 2:

General **urban** NO_2 (expressed as N) concentration range: 9 – 39 μg N m^{-3}

General **suburban** NO_2 (expressed as N) concentration range: 3 – 9 μg N m^{-3}

General **rural** NO_2 (expressed as N) concentration range: 0.06 – 3 μg N m^{-3}

Similar ranges have been published by Hanson and Lindberg (1991). The study area may be described as rural, but influenced by regional pollution and would likely fall into the higher rural concentration range or lower suburban concentration range.

Table 2 – NO_2 concentrations measured or quoted in previous studies (the degree of shading indicates general degree of pollution, i.e. darker areas are more polluted).

Environment / comment	Ambient concentration $\mu g\ N\ m^{-3}$	Reference
Denver,winter morning	46	Cadle *et al.* 1982
Indonesia, Jakarta,1996, polluted environment	17.33	Gillett *et al.* 2000
Indonesia, Jakarta,1992, polluted environment	16	Gillett *et al.* 2000
Pakistan, close to city, 1991 – 1993, annual mean	11.6– 14.5	Maggs *et al.*, 1995
Polish industrialised area	10.6	Bytnerowicz *et al.*, 1999
Yearly av. Netherlands 1979-1990	9 (NO=4)	Erisman, 1993
Nightime rural Ontario, 50kms N of Toronto, NO 3ppt	2.9 – 9.88 (4.65 & 7,56 average)	Makar *et al.*, 1998
Switzerland grass *diurnal*	5.46	Hesterburg, 1996
Indonesia, Bogor, polluted environ	4.30	Gillett *et al.*, 2000
100 kms out of Sydney, around a power station with city close by, yearly mean	3.6	Ayers *et al.*, 1995
Nightime rural Ontario, 50kms N of Toronto	2.91-9.88	Makar *et al.*, 1998
Poland rural forest (40 kms from industrial)	2.6	Szarek, 1995
Polish mountain forest	2.42	Bytnerowicz *et al.*, 1999
Czechoslovakia, farm, 1988	0.61 – 5.75 median = 2.4	Adema *et al.*, 1992
Abbeville,USA,rural,summer/spring	~2	Cadle *et al.*, 1982
California rural	0.58 – 2.9	Bytnerowicz *et al.* 1999
USA rural forests	0.7 – 2.6	Lovett 1992
Typical polluted	1.16	Soderlund, 1981
Mountain subject to pollution from Freiburg carried by valley winds. Polluted period	Up to 3.49 (to 0.87 after 12h)	Patz *et al.*, 2000
Mountain subject to pollution from Freiburg carried by valley winds.unpolluted period	~ 0.87 (NO_x)	Patz *et al.*, 2000
Indonesia, Bukit Koto Tabang, unpolluted environment	0.70	Gillett *et al.*, 2000
100 kms out of Sydney, 3 sites around a power station, no nearby city, yearly mean	0.58, 0.76, 0.70	Ayers *et al.*, 1995
Rural forestry area N. America 350 kms from industrial area. NO_x during pollution episode	0.23 – 1.51 (0.66 mean)	Thornberry *et al.*, 2001
Rural forestry area N. America 350 kms from Ind. NO_x during unpolluted episode	0.09 – 0.7 (0.27 mean)	Thornberry *et al.*, 2001
Rural Colarado Mnts. NO_x. Mostly unpolluted	0.04 – 1.16 (med. 0.17)	Parrish *et al.*, 1986
Typical rural	0.06	Soderlund, 1981

With regards nitrogen dioxide removal from the atmosphere, deposition may be either direct dry deposition or dry deposition following conversion to gaseous HNO_3, particulate NO_3^- or HONO. Wet deposition as NO_3^- will also occur (Fowler *et al.*, 1998) (Figure 4). Deposition characteristics of the conversion products will be dealt with in later subsections but as far as dry deposition of nitrogen dioxide is concerned the following points are relevant. In general, nitrogen dioxide has relatively low rates of deposition and in the absence of oxidation to HNO_3 or aerosol NO_3^-, the atmospheric lifetime of NO_2 is relatively long with a resultant regional influence (Fowler *et al.*, 1998). With regards sites of deposition, Fowler *et al.* (1989) described the exchange of NO_2 and NO with vegetation as being more complex than most pollutants. Nitrogen dioxide interacts primarily with leaves by diffusion through the stomata, with cuticle uptake 1-2 orders of magnitude less than that via stomata (Hanson and Lindberg, 1991). Diffusion of NO_2 through the stomata occurs not only from the atmosphere into the plant but physiological processes within plants may produce NO_2 or NO and may emit these gasses through the stomata. This along with the rapid conversion of soil emitted NO to NO_2 makes the evaluation of NO_2 deposition a bi-directional issue (as described above in the section on NO). A further point of importance regarding uptake of NO_2 by the stomata is that there are indications that the rate of uptake increases in proportion to ambient NO_2 concentrations (Sinn *et al.*, 1984). Furthermore, indications are that there is a minimum value below which there is no uptake viz. 1.3 nl L^{-1} (2.4 μg m^{-3} or 0.75 μg N m^{-3}) (Johansson, 1987). Fowler *et al.* (1991) discussed a number of previous measurements and also highlighted the change in deposition velocity with change in NO_2 concentration. They made the following summation, "..it is probable that NO_2 deposition on vegetation in rural atmospheres varies from 1 to 3 mm s^{-1} in the concentration range 1 – 5 ppb NO_2 (0.6 – 2.9 μg N m^{-3}), to 6 or 8 mm s^{-1} at concentrations of ≥ 20 ppb (11.6 μg N m^{-3})..." These concentration dependant velocities would indicate little or no deposition at concentrations common in rural areas of the United States (Hanson and Lindberg, 1991). Regarding the present study, concentrations are likely to be on the higher end of typical rural concentrations (as discussed above). However, the concentrations are close enough to the compensation point for there to be a degree of uncertainty about actual deposition amounts. Table 3 lists deposition velocities measured in previous studies.

Table 3 – NO_2 deposition velocities measured or quoted in previous studies

Environment / comment	Deposition velocity (cm s^{-1})	Reference
Trees geometric mean	2.4 ± 0.8	Hanson & Lindberg, 1991
Alfalfa (calculated from Hill, 1971).	1.9	Sehmel, 1980
grass	0.8	Garland, 1978
crops geometric mean	0.7 ± 0.6	Hanson & Lindberg, 1991
Netherlands	0.33	Erisman *et al.*, 1989
-	0.25	Dollard, 1987
Representative mean	0.25	Penner, 1991
Variance according to concentration	0.1 – 0.8	Fowler *et al.*, 1991
For wheat to grass from literature	0.1-0.7	Goulding *et al.*, 1998
Jakarta, 1992, polluted environment, inferential Vd	0.21	Gillett *et al.*, 2000
Yearly av. Netherlands 1979-1990	0.2	Erisman, 1993
Switzerland grass *diurnal*	0.11- 0.24	Hesterburg, 1996
average over 24 hrs over moorland	0.1 – 0.2	Fowler *et al.*, 1998

Hanson and Lindberg (1991) summarised whole canopy deposition velocities ranging from 1 to 2.8 cm s^{-1} with the geometric means for trees equal to 2.4 cm s^{-1} and that for crops equal to 0.7 cm s^{-1}. However they point out that the methods used to obtain these values suffered from a number of problems including the bi-directional flux issue. Furthermore, since NO_2 is taken up mainly through the stomata, nightime deposition is almost completely eliminated (Hanson *et al.*, 1989) and an average 24 hour deposition velocity will be smaller than deposition velocities recorded during the day. Fowler *et al.* (1998) quoted an average deposition velocity over a 24 hour period of 0.1 to 0.2 cm s^{-1} (thus taking into account the effect of soil emissions throughout the period). This is smaller than the value quoted for crops by Hanson and Lindberg (1991), but is probably a most appropriate average deposition velocity to use for short vegetation. This more appropriate deposition velocity is similar to that of nitric oxide, and again partially explains the low importance of these gases in terms of deposition.

Nitric acid vapour (HNO_3)

HNO_3 can dry deposit, wet deposit or react with alkaline aerosols (Bytnerowicz and Fenn, 1996). Parrish *et al.* (1986) mention that a number of studies indicate it to be the dominant source of acid precipitation in the western United States and it is an obvious choice for inclusion in this study. The primary source of HNO_3 is the oxidation of NO_2. This may occur directly by reaction with OH radicals or indirectly by reaction with ozone (Warneck, 1988). In the latter case, the NO_3 radical is formed first. This

associates with NO_2, to form N_2O_5 that reacts with water to form HNO_3. This second process is important at night whereas the direct oxidation path occurs in daylight. The latter is enhanced in summer when insolation, absolute humidity and ozone are at maximas (Parrish *et al.*, 1986). The time constant for the direct oxidation pathway is approximately one day and the HNO_3 produced is the stable end product of NO_2 oxidation (Warneck, 1988). Roberts *et al.* (1984) have shown that direct oxidation of NO_2 to HNO_3 appears to be the principal removal mechanism for NO_2 from aged plumes. Bytnerowicz *et al.* (1987) also make the point that nitric oxide and nitrogen dioxide (NO_x) predominate near anthropogenic sources, whereas nitric acid is prevalent at more remote locations. The NO and NO_2 emissions transported to the study area are therefore likely to have been converted to HNO_3 to a large degree. Bytnerowicz *et al.* (1987) further state that "... it appears that in humid areas, a few hundreds of kilometres or less downwind of a NO_x source, nitric acid dry deposition may be of the same magnitude as nitrate wet deposition ...", indicating the likely importance of HNO_3 to deposition at the study site. HNO_3 deposits readily by wet and dry deposition, as discussed further below. It may also become associated with aerosol particles. This occurs by reaction with NH_3 or alkaline elements in soil or sea salt particles. The reaction products of the former are relatively stable, whereas ammonium nitrate particles formed by reaction with ammonia are thermally unstable. High NH_3 and low temperatures are required to maintain ammonium nitrate concentrations. A further factor promoting conversion to particles is high humidity. These physical and chemical factors affecting HNO_3 concentrations can be considered in light of the possible pathways by which a pollutant plume may reach the study site, as discussed in section 2.2. The mesoscale pathway from the ETH to the study site is of long enough duration (i.e one day at typical wind speeds) for significant conversion of NO_2 to HNO_3, and short enough duration for the HNO_3 and particulate NO_3^- to have not been affected too radically by deposition.

In terms of typical ambient concentrations, Table 4 documents concentrations, measured or quoted in previous studies. The table lists the higher concentrations from polluted, urban type areas first followed by the lower concentrations typical of sub-urban and urban type areas.

Table 4 – HNO_3 concentrations, measured or quoted in previous studies.

Comments	Concentration $\mu g\ N\ m^{-3}$	Reference
Nightime rural Ontario, 50kms N of Toronto	1.27 – 3.07	Makar *et al.*, 1998
Summer California day influenced by photochemical smog	2.51	Grosjean & Bytnerowicz 1993
3 forest sites across Denmark 1985-1993, 24h av. yearly means, $HNO_3 + NO_3$	± 0.8 –1.75	Hovmand and Andersen 1995
Indonesia, 1992, Jakarta, polluted env. inferential Vd	1.4	Gillett *et al.*, 2000
Mountain subject to pollution from Freiburg carried by valley winds.polluted period.Summer	Up to 1.28	Patz *et al.*, 2000
Pennsylvania mountains	1.19	Pierson *et al.*, 1989
Suburban - urban	0.4 – 1.06	Harrison *et al.*, 1996
Pennsylvania mountains	0.99	Pierson *et al.*, 1989
NE U.S.A. rural, polluted source winds	0.99	Lefer *et al.*, 1999
100 kms out of Sydney, around a power station with city close by, yearly mean	0.87	Ayers *et al.*, 1995
Urban USA (Michigan, spring)	0.77	Cadle *et al.*, 1982
Switzerland unpolluted, 2x winter	Up to 0.76	Oberholzer ,1993
Summer day UK	0.71	Dollard *et al.*, 1987
Illinois day average	0.71	Huebert and Robert , 1985
Poland urban Autumn daytime	0.4 - 0.71	Bytnerowicz *et al.*, 1999
Indonesia,1996, Jakarta, polluted env.	0.7	Gillett *et al.*, 2000
Oak Ridge,USA, top of 27m high forest, annual mean	0.65	Taylor *et al.*, 1993
Summer Polluted Germany	0.64	Meixner *et al.*, 1985
Swedish rural agric.	0.64	Hesterburg *et al.*, 1996
US forests > 1yr	0.18 – 0.62	Lovett, 1992
Polluted San Joaquin Valley, California, boundary layer	0.62	Lebel *et al.*, 1990
Summer, Michigan	0.6	Cadle, 1985
Typical polluted	0.58	Soderlund, 1981
Northern Europe range	0.058 – 0.581	Fowler *et al.*, 1991
Poland rural Autumn daytime av.	0.1 - 0.53	Bytnerowicz *et al.*, 1999
Urban USA (Commerce city, winter)	0.49	Cadle *et al.*, 1982
Summer UK	0.47	Dollard *et al.*, 1987
Summer California night	0.46	Grosjean & Bytnerowicz 1993
Western U.S.A. boundary layer av.	0.45	Lebel *et al.*, 1990
Mountain subject to pollution from Freiburg carried by valley winds, unpolluted period, Summer	~ 0.44	Patz *et al.*, 2000
Rural USA (Abbesville, summer)	0.42	Cadle *et al.*, 1982
24h rural forestry N Am. 350 kms from ind.pollut.	0.23 – 0.73 (0.41 mean)	Thornberry *et al.*, 2001
Average across 6 USA sites	0.41	Cadle *et al.*, 1982
Indonesia, Bogor, polluted environ	0.41	Gillett *et al.*, 2000
Winter, Michigan	0.4	Cadle, 1985
NE U.S.A. rural, intermediate source winds	0.38	Lefer *et al.*, 1999
Year av. Rural UK	0.37	Dollard *et al.*, 1987
Japan, annual av.	0.36	Matsumoto & Okita, 1998

Comments	Concentration $\mu g\ N\ m^{-3}$	Reference
Urban USA(Warren,winter)	0.31	Cadle *et al.*, 1982
100 kms out of Sydney, 3 sites around a power station, no nearby city, yearly mean	0.29, 0.24, 0.27	Ayers *et al.*, 1995
Northern Europe summer av.	0.29	Fowler *et al.*, 1991
Central Africa, dry season	0.29 (1998),0.23 (1999)	Galy-Lacaux *et al.*, 2001
NE U.S.A. rural, unpolluted source winds	0.28	Lefer *et al.*, 1999
Winter day UK	0.27	Dollard *et al.*, 1987
Winter Polluted Germany	0.24	Meixner *et al.*, 1985
Arizona desert day	0.24	Benner *et al.*, 1991
UK rural	0.23	Acid Deposition in the UK
Winter UK	0.23	Dollard *et al.*, 1987
Netherlands, yearly av. 1979-1989	0.22	Erisman, 1993
Rural USA(Luray,summer/spring)	0.21	Cadle *et al.*, 1982
Summer night UK	0.2	Dollard *et al.*, 1987
Maine, USA, forest, mean	0.18 ± 0.1	McLaughlin *et al.*, 1996
Urban USA (Warren,fall)	0.17	Cadle *et al.*, 1982
NE USA high elev. forest annual mean 1986-1995	0.17	Miller and Friedland (1999)
Illinois day range morning-afternoon	0.38-0.87	Huebert and Robert, 1985
Colorado high elev. polluted source winds	0.15	Williams *et al.*, 1997
Winter night UK	0.15	Dollard *et al.*, 1987
Denmark, 1993, mixed forest/ heathland. Relatively high ammonia emissions	av. = 0.15 (<.02-.41)	Andersen and Hovmand 1995
Rural Colarado Mnts. Summer av. mostly unpolluted source winds	0.14	Parrish *et al.*, 1986
Indonesia, Bukit Toko Tabang, unpolluted environ.	0.12	Gillett *et al.*, 2000
Switzerland with farming and sewerage influence	Up to 0.12	Oberholzer, 1993
Sahelian region, Niger, dry season mean	0.11	Galy-Lacaux *et al.*, 2001
Central Africa, wet season	0.05 (1998), 0.11 (1999)	Galy-Lacaux *et al.*, 2001
Colorado high elev. Unpolluted source winds	0.07	Williams *et al.*, 1997
Summer High Alpine	0.07	Kasper & Puxbaum, 1998
Rural Nevada and Utah, boundary layer	0.07	Lebel *et al.*, 1990
Typical rural	0.06	Soderlund, 1981
Rural Colarado Mnts. Winter av. mostly unpolluted source winds	0.04	Parrish *et al.*, 1986
Winter High Alpine	0.03	Kasper & Puxbaum, 1998
Sahelian region, Niger, wet season mean	0.03	Galy-Lacaux *et al.*, 2001

Figure 10 is a graphical representation of some of the values in Table 4. The figure gives a visual summary of the ranges of nitric acid concentrations quoted or measured in literature for urban, sub-urban and rural type environments. The tabulated and graphical data indicate the underlying approximate ranges of HNO_3 concentration dependant on the degree of pollution of the environment. Key references for the categories are listed (overlaps between divisions occur).

Polluted areas (0.4-2.51 μg N m^{-3})	0.4-1.06 (Harrison *et al.* 1996)
	0.7-1.40 (Gillett *et al.* 2000)
	0.87 (Ayers *et al.* 1995)
	2.51 (Grosjean & Bytnerowicz 1993)
Unpolluted areas (0.03-0.14 μg N m^{-3})	0.03-0.07 (Kasper and Puxbaum 1998)
	0.03-0.11 (Galy-Lacaux *et al.* 2001)
	0.12 (Gillett *et al.* 2000)
	0.04-0.14 (Parrish *et al.* 1986)
	0.09 (Williams *et al.* 1997)
Rural areas subject to varying degrees of transported pollution (0.14-0.62 μg N m^{-3})	0.41 (Thornberry *et al.* 2001)
	0.41 (Gillett *et al.* 2000)
	0.24-0.29 (Ayers *et al.* 1995)
	0.18-0.62 (Lovett 1992) (a range across forests in the USA that may represent essentially rural areas subject to varying amounts of transported pollution)

Further analysis of typical HNO_3 concentrations may be made by comparing studies that measured NO_2 or NO_x along with nitric acid. Such studies are shown in Table 5. Some of the data has been represented graphically in Figure 11 with a linear trend fitted to the data. In Figure 12, the fit has been improved by removing the higher nitrogen dioxide concentration values. This would be appropriate since high values of NO_2 are not likely to occur at the study site. The analysis presented in Figure 12 may be useful in inferring appropriate HNO_3 concentrations for the study site.

With regards depositionary characteristics, HNO_3 is a very reactive gas that adsorbs readily to most surfaces (as opposed to being taken up via the stomata) after diffusing through the quasi-laminar boundary layer (Huebert and Robert, 1985). This is reflected in its quoted canopy resistance of virtually zero (Huebert and Robert, 1985). Table 6 is a compilation of deposition velocities measured or quoted in other studies. Division has been made in the table between: a general division, in which details of vegetation were not available; short vegetation; and forests.

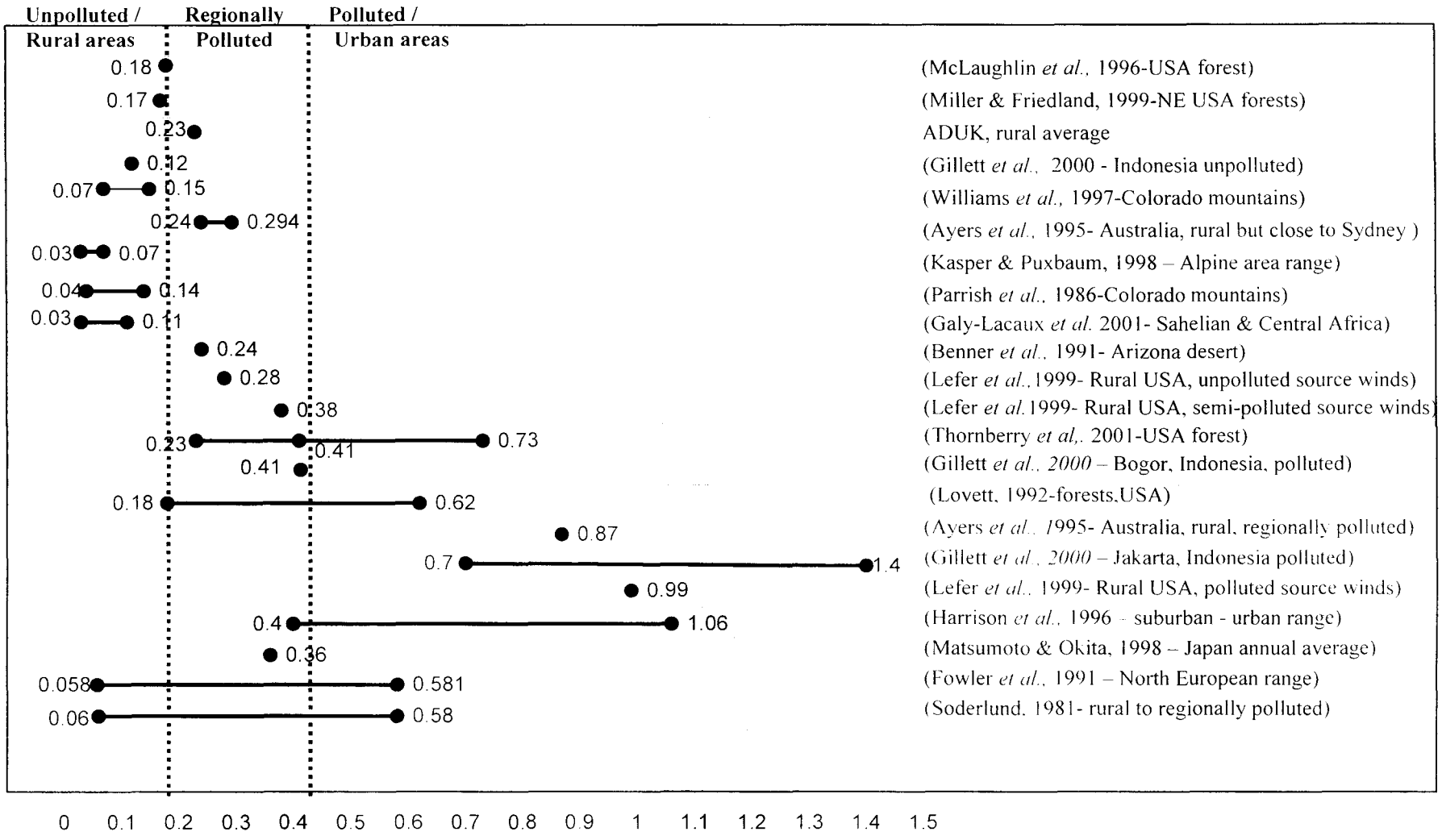

Figure 10 – Quoted and measured nitric acid values from previous studies.

Table 5 - Studies in which nitrogen dioxide and nitric acid were measured ($\mu g\ N\ m^{-3}$)

Comment	NO_x	NO_2	HNO_3	Study
Polluted August	0.66		0.55-0.73	Thornberry *et al.*, 2001
Unpolluted August	0.27		0.23-0.33	
polluted		16.3	1.4	Gillett *et al.*, 2000
polluted		17.3	0.7	
intermediate		4.3	0.4	
unpolluted		0.7	0.12	
-		5.47	0.96	Hesterburg *et al.*, 1996
-	0.29-4.07		0-1.16	Patz *et al.*, 2000
Rural, polluted source winds	4.7		0.99	Lefer *et al.*, 1999
Rural, intermediate source winds	3.03		0.38	
Rural, unpolluted source winds	0.78		0.28	
100 kms out of Sydney, around a power station with city close by, yearly mean		3.6	0.87	Ayers *et al.*, 1995
100 kms out of Sydney, site around a power station, no nearby city, yearly mean		0.58	0.29	
100 kms out of Sydney, site around a power station, no nearby city, yearly mean		0.76	0.24	
100 kms out of Sydney, site around a power station, no nearby city, yearly mean		0.7	0.27	
100 kms out of Sydney, site around a power station, no nearby city, yearly mean		0.7	0.27	
Switzerland unpolluted, 2x winter			Up to 0.76	Oberholzer, 1993
Switzerland with farming and sewerage influence			Up to 0.12	
polluted	1.16		0.58	Soderlund, 1981
rural	0.06		0.06	
Netherlands, yearly av. 1979-1989		9	0.22	Erisman, 1993
Abbeville, USA, rural		~2	0.42	Cadle *et al.*, 1982

Deposition velocities of 1.3 - 6.0 cm s^{-1} were calculated by Lovett (1992) using a model slightly modified from Hicks *et al.* (1987). In the case of nitric acid the use of the Hicks model is appropriate since the deposition of nitric acid is not subject to bi-directional influences. In the study by Lovett (1992), nitric acid vapour was the dominant species contributing to dry deposition, a reflection of its high deposition velocity (as opposed to NO_2 which had higher concentrations but lower deposition velocities). This is opposite to the study by Hesterburg *et al.* (1996) in which NO_2 dry deposition was twice as much as HNO_3. However the average concentrations of HNO_3 were low in the latter (0.6 $\mu g\ m^{-3}$).

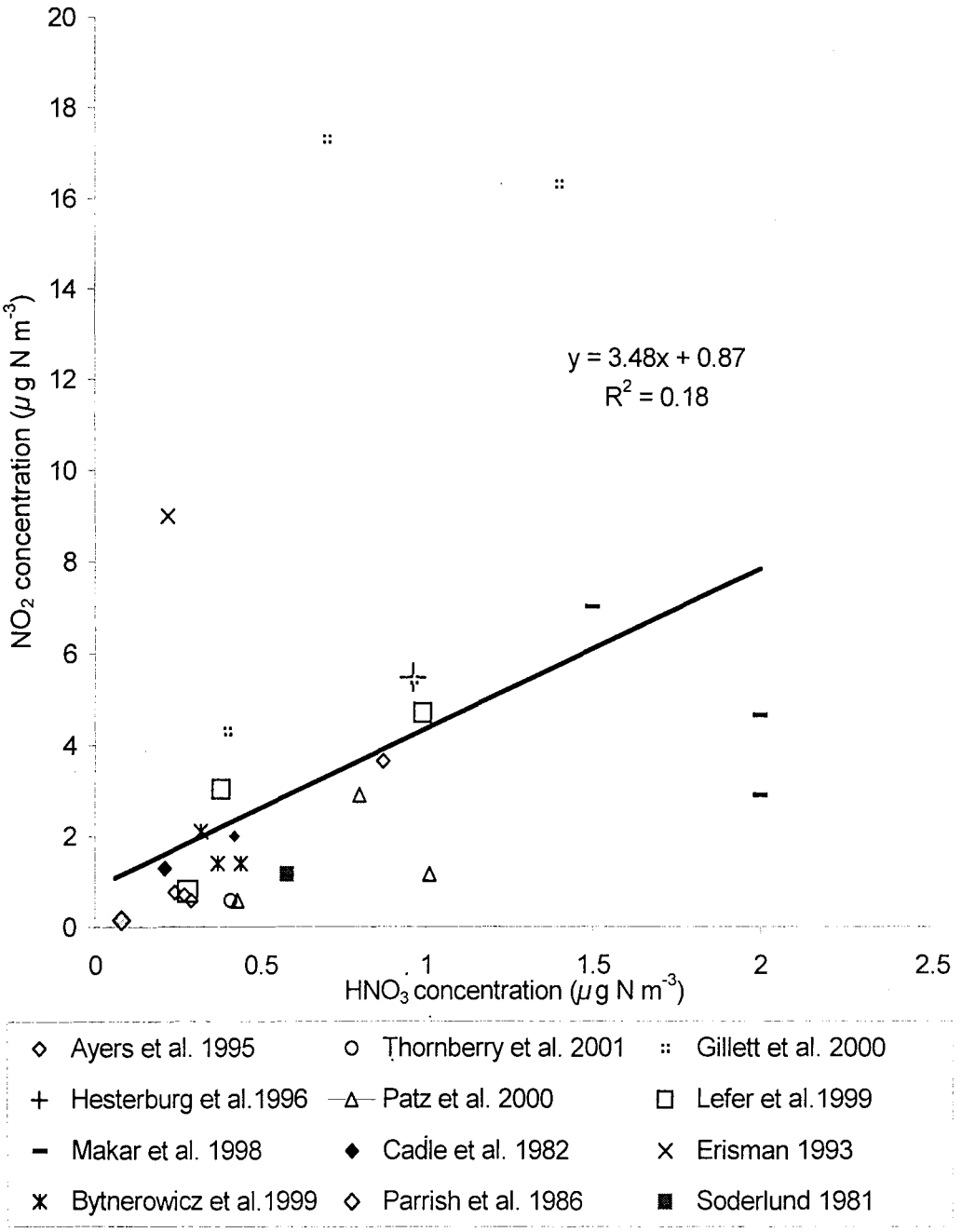

Figure 11 - Nitrogen dioxide and nitric acid concentrations measured simultaneously from a few studies.

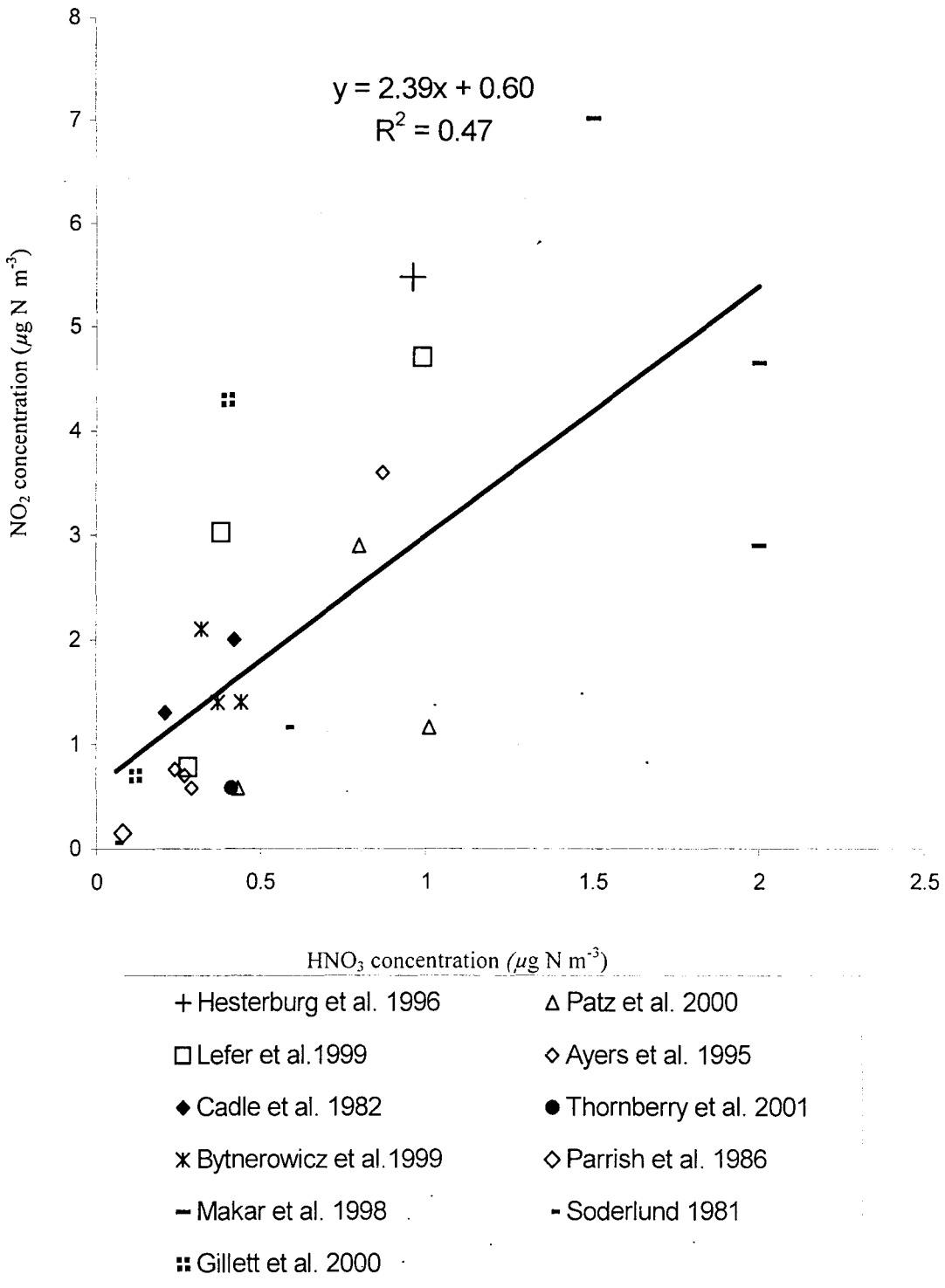

Figure 12 – NO_2 and HNO_3 concentrations measured simultaneously from a few studies, high NO_2 values removed

Table 6 - Deposition velocities for nitric acid measured or quoted in previous studies

Deposition velocity (cm s^{-1})	Comments	Reference
GENERAL		
0.90	Indonesia, 1992, Jakarta, polluted env. inferential Vd,annual average	Gillett *et al.*, 2000
1.0	Assumed annual av.	Ayers *et al.*, 1995
2.5	Netherlands, yearly av. 1979-1989	Erisman, 1993
1.6 – 2.62	North America annual avs. for six sites	Brook *et al.*, 1995
SHORT VEGETATION		
0.52	grass, windspeed = 1m/s	Fowler *et al.*, 1989
0.76	moor, windspeed = 1m/s	Fowler *et al.*, 1989
1.43	cereal, windspeed = 1m/s	Fowler *et al.*, 1989
2.0	Geometric mean of previous studies - crops	Hanson and Lindberg, 1991
2.35	grass, windspeed = 4m/s	Fowler *et al.*, 1989
2.5 ± 0.9	Illinois day average	Huebert and Robert, 1985
3.33	moor, windspeed = 4m/s	Fowler *et al.*, 1989
5.0	cereal, windspeed = 4m/s	Fowler *et al.*, 1989
FORESTS		
1	Denmark, 1993, mixed forest/ heathland. Relatively high ammonia emissions	Andersén and Hovmand, 1995
2.14	Used average of widely ranging values across a number of beech and maple stands	Lovett & Reuth, 1999
3.297	NE USA high elev. forest annual mean 1986-1995	Miller and Friedland, 1999
3.31 ± 0.516	Maine, USA, forest, weekly mean	McLaughlin *et al.*, 1996
4.0	Geometric mean of previous studies - forests	Hanson and Lindberg, 1991
4.0	forest, windspeed = 1m/s	Fowler *et al.*, 1989
7.6	Colorado, 12m high spruce fir, 13x daytime only, high turbulence	Sievering *et al.*, 2001
10.0	forest, windspeed = 4m/s	Fowler *et al.*, 1989

The differing NO_2 to HNO_3 ratios are likely a reflection of distance of the sources of the NO_x to the study sites. With regards more averaged deposition velocity calculations, Huebert and Robert (1985) calculated a daytime average deposition velocity of 2.5 cm s^{-1} over grass. Since the deposition is not stomata dependant they state that the deposition velocity is not expected to decrease overnight. Another study (Lovett and Reuth, 1999) calculated a similar deposition velocity of 2.14 cm s^{-1} using a model with site-specific canopy and meteorological data for beech and maple stands.

Ammonia gas (NH_3)

Part of this discussion includes aspects of deposition of ammonium aerosols that form from ammonia gas. However the discussion will focus primarily on ammonia gas and ammonium aerosols will be discussed further in a later section.

Emitted ammonia returns to the surface mainly in the form of dry deposition of ammonia and wet deposition of ammonium. Ammonium will also be present in cloud droplets and may deposit by cloud droplet interception. Dry deposition of ammonium may also occur. Atmospheric inputs of reduced nitrogen as ammonia and ammonium by dry and wet deposition may represent a substantial contribution to the acidification and nitrogen eutrophication of semi- natural ecosystems (Fowler *et al.*, 1989). The sources of ammonia are variable and include (Warneck, 1988):

- emissions from agricultural activity (volatilisation from fertilisers, urea and faecal decomposition);
- emissions from soils and vegetation;
- emissions from biomass burning and coal burning; and
- emissions from the sea.

Of the above ammonia sources, agricultural activities, namely excreta from domestic animals and fertilisers, are the major global source of ammonia (Asman *et al.*, 1998). The effect of proximity to agricultural activity on nitrogen deposition to an area is well illustrated by comparing the study of Hesterburg *et al.* (1996) with another relatively comprehensive study of nitrogen deposition done by Lovett (1992) in which wet deposition of NO_3^- and NH_4^+ and dry deposition of HNO_3 vapour and particulate NO_3^- and NH_4^+ were considered. It is notable that Lovett did not evaluate the form of nitrogen contributing most to deposition in the study by Hesterburg *et al.* (1996), namely dry NH_3. Lovett quotes a study by Tjepkema *et al.* (1981) as showing 'NH_3 to be low in both concentration and deposition to the sort of rural, non-agricultural areas that characterise most sites in the study'. This correlates with the recognised agricultural influence to the study by Hesterburg *et al.* (1996). The result is the removal in theory of the 46.6% contribution of NH_3 dry deposition to total deposition in the study by Hesterburg *et al.* (1996). The description of a site as being under the influence of agricultural activity, and therefore subject to NH_3 dry deposition to a

significant extent, is not an easily quantifiable element. However Asman *et al.* (1998) state that '...concentrations of NH_3 decrease rapidly from source (within the first 1 –2 km)...'. Furthermore, they make the point that although almost all NH_x emissions occur as NH_3, there is a relatively fast conversion rate of NH_3 to particulate NH_4^+ which has a small dry deposition velocity and is removed predominantly by wet deposition. Thus the further away from a source of NH_3 you go, dry deposition of NH_3 decreases while wet deposition of NH_4^+ increases.

The present study area will be evaluated in terms of a possible agricultural influence using the above qualitative parameters. Penner *et al.* (1991) noted the influence of biomass burning in the southern African region (as described above under the NO section) and since biomass burning emits NH_3 the possible influences on the study area need to be considered.

Table 7 lists ammonia concentrations measured or quoted in other studies. Shaded areas indicate studies in which an agricultural influence is mentioned. Concentrations range from 0.04 to 20.5 μg N m^{-3}. Areas under the influence of agriculture report concentrations from 0.82 μg N m^{-3} upwards, although studies not indicated to be influenced by agricultural activity report concentrations above this. The general concentration range quoted by Warneck (1988) of 0.17– 6.6 μg N m^{-3} appears to be reasonable. Values higher than this would probably only occur in distinctly agricultural areas.

Besides the general emission influences on NH_3 concentrations described above, meteorological – temperature and humidity – and chemical – sulphate and nitric acid concentrations – also play roles in determining ambient NH_3 concentrations (Warneck 1988). These factors variably increase or decrease emission and deposition or influence conversion of ammonia gas to particles. Before discussing these factors and their affects on ammonia concentrations a more detailed discussion of ammonia deposition is necessary. Many experiments using dynamic chambers with concentrations much larger than typical field conditions have shown that NH_3 is predominantly taken up by stomata with rates related to photosynthetically active radiation intensity and CO_2 fluxes.

Table 7 - Ammonia gas concentrations measured or quoted in other studies.(Shaded areas indicate studies in which an agricultural influence is mentioned).

Environment/comment	Concentration $\mu g\ N\ m^{-3}$	Reference
Massachusetts,winter	0.014	Tjepkema *et al.*, 1981
Night 1, rural Ontario, 50 kms N of Toronto	0.04	Makar *et al.*, 1998
Niwot Ridge,Colorado,winter	0.08	Langford *et al.*, 1992
Massachusetts,summer	0.11	Tjepkema *et al.*, 1981
Autumn, Sweden	0.17	Ferm, 1979
IFS study	0.2	Lovett, 1992
Allegheny mountain, Conneticut, Autumn	< 0.21	Pierson *et al.*, 1989
Niwot Ridge,Colorado, summer	0.21	Langford *et al.*, 1992
Denmark 1985-1993, 24h av. yearly means, low agriculture,	*0.25*	Hovmand and Andersen 1995
Winter, forest, Midwest USA	0.25	Pryor *et al.*, 2001
South Scotland moor, background value to above 1995 - 1996	0.25	Fletchard and Fowler, 1998
Night 2, rural Ontario, 50kms N of Toronto (0.04 -0.5 range)	*0.25*	Makar *et al.*, 1998
Compensation point forest	0.26	Warneck, 1988
Compensation point for forests	0.26	Langford & Fehsenfeld, 1992
Newton, Connecticut, summer	0.48	Keeler *et al.*, 1991
Denmark 1985-1993, 24h av. yearly means, low agriculture,	*0.5*	Hovmand and Andersen 1995
Spring, forest, Midwest USA, 0.5-0.99 range	0.75	Pryor *et al.*, 2001
Denmark, 1991 – 1993, mixed forest/ heathland. Relatively high agricultural emissions (0.36-1.9 range)	0.82	Andersen and Hovmand 1995
Compensation point for Dutch heathlands usually below this	0.83	Duyzer, 1994
Boulder, Colorado, summer	0.84	Langford *et al.*, 1992
Switzerland unpolluted, 0.12-1.74 range	0.93	Oberholzer *et al.*, 1993
mean, Scotland moor in agricultural area, 2 weeks summer values up to 9.92	0.93	Milford *et al.*, 2001
Sahelian region, semi-arid savanna, Banizoumbo, Niger, dry season	0.99	Galy-Lacaux *et al.*, 2001
Typical rural	1.16	Soderlund, 1981
Compensation point grass	1.32	Warneck, 1988
Rural? central south England, Autumn	1.37	Lee *et al.*, 1999
Rural continental atmosphere,winter	1.4	Georgii and Lenhard, 1978
Colchester, annual, 19 rural sites	1.95	Allen *et al.*, 1988
Sahelian region, Banizoumbo, Niger, semi-arid savanna ,wet season, high domestic animal densities	1.49	Galy-Lacaux *et al.*, 2001
Denmark 1985-1993, 24h av. yearly means, high agriculture, 1-2 range	1.5	Hovmand and Andersen 1995
West Germany, rural, winter	1.57	Lenhard and Gravenhorst 1980
Swiss Alps, summer	1.65	Georgii and Lenhard, 1978
Katibougou, Mali, semiarid savanna, dry season	1.65	Galy-Lacaux *et al.*, 2001
Ngola, Central Africa, humid savanna, wet season, 1999	1.65	Galy-Lacaux *et al.*, 2001

Environment/comment	Concentration $\mu g\ N\ m^{-3}$	Reference
Average weekly concentration. 1995-1996 Danish heath, agricultural influence.	1.69	Hansen, 1999
Typical polluted	1.74	Soderlund, 1981
0.2 - 3.7 range	1.95	Sutton *et al.*, 1993a
Denmark forest mean, range 0.05-4.00	2	Andersen *et al.*, 1993
ADUK, range 0.058 – 4.64	2	ADUK
South Scotland moor, downwind of agricultural area 1995-1996	2.07	Fletchard and Fowler, 1998
Compensation point, 1.7-2.9	2.3	Farquhar *et al.*, 1980
Ngola, Central Africa, humid savanna, wet season, 1998	2.31	Galy-Lacaux *et al.*, 2001
Rural? central south England, winter	2.4	Lee *et al.*, 1999
East Germany, grassland, agricultural area, late summer, 1995, compensation point 0.17-2.47	2.56	Spindler *et al.*, 2001
Weekly average wind-weighted conc. 1995-1996. Danish heath, agricultural influence 0.35-4.88 range	2.62	Hansen, 1999
Katibougou, Mali, semiarid savanna, wet season	2.64	Galy-Lacaux *et al.*, 2001
Polish mountain forest, 0.4-4.96 range	2.68	Bytnerowicz *et al.*, 1999
Ngola, , humid savanna, Central Africa dry season 1998	2.72	Galy-Lacaux *et al.*, 2001
Rural? central south England, summer	2.79	Lee *et al.*, 1999
Ngola, , humid savanna , Central Africa dry season, 1999	2.88	Galy-Lacaux *et al.*, 2001
Netherlands heath(av. of 4 sites 2.06, 2.15, 2.23, 9.09)	3.06	Duyzer, 1994
Boulder, Colorado, summer	3.22	Langford *et al.*, 1992
Typical continental concentration, range 0.17-6.6	3.39	Warneck, 1988
Compensation point range for short vegetation, 1.25-5.64	3.45	Warneck, 1988
West Germany,summer	4	Lenhard and Gravenhorst 1980
Rural continental atmosphere,summer	4.5	Georgii and Lenhard (1978)
Typical field concentration .0.1-10	5	Sutton, 1993c
Yearly av. Netherlands 1979-1990	5.79	Erisman, 1993
Switzerland grass, agricultural area	7.6	Hesterburg, 1996
Switzerland with farming and sewerage influence 0.35-16.86 range	8.5	Oberholzer *et al.*, 1993
Colchester, annual, next to livestock farms	20	Allen *et al.*, 1988
Up to 33 at source down to ± 8, 300m from agricultural source	20.5	Adema *et al.*, 1992

At more typical concentrations (0.1-10 $\mu g\ m^{-3}$) (Sutton *et al.*, 1993c) experiments have shown absorption and emission from plants (Sutton *et al.*, 1993c). Micrometeorological methods (that allow quantification of net flux over plant canopies over large areas) have also shown that both emission and deposition may occur dependant on environmental conditions, ecosystem type and plant growth stage (Sutton *et al.*, 1995). The idea of a compensation point as described in the NO section

above is thus relevant and was first modelled by Farquhar *et al.* (1980) for ammonia assuming that exchange takes place through the stomata depending on the NH_4 concentration in the apoplast. The situation may be modelled by the equation:

$$\mathbf{NH_3\ flux} = (\mathbf{C_{air}} - \mathbf{X_s}) / \mathbf{r_a} + \mathbf{r_b} + \mathbf{r_s}$$

X_s = stomatal compensation point

Both the apoplastic NH_4^+ concentration and the pH are critical in determining the compensation point. However temperature also plays a role. The temperature response of the stomatal compensation point is also substantial and increases in temperature can lead to changes from deposition to emission (Asman *et al.*, 1998). Higher air temperature increases the vapor pressure of ammonia above the ammonium dissolved in the water film lining the stomatal cavities, increasing the ammonia emitted by the canopy (Langford and Fehsenfeld, 1992). This increase in canopy emission with increased temperatures coincides with greater emissions from sources such as fertilisers and animal waste with increased temperatures as discussed further below.

The above is a simplistic model in that deposition rates measured in the field indicate that NH_3 has a high affinity for leaf cuticles as well (Sutton *et al.*, 1993a). This observation promotes a fine-tuning of the above model to incorporate a cuticular resistance $\mathbf{r_w}$ that allows calculation of a canopy concentration as a result of competing stomatal exchange and deposition to leaf cuticles.

$$\mathbf{NH_3\ flux} = (\mathbf{C_{air}} - \mathbf{X_c}) / \mathbf{r_a} + \mathbf{r_b} + \mathbf{r_c}$$

r_c = canopy resistance = stomatal resistance + cuticular resistance

X_c = canopy compensation point smaller than Xs

Sutton *et al.* (1995) proposed the above and applied it in comparison to fluxes measured by the micrometeorological aerodynamic gradient method to an agricultural grassland with good results (Sutton *et al.*, 1997).

The above model may be further refined by taking into account exchange with and emissions from ground concentrations and leaf litter concentrations. In situations where NH_3 dry deposition occurs to the canopy as a whole, the ground surface is a minor sink. The situation is different if the soil surface or leaf litter layer is a large source of NH_3 emission, as may be the case where fertiliser is applied. The potential for emissions from leaf litter in semi-natural and forest ecosystems is, however,

unquantified (Asman *et al.*, 1998). However, deposition has been shown to dominate over unfertilised semi-natural systems (Sutton *et al.*, 1993 a, b). Larger values of $[NH_4^+]$: $[H^+]$ occur in agricultural plants compared with semi-natural plants and this is closely related to the available N supply from fertilisers resulting in the aforementioned tendency (Asman *et al.* 1998). The most likely reason for this is that nitrogen fertilisation raises X_s so promoting emission (Sutton *et al.* 1995). Warneck (1988) describes several studies as showing that compensation points for forests (frequently < 0.63 μg N m^{-3}, often around 0.25μg N m^{-3}) are lower than those for agricultural crops (1.26 μg N m^{-3} – 5.65μg N m^{-3}).

Having discussed the more detailed parameters regarding NH_3 deposition to plants, other general factors influencing emissions and deposition can be addressed. Increased temperatures generally increase volatilisation / exhalation of NH_3 from emission sources and the generally strong correlation of ambient concentrations with temperature suggests that soils and / or vegetation are significant sources of atmospheric ammonia. Higher humidity or wet conditions generally lower ambient NH_3 concentrations. Moist soils generally 'emit' less NH_3 (the reaction $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$ is shifted to the right with increasing water content). Deposition to leaf cuticles is also enhanced under wet conditions thus lowering ambient concentrations. Wet deposition also obviously acts to lower ambient concentrations.

Regarding the chemical factors mentioned above, NH_3 reacts with acidic gases and aerosols e.g. H_2SO_4, HNO_3 and HCl to form ammonium particles in various forms e.g. NH_4SO_4 and NH_4NH_3. The reaction rate depends on acid concentration, humidity and temperature and NH_4^+ containing aerosols are formed (Stelson *et al.*, 1979 and Huntzicker *et al.*, 1980). Tang (1980) predicted that a primary control on the gaseous / particulate partitioning of ammonia is the level of atmospheric SO_4^{2-}. Langford *et al.* (1992) indicated that for sulphate concentrations below about 2 μg m^{-3} most of the ammonia is present in the gas phase whilst at concentrations above approximately 20 μg N m^{-3} less than 5% of NH_3 remains in the gas phase. The sulphur emissions associated with the ETH region may therefore have an effect on ammonia versus ammonium concentrations and as a result affect the atmospheric lifetime of nitrogen being emitted and impact on the amount of emitted nitrogen being transported to the

study site. The two gases SO_2 and NH_3 may further interact at the surface at which deposition is occurring. An example of this is described by Houdijk (1990), in which the high deposition of NH_3 in areas with intensive livestock production was assumed to decrease the acidity of the absorbing surfaces, thereby increasing the buffering of protons generated in SO_2 dissolution and increasing the deposition of the SO_2. Thus by affecting the alkalinity of the absorbing surface, the two gases can affect r_c values for each other. This scenario occurs when surfaces are wet. When surfaces are dry, SO_2 deposition becomes dependant on stomatal uptake as opposed to deposition to surfaces (Erisman *et al.*, 1993). The factors described above result in seasonal and diurnal variation in ambient concentrations of NH_3 (Warneck, 1988; Tjepkema *et al.* 1981; Langford *et al.*, 1992 and Lefer and Talbot, 1999). Summer values are generally greater than winter values and concentrations generally peak at midday and are at their lowest in the early morning hours. Table 8 below summarises the major factors affecting ammonia concentrations in terms of this study. The factors can be used in the evaluation of an appropriate concentration for NH_3 at the study site.

Table 8 - Possible factors causing seasonal variation in ammonia concentrations

	Summer	Autumn	Winter	Spring	
Biomass burning			+⇧	+⇧	Increased biomass burning in late winter/early spring increases spring concentrations
Temperature	+⇧		- ⇩		Higher temperatures in summer increase concentrations, lower temperatures in winter decrease concentrations
Rainfall removal	+⇩		-⇧		Higher rainfall in summer decreases concentrations, low rainfall in winter increases concentrations
Humidity	+⇩		-⇧		As above
Turbulence (dry deposition)				+⇩	Higher turbulence increases dry deposition in spring and lowers concentrations
Sulphate concentration			+⇩		Winter low due to greater conversion to ammonium as a result of interaction with sulphate, Summer high
Nitric acid concentration	+⇩		-⇧		higher summer HNO_3 concentrations, greater conversion to NH_4+ from interaction with HNO_3, lower NH_3 concentrations. reverse in winter

Regarding deposition velocities for NH_3, seasonal variations result from the variability of factors controlling deposition velocities viz. rates of turbulent mixing and canopy resistance. They are closely coupled with meteorological variables such as

wind speed, temperature, stability, precipitation and canopy wetness. Fletchard and Fowler (1998) describe surface wetness as being important in canopy resistance variance. They found canopy resistances under wet conditions to be approximately one third of that under dry conditions. They further mention the fact that although surfaces may appear dry, high relative humidity near the leaf surface may be enough to produce the reduction in canopy resistance. A positive correlation between canopy resistance and temperature above 0° C was also found. Higher temperatures promoted evaporation of surface water films, thus acting against the previously mentioned surface wetness effect. Duyzer (1994) indicated the reduced solubility of NH_3 at higher temperatures as a further possible factor regulating a canopy resistance/ temperature correlation. Non-withstanding the above complexities, deposition velocities for NH_3 fall within a general range indicated in Table 9. The various studies above are in general agreement, with deposition velocities differing for short vegetation and forests. In general terms, Hanson and Lindberg (1991) give average deposition velocities for short vegetation of 0.7 cm s^{-1} and for forests of 2.3 cm s^{-1}. Maximum deposition velocities given by Fowler *et al.* (1999) are 2.14 cm s^{-1} and 5.56 cm s^{-1} for short vegetation and forests respectively.

Table 9 - Ammonia deposition velocities measured or quoted in other studies

Environment/comment	Dep. vel. cm s^{-1}	Reference
Non agricultural vegetation	0.1-1.1	Sutton *et al.*, 1993a
Grassland geometric mean	0.7	Hanson & Lindberg, 1991
Danish heath, agricultural infl.	0.83	Hansen, 1999
Conifer forests	1.0	Lindberg *et al.*, 1990
-	Up to 2	Warneck, 1988
South Scotland moor, downwind of agricultural area 1995-1996	1.17	Fletchard and Fowler, 1998
8 studies	0.31-2.6	Hanson & Lindberg, 1991
Netherlands heath (24hrs)	1.4	Duyzer, 1994
Switzerland grass, agricultural area	0.13-1.4	Hesterburg *et al.*, 1996
Scotland moor in agricultural area, summer	1.9 mean	Milford *et al.*, 2001
Denmark, 1991 – 1993, mixed forest/ heathland. Relatively high ammonia emissions	2 av.	Andersen and Hovmand, 1995
Max. for grassland	2.14	Fowler *et al.*, 1999
Pinus	1.8-2.6	Hanson & Lindberg, 1991
Trees geometric mean	2.3	Hanson & Lindberg, 1991
Denmark forest mean	2.6	Andersen *et al.*, 1993
Max. for forest	5.56	Fowler *et al.*, 1999
To grass	10	Hutchinson *et al.*, 1972

In conclusion, the factors that may result in the variance of both concentrations of NH_3 as well as deposition velocities make the quantification of NH_3 deposition relatively complex.

Aerosol particles - NO_3^- and NH_4^+

The concentrations of these two aerosols are first discussed, followed by a discussion on particle deposition velocities that is applicable to both species

Nitrate particles are present and distributed in the continental aerosol across the entire 0.1 – 10 μm size range (Warneck, 1988). A bimodal distribution is often found (Junge, 1963) with the first maximum in the accumulation mode (0.3 μm) associated with ammonium (point 4 below). The second maximum appears in the coarse particle mode (>1 μm) where nitrate is associated with sodium, potassium and earth alkaline elements (points 1,2,3 below). A shift from coarse particle mode to accumulation mode with increasing concentration has been noted (Warneck, 1988). This possibly indicates that accumulation mode nitrate is associated with polluted air masses.

The sources of NO_3^- are:

- the conversion of HNO_3^- to form sodium nitrate and liberating HCl by interaction with sea salt (Brimblecombe and Clegg, 1988);
- N_2O_5 reacts with aqueous chloride to form $ClNO_2$ and NO_3^- (Finlayson-Pitts *et al.*, 1989);
- Similar type reactions may occur with carbonates in mineral dusts releasing carbon dioxide and forming stable nitrate salts (Warneck, 1988); and
- NH_3 reacts with HNO_3 and HCl to form NH_4NO_3 and NH_4Cl (Warneck, 1988).

Accumulation mode nitrate (NH_4NO_3) is volatile and establishes an equilibrium with its gas phase precursors NH_3 and HNO_3 (Stelson and Seinfeld, 1982). Lower temperatures favour the existence of the volatile aerosol, whilst low concentrations of NH_3 often limit the amount formed (Warneck, 1988). HNO_3 concentrations will also obviously affect NH_4NO_3 and the high deposition velocity and removal of HNO_3 is relevant. Humidity is also a factor with higher humidity increasing the liquid water capacity of aerosols and favouring NH_4NO_3 production. Warneck (1988) describes the concentrations of nitric acid and nitrate as being generally comparable with the ratio being of the order of unity. Table 10 gives concentrations of nitrate aerosol measured or quoted in previous studies. The concentrations range from a high value of 1.78 μg N m^{-3} in rural England to low values of 0.04 μg N m^{-3} in Colorado. Low values from

remote high elevation sites vary from 0.04 μg N m^{-3} to 0.09 μg N m^{-3}. Higher values range up to 2.74 μg N m^{-3} but are more commonly between 1 to 2 μg N m^{-3}.

Ammonium arises from gas to particle conversion processes, the neutralisation of sulphuric acid by gaseous ammonia and the interaction of ammonia with nitric acid:

$$NH_3 + HNO_3 \rightleftharpoons NH_4NO_3$$

$$NH_3 + H_2SO_4 \rightleftharpoons NH_4SO_4$$

In general terms therefore high ammonia, sulphate and nitric acid concentrations favour the production of ammonium. In terms of a likely annual average ammonium concentration for the study site, Table 11 may be used for guidance.

Table 10. Particulate nitrate concentration measurements from other studies

Comments	Concentration μg N m^{-3}	Reference
Northern Alps 1969-1973	0.23	Warneck, 1988
Colorado,high elev.	0.04	Williams *et al.*, 1997
Rural NA forest,summer	0.14	Lefer and Talbot, 2001
Sahelian region, Niger,wet season	0.3 ! 0.1	Galy-Lacaux *et al.*, 2001
Sahelian region, Niger, dry season	0.6 ! 0.1	Galy-Lacaux *et al.*, 2001
Skukuza	0.54	Maenhaut *et al.*, 2002
Japan, annual av.	0.48	Matsumoto & Okita, 1998
Rural? central south England, summer	0.92	Lee *et al.*, 1999
Rural? central south England, autumn	1.15	Lee *et al.*, 1999
Rural? central south England, winter	1.78	Lee *et al.*, 1999
Netherlands yearly av.1979-1989	1.58	Erisman, 1993
100 kms out of Sydney, site around a power station, no nearby city, yearly mean	0.21	Ayers *et al.*, 1995
NE USA high elev. forest annual mean 1986-1995	0.046	Miller and Friedland (1999)
Summer ,Michigan, suburban	0.69	Cadle, 1985
Winter, Michigan, suburban	0.62	Cadle, 1985
Summer regionally Polluted Germany	1.04	Meixner *et al.*, 1985
Winter regionally Polluted Germany	1.74	Meixner *et al.*, 1985
Summer High Alpine	0.09	Kasper & Puxbaum, 1998
Winter High Alpine	0.07	Kasper & Puxbaum, 1998
Nightime rural Ontario, 50kms N of Toronto, across 0.1-10 µm.	1.26 - 2.74	Makar *et al.*, 1998
Range across Europe	0.09 – 1.6	Schaap *et al.*, 2002

Table 11 - Ammonium concentrations measured or quoted in other studies

Comments	Conc.(μg N m^{-3})	Reference
Northern Alps	1.01	Warneck, 1988
Summer,West Germany	4.62	Georgii & Lenhard, 1978
Winter,West Germany	2.02	Georgii & Lenhard, 1978
Western Germany, Summer	3.81	Lenhard & Gravenhorst 1980
Western Germany, 100m,Winter	2.01	Lenhard & Gravenhorst 1980
Sweden, Autumn	0.87	Ferm, 1979
West Germany, Summer	2.88	Goethel, (1980)
West Germany, Winter	2.71	Goethel, (1980)
U.K. rural sites	3.06	Allen *et al.*, 1988
U.K. agricultural sites	3.69	Allen *et al.*, 1988
U.K.	3.69	Harrison and Allen, 1991
Massachusetts, Summer	1.64	Tjepkema *et al.*, 1981
Massachusetts, Winter	0.76	Tjepkema *et al.*, 1981
Allegheny Mountain, Summer	2.42	Pierson *et al.*, 1989
Boulder,Colorado, Summer	0.62	Langford *et al.*, 1992
Boulder,Colorado, Summer	0.41	Langford *et al.*, 1992
Niwot ridge,Colorado,Summer	0.20	Langford *et al.*, 1992
Niwot ridge,Colorado,Summer	0.13	Langford *et al.*, 1992
Conneticut,Summer	1.57	Keeler *et al.*,. 1991
Rural NA forest, Summer	0.84	Lefer and Talbot, 2001
Netherlands heath, (av.of 4 sites)	5.13	Duyzer, 1994
Sahelian region, Niger, wet season	0.1	Galy-Lacaux *et al.*, 2001
Sahelian region, Niger, dry season	0.2	Galy-Lacaux *et al.*, 2001
Range over 2 nights rural Ontario, 50kms N of Toronto, 0.1-10 μm particle size	2.56 – 4.51	Makar *et al.*, 1998
Rural? central south England, Summer	2.68	Lee *et al.*, 1999
Rural? central south England, Autumn	2.08	Lee *et al.*, 1999
Rural? central south England, Winter	4.06	Lee *et al.*, 1999
NE USA high elev. forest annual mean 1986-1995	0.344	Miller and Friedland (1999)
Netherlands yearly av.1979-1989	3.57	Erisman, 1993
Skukuza	0.66	Maenhaut *et al.*, 2002
3 sites across Denmark 1985-1993, 24h av. yearly means, HNO3 + NO3	± 1.9 – 3.4	Hovmand and Andersen 1995

Regarding deposition, both wet and dry processes are relevant to particles. The discussion below describes the dry deposition of particles and applies to both NO_3^- and NH_4^+.

The process of removal of particles from the atmosphere depends on the size of the particle. For nitrate and ammonia the relevant size classes, as discussed previously, are the accumulation and coarse modes. One of the processes for removal of larger particles from the atmosphere is gravitational settling. However gravitational settling velocities for these classes are small and may be ignored (Fowler *et al.*, 1999). Other processes promoting removal such as interception, impaction and Brownian diffusion through the sub-viscous layer are also poorly developed in the 0.1 – 1 μm size range. The fairly low deposition velocities produced by early work for this size range was

consistent with the lack of efficient depositionary mechanisms. However, more recent work (summarised by Gallagher *et al.*, 1997) show larger dry deposition velocities for which there is no underlying theoretical framework (Fowler *et al.*, 1999). Fowler *et al.* (1999) assume a deposition velocity of 0.5 cm s^{-1} for particles in the size range 0.1 – 2 μm for forests as opposed to earlier wind tunnel studies that indicate lower values of 0.01 – 0.1 cm s^{-1}. Table 12 lists deposition velocities measured in other studies.

Table 12 - Particulate deposition velocities measured or quoted in other studies.

Comments	Deposition velocity (cm s^{-1})	Reference
Netherlands heath	0.17 (24hrs)	Duyzer, 1994
German forest, 1992	0.47	Peters and Brucknr-Schatt,1995
NE USA high elev. forest	0.06 (1μm)0.82 (2.5μm)	Miller and Friedland, 1999
Netherlands yearly av. 1979-1989	0.4	Erisman, 1993

The studies on forests indicate larger deposition velocities than those to the one study on shorter vegetation (Duyzer, 1994). This is consistent with ideas that there are larger inputs of aerosol particles (as well as cloud and rain droplets) to forests (White and Turner, 1970; Mayer and Ulrich, 1974). Furthermore, Fowler *et al.* (1989) indicated that sub-micrometre particles in high elevation sites in the United Kingdom are frequently activated into cloud droplets in the size range 5 – 10 μm. These droplets are efficiently captured by forest canopies by the processes of impaction and sedimentation, and the process may increase the depositionary effect of ammonia and nitrate particles to the forested area in this study.

Other nitrogen compounds

Recent work has indicated the possible importance of organic nitrogen to deposition (Neff *et al.*, 2002). The following summary details relevant points regarding Atmospheric Organic Nitrogen (AON) and has been summarised from this work. AON may be deposited by both wet and dry processes, and is present in a variety of forms that may be divided conceptually into three classes.

Organic nitrates: oxidised end products of reactions of hydrocarbons with NO_x in polluted air masses. PAN is one of the more important species and may contribute 15 – 30 % of total N concentration in non-urban sites. PAN fluxes range between 0.1 and 2 kg N ha^{-1} yr^{-1} with average deposition between 0.3 and 0.62 kg N ha^{-1} yr^{-1} in North America and Europe. It is produced through photo-chemically mediated reactions of

non-methane hydrocarbons (NMHC) and NO_x, and occurs in polluted and remote areas. NMHC are emitted notably by plants and fossil fuel combustion. In the former a correlation exists with temperature resulting in seasonal emission variances PAN plays a further important role in that it has a relatively long lifetime and may act as a resevoir species for its shorter lived precursor NO_x. It may therefore facilitate the transport of NO_x concentrations from the ETH. Its lifetime is temperature dependant and longer transport distances can be expected in cooler seasons.

Reduced AON: primarily includes gas phase or aerosol amine N and urea that can be injected into the atmosphere in marine or agricultural surroundings. Sources of reduced organic nitrogen include oceanic, agricultural and biomass burning emissions. These compounds are highly reactive and have a short lifetime. The relevance to the study area is therefore probably low.

Biological and particulate forms of AON with terrestrial sources e.g. bacteria, dust, pollen. These may be reduced or oxidised. Bacterial nitrogen deposition appears not to be significance to local or global fluxes. Dust deposition is likely to be of some significance and conservative estimates based on dust deposition and percentage organic content result in estimates of 0.02 – 0.4 kg dust AON ha^{-1} yr^{-1}.

In summary, of the variable sources of AON only organic nitrate species and dust fluxes appear to have sufficient atmospheric concentrations or fluxes to account for a large portion of the observed AON fluxes at most sites.

Conclusion

The discussion above has been aimed at providing a background for the proposed study. The link between nitrate leaching and nitrogen deposition from the atmosphere has been proposed and investigated by previous workers and provides a rationale for the proposed study. The theory related to nitrogen deposition and the previous work done in this field has indicated the forms of deposition as well as possible methods of study that will be relevant to the proposed study, considering that direct measurement of many of the factors will not be attempted. The proposed methods of the study are discussed in the next chapter.

CHAPTER 3 - METHODOLOGY

Quantification of deposition of a substance to a surface is often quoted in the form of kg ha^{-1} $year^{-1}$ and therefore involves the determination of three basic elements – an amount of nitrogen, a surface area and a time component. The details for the latter two are the same for wet and dry deposition whilst they differ for determination of the amount of nitrogen.

With regards the time component, since the study is not measuring the variables directly and furthermore that the aim is to achieve a best estimate, data has been obtained and used from different years depending on availability. These data have been combined in the calculations to give an assumed average value for a year even though their collection has not necessarily been done simultaneously. A further aspect of this is that data are not always available for the study area and best estimates are used from other areas in certain instances. The details and justifications for these estimates are given in the rest of the discussion in this chapter.

In terms of the area component, an area subject to atmospheric deposition relevant to the measured nitrogen concentrations in streams as done by Nowicki (1997) needs to be defined. It is proposed that an area of influence may be defined by the catchment areas of the two streams (Figure 3) as a best estimate.

The discussion of the calculations of the amounts of nitrogen deposited needs to be done in terms of quantification of wet and dry deposition and deposition via cloud droplet interception.

3.1 Wet Deposition

The amount of chemical compounds received per unit area of the surface is equal to the amount of precipitation per unit area of a rainfall sample multiplied by the measured concentration of the 'pollutant' in the sample (Zunckel, 1998). The two variables that need to be obtained to perform this calculation are therefore an average amount of precipitation for a year for the study area as well as average concentrations of the ions NO_3^- and NH_4^+ in solution in the rainwater. This information has been obtained from data collected by the Kiepersol Joint Venture Project. Amounts and

chemistry of rainwater have been collected by Eskom (the South African parastatal electricity provider) and other partners since 1984 at a number of sampling stations across South Africa. One of the sites is at Blyde river, (approximately 30 km north of the study site). The chemical information recorded at this station for the years 1995-1999 has been used as the best estimate of precipitation chemistry characteristics for this study. Rainfall amounts have been obtained on site from measurements made by Global Forestry Products at their Klipkraal rainfall measurement station. The method shown below has been used to combine the Blyde river chemistry with the Klipkraal rainfall amounts to obtain wet deposition amounts.

Nitrogen deposited in rainfall event = nitrogen concentration measured in event x rainfall amount in event (where an event is a rainfall episode within any given month). In certain instances, the cumulative rainfall amount from the various events within a month at the measuring site amounted to less than that recorded at the study site. In these instances the rainfall amounts have been scaled up to equal that at the study site. The additional rainfall has been divided equally between the events within a month.

3.2 Dry Deposition

Dry deposition is the removal of particles or gases from the atmosphere through the delivery of mass to the surface by non-precipitation atmospheric processes and the subsequent chemical reaction with or physical attachment to vegetation, soil or the built environment (Dolske and Gatz, 1985).

The inferential method (presented by Hicks *et al.*, 1987) makes use of an understanding of the dry deposition process and routinely monitored meteorological parameters to infer deposition velocities. This inferred parameter is the factor linking the rate of dry deposition of a pollutant and its concentration in the atmosphere:

$$V_d = -F / C$$

F = dry deposition rate (negative sign is convention and indicates downward flux)

C = atmospheric concentration

The variables that need to be quantified are therefore ambient concentrations of the nitrogen species relevant to deposition and corresponding deposition velocities. The

species relevant to a nitrogen deposition study have been discussed in the literature review. The following species have been chosen to form part of this investigation:

1) Nitrogen dioxide gas (NO_2);
2) Nitric acid vapour (HNO_3);
3) Ammonia gas (NH_3);
4) Ammonium aerosols (NH_4^+);
5) Nitrate aerosols (NO_3^-); and
6) Organic nitrogen.

Due to technical and financial constraints, direct measurement of ambient concentrations and flux measurements have not been performed in this study. A combination of the methods outlined below has been used to estimate deposition amounts for the study area.

Regarding *ambient concentrations* :-

- **For nitrogen dioxide and ammonia gas** information from the DEBITS passive sampling program has been used. Prof. K. Pienaar of the University of Potchefstroom S.A. has made available ambient NO_2 and NH_3 concentrations measured to date at a number of sampling stations. The closest sampling station is that at Palmer (Figure 2 & 3). Only NO_2 values are available for this station and NH_3 values have been provided at other stations as possible surrogates. Prof. Pienaar has further provided a single average long-term value for NO_2 concentrations at Palmer as calculated by himself from various sources. These averages have been calculated for Autumn, Winter, Spring and Summer. This seasonal type of evaluation has been attempted in all calculations where possible. The logic of this is that there is strong seasonal variance of factors controlling deposition, the most obvious example being rainfall amount. Thus deposition amounts should vary with season and the detailing of this could be of use in determining the possible link between deposition and leaching.
- **For nitric acid, nitrate and ammonium particles** no data are available, therefore a value has been obtained from literature using qualitative characteristics (such as site proximity to pollution sources) as guiding principles.

With regards the ***deposition velocities:-***

- **For nitric acid and particles** the inferential model as described by Hicks *et al.* (1987) is utilisable for calculation of an appropriate deposition velocity using site-

specific data. The model was obtained from M. Zunckel (CSIR), who was supplied with it by the Atmospheric Turbulence and Diffusion Division of the National Oceanic and Atmospheric Administration. The model required the following meteorological inputs - wind speed, wind direction, dry and wet bulb temperature, global solar radiation, atmospheric pressure, rainfall and standard deviation of wind direction – measured as hourly averages. This information was obtained from the South African Weather Bureau station situated in the town of Graskop. The town is 20 kms of the study site and provides a good representation of the meteorological parameters relevant to deposition in the area. Data were collected and inputted to the model for a week in Summer, Winter, Autumn and Spring of 1999. The week was chosen as close to the middle of the season as possible, depending on the availabilty of data. This allowed an evaluation of the changing deposition characteristics of the seasons.

- **For nitrogen dioxide and ammonia** no data or models were available and deposition velocities have been approximated from literature using qualitative characteristics (such as site proximity to pollution sources) as guiding principles.

For organic nitrogen no data are available. As discussed in the literature review, recent work (Neff *et al.,* 2002) has highlighted the possible importance of organic nitrogen deposition. As such, estimation of possible organic nitrogen deposition amounts for the study area is made based on information from Neff *et al.* (2002), in conjunction with qualitative characteristics of the study site (such as site proximity to pollution sources). An attempt at detailing concentrations and deposition velocities is not made.

3.3 Cloud Droplet deposition

A previous study has analysed cloud droplet deposition using a mist collector (Olbrich, 1993). This information was used to supplement the dry and wet deposition estimates obtained in this study to give a complete picture of deposition for the area.

CHAPTER 4 – RESULTS AND DISCUSSION

4.1 Wet Deposition

The factors affecting wet deposition – rainfall amounts and ammonia and nitrate concentrations and deposition velocities are discussed below before detailing deposition amounts.

Rainfall

Monthly rainfall amounts (supplied by Global Forestry Products) for the study area are shown in Figure 13 for the years 1995 to 1999 along with the average calculated for these years. Rainfall occurs mostly in the summer months December to February and is at its minimum in the winter months of June and July.

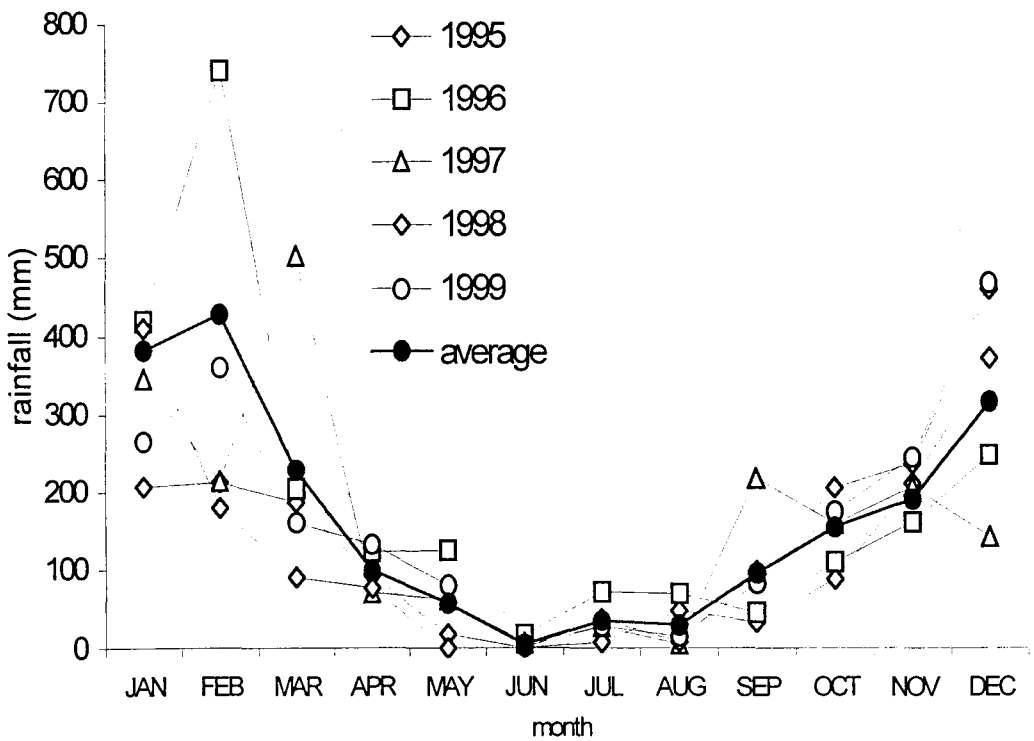

Figure 13 - Monthly rainfall amounts recorded at the study site for the years 1995-1999 and the average thereof.

Ammonia and Nitrate concentrations

Figures 14 and 15 show the monthly range of nitrate and ammonium concentrations measured from 1995 to 1999 along with the average. Figure 16 a-e show the concentrations for each individual year and Figure 16 f shows the average again for comparison. Concentrations of ammonium and nitrate in rainfall at the study site have an annual average calculated from all the data of 18.4 μeq l^{-1} ammonium and 19.2 μeq l^{-1} nitrate. Besides being similar in amount, they also follow very similar patterns in terms of monthly variation. For the most part of the year, ammonium and nitrate concentrations remain in a range of 10 to 30 μeq l^{-1} and often below 20 μeq l^{-1}. Such concentrations are not uncommon in comparison to other areas around the world, as shown in Table 13. Values from other studies range from 1-2 μeq l^{-1} in remote, unpolluted areas to 50 μeq l^{-1} and higher in polluted urban areas. The studies in which values similar to the present study are reported (i.e. ranging from 10 – 30 μeq l^{-1}), occur in areas subject to varying amounts of pollution. In terms of the Southern African region, the values for this study fall between those quoted by Mphepya (2002) for Amersfoort, a relatively more polluted site, and Louis Trichardt, a relatively less polluted site. Average annual concentrations for these sites are 22.3 μeq l^{-1} ammonium and 25.0 μeq l^{-1} nitrate and 9.7 μeq l^{-1} ammonium and 8.0 μeq l^{-1} nitrate respectively.

What is fairly unusual are the high concentrations recorded at the study site for the month of September. The discussion below aims to explain the September peak as well as the general concentration variance for the rest of the year. Although not consistently the case (notably 1996), concentrations generally increase slightly from the month of January through to August before increasing dramatically in the month of September. This general trend may be promoted by two meteorological features - rainfall and regional pressure systems. The seasonal distribution of the concentrations of ammonium and nitrate in rainfall should depend on the interplay between the amount of rainfall and concentrations of the precursor compounds (ammonia gas and ammonium particles for ammonium and nitric acid and nitrate particles for nitrate) in the air. Ambient concentrations of the various nitrogen compounds at the study site result most likely from transported 'pollution', since there are no major local emission or pollution sources.

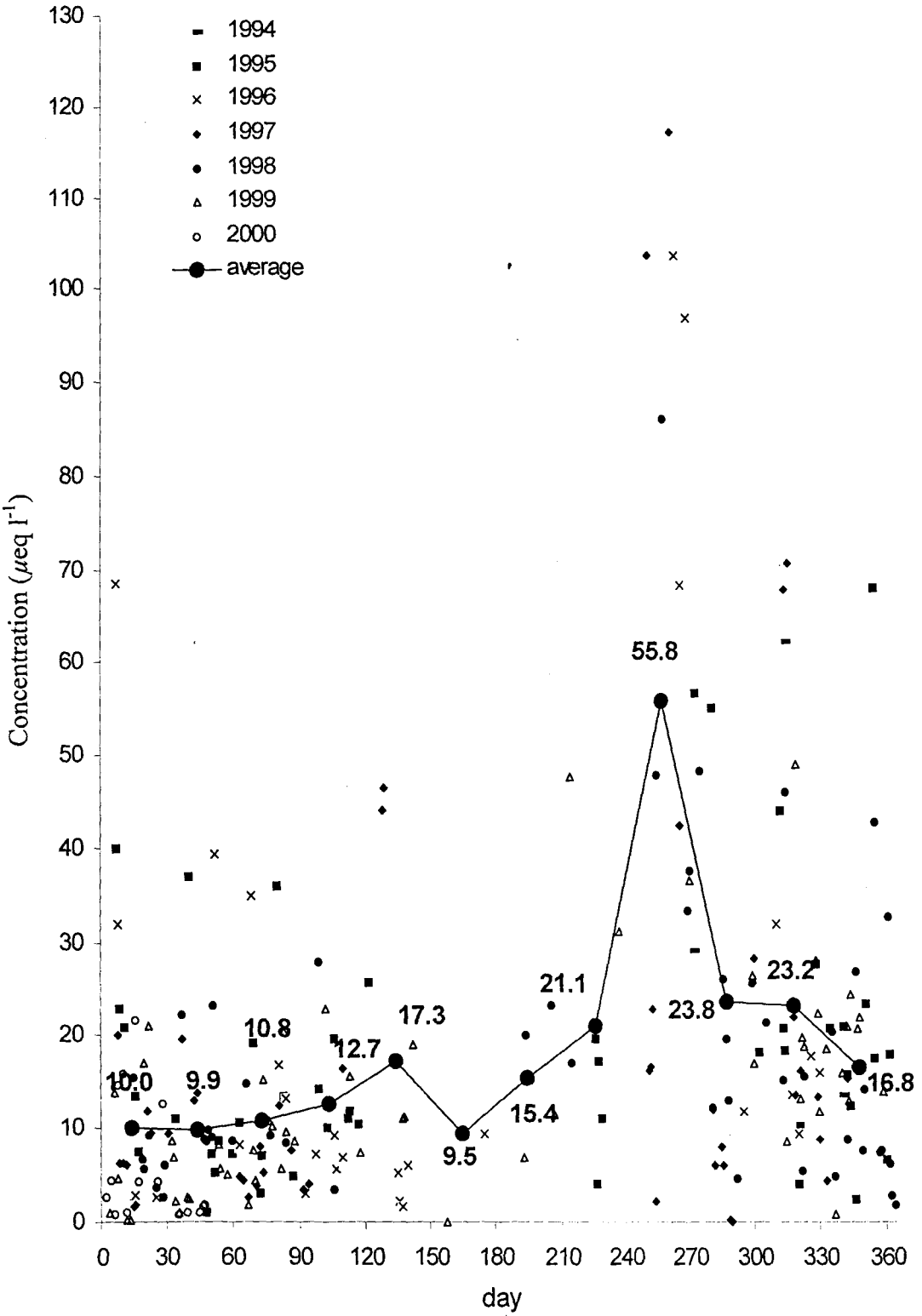

Figure 14 - Nitrate concentrations in rainfall for the years 1994-2000 (outliers removed) and the average monthly nitrate concentrations

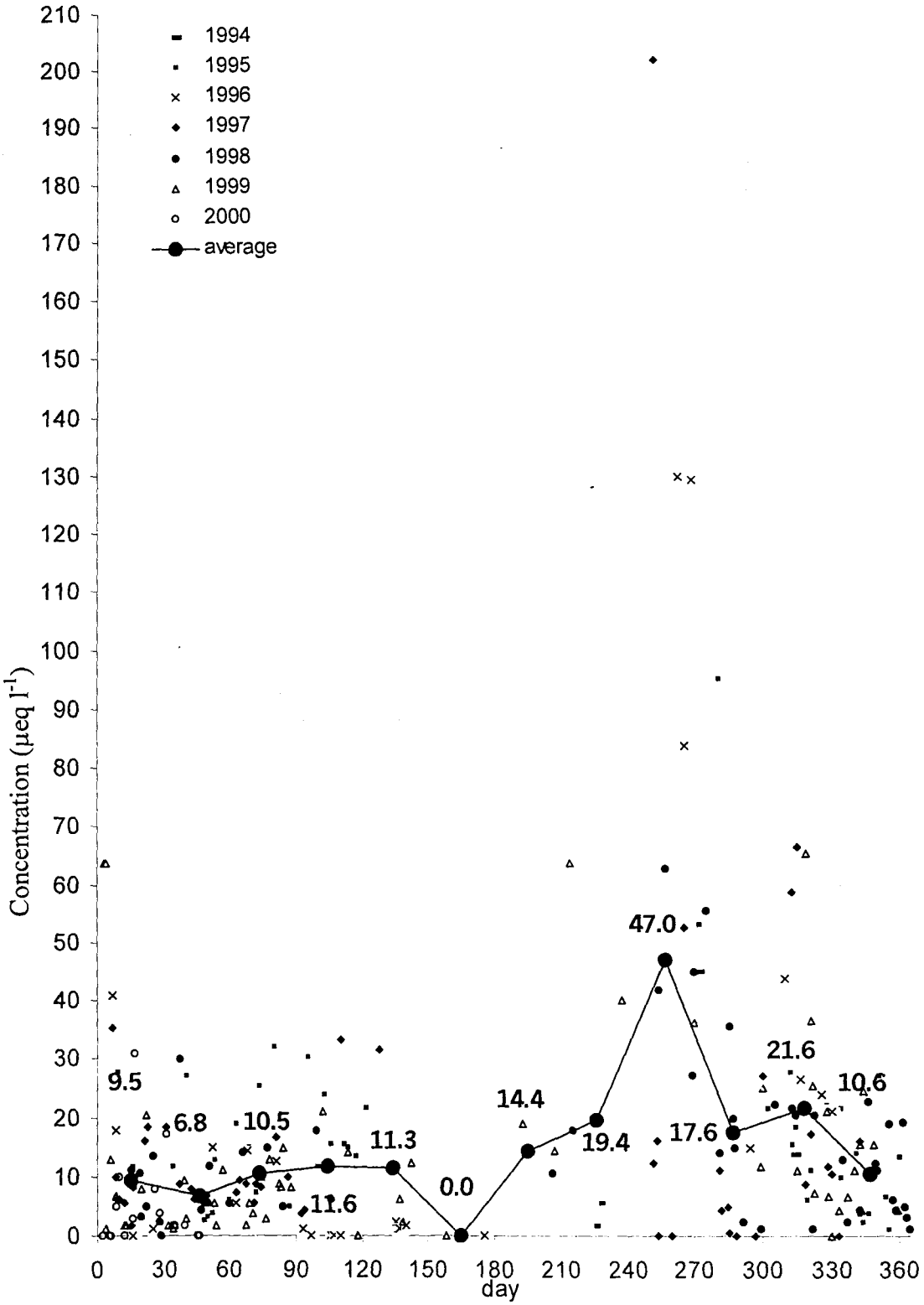

Figure 15 - Ammonium concentrations in rainfall for the years 1994-2000 (outliers removed) and the average monthly ammonium concentrations.

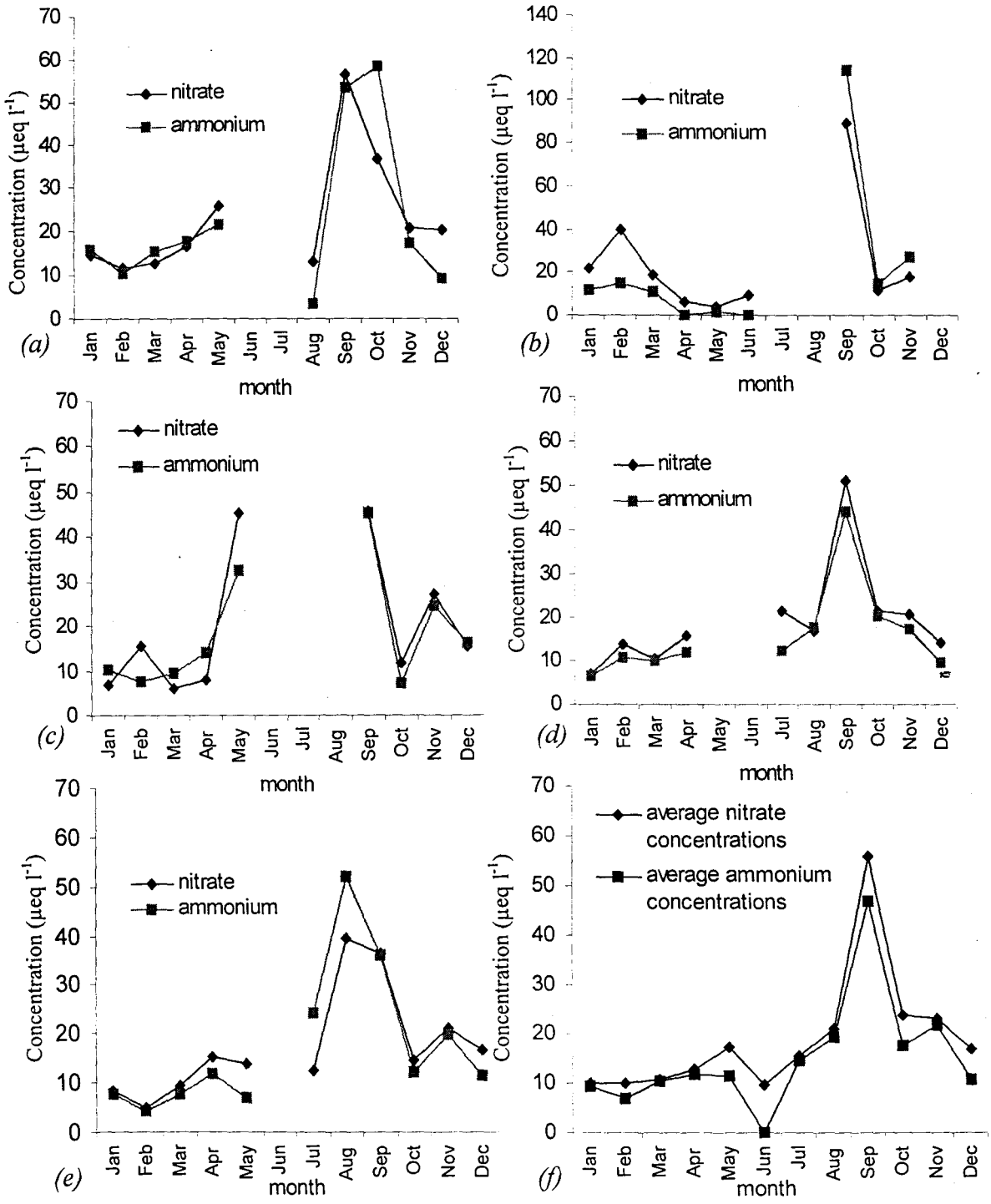

Figure 16 - Average monthly nitrate and ammonium concentrations in rainfall for the years 1995(a), 1996(b), 1997(c), 1998(d), 1999(e) and the average of 1995-1999(f).

Table 13 - Ammonium and nitrate concentrations in rainfall from other studies.

Comment	NH_4^+ conc. ($\mu eq\ l^{-1}$)	NO_3^- conc. ($\mu eq\ l^{-1}$)	Study
Amsterdam Island, Indian Ocean, 1120 mm av. annual rain	2.4	1.6	Galloway and Gaudry, 1984; Moody *et al.*, 1991
Bermuda 1979 –1980, 1131 mm av. annual rain	4.8 ± 7.1	7.9 ±9.1	Galloway and Gaudry, 1984; Moody *et al.*, 1991
Southern California, 70 kms from LA basin ,winter rainfall (low pollution period) ~ 450mm annual rainfall	~1.82	~2.85	Padgett *et al.*, 1999
Australia, 100 kms NW Sydney, rural area with small towns and power stations 20 kms from sites. Site 1 on outskirts of town.	11.71 11.34 10.42 10.35	7.89 5.95 7.5 7.89	Ayers *et al.*, 1995 Site1 Site2 Site 3 Site 4
As above except 30 kms from LA basin	~7.36	~7.57	Padgett *et al.*, 1999
Sinhagad, India, rural, high elevation, June-September 1992, means and standard deviations	7.2 ± 6.7	15.2 ± 11.2	Naik *et al.*, 1995
Japan, annual means and range of annual mean in parantheses, 1989-1993	18.3 (0.55-29.8)	14.1 (1.8-25.0)	Hara *et al.*, 1995
USA forest, Central Maine, 1988-1993, 1063 mm av. Annual rain	14	18	McLaughlin *et al.*, 1996
without September values	16.41	17.97	This study
Including September values	18.42	19.17	This study
Turkey Lake, Canada,1980-2000,908-1543 mm annual rainfall	~13	~21	Sirois *et al.*, 2001
New Hampshire, 1963 - 1974	12.1	23.1	Likens *et al.*, 1977
Sub-alpine NE USA forest, 1278 mm av. annual rain	14.9	23.3	Miller and Friedland, 1999
New Hampshire coast, 1994 – 1997, 1120 mm av. annual rain	11 - 17	22 - 27	Jordan and Talbot, 2000
Range across USA	0 – 45	0 - 33	Nilles and Conley, 2001
Sites from 2 – 20 km downwind of industrial area, India, 1234 mm rainfall	7.8 – 41.1	13.1 – 29.4	Singh and Agrawal, 2001
Colorado, June/September 2000, 32 precip. events downwind of power plants	4.27 – 104.69 range, 22.4 median	8.73 – 127.73 range, 32.8 median	Williams and Manthorne, 2001
Pyrenees, NE Spain, acidic group of precipitation	32.4	25.1	Camarero and Catalon, 1993
Deuselbach, Germany,1982-1995, approximate range of annual means	38 - 22	48 - 27	Fricke *et al.*, 1997
Denmark av. Deposition 1989-1994. site with relatively little pollution impact, ~~800 mm rainfall	~~38	~~35	Hovmand and Andersen, 1995
Denmark av. Deposition 1989-1994. site impacted by city and power plant emissions,~~800 mm rainfall	~~42	~~33	Hovmand and Andersen, 1995
Denmark av. Deposition 1989-1994. site impacted	~~55	~~38	Hovmand and

Comment	NH_4^+ conc. ($\mu eq\ l^{-1}$)	NO_3^- conc. ($\mu eq\ l^{-1}$)	Study
by agricultural emissions,~~800 mm rainfall			Andersen, 1995
Thessaloniki, Greece, urban, 1993-1994, local origin for NH_4^+, NO_3^-, 8 month means	60	24	Samara and Tsitouridou, 1999
South Poland, 1991-1994, moderate pollution, agricultural area	130	12	Szarek, 1995

In high rainfall periods, i.e. summer months, frequent washout of pollution from the air should lower the amount of pollution reaching the study site. A further possible factor contributing to higher ambient concentrations of precursors in winter is the increased frequency of inversions and regional high-pressure systems. This would prevent the dispersal of pollution from the region and enhance local or mesoscale transport from pollution sources to the study area. Thus generally lower concentrations in rainfall should prevail in the summer months and higher concentrations in the winter months as borne out by Figure 16 (a), (c), (d), (e) and (f). The obvious exception to the rule is the year 1996 (Figure 16 (b)). The decline in concentrations from the month of February to July evident in that year is likely to have been caused by extreme washout of precursor compounds by the abnormally high rainfall amount (800 mm) in February of that year (see Figure 13). The high concentration values evident in all years in September may result partially from a build-up of concentrations in low rainfall Winter months. However, biomass burning occurs in late Winter and early Spring and the correlation with the high September concentration values seems obvious. Furthermore, it is possible that biomass burning emissions previously contained by stagnant Winter meteorology are transported to the study site more easily as the more turbulent and dispersive conditions of Spring and Summer begin to prevail. Increasing amounts of rainfall in the Summer months would begin to wash precursor concentrations from the atmosphere once again resulting in lowered concentrations from September through to the lows of January and February.

Wet Deposition amounts

Wet deposition amounts for each rainfall event have been calculated by multiplying the amount of rainfall recorded for the event by the ammonium and nitrate concentrations in the rainfall obtained by chemical analysis of the rainfall. In a few instances, outliers in the concentration data have been replaced with average concentrations. Anomalous deposition amounts resulting from incomplete sampling have also been adjusted using average data. The adjustments are detailed in Appendix 2. The figures below show the monthly amounts deposited for each year as calculated by adding the amounts deposited by each event within a month for each year. Included with each graph is average monthly nitrate and ammonium deposition amounts, calculated from all the monthly data for the years 1995 –1999.

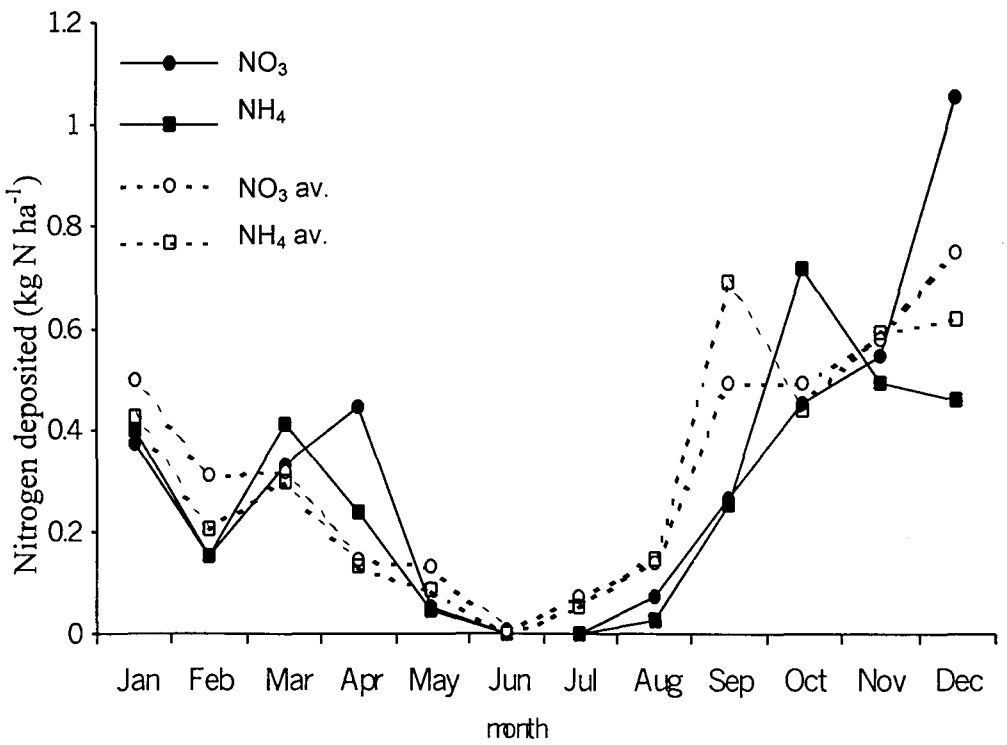

Figure 17 - Monthly nitrate and ammonium deposition 1995

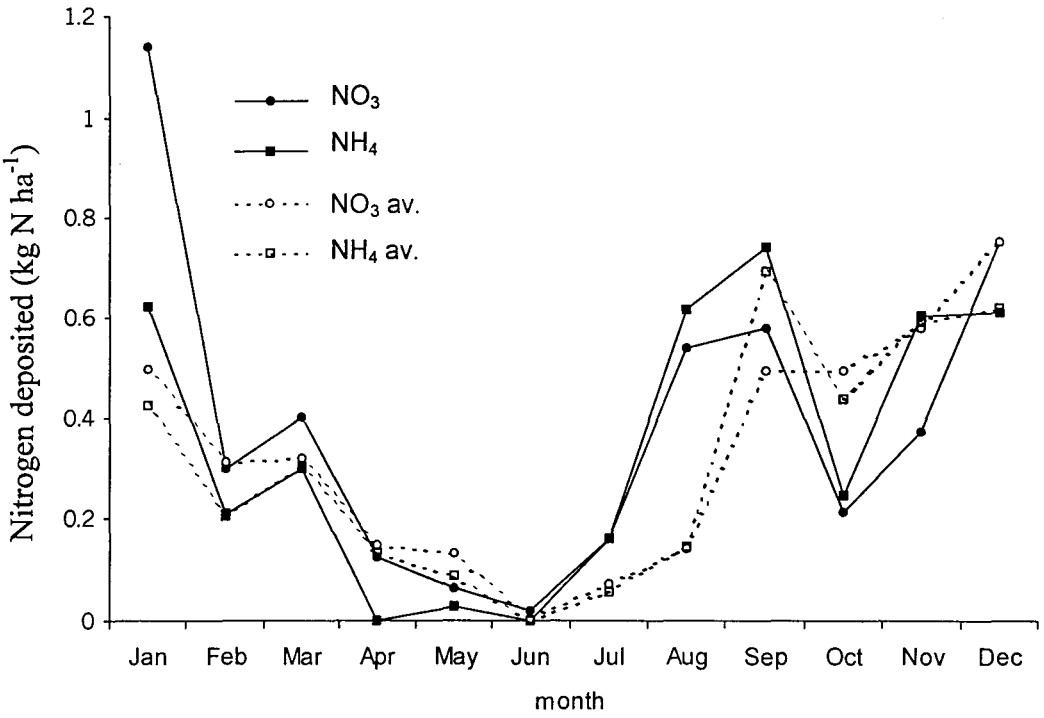

Figure 18- Monthly nitrate and ammonium deposition 1996

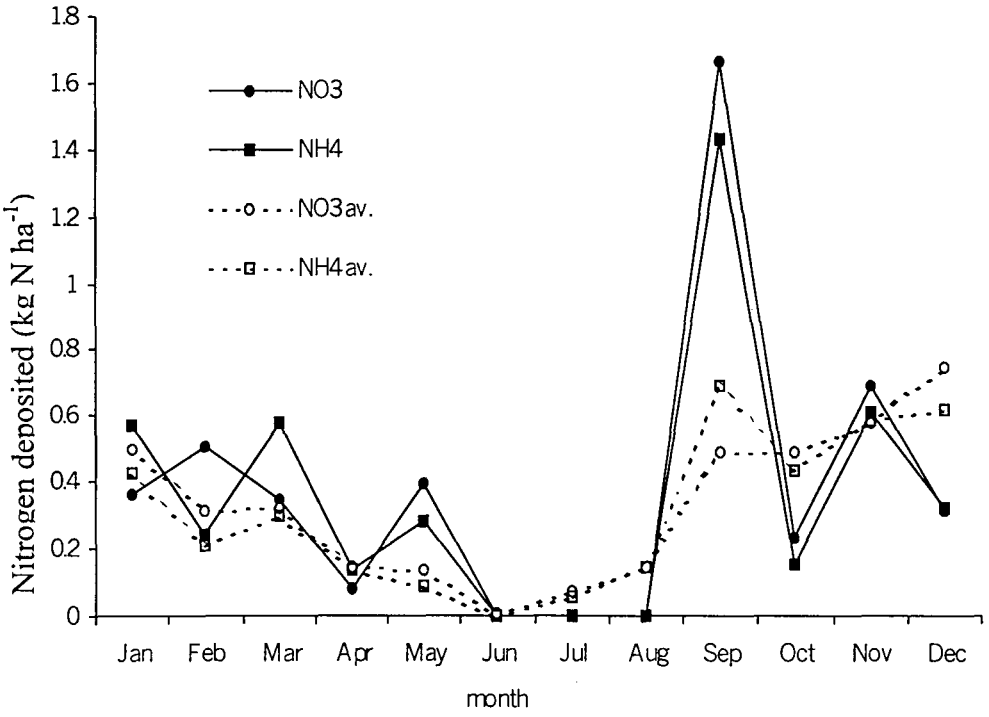

Figure 19- Monthly nitrate and ammonium deposition 1997

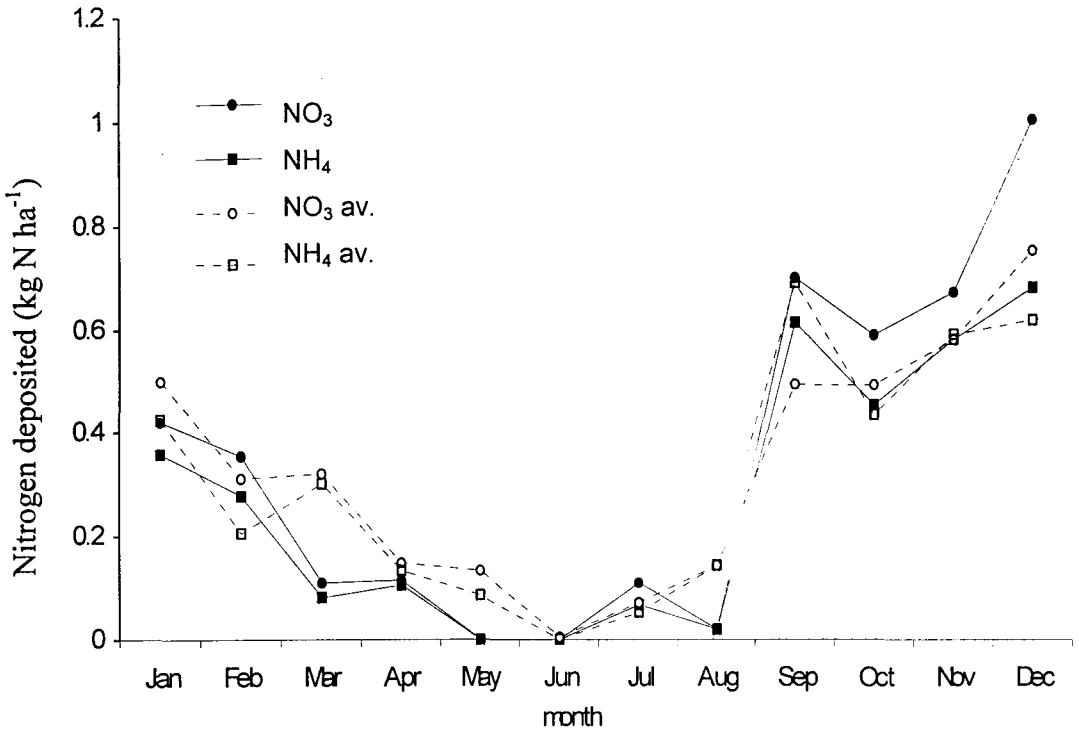

Figure 20 - Monthly nitrate and ammonium deposition 1998

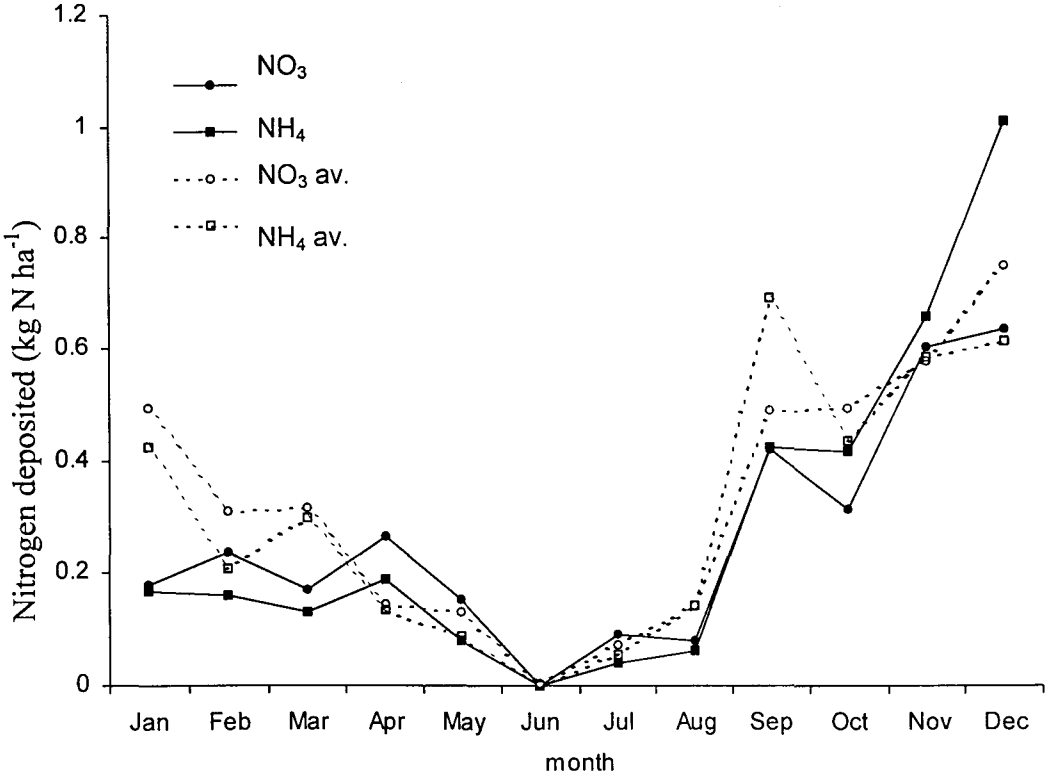

Figure 21 - Monthly nitrate and ammonium deposition 1999

Figure 22 compares the average wet deposition per month with the monthly average ammonia and nitrate concentrations in rainfall and average monthly rainfall amounts for the period 1995-1999.

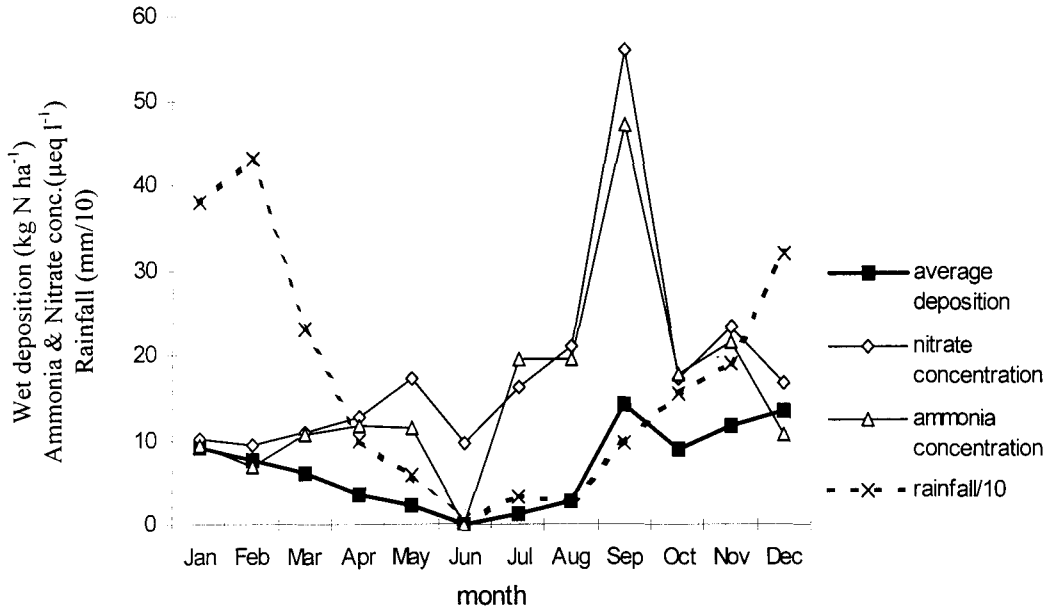

Figure 22 - Comparison of the average wet deposition per month with the monthly average ammonia and nitrate concentrations in rainfall and average monthly rainfall amounts for the period 1995-1999

Discussion

The graphs in Figures 17 – 22 illustrate a number of points. Monthly ammonia and nitrate deposition amounts are similar, reflecting the similar concentrations. In terms of annual deposition amounts, Table 14 shows generally similar amounts for all of the years with 1996 being slightly elevated. No obvious trend in deposition amount with time is apparent.

Table 14 -Annual ammonium, nitrate and total nitrogen deposited

Year	Ammonium deposited (kg N ha^{-1} yr^{-1})	Nitrate deposited (kg N ha^{-1} yr^{-1})	Total Nitrogen deposited (kg N ha^{-1} yr^{-1})
1995	3.18	3.88	7.05
1996	4.48	6.09	10.57
1997	4.33	4.58	8.91
1998	3.23	4.09	7.32
1999	3.34	3.16	6.50
average	3.71	4.12	7.84

Monthly nitrate and ammonium deposition amounts also follow a similar monthly pattern – intermediate to occasionally high deposition amounts in January decline to minimum deposition amounts in June/July, followed by an increase to maximum deposition amounts in September to December. This pattern is also relatively consistent across the years. The monthly deposition amounts generally follow the same trend as monthly rainfall amounts. This is in keeping with the generally consistent ammonia and nitrate concentration levels throughout a year (as discussed in the previous section) as opposed to the more variable rainfall amounts. Thus for instance the general slight increase in concentration from Summer to Winter is overshadowed by the decrease in rainfall amount resulting in the observed decrease in deposition amounts. The deposition amount/rainfall amount correlation is disrupted only in the month of September. The abnormally high ammonia and nitrate concentrations measured in this month play a more dominant role than rainfall amounts in determining deposition amounts during this period.

4.2. Dry Deposition

Gas and particle concentrations are discussed first, followed by a discussion on deposition velocities and deposition amounts.

Gas and Particle Concentrations

Nitrogen Dioxide Concentrations

The graph below shows the nitrogen dioxide concentrations measured by passive samplers at certain of the Kiepersol Joint Venture monitoring sites for the period November 99 to November 2000. Included in the graph are the average values calculated from all the sites.

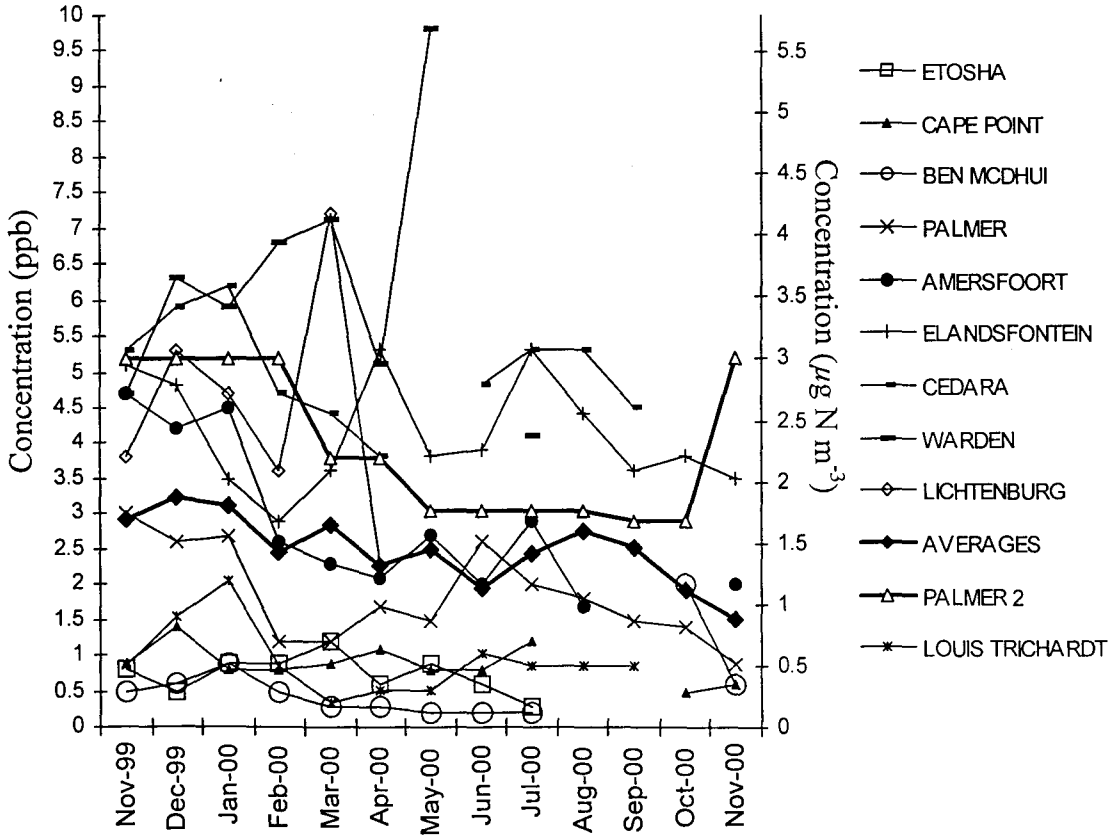

Figure 23 - Nitrogen dioxide concentrations measured by passive samplers at various locations in southern Africa by the Kiepersol Network.

Note that the Palmer 2 values are long term averages provided by Prof. Pienaar. The values range from 5.7 μg N m^{-3} (9 ppb) to 0.12 μg N m^{-3} (0.28 ppb) with an average of 1.51 μg N m^{-3} (2.6 ppb).

The data can be viewed as falling into high, medium and low ambient concentration groups that reflect the influence of distance from pollution sources. Consideration of the study site's position with regards pollution sources, it seems reasonable to view the site as falling between the medium and low groups, with a bias towards the medium group.

Low concentration group - Etosha, Ben McDhui, Cape Point, Louis Trichardt
Medium concentration group – Palmer and possibly Amersfoort
High concentration group – Elandsfontein, Cedara, Lichtenburg, Warden

The Palmer site would be the best approximation in light of its closest proximity to the study site as well as its similar elevation (generally speaking on the high-veldt) and atmospheric characteristics relevant to pollution studies. The concentrations resulting from the above considerations are shown in Table 15.

Table 15 - Nitrogen Dioxide Concentrations (μg N m^{-3}) for use in flux calculations

	Summer	Autumn	Winter	Spring	Year Average
High	1.9	1.4	1.1	1.1	1.4
Low	1	0.7	0.6	0.6	0.7
Likely	1.4	1.0	0.8	0.8	1.0

Nitric Acid Vapour

Since no nitric acid measurements are available for the study site, an approximation will need to be made using information from other studies. The principle guiding factor in determining an appropriate value from those listed in Table 4 will be the degree of pollution to which the study area is subjected in terms of the principle precursor gas for nitric acid – NO_x. This factor has already been discussed in the section on nitrogen dioxide concentrations and the study site may be described as falling between polluted and unpolluted regions. Taking this and the discussion on nitric acid concentrations in the literature review into account, it is considered that the values recorded by Lovett (1992) –

0.18 to 0.62 μg N m^{-3} – for rural forests across the USA represent a reasonable range for estimation of nitric acid values for this study. The extremes as well as the average of the two will be used as surrogates for yearly averages to allow for high, low and likely type computations.

The variation from Summer maxima to Winter minima have been incorporated by computing Summer values approximately twice that of Winter (as evidenced by general trends in the data above) and taking Spring and Autumn values 1.5 times that of Winter, whilst keeping the yearly average the same. These calculations result in the concentrations listed in Table 16.

Table 16. Nitric acid concentrations (μg N m^{-3}) for deposition calculations

	Summer	Autumn	Winter	Spring	Year average
High	0.83	0.62	0.41	0.62	0.62
Low	0.24	0.18	0.12	0.18	0.18
Likely	0.534	0.4	0.267	0.4	0.4

Ammonia gas concentrations

Figure 24 shows ammonia concentrations measured by passive samplers at certain of the Kiepersol Joint Venture monitoring sites for the period November 1999 to November 2000. The values range from 4.65 μg N m^{-3} - 0.35 μg N m^{-3} (8 to 0.6 ppb). Included in the graph is the average monthly values calculated from all the sites and these range from 2.67 μg N m^{-3} - 1.16 μg N m^{-3} (4.6 to 2 ppb). The average value for all the data is 1.9 μg N m^{-3} (3.4 ppb). The average for each site ranged from 1.7 μg N m^{-3} (2.92 ppb) at Ben Mc Dhui to 2.5 μg N m^{-3} (4.3 ppb) at Lichtenburg. Note that in some instances these values approach an average annual value but in other instances only a few months of the year were sampled. The high value for Lichtenburg was calculated from the first six months, which tended to be skewed towards higher values as shown in the graph.

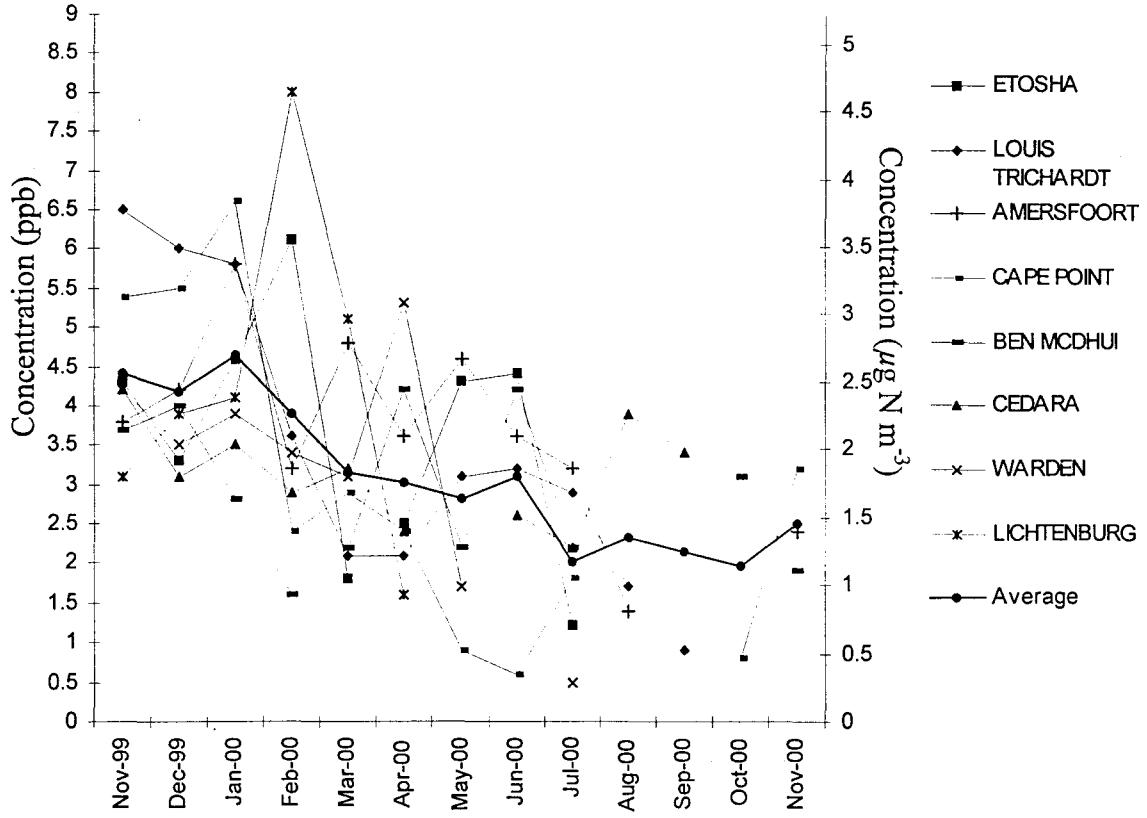

Figure 24- Ammonia concentrations measured by passive samplers at various locations in Southern Africa by the Kiepersol Network.

A more reasonable higher average would be 2.22 μg N m^{-3} (3.82 ppb) calculated from the Amersfoort data (sampled ten of the twelve months). Figure 24 illustrates the general lack of a trend in the data with regards location as well as the relatively high variance of concentrations that any one locality may experience. A factor that might promote the lack of a distinct geographical trend in the data is the fact that ammonia not converted to ammonium particles is deposited within a few kilometres from its source. In other words ammonia is not a 'long lived' gas and is unlikely to present a strong regional signature. A strong signature would only likely present itself as a local feature i.e. close to point sources such as cattle feedlots etc. The values measured were at sites situated in order to avoid point source contamination and would therefore represent background type values that should not be as geographically distinct as for instance nitrogen dioxide. However, this argument does not totally account for the variable nature of the measured

concentrations at any particular site. This variability appears to be relatively erratic, without any clear seasonal trend.

Factors affecting ammonia concentrations have been tabulated in Table 8. Many of the factors work against each other – the higher emissions during summer as a result of higher temperatures are counteracted by greater washout and deposition and vice versa for winter. The greater conversion to particulate via interaction with sulphate concentrations during winter is counteracted by the lower conversion via interaction with nitric acid and vice versa. Thus the observed data as well as theoretical considerations do not allow for an obvious seasonal variation in ammonia concentrations.

In light of the lack of clarity with regards trends, both temporal and geographical, concentrations at the study area have been estimated using the Amersfoort 'annual' average (2.22 μg N m^{-3}) for a high value and the Ben Mc Dhui 'annual' average (1.7 μg N m^{-3}) for a low value. The mean of these two values (1.96 μg N m^{-3}) will have to suffice as a likely value.

Particulate Ammonium

In the absence of measurements of ammonium at the study site, concentrations will have to be estimated using measurements from other studies in combination with analysis of factors affecting ammonium concentrations in general.

As discussed previously, NH_4 arises from gas to particle conversion processes – the neutralisation of sulphuric acid by gaseous ammonia and the interaction of ammonia with nitric acid. In general terms therefore high ammonia, sulphate and nitric acid concentrations favour the production of ammonium. Ammonia emissions near to the study site are considered to be low due to the lack of agricultural activity. Furthermore, the concentrations of sulphate measured by Zunckel (1999) near the study site are on the lower end of concentrations described by Warneck (1988) to affect the conversion process described above. At such levels of sulphate, most of the reduced nitrogen should remain in the gas phase (not considering possible effects of conversion to ammonium

nitrate via reaction with nitric acid). Thus processes such as precursor emission and conversion near to the study site should not be important in acting to increase ammonium concentrations. A more important process would be emission and conversion processes further away from the study site followed by effective transport to the study site. As discussed in the section on ammonia concentrations, the definition of seasonal type variance in ammonia concentrations is not possible. However, higher sulphate concentrations in Winter (Zunckel, 1998) (increasing the conversion of ammonia to ammonium sulphate) as well as lower temperatures favouring the stability of ammonium nitrate, should act to increase the amounts of particulate nitrogen during Winter. Furthermore, in terms of transport to the study area, ammonium is not dry deposited easily and removal from the atmosphere depends largely on wet deposition. Lower rainfall during Winter months therefore favours a longer residence time of ammonium in the atmosphere and a higher possibility of ammonium reaching the study site. Inversion type conditions during winter also favour higher concentrations of the ammonium within the boundary layer, possibly allowing more efficient transport near to the surface. The combined effect of these factors should be to increase ammonium concentrations at the study site during Winter relative to Summer. However, due to the complexity of the above arguments, a seasonal variation in ammonium concentrations is not attempted for the ammonia approximations in this study.

A likely annual average ammonium concentration for the study can be estimated from the information from previous studies (Table 11). The concentrations range from a high value of 5.13 μg N m^{-3} in Holland to low values of 0.1 μg N m^{-3} in Niger. The yearly average of 3.57 μg N m^{-3} in Holland reflects the generally accepted influence of intense agricultural activity and is not considered relevant to the present study. The value measured at Skukuza (0.66 μg N m^{-3}) is obviously the best approximation that can be made for a likely value. High and low concentration estimates are difficult to evaluate. The value recorded in Niger (0.1 μg N m^{-3}) is taken as a low value. It is the lowest value recorded in Table 11 and is not radically different to the chosen likely value. Furthermore it represents a rural African type environment obviously not influenced by intense agricultural activity. The values listed in Table 11 are less useful in terms of choosing a

high estimate for the study area. Most areas affected by agricultural activity appear to have values in the vicinity of 3 μg N m^{-3} or larger. A high estimate for the study area has been taken as half this amount i.e. 1.5 μg N m^{-3}.

Particulate Nitrate

In the absence of site information with regards nitrate concentrations, an estimate is made from measurements from other studies (Table 10) using various qualitative guidelines. As with particulate ammonium, factors affecting seasonal concentration variance are complex. For example, decreases in temperature during winter may favour relatively higher concentrations whilst lower humidities may decrease the concentrations. Seasonal variance in concentration has therefore not been attempted. The value measured at Skukuza (0.56 μg N m^{-3}) is obviously the best approximation that can be made for a likely value. Low values from remote high elevation sites vary from 0.04 µg N m^{-3} to 0.09 µg N m^{-3} and a value of 0.1 μg N m^{-3} is taken as a low estimate. Higher values range up to 2.74 μg N m^{-3} but are more commonly between 1 to 2 μ g N m^{-3}. A high estimate is taken as 1.0 μg N m^{-3}.

Summary of Concentrations

The concentrations used in this study are summarised in Appendix 3.

Gas and Particle Deposition Velocities

As discussed in the methods section, deposition velocities for this study have been inferred using the Hicks model or estimated from literature. In either case a difference between grassland and forest deposition velocities can be expected, as discussed in the literature review. As such, deposition velocities for each of the relevant nitrogen species have been reported below for the forested area and the grassland area separately.

Nitrogen Dioxide Deposition Velocities

Nitrogen dioxide deposition velocities have been estimated using measurements from other studies, as listed in Table 3. The estimated values for this study are listed in Table 17 below.

Table 17 -Nitrogen Dioxide deposition velocities (cm s^{-1})

	Forest				Grassland				Reference
	Sum	**Aut**	**Win**	**Spr**	**Sum**	**Aut**	**Win**	**Spr**	
High	1.2	1.2	1.2	1.2	0.35	0.35	0.35	0.35	Hanson & Lindberg, 1991
Low	0.35	0.18	0	0	0.1	0.05	0	0	
Likely	0.51	0.51	0.51	0.51	0.15	0.15	0.15	0.15	Forest - inference from Hanson & Lindberg, 1991 & Fowler *et al.*, 1998, Grassland - Fowler *et al.*, 1998

The high values are calculated from Hanson & Lindberg (1991) by taking their geometric mean values of previous studies and dividing by two. This is done because their studies comprise daylight values. Nitrogen dioxide nightime deposition velocities are considered negligible due to stomatal control and thus daytime values may be divided by two to obtain an estimate of 24 hour deposition velocities. The likely value for grasslands (0.15 cm s^{-1}) is taken from a study averaging over 24 hours (Fowler *et al.*, 1998). This is considered a likely value since it takes into account emissions of NO. The scaling down factor necessary to produce this likely value for grasslands from the Hanson and Lindberg grassland value is used to produce a likely forest value from the Hanson and Lindberg value for forests. For the low deposition velocity values, 0.1 cm s^{-1} has been taken as a starting point for the grasslands, since it is recorded as the lowest deposition velocity in a number of previous studies (see Table 3).

As discussed previously, the concept of a compensation point is relevant to nitrogen dioxide. Previous studies indicate it to be in the vicinity of 0.6-0.7 μg N m^{-3}. The concentration values for Summer in the low deposition analysis are just above this range (1 μg N m^{-3}) and the low deposition value above has been used (0.1 cm s^{-1}). The value for the forest has been scaled up by the same factor used for the medium analysis and a deposition velocity of 0.35 cm s^{-1} is the result. The concentration values for the Winter and Spring seasons fall below the compensation point range, and the deposition velocities have been taken as 0 cm s^{-1}. The concentration values for Autumn in the low analysis are at the compensation point and a value of 0.05 cm s^{-1} has been used for the grassland. This is relatively arbitrarily chosen as the midpoint between the Summer and Winter and Spring velocities. This has been scaled up for forests again, giving a deposition velocity of 0.18 cm s^{-1}.

Nitric Acid Deposition Velocities

Nitric acid deposition velocities were calculated using the Hicks inferential model. Inputs to the model included wind speed, wind direction, sigma theta (standard deviation of the horizontal wind direction), global radiation, temperature, humidity, surface wetness, rainfall. This information has been inputted in the form of hourly averages for each hour of one week in Summer, Autumn, Winter and Spring 2000. The model outputs for each hour in terms of the deposition velocity for SO_2, O_3, HNO_3 and particles are shown in Figures 25 - 28. For reasons described later in this discussion, the model outputs are relevant to a grassland area only and deposition velocity values for forests are dealt with after the discussion on the grassland model outputs.

The typical diurnal variation of deposition velocities, from negligible nightime values to maximum daytime values, as a result of atmospheric stability variation is clearly evident in the figures. The extended daylight hours during summer relative to winter are reflected in the graphs by the deposition velocity variance and this results in an almost five hour longer period of significant deposition conditions during summer. Besides the duration of the deposition period, seasonal variance in maximum deposition also occurs. This is illustrated in Figure 29 - the average hourly deposition velocity for the Summer, Autumn,

Winter and Spring period. Winter is again characterised by conditions less conducive to deposition, having lower average hourly deposition velocities throughout the day. The highest deposition velocities occur in the Autumn morning period whilst the Spring period is also characterised by occasional slightly higher deposition velocities than Summer and Winter.

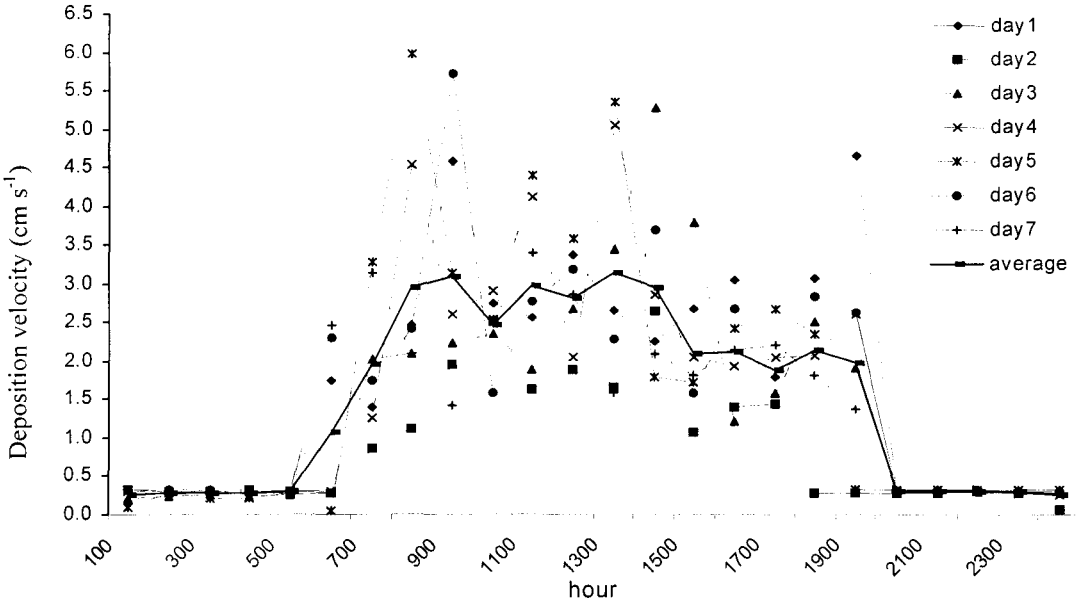

Figure 25 – Nitric Acid deposition velocities for grasslands – seven days in January (Summer) and the average

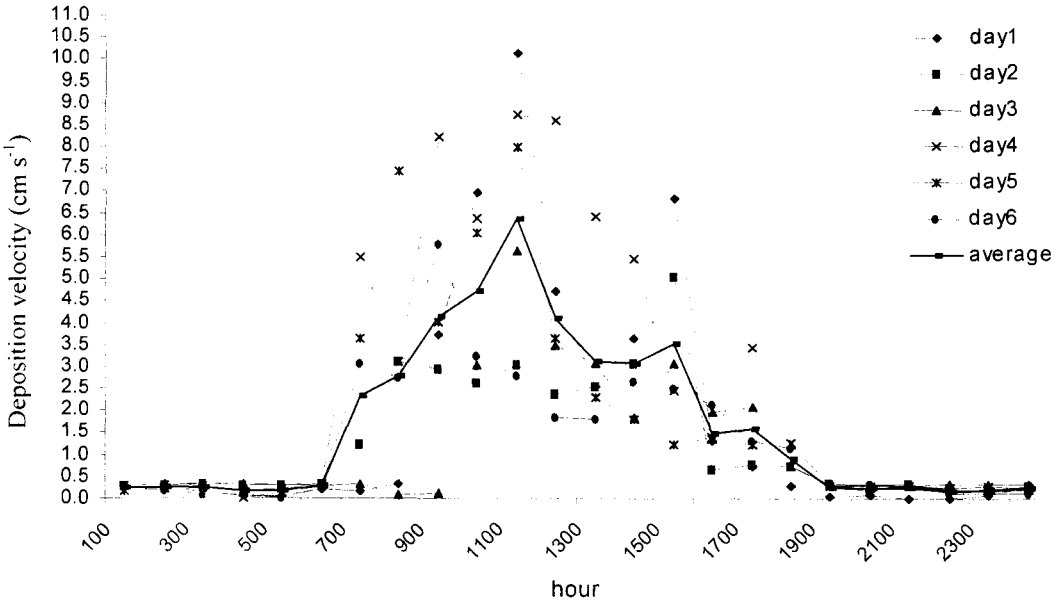

Figure 26 – Nitric acid deposition velocities for grasslands – six days in April (Autumn) and the average

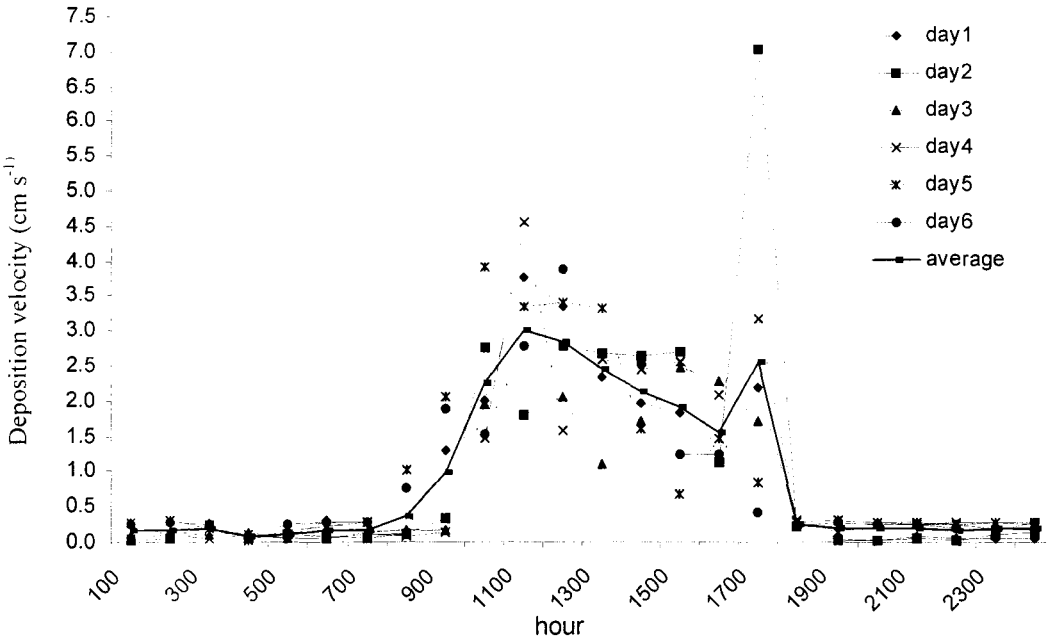

Figure 27 – Nitric Acid deposition velocities for grasslands – six days in July (Winter) and the average

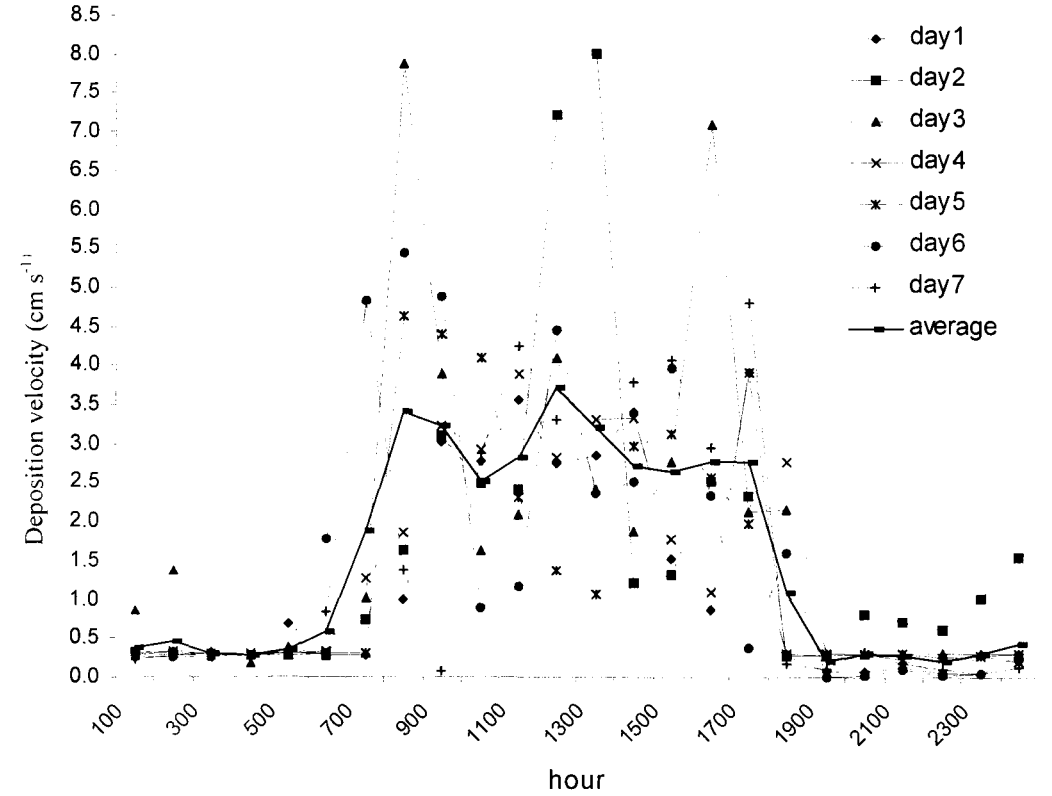

Figure 28 – Nitric Acid deposition velocities for grasslands – six days in October (Spring) and the average

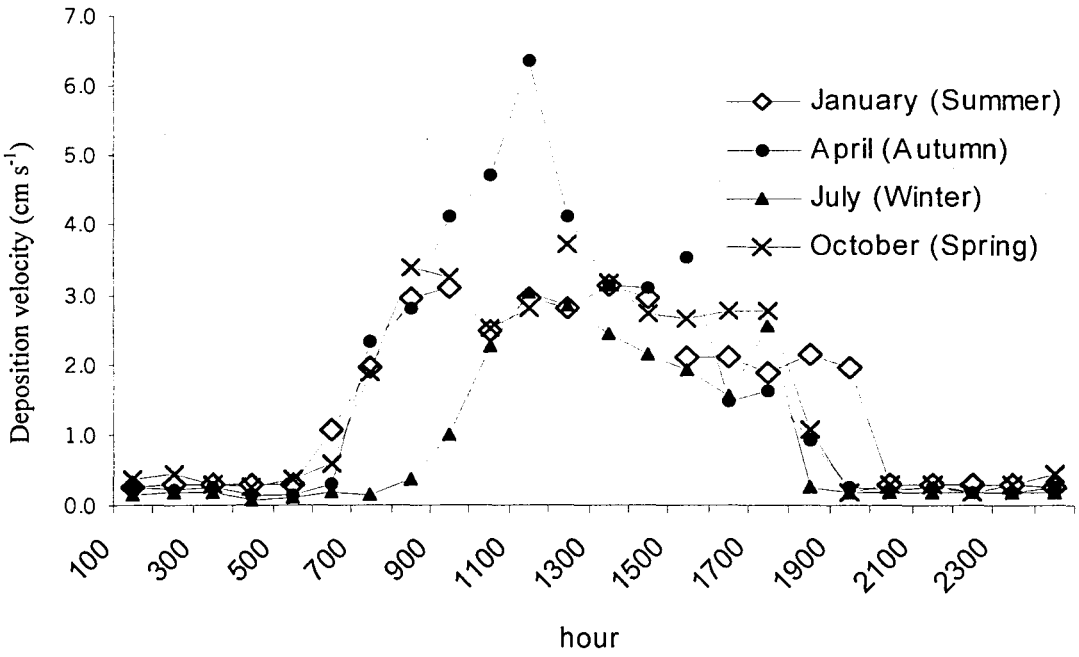

Figure 29 - Seasonal comparison of average hourly nitric acid deposition velocities

The seasonal variance in average deposition velocities is clearly illustrated in Figure 30, where Autumn has the highest average followed by Spring, Summer and Winter. Deposition velocities depend on a variety of parameters including meteorological characteristics as well as surface features. Nitric acid is generally described in literature as having surface resistances close to zero. This is borne out by the models lack of sensitivity to changes in the LAI parameter for nitric acid and seasonal deposition velocity variance for nitric acid is not affected by seasonal changes in LAI.

Figure 31 shows the seasonal variance of other input parameters to the Hicks model.

Comparing Figures 29 and 31, it may be seen that average seasonal nitric acid deposition velocities follow a similar seasonal variation as sigma theta and temperature. Figure 32 is a plot of average hourly sigma thetas (standard deviation of the horizontal wind velocity), for the various seasons. In comparing Figure 29 with Figure 32, it can be seen that the deposition velocity peaks in Autumn coincide with peaks in sigma theta. The coincidence in the Spring peaks, although less obvious, are also discernible. Figure 32 also illustrates the fact that sigma thetas do not drop off as significantly during periods of darkness as much as the deposition velocities do, indicating the contribution of insolation to deposition velocities.

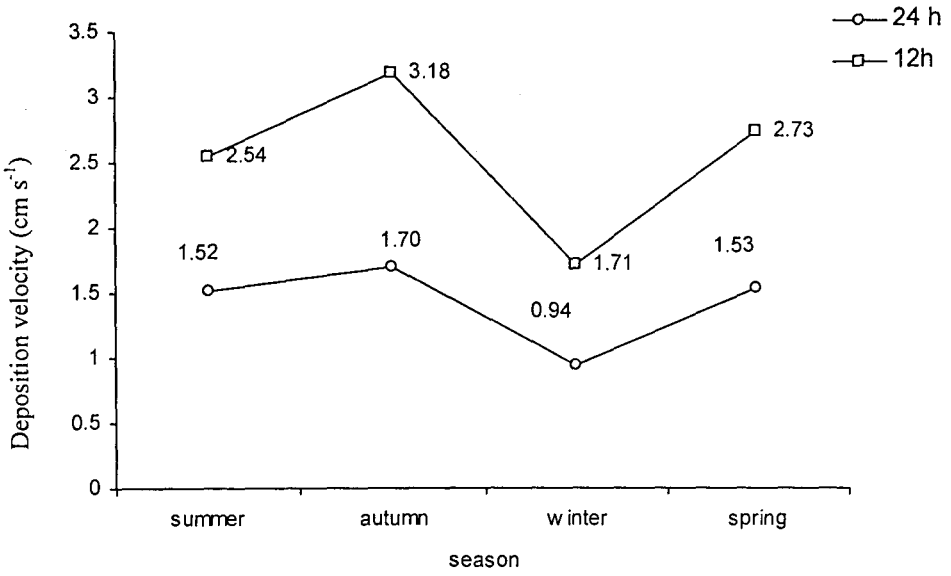

Figure 30 – Average nitric acid deposition velocities calculated for 12 hour (daylight) and 24 hour periods, showing seasonal variance

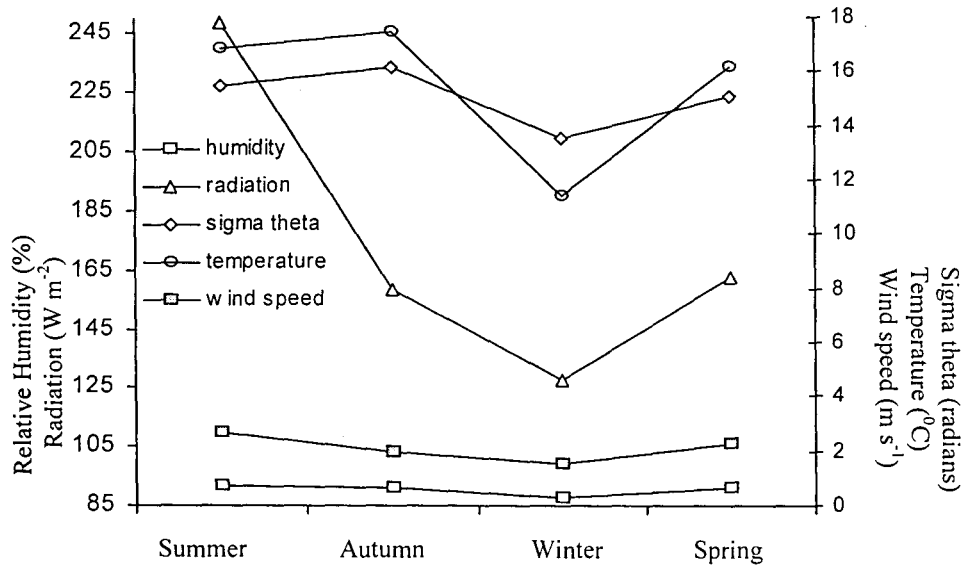

Figure 31– Seasonal average humidity, radiation, sigma theta, temperature and wind speed

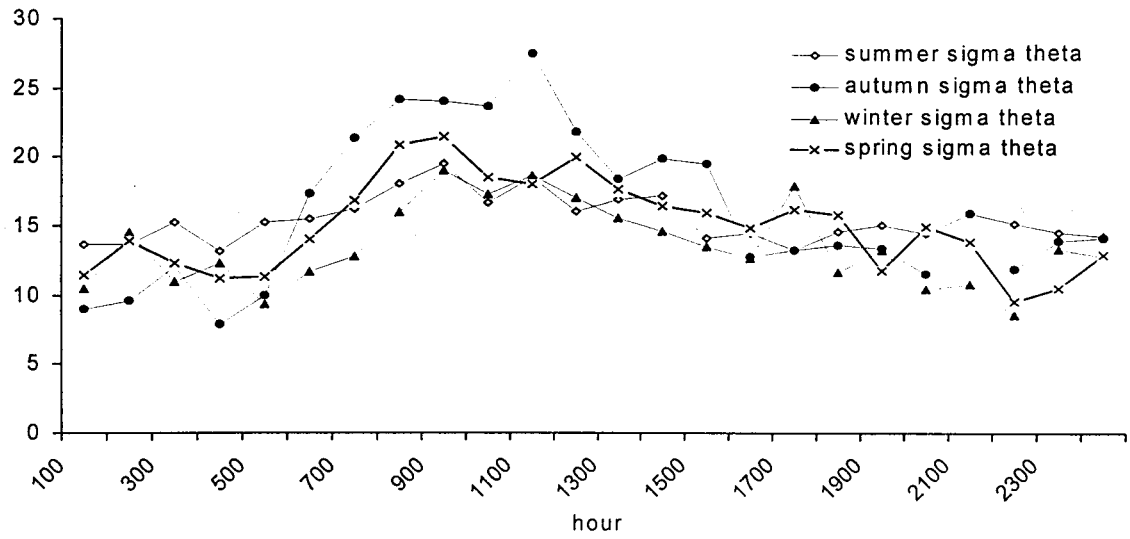

Figure 32 – Average hourly sigma theta variation for Summer, Autumn, Winter and Spring

The seasonal variance in the deposition characteristics of the atmosphere result from an interplay between wind and insolation variance. The former has a strong influence on deposition velocity magnitudes, the latter has an important influence on the length of the depositionary period.

In comparing the deposition velocities calculated using the Hicks inferential model with deposition velocities from literature, it may be seen that the calculated deposition velocities are closer to deposition velocities characteristic of low vegetation rather than forests. Fowler (1991) shows deposition velocities for varying types of vegetation typical of certain wind speeds. The average annual wind speed for the study site is 2 m s^{-1}. Inference between the deposition velocities for moors at wind speeds of 1 and 4 m s^{-1}, as given by Fowler (1991), gives a deposition velocity of ~1.52 cm s^{-1}. This is close to the average annual deposition velocity calculated for this study – 1.42 cm s^{-1}. The fit of the calculated deposition velocities with those calculated in other studies for low vegetation, is consistent with the fact that the meteorological data used as inputs to the Hicks model for this study were obtained from the weather station in the town of Graskop, a site in the middle of a grass covered field with low buildings in the general surrounds. The values calculated have therefore been taken as likely values for the grassland site. Measurements taken in other sites, as well as theoretical calculations (especially Fowler *et al.*, 1991), indicate forests to have deposition velocities approximately twice that of shorter

vegetation under the same meteorological conditions. The likely values for deposition velocities to the forested areas have therefore been taken as twice that of the values calculated by the Hicks inferential model. A low estimate has been calculated by assuming that meteorological variables measured by the weather station in Graskop represent conditions close to those above a forest canopy. The Hicks deposition velocities have then been taken as representative of the forest site, and the grassland velocities have been taken as half these values. For the high estimate, annual average wind speed has been increased from ~2 m s^{-1} to 3 m s^{-1}. Using an approximate wind speed/deposition velocity relationship from Fowler (1991)(as described above), this would result in an annual average deposition velocity of ~ 2.3 cm s^{-1}. This value is again multiplied by two to obtain a high annual average deposition velocity for forests – 4.6 cm s^{-1}. The seasonal variations have then been applied to the annual averages to produce high seasonal deposition velocity estimates shown in the table below.

Table 18 - Nitric acid deposition velocities (cm s^{-1})

	Forest					Grassland				
	Sum	**Aut**	**Win**	**Spr**	**Annual av.**	**Sum**	**Aut**	**Win**	**Spr**	**Annual av.**
High	4.9	5.1	3.03	4.94	4.6	2.46	2.75	1.49	2.50	2.3
Low	1.52	1.70	0.94	1.53	1.42	0.76	0.85	0.46	0.77	0.71
Likely	3.04	3.40	1.88	3.06	2.85	1.52	1.70	0.94	1.53	1.42

Ammonia Deposition Velocities

Estimates of ammonia deposition velocities using values recorded in other studies (Table 9) have been made and are shown in Table 19. Seasonal variation of ammonia deposition velocities is not often referred to in the literature, or measured in previous studies. Certain studies have indicated a dependence of ammonia deposition velocities on seasonally varying factors such as humidity and temperature, but these are not easily resolvable due to their possible interference. As such, an attempt to estimate seasonal variance for ammonia depostion velocities for this study has not been made.

Table 19. Ammonia deposition velocities (cm s^{-1})

	Forest	**Grassland**	**Reference**
High	5.56	2.14	Fowler *et al.* 1999
Medium	2.3	0.7	Geom. mean Hanson and Lindberg 1991
Likely	2.3	0.7	Geom. mean Hanson and Lindberg 1991

Nitrate and Ammonium Particle Deposition Velocities

Particulate deposition velocities for both nitrate and ammonium were calculated using the Hicks inferential model. The deposition velocity results are shown in the figures below.

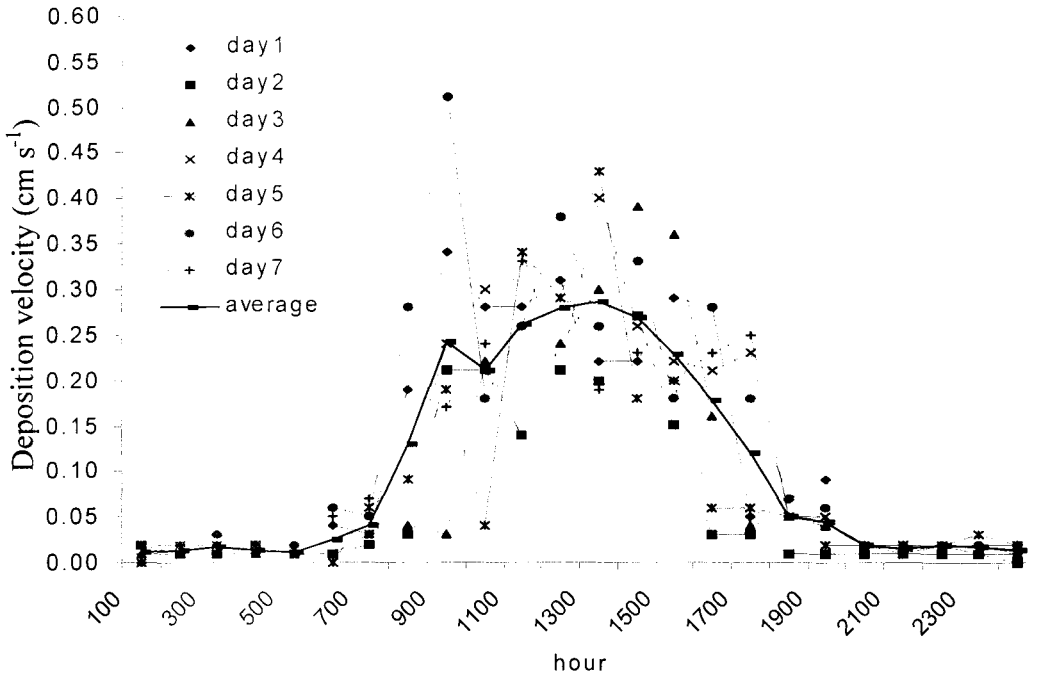

Figure 33 – Particulate deposition velocities – seven days in January and the average

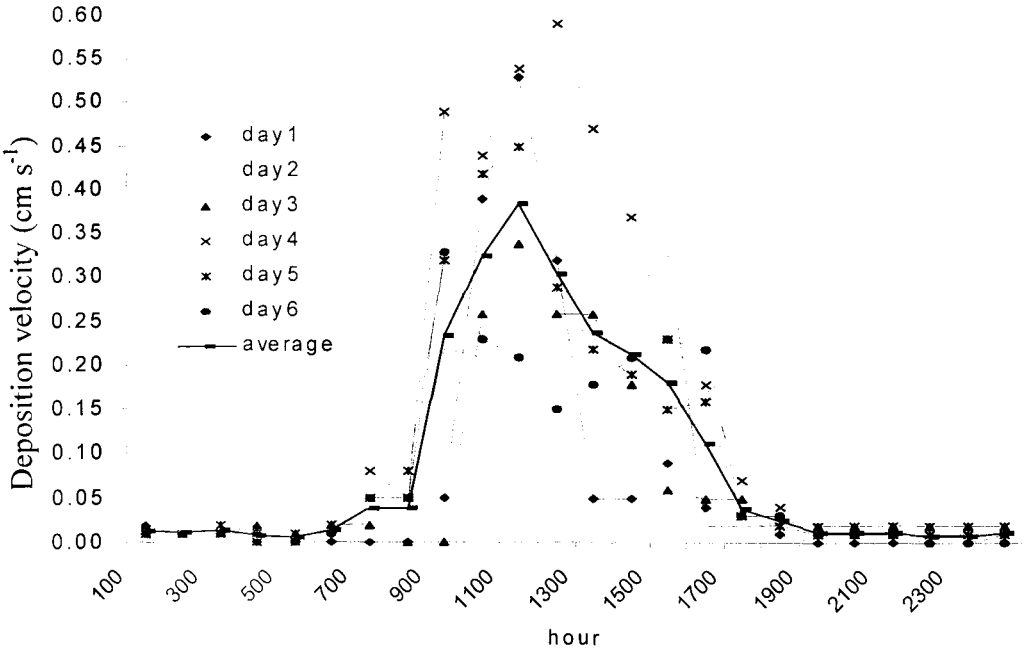

Figure 34 - Particulate deposition velocities – six days in April and the average

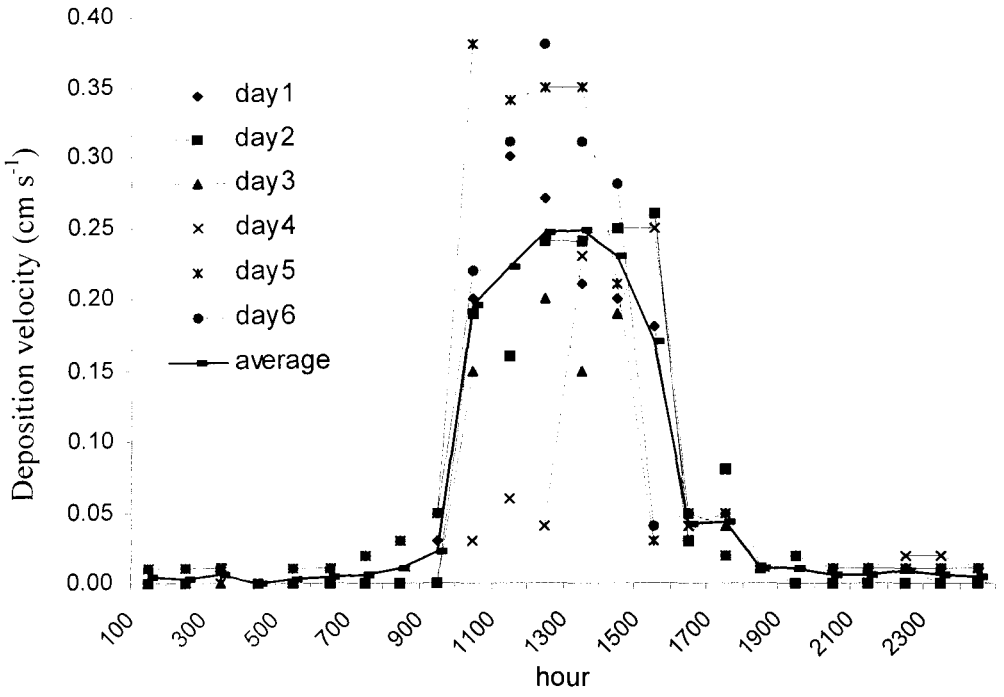

Figure 35 - Particulate deposition velocities – six days in July and the average

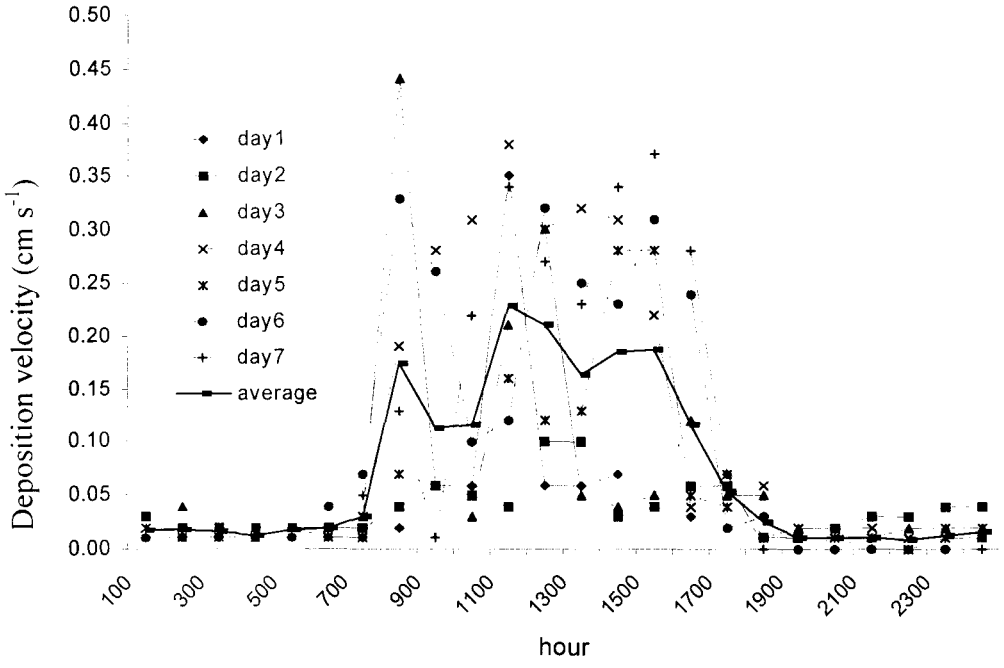

Figure 36 - Particulate deposition velocities – six days in October and the average

No significant variation of deposition velocity occurred for particulates when LAI was varied seasonally. A seasonal difference in deposition velocities did occur as a result of other factors varying. This may be seen in Figure 37 and 38.

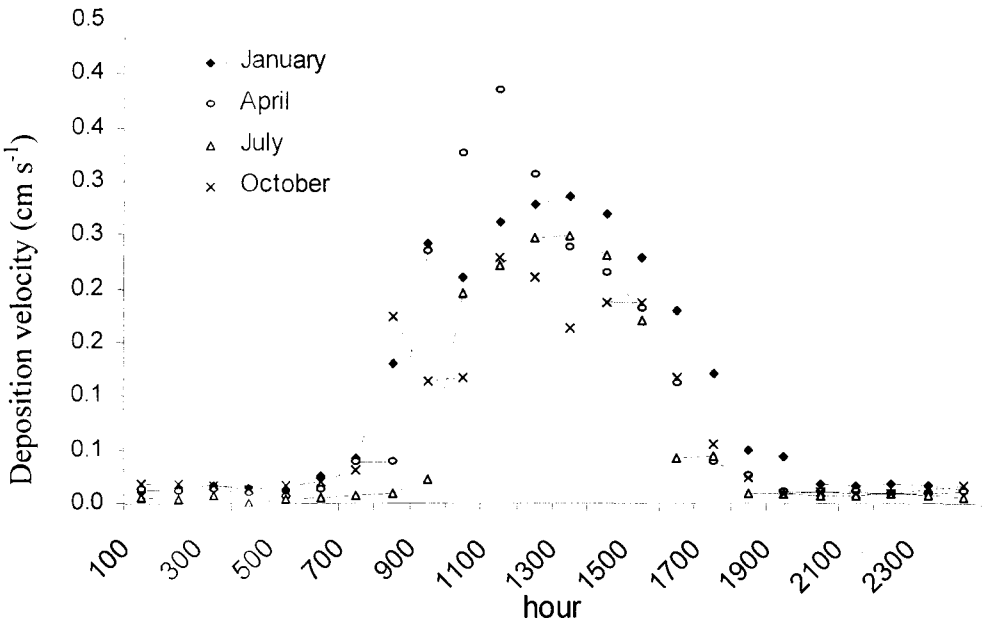

Figure 37 - Seasonal comparison of average hourly particulate deposition velocities

As with nitric acid, a comparison between seasonal average deposition velocities (Figure 38) and the average values for the inputs to the Hicks model (Figure 39) may be made. The seasonal pattern for the deposition velocities may be explained by influencing the sigma theta and temperature pattern with that of the other variables.

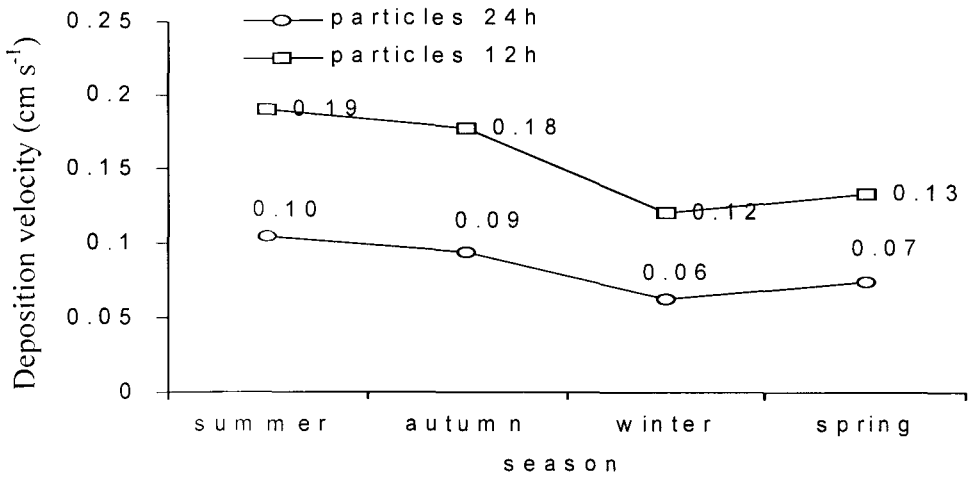

Figure 38 - Particle deposition velocities, seasonal variance

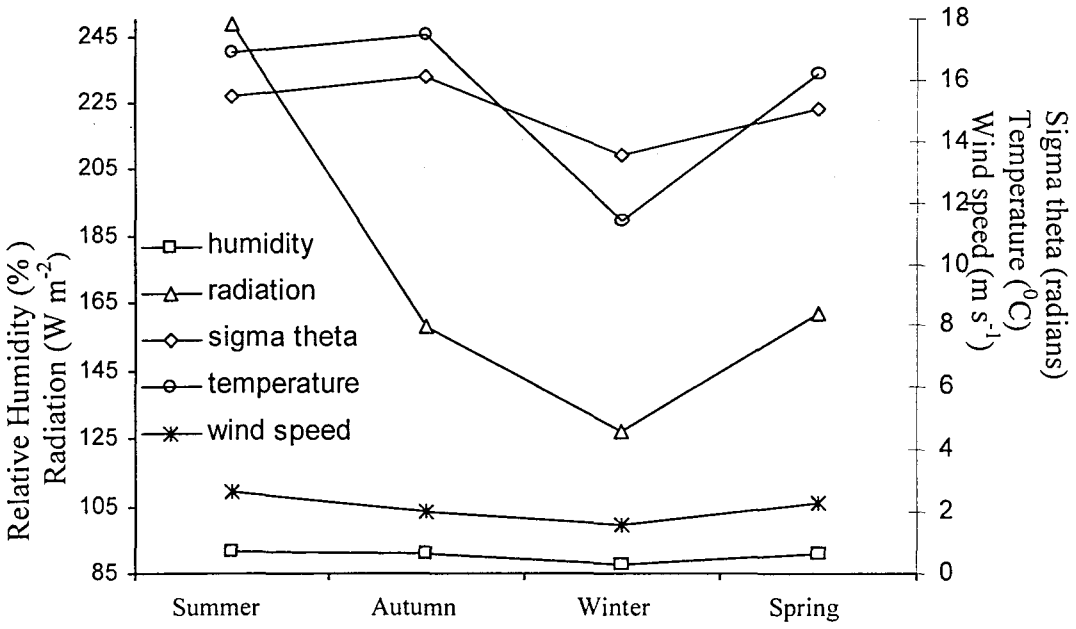

Figure 39 - Seasonal average humidity, radiation, sigma theta, temperature and wind speed

Ammonium is present as particles in the sub-micron size. Warneck (1988) presents data that shows deposition velocities for this size range of particles as being between 0.01 and 0.1 cm s^{-1} for typical atmospheric conditions over grasslands. This is consistent with the deposition velocities produced by the Hicks model for this study. The assumption that the meteorological conditions measured in the town of Graskop are consistent with conditions over grassland in that area seems valid. The deposition velocities calculated will therefore be used for likely grassland conditions. Warneck also shows minimum deposition velocities for sub-micron particles to be 0.01 cm s^{-1}. This is taken as a low annual average and seasonal variance applied to it. The data presented by Warneck show deposition velocities for sub-micron particles to forests to be of an order of magnitude larger than the deposition velocities to grasslands. A reasonable average is 0.5 cm s^{-1} and an upper limit as 1 cm s^{-1}. These values are taken as annual averages for likely and high scenarios and the seasonal variance is applied. A low annual average deposition velocity is estimated as being 0.1 cm s^{-1}.

Table 20 - Ammonium deposition velocities for deposition calculations

	Forest					Grassland				
	Sum	Aut	Win	Spr	Annual av.	Sum	Aut	Win	Spr	Annual av.
High	1.25	1.13	0.75	0.89	1.00	0.50	0.45	0.30	0.35	0.40
Low	0.13	0.11	0.08	0.09	0.10	0.01	0.01	0.01	0.01	0.01
Likely	0.63	0.56	0.38	0.10	0.50	0.1	0.09	0.06	0.07	0.08

Nitrate in the continental aerosol is distributed over the entire 0.1 – 10 μm size range. A bimodal size distribution is often observed. The first maximum occurs in the accumulation mode, where nitrate is associated with ammonium. The second appears in the coarse mode, where sodium, potassium and earth alkaline elements are the principal cations. Nitrate in the coarse particle mode is always present, whereas nitrate in the accumulation mode (ammonium nitrate) is an indicator of more polluted environments (high precursor concentration – ammonia and nitric acid). The concentrations measured at Skukuza (0.56 μg N m^{-3}) are at a high enough level for the size distribution to be biased towards the sub-micron range. The deposition velocities described above for ammonium particles will therefore also be used for the nitrate particles. For the low concentration estimation, the particle size distribution is biased towards the larger than 1 μm size. Deposition velocities for particles of this size range are approximately 1 cm s^{-1}.

The table below summarises all the deposition velocity estimations for this study.

Table 21 – Summary of deposition velocities (cm s^{-1}) used in this study

		Forest					Grassland				
		Sum	Aut	Win	Spr	av.	Sum	Aut	Win	Spr	av.
HNO_3	High	4.90	5.10	3.03	4.94	4.60	2.46	2.75	1.49	2.50	2.30
	Low	1.52	1.70	0.94	1.53	1.42	0.76	0.85	0.46	0.77	0.71
	Likely	3.04	3.40	1.88	3.06	2.85	1.52	1.70	0.94	1.53	1.42
NO_2	High	1.20	1.20	1.20	1.20	1.20	0.35	0.35	0.35	0.35	0.35
	Low	0.35	0.18	0.00	0.00	0.13	0.10	0.05	0.00	0.00	0.04
	Likely	0.51	0.51	0.51	0.51	0.51	0.15	0.15	0.15	0.15	0.15
NH_3	High	5.56	5.56	5.56	5.56	5.56	2.14	2.14	2.14	2.14	2.14
	Low	1.80	1.80	1.80	1.80	1.80	0.10	0.10	0.10	0.10	0.10
	Likely	2.30	2.30	2.30	2.30	2.30	0.70	0.70	0.70	0.70	0.70
NH_4^+	High	1.25	1.13	0.75	0.89	1.00	0.50	0.45	0.30	0.35	0.40
	Low	0.13	0.11	0.08	0.09	0.10	0.01	0.01	0.01	0.01	0.01
	Likely	0.63	0.56	0.38	0.10	0.50	0.10	0.09	0.06	0.07	0.08
NO_3^-	High	1.25	1.13	0.75	0.89	1.00	0.50	0.45	0.30	0.35	0.40
	Low	0.13	0.11	0.08	0.09	0.10	0.01	0.01	0.01	0.01	0.01
	Likely	0.63	0.56	0.38	0.10	0.50	0.10	0.09	0.06	0.07	0.08

Dry Deposition Amounts

Dry deposition amounts for the various nitrogen species, calculated from the concentrations and deposition velocities discussed in the previous section, are shown below. Dry deposition amounts are also tabulated in Appendix 4.

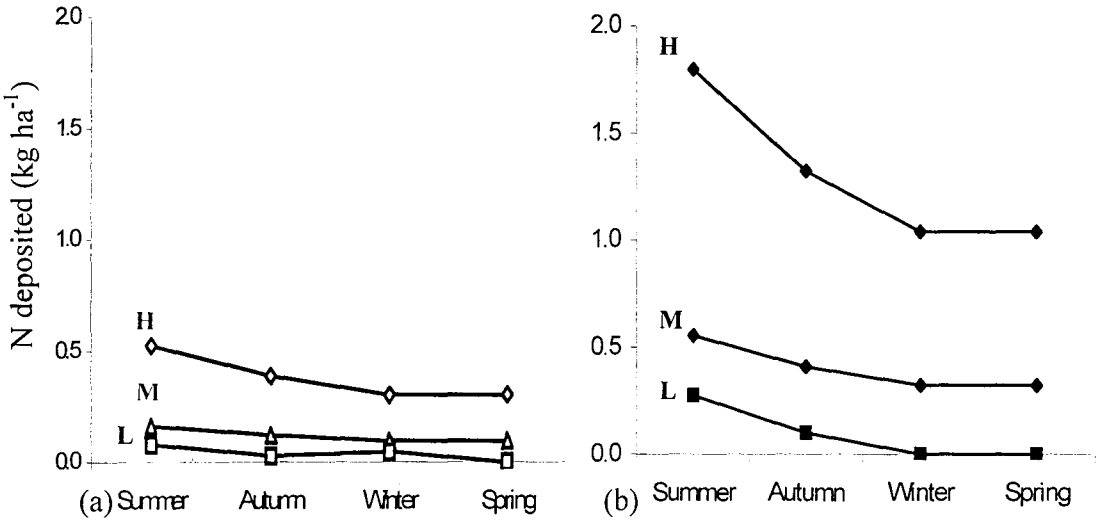

*Figure 40 – High (**H**), likely (**M**) and low (**L**) nitrogen dioxide deposition to grasslands (a) and forests (b).*

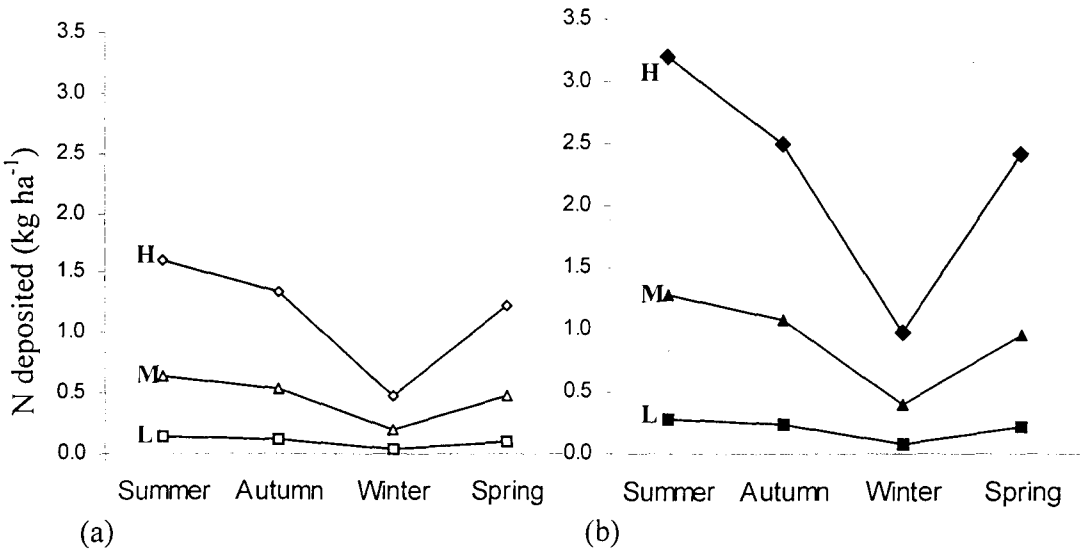

Figure 41 – High, likely and low nitric acid deposition to grasslands (a) and forests (b)

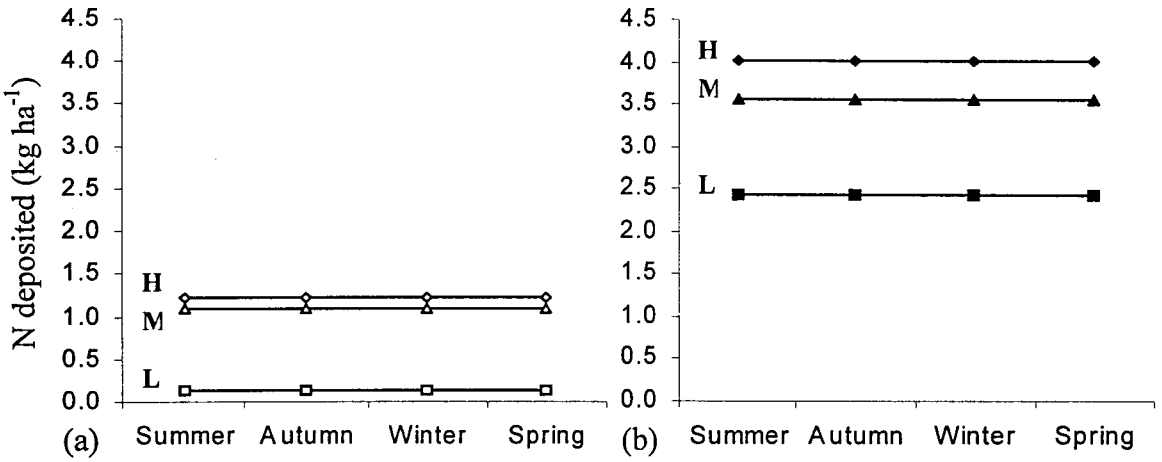

Figure 42-High and low ammonia deposition to grasslands (a) and forests (b).

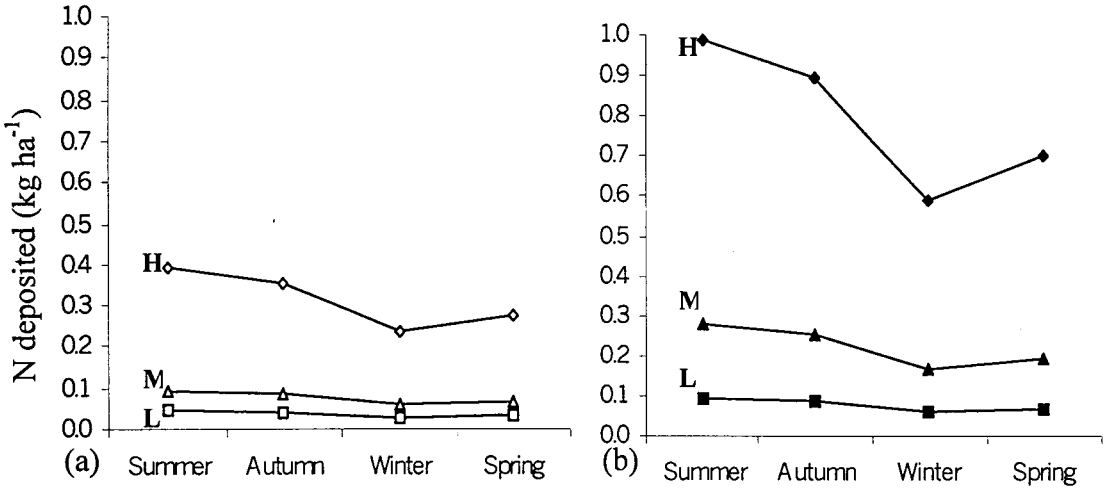

Figure 43- High and low nitrate particle deposition to grasslands (a) and forests (b)

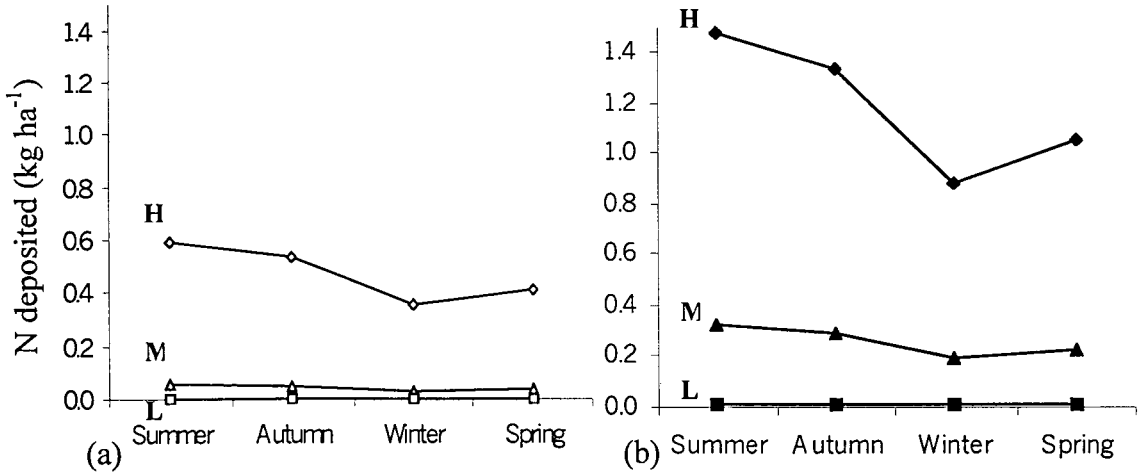

Figure 44- High and low ammonium particle deposition to grasslands (a) and forests (b)

4.3 Cloud droplet deposition

Cloud droplet deposition is the term used to describe the deposition of low-lying cloud or mist droplets to the surface. A study has been made of this by K Olbrich (1993) in the general area of the study site and information from that study will be used in the present study to complement the wet and dry deposition calculations and provide a more complete picture of nitrogen deposition at the study site.

Mistfall is as important as rainfall in terms of quantity in the study area. The figure below shows mistfall recorded in the study by Olbrich as well as that recorded at Bakenkop, approximately 20 kms from this study site. Included is the average rainfall for this study.

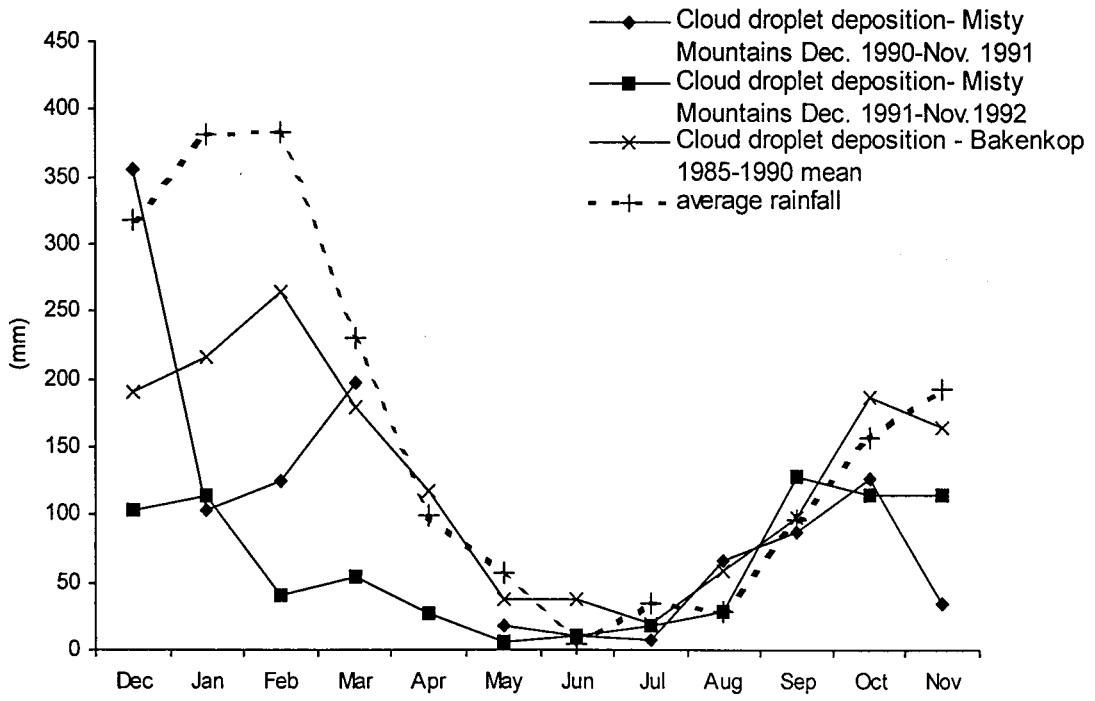

Figure 45 – Cloud droplet deposition in the vicinity of the study area compared to average rainfall

Monthly rainfall amounts and cloud droplet deposition amounts are indeed similar, although rainfall is generally higher in the months of December, January and February. Olbrich noted that the cloud droplet deposition for the first part of the year 1991-1992 at Misty Mountain was relatively low, as was rainfall. This needs to be taken into account in determining deposition amounts, as is discussed further below.

As with dry and wet deposition, an attempt at defining possible seasonal deposition from cloud droplets will be made. The monthly moisture deposition from cloud droplets in the figure above have been combined into seasonal moisture deposition amounts in the figure below. Included is the average seasonal rainfall amounts, illustrating the similarity in amounts and pattern once again. The seasonal moisture deposition from cloud droplets will be combined with the nitrogen chemistry recorded by Olbrich to obtain seasonal ammonium and nitrate deposition amounts.

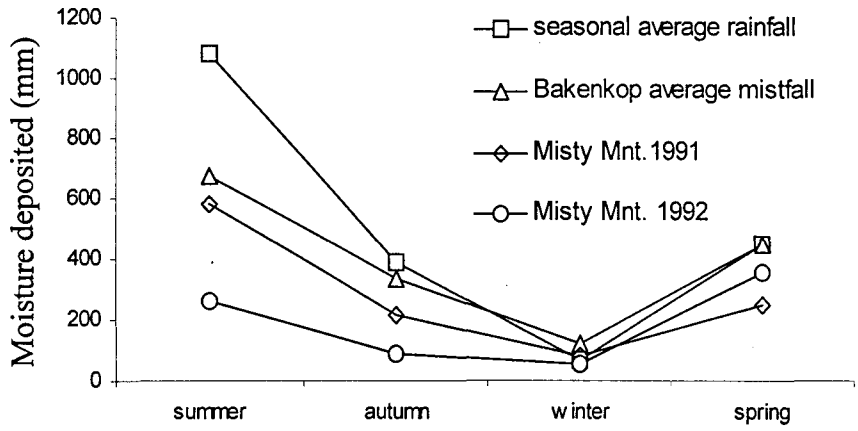

Figure 46 - Comparison of seasonal average mistfall and rainfall

Olbrich analysed the chemistry of 15 mist samples collected over the period December 1991 to January 1993. The nitrate concentrations in these samples had a mean of 127.2 μeq l^{-1} and the ammonium a mean of 60.4 μeq l^{-1}. These concentrations are significantly higher than concentrations in rainfall in the area. This is also the case in Olbrich's study, in which the chemistry of rainfall samples taken over the period September to November 1992 were compared to the chemistry of mist over the same period. Mean ammonium and nitrate concentrations in the rainfall were 24.9 μeq l^{-1} and 20.1 μeq l^{-1} respectively, compared to concentrations in the mist of 95.6 μeq l^{-1} and 60.3 μeq l^{-1}. The relatively high concentrations in the mist reported by Olbrich are not unusual, compared to concentrations in mist or intercepted clouds reported in other studies, as detailed in Table 22.

Table 22 –Cloud droplet chemistry recorded in previous studies.

Locality	NH_4^+ conc. ($\mu eq\ l^{-1}$)	NO_3^- conc. ($\mu eq\ l^{-1}$)	Comments	Reference
North England	358	349	Close to urban areas	Fowler *et al.*, 1995
South Scotland	267	291	Rural, 50 kms from urban pollution source	Fowler *et al.*, 1995
Northern central Europe	410	280	-	Acker *et al.*, 1995
East Europe	28.8	3.2	precipitating	Petrenchuk and Selezneva 1970
East Europe	11.1	16.1	Non-precipitating	Petrenchuk and Selezneva 1970
South England	22.1	18.6	Non precipitating	Oddie, 1962
Whiteface Mt. New York	140-215	32-89	Intercepted cloud	Munger *et al.*, 1983
Germany	185.6	183.7	Intercepted cloud	Mrose, 1966
Germany	710	225	Mountain fog	Wobrock *et al.*, 1994
California	1220-3250	1290-2380	Ground fog	Munger *et al.*, 1983
Chile	5.1	4.9	Remote site	Weathers *et al.*, 2000

The high concentrations in mist/fog or intercepted cloud probably results from the interaction of the mist/fog or intercepted cloud with particulate matter/aerosols at the ground level, these being elevated relative to concentrations at normal cloud level (Warneck, 1988). As such, the concentrations of ammonium and nitrate in the mist reflect the concentrations of the ammonium and nitrate aerosols as well as nitric acid and ammonia concentrations in the atmosphere where the mist forms. The fact that nitrate concentrations in the mist at Misty Mountain are higher than ammonium concentrations is consistent with the idea that the study site is probably more affected by combustion type pollution (nitrogen oxides) rather than agricultural type pollution (ammonia/ammonium).

Olbrich combined the average concentrations described above with the recorded mist-fall for the period July 1991 to June 1992 to obtain nitrogen deposition amounts of 12 kg N ha^{-1} yr^{-1} in the form of nitrate and 5.7 kg N ha^{-1} yr^{-1} in the form of ammonium. Olbrich noted further that these amounts were calculated using the relatively dry 1991-1992 year and that this likely has an effect on deposition amounts. For this study, the amounts have been broken up into seasonal deposition amounts by multiplying the average concentrations with the seasonal cloud droplet deposition. For the latter, the 1990-1991

data has been used rather than the 1991-1992 'dry' year data. This approach obviously suffers from the flaw of not taking into account possible seasonal variation of chemistry, these data not being available.

The deposition amounts detailed in Table 23 reflect deposition to a cloud droplet collector. The cloud droplet collector would define the probable deposition to forests rather than grasslands. Forests are generally viewed as being four times more efficient at capturing cloud droplets as grasslands (Unsworth and Crossley 1987). To obtain likely seasonal deposition amounts to grasslands, the forest deposition amounts have been divided by four.

Table 23 - Possible seasonal nitrogen deposition from cloud droplets

		Cloud droplet deposition (mm)	**Concentration (μeq l^{-1})**	**Seasonal amount deposited to forests (kg N ha^{-1})**	**Seasonal amount deposited to grasslands (kg N ha^{-1})**
Summer	Nitrate	671	127.2	12.00	3.00
	Ammonium	671	60.4	6.00.	1.50
Autumn	Nitrate	333	127.2	6.00	1.50
	Ammonium	333	60.4	3.00	0.75
Winter	Nitrate	117	127.2	2.00	0.50
	Ammonium	117	60.4	1.00	0.25
Spring	Nitrate	448	127.2	8.00	2.00
	Ammonium	448	60.4	4.00	1.00
Annual	Nitrate	1569	127.2	28.00	7.00
	Ammonium	1569	60.4	14.00	3.50
Annual	Nitrate + Ammonium	1569	-	42.00	10.50

CHAPTER 5 – TOTAL DEPOSITION

5.1 Total Deposition

The individual components of wet and dry deposition are shown in the graphs below for grasslands and forests. The components are also detailed in Table 24.

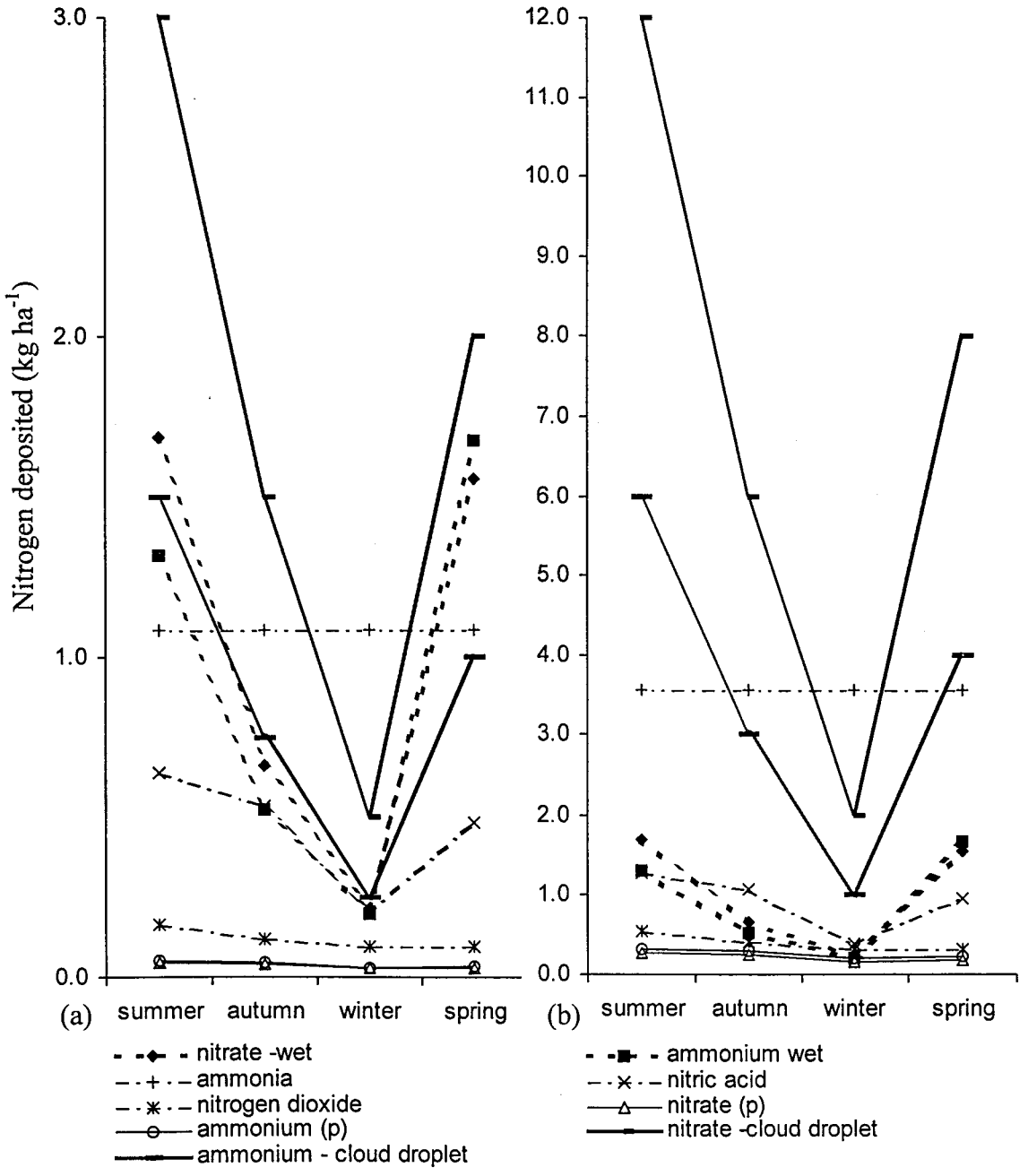

Figure 47 - Individual components of wet and dry deposition to grasslands (a) and forests (b).

The graphs above highlight the strong seasonal variance in deposition for the various individual components, as discussed in previous sections, as well as the notable increase in deposition to forests relative to grasslands. In general terms, Figure 47 indicates the deposition from the individual components of cloud droplet deposition to be most important followed by the components of wet deposition and then the components of dry deposition. Another generally consistent trend is the slight dominance of the nitrate component of the wet and cloud droplet contributions over the ammonium component. The exception to the general dominance of wet over dry deposition occurs during the dry season (winter) when the dominant dry deposition component, ammonia, becomes the largest individual contributor to nitrogen deposition. It should be noted however, that an estimate of seasonal variance in ammonia deposition was not attempted for this study. Nitric acid is the second largest component of dry deposition, followed by nitrogen dioxide and the particulates. Nitric acid deposits in amounts slightly below the individual wet deposition amounts in Summer and Spring but equals them in the dry months of Autumn and Winter.

With forests the influence of a rougher surface increases the likely deposition of dry components. This is most noticeable in ammonia, which dominates the wet components regardless of season. The greater interceptive capabilities of the forest reflect in the more obvious dominance of cloud droplet deposition over other components. However ammonia gas remains the largest single contributor during Winter. Furthermore, it now dominates the individual wet deposition components across all seasons. In both grasslands and forests, ammonia deposition competes well with ammonium cloud droplet deposition. Nitric acid becomes as important as the wet deposition components in forests whilst nitrogen dioxide and particulates remain the least influential components of deposition.

The graphs below show the total wet, total dry, total cloud droplet and total wet, dry and cloud droplet deposition to forests and grasslands. The graphs again highlight the seasonal variation in deposition as well as the difference in deposition amounts between forests and grasslands. In general terms, the three deposition classes contribute fairly similar amounts towards deposition in the case of grasslands. For forests, the three

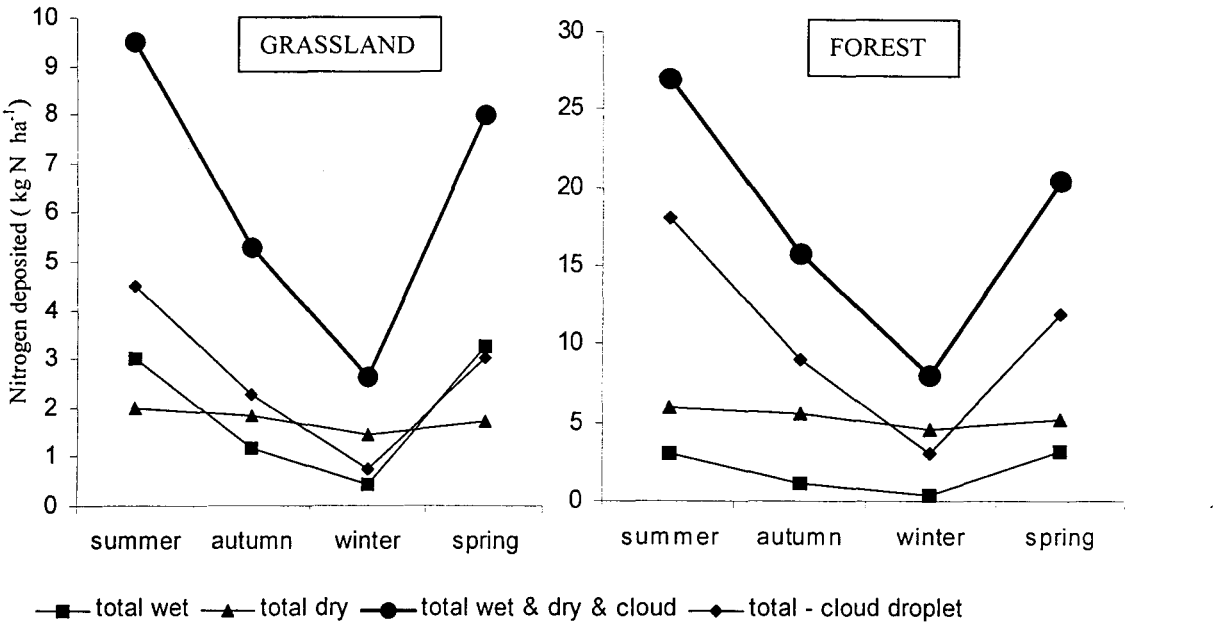

Figure 48 – Total seasonal nitrogen deposition amounts to grasslands and forests

classes differ more in terms of amounts deposited. The increased importance of dry deposition to forests is also highlighted in Figure 48.

As a concluding remark to this description of total deposition amounts, it is appropriate to reiterate that there are a number of nitrogen species that have not been included in the analysis of nitrogen deposition in this study. This is as a result of them being generally identified in the literature and previous studies as not contributing significant amounts to deposition. However it is possible that in combination they may increase the amounts described above by a few kilograms. Of relative note is the possible contribution from AON. As discussed in the literature review, dust and PAN contributions would likely to be more important with regards this study. Neff *et al.*(2002) indicate the average range for nitrogen deposition from PAN to be between 0.3 and 0.62 kg N ha^{-1} yr^{-1}. Due to the large influence of fossil burning in the region of this study, an appropriate estimate for this study may be 0.6 kg N ha^{-1} yr^{-1}. For dust, Neff *et al.*(2002) indicate the average range to be between 0.02 – 0.4 kg dust AON ha^{-1} yr^{-1}. In combination therefore, PAN and dust are likely to increase the total deposition amounts described above by not more than 1 kg N ha^{-1} yr^{-1}.

5.2 General Discussion

The deposition amounts to grasslands and forests in this study are compared in Table 24 with other studies. The studies have been selected because they are relatively comprehensive, incorporating most relevant nitrogen species and types of deposition. These comparisons provide an opportunity to highlight possible discrepancies between the deposition amounts calculated in this study and those reported in other studies.

Hesterburg *et al.*,1996 – the site is a rural grassland and deposition amounts compare reasonably with the grassland site of this study if the intense agricultural influence at the Swiss site is accounted for.

Harrison and Allen, 1991 – this study lacks land cover detail and may be viewed as an average type of deposition amount encompassing a range of land types i.e. grasslands to forests. Viewed in this light, the fact that the deposition values fall between that estimated for forests and grasslands in this study makes the study reasonably congruent with this study.

Cuesta-Santos *et al.*, 2001 – the study encompasses a number of sites across Cuba, both relatively polluted and unpolluted. The range of deposition values are comparable to the grassland area in this study, although one of the areas is reported to be forested. It is notable that the area described to be under the influence of agricultural activity has annual nitrogen deposition from ammonia of approximately 11.5 kg N ha^{-1}. This is higher than the grassland value for this study but lower than the forest study.

Miller and Friedland, 1999 – This study is well suited for comparison since it also investigates deposition to a high elevation rural forested area subjected to regional pollution. Unfortunately, the dry deposition analysis for the study did not account for ammonia and nitrogen dioxide, making a comparison for this category difficult. However, the study by Miller and Friedland is one of few studies in which an attempt has been made to account for cloud droplet deposition. The fact that the site is subject to

Table 24 – Details of deposition amounts (kg N $ha^{-1}yr^{-1}$) calculated for this study in comparison with other comprehensive studies. Values in parantheses indicate ranges.

	This study		**Hesterburg *et al.*, 1996**	**Harrison & Allen (1991)**	**Cuesta-Santos *et al.*, 2001**	**Miller & Friedland (1999)**	**Fowler *et al.*, 1989**		**Fowler *et al.*, 1999**			
	Forest	Grassland	Switzerland – grass	Eastern England	Cuba*	NE USA forest	Scotland forest	Scotland moor	Scotland forest unpolluted	Scotland moor unpolluted	Europe forest polluted	Europe moor polluted
NO_2	1.6 (0-5)	0.5 (0-2)	2.8	2.8	1.42 (0.5-3.4)	-	4.2 NO_2+HNO_3	2.2 NO_2+HNO_3	0.6	0.6	1.9	1.8
HNO_3	3.7 (1-9)	1.9 (0-5)	1.4	1.6	-	2.15			-	-	-	-
NH_3	14.2 (10-40)	4.3 (0-15)	13.0	8.6	6.64 (3.8-11.5)	-	9.3	1.8	4.2	2.7	34.5	22.6
NH_4^+	1 (0-5)	0.2 (0-2)	1.1	0.9	1	0.06	-	-	1.0	0.3	4.9	1.8
NO_3^-	0.9 (0-3)	0.1 (0-1)	-	0.7	0.1	-	-	-	0.6	0.2	11.7	4.1
Total dry	**21.4 (10-60)**	**7 (0-25)**	**16.9**	**14.6**	**9 (5.4-16)**	**2.21 (<1 - 6)**	**13.5**	**4**	**6.4**	**3.8**	**53**	**30.3**
NH_4^+wet	3.7	3.7	3.4	3.9	5.8 (3.5-9.2)	2.64	4.5	4.5	2.4	2.4	11.3	11.3
NO_3^-wet	4.1	4.1	5.6	3.2	1.8 (1.4-2.6)	4.14	3.5	3.5	1.9	1.9	5.2	5.2
Total wet	**7.8**	**7.8**	**9.0**	**7.1**	**7.7**	**6.78 (6-9)**	**8**	**8**	**4.2**	**4.3**	**16.5**	**16.5**
Total wet + dry	**29.2 (18.6-63.8)**	**14.8 (8.3-32.2)**	**27.9**	**21.7**	**16.7 (9.9-35)**	**8.99**	**21.5**	**12**	**10.6**	**8.1**	**69.5**	**46.8**
NH_4^+ cloud	14	3.5	-	-	-	3.74	1.0	0.2	-	-	-	-
NO_3^- cloud	28	7	-	-	-	4.49	0.9	0.2	-	-	-	-
Total cloud	**42**	**10.5**	-	-	-	**8.23 (1-15)**	**1.9**	**0.4**	-	-	-	-
Total wet + dry + cloud	**71.2 (60-106)**	**25.3 (19-43)**	-	-	-	**17.22**	**23.4**	**12.4**	-	-	-	-

* values estimated from graphs

similar precipitation amounts as the present study site also makes a comparative evaluation of wet and cloud droplet deposition more reasonable. Wet deposition amounts are consistent with this study, as they are across most of the studies. However, the present study approximates cloud droplet deposition to be about six times greater than the North American study. The discrepancies relate largely to the amount of moisture transferred to the surface by the cloud droplets. In the North American study, the moisture transferred by cloud droplets varies between six and forty percent of that transferred by precipitation. In this study, the percentage varies from fifty to one hundred percent. In the North American study cloud droplet deposition velocities formed the basis for calculation, as opposed to this study in which amounts of moisture transferred were based on mist collectors.

Fowler *et al.*, 1989 – A discrepancy in cloud droplet deposition amounts is again apparent in comparison with this study. In the study by Fowler *et al.* 1989, moisture transferred is only ten percent of that transferred by precipitation. Regarding dry deposition, the study by Fowler *et al.* 1989 provides a useful comparison for evaluating the relative change between deposition to forests and deposition to shorter vegetation. The approximate increase by three and a half fold in the study by Fowler *et al.* 1989 is similar to the increase of approximately three fold in the present study. Furthermore, although absolute amounts deposited by cloud droplets differ for the two studies, the factor by which cloud droplet deposition to forests increases relative to that of shorter vegetation is similar. This study used a factor of four, which is similar to that recorded in the Scottish study.

Fowler *et al.*, 1999 – In this case, the deposition amounts to forests is increased by a factor of approximately 1.7 only relative to shorter vegetation. The analysis however, does not include nitric acid.

The comparative analysis above places the deposition amounts calculated in this study in context with other comprehensive studies. The amounts for this study are generally congruent with the other studies except for the cloud droplet deposition amounts.

CHAPTER 6 – FINAL DISCUSSION AND CONCLUSIONS

6.1 Final discussion

One of the widely discussed consequences of the alteration of nitrogen cycling by recent anthropogenic activities, is the acceleration of nitrogen fixation in landscapes and the delivery of nitrogen to waterbodies (Galloway *et al.,* 1995; Vitousek *et al.* 1997). Indeed, the relatively elevated nitrate concentrations in streams draining forested as opposed to grassland catchments in the study area (Nowicki, 1977) indicated the requirement for a better understanding of nitrogen dynamics at the study site. The exact source of increased nitrogen loading in water bodies has received considerable attention in recent years. A number of causes have been postulated, including the focus of this study, the atmospheric deposition component of nitrogen cycling.

This study has initiated a step towards the better understanding of nitrogen deposition against the backdrop of a relatively unique combination of atmospheric and landscape features. These include in particular the regional pollution/dispersion/deposition cycle and the juxtaposition of natural and exotic ecosystems. The study has indicated that at least in terms of annual inputs to the nitrogen cycle in the area, deposition from the atmosphere should be considered an important roleplayer. Average deposition amounts are similar to or at least approach nitrogen mineralisation amounts at nearby sites of 50-70 kg N ha^{-1} yr^{-1} (Ndala, 2001). This relative importance of the nitrogen deposition component in nitrogen cycles is consistent with other studies. For instance, Boyer *et al.* (2002) describe atmospheric deposition in the northeastern U.S.A. as being the largest single source input overall to an area comprised of a number of catchment types. Although within the overall study area the major source varied according to the land use type, it is relevant to this study that in forested areas, the atmospheric deposition component was significantly higher than other inputs. However, the quantification of atmospheric deposition amounts gives only a partial understanding of nitrogen cycling at the study site. Postulation of a possible link between nitrogen deposition amounts and stream nitrogen contents for instance, requires further work. This has been highlighted in

recent work by Mayer *et al.* (2002), in the same study area as Boyer *et al.* (2002), using isotopic discrimination methods to elucidate the source of riverine nitrate. The study indicated that in predominantly forested watersheds, the nitrate in rivers was derived almost exclusively from soil nitrification processes, with only potentially minor contributions from atmospheric deposition, despite the relative importance of nitrogen inputs from atmospheric deposition.

Besides the scope for future work described above, this study has also identified particular areas, in terms of the deposition amounts calculated in this study, that require more research. The technical, financial and time constraints of this study have required the use of a variety of methods and data sources to calculate deposition amounts. The methods and data sources vary in terms of reliability and the probable degree of accuracy with which they reflect actual deposition amounts. As such, a critical discussion on data reliability and levels of confidence associated with the deposition amounts is given below in order to highlight these areas for future work

Wet deposition amounts are well constrained, being based on actual measurements as opposed to inferences. The data used were collected close enough to the study site for there to be no reasonable doubt as to its suitability for the study. The dry deposition calculations are less well constrained than the wet deposition calculations, with inferential methods and estimates based on data from surrounding areas and literature being used. In certain instances data were used from sites close enough to the study site for there to be no reasonable question as to their validity in approximating conditions at the study site reasonably accurately. In other instances, data were used from further afield. To reasonably constrain the estimates in all cases, qualitative (e.g. degree of agricultural activity around the study site) and quantitative information (e.g. meteorological information) have been used as guidelines. Furthermore, the analysis has been expanded to include a range of conditions to produce high and low deposition estimates for the study area.

Of the components of dry deposition, the ammonia deposition component has the most uncertainty attached to it since the factors controlling ammonia concentrations and deposition velocities are relatively complex. The importance of any uncertainty associated with the ammonia amounts is also compounded by the fact that ammonia contributes a relatively high proportion to the total dry deposition amounts. However, in comparison to other studies, the high values indicated in this study are not unreasonable. ADUK (Acid Deposition in the United Kingdom) report annual nitrogen deposition amounts attributable to ammonia, over the majority of U.K. moorlands, of between 8 and 16 kg N ha^{-1} yr^{-1}. It is further stated in the report that deposition to forests is approximately 3.5 times these amounts. However, the importance of dry deposition of ammonia indicated by this study, highlights it as a prime candidate for future investigation.

Another significant contributor to deposition amounts is that associated with cloud droplets. There are relatively few cloud droplet deposition studies reported in the literature, but the two used for comparative purposes in this study have lower deposition amounts than those calculated for this study. As discussed in the previous section, the anomaly appears to be in the amounts of moisture deposited rather than the concentration component. The different methods used in this study and the comparative studies to account for moisture deposited lie behind the incongruous deposition values. As such the cloud droplet deposition values for this study have the least amount of certainty associated with them and further investigation is recommended. In particular, the liquid water content of intercepted clouds or mist in the study area needs to be ascertained in order that the inferential methods of cloud droplet deposition used in other studies can be used for this study site.

6.2 Conclusions

The conclusions that may be drawn from this study are summarised below in terms of the aim, objectives, hypotheses and key questions of the study.

Aim

The aim of the project is to quantify the deposition of nitrogen from the atmosphere to a predominantly grassland area as opposed to a predominantly forested area.

Total deposition amounts to forests of approximately 70 kg N ha^{-1} yr^{-1} exceed the approximately 25 kg N ha^{-1} yr^{-1} deposited to adjacent grasslands by a factor of almost three.

Objectives

To quantify and interpret wet deposition patterns for the period 1995 -1999 for the study areas.

Wet deposition amounts varied from 6.5 to 10.6 kg N ha^{-1} yr^{-1} with no obvious pattern across the years.

To quantify dry deposition for the period 1999 –2000 for the study areas.

Dry deposition amounts were approximated to 21 and 7 kg N ha^{-1} yr^{-1} for forests and grasslands respectively.

To better understand the role of nitrogen deposition and nitrogen loss on nutrient cycling in the selected sites.

Average deposition amounts are similar to or at least approach nitrogen mineralisation amounts at nearby sites of 50-70 kg N ha^{-1} yr^{-1}. Nitrogen fixation in savanna sites having nodule bacterial associations is shown to be approximately 19 kg N ha^{-1} yr^{-1}. These data show that the impact of nitrogen deposition on the functioning of the ecosystems is marked. The fact that deposition amounts to forests are almost three times that to grasslands may be significant in terms of the elevated nitrate concentrations observed in streams draining the forested areas relative to the grassland areas.

Hypotheses

Dry deposition of nitrogen from the atmosphere to a predominantly forested area is larger than that to a predominantly grassland area.
Evidence from the study supported this hypothesis.

Wet deposition of nitrogen to the study sites is larger than dry deposition.
The hypothesis was upheld for grasslands but was rejected for forests, although the wet deposition to grasslands in general terms approximately equals the dry deposition.

Key Questions

What chemical forms / species of nitrogen are deposited in the greatest amounts?
The relative importance in terms of deposition amounts for individual species differs for grasslands and forests. For grasslands the order of importance is nitrate cloud, ammonia dry, nitrate wet, ammonium wet, ammonium cloud, nitric acid, nitrogen dioxide and finally ammonium and nitrate particles. For forests, the increased turbulence and interceptive properties resulted in an increase in the amounts of cloud droplet and dry deposition. Cloud droplet deposition of nitrate significantly exceeds any other species/form of deposition. Cloud droplet deposition of ammonium and dry deposition of ammonia are approximately equal and are followed by the wet deposition components. The remainder of the dry components retain the same order as in the grasslands analysis, namely nitric acid first, followed by nitrogen dioxide and the particulates.

How has wet deposition changed over time?
No trend in wet deposition amounts is apparent. This is not surprising since five years of analysis is probably too short a time period for a trend to become apparent. Furthermore, it is unlikely that emission abatement procedures have changed significantly over the time period in question.

What are the factors controlling the amount of deposition?
For wet deposition, rainfall amounts appear to be the generally dominant factor controlling deposition. Slightly higher concentrations in winter months relative to

summer months may relate to the lowered regional dispersive qualities of the atmosphere in combination with a lower 'washout' of pollutants in winter. However these effect are suppressed by the more dominant role of rainfall. The concentration factor, however, becomes important in the month of September, indicating the emissions related to biomass burning as an important factor in wet deposition.

For dry deposition, this study has combined available data with estimates from literature to allow a comprehensive evaluation of nitrogen deposition. Possible controlling factors to deposition can only really be evaluated from the available data and the following discussion makes a distinction between the two methods. In general terms, the effects indicated in literature on dry deposition velocities, resulting from changes in the surface from forested to grassland area, were assumed in this study. The Hicks inferential model indicated that changes in meteorological conditions with the seasons result in seasonal variation of deposition velocities for nitric acid and particulates. Seasonal change in daylight hours also affects the period in which significant deposition occurs. Seasonal variation of deposition velocities for ammonia and nitrogen dioxide were not resolvable using approximations from literature. With regards concentrations, a seasonal variation in nitrogen dioxide concentrations is indicated by Prof. K. Pienaar (pers. comm. 2002). Seasonal variations in nitric acid concentrations indicated from literature were assumed. For ammonia, available data indicated no general trend in concentration with season. Evaluation of possible controlling factors using literature as a guideline also indicated no clear trend. As such, seasonal variation in ammonia concentration was not resolvable. For particulates, data was not available to evaluate seasonal concentration variation and as far as a possible evaluation using information from literature was concerned, no clear trend was inferrable. Overall, total dry deposition amounts have a seasonal variance that may be attributed to both concentration and deposition velocity variance. The latter undoubtedly relate to distinct meteorological changes with season. The controls on concentration variation are less clear. The unusual emission and dispersion qualities of the region should play an important role, but at present available data (i.e. nitrogen dioxide and ammonia concentrations from the DEBITS program) are not obviously reconcilable with these factors.

With regards cloud droplet deposition, seasonal variation in the amount of moisture deposited plays a role in controlling deposition amounts. Data were not available to evaluate seasonal variation in concentrations.

In a general context, the position of the study site is such that a number of factors on varying scales combine to produce a quite particular deposition scenario. The southern African region, and in particular the ETH region, is characterised by a complex emission and dispersion regime. The effects of this on the study site have been evaluated in a qualitative manner, but a better understanding of possible mesoscale pollution transport patterns, as well as the possible role of regional inversions in controlling pollution plumes and their dispersion and deposition qualities, is needed. The coincidence of forestry areas in a region of high humidity and mist formation has also been indicated by this study to be an important area for future work.

APPENDIX 1 – ATMOSPHERIC NITROGEN CHEMISTRY
(Details of chemical reactions numbered in figure 6.)

1) NO is formed in the combustion process e.g. fossil fuel burning and biomass burnung
2) NO reacts with ozone to form NO_2 in a few seconds
3) NO_2 is photolysed back to NO in a few minutes of being formed, with the production of ozone. This reverse reaction does not occur at night and NO levels usually drop as do ozone concentrations.
4) NO is also produced during lightning episodes.
5) The relatively stable NO_2 produces higher oxides of nitrogen – NO_3 – from the reaction with ozone (further adding to ozone depletion during the night). During the night the NO_3 radical takes over from the OH radical as being the most important oxidant in the atmosphere. In the daytime, NO_3 is not stable and is photolysed back to NO_2.
6) N_2O_5 is produced from NO_2 and NO_3. The reverse reaction may also occur. N_2O_5 is also unstable in sunlight and is photolysed to NO_2. The reaction to N_2O_5 at night depletes NO_2 at night. These nighttime reserves of N_2O_5 photolyse rapidly during the day resulting in rising NO_x concentrations.
7) HNO_3 is also the major conversion product of NO_x and is formed from the reaction of NO_2 with hydroxy (OH) radicals. This is an important process in the sunlit atmosphere with daytime conversion rates approaching 10 – 30% per hour in summer and 1 % in winter.
8) The night-time formation of the higher oxides of nitrogen is one of the more important conversion routes of NO_x to HNO_3 via the reaction of N_2O_5 with water. HNO_3 is slightly unstable and may photolysise back to NO_2, however this occurs at inconsequential rates.
9) HNO_3 is highly reactive and is readily taken up by soil, vegetation and water surfaces. Dry deposition is its major removal mechanism and HNO_3 has a lifetime in the atmosphere of a few hours to tens of hours.
10) HNO_3 reacts with NaCl to form particulate $NaNO_3$ and HCl.
11) HNO_3 reacts with NH_3 to form NH_4NO_3 particles.
12) N_2O_5 reacts with NaCl to form $NaNO_3$ and $ClNO_2$.

13) NH_3 stems from agricultural activity mostly. Because of its alkaline nature it is taken up readily by damp soil and vegetation giving it a relatively short lifetime in the atmosphere.

14) However, NH_3 may convert to ammonium particles by for instance reaction with sulphate to form ammonium sulphate,or with HNO_3 to form ammonium nitrate. Particles have a longer atmospheric lifetime in terms of dry deposition but they undergo effective wet deposition.

15) N_2O is the oxide of nitrogen present in the atmosphere at highest concentrations from the surface to the mid-stratosphere except in polluted regions. It is mainly sourced from the soil. It is un-reactive in the troposphere and makes its way into the stratosphere. Here it plays a role in ozone destruction along with NO from jet fuel. The oxides of nitrogen eventually transform to HNO_3 which leaks back into the troposphere and plays a role as previously described.

APPENDIX 2 -ADJUSTMENTS TO WET DEPOSITION AMOUNTS

a) An anomalously high April 1995 nitrate deposition amount results from a concentration outlier of 588 μeq. l^{-1}. This value has been changed to an average April concentration value of 12.67 μeq. l^{-1}.

b) An anomalously high February 1996 deposition amount results because only one rainfall event was sampled for, and this event had relatively high concentration values. Extrapolation of this high value to incorporate all the rainfall for the month gives an anomalously high deposition amount. An average value for February ammonium deposition obtained from averaging the February values from 1995,1997,1998 and 1999 is considered a better representation. The same type of averaging was done for December since no sampling was done for this month in 1996. Furthermore an ammonium value of 217 μeq. l^{-1} in March was considered to be an outlier and changed to an average March value of 10.5μeq. l^{-1}. An ammonium value of 210 μeq. l^{-1} in October was also considered an outlier and changed to 17.6 μeq. l^{-1}. A nitrate value of 122.4 μeq. l^{-1} in October of was also changed to an average type value of 23.78 μeq. l^{-1}.

APPENDIX 3 – SUMMARY OF GAS AND PARTICLE CONCENTRATIONS (μg N m^{-3})

		Sum	Aut	Win	Spr	av.
NO_2	High	1.90	1.40	1.10	1.10	1.4
	Low	1.00	0.70	0.60	0.60	0.70
	Likely	1.40	1.00	0.80	0.80	1.00
HNO_3	High	0.83	0.62	0.41	0.62	0.62
	Low	0.24	0.18	0.12	0.18	0.18
	Likely	0.53	0.40	0.27	0.40	0.40
NH_3	High	2.22	2.22	2.22	2.22	2.22
	Low	1.96	1.96	1.96	1.96	1.96
	Likely	1.70	1.70	1.70	0.70	1.70
NH_4^+	High	1.50	1.50	1.50	1.50	1.50
	Low	0.10	0.10	0.10	0.10	0.10
	Likely	0.66	0.66	0.66	0.66	0.66
NO_3^-	High	1.00	1.00	1.00	1.00	1.00
	Low	0.10	0.10	0.10	0.10	0.10
	Likely	0.56	0.56	0.56	0.56	0.56

APPENDIX 4 – DRY DEPOSITION AMOUNTS

High, low and likely dry deposition amounts (kg N ha^{-1}) for the various nitrogen species are tabulated below.

		High		Low		Likely	
		grass	forest	grass	forest	grass	forest
NO_2	Summer	0.52	1.80	0.08	0.28	0.16	0.55
	Autumn	0.39	1.32	0.03	0.10	0.12	0.41
	Winter	0.30	1.04	0.05	0.00	0.1	0.32
	Spring	0.30	1.04	0.00	0.00	0.1	0.32
	Annual	1.51	5.20	0.16	0.38	0.48	1.61
HNO_3	Summer	1.61	3.21	0.14	0.29	0.64	1.28
	Autumn	1.34	2.49	0.12	0.24	0.54	1.07
	Winter	0.48	0.98	0.04	0.09	0.20	0.40
	Spring	1.22	2.42	0.11	0.22	0.48	0.97
	Annual	4.65	9.1	0.41	0.84	1.86	3.71
NH_3	Summer	1.23	4.03	0.13	2.41	1.08	3.55
	Autumn	1.23	4.03	0.13	2.41	1.08	3.55
	Winter	1.23	4.03	0.13	2.41	1.08	3.55
	Spring	1.23	4.03	0.13	2.41	1.08	3.55
	Annual	4.92	16.12	0.52	9.64	4.32	14.20
NO_3^-	Summer	0.39	0.99	0.09	0.09	0.04	0.28
	Autumn	0.36	0.89	0.09	0.09	0.04	0.25
	Winter	0.24	0.59	0.06	0.06	0.03	0.17
	Spring	0.28	0.70	0.07	0.07	0.03	0.19
	Annual	1.27	3.17	0.22	0.22	0.14	0.89
NH_4^+	Summer	0.59	1.48	0.00	0.01	0.05	0.33
	Autumn	0.53	1.34	0.00	0.01	0.05	0.29
	Winter	0.36	0.89	0.00	0.01	0.03	0.20
	Spring	0.41	1.05	0.00	0.01	0.04	0.23
	Annual	1.89	4.76	0.00	0.04	0.17	1.05

REFERENCE LIST

Aber, J.D., Nadelhoffer, K.J., Streudler, P. and Mellilo, J.M. (1989). Nitrogen saturation in northern forest ecosystems. *Bioscience*, 39: 378 – 387.

Acid Deposition in the United Kingdom (ADUK)1992-1994. (1997). Fourth Report of the Review Group on Acid Rain. AEA Technology plc.

Acker, K., Möller, D., Wieprecht, W. and Naumann, St. (1995). Mt. Brocken, a site for a cloud chemistry measurement programme in Central Europe. *Water, Air and Soil Pollution*, 85: 1979-1984.

Adema, E.H., Mejstrik, V. and Binek, B. (1992). The determination of NH_3 – concentration gradients in a spruce forest using a passive sampling technique. *Water, Air and Soil Pollution*, 69: 321-335.

Agren, G.I. and Bosatta, E. (1988). Nitrogen saturation of terrestrial ecosystems. *Environmental Pollution*, 54: 185 – 197.

Allen, A.G., Harrison, R.M. and Wake, M.T. (1988). A meso-scale study of the behaviourof atmospheric ammonia and ammonium. *Atmospheric Environment*, 22: 1347-1353.

Andersen, H.V., Hovmand, M.F., Hummels, H.O.J and Jensen, N.O. (1993). Measurement of the ammonia flux to a spruce stand in Denmark. *Atmospheric Environment,* 27A: 189-210.

Andersen, H.V. and Hovmand, M.F. (1995). Ammonia and nitric acid dry deposition and throughfall. *Water, Air and Soil Pollution,* 85: 2211-2216.

Asman, W.H., Sutton, M.A. and Schjorring, J.K. (1998). Ammonia: emission, atmospheric transport and deposition. *New Phytologist*, 139: 27-48.

Ayers, G.P., Malfroy, H., Gillett, R.W., Higgins, D., Selleck, P.W. and Marshall, J.C. (1995). Deposition of acidic species at a rural location in New South Wales, Australia. *Water, Air and Soil Pollution,* 85: 2089-2094.

Benner, C.L., Eatough, D.J., Eatough, N.L. and Bhardwaja, P. (1991). Composition of annular denuder and filter pack collection of HNO_3 (g), HNO_2 (g), SO_2 (g) and particulate phase nitrate, nitrite and sulfate in the south western desert. *Atmospheric Environment*, 25A: 1537-1545.

Beswick, K.M., Hargreaves, K., Gallagher, M.W., Choularton T.W, and Fowler, D. (1991). Size resolved measurements of cloud droplet deposition velocity to a forest using an eddy correlation technique. *Quarterly Journal of the Royal Meteorological Society,* 117: 623-645.

Böttger, A., Ehhalt, D.H. and Gravenhorst, G.(1978). Atmosphärische Kreisläufe von Stickoxiden und Ammoniak, report no. 1558. Kernforschungsanlage Jülich, Germany.

Boyer, E.W., Goodale, C.L., Jaworski, N.A. and Howarth, R.W. (2002). Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A. *Biogeochemistry,* 57/58: 137-169.

Brimblecombe, P. and Clegg, S.L. (1988). The solubility and behaviour of acid gases in the marine aerosol. *Journal of Atmospheric Chemistry,* 8: 1-18.

Brook, J.R., Sirois, A. and Clarke, J.F. (1995). Comparison of dry deposition velocities for SO_2, HNO_3, and SO_4^{2-} estimated with two inferential models. *Water, Air and Soil Pollution,* 87:205-218.

Bytnerowicz, A., Miller, P.R. and Olszyk, D.M. (1987). Dry deposition of nitrate, ammonium, and sulfate to a Ceanothus crassfolius canopy and surrogate surfaces. *Atmospheric Environment,* 2: 1749 – 1757.

Bytnerowicz, A. and Fenn, M.E. (1996). Nitrogen deposition in California forests. A review. *Environmental Pollution*, 92: 127-146.

Bytnerowicz, A., Godzik, S., Poth, M., Anderson, I., Szdzuj, J., Tobias, C., Macko, S., Kubiesa, P., Staszewski, T. and Fenn, M. (1999). Chemical composition of soil and vegetation in forests of the Silesian Beskid Mountains, Poland. *Water, Air and Soil Pollution,* 116: 141-150.

Cadle, S.H., Countess, R.J. and Kelly, N.A. (1982). Nitric acid and ammonia in urban and rural locations. *Atmospheric Environment,* 16: 2501- 2506.

Cadle, S.H. (1985). Seasonal variation in nitric acid, nitrate strong aerosol acidity, and ammonia in urban areas. *Atmospheric Environment*, 19: 181-188.

Cape, J.N. and Unsworth, M.H. (1987). Deposition, uptake and residence of pollutants. In: *Air Pollution and Plant Metabolism*. Schulte-Hostede, S., Darral, N.M., Blank, L.W. and Wellburn, A.R., editors. Elsevier Applied Science.London, 1987.

Cole, D.W. (1992). Nitrogen chemistry, deposition, and cycling in forests. In: *Ecological Studies 91, Atmospheric deposition and Forest Nutrient Cycling.* Johnson, D.W. and Lindberg, S.E., editors. Springer –Verlag, New York.

Cuesta-Santos, O., Collazo, A., Wallo, A., Labrador, R., Gonzalez, M. and Ortiz, P. (2001). Deposition of atmospheric nitrogen compounds in humid tropical Cuba. In: *Optimizing Nitrogen Management in Food and Energy production and Environmental protection : proceedings of the 2nd International nitrogen Conference on Science and Policy. The Scientific World* 1(S2), 238-244.

Dempster, J.P. and Manning, W.J., editors. (1988). Special Issue: Excess Nitrogen Deposition. *Environmental Pollution*, 54: 185–197.

Dise, N.B. and Wright, R.F. (1995). Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management*, 41: 65-80.

Dollard, G.J., Davies, T.J. and Lindstom, J.P.C. (1987) Measurement of dry deposition of some trace gases. In: *Physico-chemical Behaviour of Atmospheric Pollutants.* Angelleti, G. and Restelli, G., editors. Reidel, Dordrecht. 470-479.

Dolske, A.D., and Gatz, D.F. (1985). A field inter-comparison of methods for the measurement of particle and gas dry deposition. *Journal of Geophysical Research*, 90: 2076-2084.

Durka, W., Schulze, E.D., Gebauer, G. and Voerteliw, S. (1994). Effects of forest decline on uptake and leaching of deposited nitrate determined from ^{15}N and ^{18}O measurements. *Nature,* 372: 765-767.

Duyzer, J. (1994). Dry deposition of ammonia and ammonium aerosols over heathland. *Journal of Geophysical Research,* 99: 18757 – 18763.

Erisman, J.W., de Leew, F.A.A.M. and van Aalst, R.M. (1989). Deposition of the most acidifying components in the Netherlands during the period 1980-1986. *Atmospheric Environment,* 23: 1051-1062.

Erisman, J.W. (1993). Acid deposition to nature areas in the Netherlands: Part 1. Methods and results. *Water, Air and Soil Pollution,* 71: 51-80.

Erisman, J.W. and Wyers, G.P. (1993). Continuous measurements of surface exchange of SO_2 and NH_3: implications for their possible interaction in the depositionary process. *Atmospheric Environment*, 27A: 1937-1949.

Eskom. (1994). Statistical Yearbook for 1993.

Farquhar, G.D., Firth, P.M., Wetselaar, R. and Weir, B. (1980). On the gaseous exchange of ammonia between leaves and the environment: determination of the ammonia compensation point. *Plant Physiology*, 66: 710-714.

Ferm, M. (1979). Method for determination of atmospheric ammonia. *Atmospheric Environment,* 13: 1385-1393.

Finlayson-Pitts, B.J., Ezell, M.J. and Pitts Jr., J.N. (1989). Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous and $ClONO_2$. *Nature*, 337: 241-244.

Fletchard, C.R. and Fowler, F. (1998). Atmospheric ammonia at a moorland site. I: The meteorological control of ambient ammonia concentrations and the influence of local sources. *Quarterly Journal of the Royal Meteorological Society,* 124: 733-757.

Fletchard, C.R. and Fowler, F. (1998). Atmospheric ammonia at a moorland site. II: Long-term surface-atmosphere micrometeorological flux measurements. *Quarterly Journal of the Royal Meteorological Society,* 124: 759-791.

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., Fletchard, C., Skibe, U., Coyle, M. and Neil Cape, J. (1998). The atmospheric budget of oxidized nitrogen and its role in ozone formation and deposition. *New Phytologist*, 139: 11-23.

Fowler, D., Fletchard, C.R., Milford, C., Hargreaves, K.A., Storeton-West, R.L., Nemitz, E. and Sutton, M.A. (1996). Measurements of pollutant concentrations and deposition fluxes to moorland at Auchencorth Moss in southern Scotland. 1995. April 1996. 47pp. Commission of the European Communities.

Fowler, D., Leith, I.D., Binnie, J., Crossley, A., Inglis, D.W.F., Choularton, T.W., Gay, M., Longhurst, J.W.S. and Conland, D.E. (1995). Orographic enhancement of wet deposition in the United Kingdom: continuous monitoring. *Water, Air and Soil Pollution*, 85: 2107-2112.

Fowler, D., Duyzer, J.H. and Baldocchi, D.D. (1991). Inputs of trace gases, particles and

cloud droplets to terrestrial surfaces. *Proceedings of the Royal Society of Edinburgh,* 97B: 35-39.

Fowler, D., Cape, J.N. and Unsworth, M.H. (1989). Deposition of atmospheric pollutants on forests. *Philosophical Transactions of the Royal Society of London, B,* 324: 247-265.

Fowler, D., Leith, I.D., Cape, J.N., Jones, A., Choularton, T.W. and Gay, M.J. (1988). Wet deposition with altitude: The role of orographic cloud. In: *Acidic deposition at high elevation sites.* Unsworth, M.H. and Fowler, D. editors. Kluwer, Dodrecht, The Netherlands. 231-259.

Fricke, W., Beilke, S., Bieber, E., Uhse, K. and Wallasch, M. (1997). Results of daily precipitation analyses in Germany from 1982 to 1995 (in German). Texte 10/97. Umweltbundesamt, Berlin.

Gallagher, M.W., Beswick, K.M., Duyzer, J., Westrate, H., Choularton, T.W., and Hummelshoj, P. (1997). Measurements of aerosol fluxes to Speulder Forest using a micrometeorological technique. *Atmospheric Environment*, 31: 359 – 373.

Galloway, J. N., Scheslinger, W. H., Levy II, H. L., Michaels, A. and Schnoor, J. L. (1995). Nitrogen fixation: anthropogenic enhancement – environmental response. *Global Biogeochemical Cycles*. 9: 235 – 252.

Galloway, J.N. and Gaudry, A. (1984). The composition of precipitation at Amsterdam Island, Indian Ocean. *Atmosphere Environment*, 18: 2649 – 2656.

Galy-Lacaux, C., Carmichael, G.R., Song, C.H., Lacaux, J.P., Al Ourabi, H. and Modi, A.I. (2001). Heterogenous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations. *Journal of Geophysical Research,* 106 (D12): 12559 – 12578.

Garland, J.A. (1978). Dry and wet removal of sulphur from the atmosphere. *Atmospheric Environment,* 12: 349-362.

Georgii, H.W. and Lenhard, U. (1978). Contribution to the atmospheric NH_3 budget. *Pure Applied Geophysics*, 116: 385-391.

Gillett, R.W., Ayers, G.P., Selleck, P.W., Tuti, M.W.H. and Harjanto, H. (2000). Concentrations of nitrogen and sulfur species in gas and rainwater from six sites in Indonesia. *Water, Air and Soil Pollution,* 120: 205-215.

Goethel, M. (1980). Untersuchung ausgewählter Quellen und Senken des atmosphärischen Ammoniaks mit einem neuen Probenahmeverfahren. Diploma-thesis. Institut für Meteorologie und Geophsik, Universität Frankfurt (Main), Germany.

Goulding, K.W.T., Bailey, N.J., Bradbury, N.J., Hargreaves, P., Howe, M., Murphy, D.V., Poulton, P.R. and Willison, T.W. (1998). Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes. *New Phytologist*, 139: 49-58.

Grosjean, D. and Bytnerowicz, A. (1993). Nitrogen air pollution at a southern California mountain forest smog receptor site. *Atmospheric Environment*, 27A: 483-492.

Hansen, B. (1999). Weekly measurements over one year of ammonia concentrations and surface exchange fluxes at a Danish heathland with passive wind-vane flux samplers in an aerodynamic gradient concentration. *Water, Air and Soil Pollution*, 113: 357-370.

Hanson, P.J., Rott, K., Taylor, G.E. Jr. Gunderson, C.A., Lindberg, S.E. and Ross-Todd, B.M. (1989). NO_2 deposition to elements representative of a forest landscape. *Atmospheric Environment*. 23: 1783 – 1794.

Hanson, P.J. and Lindberg, S.E. (1991). Dry deposition of reactive nitrogen compounds: a review of leaf, canopy, and non-foliar measurements. *Atmospheric Environment,* 25: 1615-1634.

Hara, H., Kitamura,M., Mori, A., Noguchi,I., Ohizumi, T., Seto, S., Takeuchi, T. and Deguchi, T. (1995). Precipitation chemistry in Japan 1989-1993. *Water, Air and Soil Pollution,* 85:2307-2312.

Harrison, R.M. and Allen, A.G. (1991). Scavenging ratios and deposition of sulphur, nitrogen and chlorine species in eastern England. *Atmospheric Environment*. 25 A: 1719- 1723.

Harrison , R.M., Peak, J.D. and Collins, G.M. (1996). Tropospheric cycle of nitrous acid. *Journal of Geophysical Research,* 101: 14429-14439.

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: 21-34.

Hicks, B.B., Baloocchi, D.D., Meyer, T.P., Hostler, Jr. P. and Matt, D.R. (1987). A preliminary multiple resistance routine for deriving dry deposition velocity from measured quantities. *Water, Air and Soil Pollution*, 36: 311-330.

Hill, A.C. (1971). Vegetation: a sink for atmospheric pollutants. *Journal of Air Pollution Control Association*, 21: 341-346.

Hovmand, M.F. and Andersen, H.V. (1995). Nine years of measurements of atmospheric nitrogen and sulphur deposition to Danish forest. *Water, Air and Soil Pollution,* 85: 2205-2210.

Houdijk, A.L.F.M. (1990). Effects due to sulfur and nitrogen deposition to forest and heather vegetation. University of Nijmegen. The Netherlands.

Huebert, B.J. and Robert, C.H. (1985). The dry deposition of nitric acid to grass. *Journal of Geophysical Research*, 90: 2085-2090.

Huntzicker, J.J., Cary, R.A. and Ling, C.S. (1980). Neutralisation of sulphuric acid aerosol by ammonia. *Environmental Science and Technology*, 14: 819-824.

Hutchinson, G.L., Millington, R.J. and Peters, D.B. (1972). Atmospheric ammonia: absorption by plant leaves. Science. 175: 771-772.

Iseman, T.M., Zak, D.R., Holmes, W.E. and Merril, A.G. (1999). Revegetation and nitrate leaching from Lake States Northern Hardwood Forests following harvest. *Soil Science Society of America Journal*, 63.

Johansson, C. (1987). Pine forest : A negligible sink for atmospheric NOx in rural Sweden. *Tellus,* 39: 426-438.

Jordan, C.E. and Talbot, R.W. (2000). Water-soluble nitrogen at the New Hampshire sea coast: HNO_3, aerosols, precipitation, and fog. *Journal of Geophysical Research*, 105: 26403 – 26431.

Junge, C.E. (1963). Air Chemistry and Radioactivity. Academic Press, New York.

Kasper, A. and Puxbaum, H. (1998). Seasonal variation of SO_2, HNO_3,NH_3, and selected aerosol components at Sonnblick (3106 m a.b.s.l.). *Atmospheric Environment*, 32:3925-3939.

Keeler, G.L., Spengler,J.D. and Castillo, R.A. (1991). Acid aerosol measurements at a suburban Conneticut site. *Atmospheric Environment*, 25A: 681-690.

Langford, A.O. and Fehsenfeld F.C. (1992). Natural vegetation as a source or sink for Atmospheric ammonia: A case study. *Science*, 255: 581-583.

Langford, A.O., Fehsenfeld, F.C., Zachariassen, J. and Schimmel, D.S. (1992). Gaseous ammonia fluxes and background concentrations in terrestrial ecosystems of the United States. *Global Biogeochemical Cycles*, 4: 459-483.

Lebel, P.J., Huebert, B.J., Schiff, H.I., Vay, S.A., van Bramer, S.E. and Hastie, D.R. (1990). Measurements of tropospheric nitric acid over the Western United States and North-eastern pacific ocean. *Journal of Geophysical Research,* 95: 10199 – 10204.

Lee, D.S., Gollard, G.J. Derwent, R.G. and Pepler, S. (1999). Observations on gaseous and aerosol components of the atmosphere and their relationships. *Water, Air and Soil Pollution,* 113: 175-202.

Lefer, B.L. and Talbot, R.W. (1999). Nitric acid and ammonia at a rural northeastern U.S. site. *Journal of Geophysical Research*, 104: 1645-1661.

Lefer, B.L. and Talbot, R.W. (2001). Summertime measurements of aerosol nitrate and ammonium at a northeastern U.S. site. *Journal of Geophysical Research*, 106, D17: 20365 – 20378.

Lenhard, U. and Gravenhorst,G. (1980). Evaluation of ammonia fluxes into the free atmosphere over West Germany. *Tellus,* 32: 48-55.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S. and Johnson, N.M. (1977). Biochemistry of a Forested Ecosystem. Springer-Verlag, Berlin.

Lindberg, S.E., Bredemeir, M., Schaefer, D.A. and Qi, L. (1990). Atmospheric concentration and deposition during growing season in conifer forests in the United States and West Germany. *Atmospheric Environment*, 24A: 2207-2220.

Louw, J.H. and Scholes, M. (2002). Forest site classification and evaluation: a South African perspective. *Forest Ecology and Management*, 171: 153-168.

Lovett, G.M. (1992). Atmospheric Deposition and Canopy Interactions of Nitrogen. In: *Ecological Studies 91, Atmospheric Deposition and Forest Nutrient Cycling.*. Johnson, D.W. and Lindberg, S.E., editors. Springer -Verlag, New York.

Lovett, G.M. and Rueth, H. (1999). Soil nitrogen transformations in beech and maple

stands along a nitrogen deposition gradient. *Ecological Applications*, 9: 1330-1344.

Maenhaut, W., Onjia, A., Xuguang, C., Cafmeyer, J., Pashnyska, V., Vermeylen, R., Vas, G. and Claeys, M. (2002). Speciation of water-soluble organic aerosol at Skukuza, during SAFARI 2000. Abstracts, IAMAS, CACGP and IGAC Joint International Symposium on Atmospheric Chemistry within the Earth System, Crete, Greece.

Maggs, R., Wahid, A., Shamsi, S.R.A. and Ashmore, M.R. (1995). Effects of ambient air pollution on wheat and rice yield in Pakistan. *Water, Air and Soil Pollution,* 85: 1311-1316.

Makar, P.A., Wiebe, H.A., Staebler, R.M., Li, S.M. and Anlauf, K. (1998). Measurement and modelling of particle nitrate formation. *Journal of Geophysical Research*, 103 (D11): 13095 – 13110.

Matsumoto, M. and Okita, T. (1998). Long term measurements of atmospheric gaseous and aerosol species using an annular denuder system in Nara, Japan. *Atmospheric Environment,* 32: 1419-1425.

Mayer, B., Boyer, E.W., Goodale, C., Jaworski, N.A., Van Breemen, N., Howarth, R.W., Seitzinger, S., Billen, G., Lajtha, K., Nadelhoffer, K., van Dam, D., Hetling, L.J., Nosal, M. and Paustian, K. (2002). Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.A.: Isotopic constraints. *Biogeochemistry,* 57: 171-197.

Mayer, R. and Ulrich, B. (1974). Conclusions on the filtering action of forests from ecosystem analysis. *Oceologia*, 9: 157-168.

McLaughlin, J.W., Fernandez, I.J. and Richards, K.J. (1996). Atmospheric deposition to a low-elevation spruce-fir forest, Maine, USA. *Journal of Environmental Quality*, 25: 248-249.

Meixner, F.X., Muller, P., Aheimer, G. and Hoeken, K.D. (1985). Measurements of gaseous nitric acid and particulate nitrate. In*: Pollutant Cycles and Transport: Modelling and Field Experiments*. De Leew, F.A.A.M. and van Egmonds, N.D., editors. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands. 103-119.

Metcalfe, S.E., Fowler, D., Derwent, R.G., Sutton, M.A., Smith, R.I. and Whyatt, J.D. (1999). Spatial and temporal aspects of nitrogen deposition. In: *The impact of nitrogen deposition on natural and semi-natural ecosystems*. Langan, S.J., editor. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Milford, C., Hargreaves, K.J., Loubet, B. and Cellier, P. (2001). Fluxes of NH_3 and CO_2 over upland moorland in the vicinity of agricultural land. *Journal of Geophysical Research*, 106: 24169-24181.

Miller, E.K. and Friedland, A.J. (1999). Local climate influences on precipitation, cloud water, and dry deposition to an Adirondack sub-alpine forest: Insights from observations 1986-1996. *Journal of Environmental Quality,* 28: 270-277.

Montgomery, E., Coyne, M.S., and Thomas, D.W. (1997). Denitrification can cause variable NO_3^- concentrations in shallow groundwater. *Soil Science*, 162: 148-156.

Moody, J.L., Pszenny, A.A.P, Gaudry, A., Keene, W.C., Galloway, J.N. and Polian, G. (1991). Precipitation composition and its variability in the southern Indian Ocean: Amsterdam Island, 1980 – 1987. *Journal of Geophysical Research*, 96: 20769-20786.

Mphepya, J.N. (2002). Atmospheric deposition characteristics of sulphur and nitrogen compounds in South Africa. Unplubished Ph.D. thesis, Potchefstroom University, South Africa.

Mrose, H. (1966). Measurements of pH and chemical analysis of rain, snow and fog water. *Tellus*, 18: 266-270.

Munger, J.W., Jacob, D.J., Waldman, J.M. and Hoffman, M.R. (1983). Fog water chemistry in an urban atmosphere. *Journal of Geophysical Research*, 88: 5109-5121.

Naik, S.M., Momin, G.A., Pillai, A.G., Safai, P.D., Rao, P.S.P. and Khemani, L.T. (1995). Precipitation Chemistry at Sinhagad – a hill station in India. *Water, Air and Soil Pollution*, 85: 2161-2166.

Ndala, S. M. (2001). Soil properties and processes driving the observed leaching of nitrate in the forested catchments of the eastern escarpment of South Africa. Unpublished M.Sc. dissertation, University of the Witwatersrand , South Africa.

Neff, J.C., Holland, E.A., Dentener, McDowell, W.H. and Russel, K.M. (2002). The

origin, composition and rates of organic nitrogen deposition; A missing piece of the nitrogen cycle? *Biogeochemistry*, 57/58: 99-136.

Nilles, M.A. and Conley, B.E. (2001). Changes in the chemistry of precipitation in the US 1981-1998. *Water, Air and Soil Pollution,* 130: 409-414.

Nowicki, T.E. (1997). The impact of plantations of pines on the chemical properties of the soils and stream waters in South African upland catchments. Unpublished Ph.D. thesis. University of Cape Town, South Africa.

Oberholzer, B., Volken, M., Collett Jr. J.L., Staehelin, J. and Waldvogel, A. (1993). Pollutant concentrations and below-cloud scavenging of selected N (III) species along a mountain slope. *Water, Air and Soil Pollution,* 68: 59-73.

Oddie, B.C.V. (1962). The chemical composition of precipitation at cloud levels. *Quarterly Journal of the Royal Meteorological Society*, 88: 535-538.

Olbrich, K.A. (1993). The chemistry and frequency of mist events on the Eastern Transvaal Escarpment. CSIR report No 18-90325-5-0 to the Department of Water Affairs.

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: 769 – 781.

Parrish, D.D., Norton, R.B., Bollinger, M.J., Liu, S.C., Murphy, P.C., Albritton, D.L. and Fehsenfeld, F.C.(1986). Measurements of HNO_3 and NO_3^- particulates at a rural site in the Colorado mountains. *Journal of Geophysical Research,* 91 (D5): 5379-5393.

Patz, H.W., Corsmeier, U., Glaser, K., Vogt, U., Kalthoff, N., Klemp, D., Kolahgar, B., Lerner, A., Neininger, B., Schmitz, T., Schultz, M.G., Stemr, J. and Volz-Thomas, A. (2000). Measurements of trace gases and photolysis frequencies during SLOPE96 and a coarse estimate of the local OH concentration from HNO_3 formation. *Journal of Geophysical Research*, 105: 1563-1583.

Penner, J.E., Atherton, C.S., Dignon, J., Ghan, S.J., Walton, J.J. and Hameed, S. (1991). Tropospheric nitrogen: a three dimensional study of sources, distributions and deposition. *Journal of Geophysical Research*, 96: 959 – 990.

Peters, K. and Bruckner-Schatt, G. (1995). The dry deposition of gaseous and particulate

nitrogen compounds to a spruce stand. *Water, Air and Soil Pollution*, 85: 2217-2222.

Petrenchuk, O.P. and Selezneva, E.S. (1970). Chemical composition of precipitation in regions of the Soviet Union. *Journal of Geophysical Research*, 75: 3629-3634.

Pierson, W.R.W., Brachaczek, W., Gorse, R.A., Japar Jr. S.M., Norbeck, J.M. and Keeler, G.J. (1989). Atmospheric acidity measurements on Allegheny Mountain and the origins of ambient acidity in the North-eastern United States. *Atmospheric Environment*, 23: 431-459.

Pryor, S.C., Barthelmie, R.J., Sorensen, L.L. and Jensen,B. (2001). Ammonia concentrations and fluxes over a forest in the Midwestern USA. *Atmospheric Environment,* 35: 5645-5656.

Raven, P.H., Evert, R.F. and Curtis, H. (1982). Biology of Plants. Worth Publishers Inc., New York.

Roberts, J.M., Fehenseld, F.C., Liu, S.C., Bollinger, M.J., Hahn, C., Albritton, D.L. and Sievers, R.E. (1984). Measurements of aromatic hydrocarbon ratios and NO_x concentrations in the rural troposphere: Observations of air mass photochemical aging and NO_x removal. *Atmospheric Environment,* 18: 2421-2432.

Samara, C. and Tsitouridou, R. (1999). Fine and coarse ionic aerosol components in relation to wet and dry deposition. *Water, Air and Soil Pollution,* 120: 71-86.

Schaap, M., Muller, K. and ten Brink, H.M. (2002). Constructing the European aerosol nitrate concentration field from quality analysed data. *Atmospheric Environment*, 36: 1323-1335.

Sehmel , G.A. (1980). Particle and gas dry deposition: a review. *Atmospheric Environment,* 14: 983-1011.

Senger, J., Hertel, O. and Palgrem, F. (1988). Urban Air Pollution – European Aspects. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Sievering, H., Kelly, T., McConville, G., Seibold, C. and Turnipseed, A. (2001). Nitric acid dry deposition to conifer forests: Niwot Ridge spruce-fir-pine study. *Atmospheric Environment,* 35: 3851-3859.

Singh, R.K. and Agrawal, M. (2001). Characterisation of wet and dry deposition in the downwind of industrial sources in a dry tropical area. In: *Optimizing Nitrogen Management in Food and Energy Production and Environmental Protection* : Proceedings of the 2nd International Nitrogen Conference on Science and Policy. *The Scientific World* 1(S2), 266-274.

Sinn, J.P., Pell, E. and Kabel, R.C. (1984). Uptake rate of nitrogen dioxide by potatoe plants. *Journal of Air Pollution Control Association,* 34: 668-669.

Sirois, A., Vet, R. and Mac Tavish, D. (2001). Atmospheric deposition to the Turkey Lakes watershed: Temporal variations and characteristics. *Ecosystems*, 4:503-513.

Soderlund, R. (1981). Dry and wet deposition of nitrogen compounds. In: *Terrestrial Nitrogen Cycles. Processes, Ecosystem Stratergies and Management Impacts. Ecological Bulletins*. Clark, F.E. and Roswell, T., editors. Swedish Natural Science Research Council, Stockholm. 33:123-130.

Spindler, G., Teichmann, U. and Sutton, M.A. (2001). Ammonia dry deposition over grassland – micrometeorological flux-gradient measurements and bi-directional flux calculations using an inferential model. *Quarterly Journal of the Royal Meteorological Society*, 127: 795 –814.

Stelson, A.W., Friedlander, S.K. and Seinfeld, J.H. (1979). A note on the equilibrium relationship between ammonia and nitric acid and particulate ammonium nitrate. *Atmospheric Environment,* 13: 369-371.

Stelson, A.W. and Seinfeld, J.H. (1982). Relative humidity and temperature dependance of the ammonium nitrate dissociation constant. *Atmospheric Environment*, 16: 982 – 993.

Stulen, I., Perez-Soba, M., De Kok, L.J. and Van Der Eeden, L. (1998) Impact of gaseous nitrogen deposition on plant functioning. *New Phytologist,* 139: 61-70.

Sutton, M.A., Fowler, D.and Moncrieff, J.B. (1993a). The exchange of atmospheric ammonia with vegetated surfaces. I. Unfertilised vegetation. *Quarterly Journal of the Royal Meteorological Society,* 119: 1023-1045.

Sutton, M.A., Fowler, D. Moncrieff, J.B and Storeton-West, R.L. (1993b). The exchange of atmospheric ammonia with vegetated surfaces. II. Fertilized vegetation. *Quarterly Journal of the Royal Meteorological Society,* 119: 1047-1070.

Sutton, M.A., Pitcairn, C.E.R. and Fowler, D. (1993c). The exchange of ammonia between the atmosphere and plant communities. *Advances in Ecological Research*, 24: 301-393.

Sutton, M.A., Schorring, J.K. and Wyers, G.P. (1995). Plant-atmosphere exchange of ammonia. *Philosophical Transactions of the Royal Society London*, 351: 261-278.

Sutton, M.A., Milford, C., Dragosits, U., Singles, R., Fowler, D., Ross, C., Hill, R., Jarvis, S.C., Pain, B.P., Harrison, R., Moss, D., Webb, J., Espenhahn, S.E., Halliwell, C., Lee, D.S., Wyers, G.P., Hill, J. and Apsimon, H.M. (1997). Gradients of atmospheric ammonia concentrations and deposition downwind of ammonia emissions : first results of the ADEPT Burrington Moor experiment. In: *Gaseous Exchange with Grassland Systems*. Jarvis, S.C. and Pain, B.P., editors. Wallingford, Oxon, U.K: CAB International: 131-139.

Szarek, G. (1995). Sulphur and nitrogen input to the Ratanica forested catchment (Carpathian foothills, Southern Poland). *Water, Air and Soil Pollution,* 85: 1765-1770.

Tang, I.N. (1980). On the equilibrium partial pressures of nitric acid and ammonia in the atmosphere. *Atmospheric Environment,* 14: 819-828.

Taylor, G.E., Jr., Owens, J.G., Grizzard, T. and Selvidge, W.J. (1993). Atmosphere x canopy interactions of nitric acid vapor in loblolly pine grown in open top chambers. *Journal of Environmental Quality*, 22: 70-80.

Thornberry, T., Carrol, M.A., Keeler, G.J., Sillman, S., Bertram, S.B., Pippin, M.R., Ostling, K., Grossenbacher, J.W., Shepson, P.B., Cooper, O.R., Moody, J.I. and Stockwell, W.R. (2001). Observations of reactive oxidized nitrogen and speciation of NO_y during the PROPHET summer 1998 intensive. *Journal of Geophysical Research,* 106, D20: 24359 – 24386.

Tjepkema, J.D., Cartica, R.J. and Hemond, H.F. (1981). Atmospheric concentration of ammonia in Massachusetts and deposition on vegetation. *Nature*, 294: 445 –446.

Turner, C.R., Wells, R.B. and Olbrich, K.A. (1996). Deposition Chemistry in South Africa. In: *Air Pollution and its Impacts On The South African Highveld.* Held. G., Gore, B.J., Surridge, A.D, Tosen, G.R., Turner, C.R. and Walmsley, R.D., editors. Environmental Scientific Association, Cleveland. 80 – 85,

Tyson, P.D. and Preston-Whyte, R.A. (2000). Weather and Climate of Southern Africa. 2nd edition. Oxford University Press, Cape Town.

Tyson, P.D., Kruger, F.J. and Louw, C.W. (1988). Atmospheric pollution and its implications in the Eastern Transvaal Highveld. South African National Scientific Programmes Report no. 150, CSIR. Environmental Scientific Association, Cleveland.

Unsworth, M.H. and Crossley, A. (1987). Consequences of cloud water deposition on vegetation at high elevation. In: *Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems.* Hutchinson, T.C. and Meema, K.M. editors. Springer-Verlag, Berlin.

Van Miegroet, H., Cole, D.W. and Foster, N.W. (1992). Nitrogen distribution and cycling. In: *Atmospheric Deposition and Forest Nutrient Cycling, Ecological Studies 91.* Johnson, D.W. and Lindberg, S.E., editors. Springer –Verlag, Heidelberg.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Scheslinger, W.H. and Tilman, D.G. (1997). Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications.* 7: 737 – 750.

Warneck, P. (1988). Chemistry of the natural atmosphere. Academic Press, New York.

Weathers, K.C., Lovett, G.M., Likens, G.E. and Lanthrop, R. (2000). The effect of landscape features on deposition to Hunter Mountain, Catskill Mountains, New York. *Ecological Applications*, 10: 5280540.

White, F. (1978). The afro-montane region. In: *Biogeography and Ecology of Southern Africa.* Werger, M.J.A., editor. Junk, The Hague, 463-513.

White, E.J. and Turner, F. (1970). A method of estimating income of nutrients in a catch of airborne particles of woodland canopy. *Journal of Applied Ecology*, 7: 441 – 461.

Williams, E.J., Roberts, J.M., Baumann, K., Bertram, S.B., Buhr, S., Norson, R.B. and Fehsenfeld, F.(1997). Variations in NOy composition at Idaho Hill, Colorado. *Journal of Geophysical Research,* 102: 6297-6314.

Williams, M.W. and Manthorne, D. (2001). Class I areas at risk: event based nitrogen deposition to a high-elevation, western site. In: *Optimizing Nitrogen Management in Food and Energy Production and Environmental Protection* : Proceedings of the 2nd International Nitrogen Conference on Science and Policy. *The Scientific World* 1(S2), 287-293.

Wobrock, W., Schell, D., Maser, R., Jaeschke, W., Georgii, H.W., Wieprecht, W., Arends, B.G., Möls, J.J., Kos, G.P.A., Fuzzi, S., Facchini, M.C., Orsi, G., Berner, A., Solly, I., Kruisz, C., Svenningsson, I.B., Wiedensohler, A., Hansen, H.C., Ogren, J.A., Noone, K.J., Hallberg, A., Pahl, S., Schneider, T., Winkler, P., Winiwaretr, W., Colvile, R.N., Choularton, T.W., Flossmann, A.I. and Borrmann, S. (1994). The Kleiner Feldberg cloud experiment, 1990, an overview. *Journal of Atmospheric Chemistry*, 19: 1-35.

Zunckel, M. (1998). Dry deposition of sulphur over South Africa. Unpublished Ph.D. thesis. University of the Witwatersrand, South Africa.