Soil Biogenic Emissions of Nitric Oxide from Arid and Semi-Arid Ecosystems

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Abstract

Nitric oxide (NO) has an important influence on a number of environmental processes including the production of ozone in the troposphere, the cycling of the hydroxyl radical and the production of nitric acid. The biogenic production of NO in the soil accounts for between 10% and 40% of the global total. A large degree of the uncertainty in the estimation of the biogenic emissions stems from a shortage of measurements in arid regions, which comprise a substantial proportion of the earth's land surface area, but have been neglected from many of the major atmospheric chemical models. This study examined the emission of NO from three ecosystems in southern Africa which cover an aridity gradient from semi-arid savannas in South Africa through arid Kalahari savannas in Botswana and the hyper-arid Namib Desert in Namibia. A laboratory method was used to determine the release of NO as a function of the soil moisture and the soil temperature. Various methods were used to up-scale the net potential NO emissions determined in the laboratory to the vegetation patch, landscape or regional level. The importance of landscape, vegetation and climatic characteristics is emphasized. In addition NO measurements were made in other regions such as in Israel, in the Amazon and in European temperate forests and pastures; these measurements did not form a major part of this PhD but are included in the discussion.

The first study occurred in a semi-arid savanna region in South Africa, where soils were sampled from 4 different landscape positions along a catenal sequence in the Kruger National Park. The maximum NO emission occurred at soil moisture contents of between 10% and 20% water filled pore space (WFPS). The highest net potential NO emissions came from the low lying Footslope landscape positions, which have the largest nitrogen (N) stocks and the largest input of N into the soil, the net potential NO emissions from the Midslope and Crest landscape positions were considerably lower. Net potential NO fluxes obtained in the laboratory were converted in field fluxes for the period 2003-2005, for the four landscape positions, using soil moisture and temperature data obtained *in situ* at the Kruger National Park Flux Tower Site. The NO emissions ranged from 1.5-8.5 kg ha^{-1} a^{-1} with the highest emissions occurring in the Footslope positions. The field fluxes were up-scaled to a regional basis using geographic information system (GIS) based techniques, this indicated that the highest NO emissions occurred from the Midslope positions due to their large geographical extent in the considered research area. Total emissions ranged from 20 x 10^3 kg in 2004 to 34x10^3 kg in 2003 for the 56000 ha Skukuza land type.

The second study occurred in an arid savanna ecosystem in the Kalahari, near the town of Tsabong, Botswana. In this study we collected soils from four differing vegetation patch types including: Pan, Annual Grassland, Perennial Grassland and Bush Encroached patches. The maximum net potential NO fluxes determined in the laboratory ranged from 0.27 ng m^{-2} s^{-1} in the Pan patches to 2.95 ng m^{-2} s^{-1} in the Perennial Grassland patches. The net potential NO emissions were up-scaled for the year December 2005-November 2006 and a region 185km x 185km in the southern Kalahari. This was done using 1) the net potential NO emissions determined in the laboratory, 2) the vegetation patch distribution obtained from LANDSAT NDVI measurements 3) estimated soil moisture contents obtained from ENVISAT ASAR measurements and 4) soil surface temperature measurements using MODIS 8 day land surface temperature measurements. This up-scaling procedure gave NO fluxes which ranged from 1.8 g ha^{-1} $month^{-1}$ in the austral winter months (June and July) to 323 g ha^{-1} $month^{-1}$ in the austral summer months (January-March). Differences occurred between the vegetation patches where the highest NO fluxes occurred in the Perennial Grassland patches and the lowest in the Pan patches. Over the course of the year the mean up-scaled NO emission for the studied region was 0.54 kg ha^{-1} a^{-1} this is within the range of pyrogenic NO emissions in African savannas and accounts for a loss of approximately 7.4% of the estimated N input to the region through atmospheric deposition and biological N fixation. The biogenic loss of NO is therefore a potentially important loss mechanism for N within this region.

The third study occurred in the hyper-arid Namib Desert in Namibia. Soils were sampled from three ecosystems; Dunes, Gravel Plains and the Riparian zone of the Kuiseb River. The net potential NO flux measured in the laboratory was used to estimate the NO flux for the whole of the Namib Desert for the year 2006 using modelled soil moisture and temperature data from the European Centre for Medium Range Weather Forecasts (ECMWF) operational model on a 36km x 35km spatial resolution. The maximum net potential NO production occurred at low soil moisture contents (<10%WFPS) and the optimal temperature was 25°C in the Dune and Riparian ecosystems and 35°C in the Gravel Plain Ecosystems. The maximum net potential NO fluxes ranged from 3.0 ng m^{-2} s^{-1} in the Riparian ecosystem to 6.2 ng m^{-2} s^{-1} in the Gravel Plains ecosystem. Up-scaling the net potential NO flux to the whole of the Namib desert gave NO fluxes of up to 0.062 kg ha^{-1} a^{-1} in the Dune ecosystem and 0.544 kg h^{-1} a^{-1} in the Gravel Plain ecosystem for 2006.

From these studies it is shown that NO is emitted ubiquitously from terrestrial ecosystems from hyper-arid regions such as the Namib Desert to topical forests, as such the NO emission potential from deserts and scrublands should be taken into account in the global NO models. The emission of NO is influenced by various factors such as landscape, vegetation and climate. This study looks at the potential emissions from certain arid and semi-arid environments in southern Africa and other parts of the world and discusses some of the important factors controlling the emission of NO from the soil.

Deutsche Zusammenfassung

Die biogene NO Produktion im Boden ist am global totalen NO Freisetzung zu 10-40% beteiligt. Die überwiegend Ungewissheit der Schätzungen stammt aus mangelnden Messungen in den ariden Regionen, welche 40% der gesamten Landfläche der Erde ausmacht. Die vorliegende Arbeit hat zum Ziel, die NO Freisetzung aus den drei Ökosystemen in südlichen Teil von Afrika, welche eine Ariditätsstufe von Semiarid Savanne in Südafrika bis extrem arid Namib Wüste in Namibia beschreibt, zu untersuchen. In dieser Arbeit wurde Laborexperiment vorgenommen, aus denen die Abhängigkeit der NO Freisetzung von Bodenfeuchte und Bodentemperatur abgleitet wurde. Es wurde unterschiedliche Methoden benutzt, um die Vegetationstypen, Landschaftsebene sowie Regionalebene bedingten Unterschiede von NO Freisetzung bezogen auf den Standort Punktmessdaten im Labor zu regionalisieren und die wichtige Bedeutung von Vegetationstypen, Landschaftsebene und Klimaverhältnisse wurde hervorgehoben.

In der ersten Studie wurde semiarid Savanne in Südafrika als Untersuchungsgebiet ausgewählt und dazu sind Bodenproben vier unterschiedlicher Landschaftsebene von Kruger National Park im Labor untersucht. Der optimale Feuchtezustand, bei dem die NO-Freisetzung ein Maximum erreicht, sind 10-40%. Hier wird die höchste NO-Freisetzung bei der tief gelegenen Landschaft beobachtet, in der die höchste Stickstoffbestände - und Zufuhr haben. Die im Labor gemessene Netto-Freisetzungsrate wurde für den Zeitraum 2003-2006 in den NO-Fluß im Feld umgewandelt, die in Verbindung mit den gemessenen Bodenfeuchten und Temperaturen für vier Standort von Kruger National Park erfolgt wurde. Es zeigt sich eine Kurvenbereich der jährlichen Freisetzungsraten von 1,5 bis 8,5 kg ha^{-1}. Es wurde punkthaft geschätzter NO-Fluß im Feld durch die Verwendung eines Geographischen Informationssystems (GIS) auf die Fläche des Untersuchungsgebiets - Skukuza übertragen und die Maximum NO wird von Mittelhang freigesetzt. Die gesamte Emission schwankt von $20x10^3$ kg in 2004 bis $34x10^3$ kg in 2003 für Skukuza Landschaft (56000 ha).

Das zweite Untersuchungsgebiet befindet sich im ariden Ökosystem Savanne – Kalahari (Botswana). Die Bodenprobe nach vier verschiedenen Vegetationstypen, die sich voneinander als Pan, annuelle Grassland, ganzjährig Grassland und Buschland unterscheidet, von Verfasser genommen. Die Maximum Netto-Freisetzungsrate ergibt sich für Pan 0.27 ng m^{-2} s^{-1}, während es bei ganzjährig Grassland 2.95 ng m^{-2} s^{-1} liegt. Die Netto-Freisetzungsrate wurde für den Zeitraum Dezember 2005 bis November 2006 für das ganze Untersuchungsgebiet übertragen. Dazu wurden zuerst die Netto-Freisetzungsrate von NO im Labor gemessen, dann die flächendeckende Daten für Vegetationstype (Landsat), Bodenfeuchte (ENVISAT ASAR) und Bodentemperatur (MODIS 8 day land surface temperature) erhoben. Der regionalisierte NO-Fluß hat gezeigt, dass die monatliche niedrigste Freisetzung in den Wintermonaten (Juni - Juli) mit einer Wert von 1,8 g ha^{-1} sich ergibt, während es im Sommer 323 g ha^{-1} erreicht. Die höchsten NO-Fluß wurde im ganzjährig Grassland und die niedrigsten im Pan gemessen. Die jährliche NO Freisetzung wurde etwa 0.54 kg ha^{-1} geschätzt, dabei gehen 7,4% von Stickstoffzufuhr der Region in die Atmosphäre verloren.

Die dritte Untersuchung wurde in extrem ariden Namib Wüste durchgeführt und dabei wurde Bodenprobe von drei verschiedenen Ökosystemen d.h. Sanddünen, kiesige Ebene und Uferbereich von Kuiseb Fluss genommen. Für die Schätzung der NO Freisetzung vom Untersuchungsgebiet wurde die Bodenfeuchte und Temperatur Modeldaten von ECMWF model für 2006 benutzt, welche eine räumliche Auflösung von 36km x 35km hat. Generell traten die höchsten Netto potentiellen NO Produktion in Sanddünnen und Flussufer mit einer Bodenfeuchte weniger als 15 % (WFPS) und Bodentemperatur 25°C, was aber in der kiesige Ebene bei 35°C der Fall ist. Die Maximum Werte ergibt sich für Flussufer 3.0 ng m^{-2} s^{-1}, wobei die Werte in kiesige Ebene bei 6.2 ng m^{-2} s^{-1} lagen. Die NO-Fluß Ergebnisse der Regionalisierung hat gezeigt, dass die Werte der jährlichen Freisetzung in Sanddünen bis 0.062 kg ha^{-1} und in der kiesige Ebene bis 0.544 kg h^{-1} erreicht.

Diese Arbeit hat sich gezeigt, dass bisherige emittierte NO von terrestrischen Ökosystem wie z. B. NO Freisetzung von Wüste und Buschland einen Beitrag zur globalen NO Modellen leisten sollte. Aus Ergebnissen wird gefolgt, dass die Landschaftsebene, Vegetation sowie Klimaverhältnisse die wichtige Einflussfaktoren für die NO Freisetzung sind. In dieser Arbeit wurde raumbezogene potentiellen NO Freisetzung unter den ariden und semiariden geographischen Gegebenheiten in südlichen Teil von Afrika und andere Teil der Erde erfasst und über die wichtige Kontrollfaktoren von NO Freisetzung von Boden diskutiert.

Preface

The thesis is divided into eight chapters.

Chapter one provides a general introduction into the biogenic emission of nitric oxide (NO) from the soil. The general introduction covers five topics including: 1) Why the biogenic production of NO is important and how it affects the chemistry of the atmosphere; 2) The biological processes that result in NO formation; 3) Environmental factors that control the biogenic formation of NO in the soil; 4) Modelling techniques that have been used to estimate the biogenic emission of NO from the soil, and 5) The aims of this study.

Chapter two is a synthesis of the most important processes in the nitrogen cycle, as it occurs in Africa. This chapter of my thesis has been published in a book titled: "Global Change Processes and Impacts in Africa: A synthesis." (2007) Edited by Otter, L. Olango, D.O. and Niang I. Chapter two covers topics including: 1) Nitrogen in African agriculture, how it is lost from agricultural systems and its means of replenishment; 2) Emissions of nitrogen-containing trace gas species, including ammonia and nitrogen oxides; 3) The sources of these gaseous emissions such as, biogenic production, pyrogenic production and biofuel burning and industrial emissions; 4) The nitrogen cycle is followed to look at the deposition of nitrogen containing chemical species from the atmosphere to the land and vegetation surface, resulting in the redistribution of reactive nitrogen, and 5) The impact of excess accumulation of reactive nitrogen species on water bodies in Africa.

Chapter three is a research study that took place in a semi-arid savanna in the Kruger National Park in South Africa. This paper is published in the journal "Biogeosciences". In chapter three we calculate the emission of NO from four landscape positions along a catenal gradient at the Kruger National Park Flux Tower Site. Measured soil moisture and temperature data is then used to up-scale the calculated NO flux to the regional (Land Type) scale.

Chapter four is a research study that took place in an arid savanna ecosystem in the southern Kalahari, near the town of Tsabong, Botswana. Chapter four is currently in press in the journal "Biogeosciences Discussions". In this study soil samples were taken from differing vegetation units in four vegetation patch types. The mean NO emissions from each of the

vegetation patches were determined as a function of the soil moisture and temperature and this information was combined with remotely sensed soil moisture content and soil temperature to allow for the estimation of NO emission for a 34225 km^2 region of the southern Kalahari for the year 2006.

Chapter five is a research study that took place in the hyper-arid Namib Desert in Namibia. This chapter is currently being prepared to be submitted to the Journal of Arid Environments. In this study the NO emission from three ecosystems is determined as a function of the soil moisture and temperature. The NO emission is then up-scaled to the whole of the Namib Desert using modelled soil moisture and temperature data.

Chapter six is a conclusion where we synthesise the results of this PhD study and show what this PhD has contributed to the state of knowledge regarding the biogenic emission of NO from arid and semi-arid regions.

Two appendices have been inserted to include work that took place during my PhD and that is discussed in the conclusion section but is not considered the main focus of the study.

Appendix 1 is a collaborative study where I worked with Dr Ilia Gelfand from the Weizmann Institute of Science, Israel. In this study we looked at the effect of afforestation on the biogenic emission of NO from a semi-arid shrubland in Israel. This chapter has been accepted for the journal Soil Biology and Biochemistry.

Appendix 2 describes the results of three smaller studies that I conducted. None of these studies is large enough to stand alone, however they are presented here since they provide interesting data for comparison with the main studies that occurred during my PhD. The three smaller studies include: 1) A study on soils from the Sahara, as far as I am aware this is the first time that the emission of NO from soils in the Sahara has been examined. 2) A study on the emission of NO from Amazon Forest soil samples in Surinam during the Gabriel campaign. These results have been compared to modelled NO emission fluxes and have been published in the journal Atmospheric Chemistry and Physics. 3) The NO emission as a function of the soil moisture and temperature was determined for soils sampled from pastures and the mineral soil from forests near Hohenpeissenburg in Bavaria, Germany.

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Chapter 1: Introduction

1.1 Importance of the biogenic production of NO from the soil

Nitrogen is an important determinant in the functioning of many ecosystems [*Matson et al.*, 2002]. Nitrogen is an essential component of many bio-molecules such as proteins and nucleic acids. Nitrogen occurs largely in the, mostly inaccessible, atmospheric pool however it is also converted into biologically available forms through the action of lightning, combustion process, biological fixation processes and industrial fixation processes. In recent years the amount of N that occurs in the available form has greatly increased due, largely to anthropogenic activity. This has many implications in that increased levels of available nitrogen allow for increased biological activity, but negative consequences such as ecosystem eutrophication, changes in species composition, eutrophication of land and water bodies, and changes in atmospheric composition can result [*Galloway et al.*, 2003; *Galloway et al.*, 2004b].

Arid and semi-arid regions encompass approximately 40% of the earth's land surface and are home to approximately 1 billion people. These lands while being important are sensitive to environmental change and desertification [*Veron et al.*, 2006]. In arid and semi-arid ecosystems N is often considered to be the second most important limiting factor for plant production after water [*Abrams et al.*, 1997; *Billings et al.*, 2002a]. In previous investigations it has been suggested that gaseous losses are an important mechanism for N loss in arid [*Austin et al.*, 2004; *Baker et al.*, 2001; *Billings et al.*, 2002a; *Billings et al.*, 2002b; *Feig et al.*, In Press-b; *Hall et al.*, 2008; *Hartley and Schlesinger*, 2000; *McCalley and Sparks*, 2008; *Schaeffer et al.*, 2003; *Schlesinger et al.*, 1996; *Smart et al.*, 1999] and semi-arid ecosystems [*Davidson et al.*, 1993; *Feig et al.*, In Press-a; *Hook and Burke*, 2000; *Kirkman et al.*, 2001; *Martin and Asner*, 2005; *Parsons et al.*, 1996]. In these studies it has been shown that under specific conditions N can be lost to the atmosphere as N_2, NO, N_2O and NH_3.

Emissions of nitric oxide (NO) and its conversion to nitrogen dioxide (NO_2) (collectively referred to as NO_x; NO_x = NO+ NO_2) are important in regulating chemical processes in the atmosphere [*Crutzen*, 1979; *Crutzen*, 1995; *Crutzen and Lelieveld*, 2001; *Levine et al.*, 1997; *Seinfeld and Pandis*, 1998]. Nitrogen oxides are key catalysts in the chemical processes that generate or destroy ozone (O_3), such as the oxidation of carbon monoxide.

The ambient mixing ratio of NO_x is a threshold which determines whether ozone is generated or destroyed [*Chameides et al.*, 1992; *Meixner and Yang*, 2006]. Most tropospheric ozone is produced in the reaction between methane and non-methane hydrocarbons with oxides of nitrogen (particularly NO_2) and the hydroxyl radical (OH^+) in the presence of NO_x. The net reaction is where NO_x gases are catalysts in the process of ozone production (for further details see [*Seinfeld and Pandis*, 1998]). In the case of methane, oxidation results in the formation of two molecules of ozone and the production of formaldehyde, the further oxidation of the formaldehyde can result in additional ozone production.

In low NO_x environments the oxidation process leads to ozone destruction [*Lindesay*, 1997]. In general, ozone is produced in industrialised areas (where there is a high production of NO_x) and is destroyed in the remote non-industrialised regions of the globe where there is lower production of NO_x [*Steinkamp et al.*, 2008]. Ozone in the troposphere is a pollutant and an effective greenhouse gas, depending on where in the atmosphere it occurs [*Scholes and Andreae*, 2000]. The production of ozone in the troposphere has serious consequences for human health and plant productivity.

Nitrogen oxides are also involved in chemical processes that result in the production or consumption of OH which is an important component of the oxidation capacity of the atmosphere [*Monks*, 2005; *Seinfeld and Pandis*, 1998; *Steinkamp et al.*, 2008].

In the chemical reactions between NO_x and OH, nitric acid is produced (eq. 1.1). Nitric acid is an important component of acid deposition and acts as a source of reactive nitrogen deposited from the atmosphere [*Logan*, 1983; *Meixner*, 1994].

$$NO_2 + OH \rightarrow HNO_3 \qquad (1.1)$$

The deposited nitric acid is involved in the acidification and eutrophication of ecosystems both of which are important global environmental issues.

1.2 Biogenic production of NO

The global emission of NO_x has been heavily affected by anthropogenic activity. It was estimated that in 1860 the global NO_x emission was 13.1 Tg a^{-1} (all units are in terms of mass of nitrogen), of which 10.5 Tg a^{-1} originated from natural sources. By the early 2000s it was estimated that the emissions of NO_x gases totalled 42-47 Tg a^{-1} [*Galloway et al.*, 2004b] [*Denman et al.*, 2007]. The most important sources are fossil fuel combustion in power-stations and vehicles (45%-67% of total), lightning (5%-16% of total), biomass burning

(13%-29%) and biogenic emission from soil (10%-40%) [*Davidson and Kingerlee*, 1997; *Denman et al.*, 2007]. The considerable uncertainty about the scale of the contribution of biogenic soil emissions of nitric oxide stems from widely differing estimates of the emission. Davidson and Kingerlee [1997] provided a global inventory of NO emissions from soils, based on field measurements world-wide, their estimate of the global NO soil source strength is 21 Tg a^{-1} (with an error margin of 4 to 10 Tg a^{-1}) (40% of the total), while the recent IPCC (2007) estimate is 8.9 Tg a^{-1} [*Denman et al.*, 2007]. The contribution of biogenic processes is particularly important in remote areas where there is little anthropogenic influence. In Africa it is thought that biogenic production of NO from the soil accounts for 40% of the total emission, even though biomass burning is also an important source [*Jaegle et al.*, 2005]. The rate of NO emission differs according to vegetation and climatic factors, in addition, some ecosystems are better studied than others and therefore the quality of estimates differs between regions.

At present a fair amount of work on biogenic NO emissions has been conducted in various ecosystems, both managed and natural:

- Managed Ecosystems
    - Agricultural soils, have extra inputs of N through the addition of organic or synthetic fertilizers, much of this additional N can be lost in the gaseous form. Studies on the production of NO in agricultural systems have been conducted by [*Akiyama and Tsuruta*, 2003; *del Prado et al.*, 2006; *Erickson et al.*, 2001; *Garcia-Monteil et al.*, 2003; *Garrido et al.*, 2002; *Keller et al.*, 1993; *Meijide et al.*, 2007; *Parton et al.*, 2001; *Pinto et al.*, 2004; *Rolland et al.*, 2008; *Stehfest and Bouwman*, 2006; *Van Dijk et al.*, 2002; *Veldkamp and Keller*, 1997; *Verchot et al.*, 2008; *Williams et al.*, 1992]. While these agricultural ecosystems are important on the global scale, the focus of this PhD study is on natural ecosystems.
- Natural Ecosystems - humid
    - Temperate grassland [*Martin et al.*, 2003a; *Martin et al.*, 1998; *Mosier et al.*, 2003; *Smart et al.*, 1999; *Stark et al.*, 2002],
    - Temperate forests (where the effect of N deposition on forested systems has been a key focus of study) [*Kesik et al.*, 2005; *Kesik et al.*, 2006; *Kitzler et al.*, 2006a; *Kitzler et al.*, 2006b; *Pilegaard et al.*, 2006; *Rosenkranz et al.*, 2006; *Schindlbacher et al.*, 2004],

- Boreal/ coniferous forests [*Koponen et al.*, 2006; *Maljanen et al.*, 2007; *Papke and Papen*, 1998; *Regina et al.*, 1998; *Stark et al.*, 2002]
- Humid tropical forests and humid savannas [*Brümmer et al.*, 2008; *Butterbach-Bahl et al.*, 2004b; *Davidson*, 1991a; *Davidson et al.*, 1993; *Erickson et al.*, 2002; *Erickson et al.*, 2001; *Garcia-Monteil et al.*, 2003; *Li et al.*, 2007; *Mosier and Delgado*, 1997; *Serca et al.*, 1998; *Van Dijk et al.*, 2002; *Veldkamp et al.*, 2008; *Verchot et al.*, 2008]

- Natural Ecosystems - dry
  - Dry tropical forests and dry savannas [*Feig et al.*, In Press-a; *Kirkman et al.*, 2001; *Martin and Asner*, 2005; *Martin et al.*, 2003a; *Otter et al.*, 1999; *Parsons et al.*, 1996; *Scholes et al.*, 1997]
  - Dry steppes [*Holst et al.*, 2007; *Mamtimin et al.*, In Prep]
  - Deserts [*Feig et al.*, In Prep; *Hall et al.*, 2008; *Hartley and Schlesinger*, 2000; *McCalley and Sparks*, 2008].

Aggregate values from these ecosystems have been previously presented in the review paper by Ludwig et al [2001]. While there have been a large number of studies, it is evident that there is a shortage of measurements from arid and semi-arid ecosystems. A recent review by Meixner and Yang [2006] identified only 13 studies in arid and semi-arid regions (mean annual precipitation less than 400mm a^{-1}) (since then four other studies have been conducted [*Feig et al.*, In Press-b; *Hall et al.*, 2008; *Holst et al.*, 2007; *McCalley and Sparks*, 2008]). This is problematic since arid and semi-arid regions account for 40% of the earth's surface [*Veron et al.*, 2006] and there is some evidence that they may be capable of sizable emissions of NO [*Davidson and Kingerlee*, 1997] (to see reported NO emissions from arid and semi-arid ecosystems see Fig. 3.9).

1.3 Factors controlling the emissions of NO from the soil

The dynamics of NO formation has been well covered in some excellent reviews namely Conrad [1996], Ludwig et al [2001], Meixner and Yang [2006] and Galbally et al [2008], therefore I will not go into great detail here, suffice to mention that NO production in the soil is principally through the biological processes of nitrification and denitrification (although abiotic NO formation in acid soils with a high NO_2^- concentration can occur, it is often considered to be unimportant, except in certain ecosystems). All microbial processes that

involve the oxidative or reductive transformation of N through the +2 valence state may act as a source or sink for NO [*Ludwig et al.*, 2001].

Denitrification is the respiratory reduction (in the absence of O_2) of NO_3^- or NO_2^- to gaseous forms of N including N_2O, NO and N_2 and is commonly associated with the loss of N from the soil. Nitric oxide is considered to be an obligate intermediate stage in the denitrification process so it is therefore assumed that NO can be both produced and consumed in the denitrification process [*Conrad*, 1996; *Coyne*, 1999; *Ludwig et al.*, 2001]. Since it is an anaerobic process, denitrification mostly occurs in waterlogged soils and is therefore unlikely to be of significance in drylands, other than in certain landscape positions (e.g. riparian zones) or in temporally limited periods, following large precipitation events when the soil is saturated.

Consensus is beginning to develop that nitrification is the main process responsible for the production of NO in drylands [*Galbally et al.*, 2008]. Nitrification is the biological oxidation of NH_4^+ to NO_3^- with an intermediate product of NO_2^-. The process of nitrification is restricted to a small number of strictly aerobic, chemoautotrophic bacterial genera [*Coyne*, 1999; *Ludwig et al.*, 2001]. Although it is a process only performed by a limited number of taxonomic groups it is considered to be of vital importance to N cycling in many natural and agricultural soils [*Garrido et al.*, 2002; *Ludwig et al.*, 2001; *Russow et al.*, 2000; *Russow et al.*, 2008].

In the soil the water filled pore space (WFPS) sets an "envelope of oxygen containing conditions, which defines the maximum NO and N_2O flux rates" [*Scholes et al.*, 1997] see also [*Skopp et al.*, 1990]. Micro-scale heterogeneity can exist since strong gradients in O_2 supply can occur over microsite scales allowing nitrification and denitrification to occur simultaneously in close proximity in the soil [*Hutchinson et al.*, 1993]. Soil water content also controls the diffusive transport of reactants and products for the processes of nitrification and denitrification [*Hutchinson et al.*, 1993; *Skopp et al.*, 1990].

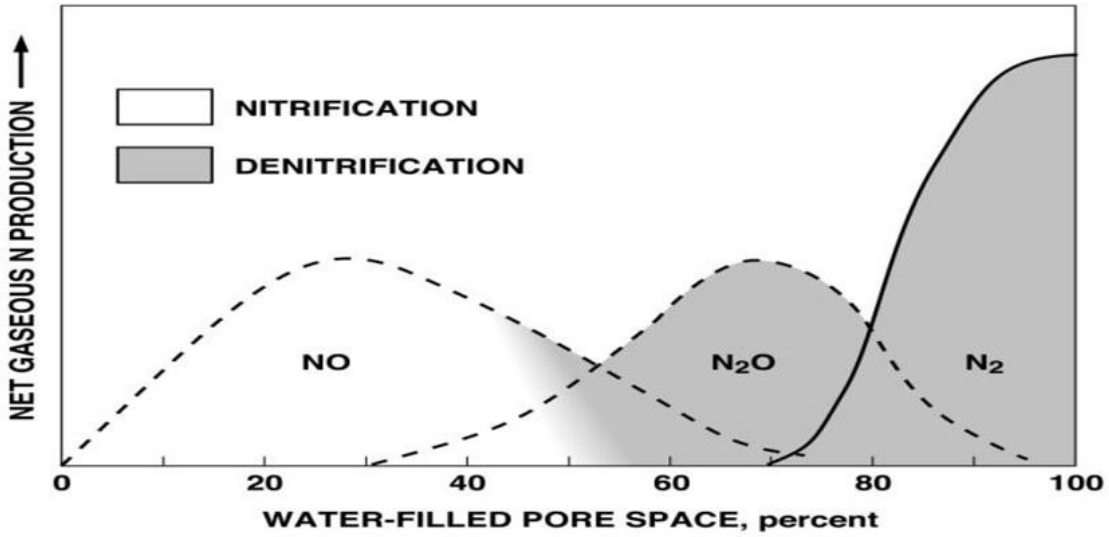

Figure 1.1 Schematic representation of the production of N containing gas species as a function of the soil WFPS from Kirkman [2000].

The microbial activity facilitating biogenic NO emissions from the soil is controlled by a number of factors including; soil moisture, soil temperature and soil nutrient concentration [*Kitzler et al.*, 2006a; *Ludwig et al.*, 2001]. These in turn are largely controlled by geographic factors, for example (a) the climatic conditions, (b) the underlying geology, (c) the position in the landscape, (d) the land use, and by biological factors such as the vegetation and the microbial consumption of NO [*Brümmer et al.*, 2008; *Davidson*, 1991b; *Galbally et al.*, 2008; *Garrido et al.*, 2002; *Ludwig et al.*, 2001; *Russow et al.*, 2000; *Russow et al.*, 2008].

1.3.1 Soil Moisture

In drier ecosystems soil moisture seems to be one of the most important factors regulating the biogenic emission of NO. When the soil moisture is too low to maintain microbial activity there are very low levels of NO emitted. When the soil moisture is too high to maintain aerobic conditions the emission of NO is negligible [*Garrido et al.*, 2002; *Meixner et al.*, 1997; *Skopp et al.*, 1990]. The optimum emission of NO seems to occur at low soil moisture levels, but where there is sufficient moisture to allow for microbial activity.

Numerous studies have examined the effects of soil moisture (commonly expressed as WFPS, although other units have been used) on N trace gas emissions. In a study where the soil water potential was maintained at low levels under laboratory conditions it was found that both NO and N_2O could be produced under aerobic conditions, but nitrification was the only process involved in the gas production under the low water conditions used in the study [*Garrido et al.*, 2002]. This is important because nitrification preferentially produces NO over N_2O

[*Conrad*, 1996]. In a field study in the Kruger National Park a savanna reserve in South Africa, NO emissions followed the predicted soil moisture curve where they were lowest at high (>54%) and at low (<8.7%) WFPS [*Parsons et al.*, 1996]. Even when desert soils are wetted emissions of N containing gasses can occur. In a study by Hartley and Schlesinger [2000] NO fluxes increased in relation to the WFPS, the increase differed according to the texture of the soil. In coarse textured soils, the increase was reported to be exponential to a level of 10% WFPS, but linear in fine textured soils which were wetted to 40% WFPS. Since the soil moisture in the study rarely exceeded field capacity, no parabolic relationship between WFPS and NO emission was found [*Hartley and Schlesinger*, 2000]. Laboratory based studies such as the type conducted by Meixner et al [1997], Meixner and Yang [2006], Van Dijk et al [2002], Yu et al [2008] and during this study are much more effective at illustrating the emission of NO as an optimum function of the soil WFPS, since measurements of the NO emission and the soil water content are conducted at a much higher resolution and across a much greater range of soil moisture contents.

Pulsing is a special situation with regard to the influence of soil moisture on the emission of NO from dry or seasonally dry ecosystems. The cyclical occurrence of favourable conditions, which result in biological activity, and unfavourable conditions, resulting in biological stasis, due to drying and rewetting cycles are most pronounced in arid and semiarid ecosystems. Wet-dry cycles affect all aspects of C and N turnover including C and N mineralization and gaseous losses. The pulsing effect is discernable within a few minutes and persists for one or more days [*Austin et al.*, 2004]. Nitric oxide fluxes in the Chihuahuan Desert increase in the wet period and after isolated storms. After artificial watering of soils the NO flux has been shown to increase by an order of magnitude within 10 minutes [*Hartley and Schlesinger*, 2000]. The emission pulse initiated on rewetting the soil could be maintained in certain vegetation communities but not in others. For example, the NO emission pulse was maintained in grassland soils but declined on subsequent rewetting in shrubland soils [*Hartley and Schlesinger*, 2000]. A number of proposals have been put forward to explain the cause of the pulsing effect:

a) Pulsing is due to a dormant water stressed microbial community activating and utilizing the available nutrients as soon as the soil becomes moist enough for microbial metabolism. In a study by Scholes et al [1997] the pulse of NO flux diminished within 72 hours but mineralization and nitrification continued at a steady pace. This suggests that the NO pulse is not directly linked to the mineralization rate

but to some rapidly depleted substrate pool [*Meixner and Yang*, 2006; *Scholes et al.*, 1997].

b) The pulsing effect is due to the NO rich soil air being displaced by water when dry soil is wetted, accounting for the very rapid onset of high NO emission following the wetting of dry soil.

c) When dry soil is wetted it results in the lysis of a large number of microbial cells in the soil, these then provide nutrients for the surviving microbial community, which can then metabolise rapidly

d) Pulsing is due to the soil microorganisms rapidly expelling intercellular solutes which had been built up in the cell as a defence against desiccation.

e) When the microorganisms are recovering from the effects of desiccation their metabolic mechanisms do not function optimally and therefore there is a leak in the system.

It seems that the NO emissions exhaust with subsequent irrigation due to the gradual depletion of the soil nutrients that have been accumulated prior to the first wetting event [*Davidson et al.*, 1993; *Garcia-Monteil et al.*, 2003; *Ludwig et al.*, 2001; *Scholes et al.*, 1997]. This has been shown in field studies such as in the Nylsvley Savanna (South Africa); where NO fluxes increased from approximately 2 ng m^{-2} s^{-1} to 76 ± 54 ng m^{-2} s^{-1}. The NO flux responded to the addition of water within 30 min and reached a peak flux between 2 and 8 hours. After peaking, the pulse reduced over a period of 72 hours to a flux of 10-30 ng m^{-2} s^{-1} and remained at that level for a further 6 days. When the soil was subsequently rewetted there was no further pulse, indicating that the pulse was due to a pool of substrate that is rapidly consumed. The pulsing effect has also been detected in laboratory studies, the greatest pulse occurred in soils that had not been well wetted from the beginning and were allowed to dry out completely; this indicates that the production of a pulse is dependent on the level of dryness attained. The second pulse of NO emissions was 35% lower than the initial pulse but the durations of the two pulses were identical [*Hutchinson et al.*, 1993]. These water induced pulses in NO emissions bore no relation to the soil NH_4^+ concentration however it was proved that the pulse was produced by autotrophic NH_4^+ oxidizers since the addition of nitrapirin (nitrification inhibitor) eliminated the NO emission [*Hutchinson et al.*, 1993]. The first pulse of NO due to rain after a prolonged dry period reportedly accounts for less than 6% of the annual NO flux in semi-arid savannas, and even less in more mesic tropical ecosystems, therefore improving this estimate is not too important in these systems, however it is important not to use the emissions after a prolonged dry period as an estimate of the average

of the wet season NO flux rate [*Scholes et al.*, 1997], this is also important for laboratory incubations in that the soil should be properly pre-incubated to avoid getting erroneous readings due to a pulse.

1.3.2 Soil Temperature

Since NO production is a microbial process it is likely to be influenced by the temperature according to the Arrhenius equation. Generally biological activity is related to the temperature, the relationship between the rate of a biological process, and a 10°C change in temperature is given by the Q_{10} relation. The activity of an enzyme approximately doubles with a 10°C increase in temperature, this has been seen in a number of studies including Feig [In Press-a], Kirkman et al [2001], Meixner and Yang [2006] and McCally and Sparks [2008]. The soil temperature is likely to modify the emission of NO as long as the soil is moist enough to allow for microbial activity but where aerobic conditions allow for nitrification. In the review on biogenic emission of NO by Ludwig et al [2001] soil temperature is mentioned as one of the most important environmental factors regulating NO emissions. This is due to the microbial nature of the NO emissions and their reliance on temperature for enzymatic activity, this reliance on temperature only occurs as long as other factors such as water and soil nutrients are not limiting. Therefore, soil temperature is a factor that modulates short term variation of NO exchange while the magnitude of the NO emission is controlled by other factors [*Ludwig et al.*, 2001]. This has been shown in experimental studies; for example, when water is not limiting in Zimbabwean systems the flux of NO is regulated by the diel variation in soil temperature [*Meixner et al.*, 1997]. In Chihuahuan Desert soils temperature interacts with soil moisture to regulate NO emissions, however NO emissions were related to temperature only at the wettest sites providing further evidence of the secondary nature of the effect of soil temperature on soil NO emissions [*Hartley and Schlesinger*, 2000]. At high soil temperatures (40-45^{o}C) NO emission fluxes have been shown to reduce [*Aranibar et al.*, 2004; *Passianoto et al.*, 2004].

1.3.3 Soil Nutrients

Soil nutrient content is another important controller of the emission of NO. Many studies have found a relationship between the emissions of NO and either the concentrations of nitrogen compounds [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Hutchinson et al.*, 1993; *Ludwig et al.*, 2001; *Meixner et al.*, 1997; *Parsons et al.*, 1996] or the N cycling rate [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Parsons et al.*, 1996]. In wet ecosystems such as humid tropical forests in Puerto Rico

[*Erickson et al.*, 2002; *Erickson et al.*, 2001] it seems that the NO emission may be primarily controlled by the concentration of NO_3^- and to a lesser extent to NH_4^+, this might indicate that the major process resulting in the release of NO under these wet (more anoxic) soils is denitrification. In dry ecosystems [*Hartley and Schlesinger*, 2000; *Meixner et al.*, 1997; *Parsons et al.*, 1996] and aerobic soil conditions in laboratory studies [*Hutchinson et al.*, 1993] the NH_4^+ concentration seems to be more important in regulating NO emissions, which might indicate to the importance of nitrification as a process resulting in the emissions of NO. Therefore, natural or anthropogenic actions that result in the modification of the inputs of nutrients or the rates of nutrient turnover are likely to have an effect on the NO production rates. Examples of studies which have found these results include inter alia:

- A review paper by Ludwig (2001) concluded that the availability of soil N has a large impact on the NO emission rate especially the availability of NH_4^+ and NO_3^- which serve as substrates for nitrification and denitrification. The application of N fertilizers was found to have a strong effect on the exchange of NO from the soil [*Ludwig et al.*, 2001], since more N is available for nitrification.
- In Puerto Rico, Erickson et al [2001] found that unfertilized sites showed consistently lower NO emissions than fertilized sites, < 1.1 ng m^{-2} s^{-1} and > 5.5 ng m^{-2} s^{-1} respectively. When the fertilized plots were omitted nitrogen oxide emissions were positively related to leaf litter N input and negatively related to the C:N ratio. Annual fluxes of N_2O and NO were related positively to soil NO_3^-, net N mineralization, net nitrification and nitrification potentials [*Erickson et al.*, 2002; *Erickson et al.*, 2001].
- In dryer ecosystems the same trends were found, fertilization of agricultural soils in Zimbabwe resulted in a significant increase in soil NO fluxes in comparison to unfertilized soils (by up to a factor of 8) [*Meixner et al.*, 1997].
- In South African savanna the initial increase in rates of NO emission with increasing soil moisture was paralleled by increases in soil NO_3^- concentration indicating nitrification [*Parsons et al.*, 1996].
- The flux of NO from Chihuahuan Desert soils was directly related to the soil NH_4^+ concentration (r^2=0.49). Therefore NH_4^+ concentration was shown to act as a secondary control of NO production in shrublands (water is primary). When the soils were fertilized with NH_4^+ and watered the NO emission was between 5 times greater (in grasslands) and 15 times greater (shrublands) than in the watered controls [*Hartley and Schlesinger*, 2000].

- Even in laboratory conditions where the soil water potential was carefully measured and maintained the NO emissions followed NH_3^+ concentration [*Hutchinson et al.*, 1993].

In natural ecosystems the soil nutrient content is modified and influenced by a number of geographic and biological factors that control the accumulation and distribution of soil nutrients. During this study we examined a number of these controlling factors such as landscape, vegetation communities and soil types.

Landscape position is known to have an important impact on many soil and ecological processes including biogeochemical processes. Nitric oxide emissions are known to vary between landscape positions and associated vegetation patterns [*Martin and Asner*, 2005; *Meixner et al.*, 1997; *Otter et al.*, 1999; *Scholes et al.*, 1997; *Scholes and Walker*, 1993]. These variations in biogenic NO emissions may be linked to: (a) the soil nutrient status, since there is often an accumulation of nutrients and clay particles at the lower portions of a slope which increase the soil's fertility status, (b) the soil water status, since a increase in soil water is expected at the lower portion of a slope due to runoff and subsurface drainage and (c) the changes in the associated vegetation communities due to changes in the above mentioned factors.
Examples of this are common in the literature [*Abrams et al.*, 1997; *Hook and Burke*, 2000; *Ludwig and Tongway*, 1995; *Ludwig et al.*, 1999a; *Ludwig et al.*, 1999b; *Myers et al.*, 2001]. One example, in short grass steppes in the United States, of a catena landscape pattern found that differences in clay content explained much of the variation in vegetation structure. Typical upland (erosional run off) and lowland plots (erosional run on) differed in soil texture with more clay occurring in the lowland plots, the soil organic matter content and hence soil C and N pools were strongly related to the soil texture and landscape position, in the study they found that localized enrichment of biologically active SOM occurs under plants but this is superimposed on the soil textural and landscape characteristics [*Hook and Burke*, 2000].

Land use and anthropogenic changes to the landscape through cultivation based agriculture and animal grazing can have important effects on the biogenic NO emissions from the soil, this occurs through:

- Direct changes in the soil chemical and physical properties such as when primary vegetation is converted to cropping systems or when forest is converted to pasture.

- Biogenic NO emissions can also be altered by changes to the vegetation, such as during the processes of desertification, which is marked by the occurrence of bush encroachment, the loss of the herbaceous layer and changes in species composition.

Changes in NO emissions due to the conversion of primary vegetation to agriculture have been reported in the humid tropical forests in Puerto Rico where, in a study looking at forest successional stages (time since abandonment of agriculture) it was found that, secondary forests had higher NO fluxes than old forest [*Erickson et al.*, 2002]. Similarly in Rondônia, Brazil clearing of tropical forests to form pastures causes a significant increase in the emission of NO from the soil [*Kirkman*, 2000]. In another study in the Amazon it was reported that both rainfall and simulated rainfall on dry forest soil resulted in a two-to-four fold increase in NO emissions from soil within a two hour period. In the same study experimental irrigation or rainfall did not cause an increase in NO emissions from pastures [*Garcia-Monteil et al.*, 2003]. Other land use issues that cause an increase in NO emissions include forest clearing [*Keller et al.*, 1993], burning [*Parsons et al.*, 1996] and fertilization of agricultural land [*Mosier and Delgado*, 1997].

Vegetation can affect the chemical composition of the soil environment through two main processes:

- The direct input of plant products into the soil either though litter fall or rhizo-deposits including the input of roots and the associated effects on soil processes [*Lamade et al.*, 1996; *Prescott et al.*, 2000]. Litter with high N is associated with high rates of decomposition and rapid soil N turnover which in turn is associated with increased emissions of NO and N_2O [*Erickson et al.*, 2001].
- Fine scale patches caused by grass tussocks or bushes obstruct surface flows of water and wind and thereby capture, concentrate and conserve runoff water and nutrients in runoff sediments and windblown litter [*Abrams et al.*, 1997; *Ludwig and Tongway*, 1995; *Ludwig et al.*, 1999a; *Ludwig et al.*, 1999b; *Tongway et al.*, 1989]. In many arid and semi-arid environments around the world limited rainfall and runoff-runon processes have led to vegetation patchiness on many types of landscapes [*Ludwig et al.*, 1999b]. Patchiness in landscapes is thought to optimize the capture and storage of limited water and nutrients within landscapes and hence maximize plant productivity within the system [*Ludwig and Tongway*, 1995]. It has been shown that there is a concentration of nutrients in patches, and this concentration can be many times the concentration of the interpatch spaces [*Tongway et al.*, 1989].

Changes in the land use may have an important impact on the distribution of vegetation patches through the landscape.

Extreme spatial heterogeneity of soil nutrient and temporal inequality of water characterize desert ecosystems. Results from the Xei and Steinberger [2001] study indicate that organic C and N in semi arid and arid ecosystems are heterogeneously distributed. Soil organic matter and available N are concentrated under shrubs in the Negev forming islands of fertility and therefore, possibly, hotspots of NO emissions [*Xei and Steinberger*, 2001].

In arid and semi-arid regions that are affected by bush encroachment or desertification, the species involved in the woody encroachment process are in the Fabaceae (legume) family [*Hagos and Smit*, 2005; *Martin and Asner*, 2005; *Ringrose et al.*, 2002; *Ringrose et al.*, 2003]. Nitric oxide emissions in Texas were highly correlated to *Prosopis* cover. In that study the lowest NO emissions reported were in areas with high amounts of bare soil and the highest in areas with high *Prosopis* cover [*Martin and Asner*, 2005].

The NO emissions in a Chihuahuan Desert differed between areas located directly under shrub canopies and between shrub canopies. Nitric oxide emission was higher under the canopy [*Hartley and Schlesinger*, 2000]. The emission of NO also differed under different vegetation types with grassland sites having a higher emission rate than creosote bush or tar bush [*Hartley and Schlesinger*, 2000]. The grassland soils have a higher potential for NO production than the shrubland soils. In these sites NO emissions may have declined with the conversion of grassland to shrubland [*Hartley and Schlesinger*, 2000], this is in contrast to the findings of Martin and Asner [2005].

In many parts of the world land cover is changing due to the encroachment of bushy vegetation. If as reported in the above mentioned study such dramatic changes in NO emissions are noted as a result of woody encroachment it might have an important impact on the regional budgets for these gases.

1.4 Modelling of NO emissions

Numerous studies have used models to estimate the biogenic emissions of NO from the soil [*Beirle et al.*, 2004a; *Beirle et al.*, 2004b; *Bruzzowe et al.*, 2003; *Ganzeveld et al.*, 2002; *Jaegle et al.*, 2005; *Martin and Asner*, 2005; *Martin et al.*, 2003b; *Steinkamp et al.*, 2008; *Xu et al.*, 2002]. These models can be broadly categorised into five main groups; the empirical models, remote sensing models, statistical models, process based models and local scale models based on soil measurements.

Various groups have tried to model NO emissions at various scales, from regional to global, recently there have been a number of papers which have reviewed the modelling work done on NO emissions [*Hutchinson et al.*, 1997; *Ludwig et al.*, 2001; *Steinkamp et al.*, 2008]. The most important global or regional models reviewed in these papers include

1.4.1 Empirical models

Empirical models function by assigning various ecosystems an emission factor, these emission factors are often modified according to parameters such as the soil moisture and the soil temperature. Although process-based models have been developed, empirical models are widely used to estimate the emissions of N trace gases due to the rudimentary knowledge of the biological processes involved in the production of the N trace gases and a shortage of data [*Wang et al.*, 2005]. A number of important empirical models have been used, including:

- Williams et al (1992) modelled NO emissions based on empirical relationships derived from measuring NO_x exchange rates. This model used soil temperature as the only major variable and grouped all the other variables into a proportionality constant that differed according to land use type [*Williams et al.*, 1992].
- The model by Yienger and Levy [1995] which is one of the most used parameterisations for the biogenic emission of NO [*Delon et al.*, 2008; *Ganzeveld et al.*, 2002; *Steinkamp et al.*, 2008]. The Yienger and Levy [1995] model is a global temperature and precipitation dependent empirical model. The global biomes that are used in this approach are water, ice, desert, tundra, grassland, scrubland, woodland, deciduous forest, coniferous forests, drought deciduous forests, rainforests and agricultural land, of the biomes water, ice, desert and scrubland are assumed not to emit NO. Included in the model are a pulsing effect and a canopy uptake effect [*Yienger and Levy II*, 1995]. This approach has been used in the ECHAM-Messy models [*Ganzeveld et al.*, 2008; *Jöckel et al.*, 2005; *Steinkamp et al.*, 2008]. The approach modelled the temperature dependence and added empirically derived functions to account for other variables, including adjustments to account for canopy reduction, pulsing, different emission relationships between wet and dry soils [*Yienger and Levy II*, 1995].

1.4.2 Remote sensing models

Nitrogen oxides are good candidates to be measured by remote sensing, since NO_2 has a very clear absorption band. Due to the rapid transformation between NO and NO_2 the emissions of

NO can be inferred from the column densities of NO_2 and the sources of NO can then be partitioned.

Using the GOME Satellite which measures the NO_2 column density in the atmosphere, and by partitioning the origin of the NO_2 into fossil fuel burning, biomass burning and biogenic emissions, it was found that the largest NO_x emissions from the soil came from tropical savanna woodland ecosystems in Africa and also from agricultural regions in western US, southern Europe and Asia. Therefore the savanna woodland regions in Africa, particularly the Sahel region was found to be an important region for NO_x emissions from the soil [*Jaegle et al.*, 2005].

1.4.3 Statistical models

Statistical models use relationships between measured NO fluxes and environmental variables, such as the soil moisture, the soil temperature, the soil nutrient concentrations, wind speed and others to predict the emission of NO from the soil. Once a model has been trained to fit to an existing data set it can then be used to predict the NO emission from measured (or modelled) environmental variables. Examples of statistical models include:

- The statistical model by Yan et al [2005], this was a model based on the field measurements of NO_x. The model estimated the emission of NO_x based on the soil organic carbon content, soil pH, land cover type, climate and nitrogen input. The statistical model by Yan et al [2005] has been used to simulate global NO_x emissions at a 0.5° resolution.
- Neural network based models have been used by [*Delon et al.*, 2008; *Delon et al.*, 2007] to estimate the emission of NO from the soil. A neural network was trained to find the best non-linear regression between NO fluxes and seven environmental variables, which were introduced step by step. The variables included the soil surface temperature, the soil WFPS, soil temperature at 20-30cm, fertilization rate, % sand in the soil, soil pH and the wind speed. This model has been used for regions of West Africa and the Sahel during the AMMA campaign. It is suggested that an artificial neural network is a good alternative to process-based biogeochemical models and large scale empirical models.

1.4.4 Process-based models

Process-based models, model the movement of nutrients through ecosystems, by looking at the important reactions, such as the rate of decomposition, the rates of nitrification and denitrification etc. The NO fluxes are normally modelled as proportion of the rate of

nitrification (typical approximately 2% of the nitrogen going through the process of nitrification is converted to NO).

- Using the Carnegie-Ames-Stanford (CASA) biosphere model Potter et al [1996] produced a process-based model based on predicted rates of gross nitrogen mineralisation with an index of the soil WFPS. This is based on the hypothesis that N mineralization and soil aeration are the dominant processes in controlling the amount and composition of the nitrogen containing trace gases emitted from the soil. This model identifies tropical dry forests and savannas as important sources of N trace gas emissions[*Potter et al.*, 1996].
- A sub-model of the Daycent model has been produced by Parton et al [2001] the N Gas Emission sub-Model of Daycent. In the Daycent model NO_x emissions are calculated from N_2O emissions by a N_2O : NO_x ratio equation, that is calculated as a function of the soil parameters, such as soil bulk density, field capacity and WFPS. The N_2O emissions as a result of nitrification are calculated from modelled soil NH_4^+ concentration, WFPS, soil temperature, pH and soil texture. The N_2O emissions as a function of denitrification are derived from calculations of the NO_3^- concentrations, WFPS, heterotrophic respiration and the soil texture. It is assumed that NO emissions are mostly due to the process of nitrification [*Parton et al.*, 2001]. This model has also been used by Davidson et al [1998].
- The Denitrification Decomposition (DNDC) Model is a process-based model that requires parameters such as the climate, the soil texture, the soil nutrient contents and land management parameters. The emission of NO in the DNDC model is calculated in a nitrification module. The DNDC model is a soil biogeochemistry model that is used for predicting soil organic matter decomposition, nitrogen turnover and N_2O production. Nitric oxide emissions from soils are directly influenced by environmental factors such as the soil temperature, the soil moisture, pH and soil substrate availability. All these factors are influenced by ecological drivers such as the climate, the soil properties the vegetation and anthropogenic disturbances [*Butterbach-Bahl et al.*, 2004a; *Kesik et al.*, 2005; *Kesik et al.*, 2006; *Li et al.*, 1996]. The DNDC model has been used on numerous occasions to estimate the emission of N_2O, CO_2, CH_4 and NO from the soil [*Kesik et al.*, 2005; *Kesik et al.*, 2006; *Norman et al.*, 2008; *Simpson et al.*, 2006; *Werner et al.*, 2007a; *Werner et al.*, 2007b]

- A nitric oxide sub-model has been incorporated into the CERES-EGC soil crop model. This sub-model simulates the emission of NO via the nitrification pathway as modulated by environmental drivers. Input parameters include the soil surface moisture content, the soil temperature and the soil ammonium content [*Rolland et al.*, 2008]. The emission of NO is proportional to the nitrification rate. The response of nitrification to the soil moisture is a linear increase from 10% to 60% WFPS followed by a linear decrease when the soil WFPS is between 60% and 80% WFPS. The temperature response was as a Q_{10} value of 2.1 based on a reference temperature of 20°C [*Rolland et al.*, 2008] .

1.4.5 Local models based on soil measurements

The model proposed by Galbally and Johnson [1989], tried to model the flux of NO by assuming that the net exchange of NO could be determined in terms of NO production, NO consumption (both measured from soil samples in the laboratory), and diffusional transport through the soil. A downside of this approach is that the production and consumption parameters have to be determined experimentally [*Galbally and Johansson*, 1989]. This approach has been found to reproduce both short term (hourly) [*Yang and Meixner*, 1997] and long term, monthly [*Van Dijk et al.*, 2002] and yearly [*Otter et al.*, 1999], measurements.

The concept behind the Galbally and Johansson model is situated between direct measurements, process-based models and empirical models, this model uses laboratory based measurements of the production of NO in the soil under varying temperatures and ambient NO concentrations to determine the flux of NO from the soil [*Galbally and Johansson*, 1989]. If the measurements are conducted over a wide range of soil moistures and varying soil temperatures then the flux of NO can be estimated for that particular type of soil as a function of the soil moisture and the soil temperature. The parameterisations that are obtained for the individual soil types can then be up-scaled to a larger region using land use distribution data and either measurements or estimates of the soil moisture and temperature [*Feig et al.*, In Press-a; *Feig et al.*, In Press-b; *Kirkman et al.*, 2001; *Van Dijk et al.*, 2002; *Yu et al.*, 2008]. The advantages of such a model are that the emission parameters are determined for the site of interest, and therefore the Galbally and Johansson model combines the advantages of empirical and process-based models. This model is particularly useful for scanning type studies that have been used during the course of this PhD study.

1.5 Aims

This PhD thesis was conceived as a scanning study where the advantages of using a local model such as the Galbally and Johansson model and laboratory based methods and to measure the biogenic emission of nitric oxide from the soil could be combined to study the emission of nitric oxide from arid and semi-arid ecosystems. For this study it was decided to focus on landscape factors such as landscape position, soil type and vegetation cover and on climatic factors such as soil moisture and temperature. These factors have all been shown to have an important influence on the emission of nitric oxide from the soil.

The aims of this study were therefore to:

- Examine the emission of NO from a range of arid and semi-arid regions
- Determine the influence of landscape and vegetation heterogeneity on the biogenic emissions of NO from the soil
- Determine the influence of the soil moisture content on the biogenic emission of NO from the soil
- Determine the influence of soil temperature on the biogenic emission of NO from the soil
- Up-scale the modelled NO emissions to the regional scale.

These aspects were examined in three main studies which occurred in southern Africa across a precipitation range from semi-arid to hyper-arid. In addition there was collaboration with scientists from the Weizman Institute for Science in Israel where the effect of afforestation on the emission of NO was determined in a semi-arid shrubland.

Chapter 2: Nitrogen in Africa

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2.1 Introduction

The productivity of many ecosystems is limited by the supply of biologically available (or reactive) nitrogen (Nr) [*Vitousek et al.*, 1997; *Vitousek et al.*, 2002b]. For many years now anthropogenic activities have been altering the nitrogen (N) cycle in the atmosphere, on land and in water, right from the local to the global scale [*Galloway et al.*, 2004b; *Nosengo*, 2003]. Over the last 100 years there has been a doubling of the amount of N transferred from the mostly biologically inaccessible atmospheric pool of N to the biologically available pools (Fig. 2.1). This doubling in the transfer of N from the unavailable form to available forms is largely as a result of human activities, mostly the production of food and energy [*Galloway et al.*, 2004b]. Important processes in which Nr is produced include the cultivation of N fixing crops, the production of fertilizer and the combustion of fossil fuel [*Vitousek et al.*, 1997].

Increases in the amount of Nr in many ecosystems have had numerous ecological consequences since Nr plays an important role in many environmental issues such as the greenhouse effect; atmospheric smog; the production of tropospheric ozone; the depletion of stratospheric ozone; acid deposition; nutrient loading and eutrophication processes in fresh water and coastal ecosystems; changes in the productivity and species composition of ecosystems and human health effects due to increases in respiratory related illnesses as a result of ozone and particulate matter inhalation [*Galloway et al.*, 2004a]. One of the important characteristics of reactive nitrogen species is that their effects are felt in a cascade (Fig. 2.2). For example one atom of N can, in sequence increase ozone in the troposphere, increase particulate matter in the atmosphere, alter the productivity of terrestrial ecosystems, acidify surface water, increase the productivity of coastal ecosystems, increase coastal eutrophication and increase the green-house potential of the atmosphere [*Galloway et al.*, 2003]. Therefore anthropogenic influences on the production and availability of Nr species, which have occurred through land use change, the production of pollutants and climate change, have a cascading effect through many other ecosystem levels.

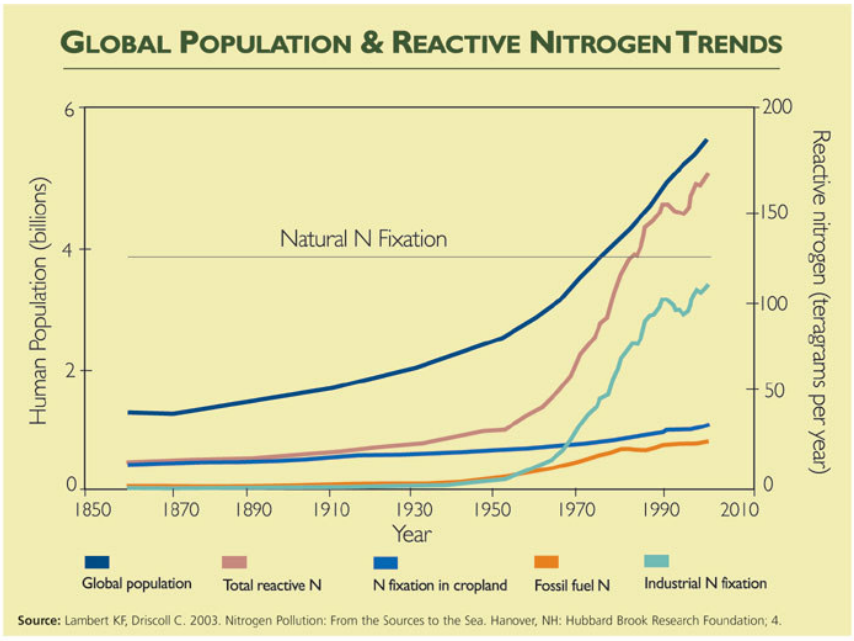

Figure 2.1: Global population trends from 1860 to 2000 (billions left axis) and Nr creation (Tg N a^{-1}; right axis). 'Haber-Bosch' is Nr creation via the Haber-Bosch process and includes the production of NH_3 for non-fertilizer purposes. 'C-BNF' is cultivation induced biological nitrogen fixation. Fossil Fuel is NO_x produced by fossil fuel combustion [*Galloway et al.*, 2003].

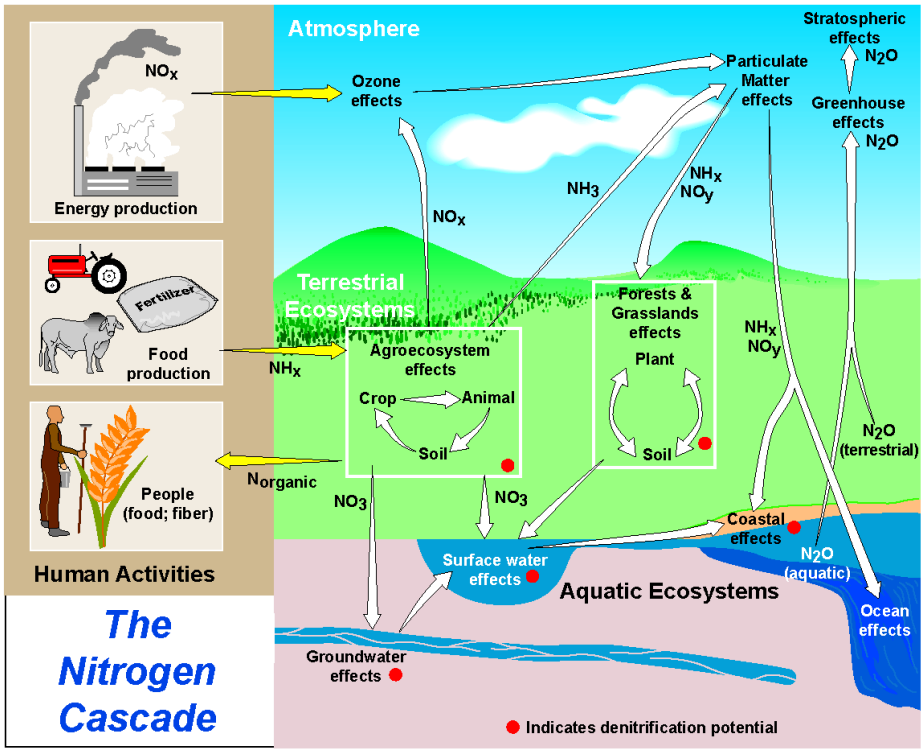

Figure 2.2 The N cascade illustrates the sequential effects that a single atom of Nr can have as it moves though the various pools [*UNEP*, 2004].

While many of these environmental issues are global their effects and severity may be different in different regions of the world. The major N issues for the African region are:

- The low use of mineral N fertilizer inputs (below 5 kg $ha^{-1}a^{-1}$) and even these low input rates are skewed towards commercial agriculture.
- The consequent unsustainability of agricultural production resulting in nutrient mining. Nutrient mining from African soils results in land degradation and decreased crop yields, which have an impact on food security and poverty in the region.
- The production and deposition of atmospheric trace gases, which have implications with regard to air quality. The production of atmospheric trace gases results from large scale biomass burning across vast areas of the continent, biogenic emissions from soil and vegetation and industry in South Africa and other localized areas in Africa [*Galloway et al.*, 2004a].
- Eutrophication caused by excessive inputs of Nr through atmospheric deposition, leaching and runoff from areas of human habitation and agricultural lands.

To date a fair amount of work has been done on N in Africa, including the production of continent wide budgets for the movement of N through the various pools and conversion processes (Fig. 2.3) [*Galloway et al.*, 2004a; Galloway et al., 2004b]. However this work has generally occurred in a discipline specific manner and there has been little attempt to compile the current state of knowledge and produce a holistic picture of the processes, problems and challenges that are specific for this continent. In this chapter we will attempt to synthesize the knowledge of N associated with Africa. In doing so we hope to make the links between terrestrial, aquatic and atmospheric processes clear.

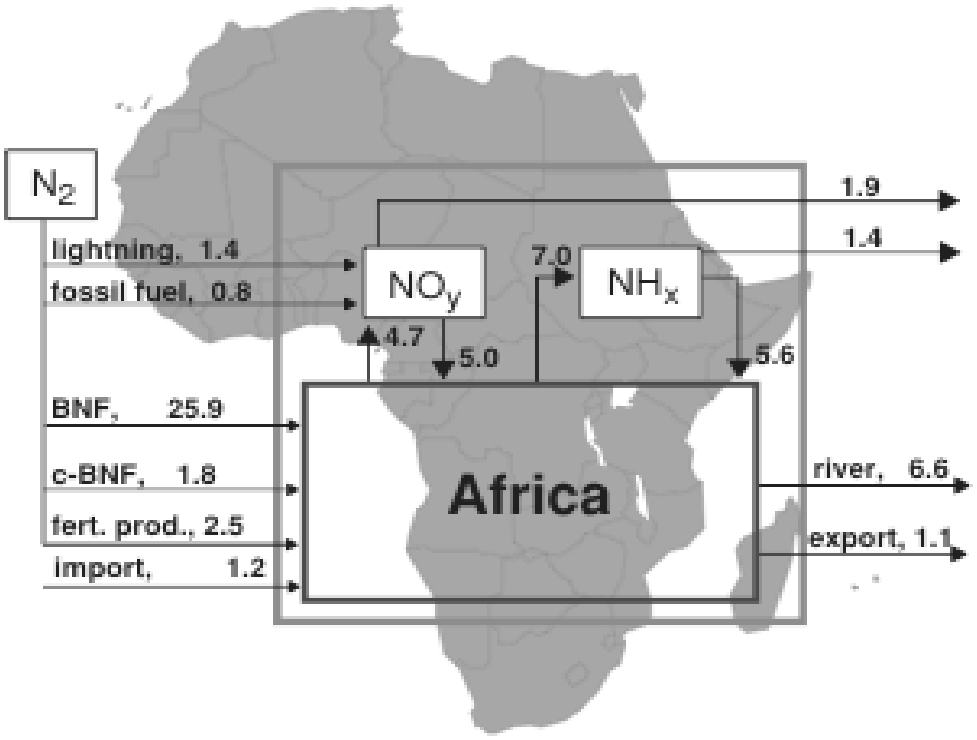

Figure 2.3: Nr Budget for Africa in the Early 1990s Tg N a^{-1} 'lightning' is Nr creation by NO_x formation during lightning; 'fossil fuel' is Nr creation by NO_x formation during fossil fuel combustion; 'BNF' is the formation of Nr through natural biological N fixation; 'c-BNF' is Nr formation during the cultivation of species that can fix N; 'fert. prod.' is Nr produced during Haber-Bosch production of fertilizer; 'import' and 'export' are Nr imports and exports in fertilizer, grain and meat; 'river' is Nr exports via rivers to the coastal zone; 'NO_y' is emission of NO_x, deposition of NO_y and atmospheric advection of both (by difference); 'NH_x' is emission of NH_3, deposition of NH_x and atmospheric advection of both (by difference) [*Galloway et al.*, 2004a].

2.2 Nitrogen in African Agriculture

One hundred and eighty million Africans do not have enough food to lead healthy and productive lives. Due to these food shortages they are more susceptible to the ravages of diseases like HIV, Malaria and Tuberculosis [*Sanchez*, 2002]. In contrast to the rest of the world, the food shortages in Africa are due to insufficient food production rather than problems with distribution and purchasing power [*Sanchez*, 2002]. In Africa per capita food production has remained stagnant since the 1960s, therefore African agriculture has effectively missed out on the improvements in agricultural production due to the green revolution, where improved crop varieties and the use of relatively high inputs of mineral fertilizer resulted in increased per capita food yields. For example in temperate regions the

yields of grain tripled with improved agricultural technologies. The techniques of the green revolution have not worked in Africa because:

- "soil fertility depletion in small holder farming in Africa is the fundamental biophysical root cause for declining per capita food production in Africa"
  - The issues of nutrient depletion have not been addressed through aid agencies or governments [*Sanchez et al.*, 1997],
- Many of the circumstances needed for the Green Revolution to succeed were missing, such as:
  - an impending crisis because of stagnant food production
  - the availability of new agricultural technologies in terms of improved varieties and crop management practices and
  - the existence of ancient farming systems, able to support relatively intensive food production over long periods [*Spencer et al.*, 1992].

The most important nutrients to have been depleted or that are in short supply in the soil are N and phosphorus (P).

2.2.1 N losses from Agriculture

It has been estimated that up to 40% of the N contribution to crops comes from N in the soil reserves [*Bationo et al.*, 1998; *de Jager et al.*, 1998a; *Roy et al.*, 2003; *Sheldrick and Lingard*, 2004]. Agriculture is, however, causing soil nutrient depletion as the nutrients removed from the soil, by farming practices and through farm products, are not being replaced (Fig. 2.4) [*Sheldrick and Lingard*, 2004; *Tan et al.*, 2005] . Nutrient depletion is considered to be a major form of soil degradation [*Roy et al.*, 2003] and human activities have resulted in the degradation of 15% of the total land area in Africa, and 65% of the agricultural land in use [*Bationo et al.*, 1998; *Chidumayo and Kwibisa*, 2003]. The reasons for land degradation in Africa are diverse but include factors such as:

- High population pressure resulting in the breakdown of traditional land management practices, such as fallow periods [*Bationo et al.*, 1998; *Chidumayo and Kwibisa*, 2003; *Sanchez et al.*, 1997; *Sanginga et al.*, 2003];
- Increased demand for agricultural produce [*Bationo et al.*, 1998; *de Jager et al.*, 1998a; *Sanginga et al.*, 2003];
- Low priority given to the rural sector by many governments and aid organisations [*Sanchez et al.*, 1997];

- The use of marginal land and ecologically sensitive land for agricultural production [*Nyamangara et al.*, 2000];
- The high cost of nutrient additions [*de Jager et al.*, 1998b; *Jayne et al.*, 2003; *Nyamangara et al.*, 2000; *Sanchez*, 2002; *Sanchez et al.*, 1997; *Sheldrick and Lingard*, 2004];
- Lack of reinvestment in soil fertility due to lack of cash, inefficient input/output markets, lack of infrastructure, ever-changing policy conditions; and
- Soils prone to degradation.

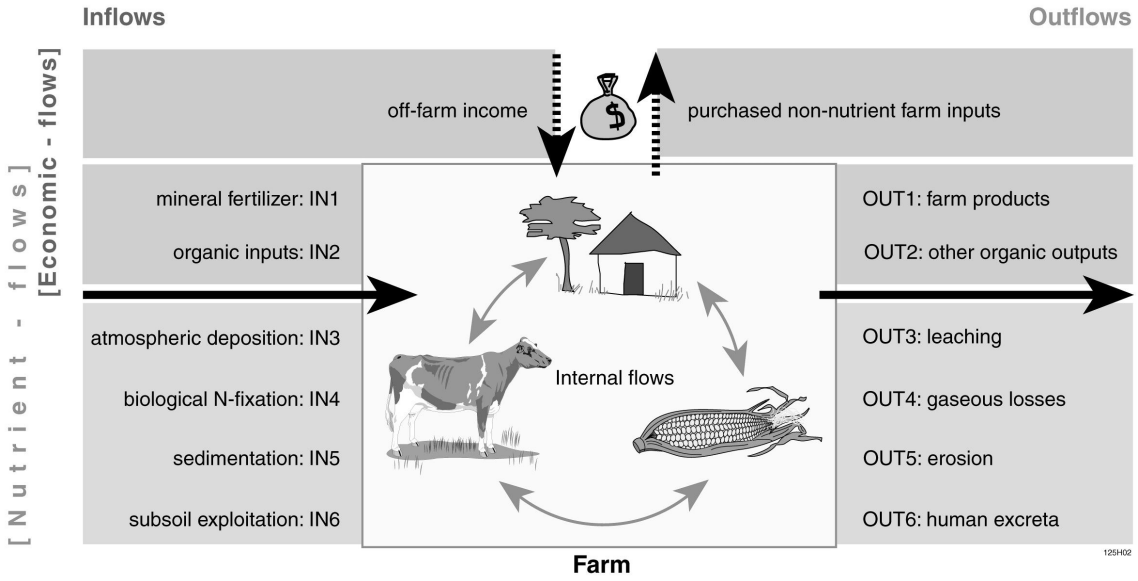

Figure 2.4: Nutrient flows and economic flows influencing the nutrient balance and household budget (after [*de Jager et al.*, 1998a; *de Jager et al.*, 1998b] in Smaling et al [2001]).

The consequences of nutrient depletion in the soil are complex but include *inter alia*:

- The low inherent fertility of a majority of the soils, often resulting in multiple constraints, at the biological, chemical and physical level, this results in low use efficiencies of the applied N fertilizer;
- A decline in crop production and food security, due to the reduction in plant yield;
- A reduction in available fodder for livestock, with a resultant decrease in livestock production;
- Damage to soil, including: increased erosion, and the further reduction in soil nutrients; compaction of the soil, leading to changes in the soil physical properties, which make plant growth more difficult; soil sealing, resulting in

reduced infiltration of water into the soil and increased run off and the consequent increase in soil erosion, reducing the quality of the soil resource even further;

- Increased poverty and decreased employment opportunities in rural areas, which lead to migrations of people from the rural areas to the urban areas, resulting in serious social problems in the urban areas;
- Increased levels of sedimentation of rivers and water storage facilities. This is due to high loads of silt, from the increased levels of soil erosion, entering the waterways;
- An increase in the release of CO_2 from the soil, due to a reduction in soil organic matter in the topsoil, which has implications for global climate change;
- Reduction in biodiversity both aboveground and belowground due to changes in the soil nutrient status, losses of topsoil through soil erosion and changes in the soil physical properties [*Sanchez et al.*, 1997];
- Shifting agriculture where new land is cleared for agricultural production when the soil fertility declines, has been blamed for deforestation of many regions [*Chidumayo and Kwibisa*, 2003];
- A mosaic of plots with varying soil fertility status within a farm and between farms as scarce organic and mineral resources are often concentrated on certain parts of the farm [*Tittonell et al.*, 2005].

The scale of nutrient depletion from African agricultural soils is alarming. Sheldrick and Lingard [2004] estimate that 3.5 Tg (million tons) of N has been lost from agricultural soils since 1961, most of it since 1985. Sanchez *et al* (1997) estimated that an average of 660 kg ha^{-1} (balance between inputs and outputs) has been lost in the last 30 years from 200 million ha of cultivated land in 37 African countries (excluding South Africa), which is a average loss of 22 kg $ha^{-1}a^{-1}$. Sheldrick and Lingard [2004] estimated the loss at 34 kg $ha^{-1}a^{-1}$.To put this in a global perspective 56% of countries are thought to experience a negative nutrient balance in agricultural systems, the average nutrient loss is thought to be 17.4 kg $ha^{-1}a^{-1}$ [*Tan et al.*, 2005], therefore the situation across most of Africa is worse than the world average. Nutrient audits have been carried out for various countries in sub-Saharan Africa (Fig. 2.5). In most cases there is a negative nutrient balance at the country level, however it must be noted that modelled nutrient balances tend to become more negative as the spatial scale of the study

increases due to methods of dealing with the internalisation of nutrient flows during the modelling process [*Schlecht and Hiernaux*, 2004; *Smaling et al.*, 2001].

The N that is lost from African agricultural systems is lost through a variety of sources, including agricultural produce, soil erosion, biogenic and pyrogenic emissions into the atmosphere and leaching.

2.2.2 Methods of N replenishment

While N is lost in African agricultural systems the rate of N replenishment is not generally sufficient to replace it. This is in contrast to what is happening in other regions of the world where the addition of too much N is producing serious adverse ecological effects, such as the acidification of soil, N deposition to surrounding areas and eutrophication of ground and surface water. The main sources of nutrient additions in African agricultural systems are in the form of animal manures and crop residues [*Chianu and Tsujii*, 2005; *Rufino et al.*, 2006; *Sanchez et al.*, 1997; *Sanginga et al.*, 2003; *Sheldrick and Lingard*, 2004]. Mineral fertilizer is used, but generally in sub-optimal quantities [*Chianu and Tsujii*, 2005]. Other inputs of soil nutrients come from non-crop/livestock residues and atmospheric deposition. Between 1996 and 1998 the input of N into agriculture was estimated at 30.9 kg $ha^{-1}a^{-1}$ [*Sheldrick and Lingard*, 2004].

Nutrient depletion (kg ha $^{-1}$ yr $^{-1}$)

	N	P	K
Low	< 10	< 1.7	< 8.3
Moderate	10 to 20	1.7 to 3.5	8.3 to 16.6
High	20 to 40	3.5 to 6.6	16.6 to 33.2
Very high	≥ 40	≥ 6.6	≥ 33.2

Figure 2.5: Classification of soil N balances for the arable land of sub-Saharan Africa (in Smaling et al [1997] adapted from Stoorvogel and Smaling [1990]).

In an attempt to reverse the trend of nutrient mining in African agriculture, various authors have called for measures to improve the soil fertility status. A variety of methods have been proposed including facilitating an increase in the use of mineral fertilizers, the use of BNF (biological nitrogen fixation) and organic residues rich in N and the use of both organic residues and mineral fertilizers. These techniques fall under the banner of Integrated Soil Fertility Management which advocates the combined application of mineral and organic inputs because (i) either of the two inputs is usually not available in sufficient quantities, (ii) both inputs are needed in the long run to sustain soil fertility and crop production, and (iii) positive interactions between both inputs could potentially result in added benefits in terms of extra grain yield or extra soil fertility increase. A *Direct* and *Indirect Hypothesis* which could form the basis for the occurrence of such benefits has been formulated by Vanlauwe *et al.* [2001]. The *Direct Hypothesis* was formulated as: *Temporary immobilization of applied fertilizer N may improve the synchrony between the supply of and demand for N and reduce*

losses to the environment. The *Indirect Hypothesis* was formulated for N supplied as fertilizer as: *Any organic matter-related improvement in soil conditions affecting plant growth (except N) may lead to better plant growth and consequently enhanced efficiency of the applied N.* The *Indirect Hypothesis* recognizes that organic resources can have multiple benefits besides the short-term supply of available N. Such benefits could be improved soil phosphorus (P) status by reducing the soil P sorption capacity, improved soil moisture conditions, less pest and disease pressure in legume-cereal rotations, or other mechanisms. Both hypotheses, when proven, lead to an enhancement in N use efficiency, through improvement of the N supply (*Direct Hypothesis*) and the demand for N (*Indirect Hypothesis*). Mechanisms supporting both hypotheses may occur simultaneously [*Vanlauwe et al.*, 2001].

To maintain food production in Africa and improve production, it will be necessary to add large quantities of high quality organic inputs and mineral fertilizers and that these additions will need to be tailor made to suit the soil type, cropping system, culture and the needs of the farmers involved [*Giller et al.*, 1997; *Nyamangara et al.*, 2000; *Quinones et al.*, 1997]. To maintain soil fertility until 2020 a minimum annual growth of 6% in fertilizer use is required [*Sheldrick and Lingard*, 2004]. Sub-Saharan Africa, however, is reported to have the lowest rate of fertilizer use in the world, only 8 kg $ha^{-1}a^{-1}$, while the average for the rest of the world was 90 kg ha^{-1} in 1997 [*Bationo et al.*, 1998]. This is due to the high cost, between 2 and 6 times higher than in Europe, North America or Asia, of inorganic fertilizers in Africa [*Bationo et al.*, 1998; *Jayne et al.*, 2003; *Sanchez*, 2002; *Sanchez et al.*, 1997; *Sheldrick and Lingard*, 2004]. While the current use of N fertiliser in Africa is low, fertiliser use is expected to double from the 1995 levels by 2030 [*Bouwman et al.*, 2005], while this will help to alleviate the problems with food production other important environmental issues, such as the production of N containing trace gases and eutrophication of water bodies may be exacerbated.

The largest source of Nr in Africa is though biological N fixation (BNF). Across Africa this accounts for the fixation of approximately 25.9 Tg a^{-1}, however this figure also includes natural areas [*Galloway et al.*, 2004a]. Nr is incorporated into agricultural production either through the manure of animals which graze in uncultivated areas or through the addition of plant biomass, obtained from uncultivated areas. The contribution of Nr from cultivated BNF is less than that which occurs in other regions of the world, particularly Asia, North America and Europe [*Galloway et al.*, 2004a] however Africa is expected to have a prominent growth of soy bean production in the next 3 decades, most of which will be used for animal fodder [*Bouwman et al.*, 2005]. While legumes are useful in fixing N (if the symbiosis works

properly) grain legumes have limited potential of replenishing soil Nr since most of the N fixed by the plant is incorporated in the grain which is removed [*Sanchez et al.*, 1997].

The temperature and amount of precipitation have an effect on the rate of N fixation, under high temperatures and drought conditions the rate on N fixation has been shown to decrease in various cultivated legumes, since nodule formation is constrained [*Carranca et al.*, 1999; *Hungria and Vargas*, 2000]. This has implications with regard to projected climatic change, if the temperature increases and the precipitation decreases, there is the potential for a decrease in the amount of N fixed through BNF, both naturally or associated with cultivation.

2.3 Nitrogen Emissions

Numerous species of Nr are emitted as gases into the atmosphere, including NO_x (which is made up of NO and NO_2 that convert rapidly between the two species in the presence of sunlight and ozone), nitrous oxide (N_2O) and ammonia (NH_3). These gases are involved in a number of atmospheric processes; they can lead to the formation of tropospheric ozone, increase the greenhouse potential of the atmosphere and facilitate the destruction of stratospheric ozone. Further more, these species of Nr also have important influences on acid deposition and the eutrophication of aquatic and terrestrial ecosystems [*Galloway et al.*, 2004a]. These issues affect both ecosystem and human health.

2.3.1 Nitrogen Oxides (NO_x)

NO_x is one of the most important species of Nr involved in the nitrogen cascade, it is produced naturally in many soils through the biological processes of denitrification and nitrification and during the burning of fossil fuels, particularly where there is high temperature combustion that causes N to be fixed from the atmosphere [*van Tienhoven et al.*, 2003]. With the increased use of fertilizer for agriculture, and combustion of fossil fuels, the emissions of NO_x have increased in the last century. In 1860 the global NO_x emission was 13.1 Tg a^{-1}, of which 10.5 Tg came from natural sources. By the early 1990's it was estimated that emissions totalled 45.9Tg a^{-1} [*Galloway et al.*, 2004a].

Emissions of the NO_x gases are important in regulating chemical processes in the atmosphere [*Levine et al.*, 1997; *Lindesay*, 1997; *Scholes and Andreae*, 2000]. These gases are key catalysts in the chemical processes that generate or destroy ozone, which is a secondary pollutant. The mixing ratio between NO and ozone (O_3) produces a threshold which determines whether ozone is generated or destroyed. Most tropospheric ozone is produced in the reaction between non-methane hydrocarbons and oxides of nitrogen (particularly NO_2)

and by the oxidation of methane by the OH radical in the presence of NO_x [*Crutzen*, 1995; *Levine et al.*, 1997; *Lindesay*, 1997; *Meixner and Yang*, 2006].

Nitrous oxide is an important greenhouse gas with a greenhouse forcing potential 200 times that of CO_2. In the stratosphere N_2O is involved in the destruction of stratospheric ozone, which protects the earths surface from harmful UV radiation [*Levine et al.*, 1997]. The lifetime of N_2O is about 120 years, therefore any changes that occur in the production of N_2O are likely to have a long term effect [*Scholes et al.*, 2003a]. N_2O is produced naturally in the soil through the bacterially mediated processes of nitrification and denitrification and through the burning of biomass. The production of N_2O has increased with the expansion of food production and the intensification of agriculture [*Scholes et al.*, 2003a].

2.3.2 Ammonia

Ammonia is important in the eutrophication of ecosystems, particularly water bodies, and in the acidification of soil. The most important sources of NH_3 in the atmosphere are agriculture, including the production of fertilizer and volatilisation of fertilizer surface-applied to the soil in the absence of sufficient rainfall, animal manures, and biomass burning [*Scholes et al.*, 2003a; *van Tienhoven et al.*, 2003].

2.4 Sources of gaseous nitrogen emissions

2.4.1 Biogenic emissions

Soils are known to be an important source of N trace gases [*Scholes and Andreae*, 2000]. The flux of NO and N_2O is the result of complex interactions between different processes in the soil, that occur simultaneously. NO and N_2O are produced during the microbial processes of nitrification and denitrification, but the relative significance of these processes differs according to the soil conditions, primarily soil moisture followed by soil temperature and nutrients [*Conrad*, 1996]. A summary of biogenic NO_x and N_2O emissions in Africa are presented in Tyson *et al* [2002]. Suffice to mention that savannas soils are a particularly important source of NO due to the high temperatures and their vast geographic extent. It appears that the production of NO is dominant over N_2O due to the long dry seasons and low water filled pore space of the soil [*Scholes and Andreae*, 2000; *Tyson et al.*, 2002]. The total biogenic NO_x emissions from southern Africa are approximately 1Tg a^{-1} [*Tyson et al.*, 2002]. Measurements of NO emissions from West and Southern Africa show that the emissions range from 0.05-100ng m^{-2} s^{-1} [*Harris et al.*, 1996; *Le Roux et al.*, 1995; *Levine et al.*, 1996;

Meixner et al., 1997; *Parsons et al.*, 1996; *Scholes et al.*, 1997; *Serca et al.*, 1998]. The emissions of NO from soils are most strongly regulated by soil moisture, soil nutrients and soil temperature [*IFA and FAO*, 2001; *Meixner et al.*, 1997; *Otter et al.*, 2002; *Otter et al.*, 1999]. Biogenic NO emissions are susceptible to alteration by changes in the amount and timing of precipitation and changes in temperature. The addition of fertilizer to agricultural land increases the amount of NO and N_2O produced since levels of soil nutrients are elevated (Table 2.1).

There is a large amount of uncertainty with regard to the role of savanna soil in N_2O production due to the scarcity of results [*Scholes and Andreae*, 2000; *Tyson et al.*, 2002]. N_2O fluxes of between 3.0 and 15 ng $m^{-2}s^{-1}$ have been reported [*Levine et al.*, 1997; *Scholes et al.*, 1997]. The biogenic production of N_2O is strongly regulated by the soil water filled pore space. As the amount of soil water increases and the number of anaerobic microsites in the soil increase more denitrification occurs. Since denitrification is the major pathway for N_2O formation there is an increase in N_2O production [*Firestone and Davidson*, 1989]. Climatic changes resulting in an alteration of the rainfall pattern are therefore likely the effect biogenic N_2O production.

Ammonia is formed in the soil during biological degradation of organic compounds and NH_4^+ yielding inorganic and organic fertilizers. Once formed in the soil ammonium can remain on the exchange sites, be nitrified to nitrate, which has the potential to produce NO and N_2O, or volatilise to the atmosphere, depending on the soil and environmental conditions [*IFA and FAO*, 2001]. Estimates of ammonia volatilisation from agricultural soils in Africa are presented in Table 2.2.

Table 2.1: N_2O and NO emission estimates from N fertilizer and animal manure application on crops and grasslands 1995. Modified from [*IFA and FAO*, 2001].

	Area (10^6 ha)	**Fertilizer N (Gg)**	**Manure (Gg)**	**N_2O Emissions (Gg)**	**NO Emissions (Gg)**
Crops					
West Africa	75	156	140	171	41
East Africa	41	109	148	78	31
Southern Africa	42	480	78	72	24
Grassland					
West Africa	48	0	137	30	26
East Africa	26	0	148	13	17
Southern Africa	24	31	78	13	14

Table 2.2: NH_3 volatilization loss estimates from Mineral N and manure application on fertilized grasslands, upland crops and wetland rice by region in Africa for 1995. Modified from IFA and FAO [*IFA and FAO*, 2001].

Region	Fertilized Grassland			Upland Crops			Wetland Rice		
	Area (10^6 ha)	N Use (Gg)	NH_3 loss (Gg)	Area (10^6 ha)	N Use (Gg)	NH_3 loss (Gg)	Area (10^6 ha)	N Use (Gg)	NH_3 loss (Gg)
Mineral N application									
West Africa	0	0	0	73	130	19	1	26	4
East Africa	0	0	0	40	109	17	1	1	0
Southern Africa	3	31	3	42	477	51	0	3	0
Animal Manure									
West Africa	48	137	35	73	137	39	1	3	1
East Africa	26	148	40	40	143	43	1	6	1
Southern Africa	24	78	20	42	78	23	0	2	0

2.4.2 Pyrogenic emissions

Africa has been called the earth's biomass burning centre. The combustion of biomass produces an immediate and significant emission of trace gases into the atmosphere [*Levine et al.*, 1997]. On a global scale biomass burning, and the burning of savannas in particular, accounts for sizable contributions of the global budgets for a number of trace gases and aerosol species including NO_x, N_2O and NH_3 gases (Table 2.3) [*Jost et al.*, 2003; *Keene et al.*, 2006; *Keil and Haywood*, 2003; *Sinha et al.*, 2004; *Yokelson et al.*, 2003]. Therefore any changes in the frequency, area burnt, timing and types of fires that occur in Africa are important in understanding the dynamics of these gases [*Korontzi et al.*, 2003]. The presence of products of biomass burning in Africa can be detected in the atmosphere as far a field as Australia [*Pak et al.*, 2003; *Tyson et al.*, 2002].

Table 2.3: Total global emissions of some important N containing trace gases, the global pyrogenic emissions of these gases, and the proportion of those emissions from Africa [*Lindesay*, 1997] (* for emissions from woodland savanna fires in Southern Africa for the period May to October 2000 from Sinha et al [2004]).

	NO_x	N_2O	NH_3
Total global emissions (Tg)	70	5.4	55.8
Global pyrogenic emissions (Tg) *(% of total emissions)*	21 (30%)	1.3 (24%)	6.7 (12%)
Pyrogenic emissions from Africa (Tg) *(% of total pyrogenic emissions)*	4.2 (20%) (6% of total global emissions)	0.52 (40%) (10% of total global emissions)	*0.137 (2%) (0.2% of total global emissions)

Most of the N that is contained in vegetation is volatilised and emitted as a mixture of N_2, NO, NO_2, N_2O and NH_3 when the vegetation is burnt [*Andreae*, 1997; *Keene et al.*, 2006]. For the savannas in the Kruger National Park, South Africa, between 14 and 33 kg ha^{-1} of the aboveground pool of N is lost in a fire [*Andreae*, 1997]. The majority is emitted as NO_x, which has reported emission factors of 0.7-2 g kg^{-1} fuel, the emission factors for NH_3 are 0.06-3.5 g NH_3 kg^{-1} fuel, however the emission of these gases depends on the type and conditions of the fuel [*Keene et al.*, 2006; *Sinha et al.*, 2003; *Yokelson et al.*, 2003].

Emissions from residual smouldering combustion (RSC) (which will occur towards the end of the fire) differ to that of flaming combustion and NH_3 becomes the major N compound emitted with a emission factor of 0.98 g NH_3-N kg^{-1} fuel, while NO_x is not detected [*Bertschi et al.*, 2003a; *Yokelson et al.*, 2003]. The NH_3 emissions are lower in fires from tropical regions than from fires in other areas [*Yokelson et al.*, 2003] . Therefore in comparison to global sources the emissions of NH_3 from savanna fires is minor [*Sinha et al.*, 2003]. Concentrations of NH_3 in the atmosphere show seasonal patterns related to the interplay between meteorological conditions and biomass burning [*Carmichael et al.*, 2003; *Galy-Lacaux et al.*, 2001; *Singha-Nkamdjou et al.*, 2003].

Projected changes in climate are likely to have an effect on the pyrogenic emissions of N containing trace gases. The area and quantity of biomass that is burnt on a yearly basis is largely dependent on the fuel load, which in turn is dependent on the precipitation [*Korontzi et al.*, 2003; *Scholes et al.*, 1996].

2.4.3 Industrial emissions and biofuels

Industry and the burning of biofuels have an important role in the production of trace gases in Africa [*Tyson et al.*, 2002]. Industrial and biofuel emissions of NO from southern Africa make a significant contribution to the global NO budget. The estimated emissions of NO from biofuel burning constitute approximately 0.16 Tg annually, while the industrial emissions from southern Africa amount to 1.75 Tg which are lower but within the same order of magnitude as NO emissions from biomass burning. A increase in the concentration of tropospheric ozone in the South Atlantic between 1977 and 2002 has been attributed to increased NO_x emissions from energy sources in Africa [*Lelieveld et al.*, 2004].

The main source of industrial emissions of NO_x gases come from the burning of coal for electricity generation in South Africa. The Mpumalanga highveld region of South Africa produced 47% of the electricity generated in Africa in 1993. The generation of electricity in

South Africa results in the production of 0.97 Tg of NO_x emissions which is 55% of the estimated NO_x emissions from industry in Africa [*Spalding-Fecher and Matibe*, 2003].

Biofuels provide between 60 and 90% of the energy requirements for many countries in sub-Saharan Africa [*Bertschi et al.*, 2003b; *Ryan and Openshaw*, 1991]. The burning of biofuel is the second most important type of biomass burning globally after savanna fires [*Yokelson et al.*, 2003]. In many regions there is a scarcity of fuel wood, which is then substituted for alternative sources of biofuel, such as agricultural waste and cow dung, thus depriving the users of a source of fertilizer for their crops [*Marufu et al.*, 1997; *Otter et al.*, 2001]. The major problem with the use of biofuels is air pollution associated with its use. During the combustion of biofuel, various trace gases including CO, CH_4, non-methane hydrocarbons (NMHC), aerosol particles, NO, N_2O and NH_3 are released into the atmosphere which (unlike CO_2) constitute a net flux into the atmosphere since they are not subsequently reabsorbed by plant growth [*Marufu et al.*, 1997]. To date the contribution of biofuel burning to the global emissions of trace gases is not well established [*Marufu et al.*, 1997]. The global emissions of NO from biofuel burning is ~2.5 Tg NO-N a^{-1} (0.065Tg NO- N a^{-1} for southern Africa) [*Ludwig et al.*, 2003; *Otter et al.*, 2001]. The emission factors change according to the type of fuel used. NO emission factors range from 0.74 g NO-N kg^{-1} fuel for charcoal (production and use), 0.8 g NO-N kg^{-1} for wood and 4.41 g NO-N kg^{-1} fuel for cattle dung [*Bertschi et al.*, 2003b; *Keene et al.*, 2006; *Otter et al.*, 2001], 0.12 g NO_2-N kg^{-1} fuel for charcoal (production and use), 0.15 g NO_2-N kg^{-1} fuel for wood [*Bertschi et al.*, 2003b] and 1.89g NH_3-N kg^{-1} fuel for charcoal (production and use), 1.06 g NH_3-N kg^{-1} fuel for wood [*Bertschi et al.*, 2003b]. In Zambia, the emissions of NH_3 from biofuel burning are significantly greater than from savanna fires [*Bertschi et al.*, 2003b].

2.5 Nitrogen Deposition

Much of the NO and NH_3 that is emitted into the atmosphere is later deposited onto the earths surface, primarily on the continents [*Galloway and Cowling*, 2002]. The Nr that is redeposited may have undergone chemical changes in the atmosphere and can be deposited in dry gaseous form as NO, NO_2, peroxyacetyl-nitrate (PAN), HNO_2, HNO_3, or in a aerosol form as aerosol nitrites (NO_2^-) or aerosol nitrates (NO_3^-). Many of these atmospheric Nr species can be taken up in atmospheric water and then deposited through wet deposition. Globally the effect of N deposition is ranked as the third most important effecter of biodiversity change after land use and global climate change. Therefore the effects of N deposition can have a

major impact on ecosystem stability. The effects include changes in C storage, changes in trace gas exchange, cation leaching from the soil, biodiversity changes and eutrophication [*Matson et al.*, 1999; *van Tienhoven et al.*, 2003]. As a result of the emissions of N trace gases and the atmospheric circulation systems that occur over southern Africa there are fairly large amounts of N deposited through wet and dry depositional processes which supply a considerable amount of N to African soils [*Lowman*, 2003; *Roy et al.*, 2003; *Tyson et al.*, 2002]. The additions of N from the atmosphere may have beneficial effects on certain communities, by providing required nutrients; however, since many species are adapted to low nutrient levels, the addition of N can change the species composition and may lead to the invasion by weeds and alien species [*van Tienhoven et al.*, 2003].

N deposition is considered to be one of the major causes of increased acidification of the soil [*Matson et al.*, 1999]. This is caused through a number of processes including the deposition of acid species [*Coleman and Thomas*, 1967] and acidification processes that occur in the soil once the Nr species has been deposited [*Jordan*, 1985].

Soil acidification constrains plant growth and ecosystem function through a number of mechanisms, namely:

- Aluminium and manganese toxicity to the plant
- Inhibition in metal cation uptake;
- Nutrient and water deficiency in plants as a result of inhibition in root growth;
- Phosphorus and molybdenum deficiency, caused by decreases in P and Mo solubility;
- An increase in leaching of certain cations such as Ca, Mg and K [*Marschner*, 1986].

Added N can be acidifying regardless of the inorganic form in which it is added, but the net change relies on the plant uptake, additions of NH_4^+ can lead to the greatest increase in acidity on a per molecule basis particularly if the NH_4^+ ion is nitrified and the nitrate is subsequently leached [*Matson et al.*, 1999]. The effects of N deposition are not limited to the area in which the trace gases are produced since there is a large degree of recirculation of trace gases over regions in Africa, which often involves trans-boundary transport and the subsequent deposition of the gases [*Tyson et al.*, 2002]. Therefore processes that occur in one country can have an effect in other countries in the region [*Fournier et al.*, 2005; *Holland et al.*, 2005; *Spokes and Jickells*, 2005].

2.5.1 Nitrogen deposition in Southern Africa

Very little is known about N deposition in southern African countries [*van Tienhoven et al.*, 2003], although some work has been done, the majority of that work occurred in South Africa. Research on N deposition in South Africa, includes estimates and measurements of both wet and dry deposition, which have been made for natural grassland near the industrial regions of South Africa [*Mphepya et al.*, 2006; *Mphepya et al.*, 2004] on the Mpumalanga escarpment, downwind of the industrial areas [*Lowman*, 2003] and savanna ecosystems upwind of the industrial areas [*Lowman*, 2003; *Mphepya et al.*, 2004; *Scholes and Walker*, 1993; *Woghiren*, 2002], downwind of the industrial areas [*Woghiren*, 2002], forest plantations on the eastern escarpment of South Africa [*Lowman*, 2003] and lake Malawi [*Bootsma et al.*, 1996]. The amount of N deposition described in these studies ranged from 2.5 kg N ha^{-1} a^{-1} to greater than 48.4 kg N ha^{-1} a^{-1} (Table 2.4).

2.5.2 Nitrogen deposition in West and Central Africa

Studies on N deposition in the major ecosystems in west and central Africa have been performed by the IDAF network. The ecosystems are semi-arid savannas (Banizoumbou, Niger; and Katibougou, Mali), humid savannas (Lamto, Ivory Coast; and Ngola, Central African Republic) and equatorial forests (Bomassa, Congo; and Zoetele', Cameroon) [*Galy-Lacaux et al.*, 2003]. The lowest total amount of wet N deposition occurred in the semi-arid sites, with the highest levels occurring in the forest and humid savannas (Table 2.5). Differences are mainly due to the amount of precipitation in each system. The highest concentrations of NH_4^+ in the precipitation were recorded in the semi-arid sites, which were attributed to strong sources of ammonia from domestic animals during the wet season. The highest concentrations of NO_3^- in the precipitation were also found in the semi-arid sites. Wet deposition is dominated by NH_4^+, which accounts for approximately 60% of the total N flux (Table 2.5) [*Galy-Lacaux et al.*, 2003].

Dry deposition is dominant in humid savanna and forest ecosystems and accounts for 60-70% of the total N deposited from the atmosphere (Table 2.5). The highest amounts of N deposition occur on the forested sites and the lowest on the semi-arid savannas. The N deposition values obtained for West and Central Africa correspond fairly well with the deposition values obtained for Southern Africa.

Table 2.4: Wet and dry N deposition to ecosystems in Southern Africa (all units are in kg N $ha^{-1}a^{-1}$) (dry deposition into Lake Malawi measured dry deposition onto a water surface particulate deposition was not measured).

	Grasslands regions			**Savanna regions**			
	Amersfoort [*Mphepya et al.*, 2004]	**Escarpment** [*Lowman*, 2003]	**Plantation forests** [*Lowman*, 2003]	**Nylsvley** [*Scholes and Walker*, 1993]	**Louis Trichardt** [*Mphepya et al.*, 2004]	**Kruger National Park** [*Woghiren*, 2002]	**Lake Malawi** [*Bootsma et al.*, 1996]
Wet deposition	48.4	7	21.4	No data	15	11.6	1.1
Dry deposition	No data	7.8	7.8	No data	No data	10	>11.3
Total	**>48.4**	**14.8**	**29.2**	**2.5**	**>15**	**21.6**	**>12.4**

Table 2.5: Yearly N deposition at the 6 IDAF sites in west and central Africa (data from Galy Lacaux [2003] (all units in kg $ha^{-1}a^{-1}$).

	Semi Arid Savanna	**Humid Savanna**	**Forest**
Wet deposition NO_3^-	0.8-1.2	1.3-1.9	1.9-2.3
Wet deposition NH_4^+	1.3-2.3	2.8-2.8	2.2-2.9
Wet deposition inorganic N	2.1-3.5	4.1-4.7	4.5-4.8
Total Wet Deposition	**4.2-7**	**8.2-9.4**	**9-9.6**
Particulate dry deposition	0.12 ±0.01	0.08 ± 0.01	0.06 ±0.01
Dry gaseous deposition NO_2	0.8±0.01	No data	1.5± 0.01
Dry gaseous deposition NH_3	3.1-5	9-12	12
Total Dry deposition	**4.0-5.9**	**9.1-12.1**	**13.6**
Total N deposition	**8.2-12.9**	**17.3-21.5**	**23.6-24.2**

2.6 Nitrogen in water bodies

Changes in the distribution and type of N in ecosystems often results in N being added to water bodies, either through leachate (mostly NO_3^-) from the soil, the addition of NH_4^+ and organic matter in waste (domestic, industrial and agricultural) and through direct atmospheric deposition onto the water body. The results of the addition of N into water bodies include:

- The process of eutrophication, which has been defined as "the increased accumulation of organic matter, usually as a result of increased nitrogen and

phosphorus inputs, but could result from the supply of excessive decomposable carbon as well" [*Nixon*, 1995].

- Surface water acidification [*Rabalais*, 2002].

The most important environmental effects of N additions would be through the processes of eutrophication. It has been reviewed in Rabalais [2002] that there is a significant relationship between nutrient loading of water bodies and algal production and biomass.
Nutrients are added to aquatic ecosystems in a number of ways, including:

- Rivers, which play a primary role in the delivery of nutrients to the oceans and other large water bodies [*Lindenschmidt et al.*, 1998; *Rabalais*, 2002].
- Atmospheric deposition, known to be a important source of Nr additions into large water bodies, can account for between 1 and 40% of the Nr input into coastal and estuarine systems [*Paerl et al.*, 2000] and up to 70% for some of the great lakes in Africa [*Scheren et al.*, 2000].
- Dust deposition (containing Fe) into the oceans can have an important effect on N fixation since, N fixation in the oceans is iron limited [*Rabalais*, 2002; *Tyson et al.*, 2002].

The extent to which the addition of N to ecosystems will affect water quality, largely depends on N cycling at the land water interface since denitrification in the riparian zone can remove Nr from water as it moves from upslope systems to streams and water bodies [*Matson et al.*, 1999; *McClain et al.*, 1994]. The main mechanism for the reduction in Nr across the riparian zone in tropical forests is thought to be denitrification [*Bowden et al.*, 1992; *Brandes et al.*, 1996]. However this leads to the production and emission of N_2O which has its own environmental consequences. Denitrification also occurs in the anaerobic sections of the water body and in the sediments, while the quantities of N containing trace gases that are emitted from African water ways is not known this source could be substantial [*Adams and Ochola*, 2002].

2.6.1 Case studies of water bodies affected by large N inputs

The problems associated with Nr entering water bodies are found in various systems throughout Africa. Many of these issues can, however, be discussed using 2 case studies; that of Lake Victoria and the Ebrie Lagoon in the Ivory Coast.

2.6.1.1 Lake Victoria

Large algal blooms are occurring more often in Lake Victoria resulting in large scale fish kills. The problem is caused by an increase of nutrient input into the lake system through atmospheric deposition, increases in the urban population surrounding the lake, and agricultural and industrial activity [*Lindenschmidt et al.*, 1998; *Scheren et al.*, 2000]. The activities that are causing the increase in nutrients in the lake include, human settlements, deforestation, crop and livestock farming, encroachment on wetlands and gold mining [*Machiwa*, 2002]. Modelled results show that the most important source of N entering lake Victoria is from atmospheric deposition and totals 85.5 Gg N a^{-1} or 71% of the total N input into the lake [*Scheren et al.*, 2000]. In rainwater samples falling on the lake in May and June 1994 dissolved N concentrations were found to be between 580 and 1906μgl^{-1} [*Lindenschmidt et al.*, 1998; *Scheren et al.*, 2000]. On lake Malawi, with similar surrounding land use practices to Lake Victoria, the N deposition was estimated to 7.5-19 kg N $ha^{-1}a^{-1}$ [*Bootsma et al.*, 1996] which is in the same range as found for N deposition calculated for other parts of Africa [*Galy-Lacaux et al.*, 2003; *Lowman*, 2003].

The other major source of N into Lake Victoria is from agriculture, which is responsible for the addition of 26 Gg a^{-1} into the lake (22% of the total) [*Scheren et al.*, 2000]. The input of N from agriculture is controlled by the land use practice, uncultivated land results in the lowest amount of N loading and pastoral land has the highest levels of N loading. One of the main causes of N loading of the Lake from agriculture is enhanced soil erosion [*Machiwa*, 2002]. The amount of N entering the lake is considerably less than the amount exported from the surrounding land, for example the amount of N exported from the lake Victoria catchments in western Kenya and Rwanda is 40-45 kg $ha^{-1}a^{-1}$, while the actual amount entering the lake is thought to be closer to the estimate for Malawi of 1.4 kg $ha^{-1}a^{-1}$ [*Scheren et al.*, 2000]. The difference in these values comes from N uptake and denitrification that occurs in the surrounding wetlands and streams. It is known that wetlands, riparian areas and estuaries are important for retaining N. However many riparian zones are being degraded, increasing the input of N into the lake [*Lindenschmidt et al.*, 1998; *Machiwa*, 2002; *Scharler and Baird*, 2005].

2.6.1.2 Ebrie Lagoon

In West Africa a similar process of increased N input is occurring in the Ebrie Lagoon in the Ivory Coast [*Scheren et al.*, 2004]. There has been a decrease in the water quality due to eutrophication as a result of high nutrient loads entering the system. The amount of N entering the lagoon is 47.9 Gg a^{-1} which comes from effluents from domestic and industrial waste in the region near Abidjan and from N from the farming activities. Overall the greatest source of N into the Ebrie lagoon is from cultivated land which accounts for 26.2 Gg a^{-1} (55%) of the N input. Uncultivated land accounts for 12.3 Gg a^{-1}(25.7%) of the total N input [*Scheren et al.*, 2004]. Other important sources of N come from unprocessed domestic sewage (8.2% of total), atmospheric deposition (7.2% of total), processed sewage (3.2% of total) and industrial sources (0.8% of total). Projections indicate that the N concentration in the Lagoon will increase by a factor of 3.5 over the period 1980-2050. Therefore if current trends continue, in the near future the Lagoon will be in a highly eutrophic state across it entire length, which will have disastrous ecological and human consequences [*Scheren et al.*, 2004].

2.7 Conclusion

The global production of Nr has more than doubled in the last century resulting in major threats to biodiversity, the availability of clean air and water and human and ecosystem health. Additions of Nr are predominantly due to anthropogenic changes in agriculture and fossil fuel combustion. In contrast to many other regions of the world, there are limited additions of Nr to the agricultural systems of Africa, and these are generally insufficient to compensate for the losses through export of agricultural products, soil erosion and emission of N containing trace gases to the atmosphere. The result of the imbalance of Nr entering and leaving agricultural systems is nutrient mining from the soil, resulting in land degradation and unsustainable agricultural production. The Nr that is lost from the agricultural lands and natural systems and the Nr produced through industry enter the atmosphere and water bodies. This Nr is redistributed through the environment, through the processes of atmospheric deposition to land and water or through transport to large water bodies via rivers and groundwater. The effects of the transfer of Nr to the atmosphere, terrestrial ecosystems and aquatic ecosystems have major effects on these ecosystem components.

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Chapter 3: Soil biogenic emissions of nitric oxide from a semi-arid savanna in South Africa

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3.1 Abstract

Soils of arid and semi-arid ecosystems are important biogenic sources of atmospheric nitric oxide (NO), however, there is still a shortage of measurements from these systems. Here we present the results of a laboratory study of the biogenic emission of NO from four different landscape positions of the Kruger National Park (KNP), a large conservation area in a semi-arid region of South Africa. Results show that the highest net potential NO fluxes come from the low lying (footslope) landscape regions, which have the largest nitrogen stocks and highest rates of nitrogen input into the soil. Net potential NO fluxes from midslope and crest regions were considerably lower. The maximum release of NO occurred at fairly low soil moisture contents of 10% – 20% water filled pore space. Using soil moisture and temperature data obtained *in situ* at the Kruger National Park flux tower site, net potential NO fluxes obtained in the laboratory were converted to field fluxes for each of the four landscape positions for the period 2003 to 2005. The highest field NO flux is from footslope positions, during each of these years and emissions ranged from 1.5 - 8.5 kg ha^{-1} a^{-1} (in terms of mass of nitrogen). Remote sensing and Geographic Information Systems techniques were used to up-scale field NO fluxes on a regional basis indicating that the highest emissions occurred from the midslope positions, due to their large geographical extent in the considered research area. Emissions for the KNP Skukuza land type (56000ha) ranged from $20x10^3$ kg in 2004 to $34x10^3$ kg in 2003. The importance of landscape characteristics in the determination of regional biogenic NO soil emissions are emphasized.

3.2 Introduction

Emissions of nitric oxide (NO) and its conversion to nitrogen dioxide (NO_2) (collectively referred to as NO_x= NO + NO_2) are important in regulating chemical processes in the atmosphere [*Crutzen*, 1995; *Crutzen and Lelieveld*, 2001; *Levine et al.*, 1997]. Nitrogen oxides are key catalysts in the chemical processes that generate or destroy ozone. The ambient NO_x mixing ratio is a threshold which determines whether ozone is generated or destroyed [*Chameides et al.*, 1992; *Crutzen and Lelieveld*, 2001; *Meixner and Yang*, 2006]. The ozone forming or destroying reactions of nitric oxide are also involved in chemical processes that result in the production or consumption of the hydroxyl radical (OH), which is the chemical species most responsible for cleaning the atmosphere [*Monks*, 2005]. Nitrogen oxides are removed from the atmosphere in a series of photochemical reactions that produce nitric acid [*Monks*, 2005]. Nitric acid is an important component of acid deposition and acts as a source of N deposited from the atmosphere, in both the wet and dry form [*Feig et al.*, 2007; *Logan*, 1983; *Remde et al.*, 1993].

In 1860 it was estimated that the global NO_x emission was 13.1 Tg a^{-1} (all values mentioned are in terms of mass of nitrogen), of which 10.5 Tg a^{-1} came from natural sources. By the early 1990s it was estimated that the emissions of NO_x gases totalled 45.9 Tg a^{-1} [*Galloway et al.*, 2004a]. The recent estimate of the Intergovernmental Panel on Climate Change is 42-47 Tg a^{-1} [*Denman et al.*, 2007]. The most important sources of NO_x is fossil fuel combustion in power stations and vehicles (45%-67% of the total) [*Denman et al.*, 2007; *Kasibhatla et al.*, 1993] followed by lightning (5%-16%) and biomass burning (13%-29%) with the biogenic emission from soil (either natural or under agriculture) accounting for between 10 % and 40 % of the total [*Davidson and Kingerlee*, 1997; *Denman et al.*, 2007]. Nitrification has long been considered the main source for NO from the soil [*Conrad*, 1996; *Coyne*, 1999; *Davidson et al.*, 1993; *Garrido et al.*, 2002; *Remde et al.*, 1989; *Russow et al.*, 2000; *Russow et al.*, 2008; *Stehfest and Bouwman*, 2006; *Tabachow et al.*, 2001]. The proportion of nitrified N emitted as NO has been shown to range between 0 and 2.5 % of the total N involved in nitrification [*Garrido et al.*, 2002]. While it is known that soil processes are responsible for a sizable proportion of the global NO_x budget, there is considerable uncertainty about exactly how much. Davidson and Kingerlee (1997) provided a global inventory of NO emissions from soils, based on field measurements world-wide. Their estimate of the global NO soil source strength is 21 Tg a^{-1} (with an error margin of 4 to 10 Tg a^{-1}), while the 4th IPCC estimate is 8.9 Tg a^{-1} [*Denman et al.*, 2007] up from the 3rd IPCC estimate of 5.6 Tg a^{-1}

[*IPCC*, 2001]. The emission of NO from soil is affected by both biotic and abiotic factors; in addition, some ecosystems are better studied than others and therefore the quality of estimates differ between regions. While temperate regions and agricultural systems have been fairly well studied, a recent review by Meixner and Yang (2006) identified only 13 studies in natural drylands (annual precipitation below 400 mm). This is unfortunate since arid and semi-arid regions make up 40% of the earth's surface area [*Veron et al.*, 2006] and are known to be an important potential source of biogenic NO emissions [*Davidson et al.*, 1993].

The microbial activity controlling biogenic NO emissions and consumption from the soil is controlled by a number of factors including soil moisture, soil temperature and soil nutrient status [*Conrad*, 1994; *Ludwig et al.*, 2001; *Meixner et al.*, 1997]. These in turn are largely controlled by geographic factors, for example the climatic conditions, the position in the landscape, the land use [*Davidson*, 1991b] and biological factors such as the vegetation.

In drier ecosystems, soil water seems to be the most important factor regulating emissions of NO. When the soil moisture is too low to maintain microbial activity there are very low levels of NO emitted [*Garrido et al.*, 2002; *Meixner et al.*, 1997] and when soil moisture level are too high to maintain aerobic conditions, the emission of NO is negligible [*Skopp et al.*, 1990]. The optimal emission of NO seems to occur at low soil moisture levels, but where microbial activity can still take place. In a previous field study in the Kruger National Park (KNP), NO emissions followed the predicted soil moisture curve where they were lowest at high (>54%) and at low (<8.7 %) values of Water Filled Pore Space (WFPS) [*Parsons et al.*, 1996]. Even when desert soils are wetted, emissions of N containing gasses can occur with the maximum emission of NO occurring at fairly low soil moisture contents (10 % WFPS) [*Hartley and Schlesinger*, 2000].

A secondary controller of biogenic NO emissions is the soil nutrient status; many studies have found a relationship between the emissions of NO and either the concentrations of ammonia or nitrate [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Hutchinson et al.*, 1993; *Ludwig et al.*, 2001; *Meixner et al.*, 1997; *Parsons et al.*, 1996] or the N cycling rate [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Parsons et al.*, 1996]. Therefore, natural or anthropogenic actions that result in the modification of the inputs of nutrients or the rates of nutrient turnover are likely to have an effect on the NO production rates.

Catenal development is an important landscape process in many of the savanna regions of southern Africa, where the distribution of soil physical and chemical properties and

vegetation community occurrence is determined by topographic position. Landscape processes, such as catenal development provide a natural example of a process that can control the distribution of moisture and nutrients across a landscape. Therefore the aim of this study was to determine the emission of NO across differing landscape positions in a semi-arid savanna ecosystem in southern Africa.

3.3 Methods and Materials

3.3.1 Site description

This research occurred at the Kruger National Park (KNP) Flux Tower site (25°01.184'S; 31°29.813'E; 365 m above sea level) which is situated in a semi-arid savanna in the north eastern part of South Africa (Fig. 3.1a), 13 km WSW of the tourist camp and administrative centre of Skukuza (for further details see [*Scholes et al.*] (2001)). It is a well characterised site that has been used in various other studies [*Scholes et al.*, 2001]. Exchanges of CO_2, energy and H_2O have been measured continuously since April 2000 using the eddy covariance technique [*Harley et al.*, 2003; *Scholes et al.*, 2001]. Meteorological parameters have been measured at the main tower, while soil moisture and temperature has been measured at various depths in the two main surrounding ecosystem types since 2000. The flux tower is positioned exactly on the ecotone between a ridge-top broad-leafed *Combretum* savanna on sandy soil, dominated by *Combretum apiculatum* and *Sclerocarya birrea* and a midslope fine leaved *Acacia* savanna on clayey soil, dominated by *Acacia nilotica, A. nigrescence* and *S. birrea.* [*Scholes et al.*, 2001] (shown in Fig. 3.1b). This characteristic catenal pattern is repeated throughout the wider region [*Venter et al.*, 2003]. The fine-leaved savannas have higher concentrations of soil nitrogen than the broad-leaved savannas (Table 3.1) [*Scholes et al.*, 2003b; *Woghiren*, 2002]. The climate at the site is semi-arid subtropical with rainfall averaging 550 mm annually. Summers are hot and wet while winters are warm and dry, for more detailed climatic information see Scholes et al (2001) and Venter et al (2003).

The soil physical and chemical properties are presented in Table 3.1 and include values reported by Woghiren (2002) and measurements conducted during this study. The soils are sandy loams in the *Crest* and midslope positions and sandy clay loams in the *Footslope* positions as determined through a sedimentation technique [*Day*, 1969]. The soil pH was determined using the method of [*Anderson and Ingram*, 1993] and ranges from 6.1 to 6.5. The total C and N was measured at the Microanalytical laboratory at the University of Mainz

using a Vario MICRO Cube universal microanalyser set up to measure total C, H, N and S content of our soil samples.

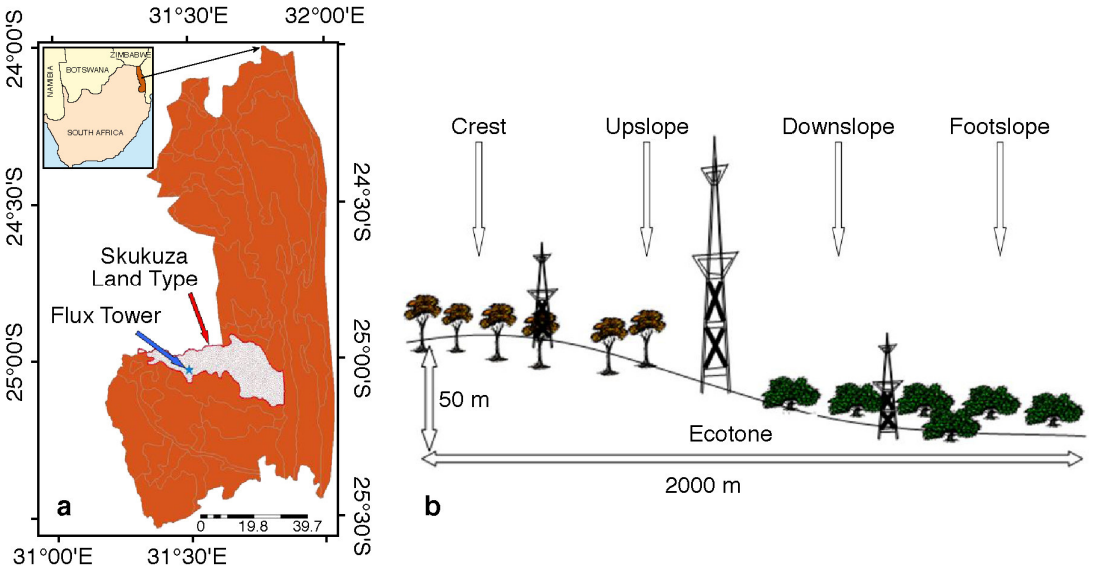

Figure 3.1 a) Map of the southern section of the Kruger National Park indicating the position of the Skukuza land type and the flux tower site, the position of the Kruger National Park in South Africa is shown in the insert. **b)**. A schematic diagram (not to scale) showing the position of the Skukuza flux tower in relation to the main ecosystem types, the smaller towers at the top and bottom of the slope are where the soil moisture and soil temperature measurements were taken.

Table 3.1 Physical and chemical properties of Skukuza KNP land type soils (all units are in terms of mass of N and mass of dry soil; numbers in brackets indicate the standard deviation of the measurements; values taken from Woghiren (2002) are marked by a star (*))

	Units	**Footslope**	**Downslope**	**Upslope**	**Crest**
Bulk Density	kg m^{-3}	1.50×10^3	1.40×10^3	1.56×10^3	1.34×10^3
Sand content	%	66.8	74.9	72.8	72.8
Silt content	%	12.1	10.0	10.1	10.1
Clay content	%	21.1	15.1	17.2	17.1
Texture		Sandy Clay Loam	Sandy Loam	Sandy Loam	Sandy Loam
pH		6.25±0.06	6.08±0.13	6.36±0.06	6.48±0.09
Total N *	kg ha^{-1}	4635	ND	ND	3318
Ammonium*	µg g^{-1}	0.15-2.41	ND	ND	1.38-2.72
Nitrate*	µg g^{-1}	0.21-2.04	ND	ND	0.01-1.24
Mean N	%	0.08% (0.00)	0.07% (0.01)	0.05% (0.00)	0.1% (0.01)
Mean C	%	0.88 (0.01)	0.83 (0.02)	0.59 (0.04)	1.12 (0.04)
Slope Class	%	0 – 2%	2 – 6%	6 – 15%	>15%

3.3.2 Sampling and instrumental set up

Soils were sampled in April 2005, using stainless steel soil cores with a length of 5 cm and radius of 2.5 cm, from four landscape positions (see Fig. 3.1b); the *Crest*, 20m upslope of the *Ecotone* referred to as "*Upslope"*, 20m downslope of the *Ecotone*, referred to as "*Downslope"* and the *Footslope*. Soil samples were comprised of 10 sub-samples taken from the top 5 cm in each of the landscape positions, the ten samples were taken in a band parallel to the *Ecotone* at approximately 1m intervals. The bulk samples were sieved through 2 mm mesh, air dried and then stored at 5 °C until analysis. When soil is rewetted after a long period of inactivity there is often a large and rapid release of NO from the soil, either as the result of displacement of NO rich air from the soil or from the rapid mineralisation of readily available nitrogen sources. This pulsing effect (a) is of short duration and is not repeated or the magnitude is greatly reduced on subsequent rewetting [*Kirkman et al.*, 2001; *Otter et al.*, 1999; *Scholes et al.*, 1997], and (b) may add to the total NO flux, but it is thought to be fairly insignificant, less than 6% of the annual NO flux [*Scholes et al.*, 1997]. Therefore, two days

before beginning the laboratory analysis, an aliquot from the soil samples was soaked with deionised water and allowed to drain freely at room temperature (22°C) to avoid the effect of pulsing after the initial wetting of soil after a long period of inactivity [*Scholes et al.*, 1997; *Snyder and Tartowski*, 2006]. The basic methodology for the laboratory measurement of NO flux from soil has been previously described [*Aranibar et al.*, 2004; *Kirkman et al.*, 2001; *Meixner and Yang*, 2006; *Otter et al.*, 1999; *Van Dijk et al.*, 2002] and is only briefly described here. A known mass of sieved, wetted soil (approximately 100 g dry weight) was placed in one of five Plexiglas chambers (volume 9.7×10^{-4} m^3) in a thermo-controlled cabinet (four chambers were used for soil samples while one was kept empty as a reference). Pressurised air that had passed through a purification system (four traps consisting of glass wool, activated charcoal, silica gel, and molecular sieve to provide a dry and "NO free" air stream) was supplied to each chamber at a flow rate of 4.2×10^{-5} m^3 s^{-1} (2.5 L min^{-1}), controlled by five mass flow controllers. The air in each chamber was well mixed using a Teflon coated fan (Micronel®, USA) in each chamber, flow rate 8.7×10^{-4} m^3 s^{-1} (52 L min^{-1}). The outlet of each chamber was connected via (a) a reverse nafion tube (Perma Pure® MD-125-127), and (b) a switching valve to a NO Chemiluminescence analyser (Eco Physics Switzerland, model CLD780TR) and a H_2O/CO_2 analyser (Rosemont Analytical, USA, Binos IR gas analyser). Occasionally, nitric oxide standard gas (200 ppm) was diluted into the air purification system via a mass flow controller (Mass-Flo® 200sccm Range, MKS instruments, USA); this allowed (a) calibration of the NO Chemiluminescence analyser and (b) control of the chamber headspace NO concentration when determining NO uptake in the soil (see below). The soil moisture content was determined by tracking the loss of water vapour throughout the measurement period and relating it to the gravimetric soil moisture content at the start and end of the measurement period. The purpose of the reverse Nafion driers is (a) to keep the humidity of the chambers' headspace air high and hence (b) to slow the dehydration of the soil, allowing the microbes in the soil time to equilibrate to changes in the soil moisture content.

3.3.3 Measurements of the net, NO release rate

The net release of NO (J_{NO}, in ng kg^{-1} s^{-1}) is calculated from the difference between the NO mixing ratio at the outlet of the reference cuvette and the outlet of each of the incubation cuvettes (since the air in the cuvette is well mixed, the air at the outlet is assumed to have the same composition as the air in the headspace) according to:

$$J_{NO} = \frac{Q}{M_{soil}}\left(m_{NO,out} - m_{NO,ref}\right) \times \left(\frac{M_N}{V_m} \times 10^3\right) \quad (3.1)$$

Where Q is the flow rate through the cuvette (4.2×10^{-5} m^3 s^{-1} or 2.5 L min^{-1}), M_{soil} is the dry mass of the soil (kg), M_N is the molar mass of N (14.0076 kg $kmol^{-1}$), V_m is the molar volume (24.465 m^3 $kmol^{-1}$ at 25°C 1013.25 hPa) and $m_{NO,ref}$ and $m_{NO,out}$ are the mixing ratios of NO in ppb, at the outlets of the control and incubation cuvettes respectively (the factor $M_N/V_m \times 10^{-3}$ is needed to convert NO mixing ratio (ppb) to NO concentration (ng m^{-3})).

The release of NO from the soil is the result of the microbial production and consumption of NO in the soil, processes that occur simultaneously [*Conrad*, 1994; *Conrad*, 1996; *Conrad and Smith*, 1995]. As a result, the NO release rate (J_{NO}) is always a net release rate. However if the NO consumption is greater than production in the soil sample then J_{NO} becomes negative. This will only occur if the in-coming (= reference) NO mixing ratio is greater than the headspace NO mixing ratio in the soil containing chamber.

It has already been shown experimentally that there is a linear relationship between the NO release rate (J_{NO}) and the rate of NO production (P) and consumption (k) [*Ludwig et al.*, 2001; *Remde et al.*, 1989] so that the measured release rates can be described according to:

$$J_{NO} = P - k \times m_{NO,out} \times \left(\frac{M_N}{V_m} \times 10^3\right) \quad (3.2)$$

This equation implies that the NO production is independent of the NO mixing ratio in the headspace ($m_{NO,out}$), while the NO consumption is dependent on the NO mixing ratio in the headspace, and can be approached as a first order decay process. To determine the values of P and k, equation (3.2) was used with the measured release rates (J_{NO}) from two sets of incubation measurements, $m_{NO,ref}$ =0 ppb and $m_{NO,ref}$ = 58 ppb. This allowed us to calculate P (ng kg^{-1} s^{-1}) and k (m^3 kg^{-2} s^{-2}), where k can be determined from the slope of equation (3.2),

$$k = \frac{\Delta J_{NO}}{\Delta[NO]} = \frac{J_{m,high} - J_{m,low}}{m_{high} - m_{low}} \times \left(\frac{V_m}{M_N} \times 10^3\right) \quad (3.3)$$

Where m_{low} is the actual NO mixing ratio (ppb) in the head space of the cuvette under fumigation with NO free air and m_{high} is the actual NO mixing ratio in the cuvette headspace under fumigation with 58ppb NO. In this study, we will present values of the NO release rate (J_{NO}) as a function of soil moisture, in terms of the soil WFPS. Water filled pore space is a useful concept because it indicates the amount of water in the soil that is available for microbial activity and also the amount of air in the soil and therefore the soil oxygen status. The WFPS is calculated (a) from the amount of water lost from the enclosed cuvettes through

evaporation during the incubation process and (b) through determining the gravimetric water content (Θ) of the rewetted sample at the start of the incubation. The WFPS is calculated according to equation (3.4):

$$WFPS = \Theta \times \frac{BD}{\left(1 - \frac{BD}{PD}\right)} \qquad (3.4)$$

Where *BD* is the soil bulk density in (kg m^{-3}) measured at the site of sampling, by driving a stainless steel core of known volume driven into the soil and removing a soil sample and drying the soil at 105°C for 48 hours, and *PD* is the particle density of the average soil mineral (quartz) with a value of 2.65×10^3 kg m^{-3} according to [*Parton et al.*, 2001].

3.3.4 Detection limit and estimation of the release rate error

The detection limit of our laboratory technique was determined in a study by Gelfand et al (in prep), but is briefly described here. Inert glass beads and autoclaved Israeli desert soils were used to measure the "blank" net release of NO. It was found that the "blank" net release of NO from the glass beads was at a rate of 0.02 ng kg^{-1} s^{-1}, with a random deviation of 0.02 ng kg^{-1} s^{-1} irrespective of the moisture content, therefore, we consider an experimentally derived detection limit for J_{NO} of 0.08 ng kg^{-1} s^{-1} this results from the mean release rate of autoclaved soils plus 3 standard deviations (corresponding to a confidence interval of 99.7 %). Similarly, the detection limit of the autoclaved soils is 0.11 ng kg^{-1} s^{-1}, therefore the more conservative estimate from the autoclaved soils is being used as our detection limit.

To quantify the precision of J_{NO} measurements, the NO net release rate was determined experimentally through the simultaneous measurement of four replicates across the full range of soil moisture. The mean standard deviation on the NO net release rate was found to be 0.03 ng kg^{-1} s^{-1} irrespective of WFPS, this is lower than the experimentally derived detection limit of J_{NO} and we therefore consider ±0.05 ng kg^{-1} s^{-1} as a conservative estimate of the experimentally derived precision of $J_{NO.}$

3.3.5 Calculation of the net potential NO flux

The laboratory derived net release of NO (J_{NO}, in ng kg^{-1} s^{-1}) from the soil was converted to a net potential NO flux (F_{lab}, in ng m^{-2} s^{-1}) using a simple diffusion based algorithm (eq. 3.5), originally developed by Galbally and Johansson [1989], modified by van Dijk et al [2002]. The net potential laboratory NO flux, as a function of WFPS and T_{soil}, is calculated according to:

$$F_{lab}(T_{soil}, WFPS) = \sqrt{BD \times k(T_{soil}, WFPS) \times D(WFPS)} \times \left(\left(\frac{P(T_{soil}, WFPS)}{k(T_{soil}, WFPS)} \right) - [NO]_{Headspace} \right) \quad (3.5)$$

where *D(WFPS),* in $m^2\ s^{-1}$, is the *WFPS* dependent diffusion coefficient of NO through the soil which is calculated after [*Moldrup et al.*] (2000), from *WFPS* and the gas diffusion constant for free air ($m^2\ s^{-1}$) equal to $1.9 \times 10^{-5}\ m^{-2}\ s^{-1}$ ([*Gut et al.*, 1998], referenced to [*Lerman*], 1979), and where $[NO]_{headspace}$ is the NO concentration (in 10^{-12} kg m^{-3}) in the headspace of the cuvette. The diffusion coefficient is dependent of the soil moisture content and the soil bulk density and therefore is calculated for each soil sample and each soil moisture interval.

For a given soil temperature, an algorithm has been developed [*Meixner and Yang*, 2006] to fit our net potential NO fluxes as a function of the WFPS (eq. 3.6). This algorithm describes the net potential NO flux as a power increase until optimal soil moisture followed by an exponential decrease:

$$F_{lab}(T_{soil} = const., WFPS) = a\,WFPS^{b} \exp(-c\,WFPS) \quad (3.6)$$

Where parameters a, b and c are related to observed values by:

$$a = \frac{F_{lab}(WFPS_{opt})}{\left[WFPS_{opt}^{\ b} \exp(-b)\right]} \quad (3.7)$$

$$b = \frac{\ln\left[\frac{F_{lab}(WFPS_{opt})}{F_{lab}(WFPS_{upp})}\right]}{\ln\left(\frac{WFPS_{opt}}{WFPS_{upp}}\right) + \frac{WFPS_{upp}}{WFPS_{opt}} - 1} \quad (3.8)$$

$$c = \frac{-b}{WFPS_{opt}} \quad (3.9)$$

Where, for a given T_{soil}, $WFPS_{opt}$ is the soil moisture where the maximum laboratory NO flux is observed, $F_{lab}(WFPS_{opt})$ is the maximum laboratory NO flux at the optimal soil moisture content, and $WFPS_{upp}$ is the soil moisture content where F_{lab} approximately equals zero ($F_{lab}(WFPS_{upp}) = 1/100\ F_{lab}(WFPS_{opt})$) for $WFPS > WFPS_{opt}$.

The temperature dependence of the laboratory NO flux was determined by measuring the net potential laboratory NO flux at two soil temperatures, 25°C and at 35°C. The temperature dependence usually shows an exponential increase and can be expressed as the increase of F_{lab} for a 10°C increase in soil temperature, otherwise known as a Q_{10} function (eq. 3.10) [*Lloyd and Taylor*, 1994].

$$Q_{10}(WFPS) = \frac{F_{lab}(T_{soil} = 35°C, WFPS)}{F_{lab}(T_{soil} = 25°C, WFPS)} \qquad (3.10)$$

The Q_{10} function can then be included into equation (3.6), as a "temperature amplification factor" of the reference NO flux (T_{ref}= 25°C), so that the laboratory NO flux can be estimated as a function of both soil temperature and soil moisture (eq. 3.11):

$$F_{lab}(T_{soil}, WFPS) = a_{Tref} WFPS^{b_{Tref}} \exp\left(c_{Tref} \times WFPS\right) \times \exp\left[\frac{\ln Q_{10}(WFPS)}{10} \times \left(T_{soil} - T_{ref}\right)\right] \qquad (3.11)$$

3.3.6 Compensation point mixing ratio

The compensation point mixing ratio ($m_{NO,comp}$) is an important concept for the bi-directional exchange of NO (see [*Conrad*, 1994]). Since it determines what the ambient mixing ratio of NO in the atmosphere has to be before a net NO uptake into the soil can occur. The compensation point mixing ratio is calculated by resolving equation (3.5) for the NO concentration where $F_{lab}(WFPS, T_{soil}) = 0$:

$$m_{NO,comp}(T_{soil,} WFPS) = \frac{P(T_{soil,} WFPS)}{k(T_{soil}, WFPS)} \times \left(\frac{V_m}{M_N} \times 10^3\right) \qquad (3.12)$$

3.3.7 Up-scaling to the landscape positions

Once we have derived the net potential NO flux (F_{lab}) from our laboratory measurements as a function of both, soil moisture and temperature, the flux of NO from the four landscape positions ($F_{NO,up\text{-}scaled}$) at the KNP Tower site could be estimated by suitable up-scaling procedures using field data of soil temperature and moisture. For that we used the half hourly soil moisture and temperature data obtained from measurement stations within the fine-leaved savanna and the broad-leaved savanna, corresponding with the *Crest* and *Footslope* landscape positions and the soil BD and D values measured at each of the landscape positions. The $F_{NO,up\text{-}scaled}$ from the two midslope positions was approached by the soil moisture and temperature data from the closest measurement site (the *Crest* for the *Upslope* position and the *Footslope* for the *Downslope* position). These soil moisture and temperature data were

used in equation (3.11) to calculate the up-scaled flux on a half hourly basis. These half-hourly flux estimates were used to calculate monthly averages of $F_{NO,up\text{-}scaled}$.

3.3.8 Up-scaling to the landscape scale

The Kruger National Park (KNP) Geographical Information System (GIS) data base divides the Skukuza land system (56000 ha) into 3 landscape positions; the *Crest* comprising 12 % of the surface area (6720 ha), the midslope comprising 80 % of the surface area (44800 ha), and the *Footslope*, comprising 8 % of the surface area (4480 ha). Since the midslope landscape position encompasses both, the *Downslope* and *Upslope* sites of our sampling scheme, the midslope area was divided equally between the *Downslope* and *Upslope* sites, giving each 40 % of the land type surface area (22400 ha). The monthly average NO fluxes for each of our designated landscape positions (section 3.2.7) were apportioned according to the proportion that each of the landscape positions comprised of the total Skukuza land type (Venter *et al,*2003) to estimate a total emission for the Skukuza land type for the years 2003-2005. This technique assumes that the soil *BD*, the soil temperature and soil moisture are the same across the whole region, for this reason the up-scaling attempt that we have made is limited to the Skukuza land type which is where the flux tower is situated, and where we can assume with reasonable confidence that on the whole similar conditions occur.

To assess the potential distribution of NO emissions from the Skukuza land type the landscape positions were associated with differing slope classes [*Venter et al.*, 2003] as shown in Table 3.1 (bottom line). Shuttle Radar Tomography Mission (SRTM) digital elevation data (supplied by the Consortium for Spatial Information, of the Consultative Group for International Agricultural Research (CGIAR-CSI)) for the classification of the slope classes was used and incorporated into a geographical information system (GIS) database to give the distribution of the landscape classes for the Skukuza land type (Fig. 3.6). The annual point NO fluxes associated with the individual landscape positions were then assigned to the corresponding slope classes to provide a distribution of the annual NO emission from the various landscape positions of the Skukuza land type.

3.4 Results

3.4.1 General behaviour of the net potential NO fluxes (F_{lab})

For the reference soil temperature of 25°C, an overview of the maximum derived net potential fluxes (F_{lab}) and the Q_{10} values are given in Table 3.2. At 25°C the maximum F_{lab} ranged

from 1.3 ng m^{-2} s^{-1} in the *Downslope* soil to 2.4 ng m^{-2} s^{-1} in the *Footslope*. At 35°C the laboratory NO flux ranged from 3.1 ng m^{-2} s^{-1} in the *Downslope* soil to 3.5 ng m^{-2} s^{-1} in the *Upslope* soil. With the full temperature dependence included, the net potential NO fluxes were calculated for the four landscape positions as a function of soil moisture and temperature and are shown in figure 3.2 a-d. Differences in the graphs reflect the differing emission potential as a function of soil WFPS and soil temperature for the individual soils. The highest F_{lab} occurs in the *Footslope*, where at 40 °C the F_{lab} is 3.2 ng m^{-2} s^{-1}, while the lowest F_{lab} (2.5 ng m^{-2} s^{-1}) occurred in the *Downslope* at 40°C.

The maximum F_{lab} for all four landscape positions was calculated to lie between 10 % and 20 % WFPS, (Table 3.2). The optimum WFPS differed according to the temperature of incubation. At 25°C, it ranged from 11 % for the *Upslope* position to 17 % in the *Footslope.* The optimum WFPS was always greater under the higher incubation temperatures and occurred at 18 % WFPS (*Footslope, Downslope, Upslope*) at 35°C. Maximum F_{lab} differed according to the incubation temperature and increased in the *Footslope*, and the two midslope positions. The measurement of F_{lab} at 35°C from the *Crest* soil was unsuccessful, since the aliquot of the corresponding soil sample got wet during the storage period between the measurements at 25°C and 35°C. Therefore, the Q_{10} value for the *Upslope* site was used for the *Crest* site to estimate the temperature dependence during subsequent up-scaling calculations.

The maximum NO consumption constant (k), calculated from equation (3.3) as a function of T_{soil} and *WFPS*, occurs at approximately the same WFPS as the maximum of F_{lab} (see Fig. 3.3), namely between $10\% - 25\%$ WFPS. The highest NO consumption occurs in the *Footslope* soils (2.7×10^{-4} m^3 kg^{-1} s^{-1}) while the consumption of the midslope and *Crest* soils appears to be similar and less than 1×10^{-4} m^3 kg^{-1} s^{-1}. In all the soils the k values were higher at the lower incubation temperatures.

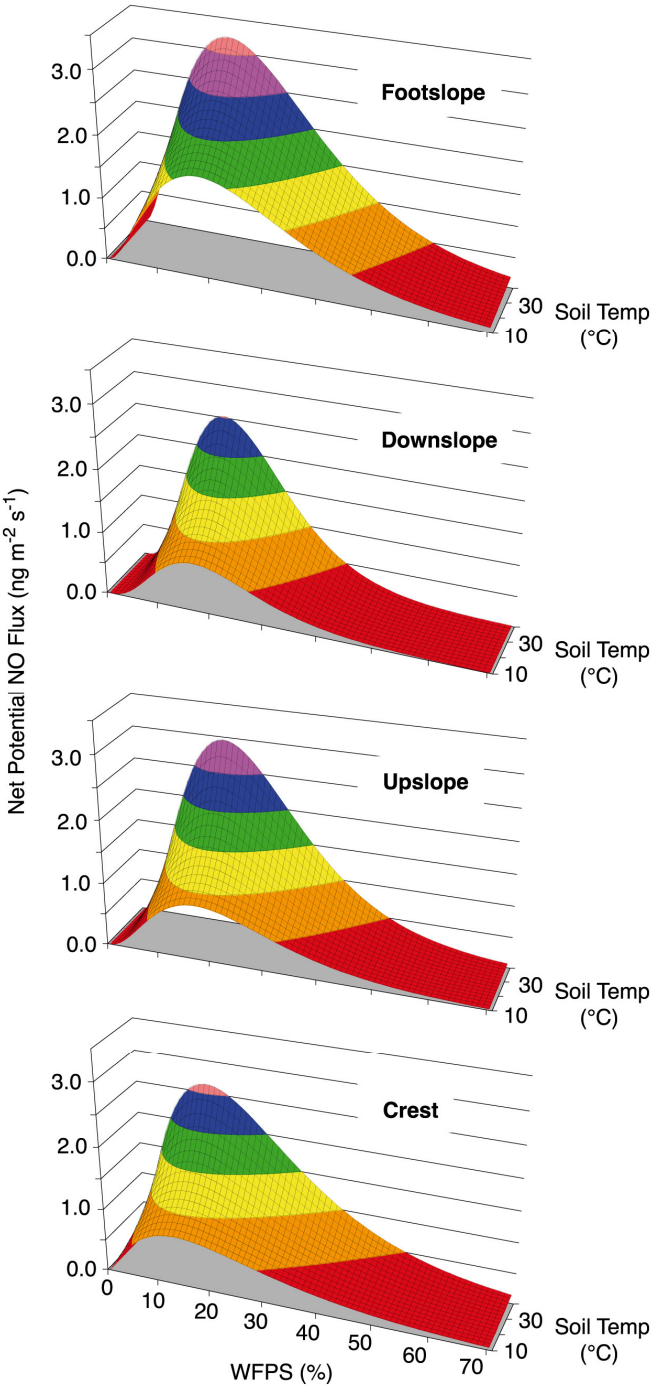

Figure 2.2 Net potential NO flux (F_{lab}) from the four landscape positions, *Footslope* (a), *Downslope* (b), *Upslope* (c), and *Crest* (d). as a function of soil moisture (WFPS) and soil temperature (mass of NO is expressed in terms of mass of nitrogen).

Table 3.2 Optimum soil moisture, maximum NO flux and Q_{10} value of Skukuza KNP land type soils (mass units are in terms of mass of N); (*) measurement failed (Q_{10} = 2.17 is used for the *Crest* soil)

	Footslope	***Downslope***	***Upslope***	***Crest***
Optimum WFPS at 25°C	17%	14%	11%	12%
Maximum net potential NO flux at 25°C (ng m^{-2} s^{-1})	2.4	1.3	1.7	1.5
Optimum WFPS at 35°C	18%	17%	18%	18%
Maximum net potential NO flux at 35°C (ng m^{-2} s^{-1})	3.5	3.0	3.5	No Data
Q_{10} Value	1.55	2.11	2.17	(*)

The compensation point mixing ratio ($m_{NO,comp}$) was calculated according to equation (3.12) from laboratory measurements derived data of *P* and *k* (each as function of T_{soil} and *WFPS*). If ambient NO equals $m_{NO,comp}$, then there is no net uptake or release of NO from the soil, since the production of NO equals the NO consumption in the soil. Figure 3.4 shows that $m_{NO.comp}$ at 25°C in each of the soils varies according to the soil moisture. The highest $m_{NO.comp}$ occurs in the *Upslope* soils where a $m_{NO,comp}$ of approximately 65-70 ppb is reached at 35 % WFPS. The *Footslope* soils have the next highest $m_{NO,comp}$, with a peak of 55-60 ppb at 40 % WFPS. The *Crest* and *Downslope* have a maximum $m_{NO,comp}$ between 45 and 50 ppb at 20 % WFPS for the *Downslope* and 27 % WFPS for the *Crest*.

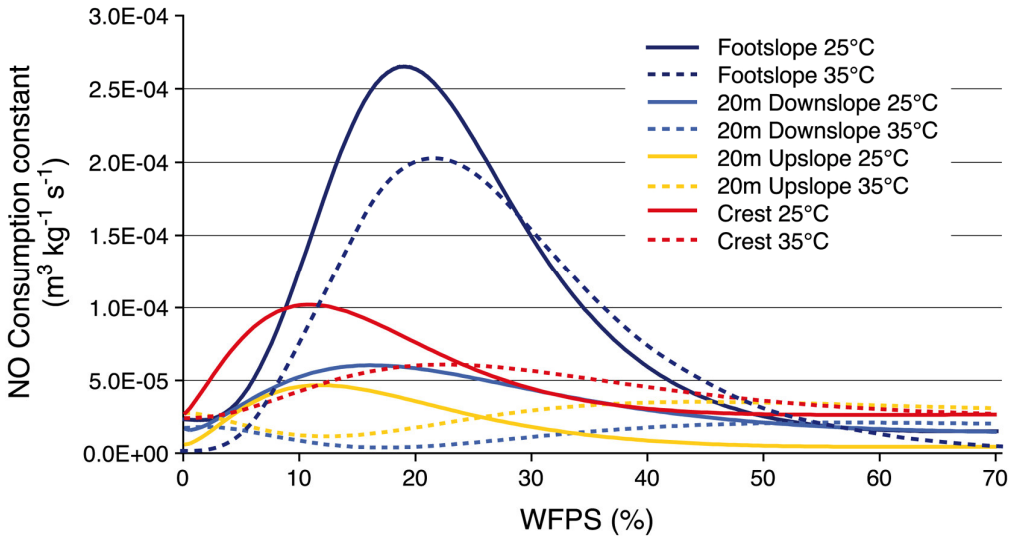

Figure 3.3 NO consumption rate (*k*) as a function of WFPS for the 4 landscape positions at 25°C and at 35°C, solid lines represent the *k* values at 25°C, while the dashed lines represent *k* at 35°C.

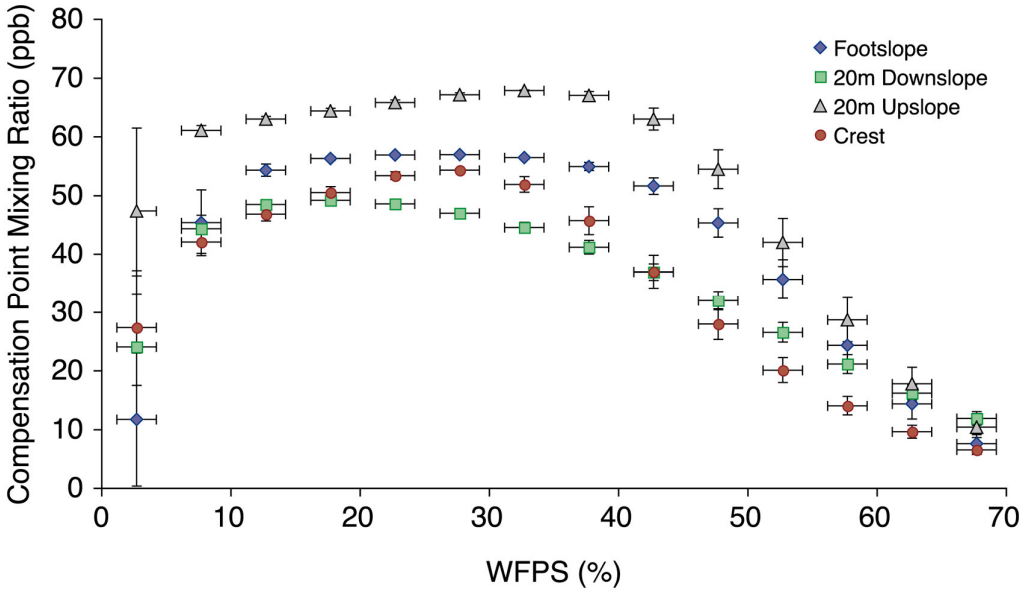

Figure 3.4 Compensation point mixing ratio ($m_{NO,comp}$) at T_{soil}=25°C as a function of *WFPS* for soils of the four landscape positions in the Kruger National Park

3.4.2 T_{soil} , WFPS, and $F_{NO,up\text{-}scaled}$ at different landscape positions

Monthly mean soil temperature and volumetric soil moisture measured at 0.05 m depth at the Skukuza flux tower site are shown in figure 3.5 for the period 2003-2005.

The average monthly soil temperature ranged from 16.5° C to 36.5° C in winter and summer respectively (Fig. 3.5b and 3.5c). There was little difference between the soils in the *Acacia* savanna (*Footslope* position) and the soils in the *Combretum* savanna (*Crest* position); although in the winter months the *Combretum* soils tend to be slightly cooler. As there was only one measuring site in each vegetation type it is not known whether this is due to small-scale variability or whether it reflects a true difference.

In the *Footslope* soils there was always a higher soil WFPS than in the *Crest* soils (Fig. 3.5c), although they generally tracked each other quite closely during the dry periods. However in the high rainfall periods (Jan-March 2004, Dec 2004-May 2005 and Nov-Dec 2005, see Fig. 3.5d), the WFPS in the lower lying *Footslope* soils was much higher than that of the *Crest* soils. This is due to the drainage effects of the slope which resulted in water accumulating in the lower slope positions and the higher clay content of the *Footslope* would increase the water holding capacity of the *Footslope* soil.

Net up-scaled mean monthly NO fluxes ($F_{NO,up\text{-}scaled}$) at the four landscape positions were estimated from T_{soil} and *WFPS* and are shown in figure 3.5a for the period 2003-2005. In these soils, $F_{up\text{-}scaled}$ ranges from less than the minimum detectable flux up to 3.5 ng m^{-2} s^{-1} and differs between the landscape positions (Fig. 3.5a). The $F_{up\text{-}scaled}$ for the *Downslope* was generally lowest and never exceeded 3 ng m^{-2} s^{-1}. The $F_{up\text{-}scaled}$ is higher for the *Footslope* area than for the *Crest* and the *Upslope* soils except for a few periods during months of heavy rainfall (see Fig. 3.5d). During these periods, the highest $F_{up\text{-}scaled}$ came from the soils above the flux tower. The *Crest* and the *Upslope* soils generally followed a similar pattern, although the $F_{up\text{-}scaled}$ from the *Upslope* soils tended to be slightly higher. Of the four landscape positions the *Footslope* soils produced the highest NO emissions per unit area over the 2003-2005 period, between 0.5 and 0.8 kg ha^{-1} a^{-1} (Fig. 3.7).

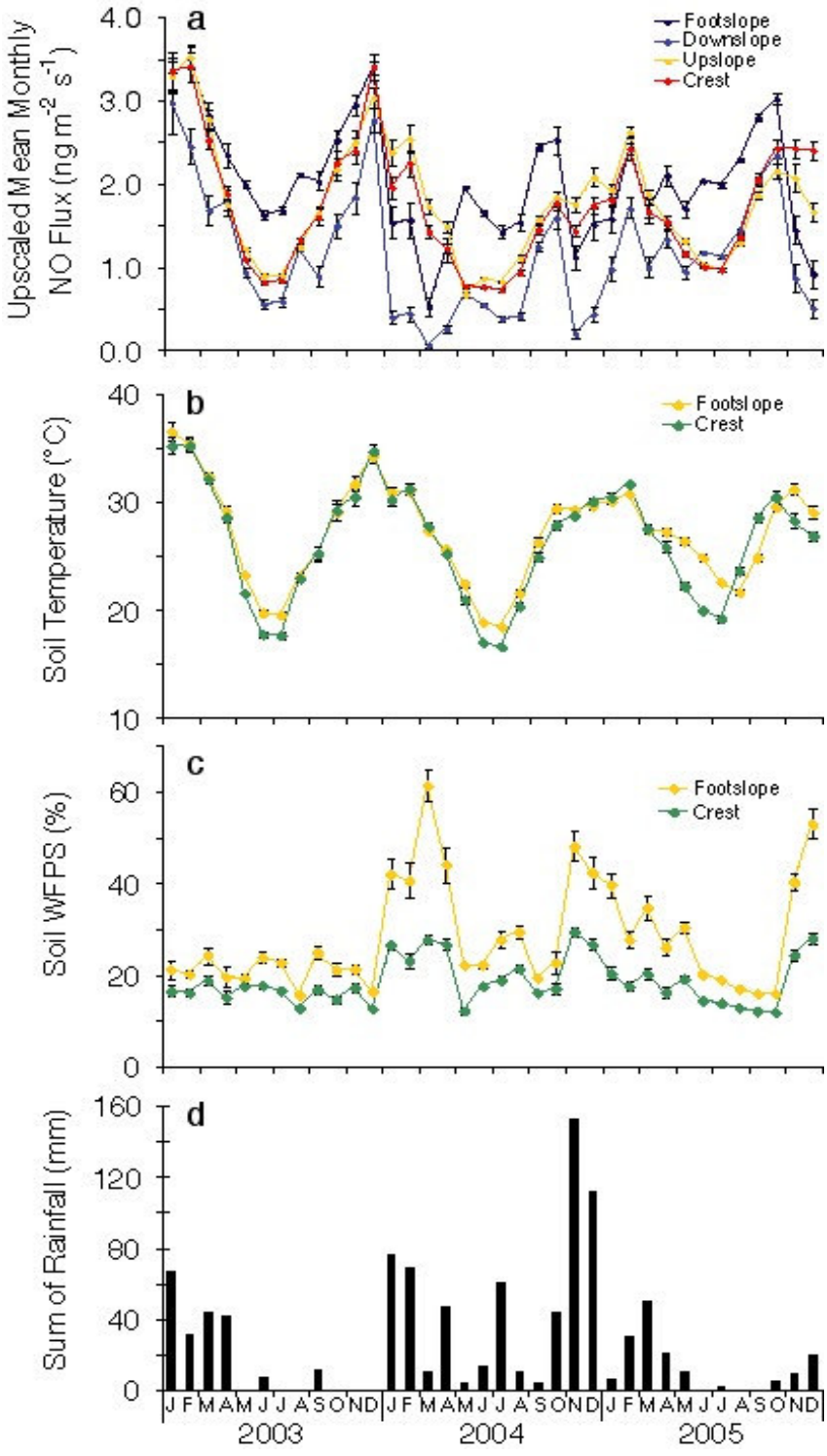

Figure 3.5 a) Monthly averages of the NO flux ($F_{NO,up\text{-}scaled}$) from soils of the four landscape positions calculated for the period January 2003 - October 2005 (error bars represent the daily variability expressed as standard error of the daily averages; mass of NO expressed in terms of mass of nitrogen). **b)** Recorded soil temperature for the period 2003-2005 **c)**. Recorded soil moisture (*WFPS*) for the period 2003-2005 Average monthly soil moisture contents and temperatures calculated from half hourly recordings in the fine-leaved Acacia savanna (*Footslope*), and the broad-leaved *Combretum* (*Crest*). Error bars indicate the monthly variability of the measurements (expressed as standard error) **d)**. Rainfall for the period 2003-2005.

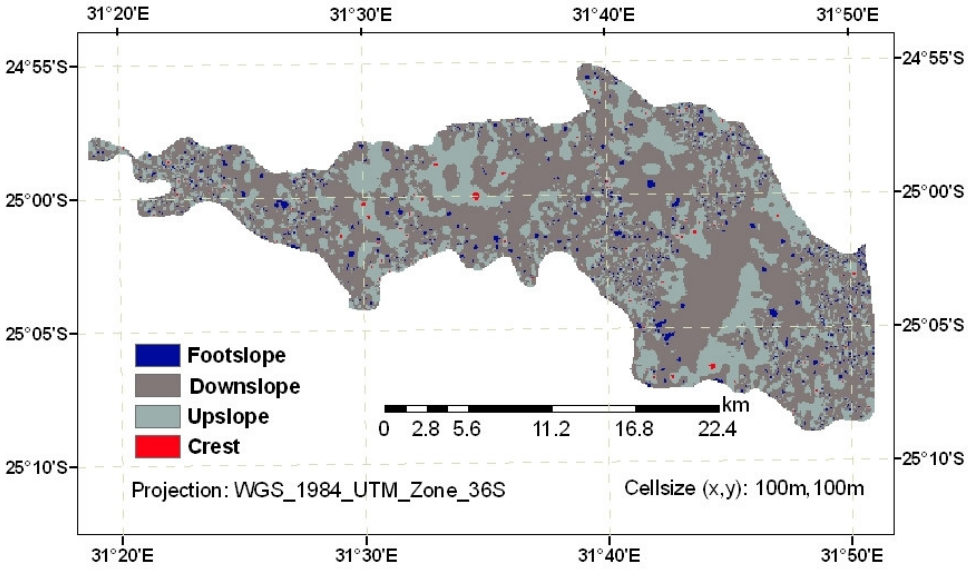

Figure 3.6 Map of the Skukuza land type showing the distribution of the different landscape positions

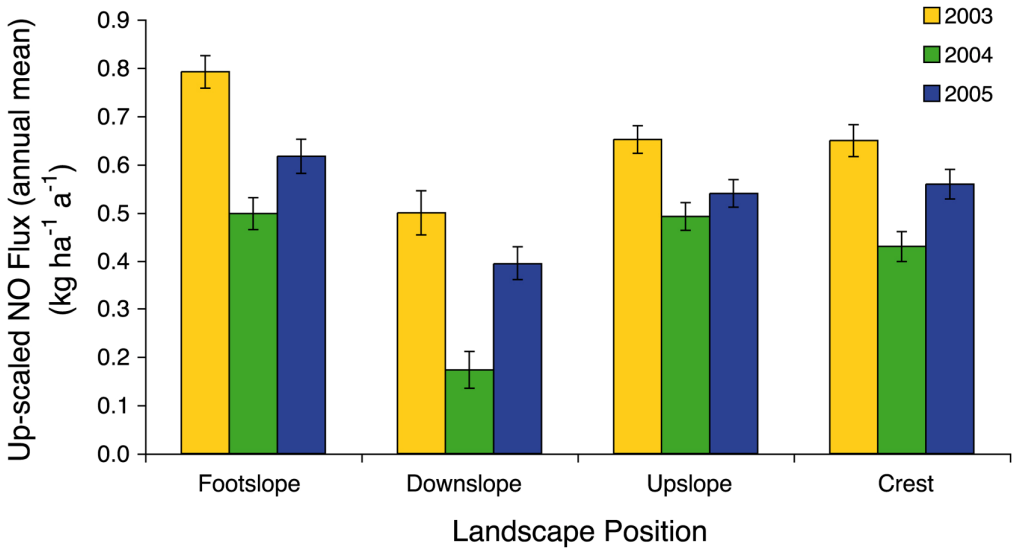

Figure 3.7 Annual means of the up-scaled NO fluxes ($F_{NO,up\text{-}scaled}$) from soils of the 4 landscape positions for the period 2003-2005; error bars represent the standard deviation of the means (mass ,of NO is expressed in terms of mass of nitrogen).

3.4.3 Estimates of NO emissions for the Skukuza land type area

When the area based annual NO fluxes were up-scaled to the entire Skukuza land type (Fig. 3.8), the total NO emission was $33x10^3$ kg in 2003, $20x10^3$ kg in 2004, and $25x10^3$ kg in 2005 (all in terms of mass of nitrogen). When the total summed emission for the Skukuza land type is divided into the constitutive land landscape positions of the original Kruger National Park (KNP) Geographical Information System (GIS) data base, the midslope positions (= *Upslope* + *Downslope*) accounted for the majority of the emissions, due to their greater geographical extent.

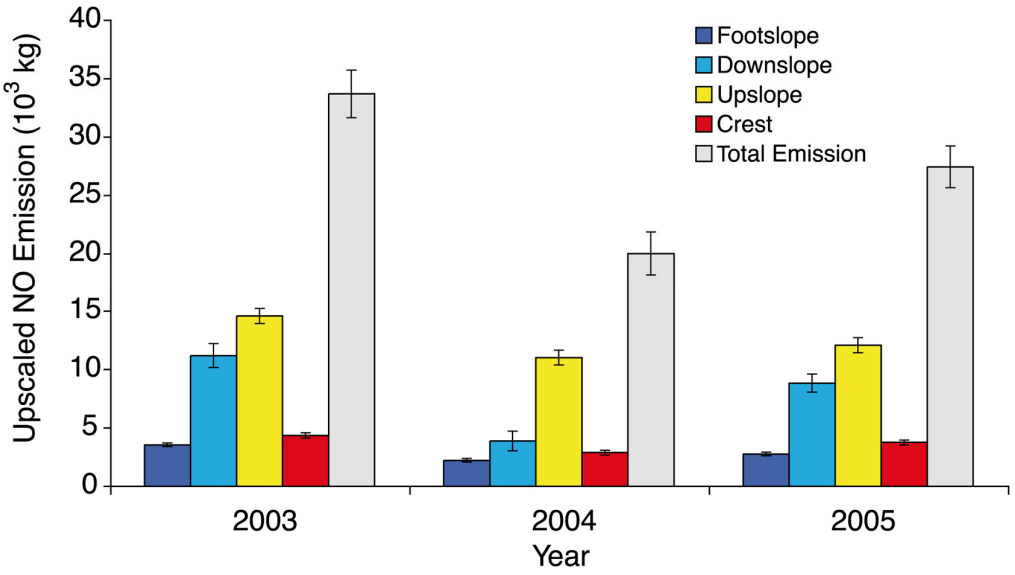

Figure 3.8 Total area weighted NO emissions (expressed in terms of mass of nitrogen) from each of the four landscape positions in the Skukuza land type for the period 2003 to 2005; errorbars represent the standard deviation of the means

3.5 Discussion

3.5.1 Net potential NO fluxes

In figure 3.9, we compare previously reported laboratory and field measurements of NO emissions from arid and semi-arid ecosystems with our net potential NO fluxes for the different landscape positions along a catenal sequence in the southern African Savanna of KNP. There have been two previous studies in the KNP, both of which were based on the use of field chambers [*Levine et al.*, 1996; *Parsons et al.*, 1996]. In both studies, which occurred on long term fire return frequency experiments approximately 30 km away from the Skukuza flux tower, the measured NO field flux was between 0.34 ng m^{-2} s^{-1} and 32 ng m^{-2} s^{-1} at a

range of soil moistures from 8.7 % to 54 % WFPS [*Levine et al.*, 1996; *Parsons et al.*, 1996]. The higher values reported in the Levine *et al* (1996) paper (see Fig. 3.9) can be attributed to measurements occurring under artificially irrigated conditions, which resulted in an increase in the emission of NO from the soil.

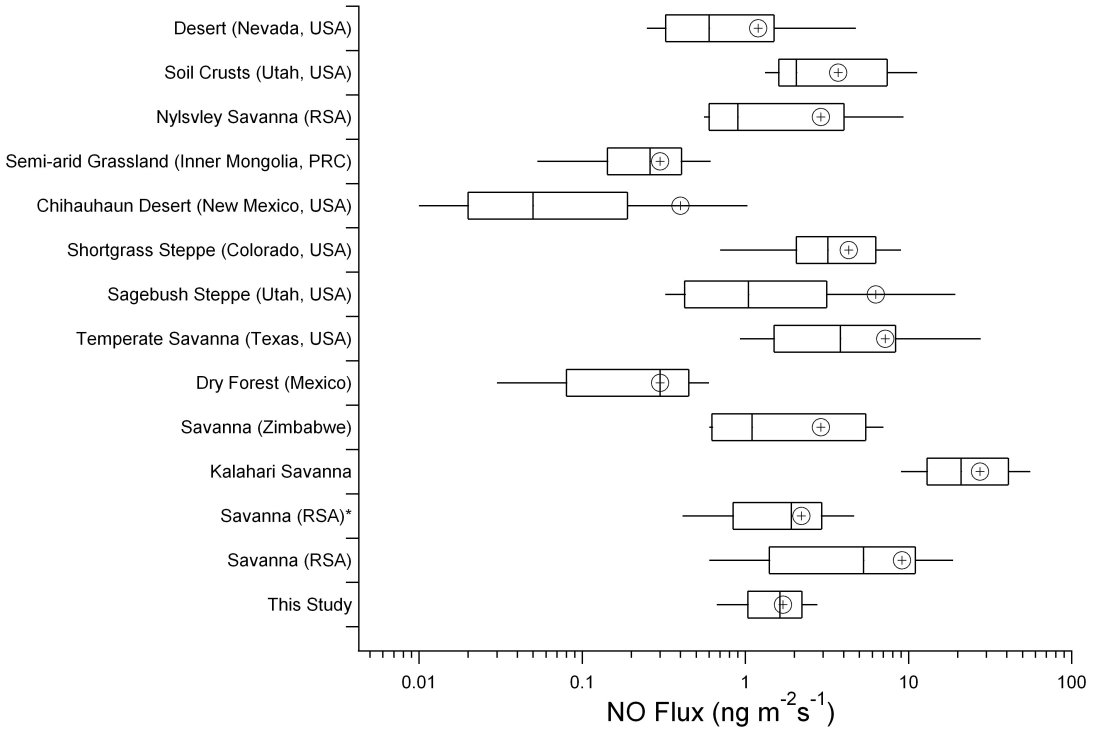

Figure 3.9 Comparison of the up-scaled NO fluxes with data reported in the literature for comparable arid and semi arid ecosystems (all expressed in terms of mass of nitrogen). Boxes in the figure indicate the inter-quartile range between the 25 and 75 percentile and the median value is marked by a vertical bar. The (horizontal) error bars represent the 10 and 90 percentile. The open circle represents the arithmetic mean of the reported data. Where the cited papers provide a mean and range of data only, values were statistically recreated to match these ranges. The reported ecosystem NO flux data is cited from:

- Desert (Nevada, USA) [*McCalley and Sparks*, 2008]
- Soil Crusts (Utah, USA) [*Barger et al.*, 2005]
- Nylsvley Savanna (RSA) [*Otter et al.*, 1999]
- Semi-arid Grassland (Inner Mongolia, PRC) [*Holst et al.*, 2007];
- Chihuahuan Desert ((New Mexico, USA) [*Hartley and Schlesinger*, 2000];
- Shortgrass Steppe (Colorado, USA) [*Martin et al.*, 1998];
- Sagebush Steppe (Utah, USA) [*Smart et al.*, 1999];
- Temperate Savanna (Texas, USA) [*Martin et al.*, 2003a];
- Dry Tropical Forest (Mexico) [*Davidson et al.*, 1993];
- Savanna (Zimbabwe) [*Kirkman et al.*, 2001];
- Kalahari Savanna (southern Africa) [*Aranibar et al.*, 2004];

- Savanna (RSA)* [*Parsons et al.*, 1996];
- Savanna (RSA) [*Levine et al.*, 1996]

Three laboratory based measurements, similar to the method used in this study, have been made in southern Africa, these include studies in Nylsvley Savanna [*Otter et al.*, 1999], the Kalahari transect [*Aranibar et al.*, 2004] and in Zimbabwe [*Kirkman et al.*, 2001]. In the Nylsvley Savanna in South Africa the NO flux ranged from 0.9-8 ng m^{-2} s^{-1} [*Otter et al.*, 1999]. For the study at Marondera (Zimbabwe) the NO flux ranged from 0.1-3.7 ng m^{-1} s^{-1} at soil moisture levels of between 9 and 15% WFPS [*Kirkman et al.*, 2001]. In a rainfall gradient transect measurement through the Kalahari it was found that the NO flux ranged from 0 to over 120 ng m^{-2} s^{-1}[*Aranibar et al.*, 2004] although it should be noted that these values are a much higher than from the other similar sites (see Fig. 3.9).

In other natural arid and semi-arid regions (mean annual precipitation <700mm) the measured median NO fluxes range from 0.07 ng m^{-2} s^{-1} to 5.3 ng m^{-2} s^{-1} (with reported values of up to 83 ng m^{-2} s^{-2} occurred during a pulsing event, such as when the soil is wetted or fertilized) [*Davidson et al.*, 1993; *Hartley and Schlesinger*, 2000; *Holst et al.*, 2007; *Martin and Asner*, 2005; *Martin et al.*, 1998; *Smart et al.*, 1999], the Aranibar et al (2004) study showed a median value of 21 ng m^{-2} s^{-1} and is far out of the range of other reported values (Fig. 3.9). Therefore in comparison with the other published studies in arid and semi-arid ecosystems the net potential NO fluxes (F_{lab}) from this study are within the range reported for both field and laboratory measurements of NO. The NO fluxes from these arid and semi-arid ecosystems tend to be fairly low in comparison with some of the values reported from temperate and tropical forests where fluxes of 22 ng m^{-2} s^{-1} [*Pilegaard et al.*, 2006] and 58 ng m^{-2} s^{-1} [*Butterbach-Bahl et al.*, 2004b] were reported in European coniferous and Australian tropical forests respectively.

3.5.2 Effect of landscape and vegetation

The biogenic emission of NO is controlled by the soil moisture, soil temperature and the soil nutrient status; it is through the combined effects of altering these modifiers of NO emission that landscape factors and vegetation can influence the production of NO from soils. Spatial and topographical factors influence the soil physical properties or the aboveground biomass; the soil physical properties and the biomass control the supply and cycling of N in the soil [*Akiyama and Tsuruta*, 2002; *Hartley and Schlesinger*, 2000; *Kirkman et al.*, 2001; *Martin and Asner*, 2005; *Martin et al.*, 2003a; *Martin et al.*, 1998; *Meixner et al.*, 1997]. In the KNP the net N mineralization has been shown to change across soil textural sequences, and is

highest in the low lying landscape positions, analogous to the *Footslope* position [*Bechtold and Naiman*, 2006; *Scholes et al.*, 2003b]. Vegetation has been shown to have an effect on the emission of NO [*Aranibar et al.*, 2004; *Davidson*, 1991a; *Hartley and Schlesinger*, 2000; *Kirkman et al.*, 2001; *Martin and Asner*, 2005; *Martin et al.*, 2003a; *Martin et al.*, 1998; *Meixner et al.*, 1997; *Ormeci et al.*, 1999; *Otter et al.*, 1999; *Pilegaard et al.*, 2006; *Scholes et al.*, 1997; *Serca et al.*, 1998; *Van der A et al.*, 2008]. This influence can be caused by the effect of:

a) Changes in the microclimate under the plant canopy, resulting in spatial heterogeneity in the soil through interacting biological and physical mechanisms;
b) Changes in the concentrations of soil nutrients; N, P and K have been shown to be enhanced under tree canopies, resulting from the relocation of absorbed nutrients and changes in the N mineralisation rates [*Rossi and Villagra*, 2003]. The increase in nutrient contents under vegetation is either caused by the vegetation trapping or accumulating nutrients [*Ludwig and Tongway*, 1995; *Ludwig et al.*, 1999b], or through biological N fixation [*Geesing et al.*, 2000; *Schulze et al.*, 1991; *Vitousek et al.*, 2002a].

At the Skukuza flux tower site, the differences in the vegetation types along the catenal sequence have caused a significant difference in the amount of biological N fixation between the vegetation types. In the *Combretum* savanna (*Crest* position) the amount of N fixed is estimated at 4.8 kg ha^{-1} a^{-1}, while in the *Acacia* savanna (*Footslope* position) it is thought to amount to 21 kg ha^{-1} a^{-1} [*Scholes et al.*, 2003b]. Although the vegetation type has a marked influence on the biological N fixation, the deposition of N from the atmosphere in the form of both wet and dry deposition is constant across the vegetation types and amounts to 21.6 kg ha^{-1} a^{-1} [*Scholes et al.*, 2003b].

These differences in the N cycling rate, the total amount of N in the system, and the amount of N entering the system by deposition from the atmosphere and biological nitrogen fixation, most likely account for the changes in the magnitude of the observed net potential NO flux. In this study there were clear differences in the NO production potential for the soils from the differing landscape positions. The highest potential NO flux occurred in the *Footslope* soils, which have been shown to have the highest total N content and N fixation rate. The lowest N emissions occurred in the less nutrient rich landscape positions (crest position Table 3.1) [*Scholes et al.*, 2003b; *Woghiren*, 2002]. Loss of N from the ecosystem through the production of NO is in the range of 0.2 – 0.8 kg ha^{-1} a^{-1} (Fig. 3.7) and therefore the loss of N

in the form of NO is between 0.5% and 2.6% of the N that enters the ecosystem through biological N fixation and wet and dry deposition from the atmosphere.

3.5.3 Effect of Soil Moisture and Temperature

The optimal soil moisture for the emission of NO from the four landscapes in the KNP was found to be between 10 % and 20 % WFPS. The optimal WFPS is the quantity of soil moisture, where the diffusion of NO through the soil is greatest, since diffusion is not limited by excessive soil moisture, while the bacterial metabolism, and therefore production of NO, is not limited by lack of soil moisture [*Skopp et al.*, 1990]. The optimum WFPS reported here correspond with the range reported in other studies in southern Africa; reported values lie between, 10 % and 23 % WFPS for a South African Savanna [*Otter et al.*, 1999], a rainfall gradient in the Kalahari [*Aranibar et al.*, 2004] and in Zimbabwe [*Kirkman et al.*, 2001]. Our study therefore confirms that the optimal NO flux occurs in a low and quite narrow range of WFPS in Southern African Savanna ecosystems (10-25 %).

The landscape position affects the soil WFPS through changes in drainage and in the water holding capacity of the soil as influenced by the soil texture. Generally over the course of the year the $F_{up\text{-}scaled}$ is higher for the *Footslope* than for the *Crest* or the *Upslope* soils since the soil WFPS is closer to the optimum. However during periods of high rainfall, the highest $F_{up\text{-}scaled}$ came from the soils above the flux tower which drained better, thereby maintaining a low soil moisture state more suitable for the production of NO. The *Crest* and the *Upslope* soils generally followed a similar pattern, although the $F_{up\text{-}scaled}$ from the *Upslope* soils tended to be slightly higher (see Fig. 3.5d).

Many previous studies have reported an exponential increase in soil NO emission with increasing temperature, where the Q_{10} value is approximately 2 [*Kirkman et al.*, 2001; *Levine et al.*, 1996; *Meixner and Yang*, 2006; *Van Dijk et al.*, 2002], which is similar to the Q_{10} values reported here (1.55-2.17). However, values of up to 4.6 have reported from the Kalahari [*Aranibar et al.*, 2004] and from shortgrass steppe ecosystems [*Martin et al.*, 1998]. Under conditions such as very high temperatures (exceeding 40 °C) there may even be a negative relationship between the NO emission and the soil temperature [*Passianoto et al.*, 2004], this indicates that a optimum soil temperature may exist, although due to the selection of incubation temperatures used in this study the position of the optimal temperature could not be determined.

The interplay between the influence of temperature and soil moisture content results in seasonal and annual patterns of NO emissions, in all the soils the lowest NO fluxes occurred

during the southern hemisphere winter months when the soil temperatures were low and increased as the soil temperatures increased in spring (September, October) and remained high during the summer, unless the soil became too wet to allow optimal NO production.

The highest $F_{up\text{-}scaled}$ occurred in 2003 and the lowest in 2004. The year 2003 was a relatively warm dry year which kept the soil WFPS low and in the range of the optimal temperature for NO production however, 2004 was a wet year and the soil was wetter than the optimum for extended periods (see Fig 3.5d).

3.5.4 NO consumption rate and compensation mixing ratio

It is known that soils can both produce and consume NO, however there have been only a very few studies that have examined the uptake of NO in the soil, and none that have investigated the NO consumption rate constant (k) or the compensation point mixing ratio ($m_{NO,comp}$) across the full range of soil water contents.

The k value found in this study is within the (very wide) range of values reported in the literature. The peak k value was found to be at the same WFPS as the peak of NO production, between 10 - 20 % WFPS and ranged between 5 and 26 $x10^{-5}$ m^{-3} s^{-1} kg^{-1} at 25 °C (Fig. 3.3). At 35 °C it was considerably lower for all the soil samples, less than $7x10^{-5}$ m^{-3} s^{-1} kg^{-1}. The highest k values were found in the *Footslope* soils, followed by the *Crest* soils. However, it appears to be a significant difference between the 2 midslope positions (*Upslope* and *Downslope*). To the best of our knowledge, there have only been four previous reports of k from drylands; these are from Nylsvley savanna in South Africa [*Otter et al.*, 1999], from the Kalahari transect in Botswana [*Aranibar et al.*, 2004], from a study in Zimbabwe [*Kirkman et al.*, 2001], and concerning an Egyptian soil [*Saad and Conrad*, 1993]. The k values found in our KNP soils were at least twice as high as those from the Nylsvley savanna and the Zimbabwe study where k values of 1.3 – 3.2 $x10^{-5}$ m^{-3} s^{-1} kg^{-1} are reported. In comparison, however, the k values reported from the Kalahari were up to two orders of magnitude higher than from the soils used in this study and ranged from 34-500 $x10^{-5}$ m^{-3} s^{-1} kg^{-1} [*Aranibar et al.*, 2004]. The k values reported in the Egyptian soils ranged from 7.2 $x10^{-5}$ m^{-3} s^{-1} kg^{-1} at 7°C to 79 $x10^{-5}$ m^{-3} s^{-1} kg^{-1} at 25 and 30°C and 40% water holding capacity [*Saad and Conrad*, 1993]. The k values reported here fit right between the ranges of values previously reported. This, however, is the first time that the k values have been reported across a full soil moisture scale; therefore, the cause of the wide range in reported k values may be that previous measurements were made at different points along the soil moisture range. Soil temperature

also has an effect on the *k* values, although the Nylsvley, Kalahari transect and Zimbabwe studies all used an incubation temperature of 25°C.

The compensation point mixing ratio, $m_{NO,comp}$, has only been investigated in three studies in southern Africa:

1. $m_{NO,comp}$ of 152 – 157 ppb have been reported from Nylsvley [*Otter et al.*, 1999].
2. Along a precipitation gradient in the Kalahari, the $M_{NO,comp}$ was reported to change with mean annual precipitation from 39 ppb at Tshane (365 mm Mean Annual Precipitation (MAP)) to 873 ppb for Mongu (880 mm MAP) [*Aranibar et al.*, 2004],
3. Kirkman et al 2001 reported that $M_{NO,comp}$ ranged from 5 – 11 ppb in the dry season in Zimbabwe and from 47 – 85 ppb during the wet season.

Our study, however, is the first to examine the effect of soil moisture on the $m_{NO,comp}$ covering as extensive a range of soil moisture contents. Within the *WFPS* range of the NO emission peak, the calculated $m_{NO,comp}$ in our study are between 40 – 70 ppb. Towards higher soil moisture conditions the compensation point mixing ratio decreases gradually to approx. 10 ppb (at 65% *WFPS*, see Fig. 3.4). The results of our study are within the range of values reported for Zimbabwe and Tshane (Kalahari), but much lower than those from Nylsvley and Mongu (Kalahari).

Knowing the *WFPS* dependent NO compensation point mixing ratios for the different Skukuza land types (as well as the average *WFPS* itself), the question could be tackled, whether the soils in KNP might ever act as a NO sink. The measured mean monthly *WFPS* at the *Crest* position ranges between 10 – 30 % (Fig. 3.5c). NO uptake would only occur (c.f. eqs. (3.5) & (3.12)), if the ambient NO mixing ratio would be higher than $m_{NO,comp}$ there (45 – 50 ppb, see Fig. 4). For the *Footslope* soils the recorded *WFPS* in the field occasionally reached levels of 60% (see Fig. 3.5c). Under these rather wet conditions the ambient concentration of NO, required before uptake could occur, would be much lower, only approximately 20 ppb. However, even an ambient NO mixing ratio of 20 ppb would be exceptionally high for such a remote location. Unfortunately, there are no measured data of ambient NO mixing ratio from Skukuza nor from the entire KNP region available. However, for comparable southern African sites, like Marondera in Zimbabwe, NO mixing ratios of 0.15 – 0.3 ppb have been reported [*Meixner et al.*, 1997]; aircraft measurements in the atmospheric boundary layer over northern Namibia revealed NO mixing ratios well below 0.5 ppb, even under conditions of high biogenic soil emissions (approx. 30 ng $m^{-2}s^{-1}$, s. [*Harris et*

al., 1996]). Using the Max Planck Institute for Chemistry Atmospheric Chemistry Model MESSy ("*Modular Earth Sub-model System*", [*Jöckel et al.*, 2005]), it was found that the modelled surface NO mixing ratio never exceeded 5 ppb , and that the mean NO mixing ratio was 0.08 ppb for the period January 2003 – October 2005. It is therefore highly unlikely that the ambient NO mixing ratio has exceeded the $m_{NO,comp}$ during 2003 – 2005. Considering the remoteness of the KNP region and the well established status as a National Park, it can be expected, that the KNP region is continuously acting as a biogenic NO source and not as a sink (like the majority of the southern African savanna ecosystems).

3.6 Conclusions

This laboratory study investigated the biogenic emission of NO from soils taken from four differing landscape positions in a semi-arid savanna under conservation land use (Skukuza, Kruger National Park, South Africa). The up-scaled emissions of NO did not exceed 3.5 ng m^{-2} s^{-2} for any of the landscape positions, even under optimal soil moisture conditions and high soil temperature; this is at the lower end of the range of previously published studies from comparable ecosystems. The optimum emission of NO occurred under fairly low soil water contents, between 10% – 20% *WFPS*. The highest NO flux came from the nutrient rich fine textured soils in the *Footslope* position, while the *Downslope*, *Upslope* and *Crest* positions had lower rates of NO emission. When the laboratory derived, net potential NO fluxes were up-scaled to the landscape level, the highest estimated NO fluxes were calculated to come from the sum of *Downslope* and *Upslope* landscape positions, because they make up the majority of the Skukuza landscape surface area. The biogenic emissions of NO from this ecosystem constitute a minor N loss mechanism and account for less than 2.6% of the N entering the system in the form of wet/ dry deposition and biological N fixation. Although soils have generally both, the potential to emit and to take up atmospheric NO, the ambient atmospheric NO mixing ratios in this remote part of Africa are highly unlikely to reach and exceed that level (i.e. the NO compensation point mixing ratio), where up-take of NO will take place. The laboratory based estimation of soil moisture and soil temperature dependent net potential NO fluxes from soil and the up-scaling procedure (using recorded soil moisture and temperature data from the field) is shown to be an effective method to quantify biogenic NO emissions on large temporal (annual) and spatial (regional) scales.

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Chapter 4: Use of laboratory and remote sensing techniques to estimate vegetation patch scale emissions of nitric oxide from an arid Kalahari savanna

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Chapter 4 is currently in press:

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4.1 Abstract

The biogenic emission of nitric oxide (NO) from the soil has an important impact on a number of environmental issues, such as the production of tropospheric ozone, the cycle of the hydroxyl radical (OH) and the production of nitric acid. Arid regions cover a significant proportion of the earth's surface; however there have been relatively few studies on the biogenic emissions of NO from these ecosystems. In this study we collected soils from four differing vegetation patch types (Pan, Annual Grassland, Perennial Grassland and Bush Encroached) in an arid savanna ecosystem in the Kalahari (Botswana). A laboratory incubation technique was used to determine the net potential NO flux from the soils as a function of the soil moisture and the soil temperature. The net potential NO emissions were up-scaled for the year December 2005-November 2006 and a region (185km x 185km) of the southern Kalahari. For that we used (a) the net potential NO emissions measured in the laboratory, (b) the vegetation patch distribution obtained from Landsat NDVI measurements, (c) estimated soil moisture contents obtained from ENVISAT ASAR measurements and (d) the soil surface temperature estimated using MODIS MOD11A2 8 day land surface temperature measurements. There are differences in the net potential NO fluxes between differing vegetation patches occur and range from 0.27 ng m^{-2} s^{-1} in the Pan patches to 2.95 ng m^{-2} s^{-1} in the Perennial Grassland patches. Up-scaling the net potential NO fluxes with the satellite derived soil moisture and temperature data gave NO fluxes of up to 323 g $ha^{-1}month^{-1}$, where the highest up-scaled NO fluxes occurred in the Perennial Grassland patches, and the lowest in the Pan patches. A marked seasonal pattern was observed where the highest fluxes occurred in the austral summer months (January and February) while the minimum fluxes occurred in the austral winter months (June and July) where the up-scaled NO fluxes were less than 1.8 g ha^{-1} $month^{-1}$. Over the course of the year the mean NO emission for the up-scaled region was 0.54 kg ha^{-1} a^{-1}, which is 2-100% of the estimated pyrogenic NO emissions from African savannas and accounts for a loss of up to 7.4% of the nitrogen (N) input to the region through atmospheric deposition and biological N fixation. The biogenic emission of NO from the soil is therefore an important mechanism of N loss from this arid savanna ecosystem and has the potential to play an important role in the production of tropospheric ozone and the OH cycle.

4.2 Introduction

The concentrations of nitric oxide (NO) and nitrogen dioxide (NO_2) (collectively known as NO_x) are important in regulating chemical reactions of the atmosphere [*Crutzen*, 1995; *Crutzen and Lelieveld*, 2001; *Monks*, 2005]. They control the production and destruction of tropospheric ozone [*Chameides et al.*, 1992; *Crutzen and Lelieveld*, 2001], are involved in the cycle of the OH radical (the most important tropospheric cleansing agent) and in the production of nitric acid (HNO_3) [*Logan*, 1983; *Meixner*, 1994; *Monks*, 2005; *Steinkamp et al.*, 2008]. The global emissions of NO_x have been severely altered by anthropogenic activity. In 1860 global NO_x emissions were estimated to be 13 Tg a^{-1} of which the majority is thought to have come from natural sources such as soils and lightning [*Galloway et al.*, 2004a]. The recent estimate of the IPCC puts total NO_x emissions at 42-47 Tg a^{-1} with the most important source being fossil fuel combustion [*Denman et al.*, 2007], and soil is thought to account for between 10 % to 40 % of the total NO emissions [*Davidson and Kingerlee*, 1997; *Denman et al.*, 2007]. Over 40% of the total NO emissions from Africa are supposed to originate from biogenic production in the soil [*Jaegle et al.*, 2004]. The wide range of uncertainty is partly due to insufficient measurements, particularly in the drylands [*Galbally et al.*, 2008]. A recent review by Meixner and Yang (2006) only identified 13 studies in natural ecosystems receiving less than 400mm rain a year (since then two other studies have occurred [*Holst et al.*, 2007; *McCalley and Sparks*, 2008]), this is problematic since drylands make up a sizable proportion of the earth's surface area and are thought to be capable of substantial emissions of NO [*Davidson and Kingerlee*, 1997].

The biogenic production of NO in the drylands is dominated by the process of nitrification [*Conrad*, 1996; *Galbally et al.*, 2008]. Nitrification is influenced by environmental factors, such as the soil moisture, the soil temperature and the soil nutrient content. These in turn are determined through the underlying geology, the climate and biotic factors such as the vegetation at the site [*Brümmer et al.*, 2008; *Davidson*, 1991b; *Galbally et al.*, 2008; *Garrido et al.*, 2002; *Ludwig et al.*, 2001; *Russow et al.*, 2000]. In drier ecosystems, soil water seems to be the most important factor regulating emissions of NO. When the soil moisture is too low to maintain microbial activity there are very low levels of NO emitted [*Galbally et al.*, 2008; *Garrido et al.*, 2002; *Meixner et al.*, 1997] and when soil moisture levels are too high to maintain aerobic conditions, the emission of NO is negligible [*Skopp et al.*, 1990]. The optimal emission of NO in drylands seems to occur at low soil moisture levels, but where microbial activity can still take place. In a previous laboratory based study in the Kalahari,

NO emissions were very low at both high and low soil moisture contents, while the optimum soil moisture for NO production was approximately 20% Water Filled Pore Space (*WFPS*) [*Aranibar et al.*, 2004]. Since the biogenic production of NO is mostly a bacterially mediated process, temperature has an important impact on the rate of the reaction, and as the environmental temperature increases so does the rate of nitrification and hence the release of NO. A number of previous studies have shown that the rate of NO increase approximately doubles with a 10°C increase in temperature [*Feig et al.*, In Press-a; *Kirkman et al.*, 2001; *McCalley and Sparks*, 2008]. The soil nutrient status is another important controller of biogenic NO emissions; many studies have found a relationship between the emissions of NO and either the concentrations of ammonia or nitrate [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Hutchinson et al.*, 1993; *Ludwig et al.*, 2001; *Meixner et al.*, 1997; *Parsons et al.*, 1996] or the N cycling rate [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Parsons et al.*, 1996]. Therefore, natural or anthropogenic actions that result in the modification of the inputs of nutrients or the rates of nutrient turnover are likely to have an effect on the NO production rates.

The Kalahari ecosystem extends from South Africa, through Botswana and into Zambia and covers an area of 2.5 million km^2, it is an ecosystem occurring on a homogenous substrate. A rainfall gradient exists, from approximately 200mm a^{-1} in the south to over 1000mm a^{-1} in the north, this results in a gradient of vegetation, from sparse arid fine leaved bush-savanna representing nutrient rich ecosystems in the south; to nutrient poor broad leaved Miombo woodland in the north [*Aranibar et al.*, 2004; *Scholes and Parsons*, 1997].

The Kalahari is currently undergoing extensive land use change associated with an increase in pastoral land use, which has been made possible with the introduction of boreholes to provide water for livestock. Grazing is concentrated around the permanent water sources and creates a distinctive disturbance pattern of concentric vegetation zones. Typically in the close vicinity to the water source there is what has been termed the “sacrifice zone” where there is heavy disturbance; this is followed by a “bush encroached” area where there is a strong increase in the proportion of woody shrub vegetation, typically dominated by *A. mellifera* [*Dougill and Thomas*, 2004; *Hagos and Smit*, 2005; *Thomas and Dougill*, 2007] resulting from the preferential use of grass species by cattle. Beyond the bush encroached zone, where there is less disturbance, the later successional stages of vegetation occur.

The vegetation is known to have an effect on the quantity and cycling of nutrients [*Hagos and Smit*, 2005]. This has been shown to influence the emission of NO from the soil, for example in Texas the emission of NO is higher under areas where there has been encroachment of *Prosopis sp*. [*Hartley and Schlesinger*, 2000; *Martin and Asner*, 2005; *Martin et al.*, 2003a]. These previous studies have either looked at the larger landscape scale [*Aranibar et al.*, 2004; *Brümmer et al.*, 2008; *Davidson*, 1991a; *Delon et al.*, 2007; *Hartley and Schlesinger*, 2000; *Jaegle et al.*, 2004; *Martin et al.*, 2003b; *Otter et al.*, 1999; *Serca et al.*, 1998] or at the vegetation canopy scale [*Barger et al.*, 2005; *Hall and Asner*, 2007; *Hartley and Schlesinger*, 2000; *Holst et al.*, 2007; *Le Roux et al.*, 1995; *Levine et al.*, 1996; *Martin et al.*, 1998; *McCalley and Sparks*, 2008; *Meixner et al.*, 1997; *Mosier et al.*, 2003; *Smart et al.*, 1999]; however there is a need to determine what occurs in the emission of NO between the plant canopy scale and the vegetation patch scale which has been examined in only very few studies [*Kirkman et al.*, 2001; *Martin and Asner*, 2005; *Scholes et al.*, 1997; *Van Dijk et al.*, 2002]. The main points of consideration in this study are (1) to determine the effect of differing vegetation cover types on the emission of NO along a disturbance gradient and (2) attempt to up-scale point measurements of NO release to a regional emission estimate for NO flux from the soil.

4.3. Methods and Materials

4.3.1 Site

The site of the research was at the Berry Bush Farm (25°56'47.73S, 22°25'39.47E, elevation 978m), a 900ha commercial ranch, situated approximately 10km north east of the town of Tsabong in the Kgalagadi District, Botswana. The ranch was formerly used for cattle and sheep farming but at the time of sampling, in May 2006, the stock densities had been reduced and it was only grazed by approximately 120 springbok and other small game. The area has been described as a grass bush savanna [*Dougill and Thomas*, 2004] and is situated on the southern portion of the Kalahari sands. The soils in the Kalahari sands are typically deficient in nutrients, deep, structureless and consist of an average of 62% fine quartz sand in all horizons [*Ringrose et al.*, 1998].

The Kalahari is in a highly seasonal (austral) summer rainfall region, with very high inter-annual variability [*Thomas and Dougill*, 2007]. Mean rainfall measured at the official meteorological station at Berry Bush Farm is 280 mm a^{-1} with a 32% annual variability for the period 1997-2005 (Personal communication Keith Thomas). At the Tsabong WMO station

(WMO Index number 68328) it has been reported that it has a mean annual rainfall of approximately 300mm with a 45% inter-annual variability [*Thomas and Dougill*, 2007]. The year of sampling, 2006, was a very wet year and 418 mm of rain had fallen by the time the soil samples were taken in May.

Four main types of vegetation patches occur on the Berry Bush Farm and are thought to represent a repeated vegetation pattern for the region. The four vegetation patches are; *Annual Grassland*, *Perennial Grassland*, bush *Encroachment* and *Pan*. From the four main types of vegetation patches that occur on the Berry Bush Farm three of the patches, namely; *Perennial Grassland*, *Annual Grassland* and *Encroachment* correspond to differing successional stages in the disturbance regime (where the *Perennial Grassland* is the least disturbed and the *Encroachment* is the most disturbed).

4.3.2 Soil and vegetation sampling

Three replicate sampling sites were selected in each of the vegetation patch types. At each of the sampling sites three 25 m transects were laid out at 120° to each other. The plant cover was estimated as the vegetation cover directly over the transect line and was assigned to various vegetation structural classes, if more than one structural unit overlapped, the larger more physically dominant was recorded. Six different vegetation structural classes have been defined which consisted of; perennial grasses, annual grasses (grasses were classified as annual or perennial species according to Van Oudtshorn [1999]), tree cover, soil crusts, bare soil and other (including shrubs and forbs). For each of the vegetation patch types the total aerial cover was estimated from the sum of the nine transects (three replicates of each vegetation patch and three 25m transects within each replicate).

In each of the sampling sites ten soil samples (approx. 150g) were taken under each of three vegetation types; tree cover, grass cover and open, these were then combined to make a representative soil sample of approximately 1.5 kg in mass (four vegetation patches, three replicates of each vegetation patch, and three vegetation types giving a total of thirty nine 1.5kg soil samples). In the *Pan* ten soil sub-samples were also taken under soil crust. The soil crusts were defined according to the classification of Dougill and Thomas [2004], however only the second and third stage crusts were sampled, since these were the most developed and were clearly discernable. The soil was air dried, sieved through 2mm mesh and stored at 5°C until use. Within each of the vegetation types the soil bulk density was measured in the first 5cm using a stainless steel soil core of known volume.

The soil texture was determined using a hydrometer technique after the method of [*Day*, 1969] and the soil pH was measured in 2.5:1 mixture in distilled water according to the method of Anderson and Ingram [1993]. Soil samples were sent to the micro analytical laboratory at the University of Mainz where total soil carbon (C) and soil nitrogen (N) content was measured using a Vario MICRO Cube universal microanalyser set up to measure total C, and N contents of the soil.

4.3.3 Laboratory incubation and net NO release from soil

Two days before beginning the measurements, the soil was soaked with deionised water and allowed to drain freely at room temperature (22°C), this was to limit the confounding effect of pulsing after the initial wetting of soil after a long period of inactivity. Pulsing is known to elicit a large but temporally limited emission. The magnitude of the pulse after rewetting the soil is variable depending on the preceding period of time in which the soil was dry. Since this can not be easily controlled and pulsing is thought to add a fairly minor contribution to the annual NO flux, (reported to be less than 6% [*Scholes et al.*, 1997]) we decided to neglect the effect of pulsing in this study, which means that the fluxes that are calculated here should be considered to be a lower limit. The basic methodology for the laboratory measurement of the NO flux from soil has been previously described [*Aranibar et al.*, 2004; *Kirkman et al.*, 2001; *Meixner and Yang*, 2006; *Otter et al.*, 1999; *Van Dijk et al.*, 2002] and was further developed by Feig et al [In Press-a] and Yu et al [2008]. It has been shown that there is good agreement between laboratory fluxes of NO calculated according to this method and the measured field fluxes [*Ludwig et al.*, 2001; *Meixner et al.*, 1997; *Van Dijk et al.*, 2002]. Briefly; a known quantity (approximately 100 g (dry weight)) of sieved, wetted soil was placed in one of five plexiglas chambers (volume 0.97 l) in a thermo-controlled cabinet. Pressurised air that had passed through a purification system was supplied to each chamber at a flow rate of 4.2×10^{-5} $m^3\ s^{-1}$ (2.5 L min^{-1}). The outlet of each chamber was connected via a reversed Naphion drier (series MD-110, Perma Pure LLC, USA) and a switching valve to a NO Chemoluminescence analyser (CLD780TR, Eco Physics Switzerland) and a H_2O/CO_2 analyser (Binos IR gas analyser, Rosemont Analytical, USA). Nitric oxide standard gas (200 ppm) was attached to the air purification system via a mass flow controller and diluted into the “zero”-gas stream; this allowed (1) the calibration of the chemoluminescence analyser and (2) for the control of the headspace NO mixing ratio when determining NO uptake in the soil (see below). The soil moisture content was determined by integrating the loss of water vapour throughout the

measurement period and relating it to the gravimetric soil moisture content at the start and end of the measurement.

4.3.4 Measurements of the net NO release rate

The net release of NO (J_{NO}, in ng kg^{-1} s^{-1}) (all units are in terms of mass of N and dry mass of soil) is calculated from the difference between the NO mixing ratio at the outlet of the reference cuvette and the outlet of each of the incubation cuvettes (since the air in the cuvette is well mixed by a microfan, the air at the outlet is assumed to have the same composition as the air in the headspace) according to:

$$J_{NO} = \frac{Q}{M_{soil}}\left(m_{NO,out} - m_{NO,ref}\right) \times \left(\frac{M_N}{V_m} \times 10^3\right) \qquad (4.1)$$

Where Q is the flow rate through the cuvette (4.2×10^{-5} m^3 s^{-1} or 2.5 L min^{-1}), M_{soil} is the dry mass of the soil (kg), M_N is the molar mass of N (14.0076 kg $kmol^{-1}$), V_m is the molar volume (24.465 m^3 $kmol^{-1}$ at 25°C, 1013.25 hPa) and $m_{NO,ref}$ and $m_{NO,out}$ are the mixing ratios of NO in ppb, at the outlets of the reference and incubation cuvettes, respectively. The factor $M_N/V_m \times 10^{-3}$ is needed to convert NO mixing ratio (ppb) to NO concentration (ng m^{-3}).

The release of NO from the soil is the result of the microbial production and consumption of NO in the soil, processes that occur simultaneously [*Conrad*, 1994; *Conrad*, 1996; *Conrad and Smith*, 1995]. As a result, the NO release rate (J_{NO}) is always a net release rate. However if the NO consumption is greater than production in the soil sample then J_{NO} becomes negative. This will only occur if the in-coming (= reference) NO mixing ratio is greater than the headspace NO mixing ratio in the soil containing chamber.

It has already been shown experimentally that there is a linear relationship between the NO release rate (J_{NO}) and the rates of NO production (P) and NO consumption (k) [*Ludwig et al.*, 2001; *Remde et al.*, 1989] so that the measured release rates can be described according to:

$$J_{NO} = P - k \times m_{NO,out} \times \left(\frac{M_N}{V_m} \times 10^3\right) \qquad (4.2)$$

This equation implies that the NO production is independent of the NO mixing ratio in the headspace ($m_{NO,out}$), while the NO consumption is dependent on the NO mixing ratio in the headspace, and can be approached as a first order decay process. To determine the values of P and k, equation (4.2) was used with the measured release rates (J_{NO}) from two sets of incubation measurements, namely using $m_{NO,ref,low}$ =0 ppb and $m_{NO,ref\ high}$ =58 ppb. This allowed us to calculate P (ng kg^{-1} s^{-1}) and k (m^3 kg^{-2} s^{-2}), where k can be determined from the slope of equation (4.2),

$$k = \frac{\Delta J_{NO}}{\Delta[NO]} = \frac{J_{NO,high} - J_{NO,low}}{m_{NO,high} - m_{NO,low}} \times \left(\frac{V_m}{M_N} \times 10^3 \right) \quad (4.3)$$

Where $m_{NO,low}$ is the actual NO mixing ratio (ppb) in the head space of the cuvette under fumigation with NO free air and $m_{NO,high}$ is the actual NO mixing ratio in the cuvette headspace under fumigation with 58ppb NO. In this study, we will present values of the NO release rate (J_{NO}) as a function of soil moisture, in terms of the soil *WFPS*. Water filled pore space is a useful concept because it indicates the amount of water in the soil that is available for microbial activity and also the amount of air in the soil (and therefore the soil oxygen status). The *WFPS* is calculated (a) from the amount of water lost from the enclosed cuvettes through evaporation during the incubation process and (b) through determining the gravimetric water content (Θ) of the wetted sample at the start of the incubation. The *WFPS* is calculated according to equation (4.4):

$$WFPS = \Theta \times \frac{BD}{\left(1 - \frac{BD}{PD}\right)} \quad (4.4)$$

Where *BD* is the soil bulk density in (kg m^{-3}) measured at the site of sampling, by driving a stainless steel core of known volume into the soil and removing a soil sample and drying the soil at 105°C for 48 hours, and *PD* is the particle density of the average soil mineral (quartz) with a value of 2.65×10^3 kg m^{-3} according to [*Parton et al.*, 2001].

4.3.5 Calculation of the net potential NO flux

The laboratory derived net release of NO (J_{NO}, in ng kg^{-1} s^{-1}) from the soil was converted to a net potential NO flux (F_{lab}, in ng m^{-2} s^{-1}) using a simple diffusion based algorithm (eq. 4.5), originally developed by [*Galbally and Johansson*, 1989], modified by van Dijk *et al* (2002). The net potential laboratory NO flux, as a function of *WFPS* and T_{soil}, is calculated according to:

$$F_{lab}(T_{soil}, WFPS) = \sqrt{BD \times k(T_{soil}, WFPS) \times D(WFPS)} \times \left(\frac{P(T_{soil,} WFPS)}{k(T_{soil}, WFPS)} - [NO]_{Headspace} \right) \quad (4.5)$$

Where $[NO]_{Headspace}$ is the NO concentration (in 10^{-12} kg m^{-3}) in the headspace of the cuvette; *D(WFPS),* in m^2 s^{-1}, is the *WFPS* dependent diffusion coefficient of NO through the soil, calculated after [*Moldrup et al.*] (2000), from the *WFPS* and the gas diffusion constant for free air (m^2 s^{-1}) equal to 1.9×10^{-5} m^{-2} s^{-1} [*Gut et al.*, 1998]. The diffusion coefficient is dependent of the soil moisture content and the soil bulk density and therefore is calculated for each soil sample and each soil moisture interval.

For a given soil temperature, an algorithm has been developed [*Meixner and Yang*, 2006] to fit our net potential NO fluxes as a function of the *WFPS* (eq. 4.6). This algorithm describes the net potential NO flux as a power increase until optimal soil moisture followed by an exponential decrease:

$$F_{lab}(T_{soil} = const., WFPS) = a WFPS^{b} \exp(-c\, WFPS) \tag{4.6}$$

Where parameters a, b and c are related to observed values by:

$$a = \frac{F_{lab}(WFPS_{opt})}{\left[WFPS_{opt}{}^{b} \exp(-b)\right]} \tag{4.7}$$

$$b = \frac{\ln\left[\dfrac{F_{lab}(WFPS_{opt})}{F_{lab}(WFPS_{upp})}\right]}{\ln\left(\dfrac{WFPS_{opt}}{WFPS_{upp}}\right) + \dfrac{WFPS_{upp}}{WFPS_{opt}} - 1} \tag{4.8}$$

$$c = \frac{-b}{WFPS_{opt}} \tag{4.9}$$

Where, for a given T_{soil}, $WFPS_{opt}$ is the soil moisture where the maximum laboratory NO release is observed, $F_{lab}(WFPS_{opt})$ is the maximum net potential NO flux at the $WFPS_{opt}$ (the optimum *WFPS*), and $WFPS_{upp}$ is the soil moisture content where F_{lab} approximately equals zero (i.e. $F_{lab}(WFPS_{upp}) = 1/100\ F_{lab}(WFPS_{opt})$) for $WFPS > WFPS_{opt}$).

The temperature dependence of the laboratory NO flux was determined by calculating the net potential NO flux at two soil temperatures, 25°C and at 35°C. The temperature dependence usually shows an exponential increase and can be expressed as the increase of F_{lab} for a 10°C increase in soil temperature, otherwise known as a Q_{10} function (eq. 4.10) [*Lloyd and Taylor*, 1994].

$$Q_{10}(WFPS) = \frac{F_{lab}(T_{soil} = 35°C, WFPS)}{F_{lab}(T_{soil} = 25°C, WFPS)} \tag{4.10}$$

The Q_{10} function can then be included into equation (4.6), as a "temperature amplification factor" of the reference NO flux (T_{ref}= 25°C), so that the laboratory NO flux can be estimated as a function of both soil temperature and soil moisture (eq. 4.11):

$$F_{lab}(T_{soil},WFPS) = a_{Tref} WFPS^{b_{Tref}} \exp\left(-c_{Tref} \times WFPS\right) \times \exp\left[\frac{\ln Q_{10}(WFPS)}{10} \times \left(T_{soil} - T_{ref}\right)\right] \quad (4.11)$$

4.3.6 Compensation point mixing ratio

The compensation point mixing ratio ($m_{NO,comp}$) is an important concept for the bi-directional exchange of NO (see [*Conrad*, 1994]). Since it determines what the ambient mixing ratio of NO in the atmosphere has to be before a net NO uptake into the soil can occur. The compensation point mixing ratio is calculated by resolving equation (4.5) for the NO concentration where $F_{lab}(WFPS,T_{soil}) = 0$:

$$m_{NO,comp}(T_{soil,}WFPS) = \frac{P(T_{soil,}WFPS)}{k(T_{soil},WFPS)} \times \left(\frac{V_m}{M_N} \times 10^3\right) \quad (4.12)$$

In equation (4.5) the last term considers the $m_{NO,comp}$ and the ambient NO concentration, however it has to be stated that the $m_{NO,comp}$ has been found to be much larger (60-90ppb, see section 4.4.2) than the ambient NO mixing ratio in the Kalahari region (<0.8ppb, see section 4.4.1).

4.3.7 Error estimation of NO release measurements

To determine the detection limit of our J release measurements, inert glass beads and autoclaved soils were used to measure the "blank" net release of NO as shown in the study of Feig *et al* [In Press-a]. It was found that the "blank" net release of NO from the glass beads was at a rate of 0.02 ng kg^{-1} s^{-1}, with a random deviation of 0.02 ng kg^{-1} s^{-1} irrespective of the moisture content, therefore an experimentally derived detection limit for J_{NO} of 0.08 ng kg^{-1} s^{-1} may be considered. This results from the mean release rate of glass beads plus 3 standard deviations (corresponding to a confidence interval of 99.7 %). Similarly, the detection limit of the autoclaved soils is 0.11 ng kg^{-1} s^{-1}, therefore the more conservative estimate from the autoclaved soils was used as our detection limit.

To quantify the precision of J_{NO} measurements, the NO net release rate was determined experimentally through the simultaneous measurement of four replicates across the full range

of soil moisture. The mean standard deviation on the NO net release rate was found to be 0.03 ng kg^{-1} s^{-1} irrespective of *WFPS*; this is lower than the experimentally derived detection limit of $J_{NO.}$ We consider ±0.05 ng kg^{-1} s^{-1} as a conservative estimate of the experimentally derived precision of J_{NO}.

An error propagation approach was used to estimate the error in the net potential NO flux [*Harris*, 1995]. The error in the net potential NO flux is derived from the error of mixing ratio measurements (i.e., error of the NO analyser), error in the determination of the bulk density, error in the determination of the consumption constant *k*, error in the calculation of the diffusion values and error in the determination of NO production values (*P*) (which can be assumed to be similar to those of the *J* release) and the error in the water vapour measurement which is mainly the *WFPS* measurements (see equation 4.5).

- The error in the $NO_{Headspace}$ measurements stems from the sensitivity of the NO analyser; using 37 different measurement periods (over 13000 individual data points) during Jan –Oct 2006 the instrument noise was found to be 0.75% of the corresponding signal.
- The error in the BD calculation was determined from:
    - The error in the balance (Model, Sartorius, Göttingen, Germany) this was found to be ±0.006 g from 20 sets of measurements in a mass range of 2-1000g. The error was determined for a mass of 150g giving a relative error of 0.004%.
    - A maximum relative error of 5% was assumed (conservatively) for determination of the volume of the soil sample which was finally used as the error of the BD calculations.
- The error in the consumption constant *k* was calculated using the absolute error calculated for *J* (0.04 ng kg^{-1} s^{-1}) and converted to a relative error using a J release value of 3.5 ng kg^{-1} s^{-1}), this and the relative error of the NO analyser (0.75%), resulted in a relative error in *k* of 1.7%.
- The noise in the water vapour measurements was determined by adding water to all the cuvettes and incubating them while there was maximum evaporation. The relative error of the water vapour measurements was estimated at 0.8%.

- The relative error in the diffusion values is derived from a 0.8% relative error in the water vapour measurements and a 5% assumed error for the bulk density measurements resulting in a relative error in the diffusion values of 5.1%
- The error in P can be calculated from the errors in J, k and the $m_{NO,headspace}$ and it is found that the absolute error of P is 0.07 ng kg^{-1} s^{-1} and if a maximum P value of 3.5ng kg^{-1} s^{-1} is assumed, this gives a relative error of 2% in P.

Propagating the errors of all these variables, results in a relative error of 4.2% of the net potential NO flux.

4.3.8 Statistics and Analysis

Calculations and graphs have all been done in EXCEL (Microsoft®), and IGOR ® Version 6.03, while statistical analysis of the soil physical and chemical properties was done using a 2 way ANOVA after checking for normality; all statistics were done using SPSS version 16.

4.3.9 Up-scaling to the regional level using remote sensing and GIS techniques

The calculated net potential NO flux values (as a function of soil moisture and temperature, see eq. 4.11) were used to create a regional estimate of the NO flux ($F_{up\text{-}scaled}$) under a GIS framework. To do this, three tools were developed for the use of remote sensing information. These were the following classification schemes of:

- Land use (vegetation patch);
- Soil temperature;
- Soil moisture.

All charts have been produced with a projection of UTM zone 34 (south) Spheroid WGS84 Datum WGS 84.

4.3.9.1 Land use classification

The region where up-scaled NO emissions were calculated is around the town of Tsabong in the southern part of the Kalahari. Up-scaling has been limited to an area the size of a Landsat image (185km x 185km, see highlighted square in Fig. 4.1). This is in the region where the field sampling took place and where the climate and soil properties are fairly homogeneous (Fig. 4.1). The four corners demarcating the region are (24°57'18.51'' S, 21°36'20.12''E), (25°02'20.31''S, 23°04'54.75''E); (26°26'58.27''S, 21°34'57.92''E) and (26°30'04.40''S,

23°05’29.43’’E). The land use for the area was described using high resolution Landsat images in combination with visual interpretation of field conditions.

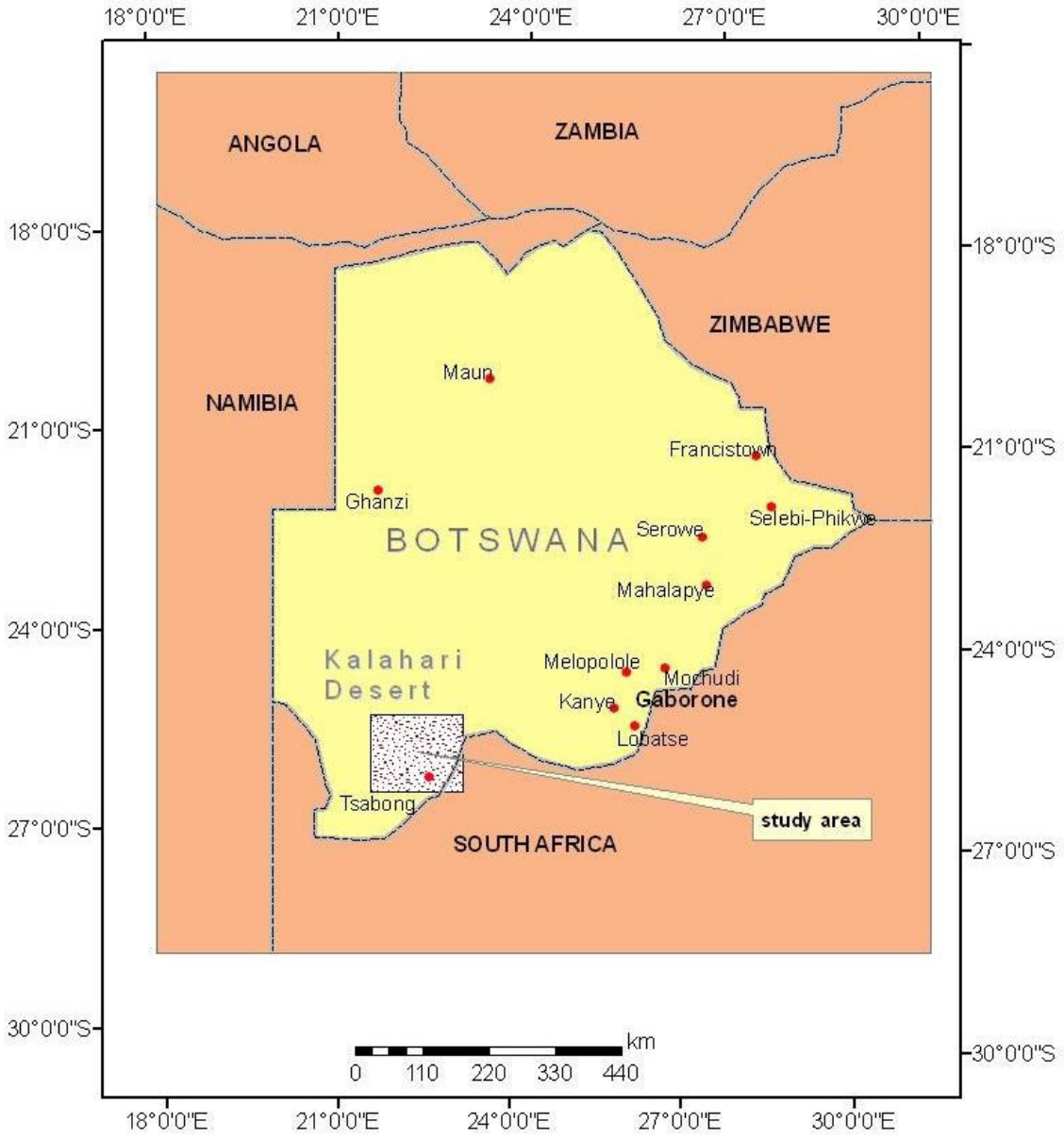

Figure 4.1 Map of Botswana and surrounding countries. The area where up-scaling of the NO flux occurred is highlighted

Multiband Landsat images for May 2000 (Landsat-7 Enhanced Thematic Mapper), positioned within Landsat path 174 row 78, were provided by the US Geological Survey (USGS) (since this is a remote rural region it was assumed that there have be no significant changes in the land use between May 2000 and May 2006). These images were rectified to UTM zone 34 S and image processing was performed using ERDAS Imagine, version 8.7.

Vegetation cover was defined using Normalized Difference Vegetation Index (NDVI) based vegetation rendering since it provides a good spectral characterization parameter [*Roettger*, 2007]. The NDVI was calculated using Landsat channels 3 (R: red) and 4 (IR: near infrared) using equation (4.13):

$$NDVI = \frac{IR - R}{IR + R} \qquad (4.13)$$

The NDVI values range from -1 to +1 and correlate with the vegetation cover; high NDVI values indicate higher biomass [Roettger, 2007] and larger plants, therefore larger vegetation (trees and shrubs) will have a higher NDVI value, while sparse vegetation and grass have lower values. Bare soil and rocks reflect in the near infrared range and therefore have NDVI values near zero, very dry soil has a negative NDVI; water, snow and clouds and reflect in the near infrared and red wavelengths and therefore have values below zero; however snow and standing water is not expected in this area.

Our classification scheme for the land use was based on the NDVI pixel value and on the "supervised classification approach", where an analyst selects "training areas" that are spectrally representative of the land cover classes of interest (ERDAS Field Guide by Leica, 2005). In this case the training areas were the vegetation patches chosen at the Berry Bush Farm where the soil samples were taken (three replicates per vegetation patch type). The vegetation patches were delineated in the field with a hand held GPS device. Parametric signatures ware developed from the NDVI values of the pixels in each vegetation patch, based on statistical parameters (maximum, minimum, mean and covariance of the NDVI matrix) of the pixels that are in the training areas at a resolution of 28m x 28m (which is smaller than the size of the vegetation patches measured in the field) [*Roettger*, 2007].

In this study NDVI values ranged from 0.29 to 0.00, which corresponds to "light to sparse vegetation cover and bare soils" [*Roettger*, 2007].

NDVI signatures for each of the patches were defined as 0.0- 0.039 for the *Pan*, 0.040- 0.057 for the *Annual Grassland*, 0.058-0.24 for the *Perennial Grassland,* and 0.25-0.29 for the *Encroachment*.

The land use distribution in this part of the Kalahari was later used for estimating the emissions of NO from the soil using MODIS land surface temperature data (LST). This data is provided at a coarser resolution (1km x1km) and it was therefore necessary to change the resolution of the land cover data from 28m x 28m (Fig. 4.7a) to that of the LST (1km x 1km)

(Fig. 4.7b), this up-scaling procedure was performed in GIS mapping, where one can accurately estimate block estimates from pixels of smaller resolution.

4.3.9.2 Soil moisture classification

The soil moisture content for the region (December 2005-November 2006) was obtained from the "Soil Moisture for Hydrometeorologic Applications in the SADC region" (SHARE) program, which is a European Space Agency project for the characterisation of soil moisture at a 1km resolution. The project uses the ENVISAT ASAR (Advanced synthetic aperture radar) sensor in the global mode, in conjunction METOP scaterometer sensors [*Wagner et al.*, 2008; *Wagner et al.*, 2007]. The spatial resolution of the SHARE soil moisture data is less than 1 km and the pixel size is 420m (aggregated to 1x1 km). The temporal resolution is variable and the satellite generally makes a pass every 3-5 days. Here the spatial distribution of soil moisture (in terms of soil Water Filled Pore Space) is mapped using GIS techniques.

4.3.9.3 Soil temperature classification

Soil surface temperature was obtained from the MODIS (Moderate Resolution Imaging Spectroradiometer) land surface temperature products MOD11*A2 Eight-Day LST*, distributed by the Land Process Distributed Active Archive Centre (LP DAAC) for the period December 2005- November 2006. Land surface temperatures (LST) (corresponding to a skin temperature) were obtained using the "screened for cloud effects and split-windows algorithm" [*Wan et al.*, 2002], and the day/night algorithm which is usually applied to tropical regions [*Wan*, 2003]. The *MOD11A2 Eight-day LST* is the average land surface temperature over an 8 day period obtained from daily products from the *MOD11A1* at a 1km spatial resolution. The land surface temperatures were mapped for the study area using ENVI 3.6 software. Comparisons of the satellite derived surface temperatures were compared with measured soil temperatures (5cm depth) at the WMO weather station at Tsabong obtained from the National Climate Data Centre (NCDC) of the National Oceanic and Atmospheric Administration (NOAA).

4.3.9.4. NO up-scaling

The emission of NO from the soil was calculated for 12 months based on the parameters obtained from the laboratory flux measurements, distribution of the vegetation patches obtained from Landsat, the soil moisture estimations obtained from the ENVSAT ASAR data

and from the MODIS land surface temperature data, using the algorithm of Meixner and Yang (2006) (See Eq 4.11).

4.4 Results

4.4.1 Soil physical and chemical properties

The soils in all the vegetation patches have a high sand content of over 70% and the soils are classified as sandy loam soils, except for the *Pan* soils which are sandy clay loam soils. The mean bulk density of the soils is between 1.4 x 10^3 kg m^{-3} and 1.5 x 10^3 kg m^{-3} and does not differ significantly between the vegetation patches.

Table 4.1: Mean soil physical and chemical properties for the vegetation patches. Values in brackets indicate standard deviation (n= 9 for the *Annual Grassland*, *Encroachment* and *Perennial Grassland*, n=12 for the *Pan*)

Patch	***Pan***	***Annual Grassland***	***Perennial Grassland***	***Encroachment***
Bulk Density (10^3 kg m^{-3})	1.4 (0.1)	1.5 (0.1)	1.5 (0.1)	1.5 (0.1)
Sand (%)	71.0 (1.7)	78.2 (1.7)	79.0 (0.8)	78.9 (1.0)
Silt (%)	7.6 (1.5)	4.1 (1.3)	4.5 (1.3)	3.8 (1.1)
Clay (%)	21.4 (1.3)	17.6 (1.3)	16.5 (1.0)	17.3 (0.5)
Texture Class	Sandy clay loam	Sandy Loam	Sandy Loam	Sandy Loam
pH	8.5 (0.1)	6.5 (0.5)	6.1 (0.5)	6.5 (0.3)
Total N (%)	0.07 (0.02)	0.07 (0.02)	0.05 (0.02)	0.06 (0.02)
Total C (%)	0.68 (0.2)	0.49 (0.2)	0.44 (0.2)	0.38 (0.1)

The mean pH in the *Annual Grassland*, *Perennial Grassland* and *Encroachment* patches ranges from 6.1-6.5 and does not differ significantly ($p>0.05$). However in the *Pan* the mean pH is 8.5 and this is significantly higher than in the other patches ($p<0.05$). Differences occur within the *Pan* patch where the Tree cover has a significantly lower pH than the Open. The pH values are 8.4 and 8.6 for the Tree cover and Open, respectively ($p<0.05$, n=3).

Table 4.2 Effect of vegetation cover unit on the soil total N and C contents (values in brackets indicate the standard deviation (n=3)

Patch	Vegetation Cover Unit	Total Nitrogen (%)	Total Carbon (%)
Pan	Tree	0.093 (0.028)	0.90 (0.114)
	Open	0.057 (0.008)	0.57 (0.103)
	Grass	0.067 (0.008)	0.66 (0.117)
	Crust	0.058 (0.010)	0.58 (0.094)
Annual Grassland	Tree	0.092 (0.025)	0.72 (0.21)
	Open	0.052 (0.003)	0.35 (0.03)
	Grass	0.055 (0.018)	0.40 (0.108)
Perennial Grassland	Tree	0.065 (0.010)	0.65 (0.074)
	Open	0.037 (0.008)	0.27 (0.081)
	Grass	0.035 (0.010)	0.38 (0.129)
Encroachment	Tree	0.076 (0.006)	0.51 (0.093)
	Open	0.050 (0.005)	0.30 (0.047)
	Grass	0.043 (0.006)	0.31 (0.06)

There are no significant differences in the mean total N contents between the vegetation patches, which range from 0.05-0.07% total N; however there are vegetation cover type related differences (Table 4.2). In the *Encroachment* and *Perennial Grassland* patches where the total N content under Tree cover is significantly higher than under the Open or Grass cover classes ($p<0.01$, n=3). There are no significant differences ($p>0.05$) in the total N continents within either the *Pan* or the *Annual Grassland* vegetation patches. The total C content of the soil does not differ between the vegetation patches; however differences occur between the vegetation cover units within the patches (Table 4.2). In the *Encroachment* patches total C is significantly higher under the Tree cover than under either the Open or Grass cover classes ($p<0.05$, n=3). In the *Perennial Grassland* the total C content under the Tree canopies is significantly higher than under the Grass or Open cover types ($p<0.05$, n=3). In the *Annual Grassland* patch the total C content under Tree cover is significantly higher than under Open ($p<0.05$, n=3) and is greater than under Grass cover at the 10% confidence interval ($p<0.1$, n=3). In the *Pan* patches the soil C content is significantly higher under the Tree canopy than under the Open or Crust cover types ($p<0.05$, n=3) and is greater than the Grass cover type ($p<0.1$, n=3).

4.4.2 Vegetation cover

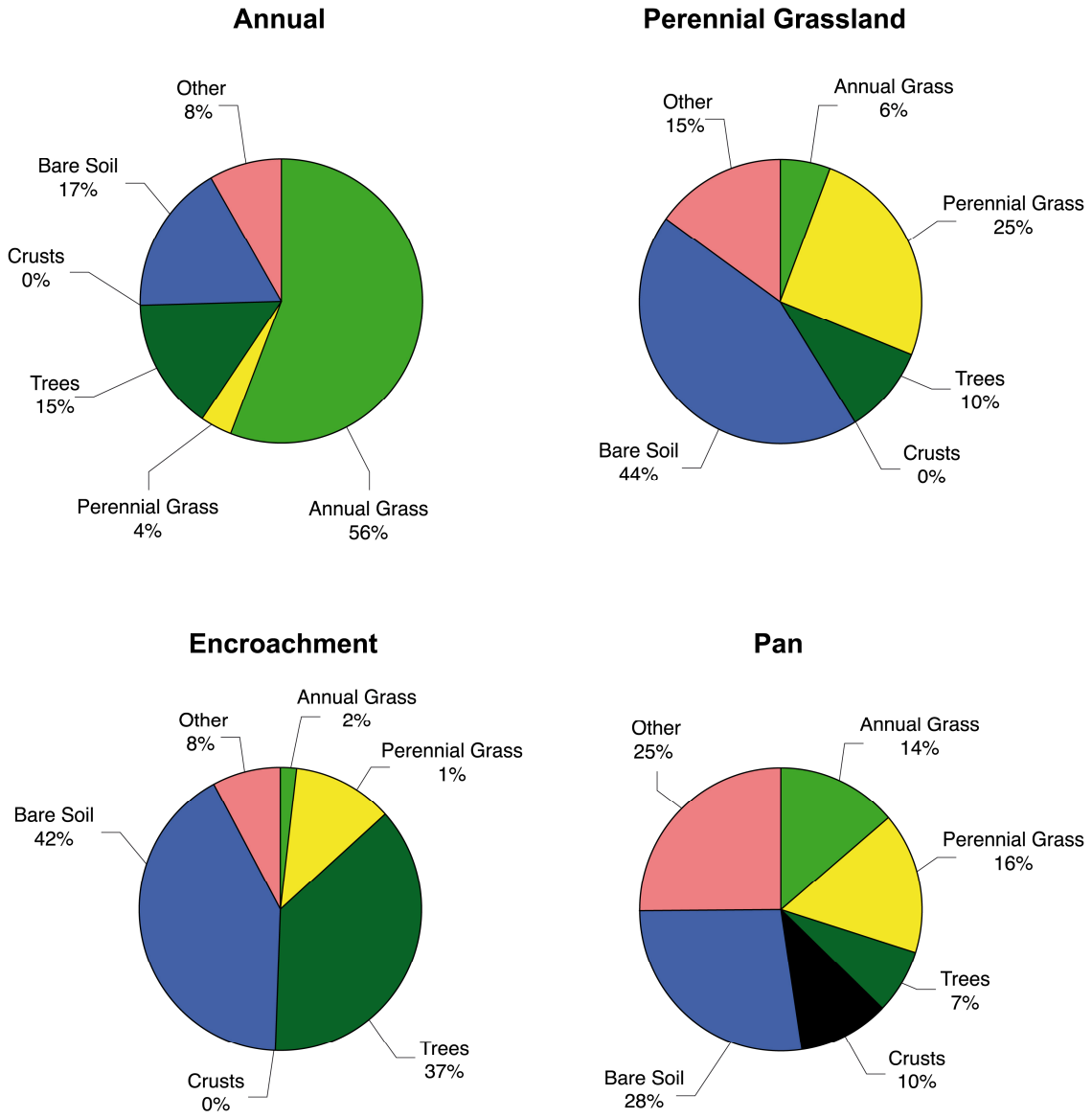

Figure 4.2 Vegetation cover in each of the selected vegetation patches

There are distinct differences in the vegetation cover patterns between the four chosen vegetation patch types.

The *Annual Grassland* patch was covered by 56% annual grass species, mostly *Schmiditia kalihariensis* (Stent). None of the other vegetation patches had a cover of annual grass species as high as the *Annual Grassland*; the *Pan* had the next highest cover with 14% annual grass cover.

In the *Encroachment* patch the vegetation cover was dominated by tree cover, almost exclusively *A. mellifera* subsp. *detinens* (Burch.), which made up 37% of the total vegetation cover in the *Encroached* patch, more than double the 7-15% tree cover in the other patches. The dominant vegetation types in the *Perennial Grassland* patches were perennial grass species, which made up 25% of the vegetation cover. In the *Pan* the vegetation composition was fairly evenly distributed between the vegetation functional types, however this was the only patch where 2nd or 3rd degree soil crusts made an important contribution to the vegetation cover. In all the vegetation patches there was a large amount of uncovered soil which ranged from 17% in the *Annual Grassland* to 45% in the *Perennial Grassland*.

4.4.3 Laboratory NO flux

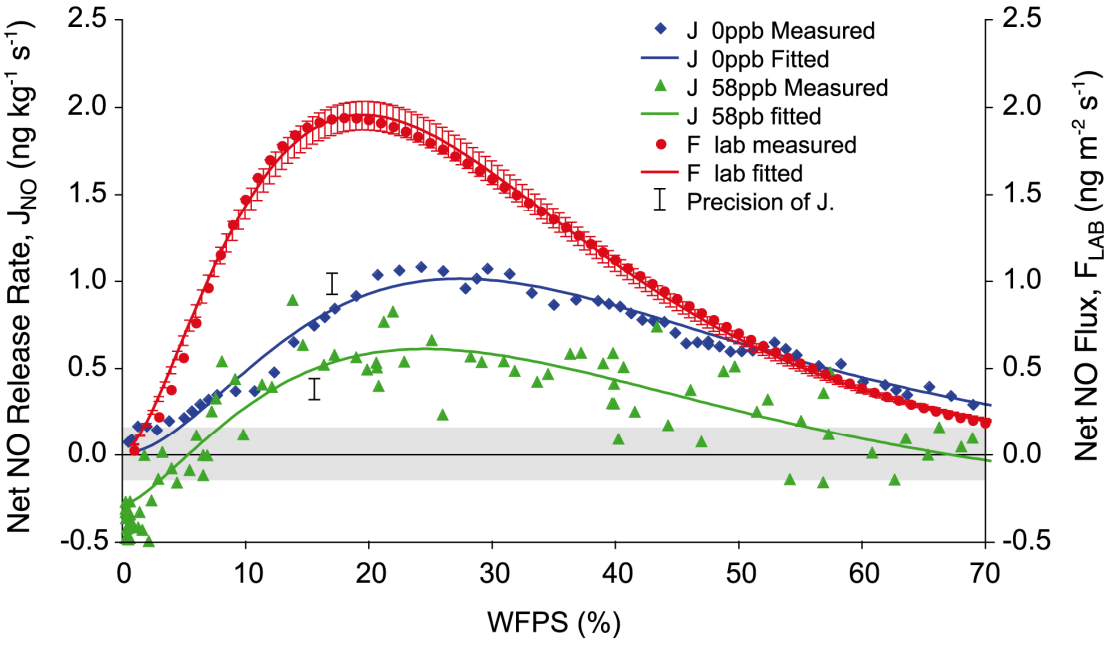

Figure 4.3 An example of the measured and fitted net NO release (J_{NO}) under low NO mixing ratios (blue), measured and fitted net NO release under high NO mixing ratios (green) and the net potential NO flux (red) for the *Annual Grassland* Grass cover at an incubation temperature of 25°C. Error bars indicate the precision for the J release measurements (0.05ng kg^{-1} s^{-1}), while the detection limit is represented by the "dead band" (0.11ng kg^{-1} s^{-1}) around zero net NO release rate (J_{NO}). The error bars on the net potential NO curve represents the calculated error using a relative error of 4.2% from the error propagation approach.

Figure 4.3 shows an example of the net NO release (*J release*) values from soils of the *Annual Grassland* patch and under Grass cover with NO free air incubation, *J release* under incubation with air containing 58 ppb NO, and the calculated net potential NO flux (F_{Lab}). Under elevated NO headspace conditions the release of NO is reduced indicating that uptake

of NO is occurring in the soil, while the shapes of the emission curves are comparable. The flux of NO has slightly differing optimal soil moisture to the two release values due to the position of the areas of NO uptake.

In all the vegetation patches the maximum net potential NO flux was below 5 ng m^{-2} s^{-1} (Fig. 4.4). The highest net potential NO fluxes occurred from the soils in the *Perennial Grassland* and *Encroachment* patches, 4.3 ng m^{-2} s^{-1} (25°C), 3.1 ng m^{-2} s^{-1} (35°C) in the *Perennial Grassland*, 3.3 ng m^{-2} s^{-1} (25°C) and 3.3 ng m^{-2} s^{-1} (35°C) in the *Encroachment* Patch. The lowest net potential NO fluxes occurred from the *Pan* where the NO flux did not exceed 0.6 ng m^{-2} s^{-1} and 1.3 ng m^{-2} s^{-1} at 25°C and 35°C, respectively. This indicates that there are differences between the vegetation patches, caused either by the soil physical properties or by the differing vegetation.

In all the patches, except the *Perennial Grassland,* the potential NO flux is greater at the 35°C incubation than the 25°C incubation. In the *Perennial Grassland* the potential flux was greater at 25°C, indicating that there is an optimum soil temperature for the emission of NO, above which the emissions start to decrease. There is no constant pattern as to which vegetation cover type produces the highest or lowest NO flux, as these change between the different vegetation patches and is not even consistent under the different temperature treatments. However at 25°C the maximum net potential NO flux tends to occur under the dominant vegetation cover unit within the vegetation patch.

- In the *Pan* patch the maximum net potential NO flux from under the *Crusts* (0.6 ng m^{-2} s^{-1}) is more than 25% higher than under any of the other vegetation cover units (0.4 ng m^{-2} s^{-1} for *Grass* and *Trees* and 0.3 ng m^{-2} s^{-1} for *Open*);
- In the *Annual Grassland* the maximum net potential NO flux under *Grass* cover (1.95 ng m^{-2} s^{-1}) is twice as high as under the highest of the other vegetation cover types (0.9 ng m^{-2} s^{-1}).;
- In the *Perennial Grassland* patch the maximum net potential NO flux of 4.3 ng m^{-2} s^{-1} occurs from the *Open* cover type, while the maximum net potential NO flux from under *Trees* is 3.2 ng m^{-2} s^{-1} and 2 ng m^{-2} s^{-1} from under the *Grass* canopy.
- In the *Encroachment* patch the maximum net potential NO flux from under the *Tree* canopies (3.3 ng m^{-2} s^{-1}) is between 25% and 50% higher than under the *Open* (1.6 ng m^{-2} s^{-1}) and *Grass* cover (2 ng m^{-2} s^{-1}).

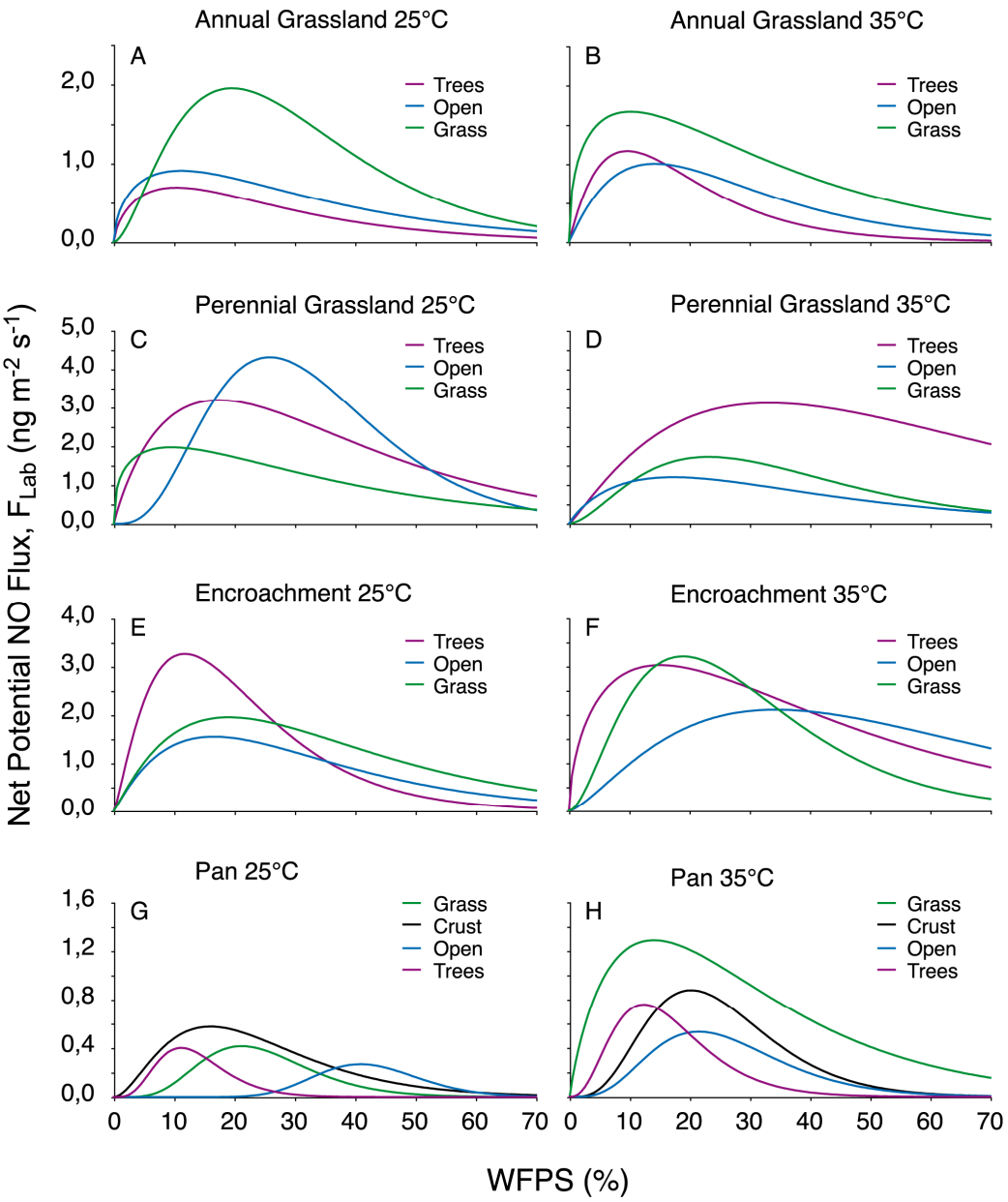

Figure 4.4: Laboratory derived net potential NO flux as a function of the soil *WFPS* at 25°C and 35°C incubation temperatures.

At 35°C these patterns have changed so that in the *Annual Grassland*, *Perennial Grassland* and *Encroachment* sites the maximum net potential NO flux comes from under the *Trees*, while in the in the *Pan* patch it occurs under the *Grass* canopy.

The median optimal *WFPS* (where F_{lab} is maximum) for all patches and covers at 25°C is 16.3 % (12.4% and 20% for 25 and 75 percentile respectively). At 35°C the median optimal *WFPS* is slightly higher at 19.3% *WFPS* (14.5% and 21.9%, for the 25 and 75 percentile, respectively), although these differences are not significant ($p>0.05$). Therefore the optimum

soil moisture for the emission of NO is fairly low (20%*WFPS* = 5.8 % Θ), as is expected since the production of NO is a result to the aerobic process of nitrification.

4.4.4 Mean net potential patch NO flux

To determine the mean net potential NO flux of an entire patch, the NO flux within each patch have been apportioned from the individual net potential NO fluxes from the corresponding vegetation cover types according to the total coverage of that vegetation cover type (as shown in Fig. 4.2). This results in mean net potential flux curves for each of the vegetation patches (Fig. 4.5). The lowest mean net potential NO flux still occurs in the *Pan* patch where the maxima are less than 0.27 ng m^{-2} s^{-1} (25°C) and 0.89 ng m^{-2} s^{-1} (35°C), respectively. The highest net potential NO flux comes from the *Perennial Grassland* patch where the maximum flux (2.95 ng m^{-2} s^{-1}) is reached at soil moisture content of 24% soil *WFPS* and a soil temperature of 25°C. In all the patches the optimal soil moisture is between 10% and 25% *WFPS*.

Temperature does not have a consistent influence on the optimal WFPS. In the *Pan* and *Perennial Grassland* patches the optimal soil moisture under the two incubation temperatures is approximately the same, however in the *Annual Grassland* the optimal *WFPS* is shifted towards dryer soil conditions at the higher incubation temperature and in the *Encroachment* it is shifted towards wetter conditions under the higher incubation temperatures. The effect of temperature is also not consistent; in the *Pan* and *Encroachment* patches an increase in temperature results in a strong increase in net potential NO flux. The Q_{10} value is 3.54 and 1.51 for the *Pan* and *Encroachment* patches respectively. However in the *Annual Grassland* these effects are not as strong. In the *Annual Grassland* the Q_{10} value is 1.07 indicating that in the 25°C to 35°C temperature range there is virtually no temperature influence on the NO flux. In the *Perennial Grassland* there is a negative temperature relationship in the 25°C to 35°C temperature range (Q_{10} = 0.61) and as the temperature increases the NO flux decreases.

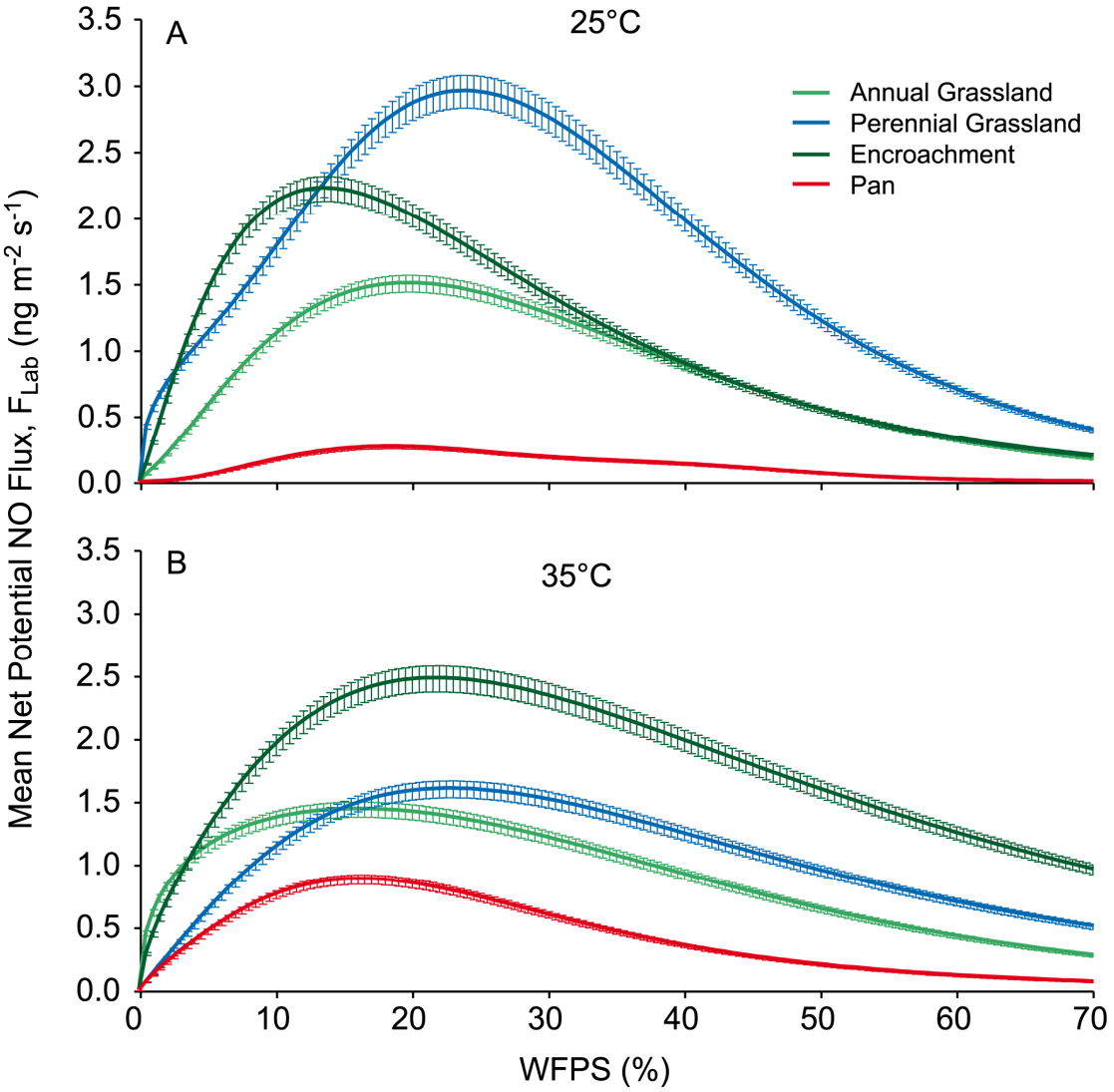

Figure 4.5 A) Mean net potential NO flux at 25°C incubation. **B)** Mean net potential NO flux at 35°C. Error bars represent the 4.2% relative uncertainty determined for the NO flux (section 2.7). The mean net potential NO flux is determined in each of the vegetation patches taking into account the proportion of vegetation cover (see Fig. 4.2).

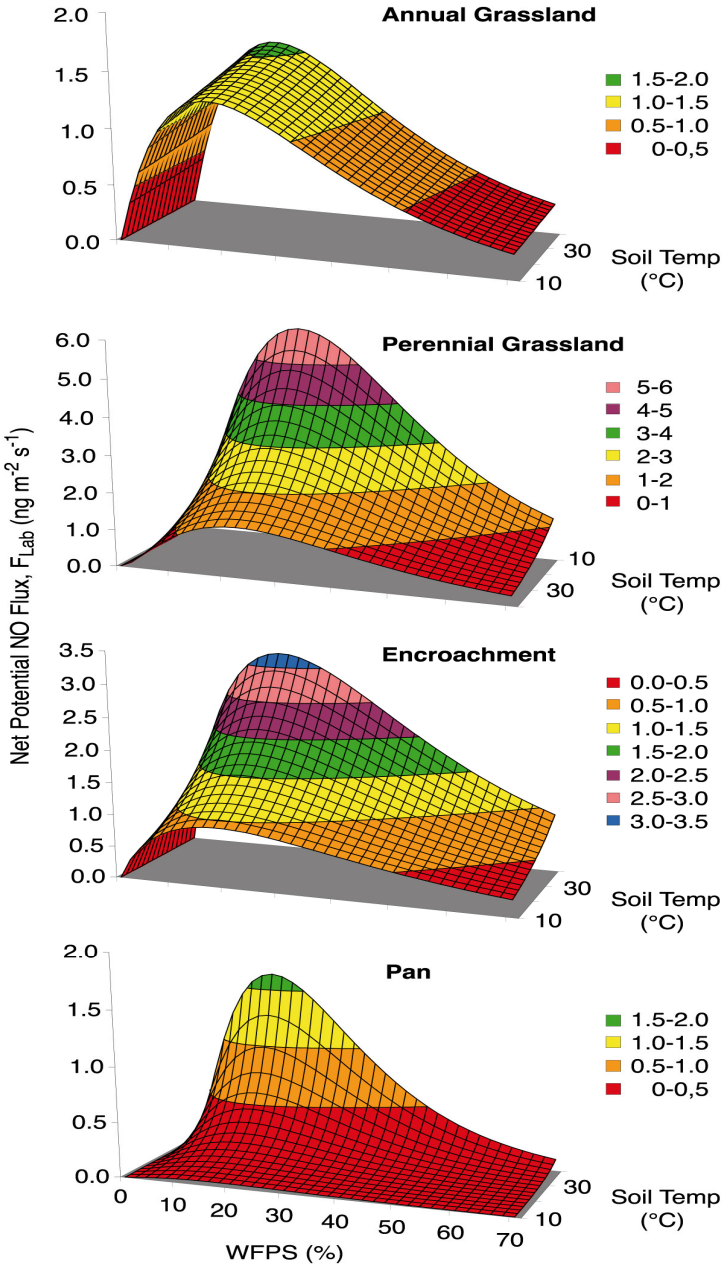

Figure 4.6 Mean net potential NO flux charts for each of the four vegetation patches as a function of both soil moisture (in terms of *WFPS*) and soil temperature. Note that the temperature scale in the *Perennial Grassland* figure is reversed and in fact shows negative temperature dependence.

Fitting the laboratory measured net potential NO fluxes as a function of both soil moisture and temperature gives the net potential flux curves as shown in figure 6. Using these curves an estimate of the net potential NO flux can be made for any known soil water and temperature content.

4.4.5 NO compensation mixing ratio and NO consumption rate

The median NO compensation mixing ratio (25°C) as a function of soil moisture is shown in Figure 4.7a. The median $m_{NO,comp}$ ranges from 61-86ppb NO with the highest median values occurring between 20% and 25% *WFPS*. The lower 25 percentile range is from 35 to 63ppb NO while the 75 percentile range is from 86 to 147 ppb NO. The $m_{NO,comp}$ does not seem to be strongly influenced by the soil moisture content (at least not in the range of soil *WFPS* found in this study section 3.6.2).

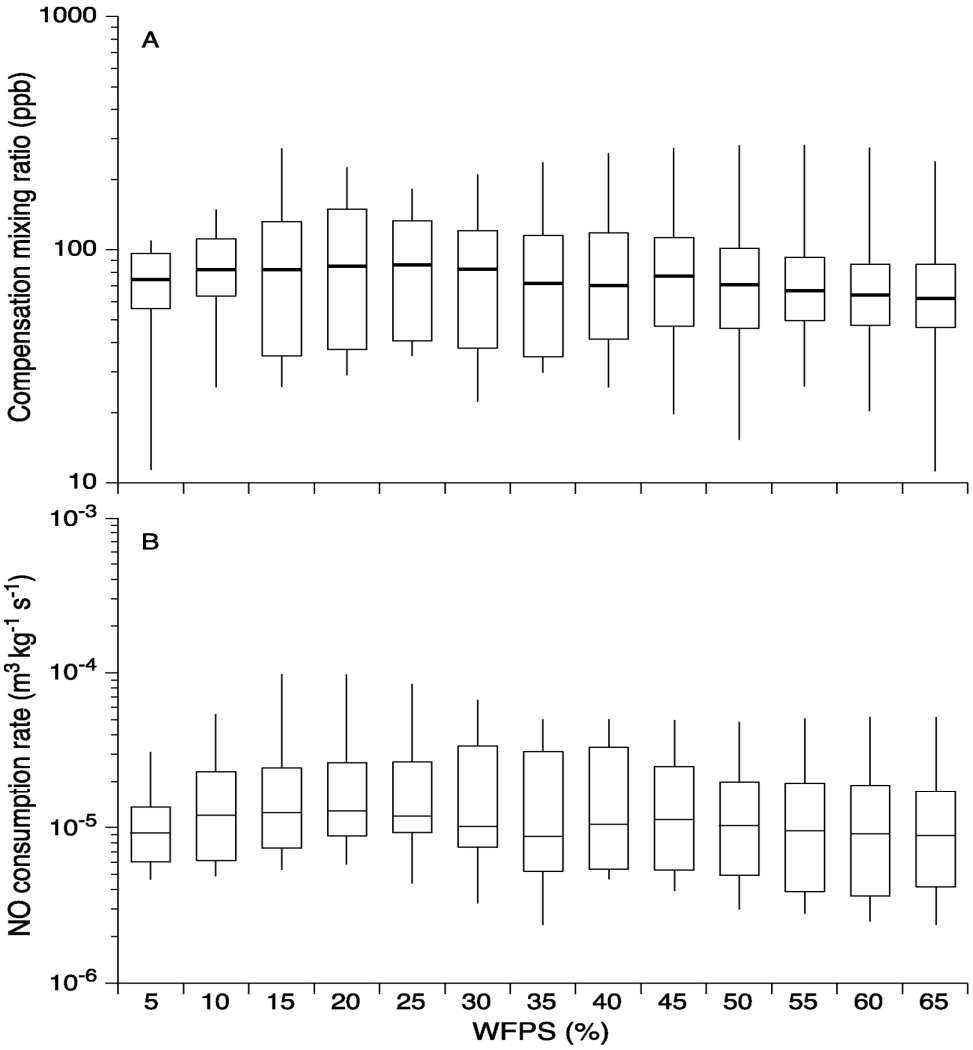

Figure 4.7 A Median $m_{NO,comp}$ at 25°C for all the soils grouped into soil *WFPS* intervals of 5% *WFPS* for the range of *WFPS* that occurred in the field. The bar indicates the median $m_{NO,comp}$ while the box and whiskers indicate the 10, 25, 75 and 90 percentile range. **B** NO consumption rate at 25°C, medians and percentiles for all the soil samples, the bar indicates the median *k* value, the box delineates the 25 percentile to the 75 percentile and the whiskers show the 10 percentile to 90 percentile range.

The NO consumption rate (*k*) at 25°C, calculated from equation (4.3) as a function of *WFPS* is shown in figure 4.7b. The maximum *k* occurs at approximately the same *WFPS* as the maximum of F_{lab} (see Fig. 4.5), namely between 10% – 25% *WFPS*, although the there are no

marked differences in *k* due to the soil moisture content. The median *k* values range from 0.9 x 10^{-5} m^3 $kg^{-1}s^{-1}$ (30%-35% *WFPS*) to 1.3 x 10^{-5} m^3 $kg^{-1}s^{-1}$ (15%-20% *WFPS*). The lower 25 percentile ranges from 3.7 x 10^{-6} (55%-60% *WFPS*) to 9.3 x 10^{-6} m^3 $kg^{-1}s^{-1}$ (20%-25% *WFPS*) and the upper 75 percentile ranges from 1.5 x 10^{-5} (2.5% -5% *WFPS*) to 3.4 x 10^{-5} x 10^{-5} m^3 $kg^{-1}s^{-1}$ (25%-30% *WFPS*).

4.4.6 NO up-scaling

Up-scaling the NO flux from the corresponding mean net potential NO flux for each of the vegetation patches (see Fig 4.6) to the regional scale required three sets of landscape based information: the vegetation patch distribution; the soil moisture content; and the soil surface temperature.

4.4.6.1 Vegetation patch distribution

Using the Landsat NDVI (see section 2.9.1) provided a high resolution distribution of the vegetation patches (28m x 28m) in this region (Fig. 4.1) of the southern Kalahari (Fig. 4.8a). The proportion of land cover from each patch type was 60.3% for *Perennial Grassland*, 26.8% for *Annual Grassland*, 6.3% for *Encroachment* and 6.6% for *Pan*. Decreasing the resolution of the vegetation patch distribution to 1km x 1km (Fig. 4.8b) did not result in any major changes in the proportion of land covered by the vegetation patches; percentage distribution was 59.9%, 26.9%, 6.4% and 6.8% for the *Perennial Grassland*, *Annual Grassland*, *Encroachment* and *Pan* respectively.

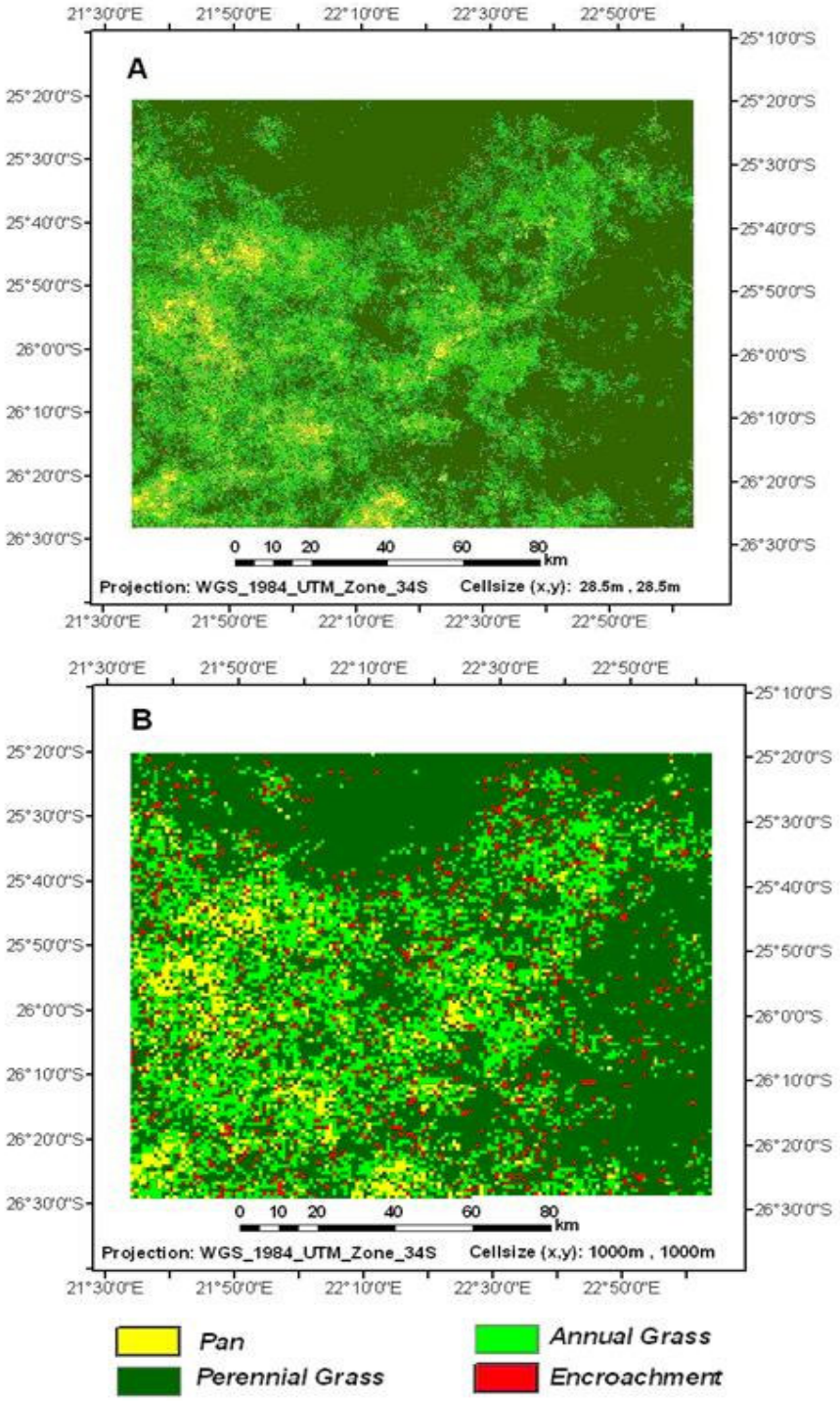

Figure 4.8A) Land cover classification at a pixel resolution of 28m x 28m **B)**. Land cover classification at a resolution of 1km x 1km.

4.4.6.2 Soil moisture

The mean monthly soil *WFPS* for the up-scaled section of the southern Kalahari for the period December 2005- November 2006 (see section 2.9.2) is presented in figure 4.9a. It can be seen

that there is considerable spatial and temporal heterogeneity in the distribution of the soil moisture. The wettest months are January and February (austral summer) where the maximum soil moisture was found to be 71% *WFPS*, and the areas of high soil moisture are widely distributed through the region. There was also an increase in the mean soil moisture content between March and May and following rains in October, although in these time periods the soil moisture distribution is patchier and less widely distributed. The soils were driest in July where the mean *WFPS* in the soils was less than 20%. Spatial differences exist where small scale convective storms occurred, creating a patchy distribution of soil moisture through the landscape. These estimates are partly corroborated from gravimetric soil moisture data in a study by [*Thomas et al.*, 2008] which occurred at the Berry Bush Farm in May 2006, which is equivalent to a soil moisture content of 22.5%-34% *WFPS* (10-15% volumetric soil moisture). The monthly range of the soil moisture contents can be seen in figure 10b, where the mean values range from 20% to 48%.

4.4.6.3 Soil surface temperature

The soil surface temperature for December 2005- November 2006 was obtained from the MODIS instrument at a resolution of 1km (see section 2.9.3) and is shown in figure 4.10a. Variations can be seen in the land surface temperature values (averaged over 8 days) which range from approximately 13°C in July (austral winter) to 47°C in January (austral summer). While some spatial differences occur across the landscape the spatial distribution is not as marked as those found in the soil moisture distribution. Figure 4.10b shows a comparison between the surface temperature obtained for the Tsabong area using the remote sensing technique and the measured mean monthly temperature measured at the Tsabong meteorological station at a depth of 5cm. It can be seen that the remote sensing estimates follow the pattern of the measured soil temperature very closely except in the austral summer months (Dec –Mar) where the soil is somewhat cooler (1-3.4°K) at a depth of 5cm than it is at the surface.

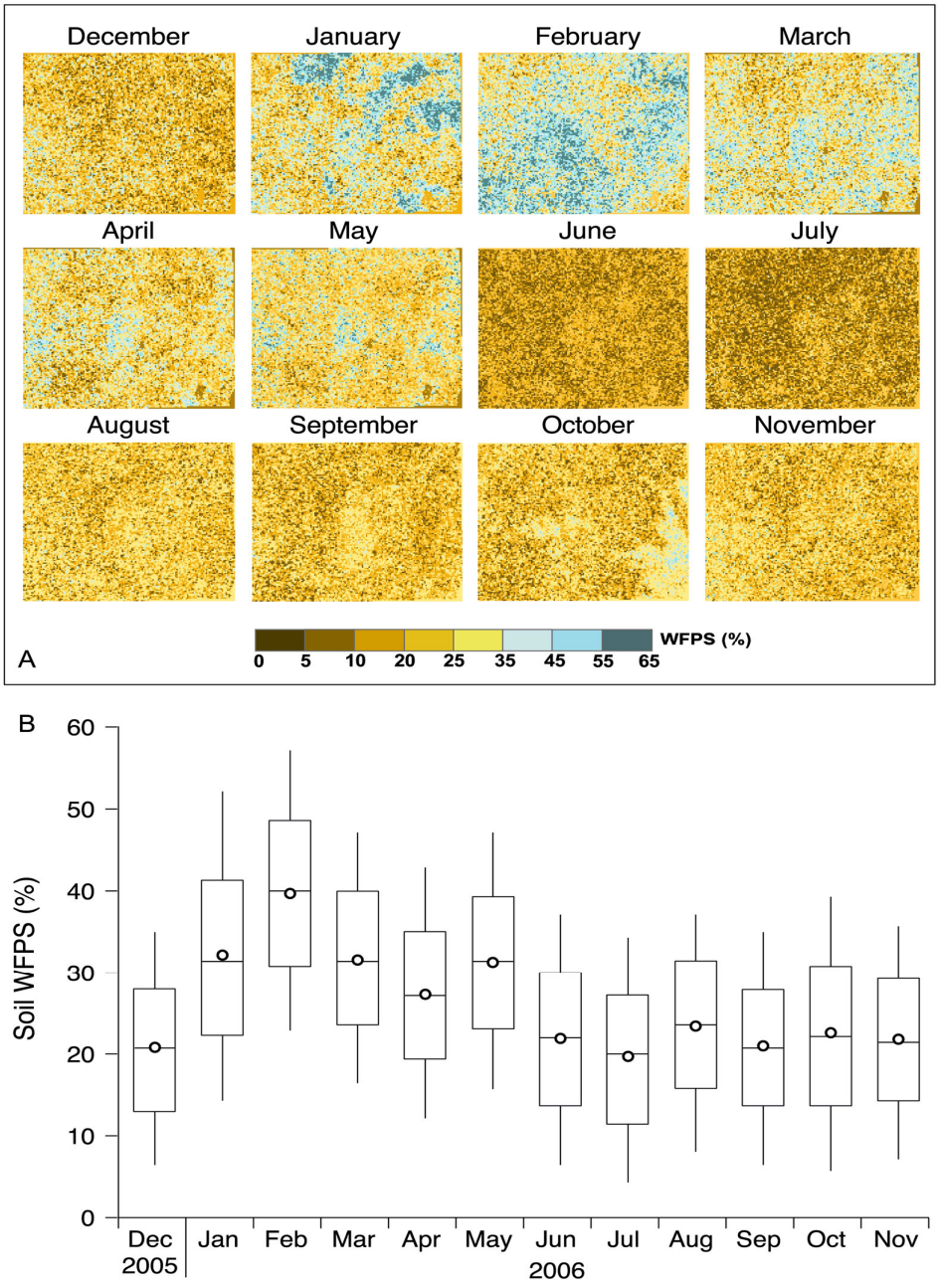

Figure 4.9a) Soil moisture classification for the period December 2005 to November 2006 in terms of Soil Water Filled Pore Space (*WFPS*), resolution 1km. These figures occupy exactly the same area and are at the same resolution as figure 8. **b)**: monthly mean soil moisture (*WFPS*) for December 2005- November 2006 from the SHARE satellite data for the research area (see Fig. 4.1 and 4.8), circles represent the mean *WFPS* across the individual pixels, the bar in the middle of the box represents the median *WFPS*, the box indicates the 25 and 75 percentiles and the whiskers represent the 10 and 90 percentile

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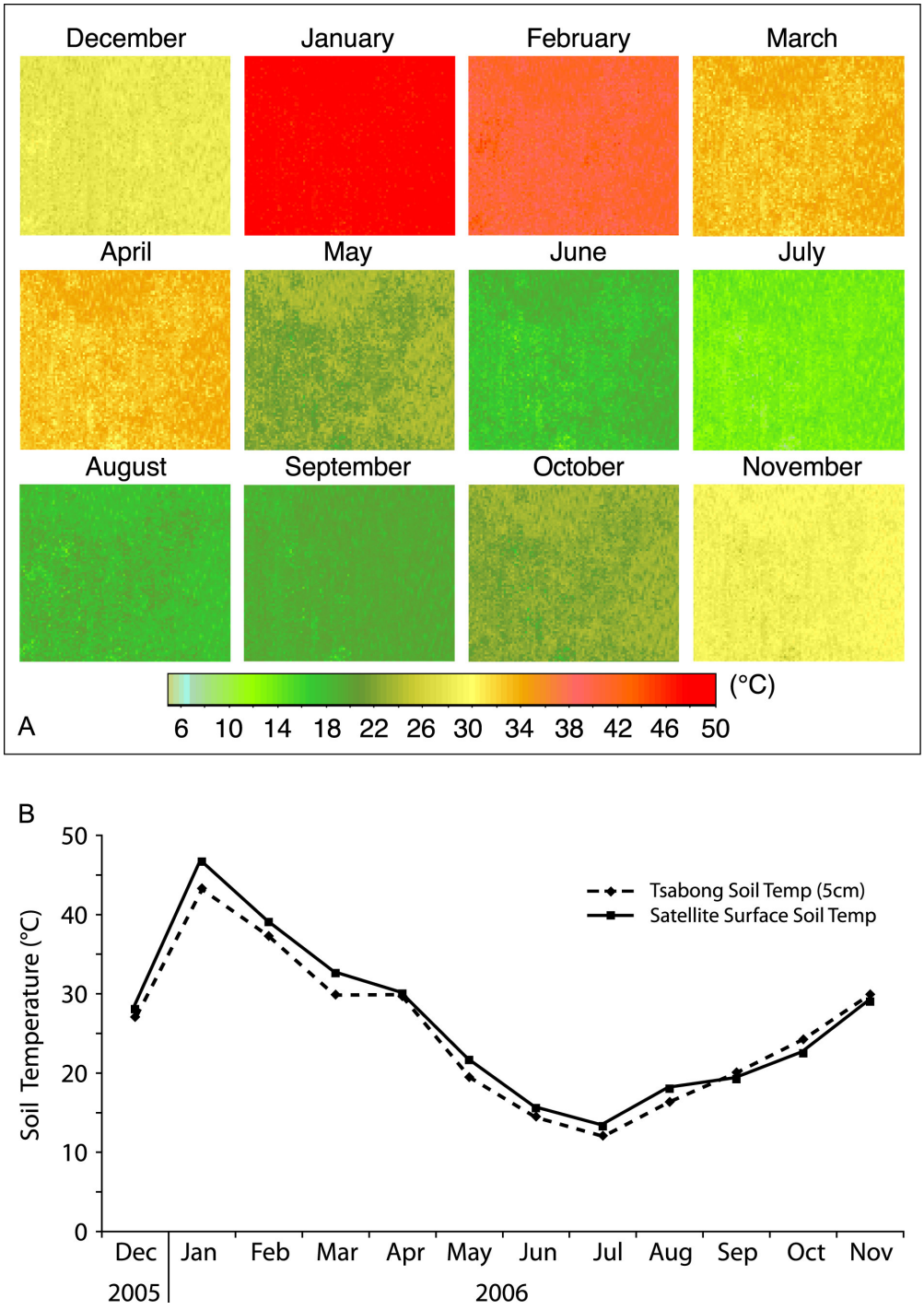

Figure 4.10a) Monthly mean soil surface temperatures for the selected site (see Fig. 4.8) (December 2005- November 2006) **b)** Comparison between the measured soil temperature (at 5cm depth) at the WMO station in Tsabong and the satellite derived surface temperature (at a 1km x 1km scale) for the pixel including the Tsabong WMO station for the period December 2005- November 2006. Deviations between the satellite and measured values arise from the depth of measurement.

4.4.6.4 Up-scaled NO fluxes

The up-scaled NO flux for the selected part of the southern Kalahari is presented in figure 4.11a. The up-scaled mean monthly flux of NO ranges from 0-323 g ha^{-1} $month^{-1}$ (0 to 13.6 ng m^{-2} s^{-1}) over the course of the year. The highest emissions of NO occurred from the least disturbed of the vegetation types, the *Perennial Grassland* where the emissions of NO reached a maximum of 323 g ha^{-1} $month^{-1}$ in some of the pixels in February 2006, although the largest mean NO emission was 240 g ha^{-1} $month^{-1}$ (9.9 ng m^{-2} s^{-1}) for February 2006. The next highest rate of NO emission occurred in the *Encroached* sites where the flux of NO reached a maximum of 143 g ha^{-1} $month^{-1}$ (5.4 ng m^{-2} s^{-1}) and the largest mean flux was 124 g ha^{-1} $month^{-1}$ (4.6 ng m^{-2} s^{-1}) in January 2006. In the *Annual Grassland* vegetation patches the greatest mean monthly NO flux was 119 g ha^{-1} $month^{-1}$ (2.0 ng m^{-2} s^{-1}) while a maximum pixel value of 216 g ha^{-1} $month^{-1}$ (3.6 ng m^{-2} s^{-1}) was recorded in March 2006. Mean up-scaled NO fluxes were lowest in the *Pan* patches and the largest mean flux was 33 g ha^{-1} $month^{-1}$ (1.4 ng m^{-2} s^{-1}) in February 2006 while the highest pixel value was 60 g ha^{-1} $month^{-1}$ (3.15 ng m^{-2} s^{-1}) which occurred in March 2006. The maximum up-scaled flux was reached in the austral summer where the greatest biogenic emissions of NO were produced in the warm, moist month of February. The lowest NO fluxes occurred in the austral winter months where the soil temperature and moisture content were at the lowest in the annual cycle. During June, July and August the flux of NO out of the soil in these ecosystems is negligible (in July 2006, the maximum NO flux was less than 1.8 g ha^{-1} $month^{-1}$).

4.5 Discussion

This study has tried to up-scale the emissions of NO from differing vegetation patches in an arid Kalahari savanna. During the course of the study three main aspects were focused on these were:

1. The soil physical and chemical properties, including the soil texture, pH the total N and C contents.
2. The net potential NO flux, which was measured in the laboratory and examines both inter and intra patch differences
3. The NO flux up-scaled to a region the size of a Landsat image (185km x 185km) using a combination of remote sensing techniques.

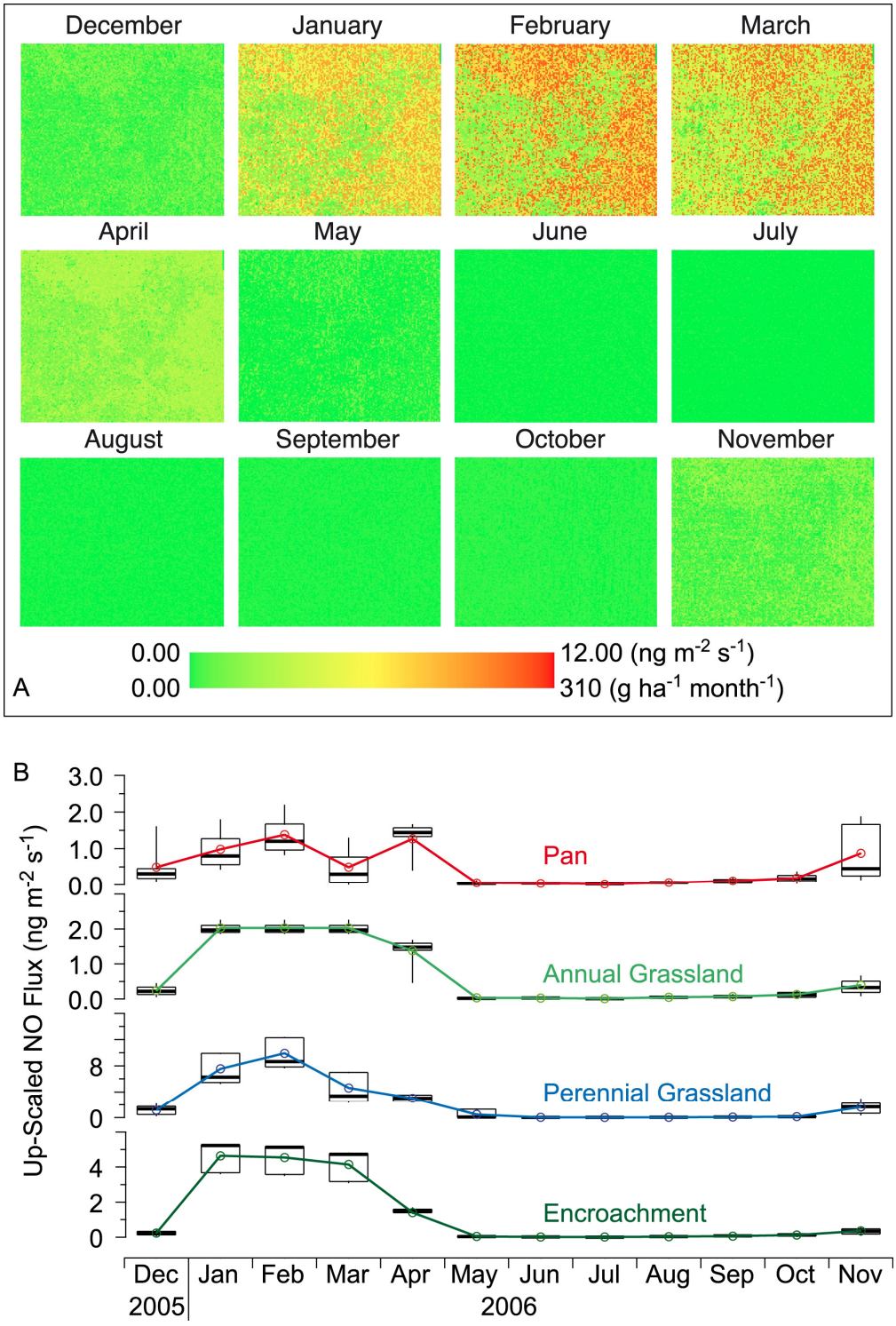

Figure 4.11: **a)** Estimation of the mean monthly up-scaled NO flux for the region of the southern Kalahari under investigation. These figures occupy exactly the same area and are at the same resolution as figure 8 **b)** monthly up-scaled NO fluxes from each of the vegetation patch types, the circle indicates the mean monthly up-scaled NO flux the solid bar indicates the median, the box indicates the region between the 25 and 75 percentiles and the whiskers indicate the 10-90 percentile range.

4.5.1 Soil physical and chemical properties

In this study we recorded soil textures consisting of 71-79% sand, 3.8-7.6% silt and 16.5-21% clay (see Table 4.1). Differences in the soil textural classes between the *Pan* and the other vegetation patches has been previously noticed, while soil textures of the *Perennial Grassland*, *Encroachment* and *Annual Grassland* are typical of the Kalahari sands. The *Pan* patches have more clayey soil and are more calcareous resulting in a higher pH [*van Rooyen and van Rooyen*, 1998].

The mean total soil C and total N values reported in this study (see Table 4.2) range from 0.2%-1% total C and from 0.03%-0.12% total N. These are at the lower end of values reported from the Kalahari in other studies, where the soil C ranges from 0.2% to 6% [*Aranibar et al.*, 2004; *Dougill et al.*, 1998; *Feral et al.*, 2003] and the reported soil N contents range from 0.025-0.045% [*Aranibar et al.*, 2004]. Few differences in the mean soil chemical properties between the differing patches occurred, however there were differences within each of the patches.

In this study, differences in the soil chemical properties were found under differing vegetation cover units within each of the patches. In most of the vegetation patches the total soil C and total soil N were higher under tree canopies than away from the canopies. This has also been found in other studies [*Dougill and Thomas*, 2004; *Hagos and Smit*, 2005]. The differences in soil nutrient concentration under the tree canopies have a number of possible causes; firstly the tree species in this region are dominated by members of the *Mimosaceae* family all of them within the *Acacia* genus. The *Acacia* genus is known to undergo the process of biological nitrogen fixation [*Dougill and Thomas*, 2002; *Scholes and Walker*, 1993; *Schulze et al.*, 1991]. It has also been proposed that the "island of fertility effect" is due to nutrients being trapped by plant stems and root systems [*Aranibar et al.*, 2004; *Hagos and Smit*, 2005; *Ludwig and Tongway*, 1995; *Ludwig et al.*, 1999b; *Tongway et al.*, 1989].

The results of the soil physical and chemical investigations show that all the vegetation patches, apart from the *Pan* soils, can be considered to be on a fairly homogenous substrate shown by the similarity in the soil textural properties, soil pH and the total C and N contents of the soil, [*Aranibar et al.*, 2004; *Scholes et al.*, 2002], however there are micro-scale differences in the soil physical and chemical properties due to the presence of differing vegetation cover. These micro-scale differences are what drive the variation in biological processes between the vegetation patches and as a result are likely to influence the net potential NO flux from the soil.

4.5.2 Net potential NO flux

This is the fifth study of the biogenic emissions of NO from soils in savanna ecosystems of southern Africa, which has been conducted using a similar laboratory technique. Other studies include:

- The Nylsvley Savanna where the flux on NO ranged from 0.12 ng m^{-2} s^{-1} to 13.86 ng m^{-2} s^{-1} with mean and median values of 2.89 ng m^{-2} s^{-1} and 0.90 ng m^{-2} s^{-1} respectively [*Otter et al.*, 1999].
- Miombo savannas and grasslands in Zimbabwe where the NO flux ranged from 0.5 ng $^{-2}$ s^{-1} to 9.4 ng m^{-2} s^{-1} with mean and median values of 2.93 ng m^{-2} s^{-1} and 1.1 ng m^{-2} s^{-1} respectively [*Kirkman et al.*, 2001].
- The Botswana Kalahari Transect where the values ranged from 8 ng m^{-2} s^{-1} to 60 ng m^{-2} s^{-1} with mean and median values of 27.4 ng m^{-2} $s^{-1}$and 21 ng m^{-2} s^{-1} respectively [*Aranibar et al.*, 2004].
- Landscape in the Kruger National Park in South Africa where the NO flux ranged from 0.06 ng m^{-1} s^{-1} to 3.52 ng m^{-1} s^{-1} and mean and median values were 1.67 ng m^{-2} s^{-1} and 1.63 ng m^{-2} s^{-1} respectively [*Feig et al.*, In Press-a].

The net potential NO fluxes calculated for the differing vegetation patches in this study (0-3.5 $ng.m^{-2}.s^{-1}$) correspond very well with the values previously reported by Otter [1999], Kirkman [2001] and Feig [In Press-b]. The reasons why the Aranibar *et al* [2004] study gave such differing results is unclear and the causes cannot currently be judged.

In other natural arid and semi-arid regions (mean annual precipitation <700mm) the measured median NO fluxes range from 0.07 ng m^{-2} s^{-1} to 5.3 ng m^{-2} s^{-1} (with reported values of up to 83 ng m^{-2} s^{-2} occurred during a pulsing event, such as when the soil is wetted or fertilized) [*Davidson et al.*, 1993; *Feig et al.*, In Press-a; *Hartley and Schlesinger*, 2000; *Holst et al.*, 2007; *Martin and Asner*, 2005; *Martin et al.*, 1998; *McCalley and Sparks*, 2008; *Smart et al.*, 1999]. The NO fluxes from these arid and semi-arid ecosystems tend to be fairly low in comparison with some of the values reported from temperate and tropical forests where fluxes of 22 ng m^{-2} s^{-1} [*Pilegaard et al.*, 2006] and 58 ng m^{-2} s^{-1} [*Butterbach-Bahl et al.*, 2004b] were reported in European coniferous and Australian tropical forests respectively.

4.5.3 Intra and inter patch variability

Within each of the vegetation patches differences in the net potential NO flux occurred under the different vegetation cover types, although the patterns were not consistent between the

vegetation patches either due to the soil nutrient status or due to changes in the microclimates under differing vegetation cover types.

Once the mean net potential NO flux was determined for each of the vegetation patches (by incorporating the proportion of different cover units within each of the vegetation patch types) it could be seen that differences in the mean net potential fluxes of NO occurred between the four vegetation patches. These emissions were affected by both the soil temperature and the soil moisture; however (like in the case of the intra-patch variability) the effect of these factors was not consistent between the vegetation patches.

The *Pan* patches produced the lowest mean net potential NO emissions (maximum emission less than 1ng m^{-2} s^{-1} at 35°C) irrespective of the soil moisture content or the soil temperature. The *Pan* however has different soil properties to the other patches (see section 3.1) while the *Perennial Grassland*, *Annual Grassland* and *Encroachment* patches can be considered to occur on the same soil type, and differences in the vegetation patterns are due to changes in the disturbance regime.

In the vegetation patches that occur on the same soil substrate the maximum mean net potential NO flux was between 1.5 ng m^{-2} s^{-2} and 3.5 ng m^{-2} s^{-2}. Of these vegetation patches the lowest emissions occurred in the *Annual Grasslands* (This is still higher than the maximum mean net potential NO flux from the *Pan*) and there did not appear to be an influence of temperature at the 25°C-35°C range. The maximum mean net potential NO flux from the *Encroachment* site is higher than that of the *Annual Grassland* and is influenced by the soil temperature where a positive temperature relationship occurs. The highest maximum mean net potential NO flux comes from the *Perennial Grassland* patches, however there is a negative temperature relationship between 25°C and 35°C. Changes in the emission patterns between the vegetation patches indicates that when there is an increase in disturbance, resulting in a change from undisturbed *Perennial Grassland* to disturbed *Annual Grassland*, there is a reduction in the emission of NO from the soil. However as the levels of vegetation disturbance (see section 4.2.1) increase to the point of forming an *Encroachment* zone the increased nutrient content and N cycling rate that occurs under the high tree cover increases the emission of NO to levels similar to that found in the undisturbed *Perennial Grassland*.

While under most of the soil types there was a positive or neutral relationship between the emission of NO and the temperature, this did not occur in the *Perennial Grassland* soils between incubation temperatures of 25°C to 35°C and a negative relationship between the soil

temperature and the flux of NO was found. A negative relationship between the soil temperature and the emission of NO has previously been reported in the field but this generally only occurs above very high soil temperatures (40°C) [*Passianoto et al.*, 2004]. It is interesting that in the study by [*Thomas et al.*, 2008] at the same site, a negative relationship between the soil temperature and the emission of CO_2 was found in the Kalahari sands (which correspond to the *Perennial Grassland* patches of this study).

4.5.4 NO consumption rate (k) and the compensation mixing ratio ($m_{NO,comp}$)

It is known that soils can both produce and consume NO, however there have been only a very few studies that have shown the uptake of NO in the soil. The uptake of NO in the soil can be described using two parameters, firstly the NO consumption rate (k) which determines the rate at which NO uptake occurs and secondly the compensation mixing ratio ($m_{NO,comp}$) which determines the ambient NO mixing ratio necessary for NO uptake to occur. Despite the fact that in the Kalahari uptake of NO is likely never to occur we would like to discuss the issue of the $m_{NO,comp}$ since there are only a few scattered reports of the k and the $m_{NO,comp}$ published.

4.5.4.1 NO consumption rate

The NO consumption rate values found in this study are within the (very wide) range of values reported in the literature, although they tend to be on the low side. The values reported in the literature range from 0.9 x 10^{-5} m^{-3} s^{-1} kg^{-1} to 500 x 10^{-5} m^{-3} s^{-1} kg^{-1}. To the best of our knowledge, there have only been five previous reports of k from drylands; these are: Nylsvley savanna in South Africa [*Otter et al.*, 1999], from a semi-arid savanna in the Kruger National Park (South Africa) [*Feig et al.*, In Press-a], from the Kalahari transect in Botswana [*Aranibar et al.*, 2004], from a study in Zimbabwe [*Kirkman et al.*, 2001], and an Egyptian soil [*Saad and Conrad*, 1993]. The median k values found in our study (0.9-1.3 x 10^{-5} m^{-3} s^{-1} kg^{-1}) correspond closely to the values reported for the Nysvley Savanna (1.3-2 x 10^{-5} m^{-3} s^{-1} kg^{-1}) [*Otter et al.*, 1999] and for Zimbabwe (1.6-3.2 x 10^{-5} m^{-3} s^{-1} kg^{-1}) [*Kirkman et al.*, 2001]. However the values reported here are lower than those reported in the Kruger National Park (10-27 x 10^{-5} m^{-3} s^{-1} kg^{-1}) [*Feig et al.*, In Press-a]; Egypt (7.2-79 x 10^{-5} m^{-3} s^{-1} kg^{-1}) [*Saad and Conrad*, 1993] or the precipitation gradient study in the Kalahari (34-500 x 10^{-5} m^{-3} s^{-1} kg^{-1}) [*Aranibar et al.*, 2004]. Due to the limited number of studies that have reported the NO consumption rate in dryland ecosystems and the inconsistencies in the values reported it

remains an open question as to how typical the values reported in this study are for dryland ecosystems.

4.5.4.2 Compensation mixing ratio ($m_{NO,comp}$)

The $m_{NO,comp}$ for NO varies with changing soil conditions and soil may change from acting as a source to acting as a sink [*Conrad and Smith*, 1995]. The results of this study (mean values from 61-86ppb) correspond very well to the values reported for other semi-arid savannas in southern Africa of which four studies have been reported (Fig. 4.12):

- Otter *et al* [1999] reported $m_{NO,comp}$ of 157±19 ppb and 152±16 ppb from the Nylsvley Savanna in South Africa for nutrient poor and nutrient rich savannas respectively.
- Kirkman *et al* [2001] reported $m_{NO,comp}$ which ranged from 5 – 11 ppb in the dry season in Zimbabwe and from 47 – 85 ppb during the wet season.
- Aranibar *et al* [2004] reported $m_{NO,comp}$ of 39ppb in the driest site of there study (Tshane) in the Botswana Kalahari Transect
- Feig *et al* [In Press-a], in a study in the Kruger National Park, South Africa, found the $m_{NO,comp}$ to be dependent on the soil moisture and the compensation mixing ratio reached a maximum of 40-70ppb at a soil moisture content of between 10% and 25% *WFPS*.

Other studies (Fig. 4.12) have shown $m_{NO,comp}$ of 140 ppb and 500 ppb in German forest, barley and meadow soils [*Bollmann et al.*, 1999; *Rudolph et al.*, 1996]. The $m_{NO,comp}$ has been shown to change according to the soil temperature. Low $m_{NO,comp}$ of 50 ppb occur at soil temperatures of 7°C and a maximum of over 1000 ppb was observed at a temperature of 40°C. However in this study the results for the three soils studied were not consistent across the range of temperatures [*Saad and Conrad*, 1993]. In a second study that examined the effect of temperature on the $m_{NO,comp}$, the highest compensation point values were observed at low and high temperatures (4 °C and 35 °C respectively), but all were in the range of 30-800 ppb [*Gödde and Conrad*, 1999]. From the published results it can be seen that the $m_{NO,comp}$ show a broad range of values and differ according to soil type, incubation temperature and soil moisture at differing set points.

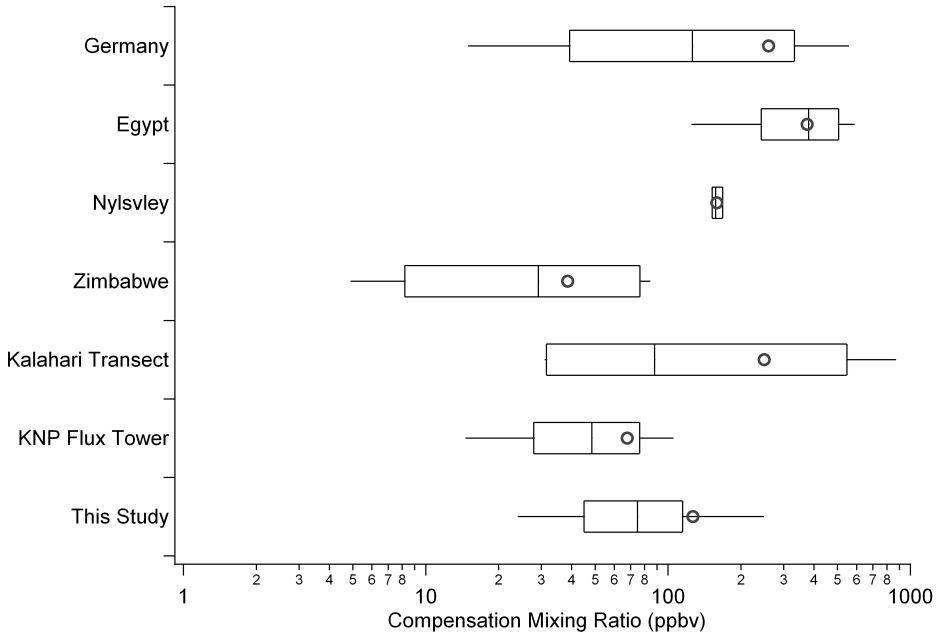

Figure 4.12 Comparison of Compensation Mixing Ratio values reported in the literature. Circles represent the mean $m_{NO,comp}$ of the studies, the bar in the middle of the box represents the median $m_{NO,comp}$, the box indicates the 25 and 75percentiles and the whiskers represent the 10 and 90 percentile. Values for "Germany" are from [*Bollmann et al.*, 1999; *Gödde and Conrad*, 1998; *Gödde and Conrad*, 1999; *Rudolph and Conrad*, 1996; *Saad and Conrad*, 1993], the values for "Egypt" are from [*Saad and Conrad*, 1993], Values for "Nylsvley" are from [*Otter et al.*, 1999], values for "Zimbabwe" are from [*Kirkman et al.*, 2001]and values for "KNP Flux Tower" are from [*Feig et al.*, In Press-a].

The calculated mean $m_{NO,comp}$ in this study are between 60 and 90 ppb, during the peak of NO emission, knowing the NO compensation point mixing ratios, the question could be tackled whether the soils in the Kalahari might ever act as a NO sink. NO uptake would only occur (see section 4.2.6), if the ambient NO mixing ratio is higher than the $m_{NO,comp}$, therefore the ambient NO concentration would need to be greater than about 5ppb for NO uptake to occur (using values above the 10 percentile range see Fig. 4.7a). However, even an ambient NO mixing ratio of 5ppb would be exceptionally high for such a remote location. Unfortunately, there are no measured data of ambient NO mixing ratio from the Kalahari available. However, for comparable southern African sites, like Marondera in Zimbabwe, NO mixing ratios of $0.15 - 0.3$ ppb have been reported [*Meixner et al.*, 1997]; aircraft measurements in the atmospheric boundary layer over northern Namibia revealed NO mixing ratios well below 0.5 ppb, even under conditions of high biogenic soil emissions (approx. 30 ng m^{-2} s^{-1}, s. [*Harris et al.*, 1996]). Using the Max Planck Institute for Chemistry Atmospheric Chemistry Model MESSy ("*Modular Earth Sub-model System*", [*Jöckel et al.*, 2005]), it was found that the

modelled surface NO mixing ratio never exceeded 0.84 ppb, and that the mean NO mixing ratio was 0.024ppb for the period January 2000 – October 2005. It is therefore highly unlikely that the ambient NO mixing ratio has exceeded the $m_{NO,comp}$ during 2006. The only chance that ambient NO mixing ratios may become high enough to allow for uptake of NO in the soil could occur are during biomass burning events where the NO mixing ratios in the biomass burning plume of semi arid savannas in South Africa range from 20-185 ppb [*Hobbs et al.*, 2003; *Yokelson et al.*, 2003]. However generally the standing biomass in this region in the Kalahari is low and the fire return frequency infrequent. Considering the remoteness of the Kalahari region and the low ambient N mixing ratios occurring there, it can be expected that the soils of the Kalahari region are continuously acting as a biogenic NO source and not as a sink.

4.5.5 Up-scaled NO fluxes

Up-scaling of the emission of NO from differing vegetation patches in the Kalahari was made using patch mean net potential NO emissions (as a function of the soil moisture and the soil temperature) and remote sensing techniques to estimate the regional soil moisture and temperature at a 1km x 1km scale for the year December 2005 to November 2006. It was found that the up-scaled NO emissions for a 185km x 185 km area around Tsabong (see Fig. 4.1) differed according to the vegetation type, and according to the season. When the mean flux of NO for the entire up-scaled region was calculated it was found that the highest monthly NO flux was 167 g ha^{-1} $month^{-1}$ which occurred in February 2006, while the lowest mean monthly fluxes totalled 0.5 g ha^{-1} $month^{-1}$ in July. Yearly emissions of NO from the soil for 2006 totalled 0.54 kg ha^{-1} a^{-1}.

Four laboratory based measurements, similar to the method used in this study, have been made in southern Africa, these include studies in Nylsvley Savanna [*Otter et al.*, 1999], in Zimbabwe [*Kirkman et al.*, 2001] in the Kruger National Park, South Africa [*Feig et al.*, In Press-a]. In the Nylsvley Savanna in South Africa the NO flux ranged from 1.4-1.6 kg ha^{-1} a^{-1} [*Otter et al.*, 1999]. For the study at Marondera (Zimbabwe) the NO flux ranged from 0.9 kg ha^{-1} a^{-1} to 1.2 kg ha^{-1} a^{-1} [*Kirkman et al.*, 2001]. In the study in the Kruger National Park, Feig *et al* [In Press-a] reported yearly NO emissions of between 0.2 kg ha^{-1} a^{-1} and 0.8 kg ha^{-1} a^{-1}. A further study that up-scaled the annual NO mission from field measurements gave estimates of 2.1 kg ha^{-1} a^{-1} to 2.7 kg ha^{-1} a^{-1} for a semi-arid savanna in South Africa [*Scholes et al.*, 2003b]. Therefore in comparison with other studies in Southern Africa the results are

comparable. The estimated up-scaled emission of NO from the field shows distinct seasonal differences, in the austral winter the soil temperature and the soil moisture content is lower than the optimum for the production of NO, this results in low NO fluxes from the soil. In January and February (the austral summer) the soil temperatures are higher (approximately 40°C) and it is the period of the year when rain occurs, the combination of warm soils and the availability of water allow the biogenic processes that result in the formation of NO to proceed optimally. The seasonal pattern with regards to the emission of NO from the soil has been previously shown in the Nylsvley study [*Otter et al.*, 1999] where the peak NO emissions seem in February and March. In the Zimbabwe study the period of peak NO emission is December [*Kirkman et al.*, 2001]. In both previous studies negligible NO emissions occur in the austral winter months.

The other major source of NO in African savanna ecosystems is pyrogenic emissions is from biomass burning. A number of estimates of the total emission of NO from African savannas have been made these include values of 1.04 Tg a^{-1} [*Scholes and Scholes*, 1998], 4.2 Tg a^{-1} [*Sinha et al.*, 2003] and 3.6 Tg a^{-1} [*Andreae*, 1997]. If the area of savannas burnt in Africa on a yearly basis is assumed to be 440 million ha [*Hao et al.*, 1996], the pyrogenic emission of NO ranges from 2.4-9.5 kg ha^{-1} a^{-1}. The pyrogenic emission of NO from African savannas is therefore higher but still comparable to the biogenic emission of NO (0.2-2.4 kg ha^{-1} a^{-1}). If one then looks at the timing of the two main types of NO emission, pyrogenic emissions occur predominantly in the austral winter (July- September), while the biogenic emissions occur in the austral summer (Jan-March see Fig. 4.11b).

The input of N into this region is largely from two sources, the deposition of N from the atmosphere and the biological fixation of N by vegetation and soil crusts. The estimated N deposition into savanna regions in Southern Africa ranges from 2.5-21.6 kg ha^{-1} a^{-1} [*Bootsma et al.*, 1996; *Feig et al.*, 2007; *Garstang et al.*, 1998; *Mphepya et al.*, 2004; *Scholes and Walker*, 1993]. Nitrogen input into the southern African savanna ecosystems through biological fixation has been estimated by Scholes *et al* [2003b] and is thought to range from 4.8 kg ha^{-1} a^{-1} to 21 kg ha^{-1} a^{-1} (approximately the same range as atmospheric deposition). Therefore the loss of N in the form of NO through biogenic gaseous emissions can be significant (1.3%-7.4% of the combined atmospheric and biological N fixation inputs) and biogenic emissions of NO from the soil can be considered to be an important pathway of N loss in the region.

4.6 Conclusion

This study has shown the usefulness of combining laboratory measurements and remote sensing data of soil moisture and temperature in the estimation of biogenic nitric oxide emissions on a regional scale; since it can incorporate heterogeneity in both the spatial and temporal scale with a fine resolution of 1km x 1km. This is a particularly useful technique for remote areas, structurally heterogeneous regions or developing countries where a network of ground based measuring stations does not exist, or can not be implemented.

Differences in the emission of NO occur at the individual plant and the vegetation patch scales. The lowest mean net potential NO emissions were recorded in the *Pan* patches and the highest emission of NO occurred from the *Perennial Grassland* vegetation patches. These emissions are controlled by the soil moisture status and the soil temperature. The vegetation cover of the Kalahari is structurally heterogeneous and changes in the vegetation dynamics as a result of anthropogenic activity or climate are likely to have an important effect on the biogenic production of NO.

The Kalahari has the potential for producing fairly high emissions of nitric oxide, particularly after periods of rainfall in the hot austral summer months, although in the dry austral winter period the emissions are negligible. This results in mean monthly emissions ranging from 0.6 g ha^{-1} $month^{-1}$ (*Pan* in July) to 240 g ha^{-1} $month^{-1}$ (*Perennial* Grassland in February) and mean annual emissions for the period December 2005 to November 2006 of 538 g ha^{-1} for the region that we studied. The total annual emission of NO results in a loss of N from the system of between 2.5%- 22% of the amount of N entering the system due to deposition from the atmosphere. The annual biogenic emissions of NO are within the same order of magnitude as the pyrogenic NO emissions (2% to 100%) and therefore are likely to play an important role in the production of ozone in the troposphere.

An analysis of the compensation point mixing ratio in this region of the Kalahari suggests that the uptake of NO into the soil will only occur under ambient NO mixing ratios greater than 10ppb, ambient NO mixing ratios of this magnitude are highly unlikely as it is expected that they will not exceed 1ppb in this region and therefore the soils of the Kalahari will act a source of biogenic NO to the atmosphere.

4.7 Acknowledgements

This paper is dedicated to the memory of Keith Thomas of Berry Bush Farm who passed away in 2006.

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Chapter 5: Biogenic emission of nitric oxide from three ecosystems in the Namib Desert: a laboratory study

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5.1 Abstract

This is the first reported study on the emission of nitric oxide (NO) from a hyper-arid ecosystem. The biogenic emission of NO from the soil is one of the major sources of NO to the atmosphere, accounting for between 10% and 40% of the total global NO emission. Nitric oxide has a major impact on a number of important environmental issues, including the production of tropospheric ozone, the cycling of the OH radical and the production of nitric acid. While arid ecosystems cover a significant portion of the earth's surface area there have been few studies in these ecosystem. Here we present the results of a laboratory based study of the net potential NO emission from soils sampled on differing ecosystem types in the vicinity of the Gobabeb Desert Research Station in the Namib Desert, Namibia. Soils were sampled from Dune, Riparian and Gravel Plain ecosystems and the net potential NO flux was determined as a function of the soil moisture content and the soil temperature. These net potential NO flux values were then used to estimate the NO flux from the Namib Desert for the year 2006, using modeled soil moisture and temperature data. The maximum net potential NO flux ranged from 3.0 ng m^{-2} s^{-1} in the Riparian ecosystem to 6.2 ng m^{-2} s^{-1} in the Gravel Plain ecosystem. The maximum production of NO occurred at low soil moisture contents in all 3 sites (<10% WFPS) and the optimal temperature was 25°C for the Dune and Riparian soils and 35°C for the Gravel Plain soils. Up-scaling the net potential NO emissions to the whole of the Namib Desert gave fluxes of 62 g ha^{-1} a^{-1} for the Dune ecosystem in 2006 and 544g ha^{-1} a^{-1} for the Gravel Plain ecosystem in 2006.

5.2 Introduction

Nitric oxide (NO) and nitrogen dioxide (NO_2) (collectively known as NO_x) are compounds that play an important role in regulating chemical reactions of the atmosphere [*Crutzen*, 1995; *Crutzen and Lelieveld*, 2001; *Monks*, 2005; *Steinkamp et al.*, 2008]. They control the production and destruction of tropospheric ozone [*Chameides et al.*, 1992; *Crutzen and Lelieveld*, 2001; *Steinkamp et al.*, 2008], are involved in the cycle of the OH radical (influencing oxidising capacity of the atmosphere) and in the production of nitric acid (HNO_3) [*Logan*, 1983; *Monks*, 2005; *Remde et al.*, 1993; *Steinkamp et al.*, 2008].

The global emissions of NO_x gases have been severely altered due to anthropogenic activities. In the 1860s global NO_x emissions were estimated to be 13 Tg a^{-1} (all units referred to in this paper are in terms of mass of nitrogen) of which the majority is thought to have come from natural sources such as soils and lightning [*Galloway et al.*, 2004a]. The most recent report of the Inter-Governmental Panel on Climate Change (IPCC) estimates that the total NO_x emissions has increased almost four fold to approximately 42-47 Tg a^{-1}. The most important source of NO_x is fossil fuel combustion (21.5-28.8 Tg a^{-1}) followed by soils (5-8 Tg a^{-1}), biomass burning (6-12 Tg a^{-1}) and lightning (1.1-6.4 Tg a^{-1}) [*Denman et al.*, 2007].

Soil is thought to account for between 10% to 40% of the total NO emissions [*Davidson and Kingerlee*, 1997; *Denman et al.*, 2007]. The importance of the biogenic source of NO varies with location; in remote or undeveloped regions the majority of the NO emissions are still from natural sources such as biomass burning or biogenic production in the soil, for example in Africa over 40% of the total NO emissions originate from biogenic production in the soil [*Jaegle et al.*, 2004].

Drylands, in particular, are responsible for a large degree of the uncertainty in the estimation of the contribution of biogenic production to the global emission of NO_x, this is partly due to insufficient measurements [*Galbally et al.*, 2008]. A recent review by Meixner and Yang (2006) only identified 13 studies in natural ecosystems receiving less than 400mm rain a year (since then three other studies have occurred [*Feig et al.*, In Press-b; *Hall et al.*, 2008; *Holst et al.*, 2007; *McCalley and Sparks*, 2008]), this is problematic since drylands make up a sizable proportion (40%) of the earth's surface area [*Veron et al.*, 2006] and are thought to be capable of substantial emissions of NO [*Davidson and Kingerlee*, 1997].

The most widely used algorithm for the simulation of biogenic NO emission from soil is the Yienger and Levi [*Yienger and Levy II*, 1995] algorithm [*Ganzeveld et al.*, 2002; *Steinkamp et al.*, 2008], it works on an empirical basis where emission factors are allocated to various

biomes, however desert and shrubland biomes are assumed to have a zero NO emission potential [*Yienger and Levy II*, 1995]. From the earlier work in arid and semi-arid shrublands and steppes [*Feig et al.*, In Press-b; *Hall et al.*, 2008; *Hartley and Schlesinger*, 2000; *Holst et al.*, 2007; *McCalley and Sparks*, 2008] it has been shown that emissions from deserts are not only possible but may be significant, it is therefore imperative to get a better understanding of the potential NO emissions from a wide range of arid ecosystems.

The biogenic production of NO in the drylands is dominated by the process of nitrification [*Conrad*, 1996; *Galbally et al.*, 2008]. Nitrification is influenced by environmental factors, such as the soil moisture, the soil temperature and the soil nutrient content. These in turn are determined through the underlying geology, the climate and biotic factors such as the vegetation at the site [*Brümmer et al.*, 2008; *Davidson*, 1991b; *Galbally et al.*, 2008; *Garrido et al.*, 2002; *Ludwig et al.*, 2001; *Russow et al.*, 2000].

In arid ecosystems, soil moisture is the most important factor regulating microbial activity in the soil, including the emissions of NO. Water affects the osmotic status of the microbial cells, the substrate availability, diffusion of gases into and out of the soil, the pH and the temperature [*Gleeson et al.*, 2008]. When the soil moisture is too low to maintain microbial activity there are very low levels of NO emitted [*Galbally et al.*, 2008; *Garrido et al.*, 2002; *Meixner et al.*, 1997] and when soil moisture level are too high to maintain aerobic conditions, the emission of NO is negligible due to reduced diffusion of oxygen into the soil and reduced ability of NO to diffuse out of the soil [*Skopp et al.*, 1990]. The optimal emission of NO seems to occur at fairly low soil moisture levels, but where sufficient moisture is present to allow microbial activity. In previous laboratory based studies NO emissions were very low at both high and low soil moisture contents, while the optimum soil moisture for NO production was in the range of 10% to 30% Water Filled Pore Space (WFPS) [*Aranibar et al.*, 2004; *Feig et al.*, In Press-a; *Feig et al.*, In Press-b; *Hartley and Schlesinger*, 2000; *Kirkman et al.*, 2001; *Meixner and Yang*, 2006; *Otter et al.*, 1999].

Since the biogenic production of NO is a bacterially mediated process, temperature has an important impact on the rate of the reaction, and as the environmental temperature increases so does the rate of nitrification and hence the release of NO. A number of previous studies have shown that the rate of NO increase approximately doubles with a 10°C increase in temperature [*Aranibar et al.*, 2004; *Feig et al.*, In Press-a; *Kirkman et al.*, 2001]. Although an optimal temperature has been shown above which the emission of NO is greatly reduced, this

optimal temperature is often said to be in the region of 40°C [*Aranibar et al.*, 2004; *Feig et al.*, In Press-b; *Passianoto et al.*, 2004; *Williams et al.*, 1992].

The soil nutrient status is another important controller of biogenic NO emissions; many studies have found a relationship between the emissions of NO and either the concentrations of ammonia or nitrate or the N cycling rate [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Parsons et al.*, 1996]. Therefore, regional differences such as changes in the soil and vegetation properties are likely to influence the NO production potential.

The Namib Desert is one of the most arid regions in the world, it is situated on the west coast of southern Africa and extends over 2000 km from South Africa in the south, through Namibia to southern Angola [*Lalley and Viles*, 2008; *Lancaster*, 2002] (Fig. 5.1). The climate is influenced by the cold Benguela Current in the Atlantic and the El Niño Southern Oscillation [*Abrams et al.*, 1997; *Southgate et al.*, 1996]. The Namib Desert extends from the Atlantic coast in the west to the base of the Great Western Escarpment in the east and is up to 150 km wide at the widest point [*Jacobson et al.*, 2000]. A strong rainfall gradient exists; from a mean annual rainfall of below 10 mm a^{-1} near the coast to approximately 100 mm a^{-1} at the base of the escarpment [*Henschel and Seely*, 2008; *Jacobson et al.*, 2000; *Southgate et al.*, 1996].

The Namib Desert is unique due to its combination of extremely low rainfall and the regular presence of fog. Fog occurs regularly at the coast but the frequency of fog decreases inland. Fog moderates the temperature and acts as an important source of moisture for the biota in the region [*Henschel and Seely*, 2008; *Olivier*, 1995]. The biomass and productivity of the Namib Desert is very low in comparison to other deserts in the world due to the hyper-arid conditions which reduce the rates of net primary productivity and decomposition [*Southgate et al.*, 1996]. In hyper-arid ecosystems, like the Namib Desert the productivity is limited primarily by the low amounts of water [*Abrams et al.*, 1997].

Moisture is obtained by the organisms living in the Namib Desert through three main forms namely rain, fog and dew, for a more in-depth discussion please refer to Henschel and Seely [2008].

There were four main points to this study (a) to determine whether or not the emission of N from soils in hyper arid ecosystems is possible, since this is the first time that such a study has been conducted, (b) to determine the net potential NO emission from the major ecosystems in the Namib, (c) to determine the influence of soil moisture and temperature (known controllers

of NO production) on the production of NO from the soil and (d) to estimate the NO emissions for the whole of the Namib Desert, using the laboratory obtained relationship between the NO flux and modelled soil moisture and temperature data.

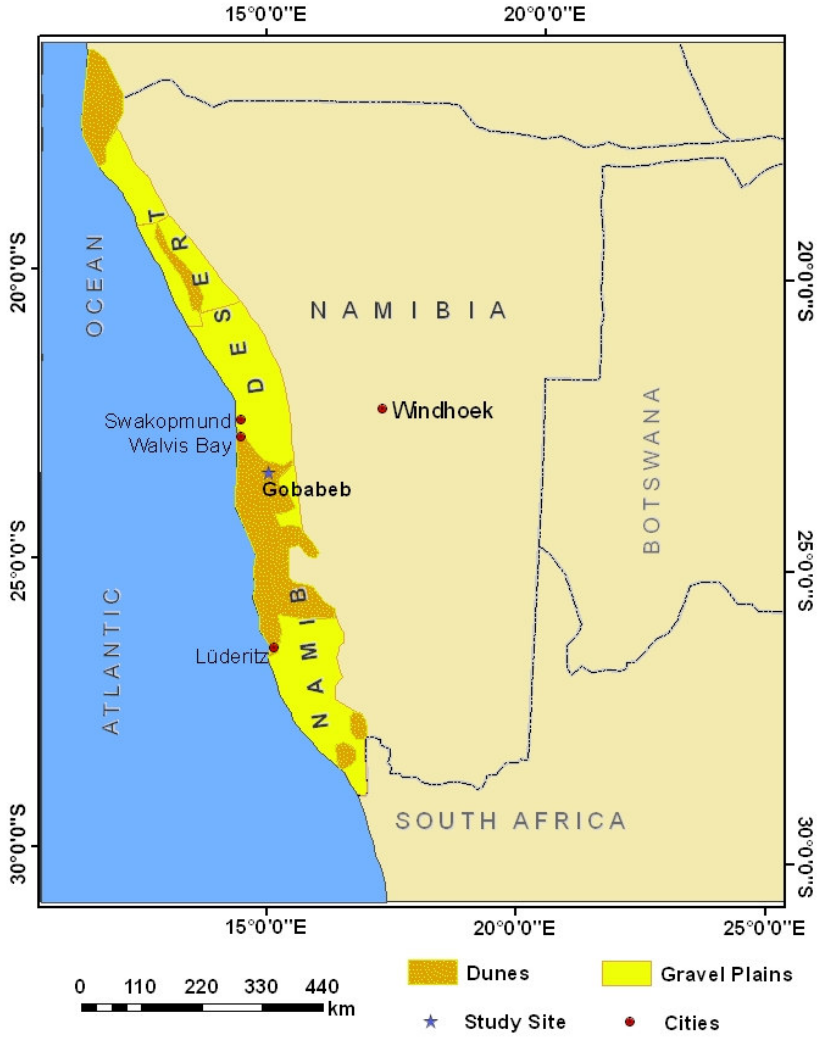

Figure 5.1 Map of the Namib Desert modified from [*Lalley and Viles*, 2008], showing the position of the Namib Desert, the regions dominated by dunes and the position of Gobabeb, the research site

5.3. Methods and Materials

5.3.1 Site

The site of this investigation is the Gobabeb Desert Research Station in the Namib Desert in Namibia (23°34'S; 15°03'E). The Gobabeb Research Station is situated on the Kuiseb River, which separates the Central Namib Dune Sea and the Gravel Plain ecosystem. The Namib Desert has 3 major types of ecosystems; Dunes, Gravel Plain ecosystems and Ephemeral Rivers.

- Dunes occur in a number of discrete positions in the Namib Desert. The major dune systems are the Cunene Sand Sea in the north, the Skeleton Coast Dunes north of Swakopmund and the Central Namib Sand Sea situated between Ludertiz and Walvisbay [*Lalley and Viles*, 2008]. For a more detailed account of the Namib Dune ecosystems see Southgate et al [1996] and Abrams et al [1997]
- Gravel Plains occur to the N and E of the Kuiseb River and to the S and E of the town of Lüdertiz (see Fig. 5.1).
- Various Ephemeral Rivers that drain the escarpment (Swakop, Kuiseb, Hoanib and Huab) cross the Namib Desert. The most striking feature of these rivers is the lush vegetation that occurs in the river channels. The soils within the rivers have been shown to have fairly high concentrations of nutrients, especially in comparison to the surrounding Dune and Gravel Plain ecosystems [*Jacobson et al.*, 2000].

Precipitation at Gobabeb Research Station averages 23 mm a^{-1} however Gobabeb is also exposed to banks of fog from the Atlantic Ocean, which contribute an average of 37 mm a^{-1} (range 16-68mm a^{-1}) to the water balance at Gobabeb [*Henschel and Seely*, 2008].

5.3.2 Soil and vegetation sampling

Soil samples comprising of 10 pooled sub-samples (top 5cm) were taken in each of the three ecosystems. In the Dune system samples were taken at 3 differing points and in each of these points two samples were taken, one from under the *Stipagrostis sabulicola* grass hummocks and one from bare soil. In the Riparian ecosystem 3 samples were taken from under tree canopies and 3 from away from tree canopies in 3 sites along the Kuiseb, one site was approximately 1.5 km upstream of the Gobabeb Research Station, one site was near the research station and one site was approximately 1.5 km downstream of the research station. From the Gravel Plains three replicate soil samples were taken from the vicinity of four sites: near the Gobabeb research station, Rooibank, Vogelfederburg, and Kleinburg.

The soil was air dried, sieved through 2mm mesh and stored at 5°C until use. Within each of the sampling sites the soil bulk density was measured in the first 5cm using a stainless steel soil core of known volume.

The soil texture was determined using a hydrometer technique after the method of [*Day*, 1969] and the soil pH in 2.5:1 mixture in distilled water according to the method of Anderson and Ingram [1993]. Soil samples were sent to the micro analytical laboratory at the University of Mainz where total soil carbon and soil nitrogen content was measured according using a Vario MICRO Cube universal microanalyser set up to measure C, H, N and S. The carbonate content was determined at the University of Mainz using the Scheibler (ISO 10693) method by acidifying the soil samples with 10% HCl and measuring the volumetric production of CO_2.

5.3.3 Laboratory incubation and soil NO flux emission

Comparisons between laboratory based technique to estimate the emission of NO from the soil and *in situ* measurements have been shown to provide highly comparable results [*Meixner et al.*, 1997; *Van Dijk et al.*, 2002] therefore the use of laboratory measurements of the emission of NO from soil provide a suitable alternative to direct measurements in the field. These laboratory techniques are particularly useful for studies in remote regions where the logistics of making direct measurements can be problematic.

Two days before beginning the analysis, the soil was soaked with deionised water and allowed to drain freely at room temperature (22°C); this was to limit the confounding effect of pulsing after the initial wetting of soil after a long period of inactivity.

The basic methodology for the laboratory measurement of the NO flux from soil has been previously described [*Feig et al.*, In Press-a; *Feig et al.*, In Press-b; *Yu et al.*, 2008]. Briefly this entails a laboratory incubation of aliquots of the soil samples at three temperatures (15°C, 25°C and 35°C) and at two ambient NO concentrations; NO free air and 50ppb NO. The flux of NO (F_{lab}) as a function of soil water-filled pore space (*WFPS*), and incubation temperature (T_{soil}) is then calculated according to the method of Galbally and Johansson [1989] as modified by Van Dijk *et al* [2002] equation (5.1) (all values are in terms of mass of nitrogen and mass of dry soil).

$$F_{lab}(T_{soil}, WFPS) = \sqrt{BD \times k(T_{soil}, WFPS) \times D(WFPS)} \times \left(\left(\frac{P(T_{soil}, WFPS)}{k(T_{soil}, WFPS)} \right) - [NO]_{Headspace} \right) \qquad (5.1)$$

Where BD is the soil bulk density (10^3 kg m^{-3}); k is the NO consumption rate (m^3 kg^{-2} s^{-2}) as a function of the soil moisture and temperature; D is the WFPS dependent diffusion coefficient for NO in soil according to Moldrup *et al* [2000]; P is the NO production rate (ng kg^{-1} s^{-1}) [*Ludwig et al.*, 2001; *Remde et al.*, 1989] and $[NO]_{Headspace}$ is the concentration (ng m^{-3}) of NO in the cuvette. For further information see [*Feig et al.*, In Press-a; *Feig et al.*, In Press-b; *Yu et al.*, 2008].

The NO flux is then fitted as a function of soil moisture as described in [*Meixner and Yang*, 2006], where the emission of NO is described as a power increase in the emission of NO to an optimal soil moisture content, followed by an exponential decrease once the soil moisture is above the optimum. Finally it is assumed that since the biogenic production of NO is a microbially mediated process NO production is therefore dependent on temperature and a Q_{10} temperature dependence "amplification factor" was included to account for changes in the NO flux between the three differing incubation temperatures. Therefore the NO flux can then be estimated as a function of soil moisture and soil temperature from equation (5.2).

$$F_{(soiltemp,WFPS)} = a_{25°C} WFPS^{b_{25°C}} \exp(-c_{25°C} \times WFPS) \times \exp\left[\frac{\ln Q_{10}}{10} \times (T_{soil} - T_{ref})\right] \quad (5.2)$$

Where a, b and c are fitting factors corresponding to measured points on the NO emission curve (for further information see Meixner and Yang 2006)[*Feig et al.*, In Press-a; *Feig et al.*, In Press-b; *Yu et al.*, 2008], Q_{10} is the temperature amplification factor and T_{ref} is the soil reference temperature of 25°C.

5.3.4 Error estimation and statistics

To determine the error of measurements an error accumulation technique was used as reported in Feig et al [In Press-b] where a relative error of 4.2% of the NO flux signal was calculated for the technique. Calculations and graphs have all been done in excel, while differences in the soil physical and chemical properties was done using a one way ANOVA and Tukey post hoc test after checking that the results followed a normal distribution, statistics were done using Statistica version 6.

5.3.5 Up-scaling of NO emissions to the whole Namib Desert

The modelled soil moisture and temperature for the Namib Desert for 2006 was obtained from the (European Centre for Medium Range Weather Forecasts) ECMWF operational model. The ECMWF model operates at a 6-hour temporal resolution and a quarter degree (latitude) by half degree (longitude) (36.95km x 35.2km) spatial resolution.

For up-scaling, the Namib Desert was divided into two main ecosystem types, Dunes and Gravel Plains (Fig. 5.1), while we realize this is a rather simplistic classification, we thought it to be satisfactory, considering the large size of the pixels used for up-scaling. The spatial classification of the Dunes in the Namib Dunes was done according to [*Lalley and Viles*, 2008] and the remaining region was classified as Gravel Plain.

The modelled soil moisture and soil temperature for the Namib Desert region, and the mapped ecosystem distribution was incorporated into equation (5.2) with the parameters (*a, b, c* and Q_{10}) for the Dune and Gravel Plain Ecosystems obtained from the laboratory measurements (Ephemeral rivers would occupy an extremely small proportion of the Namib Desert and are therefore neglected from the up-scaling procedure).

5.4 Results

5.4.1 Soil physical and chemical properties

The three ecosystems differed in the soil chemical and physical properties (Table 5.1), the Dunes had the greatest sand content in the soil and the lowest total soil carbon and nitrogen contents, while the Gravel Plains had the highest mean total soil carbon content of 0.6% this is partially due to the carbonate content of the soils which accounts for 61% of the total soil carbon content in the Dune and Riparian ecosystems. The carbonate values for the Riparian system may have been affected by the presence of sulphide, since the soils had a high total S content.

5.4.2 Net potential NO flux

There was a large amount of variation in the NO emissions of the differing samples, therefore no significant differences in the NO emission between the NO emission from the vegetated and bare samples (Dune and Riparian) could be determined. As a result the vegetation was not included as a contributing factor in the further discussion of the NO emission. The mean net potential NO flux for the Dune ecosystem is shown in figure 5.2a. In the Dune ecosystem the potential NO flux was highest at an incubation temperature of 25°C, with a peak mean net potential NO flux of 5.6 ng m^{-2} s^{-1}, although there was a great deal of variation between the samples (as shown by the standard deviation at the peak of measurement) the peak emission occurs at a soil moisture content of 7.5% WFPS (1.68% $\Theta_{g/g}$). At 15°C the mean peak emission is lower, 2.2 ng m^{-2} s^{-1} and occurs at a soil moisture content of 6 % WFPS (1.34% $\Theta_{g/g}$). When a higher incubation temperature was used (35°C) the peak NO flux was lower

than at 25°C and the mean was 1.2 ng m^{-2} s^{-1} at a soil moisture content of 10 % WFPS (2.25 % $\Theta_{g/g}$).

Table 5.1 The main soil physical and chemical properties in the three major ecosystems in the Namib Desert *the carbonate content of the Gravel Plains soil could not be determined, since the Gravel plain soils had a high total sulphur content

	Mean C (%)	$CaCO_3$ C (%)	Mean N (%)	Mean pH	Bulk Density	% Sand	% Silt	% Clay	Texture
Dune	0.10 (0.01)	0.06 (0.05)	0.03 (0.01)	8.12 (0.81)	1.65 (0.08)	83.6 (0.83)	1.33 (0.52)	15.03 (0.65)	Loamy sand
Riparian	0.41 (0.26)	0.25 (0.11)	0.05 (0.03)	7.52 (0.59)	1.41 (0.17)	73.7 (5.16)	10.21 (4.29)	16.06 (1.43)	Sandy Loam
Gravel Plain	0.6 (0.46)	*1.93 (0.6)	0.04 (0.02)	8.18 (0.2)	1.55 (0.22)	62.7 (7.1)	15.18 (4.49)	22.12 (3.94	Sandy clay loam

Figure 5.2b shows the net potential emission of NO from soils taken in the Riparian ecosystem. In the Riparian ecosystem at 15°C incubation the maximum mean NO Flux was 0.74 ng m^{-2} s^{-1} and the optimal flux occurred at 7.5 % WFPS (2.5% $\Theta_{g/g}$). At an incubation temperature of 25°C the highest NO flux was recorded, with a mean flux of 3.04 ng m^{-2} s^{-1} occurring at a soil moisture content of 7.5 % WFPS (2.5% $\Theta_{g/g}$). At an incubation temperature of 35°C the maximum mean net potential NO flux was lower than at 25°C, 2.07 ng m^{-2} s^{-1} at a soil moisture content of 7.5 % WFPS (2.5% $\Theta_{g/g}$).

The net potential NO flux for soils sampled in the Gravel Plain ecosystem is shown in figure 5.2c. In the Gravel Plans soils at an incubation temperature of 15°C the maximum NO flux of 2.42 ng m^{-2} s^{-1} occurred at a very low soil moisture content of 3 % WFPS (0.8% $\Theta_{g/g}$). At an incubation temperature of 25°C the peak mean net potential NO flux was found to be 4.85 ng m^{-2} s^{-1} at a soil moisture content of 4.5% WFPS (1.2 % $\Theta_{g/g}$) and at an incubation temperature of 35°C the peak mean NO flux 6.17 ng m^{-2} s^{-1} occurred at 9 % WFPS (2.4% $\Theta_{g/g}$).

The NO flux in the Dune and Riparian ecosystem shows a similar pattern in that the maximum flux occurs at 25°C and the emissions of NO at 15°C and at 35°C are considerably lower. The optimal soil moisture in these two ecosystems is constant across the differing incubation temperatures and the peak emission occurs at approximately 7% WFPS. The Gravel Plain soils behave slightly differently and the emissions increase with temperature up

to at least 35°C, which is where the maximum emission occurs. The optimal soil moisture at all three ecosystems is below 10% WFPS.

When the relation between the soil NO emission and the soil moisture and the soil temperature was combined (eq. 5.1) potential NO emission profiles as a function of both the soil moisture and the soil temperature could be produced. This is shown in figures 5.3 a, b and c and represents the fluxes of NO as a function of soil moisture and temperature that will be used during the up-scaling for the Namib Desert.

5.4.3 NO up-scaling

When the soils were sampled measurements of the soil temperature were made at the sites in the gravel plains. For the week from the 1-7 September 2006 a strong daily pattern in the soil temperature could be seen where the soil temperature fluctuated from a day time maximum of nearly 50°C to a night time minimum of 11°C. Differences were found in the maximum temperatures between the sites and the daily maximum ranged from 35°C in Kleinburg and 51°C in Vogelfederberg, while the minimum temperatures were fairly similar.

Figure 5.4b shows a comparison between the measured soil temperature in the Gravel Plains at Gobabeb and the modelled soil temperature for the pixel encompassing Gobabeb. In general the model that we have used has a close correspondence to the measured soil temperatures, this is particularly impressive considering the differing scales of the model (quarter degree by half degree grid size), the only time that the model does not seem to accurately predict the measurements is at 18:00 when it underestimates the soil temperature by 25%- 35%.

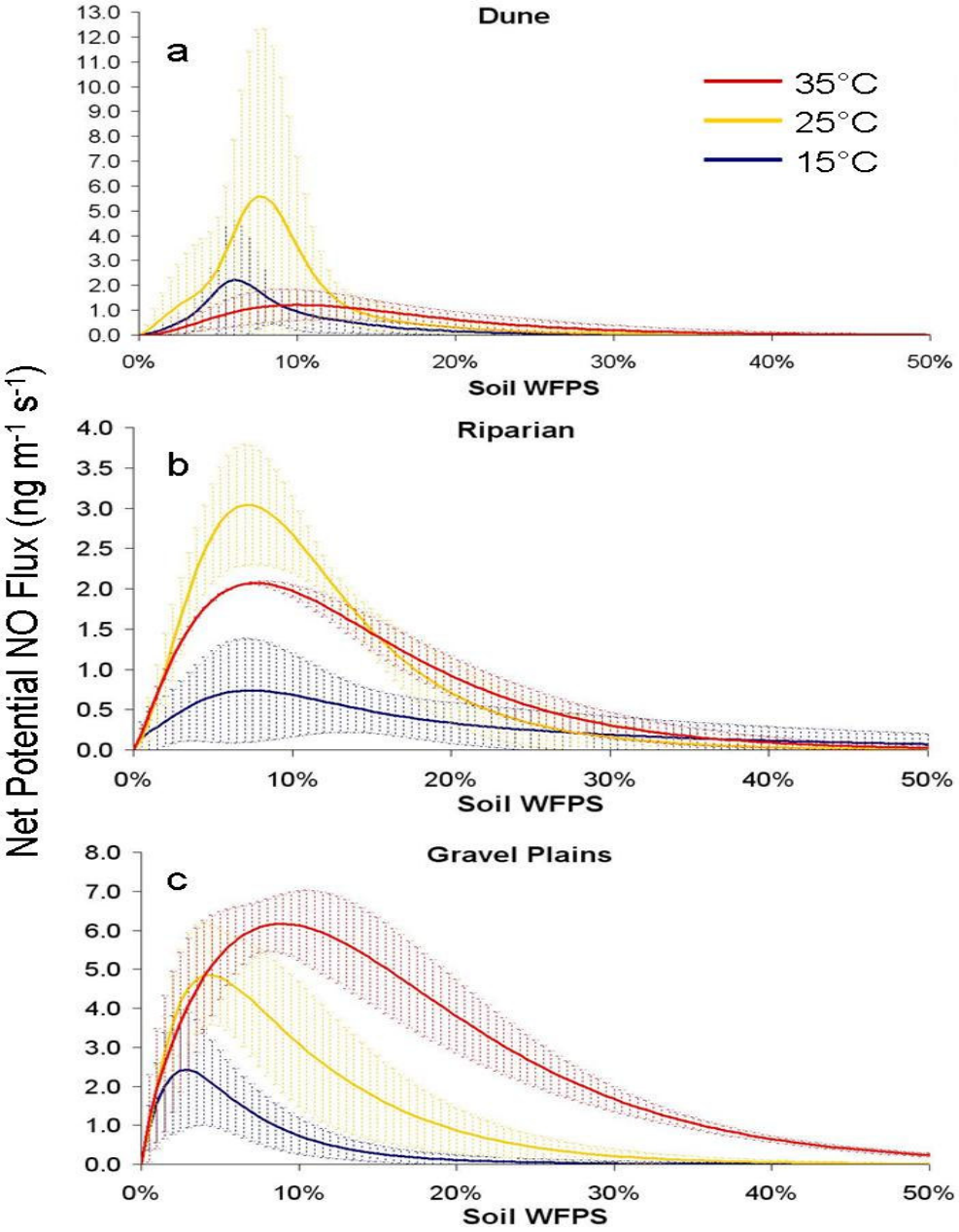

Figure 5.2a) Mean flux of NO from the Dune Ecosystem at 15°C, 25°C and 35°C incubation temperatures, error bars represent the standard deviation of 6, 4 and 4 measurements made at 15°C, 25°C and 35°C respectively. **b)** Mean flux of NO from the Riparian Ecosystem at 15°C, 25°C and 35°C incubation temperatures, error bars represent the standard deviation of 6, 4 and 2 measurements at 15°C, 25°C and 35°C respectively. **c)** Mean flux of NO from the Gravel Plain Ecosystem at 15°C, 25°C and 35°C incubation temperatures, error bars represent the standard deviation of 8, 4 and 3 measurements at 15°C, 25°C and 35°C respectively.

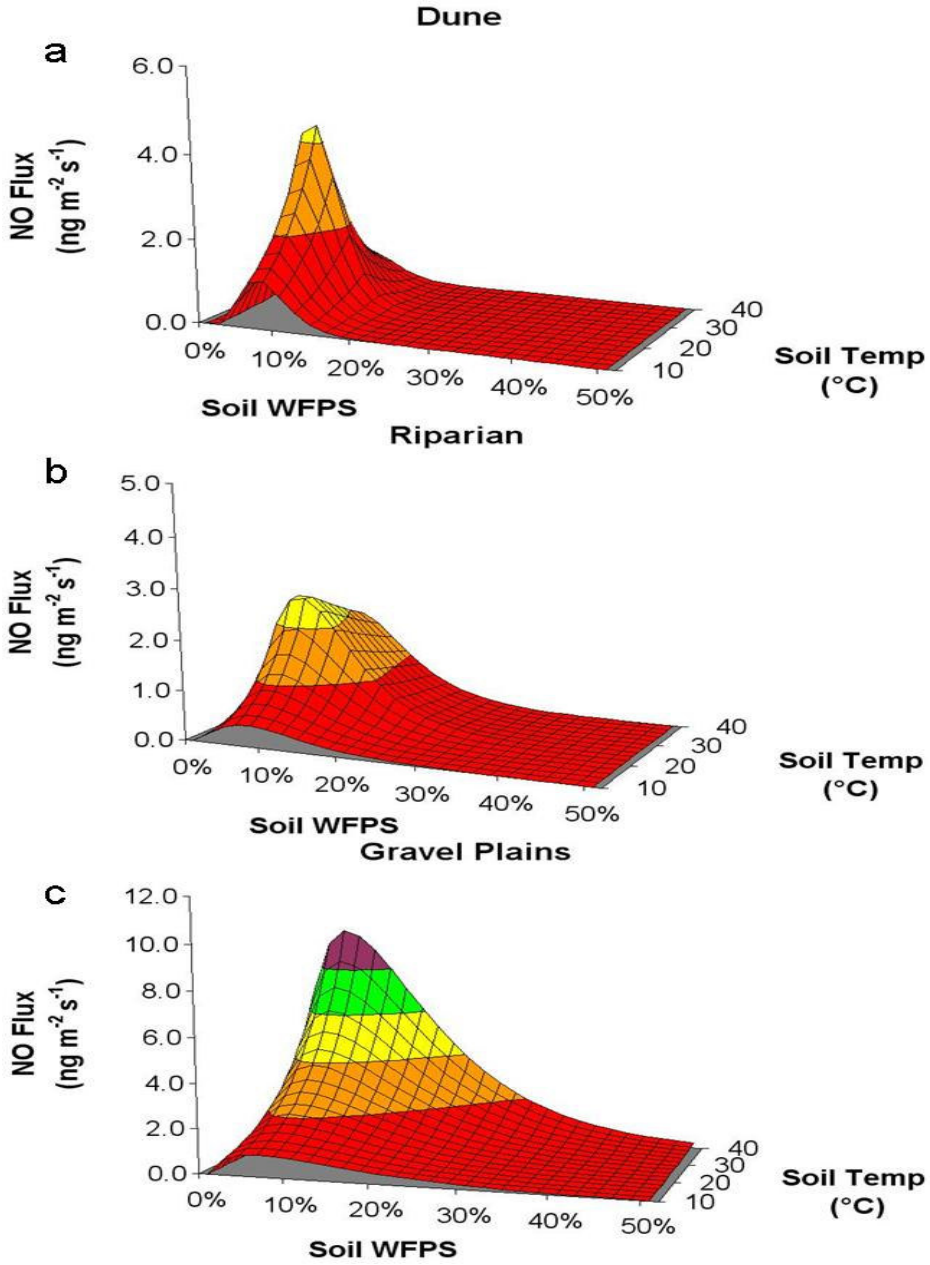

Figure 5.3 Potential flux of NO as a function of soil moisture and temperature **a)** for the Dune Ecosystem **b)** for the Riparian Ecosystem **c)** for the Gravel Plain Ecosystem

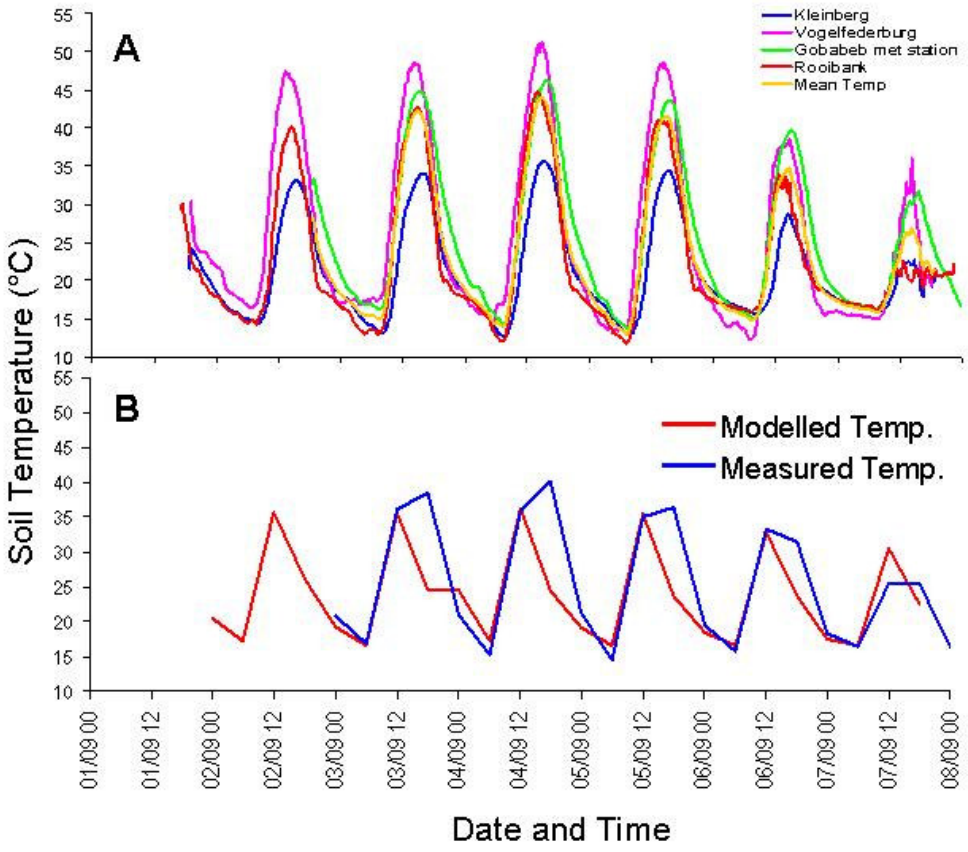

Figure 5.4 a) Soil temperature measured at a depth of two cm at four sites in the Gravel Plain Ecosystem, the X axis indicates the day, month and time of measurement. **b)** Comparison between the measured soil temperature at the Gobabeb Research Station and the modelled soil temperature for the pixel encompassing Gobabeb

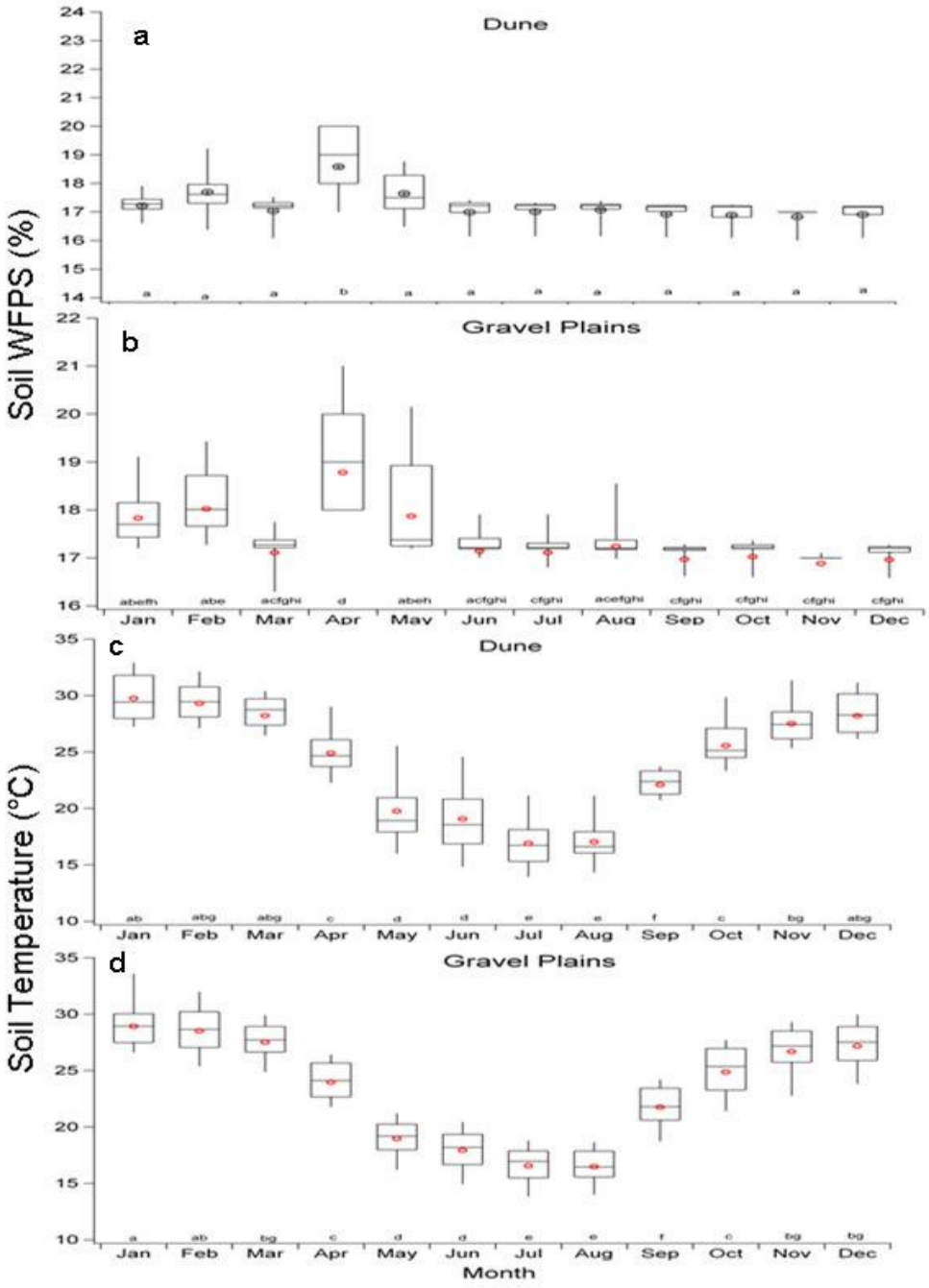

Figure 5.5a Monthly mean soil WFPS for the Dune Ecosystem, equivalent letters indicate that there is no statistically significant difference in the soil WFPS between the months ($p>0.05$ $n=37$) **b)** Monthly mean soil WFPS for the Gravel Plain Ecosystem, equivalent letters indicate that there is no statistically significant difference in the soil WFPS between the months ($p>0.05$ $n=63$). **c)** Mean monthly soil temperature distribution for the pixels in the Dune Ecosystem, corresponding letters indicate that there is no significant difference in the mean monthly soil temperature ($p>0.05$ $n=37$). **d)** Mean monthly soil temperature distribution for the pixels in the Gravel Plain Ecosystem, corresponding letters indicate that there is no significant difference in the mean monthly soil temperature ($p>0.05$ $n=37$).

Differences occurred in the modelled mean annual soil WFPS between the Dune and Gravel Plain ecosystems (Fig. 5.5a and 5.5b), while the modelled mean WFPS difference is small, 17.2% and 17.4% for the Dune and Gravel Plains respectively the difference is statistically significant ($p=0.014$, $n=1140$). In the Dune ecosystem April is significantly ($p<0.05$) wetter than any of the other months (due to the heavy rains that occurred in April 2006 [*Muller et al.*, 2008]), while no significant differences in modelled monthly soil moisture occur during the rest of the year. In the Gravel Plains the modelled monthly differences in the soil WFPS is not as clear but April is still significantly wetter than any of the other months.

There are no significant differences in the modelled annual mean temperatures between the Dune and Gravel Plain ecosystems (see Fig. 5.5c and 5.5d). In both ecosystems the modelled soil temperature can be divided into the hot conditions of November- March, which occur during the austral summer, the warming and cooling periods of April and October, early winter in May and June, late winter in July and August and Spring in September. Over the course of the year the mean monthly pixel temperatures range between 12°C and 36°C. Across all the months there are no significant differences between the Dune and Gravel Plain ecosystems.

Once we had estimates of the soil temperature and the soil moisture contents, obtained from the model and we had the net potential NO flux as a function of the soil moisture and temperature for the Gravel Plains and the Dune ecosystems, we were able to model the emission of NO in the Namib for the year 2006 figures 5.6 shows the mean NO flux calculated for each quarter degree by half degree pixel for the year 2006, these are mean values made up of 112-124 modelled temperature and moisture data points, taken on a 6 hourly basis.

For individual pixels the mean monthly up-scaled NO emissions ranged from 0.02 ng m^{-2} s^{-1} to 4.31 ng m^{-2} s^{-1}. The NO emissions from the Gravel Plain ecosystems were higher than from the Dune ecosystems and the mean up-scaled NO emissions increased in conjunction to the rainfall gradient in an easterly direction. In January there is a peak of NO emission in the Lüderitz region, as seen by the red colour, these high emissions are due to the high soil temperatures that occurred at this time, which reached 49°C, these high soil temperatures may be above the optimal soil temperature and as a result this could lead to an over estimation of the NO flux from the soils. A significant difference in the NO flux occurs between the Gravel Plain and the Dune ecosystems ($p<0.05$) and at no point during the year are the NO emissions from the Dunes and the Gravel Plains significantly similar (Fig. 5.7a and 5.7b).

The NO emissions in the Gravel Plains ecosystems (Fig. 5.7b) were higher (mean monthly fluxes from 2.2-2.4 ng m^{-2} s^{-1}) in the austral summer months of January, February, March, November and December and lower in the cooler austral winter months of May - August (mean monthly fluxes from 0.98-1.15 ng m^{-2} s^{-1}) closely resembling the pattern of soil temperature (see Fig. 5.5d). This pattern was not as marked in the Dune ecosystem (Fig. 5.7a) where the NO flux remains fairly consistent throughout the year.

The NO flux from the Central Namib Dune Sea and the Cunene Dune Sea were always very low and the mean NO flux did not exceed 1.20 ng m^{-2} s^{-1} from any pixel, in these regions. In the Gravel Plains ecosystems the NO flux tended to be higher and mean monthly pixel values ranged from 0.63- 4.31 ng m^{-2} s^{-1}.

The mean NO flux in the Dune ecosystem amounts to 62.06 g ha^{-1} a^{-1} for the year 2006, since the Dune ecosystem in the Namib Desert encompasses an area of approximately 4.8 million ha the emission of NO from the Dune Ecosystem amount to 62 Mg NO in 2006 (in terms of mass of N). The Gravel Plains which showed a mean up-scaled NO emission of 544g ha^{-1} a^{-1} and encompassed an area of approximately 8.2 million ha produced approximately 4461 Mg of NO in 2006. Therefore in 2006 the total NO emission from the Namib Desert is approximately 4.5Gg, of which the majority came from the Gravel Plain Ecosystem.

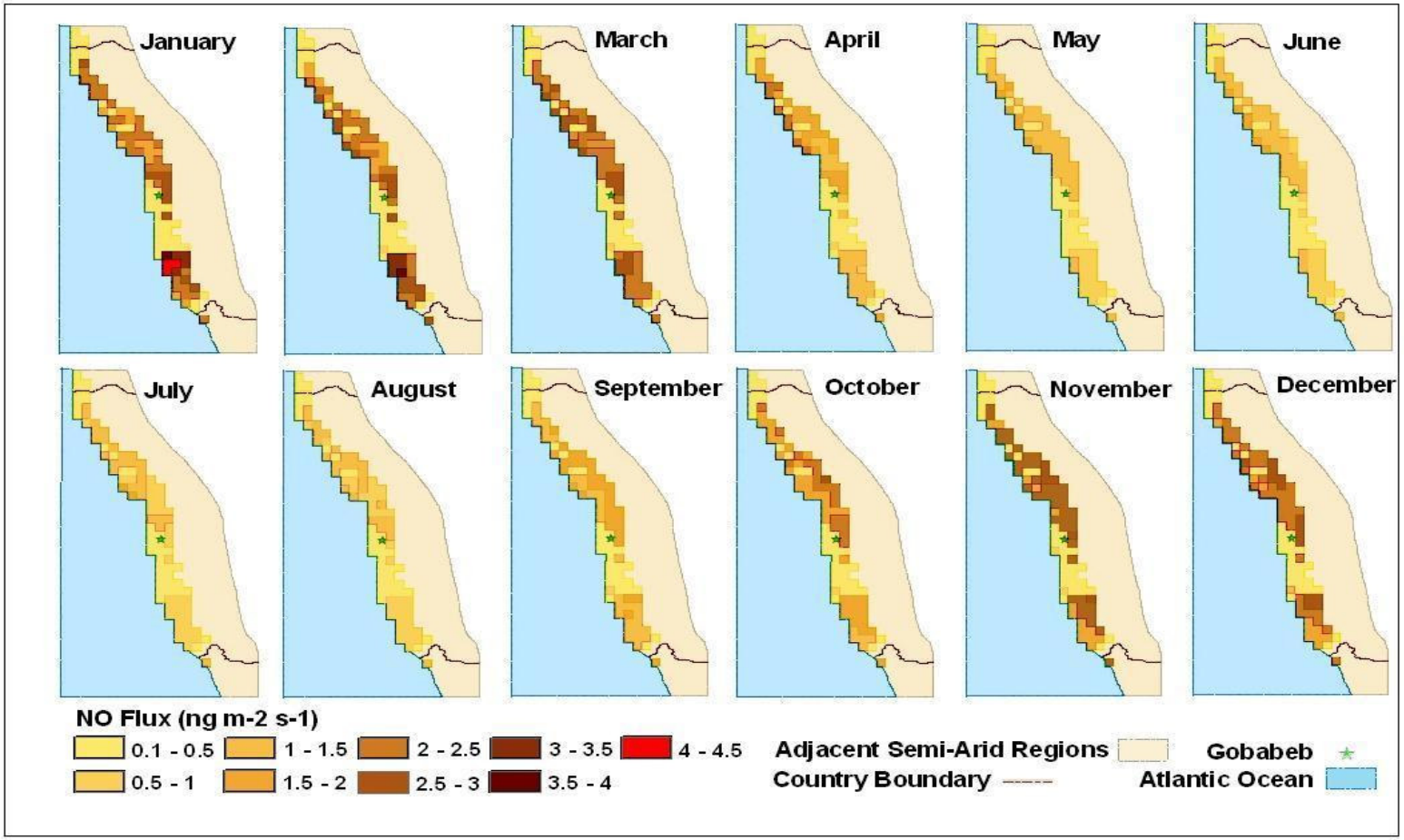

Figure 5.6 Modelled mean monthly NO flux in the Namib Desert for the year 2006

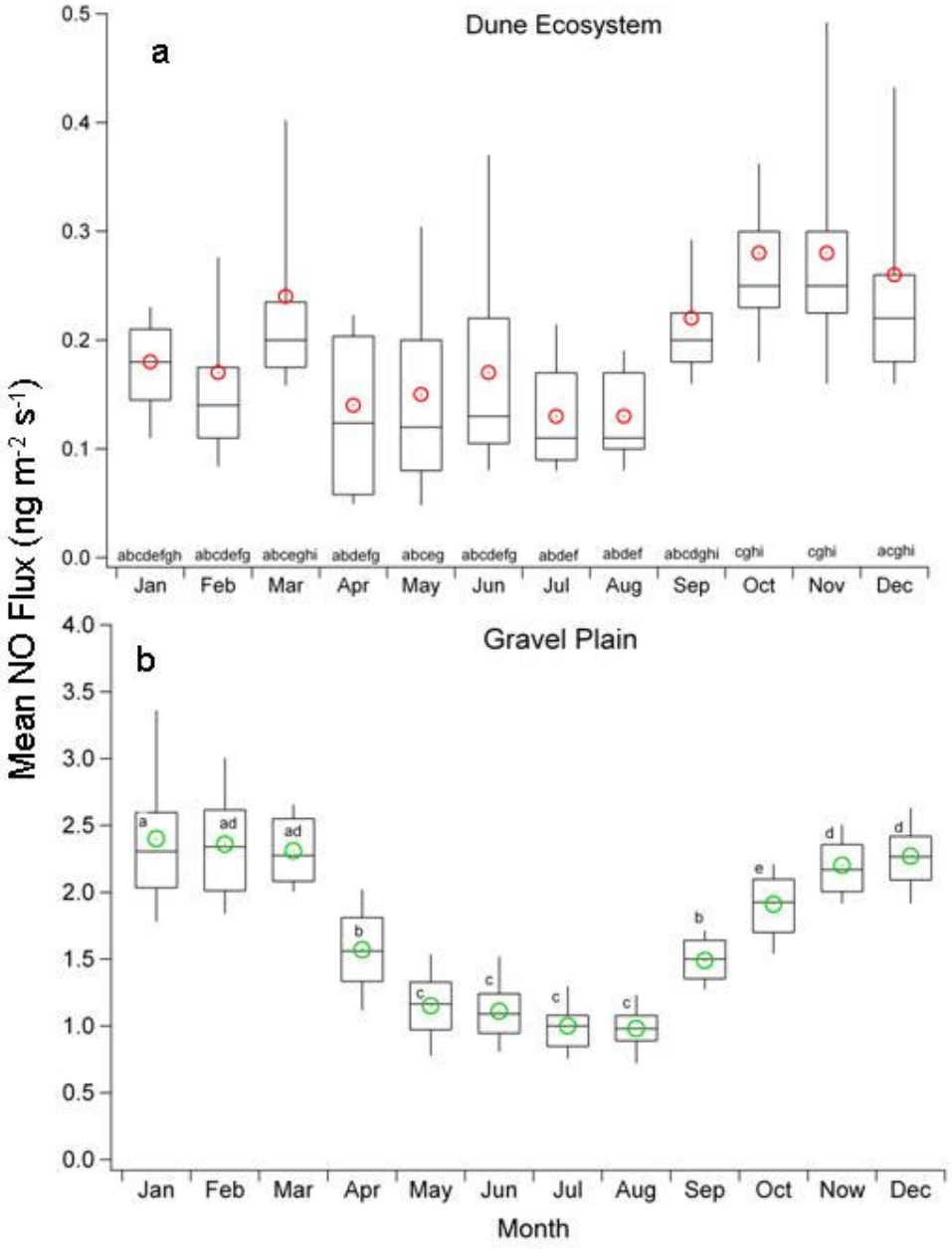

Figure 5.7a Mean monthly NO flux from the Dune Ecosystem, identical letters indicate that there is no significant between the up-scaled mean monthly NO flux **b** Mean monthly NO flux from the Gravel Plain Ecosystem, identical letters indicate that there is no significant between the up-scaled mean monthly NO flux

5.5. Discussion

5.5.1Net potential NO flux

To the best of our knowledge this is the first time that such a study has been conducted on the emission of NO from a hyper-arid ecosystem. Previously it had been thought that deserts were not able to produce sizable biogenic emissions of NO and have therefore been left out of many of the global NO models, an example is the Yienger and Levy [1995] algorithm which is one of the most commonly used NO emission models. Of the few studies in deserts: Hartley and Schlesinger [2000] showed that substantial NO emissions (up to 4.6 ng m^{-2} s^{-1}) could occur under suitable conditions, particularly after wetting of the soil; similarly McCalley and Sparks [2008] showed NO emissions of up to 6.2 ng m^{-2} s^{-1} in the Mojave Desert, Nevada USA; Hall et al [2008] showed NO fluxes of up to 22 ng m^{-2} s^{-1} following irrigation of desert soils and Feig et al [In Press-b] showed that a net potential NO flux of 3 ng m^{-2} s^{-1} is possible in the Kalahari. These maximum emission rates are comparable with reported emission rates from tropical forests 6.9 ng m^{-2} s^{-1} [*Van Dijk et al.*, 2002], 8.25 ng m^{-2} s^{-1} [*Passianoto et al.*, 2004]. During this study peak mean net potential NO fluxes of between 2.6 ng m^{-2} $s^{-1}$and 7.2 ng m^{-2} s^{-1} were obtained. The net potential emission of NO from the soil is largely controlled by the soil moisture and the soil temperature. In the Namib Desert the optimal soil moisture for the emission of NO is below 10% WFPS, (this is the lowest optimal soil moisture that has been reported in the literature). For comparison it was reported that in the Chihuahuan Desert the NO emissions reached a maximum at approximately 10% WFPS [*Hartley and Schlesinger*, 2000]; in the Kalahari, Feig et al [In Press-b] and Aranibar *et al* [2004] found that the optimal emission of NO occurred at a WFPS of between 10% and 25%. Similarly in semi-arid ecosystems of southern Africa the optimal soil moisture was found to be between 15% and 20% WFPS [*Feig et al.*, In Press-a; *Kirkman et al.*, 2001]. The low optimum soil moisture for the emission of NO in the Namib Desert implies that the production of NO is possible even under dry conditions and there is substantial NO emission from the soil. It must however be borne in mind that in this study we have tried to eliminate the confounding effect of pulsing, since pulses may result in a greatly increased NO emission for a short period following a precipitation event [*Hall et al.*, 2008; *McCalley and Sparks*, 2008; *Scholes et al.*, 1997].

The second major controller of the biogenic NO flux from ecosystems is the soil temperature. It seems that the soil temperature is a secondary controller of the NO flux in arid ecosystems since it only has an influence when the soil is moist enough to allow for the production of NO. As reported in the literature there is generally a positive relationship between the soil temperature and the emission of NO, and this has often been reported to follow an exponential relationship. In numerous studies a Q_{10} temperature amplification factor of approximately two has been given [*Aranibar et al.*, 2004; *Feig et al.*, In Press-a; *Kirkman et al.*, 2001; *Van Dijk et al.*, 2002]. Previously it has been reported that the maximum temperature for the production of NO is fairly high, in the region of 40°C [*Aranibar et al.*, 2004; *Passianoto et al.*, 2004; *Williams et al.*, 1992]. However in the soils sampled in the Namib Desert the issue of temperature dependence of NO emission seems to be rather more complicated. In two of the three ecosystems studied (Dune and Riparian) an optimal temperature of 25°C has been found, above which the emissions of NO decrease. In the Gravel Plains ecosystem the optimum temperature was not reached under our experimental conditions (maximum temperature 35°C). One would expect that in a hot environment such as the Namib Desert the microorganisms responsible for the production of NO would be adapted to high temperatures. It is therefore surprising that the optimal temperature in the Dune and Riparian ecosystems is lower than in cooler more mesic regions. One possible reason for this unexpected pattern between the NO emission and the temperature is that the microorganisms may be adapted to metabolise when water is available, and in the dune fields of the Namib, one of the main sources of water is the deposition of fog and dew, both of which occur predominantly at night when it is cool. During the day when the soil surface starts warming up, most of the moisture in the soil surface would evaporate quickly and the NO production would then be limited by a lack of water.

5.5.2 Up-scaled NO flux

The emission of NO from the Namib Desert shows distinct landscape and seasonal patterns. The lowest mean up-scalded NO emission occurs in the Dune ecosystem (0.13-0.28 ng m^{-2} s^{-1}), while higher NO emissions occur in the Gravel Plain ecosystems (0.98-2.4 ng m^{-2} s^{-1}). This is due to the differences in the temperature dependence of the NO emission in the two ecosystems since the differences in the soil

moisture are fairly small (0.2% WFPS) and it can be seen that the emissions of NO do not track the increase in the soil WFPS that occurred in April 2006, following the heavy rains reported in the area [*Muller et al.*, 2008].

There is also a seasonal pattern with regard to the emission of NO where higher NO emissions occur in the austral summer months. This is particularly pronounced in the Gravel Plains ecosystem where the NO emission closely tracks the soil temperature. For the Dune ecosystem a maximum temperature was observed and this tempered the influence of soil temperature on the NO emission.

This technique may at times underestimate the NO emissions from the Namib since we employ a pre-incubation procedure to limit the influence of the NO pulse that occurs when dry soil is first wetted, it is likely that this NO pulse provides a major component in the annual NO budget after rain, for example the study by Hall et al [2008] fluxes of up to 22 ng m^{-2} s^{-1} were observed after simulated rain, and pulses of up to 35 ng m^{-2} s^{-1} were reported by McCalley and Sparks [2008]. Secondly our soil moisture model does not account for precipitation in the form of dew and fog, which plays an important role in the water balance [*Henschel and Seely*, 2008; *Walter*, 1937], particularly in the coastal regions of the Namib, although the effect of dew and fog may be difficult to quantify, precipitation from fog is greater than from rain at Gobabeb [*Henschel and Seely*, 2008]. In other arid and semi arid ecosystems dew and fog play an important role in the total water balance [*Beysens et al.*, 2005; *Jacobs et al.*, 2002; *Kidron*, 2000; *Kidron et al.*, 2002; *Malek et al.*, 1999; *Moro et al.*, 2007]. While the Namib is one of the most arid regions on earth and the amount of rainfall is severely limiting to biological activity, approximately 40% of the days have some form of precipitation which results in the soil surface being wet for an estimated 590 hours [*Henschel and Seely*, 2008]. These periods where soil moisture is present may allow for some, albeit limited, biological activity to occur, however it is very difficult to scale up the contribution of these diverse water sources to the total moisture input into the Namib ecosystems

The up-scaled emissions of NO ranged from 62-544 g ha^{-1} a^{-1} for the Dune and Gravel Plain ecosystems respectively, this produces a total emission of 4.5Gg of NO from the 13 million ha of the Namib Desert in 2006. The 4.5 Gg is less than 0.01% of the estimated total biogenic emission of NO from soils (5-8 Tg)[*Denman et al.*, 2007]. Hyper-arid regions cover an area of approximately 1 billion ha [*Lal*, 2001] if the

annual NO emission fluxes for the Dune Ecosystem are assigned to the entire area covered by hyper arid ecosystems a total NO emission of 62 Gg a^{-1} (0.5% of the global total biogenic emission) is possible from hyper-arid ecosystems. However if the NO flux from the Gravel Plains ecosystem is assigned total annual NO emissions from hyper-arid ecosystems could amount to 544 Gg a^{-1} which would account for an additional 4.2% of the estimated total biogenic NO emission. This should be included in the global NO budgets since it is currently neglected due to the commonly used empirical NO models that do not include emissions from deserts.

5.6 Conclusions

This is the first study to look at the emission of NO from a hyper-arid ecosystem, the study occurred at the Gobabeb research station in the Namib Desert, Namibia. Soil samples were taken under three different ecosystem types; Dunes, Riparian and Gravel Plains and the net potential NO flux was determined using a laboratory incubation technique as a function of the soil moisture content and the soil temperature. It was found that the both the soil moisture and the soil temperature had an important influence on the flux of NO where the optimum NO flux occurred a low soil moisture contents (<10% WFPS) and therefore it appears that the microbial communities responsible for the production of NO are adapted to the hyper arid conditions. The influence of temperature was variable between the different soils, in the Dune and Riparian soils the maximum NO flux occurred under the 25°C incubation conditions; however in the Gravel Plains ecosystem the NO flux increased with temperature to the maximum incubation temperature used in this study, 35°C. It therefore seems that an optimum soil temperature for the emission of NO is likely to occur and in the dune and Riparian ecosystems this appears to be considerably lower than in other more mesic ecosystems where the maximum emission of NO occurs at a temperature of approximately 40°C. Difference in the net magnitude of the net potential NO fluxes occurred between the various ecosystems. The maximum net potential NO flux ranged from 3.04 ng m^{-2} s^{-1} in the Riparian (25°C), 5.6 ng m^{-2} s^{-1} in the dunes (25°C) to 6.17 ng m^{-2} s^{-1} in the Gravel Plains (35°C). This study shows that contrary to the assumptions of a number of the major empirical models of NO emission, Desert ecosystems and even hyper-arid ecosystems have the potential to emit NO when there is sufficient soil moisture to allow the NO emissions to occur, it

is also important to note that the optimum soil moisture for the production of NO is low and therefore there is the potential for the production of NO even after small precipitation events. It seems that in some of the studied ecosystems the optimum temperature for NO emission is lower that that found in more mesic regions, this may be an adaptation of the microbial communities to activate following precipitation events such as fog or dewfall which are an important moisture source in the Namib and predominantly occur under cool night time conditions.

The net potential NO fluxes measured in the laboratory were up-scaled to the whole of the Namib Desert, using a GIS based technique where the Namib Desert region was divided into Dune and Gravel Plain ecosystems and the soil moisture and temperature was estimated using the ECMWF operational model. The up-scaled emissions ranged from 62-544 g ha^{-1} a^{-1} for the Dune and Gravel Plain ecosystems respectively, and the total up-scaled emission of NO from the Namib Desert for the year 2006 is estimated at 4.5 Gg. Using the emissions of NO calculated in this study to estimate the total contribution of hyper-arid ecosystems to the global NO budget, these ecosystems could add 0.5-4.2% to the total NO budget.

5.7Acknowledgements

The research of Gregor Feig has been made possible by a bursary from the German Academic Exchange Service (DAAD). We would also like to thank Helen Kolb and the staff at Gobabeb for all their help during the field sampling. Thanks also to Joh Henschel, for help in obtaining permits to work at Gobabeb.

Chapter 6: Executive Summary and Conclusions

This study has looked at the net potential flux of nitric oxide from a number of arid and semi-arid ecosystems using a laboratory technique followed by an up-scaling procedure where the laboratory flux, as a function of the soil moisture and temperature, is combined with measured, modelled or remotely sensed soil moisture and temperature data.

The conclusion chapter is structured in such a way that there is first an executive summary of the various studies that occurred during my PhD, this is followed by specific discussion about: 1) The fluxes of NO from the sites studied during the course of this PhD, which have been compared to studies published in the literature; 2) The effect of soil moisture content on the emission of NO from the soil in arid and semi-arid regions; 3) The effect of the soil temperature on the emission of NO from the soil in arid and semi-arid regions; 4) The effect of the soil nutrient content on the flux of NO from arid and semi-arid regions; 5) A discussion about the NO consumption rate and the compensation mixing ratio, and 6) Some final remarks about future options for this research.

6.1 Executive summary

During the course of this PhD three full studies on the biogenic emission of NO have been conducted and prepared for publication where I am the first author. A collaborative study has been conducted with scientists from Israel, this has been prepared for publication where I am the second author. In addition other laboratory NO measurements were made, including studies on soils sampled in the Sahara, Bavaria and Surinam.

6.1.1 Soil biogenic emissions of nitric oxide from a semi-arid savanna in South Africa

In the first study (Chapter 3) [*Feig et al.*, In Press-a], which occurred in a semi-arid savanna in the Kruger National Park (South Africa) we looked at the emission of NO from differing landscape positions on a catenal sequence. It was found that the highest net potential emissions of NO occurred from the nutrient rich, low lying positions of the landscape and lower net potential emissions of NO occurred from the nutrient poor sandy soils of the upper slope positions. Across the landscape positions the net

potential flux of NO did not exceed 3.5 ng m^{-2} s^{-1}. The maximum net potential NO emission occurred at a soil moisture content of between 10% and 20% WFPS.

The emission of NO was up-scaled to the Land Type level, using measured soil moisture and temperature data obtained at the Kruger National Park Flux tower site. It was found that the Midslope positions had the greatest contribution to the emission of NO due to their large geographical extent. Emissions of NO ranged from 0.15-8.5 kg ha^{-1} a^{-1} and were affected by the landscape position and the climatic conditions that occurred during the year. The emission of NO from the savannas of the KNP accounts for approximately 2.6% of the annual input of nitrogen into the ecosystem in the form of biological nitrogen fixation and deposition from the atmosphere.

6.1.2 The use of laboratory and remote sensing techniques to estimate patch scale emissions of nitric oxide from an arid Kalahari savanna

The second study (Chapter 4) [*Feig et al.*, Submitted] occurred in an arid savanna in the Kalahari, Botswana. The emission of NO was determined from under various types of vegetation cover, including tree cover, bare soil, soil crusts and grass cover. There were differences in the net potential NO flux between the differing vegetation cover units although these were not consistent between the vegetation patches. The emissions of NO at the patch scale were determined by averaging the emissions across the patch where the contribution of each of the vegetation cover units was scaled to correspond to the proportion of the cover that vegetation unit contributed to the patch. The highest NO emissions came from the Perennial Grassland patches and the lowest mean net potential NO emissions came from the Pan patches. The optimum WFPS for each of the patches ranges from 10%-25% and the mean net potential NO flux ranges from 0.27 ng m^{-2} s^{-1} for the Pan patch and 2.95 ng m^{-2} s^{-1} for the Perennial Grassland patch.

Up-scaling was performed using GIS and remote sensing techniques. The distribution of vegetation patches in this region of the Kalahari was obtained through LANDSAT NDVI measurements where a signature was determined for each of the vegetation patches by marking out the dimensions of the patches in the field. The soil moisture for the region was obtained for the region using microwave reflectrometry data from the ASAR instrument on ENVISAT, run by the "Soil Moisture for Hydrometeorologic Applications in the SADC Region" (SHARE) project. The soil surface temperature was obtained for the region using the MOD11A2 eight day land

surface temperature data. Up-scaling the net potential NO fluxes with the satellite derived soil moisture and temperature data gave NO fluxes of up to 323 g ha^{-1} $month^{-1}$, where the highest up-scaled NO fluxes occurred in the Perennial Grassland patches, and the lowest in the Pan patches. A marked seasonal pattern was observed where the highest fluxes occurred in the austral summer months (January and February) while the minimum fluxes occurred in the austral winter months (June and July), and were less than 1.8 g ha^{-1} $month^{-1}$.

6.1.3 Biogenic emissions of nitric oxide from three ecosystems in the Namib Desert: a laboratory study

The third study (Chapter 5) conducted during the course of this PhD was in the Namib Desert in Namibia [*Feig et al.*, In Prep], where the research was conducted at the Gobabeb Research Station. In this study soils were sampled in the three main ecosystem types in the Namib Desert; Dune fields, Gravel Plain Ecosystem and the Riparian ecosystem of the Kuiseb River. The maximum net potential flux of NO occurred at very low soil water contents (<10% WFPS) and ranged from 3 ng m^{-2} s^{-2} in the Riparian ecosystem to 6.2 ng m^{-s} s^{-1} in the Gravel Plain ecosystem. When these net potential NO fluxes were up-scaled for the whole of the Namib Desert using modelled soil moisture and soil temperature data from the ECMWF operational model, up-scaled NO fluxes of up to 0.062 kg ha^{-1} a^{-1} in the Dune ecosystems. The up-scaled emissions of NO were considerably higher in the Gravel Plain ecosystem and were estimated to be 0.544 kg ha^{-1} a^{-1}. These are fairly large potential NO emissions and are comparable to arid and semi-arid savanna ecosystems. If the potential NO fluxes are applied to other hyper-arid ecosystems around the world we can add up to 4.5% to the global NO budget.

6.1.4 Effects of semi-arid shrubland afforestation on biogenic NO emissions from soil

In addition to the three main studies carried out during the course of this PhD I was involved in a collaborative study with a graduate student from The Weizmann Institute of Science (Appendix 1) [*Gelfand et al.*, In Prep]. During this study we examined the effect of afforestation on the biogenic fluxes of NO from the soil in Southern Israel. Comparisons were made between the net potential NO flux from soils taken from a 40 year old pine afforestation site (Yatir Forest) and the adjacent shrubland (samples taken both under shrub canopy and between shrub canopies). The

three microsites differed in the NO release rates and also showed high inter-seasonal variability in their NO emission rates, responses to the soil moisture content and response to soil temperature. Up-scaling of the NO flux to the ecosystem level was performed using measured data from the Yatir Forest Flux Tower. The up-scaling results showed that afforestation of semi-arid shrubland has the potential of reducing the NO flux by up to 65% compared with the natural shrubland.

6.1.5 Other studies

Three other sets of measurements were conducted during the course of this study (Appendix 2), while these measurements did not result in stand alone publications, the measurements from the tropical rain forests in Surinam have been published [*Ganzeveld et al.*, 2008].

In the first of the ancillary measurements, soils were sampled along a transect through the Sahara in Libya. In total four soil samples were taken but in three of the four samples the release of NO (J) was less than the detection limit of our instrumentation, and therefore the NO flux, compensation mixing rate, or compensation point mixing ratio could not be determined. However the fourth sample did release NO at a sufficient rate to allow for measurement and the flux of NO was found to reach a peak of 0.7ng m^{-2} s^{-1} at a soil moisture content of 9% WFPS.

In the second of the ancillary measurements two soil samples were taken from the Amazon Rainforest during the Gabriel campaign, the NO flux from these soils was determined at two temperatures and a range of soil WFPS and the potential NO flux as a function of soil temperature and moisture was used for model comparison, these results are published in Ganzeveld et al [2008].

In the final set of ancillary measurements forest mineral soils and pasture soils from Hohenpeissenberg in Bavaria were measured as part of the SALSA campaign.

These measurements combined with values reported in the literature give us sufficient data so that we can start looking at some of the processes that control the emission of NO from the soil.

6.2 NO emission from arid and semi-arid ecosystems

While there have been a large number of studies on the biogenic emission of NO from the soil there is a dearth of information on the emission of NO from arid and semi-arid regions. This study has attempted to address that knowledge gap; this was achieved by doing the first full study on the NO emission from a hyper-arid region in the Namib, by examining vegetation and vegetation patch scale effects on the emission of NO in the Kalahari; by looking at the influence of landscape position on NO emission in a semi-arid savanna in South Africa and by providing the first study on the emission of NO from the Sahara Desert as well as two additional sites in tropical rainforests and moist temperate forests and pastures. What this study has shown is that the biogenic production of NO can occur almost ubiquitously, from hyper-arid deserts such as the Namib Desert to tropical forests such as the Amazon.

Figure 6.1 shows a comparison of the up-scaled NO fluxes calculated during this study with values that have been previously published. It can be seen that the up-scaled NO fluxes obtained during this PhD study are within the range of values published in previous studies either through modelling of NO fluxes [*Kirkman et al.*, 2001; *Otter et al.*, 1999], or measured in the field [*Barger et al.*, 2005; *Davidson et al.*, 1993; *Hartley and Schlesinger*, 2000; *Holst et al.*, 2007; *Levine et al.*, 1996; *Martin et al.*, 2003a; *Martin et al.*, 1998; *McCalley and Sparks*, 2008; *Parsons et al.*, 1996; *Smart et al.*, 1999]. Therefore it seems that the up-scaling method that we have used during this study reproduces the range of NO fluxes fairly well. The up-scaled NO fluxes from the KNP (1.7 ng m^{-2} s^{-1}, 1.63 ng m^{-2} s^{-1}, 1.07 ng m^{-2} s^{-1}, 2.18 ng m^{-2} s^{-1} for the mean , median, 25 percentile and 75 percentile respectively) correspond very well with the range of NO fluxes reported in the other studies that took place in southern African savannas for example Kirkman et al [2001] (2.93 ng m^{-2} s^{-1} , 1.1 ng m^{-2} s^{-1} , 0.68 ng m^{-2} s^{-1}, 5.4 ng m^{-2} s^{-1} for the mean , median, 25 percentile and 75 percentile respectively); Parsons et al [1996] (2.25 ng m^{-2} s^{-1} , 1.95 ng m^{-2} s^{-1} , 0.9 ng m^{-2} s^{-1} , 2,86 ng m^{-2} s^{-1} for the mean , median, 25 percentile and 75 percentile respectively) and Levine et al [*Levine et al.*, 1996] (9.06 ng m^{-2} s^{-1} , 5.3 ng m^{-2} s^{-1}, 1.4 ng m^{-2} s^{-1} , 10.4 ng m^{-2} s^{-1} for the mean , median, 25 percentile and 75 percentile). The higher values in the Levine et al [1996] are due to the fertilization and irrigation that occurred.

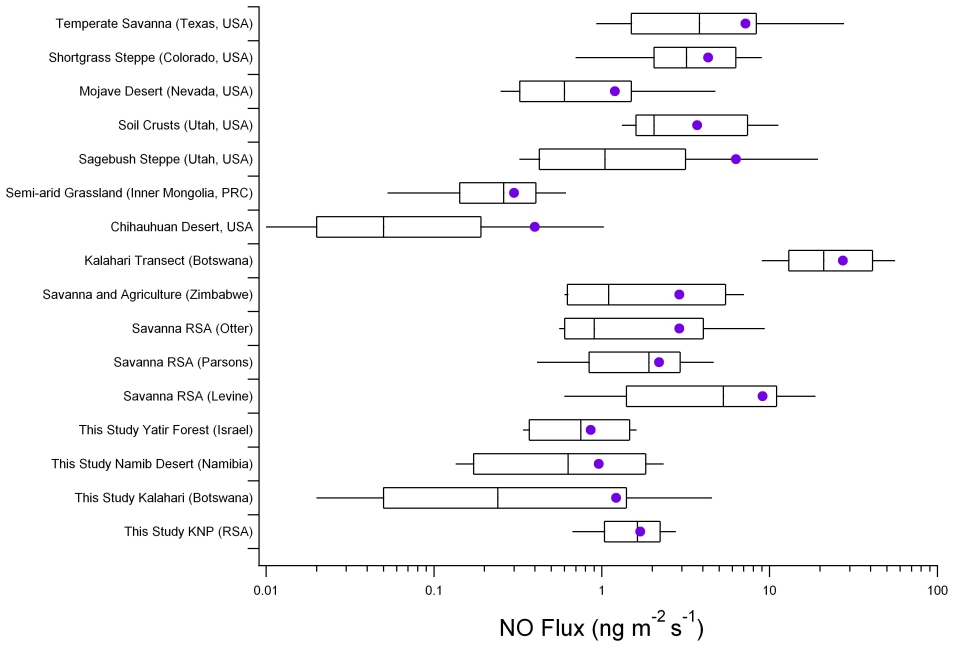

Figure 6.3 Comparison of the up-scaled fluxes of NO determined during this study with data reported in the literature for comparable arid and semi-arid ecosystems (all expressed in terms of mass of nitrogen). Boxes in the figure indicate the inter quartile range between the 25th and 75th percentile and the median value is marked by a vertical bar. The horizontal error bars represent the 10th and 90th percentile, and the blue circle represents the arithmetic mean of the reported data. Where the cited papers provide a mean and range of data only, values were statistically recreated to match these ranges. The reported flux data is cited from:

- Temperate Savanna (Texas USA) [*Martin et al.*, 2003a]
- Shortgrass Steppe (Colorado, USA) [*Martin et al.*, 1998]
- Mojave Desert (Nevada, USA) [*McCalley and Sparks*, 2008]
- Soil crusts (Utah, USA) [*Barger et al.*, 2005]
- Sagebush steppe (Utah, USA) [*Smart et al.*, 1999]
- Semi-arid grassland (Inner Mongolia PRC) [*Holst et al.*, 2007]
- Chihuahuan Desert (USA) [*Hartley and Schlesinger*, 2000]
- Kalahari Transect (Botswana) [*Aranibar et al.*, 2004]
- Savanna RSA (Otter) [*Otter et al.*, 1999]
- Savanna RSA (Parsons) [*Parsons et al.*, 1996]
- Savanna RSA (Levine) [*Levine et al.*, 1996]
- This Study Yatir Forest (Appendix 1)
- This Study Namib Desert (Chapter 5)
- This Study Kalahari (Chapter 4)
- This Study KNP (Chapter 3)

The up-scaled NO emissions for the Namib Desert (0.96 ng m^{-2} s^{-1}, 0.63 ng m^{-2} s^{-1}, 0.18 ng m^{-2} s^{-1}, 1.66 ng m^{-2} s^{-1} for the mean, median, 25 percentile and 75 percentile

respectively) and the Yatir Forest (0.86 ng m^{-2} s^{-1}, 0.75 ng m^{-2} s^{-1}, 0.43 ng m^{-2} s^{-1}, 1.18 ng m^{-2} s^{-1} for the mean, median, 25 percentile and 75 percentile respectively) correspond well to the Mojave Desert [*McCalley and Sparks*, 2008] (1.23 ng m^{-2} s^{-1}, 0.6 ng m^{-2} s^{-1}, 0.4 ng m^{-2} s^{-1}, 0.9 ng m^{-2} s^{-1} for the mean, median, 25 percentile and 75 percentile respectively) although they are higher than what was reported for the Chihuahuan Desert [*Hartley and Schlesinger*, 2000] (0.35 ng m^{-2} s^{-1}, 0.05 ng m^{-2} s^{-1}, 0.018 ng m^{-2} s^{-1}, 0.17 ng m^{-2} s^{-1} for the mean, median, 25 percentile and 75 percentile respectively).

What can be seen from these studies is that the NO emissions from deserts have the NO fluxes that are within the range of those reported for savanna and grassland ecosystems (except in regions of the Sahara). This becomes important when considering the emission of NO from the soil on a global scale. Many of the most important global modelling schemes for biogenic NO emission neglect emissions from desert and arid shrubland ecosystems. This may result in a significant underestimation of the global biogenic NO flux, and correcting this should reduce the uncertainty in the scale of the biogenic contribution to the total biogenic NO emission.

6.3 Soil Moisture Content

As shown in Chapter 1 the emission of NO from the soil is a microbiologically mediated process, dominated by nitrification. The rate of nitrification and the emission of NO are influenced by a large number of factors the most important include the soil water content, the soil temperature, the soil nutrient status, and soil physical properties.

The soil moisture content determines the soil oxygen status and hence controls nitrification (which is an aerobic process) and the diffusion of NO out of the soil. The biogenic emission of nitric oxide as a function of the soil moisture is a prime example of how the rate of a microbiological process can be controlled by the soil moisture content. At low and high WFPS there are low or no emissions of NO from the soil [*Parsons et al.*, 1996]. A characteristic NO emission curve as a function of soil moisture can be seen in soils sampled from many environments. In figure 6.1a-d we have presented the release of NO as a function of the soil WFPS (normalized against

the maximum NO release). The NO release is the primary data source and it can be seen that for 12 differing soils the shape of the emission curve is generally very similar.

Looking at the production of NO as a function of the soil WFPS in these 12 examples it can be seen that the production of NO occurs across a wide range of ecosystems (Hyper-arid Desert, Savanna, European Pastures and Tropical Forests) and the net NO release to WFPS relation shows a similar shape. There is an optimum WFPS value, where the net NO release rate is at a maximum and on either side of this optimum the NO production rate decreases. This curve has been described by Meixner and Yang [2006] as a power increase in the NO production with increasing soil moisture to the optimum soil moisture content, followed by an exponential decrease once the soil moisture content is above the optimum. Fitting parameters for this curve are deduced from three points of the emission curve: the NO release rate at the optimum soil moisture content; the optimum soil moisture content, and the upper soil moisture content where emission ceases (defined to be 1% of the maximum emission flux). We have found that these fitting parameters determine the shape of the emission of NO as a function of the soil water content in all the soils that we have studied. With the large range of ecosystems studied (as shown in Fig. 6.2) it can be seen that while the emission curves from all of the ecosystems have a similar shape they tend to separate according to the position of the optimal soil moisture level for the production of NO. Therefore the question could be asked “what causes this segregation of optimal soil moisture for NO production?”

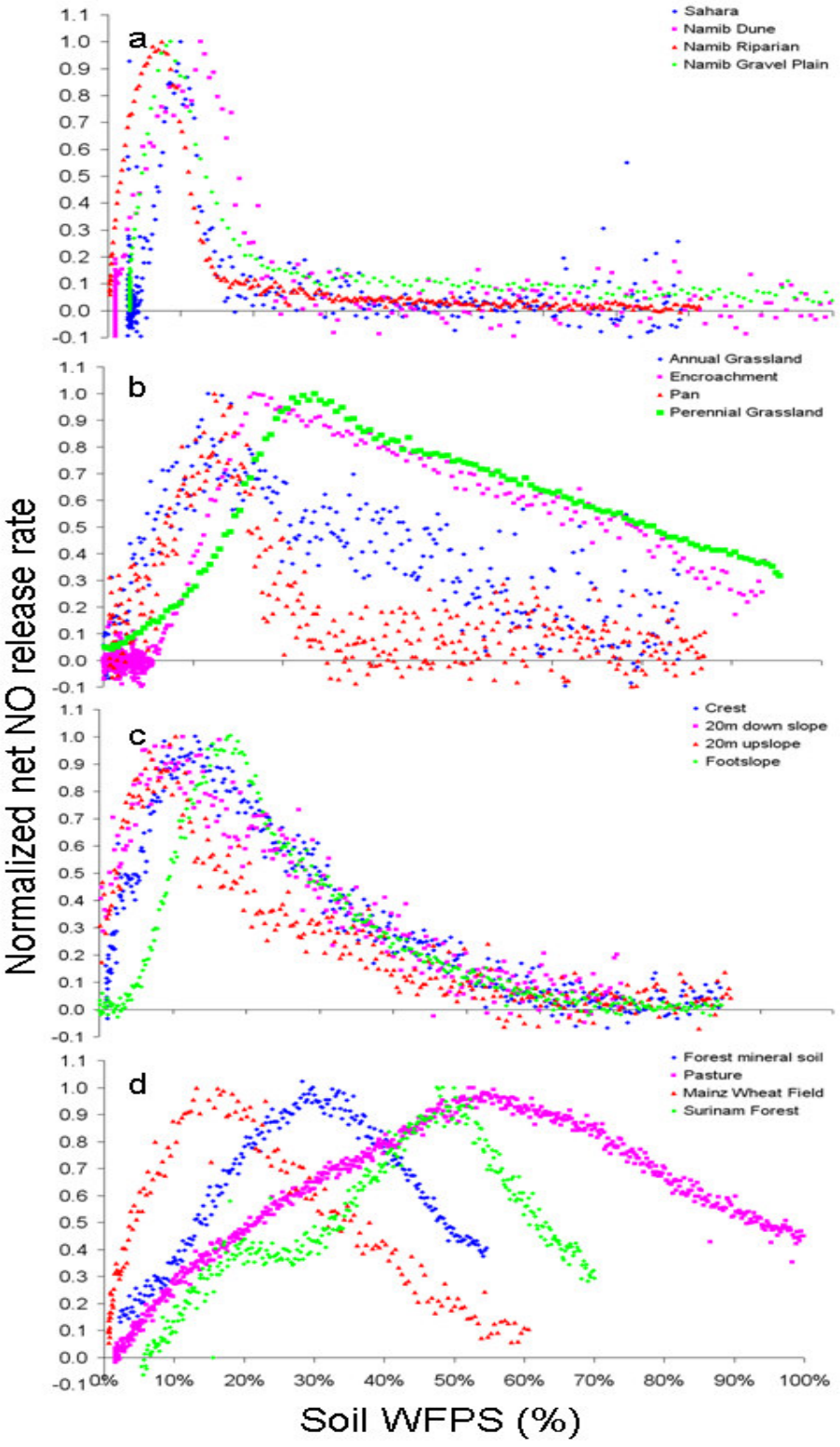

Figure 6.2a) NO release form soils sampled in twodesert ecosystems in Africa, the Namib Desert and the Sahara Desert **b)** NO release from soils sampled in a arid savanna ecosystem in southern Africa **c)** NO release from soils sampled in semi-arid savanna ecosystem in South Africa **d)** NO release from soils sampled in mesic and humid ecosystems in Europe and South America

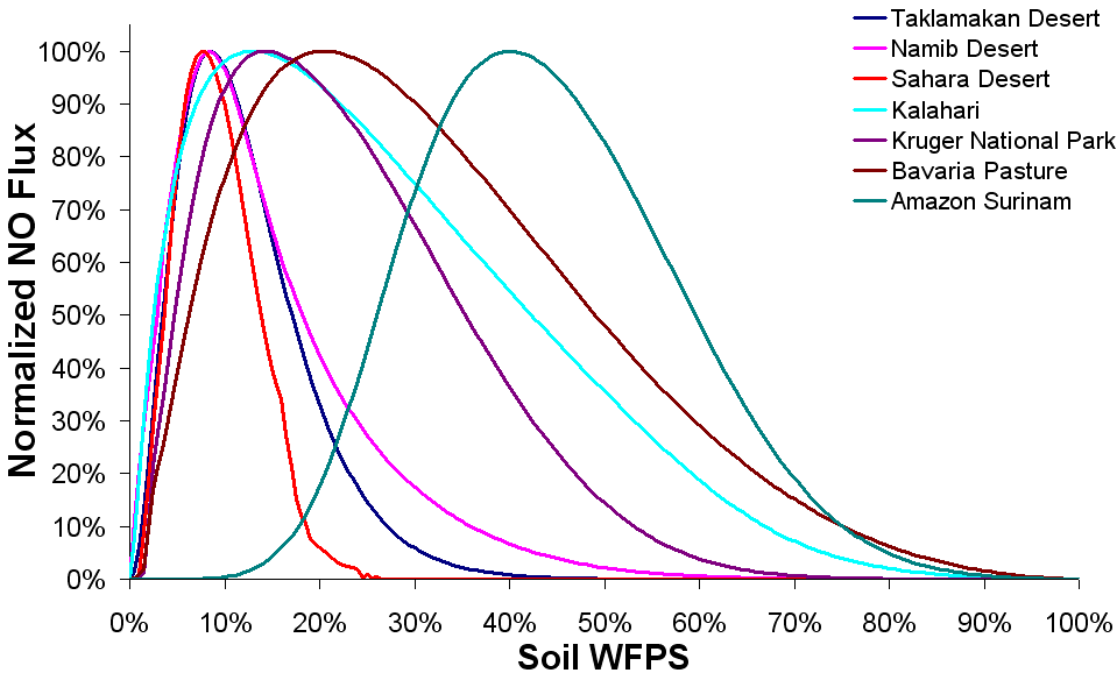

Figure 6.3 Normalized NO flux from a variety of the ecosystems studied. Values are normalized against the maximum NO flux for the sample.

The mean annual precipitation (MAP) of the ecosystems studied (or where data could be found from other sources e.g. [*Mamtimin et al.*, In Prep]) ranges from <20 mm a^{-1} in the Namib, Sahara and Taklimakan Deserts [*Mamtimin et al.*, In Prep] to over 2200 mm a^{-1} in the tropical rain forest of Surinam, as the ecosystems get wetter the optimum soil moisture levels shift. With the wide range of ecosystems that we have studied the effect of MAP on the optimum soil moisture content for the production of NO can be examined.

In figure 6.4 it can be seen that as the mean annual precipitation of the ecosystem increases, so does the optimum soil WFPS (the R^2 value of the regression through the median values is 0.92 n=11). In the hyper-arid ecosystems of the Sahara, the Taklimakan and the Namib Desert which receive a MAP of less than 50 mm a^{-1} the median optimum WFPS for these soils ranges between 5 % and 10 % WFPS. In the semi-arid ecosystems of NE China (published in [*Yu et al.*, 2008]) and southern African savanna ecosystems that receive a MAP of between 250 mm and 1000 mm a^{-1} precipitation the median optimum WFPS ranges between 10 % and 20 %. In the temperate forests of Germany which receive slightly over 1000mm MAP the optimum

WFPS is approximately 30 % while in the humid tropical forests of Surinam (MAP >2000mm a^{-1}) the mean optimum WFPS is approximately 35 %.

The MAP is obviously quite a good parameter for examining the relationship of the optimum WFPS between the differing ecosystems, since it influences a number of other characteristics such as the soil pH, and the soil bulk density, which may play a role in influencing the emission of NO from the soil. The association between the mean annual precipitation and the optimal WFPS for NO emission has previously been noted in European forest soils [*Schindlbacher et al.*, 2004], where it was suggested that the relationship may be due to the adaptation of the microbial communities to drought conditions.

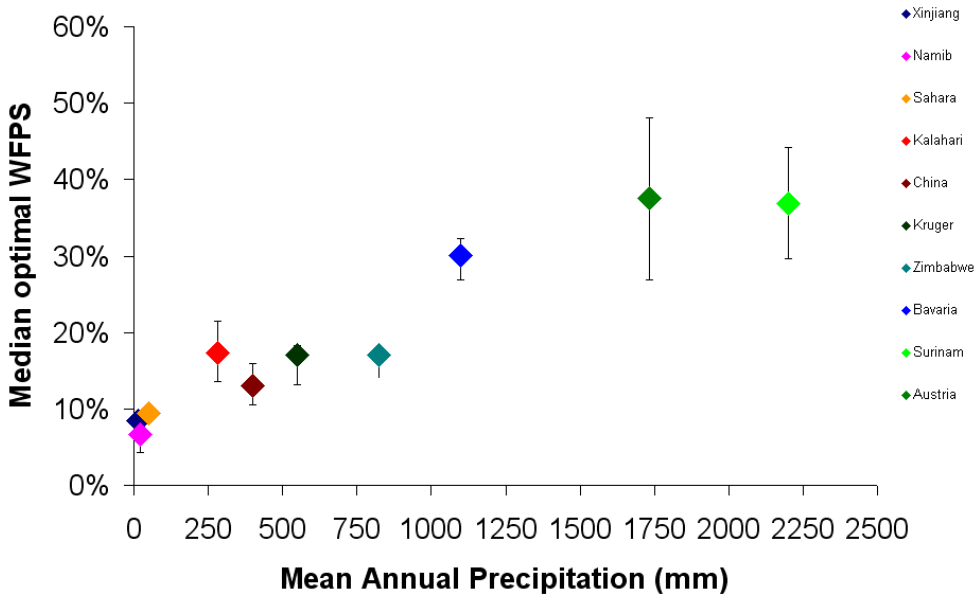

Figure 6.4 Median optimum WFPS as a function of the mean annual precipitation, error bars indicate the 25 and 75 percentile range. Some of the values have been obtained from the literature: Austria comes from the Kitzler et al [2006a] China comes from Yu et al [2008], Zimbabwe comes from Kirkman et al [2001], Xinjiang comes from Mamtimin et al [In Prep].

6.4 Soil Temperature Effect

Temperature is known to have a marked effect on the emission of NO (chapter 1) (see also [*Kitzler et al.*, 2006a; *Schindlbacher et al.*, 2004]), many previous studies have suggested that there is approximately a doubling in the rate of NO emission with a 10°C increase in the soil temperature, and this corresponds well with the temperature influence on soil respiration (Fig. 6.5). It can be seen in figure 6.5 that the Q_{10}

temperature amplification factor (fitted for the NO emissions) ranges between 1.5 and 2.5, with the exception of the Hohenpeissenberg soils where there seemed to be little influence of the soil temperature in the range of 15°C to 25°C, and the soils from the Yatir forest in Israel. In some cases there is quite a large variation around the mean. Of particular interest are the Namib Desert and Kalahari studies where in some cases the Q_{10} value is below 1, indicating that there is an inverse relationship between the temperature and the NO emission rate. These particular situations occurred where the optimum temperature for the production of NO in the soil was exceeded (see chapter 5).

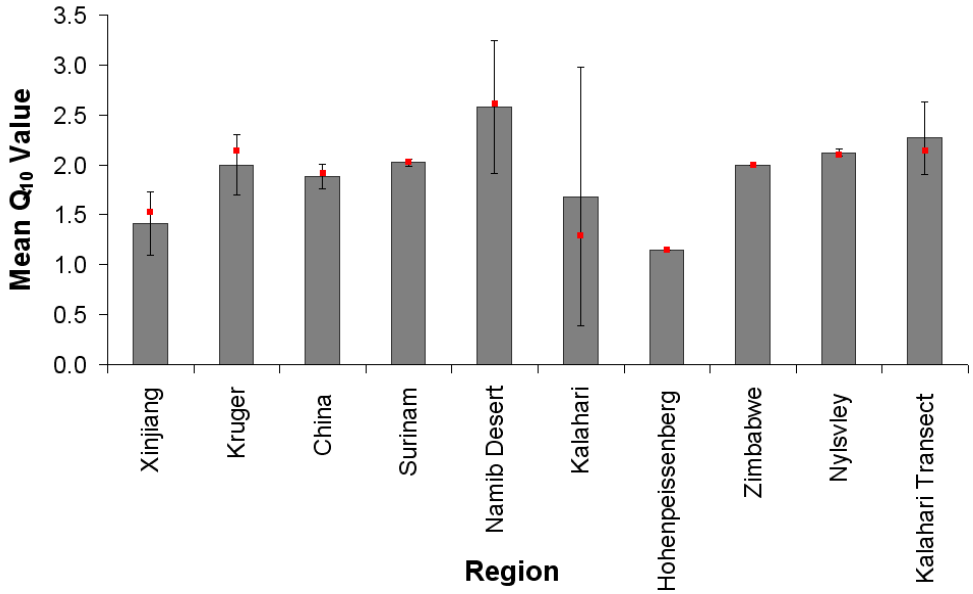

Figure 6.5 Mean reported Q_{10} value for ecosystems examined in this study and selected published values. Error bars indicate the standard deviation around the mean and the red point represent the median Q_{10} value of the measurements. A number of these values have been obtained from studies reported in the literature Xinjiang comes from [*Mamtimin et al.*, In Prep], China comes from [*Yu et al.*, 2008], Zimbabwe comes from [*Kirkman et al.*, 2001], Nylsvley comes from [*Otter et al.*, 1999] and Kalahari Transect comes from [*Aranibar et al.*, 2004].

A number of studies have shown a link between the soil moisture content and the Q_{10} temperature amplification factor values [*Kutsch et al.*, 2008]. The types of laboratory experiments that have been conducted during the course of this PhD offer the opportunity to examine the influence of soil moisture on the Q_{10} of NO emission. In figure 6.6 which shows the Q_{10} temperature amplification factor as a function of the soil WFPS, for a selection of soils, there is a clear relationship between the Q_{10} and the soil WFPS in two of the three soils, where the maximum Q_{10} occurs at approximately the same WFPS as the peak in NO emissions, however in the 3rd soil this is not the case. In many of the other sites that have been studied there is similar

ambiguity about the influence of soil WFPS on the Q_{10} temperature amplification factor. While it is tempting to look at the data from the two sites in the Kruger Park and try and draw conclusions relating to the Q_{10} of the WFPS, I do not believe that there is sufficient evidence to confirm any consistent relationship between the Q_{10} and the soil WFPS, this would be a interesting topic for future study.

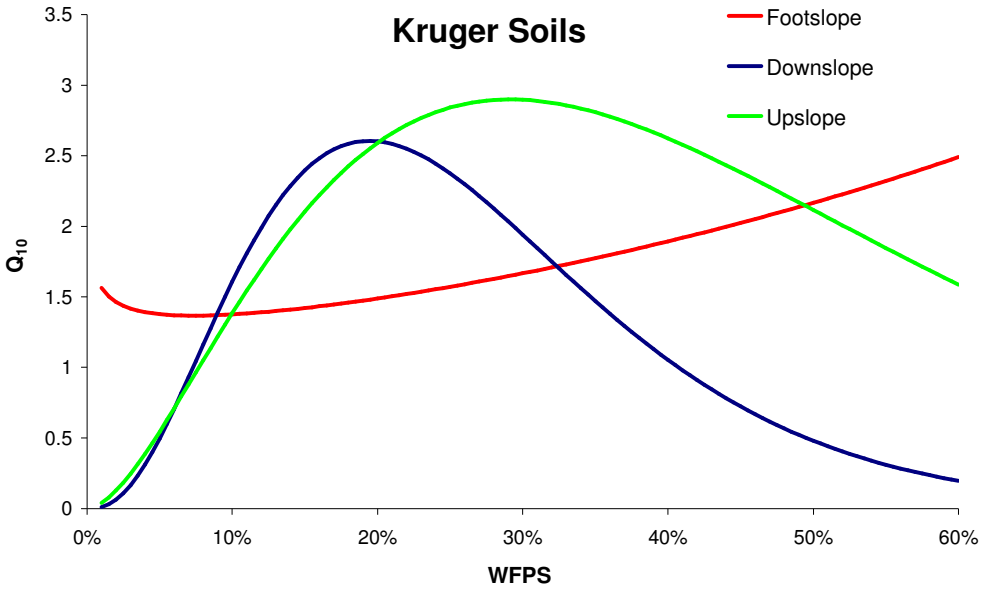

Figure 6.6 Temperature amplification factor (Q_{10}) as a function of the soil WFPS in semi-arid Savanna soils of the Kruger National Park, South Africa

In the study that occurred in the Namib Desert we were fortunate to be able to examine the Q_{10} temperature effect under two different temperature ranges, firstly between 15°C and 25°C and also between 25°C and 35°C. At both temperature ranges no clear patterns emerged between the Q_{10} and the soil WFPS. However we did find that in some of the sites (Riparian and Dune) the NO emission did not increase with the temperature to 35°C, instead there was an increase in NO emission between 15°C and 25°C and a decrease in NO emission between 25°C and 35°C (see Fig. 5.3). This NO emission, soil temperature relationship differed between the Dune (strong decrease in NO flux in temperatures above 25°C), the Riparian (moderate decrease in NO flux under incubation temperatures greater than 25°C) and the Gravel Plains (increase in NO flux with increasing soil temperature up to 35°C). This implies that there is an optimal temperature for the emission of NO, above which emissions decrease; this is an important finding since a number of previous studies that have examined increase in NO emission with the soil temperature and have not seen an upper limit to the temperature relationship [*Meixner and Yang*, 2006; *Otter et al.*,

1999] and it is only in a very few studies and under high soil temperatures (>40°C) that a decrease in soil NO emission has been reported [*Aranibar et al.*, 2004; *Passianoto et al.*, 2004]. Unfortunately due to the limited range incubation temperatures chosen during this study (limited by the time period required to incubate soils), we have only been able to examine the optimal temperature for NO emission under a fairly course resolution.

6.5 Soil Nutrient Content

The soil nutrient status is known to have an important influence on the emissions of NO from the soil. In many previous field studies a relationship between the emissions of NO and the and the concentrations of nitrogen containing compounds [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Hutchinson et al.*, 1993; *Ludwig et al.*, 2001; *Meixner et al.*, 1997] or the N cycling rate [*Erickson et al.*, 2002; *Erickson et al.*, 2001; *Hartley and Schlesinger*, 2000; *Parsons et al.*, 1996]. It has been suggested that in humid ecosystems the emission of NO is primarily controlled by the NO_3^- concentration and to a lesser extent the NH_4^+ concentration [*Erickson et al.*, 2002; *Erickson et al.*, 2001], while in arid ecosystems the production of NO is controlled by the NH_4^+ concentration [*Hartley and Schlesinger*, 2000]. It was thought that the concentrations of NO_3^- and NH_4^+ would have been altered due to the sampling process and storage of soils that was necessary to conduct the laboratory NO measurements that we have performed. Therefore we only measured the total soil N content during these studies. In figure 6.7 the maximum NO flux against the total soil nitrogen is presented. For some of the sites there is a strong positive relationship between the total N content and the maximum NO flux. In the Nylsvley study [*Otter et al.*, 1999] the R^2 value of the relationship was found to be 0.99 n=3. Similarly in the Namib soils (chapter 5) a positive relationship existed (R^2=0.26 n=9). However in some of the other ecosystems that we have studied there appears to be a negative relationship between the total N content and the maximum NO flux, for example in soils from the Kalahari (Chapter 4) there is a negative relationship (R^2=0.9 n=4 this analysis was done using the mean patch scale values), and in the soils from China [*Yu et al.*, 2008] and from the Kruger National Park there the total N content has little influence on the maximum NO emission. Therefore it appears that the magnitude of the NO emission flux is not dependent on the total N content and if one is interested in

determining the effect of soil nutrients on the emission of NO it is not sufficient only to measure the total N content, but the NH_4^+ and NO_3^- concentrations would need to be examined more closely.

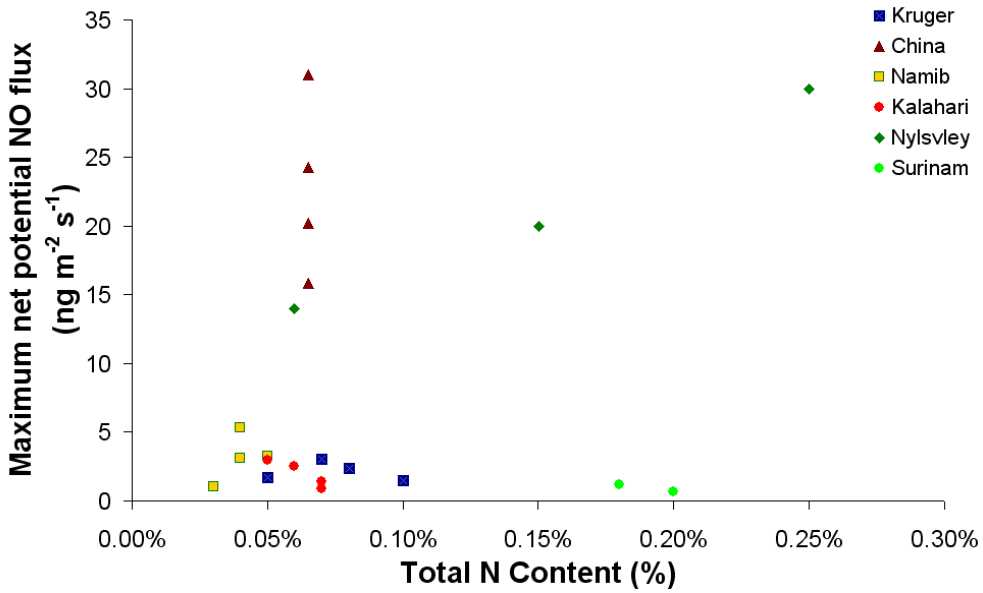

Figure 6.7 The maximum net potential NO flux as a function of the total nitrogen in soil. Data in this figure is taken from a variety of sources: Kruger is from Chapter 3, China is from [*Yu et al.*, 2008], Namib is from Chapter 5, Kalahari is from Chapter 4 and Nylsvley is from [*Otter et al.*, 1999].

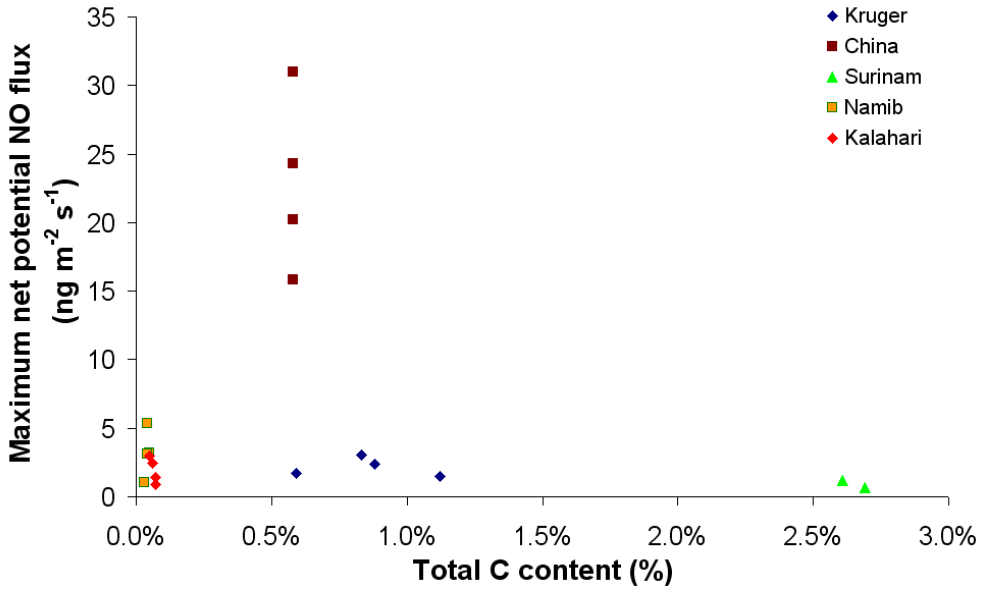

Figure 6.8 The maximum net potential NO flux as a function of the total soil carbon content. Data used in this figure has been obtained from a variety of sources: Kruger is from the Kruger National Park

(Chapter 3), China is from [*Yu et al.*, 2008], Surinam is from Appendix 2, Namib from Chapter 5 and Kalahari from Chapter 4.

The maximum net potential NO flux for the ecosystems that we have studied does not have a strong dependence on the total carbon content (Fig. 6.8). This is in contrast to the study by Ashuri [2008], which used similar methods to this study, where it was found that the soil organic carbon content (as measured by loss of mass on ignition) was significantly correlated to the maximum NO release. That study, however, was limited to the catchment scale and predominantly conducted on agricultural soil and those findings appear not to be transferable between regions. On the inter-regional scale it is to be expected that other factors have a greater influence on controlling the magnitude of the net potential NO emissions from the soil.

6.6 Compensation mixing ratio and NO consumption rate

It is known that soils simultaneously produce and consume NO; however there have been very few studies that have looked at the process of NO uptake in the soil. During the course of this PhD we have managed to add considerably to the number of studies on the uptake of NO in the soil from a wide range of ecosystems. The uptake of NO into the soil is described by two differing parameters, firstly there is the NO consumption rate (k) which determines the rate at which NO is taken up, secondly there is the NO compensation mixing ratio ($m_{NO,comp}$)which is the ambient NO concentration where NO production is equal to NO consumption and the net NO release rate is zero.

6.6.1 Compensation mixing ratio ($m_{NO,comp}$)

The $m_{NO,comp}$ varies with the changing soil conditions (see Fig. 3.4, 4.7a, A2.4, A2.9 A2.14), potentially the change in the $m_{NO,comp}$ could switch the soil from being a net source of NO to being a net sink of NO [*Conrad and Smith*, 1995]. The results of this study (means range from 10ppb-126ppb) correspond very well with reported values from other arid and semi-arid regions (means from 38ppb-375ppb) (Fig. 6.9). Since we know the range on NO mixing ratios that is necessary before the soils change from being a source of NO to being a sink for NO, the question can be asked whether it is ever likely that soils from arid and semi-arid regions will act as a sink for NO?

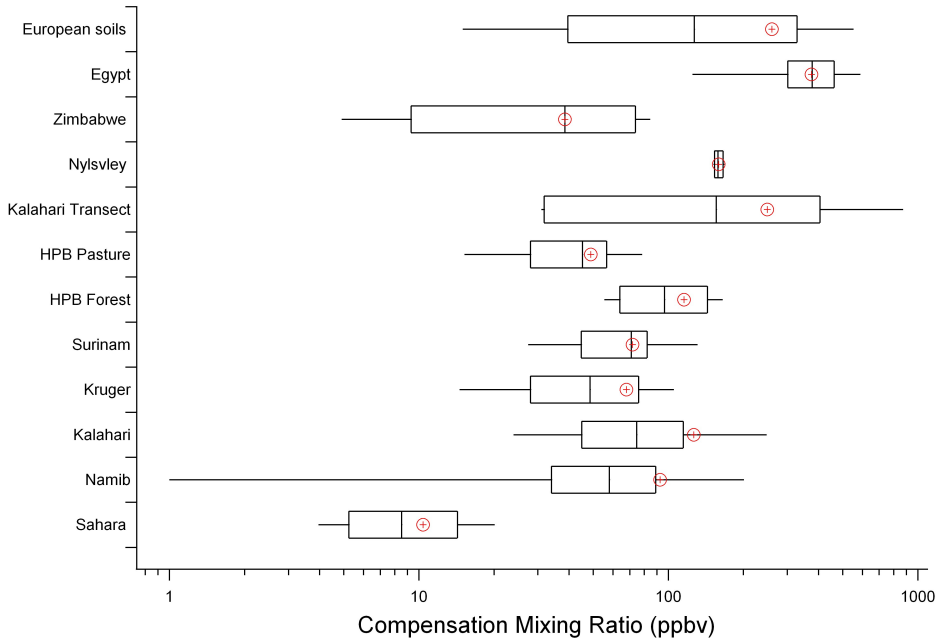

Figure 6.9 Comparison of compensation mixing ratio values reported during this study with the values reported in the literature. Circles represent the mean $m_{NO,comp}$ of the studies, the bar in the middle of the box represents the median $m_{NO,comp}$, the box represents the 25 and 75 percentiles and the whiskers represent the 10 and 90 percentile. Values European soils are from [*Bollmann et al.*, 1999; *Gödde and Conrad*, 1998; *Gödde and Conrad*, 1999; *Rudolph et al.*, 1996; *Saad and Conrad*, 1993], the values for Egypt are from [*Saad and Conrad*, 1993],values for Zimbabwe are from [*Kirkman et al.*, 2001] values for Nylsvley are from [*Otter et al.*, 1999], values for Kalahari Transect are from [*Aranibar et al.*, 2004]. HPB pasture and HPB forest are for the Hohenpeissenburg Pasture and forest soils respectively. The $m_{NO,comp}$ values presented here are those which correspond to a soil WFPS where there was NO production occurring.

In chapters 3, 4 and A1, it has been discussed that in the Kruger National Park, and in the Tsabong region of the Kalahari the ambient NO mixing ratio is very low (never exceeding 5ppb), while in the Yatir Forest the annual mean NO mixing ratio is 2.39 ±0.56ppb). It can therefore be assumed that due to the low ambient NO mixing ratios that occur in the research sites and the relatively high $m_{NO,comp}$ values, net uptake of NO into the soil is highly unlikely and may be limited to periods of abnormally high NO concentrations, such as during biomass burning events.

With NO fluxes such as these the annual production of NO ranges from 0.2-0.8 kg $ha^{-1}y^{-1}$ in the Kruger National Park (up to 2.6% of the total N entering the system through atmospheric deposition and biological N fixation), 0.54 kg ha^{-1} a^{-1} for the Kalahari (1.3-7.4% of the total input of N into the ecosystem through atmospheric deposition and BNF), 0.062-0.54 kg ha^{-1} a^{-1} for the Namib Desert , 0.13-0.49kg $ha^{-1}a^{-1}$ for the

Yatir Forest and surrounding shrubland. These emissions of NO therefore act as a potentially important N loss mechanism for the soils.

6.7 Final remarks

From the measurements conducted during this study, where the focus has been on the emission of NO from arid and semi-arid ecosystems and in other measurements made during the course of my time in Mainz and previously published values a number of conclusions can be drawn:

1. Nitric oxide appears to be emitted ubiquitously from the terrestrial ecosystems, ranging from hyper-arid ecosystems in the Namib Desert, the Sahara Desert and the Taklimakan Desert where the mean annual precipitation is below 50 mm to tropical forests with mean annual precipitation of over 2000 mm a^{-1}. As such the global models of NO emissions which currently exclude deserts as a source of NO should be updated, since the production of NO from desert soils may be important and add a significant amount of NO to the atmosphere. The fact that there is very little vegetation cover in arid environments means that there is reduced vegetation canopy uptake of NO_x and that the majority of the NO produced will escape the vegetation canopy.
    a. Drylands cover 40% of the earth's surface area [*Lal*, 2000] this amounts to an area of approximately 6.1 billion ha. The hyper-arid regions cover approximately 1 billion ha and it was shown in Namib Desert study (Chapter 5) that hyper-arid ecosystems have the potential of contributing between 62-544 Gg a^{-1} to the total annual NO budget (0.7%-6.1% of the 2007 IPCC estimate on biogenic NO emission 8.9 Tg a^{-1}). Many of the important models looking at the emission of NO from the soil (for example [*Yienger and Levy II*, 1995]) state that there is no NO produced in deserts or arid scrublands, here we prove that this is not the case, and it is therefore imperative that estimates of NO emission from these regions be included in the global NO emission models.
2. From all these diverse ecosystems it appears that the emission of NO is primarily controlled by two factors, the soil moisture content and the soil temperature. From the literature we know that the nutrient concentrations are

important, however closer examination of the soil nutrient effect was beyond the scope of this project as it was conceived.

a. The emission of NO as a function of the soil moisture content follows a distinct curve where there is optimal water content. If the soil is wetter or dryer than this optimal then the emissions are reduced. Looking at the range of ecosystems it appears that the optimal soil moisture content is influenced by the mean annual precipitation, in hyper-arid regions where mean annual precipitation is less than 50mm a^{-1} the optimum WFPS is between 5% and 10%. In humid ecosystems such as temperate or tropical forests where the mean annual precipitation is greater than 1500 mm a^{-1} the optimum WFPS is 30%-40%.
b. Temperature has an important influence on the emission of NO. In most ecosystems that we have studied the emission of NO tends to approximately double with a 10°C increase in temperature, however it appears that the soil temperature also has an optimum, above which the emission of NO decreases. To date we have not measured enough soils, or used a wide enough temperature range to determine where the optimum temperature for all these ecosystems is. Future studies using this method should consider examining the influences of soil temperature more closely. Currently the soil incubation technique that we have used has a high resolution with the soil moisture (approximately 0.5% WFPS) while the resolution of the temperature effect is both course and rather crude, since a maximum of three differing incubation temperatures have been used.
c. The feedback that occurs between the important components of the emission of NO, such as the optimum soil moisture level and the optimum soil temperature and environmental factors such as the mean annual precipitation of the soil temperature imply that the emission of NO is a dynamic process and that the microorganisms responsible for the emission of NO adapt to the environment in which they occur.

3. The small scale vegetation patch and landscape properties have a large effect on the emission of NO from the soil. Therefore in any attempt to estimate regional emissions of NO heterogeneity in terms of soil, vegetation and landscape position will need to be considered.

4. It has been found that the emission of NO is an important loss mechanism for N in the ecosystems that have been studied. Emissions range from 0.06-0.8kg $ha^{-1}a^{-1}$ for the ecosystems that have been studied. For the Kalahari and Kruger sites this NO loss accounts for approximately 1.3-7.4% of the total N input to these systems.

During the course of this PhD we have been able to study the emission of NO from arid and semi-arid ecosystems that have never been studied before, and scale up the estimates of NO emissions spatially to the regional scale and temporally to the seasonal, annual or multiyear scale. This PhD has resulted in three first author publications that have been published or are currently in press, in addition two papers are in preparation and there have been two papers published or submitted where data from this thesis has been used.

Appendix 1: Effects of semi-arid shrubland afforestation on biogenic NO emission from soil

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A1.1 Abstract

Nitric oxide (NO) plays a central role in the formation of tropospheric ozone, hydroxyl radicals, as well as of nitrous and nitric acids. Global NO emissions from the terrestrial biomes to the atmosphere were estimated to be 30 to 50 Tg a^{-1}, with roughly equal contributions from anthropogenic and natural sources. The large uncertainty of the global estimations is partly due to the small number of measurements (both laboratory and field) in the drylands.

The main objective of the presented research was to study the influence of afforestation on soil NO fluxes in the semi-arid afforestation system in Southern Israel (precipitation ~280 mm). For estimation of soils NO emissions, laboratory incubations were carried out on under well-defined conditions of soil moisture and temperature with soils from the native shrubland (taken both under shrub canopy and in the inter-shrub areas), and from the adjacent 40-year old pine afforestation site (Yatir forest). While the different microsites differed in NO release rates, they all exhibited high inter-seasonal variability in NO emission rates, soil moisture, and in temperature responses. Based on the laboratory results and field measurements of soil moisture and temperature, we up-scaled soil-atmosphere NO fluxes to the ecosystem level.

The results indicated that afforestation of the semi-arid shrubland resulted with reduced NO emission from the soil by about 65%. Our results also indicated the need to consider seasonal sampling of soils, incubation under corresponding field conditions and explicit determination of the NO consumption constants for the specific soil, for up-scaling purposes.

A1.2 Introduction

Afforestation in semi-arid regions can increase the carbon sequestration capacity of these areas [*Grünzweig et al.*, 2003]. Changes in land cover or land management practices are associated with changes in trace-gas emissions, which are generally not well characterized. For example, environmental benefits from the increases in carbon sequestration may be negated by associated increases in emission of other primary and secondary greenhouse gases, such as nitrous oxide (N_2O) and nitric oxide (NO) [*Smith and Conen*, 2004]. In Texas, woody vegetation encroachment resulted in increased NO emissions from 0.15 to 2.85 kg ha^{-1} a^{-1} (all emission values are in terms of the mass of nitrogen) [*Martin et al.*, 2003a]. However, afforested sites in Costa Rica have been shown to have lower NO emission rates than pastures and banana plantations (0.9 to 8.9 and 15.6 kg ha^{-1} a^{-1}, respectively; [*Reiners et al.*, 2002]). To the best of our knowledge, no studies on the influence of afforestation of semi-arid shrubland on NO fluxes have been reported.

Emissions of NO and its conversion to NO_2 are important in regulating chemical processes in the atmosphere [*Chameides et al.*, 1992; *Crutzen*, 1979; *Crutzen*, 1995; *Levine et al.*, 1997]. The secondary greenhouse gas, NO, is a highly reactive gas and it has a rapid chemical inter-conversion with ozone (O_3) and nitrogen dioxide (NO_2). Both NO and NO_2 are key catalysts in those (photo-) chemical reactions that generate and destroy the primary greenhouse gas O_3 and are commonly referred to as NO_x ($NO+NO_2=NO_x$; [*Meixner*, 1994]. Thus, the ambient mixing ratio of NO_x creates the threshold (around 30 ppt) that determines whether tropospheric O_3 is created or destroyed [*Levine et al.*, 1997; *Lindesay*, 1997; *Meixner and Yang*, 2006]. The removal of tropospheric NO_x is through a series of photochemical reactions that finally produce nitrous and nitric acid and/or aerosol nitrate, which is also an important component of acid rain. Both wet and dry deposition of nitric acid and aerosol nitrate are an atmospheric source of N to terrestrial and marine ecosystems [*Logan*, 1983; *Meixner*, 1994].

According to current knowledge, NO (as well as N_2O) is produced in soils nearly ubiquitously [*Conrad*, 1996; *Conrad et al.*, 2000]; and therefore, soil emissions constitute a continuous background flux of NO to the atmosphere [*Davidson*, 1991a]).

Global inputs of NO_x to the atmosphere are estimated to be between 33 and 50 Tg a^{-1}, where anthropogenic sources account for approximately 50% (~21 Tg) and where soils contribute between 18 and 40% of the total emission, with a relatively large uncertainty of 4 to 10 Tg N a^{-1} [*Davidson and Kingerlee*, 1997]. As can be seen from these estimates, there is still large uncertainty in estimating NO_x fluxes from terrestrial biomes. However, despite considerable uncertainties, there is substantial evidence that soil emissions significantly contribute to the tropospheric NO_x budget even in industrialized regions of the globe [*Davidson and Kingerlee*, 1997; *Ludwig et al.*, 2001; *Williams*, 1992]. Emissions from semi-arid and arid lands, in particular, contribute to uncertainties because of the very small number of NO_x flux measurements. The recent review by Meixner and Yang [2006] identified only 13 studies on natural semi-arid and arid ecosystems (annual precipitation below 400 mm), including two studies from the Mediterranean region. If current and future efforts to reduce NO_x emissions from vehicles and fossil-fuel burning are successful, then the relative importance of biogenic emissions will grow considerably. Whereas biogenic emissions from natural systems are part of the natural background levels, the increased use of fertilizers as well as land use changes may significantly influence the global NO_x budget.

The net flux of NO from soils is mainly influenced by soil N content, temperature, moisture, and texture [*Ludwig et al.*, 2001; *Martin et al.*, 1998; *Skiba et al.*, 2006]. Soil cover has a regulatory role in determining the flux of NO to the atmosphere, since NO emitted from vegetated soils is converted into NO_2 by O_3 within most plant canopies and can then be re-deposited on the vegetation surface (in gaseous form; [*Ludwig et al.*, 2001]). In addition, direct (stomatal) uptake of NO_2 by plants is well known, whereas for NO this uptake pathway is generally not as important [*Hereid and Monson*, 2001; *Meixner*, 1994; *Sparks et al.*, 2001]. Recent studies have shown that NO plays an important role as a signalling molecule in plants, affecting a broad range of plant physiological activities, from stomatal closure to regulating mitochondrial and chloroplast functions [*Neill et al.*, 2003; *Shapiro*, 2005; *Stöhr and Ullrich*, 2002].

Given the importance of biogenic NO_x emission from soils and its sensitivity to land use changes and the environmental conditions of specific sites, our objective was (a) to evaluate the potential NO emission rates from soils in the semi-arid Yatir forest across different seasons, (b) to compare it to that in the surrounding "native" shrubland, and (c) to use a simple up-scaling procedure to extrapolate the results in

order to estimate the consequences of afforestation on biogenic soil NO emissions at the ecosystem scale.

A1.3 Materials and Methods

A1.3.1 Site description

Our field research site is located in the Yatir Forest (31°20'49.2''N, 35°03'07.2''E), a ~2800 ha pine afforestation system and surrounding shrubland at the transition zone between the semi-arid and Mediterranean climates, at a mean altitude of about 650 m a. s. l. The mean annual precipitation at the Yatir forest is 280 mm (the last 30 years). Trees are ~90% *Pinus halepensis* Mill. [*Ne'eman and Trabaud*, 2000] planted by the Jewish National Fund (JNF) during 1965 to 1969. The main shrubland plant is *Sarcopoterium spinosum* L. [*Litav and Orshan*, 1971]. Precipitation occurs only between October and April, with high inter- and intra-annual variations. The mean annual temperature is ~17°C, with average maximum and minimum for the studied years (2005 to 2006) of 32.3°C and 6.9°C, respectively. The mean wet and dry period temperatures are 13°C and 31°C, respectively. Wet period temperatures during the studied years had two distinct periods of lower average temperatures in November-February (12°C) and higher average temperatures in February-May (17°C). With a depth of 0.2 to 1 m, the soil is of Aeolian origin with pH 7.6±0.2 (1:1 water, and confirmed by additional analysis in the local Agricultural Extension Laboratory) above chalk and limestone. The mean soil bulk density is 1.65×10^{3} kg m^{-3}. The particle size distribution of the soils is silty-clay (USDA) and there was no distinct organic or litter layer, as noted earlier [*Grünzweig et al.*, 2003]. The site includes a 19-m flux tower for ecosystem-level measurements of net ecosystem CO_2 exchange (NEE), as well as a set of meteorological measurements [*Grünzweig et al.*, 2003].

A1.3.2 Soil sampling and field methods

Soil samples were collected inside the Yatir forest (*forest*) and in the surrounding shrubland. The shrubland sites were divided into two microsites: (1) under shrub canopy (*shrub*) and (2) at inter-shrub interval soils (*annuals*). Soil sampling was done during October 2005, February 2006, and May 2006. Three sampling dates represented the main seasons; they differ in water content and the temperature of the soils (see section ***Up-scaling approach*** for details). Three representative plots of

approximately 1 ha size in each location were chosen. At each plot, five random replications of mineral soil samples were taken from depths of 0 to 10 cm using a 50-mm diameter corer (Ben Meadows Company, Canada). The samples were then brought to the laboratory on the day of sampling, sieved (2 mm), bulked, homogenized, and stored in a refrigerator (4°C). The soil samples from October 2005 and May 2006 were practically air-dried. The October 2005 soils had gravimetric water content (GWC) of 3.8, 4.8, and 4.8% for *annuals* and vegetation-covered soils (*forest* and *shrub*). The soil samples from May 2006 had a GWC of 5.4, 7.2, and 7.6% for *annuals*, *shrub,* and *forest* soils. Soils from February 2006 had a GWC of 16.5, 20.8, and 22.2% for *annuals*, *shrub,* and *forest* soils, respectively. The February 2006 samples were slightly dried prior to sieving and storage. Samples used for incubations were delivered under cool conditions (~ 5°C) to Mainz, Germany. The *in situ* soil water content and temperature were measured at the Yatir flux tower site [*Grünzweig et al.*, 2003]. The temperature was measured with T-type thermocouple sensors placed at a 6 cm depth. Sensors were placed under the tree canopy and in a clearing for representing *annuals*- and canopy-covered soils (i.e., *forest* and *shrub*). The volumetric water content (VWC) of the soil was measured with the Time-Domain Reflectrometry (TDR) sensor (IMKO, Germany). The sensors were placed at the same plots as the temperature sensors, at 5 cm depth. The average water content measured by TDR sensors was in good agreement with destructive measurements of the soil water content at the forested and shrubland sites (0 to 10cm soil layer, core sampling; Raz-Yaseef, N., unpublished data). Both water and temperature were measured with half-hour resolution and have been averaged to yield daily means.

A1.3.3 Laboratory incubations

The procedure for soil incubation and laboratory NO flux measurements has been described in detail elsewhere [*Otter et al.*, 1999; *Van Dijk et al.*, 2002; *Van Dijk and Meixner*, 2001]. In short, the system for laboratory incubations contains five parallel flow-through chambers (0.9 l volume), four for soil samples, and one (without soil) for reference. Micro-fans in the head-space of the chambers ensured well-mixed conditions within the incubation chambers. The NO was measured by a chemiluminescence trace gas analyzer PLC760 (Ecophysics AG, Switzerland). In addition, the evaporation rate was measured by using an infrared H_2O/CO_2 gas analyzer (BINOS, Rosemont). Laboratory incubations were made using ~100 g sub-

samples of the soil samples brought from Israel. Before incubation, the sub-samples were wetted by saturation (deionized water) to water-holding capacity, and pre-incubated at room temperature (~24°C) for ~72 h. The pre-incubation was performed to standardize conditions within the soil sub-samples, since the soils had differing water contents and had experienced different refrigerating periods during storage. For estimating zero-activity, we performed incubations with autoclaved soils.

The net NO release from soil samples was calculated from the difference between the NO mixing ratio at the outlet of the reference chamber and the outlet of each incubation chamber. The net NO release rate (J_{NO}, in ng kg^{-1} s^{-1}) is calculated according to:

$$J_{NO} = \frac{Q}{M_{soil}} \left(m_{NO,out} - m_{NO,ref} \right) \frac{M_N}{V_m} \times 10^{-3} \quad \text{(A1.1)},$$

where Q is the flow rate through cuvette (4.17×10^{-5} m^3 s^{-1} or 2.5 l min^{-1}), M_{soil} is the soil dry mass (kg), and $m_{NO,ref}$ and $m_{NO,out}$ are the NO mixing ratios (in ppb or 10^{-9}) at outlets of the reference and the incubation chambers, respectively. The conversion factor (ppb to ng m^{-3}) is defined by $M_N/V_m\times10^{-3}$, where M_N is the molecular mass of nitrogen (kg $kmole^{-1}$), and V_m is the molar volume (m^3 $kmole^{-1}$).

The release of NO from the soil results from microbial NO production and NO consumption, which operate simultaneously [*Conrad*, 1994; *Conrad*, 1996]. Consequently, the NO release rate (J_{NO}) observed during incubation (eq. A1.1) is always a net release rate. If NO consumption overrides NO production in the soil sample, then J_{NO} becomes negative. According to equation (A1.1), this only occurs if the incoming NO mixing ratio (which is equal to $m_{NO,,ref}$) exceeds the headspace NO mixing ratio (which is equal to $m_{NO,,out}$ due to well-mixed conditions within the incubation chamber. Remde et al [1989], Ludwig et al [*Ludwig et al.*, 2001], and van Dijk and Meixner [2001] have shown that there is a linear relationship between the J_{NO}, and the rates of NO production, P, and consumption, k. Therefore measured release rates, J_{NO}, can be described as:

$$J_{NO} = P - k \times m_{NO,out} \times \frac{M_N}{V_m} \times 10^{-3} \quad \text{(A1.2)},$$

Equation (A1.2) implies that the NO production rate P is independent of the headspace NO mixing ratio ($m_{NO,,out}$), whereas the first-order NO consumption rate, k (m^3 kg^{-1} s^{-1}), is dependent on it. In order to determine P we used equation (A1.2) with measured fluxes (J_{NO}, eq. A1.1); k was obtained from Otter et al [1999], or estimated based on our own laboratory results (see below).

We present the results of NO release rates as a function of the Water Filled Pore Space (WFPS). WFPS was determined from (a) the amount of water lost by evaporation from the enclosed soil sample during incubation, and (b) the gravimetric water content of the sample (by drying a subsample at 105°C for 48 h):

$$WFPS = GWC \times BD / (1 - (BD / 2.65 \times 10^{-3})) \quad \text{(A1.3)},$$

where GWC is the gravimetric water content in %; BD is the bulk soil density (kg m^{-3}), and the particle density of the average mineral (quartz) soil is 2.65×10^3 kg m^{-3} according to [*Parton et al.*, 2001].

The temperature response of the soil NO release was derived from two sets of measurements of the NO release rate (each on another set of sub-samples of the same soil), where the sub-samples were always identically treated except for incubation at 18°C and 28°C, respectively.

Finally, equation (A1.2) is extended to describe the net NO release rate and its partitioning (P and k), for each soil sample, as a function of the relevant variables, headspace NO mixing ratio (= $m_{NO,,out}$), $WFPS$, and soil temperature (T_{soil}):

$$J_{NO}(m_{NO,out}, WFPS, T_{soil}) = P(WFPS, T_{soil}) - k(WFPS, T_{soil})\, m_{NO,out} \frac{M_N}{V_m} \times 10^{-3} \quad \text{(A1.4)},$$

A1.3.4 Error estimation

We found that autoclaved soils release NO at a rate of 0.05 ng kg^{-1} s^{-1} with a random deviation of 0.02 ng kg^{-1} s^{-1} at all WFPS. Therefore, we considered a NO release of 0.11 ng kg^{-1} s^{-1} (release rate of autoclaved soils plus three standard deviations from the mean release rate, with a confidence interval of 99.7%) as the experimentally derived detection limit for J_{NO} of our incubation technique. Furthermore, the error of the NO release rate measurements was determined experimentally by incubation of soils in four replicates. The mean standard deviation of the NO release rate in four replicates was found to be 0.03 ng kg^{-1} s^{-1} for all WFPS, i.e., lower than the experimentally derived detection limit of J_{NO} as well as the error that would result from the detection

limit of the NO mixing ratio by the chemiluminescence analyzer used. Based on these observations, we consider ± 0.05 ng kg^{-1} s^{-1} as a conservative estimate of the overall experimental error of J_{NO}.

A1.3.5 Up-scaling approach

NO release rates (J_{NO}), derived from laboratory incubations and parameterized for measured T_{soil}, WFPS, and m_{NO}, were up-scaled to estimate field net NO fluxes (F_{NO}) by applying the field measurements of these parameters. Similar up-scaling has already been reported by Kirkman *et al*., [2001], and verification of the up-scaling procedure has been repeatedly performed by demonstrating that NO fluxes, measured in the field by the dynamic chamber technique, were in good agreement with those derived from laboratory incubations on soil samples (taken from the top soil of dynamic chambers' enclosures, e.g., Ludwig *et al*., [2001], van Dijk *et al*., [2002]). Up-scaling is achieved by applying the modified (see below) algorithm developed by [*Galbally and Johansson*, 1989] and subsequently improved by [*Kirkman et al.*, 2001; *Meixner et al.*, 1997; *Meixner and Yang*, 2006; *Van Dijk et al.*, 2002; *Van Dijk and Meixner*, 2001]:

$$F_{NO}(WFPS) = \sqrt{D(WFPS)\,BD\,k}\left(\frac{P(WFPS)}{k} - m_{NOamb}\frac{M_N}{V_m}\times 10^{-3}\right)$$

(A1.5),

where F_{NO} is the estimated net NO flux (ng m^2 s^{-1}), BD is the bulk density of soil (kg m^{-3}), k is the NO consumption rate (m^3 kg^{-1} s^{-1}), D is the effective diffusion coefficient of NO in soil (in m^2 s^{-1}) calculated accordingly to [*Moldrup et al.*, 2000], P is the NO production rate (ng kg^{-1} s^{-1}) calculated from measured J_{NO} (Eq. A1.1) using equation (A1.4), and m_{NOamb} is the ambient NO mixing ratio (ppb). 2005 to 2006 field data of the NO mixing ratio (average of 2.39±0.56 ppb) were provided by the Israeli Ministry of Environmental Protection, from measurements at the Gush Ezion air quality monitoring station (distance of ~35 km from our research site; http://www.sviva.gov.il). Since corresponding soil moisture and soil temperature data were calculated as daily means, F_{NO} was up-scaled on a daily basis for all studied soils, for each sampling season and location (i.e., October 2005, February 2006, and May 2006, *forest*, *annuals,* and *shrub* soils).

In contrast to Meixner & Yang, [2006], we used in equation (A1.5) a constant NO consumption rate, *k,* (rather than *k*(WFPS)). We used two different *k* values for equation (A1.5). Firstly, we estimated *k* values of studied soils, based on lab incubations of the studied soils (in the WFPS interval of 5-18%). The *forest* soils have average *k* value of 0.67×10^{-5} m^3 kg^{-1} s^{-1}. The *annuals* soils have average *k* value of 3.65×10^{-5} m^3 kg^{-1} s^{-1}. We did not succeed to measure any *k* value for *shrub* soils, however, we assume that *shrub* soils are represent intermediate stage between fully plant covered *forest* and annuals covered *annuals* soils. Therefore we can assume that *k* values for the *shrub* soils need to be in between the measured *k* (1.58×10^{-5} m^3 kg^{-1} s^{-1}). The above mentioned *k* values are consistent with other, literature published *k* values (see below).

Secondly, we used a constant *k*-value of 1.6×10^{-5} m^3 kg^{-1} s^{-1} for the *forest*, *annuals,* and *shrub* soils, which was obtained from the report of Otter *et al* [1999] for semi-arid savannas, and which is in the range of *k* values for a wide range of soils [*Bollmann et al.*, 1999; *Gödde and Conrad*, 2000; *Rudolph et al.*, 1996].

Finally, we calculated gross F_{NO} for estimation of maximum NO flux from the studied soils. To this end we used uncorrected J_{NO} (eq. A1.2) data for fitting procedure (see below) and converted laboratory measured flux of ng kg^{-1} s^{-1} to ng m^{-2} s^{-1} using field BD for 0-10 cm soil layer. We assumed that main contribution to the soil NO flux is from this or shallower soil depth (c.f. [*Conrad*, 1994; *Remde et al.*, 1993]).

To describe the dependence of F_{NO} on WFPS at a constant reference soil temperature (T_{ref} = 28°C), we made use of equation (A1.5) to calculate data pairs (F_{NO}, WFPS) from our observations and fitted them similarly to the Meixner & Yang, [2006] procedure by a mathematical algorithm (OriginLab Corp., MA, USA):

$$F_{NO}\left(WFPS, T_{ref}\right) = y_{0T_{ref}} + \frac{A_{T_{ref}}}{w_{T_{ref}}\sqrt{\pi/2}} \times e^{b}$$

(A1.6), where $b = -2 \times \frac{(WFPS - X_{cT_{ref}})^2}{w_{T_{ref}}^{\ 2}}$ and from which y_{oTref}, A_{Tref}, w_{Tref}, X_{cTref}, can be derived.

Similar to [*Van Dijk et al.*, 2002; *Van Dijk and Meixner*, 2001], we assumed the dependence of F_{NO} on soil temperature to be an exponential relationship (the general form of temperature dependence for enzymatic processes). To quantify the relationships, we utilized our measurements on J_{NO} at two different incubation

temperatures (see ***Laboratory incubations***). The response of the NO release to soil temperature could be directly determined for any given WFPS in terms of Q_{10}, i.e.:

$$Q_{10}(WFPS) = J_{NO}(WFPS, T_{soil} = 28°C) / J_{NO}(WFPS, T_{soil} = 18°C)$$

(A1.7),

For the up-scaling procedure, we assumed that Q_{10} for F_{NO} (field) is the same as Q_{10} for J_{NO}, (lab) since both are assumed to be driven by the same microbial processes.

Finally, we combined the functional dependence of F_{NO} on soil moisture and soil temperature (Eqs. A1.6 and A1.7) and calculated the field net NO fluxes, F_{NO} (in ng m^{-2} s^{-1}), according to:

$$F_{NO}(WFPS, T_{soil}) = y_{0\,T_{ref}} + \frac{A_{T_{ref}}}{w_{T_{ref}}\sqrt{\pi/2}} \times e^{b} \times \exp\left[0.1 \times \ln Q_{10} \times \left(T_{soil} - T_{ref}\right)\right]$$

(A1.8),

where parameters as above and *WFPS* is calculated from the field measurements of VWC and field soil BD (see eq. A1.3), T_{soil} is the soil temperature at 6 cm depth, and T_{ref} is the incubation temperature (28°C; see ***Soil sampling and field methods*** and ***Laboratory incubations*** sections).

In order to up-scale the laboratory measurements, we divided the yearly data set (daily averages) of the field soil water content (5 cm depth) and soil temperature (6 cm depth) measured continuously in three different sections. These correspond to three different periods characterized by different field temperatures and WFPS dynamics, as well as by different NO release patterns during the laboratory incubations.

The three time periods that we defined were *dry-rewetting, wet,* and *drying*. The *dry-rewetting* period had two sub-periods: *dry* and *rewetting* periods, which will be referred to as *dry* and *rewetting*, respectively. The first, *dry*, sub-period (20 July to 10 October), was characterized by a stable WFPS of ~14% and a soil temperature well above 20°C (20 to 35°C). The second sub-period (*rewetting*), is the period from the first rain event with consequent drying of soil to almost *dry* period WFPS values. This period lasted from 11 October, when the first rain event took place, to 25 December, when the second significant rain event occurred (after which soils reached ~66% WFPS). During *rewetting*, WFPS varied from 14% to a maximum > 48% and, following drying of the soil, down to 26% again. The soil temperature during *rewetting* decreased from >20°C to ~15°C. The *wet* season ranged from December 25, 2005 to April 17, 2006, during which the WFPS remained quite high, between 40%

and 73%. The mean daily soil temperature was generally 10°C to 15°C, with a minimum of ~7°C. The *drying* season was taken to be from April 18, 2006 to July 19, 2006, accordingly to changes in WFPS and soil temperature. During the *drying* season, the soil temperature increased to >20°C and WFPS decreased back to the *dry* sub-period values of ~14% and remained stable.

We used the seasonally determined J_{NO}-values derived from the laboratory incubations of the soil samples from October 2005 (*dry-rewetting*), February 2006 (*wet*), and May 2006 (*drying*) and linearly interpolated (weighted linear interpolation) between the seasons to estimate the transitions between seasons. The soil temperature measurements from soils at a forest clearing were used for up-scaling the *annuals* NO emissions, and soil temperatures measured under the tree canopy were used for up-scaling *forest* and *shrub* NO emission (there were no continuous temperature measurements in the shrubland). The ambient NO mixing ratios we used for upscaling were provided by the Israeli Ministry of Environmental Protection and were 2.66±0.67 ppb for the *dry-rewetting* season, 2.42±0.61 ppb for the *wet* season, and 2.14±0.33 ppb for the *drying* season, respectively. Free surface area, s_i, was corrected for rocks, stamps, and tree stems (the latter two were insignificant) from 10 random transect walks during which a one-meter resolution description of the soil cover (i.e., free soil, rock, stamps and stems) was done. The sampling was performed on four, 30x30 m size, representative plots in the forest and four plots in the surrounding shrubland.

A1.3.6 Data processing

The data processing and calculations were done in Excel (Microsoft, USA) and with Origin graphing and analysis software (OriginLab Corp., MA, USA).

A1.4 Results

A1.4.1 Laboratory results

A1.4.1.1 NO release rates from different sites and seasons

The NO release rates from all soils had strong seasonal and spatial variability, as shown in figure A1.1 (a – c), where NO release rates are shown which have been sampled in October 2005, February 2006, and May 2006 from *forest*, *shrub*, and *annuals* soils (all results obtained at T_{soil} = 28°C and $m_{NO,ref}$ = 0 ppb). Maximum NO

release rates occurred in the soils sampled in October 2005 and the minimum NO release rates occurred in the soils sampled in February 2006. *Forest* and *shrub* soil samples from October 2005 had lower maximum release rates than the *annuals* soils. The NO release rates were 63.7% and 58.5% lower for *forest* soils and *shrub* soils (1.32, 1.51 and 3.64 ng kg^{-1} s^{-1}, respectively for *forest*, *shrub,* and *annuals* soils). All soils sampled in February 2006 had low maximum release rates of 0.12, 0.29, and 0.38 ng kg^{-1} s^{-1} for the *forest*, *shrub*, and *annuals* soils, respectively. The February 2006 results indicated 68.4% and 23.7% lower maximum release rates for *forest* soils and soils, respectively, under *shrub,* compared with the *annuals* soil, similar to the soils sampled in October 2005 (Fig. A1.1).

However, the soil samples from May 2006 showed a different NO release pattern. In all samples, the maximum release rates were higher than from the soils sampled in February 2006. The maximum release rates from the *shrub* soils were higher than those from *annuals* and *forested* soils: 1.03, 0.74, and 0.35 ng kg^{-1} s^{-1}, respectively.

$WFPS_{opt}$ (i.e., WFPS at maximum NO release rates for a given soil) can be used as a first approximation for (a) the microbial process responsible for the emitted NO (e.g., anaerobic or aerobic metabolism) and (b) the maximum potential rate of the NO production process [*Conrad*, 2002; *Williams*, 1992]. We found that soils sampled during different seasons exhibited comparable $WFPS_{opt}$. The *forest* samples in all incubations showed a $WFPS_{opt}$ at ~24%. The $WFPS_{opt}$ for NO release from the *shrub* soils changed from 26% (October 2005), to 32% (February 2006), and 23% (May 2006). Soil samples from the *annuals* soils revealed a $WFPS_{opt}$ of 27% (October 2005 and February 2006), and 24% (May 2006).

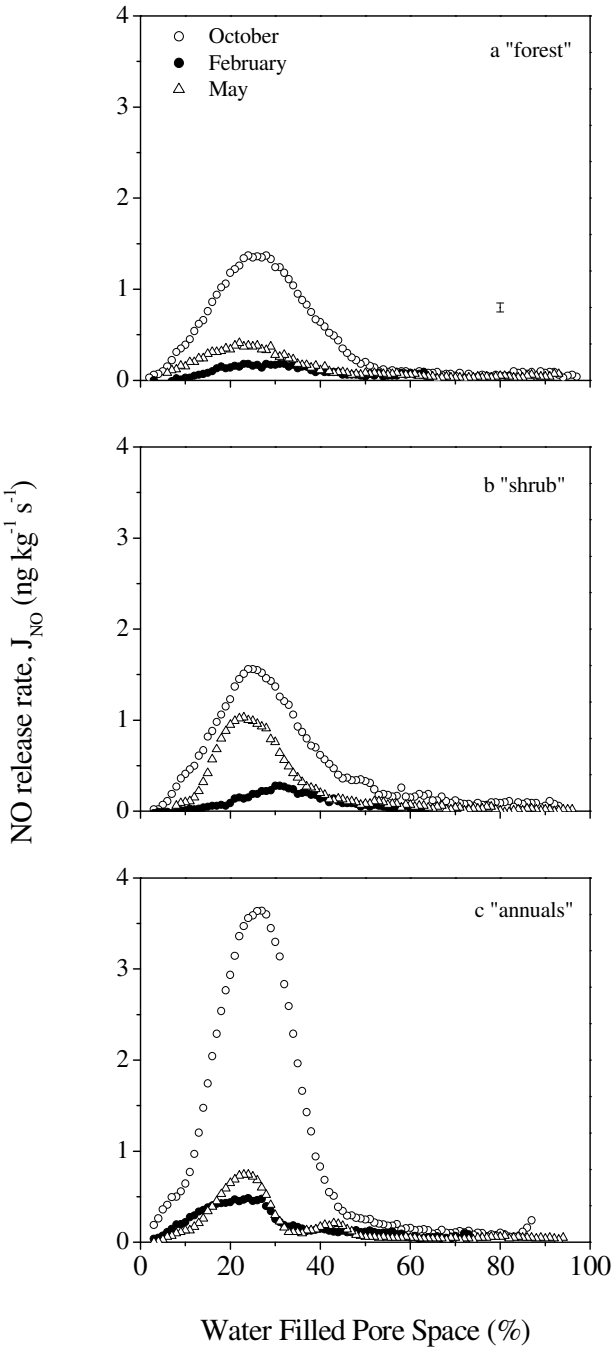

Figure A1.1 Seasonal variability of the release rate J_{NO} (at T_{soil} = 28°C and $m_{NO,ref}$ = 0 ppb) from soil samples of (a) Yatir forest soil (*forest*), (b) surrounding shrubland soil (under shrub canopy; *shrub*), and (c) inter-shrub (*annuals*) soil; open circles, filled circles, and open triangles represent soils sampled in October 2005, February 2006, and May 2006, respectively. A representative error of J_{NO}

measurements (0.05 ng kg^{-1} s^{-1}, in terms of mass of N; see section *Error estimation*) is shown in figure 6.1a.

A1.4.1.2 The temperature response of net NO release rates

The corresponding results for temperature response in different soils (obtained at $m_{NO,ref} = 0$ ppb) are shown in figure A1.2 (a – f). The reduction of incubation temperature from 28°C to 18°C of the Yatir forest soils sampled in October 2005 and May 2006, resulted in a similar shift of $WFPS_{opt}$, namely, from approximately 24% toward 40% (Fig. A1.2 a, b). In contrast, *annuals* soils showed a decrease in the $WFPS_{opt}$ when incubated at 18°C, and corresponding $WFPS_{opt}$ values were shifted from 24 to 27% (28°C) toward 17 to 21% (18°C) (see Fig. A1.2 e, f). *Shrub* soils showed a shift of the $WFPS_{opt}$ from 26% (28°C) to 62 % (18°C) for the October 2005 samples and from 23% (28°C) to 32% (18°C) for the May 2006 samples (Fig. A1.2 c, d).

For the sake of simplicity, we would like to consider the observed temperature dependence of J_{NO} for the different soil samples in terms of $Q_{10}^{*} = Q_{10}(WFPS_{opt})$, calculated as the ratio of $J_{NO}(WFPS_{opt}, 28°C)$ and $J_{NO}(WFPS_{opt}, 18°C)$. The Q_{10}^{*} value was strongly dependent on the soil origin (i.e., *forest*, *shrub,* and *annuals* soils) and the sampling period. Whereas the *forest* soils from October 2005 showed a Q_{10}^{*} of 4.1, the *forest* soil samples from May 2006 showed virtually no temperature response (Q_{10}^{*} = 1.1; Fig. 2 a, b). The *shrub* soils revealed a Q_{10}^{*} from 4.4 to 3.0, and the *annuals* soils revealed a Q_{10}^{*} from 3.5 to 0.95 for the October 2005 and May 2006 samples, respectively (Fig. A1.2 c, d, e, and f).

Integration of the overall mass of NO released from the soils during the entire incubation with different temperatures revealed the following results: *forest* soils showed a NO release reduction by a factor of 3.9 and 0.9, *shrub* soils showed a reduction of 10.5 and 2.9, and *annuals* soil showed a reduction of 3.1 and 0.8 for the October 2005 and May 2006 soil samples, respectively.

To summarize, a reduction of the incubation temperature by 10°C resulted in changes in both the $WFPS_{opt}$ and the Q_{10}^{*} of the different soils on both spatial (i.e., between soils with different vegetation cover) and temporal (i.e., seasonal) scales (Fig. A1.2).

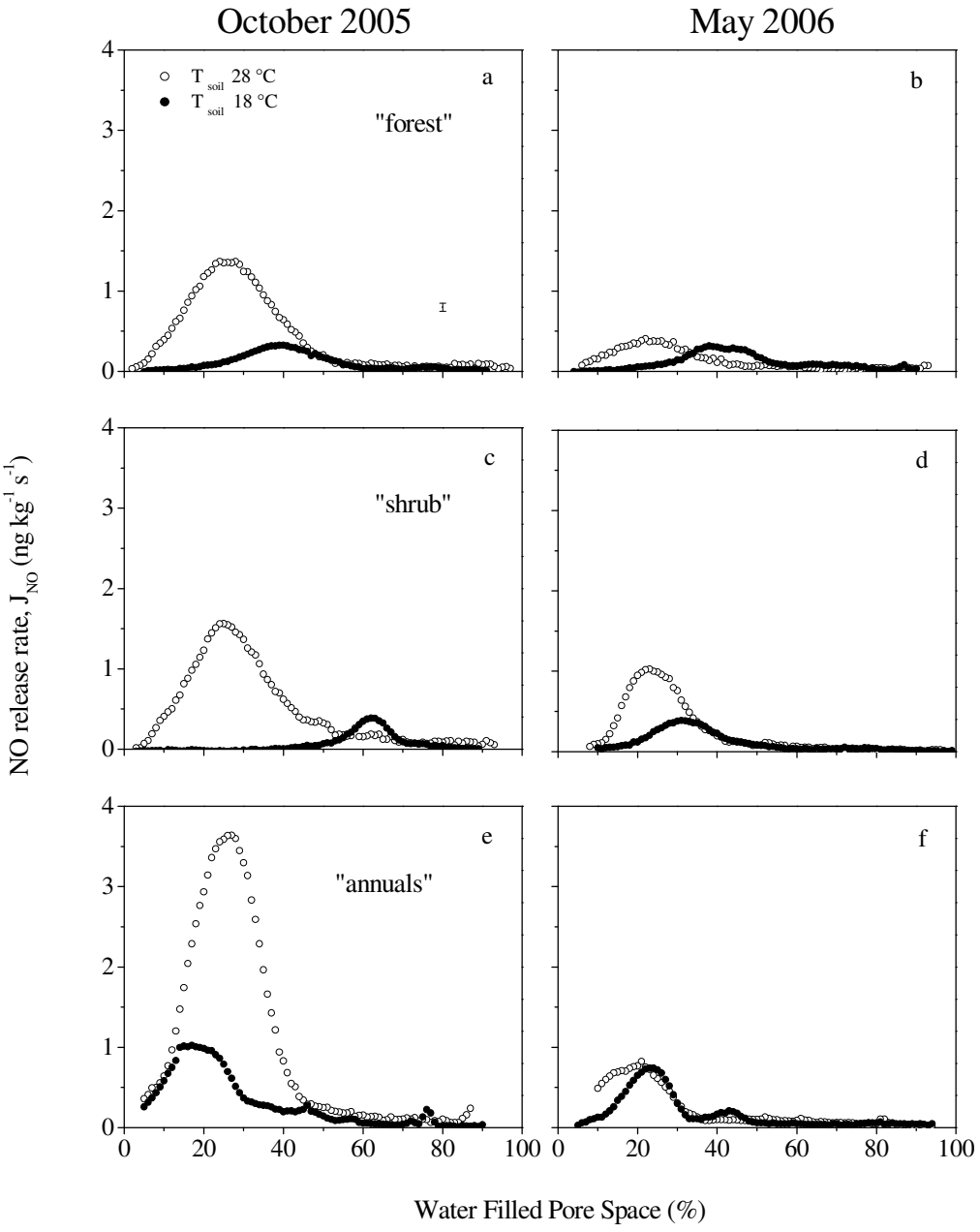

Figure A1.2 Temperature dependence of NO release rates J_{NO} (ng kg^{-1} s^{-1}; in terms of mass of N) of soils sampled in October 2005 and May 2006 and incubated at $m_{NO,ref}$ = 0 ppb: Yatir forest (*forest*; a, b); under shrub canopy (*shrub*; c, d), and inter-shrub soils (*annuals*; e, f). Open circles represent incubations at T_{soil} = 28°C and filled circles at T_{soil} = 18°C, respectively. A representative error of J_{NO} measurements (0.05 ng kg^{-1} s^{-1}, see *Error estimation*) is shown in figure 2a.

A1.4.2 Up-scaling results

In order to evaluate the effect of afforestation of the shrubland on biogenic soil NO emissions, we up-scaled the laboratory measurements, using field measured soil temperature and water content. Results of our up-scaling exercise, namely, annual cycles of the daily F_{NO}-estimates for *forest*, *shrub*, and *annuals* soils are shown in figure A1.3 (a to c), together with the annual course of mean daily soil temperatures and soil moistures (WFPS). The results from figure A1.3 were integrated for each of the three 'seasons' and given as mean daily sums (to fit with the time scale of the environmental measurements) in Table A1.1.

Up-scaled NO emissions were found to be sensitive to measured T_{soil}, WFPS, specific soils, and exhibited distinctive seasonal patterns. Maximum NO emissions were calculated during the *dry-rewetting* season, when the WFPS was stable (around 14%), and T_{soil} increased above 20°C. The highest emission rates were calculated from the *annuals* soils and the minimum emission rates were from *forest* soils (Fig. A1.3; Table 6.1). We were able to show the emission peak after the first significant rain event (November 21, 2005) and subsequent drying in all three studied ecosystems (Fig. A1.3, "December"). An additional peak of NO emission occurred during the *drying* period after the *wet* season, along with the rise in soil temperature (Fig. A1.3b, c, "May – June"). However, this peak was almost absent in the *forest* soil. Low emissions during the *wet* season were calculated for all ecosystems, because of (a) low release rates observed during the corresponding laboratory incubations (see Fig. A1.1), and (b) high WFPS and low soil temperatures measured in the field (Fig. A1.3).

Table A1.1. Mean daily ($D(NO)_i$) and annual ($A(NO)_i$) NO emission rates for different seasons and soils of the Yatir forest and shrubland ecosystems. Number of days of each season (j in Eq. A1.9 used for upscaling), where *dry-rewetting=20 July 2005 to 24 December 2005*; *wet=25 December 2005 to 17 April 2006; drying=18 April 2006 to 19 July 2006*. The type of micro-site (i used in Eq. A1.9 for upscaling): *forest, shrub* (i.e. under-shrubs samples*), annuals* (inter-shrub samples), are indicated and the under-shrub and inter-shrub components are integrated into the *shrubland* ecosystem; s_i is the respective free soil surface area (corrected for contribution of rocks, stamps, and stems). Estimates are based on lab incubations of soil samples collected in the different seasons and microsites using a mean literature k value for semi-arid environment, or (given in parentheses) using microsite-specific values based on limited estimates of k using our soil samples [a] and using gross emission rates [b] (see ***Methods*** section).

		Seasonal mean of daily NO emissions $D(NO)_I$ [mg m^{-2} d^{-1}]			
		microsite (i)			
Season	Days (j)	*shrub*	*annuals*	*shrubland*	*forest*
Area contribution s_i (in %)		25±3	56±2	81±3	86±5
dry-rewetting	158	0.06 (0.14) [a] (1.66) [b]	0.25 (0.17) [a] (11.73) [b]	0.16 (0.13) [a] (13.40) [b]	0.06 (0.12) [a] (5.09) [b]
Wet	114	0.01 (0.00) [a] (0.15) [b]	0.00 (0.00) [a] (0.66) [b]	0.00 (0.00) [a] (0.81) [b]	0.00 (0.00) [a] (0.54) [b]
Drying	93	0.05 (0.08) [a] (1.39) [b]	0.11 (0.02) [a] (5.20) [b]	0.07 (0.07) [a] (6.59) [b]	0.03 (0.04) [a] (3.01) [b]
Annual rate	365	0.04 (0.08) [a] (1.12) [b]	0.14 (0.08) [a] (6.61) [b]	0.09 (0.06) [a] (7.73) [b]	0.03 (0.06) [a] (3.14) [b]
Annual mean NO emission $A(NO)_i$ (kg $ha^{-1}a^{-1}$) (season and area weighted)				**0.32** **(0.24)** [a] **(28.15)** [b]	**0.11** **(0.20)** [a] **(11.44)** [b]

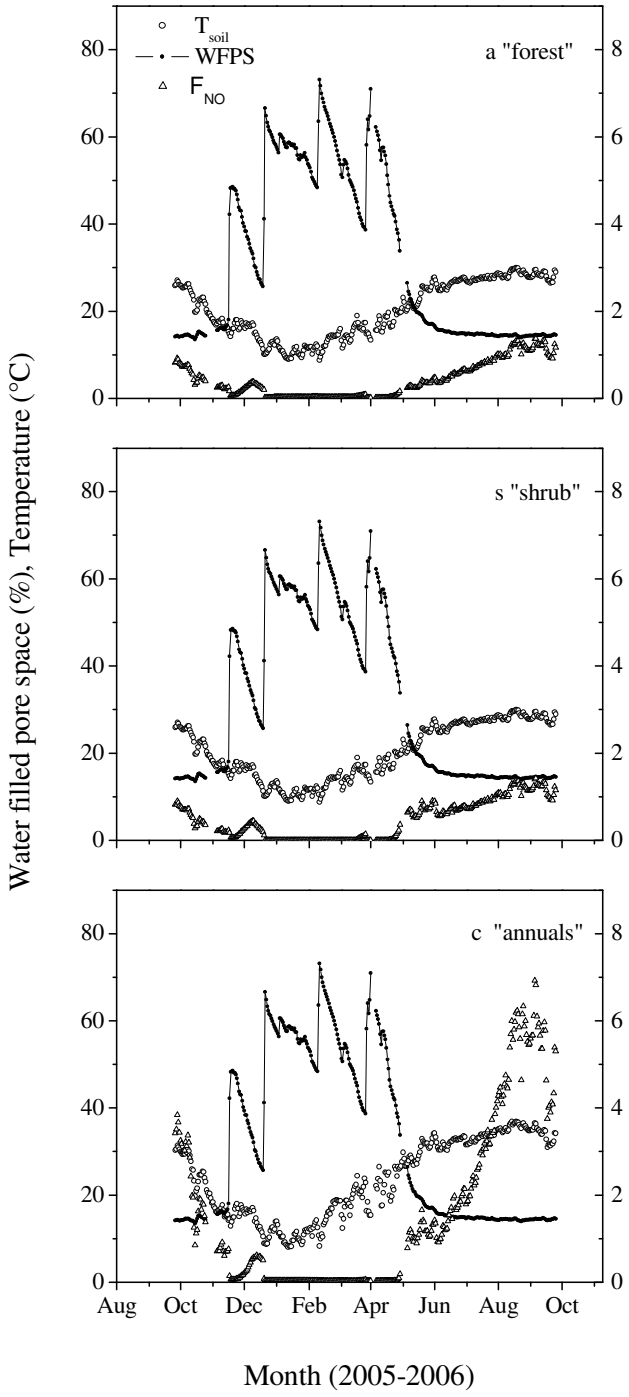

Figure A1.3 Results of up-scaling NO emission fluxes from laboratory incubations of soil samples from the Yatir forest ecosystem based on measurements of soil water content (at 5 cm depth) and soil temperature (at 6 cm depth) in the field; (a) Yatir forest (*forest*), (b) under shrub canopy (*shrub*), and (c) inter-shrub (*annuals*), soil. Open circles indicate soil temperature (°C), open triangles indicate the

NO emission flux (ng m^{-2} s^{-1}, in terms of mass of N), and dash line represents water filled pore space (%).

Seasonal trends in mean daily NO emissions and mean annual NO emissions ($A(NO)_i$) of each soil cover type (i = *forest*, *shrub*, *annuals*; Table A1.1) were calculated by summing up individual daily $D(NO)_i = F(NO)_i \times (8.64\times10^{-2})$ emission rates over the corresponding number of days (j) of each season, considering the relative free soil area s_i (i.e., after subtracting the estimated area of rocks, stamps, and stems, see section A1.2.5) of the individual microsites:

$$A(NO)_i = s_i \times \left(\sum_{j=1}^{j=158} D(NO)_{dry-rewetting,i,j} + \sum_{j=1}^{j=114} D(NO)_{wet,i,j} + \sum_{j=1}^{j=93} D(NO)_{drying,i,j} \right) \times 10^{-2}$$

(A1.9),

where i = *forest*, *shrub*, *annuals*, s_i is in %, $D(NO)_i$ is in mg m^{-2} d^{-1}, and $F(NO)_i$ is in ng $m^{-2}s^{-1}$ (in terms of the mass of nitrogen). The season- and area-weighted mean annual biogenic NO emission for the *forest* soil was 0.11±0.01 kg ha^{-1} a^{-1}, whereas emission from surrounding shrublands (*shrub* covered and *annuals* soils) was 0.32±0.02 kg ha^{-1} a^{-1} (about 67% of soil NO emission reduction; Table A1.1).

Annual NO emission rates, calculated using microsite specific values based on limited estimates of k using our soil samples showed different results. The season- and area-weighted mean annual biogenic NO emission for the *forest* soil was 0.20 kg h^{-1} a^{-1} whereas emission form surrounding shrublans was 0.24 kg h^{-1} a^{-1} (about 17% of soil NO emission reduction, Table A1.1). To eliminate k related differences between the estimation of annual NO emission rates we calculated "gross" emission rates using our lab measured J_{NO} (see ***Up-scaling approach***). The season- and area-weighted mean annual biogenic NO emission for the *forest* soils accordingly to this calculation was 11.44 kg h^{-1} a^{-1} whereas emission from the shrubland was 28.15 kg h^{-1} a^{-1} (more then 55% of soil NO emission reduction, Table A1.1).

A1.5 Discussion

A1.5.1 Effects of the environmental variables on NO emission

The laboratory incubations of the soils revealed a seasonal pattern, with the highest NO release rates from soils sampled in the *dry-rewetting* season, and the lowest release rates from soil samples in the middle of the *wet* season (Fig. A1.1). These seasonal trends can be explained by corresponding patterns of soil temperature and

soil water content and assuming continuous adaptation of the soil microbial community to the changing conditions [*Harris et al.*, 1996; *Johansson and Sanhueza*, 1988; *Levine et al.*, 1997; *Scholes et al.*, 2003a; *Smith et al.*, 2003]. The estimate from our up-scaling approach of high ecosystem-scale NO emissions after rewetting of dry soils is consistent with other studies of semi-arid ecosystems, which have also attributed high NO emission to the increase in water availability for microbial activity [*Davidson et al.*, 1993; *Hartley and Schlesinger*, 2000; *Martin et al.*, 2003a; *Meixner et al.*, 1997]. We attribute both the low NO release rates derived from laboratory incubations and the low NO emission rates obtained from up-scaling during the *wet* season to the fact that during this season (a) the soils are too wet to allow good aeration, and (b) the soil temperature is markedly below the optimum for microbial activity (WFPS>40%; T<15°C; [*Conrad*, 1996; *Meixner and Yang*, 2006; *Williams*, 1992]). Decreases of NO flux during high soil moisture regimes were also shown by [*Rosenkranz et al.*, 2006] and were partly attributed to enhanced aerobic NO consumption by heterotrophic nitrifiers [*Rosenkranz et al.*, 2006]. Alternatively, the decrease of NO flux with increasing soil water content could also be explained by a decrease in nitrification activity due to reduced diffusion of the oxygen into the soil. However, this is inconsistent with in situ nitrification activity and mineralization rates in soils that showed opposite trends, namely, an increase to ~0.4 μg g^{-1} $week^{-1}$ (in terms of soil dry weight) from virtually zero, with increasing soil water content [*Gelfand and Yakir*, 2008]. During the *drying* season, soils showed intermediate NO emission rates; lower than during *dry-rewetting* seasons and higher than *wet* season rates (Table A1.1). We can explain these findings by the increase in soil temperature, together with a decrease in the soil water content towards optimum conditions ($WFPS_{opt}$) for NO emission. We hypothesize that the seasonal pattern of NO emission from soils is due to gradual changes in both soil temperature and soil water content, which induce activation of different microbial sub-populations [*Avrahami*, 2002; *Avrahami and Bohannan*, 2007]. During the start of the *rewetting* season, nitrifying bacteria have a temporal advantage regarding N supply because of their fast recovery from drought and because of their relative tolerance to high-temperatures [*Gelfand and Yakir*, 2008; *Hastings et al.*, 2000].

Two mechanisms for NO formation in soils from seasonally dry tropical forests have been proposed by Davidson et al [1993], namely, oxidation of ammonia and the chemo-denitrification of HNO_2 (nitrous acid), an intermediate of both the nitrification

and denitrification processes. Both mechanisms would take place in our ecosystem. Our previous study of soils representing the *dry-rewetting* season from our ecosystems indicated high activity of ammonia oxidizing microorganisms and a temporal delay between the ammonia and nitrite oxidation [*Gelfand and Yakir*, 2008]. The second proposed mechanism for NO formation is self-decomposition of HNO_2 and the possible reaction of HNO_2 with soil organic matter. This NO formation pathway is generally expected to be more important in acidic soils (pH < 5.5; [*Van Dijk et al.*, 2002]). However, during nitrification, both nitrite (NO_2^-) and H^+ may accumulate and possibly result in acidified microsites, even in alkaline soils, where conditions can favor the formation of HNO_2 and therefore NO. Finally, nitrite was shown to enhance NO production in the soils [*Davidson et al.*, 1993]. From the above, we can conclude that enhanced NO emission during the *dry-rewetting* season is consistent with both the presence of HNO_2 and the relatively high ammonia concentration in the soil.

The possibility of NO uptake by the soil was noted in the past and was assumed to be an integral part of the N metabolism in soil; a corresponding concept of a NO compensation mixing ratio in soils was defined by [*Conrad*, 1994]. According to equation (A1.5), the NO compensation mixing ratio is given by $m_{NO,comp} = P/k$ [*Remde et al.*, 1993]. From our deduced *k*-values (see section A1.2.5) and from the range of J_{NO} (observed at $m_{NO,ref}$ = 0 ppb; Fig. A1.1), we estimated the NO compensation mixing ratios for *forest*, *shrub*, and *annuals* soils to be 149.3, 170.8, and 413.6 ppb NO. These NO compensation mixing ratios fall within the wide range of values reported from laboratory study (15 to 600 ppb; [*Remde et al.*, 1993; *Remde et al.*, 1989]. As discussed previously [*Otter et al.*, 1999] and references within) these values are much higher than those found in field studies. A sensitivity test using our data indicated that up scaling of NO incubation data to the field scale, critically depended on considering the large seasonal changes in J_{NO} (Fig. A1.3) and reliable estimate of *k*, and is less sensitive to variations in WFPS and temperature. In our scaling up experiment, there was no indication of no nitric oxide uptake fluxes (NO deposition), which is most likely because the low ambient NO mixing ratios (annual mean 2.39±0.56 ppb, see section A1.2.5) never exceeded the estimated NO compensation mixing ratio.

Similar values of $WFPS_{opt}$ for *forest*, *shrub*, and *annuals* soils (Fig. A1.1) pointing towards similar composition of microbial populations in these soils. Thus, the

difference in NO release rates among sites and seasons might be explained by changes in the microbial activity rates and the influence of plant activity, such as N uptake from the soil and microsite conditions, such as carbon availability for heterotrophic microbes [*Cookson et al.*, 2007; *Hackl et al.*, 2004; *Hartley and Schlesinger*, 2000; *Meixner et al.*, 1997].

Rates of NO release in soils with different vegetation cover revealed different dependencies on soil temperature (Fig. A1.2). The observed Q_{10}* of the NO release appears to be not only soil specific, but also season specific. Similar seasonal and spatial variations in Q_{10} were recently shown for CO_2 efflux in a Sierra Nevada forest plantation [*Xu and Qi*, 2001]. Soil temperature controls on the NO emission (e.g., Q_{10}) seem to be more important for short-term variations of the NO release, whereas the magnitude of the biogenic release rates is predominantly controlled by other seasonal factors such as soil water content and N availability [*Meixner and Yang*, 2006]. From figure A1.2, it can be seen that for our *forest*, *shrub*, and *annuals* soils, there is no simple relationship between soil temperature, and NO release rates cannot be simply explained by $Q_{10} = 2$ or any alternative constant [*Brierley et al.*, 2001; *Fierer et al.*, 2003; *Gödde and Conrad*, 1999; *Wang et al.*, 2004]. The Q_{10}* calculated for our soils ranged from 0.95 up to 4.4.

Our results show that when considering the annual time-scale, inter-seasonal variations in soil NO release, as well as factors influencing it, must be considered. When taken into account, the average soil NO release rates for our ecosystems were on the lower end of published NO release rate estimates in other semi-arid biomes [*Davidson and Kingerlee*, 1997; *Meixner and Yang*, 2006]. Specifically, published NO release estimates for semi-arid and arid ecosystems range from 1.8 to 3.8 ng m^{-2} s^{-1} for dry tropical forests [*Davidson et al.*, 1993]), 0.1 to 3.7 ng m^{-2} s^{-1} for Miombo woodland and grassland in Zimbabwe [*Kirkman et al.*, 2001], 0.3 to 21.9 ng m^{-2} s^{-1} for South African savannas [*Parsons et al.*, 1996], and 0 to 4.9 ng m^{-2} s^{-1} for the Chihuahuan Desert, New Mexico [*Hartley and Schlesinger*, 2000]. The annual, seasonally weighted mean NO release values in our ecosystems were 0.4, 0.5 and 1.6 ng m^{-2} s^{-1} for the *forest*, *shrub* and *annuals* soils, respectively (converted from Table A1.1).

A1.5.2 Influence of afforestation on the NO emission

Information on the influence of land use change on NO emission, including type of vegetation covers or proportion among microsites (e.g., *shrub* and *annuals* types) is limited at present. NO emissions were shown to decrease with decreasing soil cover [*Davidson et al.*, 1993; *Martin and Asner*, 2005], grassland and savanna soils were shown to be stronger sources of NO emission than soils with greater vegetation cover [*Kirkman et al.*, 2001; *Williams*, 1992]. Note that in the shrubland, the emission estimate is sensitive to the proportions of *shrub* and *annuals* soil covers since both had different average release rates (0.04 and 0.14 mg m^{-2} d^{-1}, respectively). The main effect observed here is therefore in going from annuals covered soil to the forest soil (release rate of 0.03 mg m^{-2} d^{-1}). Considering the proportion of land cover by shrubs and annuals soil (see Table A1.1), the up-scaled rates for our particular case indicated ~65% apparent reduction in NO release rates (from 0.32 to 0.11 kg ha^{-1} a^{-1}) associated with the afforestation.

However, when using lab estimated *k* values and gross emission values, large differences in soils NO emission reduction were observed. Use of lab estimated *k* values for upscaling procedure revealed only 17% reduction (0.24 to 0.20 kg ha^{-1} a^{-1}) of annual NO emission and gross emission rates showed 59% (28.15 to 11.44 kg ha^{-1} a^{-1}) of reduction. These differences in estimation of afforestation effect reveal need in further research and better understanding of the processes that lead to NO consumption by soils and particularly better estimation of the NO consumption factor (*k*).

Despite of fact that use of different parameterization for upscaling method resulted in different estimation of afforestation effect on the soil NO emission we can point on the strong tendency to emission reduction. We speculate that the reduction in NO flux is due to increased N uptake by the forest trees (there was ~2.5-fold increase in ecosystem organic carbon stock, associated with afforestation), reducing soil N availability for nitrification [*Grünzweig et al.*, 2007; *Jackson et al.*, 1989; *Kaye and Hart*, 1997; *Zak et al.*, 1990].

The importance of the seasonal effect was especially apparent in up-scaling the laboratory results to the ecosystem scale (Fig. A1.3). For example, if we would calculate the annual NO release rates for the Yatir forest with the data from the laboratory incubations of the October 2005 samples alone, we would overestimate the

annual release rates by 48%. Similarly, if we would use data from the February 2006 soil samples alone, we would underestimate the annual release rates by 73%.

Because of the observed sensitivity to sampling location, date, soil cover and consumption rate in the semi-arid ecosystems, it seems important that further studies using soil samples incubations should consider (a) at least one soil sample per distinct season, (b) incubation of the samples under corresponding field conditions (e.g., average field water content and soil temperature at the time of soil sampling) and (c) explicit determination of the *k*-values.

A1.6 Conclusions

Soils from the Yatir forest and surrounding shrubland were analyzed to examine the effects of afforestation on NO emission. All studied soils showed considerable variability in the seasonal and spatial patterns of NO release rates and NO emissions. The seasonal pattern of laboratory-derived NO release rates were used, together with data from soil moisture and soil temperature measurements in the field, to up-scale NO emissions to the ecosystem scale. We found that afforestation in the semi-arid northern Negev shrubland reduced soil NO emissions by about 65% in comparison with the native shrubland. The average annual NO emissions from *forest*, *shrub*, and *annuals* soils (12.9, 15.4 and 49.4 mg m^{-2} a^{-1}) are at the lower range of previous estimates for biogenic NO emission from arid and semi-arid ecosystems. We emphasize the predictive power of our up-scaling procedure, which is based on (a) seasonal soil sampling, (b) incubation under a corresponding soil moisture, temperature, and ambient NO mixing ratio, and (c) application of a comprehensive and validated up-scaling algorithm.

A1.7 Acknowledgements

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Appendix 2: Other Studies

Section 3 in this chapter has been published in:

> Ganzefeld L.N., Eerdekens G., Feig G.T., Fisher H., Harder H., Königstedt R., Kubistin D., Martinez M., Meixner F.X., Scheeren B., Sinha V., Taraborrelli D., Williamn J., Vilà-Guerau de Arellano J., and Lilieveld J. **Surface and boundary layer exchanges of volatile organic compounds, nitrogen oxides and ozone during the GABRIEL Campaign**, *Atmospheric Chemistry and Physics*, 8, 6223-6243, 2008

A2.1 Introduction

During the course of this PhD the emission of NO from soils sampled in a number of other places was measured. These measurements formed parts of other studies, or occurred when opportunities for obtaining soil samples from other regions were presented. While these studies were individually not large enough to constitute entire chapters on their own, I believe that they should be included as their results do reflect on the overall findings, and should be discussed within the context of this study.

A2.2 Sahara

In January 2006 four soil samples were taken along a transect through Libya. Soil sampling and the measurement of the net potential NO flux was carried out in the same way as in the other studies, although the soils were only incubated at one temperature, 25°C and two NO concentrations, 0ppb NO and 56ppb NO.

- The first set of samples, (Libya 1) was taken at 31°52'52.00''N 11°32'16.00''E approximately 500m off the side of the road 40 km from the town of Nalut.
- The second set of samples, (Libya 2) were taken at 28° 31'12.77 N; 12°30'47.78E
- The third set of samples (Libya 3) were taken at the oasis of Oum el Rhessas 26°52'55.66''N; 13°17'55.47''E. This is a salt water oasis, however the small scale cultivation of date palms occurred and there was evidence of the activity of livestock such as camels and goats.
- The fourth set of samples (Libya 4) were taken outside the town of Ghat 25°00'03.04"N; 10°10'54.33" E.

Of the four sites that were sampled the net release of NO from three of the sites (Libya 1, Libya 2, Libya 4) was less than the detection limit of our laboratory method (J= 0.1 ng kg^{-1} s^{-1} see chapters 3.3.4 and 4.3.7) and therefore there was no clear evidence of the production of NO at these sites. The 3rd site (Libya 3) which was situated at the oasis of Oum el Rhessas showed an emission of NO that was sufficient to measure and therefore further analysis is based on that sample.

A2.2.1 NO flux

The maximum NO flux occurred at 9.4% WFPS and reached a maximum of 0.67 ng m^{-2} s^{-1}. In figure A2.1 the calculated and the fitted NO flux for Libya 3 is shown. Unfortunately the temperature dependence for the soils of the Sahara was not determined and therefore we were not able to discuss the effect of incubation temperature.

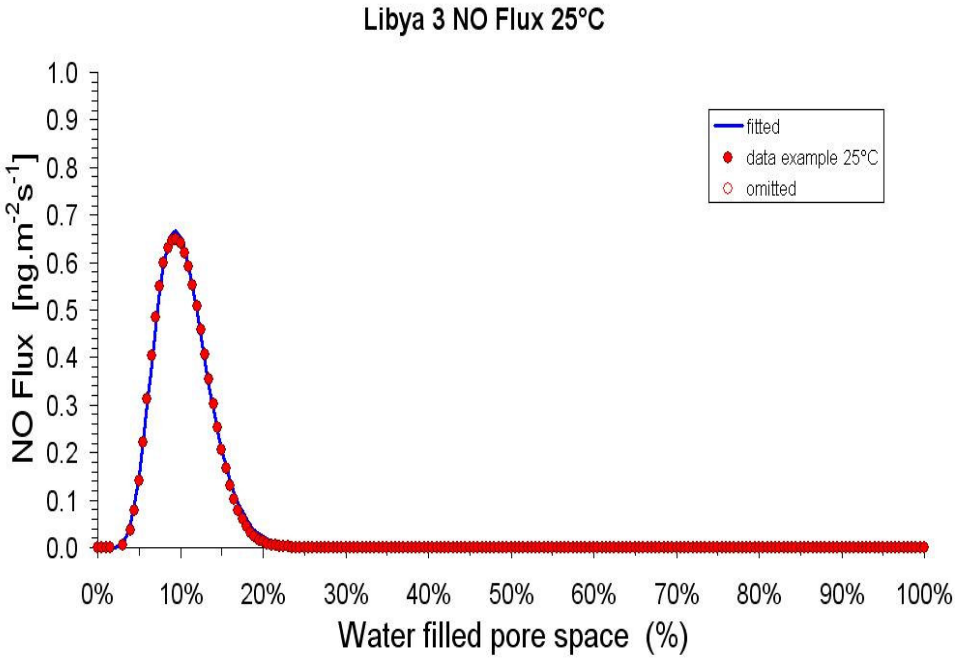

Figure A2.1 Potential Flux of NO Libya 3 soils at an incubation temperature of 25°C

The optimal WFPS found in the Sahara is very similar to that found in the hyper-arid Namib Desert [*Feig et al.*, In Prep] (chapter 5) where the optimal soil moisture ranges from 4.5% for the Gravel plains ecosystem to 10% in the Riparian Ecosystem.

A2.2.2 Consumption mixing ratio (*k*) and compensation mixing ratio ($m_{NO,comp}$)

The NO consumption rate (*k*) (Fig. A2.2) and the compensation mixing ratio show a similar pattern to the NO flux; where a maximum is reached at a soil moisture content of 9.5% WFPS. The NO consumption rate reaches a peak of 4.2x 10^{-5} at 9.5% WFPS. At soil moisture contents below 2% WFPS and above 20% WFPS the NO emission and consumption activity are greatly reduced.

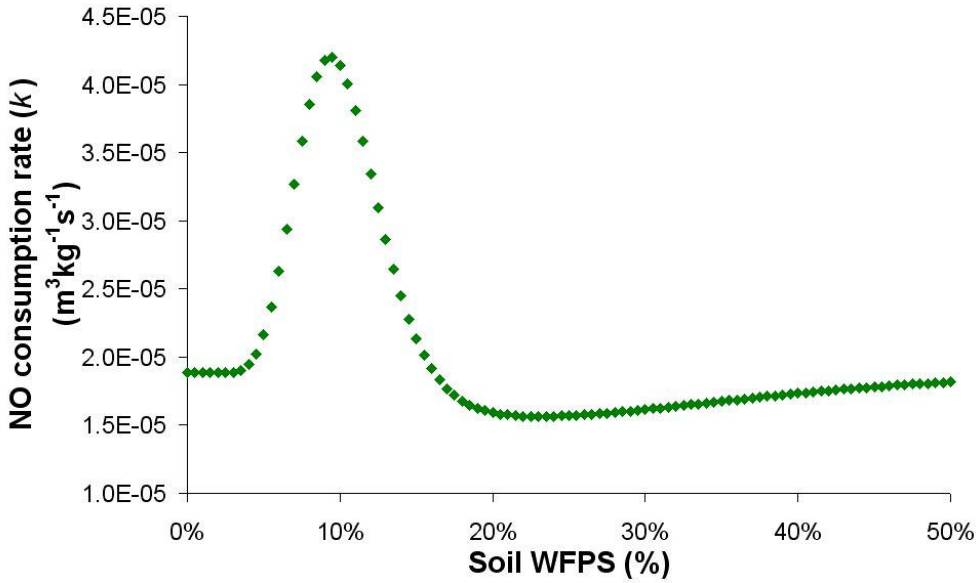

Figure A2.2 NO consumption rate k for Libya 3 soils at 25°C incubation

The compensation mixing ratio is shown in figure A2.3. The $m_{NO,comp}$ reaches a peak of 27 ppb at 9.5% WFPS, which is the same WFPS where the optimal NO flux occurs. The peak $m_{NO,comp}$ for the Sahara soils is within the dry season range of values for Zimbabwe reported by [*Kirkman et al.*, 2001] and is in the lower end of the range of values reported in the Kalahari [*Aranibar et al.*, 2004; *Feig et al.*, In Press-b] (see Fig. 4.12). For a full comparison with reported values from other studies see figure 6.9.

To the best of our knowledge this is the first time that the emission of NO has been examined from the Sahara Desert. Of the four samples that were taken three of them showed no detectable release of NO, it must therefore be assumed that the emission of NO in large regions of the Sahara does not occur and that NO emission is limited to discrete points in the landscape, such as in the vicinity of oases. The difference between the general absence of potential NO emission in the Sahara and the ubiquitous potential for NO emission in the Namib, which has similar levels of mean annual precipitation, may be due to the regular occurrence of fog events in the Namib, which do not occur in the Libyan section of the Sahara. These fog events may provide sufficient moisture to the microbial community in the soil surface to maintain a viable microbial population that can respond when the soil becomes moist. It is known that in certain hyper-arid deserts the conditions are so unfavourable to biological activity that virtually all signs of life are absent [*Navarro-Gonzalez et al.*, 2003] such a

situation may have occurred with regard to the populations of nitrifying bacteria in the Sahara.

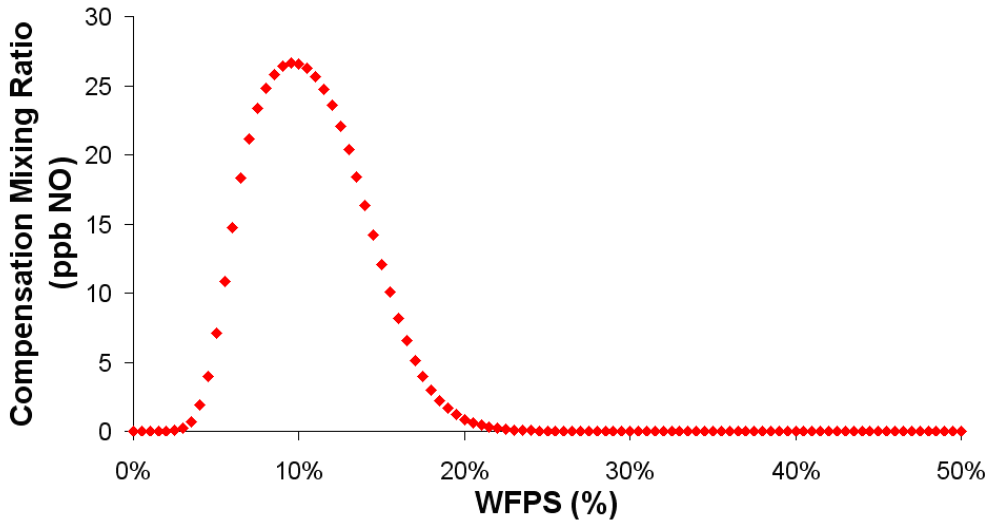

Figure A2.3 NO consumption rate (k) and the NO compensation mixing ratio for Libya 3 soils at 25°C incubation as a function of the soil WFPS.

A2.3 Surinam

During the GABRIEL experiment that took place in Surinam during October 2005, soils were sampled from two sites within the Amazon rainforest near the town of Brownsburg. This data has been used in the publication by Ganzeveld et al [2008]. For the Ganzeveld [2008]study the net release of NO from the soil (*J*) was determined under two NO concentrations; 0ppb NO and 56ppb NO and also under two temperatures; 25°C and 35°C. This truncated measurement (incubation of the soil under 56ppb NO at a 35°C incubation temperature did not occur) allowed us to determine the NO flux at 25°C and determine the Q_{10} temperature dependence for the release of NO, which we assumed would be the same as for the release of NO. The optimum WFPS differed between the two sites and ranged from 30%-40% WFPS at site 1 and from 50%-60% in site 2.

A2.3.1 Net NO release (*J*)

In figures A2.4a and A2.4b the net potential NO release (*J*) values of the Surinam 1 and Surinam 2 soils, respectively, are shown. The optimal release of NO at 25°C and under 0ppb NO concentration ranged from 1.5-2 ng kg^{-1} s^{-1} and occurred at a soil WFPS of 47.5% and 32.5% for the Surinam 2 and Surinam 1 soils respectively. In both soils the release of NO under higher ambient (56ppb) NO concentrations was approximately 0.5 ng kg^{-1} s^{-1} lower than the low ambient NO concentration incubation, indicating uptake of NO by the soil. When the incubation temperature was increased to 35°C there was a substantial increase in the net potential NO release. The Q_{10} value of the net potential NO release ranged from 1.95 for Surinam 1 to 2.16 for Surinam 2.

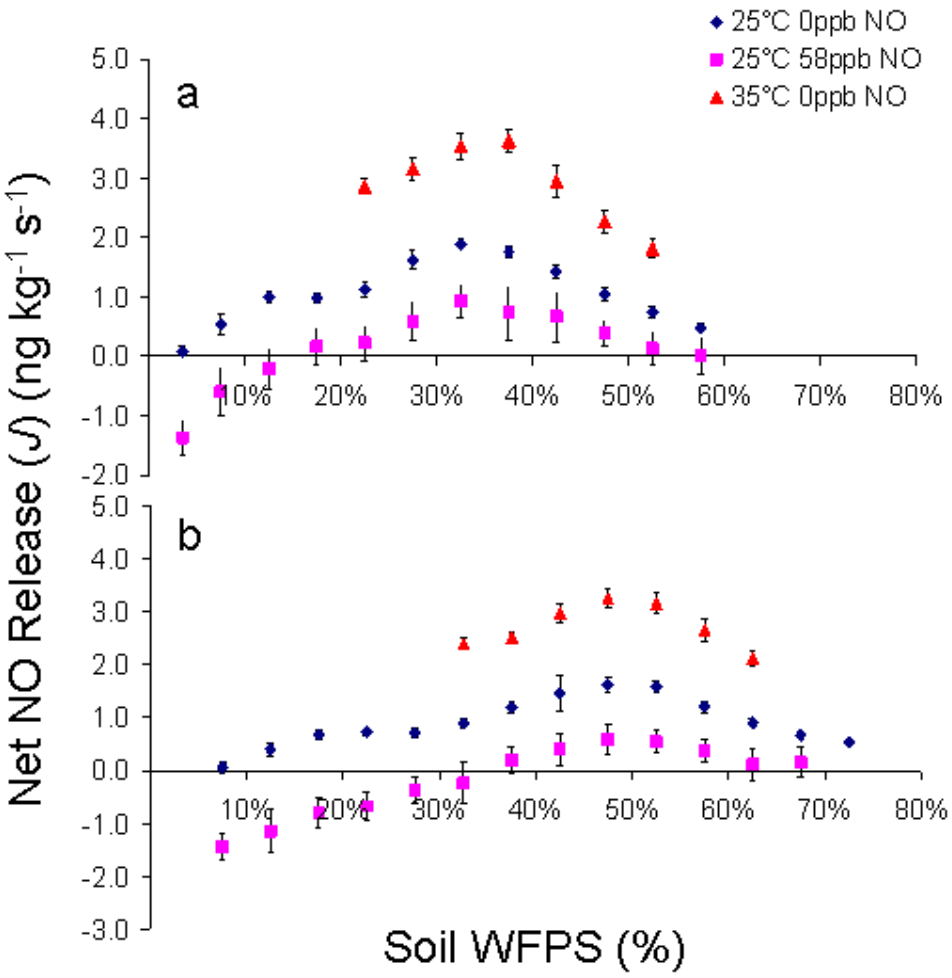

Figure A2.4 a) *J* release under differing incubation temperatures and NO concentrations for sample Surinam 1 **b)** for sample Surinam 2

A2.3.2 Net potential NO flux

The values of the net potential NO flux (at a 25°C incubation temperature) that were calculated for Surinam 1 and Surinam 2 peaked at 1.17 ng m^{-2} s^{-1} and 0.68 ng m^{-2} s^{-1} respectively (Fig. A2.5 a and b). The optimal net potential flux of NO occurs at a soil moisture content of 33% WFPS in Surinam 1 and 41% WFPS for Surinam 2. The NO fluxes that have been recorded here are fairly low but are comparable to the recorded NO emissions from other studies in the Amazon where reported emissions are in the range of 2-10 ng m^{-2} s^{-1} [*Passianoto et al.*, 2004; *Van Dijk et al.*, 2002; *Verchot et al.*, 2008].

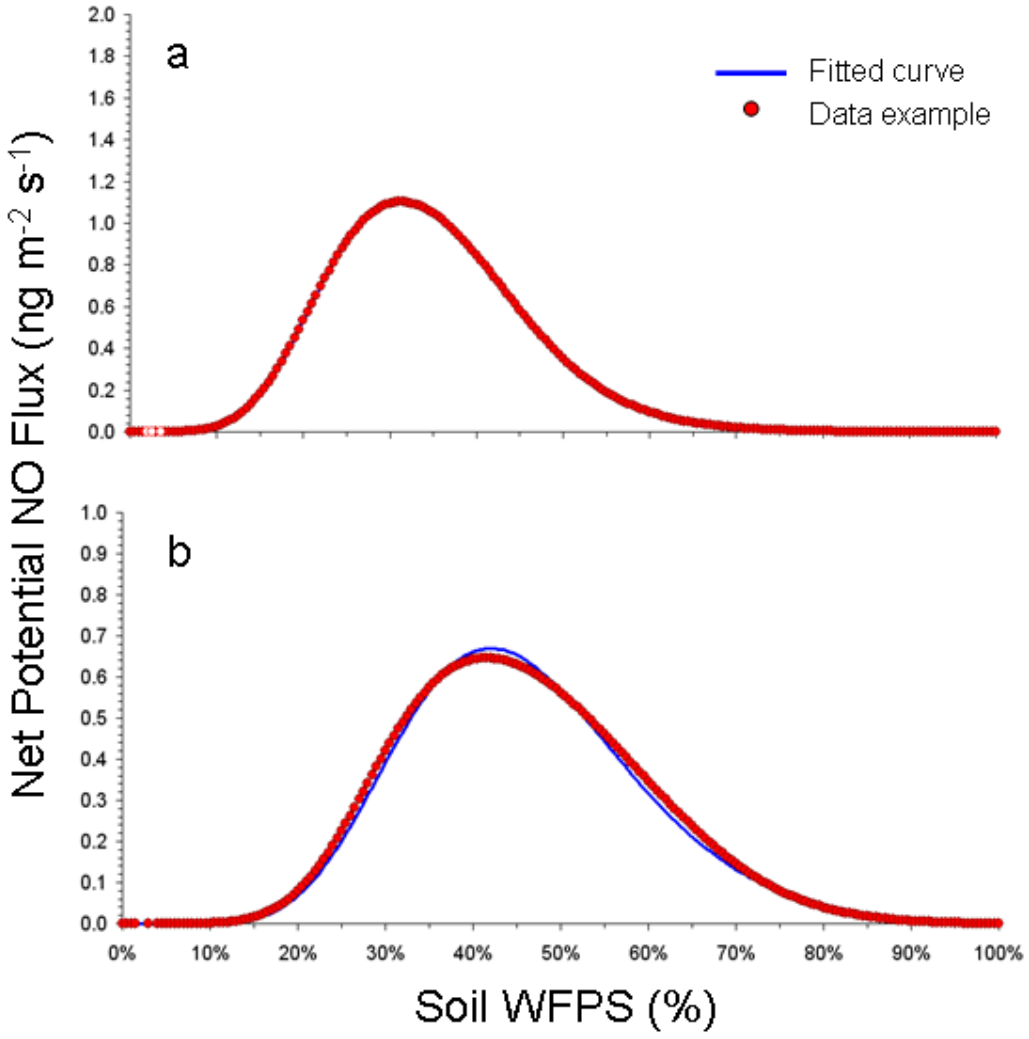

Figure A25a) The net potential NO flux at 25°C for Surinam 1 **b)** The net potential NO flux at 25°C for Surinam 2 soils

A2.3.3 NO consumption ratio (*k*) and compensation mixing ratio ($m_{NO,comp}$)

The NO consumption rate of the Surinam soils is shown in figure A2.6. The NO consumption rate is affected by the soil water content. During the peak of the NO flux 20%-50% WFPS in Surinam 1 and 25%-65% in Surinam 2 the NO consumption rate is between 2 x 10^{-5} and 4 x 10^{-5} m^3 kg^{-1} s^{-1}. In the (limited number of) previous studies that have looked at the NO consumption rate, reported values range from 0.9-500 x 10^{-5} m^3 kg^{-1} s^{-1} (see 4.5.4.1) [*Feig et al.*, In Press-a; *Feig et al.*, In Press-b; *Kirkman et al.*, 2001; *Otter et al.*, 1999; *Saad and Conrad*, 1993]. The values in this study increase quite substantially at both high and low soil WFPS, this may be an artefact of the measurement method, since the NO consumption rate is determined from the difference in the NO release between incubations under differing NO concentrations. At high and low soil WFPS the release of NO is low and therefore any minor inaccuracies in the measured NO release rate will have a large impact on the reported *k* values.

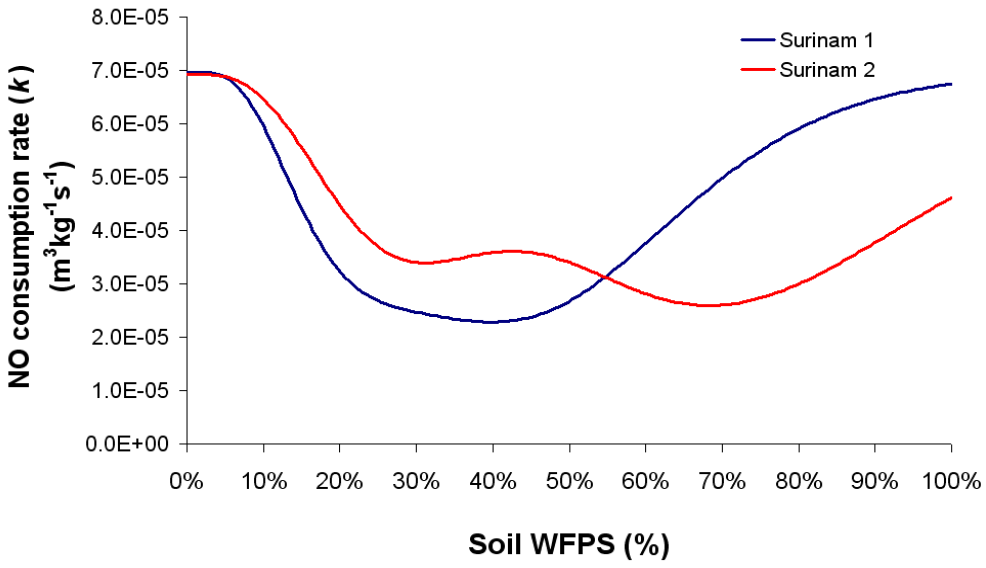

Figure A2.6 The NO consumption rate for the Surinam soils

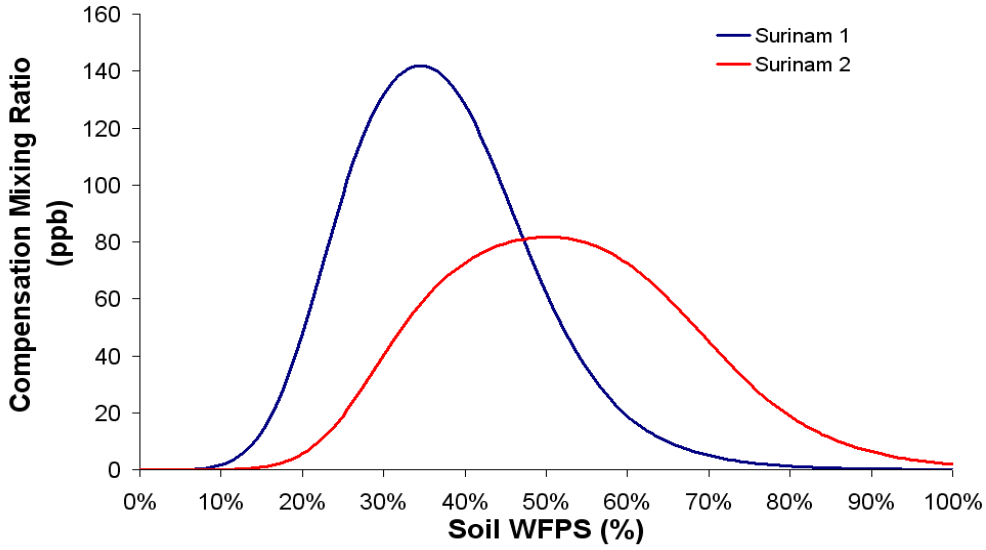

Figure A2.7 Compensation mixing ratio for Surinam soils

The compensation point mixing ratios for Surinam 1 and Surinam 2 at 25°C incubation are shown in figure A2.7. Once again it appears that the $m_{NO,comp}$ is affected by the soil WFPS and it follows a similar relationship to the NO flux. Maximum $m_{NO,comp}$ range from 80ppb NO for the Surinam 2 soils to approximately 140 ppb NO for Surinam 1.

A2.4 Hohenpeissenberg

As part of the Salsa campaign that took place in Hohenpeissenberg in Bavaria during 2005 the net potential NO fluxes as a function of the soil moisture and temperature were determined for a number of soils using the laboratory method.

A2.4.1 Pasture soils

First of all the NO flux for two pasture soils (Bauhof and Fetch Wiese) was determined at 15°C and at 25°C. Figure A2.8 shows the flux of NO at two temperatures (15°C and 25°C) for the sample "Bauhof Wiese".

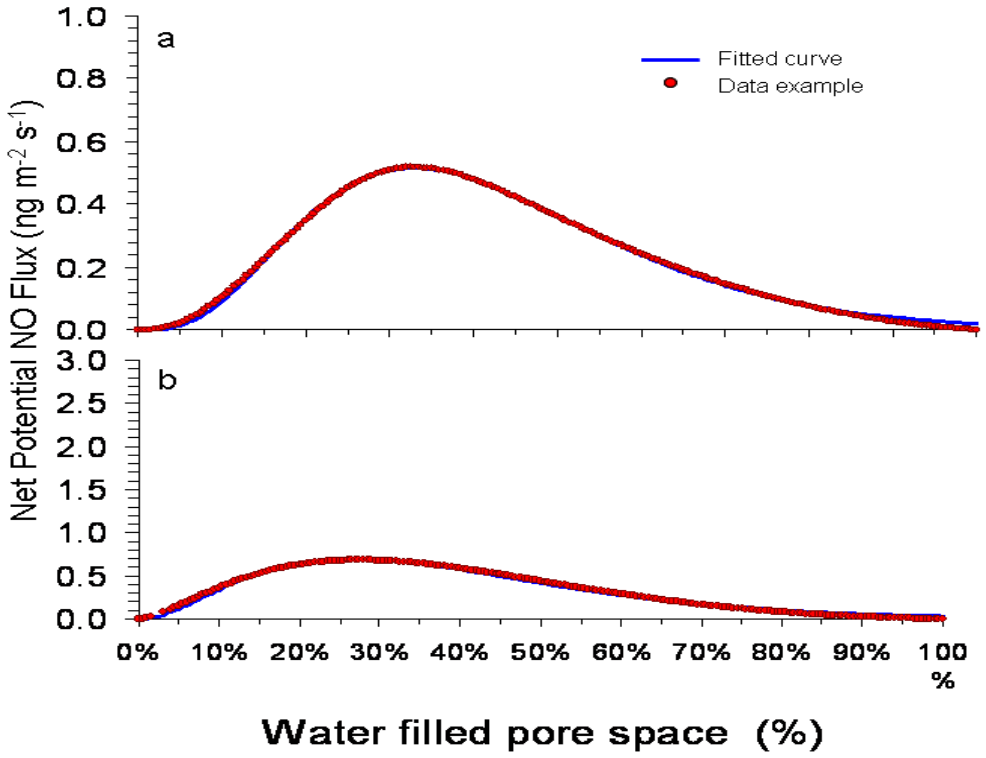

Figure A2.8 The potential NO flux for Bauhof Wiese at **a)** 15°C incubation and **b)** 25°C incubation

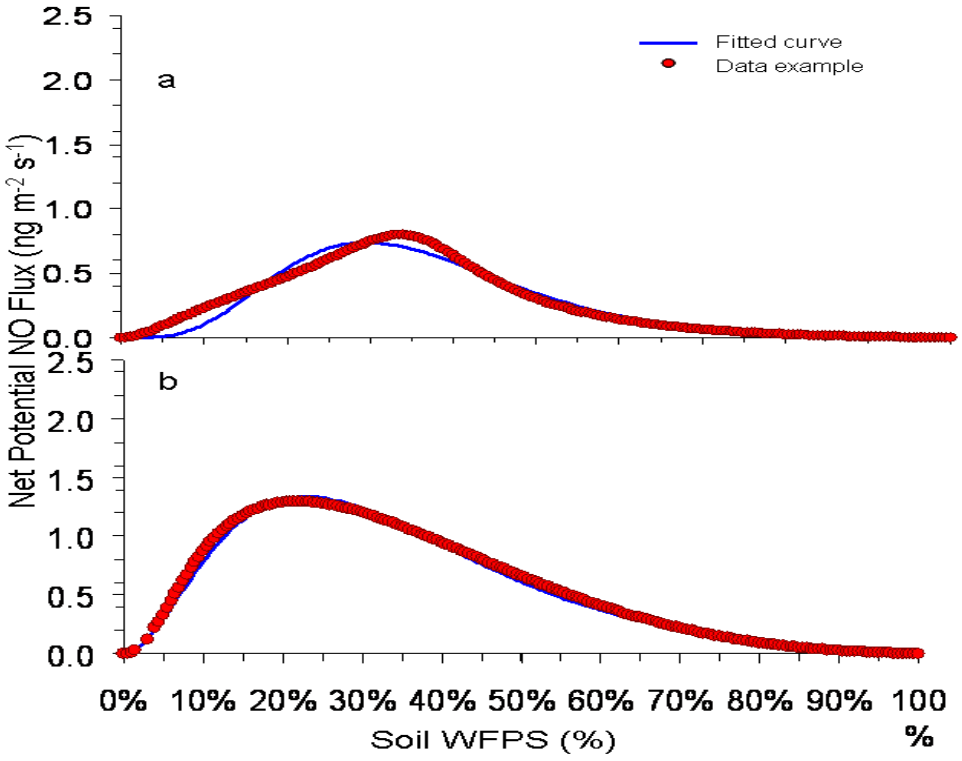

Figure A2.9 The NO flux for Hohenpeissenberg Fetch Wiese at **a)** 15°C and **b)** 25°C

A2.4.2 Hohenpeissenberg forest mineral soils

The NO flux from the mineral soil sampled from two forests was determined during the SALSA campaign in Hohenpeissenberg. The first sample came from the slopes of the Hohenpeissenberg meteorological observatory (Observatory); this was on a steep slope and the dominant vegetation was spruce (*Picea abies*).The second sample (Forest 2) came from a mixed deciduous forest. When the samples were taken the organic and litter layers were removed and the samples were taken from the top 5cm of the mineral soil as previously described.

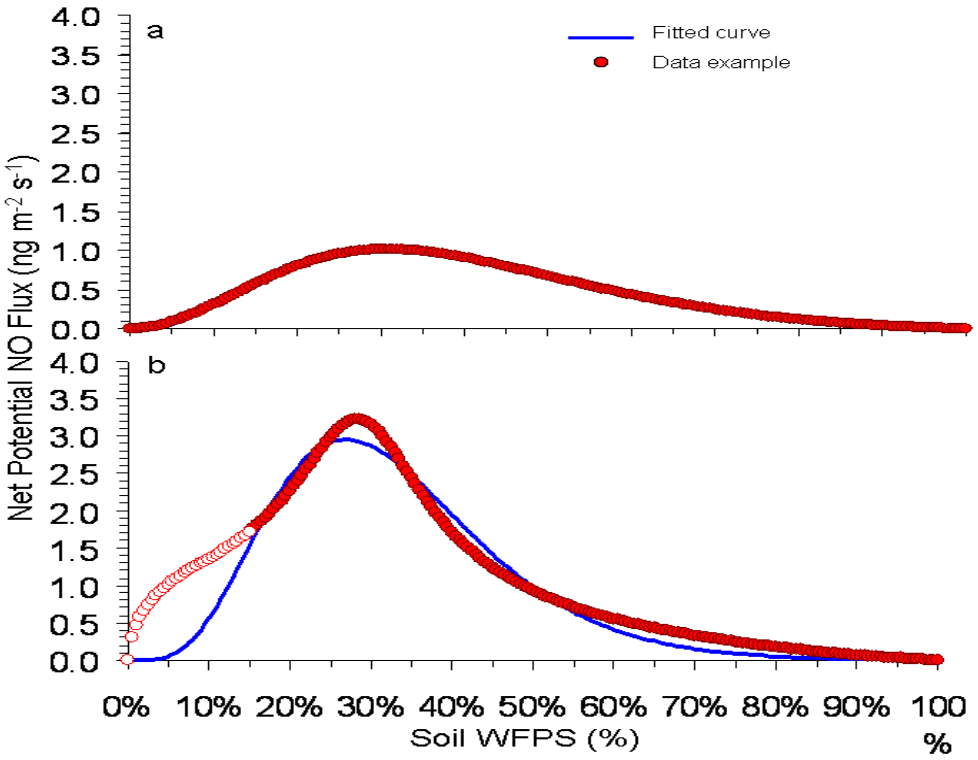

Figure A2.40 a) The NO flux from Hohenpeissenburg Forest 2 mineral soil at 15°C **b)** The NO flux from Hohenpeissenburg Observatory mineral soil at 15°C

A2.4.3 Uptake and consumption of NO

The NO consumption rate (Fig. A2.11a) ranges from 1-18 x 10^{-5} m^3 kg^{-1} s^{-1}. There does not seem to be a difference in the Pasture and Forest soils. The effect of soil moisture is variable, in the "Fetch Wiese" at 25°C incubation the uptake of NO follows the same relationship with the soil moisture content as the NO flux. However this pattern is not repeated in the other soils. In the Pasture Wiesa soils where the NO consumption rate was determined at two incubation temperatures the consumption of NO was greater at the higher incubation temperature than at the lower temperature.

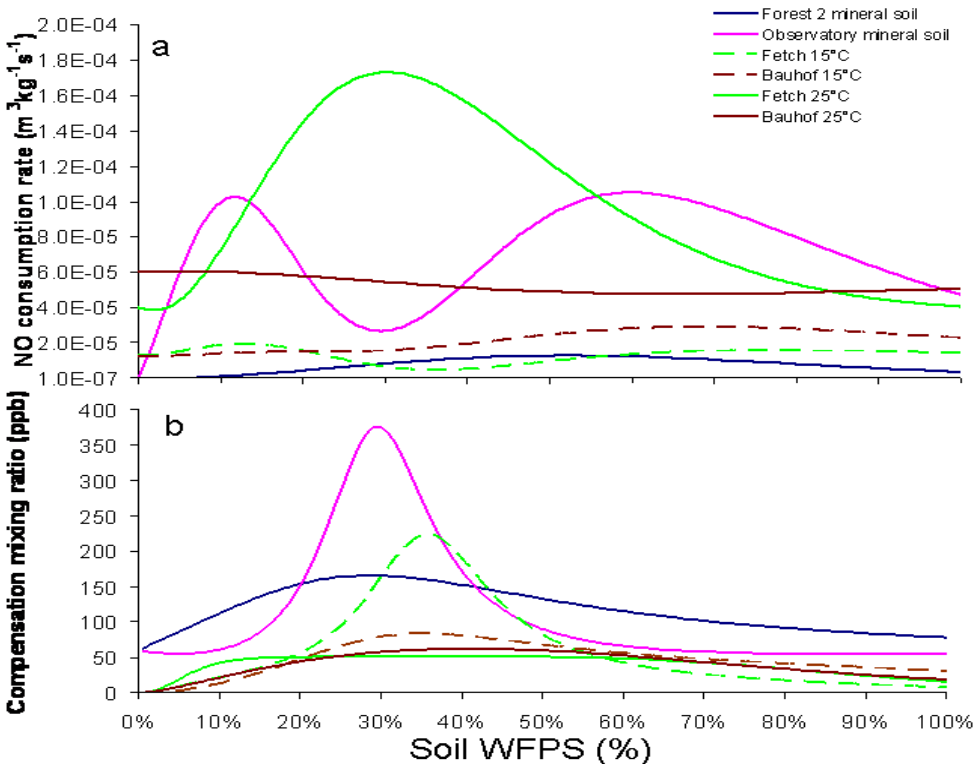

Figure A2.11 a) NO consumption rate for the soils from Hohenpeissenberg **b)** NO compensation mixing ratio

The compensation mixing ratio ($m_{NO,comp}$) for the soils from Hohenpeissenberg reached a maximum of between 50 and 380ppb. The $m_{NO,comp}$ was generally higher (175ppb and 380ppb for Forest 2 and Observatory mineral soils respectively) in the forest soils than in the Pasture soils (less than 75ppb except for Fetch Wiesse at a incubation temperature of 15°C where the $m_{NO,comp}$ peaked at 220ppb).

A2.5. Concluding remarks

The data presented in Appendix 2 were never designed to form stand alone studies but sampling was designed to contribute to other studies, however this data is still useful when trying to generalise the patterns of NO release, flux and uptake. These data will therefore be used in the conclusions chapter (Chapter 6).

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