Nitric oxide emissions from soils: effects of deforestation

Stikstofmonoxide emissies uit bodems: effecten van ontbossing

(met een samenvatting in het Nederlands)

Proefschrift ter verkrijging van de graad van doctor aan de Universiteit Utrecht
op gezag van de Rector Magnificus, Prof. dr. W.H. Gispen, ingevolge het besluit
van het College voor Promoties in het openbaar te verdedigen op 11 juni 2001
des middags te 16:15 uur

door

Saskia Maria van Dijk

Geboren op 1 mei 1974, te Amstelveen

Promotor:	Prof. dr. J. Lelieveld Faculteit Natuur- en Sterrenkunde, Universiteit Utrecht Max Planck Institute for Chemistry, Mainz, Germany
co-promotor:	Prof. dr. F.X. Meixner Department of Physics, University of Zimbabwe (Harare) Max Planck Institute for Chemistry, Mainz, Germany

Printed by Universal Press, Veenendaal, the Netherlands
ISBN 90-393-2741-6

Cover image by Greg Roberts

"Rustig blijven, ’t is niet moeilijk, toch niet onderschatten"

CONTENTS

SAMENVATTING

Dit promotieonderzoek richtte zich op de vraag wat het effect van ontbossing is op de emissies van stikstofmonoxide (NO) uit bodems in het Amazone-gebied. Stikstofoxiden spelen een belangrijke rol bij de fotochemische productie van ozon in de troposfeer. De ontbossing op grote schaal van het Amazone-gebied in Zuid Amerika verandert de fysische en chemische eigenschappen van de bodems, die op hun beurt tot grote veranderingen in de emissies van gassen uit de bodem leiden. De metingen werden uitgevoerd als onderdeel van het Europese project "European Studies on Trace Gases and Atmospheric Chemistry" als een bijdrage aan het internationale project "Large Scale Biosphere-Atmosphere Experiment in Amazonia" (EUSTACH-LBA).

Onze meetgegevens tonen dat de produktie van NO in bodems van oude weilanden duidelijk minder is dan die in bodems van primaire regenwouden. Een aantal mogelijke oorzaken kon worden aangetoond. Ten eerste duiden de hoge nitraat- en lage ammonium-concentraties in bosbodems in vergelijking tot weilanden op een hogere microbiologische activiteit en zodoende een hogere produktie van NO in regenwoud-bodems. Ten tweede is de zuurgraad in de bosbodems zo hoog dat extra produktie van NO via chemische reacties kan plaatsvinden.

Uit de gegevens van de produktie en consumptie van NO en de gemeten effectieve diffusie van NO in bodem zijn de emissies van NO uit de bodems van een regenwoud en een 22-jaar oud weiland berekend. De bodem van het regenwoud emitteerde het meeste NO. Naast de hierboven genoemde verschillen die de productie beinvloeden, kon een ander effect worden aangewezen. De omzetting van regenwoud tot weiland leidt tot compactie van de bodem, wat resulteert in een verlaagde diffusie van NO door de bodem en uiteindelijk tot kleinere emissies uit de bodem van het weiland.

Voor beide ecosystemen kwamen de berekende NO-emissies goed overeen met NO-emissies die gedurende veldwerk-activiteiten op precies dezelfde locaties waren gemeten. Deze methode lijkt daarom niet alleen geschikt voor het in detail bestuderen van productie en consumptie van NO, maar ook om NO-emissies uit bodems te bepalen in verschillende ecosystemen tegen zo laag mogelijk kosten.

Om een beter inzicht te krijgen onder welke condities maximale NO emissies uit de bodem treden, werden monsters onderzocht met betrekking tot de bodemtextuur. De optimale vochtigheid correleerde met het kleigehalte van de bodems. De situatie waarbij het water uit de relatief grote poriën gedraineerd was, terwijl de kleinere poriën nog gevuld waren met water, resulteerde voor alle bodems in maximale NO-emissies, ongeacht bodemtextuur. Dit duidt aan dat de voorspelling van NO-emissies uit bodems met verschillende bodemtexturen vereenvoudigd kan worden door het gebruik van de drainage-staat (matric potential) van de bodem in plaats van het gebruik van bodem vochtigheid.

Tenslotte wordt een beeld geschetst van de te verwachten ontwikkelingen in het Amazone gebied. Er wordt voorgesteld dat verhoogde antropogene emissies van stikstof-verbindingen zouden kunnen leiden tot een verhoogde N-depositie vanuit de atmosfeer. We presenteren meetresultaten van NO-bodem-emissies uit bossen in Europa met hoge N-depositie vanuit de atmosfeer. Hogere N-depositie leidde tot hogere NO-emissies uit de bodem. De fotochemische productie van ozon in het Amazone gebied is vooral afhankelijk van de NO-concentratie, en wordt sterk beinvloed door de grootschalige ontbossing van het Amazonegebied.

SUMMARY

Nitrogen oxides play an important role in the photochemical production of ozone in the troposphere. Large scale deforestation in the Amazon Basin (South America) affects the physical and chemical soil properties that in turn alter the biogenic emissions from the soils. This thesis concentrates on the effects of deforestation on nitric oxide (NO) emissions from soils within the Brazilian Amazon. The study was carried out as part of the European project "European Studies on Trace Gases and Atmospheric Chemistry" as a contribution to "Large Scale Biosphere-Atmosphere Experiment in Amazonia" (EUSTACH-LBA).

Our measurements showed that the NO production is higher in forest soils than in old pasture soils. Higher nitrate and lower ammonium concentrations in forest soils compared to pastures suggest higher microbial activity (and hence higher production) in forest soils. Also, the production of NO through chemical reactions under acid conditions could explain higher NO production in the acidic forest soils compared to the more neutral pastures.

NO production and consumption were converted into NO emissions from soil using a simple diffusion algorithm. NO emissions were higher from forest soils compared to old pastures. Besides the aforementioned differences that influenced the NO production, another effect of deforestation was determined. The conversion from forest to pasture decreased the soil pore volume, and consequently the diffusion of NO through the soil, explaining the smaller emissions of NO from pastures.

Our laboratory derived NO emissions agreed well with NO emissions from field measurements, for two different ecosystems (primary forest and 22 years old pasture) during the full measurement campaign. This indicates that such laboratory measurements are a powerful tool to study NO production and consumption in detail under controlled conditions, as well as to establish NO emissions from a variety of ecosystems on a cost-effective basis.

The moisture conditions for which the NO emissions from soil are highest (*optimum soil moisture*) were examined in detail with respect to the soil texture. Optimum soil moisture depended strongly on the soil texture. However, for all soil textures, maximum NO was emitted from soil when the relatively larger pores were drained, whereas the smaller pores were water-filled. Models that predict NO emissions from soils would benefit from considering the different soil textures.

Finally, future developments within the Amazon are evaluated, and it is proposed that increased anthropogenic emissions of reactive nitrogen species could lead to higher N-deposition from the atmosphere. We present NO emissions from forest soils in Europe which receive high amounts of nitrogen by atmospheric deposition. Higher N-input to the soils from the atmosphere resulted in higher NO emissions from soils. The photochemical production of ozone in the Amazon largely depends on the concentrations of NO (and NO_2), and is strongly influenced by the large scale deforestation of the forest ecosystems in the Amazon.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Background

Nitric oxide (NO) plays an important role in atmospheric chemistry. The removal of trace gases from the atmosphere is mostly through oxidation processes that involve reactions with hydroxyl radicals (OH) and ozone (O_3). NO significantly influences the oxidative capacity of the troposphere, especially by its catalytic behaviour in the photochemical formation of O_3 [*Graedel and Crutzen*, 1993]. When mixtures of NO and O_3 are exposed to ultraviolet light, an equilibrium is established in which NO reacts with O_3 to form nitrogen dioxide (NO_2) and oxygen (O_2) and visa versa. In this equilibrium one O_3 molecule is produced for every O_3 molecule that is consumed (eq. 1.1, 1.2 and 1.3).

$$NO + \mathbf{O_3} \rightarrow NO_2 + O_2 \qquad (1.1)$$
$$NO_2 + h\nu \rightarrow NO + O \qquad (1.2)$$
$$O + O_2 \rightarrow \mathbf{O_3} \qquad (1.3)$$

Furthermore, absorption of solar ultraviolet radiation by O_3 molecules leads to the generation of excited $O(^1D)$-atoms that can react with water vapour to form very reactive OH radicals (eq. 1.4 and 1.5) [*Crutzen and Zimmermann*, 1991].

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (\leq 310\ \text{nm}) \qquad (1.4)$$
$$O(^1D) + H_2O \rightarrow 2\ OH \qquad (1.5)$$

These OH radicals rapidly oxidise hydrocarbons (RH) to produce peroxy radicals, such as HO_2 and RO_2. When NO can reacts with RO_2 (eq. 1.6), additional O_3 is produced through the photolysis of NO_2 (eq. 1.2 and 1.3) without the prior destruction of O_3 (eq. 1.1).

$$NO + RO_2 \rightarrow NO_2 + RO \qquad (1.6)$$

Whether OH and O_3 are generated or destroyed during these oxidation processes, depends strongly on the NO_x (NO and NO_2) concentration in the atmosphere. When NO_x is low, HO_2 reacts with HO_2 and RO_2 forming H_2O_2 and RO_2H, which are removed from the atmosphere by wet and dry deposition. Therefore, at low NO_x levels, OH concentrations are suppressed. When concentrations of NO_x are sufficiently high, HO_2 will react NO, which leads to the photochemical formation of O_3 (see eq. 1.2, 1.3 and 1.6) [*Crutzen and Zimmermann*, 1991].

Strong light intensities and high concentrations of water vapour in the tropical region generally lead to high OH concentrations in the tropical troposphere. About 70% of the global atmospheric oxidation of trace gases is believed to take place in the tropical troposphere [*Crutzen and Zimmermann*, 1991]. The tropics are therefore an important research area for NO_x.

Table 1.1 *Global emissions*[*] *of* NO_x *in Tg N* $year^{-1}$. *Reproduced from Mosier [2001].*

SOURCE	*Holland et al.*, [1999]		*Delmas et al.* [1997]	
		Tg N $\mathbf{year^{-1}}$		
Fossil fuel combustion	20	(20–22.4)	22	(15–29)
Aircraft emissions	0.6	(0.23–0.6)	0.4	(0.5–0.6)
Lightning	5.1	(3–25)	2.0	(1–4)
Biomass burning	6.0	(3–13)	7.0	(3–10.4)
Soil NO_x emissions	4.76	(4–21)	5.5	(3.3–7.7)
Natural	-	(4–15.5)	-	
Agricultural	-	(1.8–5.4)	-	
NH_3 oxidation	-	(0.5–3)	-	
Stratospheric injection	0.5	(0.1–0.6)	-	
Total	**36.1**	**(23–81)**	**38.2**	**(23.7–53.8)**

([*]Numbers presented are mean emission estimates from five different 3-dimensional chemical transport models, numbers in parentheses are the range of model output values.)

On a global scale, the main sources of NO_x are combustion of fossil fuel, lightning and biomass burning (Table 1.1). On a local scale, biogenic emissions of NO from soils can be an important source, especially in remote areas where emissions from the combustion of fossil fuel are relatively small. The Amazon in South America is a large tropical ecosystem that faces rapid development. Combustion of fossil fuel is (still) a negligible source of NO_x in the Amazon, but the burning of vast areas of primary forest leads to high pyrogenic emissions of NO_x. Each year, an area of about 19000 km^2 of primary forest (about half the size of the Netherlands, or 2700000 football fields) is deforested and burned within the Brazilian Amazon [*Nepstad et al.*, 1999a].

Current and future deforestation and land use changes in the Amazon will affect the physical and chemical characteristics of the corresponding soils. For instance, the conversion from forest to pasture has been shown to change the organic carbon contents and the inorganic nitrogen contents in soil, as well as rates at which nutrients are turned over (*Reiners et al.*, 1994; *Veldkamp*, 1994; *Moraes et al*., 1996; *Neill et al.*, 1999). Consequently, biogenic emissions from soils are expected to change. NO emissions from forest soils have been shown to increase directly after burning [*Neff et al.*, 1995], and to decrease below original values after several years [*Keller et al.*, 1993].

Investigation of the ecological functioning of the Amazon and evaluation of the effects of land-use changes on this ecological functioning are the main aims of the long-term international project ”Large Scale Experiment in Amazonia” (LBA). Within these research aims, the European project "European Studies on Trace Gases and Atmospheric Chemistry" (EUSTACH) concentrates on the thematic areas of carbon storage, atmospheric chemistry and biogeochemistry. This Ph.D. work was carried out as part of LBA-EUSTACH at the Biogeochemistry Department of the Max Planck Institute for Chemistry in Mainz, Germany. The overall objectives were to quantify biogenic emissions of NO from primary forest soils and pastures, and thus quantify the effect of forest-to-pasture conversion on these emissions.

An introduction in the biogenic emission of NO from soil and the controlling parameters are given in sections 1.2–1.3. The objectives of this Ph.D. work, including an outline of the thesis are given in sections 1.4–1.5.

1.2 Biogenic emissions of nitric oxide from soil

NO is produced in soil both through biological and chemical processes. Nitrification (authotrophic and heterotrophic) and denitrification are considered the most important processes for the microbial production of NO in soil, although other processes have been observed. Most of the information given in this section is from *Conrad* [1996a].

Autotrophic nitrification is the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-). This is carried out in two steps by two different groups of microorganisms; *Nitroso*-bacteria and *Nitro*-bacteria. The *Nitroso*-bacteria oxidise NH_4^+ to hydroxylamine (NH_2OH), and finally to nitrite (NO_2^-) (eq. 1.7). The *Nitro*-bacteria oxidise NO_2^- to NO_3^- (eq. 1.8).

$$NH_4^+ \rightarrow NH_2OH \rightarrow NO_2^- \qquad (1.7)$$

$$NO_2^- \rightarrow NO_3^- \qquad (1.8)$$

In equation 1.7, the oxidation of NH_4^+ to NH_2OH requires the presence of oxygen (O_2), whereas the further oxidation to NO_2^- is not oxygen-limited. Instead of O_2, NO_2^- can be used as an electron acceptor, and as a result NO is produced. The reduction of NO_2^- to NO consumes 2 protons, and thus could be important in regulating the pH in the bacteria. NO is also produced in this manner under oxic conditions. Heterotrophic nitrification is the oxidation of organic nitrogen and inorganic nitrogen species to NO_2^- and NO_3^-. Heterotrophic nitrifiers include bacteria and fungi. There are probably numerous different biochemical pathways, and these are still unknown.

Denitrification is the reduction of NO_3^- to the gaseous endproducts N_2O and N_2 (eq. 1.9). NO is produced as an intermediate product, and can escape it's fate of further reduction. Denitrification generally occurs under anaerobic conditions, although aerobic denitrifiers and heterotrophic nitrifiers have been found to denitrify NO_3^- under aerobic conditions.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO\ (g) \rightarrow N_2O\ (g) \rightarrow N_2\ (g) \qquad (1.9)$$

Besides the reduction of NO_3^- by denitrifying microorganisms, there are several other biological mechanisms that reduce NO_3^- and consequently produce NO. For instance, nitrate respiration (eq. 1.10) or DRNA (Dissimilatory Reduction of Nitrate to Ammonium) (eq. 1.11). However, nitrification (under oxic conditions) and denitrification (under anoxic conditions) are the major microbiological sources of NO production in soil.

$$NO_3^- \rightarrow NO_2^- \qquad (1.10)$$
$$NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ \qquad (1.11)$$

Another pathway for NO production is through chemical reactions. Nitrous acid (HNO_2) and NO_2^- are chemically unstable in acid soil ($pH<5.5$), especially in combination with a high organic matter content [*Blackmer and Cerrato*, 1986]. These species have been shown to participate in several chemical reactions that produce NO (eq. 1.12, 1.13 and 1.14), generally referred to as chemodenitrification [*Serca et al.*, 1994].

$$3\ NO_2^- + 2\ H^+ \rightarrow 2\ NO\ (g) + NO_3^- + H_2O \qquad (1.12)$$
$$2\ HNO_2 \rightarrow NO + NO_2 + H_2O \qquad (1.13)$$
$$NO_2^- + NO_2\ (g) \rightarrow NO_3^- + NO\ (g) \qquad (1.14)$$

The NO_2^- concentration in soil is generally small. However, NO_2^- is formed as an intermediate product in many microbiological processes, such as nitrification, denitrification, nitrate respiration and DRNA (equations 1.7, 1.8, 1.9, 1.10 and 1.11). The production of NO_2^- (and HNO_2) thus may be biological, its evolution (biological oxidation/reduction or chemical reaction) depends largely on its chemical stability in soil.

In all the aforementioned processes NO can be produced as a gaseous (intermediate) product and consequently can escape the soil to the atmosphere. However, part of that NO is simultaneously consumed in soil. For instance, as was shown in equation 1.9, NO is a substrate for denitrification and can be reduced to the gaseous endproducts N_2O and N_2. This mechanism functions both under oxic and anoxic conditions. Several groups of microorganisms have been identified that consume NO through biological oxidation and reduction, such as autotrophic and heterotrophic nitrifiers and methanotrophic bacteria, but many others are probably still unknown [*Baumgärtner et al*., 1996; *Rudolph et al*., 1996a; *Krämer et al.*, 1990].

Generally the result of simultaneous production and consumption of NO in soil is a net release from the soil to the atmosphere, although deposition of NO can occur at high ambient NO concentrations [*Meixner*, 1994]. If the soil is covered by tall vegetation (e.g. forest canopy), not all NO emitted from the soil might leave the canopy. When passing the trunk and canopy spaces, a substantial part of the biogenically emitted NO can react with ozone (mixed into the canopy from aloft) to form nitrogen dioxide (NO_2). This NO_2 can escape the canopy or can be deposited to vegetation, reducing the potential biogenic NO flux from the forest ecosystem to the atmosphere [*Ammann et al*., 1999; *Jacob and Wofsy*, 1990; *Meixner*, 1994; *Rummel et al.*, submitted].

1.3 Regulation of the biogenic emissions of nitric oxide from soil

NO emissions are thought to be largely controlled by substrate availability, soil temperature, soil moisture and soil acidity (pH) [e.g. *Davidson et al*., 2000]. As was explained above, the production of NO is possible through various microbial and chemical processes with different substrates. Indeed, several authors have reported increasing NO emissions upon additions of ammonium [*Parsons and Keller*, 1995; *Vermoesen et al.*, 1996], others upon additions with nitrate (denitrification, nitrate respiration, DRNA?) [*Bakwin et al*., 1990; *Cardenas et al*., 1993, *Vermoesen et al*., 1996; *Thornton et al.*, 1998]. No general agreement has been reached. Often, no correlation is found between the observed NO flux and the nutrient-pools, and it appears more useful to consider the rates at which nutrients are processed and transformed in soil (e.g. mineralization, nitrification and denitrification) [see *Davidson et al.*, 2000].

Soil acidity may influence the microbial processes in several ways. Soil pH regulates the liberation of elements (e.g. phosphate availability) and the speciation of acid/base-complexes (e.g. NO_2^-/HNO_2) [*Sposito*, 1989], which in turn could influence (or serve as substrate for) the various NO production processes. For example, whereas biological nitrification is inhibited at low pH [*Tietema et al.*, 1992; *Gödde*, 1999], chemodenitrification occurs mostly under acid conditions [*Blackmer et al.*, 1986; *Serca et al*., 1994].

As for the controlling parameters of soil temperature and soil moisture, results from field studies show good agreement. The NO flux increased exponentially with soil temperature, which is generally observed for microbial processes [e.g. *Williams et al*., 1987]. In dry soil, the relation with soil temperature might be less pronounced [*Cardenas et al.*, 1993; *Sullivan et al.*, 1996]. This indicates that soil moisture plays an important role in emissions of NO from soil.

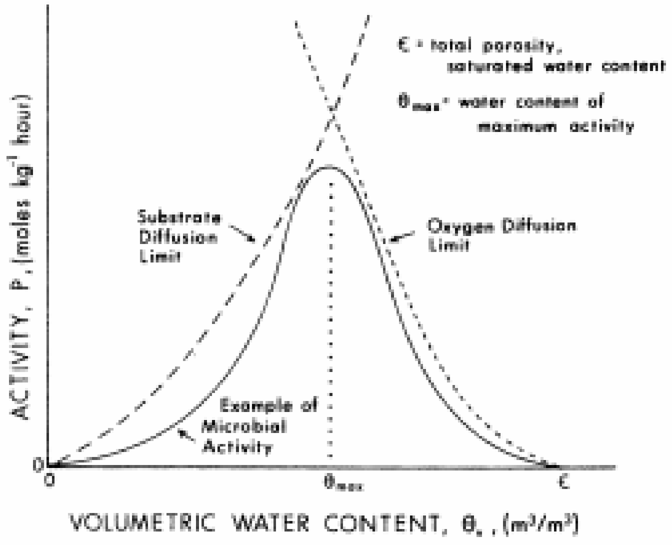


Figure 1.1 Aerobic microbial activity as a function of volumetric water content (reproduced from *Skopp et al.*, [1990])

Many studies have shown that NO emissions were maximum at an intermediate soil moisture (*optimum soil moisture,* θ_{opt}) [*Cardenas et al*., 1993; *Grundmann et al*., 1995; *Sullivan et al*., 1996; *Scholes et al.*, 1997; *Martin et al*., 1998; *Parsons et al*., 1996; *Pilegaard et al*., 1999*; Otter et al*., 1999; *Peirce and Aneja*, 2000]. Figure 1.1, reproduced from *Skopp et al.* [1990], demonstrates aerobic microbial activity versus soil moisture. At low soil moisture (aerobic conditions), the microbial activity increases with soil moisture, since substrate diffusion is enhanced through water films. At high soil moisture (anaerobic conditions), oxygen-supply is limited and the aerobic microbial activity decreases with further wetting of the soil. [*Skopp et al*., 1990; *Linn and Doran*, 1984]. An intermediate soil moisture exists, where the limiting effects of substrate diffusion (through water films) and O_2 supply are equal, and consequently aerobic microbial activity (e.g. nitrification) is maximum (optimum soil moisture, θ_{opt}). Maximum aerobic microbial activity was suggested to occur at approximately 0.60 water-filled pore space (WFPS). [*Davidson*, 1993; *Linn and Doran*, 1984]. For emissions of NO from soils, however, a range of optimum moistures (θ_{opt}) is given in the literature, ranging from 0.20 to 0.70 WFPS [*Cardenas et al.*, 1993; *Grundmann et al.*, 1995; *Scholes et al.*, 1997; *Martin et al.*, 1998; *Pilegaard et al.*, 1999; *Peirce and Aneja*, 2000]. Optimum soil moisture for emission of NO from soil exists where conditions for NO production (microbial activity and/or chemical processes) and gas diffusion (NO escapes the soil towards the atmosphere) are optimized. Since NO can be produced both under aerobic and anaerobic conditions [*Conrad*, 1996a], θ_{opt} for the emission of NO from soil may be different from 0.60 WFPS.

When examining soils from different regions, one encounters different soil textures and moisture regimes that could influence the optimum moisture for NO emissions from soil. For instance, a coarse-textured soil generally has a relatively smaller total pore volume, compared to a fine-texture soil [*Hillel*, 1982]. Thus, at identical soil moisture (mass of water per mass of soil), a coarse-textured soil would be relatively wet compared to a fine-textured soil.

Matric potential (kPa) is an expression which characterizes the tenacity with which soil water is held by the soil matrix [*Hillel*, 1982]. The relation between matric potential and the soil water content (also, water retention curve or water release characteristics) thus depends on the soil matrix, as is shown in Figure 1.2.

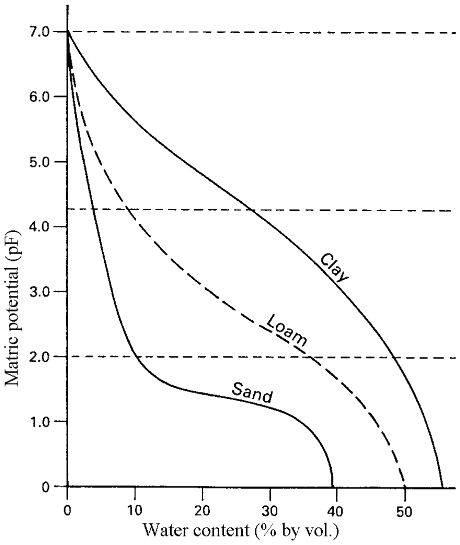


Figure 1.2 Water release characteristics of three different soil textures: sand, loam and clay. Matric potential is presented on a log scale (pF): pF 2.0 indicates a matric potential of –100 hPa (or –10 kPa). Figure was reproduced from *Monteith and Unsworth* [1990].

At a given matric potential, a fine-textured soil (clay) with relatively fine pores will retain more water than a coarse-textured soil (loam or sand) with relatively large pores. In addition, gas diffusion through the soil is more effective in a coarse-textured soil with relatively larger pores compared to a fine-textured soil with relatively fine pores [*Currie*, 1983]. Therefore, differences in the soil textural and soil structural properties are expected to lead to differences in the optimum moisture conditions for NO emissions from soils. In order to simplify the prediction of NO emissions from soils over extended regions, the optimum soil moisture should be studied in more detail with respect to the soil texture and soil structure.

1.4 Objectives

The overall objective of this work was to quantify biogenic NO emissions from primary forest soils and pastures within the Brazilian Amazon, and thus determine the effect of deforestation on biogenic emissions of NO from soils.

Field measurements with (dynamic or static) chambers have been successfully applied to quantify net NO emissions from soil. However, these measurements generally impose high demands on resources (transport, power supply, finances, etc.), especially when measurements take place in remote parts of the world. Laboratory studies offer a controlled environment which is necessary to study particular aspects of the NO production and consumption in detail. Often, field measurements need to relate back to these laboratory studies to understand the results obtained. It would be more practical and more cost-effective to be able to collect soil samples and quantify net NO emissions from soil samples in the laboratory.

Galbally and Johansson [1989] developed a simple diffusion-based algorithm to quantify net NO emissions from laboratory results on the NO production and consumption in soil samples. It has been shown that these laboratory-derived NO emissions agreed well with NO emissions from field measurements (with dynamic chambers) [*Galbally and Johansson,* 1989*; Remde et al.*, 1993; *Rudolph et al.*, 1996b]. In later studies, the algorithm was modified to include the dependence of the net NO emissions on soil temperature and soil moisture [*Yang and Meixner*, 1997; *Otter et al.*, 1999]. However, NO production and consumption have been observed to depend differently on controlling soil parameters, such as O_2 availability, soil pH, nutrient content, and soil moisture and soil temperature [*Krämer and Conrad*, 1991; *Baumgärtner and Conrad*, 1992; *Saad and Conrad*, 1993; *Dunfield and Knowles*, 1999; *Conrad*, 2000]. Therefore, it is more appropriate to describe the individual processes each as a function of soil temperature and soil moisture, rather than examining the resulting net NO emissions.

In this study, NO production and consumption were studied individually with respect to soil temperature and soil moisture. Finally, biogenic emissions of NO were quantified from the relations of NO production and consumption with soil temperature and soil moisture, and the diffusion based algorithm of *Galbally and Johansson* [1989].

In order to quantify the direct effect of deforestation on the biogenic NO emissions from soils, soil samples were collected from primary forests, secondary forests and pastures within the Brazilian Amazon, and results of their corresponding NO production, NO consumption and net NO emissions were intercompared.

In addition, as alluded to in the previous section, some uncertainty exists about the optimum moisture conditions under which NO is emitted from soil. Soil texture is an important characteristic that partly controls the soil moisture conditions, and therefore may influence the optimum moisture conditions for maximum NO emission. For this reason, a series of soil samples, with varying soil textures, from the Brazilian Amazon were examined with respect to the corresponding optimum moisture conditions for which maximum NO emissions were observed.

The three main aims of this research are given below:

I. Determine NO production and consumption in soil samples from primary forest and pastures in the Amazon, and study these processes in detail with respect to soil temperature, soil moisture and nutrients.

II. Quantify net NO emissions from forest and pasture soils in the Brazilian Amazon, using the dependency of NO production and consumption with soil temperature and soil moisture from laboratory experiments. Test these laboratory-derived NO emissions with net NO emissions from field-measurements, and finally find the direct effect of deforestation on the NO emissions from soils.

III. Establish the optimum moisture for NO emissions from a series of different soils in the Amazon. More specifically, examine the effect of soil texture on the optimum moisture conditions under which NO is emitted from the soil.

1.5 Outlook, and further objectives

As was mentioned in the previous paragraph, the main aim of this thesis was to quantify the effect of deforestation on the biogenic emissions of NO from soils in the Amazon. For this reason, NO emissions were determined in soil samples from primary forest and pastures. Differences in the soil emissions of NO between primary forest and pastures will be attributed to be the direct effect of deforestation. However, besides the difference in the biogenic NO emissions from primary forest soils and pastures that is directly measurable, there are additional indirect effects that should be considered when evaluating the effects of deforestation on the biogenic NO emissions from soils.

Until now, the Brazilian Amazon has been a relatively undisturbed ecosystem in terms of human activities. However, recently the Brazilian government has launched the project "Avança Brasil 2000–2003" (http:\\www.abrasil.gov.br). This project aims, amongst others, to enhance the economical development of the state of Amazonas, in the North West of the Brazilian Amazon. As part of the project, roads and railways (4500 and 1600 km respectively) will be constructed within the Brazilian Amazon. Currently, an area of approximately 19,000 km^2 of primary forest is deforestated and burned each year. The developments within the project "Avança Brasil" are expected to induce additional deforestation of about 80,000–180,000 km^2 within the next 25–30 years [*Nepstad*, personal communication]. Thus, the Brazilian Amazon continues to face large scale deforestation in the near future. Increased human activities, related to a better infrastructure, will enhance anthropogenic emissions in the Brazilian Amazon. These anthropogenic emissions can become of great environmental significance in the natural surroundings of the Brazilian Amazon, and should be considered as (indirect) effects of deforestation.

During the last two centuries, large scale development of temperate ecosystems in the Northern Hemisphere has lead to strongly enhanced anthropogenic emissions into the atmosphere. This increase was mainly due to increased combustion of fossil fuel, and intensification of industry and agriculture. Globally, the emissions of reactive nitrogen have increased several fold due to anthropogenic influences, with the steepest increase during the last 50 years [*Holland et al.*, 1999]. These reactive nitrogen emissions, such as nitrogen oxides (NO_x) and ammonia (NH_3), have driven an increase in nitrogen input to the terrestrial ecosystem by atmospheric deposition [*Vitousek et al.*, 1997].

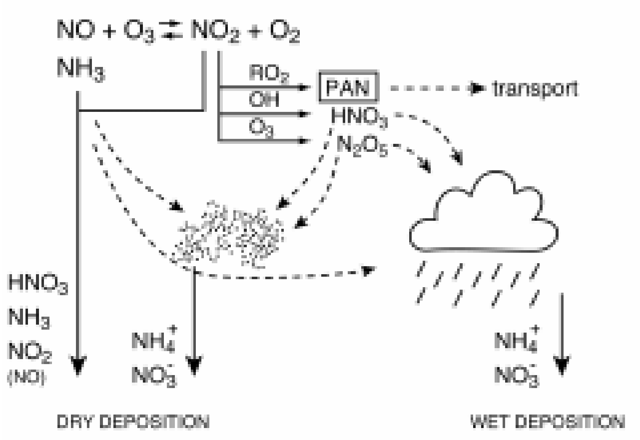


Figure 1.3 Schematic of the important pathways of NO and NH_3 within the atmosphere.

After their emission into the atmosphere, nitric oxide and ammonia can undergo several processes, including reactions with radicals, and uptake of the gases in aerosols and clouds. Figure 1.3 presents the most important processes in the atmosphere for NO and NH_3 (reproduced from *Duyzer* [1995]). As was mentioned above (see section 1.1), NO reacts rapidly with O_3 to form NO_2. The formed NO_2 can react with a peroxy radical (RO_2, or more specifically $CH_3C(O)O_2$) to form peroxy acetyl nitrate (PAN). PAN is a relatively unreactive species and consequently can transport the nitrogen away from its source. However, generally, NO_2 reacts more rapidly with ozone (O_3) or hydroxy radicals (OH). The result is the formation of HNO_3 and N_2O_5. These latter compounds are easily dissolved in cloud droplets or taken up in aerosol particles to form nitrate (NO_3^-). HNO_3 is also very rapidly deposited onto surfaces [*Huebert and Robert*, 1985]. Similarly, NH_3 can be deposited, or taken up in clouds and aerosols to form ammonium (NH_4^+). Finally, the nitrogen species are removed from the atmosphere by wet deposition (precipitation), and the dry deposition of gases and aerosols (for more details see *Meixner* [1994]). Thus, in polluted areas with high emissions of reactive nitrogen species, soils can receive high levels of nitrogen by atmospheric deposition (HNO_3, NH_3, NO_2, NO_3^- and NH_4^+). These high levels of atmospheric nitrogen largely affect the cycling of nutrients in soil, leading to eutrophication and acidification [*Goulding et al.*, 1998; *van Breemen et al.*, 1982]. Furthermore, as was mentioned in paragraphs 1.1 and 1.2, NO_3^- and NH_4^+ are substrates for several microbial processes that are directly related to the production of NO in soils. Thus, increased nitrogen input to the soil by atmospheric deposition is likely to increase the biogenic NO emissions from soils [*Butterbach-Bahl et al.*, 1997].

Earlier in this paragraph, it was mentioned that current and future deforestation in the Brazilian Amazon are expected to increase human activities in the near future. The development of the temperate ecosystems during the last 200 years in the Northern Hemisphere demonstrated an increasing nitrogen deposition from the atmosphere to the ecosystems. It is therefore suggested that the current and future developments in the Brazilian Amazon also will enhance the atmospheric deposition of nitrogen, and possibly the NO emissions from soil. This can be interpreted as an additional (indirect) effect of deforestation on the NO emissions from soil.

For the reasons given above, the final part of this thesis concentrates on the biogenic emissions of NO from soils in areas with high levels of atmospheric nitrogen deposition. These are very high levels of N deposition, but could represent the future of some areas in the Amazon. NO emissions were measured from soils in the vicinity of poultry and pig farms in Scotland, which receive high loads of atmospheric nitrogen through the dry deposition of NH_3. In addition, results are presented from trace gas measurements in two forest plantations and on intact peat cores, that received extra input of nitrogen through acid mist. Finally, NO emissions were studied from soils at "Speulderbos" in the Netherlands. This research area has been a focus of several studies that deal with the impact of high nitrogen deposition on the nitrogen cycling in forest ecosystems, since it receives extremely high background values of nitrogen deposition (up to 70 kg N ha^{-1} y^{-1}). To summarize, in addition to the objectives mentioned in paragraph 1.4, emphasis was placed on the following:

IV. Study the effect of increased atmospheric nitrogen deposition on the biogenic emissions of N_2O and NO from soil.

V. Measure biogenic emissions of NO from soils in areas with very high atmospheric nitrogen loads.

1.6 Outline of the thesis

As part of the LBA-EUSTACH project, biogenic emissions of NO were studied from primary forest soils and pastures in the Brazilian Amazon. Because of difficulties with the export of any material that contains genetic information from Brazil, such as soil samples, a laboratory was build in Ji-Paraná (RO, Brazil). Experiments were conducted on soil samples in the laboratory in Brazil from March to November 1999.

In **Chapter 2**, the production and consumption of NO in soil samples from a primary forest and a 22 year old pasture is described in detail with respect to soil moisture and soil temperature. In addition, experiments were conducted in which the response of NO production to the addition of nutrients was monitored on samples from similar soils within approximately 100 km distance. The differences in the nutrient contents between forest and pasture soils provide an explanation for the higher NO production in forest soils..

Chapter 3 reports the quantification of the net NO emissions from the relations of NO production and consumption with soil temperature and soil moisture that were presented in Chapter 2. Thereafter, these laboratory-derived NO emissions were compared to NO emissions from dynamic chamber measurements in the field. In addition to the differences in the nutrient contents as was mentioned in Chapter 2, differences in the soil acidities and the gas diffusion of NO in the soils may explain the lower net NO emissions from pasture soils.

In **Chapter 4**, the optimum moisture conditions for NO emissions from soil were studied for a series of soil samples. In total, 35 soil samples were collected to cover a wide range of different soil textures within the Brazilian Amazon. The goal was to find whether differences in soil texture are reflected in the optimum field conditions under which NO is emitted from soil. In addition, water-release characteristics of the soil samples were determined using a simple tension-table, and corresponding pore size distributions were calculated. Finally, using these water-release characteristics, NO is presented as a function of matric potential.

The direct effect of deforestation on the biogenic NO emissions from soil within the Brazilian Amazon was quantified by comparing results on the production and consumption of NO from primary forest and pasture soils. In addition, an indirect effect of deforestation is the intensification of human activities in the newly deforested area. In the Northern Hemisphere, increasing human activities over the last 200 years have resulted in enhanced anthropogenic emissions from the combustion of fossil fuel, and the intensification of agriculture and industry. Moreover, these anthropogenic emissions have driven an increased deposition of reactive nitrogen, which have largely affected the nutrient status in soils. As was discussed in section 1.5, the Brazilian Amazon faces further rapid deforestation related to economical development in the near future. Considering the developments on the Northern

Hemisphere, NO emissions from soils within the Brazilian Amazon are likely to undergo changes due to an increased input of nitrogen to the soils.

Chapter 5 discusses the effect of increased N-deposition on the NO emissions. As part of a research project at the Centre for Ecology & Hydrology (UK), trace gas fluxes (N_2O and NO) from soils in the United Kingdom were studied with respect to their corresponding N-deposition. Emissions of N_2O and NO are presented from soils in an area around poultry and pig farms with increased N-depositions. In addition, results are shown on the N_2O and NO emissions from acid mist experiments on intact peat monoliths and in two Sitka spruce forest plantations.

Chapter 6 presents results of field measurements on the exchange rates of nitrogen oxides in forest ecosystems with extremely high N-deposition in the Netherlands. NO fluxes are presented from sandy and clayey soils, in a Douglas fir forest and a beech forest. This work was carried out as part of the European project FOREXNOX, coordinated by the Netherlands Organisation for Applied Scientific Research (TNO).

Finally, in **Chapter 7**, results from the previous chapters are combined and discussed in a broader perspective.

CHAPTER 2

Production and consumption of NO in forest and pasture soils from the Amazon Basin: a laboratory study

Saskia M. van Dijk and Franz X. Meixner

ABSTRACT

As part of the LBA-EUSTACH project, NO production and the rate constant of NO consumption in soil samples from Amazonian forest and pasture sites were determined in the laboratory. The purpose was to study NO production and consumption in soils from both types of land use as functions of soil temperature and soil moisture. NO production increased exponentially with soil temperature. The degree of increase depended on soil moisture, indicating that the response of NO production to a change in soil temperature is most pronounced at a certain intermediate soil moisture. NO production peaked at a soil moisture of 0.10 g/g, corresponding to 0.27 and 0.38 water-filled pore space for forest and pasture soils, respectively. The optimum soil moisture for which maximum NO release was observed was independent of soil temperature. NO consumption was most efficient at high soil temperatures and under dry soil conditions. NO release was approximately 10 times larger for forest than pasture soil. The difference may be related to the higher NO_3^- content in forest soil.

Submitted in final form to *Water, Air, and Soil Pollution*, 2001

2.1. INTRODUCTION

The tropical troposphere is believed to be responsible for about 70% of the global atmospheric oxidation of trace gases (*Crutzen and Zimmermann*, 1991). The tropospheric oxidative capacity is significantly influenced by nitrogen oxides NO_x (NO_x = NO + NO_2), especially by the catalytic behaviour of NO_x in photochemical ozone formation (*Graedel and Crutzen*, 1993). Tropical nitric oxide (NO) arises mainly from pyrogenic emissions released during biomass burning (*Andreae et al.*, 1996) and from biogenic emissions from soil. In the uppermost soil layers, NO is simultaneously produced and consumed by microbiological processes (*Conrad*, 1996a), which comprise of nitrification (the oxidation of organic nitrogen and ammonium to nitrate) and denitrification (the reduction of nitrate). On a global scale, net NO emissions into the atmosphere are larger than NO dry deposition (*Meixner*, 1994; *Davidson and Klingerlee*, 1997). However, if the soil is covered by tall vegetation, not all NO emitted from the soil might leave the canopy. When passing the trunk and canopy spaces, a substantial part of the biogenically emitted NO can react with ozone (mixed into the canopy from aloft) to form nitrogen dioxide (NO_2), which can be deposited to vegetation elements (*Jacob and Wofsy*, 1990; *Meixner* 1994; *Ammann et al.*, 1999).

While chamber measurements and micrometeorological techniques have been successfully applied to quantify soil NO emissions in the field, the investigation of the controlling parameters of biogenic NO emissions (soil moisture, soil temperature and soil nutrient content) usually requires well-defined (laboratory) conditions (*Ludwig et al.*, 2001). It has been demonstrated that NO emissions, which were derived by laboratory measurements on soil samples, agreed with NO emissions which were measured in the field by use of dynamic chambers (*Remde et al.*, 1993; *Yang and Meixner*, 1997; *Otter et al.*, 1999; *Ludwig et al.*, 2000). Moreover, biogenic net NO emissions were parameterized in terms of soil temperature and soil moisture (*Yang and Meixner*, 1997; *Otter et al.*, 1999). However, NO is produced and consumed in soil through individual processes (*Conrad*, 1996a), and these processes should therefore be studied separately with respect to their controlling parameters, rather than the resulting net NO emissions.

Current and future deforestation and land use changes in the Amazon Basin will affect physical and chemical characteristics of corresponding soils (*Moraes et al.*, 1996; *Neill et al.*, 1999; *Andreae et al.*, 2000). Conversion from forest to pasture has been shown to slow down mineralization and nitrification rates, change nutrient pools in soil (*Neill et al.*, 1999), and decrease the soil NO emissions (*Keller et al.*, 1993; *Garcia-Montiel et al.*, 1999). Consequently, tropical NO emissions will change on a large scale, which will have a significant impact on the regional and global tropospheric chemistry.

In this study, microbial NO production and consumption were studied separately in the laboratory on soil samples from Amazonian forest and pasture sites. Results are presented with respect to soil temperature, soil moisture, and nutrient additions.

2.2 METHOD

2.2.1 Site characteristics

During September 1999, soil was collected from the primary rainforest in the Biological Reserve Jaru (10°05' S, 61°55' W), and from the pasture on Fazenda Nossa Senhora (10°45' S, 62°21' W), both in the state of Rondônia, Brazil. At both sites, mean annual air temperature is 25 ºC and precipitation is approximately 2200 mm a year. The pasture was first burned in 1977. After a sequence of rice/bean plantations, the land was ploughed (1992) and turned into pasture with predominantly tropical grass vegetation (*Brachiaria brizantha)*. Both the forest and pasture have acidic loamy sand soils of the type Podzolico vermelho-amarelo, comparable to the orthic acrisol in the FAO (Food and Agricultural Organization, United Nations) classification. Field bulk densities (BDs) were determined from undisturbed soil cores (diameter 0.05 m, height 0.05 m) with a precision of 3%. The ammonium and nitrate concentrations in extracts (2M KCl) of the soil samples were determined with spectrometry. Table 2.1 presents some soil characteristics of the forest and pasture field sites.

Beside the two main sampling sites described above, additional samples were collected from forest and pasture soils of the type Podsolico vermelho-amarelo at Fazenda Nova Vida (10°30' S, 62°30' W). The site is described in detail by *Neill et al.* (1999).

Table 2.1. Soil characteristics of the forest and pasture soils.

	Sand, %	Silt, %	Clay, %	pH	BD, kg/dm^3	Porosity, %	NH_4^+, mg/kg	NO_3^-, mg/kg
Forest	80	7	13	3.5	1.33	54	9.38^b	11.79^b
Pasture	84	5	11	5.2	1.56^a	41	16.81^b	5.25^b

Values are from single measurements (n = 1) except when indicated otherwise

[a] Mean value of 4 measurements (n = 4), with a standard deviation of 0.05

[b] February 2000, soil nutrient contents were determined again on new samples from forest (n = 2) and pasture (n = 1) soils. NH_4^+ and NO_3^- were 10.47±1.5 and 13.16±1.9 in forest soil, and 23.02 and 7.19 in pasture soil, respectively.

2.2.2 Experimental setup

Net NO release was determined in the laboratory from soil samples for a broad range of soil temperatures T (10–35ºC) and soil moistures θ (0–100% water-filled pore space (WFPS)) and for various ambient NO mixing ratios (0–130 ppb). The experimental setup (see Fig.2.1), first described by *Yang and Meixner* (1997), was slightly modified.

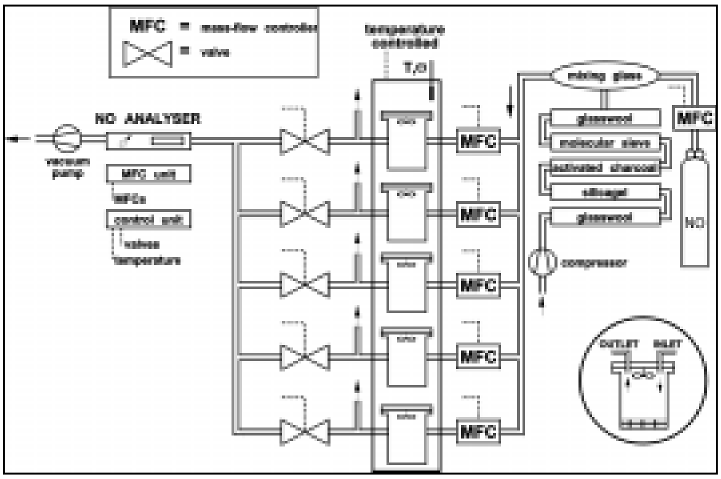


Figure 2.1. Experimental setup for laboratory investigation of NO production and consumption in soil samples.

In short, approximately 0.060 kg of dry soil was placed in a Plexiglas cuvette of approximately 1-litre volume, and either zero air (NO-free) or air with a certain NO mixing ratio was flushed through the headspace of the cuvette at a flow rate of 4.17×10^{-5} m^3 s^{-1}. NO was measured by a chemiluminescence analyser (TECAN AL 770 PPT, Ecophysics, Switzerland). The instrument was calibrated using NO gas standards (200 ppm; Messer Griesheim, Germany) and a home-built gas dilution system, consisting of a mass-flow controller (0–10 mL min^{-1}; Bronckhorst, Netherlands) and a glass-mixing chamber. Calibration was conducted every 4 weeks in the range from 0 to 200 ppb NO mixing ratio. The standards could be reproduced with a precision better than 3%. With an integration time of 10 seconds, the detection limit of the NO analyser was 100 ppt (2σ).

Net NO release (J) (i.e., the released mass of NO-N per soil mass – time) was calculated from the difference in the NO mixing ratios at the inlet ($[NO]_{in}$ in ppb) and outlet ($[NO]_{out}$ in ppb) of the soil cuvette, the soil mass (M_{soil} in kg) and the flow rate of the carrier gas (Q in $m^3 s^{-1}$):

$$J = (Q/M_{soil})\ ([NO]_{out} - [NO]_{in})\ (M_N/V_m) \qquad (2.1)$$

where the ratio (M_N/V_m) is used to convert NO mixing ratios (ppb) into gas density units (ng m^{-3}). M_N is the molecular weight of nitrogen (14.0 g $mole^{-1}$) and V_m is the molar volume (2.45×10^{-2} m^3 $mole^{-1}$) at 298 K. NO release could be determined above 0.04 ng kg^{-1} s^{-1}. It should be emphasized that net NO release is negative ($J<0$) when NO consumption exceeds the NO production in soil ($[NO]_{out}<[NO]_{in}$). This will also be referred to as net NO release. In total, soil samples in four measurement cuvettes and one blank cuvette were analysed in turn, by switching a valve manifold system every 1.5 minutes. The cuvettes were enclosed in a climate chamber, which enabled the control of soil temperature either at constant temperature or by continuous heating at 0.25 ºC/min. Soil temperature was measured in the centre of two soil samples, since no significant thermal gradient within the sample was detected. Soil moisture was calculated every hour from the gravimetrically measured water loss of the soil sample in the measurement cuvettes. Variation in the initial gravimetric water content of replicate soil samples ($n = 5$) was 5%. Water loss during the experiment was measured using a balance (PG5002-S, Mettler Toledo) with an accuracy of 0.01 g. Considering a typical sample amount of 0.06 kg dry soil, gravimetric moisture content could be determined within 2% in all cases. The hourly gravimetric water contents were fitted with Gaussian functions in order to derive soil moisture data for the full measurement period. For saturated soils to soils with approximately 0.06 g H_2O/g soil, negligible uncertainty was introduced by interpolating the hourly moisture measurements. However, for relatively dry soils (<0.06 g/g) the Gaussian curve was extrapolated to calculate the moisture content. In these cases, the maximum deviation from zero that was calculated for completely dry soil was –0.025 g/g. For this reason, the maximum absolute error in the soil moisture content due to the fitting method was estimated to be ± 0.025 g/g. The use of an inverted Nafion dryer system, which extracts water vapour from the outlet air of every cuvette and directs it back into the atmosphere of the soil cuvettes, enabled measurements at approximately constant soil moisture. The typically observed water loss rate with the inverted Nafion dryer was 0.37 g H_2O h^{-1} (without Nafion dryer 1.79 g H_2O h^{-1}), which corresponded to a reduction in the soil moisture content of only 1% per hour. Soil samples were composed of 6 subsamples from a 10 x 10 m^2 sampling plot. Samples were cooled during transport and stored in the laboratory at 4 ºC. Large pieces of roots and rock were removed by sieving the soil samples at 2 mm. All experiments were conducted within 1 month after sampling. Each experiment was initiated with pristine soil. Soil samples were packed in the cuvette to their equivalent field bulk density. The soil was allowed to adjust to the soil temperature set point for approximately 30 minutes, after which NO release measurements were initiated. Gravimetric soil moisture (g/g) was converted into water filled pore space (WFPS) using the field bulk density. The individual subsamples proved excellent duplicates, a typical example is shown in Table 2.2. NO release was measured from four replicate samples of a pasture soil (P87) from Fazenda Nova Vida (for details on the pasture site see *Neill et al.* [1999]). The variation in the NO release amongst the replicate soil samples was in all cases within 10%. After the first experiment the samples were stored for 17 days at 4 ºC. Repetition of the experiment using two of the replicate samples, indicated that the results could be reproduced within 0.02 ng NO-N kg s^{-1}, which corresponds to a precision of 15%. Nevertheless it was decided to take fresh soil from the sample bag for each new experiment.

Table 2.2. NO release (ng NO-N kg^{-1} s^{-1}) from replicate soil samples (soil moisture = 0.10 g/g) of a pasture (P87) at Fazenda Nova Vida.

Individual Subsamples:	Nov 10th 1998 NO release	Nov 28th 1998 (repeated experiment) NO release
A	0.14	0.12
B	0.15	0.12
C	0.13	not measured
D	0.14	not measured
Replication	within 6%	within 1%

2.2.3 Experiments

Net NO release by soil samples has been observed to be linearly related to the NO mixing ratio in the head space of the measurement cuvette (cf. *Remde et al.*, 1993). Consequently, the NO consumption process is assumed a first-order reaction with respect to the NO mixing ratio [NO]. Therefore by conducting a series of experiments at varying NO mixing ratios (0, 80 and 130 ppb), the rate constant of NO consumption k can be determined from the slope of the corresponding plot of J versus [NO] (i.e., $k = \Delta J/\Delta[NO]$). Selection of 0, 80 and 130 ppb was made since the NO compensation points (Conrad, 1996b) (and ambient NO mixing ratio) were typically 76.0 ppb (2.6 ppb) and 10.2 ppb (0.37 ppb) for the forest and pasture, respectively. Furthermore, the NO production P equals the release of NO at [NO] = 0 (i.e., P is the y-axis intercept of the linear regression line of J versus [NO]). The rate constant k was determined for soil samples at 3 different soil temperatures (16, 26 and 32 ºC) and at the whole range of soil moistures (0–100% WFPS). NO production P was derived directly from measurements of NO release J at NO-free air. Since the NO mixing ratio is determined in the headspace of the cuvette ([NO] slightly above zero), P equals J only by approximation.

For both the forest and the pasture soils, the difference between the observed J and P (i.e., J at [NO] = 0) was estimated to be less than 5%. The dependence of NO production P on soil temperature and soil moisture was determined from several experiments. These included measurements at constant soil temperatures with varying soil moistures (0–100% WFPS) and measurements at constant soil moistures with varying soil temperatures (10–35 ºC). In addition, experiments were conducted to determine the response of NO release to additions of NH_4^+ and NO_3^-. Soil samples, with the original field moisture content (ranging from 0.20 to 0.35 g/g), received 0, 80, 400 or 800 mg N/kg dry soil in 3-ml demineralized water from either a NH_4Cl or a KNO_3 solution, and the net NO release from soil was determined.

2.3 RESULTS AND DISCUSSION

2.3.1 NO production *P*

Figure 2.2 shows NO production *P* (i.e., NO release at $[NO]_{in} \approx 0$) in forest and pasture soils at a constant soil temperature of 25 °C. Maximum NO production was 2.7 and 0.26 ng N kg^{-1} s^{-1} in soils from the forest and the pasture, respectively. NO production peaked at a soil moisture of approximately 0.10 g/g for both samples, which is equivalent to 0.27 WFPS for the forest and 0.38 WFPS for the pasture. The soil moisture where NO production peaked (θ_{opt}, optimum soil moisture) did not change significantly with soil temperature (results not shown). Gas-diffusion limitation under wet soil conditions (Skopp et al., 1990) and substrate-diffusion limitation under dry soil conditions (*Linn and Doran*, 1984) result in a specific shape of the *P* response to soil moisture and consequently in the existence of θ_{opt}.

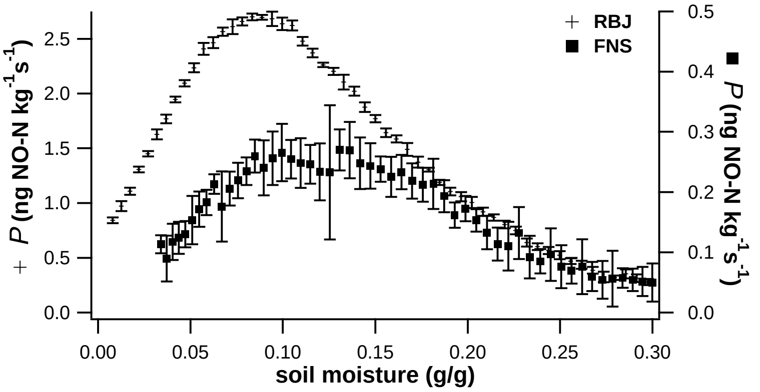


Figure 2.2. NO production *P* in forest (RBJ) and pasture (FNS) soils as a function of soil moisture (data are mean values (n = 6), the standard deviation is indicated by error bars).

For both soils, the NO production *P* increased exponentially with soil temperature ($P = A \exp^{BT}$), as presented in Figure 2.3a for the forest soil. An exponential increase with soil temperature is generally found for microbial processes (*Conrad*, 1996b), including nitrification (*Focht and Verstraete*, 1977) and denitrification (*Galbally*, 1989), and was observed in numerous NO field studies (*Johansson*, 1984; *Williams and Fehsenfeld*, 1991). The strongest increase with soil temperature can be observed for intermediate moisture of 0.10 g/g. The exponential relation can be written as the linear equation $\ln P = \ln A + BT$. Both $\ln A$ and B show a parabolic behaviour with respect to soil moisture (see Figure 2.3b). In extremely dry and extremely wet soil, the increase of NO production with soil temperature is less pronounced than at more intermediate soil moistures. Exponential relations were also found for the pasture soil, with different A, but nearly identical *B* coefficients. This indicates that whereas the magnitude of NO release from forest and pasture soils differed considerably, the increase of NO release with soil temperature was similar for both soils.

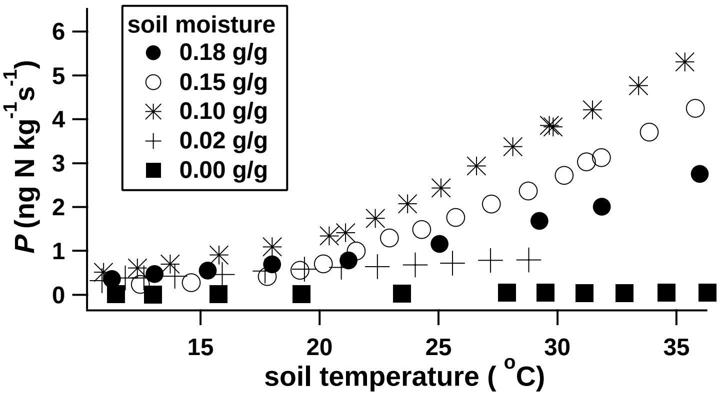


Figure 2.3a. NO production P in forest soil as a function of soil temperature. Soil moisture is indicated by the symbols in the legend. Error bars are within the size of the symbols.

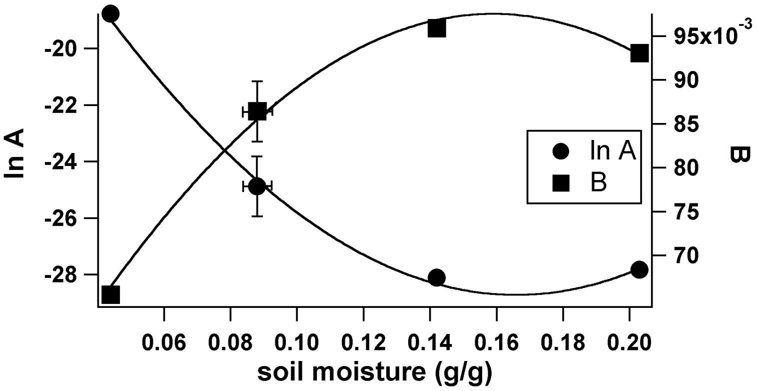


Figure 2.3b. The dependence of NO production P in forest soil on soil temperature. The parameters ln A and B of the linear equation $\ln P = \ln A + BT$ show a parabolic behaviour with respect to soil moisture. Typical error bars are shown.

2.3.2 Rate constant of NO consumption *k*

Values of the NO consumption rate constant k showed a clear dependence on soil moisture and soil temperature (Figure 2.4). Also included in the figure are results from the soil samples collected at Fazenda Nova Vida that illustrate the same findings. k decreases with soil moisture and increases with soil temperature. This indicates that NO consumption is favoured at high soil temperatures and under dry soil conditions. The dependence on soil temperature can be explained by the microbial nature of the consumption processes, both through reduction (*Krämer et al.*, 1990; *Bender and Conrad*, 1994) and through oxidation (*Koschorreck and Conrad*, 1997). In agreement with our results, *Gödde and Conrad* (1999) found decreasing NO consumption with increasing soil moisture and attributed this to the O_2-limiting conditions under wet soil.

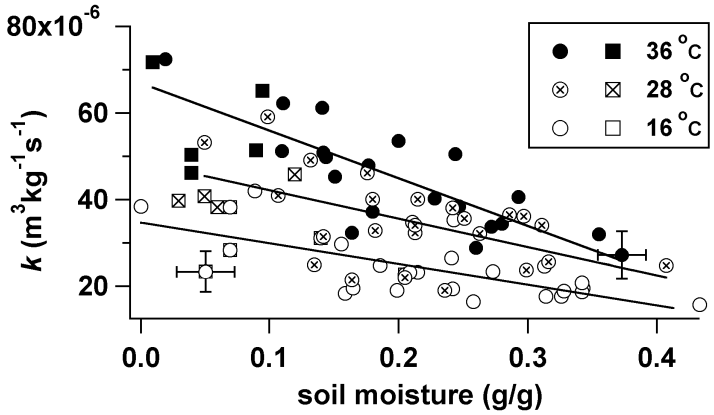


Figure 2.4. Rate constants of NO consumption *k* in forest and pasture soils as a function of soil moisture and soil temperature (squares). Additional data that illustrate the same findings for soil samples from Fazenda Nova Vida (circles) are included. Typical error bars are shown.

2.3.3 Differences between forest and pasture soils

NO production in forest soil was approximately 10 times higher than in pasture soil (Figure 2.2). The forest and pasture soils have comparable contents of total inorganic nitrogen (NH_4^+ + NO_3^-). However, the forest soil contains more NO_3^- and less NH_4^+ compared to the pasture (see Tab. 2.1). Differences in the relative portions of the inorganic nitrogen contents may reflect differences in the NO production in both soils. In order to find the response of NO production to additions of NH_4^+ and NO_3^-, we conducted a series of experiments in the laboratory on similar forest and pasture soils from Fazenda Nova Vida (within approximately 100 km distance from Reserva Biologica Jaru and Fazenda Nossa Senhora). Almost no increase of the net NO release upon addition of NH_4Cl solutions was observed, whereas the addition of KNO_3 solutions resulted in enhanced NO release (Figure 2.5). This indicates that NO_3^- consumption may be an important pathway for NO production in these soils. However, the following must be considered. The nutrients were added and mixed into field moist soil of approximately 50–100% WFPS (section 2.2.2). These relatively wet conditions may well have favoured denitrification, and consequently resulted in higher NO production in soil after addition of NO_3^-. Our results may therefore indicate the potential of NO production through the consumption of NO_3^-. It does not prove that nitrate consumption was indeed the dominating NO production process in the investigated soils.

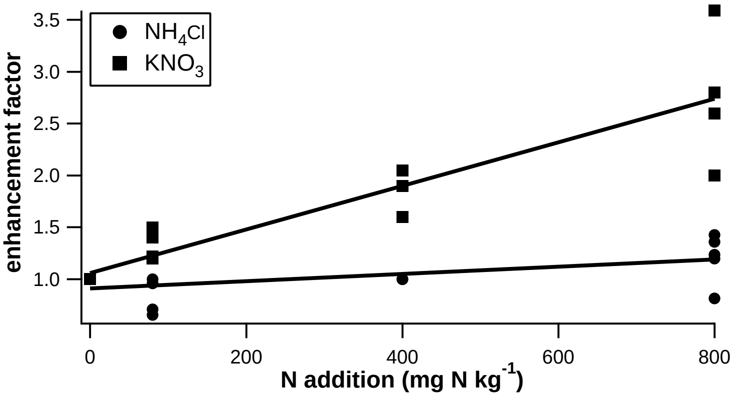


Figure 2.5. The response of net NO release from field moist soils at 25 °C to additions of NH_4Cl and KNO_3. The enhancement factor equals the observed NO release divided by net NO release from a control sample without N-addition. Experiments were conducted with forest and pasture soils from Fazenda Nova Vida.

While there is agreement on higher NO fluxes from tropical forest soils compared to pasture soils, contrasting results are found in the literature concerning the control of NO production by nutrients in soils. For mid-latitude soils, *Ludwig et al.* (2000) observed a significant log-linear dependence of NO emissions on soil NO_3^- for different European semi-natural and agricultural sites (with which our data also agrees). *Vermoesen et al.* (1996) attributed NO production at low pH to NO_3^- and at higher pH values to NH_4^+. In agreement to our findings, *Cardenas et al.* (1993) found that NO emissions from acidic tropical soil were strongly stimulated by NO_3^- and only very weakly by addition of NH_4^+. *Bakwin et al.* (1990) also found higher NO fluxes after the addition of NO_3^- compared to NH_4^+ and suggested a reductive pathway (denitrification) for the NO production in Amazonian soils. In contrast, *Parsons and Keller* (1995) observed a significant increase of the NO emissions to additions of NH_4^+, but no significant increase to additions of NO_3^- in intact soil cores from a forest in Costa Rica. Furthermore, NO release from an old pasture (>20 years) did not show any response to additions of NH_4^+ and NO_3^-. During earlier work in Costa Rica, *Keller et al.* (1993) measured higher NO fluxes from primary forest soils compared to old pastures (>10 years). These lower pasture emissions were thought to arise from the nitrogen-poor soil conditions of pasture soil. As was mentioned above, our results showed higher NO production in forest soil, but with similar conditions of total inorganic nitrogen on both sites (see Tab. 1). *Garcia-Montiel et al.* (1999) also measured highest NO emissions from forest soils at Fazenda Nova Vida, with similar total inorganic nitrogen contents and more inorganic nitrogen in the form of NO_3^- in forest soil compared to pasture (*Neill et al.*, 1999).

It has been shown repeatedly that pastures are dominated by NH_4^+, whereas forest soils contain a higher portion of the mineral nitrogen in the form of NO_3^- (*Piccolo et al.*, 1994;

Neill et al., 1997; *Verchot et al.*, 1999, see also *Davidson et al.*, 2000). These authors suggested that the higher NO_3^- content in forest soil are a result of rapid nutrient cycling from NH_4^+ (and organic N) to NO_3^-. Moreover, high NO emissions from forest soils would thus result from (rapid) nitrification. Similarly, they suggested that the higher portions of NH_4^+ in pastures indicate relatively slow nitrification, which in turn would explain the lower NO emissions from pastures. Unfortunately, nitrification and mineralization rates are not known for our forest and pasture samples. However, this interpretation seems applicable to our results of high NO_3^- in forest soils with high NO production, and low NO_3^- in pasture with low NO production. In addition, maximum NO production was found at 0.27 and 0.38 WFPS for the forest and pasture respectively, which indicates aerobic conditions in both cases. Aerobic conditions are generally thought to favour nitrification, although denitrification has also been observed under aerobic conditions (*Remde and Conrad*, 1991; see also *Conrad*, 1996b).

2.3 CONCLUSIONS

A laboratory method has been applied to investigate the role of soil temperature, soil moisture and soil nutrients (the most important controllers of biogenic NO emission) on NO production and NO consumption processes in Amazonian primary forest and pasture soils. This is a substantial step forward as earlier laboratory work (*Yang and Meixner*, 1997; *Otter et al.*, 1999) was confined to the parameterization of net NO emission. NO production was found to increase exponentially with soil temperature. Under very dry and very wet soil conditions, the response of the NO production to a change in temperature was less pronounced than under conditions of intermediate soil moisture. NO production peaked, independent of soil temperature, at soil moisture of 0.10 g/g corresponding to 0.27 WFPS and 0.38 WFPS for the forest and pasture soils, respectively. NO consumption was most effective at high soil temperatures (> 25°C) and under dry soil conditions (<0.20 g/g). Rate constants of NO consumption were within 5% of NO production and showed comparable values for forest and pasture soils. NO production, and consequently net NO release, was generally 10 times higher in forest soil compared to pasture. There is some evidence, that this observation mirrors differences in the nutrient pools. Nutrient addition experiments indicated the potential for NO production through the consumption of NO_3^-. Higher soil NO_3^- content has been observed in our forest soil (as compared to pasture) and may have led to a higher NO production compared to pasture soils. On the other hand, the higher NO_3^- content in forest soil suggests rapid nitrification, which could suggest that NO was produced by the consumption of NH_4^+ and/or organic N rather than NO_3^-. Whether these or other processes (e.g. chemodenitrification) have contributed to the observed NO release awaits further investigation. Most likely, microbial inhibition-experiments could bring more insight, which biological and/or chemical processes dominated in these soils. Finally we like to state, that our findings—notably the high NO release from Amazonian forest soils—are not necessarily equivalent to higher NO fluxes out of the forest canopy, since in-canopy conversion of NO to NO_2 (through reaction with ozone) may reduce the biogenic NO emission of forest soils (*Ammann et al.*, 1999).

2.4 ACKNOWLEDGEMENTS

The authors would like to thank the Federal University of Rondônia (UNIR) and the National Institute for Colonisation and Agriculture (INCRA) in Ji-Paraná, Brazil for their support. Paul Steudler and Diana Garcia (The Ecosystems Center, Woods Hole, USA) are kindly thanked for their help in enabling us to collect soil at Fazenda Nova Vida. The European Union and the Max Planck Society gave financial support through the LBA-EUSTACH project (ENV4-CT97-0566).

CHAPTER 3

Biogenic NO emissions from forest and pasture soils: relating laboratory studies to field measurements

S.M. van Dijk, A. Gut, G.A. Kirkman, B.M. Gomes, F.X. Meixner, M.O. Andreae

ABSTRACT

During September and October 1999, dynamic chamber measurements were carried out to determine NO fluxes from a primary forest soil and an old pasture in the Brazilian Amazon, as part of the LBA-EUSTACH project. In addition, soil samples were collected from these two sites and laboratory experiments were conducted to determine the NO production and consumption rate constant as functions of soil temperature and soil moisture. These laboratory results were converted into NO fluxes using a simple algorithm, which required additional information on the gas-diffusion in soil, the soil bulk density and the field conditions (soil temperature, soil moisture). Considering the entire measurement period, the calculated and measured NO fluxes agreed well, both for the forest (6.9 ± 2.9 ng m^{-2} s^{-1} and 5.0 ± 4.6 ng m^{-2} s^{-1}, respectively) and the pasture (0.67 ± 0.09 and 0.65 ± 0.37, respectively). Forest to pasture conversion decreased NO production, as well as gas-diffusion, and finally resulted in smaller NO fluxes from pasture than forest soil.

Also submitted to *J. Geophys. Res.*

3.1 INTRODUCTION

Nitrogen oxides ($NO_x = NO + NO_2$) contribute largely to the oxidative capacity of the troposphere by the catalytic behaviour of NO_x in the photochemical formation of ozone (O_3)[*Graedel and Crutzen*, 1993]. In the tropical Amazon basin, sources of NO_x are mainly from biomass burning [*Andreae et al.*, 1996] and biogenic emissions from the soil [*Davidson* et al., 2000]. Production of nitric oxide (NO) in soil can occur both through biological (e.g., nitrification and denitrification) and chemical processes (chemodenitrification). Nitrification is the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-) (eq. 3.1). Besides this pathway (autotrophic nitrification), heterotrophic bacteria have been found to oxidise NH_4^+ and organic nitrogen species to NO_2^- and NO_3^- (heterotrophic nitrification) (see *Conrad* [1996a]).

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \qquad (3.1)$$

Biological denitrification is the reduction of NO_3^- to NO_2^-, with endproducts N_2O and N_2 (eq. 3.2). Denitrification generally occurs under anaerobic conditions, although aerobic denitrifiers and heterotrophic nitrifiers have been found to denitrify NO_3^- under aerobic conditions (see *Conrad* [1996a]).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (3.2)$$

Another pathway for NO production is through chemical reactions. Nitrite (NO_2^-) and nitrous acid (HNO_2) become chemically unstable in acid soil ($pH < 5.5$), especially in combination with a high organic matter content [*Blackmer and Cerrato*, 1986]. The concentrations of these species are generally low in soil. However, NO_2^- is produced as an intermediate product both during nitrification and denitrification, and hence can react chemically directly after its (biological) formation in acid, organic soils. Several chemical reactions are known to produce NO (equations 3.3, 3.4 and 3.5), these are generally referred to as chemodenitrification [*Serca et al.*, 1994].

$$3\,NO_2^- + 2\,H^+ \rightarrow 2\,NO\,(g) + NO_3^- + H_2O \qquad (3.3)$$

$$2\,HNO_2 \rightarrow NO\,(g) + NO_2\,(g) + H_2O \qquad (3.4)$$

$$NO_2^- + NO_2\,(g) \rightarrow NO_3^- + NO\,(g) \qquad (3.5)$$

NO is also consumed in soil, it is a substrate for denitrification and various other biological reduction and oxidation processes [*Baumgärtner et al.*, 1996; *Rudolph et al.*, 1996a; *Krämer et al.*, 1990]. NO production and consumption occur simultaneously in soil.

NO production generally exceeds consumption, which results in net release of NO from the soil to the atmosphere [*Davidson and Klingerlee*, 1997; *Meixner and Eugster*, 1999].

Whereas net fluxes of NO from soil are generally measured in the field, NO production and consumption are determined on soil samples under controlled conditions in the laboratory. However, net NO fluxes have also been derived from soil samples in the laboratory. Those net NO fluxes agreed with NO fluxes that were measured at corresponding field sites by use of dynamic chambers [*Galbally and Johansson*, 1989; *Remde et al.*, 1993; *Rudolph et al.*, 1996b; *Gut et al.*, 1999; *Otter et al.*, 1999; *Ludwig et al*., 2000]. Examining soil samples in the laboratory is a more straightforward and less expensive way to quantify NO fluxes, especially when focussing on differences between ecosystems. As part of the project “European Studies of Trace gases and Atmospheric Chemistry as a contribution to the Large Scale Biosphere-Atmosphere Experiment in Amazonia“ (LBA-EUSTACH), we present results from laboratory studies on soil samples from the Brazilian Amazon and compare these to results from field measurements at exactly those locations where the samples were taken.

3.2 METHOD

3.2.1 Field measurements

During 6 weeks between September and October 1999, NO fluxes were determined in the field at a primary forest in Reserva Biologica Jaru (10°05' S, 61°55' W) and at an old pasture at Fazenda Nossa Senhora (10°45' S, 62°21' W). Both sites are situated in the state of Rondônia (Brazil), where rapid deforestation has been taking place since the last 25 years. Mean annual temperature is 25 ºC and precipitation is approximately 2200 mm a year. Reserva Biologica Jaru is an undisturbed primary forest reserve, whereas the pasture site (burned first in 1977) is covered predominantly with tropical grass vegetation (*Brachiaria brizantha)*. For further details about the measurement sites, see *Andreae et al*. [2001].

Exchange rates of NO between the soil and the atmosphere were determined with dynamic chambers. The chambers (11.8 L volume), covering a surface of 0.066 m^2, were placed directly on the soil surface and sealed with Teflon foil and sand, to avoid cutting the dense root mat. A funnel was mounted on the chamber outlet, on top of the cover, to allow wetting of the soil by rain. A micro-fan pushed ambient air through the chamber, replacing the chamber volume about 3.3 times per minute. A second micro-fan, mounted within the chamber, ensured well-mixed conditions. A detailed description of the field-measurements at the forest (Reserva Biologica Jaru) is given by *Gut et al.* [2001] and at the pasture (Fazenda Nossa Senhora) by *Kirkman et al.* [2001].

In addition, the soil bulk density coefficient was measured from the surface flux and the activity gradient of ^{222}Rn. The ^{222}Rn surface flux was measured using static chambers [*Gut et al.*, 2001]. For the ^{222}Rn-activity gradient (between 3-cm soil depth and ambient), hydrophobic, gas permeable tubes (1.5 m length, Accurel V8/2 ™) were buried 6 months prior to measurements. The methodological concept is based on diffusion from the air-filled pore space of the soil to a small air stream in the tubes. To avoid enrichment or depletion of ^{222}Rn in the soil, the sampled air was recycled into the tubes after detection [see *Gut et al.*, 1998]. Soil bulk diffusion was parameterised with air-filled pore space and scaled with the ratio of the NO molecular diffusion coefficient over the ^{222}Rn molecular diffusion coefficient of 1.5 to obtain the NO bulk diffusion coefficient in soil. The diffusivity of NO through the soil pores was measured for 2 weeks in forest soil, and in addition measurements were conducted during several days at the pasture site.

3.2.2 Laboratory experiments

Soil samples were collected from the same locations where NO fluxes were measured with dynamic chambers (as described in Section 3.2.1), from the primary forest in the Reserva Biologica Jaru and from the pasture at Fazenda Nossa Senhora on 26 and 28 September 1999 respectively. In order to avoid small-scale soil inhomogenities, soil was collected exactly where the dynamic chambers were located. Additional soil samples were collected from other parts of the Amazon Basin (the states of Amazonas and Para) during three sampling campaigns in March, June and September 1999. Geographical coordinates of the sampling locations, as well as a description of several physical (bulk density, porosity, sand/silt/clay content, water-release characteristics, pore-size distribution) and chemical soil properties (organic carbon, inorganic nitrogen content, pH, CEC, etc.) of the samples were presented by van Dijk and Meixner [2001a, 2001b].

In short, the soil samples from Reserva Biologica Jaru (RBJ) and Fazenda Nossa Senhora (FNS) both consisted of a loamy-sand texture (approximately 10% clay and 80% sand), with pH (0.01 M $CaCl_2$) of 3.5 and 5.2 respectively. Field cores (0.05 m. Ø, 0.05 m. height) showed soil bulk densities of 1.33 g/cm^3 and 1.56 g/cm^3 for RBJ and FNS respectively. The samples (RBJ and FNS) were taken into the laboratory in Ji-Paraná (RO, Brazil), where NO production (P) and the rate constant of NO consumption (k) were determined as functions of soil temperature (T) and soil moisture (θ). Figure 3.1 gives a simplified graphical presentation of a single measurement cuvette. In total, four individual measurement cuvettes (each containing a soil sample, packed to the corresponding field bulk density) and one blank cuvette were continuously flushed with dry air (4.2×10^{-5} m^3 s^{-1}), having NO concentrations ranging from 0 to 7.5×10^3 ng m^{-3}.

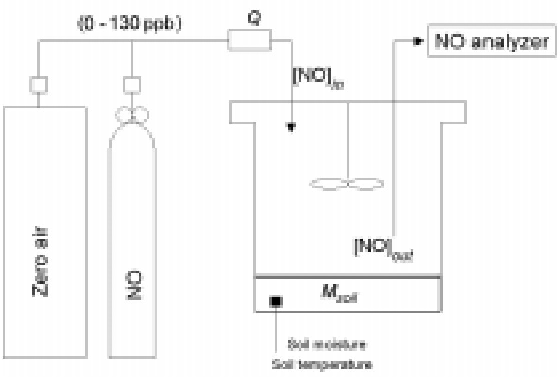


Figure 3.1. Simplified graphical presentation of a single measurement cuvet containing a soil sample.

Net NO release (or uptake) by the soil samples is determined by measuring the corresponding concentrations before and after passing the cuvettes: net NO release $J = (Q/M_{soil})$ $([\mathrm{NO}]_{out} - [\mathrm{NO}]_{in})$, where Q is the flow rate, M_{soil} is the equivalent dry soil mass and $[\mathrm{NO}]_{out}$ and $[\mathrm{NO}]_{in}$ are the NO concentrations at the inlet and outlet respectively. A micro-fan ensures well mixed conditions within the chamber, therefore the (ambient) NO concentration in the headspace of the cuvette equals the outlet concentration $[\mathrm{NO}]_{out}$.

Whereas NO production is independent of the ambient NO concentration (above the soil), NO consumption processes are assumed to be first-order reactions with the ambient NO concentration [*Remde et al.*, 1989] (see figure 3.2). Hence, the rate constant of NO consumption (k) equals the slope of J with the NO concentration in the headspace of the cuvette. Furthermore, at zero ambient NO, where NO consumption is zero, net NO release equals NO production (P). Thus, NO production is found by extrapolation of the regression ($\Delta J/\Delta[\mathrm{NO}]_{\mathrm{out}}$) to the y-intercept ($[\mathrm{NO}]_{out}=0$). See also the following paragraph (Section 3.2.3).

All cuvettes were placed in a small climate control chamber, which enabled the determination of NO production and the NO consumption rate constant in soil samples for a range of soil temperatures (10–35 °C) and soil moistures (0–100 % water-filled pore space). Soil temperature was measured in the middle of the soil samples. Gravimetric water content was calculated every hour from the soil samples, using the equivalent dry weight soil-mass (calculated from the initial gravimetric water content). NO was measured by a chemiluminescence analyser (TECAN AL 770 PPT, Ecophysics, Switzerland), with a detection limit of 100 ppt. This enabled the detection of NO release from soil at 0.04 ng NO-N $\mathrm{kg}^{-1}\ \mathrm{s}^{-1}$. *Van Dijk and Meixner* [2001a] give a more detailed explanation of the laboratory set-up and the error assessment of the system (see Chapter 2).

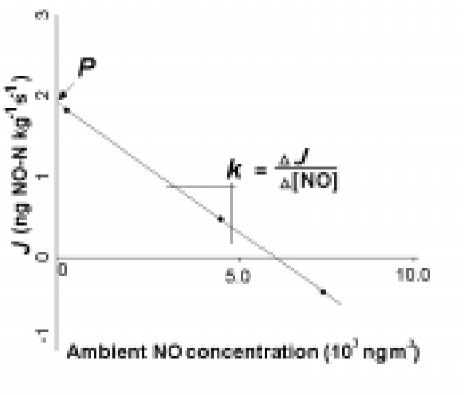


Figure 3.2. NO release (or uptake) (ng NO-N kg^{-1} s^{-1}) versus the ambient NO concentration (ng m^{-3}).

3.2.3 The diffusion algorithm of Galbally and Johansson [1989]

It was already mentioned above that NO production and consumption occur simultaneously in soil, and that this generally results in net release (J) of NO by the soil (eq. 3.6). The simultaneous occurrence of these processes has lead to the concept of compensation concentration ($[NO]_c$), the NO concentration where production equals consumption ($J = 0$) (eq. 3.7) [*Conrad*, 1996b; *Conrad*, 1994].

$$J = P - k\,[\mathrm{NO}]_{amb} \tag{3.6}$$

$$[\mathrm{NO}]_c = P / k \tag{3.7}$$

where P is NO production (mass of NO-N per mass of dry soil and time), $[NO]_{amb}$ is the ambient NO concentration (mass of NO-N per volume), and k is the rate constant of NO consumption (volume of NO-N per mass of dry soil and time). As mentioned above, NO production generally exceeds NO consumption, therefore NO is formed in soil and can escape to the atmosphere. However, the amount of NO that escapes the soil depends on the effective gas diffusion through the soil pores. Gas diffusion generally is faster through large and open pores, while small pores and water-filled pores result in slower gas-diffusion in soil [*Currie*, 1983]. *Galbally and Johansson* [1989] developed a simple diffusion-based algorithm to transform the laboratory derived NO release (mass of NO-N per mass of dry soil and time) into a net NO flux (mass of NO-N per area and time). The net NO flux derived from laboratory measurements will be denoted as F_{lab}, and is calculated according to equation (3.8). Similarly, the net NO flux derived from field measurements will be denoted as F_{field}.

$$F_{lab} = \sqrt{BD \cdot k \cdot D} \times \left([\mathrm{NO}]_{amb} - \left(\frac{P}{k} \right) \right) \tag{3.8}$$

Besides *P* and *k*, information is needed about the soil bulk density (*BD*), the diffusion coefficient (*D*) of NO through the soil and the ambient NO concentration. Chapter 3.3.5 provides a sensitivity analysis of F_{lab} on the parameters (*P*, *k*, *BD*, *D*, $[\mathrm{NO}]_{amb}$) in the Galbally and Johansson algorithm. Several studies have tested this algorithm by calculating NO fluxes directly from laboratory results on *P* and *k* (for a given soil temperature and a given soil moisture), and generally found good agreement with NO fluxes from field measurements [*Galbally and Johansson,* 1989*; Remde et al.*, 1993; *Rudolph et al.*, 1996b]. In later studies, the algorithm was modified to include the dependence of the NO flux on soil temperature and soil moisture. A reference NO flux was calculated from *P* and *k* (for a reference soil temperature and reference soil moisture) and multiplied by two functions that described the dependence of the NO flux on soil temperature G*(T)*, and soil moisture H*(θ)* respectively (eq. 3.9) [*Yang and Meixner*, 1997; *Otter et al.*, 1999].

$$F_{lab}(\theta, T) = F_{lab}(\theta_{ref}, T_{ref}) \times \mathrm{G}(T) \times \mathrm{H}(\theta) \tag{3.9}$$

This concept assumes that both functions are independent of each other: that the effect of soil temperature on the NO fluxes is independent of soil moisture, and visa versa. However, results from laboratory studies and field measurements already have suggested otherwise. For instance, NO fluxes were hardly stimulated by soil temperature in dry soil [*Anderson and Poth*, 1989; *Cardenas et al.*, 1993], while under sufficiently wet conditions NO fluxes increased exponentially with soil temperature [review by *Williams et al.*, 1992]. Furthermore, NO production and the NO consumption rate constant have been observed to depend differently on soil parameters, such as O_2 availability, soil pH, nutrient content, and soil moisture and soil temperature [*Krämer and Conrad*, 1991; *Baumgärtner and Conrad*, 1992; *Saad and Conrad*, 1993; *Dunfield and Knowles*, 1999; *Conrad*, 2000]. Therefore, rather than parameterizing the resulting net NO flux (F_{lab}), it seems more appropriate to regard *P* and *k* as individual processes and describe each as a function of soil temperature and soil moisture individually. F_{lab} would then be determined from the following equation.

$$F_{lab}(\theta, T) = \sqrt{BD \cdot k(\theta, T) \cdot D} \times \left([\mathrm{NO}]_{amb} - \left(\frac{P(\theta, T)}{k(\theta, T)} \right) \right) \tag{3.10}$$

Consequently, in the present study, *P* and *k* were investigated in soil samples from forest and pasture soils with respect to soil moisture and soil temperature in the laboratory. Moreover, using the observed relations and information (soil moisture, soil temperature, ambient NO concentration, bulk gas-diffusion of NO in soil, and the soil bulk density) measured at both field sites (RBJ and FNS), NO fluxes were calculated according to the modified algorithm of eq. (3.10). Then, we compared these laboratory derived NO fluxes (from soil samples) to field derived NO fluxes (from field-measurements with dynamic chambers) at the same locations.

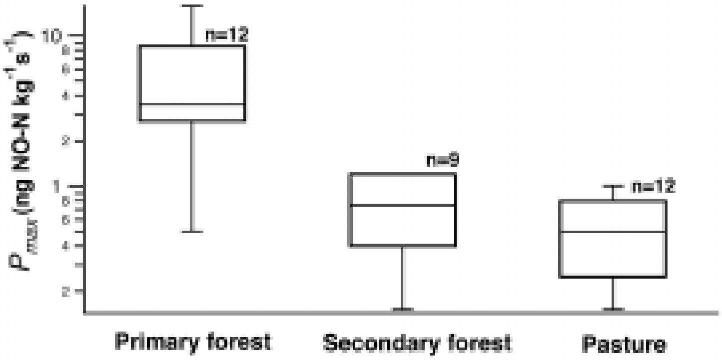


Figure 3.3. Maximum observed NO production P_{max} in soils from primary forests, secondary forests, and pastures. Indicated are averages values of P_{max} from soil samples that were collected in primary forest (*n*=12), secondary forest (*n*=9) and pastures (*n*=12), the corresponding standard deviations are indicated by error bars.

3.3 RESULTS AND DISCUSSION

3.3.1 NO production *P*

Figure 3.3 presents the maximum NO production (P_{max}) observed in the 35 soil samples (classified in primary forest, secondary forest and pasture) that were collected in the Amazon Basin. Soils covered by primary forest exhibited the highest P_{max}, whereas P_{max} in soils from secondary forests and pastures were equally low. Similar findings have been shown before, both in laboratory and in field studies. *Garcia-Montiel et al.* [1999] and *Verchot et al.* [1999] studied trace gas emissions from forest and pasture soils in the Brazilian Amazon, and measured the highest NO fluxes from forest soils.

Furthermore, *Parsons and Keller* [1995] observed higher NO production in intact cores from forest soils compared to soil cores from old pastures (>20 year) in Costa Rica. Their results agreed with earlier fieldwork in Costa Rica, showing higher NO fluxes from forest soils and decreasing NO fluxes with increasing pasture age. The lower NO fluxes were explained by poor nitrogen conditions in pasture soils [*Keller et al.*, 1993]. Unfortunately, data on the nitrogen conditions in our soil samples were not available. Only the inorganic nitrogen concentrations (NH_4^- and NO_3^-) were determined in samples from Reserva Biologica Jaru (RBJ) and Fazenda Nossa Senhora (FNS). While the total inorganic nitrogen contents (NH_4^+ and NO_3^-) were similar in both RBJ and FNS, the forest contained more NO_3^- than the pasture soil [v*an Dijk and Meixner*, 2001a]. There is general agreement in the literature that forest soils are dominated by NO_3^-, whereas pastures contain more NH_4^+ [*Neill et al.*, 1999; *Verchot et al.*, 1999]. However, there is less agreement on what causes the higher NO production in forest soils.

On one hand, the higher NO_3^- concentration in forest soils, together with higher NO fluxes from forest soils, might suggest that NO_3^- is a substrate for NO production. Indeed, nutrient-addition experiments on soils from forests and pastures in the Amazon showed an increase in NO production with additions of KNO_3 but not with NH_4Cl [*Bakwin et al.*, 1990*; van Dijk and Meixner*, 2001a]. This suggested that there is a potential for NO_3^- consumption in these soils. However, it does not prove the importance of nitrate consumption (nitrate respiration, denitrification, DNRA) for the production of NO in these soils.

On the other hand, the higher NO_3^- concentration in forest soil might have accumulated as a result of rapid transformation from organic N and NH_4^+ to NO_3^- [*Davidson et al.*, 2000; *Neill et al.*, 1999; *Verchot et al.*, 1999]. Hence, the high NO production in forest soil would then have resulted from the consumption of organic N and NH_4^+ (nitrification). Similarly, the higher fractions of NH_4^+ in pasture soils would indicate a slower nutrient cycling (from NH_4^+ to NO_3^-), and thus NO production from nitrification would be smaller. Unfortunately, no data were available on the nutrient cycling in the different soil samples and therefore no statement can be made on what microbial processes produced NO in the soils.

In the following chapter, NO production in the soil samples is related to their corresponding soil acidities, since this is an informative soil parameter that influences several soil processes including microbial activity [*Conrad,* 1996b]. For instance, in forest soils in the Netherlands, *Tietema et al.* [1992] observed decreasing nitrification rates with decreasing soil pH between pH 4.4 and pH 3.45. At pH values below 3.34, no significant nitrate production was measured [*Tietema et al.,* 1992]. *Gödde* [1999] also found no nitrate production in acidic (pH 3.31 and pH 2.80) forest soils from mid-latitudes and concluded that nitrification was inhibited at low soil pH.

3.3.1.1 NO production P_{max} versus soil pH

Figure 3.4a presents the P_{max} versus soil pH for all samples. In general, P_{max} is highest under acidic conditions. Below pH 4.0, P_{max} increases sharply with decreasing soil pH.

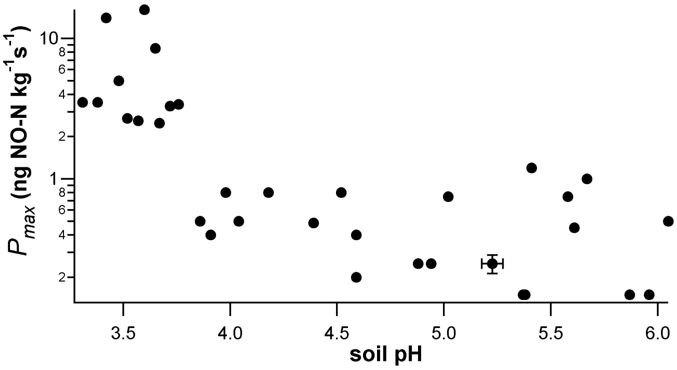


Figure 3.4a. Maximum observed NO production P_{max} versus soil acidity (pH). A typical error bar is included.

Van Cleemput and Baert [1984], as well as *Blackmer and Cerrato* [1986], report that NO_2^- is unstable under acidic soil conditions (pH < 5.5) and reacts to form NO, especially in soils with relatively high organic matter content. Thus, our results (increasing *P* with decreasing soil pH below 4.0) may suggest the production of NO through chemodenitrification under acidic soil conditions.

It must, however, be stated that low soil pH was almost exclusively found in our forest soils and high pH was limited mostly to pastures. Figure 3.4b shows P_{max} versus soil pH, classified by vegetation type (primary forest, secondary forest and pasture).

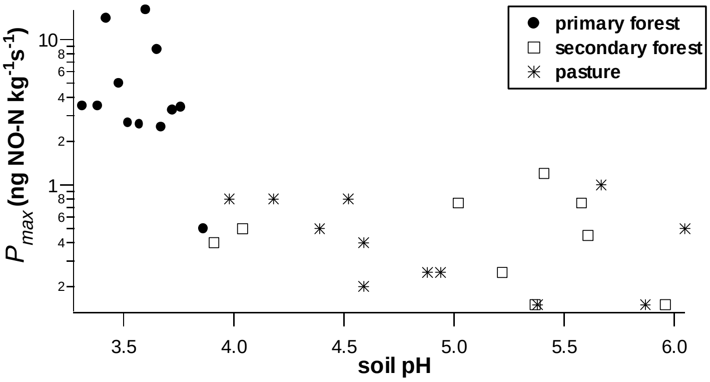


Figure 3.4b. P_{max} versus soil acidity (pH). Soil samples (shown in Figure 3.4a) are classified here by vegetation type (primary forest, secondary forest and pasture).

It can be seen that the distinction in low pH and high pH resembles the distinction in primary forest soils and secondary forest and pasture soils.

It can not be excluded that there is a further explanation for the higher P_{max} in primary forest soils compared to pastures and secondary forest soils. P_{max} was correlated to the other investigated soil characteristics (sand/silt/clay content, organic carbon, phosphorus, CEC, individual cation concentrations, exchangeable aluminium). However, none of these other soil characteristics correlated significantly with P_{max}.

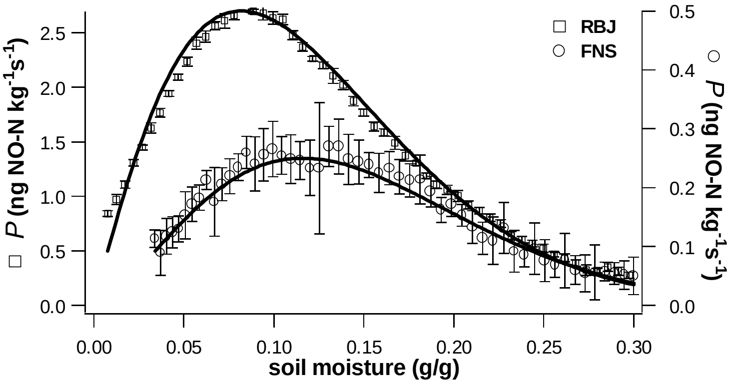


Figure 3.5. Curve fits of NO production *P* in soil samples from RBJ and FNS versus soil moisture. Data as in Figure 2.2 (Chapter 2).

3.3.1.2 NO production *P* versus soil moisture θ and soil temperature *T*

Figure 3.5 presents NO production at constant soil temperature of 25 °C versus soil moisture for the pasture (FNS) and the forest soil (RBJ). The data represent 1-minute average values, consisting of 6 consecutive (10 second) measurements. The error bars in Figure 3.5 indicate the scatter (standard deviation, $n = 6$) within these averages. Both for RBJ and FNS, the average variation in *P* was 0.03 ng NO-N kg^{-1} s^{-1}, which corresponds to 4% and 25% respectively. Relatively, the scatter in data of *P* was larger for FNS, since measurements were closer to the detection limit ($\approx$ 0.04 ng NO-N kg^{-1} s^{-1}). For both soils, NO production was maximum at an intermediate soil moisture (θ_{opt}) of about 0.10 g/g. These observations agreed well with the field-data from RBJ, where maximum NO production was observed at approximately 0.14 g/g (*Gut*, personal communication). The concept of optimum soil moisture is well understood. Under very dry soil conditions, substrate diffusion through water films (around soil particles) to microbial active cells is limited [*Linn and Doran*, 1984]. In contrast, under very wet soil conditions, oxygen diffusion may inhibit NO production, and diffusion of NO through pore spaces to the atmosphere is limited [*Skopp et al.*, 1990, see also *Davidson*, 1993].

NO production (at constant soil temperature) was described as a function of soil moisture. For this reason, Poisson functions were fitted to the data series in Figure 3.5. Results are shown for RBJ and FNS in eq. (3.11) and (3.12), respectively.

$$P_{RBJ}(\theta, T_{ref}): \qquad P = 2.7 \cdot \left(\frac{\theta}{0.082}\right)^{1.00} \cdot \mathrm{EXP}\left\{0.67 \cdot \left(1 - \left(\frac{\theta}{0.082}\right)^{1.49}\right)\right\} \tag{3.11}$$

$$P_{FNS}(\theta, T_{ref}): \qquad P = 0.25 \cdot \left(\frac{\theta}{0.116}\right)^{1.44} \cdot \mathrm{EXP}\left\{0.89 \cdot \left(1 - \left(\frac{\theta}{0.116}\right)^{1.62}\right)\right\} \tag{3.12}$$

Equation (3.11) and (3.12) predict NO production for a constant reference soil temperature of 25 ºC (T_{ref} = 298 K). However, at a given soil moisture, NO production was observed to increase exponentially with soil temperature ($P(T+\Delta T) = P(T) \times \mathrm{EXP}\{B \cdot \Delta T\}$). The degree of increase of P with T (indicated by the B-coefficient) depended on soil moisture. Figure 3.6 presents B-coefficients for the forest (RBJ) and pasture (FNS) soils versus soil moisture.

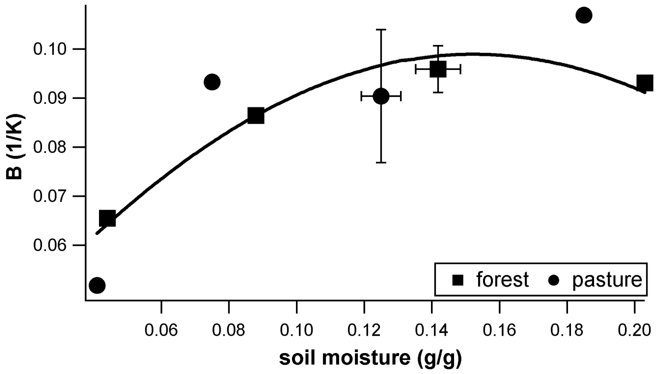


Figure 3.6. B-coefficient, indicating the increase of NO production P with soil temperature, versus soil moisture, both for the forest and pasture soils. Typical error bars for the forest and pasture soils are shown.

The degree of increase (B-coefficient) could be described by a parabolic function with soil moisture $B(\theta)$ (see equation 3.13).

$$B_{RBJ,\,FNS}(\theta): \qquad B = -0.62 + 0.72 \cdot \mathrm{EXP}\left\{-\frac{(\theta - 0.16)}{0.49}\right\} \tag{3.13}$$

This indicates that P increased most pronounced with soil temperature at a certain intermediate soil moisture (further details by *van Dijk and Meixner* [2001a]). By implementing the B-coefficient as a function of soil moisture ($B(\theta)$) into the exponential relations in eq. (3.11) and (3.12) , NO production could be described at any soil moisture and any soil temperature. Equation (3.14) and (3.15) describe the dependence of P on soil temperature (at any θ) for RBJ and FNS, respectively.

$$P_{RBJ}(\theta, T): \qquad P = P_{RBJ}\,(\theta, T_{ref}) \times \mathrm{EXP}\{B \cdot\, (T - T_{ref})\} \tag{3.14}$$

$$P_{FNS}(\theta, T): \qquad P = P_{FNS}(\theta, T_{ref})\ \times \mathrm{EXP}(B \cdot\, (T - T_{ref})\} \tag{3.15}$$

For clarity, Figure 3.7 gives a graphical presentation of the NO production in soil from RBJ versus soil moisture and soil temperature, created from eq. (3.14). For any given temperature, there is a clear optimum soil moisture for with NO production is maximum. At the same time, for any given soil moisture, NO production increases with soil temperature following an exponential relation, depending on the moisture content of the soil.

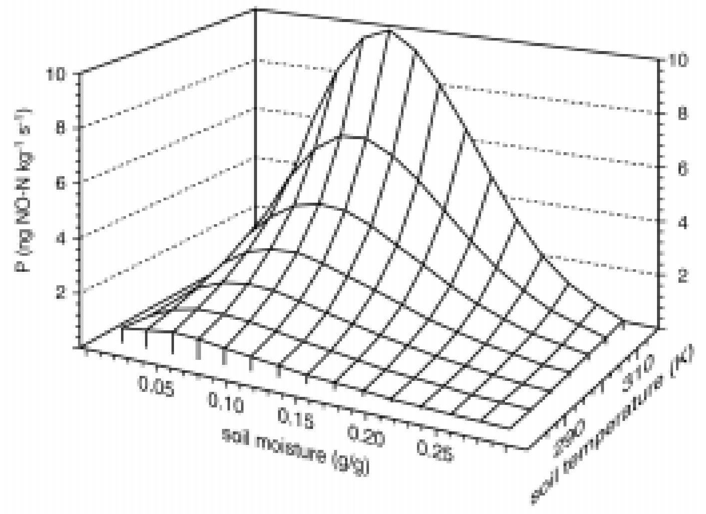


Figure 3.7. NO production P in forest soil (RBJ) versus soil temperature and soil moisture.

By describing the measured data of P from RBJ and FNS with functions, some error was introduced depending on the goodness of fit. The relative error between the observations and the predicted values (by functions) was calculated by dividing the root mean squared error (RMSE) by the mean of the observations. For RBJ and FNS, P was described with a relative error of 6% and 8% respectively.

3.3.2 NO consumption rate constant *k*

Results on k in forest and pasture soils from the Brazilian Amazon (including RBJ and FNS) have been described by *van Dijk and Meixner* [2001a]. In short, k showed similar values for forest and pasture soils, ranging from 16.4×10^{-6} to 80.5×10^{-6} and from 15.7×10^{-6} to 72.4×10^{-6} m^3 kg^{-1} s^{-1} respectively. The uncertainty in the measurement of k was assumed to be approximately 20%. The first-order rate constant of NO consumption is a kinetic parameter, and thus does not depend on soil characteristics such as soil packing [*Galbally and Johansson*, 1989]. However, k is largely determined by what type of microbial consumption takes place in the soil. Since the data showed similar values of k, it is suggested that the consumption processes were similar in the different soils. Our results are on the high side of the range of k values that were observed in other studies, ranging from 0.5×10^{-6} to 60×10^{-6} m^3 kg^{-1} s^{-1} [*Saad and Conrad*, 1993; *Baumgärtner and Conrad*, 1992; *Bollman and Conrad*, 1997]. NO consumption was maximum at high soil temperature and dry soil conditions. Several studies have shown NO consumption under aerobic and anaerobic conditions by denitrification and by heterotrophic and methanotrophic bacteria [*Baumgärtner et al.*, 1996; *Koschorreck and Conrad*, 1997; *Rudolph et al.*, 1996b; *Bender and Conrad*, 1994; *Krämer et al.*, 1990]. In agreement with our findings, *Gödde and Conrad* [1999] explained NO consumption in dry soil by aerobic consumption processes, with O_2-limiting conditions under wet soil. Our data demonstrated the same trend with respect to soil temperature and soil moisture; therefore k was described for all soil samples simultaneously as a function of T and θ (see Figure 2.4). The dependency of k on T and θ was described by a linear fit (eq. 3.16).

$$k(\theta, T): \qquad k = 0.0283 - (0.0009 - 0.0014\theta)\cdot(T - 300) + (0.3795 - 0.0014T)\cdot(\theta) \qquad (3.16)$$

By describing the data with the function in eq. (3.16), k could be predicted with a relative error of 25% (derivation explained in chapter 3.3.1.2). The sensitivity of F_{lab} (eq. 3.8) in the modified algorithm of Galbally and Johansson to the uncertainty in k is given in chapter 3.3.5.

3.3.3 Gas diffusion *D*

The bulk diffusion of NO in soil (D) was measured in the field at the forest and pasture sites. *Gut et al.* [2001] report in detail on the gas diffusion in soil at RBJ. The gas diffusion decreased with increasing soil moisture, since diffusion is limited when the pores become water-filled. Equation (3.17) presents the relation of D at RBJ (D_{RBJ}) with the air-filled pore space, the fraction of the air-filled pore volume to the total pore volume in soil ($\varepsilon_{\mathrm{air}}$).

$$D_{RBJ} = 2.2 \times 10^{-6} (\varepsilon_{\mathrm{air}})^{1.346} \qquad (3.17)$$

The diffusion of NO in pasture soil at FNS (D_{FNS}) is presented by *Kirkman et al.* [2001]. Data were collected during several days, resulting in information about D in pasture soil only for a narrow soil moisture regime. Therefore, a general relation of D with the air-filled pore space could not be established directly. However, D_{FNS} was compared to D_{RBJ} for the moisture regime that was covered by the field measurements at FNS. For this particular moisture regime, the gas diffusion in pasture soil was approximately 23% smaller than in forest soil. Finally, the relation of D_{FNS} with $\varepsilon_{\mathrm{air}}$ was assumed similar to D_{RBJ} (equation 17), with the difference that the gas diffusion in pasture was 0.77 times the gas diffusion in forest soil (see eq. 3.18).

$$D_{FNS} = 0.77\, D_{RBJ} \approx 1.7 \times 10^{-6}\, (\varepsilon_{\mathrm{air}})^{1.346} \tag{3.18}$$

Results from laboratory experiments also suggested a less effective gas diffusion in pasture compared to forest soil. The bulk density of the pasture soil (1.56 g/cm^3) was considerably higher than the bulk density of the forest soil (1.33 g/m^3). Considering that both soils are loamy sand soils with almost identical particle-size distributions (Section 3.2.2), the higher bulk density in pasture soil suggests the effect of soil compaction. The conversion from forest to pasture generally leads to soil compaction (by cattle) [*Neill et al.*, 1997], which results in an increase in the soil bulk density and consequently a decrease in the pore volume. Diffusion of gas takes place in the open pore volume. Thus, the higher bulk density in pasture soil (smaller pore volume) would result in a decreased gas diffusion compared to forest soil. Several studies presented diminished gas-diffusion in compacted soils, ranging from 20% to 95% slower, depending upon the degree of compaction [*Ball et al.*, 1981; *Currie*, 1984]. Compaction of the soil has been shown to largely reduce the fraction of larger pores (>60 μm) to the total pore volume [*Currie*, 1984; *Bullock et al.*, 1985; *Richard et al.*, 2000]. *Van Dijk and Meixner* [2001b] present pore-size distributions (volume fraction of a certain pore size to the total pore volume) for forest and pasture soils from the Amazon Basin (Chapter 4).

Figure 3.8 demonstrates the volume fraction of large pores (> 60 μm) to the total pore volume ($\varepsilon_L/\varepsilon$) against the sand content, for forest and pasture soils. In general, $\varepsilon_L/\varepsilon$ increases with sand content. This is well understood. Coarse textured soil (sandy soils) generally have a larger fraction of large pores than fine textured soils (clay soils) [*Hillel*, 1982]. Furthermore, at identical sand content, $\varepsilon_L/\varepsilon$ is clearly smaller in pastures than in forest soils. Most likely, compaction by cattle caused the larger pores in the top layer of the pasture soil to collapse. Gas diffusion in soil is mostly through the larger pores, whereas small pores hardly contribute to the aeration of the soil. [*Currie*, 1983]. Thus, our laboratory results of high soil bulk density and smaller fraction of large pores in pasture soil support the outcome from field measurements of less effective gas diffusion in pasture (FNS) compared to forest soil (RBJ).

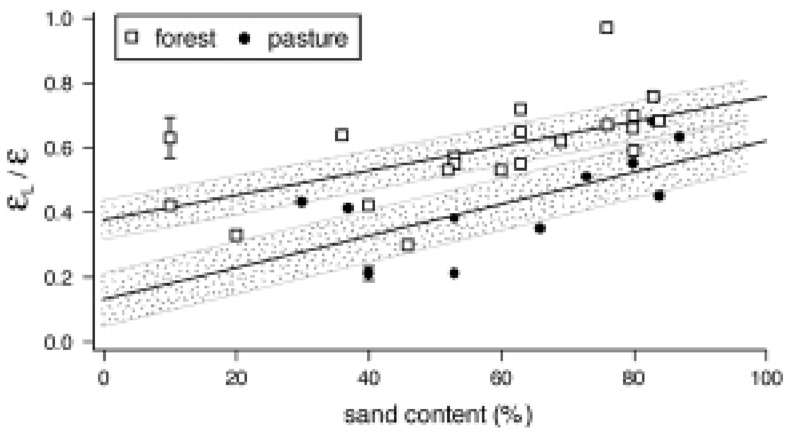


Figure 3.8. The volume fraction of large pores (> 60 µm) to the total pore volume ($\varepsilon_L/\varepsilon$) against the sand content. Results are shown from all soil samples, classified by vegetation type: forest (primary and secondary) and pasture. Indicated are error bars, 95% confidence levels (grey shaded areas), and regression trends for the forest ($r^2 = 0.35$, $n = 22$) and pasture soils ($r^2 = 0.45$, $n = 17$), respectively.

3.3.4 Comparing F_{lab} and F_{field}

We would like to emphasize that all information to calculate NO fluxes from laboratory experiments (F_{lab}) was obtained independently from the NO fluxes that were measured in the field (F_{field}). The gas diffusion (Section 3.3.3) and soil bulk density (Section 3.2.2) were determined in the field. NO production (Section 3.3.1.2) and the NO consumption rate constant (Section 3.3.2) were determined in the laboratory as functions of θ and T, which enabled the calculation of F_{lab} for any combination of θ, T and $[NO]_{amb}$. Finally, F_{lab} was calculated for RBJ and FNS according to eq. (3.10), using the observed relations of $P(\theta, T)$ and $k(\theta, T)$, information about D, BD and $[NO]_{amb}$ and the field conditions (θ, T and $[NO]_{amb}$) at the time of measurement of the NO fluxes with dynamic chambers in the field (F_{field}).

3.3.4.1 Forest (Reserva Biologica Jaru)

Figure 3.9a presents the soil temperature and soil moisture at RBJ during the month of October 1999. Original data with a 30-minute time resolution were averaged over 12-hour periods. Soil temperature varied only slightly from 23 °C to 25 °C, whereas soil moisture ranged widely from dry soil to 0.24 g/g (0.60 water-filled pore space). Median NO ambient mixing ratio was approximately 2.6 ppb. F_{lab} (eq. 3.10) was not significantly influenced by the ambient NO mixing ratio, since $P_{RBJ}(\theta, T)/k(\theta, T)$ was considerably higher (median 76 ppb). *Gut et al.*, [2001] measured the NO compensation concentration (P/k) directly in soil from RBJ, and found $[NO]_{amb}$ / $[NO]_c$ < 0.06 over the full measurement period. Figure 3.9b presents F_{field} and F_{lab} from the forest soil during October 1999. Values of F_{field} were averaged over three individual chamber measurements and over 12 hours. The 12-h variation in F_{field} is indicated by error-bars, whereas grey shading indicates the variation in F_{lab}.

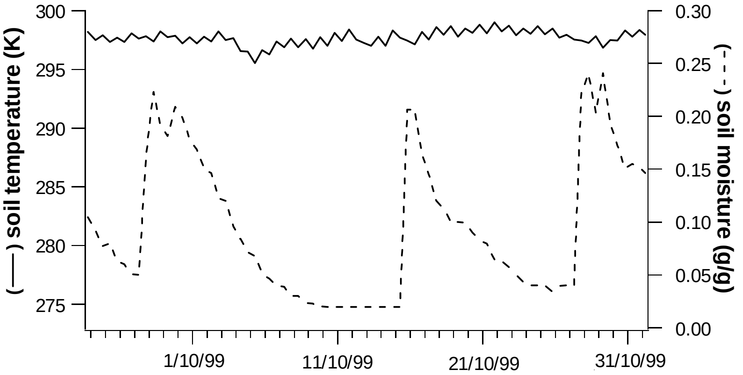


Figure 3.9a. Soil temperature and soil moisture at the forest site (RBJ) for the month October in 1999.

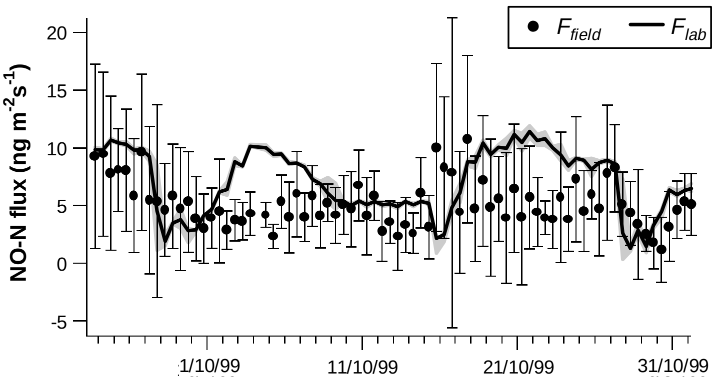


Figure 3.9b. Measured NO fluxes (F_{field}) and calculated NO fluxes (F_{lab}) at the forest site (RBJ) for the month October in 1999. Data of F_{field} are average values (3 chambers, 12 hours) and error bars indicate the corresponding standard deviations. The grey shaded area indicates the variation in F_{lab} over 12-hour intervals.

Considering the entire measurement period, there was good agreement between the calculated NO fluxes (median 7.2, mean 6.9 ± 2.9 ng m^{-2} s^{-1}) and the measured NO fluxes (median 4.3, mean 5.0 ± 4.6 ng m^{-2} s^{-1}). However, on some occasions there were significant discrepancies. Especially around 4 and 21 October, F_{lab} predicts considerably higher NO fluxes than were measured in the field. At both occasions, the soil moisture (as observed in the field) is around 70.10 g/g (see Figure 3.9a). Laboratory experiments showed highest NO production at approximately 0.10 g/g, causing F_{lab} to peak at this moisture. In the field, however, maximum NO fluxes were observed at a soil moisture around 0.14 g/g (see Section 3.3.1.2). Difficulties arise since soil moisture was determined by two different methods. While gravimetric water content was determined in the laboratory (Section 3.2.2), Time-Domain Reflectometry (TDR) measurements in the field resulted in volumetric water content [*Gut et al.*, 2001]. The volumetric water content was converted into gravimetric water content using the soil bulk density. Discrepancies caused by the conversion from TDR measurements to gravimetric soil moisture may have led to errors in the estimation of NO production, and hence in the prediction of F_{lab}. The precision of the TDR measurements was better than 1%, however due to soil inhomogenities the uncertainty in the field calibration was approximately 20%. As mentioned previously, the variation in the gravimetric soil moisture was within 5%. Therefore, the maximum error in the comparison of the two moisture methods would be 25%, which would result in an error in F_{lab} of approximately 1 ng NO-N kg^{-1} s^{-1}. On one other occasion (17 October) heavy rainfall after a period of drought resulted in high NO fluxes (F_{field}) which are not matched by the laboratory results (F_{lab}). These large emissions of NO from the soil upon rainfall (pulsing), due to a sudden mineralization of nutrients that accumulated in the dry period [*Gut et al.*, 2001], were not simulated in the laboratory and thus were not predicted by F_{lab}. This is also seen in Figure 3.10, which presents the cumulative probability for values of F_{lab} and F_{field}. F_{field} covers a broad range from –20 to 45 ng m^{-2} s^{-1}, whereas F_{lab} varies from 0.06 to 12 ng m^{-2} s^{-1}.

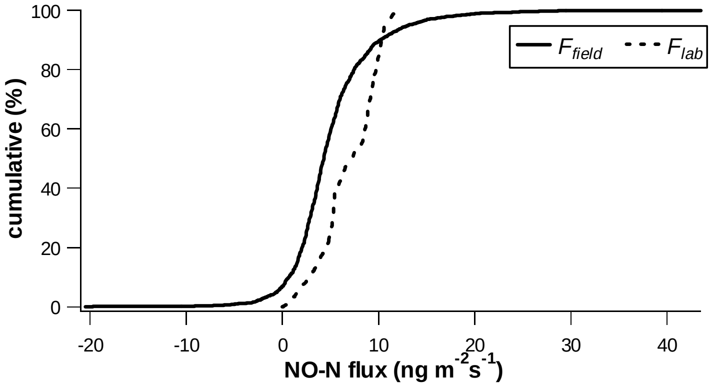


Figure 3.10. Histogram (cumulative percentage) of the measured NO fluxes (F_{field}) and the calculated NO fluxes (F_{lab}) at the forest site (RBJ).

F_{lab} does not predict negative NO fluxes (deposition) or extremely high NO fluxes (pulsing) that were observed in the field. Therefore, F_{lab} could not predict daily NO fluxes. However, over the entire measurement period, mean and median values of F_{lab} and F_{field} were equal within 1 standard deviation, indicating good agreement between the laboratory-derived and field-derived NO fluxes.

3.3.4.2 Pasture (Fazenda Nossa Senhora)

Figure 3.11a shows soil temperature and soil moisture at FNS for October 1999. Soil temperature varied from 22 ºC to 28 ºC, and soil moisture ranged only slightly from 0.06 to 0.14 g/g (or from 0.20 to 0.50 water-filled pore space). The median ambient NO mixing ratio was approximately 0.37 ppb. Again, F_{lab} (eq. 3.10) was not significantly influenced by the ambient NO mixing ratio, since $P_{FNS}(\theta, T)/k(\theta, T)$ was considerably larger (median 41 ppb).
In Figure 3.11b, the calculated NO fluxes from laboratory experiments are compared with the NO fluxes from field measurements at the pasture during October 1999. Again, values of F_{field} were averaged over three individual chambers and 12 hours. Error bars and grey shading indicate the 12-h variation for F_{field} and F_{lab}, respectively. Over the entire measurement period, F_{lab} (median 0.67, mean 0.67 ± 0.09 ng m^{-2} s^{-1}) agreed very well with F_{field} (median 0.53, mean 0.65 ± 0.37 ng m^{-2} s^{-1}).

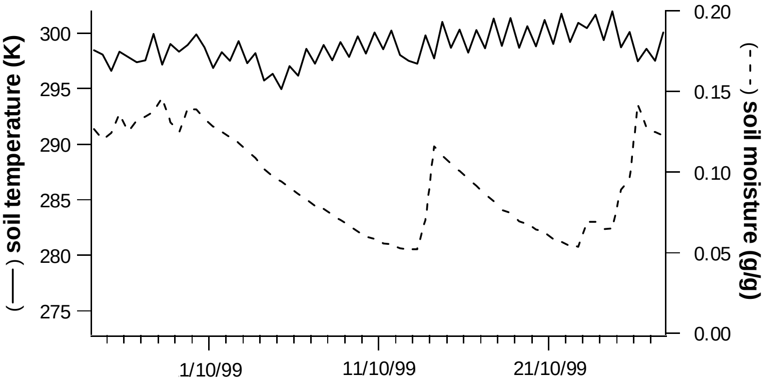


Figure 3.11a. Soil temperature and soil moisture at the pasture site (FNS) from September to October in 1999.

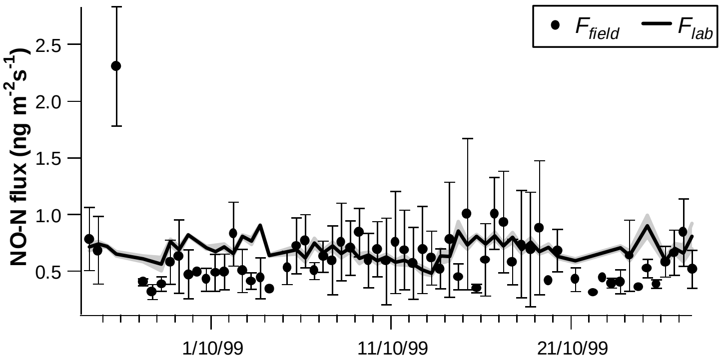


Figure 3.11b. Measured NO fluxes (F_{field}) and calculated NO fluxes (F_{lab}) at the pasture site (FNS) from September to October in 1999.

Figure 3.12 presents a histogram (cumulative percentage) for F_{field} and F_{lab}. F_{lab} covered a smaller range of NO fluxes (0.42–1.04 ng m^{-2} s^{-1}) than F_{field} (0.27–3.16 ng m^{-2} s^{-1}), but the laboratory-derived and field-derived NO fluxes were not significantly different ($p < 0.01$).

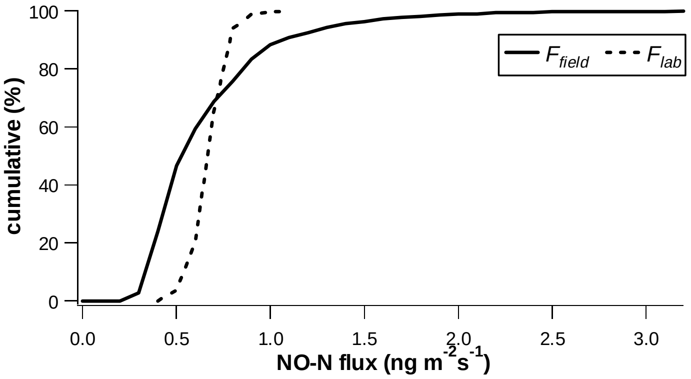


Figure 3.12. Histogram (cumulative percentage) of the measured NO fluxes (F_{field}) and the calculated NO fluxes (F_{lab}) at the pasture site (FNS).

The NO fluxes (F_{field}) from the pasture soil (FNS) were approximately 11 times smaller than from the forest soil (RBJ) (Section 3.3.4.1). The NO production was about 10 times smaller and the gas diffusion was 23% less effective in pasture soil. It is concluded that the conversion from forest to pasture decreased NO production, and compaction of the pasture soil most likely decreased the gas diffusion, which finally resulted in these small NO fluxes from pasture compared to forest soil.

3.3.5 Sensitivity analysis on the parameters: *P, B, k, D, BD* and $[NO]_{ambient}$

In order to establish the sensitivity of F_{lab} towards its parameters, the modified algorithm (eq. 3.10) was tested for relative changes in the six parameters (see also *Remde et al*. [1993]). The NO fluxes from RBJ (as presented in Figure 3.9b) were averaged over the entire measurement period to obtain the reference NO flux ($F_{lab, ref}$). The parameters that were used to calculate these NO fluxes (see Sections 3.3.1.2–3.3.4.1) will be denoted as P_{ref}, B_{ref}, k_{ref}, D_{ref} BD_{ref} and $[NO]_{amb, ref}$. Then, the relative change in F_{lab} was investigated for a relative change in any of the parameters between 0.1 and 2.0. While one of the parameters was changed with respect to the reference value, the other parameters remained constant. The modified NO fluxes were calculated for the entire measurement period, and averaged to one value ($F_{lab, mod}$). Figure 3.13 shows the relative change in F_{lab} ($F_{lab, mod} / F_{lab, ref}$) as a result of the relative change of any property (X_{mod}/X_{ref}), for the properties *P, B, k, D, BD* and $[NO]_{amb}$.

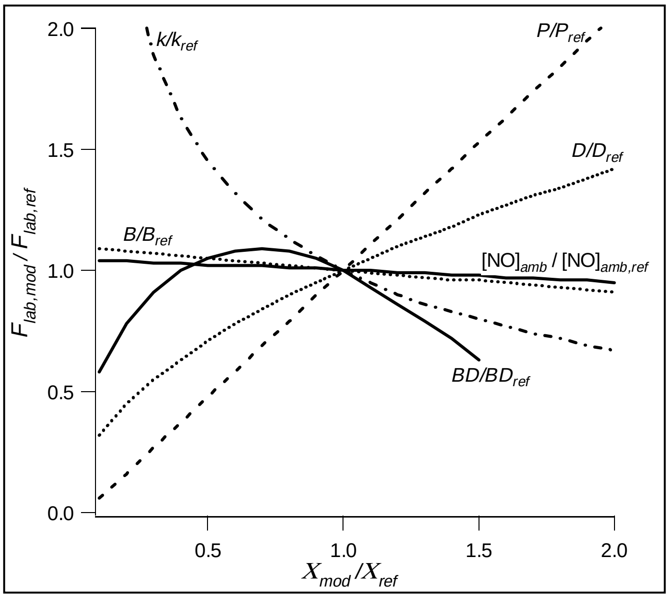


Figure 3.13. Sensitivity analysis, indicating the relative changes in the calculated NO flux ($F_{lab, mod}/F_{lab, rer}$) for changes in any of the parameters (X_{mod}/X_{ref}). Shown are the parameters: *P*, *k*, *D*, *BD*, $[NO]_{amb}$.

As can be seen by the slopes of the curves in Figure 3.13, the algorithm is most sensitive towards *P* and *k*, less sensitive towards *BD* and *D*, and relatively insensitive towards $[\mathrm{NO}]_{amb}$ and *B* (the increase of *P* with soil temperature). In order to give an impression of the error that could be introduced by the various parameters, the reliability of the individual parameters is briefly discussed. The reliability of the parameters *P*, *k*, *D*, *BD* and $[NO]_{amb}$ depends on the measurement error or the error by fitting the data with functions. For instance, *P* was described with an uncertainty of 6% for RBJ and 8% for FNS, whereas the measurement error in *P* was estimated to be 4% and 25% for RBJ and FNS respectively (see chapter 3.3.1.2). This indicates for RBJ that higher uncertainty resulted from fitting the data with a function, whereas for FNS the measurement of *P* introduced the largest uncertainty. As a result, $F_{lab, mod} / F_{lab, ref}$ would observe a relative change of approximately 0.06 and 0.25 for RBJ and FNS respectively. Largest uncertainty in *k* was due to fitting the data, which led to an error in *k* of approximately 0.25 for both soils. Even though the algorithm is also very sensitive towards *k*, errors in *k* would result in a relative change in F_{lab} of less than 0.15 for both soils. As was mentioned above, the algorithm is relatively sensitive towards *BD* and *D*. Field bulk density was determined within 5%, which corresponds to a relative change in F_{lab} of approximately 0.04. Data of the bulk diffusion *D* in soil from RBJ were determined with an error of approximately 16%. This would result in a change in $F_{lab, mod} / F_{lab, ref} < 0.10$. Although the absolute value of *D* in pasture was measured directly in the field, the largest uncertainty in

F_{lab} from FNS most likely resulted from not knowing the exact relation of D_{FNS} with $\varepsilon_{\mathrm{air}}$ and applying the relation of D_{RBJ} with $\varepsilon_{\mathrm{air}}$ instead. Several models exist that could be applied to predict D [*Jin and Jury*, 1996; *Moldrup et al*., 1997]. However, these models describe values of D over a wide range, and consequently calculations of F_{lab} would differ more than by using the measured D_{FNS}. Propagation of the error in the individual parameters (P, k, BD and D) indicated that the relative errors in F_{lab} were approximately 25% for RBJ and 40% for FNS.

3.4 CONCLUDING REMARKS

Finally, our findings demonstrate the suitability of the modified algorithm from *Galbally and Johansson* [1989] to predict NO fluxes using information on the NO production and consumption rate constant, and the diffusion of NO in soil. In some cases, there were significant discrepancies between the laboratory derived NO fluxes (F_{lab}) and the NO fluxes from field measurements with dynamic chambers (F_{field}). However, when considering the entire measurement period, F_{lab} agreed well with F_{field}. This suggests that the modified algorithm could be applied to determine NO fluxes over a relatively longer time scale, for instance to establish seasonal differences within an ecosystem. Furthermore, the NO fluxes from pasture were approximately 11 times smaller than from forest soil, and both for the forest and the pasture F_{lab} and F_{field} agreed well. This confirms the potential of the algorithm to scan soil samples in the laboratory and obtain information about the biogenic NO fluxes from the soil. NO fluxes from different ecosystems may even vary over 4 orders of magnitude [*Davidson and Klingerlee,* 1997; *Ludwig et al.*, in press]. Thus, the combination of laboratory experiments and the modified algorithm from G*albally and Johansson* [1989] could be a powerful tool to establish NO fluxes from soils from various ecosystems.

3.5 ACKNOWLEDGMENTS

The authors would like to thank the Federal University of Rondônia (UNIR) and the National Institute for Colonisation and Agriculture (INCRA) in Ji-Paraná, the state of Rondônia, Brazil for their support. Our colleague Christof Ammann is thanked for numerous valuable discussions. The European Union and the Max Planck Society provided financial support through the LBA-EUSTACH project (ENV4-CT97-0566).

3.6 NOMENCLATURE

J	NO release or uptake	(ng kg^{-1} s^{-1})
P	NO production	(ng kg^{-1} s^{-1})
k	rate constant of NO consumption	(m^3 kg^{-1} s^{-1})
$[NO]_{in}$	NO concentration of inlet air	(ng m^{-3})
$[NO]_{out}$	NO concentration of outlet air	(ng m^{-3})
$[NO]_{amb}$	ambient NO concentration	(ng m^{-3})
$[NO]_c$	NO compensation concentration	(ng m^{-3})
F_{lab}	NO flux from soil, calculated by eq. (8)	(ng m^{-2} s^{-1})
F_{field}	NO flux from soil, measured in the field	(ng m^{-2} s^{-1})
BD	soil bulk density	(kg/m^3)
D	molecular diffusion of NO through soil	(m^2/s)
T	soil temperature	(K)
B	coefficient in the exponential relation of P with T	(1/K)
θ	soil moisture	(g/g)
θ_{opt}	optimum soil moisture	(g/g)
$\varepsilon_L/\varepsilon$	volume of large pores (>60 μm) to the total pore volume	(m^3/m^3)
ε_{air}	air-filled pore volume to the total pore volume	(m^3/m^3)
$_{RBJ}$	subscript indicating Biological Reserve Jaru (forest)	
$_{FNS}$	subscript indicating Fazenda Nossa Senhora (pasture)	
$_{ref}$	subscript indicating ”reference”	
$_{mod}$	subscript indicating "modified"	

CHAPTER 4

The effect of soil texture on nitric oxide release from soils in the Amazon

S.M. van Dijk and F.X. Meixner

ABSTRACT

Nitric oxide (NO) emissions from soil are maximum at *optimum soil moisture.* A range of optimum soil moistures is given in the literature. Our objective was to find whether differences in soil texture are reflected in the optimum soil moistures under which NO is emitted from soil. Soil samples were collected in the Brazilian Amazon and covered a series of textures, ranging from loamy sand to clay. NO release was determined from these soil samples in the laboratory as a function of soil moisture at a constant soil temperature of 25 ºC. Several expressions of soil moisture were compared: gravimetric water content, volumetric water content, and water-filled pore space. In addition, water release characteristics of the soils were analyzed using a tension table. Different optimum soil moistures were observed for different textures. Optimum soil moisture (gravimetric, volumetric, and water-filled pore space) correlated positively with clay content, indicating wetter optimum conditions for NO emissions from soils with a higher clay content. Best correlation was found using gravimetric water content ($r^2 = 0.75$, $n = 35$). Fine-textured soils (clay) had larger pore volumes, and thus could contain more water than coarse-textured soils (sand). Also, the fine-textured soils had larger fractions of smaller pores compared to the coarse-textured soils, and thus retained more water at identical matric potential. For this reason, NO release was presented as function of matric potential. All samples, independent of soil texture, showed optimum soil moisture at a matric potential close to –10 kPa. This suggests that the situation where larger pores are drained (promoting gas diffusion) and smaller pores are water-filled (promoting microbial activity) is optimal for NO release from soil.

Also submitted to *Soil Sci. Soc. Am. J.*

4.1 INTRODUCTION

Nitrogen oxides (NO and NO_2) contribute considerably to the oxidative capacity of the troposphere, especially by their catalytic action in the formation of ozone [*Graedel and Crutzen*, 1993]. Besides emissions of nitric oxide (NO) from fossil fuel combustion, biomass burning and lightning, NO emissions from soils can be an important source in remote areas for tropospheric NO [*Holland et al.*, 1999]. NO is simultaneously produced and consumed in soil [*Remde et al.*, 1989], which generally results in a net NO emission from the soil to the atmosphere [*Davidson and Klingerlee*, 1997]. NO can be produced under aerobic and anaerobic conditions by biological nitrification (oxidation of ammonium and organic nitrogen to nitrate) and denitrification (reduction of nitrate), and by chemical denitrification. Biological nitrification is considered to occur exclusively under aerobic conditions, whereas biological denitrification generally takes place under anaerobic conditions, although exceptions have been shown [*Conrad*, 1996]. Net NO emissions from soil generally increase exponentially with soil temperature (15–35 °C)[*Williams et al.*, 1992]. The degree of increase has been shown to depend on soil moisture [*van Dijk and Meixner*, 2001a; *Davidson et al.*, 1998]. Less well established is the direct relation of NO emission with soil moisture.

Soil moisture can be expressed by various quantities: gravimetric water content θ_g (mass of H_2O per mass of dry soil), volumetric water content θ_v (volume of H_2O per volume of dry soil) and water-filled pore space θ_{wfps} (volume of H_2O per pore-volume in soil). The quantities of soil moisture are converted using equations (4.1) and (4.2), where ε is the total pore-volume of the soil, and ρ_{soil} and ρ_{water} are soil bulk density (g/cm^3) and density of water (g/cm^3), respectively.

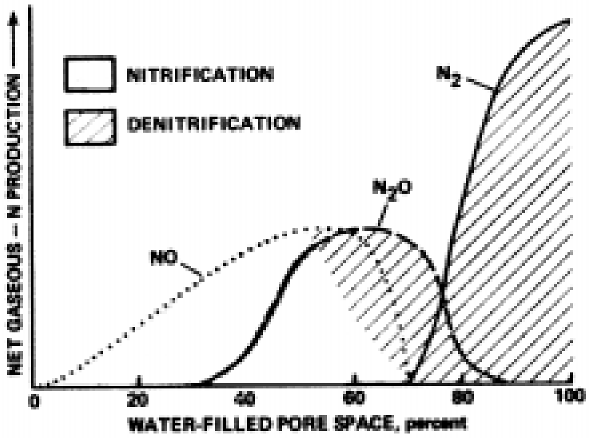
$$\theta_v = \theta_g \cdot \left(\frac{\rho_{soil}}{\rho_{water}} \right) \tag{4.1}$$

$$\theta_{wfps} = \frac{\theta_v}{\varepsilon} = \frac{\theta_g}{\varepsilon} \cdot \left(\frac{\rho_{soil}}{\rho_{water}} \right) \tag{4.2}$$

Matric potential (kPa), is an expression of the energy potential of soil water that results from the capillary and adsorptive forces due to the soil matrix [*Monteith and Unsworth*, 1990]. Matric potential generally has negative values; and at lower (more negative) matric potential, less water is retained in the soil pores and consequently the soil is dryer. Not all moisture quantities are suitable for comparing different soils. A gravimetric water content of 0.20 may be relatively dry for a fine-textured soil (larger pore volume) and relatively wet for a coarse-textured soil (smaller pore volume).

Likewise, a similar volumetric water content will seem wetter in a soil with finer pores compared to a soil with larger pores. These differences arise mainly from differences in soil texture and soil structure: soil texture refers to the particle size distribution, while soil structure is the arrangement and organization of the particles in the soil [*Hillel*, 1982; *Davidson*, 1993]. Since "water-filled pore space" and "matric potential" account for differences in soil texture and soil structure, respectively, they are generally the more suitable quantities to compare soil moisture of different soils.

Figure 4.1 Proposed relative contributions of nitrification (white) and denitrification (cross hatched) to emissions of NO and N_2O as a function of WFPS (reproduced from *Davidson* [1991] and *Davidson et al.* [2000]).



Shapes of the curves, the curve heights, WFPS optima, and the inflection points were largely educated guesses based on the limited field and laboratory data available.

Davidson [1991] presented a model of the relationship between WFPS and relative fluxes of NO and N_2O (see Figure 4.1). This model predicts NO production by nitrification < 0.60 WFPS, and N_2O production by denitrification > 0.60 WFPS, and that the emission ratios of N_2O to NO should be about 1 at 0.60 WFPS. This is explained by the following. Figure 4.2 shows aerobic microbial activity (such as nitrification) versus soil moisture, as was presented by *Skopp et al*. [1990]. At low soil moisture (aerobic conditions), the microbial activity increases with soil moisture, since substrate diffusion is enhanced through water films. At high soil moisture (anaerobic conditions), oxygen-supply is limited and the aerobic microbial activity decreases with further wetting of the soil. [*Skopp et al.*, 1990; *Linn and Doran*, 1984]. Aerobic microbial activity is maximum at an intermediate soil moisture, where both substrate diffusion and oxygen supply are optimized. Soil moisture of 0.60 WFPS was found to be a threshold between aerobic and anaerobic conditions, with maximum aerobic microbial activity at approximately 0.60 water-filled pore space [*Linn and Doran*, 1984].

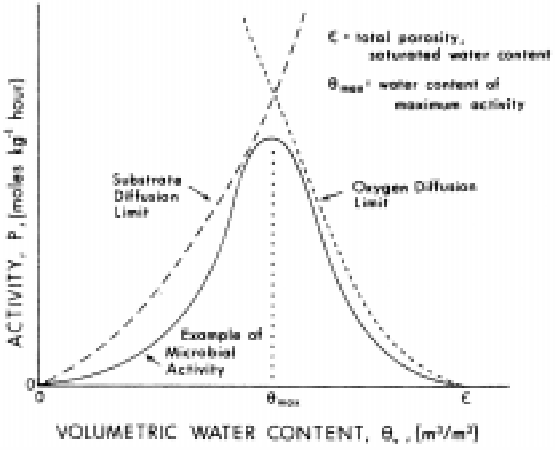


Figure 4.2. Aerobic microbial activity versus soil moisture (reproduced from *Skopp et al.*.[1990]).

Davidson et al. [2000] suggest maximum NO production due to nitrification at field capacity, which is defined as the soil's water content after excess moisture has drained freely from that soil. At field capacity, soil micropores are water-filled, which permits microbial activity without water stress, and soil macropores are air-filled, which permits relatively good aeration of the bulk soil. Field capacity therefore offers optimum conditions for nitrification. The moisture content of many soils is about 0.60 WFPS at field capacity. For this reason, maximum NO production is expected at about 0.60 WFPS, as was indicated in Figure 4.1. However, as NO can be produced both under aerobic and anaerobic conditions [*Conrad*, 1996], the optimum soil moisture for NO production in soil may be different from the optimum soil moisture for aerobic microbial activity (0.60 WFPS). Several studies presented maximum NO emissions at an intermediate soil moisture (*optimum soil moisture)*. A range of optimum soil moistures found in the literature is presented in Table 4.1. Since soil texture and soil structure largely determine the water holding capacity of the soil, the question arises about the effect of these soil properties on the optimum soil moisture conditions for NO emission from soil.

As part of the project "European Studies of Trace gases and Atmospheric Chemistry as a Contribution to the Large Scale Biosphere-Atmosphere Experiment in Amazonia“ (LBA-EUSTACH) [*Andreae et al.*, 2001], biogenic emissions of NO were studied in detail in the laboratory on a series of soil samples with respect to soil moisture (at constant soil temperature at 25 °C). In the present study, the goal was to find how differences in soil texture are reflected in the optimum moisture conditions, expressed in different quantities, under which NO is emitted from soil. Moreover, what moisture-quantities allow the identification of optimum field conditions independent of soil texture/structure?

Table 4.1. Optimum soil moisture for which maximum NO emissions were observed in the field, as presented in the literature. Optimum soil moisture is presented as gravimetric water content θ_g *(opt)*, volumetric water content θ_v *(opt)* and water-filled pore space θ_{wfps} *(opt)*.

	Measurement location	Field description	Sand %	Silt %	Clay %	ρ_{soil} g/cm^3	ε	$\theta_g(opt)$	$\theta_v(opt)$	$\theta_{wfps}(opt)$
Cardenas et al., 1993	Venezuela	Savanna	70	13	17	1.5	0.43	0.12	0.18	0.41
Martin et al., 1998	Colorado (USA)	Steppe	72	15	13	1.4	0.49	0.13	0.17	0.35
Martin et al., 1998	Colorado (USA)	Steppe	42	18	30	1.3	0.50	0.25	0.33	0.66
Scholes et al., 1997	South Africa	Savanna	83	12	5	1.6	0.40	0.07	0.12	0.30
Parsons et al., 1996	South Africa	Savanna	85	5	10	1.6	0.40	0.07	0.12	0.30
Parsons et al., 1996	South Africa	Savanna	83	7	11	1.6	0.40	0.07	0.12	0.30
Parsons et al., 1996	South Africa	Savanna	36	8	56	1.7	0.36	0.06	0.11	0.30
Pilegaard et al., 1999	Norway	spruce forest	-	-	4	1.4	0.48	0.07	0.10	0.20
Otter et al., 1999	South Africa	Savanna	74	6	20	1.6	0.40	0.08	0.12	0.30
Otter et al., 1999	South Africa	Savanna	71	7	22	1.6	0.40	0.11	0.18	0.44
Otter et al., 1999	South Africa	Floodplain	34	12	54	1.1	0.59	0.27	0.30	0.50
Peirce and Aneja, 2000	N.Carolina(USA)	Agricultural	60	23	17	1.3	0.52	0.18	0.23	0.45
Grundmann et al., 1995	France	Agricultural	41	38	18	1.2	0.54	0.20	0.24	0.44

4.2 SITE DESCRIPTION AND SOIL CHARACTERISTICS

During two sampling campaigns in June and September 1999, a total of 35 composite soil samples were collected from forest and pasture sites in the Amazon Basin in the states of Rondônia, Amazonas and in the Tapajós National Forest of Pará. Table 4.2 presents the geographical coordinates of the sample locations. The state Rondônia has been colonised since the 1970‘s and experiences the most rapid deforestation in the Amazon basin. The Tapajós National Reserve is a protected forest, and also the Amazonas sampling site was relatively undisturbed. The three sampling locations experience comparable mean annual temperatures of approximately 25–27 °C. Amazonas and the Tapajós National Reserve have relatively constant temperatures throughout the year. Rondônia experiences some seasonal variability, with October (25.5 °C) and July (22.6 °C) as the hottest and coldest months. Rainfall at the three sites is also comparable, with a mean annual precipitation of approximately 2200 mm. There is only little rain during the 5-month dry season, which takes place from June to August, from June to September and from July to November for Rondônia, Amazonas and the Tapajós

National Forest, respectively. Wet deposition rates of ammonium (NH_4^+) and nitrate (NO_3^-) at the Amazonas sampling site were approximately 3.45 and 0.82 kg ha^{-1} yr^{-1}, respectively, [*Filoso et al.*, 1999]; and Rondônia had similar NO_3^- compositions in rain water as the Amazonas site (*Fernandes*, personal communication).

Soils were generally of the types red-yellow latosol (or yellow latosol) and red-yellow podsol, comparable to the ferralsols and acrisols, respectively, in the FAO classification (Food and Agriculture Organization, Italy). These soils are generally acidic and have a low base saturation and exchange capacity. Soil samples were composed of 6 sub-samples, taken from the top 0.05-m soil of a 10 x 10 m^2 sampling area. Samples were cooled during transport and stored in the laboratory at 4 °C. Large pieces of rock and root matter were removed.

Bulk densities (g/cm^3) were determined from undisturbed topsoil cores (0.05-m diameter, 0.05-m depth) taken in the field together with the soil samples. Variation in the soil bulk density due to soil inhomogenities was approximately 0.05 g/cm^3, or less than 5%.

In addition, physical (particle-size distribution) and chemical (soil acidity, organic matter content, phosphorus, and the individual cation concentrations) properties of the sampled soils were analyzed in a commercial laboratory (Planacampo) in Rolim da Moura, Brazil. Samples were air dried and sieved on 2-mm prior to analysis. Particle-size distributions were determined with the pipet method [see *Gee and Bauder*, 1986]. A textural triangle (Figure 4.3) presents the wide range of textural classes that was covered by the sampled soils, ranging from loamy sand (87% sand and 10% clay) to clay (11% sand and 81% clay). Soil pH (2.5:1) was measured in 0.01 M $CaCl_2$. Plant available phosphorus was extracted from 10 cm^3 dry soil with 100 ml Mehlich solution (HCl and H_2SO_4) and analysed with the ascorbic acid method by spectrophotometry [see *Kuo*, 1996]. Organic matter was calculated (factor 1.72) from the dichromate oxidation of organic carbon. Cation exchange capacity, the individual cation concentrations of potassium, calcium, magnesium and exchangeable aluminium were measured with spectrophotometry from extractions (10 cm^3 dry soil) with ammonium acetate (pH 7). Further details on the analysis procedures are given by *Klute* [1986] and *Bartels* [1996]. Table 4.2 presents a description of the soil samples, including some of the physical and chemical properties.

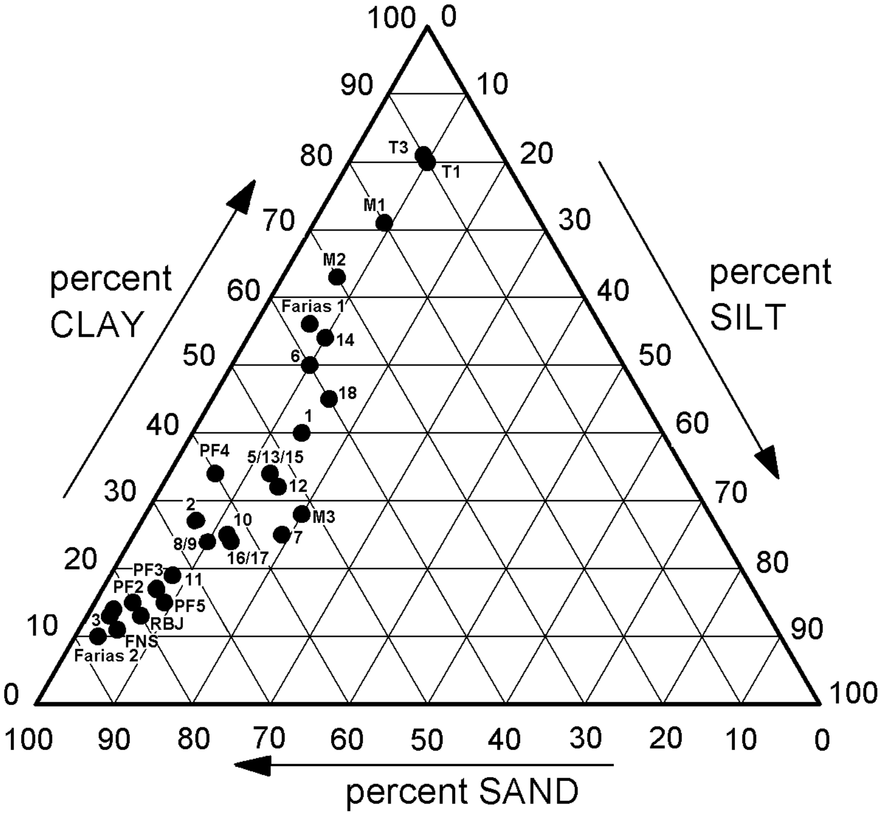


Figure 4.3. Textural triangle, presenting the sand, silt and clay percentages of the soil samples.

Table 4.2. The coordinates of the collected soil samples and a selection of their most important physical and chemical properties († Vegetation type: PF = primary forest, SF = secondary forest, P = pasture; ‡ indicates whether water release characteristics were determined: "yes" or "no").

CODE	Coordinates	Soil type	Veg †	Sand %	Silt %	Clay %	BD g/cm^3	ε	pH	org.Mat g/kg	PO_4-P mg/dm^3	CEC Cmol$_c$/dm^3	Acid %	ψ_m ‡
SJT1	11°34 S 61°76 W	Red yellow Latosol	SF	46	14	40	1.16	0.56	5.6	24.8	2.2	12.71	25	no
SJT2	11°29 S 61°89 W	Red yellow Latosol	P	66	7	27	1.46	0.45	5.4	26.8	4.2	10.33	42	no
SJT3	11°62 S 61°20 W	Quartzite	P	83	3	14	1.09	0.59	5.6	14.1	10.7	9.66	39	no
SJT4	11°62 S 61°21 W	Quartzite	P	80	5	15	1.24	0.53	5.0	21.5	4.1	10.96	52	yes
SJT5	11°58 S 61°28 W	Red yellow Podsol	P	53	13	34	1.20	0.55	4.4	38.9	5.6	5.44	78	no
SJT6	11°55 S 61°31 W	Red yellow Podsol	SF	40	10	50	1.10	0.58	3.7	28.2	3	9.81	85	no
SJT7	11°42 S 61°65 W	Red yellow Latosol	P	56	19	25	1.48	0.44	3.7	22.8	3.5	7.23	79	no
SJT8	10°79 S 62°05 W	Red yellow Latosol	P	66	10	24	1.46	0.45	3.7	18.1	40.7	7.73	80	no
SJT9	10°78 S 62°05 W	Red yellow Podsol	SF	66	10	24	1.50	0.43	3.9	23.5	14.4	8.84	87	no
SJT10	10°79 S 62°05 W	Red yellow Podsol	SF	63	12	25	1.06	0.60	3.6	45.0	8.2	7.29	56	no
SJT11	10°79 S 62°05 W	Red yellow Podsol	P	73	8	19	n.d.	n.d.	3.5	33.6	62.8	9.17	50	no
SJT12	10°72 S 62°25 W	Red yellow Podsol	SF	53	15	32	1.11	0.58	3.8	36.9	65.9	7.83	54	no
SJT13	10°49 S 62°43 W	Red yellow Podsol	P	53	13	34	1.14	0.57	5.0	34.9	4.1	9.51	39	no
SJT14	10°28 S 62°69 W	Red yellow Latosol	SF	36	10	54	0.80	0.70	5.2	25.5	4	9.24	58	no
SJT15	10°12 S 62°94 W	Yellow Latosol	SF	53	13	34	1.02	0.62	4.9	37.6	28.1	8.66	46	no
SJT16	9°95 S 63°05 W	Yellow Latosol	SF	63	13	24	1.03	0.61	5.5	29.5	4.8	10.71	64	no
SJT17	9°99 S 63°02 W	Yellow Latosol	SF	63	13	24	0.92	0.65	4.7	30.9	5.2	9.26	87	yes
SJT18	10°06 S 62°98 W	Yellow Latosol	P	40	15	45	1.22	0.54	5.2	30.2	3.7	11.73	52	no
PF.1	10°05 S 61°55 W	Red yellow Latosol	PF	83	3	14	1.35	0.49	4.5	8.7	2.3	10.15	59	yes
PF.2	10°05 S 61°55 W	Red yellow Latosol	PF	80	5	15	1.30	0.51	4.2	17.4	3.2	9.48	22	yes
PF.3	10°04 S 61°56 W	Red yellow Latosol	PF	76	7	17	1.13	0.57	4.6	16.8	3.0	11.53	22	no
PF.4	10°04 S 61°56 W	Red yellow Latosol	PF	60	6	34	1.10	0.58	4.6	13.4	1.0	10.3	42	no
PF.5	10°05 S 61°55 W	Red yellow Latosol	PF	76	9	15	1.22	0.54	5.9	13.4	3.9	10.08	41	yes
PF.7	10°05 S 61°55 W	Red yellow Latosol	PF	80	7	13	1.22	0.54	5.7	n.d.	n.d.	n.d.	n.d.	yes
SF	-----------------------	Red yellow Latosol	SF	80	7	13	1.30	0.51	5.4	n.d.	n.d.	n.d.	n.d.	yes
RBJ	10°05 S 61°55 W	Red yellow Latosol	PF	80	7	13	1.22	0.54	6.1	n.d.	n.d.	n.d.	n.d.	yes
FNS	10°45 S 62°21 W	Red yellow Latosol	P	84	5	11	1.56	0.41	4.0	n.d.	n.d.	n.d.	n.d.	yes
M1	3°13 S 60°87 W	Yellow Latosol	PF	20	9	71	1.08	0.59	4.9	n.d.	n.d.	n.d.	n.d.	yes
M2	3°19 S 60°12 W	Yellow Latosol	P	30	7	63	0.94	0.65	4.4	n.d.	n.d.	n.d.	n.d.	no
M3	3°24 S 60°37 W	Yellow Latosol	PF	52	20	28	0.88	0.67	4.9	n.d.	n.d.	n.d.	n.d.	no
T1	3°02 S 54°97 W	Yellow Latosol	PF	10	10	80	0.99	0.63	3.4	n.d.	n.d.	n.d.	n.d.	yes
T2	3°02 S 54°97 W	Yellow Latosol	PF	84	3	13	1.40	0.47	3.5	n.d.	n.d.	n.d.	n.d.	no
T3	2°86 S 54°96 W	Yellow Latosol	PF	10	9	81	0.74	0.72	3.4	n.d.	n.d.	n.d.	n.d.	yes
Farias1	3°02 S 54°89 W	Podsol	P	37	7	56	1.21	0.54	3.3	n.d.	n.d.	n.d.	n.d.	no
Farias2	3°03 S 54°88 W	Podsol	P	87	3	10	1.41	0.47	3.6	n.d.	n.d.	n.d.	n.d.	yes

4.3 METHOD

From June to October 1999, NO release was determined from soil samples in the laboratory in Ji-Paraná (Rondônia, Brazil). The experimental setup was described in detail by Yang et al. [*van Dijk and Meixner*, 2001a; *Yang and Meixner*, 1997]. Each experiment was initiated with pristine soil and all experiments were conducted within 3 months after sampling. A soil sample (with an equivalent of 0.06-kg dry soil) was packed into a measurement cuvette (0.092-m diameter and 0.136-m height), corresponding to its field bulk density. The soil was allowed to adjust to the soil temperature set point for approximately 30 minutes, after which NO release measurements were initiated. The soil sample was flushed with dry, NO-free air at a flow rate of 4.17×10^{-5} m^3 s^{-1}. In total, four measurement cuvettes and one blank cuvet were flushed continuously with dry NO-free air and the NO mixing ratio was analysed at the inlet and outlet of the measurement cuvettes, interchanging the cuvette every 1.5 minutes. NO was measured by a commercial chemiluminescence analyzer (TECAN AL 770 PPT, Ecophysics, Switzerland), with a detection limit of 100 ppt. The instrument was calibrated using zero air and NO gas standards (200 ppm, Messer Griesheim, Germany). Further information about the experimental setup is given by *van Dijk and Meixner* [2001a] (Chapter 2).

Cuvettes were placed in a small climate chamber, which enabled the control of soil temperature. Soil temperature was measured in the middle of the soil samples. Gravimetric water content was calculated every hour from the soil samples using the equivalent dry weight soil mass (calculated from the initial gravimetric water content) and the water loss during the experiment. Hourly gravimetric water contents were fitted with Gaussian functions, and interpolation between hourly measurements produced soil moisture data for the full measurement period. During the last part of the experiment, when the soils were almost dry (approximately <0.06 g/g), the Gaussian curve was extrapolated to compute the moisture content. In these cases, the maximum error in the soil moisture content due to the fitting procedure was ± 0.025 g/g. However, for most of the experiment, gravimetric water content was measured with a precision equivalent to the precision in the initial gravimetric water content (≈ 5%). The gravimetric water content (g/g) was converted into volumetric water content (cm^3/cm^3) and into water-filled pore space (cm^3/cm^3), using the field bulk density (see equations 4.1 and 4.2). The uncertainty in the determination of the field bulk density due to inhomogenities in the soil was approximately 0.05 g/cm^3 or 5%. Following the propagation of error due to the combined uncertainties in the gravimetric soil water content and the field bulk density, the uncertainties in the volumetric water content and water-filled pore space were estimated to be 6% and 8% respectively.

NO release J (NO-N ng kg^{-1} s^{-1}) was calculated from the difference in the NO mixing ratio between inlet $[NO]_{in}$ and outlet $[NO]_{out}$ of the measurement cuvette, the flow rate through the cuvette Q, and the sampling weight M_{soil}. The calculation is given in eq. (4.3), where M_{N} is the molecular weight of nitrogen (14.0 kg kmole^{-1}) and V_{m} is the molar volume (24.5 m^3 kmole^{-1}). NO release was determined for a range of moistures (0–100% WFPS), while the soil samples dried out at constant soil temperature of 25 °C. And likewise, for two soil samples (FNS and RBJ) at 17 °C and 33 °C.

$$J = \left(\frac{Q}{M_{soil}}\right) \cdot \left([\mathrm{NO}]_{out} - [\mathrm{NO}]_{in}\right) \cdot \left(\frac{M_N}{V_m}\right) \tag{4.3}$$

In addition to the measurements of NO release, water release characteristics of the soil samples were determined. The water release characteristics (water retention curves) were determined with a tension table, by placing water-saturated soil samples on a filter unit and applying a certain suction (or matric potential). Water is drained from the soil samples and escapes the tension-table via drainage channels [*Clement*, 1966]. The relation of soil moisture with matric potential (or suction) gives the water release characteristics. A simple water tension table system, as described by *Ball and Hunter* [1988], was modified by placing a 0.02 m layer of very fine silica gel (10–40 µm, SIGMA, Germany) on top of the filter unit. This enabled measurements up to –22.5 kPa. Matric potential of –22.5 kPa was the highest suction that could be determined. At even lower values air entered the system through the filter unit and the tension was lost. Before initialising measurements, each soil sample was packed in a Plexiglas ring (0.08-m. diameter and 0.05-m. height) and adjusted to their corresponding field bulk density with a 2-kg copper weight. After saturating the soil sample overnight in a water bath, matric potential was applied. This was repeated for matric potential of –0.5, –1.5, –5.0, –10, –15, and –22.5 kPa. After incubation at matric potential for 48 hours, the gravimetric water content was determined (104°C). Results from replicate soil samples indicated that the gravimetric water content at a certain matric potential could be determined within 10% (–5 kPa), 15% (–10 kPa) and 20% (–15 kPa) respectively. At a matric potential of –22.5 kPa, replicates indicated variation in the gravimetric water content between 6% to 88%. Pore size distributions were calculated from the water retention curves according to *Danielson and Sutherland* [1986] (eq. 4.4):

$$\Delta P = \frac{2\sigma}{r_c} cos\theta \tag{4.4}$$

Where ΔP (Pascal) is the pressure difference between two matric potential measurements, σ equals the surface tension of water (J m^{-2}), r_c (m) is the curvature of the meniscus, and θ (degrees) is the contact angle of water to the solid. If θ is assumed to be zero, the cosine becomes unity, and the radius of the meniscus curvature is equal to r_p (m), the radius of a circular capillary tube of size equivalent to that of the pore (eq. 4.5). Finally, equation (4.6) is generally used to calculate the equivalent pore diameter (see for example, *Hillel* [1971]).

$$\Delta P = \frac{2\sigma}{r_p} \tag{4.5}$$

$$r_p = \frac{2\sigma}{\Delta P} \approx \frac{0.3}{\Delta P} \tag{4.6}$$

In this study, NO release is presented as a function of soil moisture (gravimetric and volumetric water content and water-filled pore space) for a range of soil textures and data are compared to results of the water retention curves.

4.4 RESULTS AND DISCUSSION

4.4.1 NO release as function of soil moisture

Figure 4.4 presents NO release (normalised to the maximum) as function of gravimetric water content at 25 °C for two soil samples (SJT9 and SJT14) with 24% and 54% clay, respectively. The soil moisture where maximum NO release is observed is the *optimum soil moisture* $\theta(opt)$. Figure 4.4 demonstrates a clear separation of the *optimum gravimetric soil moisture* $\theta_g(opt)$ for the two samples, 0.10 g/g and 0.18 g/g for the samples with 24% and 54% clay respectively. Considering all soil samples, a wide range of $\theta_g(opt)$ was observed, ranging from 0.04 g/g to 0.38 g/g.

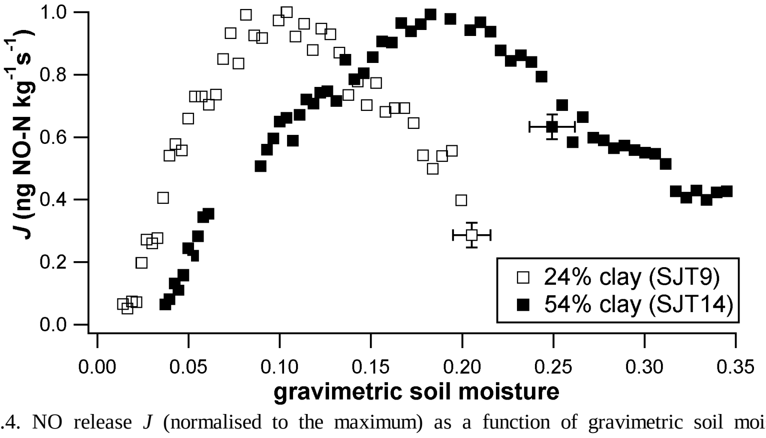


Figure 4.4. NO release *J* (normalised to the maximum) as a function of gravimetric soil moisture for two samples (sjt9 and sjt14) with 24% and 54% clay content, respectively. Typical error bars are shown.

As is shown in Figure 4.5, $\theta_g(opt)$ correlated positively with the clay content of the soil sample ($r^2 = 0.75$, $n = 35$). This indicates that maximum NO emissions from soil with a high clay content are observed at a higher gravimetric water content compared to soils with a low clay content. This is due to differences in soil texture (particle size), which produce differences in bulk density, with larger pore volumes for clay and smaller pore volumes for sandy soil [*Hillel*, 1982]. For this reason, gravimetric water content (θ_g) is usually converted to volumetric water content (θ_v) and water-filled pore space (θ_{wfps}). Converting to θ_{wfps} is thought to compensate for texture differences and hence enables comparison amongst different soils. In total, NO release was highest at θ_{wfps} between 0.11 cm^3/cm^3 and 0.64 cm^3/cm^3. Figure 4.6 and Figure 4.7 present optimum soil moisture, expressed as optimum volumetric soil moisture $\theta_v(opt)$ and optimum water-filled pore space $\theta_{wfps}(opt)$ respectively, as a function of the clay content of the soil samples. Figure 4.5, 4.6 and 4.7 basically reveal the same positive correlation between optimum soil moisture and clay content, irrespective of soil moisture quantity (gravimetric, volumetric, water-filled pore space), as can be seen in equations (4.7), (4.8) and (4.9), respectively.

$$\theta_g(opt) = 0.04 + \mathbf{0.004}\cdot\text{Clay-content} \qquad (r^2 = 0.75,\ n = 35) \qquad (4.7)$$
$$\theta_v(opt) = 0.08 + \mathbf{0.003}\cdot\text{Clay-content} \qquad (r^2 = 0.57,\ n = 35) \qquad (4.8)$$
$$\theta_{wfps}(opt) = 0.19 + \mathbf{0.004}\cdot\text{Clay-content} \qquad (r^2 = 0.33,\ n = 35) \qquad (4.9)$$

However, the scatter increases considerably when changing moisture units from gravimetric to volumetric to water-filled pore space, which is expressed by decreasing r^2 from 0.75 to 0.57 to 0.33, respectively. The larger scatter in Figures 4.6 and 4.7, as compared to Figure 4.5, is induced by the uncertainty in the field bulk density (see section 4.3). Consequently, in this study gravimetric water content was the more suitable parameter when comparing amongst soils with a given soil texture. Other field studies presented optimum soil moistures for NO emissions from measurement sites with different soil textures (see Table 4.1). The optimum field conditions for NO emission and their corresponding clay content, from Table 4.1, were inserted in Figures 4.5, 4.5 and 4.6. The literature data correspond well to the correlation between *optimum soil moisture* (irrespective of moisture-quantity) and clay content that was observed in our laboratory studies.

So far, the presented NO release was determined as a function of soil moisture at a constant temperature of 25 ºC. In order to find whether the optimum soil moisture changes with soil temperature, additional experiments were conducted for 2 samples (FNS and RBJ) at 17 ºC and 33 ºC. A significant change of θ_{opt} with temperature could not be observed in our data (data not shown). In contrast to our results, *Grundmann et al*. [1995] found a parabolic relation between the optimum soil moisture for nitrification (NO production) and soil temperature, with minimum optimum soil moisture at 20–25 º C.

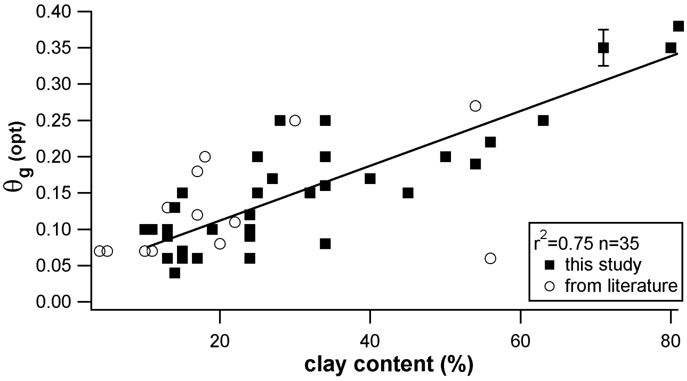


Figure 4.5. *Optimum gravimetric soil moisture θ_g (opt)* as a function of clay content (data from the literature are not included in the regression analysis).

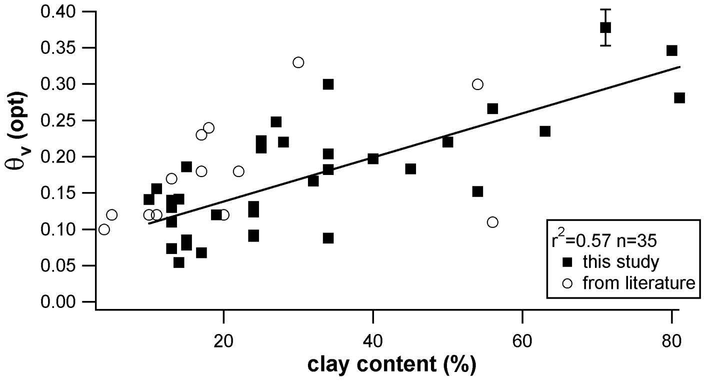


Figure 4.6. *Optimum volumetric soil moisture θ_v* (opt) as a function of clay content (data from the literature are not included in the regression analysis).

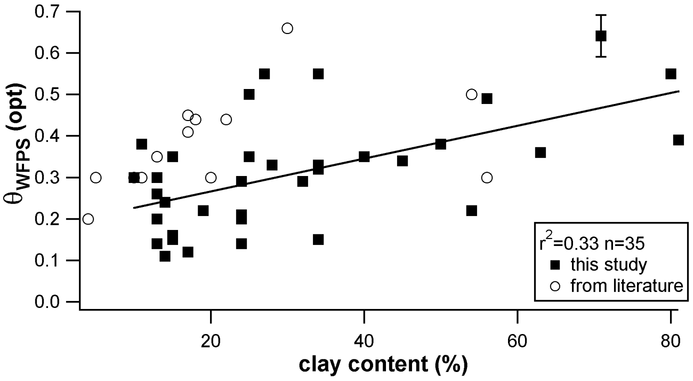


Figure 4.7. *Optimum water-filled pore space θ_{WFPS}* (opt) as a function of clay content (data from the literature are not included in the regression analysis).

As mentioned previously, WFPS is expected to compensate for differences in soil texture. Hence, maximum NO release was expected at one specific value of θ_{WFPS} (opt), independent of soil texture. However, θ_{WFPS} (opt) ranged from 0.11 to 0.64 cm^3/cm^3, and θ_{WFPS} (opt) increased with increasing clay content (Figure 4.7). Figure 4.8a and 4.8b present *J* (normalised to the maximum) as a function of WFPS for two groups of soil samples with a clay content below and above 30%, respectively. Data were grouped in 0.10 WFPS intervals. Presented are the average values of *J* for the 0.10 WFPS intervals (closed circles). The box dimensions represent the 0.10 WFPS intervals (horizontal) and the corresponding standard deviations (vertical). Values of *J* widely range at each WFPS interval, for both texture groups (A and B). Furthermore, there is a clear distinction in the optimum water-filled pore space for the two texture groups (0.25 WFPS for A and 0.45 WFPS for B). This indicates that WFPS could not account for differences in the optimum moisture conditions due to differences in the soil texture and soil structure.

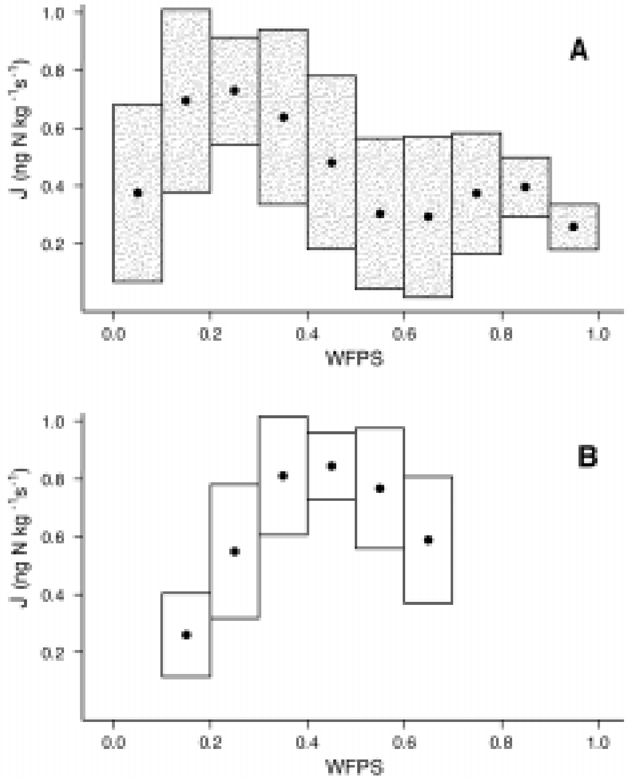


Figure 4.8. NO release *J* (normalised to the maximum) as a function of WFPS for two groups of soil samples[‡] with clay content < 30% clay (A) and > 30% clay (B). Closed circles indicate average values of *J* ($n = 10$ in A) ($n = 3$ in B) for 0.10 WFPS intervals. Box dimensions around the averages indicate the 0.10 WFPS intervals (horizontal) and the corresponding standard deviations (vertical) ([‡] sample numbers are indicated in Table 4.2).

4.4.2 Water release characteristics

Figure 4.9 presents the water retention curves for a selection of 5 soil samples having a wide range of clay contents (10–81%). In general, soil moisture decreases with decreasing (more negative) matric potential. Furthermore, when comparing results amongst different samples, it is seen that at a given matric potential (ψ_m) the soil with the highest clay content is wettest and soil moisture decreases with decreasing clay content.

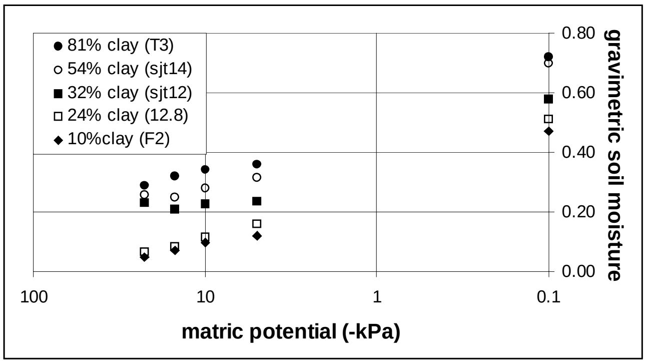


Figure 4.9. Water retention curves for a selection of 5 soil samples that cover a wide range of clay content.

The ability of the soil to retain water at a certain matric potential depends largely on the soil structure. Fine-textured soils (relatively high clay content) generally contain a relatively larger pore volume consisting of small pores. Similarly, coarse textured soils (with a more sandy composition) contain a relatively smaller pore volume, mainly consisting of larger pores [*Monteith and Unsworth*, 1990]. Smaller pore spaces introduce larger capillary forces. Consequently, fine-textured soils will retain more water than coarse-textured soils at identical matric potential. The pore size distributions of our soil samples (the individual contributions of a certain pore size to the total volume of the pore space) were calculated from the water retention curves and soil bulk density data, according to eq. (4.6).

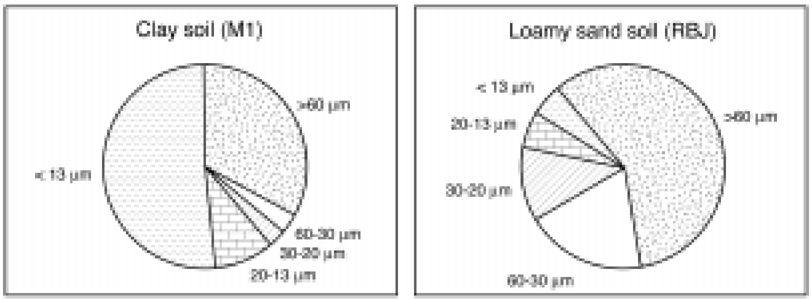


Figure 4.10. Pore size distributions for (a) a clay soil (M1) and (b) a loamy sand soil respectively.

Figure 4.10a and 4.10b present the pore size distributions for a loamy sand soil (RBJ) and a clay soil (M1) respectively. More than 50% of the loamy sand pore volume consisted of pores larger than 60 μm, whereas the clay soil had approximately 70% of pores smaller than 60 μm. These differences in soil structure, having smaller pores in the clay soil than the sandy loam, are reflected in the different soil moistures at similar matric potential.

4.4.3 NO release as function of matric potential

As a quantity that takes into account differences in soil structure, gravimetric water content from the NO release measurements was converted into matric potential (kPa), using the corresponding water retention curves (see Figure 4.9). Figure 4.11 presents the normalised NO release (as in Figure 4.8a and b) as a function of the calculated matric potential. Data were grouped in 2.5 matric potential intervals. Presented are average values of *J* (closed circles). Box dimensions represent the 2.5 matric potential intervals (horizontal) and the corresponding standard deviations (vertical).

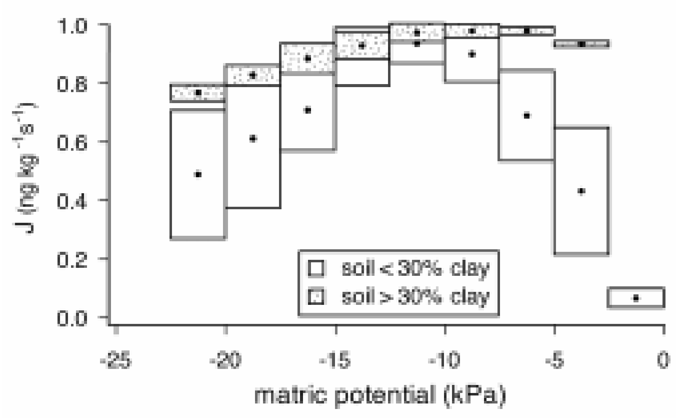


Figure 4.11. NO release *J* (normalised to the maximum) as a function of matric potential ‡. Indicated are averaged values of *J* for soil samples below (n = 10) and above (n = 3) 30% clay respectively. Box dimensions around the averages indicate the 2.5 matric potential intervals (horizontal) and the corresponding standard deviations (vertical) (‡ Samples are indicated in Table 4.2).

NO release was highest at ψ_m between approximately –9 to –11 kPa. The parabolic nature of the curve is a result of the simultaneously limiting processes of substrate diffusion and gas diffusion, as was mentioned in the "Introduction". At very negative matric potential (dry soil conditions), the substrate diffusion within water films (around soil particles) to metabolically active sites is limited [*Griffin*, 1981; *Zak et al.*, 1999]. In addition, *Csonka* [1989] suggests that decreasing (more negative) matric potential increases ion concentrations in soil solution, which causes microorganisms to accumulate ions in their cells in order to maintain osmotic balance. These high intracellular ion concentrations can alter enzyme conformation and reduce microbial activity. Both arguments support the idea of low microbial production of NO at low matric potential. At high matric potential (near zero), soils are near saturation, and consequently the gas diffusion of NO through the soil pores to the atmosphere is limited.

The striking result of Figure 4.11 is that both texture groups show maximum NO release at ψ_m close to –10 kPa. This may be explained by the following. At a certain matric potential, only pores with a certain pore size (capillary force) will be water-filled, and all pores larger than those will have drained their water [*Danielson and Sutherland*, 1986]. Several classifications of pore sizes exist that are based on the different functions of the pore size classes in soil [*Luxmoore et al.*, 1990; *Perret et al.*, 1999]]. In general, a distinction is made in micropores (retain water), mesopores (regulate conduction of water by rapid capillary flow), and macropores (responsible for aeration and rapid drainage) [*Monteith and Unsworth*, 1990]. Gas diffusion in soil is mainly through the relatively larger pores (meso and/or macropores), whereas the micropores hardly contribute to the gas diffusion [*Currie*, 1983].

Both texture groups had maximum NO release at $\psi_m \approx -10$ kPa, which is equivalent to a pore diameter of approximately 30 μm (eq. 4.6). This suggests that soil conditions where the relatively larger pores (>30 μm) have drained (and smaller pores are water-filled) were optimum for NO release from soil. By comparing the soils at the level of their pore size distributions, differences in soil texture and soil structure are compensated, and therefore maximum NO release was found at identical ψ_m, independent of soil texture. The situation when large pores have drained has been described as field capacity (FC). Strictly, FC is defined as the water content that the soil will hold after excess gravitational water has drained away and after the rate of downward water movement has decreased [*Veihmeyer and Hendrickson*, 1931]. For different soils, FC will be at different matric potentials (generally between –5 and –33 kPa [*Monteith and Unsworth*, 1990]). In this study we find optimum field conditions for NO emission at identical matric potential for all soils. Therefore, we could suggest that maximum NO emissions were found at field capacity in the sense that the relatively larger pores are open (enabling gas diffusion) and the small pores are water-filled (enabling microbial activity), but not according to the strict definition of field capacity.

As in Figures 4.4 and 4.8a and 4.8b, the shape of the curve in Figure 4.11 is different for clayey and sandy texture groups. Differences in the volume fractions of individual pore sizes between clayey and sandy soils may explain the different responses of the (normalised) NO release to a change in matric potential. The higher volume fraction of large pores in sandy soils, compared to clayey soils, would result in a more dramatic impedance of the gas diffusion at high matric potential. Hence, NO release would decrease more rapidly with increasing matric potential in sandy soils than in clayey soils.

4.5 CONCLUDING REMARKS

In this study, matric potential close to –10 kPa resulted in maximum NO release from all soil samples (independent of soil texture), whereas other soil moisture quantities (gravimetric water content, volumetric water content, and water-filled pore space) demonstrated different optimum soil moistures for different soil textures. This suggests that soil structure (pore-size distribution), rather than the soil texture (total pore volume) determined the optimum conditions for NO emissions from soil. Soil structure (pore diameter) largely determines the water retention properties [*Hillel*, 1982], and directly affects the gas diffusion through the soil [*Currie*, 1983; *Jury et al.*, 1991; *Borken and Brumme*, 2000]. Thus, as a measure that takes into account differences in soil structure, matric potential was the more suitable quantity in explaining the optimum field conditions for NO release from different soil textures. Several field studies have shown the use of matric potential. *Borken and Brumme* [2000] tested the relationships between CH_4 oxidation rates, water-filled pore space, ψ_m, gas diffusion, and soil temperature and found ψ_m the best predictor for methane fluxes from soil. *Zak et al.* [1999] measured highest CO_2 respiration in soil at a matric potential of –10 kPa and declining soil respiration when matric potential decreased to –300 kPa. Unfortunately no data were presented for matric potential between 0 and –10 kPa. In agreement with our findings, *Miller and Johnson* [1964] presented maximum CO_2 production and maximum nitrification in soils at approximately –15 kPa, with lower rates at both higher and lower ψ_m.

This study dealt with NO release from soil samples in the laboratory. However, it has been demonstrated repeatedly that these laboratory results can be converted into NO fluxes, using a simple diffusion algorithm by *Galbally and Johansson* [1989]. Good agreement (5–40%) has been obtained between calculated NO fluxes from laboratory experiments and NO fluxes from field measurements [*Galbally and Johansson*, 1989; *Remde et al.*, 1993; *Rudolph et al.*, 1996; *Gut et al.*, 1999; *Otter et al.*, 1999; *Ludwig et al.*, 2000; *van Dijk and Meixner*, 2001b; *Gut et al.*, 2001]. Thus, our results of maximum NO release from soils may be equivalent to maximum NO emissions from soils at matric potential close to –10 kPa. It should be investigated in the field whether our observed relation indeed holds for NO emissions from soils, including soils outside the tropical region. If so, the use of matric potential could simplify the prediction by models of NO fluxes from different ecosystems (having largely varying soil textures). Matric potential is easily obtained from pedo-transfer functions, using the water content and the soil texture (sand, silt and clay content). For instance, *Tomasella and Hodnett* [1998] developed pedo-transfer functions for a wide range of soil textures from the Amazon. Finally, please note that our results were normalised to the corresponding maximum. Thus, although the use of matric potential could support the prediction of normalised NO emissions from soils with varying textures, it is still necessary to predict the different magnitudes of individual emissions of NO from different ecosystems.

4.6 ACKNOWLEDGEMENTS

The authors kindly thank Beatriz Gomes, Eliomar, and Aparecida da Silva of the Federal University of Rondônia (UNIR, Ji-Paraná), Michael Keller, Yara Ferreira, Janice Wiles and Lisa Zweede (LBA-Ecology project), Gilberto (INPA, Manaus), Senhor Cravo and Senhor Oliveira (EMBRAPA, Manaus) and Raimundo Cosme (EMBRAPA, Santarem) for enabling the collection of soil samples in Amazonas and in the Tapajós National Forest. Jao Luiz Estevez, Claudionor and Eduardo (INCRA, Ji-Paraná) and Jonathan Williams, Marcos Antonio Lima Moura, and Jadson Dias and Hudson da Silva are most kindly thanked for their valuable help during sampling campaigns. Comments on the water retention measurements by Isabel Cousin during the conference in Nice (2000) by the European Geophysical Society have been most appreciated. The European Union and the Max Planck Society provided financial support through the LBA-EUSTACH project (ENV4-CT97-0566).

CHAPTER 5

Soil nitrous oxide and nitric oxide emissions as indicators of the exceedance of critical loads of atmospheric N deposition in seminatural ecosystems

U. Skiba, L. Sheppard, C.E.R. Pitcairn, I. Leith, A. Crossley, S. van Dijk,
V. H. Kennedy and D. Fowler

ABSTRACT

Elevated N deposition caused by ammonia emissions from poultry and pig farms, and supplemented N concentrations in acid mist in field and chamber experiments increased soil available NH_4^+ and NO_3^- concentrations and emissions of N_2O and NO. In a 'pristine' soil, not previously exposed to high N deposition rates, an initial threshold of 40 kg ha^{-1} $year^{-1}$ was required to increase N_2O emissions. For all data described here on average 0.76% (range 0.2 to 15%) of the elevated N deposited was emitted as N_2O. For soils exposed to long-term and large N deposition rates N_2O losses >3% of the N deposition rate were calculated. This suggests that N_2O losses of more than 3% of the N input can be indicative of soil ecosystems where the N input exceeds its demand. For NO a more limited data set showed losses ranging from 1.3 to 20% of the elevated N input. It was calculated that NH_3 emissions from all intensive pig and poultry farms in Great Britain accounted for 18 t N_2O–N $year^{-1}$ and that poultry farms accounted for less than 3 t NO–N $year^{-1}$.

Also published in *Environmental Pollution*, 102, S1 457–461, 1998

5.1 INTRODUCTION

In the UK total annual N deposition ranges from <10 to >30 kg N ha^{-1} y^{-1} (INDITE, 1994). Large deposition rates are measured in close vicinity to cities, in rural areas in close proximity of intensive livestock farms and in upland areas, receiving high rates of cloud droplet deposition. Atmospheric N deposition in non- agricultural ecosystems therefore, can present an important source of N, in some situations improving the growth of the vegetation, while in others causing changes in plant species composition (Pitcairn *et al*., 1998) and eutrophication of the ecosystem.

In soil, elevated inputs of N are known to increase rates of nitrification and denitrification and associated production and emission of nitrous oxide (N_2O) and nitric oxide (NO) (Skiba *et al*., 1993). In the atmosphere, both gases are involved in important chemical reactions. Nitrous oxide is a greenhouse gas and in the stratosphere is involved in reactions leading to ozone destruction (IPCC, 1997). Nitric oxide is closely coupled to the production of tropospheric ozone and acid rain (Crutzen, 1983). It is therefore important to quantify all effects that lead to the increase of emissions of N_2O and NO to the atmosphere. Here we report on how elevated atmospheric N deposition rates to forests downwind from NH_3 emitting poultry and pig farms and from field and open top chamber (OTC) experiments, where varying rates of N have been applied as a fine mist to sitka spruce, *Calluna vulgaris* and moorland grasses, increase soil emissions of N_2O and NO.

5.2 SITE DESCRIPTION AND METHODS

Poultry farm A is situated in a rural area of southern Scotland and houses approximately 120,000 birds managed on a 44-day cycle. Poultry farm B is situated in the central belt of Scotland, in close vicinity of motorways and airfields, containing 340,000 birds. The pig farm is situated in a rural area in eastern Scotland, containing 200 sows and about 2000 piglets. The poultry farms have been operating for over 15 years and the pig farm for 46-years. All lie in close vicinity to mixed woodlands. Atmospheric NH_3 concentrations were measured by passive diffusion along a transect of the prevailing wind direction above and below the poultry and pig units over a one year period (1995 to 1996 at the poultry farms and 1996 to 1997 at the pig farm) (Pitcairn *et al*. 1998). Nitrous oxide was measured at several distances (Table 5.1) downwind from poultry farm A on 5 occasions between September and November 1995 and from poultry farm B and the pig farm on 5 and 3 occasions, respectively, between May and August 1997. N_2O and NO were measured from poultry farms A and B on 3 (A) and 2 (B) occasions in September/October and November 1997.

Deepsyke Forest, in the Scottish borders, is a 10-year Sitka spruce plantation growing on a drained moorland, in which groups of 10 trees were treated with acid mist at pH 2.5 (H_2SO_4 and NH_4NO_3) providing 48 kg N ha^{-1} y^{-1} (single dose, S) or 96 kg N ha^{-1} y^{-1} (double dose, D) and enhancing precipitation by 10%. The control at pH 5 provided 2 kg N ha^{-1} y^{-1} and annual wet and dry deposition of N contributed a further 6.7 kg N ha^{-1} y^{-1} to all treatments (Sheppard *et al.*, 1998). Treatments were replicated over 4 blocks. Nitrous oxide fluxes were measured between April and August during the first and second year of spraying. Average weekly inputs of N for the measurement period were 1.7 (S 1996), 2.8 (D, 1996), 1.9 (S, 1997) and 3.7 (D, 1997) kg N ha^{-1} y^{-1}.

Glencorse, SE Scotland, is an 18-year old, physiologically mature Sitka spruce plantation growing on ex-agricultural land. Groups of trees were sprayed with acid mist as above for the single dose. Control plots were not sprayed. Nitrous oxide and NO fluxes were measured in July and September 1991, during the second year of treatment.

Intact peat monoliths (10 l) of pure *Calluna vulgaris* from a moorland in NE England and moorland grasses with some *Calluna* from North Scotland were collected in 1995 and were maintained in OTC's at ITE. Monoliths were sprayed 2 to 3 times per week with simulated rainwater enriched with solutions of nitrogen (NH_4NO_3) to provide an annual input of 2, 20, 40, 60, 80 or 100 kg N ha^{-1} y^{-1} (Pardiwala, 1997). Nitrous oxide fluxes were measured on 2 occasions 1 year after treatments started and on 5 occasions during the second year of treatment.

Nitrous oxide fluxes at the farm sites and in the field experiment were measured by the static chamber method. Small round frames (22 l volume) were inserted into the ground for the duration of the experiment (MacDonald *et al.*, 1997). In the OTC's, a 10 l box with a stirring fan was fixed temporarily over the monolith and sealed to form a static chamber. Chambers were sealed for 1 hour for flux measurement, when gas samples were withdrawn by syringe and were analysed by ECD gas chromatography for N_2O. Soil temperature was measured and soil samples were collected for analysis of available soil NH_4^+ and NO_3^- (Grimshaw, 1989) and volumetric soil water content.

Nitric oxide fluxes were measured by the dynamic chamber method (Skiba *et al.*, 1993). Frames (0.95 m^2 × 0.15 m depth) were inserted into the ground onto which a 0.55 m^3 Perspex chamber was attached for the duration of the flux measurements. Ozone free air was pushed through the chamber at a flowrate of 60 l min^{-1}, inlet and outlet air was sampled at intervals of 3 min and was analysed for NO, NO_2 by chemiluminescence and O_3 using a UV photometric analyser.

Table 5.1. The effect of NH_3 deposition on the soil available N concentrations and NO and N_2O fluxes

Site and distance (m)	Total N deposition[1] (kg N ha^{-1} y^{-1})	N_2O flux[2] µg N m^{-2} h^{-1}	NO flux[3] µg N m^{-2} h^{-1}	volumetric water content m^3 m^{-3}
Poultry farm A				
15	40.9	4.1 (10.1)[4]	21.8	24.5 (33)[4]
100	22.0	1.7 (3.8)	3.3	38 (35)
276	11.4	1.4 (2.4)	3.3	32 (30)
Poultry farm B				
30	80.1	55.7	131.2	21.7
50	52.1	43.8	158.5	25.7
110	24.9	17.3	n.d.	40.5
250	17.4	12.9	79.6	29.8
Pig farm				
15	56.3	8.4	n.d	20.4
34	37.7	11.3	n.d	19.2
116	23.6	3.8	n.d	33
1000	12	0.9	n.d	27

[1] NH_3 deposition was measured by passive diffusion for a one year period in 1995/96 at the poultry farms and in 1996/1997 at the pig farm, oxidised N deposition rates were modelled (INDITE, 1994).

[2] mean flux from 3 chambers sampled on 3 (farm A), 7 (farm B) and 3 (pig farm) dates.

[3] mean flux from 2 chambers sampled on 3 (farm A) and 2 (farm B) dates, n.d = not determined.

[4] values in brackets are means from 5 sampling occasions in 1995 (Skiba et al, 1996).

Typical standard errors of the mean were 67% for N_2O, 38% for NO and 18% for the soil water content.

5.3 RESULTS AND DISCUSSION

The poultry and pig farms were a source of NH_3. Total annual N deposition rates at the woodland edge, closest to the poultry and pig farm buildings were 41, 81 and 56 kg N ha^{-1} y^{-1}, respectively (Table 5.1). Deposition rates declined rapidly with distance away from the farm buildings, and were reduced by at least 50% 100 m downwind, approaching background, upwind values (12 to 17 kg N ha^{-1} y^{-1}) at a distance of about 300 m from the poultry houses and 1000 m from the pig farm (Table 1). The increased N deposition downwind of the farms increased soil available NH_4^+ and NO_3^- concentrations in a linear fashion (Fig. 5.1). It is therefore not surprising to measure increased emissions of N_2O and NO in close vicinity to the livestock buildings (Table 5.1). Previous measurements at poultry farm A showed that N_2O emissions were positively correlated with soil available NH_4^+ and NO_3^- concentrations ($r^2 = 0.75$ for NH_4^+ and $r^2 = 0.62$ for NO_3^-, Skiba et al., 1996).

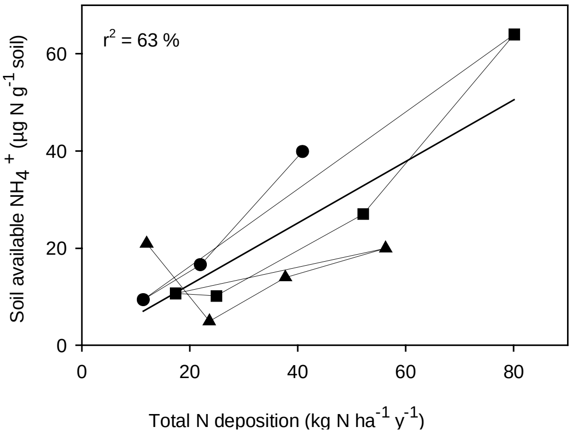


Figure 5.1. The effect of N deposition on the soil available NH4+ concentration downwind of poultry farm A (1995) (●), poultry farm B (1997) (■) and the pig farm (1997) (▼).

The largest emissions were measured from poultry farm B, which even at the control site, emitted significantly more N_2O and NO than at any site downwind of poultry farm A or the pig farm. Large emissions coincided with significantly larger total soil available N concentrations, in particular soil NO_3^-. Downwind of farm B mean soil NO_3^- concentrations in samples collected between July and November 1997 ($n = 4$) were 65, 42 and 14 μg NO_3^- - N g^{-1} dry soil 30, 50 and 250 m away, whereas the mean concentration in samples collected 16, 100 and 276 m downwind of farm A in September 1995 and September, November 1997 ($n = 8$) were only 4.0, 1.8 and 1.1 μg NO_3^- - N g^{-1} dry soil.

Differences in soil physical properties were unlikely to account for this large difference in soil N between the sites. All soils were brown forest soils, with very similar volumetric water contents (Table 5.1). The large NO_3^- concentrations at farm B are difficult to explain although, heavy vehicle and air traffic have probably increased the local total N deposition above the value based on the 20 km^2 scale at which N deposition was modelled (INDITE, 1994).

Nitrous oxide and NO emissions expressed as a percentage loss of the elevated N input $((N_2O_{\text{high N input}} - N_2O_{\text{background N input}})$ / (high N input – background N input)) × 100 differed widely between sites. Emission factors within a radius of 100 m of poultry farm A were 1.7% for N_2O and 2.2% for NO. The fractional emission losses, however, were much larger for poultry farm B, receiving larger N deposition rates (6.3% for N_2O and 13.6% for NO), and the pig farm, which has been operating 46 years (12.7% for N_2O). Based on these emission factors it was calculated that NH_3 deposition within a 100 m radius of all poultry and pig farms in the UK was responsible for <1 t N_2O - N $year^{-1}$ and <3 t NO - N $year^{-1}$ for the poultry farms and approximately 18 t N_2O - N $year^{-1}$ for pig farms. This is a small percentage of the UK total soil N_2O emission (68 kt N_2O - N $year^{-1}$, Skiba et al., 1998).

As in the above field observations also experimental applications of acid mist to mineral soil (pH in $CaCl_2$ = 4.6) and organic soil (pH in $CaCl_2$ = 3) increased soil available NH_4^+ and NO_3^- concentrations and consequently emissions of N_2O and NO. However, it was interesting that for the mineral soil a response was observed when the acid mist treatment provided an input of 48 kg N ha^{-1}, whereas only the 85 kg N ha^{-1} treatment stimulated a response on the organic soil. For the mineral, previously agricultural soil, during the second year of treatment, an input of 48 kg N ha^{-1} increased NO emissions 10 fold and N_2O emissions and NO_3^- about 5 fold (Fig. 5.2).

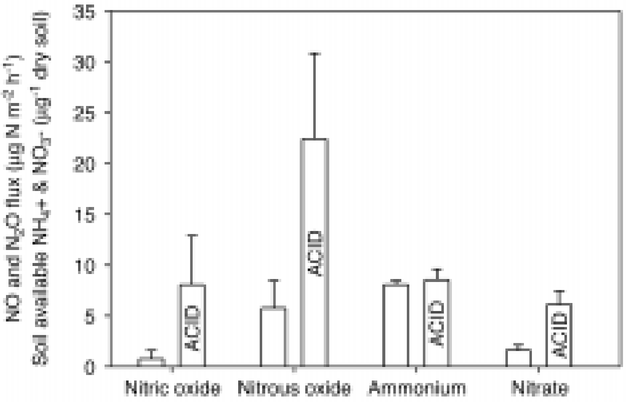


Figure 5.2. The effect of acid mist (Acid = 48 kg N ha^{-1} $year^{-1}$) and adjacent control plots (empty bars) on soil N concentrations and trace gas emissions at Glencorse, a mineral soil planted with sitka spruce. The bars represent means and standard error of the means, *n* =4.

On the organic soil an input of 85 kg N ha^{-1} increased the emission of N_2O and soil available NH_4^+ concentrations during both spraying periods ($p < 0.05$, $n = 8$) from 3.6 to 10.6 µg N_2O-N m^{-2} h^{-1} and 8.7 to 13.2 µg NH_4^+- N g^{-1} soil. The lack of response to the single dose treatment suggests that most of the N applied was immobilised. However, continuous applications of smaller rates of N will eventually exceed immobilisation rates and increase N_2O emissions, as suggested by a comparison of N deposition and N_2O emissions at a low altitude and high altitude sitka spruce plantations and moorland on acid peaty soils. This study showed that even for an acid organic rich soil 1% of the increased N deposition at the high altitude was emitted as N_2O (MacDonald *et al.*, 1997).

Restricted responses to N additions were also observed for the peat monoliths of *Calluna* and moorland grasses. For both plant communities N_2O emissions only increased significantly when the N input exceeded 40 kg N ha^{-1} y^{-1} (Fig. 5.3). After the first year of treatment N_2O emissions from the grass monoliths were significantly smaller than from the *Calluna* monoliths, especially for the 80 and 100 kg N ha^{-1} y^{-1} doses. This difference was not observed after the second year of treatment. The *Calluna* monoliths were collected from a moorland in NE England were N deposition rates exceed 30 kg N ha^{-1} y^{-1}, whereas the grass monoliths from the North of Scotland had only experienced N input rates of less than 15 kg N ha^{-1} $year^{-1}$ (INDITE, 1994).

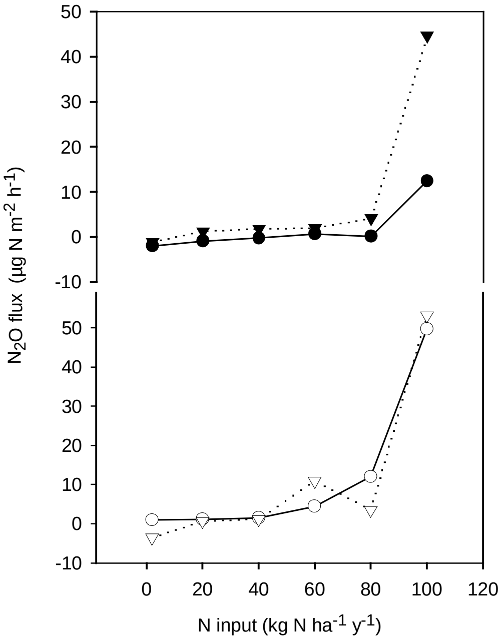


Figure 5.3. The effect of increasing N concentrations in rain on the emissions of N_2O from *Calluna* (open symbols) and moorland grasss (closed symbols) 1 year (circles) and 2 years (triangles) after treatment started.

Previous exposure to high N deposition rates, implies the presence of larger nitrifying and denitrifying microbial communities, thus a faster response to further increases in N input compared to a soil not previously exposed to high N. This 'memory effect' of a soil can be long lasting and may explain the differences in the behaviour of *Calluna* and grass monoliths and also the differences in response to acid mist at the ex-agricultural site (Glencorse) and the peat (Deepsyke forest). *Mosier et al.* (1996) reported that for a prairie grassland in North America the effect of N fertilization on N_2O remained evident 12 and 13 years later. However, for the monoliths, it is also possible that the competition from the grasses was high, leaving less N available for microbial activities.

The enhanced N_2O emissions caused by increased deposition of atmospheric N described in this work and from upland forests and moorlands by MacDonald *et al*. (1997) and Skiba *et al*. (1997) were expressed as percentage of the elevated N inputs. The spread in % emission losses was large and ranged from –0.22 to 14.7%, with a median value of 0.76% (*n* = 38) (Fig. 5.4). This median value is not unreasonable, the IPCC (1997) adopted a value of 1% in their calculations of N_2O emissions from N deposition at the global scale. The scatter of the data in Fig. 5.4 at first sight is alarming. However, all N_2O losses >3% were calculated for soils that were exposed to long-term and/or large N inputs: poultry farm B with unusually large NO and N_2O emissions, the pig farm with 46 years of continuous high N inputs, the sitka spruce experiment on the ex-agricultural soil and the 100 kg N ha^{-1} y^{-1} dose in the OTC's. This implies that a N_2O emission >3% of the N deposited above background values can be indicative of a soil ecosystem where N input exceeds its demand.

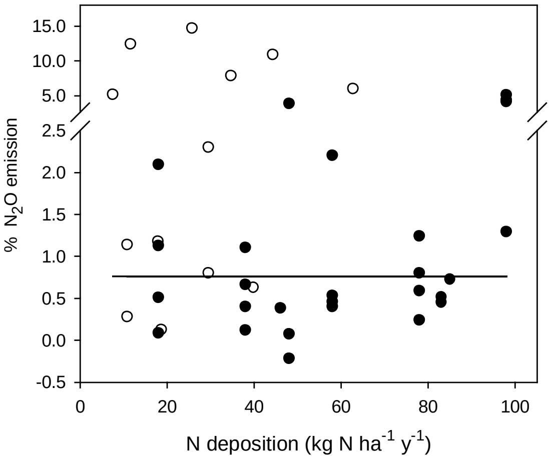


Figure 5.4. The effect of N deposition on N_2O emissions where N_2O is given as a % of the additional N deposited to a range of forest, heather and grass moorland sites reported in this study and in Skiba et al (1997). Open circles show results from field measurements and closed circles from experimental applications of N. The solid line represents the median % N_2O loss (0.76 %), calculated from this data set.

For NO the data was not extensive enough to draw such conclusions, but as for N_2O, emission factors were largest downwind of poultry farm B, where N deposition rates were very high. It can be concluded from the above studies, that for a soil not previously exposed to high N inputs, an initial threshold N deposition rate of at least 40 kg N ha^{-1} $year^{-1}$ is required before increasing the N_2O emissions above background values. However long-term exposure to relatively low elevated N deposition rates (as low as 10 kg N ha^{-1} $year^{-1}$ above background deposition rates) can cause N_2O to be emitted in excess of 3% of the annual N input (Fig. 5.4). This work suggests that measurements of soil N_2O and NO emissions may be useful as indicators of soils for which the supply of N exceeds its demand, and therefore may also be indicative of other problems arising from excess N input, such as NO_3^- leaching.

5.4 ACKNOWLEDGEMENTS

The authors wish to thank the landowners for access on their land and NERC for financial support.

CHAPTER 6

Nitric oxide emissions from forest soils in the Netherlands

Saskia M. van Dijk and Jan H. Duyzer

ABSTRACT

Nitric oxide (NO) fluxes to the atmosphere were determined from different soil types in coniferous forest and deciduous forest in the Netherlands. Dynamic chambers were used to determine the emission every week throughout a year. Forest type and soil texture are important parameters leading to large differences in fluxes between sites. High fluxes of up to 178 ng m^{-2} s^{-1} were observed in summer in a Douglas fir forest on a sandy soil. In a nearby beech forest, on the same soil, fluxes up to 63 ng m^{-2} s^{-1} were observed. Emissions from clayey soils in a beech forest were much lower, ranging from 0 to 14 ng m^{-2} s^{-1}. Besides the important effect of the forest community type and the soil texture on the NO flux, a strong positive correlation with soil temperature was observed (accounting for up to 70% of the variance). Soil moisture could explain up to 60% of the variance of the NO flux. It seems that an optimum range of intermediate moisture contents exists, ranging from 30% to 45% dry weight, or from 55% to 85% water-filled pore space approximately, where high temperatures lead to high emissions.

Also published in *J. Geophys. Res.* 104, D13, pp. 15955-15961, 1999

6.1 INTRODUCTION

Nitrogen oxides, together with hydrocarbons, play an important role in atmospheric ozone formation [*Crutzen*, 1983]. Furthermore, the oxidation of nitrogen dioxide to nitric acid is a major contributor to acid precipitation [*Logan*, 1983]. Policies to reduce levels of tropospheric ozone are often based on computer simulation models that rely on estimates of emissions from all relevant sources of hydrocarbons and nitrogen oxides. Especially on a global scale, the contribution of emissions of nitric oxide (NO) from natural sources to the NO_y (NO plus other nitrogen oxides) budget is significant [*Davidson*, 1991]. Few data are available on the emission rates of these trace gases from soils in temperate forests.

Earlier studies indicated that NO emitted from the soil is mainly produced by biological nitrification, the oxidation of organic nitrogen and/or ammonium (NH_4^+) to nitrate (NO_3^-) [*Lipschultz et al.*, 1981], and denitrification, the reduction of nitrate NO_3^- to NO, nitrous oxide (N_2O) and nitrogen [*McKenny et al.*, 1982]. The NO flux from soil has been found to be strongly positively linked to temperature [*Slemr and Seiler*, 1984; *Skiba et al.* 1992]. A very small temperature response of NO emissions to temperature has been observed from extremely dry soils [*Cardenas et al.*, 1993; *Ludwig*, 1994], indicating that soil moisture has an important control on the NO flux. Also, a strong link between rainfall amount and NO flux has been observed [*Skiba et al.*, 1992]. Other controlling variables are the availability of NO_3^- and NH_4^+ [*Galbally*, 1989], soil acidity [*van Cleemput and Samater*, 1996] and organic substrate [*Slemr and Seiler*, 1984]. *Meixner* [1994] gives a comprehensive review on the NO flux from soil and the main regulating parameters.

The Netherlands Organization for Applied Scientific Research (TNO) coordinated a European project (FOREXNOX) in which measurements of exchange rates of nitrogen oxides were carried out in various forests across Europe. The aims of this study were to establish NO fluxes at the soil-atmosphere interface in different forests as well as from different soils and to determine key factors regulating this flux. For this purpose, experiments were designed to cover a wide variety of conditions. These included measurements in areas with high (Netherlands) and low (Scotland) nitrogen inputs from the atmosphere, in deciduous and coniferous forests, and measurements from different soil textures (sandy and clayey soils). In this paper, the measurements carried out in the Netherlands are presented. Measurements were carried out throughout the year, which made it possible to determine emissions under varying conditions with respect to soil temperature and wetness.

6.2 METHOD

6.2.1 Experimental

Dynamic open chamber techniques as described by *Mosier* [1989] were used to measure the nitric oxide flux from soil. The stainless steel chambers (1.50 x 0.30 x 0.25 m) were sunk in the soil to about 0.10 m, giving a total volume of 0.0675 m^3. Two fans were attached to the Plexiglas lid on top of the chamber to achieve adequate mixing of the air inside the chamber. The lid was placed on top of the chambers half an hour prior to the start of measurements. Using a ventilator, ambient air was pushed through a funnel over the enclosed soil within the chamber. The flow rate ranged from 0.008 to 0.010 m^3 s^{-1}. This suggests that small pressure differentials, induced by pushing the air over the soil, were not found to influence the NO flux. NO concentrations at the inlet and outlet of the chamber were determined using a Thermo Environmental Instruments 42 W monitor based on the chemiluminescent reaction between NO and ozone. The detection limit of the instrument was 0.1 ppb. Calibration of the instruments was carried out at the laboratory using permeation tubes for NO_2 and primary standard for NO (50.03 ppm certified by the Dutch NMI). A mobile calibration unit was used in the field prior to each measurement campaign. The sampling procedure and data logging were controlled using a Campbell 21 X. Each measurement sequence took about 1 hour, after which the Plexiglas lid was opened and measurements were made from the next chamber. In addition several physical and chemical aspects of the soil were monitored. Soil temperature, at a depth of 0.05 m, was recorded simultaneously with the chamber experiments. The gravimetric water content of the soil was determined for each experimental site.

From July 1996 to August 1997 NO fluxes were determined on one day every week at Speuld in the central part of the Netherlands. In addition, NO fluxes were measured at Hollandse Hout during two field campaigns in summer 1997. Table 6.1 presents various physical and chemical soil characteristics observed at Speuld and Hollandse Hout. Atmospheric deposition levels are relatively high for both study areas, averaging 40 kg N ha^{-1} y^{-1} and 30 kg S ha^{-1} y^{-1} [*Heij and Schneider*, 1991].

The study area at Speuld is a 35 year old forest stand which has several different plantations all on identical coarse textured acidic soil (Table 6.1). In total three, permanently installed, chambers were operational at Speuld, providing NO fluxes from three different experimental plots. NO emissions were determined in a Douglas fir (*Pseudotsuga menziesii*) plantation and a beech (*Fagus*) plantation. Since these two forest types were stocked on the same sandy soil, results could be used to study the impact from tree species on the NO fluxes. Additionally a third experimental site, situated within the Douglas fir plantation, was weekly supplied with 8 ml of an ammonium/nitrate/sulfate solution, having concentrations of 0.042, 0.010 and 0.016 mol kg^{-1} respectively. By this procedure, this site would receive an amount of nitrogen and sulfate equivalent to twice the normal annual deposition.

Table 6.1 Summary of the different experimental sites at Speuld (52°13′N, 5°39′E) and Hollandse Hout (52 °26′N, 5°28′E).

	SPEULD			HOLLANDSE HOUT
Forest community	Douglas Fir	Douglas Fir	Beech	Beech
Soil texture	Loamy sand	Loamy sand	Loamy sand	Heavy clay
Soil classification	Podsol	Podsol	Podsol	Luvisol
Soil acidity (pH H_2O)	3.7	3.7	3.7	6.8
Org.matter% (0-5 cm)	15	15	15	5
Org.matter% (>50 cm)	1.5	1.5	1.5	5
$CaCO_3$%	0	0	0	1
NH_4^+/NO_3^- (mg N kg^{-1})	4.9/3.8	-	-	-
Special		N added		

In addition to the continuous flux measurements at the study area at Speuld, two other dynamic chambers were installed at Hollandse Hout in March 1997. NO flux measurements were determined from two identical sites at Hollandse Hout during two field campaigns of several days in summer 1997. The study area at Hollandse Hout is a beech (*Fagus*) plantation in a 25 year old forest which has several different forest communities. The soil has a very fine soil texture, consisting mainly of heavy clay (see Table 6.1). Comparison of the NO fluxes from the beech plantation at Speuld (sandy soil) and the beech plantation at Hollandse Hout (clayey soil) could be used to study the impact of soil texture on the NO flux.

6.2.2 Calculation

The NO flux was calculated from the difference in NO mixing ratios [ppb] between inlet and outlet of the dynamic chamber and was corrected for bias due to chemical reactions between NO, NO_2 and O_3 (see below). The fluxes were calculated from the following equation:

$$F_{NO} = \left\{ \frac{Q}{A}(c_{out} - c_{in}) + F_{cor} \right\} \frac{M_N}{V_m} \qquad (6.1)$$

Where F_{NO} [ng NO-N m^{-2} s^{-1}] is the NO flux, Q [m^3 s^{-1}] is the flow rate through the chamber, A [m^2] is the area enclosed by the frame and V_m [m^3 mol^{-1}] and M_N [kg mol^{-1}] are the molar volume and molar weight of nitrogen respectively. F_{cor} is a factor used to correct for the amount of NO consumed in the reaction with O_3 (to form NO_2), taking place in the enclosure, and can be found by estimating the average reaction rate in the enclosure during monitoring. Air was alternately sampled and analyzed at the chamber inlet and chamber outlet, switching every 3 minutes. Preliminary analysis of the data showed that a sudden unambiguously high or low ambient NO mixing ratio could result in errors in the calculated flux. Therefore, the NO flux was numerically filtered to prevent bias from strong variations of the ambient NO mixing ratios. Averaging two successive NO mixing ratios of the ambient air effectively removed sudden leaps and proved to be a good method to reduce the variance in the calculated NO flux. Only a few flux measurements with large fluctuations of the NO mixing ratios at the inlet were rejected. In total approximately 4000 successful 6 minute NO flux measurements resulted in 300 hourly average NO emission rates. The data set was tested for normal distribution (histograms) and parametric statistical tests (t tests) were used to determine significant differences between experimental sites.

6.3 Results and Discussion

Figure 6.1 presents the hourly averaged NO emissions observed at the different experimental sites at Speuld and Hollandse Hout. The NO fluxes were found to differ considerably throughout the measuring period. The NO fluxes at Speuld were very high, varying from hardly detectable in winter to 180 ng m^{-2} s^{-1} in summer in a Douglas fir and up to 65 ng m^{-2} s^{-1} in the beech plantation. The average observed NO flux from the beech plantation at Hollandse Hout ranged from 0 to 15 ng m^{-2} s^{-1}.

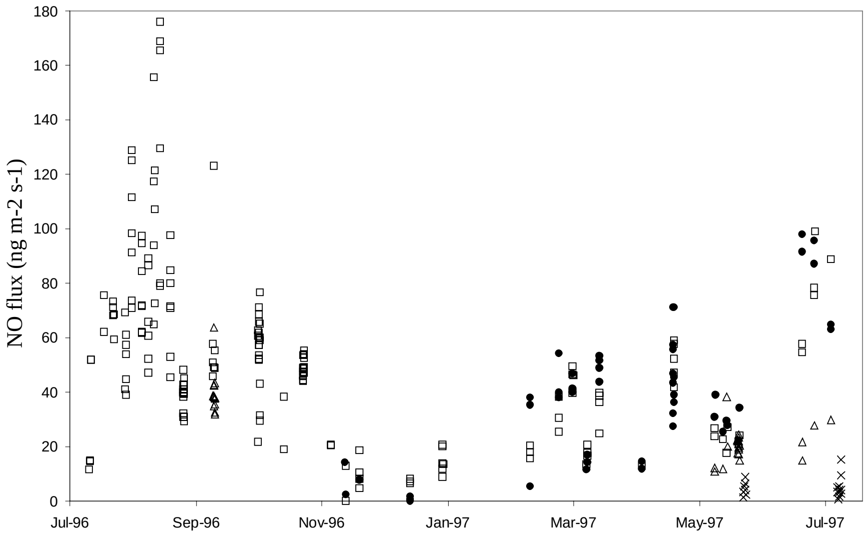


Figure 6.1. Hourly averaged NO fluxes observed at the different experimental sites at Speuld and Hollandse Hout.

Maximum NO fluxes are found during summer and minimum NO fluxes are found during winter. Open squares = Douglas fir, sandy soil; closed circles = Douglas fir extra N sandy soil; open triangles = Beech, sandy soil; crosses = Beech, clayey soil.

Compared to results from other relevant studies, the NO fluxes observed at Speuld and Hollandse Hout were relatively high. In analogue studies in temperate coniferous forests in Germany and Norway, NO fluxes were reported, ranging from 0.14 to 6.7 ng m^{-2} s^{-1} [*Papen et al.*, 1993] and from 0.3 to 21 ng m^{-2} s^{-1} [*Pilegaard et al.*, 1998] respectively. The relatively high NO fluxes observed during our study may well result from the high atmospheric N deposition. *Butterbach-Bahl et al.* [1997] also found relatively high NO emissions up to 28 ng m^{-2} s^{-1} and 40 ng m^{-2} s^{-1} from sandy soils in deciduous and coniferous forest respectively. These values were thought to originate from the high annual atmospheric deposition level of 35 kg N ha^{-1} y^{-1}, comparable to the N deposition at Speuld.

6.3.1 Soil Temperature

As a microbiological process, nitric oxide production is strongly linked to temperature, causing higher fluxes from soil in summer. At most 70% of the variance in the determined NO flux was explained by soil temperature. Figure 6.2 shows the NO emission as a function of temperature for all sites. The activation energy was 85 kJ mol^{-1}, as was calculated according to the Arrhenius equation for data from the Douglas fir stand on sandy soil. At this experimental site NO fluxes were determined during a complete year. The activation energy agrees well with values reported in other studies, ranging from 44 to 103 kJ mol^{-1} [*Johansson and Granat*, 1984; *Skiba et al.*, 1992]. This indicates a 2 to 3 fold increase in the NO emission for each 10 degrees rise in temperature, as is commonly observed for microbiological processes [*Focht and Verstraete*, 1977; *Galbally*, 1989].

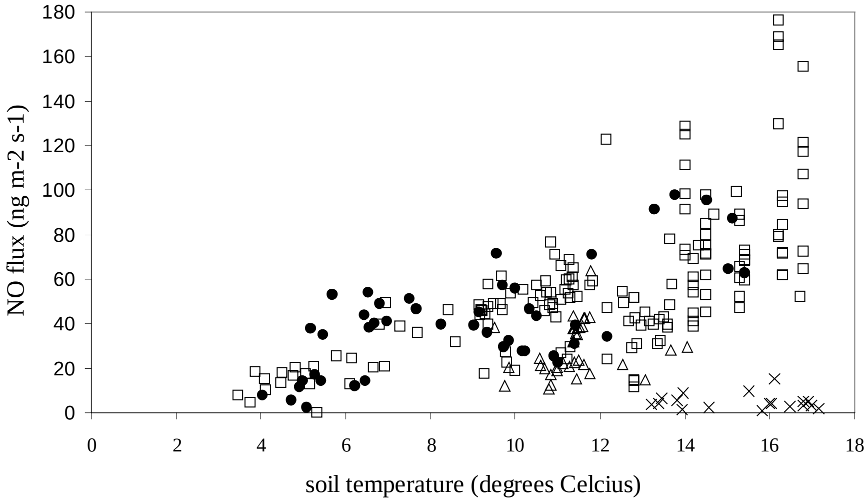


Figure 6.2. NO flux related to the temperature. The activation energy calculated according to the Arrhenius equation for data from Douglas Fir on sandy soil is 85 kJ mol^{-1}. Symbols are as in Figure 6.1.

6.3.2 Soil Moisture

As is shown in Figure 6.3, a high NO emission rate was found particularly at a high soil temperature. Furthermore it can be seen that maximum fluxes were observed at a specific range of soil moistures. If soil conditions are extremely dry, the microbial community suffers from water stress, limiting the biological production of NO. For instance, *Cardenas et al.* [1993] found hardly any effect on soil temperature at very dry soil conditions. Several studies have shown an explosion of NO emissions after wetting extremely dry soil, suggesting that the NO production in soil was water limited [*Johansson et al.*, 1988; *Meixner et al.*, 1997; *Scholes et al.*, 1997]. On the other hand, when soil pores are filled with water, this drastically affects the escape of NO to the atmosphere [*Galbally*, 1989]. An optimum soil water content offers sufficiently moist conditions to enable microbial activity without disabling gas diffusion through the soil.

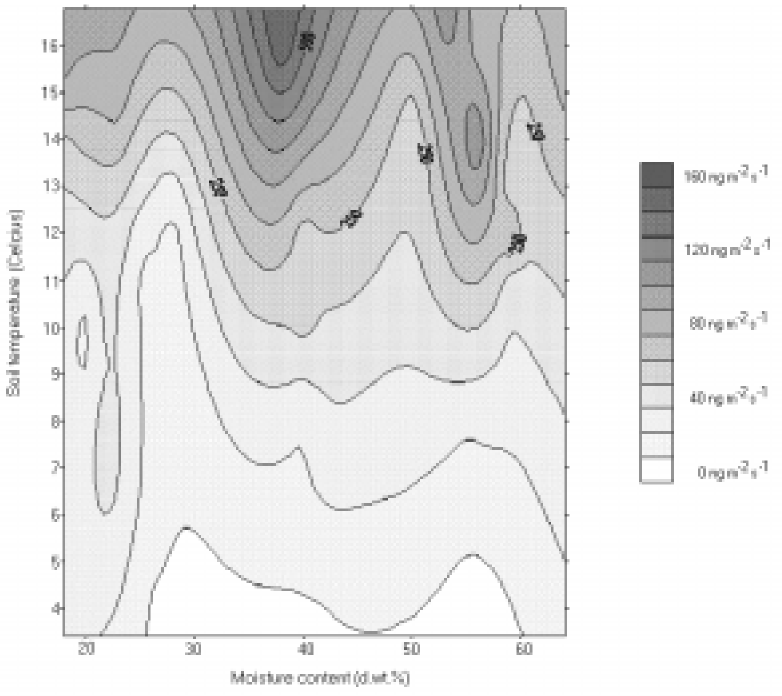


Figure 6.3. NO emissions from the sandy soil site in the Douglas fir plantation related to both the temperature and the soil water content. High NO fluxes are restricted to a relatively high soil temperature, and maximum fluxes are observed

at a certain intermediate range of soil water content (30%-45% dry weight).

Laboratory studies [*Linn and Doran*, 1984] indicated that production of trace gases (CO_2, N_2O) in soil through aerobic microbial processes is at a maximum at a water-filled pore space of 60% (Water-filled pore space is the ratio of volumetric soil water content to total soil porosity [*Hillel*, 1980]). Water-filled pore space of 60% appeared to be the threshold between water limiting and aeration limiting processes and was also suggested to be the optimum for NO emission from soil [*Davidson*, 1993].

During our experiment, maximum NO fluxes from sandy soil in coniferous forest were found at a soil water content varying between 30% and 45% (dry weight), at a water-filled pore space (WFPS) between 55% and 85% (Figure 3). NO production is possible not only through aerobic nitrification, but also through microbial processes under anaerobic conditions [*Firestone and Davidson*, 1989] and therefore the optimum soil water content for NO emission may be higher than 60% WFPS.

The range of optimum water content is well in line with the field capacity of the sandy soils at Speuld, approximately 85% and 40% WFPS, in the soil layers from 0 to 0.06 m and from 0.08 to 0.14 m. depth respectively. Compared to our findings, results from a study in Venezuela showed maximum NO emissions from a sandy soil at a much lower water content, ranging from 10 to 20% (dry weight) [*Cardenas et al.*, 1993].

Possibly, in a certain region, the established microbial community has adapted to the prevailing environmental conditions. Therefore, the optimum soil water content at which microbial production, together with gas diffusion, leads to maximum NO emission depends on the water regime of the study area. This implies that the optimum soil water content for maximum NO emission under slightly wetter soil conditions (the Netherlands) would be higher than for slightly dryer conditions (Venezuela), explaining the relatively higher optimum soil moisture found during this study.

6.3.3 Atmospheric nitrogen input

Figure 6.1 shows NO fluxes from two experimental sites in a Douglas fir forest at Speuld, having two different annual atmospheric N deposition levels. There is widespread evidence that the availability of organic and inorganic nitrogen in soils has a strong impact on NO emission rates [*Slemr and Seiler*, 1984]. For instance, the average NO flux from soils in a Sitka spruce forest in Scotland changed from 0.53 ng m^{-2} s^{-1} to 4.6 ng m^{-2} s^{-1} upon addition of nitrogen containing acid mist [*Skiba et al.*, 1994]. However, the experimental site at Speuld that received an additional amount of nitrogen in addition to the annual atmospheric deposition level was not found to have significantly higher NO emissions.

It is thought that the high annual deposition levels of N and S from the atmosphere at Speuld (40 kg $ha^{-1}y^{-1}$ and 30 kg $ha^{-1}y^{-1}$ respectively [*Heij and Schneider*, 1991]) have saturated the soil with nutrients. Addition of extra N would therefore not result in an increase in the NO flux from soil. This finding is in line with experiments carried out by *Koopmans* [1996] who showed on the basis of nitrogen leaching experiments that soils at Speuld are indeed nitrogen saturated.

Table 6.2. Comparison of the hourly average NO emissions (average and standard deviation) for the different experimental sites at Speuld and Hollandse Hout.

Location	Measuring period	Average flux ng m^{-2} s^{-1}	St.dev	n	Significant difference
Douglas	Nov 96 - Aug 97	32.0	21	46	
Douglas N added	Nov 96 - Aug 97	39.0	16	46	No
Douglas sandy soil	May 97 – July 97	49.7	29.7	20	
Beech sandy soil	May 97 – July 97	20.6	6.1	20	Yes[1]
Beech sandy soil	May 97 - July 97	21.7	6.4	21	
Beech clayey soil	June 97 - July 97	3.2	4.8	21	Yes[1]

[1] NO fluxes are significantly different ($p<0.01$) by paired t-tests.

6.3.4 Soil texture and forest type

Figure 6.1 and Figure 6.2 show that differences in forest type, or differences in soil parameters due to differences in forest type, influenced the NO flux from soil. Table 6.2 compares the average NO flux and standard deviations found for the different experimental sites. NO emission rates from sandy soil in Douglas fir forest were approximately 30 ng m^{-2} s^{-1} higher than NO fluxes from sandy soil in beech forest. It remains uncertain which soil properties could have caused the higher flux from soil in coniferous forest, since the physical and chemical soil characteristics that were monitored at the two different experimental sites were all similar. The soil NH_4^+ and NO_3^- concentrations, found to be strongly positively linked to NO fluxes [*Slemr and Seiler*, 1984], were unfortunately not measured at the different experimental sites. Similar experiments in Germany also demonstrated a smaller NO flux from soil in deciduous forest than from soil in coniferous forest. These differences were suggested to arise from differences in the soil microbial populations/processes and different turnover ratios of organic matter due to differences in litter quality [*Butterbach-Bahl et al.*, 1997].

Another possible cause for the difference could be the influence of the leaves on the penetration of direct sunlight, thereby increasing soil temperature in the coniferous forest compared to deciduous forest, or the difference in throughfall amount and composition on soil processes. In a beech forest, most of the nutrients reach the soil through stem flow, making inorganic nitrogen compounds available for NO flux processes mainly directly around the stem [*Thimonier*, 1998]. Also, coniferous forest has been found to take up more atmospheric nitrogen than a beech forest [*Schaeffer*, 1990], this would result in a higher inorganic nitrogen concentrations in soil, and therefore in a higher NO flux from soil under coniferous forest compared to beech. In a study concerning soil gas transport, *Ball et al.* [1997] found an impact of the structure of the leaf litter layer on the gas diffusion from soil. The laminar structure of a bed of deciduous leaves, compared to that formed by coniferous needles induces a barrier to gaseous diffusion. This is in line with our findings, where a smaller NO flux from soil within a deciduous plantation compared to coniferous forest was observed. The very large difference observed during our experiments in the emission rates from the two forest types indicates that the forest community is of major importance to the NO flux from soil.

Table 6.2 shows the average NO fluxes from two different soil textures. The NO emission rates from sandy soil were higher than the NO emission rates from clayey soil, on average differences of approximately 20 ng m^{-2} s^{-1} were observed. The total pore volume of a fine textured soil (clay) is somewhat larger, but the pores itself are smaller than those of the coarse textured sandy soils [*Hillel*, 1980]. It is suggested that –under similar field conditions- molecular diffusion was slower through the smaller pores in the clayey soil, and that the microbiologically produced NO gases were consumed in various reactions [*van Cleemput and Samater*, 1996]. *Butterbach-Bahl et al.* [1997] and *Papen et al*. [1993] reported a reduction in the NO flux from a spruce forest floor when liming the soil (de-acidification). This is in line with our findings of smaller NO fluxes from the less acidic clayey soils at Hollandse Hout, when compared to the high fluxes observed at the acidic sandy soils at Speuld. Under the acidic conditions (pH<5.5) and high levels of organic matter at Speuld, nitrite (NO_2^-) can spontaneously decompose to form NO and NO_2 [*Nelson*, 1982]. This chemical denitrification has been shown to contribute considerably to the NO flux [*van Cleemput and Samater*, 1996]. Whether differences in soil texture alone or additional soil characteristics, such as soil pH, are responsible for the larger NO flux from sandy soil remains unresolved.

6.4 Concluding remarks

From our study it can be concluded that the environmental factors controlling emissions of NO from soil are soil temperature and water content. Our studies showed that the NO flux from soil is positively correlated to soil temperature, a rise of 10 degrees in the temperature doubling the microbial production rate of the trace gas. Maximum emission rates from soil observed at an intermediate range of soil moisture contents, where conditions stimulating both microbial production and molecular diffusion are optimal. Our results show maximum NO emissions from soil at a soil water content ranging from 30 to 45% dry weight, or from 55% to 85% WFPS respectively.

Across the landscape, differences in soil texture and forest community type are probably the most important parameters. Differences in the NO flux between sandy and clayey soils can be very large. The forest type most likely introduces differences in the microbial community and in the leaf litter covering the forest floor, hence strongly influences both NO production and gas diffusion from soil. Also, differences in stem flow and throughfall of different forest species determine the soil nutrient content. The emissions observed in our studies in the Netherlands were very large. It has been suggested that these large fluxes are linked to the large input of nitrogen from the atmosphere in these regions. An artificially increased nitrogen input from the atmosphere, however, did not increase the NO emission. This phenomenon is probably linked to the soil already being saturated with nitrogen.

On the basis of our study and literate information we conclude that when estimating the NO flux from natural environments on regional scale it is important to take into account differences in forest type, soil texture and perhaps even nitrogen input from the atmosphere. These quantities are likely to differ on a regional scale and are found to have a major influence on the magnitude of the NO flux from soil.

6.5 Acknowledgements

The financial support for our study provided by the Commission of the European Communities (DGXII) is kindly acknowledged. The authors would also like to thank the Faculty of Earth Sciences in Utrecht for permission to use the laboratory for chemical analysis of the soil samples. Discussions with Dr. Simon Vriend (University of Utrecht) and Dr. Albert Tietema (University of Amsterdam) were greatly appreciated. We thank the Boswachterij Flevoland and RIVM for their permission to carry out fieldwork on their properties. The help of Hilbrand Weststrate in the experimental work is kindly acknowledged. The anonymous reviewers are thanked for thorough reviews and useful suggestions.

CHAPTER 7

CONCLUSIONS, OUTLOOK AND RECOMMENDATIONS

7.1 Conclusions

Removal of trace gases from the atmosphere takes place mostly through oxidation processes that involve reactions with hydroxyl radicals (OH) and ozone (O_3). Because of favourable conditions for the formation of OH radicals in the tropics, about 70% of the oxidation of gases occurs in the tropical troposphere. Nitrogen oxides strongly influence the oxidative capacity of the atmosphere, especially by the catalytic behaviour of nitric oxide (NO) in the photochemical formation of O_3. Special notice has been given to the Amazon in South America. This tropical ecosystem, which covers a vast area of 7 million km^2 and contains almost half of the world's undisturbed tropical evergreen forest, is facing rapid deforestation and cultivation. As a result of changes in the physical and chemical soil properties (such as nutrient turnover rates, nutrient pools, and bulk density), major changes in the biogenic emissions of NO from soils can be expected and hence the budgets of trace gases in the troposphere may be altered.

In this study, biogenic NO emissions from soils were quantified from laboratory results of NO production and consumption in soil samples, and the in-situ measured NO diffusion through soil. Earlier studies have already shown good agreement between laboratory derived NO emissions, and NO emissions that were measured in the field [*Galbally and Johansson*, 1989*; Remde et al.*, 1993; *Rudolph et al.*, 1996b]. In more recent studies, a standard NO flux was derived from laboratory experiments at reference conditions (soil temperature and soil moisture), and multiplied by the relations of net NO emissions with soil temperature and soil moisture [*Yang and Meixner*, 1997; *Otter et al.*, 1999]. These studies also showed good agreement (10–80%) between the two methods. However, net NO emissions generally are the result of simultaneous production and consumption of NO in soil, which depend differently on their controlling parameters (see section 1.4). Therefore, in the present study, the original algorithm by *Galbally and Johansson* [1989] was modified to include the individual relations of NO production and consumption with respect to soil temperature and soil moisture. Finally, using the modified algorithm, NO emissions were quantified for a primary forest soil and a 22 year old pasture, over a period of 4 weeks.

The laboratory derived NO emissions agreed well with the NO emissions from field measurements with dynamic chambers (see section 3.4). In some cases there were significant discrepancies between the two methods. However, considering the average NO emissions over the full measurement periods, good agreement (5–40%) was observed for both of the two very different ecosystems (see section 3.3.4.2). The difference in the NO emissions between the forest and the pasture soil was approximately one order of magnitude.

Considering the large variety of ecosystems, NO emissions may even vary over 4 orders of magnitude [*Davidson and Klingerlee*, 1997]. This indicates the potential of these laboratory studies to determine NO emissions from various ecosystems on a cost-effective basis, compared to the more expensive field studies. In addition, these laboratory studies offer the possibility to examine the individual processes of NO production and consumption under controlled conditions with respect to their controlling parameters (e.g. soil temperature, soil moisture, soil acidity and nutrient content). This is done in order to study the effects of these controlling parameters on the NO production and consumption in detail, and find explanations for the differences in the NO emissions between ecosystems, and for the temporal differences within one ecosystem.

Our observations showed that NO production in soils from old pastures was much smaller than in soils from primary forests (see sections 2.3.1 and 3.3.1). Rates of NO consumption were similar in both soils, indicating that the conversion from forest to pasture did not alter the consumption processes significantly (see sections 2.3.2 and 3.3.2). Differences in the NO production may reflect differences in the nutrient contents of the forest and pasture soils. Whereas the total inorganic nitrogen concentrations (sum of NO_3^- and NH_4^+) were approximately equal in the pasture and forest soils, the relative proportions of the inorganic nitrogen species were different (see section 2.2.1). Forest soil contained higher concentrations of nitrate and lower concentrations of ammonium than pasture soil, which could explain the differences in NO production (see section 2.3.3).

It is still not clear in the literature under what circumstances NO_3^- and/or NH_4^+ are consumed as substrates for the production of NO. It is generally thought that NO is produced under anaerobic conditions by the reduction of NO_3^- (denitrification), and under aerobic conditions by the oxidation of NH_4^+ and organic N (nitrification) [see *Conrad*, 1996a]. We studied the response of NO production to the addition of solutions of KNO_3 and NH_4Cl in relatively wet soils from forest and pastures. NO production increased after adding exogenous NO_3^-, and not after NH_4^+ (see section 2.3.3). This indicated the potential for NO production through the consumption of NO_3^- (denitrification, nitrate-respiration or DNRA). However, it is not said that this is the dominant microbial process responsible for NO production in these soils. In fact, the relative proportions of the inorganic nitrogen concentrations might even suggest otherwise. The high concentrations of NO_3^- in forest soil suggest a rapid turnover of nutrients from NH_4^+ to NO_3^-, whereas low NO_3^- concentrations in pasture soil suggest a slow cycling of nutrients [e.g. *Davidson et al.*, 2000]. Higher NO production in forest soil could thus arise from rapid nitrification in the microbially active forest soil compared to the more conservative pasture.

Furthermore, chemical reactions (chemodenitrification) may have contributed to the production of NO, as is suggested by the observed positive correlation of NO production with soil acidity (see section 3.3.1.1). In the acid, organic rich soils of the primary forests, NO_2^- and HNO_2 become chemically unstable and decompose to produce NO [*Blackmer and Cerrato*, 1986; *Serca et al.*, 1994]. Chemodenitrification would be less important in the pasture soils, where pH values are closer to neutral. Thus, chemodenitrification could explain the higher NO production in forest soils compared to pastures. However, it must be stated that high soil acidity and high NO production was exclusively found in forest soils, whereas more neutral soil pH and low NO production were restricted to pastures. Perhaps other soil processes and/or parameters that so far have not been identified could explain the differences in NO production as well as the differences in soil pH between the forest and pasture soils.

Another soil parameter that is generally strongly influenced by the conversion from forest to pasture is the soil bulk density. Our observations showed that the soil bulk density of a 22 year old pasture (1.56 g/cm^3) was much higher than the primary forest soil (1.33 g/cm^3). Both soils consisted of similar soil texture (loamy sand). Therefore, the increase in the soil bulk density suggests the effect of soil compaction by cattle and machines on pastures. Soil compaction decreases the total pore volume, and hence decreases the gas diffusion in soil. Differences in the soil structure, or in the pore size distributions, between the forest and pasture soils also suggested a diminished gas diffusion in pasture soils. Gas diffusion takes place mostly through the relatively large pores [*Currie*, 1983], and particularly the fraction of larger pores was reduced in pastures compared to forest soils (see section 3.3.3). Indeed, field measurements confirmed that the gas diffusion was approximately 23% less effective in pasture than in forest soil [*Kirkman et al.*, submitted]. However, the reduction in the biogenic NO emissions from pasture soil compared to forest soil was mostly due to a reduction in the NO production. Production of NO was approximately 10 times smaller in pasture soil, whereas the diffusion of NO through the soil was 23% less effective in pasture soil compared to forest soil. The combination of these two factors resulted in approximately 11 times smaller NO emissions from the 22 year old pasture compared to primary forest soil (see section 3.4).

In order to be able to predict NO emissions from soils over large regions, it is important to develop a better understanding of the controlling behaviour of the moisture content on these biogenic emissions. Some uncertainties exist concerning the optimum moisture conditions under which maximum NO is emitted from the soil. Our results showed that soils with different soil textures have widely varying optimum moisture conditions, ranging from 0.04 to 0.38 g/g (0.11 to 0.64 water-filled pore space). Moreover, optimum soil moisture correlated with the clay content of the soil samples. Strong correlation between optimum soil moisture and clay content was observed for all moisture units that were compared (gravimetric water content, volumetric water content and water-filled pore space). Of these three moisture units, gravimetric water content appeared the best parameter to compare optimum soil moisture conditions amongst soils of a given soil texture (see section 4.4.1).

The observed correlation between optimum soil moisture and clay content can be explained by differences in the soil structure of the soil samples. Clay soils generally have larger total pore volumes compared to sandy soils. This indicates that clay soils can contain more water than sandy soils. Furthermore, clay soils generally have relatively small pores, whereas sandy soils consist mainly of relatively large pores. Because of these differences in the pore sizes, clay soils generally have stronger water retention properties than sandy soils and therefore retain more water under identical circumstances. This was confirmed by laboratory measurements on the Brazilian soil samples. A simple water retention table was used to determine the moisture content of the soil samples for a range of given matric potentials. At identical matric potential, it was observed that soil samples with a higher clay content retained more water than sandy soils (see section 4.4.2). The results from these experiments were compared to the observed optimum soil moistures for the different soil textures.

For all soil textures, maximum NO emissions were found at identical matric potential. At this particular matric potential, water had drained from the relatively large pores, whereas the small pores were still water-filled. It was suggested that NO is produced in the small water-filled pores, while the diffusion of NO from the soil to the atmosphere occurs mainly through the relatively large open pores in the soil. This explains that all soil textures demonstrated maximum NO emissions at identical matric potential, where the large pores were open for diffusion. Because of the aforementioned differences in the soil structure, soils with different clay contents had largely varying soil moistures at this particular matric potential. Clay soils, with relatively small pores, retained more water, and consequently had a higher moisture content than sandy soils. Hence, the observed correlation between optimum soil moisture and clay content of the soil samples. By accounting for these differences in the soil structure (pore size), optimum soil moistures could be described independent of soil texture (clay content).

Finally, our findings could be used to simplify the prediction of NO emissions from soils with different textures within the Amazon. As was mentioned above, maximum NO emissions were observed when only the relatively large pores had drained. Pedotransfer functions exist for a range of soil textures, that describe their corresponding water retention characteristics. Using the pedotransfer function for a given soil texture, the soil moisture content can be determined at which the relatively large pores are open for diffusion. For a wide range of soils within the Amazon with largely varying soil textures, these pedo-transfer functions have already been measured [*Tomasella and Hodnett*, 1998]. Together with our findings, these could be used to predict the soil moistures at which maximum NO is emitted from soils with different soil textures.

It should be noted that our results can only be used to find the optimum moisture conditions at which maximum NO emissions are found for the different soil textures. The magnitude of the NO emissions will be different for each of the individual soils, and still depends on the controlling parameters, such as microbial activity, substrate availability, soil acidity, soil moisture and soil temperature. In order to be able to predict the magnitude of the NO emissions for the individual soils, we propose that the observed positive correlation between the NO production and soil acidity could be used, to indicate high NO emissions from soils with high soil acidity and low NO emissions from soils with neutral pH-values.

7.2 Outlook

At a first glance, our findings of lower biogenic emissions of NO from pastures than from forest soils seem to imply a potential reduction in the photochemical formation of ozone. However, several other indirect effects of the conversion from forest to pasture on the tropospheric NO budget should be taken into consideration.

- Although the forest soils demonstrated the highest emissions of NO, not all of the NO that is emitted from the forest floor escapes the canopy to the atmosphere. Within the canopy, NO is rapidly converted (by O_3) to nitrogen dioxide (NO_2), which can be deposited on the soil and on leaf surfaces [*Kaplan et al.*, 1988]. This greatly reduces the flux of NO into the atmosphere. *Ammann et al.* [1999] and *Rummel et al.* [submitted] quantified the net NO flux that escapes the forest canopy into the atmosphere. Figure 7.1 a and b present two situations within the forest canopy, during the day and the night respectively.

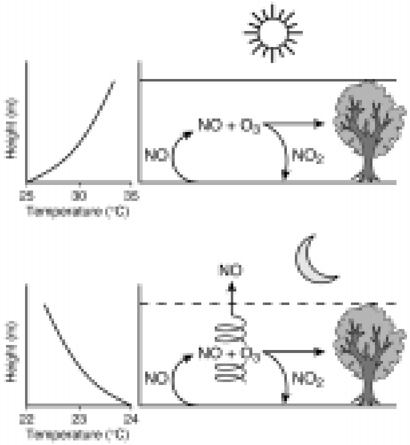


Figure 7.1 Temperature profile and schematic of the in-canopy situation during day (a) and night (b).

During daytime (Figure 7.1 a), warm air in the top of the canopy and colder temperatures in the shadow of the canopy near the soil provide stable conditions. During these stable conditions, almost all NO can react with O_3 (entrained from above the canopy) to form NO_2, which in turn is partly deposited on the soil and on leaf surfaces within the canopy. Consequently, during daytime, less than 10% of the soil emitted NO escapes the forest canopy into the atmosphere [*Rummel et al.*, submitted]. At night however (Figure 7.1 b), the temperature profile within the forest canopy is reversed, since the air in the top of the canopy experiences strong radiative cooling. Mixing of the colder air from above, with warm air near the surface maintains the turbulence within the canopy [*Fitzjarrald and Moore*, 1990]. This causes some of the NO to be swept out of the canopy into the atmosphere. Due to the large differences during day and night, it is not easy to define how much in total of the NO soil emissions reaches the atmosphere. It has been concluded that the net NO flux from the forest system out of the canopy to the atmosphere is small compared to the NO emission from the forest soil [*Ammann et al.*, 1999; *Jacob and Wosfy*, 1990; *Rummel et al*., submitted]. However, which fraction of the NO_2, that is formed within the canopy by the reaction of NO with O_3, is re-deposited onto soil and leaf surfaces and how much escapes the canopy into the atmosphere is still largely unknown [*Lerdau et al.*, 2000].

While only a small fraction of the NO that is emitted from the forest soil escapes the forest canopy, NO that is emitted from pasture soil directly enters the troposphere. The reduction of the NO flux out of the canopy by reaction with O_3 and deposition of NO_2 within the forest canopy should be taken into account when comparing biogenic emissions of NO from forest and pasture soils.

- Although old pastures generally emit less NO than forest soils, recently burned pastures have shown enhanced NO emissions for a period of 1–5 years [*Keller et al.*, 1993; *Neff et al.*, 1995]. This has been explained by enhanced availability of nutrients directly after slash and burn of the forest. Besides increasing the nutrient stocks in soil, the ashes introduce high concentrations of basic cations that raise the pH in soil, which further enhances the availability of nutrients, and consequently stimulates the productivity [*Jordan*, 1989]. Increased microbial activity, related to the higher availability of nutrients, enhances the NO emissions from recently burned pasture soils.

- The combustion of forest biomass during the conversion from forest to pasture results in large pyrogenic emissions of NO and hydrocarbons. Recently, *Andreae and Merlet* [submitted] presented a review on the emission factors (g species kg^{-1} dry matter burned) for a large variety of compounds that are emitted during the combustion of several different biomass sources. The authors estimated that approximately 1.6 $\pm$ 0.7 grams of NO_x (mostly as NO) are released per kilogram of dry matter during the combustion of tropical forest, resulting in approximately 1.0 Tg N year^{-1} for this source alone on a global scale. For comparison, on a global scale, soil emissions of NO are estimated to contribute approximately 4.76 or 5.5 Tg N year^{-1} (see Table 1.1). It should also be mentioned that NO emissions from soil occur continuously throughout the year, whereas pyrogenic NO emissions from biomass burning are mostly restricted to the dry season. Thus, the individual contributions of these sources to the NO_x budget vary over the year, and pyrogenically emitted NO may be a very strong source compared to the biogenic NO emissions in the dry (burning) season.

- Each year, an area of about 75,000 km^2 is burned within the Brazilian Amazon [*Nepstad,* 1999a]. About 25% of this area was primary forest that has been actively deforested. About 75% of the total burned area had already been deforested previously, or was primary forest that burned accidently due to increased susceptibility to drought and escaping fires from other locations. Selective logging of primary forest, damages the forest and increases its susceptibility to fires in times of drought, which can lead to accidental deforestation of primary forest [*Nepstad et al*., 1999b]. After the initial burn to clear the forest, the land is used for shifting-cultivation agricultural practises and cattle pastures. These land uses generally require additional burns, in order to clear the invaded pastures and enhance soil productivity. This indicates that after the initial combustion of primary forest, the pastures remain a source of pyrogenically emitted NO. The emission factors of NO_x from the combustion of grassland are even larger than those from the combustion of tropical forest, 3.9 $\underline{+}$ 2.4 and 1.6 $\underline{+}$ 0.7 grams of NO_x kg^{-1} dry matter burned respectively [*Andreae and Merlet,* submitted]. These pyrogenic emissions (initial and additional burns) are a major source for the global budget of NO_x in the troposphere, contributing approximately 6.0 or 7.0 Tg N year^{-1} (see Table 1.1).

- Further agricultural activities on the deforested land demand the application of fertilizers, since crop productivity decreases sharply over the course of cultivation after forest conversion. The following information is from *Jordan* [1989]. After an initial increase in the nutrients and pH by the input of ashes into the soil, nutrient stocks decline gently, and available phosphorus declines rapidly as a result of acidification of the soil. About 3 years after conversion of the forest, the organic matter from the original forest biomass has disappeared, and nutrients are no longer replenished in soil. Crop productivity therefore depends strongly on the application of fertilizer to the soil. It is well known that soil NO emissions increase after the addition of N-fertilizer [e.g. *Bouwman*, 1998]. In the tropics this effect is even larger than in the temperate zone. Due to warmer conditions, a higher percentage of the applied nitrogen fertilizer is emitted as NO [*Veldkamp and Keller*, 1997a; 1997b].

- Finally, the conversion from primary forest to pasture can be expected to introduce anthropogenic emissions of reactive nitrogen (NO and NH_3). Table 7.1 presents the global NH_3 emission estimates. It can be seen that biomass burning and agriculture (animals, crops, and fertilizer application) are important sources of NH_3.

Table 7.1 Total global NH_3 emission estimates (reproduced from *Mosier* [2001]).

Source	NH_3-N Emission (Tg N year^{-1})	
	Estimate	Uncertainty of estimate
Excreta from domestic animals	**21.6**	**10–30**
Excreta of wild animals	0.1	0–1
Synthetic fertilizers	**9.0**	**4.5–13.5**
Biomass burning	**5.9**	**3–7**
Soils under natural vegetation	2.4	0–10
Oceans	8.2	3–16
Fossil fuel combustion	0.1	0–0.2
Industrial processes	0.2	0.1–0.3
Human excreta & pets	2.6	1.3–3.9
Crops & crop decomposition	**3.6**	**1.4–5.0**
Total Emission	54	40–70

Considering the planned developments within the Amazon it is suggested that future emissions from biomass burning and intensification of agriculture, related to a larger deforested area, in the Amazon lead to higher concentrations of NO and NH_3 in the troposphere (see section 1.5). At the moment it is impossible to estimate to what extend these emissions will become important in the Amazon. However, it is known that, on the Northern Hemisphere, anthropogenic emissions of these reactive nitrogen species have driven an increase in the N-deposition from the atmosphere to the soil (see section 1.5). If the natural surroundings of the Amazon also face increased N-input to the soils, due to increasing emissions of NO and NH_3 from biomass burning and intensification of agriculture, this could increase the biogenic emissions of NO from soils.

Our observations from field studies in the United Kingdom around poultry farms showed higher NO emissions closer to the farm, where higher NH_3 concentrations lead to higher N-input to the soil (see Chapter 5). Furthermore, results from acid-mist experiments on two deciduous forest ecosystems also confirmed that NO emissions increased with extra N-input onto the soil (see section 5.3). In addition, NO emissions were measured from forest soils in a research area in the Netherlands, which received the highest atmospheric N-deposition rates amongst Europe (see Chapter 6). The extremely high N-input from the atmosphere resulted in extremely high NO emissions from the Dutch forest soils. Furthermore, it was observed that application of additional inorganic nitrogen on top of the very large N-input from atmospheric deposition in the Dutch forest did not significantly enhance the NO emissions from the soil (see section 6.3.3). The forest ecosystem had already reached the state of N-saturation, where the availability of inorganic nitrogen in soil exceeds the demand by plants and microbes [*Koopmans*, 1996]. This indicates that there may be a natural limit to the increasing biogenic emissions of NO from soil, and an endless continuous increase of the NO emissions with N-deposition is not to be expected.

However, the results of these field studies indicate a strong dependency of the biogenic NO emissions from soils on the N-input from atmospheric deposition. If the N-input to the soils in the Amazon increases, due to enhanced N-deposition from the atmosphere as a result of higher anthropogenic emissions of reactive nitrogen species, it can be expected that this will enhance the biogenic emissions of NO from the soils in the Amazon.

Especially in the natural surroundings of the Amazon, the consequences of more NO would be very large on the local chemistry of the troposphere. As was outlined in the Introduction (section 1.1), in the presence of sunlight and the oxidation products of hydrocarbons, nitrogen oxides lead to the very rapid formation of ozone [*Graedel and Crutzen*, 1993]. The forest ecosystems in the Amazon provide a major biogenic source of reactive hydrocarbons, thus the concentrations of such compounds (e.g. isoprene) in the local troposphere are generally high [*Jacob and Wofsy*, 1988; *Kesselmeier et al.*, 2000].

Concentrations of nitrogen oxides, however, are generally low, since a large part of the biogenically emitted NO from the forest soils is re-deposited within the forest canopy [*Ammann et al.*, 1999; *Jacob and Wofsy*, 1988; *Rummel et al.*, submitted]. Thus, the photochemical formation of ozone is very sensitive to NO_x concentration in the atmosphere, and consequently depends strongly on the source strength of nitrogen oxides. The addition of extra NO_x, in the presence of high concentrations of reactive hydrocarbons and strong sunlight intensity, will rapidly produce ozone. This is demonstrated in Figure 7.2, which presents the ozone production rates as a function of the mixing ratios of the reactive hydrocarbons and NO_x.

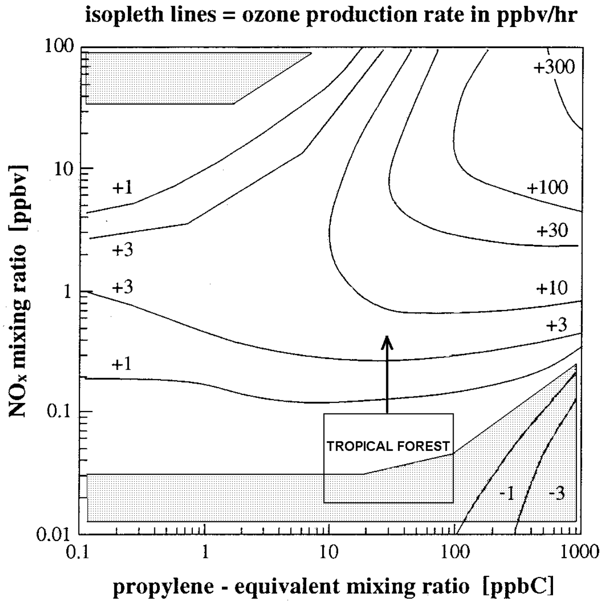


Figure 7.2. Ozone production rate as a function of propylene-equivalent and NO_x mixing ratios (reproduced from *Chameides et al.*, [1992]). Each hydrocarbon has a defined propylene-equivalent, based on its relative reactivity compared to the reactivity of propylene. If some hydrocarbon species has an atmospheric concentration of 10 ppb and is twice as reactive, its propylene-equivalent would be 20 ppb.

Indicated are the ranges of mixing ratios (box) that were encountered in the tropical forest in the Amazon during the wet season. This range can be considered as a natural situation without the influences of biomass burning, and is characterized by almost no O_3 production, or even O_3 destruction (grey area). In this area of the graph, the ozone production rate strongly increases with the NO_x mixing ratio. This indicates the sensitivity of the ozone production rate on the NO_x concentration in the tropical forest ecosystems within the Amazon.

Combustion of forest biomass, related to the ongoing economical developments in the Amazon, will lead to large pyrogenic emissions of hydrocarbons and NO_x, and consequently to higher NO_x concentrations in the troposphere. Considering the sensitivity of the ozone production rates on the concentration of nitrogen oxides, this has the potential to greatly enhance the local tropospheric ozone concentrations, which in turn can affect human health and the quality of the forest ecosystems within the Amazon [*Mckee*, 1994; *Skarby and Sellden*, 1984].

7.3 Recommendations

For a more profound understanding of the conditions under which NO is produced in soil, and to be able to predict the magnitude of NO emissions from soils, it is necessary to continue to examine the production and consumption of NO in detail, especially with respect to the corresponding controlling factors nutrient content and soil acidity.

As was discussed in section 2.3.3, differences in the inorganic nitrogen concentrations between forest and pasture could reflect differences in the production of NO in these soils. The generally accepted explanation is that rapid cycling of nutrients in forest soils causes the higher NO_3^- and lower NH_4^+ concentrations in forest soils compared to pastures [e.g. *Davidson*, 2000]. According to this hypothesis, the high emissions of NO from forest soils are a product of rapid nitrification under aerobic conditions. Denitrification is thought to occur only under anaerobic conditions and, therefore, is not considered to be an important process that produces NO in aerated (aerobic) soil.

In contrast to this explanation however, we would like to propose that it is still possible that NO is produced in soil by consumption of NO_3^- (denitrification). Many (heterotrophic) nitrifying bacteria have been found that are able to denitrify, even under aerobic conditions [*Conrad*, 1996a]. Also, *Goedde* [1999] found that denitrifying bacteria are better adapted to higher soil temperatures (25–35°C) than nitrifying bacteria. Several studies have presented nutrient-addition experiments on tropical soils that showed increasing production of NO after additions of NO_3^-, and no response of the NO production after additions of NH_4^+ [*Cardenas et al.*, 1993; *Bakwin et al.*, 1990; *van Dijk and Meixner*, submitted-a]. These results indicate the potential of NO_3^- consumption in the corresponding tropical soils, and may even suggest the absence of autotrophic nitrifying bacteria. Of course, these nutrient-addition experiments give no information about the presence or absence of heterotrophic nitrifying bacteria. Thus, it is still possible that NO was indeed produced through (heterotrophic) nitrification.

On the other hand, it still cannot be excluded that NO is produced through the consumption of NO_3^-. In which case the higher concentrations of NO_3^- in forest soils compared to pastures would explain the higher production of NO in forest soils. High concentrations of NO_3^- and rapid consumption of NO_3^- can co-exist in soil, as long as the supply of NO_3^- is equal to (or exceeds) the consumption of NO_3^-. Indeed, nitrification rates are generally high in forest soils, which supplies the soil with NO_3^- at a high rate [*Reiners et al.*, 1994; *Piccolo et al.*, 1994; *Neill et al.*, 1997a; *Neill et al.*, 1999; *Veldkamp et al.*, 1999; *Verchot et al.*, 1999].

From the nutrient experiments and turnover rates only, its seems impossible to determine whether NO is produced through the oxidation of NH_4^+ (and/or organic nitrogen) or the reduction of NO_3^-. Microbial inhibition experiments and nutrient-addition experiments with isotopically labelled nitrogen compounds, together with detailed information about the nutrient cycling rates, could bring more insight in the processes that are responsible for the biogenic emissions of NO from soils, under aerobic and anaerobic conditions.

A second issue that needs further attention arises from the differences that were observed in the optimum moisture conditions for the Brazilian and Dutch soils, and leads to the question of whether there are global differences in the optimum soil moistures for NO emissions that are induced by different climate zones.

In this study, we presented results on the optimum soil moistures for NO emission from tropical soils in a region with high soil temperatures and large seasonal differences in the annual precipitation. These results showed that the optimum soil moisture conditions for NO emissions correlated positively with the clay content of the soils (see section 4.4.1). Furthermore, in section 6.3.2, we presented NO emissions from a loamy sand soil in a Douglas fir forest in the Netherlands, which were maximum at a soil moisture content ranging from 0.30 to 0.45 g/g (or 55 to 85% water-filled pore space). Assuming a clay content for the Dutch loamy sand soil of approximately 10 %, these latter results do not agree with the observed correlation of optimum soil moisture with clay content of the Brazilian soil samples (section 4.4.1). According to this correlation, the loamy sand soil in the Dutch forest should have shown maximum NO emissions at a soil moisture around 0.10 g/g. Three explanations can be considered.

Firstly, perhaps field measurements were not successful in determining the optimum soil moisture. Earlier research on soils in the Dutch forest demonstrated that soil moisture ranged from approximately 0.2 to 2.0 g/g between 1992 and 1993 [*Koopmans*, 1996]. It is suggested that the Dutch loamy sand soil never became dry enough to reach the optimum soil moisture that is predicted by the correlation with clay content, namely 0.10 g/g (section 4.4.1). Instead, maximum emissions were observed at a higher soil moisture (0.30–0.45 g/g). This is one probable explanation. However, field measurements were taken over a year, with soil moisture ranging from 0.22 to 0.74 g/g, and showed highest NO emissions around 0.30–0.45 g/g. Laboratory studies on soil samples could confirm whether the optimum moisture conditions for NO emissions from the Dutch loamy sand soils are, as was observed in the field, at a soil moisture of about 0.30–0.45 g/g. If so, there indeed are major differences between the optimum soil moistures for which maximum NO emissions are observed from Dutch and Brazilian soils.

Secondly, as was mentioned above, the Brazilian soils demonstrated maximum NO emissions at a whole range of soil moistures, depending on the clay content. However, all Brazilian soil samples showed maximum NO emissions at a particular matric potential, where the larger pores were open for diffusion (matric potential ≈ –10 kPa, see section 4.4.3). It would be interesting to measure the water retention characteristics of samples from the Dutch loamy sand soils. Perhaps these Dutch loamy sand soils have much stronger water retention properties than the Brazilian loamy sand soils, due to different soil structures. Indeed, the Dutch loamy sand soil showed very wet conditions throughout the year, ranging from 0.2 to 2.0 g/g between 1992 and 1993, which could suggest that the soils have very strong water retention properties. Possibly, at a matric potential close to –10 kPa, the Dutch loamy sand soil have a soil moisture of approximately 0.30–0.45 g/g. This would indicate that the optimum moisture conditions are identical for the Dutch soil as well as for the Brazilian soils. If so, it is suggested that the gas diffusion through the soil, leading to maximum NO emissions when the relatively large pores are open, largely determines the optimum conditions for NO emissions from soil.

Thirdly, however, the proposed measurements could also demonstrate that the NO emissions from the Dutch loamy sand soils are maximum at completely different moisture conditions than expected from results of the Brazilian soil samples. Perhaps, milder temperatures and more uniformly distributed precipitation in the temperate region compared to the tropics give rise to different microbial cultures that produce NO under different conditions to those encountered in the tropical region. As was mentioned before, denitrifying bacteria are better adapted to higher soil temperatures (25–35°C), whereas nitrifying bacteria prevail at lower soil temperatures (15–25°C) [*Gödde*, 1999]. This implies that there may be regional differences, related to different climate zones, in the optimum moisture conditions for the NO production in soils, and NO emission from soils. So far, it remains unclear whether differences in the climate zones result in differences in microbial cultures and hence in other optimum moisture conditions, whether tropical and temperate ecosystems have identical optimum moisture conditions for NO emission from soil.

Bibliography

Ammann, C., A. Gut, U. Rummel, F. Meixner, S.T. de Oliva, T.M. Tavares, and M.O. Andreae, Primary emission and canopy exchange of nitrogen oxides in an Amazonian rain forest, *EOS Transactions, AGU*, *80* (46), F419, 1999.

Anderson, I.C., and M.A. Poth, Semiannual losses of nitrogen as NO and N_2O from unburned and burned chaparral, *Global Biogeochemical Cycles*, *3* (3), 121-135, 1989.

Andreae, M.O., E. Atlas, H. Cachier, I. Cofer, W. R., G.W. Harris, G. Helas, R. Koppmann, J.-P. Lacaux, and D.E. Ward, Trace gas and aerosol emissions from savanna fires, in *Biomass Burning and Global Change*, edited by J.S. Levine, pp. 278-295, MIT Press, Cambridge, Mass., 1996.

Andreae, M.O., P.J. Crutzen, J. Lelieveld, J. Grace, P. Kabat, R. Valentini, A.D. Culf, and F.X. Meixner, European studies on trace gases and atmospheric chemistry as a contribution to the large scale biosphere-atmosphere experiment in Amazonia (EUSTACH-LBA), in *European Climate Science Conference, October 19-23, 1998, Vienna City Hall, Vienna (Austria)*, edited by A. Gazhi, and I. Troen, European Commission, Research DG, Biodiversity and Global Change Unit DI/1, Rue de la Loi 200, B-1049 Brussels, Belgium, CD-Rom, article no. 86, 2000.

Andreae, M.O., S.S. de Almeida, P. Artaxo, C. Brandao, F.E: Carswell, P. Ciccioli, A. Culf, J.L. Estevez, J. Gash, J. Grace, P. Kabat, J. Lelieveld, Y. Malhi, A.O. Manzi, F.X. Meixner, A. Nobre, C. Nobre, M.A. de Lourdes Ruivo, M.A: Silvia-Dias, P. Stefani, R. Valentini, and M. Waterloo, Towards an understanding of the biogeochemical cycling of carbon, water, energy, trace gases, and aerosols in Amazonia: An overview of the LBA-EUSTACH experiments, *J. Geophys. Res.*, submitted, 2001.

Andreae, M.O., and P. Merlet, Emission of trace gases and aerosols from biomass burning, *Global Biogeochemical Cycles*, accepted, 2001.

Bakwin, P.S., S. Wofsy, S.M. Fan, M. Keller, S.E. Trumbore, and J.M. da Costa, Emission of nitric oxide (NO) from tropical forest soils and exchange of NO between the forest canopy and atmospheric boundary layers, *J. Geophys. Res.*, *95* (D10), 16,755-16,764, 1990.

Ball, B.C., t.l.W. Harris, and J.R. Burford, A laboratory method to measure gas diffusion and flow in soil and other porous materials, *Journal of Soil Science*, *32*, 323-333, 1981.

Ball, B.C., and R. Hunter, The determination of water release characteristics of soil cores at low suctions, *Geoderma*, *43*, 195-212, 1988.

Ball, B.C., K.E. Dobbie, J.P. Parker, and K.A. Smith, The influence of gas transport and porosity on methane oxidation in soils, *J. Geophys. Res.*, *102* (D19), 23,301-23,308, 1997.

Bartels, J.M., *Methods of Soil Analysis, Part 3. Chemical Methods*, pp. 1390, Soil Science Society of America, Madison, WI, 1996

Baumgärtner, M., and R. Conrad, Effects of soil variables and season on the production and consumption of nitric oxide in oxic soils, *Biol. Fert. Soils*, *14*, 166-174, 1992.

Baumgärtner, M., M. Koschorreck, and R. Conrad, Oxidative consumption of nitric oxide by heterotrophic bacteria in soil, *FEMS Microbiology Ecology*, *19*, 165-170, 1996.

Bender, M., and C. Conrad, Microbial oxidation of methane, ammonium and carbon monoxide, and turnover of nitrous oxide and nitric oxide in soils, *Biogeochemistry*, *27*, 97-112, 1994.

Blackmer, A.M., and M.E. Cerrato, Soil properties affecting formation of nitric oxide by chemical reactions of nitrite, *Soil Sci. Soc. Am. J.*, *50*, 1215-1218, 1986.

Bollman, A., and R. Conrad, Enhancement by acetylene of the decomposition of nitric oxide in soil, *Soil Biol. Biochem.*, *29* (7), 1057-1066, 1997.

Borken, W., and R. Brumme, Effects of prolonged soil drought on CH4 oxidation in a temperate spruce forest, *J. Geophys. Res.*, *105* (D6), 7079-7088, 2000.

Bouwman, A.F., Nitrogen oxides and tropical agriculture, *Nature*, 392, 866–867, 1998.

Bullock, P., A.C.D. Newman, and A.J. Thomasson, Porosity aspects of the regeneration of soil structure after compaction, *Soil&Tillage Research*, *5*, 325-341, 1985.

Butterbach-Bahl, K., R. Gasche, L. Breuer, and H. Papen, Fluxes of NO and N_2O from temperate forest soils: impact of forest type, N deposition and of liming on the NO and N_2O emissions, 48, 79-90, 1997.

Cardenas, L., A. Rondon, C. Johansson, and E. Sanhueza, Effects of soil moisture, temperature, and inorganic nitrogen on nitric oxide emissions from acidic tropical savannah soils, *J. Geophys. Res.*, *98* (D8), 14,783-14,790, 1993.

Chameides, W.L., F. Fehsenfeld, M.O. Rodgers, C. Cardelino, J. Martinez, D. Parrish, W. Lonnenman, D.R. Lawson, R.A. Rasmussen, P. Zimmerman, J. Greenberg, P. Middleton, and T. Wang, Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, 97 (D5), 6037–6055, 1992.

Clement, C.R., A simple and reliable tension table, *Journal of Soil Science*, *17* (1), 133-135, 1966.

Conrad, R., compensation concentration as critical variable for regulating the flux of trace gases between soil and atmosphere, *biogeochemistry*, *27*, 155-170, 1994.

Conrad, R., Metabolism of nitric oxide in soil and soil microorganisms and regulation of flux into the atmosphere, in *Microbiology of atmospheric trace gases: sources, sinks and global change processes*, edited by J.C. Murrell, and D.P. Kelly, Springer-Verlag, Berlin, 1996a.

Conrad, R., Soil microorganisms as controllers of Atmospheric trace gases (H_2, CO , CH_4, OCS, N_2O and NO), *Microbiological reviews*, 609-640, 1996b.

Conrad, R., Evaluation of data on the turnover of NO and N_2O by oxidative versus reductive microbial processes in different soils., *submitted to Phython*, 2000.

Crutzen, P.J., Atmospheric interactions-homogeneous gas phase reactions of C, N, and S compounds, in *The Major Biochemical Cycles and their Interactions*, edited by B. Bolin, and R.B. Cook, John Wiley, Chichester, 1983.

Crutzen, P.J., and P.H. Zimmermann, The changing photochemistry of the troposphere, *Tellus*, *43AB*, 136-151, 1991.

Csonka, L.N., Physiological and genetic responses of bacteria to osmotic stress, *Microbiol. Rev.*, *52*, 121-147, 1989.

Currie, J.A., Gas diffusion through soil crumbs: the effect of wetting and swelling, *Journal of Soil Science*, *34*, 217-232, 1983.

Currie, J.A., Gas diffusion through soil crumbs: the effects of compaction and wetting, *Journal of Soil Science*, *35*, 1-10, 1984.

Danielson, R.E., and P.L. Sutherland, Porosity, in *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*, edited by A. Klute, pp. 1188, Soil Science Society of America, Madison, WI, 1986.

Davidson, E.A., Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems, in *Microbial production and consumption of greenhouse gases: methane, nitrogen oxides and halomethanes*, edited by J.E. Rogers, and W.B. Whitman, American Society for Microbiology, Washington DC, 1991.

Davidson, E.A., Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil, in *The biogeochemistry of global change: radiatively active trace gases.*, edited by R.S. Oremland, pp. 369-386, Chapmann&Hall, New York, 1993.

Davidson, E.A., and W. Klingerlee, A global inventory of nitric oxide emissions from soils, *Nutrient Cycling in Agroecosystems*, *48*, 37-50, 1997.

Davidson, E.A., E. Belk, and R.D. Boone, Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest, *Global change biology*, *4*, 217-227, 1998.

Davidson, E.A., M. Keller, H.E. Erickson, L.V. Verchot, and E. Veldkamp, Testing a conceptual model of soil emissions of nitrous and nitric oxides, *Bioscience*, *50* (8), 667-680, 2000.

Dunfield, P.F., and R. Knowles, Nitrogen monoxide production and consumption in an organic soil, *Biology and fertility of soils*, *30*, 153-159, 1999.

Duyzer, J., Dry deposition of nitrogen compounds to seminatural ecosystems, Ph.D. thesis, Universiteit Utrecht, Utrecht, 1995.

Erisman, J.W., and G.P.J. Draaiers, Atmospheric deposition in relation to acidification and eutrophication, *Stud. Environ. Sci.*, *63*, 253-357, 1995.

Fehsenfeld, F.C., J. Calvert, R. Fall, P. Goldan, A.B. Guenther, C.N. Hewit, B. Lamb, S. Liu, M. Trainer, H. Westberg, and P. Zimmerman, Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Global Biogeochemical Cycles*, *6* (4), 389-430, 1992.

Filoso, S., M.R. Williams, and J.M. Melack, Composition and deposition of throughfall in a flooded fores archipelago (Negro River, Brazil), *Biogeochemistry*, *45*, 169-195, 1999.

Firestone, M.K., and E.A. Davidson, Microbiological bases of NO and N_2O production and consumption in soil, in *Exchange of trace gases between terrestrial ecosystems and the atmosphere*, edited by M.O. Andreae, and D.S. Schimel, pp. 7-21, John Wiley & Sons, New York, 1989.

Fitzjarrald, D.R., and K.E. Moore, Mechanisms of nocturnal exchange between the rainforest and the atmosphere, *J. Geophys. Res.*, *95* (D10), 16839-16850, 1990.

Focht, D.D., and W. Verstraete, Biochemical ecology of nitrification and denitrification, *Adv. Microbiol. Ecol.*, *1*, 135-214, 1977.

Galbally, I.E., Factors controlling NO_x emissions from soils, in *Exchange of trace gases between terrestrial ecosystems and the atmosphere*, edited by M.O. Andreae, and D.S. Schimel, pp. 189-207, John Wiley, New York, USA, 1989.

Galbally, I.E., and C. Johansson, A model relating laboratory measurements of rates of nitric oxide production and field measurements of nitric oxide emission from soils, *J. Geophys. Res.*, *94* (D5), 6473-6480, 1989.

Garcia-Montiel, D.C., P. Steudler, P.A. Mellilo, J.M. Neill, B. Piccolo, and C.C. Cerri, Patterns of NO, N_2O and CO_2 emissions from Brazilian forest and pastures following a simulated rain event, in *EOS Transactions*, pp. F42, American Geophysical Union, 1999.

Gödde, M., and R. Conrad, Simultaneous measurement of nitric oxide production and consumption in soil using a simple static incubation system and the effect of soil water content on the contribution of nitrification, in *Stickoxidumsetzung durch Nitrifikation und Denitrifikation in Boeden under dem Einfluss verschiedener Bodenvariablen, Edition Wissenschaft, Reihe Biologie*, edited by M. Gödde, pp. 114-131, Tectum Verlag, Marburg, Germany, 1999.

Gödde, M., Stickoxidumsetzung durch Nitrifikation und Denitrifikation in Boeden unter dem Einfluss verschiederner Bodenvariablen, Universitaet Marburg, Marburg, 1999.

Goulding, K.W.T., N.J. Bailey, N.J. Bradbury, P. Hargraeves, M. Howe, D.V. Murphy, P.R. Poulton, and T.W. Willison, Nitrogen deposition and its contribution to nitrogen cycling and associated processes, *New Phytologist*, *139* (1), 49-58, 1998.

Graedel, T.E., and P.J. Crutzen, *Atmospheric change: An earth system perspective*, 446 pp., W.H. Freeman and Company, New York, 1993.

Griffin, D.M., Water and microbial stress, in *Advances in microbial ecology*, edited by M. Alexander, Plenum Publ., New York, 1981.

Grimshaw, H.M., Analysis of soils, in *Chemical analysis of evological materials*, edited by S.E. Allen, pp. 7-45, Blackwell Scientific Publications, Oxford, 1989.

Grundmann, G.L., P. Renault, L. Rosso, and R. Bardin, Differential effects of soil water content and temperature on nitrification and aeration, *Soil Sci. Soc. Am. J.*, *59*, 1342-1349, 1995.

Gut, A., A. Blatter, M. Fahrni, B.E. Lehmann, A. Neftel, and T. Staffelbach, A new membrane tube technique (METT) for continuous gas measurements in soils, *Plant and Soil*, *198*, 79-88, 1998.

Gut, A., A. Neftel, R. Staffelbach, M. Riedo, and B.E. Lehmann, Nitric oxide flux from soil during the growing season of wheat by continuous measurements of the NO soil-atmosphere concentration gradient: a process study, *Plant and Soil*, *216*, 165-180, 1999.

Gut, A., S.M. van Dijk, M. Scheibe, U. Rummel, M. Welling, and F.X. Meixner, NO flux from an Amazonian rain forest soil: Continuous measurements of the flux and No soil compensation concentration, *J. Geophys. Res.*, submitted, 2001.

Heij, G.T., and T. Schneider, Acidification research in the Netherlands, in *Final report of the Dutch priority programme of acidification*, edited by RIVM, pp. 60-275, Elsevier, 1991.

Hillel, D., *Soil and Water: Physical Principles and Processes*, 288 pp., Academic Press., New York and London, 1971.

Hillel, D., *Introduction to soil physics*, Acad. Press, New York, 1982.

Holland, E.A., F.J. Dentener, B.H. Braswell, and J.M. Sulzman, Contemporary and pre-industrial global reactive nitrogen budgets, *Biogeochemistry*, *46*, 7-43, 1999.

Huebert, B.J., and C.H. Robert, The dry deposition of nitric acid to grass, *J. Geophys. Res.*, *90* (D1), 2085-2090, 1985.

INDITE, *Impacts of nitrogen deposition on terrestrial ecosystems*, 100 pp., UK Review Group, Department of the Environment, London, 1994.

IPCC (Intergovernmental Panel of Climate Change), *Greenhouse Gas Inventory Workbook. Revised 1996 IPCC guidelines for National Gas Inventories. Vol. 2*, IPCC, Bracknell, UK, 1997.

IPCC (Intergovernmental Panel on Climate Change), *WG III Assessment Report*, 2001.

Jacob, D.J., and S.J. Wofsy, Photochemistry of biogenic emissions over the Amazon forest, *J. Geophys. Res.*, *93*, 1477-1486, 1988.

Jacob, D.J., and S.C. Wofsy, Budgets of reactive nitrogen, hydrocarbons, and ozone over the Amazon forest during the wet season, *J. Geophys. Res.*, *95* (D10), 16737-16754, 1990.

Jin, Y., and W.A. Jury, Characterizing the dependence of gas diffusion coefficient on soil properties, *Soil. Sci. Soc. Am. J.*, *60,* 66-71, 1996.

Johansson, C., Field measurements of emission of nitric oxide from fertilised and unfertilised soils in Sweden, *J. Geophys. Res.*, 429-442, 1984.

Johansson, C., and L. Granat, Emission of nitric oxide from arable land, *Tellus*, *36B*, 25-37, 1984.

Johansson, C., and E. Sanhueza, Emission of NO from tropical savanna soils during raining season, *J. Geophys. Res.*, *93*, 14193-14198, 1988.

Jordan, C.F., *an Amazonian rain forest: the structure and function of nutrient stressed ecosystem and the impact of slash and burn agriculture*, United Nations Educational, Scientific and Cultural Organization and The Parthenon Publishing Group, Butler and Tanner Ltd., London, 1989

Jury, W.A., W.R. Gardner, and W.H. Gardner, *Soil Physics*, 328 pp., Wiley, New York, 1991.

Kaplan, W.A., S.C. Wofsy, M. Keller, and J.M. da Costa, Emission of NO and deposition of O3 in a tropical forest system, *J. Geophys. Res.*, *93* (D2), 1389-1395, 1988.

Keller, M., E. Veldkamp, A.M. Weitz, and W.A. Reiners, Effect of pasture age on soil trace-gas emissions from a deforested area of Costa Rica, *Nature*, *365*, 244-246, 1993.

Kesselmeier, J., U. Kuhn, A. Wolf, M.O. Andreae, P. Ciccioli, E. Brancaleoni, M. Frattoni, A. Guenther, J. Greenberg, P. de Castro Vasconcellos, T. de Oliva, T. Tavares, and P. Artaxo, Atmospheric Environment, *34*, 4063-4072, 2000.

Kirkman, G.A., A. Gut, C. Ammann, L.V. Gatti, M.A.L. Silva Dias, M.A.L. Moura, and F.X. Meixner, Surface exchange of nitrogen dioxide, nitric oxide and ozone at a cattle pasture in Rondonia, Brazil, *J. Geophys. Res.*, submitted, 2001.

Klute, A., *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*, pp. 1188, Soil Science Society of America, Madison, WI, 1986.

Koopmans, C.J., The impact of reduced nitrogen deposition on nitrogen cycling in Dutch forest ecosystems, Ph.D. thesis, Universiteit van Amsterdam, Amsterdam, 1996.

Koschorreck, M., and R. Conrad, Kinetics of nitric oxide consumption in tropical soils under oxic and anoxic conditions, *Biol. Fert. Soils.*, *25*, 82-88, 1997.

Krämer, M., M. Baumgärtner, M. Bender, and R. Conrad, Consumption of NO by methanotrophic bacteria in pure culture and in soil, *FEMS Microbiology Ecology*, *73*, 345-350, 1990.

Krämer, M., and R. Conrad, Influence of oxygen on production and consumption of nitric oxide in soil, *Biol. Fert. Soils*, *11*, 38-42, 1991.

Kuo, S., Phosphorus, in *Methods of Soil Analysis, Part 3. Chemical Methods*, edited by J.M. Bartels, pp. 1390, Soil Science Society of America, Madison, WI, 1996.

Lerdau, M.T., J.W. Munger, and D.J. Jacob, The NO_2 flux conundrum, *Science*, *289*, 2291-2293, 2000.

Linn, D.M., and J.W. Doran, Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils, *Soil Sci. Soc. Am. J.*, *48*, 1267-1272, 1984.

Lipschultz, F., O.C. Zafiriou, S.C. Wofsy, M.B. McElroy, F.W. Valois, and S.W. Watson, Production of NO and N_2O by soil nitrifying bacteria, *Nature*, *294*, 641-643, 1981.

Logan, J.A., Nitrogen oxides in the troposphere: Global and regional budgets, *J. Geophys. Res.*, *88*, 10785-10807, 1983.

Ludwig, J., Untersuchungen zum Austausch von Stickoxiden zwischen Biosphäre und Atmosphäre, University of Bayreuth, 1994.

Ludwig, J., F.X. Meixner, B. Vogel, and J. Foerstner, Soil-air exchange of nitric oxide: an overview of processes, environmental factors, and modeling studies, *Biogeochemistry*, 52, 225-257, 2001.

Luxmoore, R.J., P.M. Jardine, G.V. Wilson, J.R. Jones, and L.W. Zelazny, Physical and chemical controls of preferred path flow through a forested hillslope, *Geoderma*, *46*, 139-154, 1990.

MacDonald, J.A., U. Skiba, L.J. Sheppard, B. Ball, J.D. Roberts, K.A. Smith, and D. Fowler, The effect of nitrogen deposition and seasonal variability on methane exidation and nitrous oxide emission rates in an upland spruce plantation, *Atmos. Environ.*, *31*, 3693-3706, 1997.

Martin, R.E., M.C. Scholes, A.R. Mosier, D.S. Ojima, E.A. Holland, and W.J. Parton, Controls on annual emisisons of nitric oxide from soils of the Colorado shortgrass steppe, *Global Biogeochemical Cycles*, *12* (1), 81-91, 1998.

McKee, D.J., *Tropospheric Ozone; Human Health and Agricultural Impacts,* CRC Press, Boca Raton, Fla., 1994.

McKenny, D.J., K.F. Shuttleworth, and W.I. Findlay, Production and loss of nitric oxide from denitrification in anaerobic Brookston clay, *Appl. Environ. Microbiol.*, *43*, 534-541, 1982.

Meixner, F.X., Surface exchange of odd nitrogen oxides, *Nova Acta Leopoldina*, *NF 70* (288), 299-348, 1994.

Meixner, F.X., T. Fickinger, L. Marufu, D. Serca, F.J. Nathaus, E. Makina, L. Mukurumbira, and M.O. Andreae, Preliminary results on nitric oxide emission from a southern African savanna ecosystem, *Nutrient Cycling in Agroecosystems*, *48*, 123-138, 1997.

Meixner, F.X., and W. Eugster, Effects of landscape pattern and topography on emissions and transport, in *Integrating Hydrology, ecosystem dynamics and biogeochemistry in complex landscapes*, edited by J.D. Tenhunen, and P. Kabat, John Wiley&Sons Ltd., New York, 1999.

Miller, R.D., and D.D. Johnson, The effect of soil moisture tension on carbon dioxide evolution, nitrification, and nitrogen mineralization, *Soil Sci. Soc. Pro.*, *28*, 644-647, 1964.

Moldrop, P., T. Olesen, D.E. Rolston, and T. Yamaguchi, Modeling diffusion and reaction in soils: VII predicting gas and ion diffusivity in undisturbed and sieved soils, *Soil Science*, *162* (9), 632-640, 1997.

Monteith, J.L., and M.H. Unsworth, *Principles of environmental physics*, Arnold, London, 1990.

Moraes, J.F.L.d., B. Volkoff, C.C. Cerri, and M. Bernoux, Soil properties under Amazon forest and changes due to pasture installation in Rondonia, Brazil, *Geoderma*, *71*, 63-81, 1996.

Mosier, A.R., Chamber and isotope techniques, in *Exchange of trace gases between terrestrial ecosystems and the atmosphere*, edited by M.O. Andreae, and D.S. Schimel, pp. 175-187, John Wiley, New York, 1989.

Mosier, A.R., W.J. Parton, D.W. Valentine, and D.S. Schimel, Long-term impact of N fertilization on N_2O flux and CH_4 uptake in the Colorado shortgrass prairie, in *Transactions of the 9th Nitrogen Workshop*, pp. 157-160, Technische Universitaet Braunschweig, Braunschweig September 1996, 1996.

Mosier, A.R., Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere, *Plant and Soil*, *228*, 17-27, 2001.

Neff, J.C., M. Keller, E.A. Holland, A.W. Weitz, and E. Veldkamp, Fluxes of nitric oxide from soils following the clearing and burning of a secondary tropical rain forest, *J. Geophys. Res.*, *100* (D12), 25913-25922, 1995.

Neill, C., M.C. Piccolo, P. Steudler, J.M. Melillo, B.J. Feigl, and C.C. Cerri, Net nitrogen mineralization and net nitrification rates in soils following deforestation for pasture across the southwestern Brazilian Amazon Basin landscape, *Oecologia*, *110*, 243-252, 1997a.

Neill, C., J.M. Melillo, P.A. Steudler, C.C. Cerri, J.F.L. de Moraes, M.C. Piccolo, and M. Brito, Soil carbon and nitrogen stocks following forest clearing for pasture in the southwestern Brazilian Amazon, *Ecological Applications*, *7* (4), 1216-1225, 1997b.

Neill, C., M.C. Piccolo, J.M. Mellilo, P.A. Steudler, and C.C. Cerri, Nitrogen dynamics in Amazon forest and pasture soils measured by 15N pool dilution, *Soil Biology and Biochemistry, 31*, 567-572, 1999.

Nelson, D.W., Gaseous losses of nitrogen other than through denitrification, in *Nitrogen in agricultural soils*, edited by F.J. Stevenson, pp. 327-364, American Society of Agronomy, Madison, 1982.

Nepstad, D.C., A.G. Moreira, and A.A. Alencar, *A Floresta em Chamas: origens, impactos e prevencao de fogo na Amazonia*, Quick Printer, Brasilia, 1999a.

Nepstad, D.C., A.Verissimo, A. Alencar, C. Nobre, E. Lima, P. Lefebvre, P. Schlesinger, C. Potter, P. Mountinho, E. Mendoza, M. Cochrane, and V. Brooks, Large scale impoverishment of Amazonian forests by logging and fire, *Nature*, 398, 505–508, 1999b.

Otter, L.B., W.X. Yang, M.C. Scholes, and F.X. Meixner, Nitric oxide emissions from a southern African savanna, *J. Geophys. Res.*, *104* (D15), 18471-18485, 1999.

Papen, H., B. Hellmann, H. Papke, and H. Rennenber, Emissions of N-oxides from Acid irrigated and limes soils of a coniferous forest in Bavaria, in *Biogeochemistry of global change: Radiatively active trace gases*, edited by R.S. Oremland, pp. 95-103, Chapman & Hall, New York, 1993.

Pardiwala, R.M., Aspects of the response of Calluna vulgaris (L.) Hull to nitrogen deposition, Master of Schience Thesis thesis, University of Edinburgh, 1997.

Parsons, D.A.B., M.C. Scholes, R.J. Scholes, and J.S. Levine, Biogenic NO emissions from savanna soils as a function of fire regime, soil type, soil nitrogen, and water status, *J. Geophys. Res.*, *101* (D19), 23683-23688, 1996.

Parsons, W.F.J., and M. Keller, Controls on nitric oxide emissions from tropical pasture and rain forest soils, *Biol. Fertil. Soils*, *20*, 151-156, 1995.

Peirce, J.J., and V.P. Aneja, Nitric oxide emissions from engineered soil systems, *Journal of environmental engineering*, *126* (3), 225-232, 2000.

Perret, J., S.O. Prasher, A. Kantzas, and C. Langford, Three-dimensional quantification of macropore networks in undistrubed soil cores, *Soil Sci. Soc. Am. J.*, *63*, 1530-1543, 1999.

Picollo, M.C., C. Neill, and C.C. Cerri, Net nitrogen mineralization and net nitrification along a tropical forest-to-pasture chronosequence, *Plant and Soil*, *162*, 61-70, 1994.

Pilegaard, K., P. Hummelshoj, and N.O. Jensen, Nitric oxide emission from a norway spruce forest floor, *J. Geophys. Res.*, *104* (D3), 3433-3445, 1999.

Pitcairn, C.E.R., I.D. Leith, L.J. Sheppard, M.A. Sutton, D. Fowler, R.C. Munro, S. Tang, and D. Wilson, The relationship between nitrogen deposition species composition and foliar nitrogen concentrations in woodland flora, *Environ. Pollut.*, *102* (S1), 457-461, 1998.

Reiners, W.A., A.F. Bouwman, W.F.J. Parsons, and M. Keller, Tropical rain forest conversion to pasture: changes in vegetation and soil properties, *Ecological Applications*, *4* (2), 363-377, 1994.

Remde, A., F. Slemr, and R. Conrad, Microbial production and uptake of nitric-oxide in soil, *Fems Microbiology ecology*, *62* (4), 221-230, 1989.

Remde, A., and R. Conrad, Metabolism of nitric oxide in soil and denitrifying bacteria, *FEMS Microbiology Ecology*, *85*, 81-94, 1991.

Remde, A., J. Ludwig, F.X. Meixner, and R. Conrad, A study to explain the emission of nitric oxide from a marsh soil, *Journal of Atmospheric Chemistry*, *17*, 249-275., 1993.

Richard, G., I. Cousin, and A. Bruand, Change in soil porosity and hydraulic properties by compaction, European Geophysical Society, 2000.

Rudolph, J., M. Koschorreck, and R. Conrad, Oxidative and reductive microbial consumption of nitric oxide in a heathland soil, *Soil Biol. Biochem.*, *28* (10/11), 1389-1396, 1996a.

Rudolph, J., F. Rothfuss, and R. Conrad, Flux between soil and atmosphere, vertical concentration profiles in soil, and turnover of nitric oxide: 1. Measurements on a model soil core, *Journal of atmospheric chemistry*, *23*, 253-273, 1996b.

Rummel, U., C. Ammann, A. Gut, F.X. Meixner, and M.O. Andreae, Eddy covariance measurements of NO flux within a rain forest, *J. Geophys. Res.*, submitted, 2001.

Saad, O.A.L.O., and R. Conrad, Temperature dependence of nitrification, denitrification and turnover of nitric oxide in different soils, *Biol. Fertil. Soils*, *15*, 21-27, 1993.

Schaefer, D.A., and W.A. Reiners, Throughfall chemistry and canopy processing mechanisms, in *Acid precipitation*, edited by S.E. Lindberg, A.L. Page, and S.A. Norton, Springer Verlag, 1990.

Scholes, M.C., R. Martin, R.J. Scholes, D. Parsons, and E. Winstead, NO and N_2O emissions from savanna soils following the first simulated rains of the season, *Nutrient cycling in Agroecosystems*, *48*, 115-122, 1997.

Serca, D., R. Delmas, C. Jambert, and L. Labroue, Emission of nitrogen oxides from equatorial rain forest in central Africa: origin and regulation of NO emissions from soils, *Tellus*, *46B*, 243-254, 1994.

Sheppard, L.J., A. Crossley, J.N. Cape, F. Harvey, J. Parrington, and C. White, Early effects of acid mist on Sitka spruce planted on acid peat, *Phyton-annales rei botanicae*, *39 (1)*, 1-25, 1999.

Skarby, L., and G. Sellden, The effects of ozone on crops and forests, *Ambio*, *13*, 68-74, 1984.

Skiba, U., K.J. Hargreaves, D. Fowler, and K.A. Smith, Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperature climate, *Atm. Environ.*, *26A* (14), 2477-2488, 1992.

Skiba, U., K.A. Smith, and D. Fowler, Nitrification and denitrification as sources of nitric oxide and nitrous oxide in a sandy loam soil, *Soil Biol. Biochem.*, *25*, 1527-1536, 1993.

Skiba, U., D. Fowler, and K.A. Smith, Emission of NO and N_2O from soils, *Environmental Monitoring and Assessment*, *31*, 153-158, 1994.

Skiba, U., M.M. Sosanza, and S. Metcalfe, An inventory of soil nitrous oxide emissions from a region in northern Britain, *submitted to Soil Use & Management.*

Skiba, U., L.J. Sheppard, C.E.R. Pitcairn, and D. Fowler, Nitrous oxide emission and methane oxidation in woodland soil downwind of a poultry farm., in *Transactions of the 9th Nitrogen Workshop, Braunschweig, September 1996*, pp. 561-564, Technische Universitaet Braunschweig, Braunschweig, 1996.

Skiba, U., L.J. Sheppard, J. MacDonald, and D. Fowler, Nitrous oxide emissions from forest and moorland soils in Northern Britain, in *Proceedings of the 7th International Nitrous Oxide Workshop, Cologne, April 1997*, pp. 247-253, Bergische Universitaet, Wuppertal, 1997.

Skopp, J., M.D. Jawson, and J.W. Doran, Steady-state aerobic microbial activity as a function of soil water content, *Soil Sci. Soc. Am. J.*, *54*, 1619-1625, 1990.

Slemr, F., and W. Seiler, Field measurements of NO and N_2O emissions from fertilized and unfertilized soils, *J. Atm. Chem.*, *2*, 1-24, 1984.

Sposito, G., *The chemistry of soils*, 277 pp., Oxford University Press, New York, 1989.

Sullivan, L.J., Environmental variables controlling nitric oxide emissions from agricultural soils in the southeast united states, *Atmospheric environment*, *30* (21), 3573-3582, 1996.

Thimonier, A., Measurement of atmospheric deposition under forest canopies: some recommendations for equipment and sampling design, *Environmental Monitoring and Assessment*, *52*, 353-387, 1998.

Thornton, F.C., N.J. Shurpali, B.R. Bock, and K.C. Reddy, N_2O and NO emissions from poultry litter and urea applications to bermuda grass, *Atmospheric Environment*, *32* (9), 1623-1630, 1998.

Tietema, A., B. Warmerdam, E. Lenting, and L. Riemer, Abiotic factors regulating nitrogen transformations in the organic layer of acid forest soils: Moisture and pH, *Plant and Soil*, *147*, 69-78, 1992.

Tomasella, J., and M.G. Hodnett, Estimating soil water retention characteristics from limited data in Brazilian Amazonia, *Soil Science*, *163* (3), 190-202, 1998.

van Breemen, N., B. P.A., E.J. Velthorts, H.F. van Dobben, T. de Wit, T.B. Ridder, and H.F.R. Reijnders, Soil acidification from atmospnheric ammonium sulphate in forest canopy throughfall, *Nature*, *299*, 548-550, 1982.

van Cleemput, O., and L. Baert, Nitrite: a key compound in N loss processes under acid conditions?, *Plant and Soil*, *76*, 233-241, 1984.

van Cleemput, O., and A.H. Samater, Nitrite in soils: accumulation and role in the formation of gaseous N compounds, *Fertilizer Research*, *45*, 81-89, 1996.

van Dijk, S.M., and F.X. Meixner, Production and consumption of NO in forest and pasture soils from the Amazon Basin: a laboratory study, *Water, soil and air pollution*, submitted, 2001a.

van Dijk, S.M., and F.X. Meixner, Nitric oxide release from soils in the Amazon Basin: the effect of soil texture/structure on optimum moisture conditions, *Soil Science Society of American Journal*, submitted, 2001b.

Veihmeyer, F.J., and A.H. Hendrickson, The moisture equivalent as a measure of the field capacity of soils, *Soil Sci. Soc. Am. J.*, *32*, 181-194, 1931.

Veldkamp, E., Organic carbon turnover in three tropical soils under pasture, *Soil Sci. Soc. Am. J.*, *58*, 175-180, 1994.

Veldkamp, E., and M. Keller, Fertilizer-induced nitric oxide emissions from agricultural soils, *Nutrient Cycling in Agroecosystems*, 48, 69–77, 1997a.

Veldkamp, E., and M. Keller, Nitrogen oxide emissions from a banana plantation in the humid tropics, *J. Geophys. Res.*, 102 (D13), 15,889–15,898, 1997b.

Veldkamp, E., E. Davidson, H. Erickson, M. Keller, and A. Weitz, Soil nitrogen cycling and nitrogen oxide emissions along a pasture chronosequence in the humid tropics of Costa Rica, *Soil Biology and Biochemistry*, *31*, 387-394, 1999.

Venterea, R.T., and D.E. Rolston, Mechanisms and kinetics of nitric and nitrous oxide production during nitrification in agricultural soil, *Global Change Biology*, *6*, 303-316, 2000.

Vermoesen, A., C.-J. de Groot, L. Nollet, P. Boeckx, and O. van Cleemput, Effect of ammonium and nitrate application on the NO and N_2O emission out of different soils, *Plant and Soil*, *181*, 153-162, 1996.

Verchot, L.V., E.A. Davidson, J.H. Cattanio, I.L. Ackerman, H.E. Erickson, and M. Keller, Land use change and biogeochemical controls on nitrogen oxide emissions from soils in eastern Amazonia, *Global Biogeochemical Change*, *13* (1), 31-46, 1999.

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

Williams, E.J., D.D. Parish, and F.C. Fehsenfeld, Determination of nitrogen oxide emissions from soils: results from a grassland site in Colorado, United States, *J. Geophys. Res.*, *92*, 2173-2179, 1987.

Williams, E.J., A. Guenther, and F.C. Fehsenfeld, An inventory of nitric oxide emissions from soils in the united states, *Journal of Geophysical Research*, *97* (D7), 7511-7519, 1992.

Williams, E.J., and F.C. Fehsenfeld, Measurement of soil nitrogen oxide emissions at three North American ecosystems, *J. Geophys. Res.*, *96*, 1033-1042, 1991.

Yamulki, S., R.M. Harrison, K.W.T. Goulding, and C.P. Webster, N_2O, NO and NO_2 fluxes from a grassland, effect of soil pH, *Soil Biol. Biochem.*, *29* (8), 1199-1208, 1997.

Yang, W., and F.X. Meixner, Laboratory studies on the release of nitric oxide from subtropical grassland soils: the effect of soil temperature and moisture, in *Gaseous Nitrogen Emissions from Grasslands*, edited by S.C. Jarvis, and B.F. Pain, CAB International, New York, 1997.

Zak, D.R., E.H. Holmes, N.W. MacDonald, and K.S. Pregitzer, Soil temperature, matric potential and the kinetics of microbial respiration and nitrogen mineralization, *Soil Sci. Soc. Am. J.*, *63*, 575-584, 1999.

Acknowledgements

During the course of my Ph.D., I was supported in many ways by a large number of people. Therefore I would like to take this opportunity to thank my family, friends and colleagues and mention the following people explicitly:

My promotor Jos Lelieveld and co-promoter Franz Meixner were instrumental in initiating this project, and I would like to thank them for the opportunity to complete my research at the Max Planck Institute in Mainz, while taking the Ph.D. exam at Utrecht University. Together, they supervised my work and offered valuable help and advice during the course of my Ph.D. I thank Franz who invited me to the Max Planck Institute, and offered the possibility to expand my horizons and strengthen my persistence during the campaign work in Brazil. Jan Duyzer first introduced me to the world of nitric oxide, and I thank him for his support, advice and friendship, and for many stimulating discussions! Many thanks also to Ute Skiba for her help and friendship, I enjoyed our adventures with the red pickup!

The overall development of this thesis was only possible through the aid of a great support team (Christof Ammann, Hermann Bange, Reinhard Gabriel, Andreas Gut, Grant Kirkman, Udo Rummel and Michael Welling). Many thanks also to the very helpful staff of the engineering workshop and the graphics department. My stay at MPI and in Mainz in general has been very pleasant, not in the least by the friendship of my international colleagues and friends. Thanks for a great time, everyone! I especially thank the members of the DDG for numerous interesting discussions. Also, I am grateful to my Dutch friends and Ph.D. colleagues (ActIva-Ext.) for their motivating emails (o.d.z. "leuk"). I hope we will continue to increase our expertise in geology during the yearly returning AKBX (Alternative Kleine Buitenland Excursie). Many thanks to Eveline (no more sitting duck), Jan (de Master), Jolt (de Boorkoning), Martijn (Yeti), JW (Blokkie), Luuk (de Kostendrukker), Annemieke, Vian and Yvonne. I am looking forward, Stephan and Melynda, to another FC-Utrecht match: the invitation to Mainz 05 still stands. Danke auch Silvi, Ursula & *Emma!*

Enquanto estive em Ji-Paraná no Brasil, muitas pessoas de diversos institutos me offereceram apoio. Agradeço a todos: Cida e Bia, obrigada pelo sua amizade e as noites com pizzas, filmes e conversas!

Mijn familie, Ria (ik heb vla voor je gekocht), Dolf (zorg dat je er niet gek van wordt), Annemarie (natuurlijk mag je blijven slapen), en Jonathan (I've put your tea on the table) bedank ik voor hun geweldige steun, liefde, humor, geduld en aanmoediging tijdens het voorbereiden van dit boekje.

Saskia

Curriculum Vitae

Saskia van Dijk was born in Amstelveen, the Netherlands, on May 1st 1974. After her ”VWO” exam from Visser 't Hooft in Leiden in 1992, she studied geology at the Department of Earth Sciences at Utrecht University. She completed her "propaedeuse" in geology in 1993, and received an MSc. in exogeneous geochemistry and environmental geochemistry in 1997. The final thesis reported on results from an integrated geochemical research project in Espírito Santo, Brazil. At the Earth Sciences Department, exchange between the Earth and the Atmosphere was generally applied as the final instrument to close the chemical budgets of nutrient cycles. During the last year of her study, she developed an interest in the field of Atmospheric Chemistry. For this reason she attended some additional lectures on "Introduction in Atmospheric Chemistry" by Prof. Peter Builtjes. It was though his help, that she was introduced to Dr. Jan Duyzer from the Netherlands Institute for Applied Science (TNO) in Delft (currently Apeldoorn). Here, she carried out fieldwork, measuring nitric oxide emissions from forest ecosystems. As part of her practical at TNO, she stayed at the Center for Ecology & Hydrology (CEH) in Edinburgh. Under the supervision of Dr. Ute Skiba, she measured emissions of nitrous oxide and nitric oxide from soils around poultry farms in Edinburgh. Directly after graduation from Utrecht University in 1997, Dr. Ute Skiba offered a position as a scientific assistant. This work involved carrying out fieldwork and performing data analysis. February 1998, she started in the research group of Prof. Franz Meixner at the Max Planck Institute in Mainz (Germany). As part of a major field campaign in Brazil, she set up a laboratory in Ji-Paraná (Brazil), and conducted experiments on the controlling parameters of production and consumption of nitric oxide in soil samples from forest and pasture soils. Her Ph.D. was completed under the supervision of promotor Prof. Jos Lelieveld of Utrecht University (Netherlands).