# University of New Hampshire University of New Hampshire Scholars' Repository

#### **Doctoral Dissertations**

Student Scholarship

Fall 1994

# Nitrous oxide emissions from tropical soils

Antonio Donato Nobre University of New Hampshire, Durham

Follow this and additional works at: https://scholars.unh.edu/dissertation

#### **Recommended** Citation

Nobre, Antonio Donato, "Nitrous oxide emissions from tropical soils" (1994). *Doctoral Dissertations*. 1806. https://scholars.unh.edu/dissertation/1806

This Dissertation is brought to you for free and open access by the Student Scholarship at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact nicole.hentz@unh.edu.

# **INFORMATION TO USERS**

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

# UMI

A Bell & Howell Information Company 300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA 313/761-4700 800/521-0600

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

· •

Order Number 9511210

# Nitrous oxide emissions from tropical soils

Nobre, Antonio Donato, Ph.D. University of New Hampshire, 1994



Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

. . . . . .

# NITROUS OXIDE EMISSIONS FROM TROPICAL SOILS

BY

#### ANTONIO DONATO NOBRE

B.Sc., Agronomical Engineering, Universidade de São Paulo, 1983 M.Sc., Tropical Ecology, INPA/Universidade do Amazonas, 1989

## DISSERTATION

# Submitted to the University of New Hampshire in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

in

Earth Sciences

September, 1994

This dissertation has been examined and approved

Dissertation Director, Dr. Robert C. Harriss, Professor Earth Sciences

Dr. John D. Aber, Professor Natural Resources

Dr. Patrick M. Crill, Research Associate Professor Earth Sciences

Dr. Mark É. Hines, Research Associate Professor Earth Sciences

James & Voyelman

Dr. James E. Vogelmann, Research Assistant Professor Complex Systems

<u>July 29, 1994</u> Date This dissertation is dedicated with love to the elemental beings of soil and air.

# ACKNOWLEDGMENTS

For the second time in my graduate life, I am able to thank my advisor, mentor and friend, Bob Harriss, for his support, tolerance, kindness, wisdom, and farsighted enthusiasm. For the longer haul, I thank my parents, Nair and Wilson, for bringing me to this wonderful planet and my brother Carlos for the early inspiration and support which lead me into science. I am indebted to Patrik Wiedemeir and Reto Stoker for giving me the opportunity to continue my crusade against the destruction of the tropical rainforest. Katherine Bolster through her delicate grace, emotional support and competent advice on programming and editing help carry me through to the completion of this dissertation.

The Complex Systems Research Center staff, namely Karen Bushold, Linda Tibbetts and Diana Wright offered the kind of encouragement and support that helped to make me have the most productive professional four years of my present life. I thank Patrick Crill and Michael Keller for introducing me and getting me to appreciate the technical side of trace-gases. I thank also Steve Frolking, Changsheng Li and John Aber for introducing me and getting me to appreciate the modeling side of trace gases and Mark Hines for acquainting me with an exciting biogeochemical way to see the world. In Costa Rica I am thankful to Rodolfo Vargas, Danilo Villegas, and Marvin Nunez for their assistance in the field and lab, and to the National Science Foundation Huerto's

iv

project, John Ewel P.I., for providing infrastructure and support on the Vegas site. I thank also for their support the staff of the La Selva Biological Station of the Organization for Tropical Studies. In Brazil I am thankful to Heloisa Miranda and Antonio Miranda at the Universidade de Brasilia (UnB), and to Braulio Dias and his staff at the Instituto Brasileiro de Meio Ambiente (IBAMA) for advice and support. I especially appreciated the use of facilities at the Roncador Reservation of the Instituto Brasileiro de Geografia e Estatistica (IBGE) and thank its staff for their support.

During the course of this study I was a doctoral fellow under the Global Change Fellowship Program of the National Aeronautics and Space Administration (NASA NGT 30059). The work in Costa Rica was partially funded by EPA (DW499347801-2) and the work in Brazil was funded by a grant (NAGW 2726) from NASA, the fire-scars project. I was granted a leave of absence from the Instituto Nacional de Pesquisas da Amazonia -INPA- in Manaus, Brazil, to complete my Graduate Studies at University of New Hampshire.

I also would like to thank a countless number of software engineers involved in the development of many commercial and scientific software used in this dissertation. Finally, I thank everybody else, including the American people, whose direct or indirect hospitality and friendship allowed me to feel at home here, far away from the place I was born.

> Copies of this work should mention its true inspirational source: © NATURE!!

> > v

#### PREFACE

This dissertation consists of two parts, each one standing alone as a comprehensive approach to its respective subject. However, when taken together these two studies encompass an interesting spectrum of possibilities for helping to solve the puzzle of the missing nitrous oxide source in the global budget. The following is a brief summary of each part.

## <u>Part I</u> - Short-Term Response Of Nitrous Oxide Emissions To Nitrogen And Carbon Additions In Two Tropical Volcanic Soils.

This part presents a detailed study of volcanic soils of high natural fertility, located at La Selva Biological Station in Costa Rica. Originally the area had a lush tropical rainforest cover, which since has been converted to agricultural use. The experiments described in this part stress two key approaches to nitrous oxide production, namely rainfall-driven episodic short-pulses of emissions, and emission-response to different kinds of fertilizers. The monitoring of soil-profile inorganic-nitrogen chemistry and soil-moisture, simultaneously with nitrous oxide production and emission over time, is, to date, unique to this study.

### <u>Part II</u> - Episodic Nitrous Oxide Soil Emissions In Brazilian Savanna (Cerrado) Fire-Scars.

The second part reports on a study of savanna ecosystems in tropical South America and their conversion to high input agriculture. The natural savanna, locally called cerrado, occurs on a highly infertile soil, as opposed to the soils in Costa Rica, which suffers periodic fires leaving behind large expanses of fire-scarred savanna. Nitrous oxide emissions for these impacted savannas previously were unknown. The first segment of this study, covering most of one rainy season, assesses several fire-scars from prescribed fires. The second segment of this study describes a series of fertilizations and subsequent episodic emissions carried out on a recently burned patch of natural savanna. This experiment was similar to the addition experiments in Costa Rica, so results could be compared and contrasted. And finally, the third segment of this study consists of monitoring episodic nitrous oxide emissions from pasture, and corn and soybean plantations, the three most common agricultural uses of the savannas.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

# **TABLE OF CONTENTS**

ACKNOWLEDGMENTSiv
PREFACEvi
LIST OF TABLESx
LIST OF FIGURES xi
ABSTRACT xiii
DADT I SHOPT-TERM RESPONSE OF NITROUS OVIDE EMISSIONS
TO NITROGEN AND CARBON ADDITIONS IN TWO TROPICAL
VOLCANIC SOILS
Introduction2
Methods
Study Site 6
Experimental Design
Field Sampling
Laboratory Analysis
Results and Discussion15
Soil Time Series Profiles15
Vegas Control Treatment15
Vegas Water Treatment16
Vegas Nitrate-N Treatment20
Vegas Nitrate-N + Glucose-C Treatment20
Flaminia Water Treatment22
Flaminia Nitrate-N Treatment
Flaminia Glucose-C Treatment24
Flaminia Nitrate-N + Glucose-C Treatment
Episodic Emission and Fluxes to the Atmosphere
Vegas
Flaminia Event #1
Flaminia Event #2 (Substrate search for $N_2O$ -production)
Importance of Episodic Nitrous Oxide Production
Conclusions

BRAZILIAN SAVANNA (CERRADO) FIRE-SCARS	5
Introduction	6
Methods	6
Study Site	6
Experimental Design	6
Field Sampling	6
Laboratory Analysis	7
Results and Discussion	7
Savanna Fire-Scar Experiments (FScars)	
Savanna Grassland (Cl)	7
Tree/shrub savanna (Cs)	7
Wooded Savanna (Ct)	
Savanna Woodland (Cd)	7
Cerrado FScars Emissions in Comparison with Emission	s in other
Similar Ecosystems	7
The Savanna Fertilization Experiment (FertEx)	
Control Treatment	
Nitrate-N Treatment	8
Glucose-C Treatment	
Nitrate-N + Glucose-C Treatment	82
Agriculture/Pasture Experiments (APEx)	8.
Corn (Zea mayz)	8
Soybean (Glycinea max)	
Pasture (Paspalum grass)	
Importance of the Conversion of Cerrado to High Input	
Agriculture	88
Conclusions	90
Bibliography	
Appendix A (diffusive leaks)	130
Annondix P (numeric data for Part I)	13'

## LIST OF TABLES

Table	e I	Page
I.1.	Physical and chemical properties of the studied soils	39
I.2.	Vegas site treatments	40
I.3.	Flaminia site treatments	41
I.4.	Vegas episodic versus background N <sub>2</sub> O emissions	42
I.5.	Flaminia episodic versus background N <sub>2</sub> O emissions	43
II.1.	Vegetation types and general properties for the savannas in central Brazil	92
II.2.	Main superficial soil properties for the savannas in central Brazil	93
II.3.	Vegetation types and treatments for savanna Fire-Scar Experiment	. 94
II.4.	Treatments for the savanna Fertilization Experiment	95
II.5.	Crop and treatments for the Agriculture/Pasture Experiment	96
II.6.	Mean N <sub>2</sub> O flux measurements for FScars	97
II.7.	Mean N <sub>2</sub> O flux measurements for FertEx	98
II.8.	Mean N <sub>2</sub> O flux measurements for APEx	99

# LIST OF FIGURES

Figures Page			
I.1.	Horizontal layout of the field experiment at Vegas and for Event #1 at Flaminia		
I.2.A.	Vegas soil time-series data for dry Control treatment45		
I.2.B.	Vegas soil time-series data for Water treatment46		
I.2.C.	Vegas soil time-series data for Nitrate-N treatment		
I.2.D.	Vegas soil time-series data for Nitrate-N + Glucose-C treatment 48		
I.3.A.	Flaminia soil time-series data for Water treatment		
<b>I.3.B.</b>	Flaminia soil time-series data for Nitrate-N treatment		
1.3.C.	Flaminia soil time-series data for Glucose-C treatment		
I.3.D.	Flaminia soil time-series data for Nitrate-N + Glucose-C treatment52		
I.4.A.	Vegas $N_2O$ emissions for the four treatments in Event #1		
I.4.B.	Vegas $N_2O$ emissions for the four treatments in Event #2		
I.4.C.	Vegas $N_2O$ emissions for the four treatments in Event #3		
I.5.A.	Flaminia $N_2O$ emissions for the four treatments in Event #1		
I.5.B.	Flaminia $N_2O$ emissions for the first four treatments in Event #257		
I.5.C.	Flaminia $N_2O$ emissions for the last three treatments in Event #2		
II.1.	The forest-savanna-grassland ecocline in central Brazil100		
II.2.A.	FScars soil time-series data for savanna grassland (Cl) site 101		
II.2.B.	FScars soil time-series data for three/shrub savanna (Cs) site102		
II.2.C.	FScars soil time-series data for wooded savanna (Ct) site103		

II.2.E	. FScars soil time-series data for savanna woodland (Cd) site	104
<b>II.3.</b> A	A. FScars N <sub>2</sub> O emissions for three/shrub savanna (Cs) site	105
II.3.B	<b>4.</b> FScars N <sub>2</sub> O emissions for wooded savanna (Ct) site	. 106
II.3.C	C. FScars N <sub>2</sub> O emissions for savanna woodland (Cd) site	107
II.4.A	. FertEx soil time-series data for Control treatment	108
11.4.B	. FertEx soil time-series data for Nitrate-N treatment	109
II.4.C	C. FertEx soil time-series data for Glucose-C treatment	110
II.4.D	. FertEx soil time-series data for Nitrate-N + Glucose-C treatment	. 111
II.5.A	. FertEx N <sub>2</sub> O emissions for Control treatment	.112
II.5.B	FertEx N <sub>2</sub> O emissions for Nitrate-N treatment	.113
II.5.C	2. FertEx N <sub>2</sub> O emissions for Glucose-C treatment	.114
II.5.D	• FertEx N <sub>2</sub> O emissions for Nitrate-N + Glucose-C treatment	115
II.6.A	APEx N <sub>2</sub> O emissions for Corn (Zea mayz) plantation	116
II.6.B	APEx N <sub>2</sub> O emissions for Soybean ( <i>Glycinea max</i> ) plantation	. 117
II.6.A	. APEx N <sub>2</sub> O emissions for Pasture ( <i>Paspalum</i> grass)	.118
A.1. \$	Scatterplot showing distribution of diffusional syringe leaks for Vegas samples collected for flux measurement	.133
A.2. S	Scatterplot showing distribution of diffusional syringe leaks for Vegas soil-gas-phase samples	.134
A.3. S	Scatterplot showing distribution of diffusional syringe leaks for Flaminia samples collected for flux measurement	.135
A.4. 5	Scatterplot showing distribution of diffusional syringe leaks for Flaminia soil-gas-phase samples	.136

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

#### ABSTRACT

#### NITROUS OXIDE EMISSIONS FROM TROPICAL SOILS

by

Antonio Donato Nobre University of New Hampshire, September 1994

Nitrous oxide ( $N_2O$ ), the third most important greenhouse trace gas in the troposphere and one contributor to ozone destruction in the stratosphere, has its concentration in the atmosphere increasing steadily over the last few decades. This study measured sources from tropical soils, potentially the highest and least studied  $N_2O$  production areas in the world.

For two tropical volcanic soils in Costa Rica the effect of water, nitrate and glucose additions on episodic emissions of nitrous oxide were studied. Magnitudes of episodic  $N_2O$  pulses, as well as overall  $N_2O$  emissions, varied considerably and consistently, depending on soil texture, soil moisture, and kind and availability of substrates. Emission pulses began within 30 minutes, peaking no later than 8 hours after wetting. Production in the soil occurred mainly in the layer between 5 and 20 cm deep, but depended directly on the temporal dynamics of the water profile. Soil inorganic nitrogen was associated with soil  $N_2O$  concentration changes. Depending on the treatment, one episodic  $N_2O$  production event driven by one moderate rain could account for less than 15% to more than 90 % of the total weekly production. Previous survey studies may have underestimated the contribution of gas emissions from tropical soils to

the global budget of  $N_2O$ , and better budgets will demand a detailed knowledge of both background emissions, and episodic emissions driven by rain events.

The seasonally burned cerrados of Brazil are the largest savanna-type ecosystem of South America and their contribution to the global atmospheric N<sub>2</sub>O budget is unknown. Results showed that N<sub>2</sub>O consumption/emission for four fire-scarred savanna ecosystems, for nitrogen and carbon fertilization and for agriculture/pasture ranged from -0.3 to +0.7, 1.8 to 9.1, and 0.5 to 3.7 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>, respectively. During the wet season the cerrado biome does not appear to be a major source of N<sub>2</sub>O to the troposphere, even following fire events. However, conversion of the cerrado to high input agriculture, with liming and fertilization, can increase N<sub>2</sub>O emissions more than ten fold.

# PART I

# SHORT-TERM RESPONSE OF NITROUS OXIDE EMISSIONS TO NITROGEN AND CARBON ADDITIONS IN TWO TROPICAL VOLCANIC SOILS

## **Introduction**

Before the industrial age, the atmospheric nitrous oxide concentration (mixing ratio) appears to have remained constant at around  $285 \pm 1$  parts per billion by volume (ppbv) for the past 3000 years (*Khalil* and *Rasmussen*, 1988). However, over the past century the mixing ratio has increased about 8%, and during the past decade it has shown a yearly increase from 0.2% to 0.3% (*Khalil* and *Rasmussen*, 1983; *Khalil* and *Rasmussen*, 1992; *Prinn* et al., 1990; *Weiss*, 1981). There is a very high likelihood that the increase in N<sub>2</sub>O atmospheric mixing ratio is directly associated with large scale human interference in the nitrogen cycle (*IPCC*, 1990). The current measured mixing ratio of N<sub>2</sub>O in the troposphere is about 310 ppbv (*IPCC*, 1990). Nitrous oxide is an important greenhouse gas and is a factor in determining the ozone concentration in the stratosphere (*Cicerone*, 1987; *Dickinson* and

2

Cicerone, 1986; Hahn and Crutzen, 1982; Singh, 1987). The current sources of  $N_2O$  are poorly known, and inputs to the atmosphere, known and estimated, account for3 only about half of the flux required to balance the relatively well known destruction rate (Kim and Craig, 1993; Robertson, 1993).

Of the presently known sources, soils are estimated to be the largest, contributing approximately 66% of total emissions (Robertson, 1993 and references therein; Davidson, 1991 and references therein); 50% of the soil emissions are currently thought to be from undisturbed ecosystems. Comparative measurements have reported higher rates of denitrification and nitrous oxide release in tropical than in temperate forests (e.g. Robertson and Tiedje, 1986; Seiler and Conrad, 1987), sometimes by a factor of 20 larger than the global mean of nitrous oxide emissions by soils (Keller et al., 1983). Denitrification in tropical soils may account for up to half of the global production of N,O (Griffiths et al., 1993). The Amazon basin, for instance, appears to be a major source of trace gases, including N<sub>2</sub>O (Matson et al., 1987). Tropical biomes cycle larger amounts of total nitrogen than boreal ecosystems (Chapin et al., 1986; Matson and Vitousek, 1987; Vitousek and Matson, 1988; Vitousek and Matson, 1993; Vitousek and Sanford, 1986). Tropospheric N<sub>0</sub> mixing ratios over that basin are higher than the global average

3

(McElroy and Wofsy, 1986), although specific sources within the region have not yet been well quantified. To date, a disproportionate amount of information has come from the developed temperate regions of the northern hemisphere (Smith and Arah, 1990; Vitousek and Matson, 1993).

Nitrous oxide production and consumption in soil have been demonstrated to be a non-continuous process in both time and space (e.g. *Terry* et al., 1981). Its episodic nature, with pulses of production associated with major transient changes in soil microsite environments, has been shown to account for significant surges of emissions to the atmosphere in relatively short spans of time (e.g. *Brumme* and *Beese*, 1992; *Davidson* et al., 1991; *Grundmann* and *Rolston*, 1987; *Johnsson* et al., 1991; *Mosier* et al., 1991; *Sexstone* et al., 1985).

Most previous survey studies carried out for tropical soils have not used high frequency (e.g. every few hours) sampling based on rain events to guide sampling. More commonly, daily sampling is conducted for only a short campaign (e.g. *Livingston* et al., 1988; *Goreau* and *Mello*, 1987; *Keller*, et al., 1983; *Matson* et al., 1990), or a few complete seasonal cycles are studied, sampling approximately every week (e.g. (*Keller* et al., 1993; *Luizão* et al., 1989).

Davidson et al. (1993) and Garcia-Mendez et al. (1991) studied a dry tropical forest and sampled rain-driven episodic events. They reported that the magnitude of the episodic events was a direct function of substrate accumulation during the dry season, and that the magnitude decreased with each successive rainfall until rain associated emissions were not distinguishable from the background. This finding might be a good approximation for most of the relatively arid and infertile nitrogen-limited natural ecosystems in the tropical and subtropical regions (see Part II). However, as these ecosystems are converted to agriculture, pasture or silviculture (*Fearnside*, 1986; *Skole* and *Tucker*, 1993), where some form of nitrogen fertilization is used (*Duxbury* et al., 1993; *Vitousek* and *Matson*, 1993), there is an increasing potential for episodic emissions to become significant.

In this paper, we report on a detailed study carried out on two tropical soils, converted previously from rainforest cover to agroforestry and pasture. The study was designed to respond to a recognized urgent need for field studies in which  $N_2O$  flux measurements are investigated in combination with processes regulating gas production and their environmental controls (*Schimel* et al., 1989). The study also was planned in conjunction with the development of a process oriented model,

DNDC (Li et al., 1992a) and (Li et al., 1992b), both efforts seeking to assess the unique role of rainfall events in soil denitrification.

#### <u>Methods</u>

#### **Study Site**

La Selva, a 3300 ha biological station of the Organization for Tropical Studies, lies between the confluence of the rivers Viejo and Sarapiqui, province of Heredia (10° 26' N; 83° 58' W, 40 m approx. elevation asl), in the transition zone from the coastal plain to the steep foothills of the Costa Rican Cordillera Central mountain range's north facing Caribbean slope. The terrain of the reserve is developed on andesitic lava flows deposited in the Pleistocene, and on alluvium, also derived from volcanic rock, overlying lava flows in terraces bordering both rivers (*Sollins* et al., 1993). Annual climatic means are about 25° C and 3720 mm precipitation (*Instituto Meteorológico Nacional*, 1988). The dry season extends roughly from December to April, and the variation in air temperature is minimal throughout the year.

One experimental site, Las Vegas annex, is located on one of those alluvial terraces at the confluence of the Viejo and Sarapiqui rivers,

about 15 m above the dry season river water level. The area had an original vegetation cover classified as wet tropical forest (*Hatshorn*, 1983), but had been converted in the 1950's to cacao cultivation, a condition in which it remained for many years until abandonment, ca. 1980 (*Griffiths* et al., 1993). In 1991 the area was cleared to bare soil for the establishment of the Huertos silvicultural experimental plots. The marginal buffer zones among Huertos plots were left to regrow with wild pioneer plants. A regrowth strip, localized on the west side of the Sendero Las Vegas, at approximate position in the La Selva GIS coordinates of -50/-375, was chosen for the experiment. The regrowth was primarily two species of fast-growing shrubs, forming a dense two meter tall cover that was clear cut to bare soil, without removal of roots, one week prior to the beginning of this experiment.

The second experimental site, *Finca* (ranch) Flaminia is located on the slope of a clayey terrain developed possibly from a higher river terrace. The finca had been under long term pasture until abandonment several months prior to the experiment. An area near and to the south of the new road to San José (Rio Frio), approximate position in La Selva GIS grid of -350/1250, was chosen for the experiment. The site was covered with 1 m tall grass that was cut down and the soil left bare. The

Flaminia experiment site was cleared and established three weeks before beginning experimental work.

The sandy lower-terrace soil in Vegas (Bambu consociation) is an andic fluventic Eutropept, rich in exchangeable bases, whereas, the clayey pasture soil in Flaminia is an upland with more weathered soil, poor in bases, and not classified but possibly a typic Tropohumult (Sollins et al., 1993) or an oxic Humitropept (Reiners et al., 1993), based in its physiographic position. Selected data from the studied soils is presented in Table I.1. Sollins et al. (1993) further describe the soils of La Selva and the region.

#### **Experimental Design**

Each of the two experimental sites (except for Event #2 in Flaminia) had one 3.2 x 3.2 m square plot subdivided into four 2.56 m<sup>2</sup> sub-plots (treatments). Each sub-plot was a 1.6 m square with four basic components or installations (Figure I.1): one PVC ring or collar inserted approximately in the center of the square; one battery of stainless steel soil-gas-phase probes for sampling at various depths, and installed to one side of the collar close to the merge of the four sub-plots, or proximal edge, and extending under the collar; one battery of tensiometers also for

sampling at various depths, and installed on the one distal or outer edge of the sub-plot, pointing to the collar; and one soil sampling soil pit lying outside the other distal edge, with the sampler operating towards the collar.

The simulated rain events were water and solution additions using a backpack sprayer and a garden watering can. All the nitrogen and carbon sources (except for dry urea in Flaminia) were dissolved immediately before irrigation in pre-stored rain water. The water or solutions were sprayed evenly onto the sub-plots over a period of 30 minutes so that they would percolate into the soil without forming standing water. The time-step used in the experiments for measurements were irregular, but followed a general scheme. For each simulated rain event, or solution addition, measurements were done at time zero, which was immediately preceding the additions, and then 30 minutes, 2, 4, 8 hours, and one day after additions, and daily thereafter, until the next rain event or completion of the experiment.

For Event # 1 at both sites (Tables I.2 & I.3), there were two fertilizer treatments and water alone as a control. The fertilizers were sodium nitrate (NaNO<sub>3</sub>) at a level of 50 kg N  $\cdot$  ha<sup>-1</sup> as the first fertilizer

treatment, and NaNO<sub>3</sub> at 50 kg N  $\cdot$  ha<sup>-1</sup> plus glucose (dextrose,  $\alpha$ -D(+) C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) at a level of 250 kg C  $\cdot$  ha<sup>-1</sup> as the second treatment. The 5:1 C:N ratio used to obtain denitrifying potential was similar to those used in soil core incubation studies (*Parsons* et al., 1993; *Schuster* and *Conrad*, 1992). In Vegas there was also one dry control, and in Flaminia there was one glucose only treatment, at a level of 250 kg C  $\cdot$  ha<sup>-1</sup>. Events #2 and #3 in Vegas were a continuation of the observation of treatments from Event #1 with supplemental water additions on the two fertilizer treatments and the water control.

Event #2 in Flaminia had a different and simplified treatment layout. At a location within ten meters from the main plot (Event #1), seven collars were installed in a line, each in the center of a  $0.5 \times 0.5$  m square plot. All the procedures for adding the solutions onto the plots were similar to that described above, except for the dry urea treatment where the urea salt (CH<sub>4</sub>N<sub>2</sub>O) was sprinkled over the dry soil one day before the irrigation in a manner similar to local agricultural practice. Carbon and nitrogen combinations and levels in the seven treatments can be seen in Table I.3. The extract of litter constituted an aqueous extract of forest-floor organic litter (from the rain-forest in the area) that was ground into a fine powder, agitated with deionized water for 1 hour, let rest for another hour, and then centrifuged at 10,000 rpm for 5 min. The

supernatant was then refrigerated until use. The resulting dark brown solution was used to simulate drainage through a soil litter layer.

#### **Field Sampling**

The enclosure technique used to quantify trace-gas exchange between soil and atmosphere has been widely used and discussed at length by Hutchinson and Mosier (1981). In this study, the two-part static vented chambers consist of a 25 cm internal diameter, 10 cm tall, polyvinylchlorine (PVC) ring or collar and a molded acrylonitrile-butadiene-styrene (ABS) plastic top 10 cm tall with a gas sampling port, a pressure equilibration port, and a lip that fits over the PVC ring (Matson et al., 1990). The chamber-top was well aerated before the beginning of each N<sub>2</sub>O flux measurement. The lip was greased lightly with silicon grease (Apiezon) and the collar capped tightly with chamber-top. Gas samples, withdrawn through an injection port, were collected using 20 ml nylon syringes (S.E.S.I., VWR Scientific) fitted with butyl rubber o-rings, and polypropylene stopcocks (Baxter Scientific), at 1, 7, 14, 21 and 28 minutes after closure. Each five syringe sample set constituted one flux measurement, after which the chamber closure was opened. Air temperature was taken during the sampling.

11

Nitrous oxide flux was calculated by regressing the  $N_2O$  mixing ratio linear change over time in the chamber enclosure (*Keller* et al., 1986).

One week prior to the experiment the collar was inserted approximately 2 cm in the top soil. Problems reported by *Matson* et al. (1990) associated with increased gas production in rainforest soils due to early insertion of rings onto the soil should not be a matter of concern at these sites, because there was no root mat covering the soil and preliminary tests in nearby forest sites (*Keller* and *Reiners*, 1994) did not indicate an insertion effect.

The sampling of soil-gas was carried out using horizontal probes made of stainless steel tubing (3.17 mm oD) formed in an L shape, installed adjacent to the PVC collar, at depths of 2, 5, 10, 20, and 40 cm (Figure I.1). The drawing portion of the probe's tubing, approximately 10 cm long, had 20 small holes drilled in its wall, distributed along its length. The upper part of the L ( 2 cm) was bonded (epoxy setting glue) to a capillary stainless steel tubing (1.59 mm oD) leading upward outside the soil. On top, a cutoff hypodermic needle (also with 1.59 mm oD), with a luer slip lock, was hooked to the stainless steel tubing, tip to tip, using a short piece of polystyrene tubing. On the slip lock end, a plastic

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

cap was used to seal the probe from the atmosphere and dirt during the intervals between sampling.

To monitor the total soil water potential (matric, pressure, gravitational and osmotic), porous-cup tensiometers (1 cm OD by 10 cm long sensing porous-cup; 1 bar air entry value) were installed horizontally in the soil close to the collars [about 25 cm away]. They were placed at the same depths as the gas probes but offset laterally to avoid interference. The water tension inside the tensiometers was measured at each time step using a calibrated electronic pressure transducer (Soilmoisture, CA) hooked to an ammeter. Gravimetric soil moisture was measured on all soil samples collected for chemical analysis.

Samples were collected for each time step, each treatment, and each depth for monitoring soil chemistry. Soil samples were extracted using a 25.40 mm oD steel tube soil sampler (Soilmoisture,CA). The sampling scheme in the immediate vicinity of the experimental plots (Figure I.1), consisted of digging one small pit (30 cm wide, 50 cm deep and 1m long) for each treatment. The samples were then drawn horizontally, within the pit, from under the experiment area at the same depths as those used for gas probes and tensiometers. The amount of earth collected corresponded to from two to three loads of the sampler, or

about 200g. Soil samples were kept in plastic bags for few hours and thereafter frozen in the same bags [-18° C] for variable periods of time, until extraction could be carried out.

#### Laboratory Analysis

Nitrous oxide was determined for 2 ml sub-samples of the 20 ml field samples, using a 8A Shimadzu gas chromatograph fitted with a stainless steel (3.2 mm oD by 2 m) column, packed with 50-80 mesh Porapaq Q, and a <sup>63</sup>Ni electron capture detector. Operating conditions were: column temperature, 63° C; electron capture detector temperature, 330° C; P5 mixture (95% Ar with 5% CH<sub>4</sub>) carrier gas with a flow rate of 30 ml · min<sup>-1</sup>. N<sub>2</sub>O and CO<sub>2</sub> were separated, but only N<sub>2</sub>O mixing ratios were quantified. Oxygen, hydrocarbons, CFC's, etc. were removed from the carrier gas with a mol-sieve purifier filter. Water vapor was removed from all samples with a pre-column of indicating moisture absorbent (Aquasorb<sup>TM</sup> - Mallinckrodt 6063). Standards (nitrous oxide in dinitrogen gas mixture) used in the analysis (343.8, 543.7 and 808.7 ppbv; Scott Specialty Gases) were calibrated against NOAA (Nitrous Oxide and Halocarbons Division, Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado) secondary standards.

The samples were held in the sampling syringes an average of 21 hours before being analyzed. Loss rates for every syringe used in the experiments were determined by leak tests and the values for analyzed  $N_2O$  mixing ratios were corrected for any diffusional leaks (see Appendix A for detail in method). Soil nitrate ( $NO_3$ ) and ammonium ( $NH_4^+$ ) concentrations were determined colorimetrically in saline soil extract (*Keeney* and *Nelson*, 1982) using an autoanalyzer (Technicon Traacs 800). Soil total elemental carbon and nitrogen were determined from oven dried and well ground soil sub-samples (*Nelson* and *Sommers*, 1982) through a flash dry combustion elemental analyzer (Carlo Erba).

## **Results and Discussion**

#### **Soil Time Series Profiles**

Figures I.2. and I.3. show time series data on experiment results for  $N_2O$  fluxes and soil-gas-phase  $N_2O$  mixing ratios, together with soil water tension and soil  $NO_3^-$  concentration profiles.

<u>Vegas Control Treatment</u>. At the sandy Vegas site, control treatment  $N_2O$  fluxes remained close to background levels throughout the period (Figure I.2.A). There was some rainfall three days before the

beginning of the experiments in Vegas, and the residual effects of that moisture in the soil can be seen in the initial days as low soil water tension and elevated N<sub>2</sub>O mixing ratios at depths of 5, 20 and 40 cm. The small oscillation in the background flux at the surface reflects these changes in the soil profile. As the soils dried due to dry weather until day 20, the soil moisture to depths of 20 cm decreased progressively to tensions in excess of 1 Bar (the limit of the tensiometers). Some low rainfall (3 mm) at the end of the experiment resulted in increased profile mixing ratios and fluxes. Changes in nitrate concentrations in the soil profile did not directly reflect changes in the associated N<sub>2</sub>O mixing ratios. This could indicate that nitrification is the main source for N<sub>2</sub>O background emissions rather than denitrification, or, that nitrous oxide is diffusing up from deeper layers where it would have been produced either by denitrification or nitrification. Degassing from ground water is also a possible source. There is a consistent upward gradient in soil N<sub>2</sub>O mixing ratios at all sampled depths, which supports the hypothesis of production at depth (for a review of denitrification in subsurface environments see Rice and Rogers, 1993).

<u>Vegas Water Treatment</u>. The time series of water tension profiles, which are averages of three separate measurement sites, indicate clearly the effects of each simulated rain event and subsequent drying

16

period (Figure I.2.B). The first event quickly lowered water tension to a depth of 10 cm, and after some lag also lowered tension slightly at 20 cm, but did not influence deeper layers.

If water seems so clearly associated with increased gas phase N<sub>2</sub>O mixing-ratios in the upper soil layers, how can be explained, before wetting, the proportionally equivalent peaks at depth 20 and 40 cm? Griffiths et al. (1993), incubating similar soils to study denitrification potential, found that N<sub>2</sub>O produced by denitrification was highest in  $O_2$ -free headspace. Considering that water temporarily fills up pore space in the upper soil layers, diffusion of atmospheric  $O_2$  into the soil could diminish, increasing the probability of a larger anaerobic fractional volume developing (Davidson, 1992; Rudaz et al., 1991; Mosier et al., 1986), therefore allowing denitrification to proceed faster in layers beneath the saturated zone. Another possible explanation is that nitrous oxide actively produced in upper layers diffuses downward. Gas diffusion from below would be inhibited. Corroborating the argument of diffusion from upper layers and consequently low denitrification at depth, the soil nitrate data showed no change at a depth of 40 cm. The nitrous oxide peak for all depths happened around 8h after the simulated rain, indicating a simultaneous response (no lag determined by diffusional constraints).

17
Even though the magnitude of the second simulated rain event was the same as the first, the soil was much drier at that time. The wetting front percolated quickly to 5 cm, but moisture was soon lost to evaporation. The water added to the top 5 cm in this event kept water tension low until the third event, when a three-fold larger simulated rain percolated quickly to the drier layers underneath, reaching 20 cm, and producing strong pulses of N<sub>2</sub>O to that depth. Lower water tensions might have induced lower O<sub>2</sub> partial pressure in the microbial microsites for a longer time than in previous events, leading to a further reduction of nitrous oxide (already diffused from the liquid into the gas-phase) to N<sub>2</sub>. In the "leaky-pipe" model (Firestone and Davidson, 1989) this would mean a regulation at the third level, where diffusion and consumption of N<sub>2</sub>O occur prior to escape from soil into the atmosphere. That would explain the sharp peaks at depths 5 and 10 cm. From 20 cm downward, there could be less consumption after the peak, which would explain the skewed tails for those depths. The bigger pulses of soil gas-phase N,O, compared with event 1 and 2, did not translate into bigger emissions at the soil surface.

The nitrate data showed consistent patterns, especially the patterns associated with water additions and resulting nitrous oxide pulses. A progressive increase during interpeak or low flux periods, like

the one shown at 2 cm, could indicate two main processes: first, nitrification occurring during periods where  $O_2$  is more plentiful, and also enhanced by moderate wetness; second, upward movement of soil solution from deeper layers to the surface by capillarity action, due to surface evaporation, would result in accumulation of nitrate at the uppermost layer and progressive loss of nitrate in deeper layers. The  $NH_4^+$ concentrations showed a remarkable similarity with  $NO_3^-$ .

There were nitrate oscillations associated with the  $N_2O$  pulses. NO<sub>3</sub><sup>-</sup> suddenly decreased in concentration, followed immediately by quick increases until NO<sub>3</sub><sup>-</sup> stabilized around background levels. This was similar to what was observed in tropical dry forest upon wetting (*Davidson* et al., 1993). This could suggest that with increased moisture, microbial communities bloom, consuming and immobilizing nitrate from the soil solution, leading to a decrease in nitrate concentration. Then, either due to exhaustion of substrate or some other regulating factor, the recently grown biomass dies, liberating part of the nitrogen that was immobilized by the microbial mass. The NH<sub>4</sub><sup>+</sup> data corroborated that interpretation, assuming that increased concentrations reflect mineralization. The subsequent stabilization in the nitrate concentrations during the dry periods suggested that the microbial community had

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

reached a quasi-equilibrium. The detailed dynamics of the soil microbiology was beyond the scope of this study.

**Vegas Nitrate-N Treatment**. In this treatment the emissions from the soil surface were very consistent with changes in soil gas mixing ratios (Figure I.2.C). There was an unexpected increase in nitrous oxide and nitrate at 40 cm prior to any change in soil moisture. In this first amendment, the top four layers showed a large increase in nitrate with the arrival of a moisture front. The first peak of mixing-ratios associated with nitrate additions exceeded the water alone treatment throughout the profile. The extra nitrate supplied clearly stimulated higher denitrification activity. This is an indication that the soil ecosystem was limited in nitrogen, a result corroborated by soil core nitrate addition experiments with pasture and forest soils in the same region (*Parsons* et al., 1993), but contradicting results of another study (*Keller* et al., 1988).

<u>Vegas Nitrate-N</u> + <u>Glucose-C Treatment</u>. After addition, the profile of  $N_2O$  mixing-ratios (Figure I.2.D) indicated that denitrification was enhanced 30 times above levels measured in other treatments. The nitrate profile showed nitrate concentrations oscillating abruptly during gas peaks, as in other treatments which received water. Most of the nitrate was consumed during and soon after Event #1 at depths of 5 and 10 cm, remaining constant in deeper levels. This suggests that microbial activity is most intense in those two layers, which increases the likelihood that  $N_2O$  is actively produced there (*Firestone* and *Davidson*, 1989), diffusing upward and downward. In the surface layer, nitrate remained high, possibly due to the addition in the amendment, but also possibly due to the progressive loss of water by evaporation during the first interpeak period. Between events 2 and 3 nitrate progressively dropped to almost zero mg  $\cdot$  kg<sup>-1</sup> of dry soil, possibly due to higher soil moisture conditions than the first interpeak.

Nitrous oxide mixing-ratios reached in the first event of the nitrate + glucose additions were 25, 40, 14, 5 times higher in layers 2, 5 & 10, 20, and 40 cm, respectively, than in equivalent layers during the nitrate treatment. The second event had mixing-ratios values only 1.2 to 1.7 times higher than the corresponding nitrate-only additions. The third event had some mixing-ratios concentrations which were even smaller than in nitrate addition. This overwhelming response to glucose after an initial application, primarily in the layers wetted by the simulated rain, indicated the high potential for denitrification in this soil. More interesting to this study was the temporary nature of the response to nitrate + glucose addition suggesting strong carbon limitation.

**Flaminia Water Treatment**. Soil gas nitrous oxide concentrations in the Flaminia pasture clayey soil (Figure I.3.A.) showed a four-fold faster and 5-10 times larger response than the equivalent treatment on the sandy soil at the Vegas site. The quick and homogeneous drop of soil moisture after a simulated rain event throughout the profile indicated higher infiltration, probably due to macropores. Except for the uppermost few centimeters which became drier, the rest of the measured profile behaved the same with respect to moisture. Because of scattered rainfall during Event #1 at Flaminia, it is not possible to compare background production with events 1 and 2 of Vegas. Nitrous oxide formed after the first brief peak, accumulated progressively at depth. Because the rain events happened during nights, peak sampling (30 min., 2, 4, and 8h) was not done. Lack of sampling of the N<sub>2</sub>O peaks makes it hard to evaluate the impact on the soil N<sub>2</sub>O mixing-ratios of different magnitudes of natural rainfalls.

A few observations should be noted about the water treatment results. After 19 + mm of rain accumulated in the third day, twice as much as the amount of the simulated rain in Event #1, there was a drop in  $N_2O$  mixing-ratios at almost all depths, associated with a big increase in  $NO_3^-$  concentration. On the fourth day, after more 78 mm of rain, the

situation reversed, with gas accumulating in the profile, and NO<sub>3</sub><sup>-</sup> substrate diminishing abruptly. The first drop in gas mixing ratios was similar to the drop that happens after each episodic pulse peak, with the increased nitrate being the result of the increased mineralization-nitrification associated with the enhanced soil moisture. The increase in nitrate is associated with the first peak for the three uppermost layers, and is relatively proportional to the amount of water going through the soil. The increase in mixing ratios by the fourth day was probably caused by denitrification soon after the natural rain, which would also explain the drop in concentration of the nitrate substrate.

**Flaminia** Nitrate-N Treatment. The nitrate treatment (Figure I.3.B) produced a significantly different response compared to the water treatment. Mixing ratios of  $N_2O$  are generally higher than those produced by water, but the dynamics of production and consumption were not symmetric as they were at the Vegas site.

After the amendment, nitrate increased immediately in the uppermost layer, and showed a progressive time lag for the increase at deeper levels. In contrast to the water treatment, nitrate in the three intermediate layers that accumulated during the first day began decreasing on the second day, reaching its lowest concentration in the third day, and

recovering by the fourth day. As seen in Vegas, nitrate in the surface soil remained high as the soil dried, but in contrast to Vegas, when more water was added, nitrate concentrations decreased and did not recover. The likely explanation is leaching of nitrate from the surface layer into layers beneath by the added water. The results of this experiment, in spite of the complicating factor of natural rainfall, strongly support the inference that nitrate dynamics in the soil profile, if studied in conjunction with soil moisture and soil  $N_2O$  mixing ratios, can be a useful indicator of conditions controlling soil  $N_2O$  production.

**Flaminia Glucose-C Treatment**. The Glucose-C treatment (Figure I.3.C) was unique to the Flaminia site, and served to separate the effect of carbon alone from that of carbon plus nitrogen. The most evident effect of carbon alone, besides the brief enhancement of  $N_2O$  in the profile following amendment, was the consumption of nitrate to the lowest concentrations observed in any of our treatments. Similar to Nitrate-N + Glucose-C at Vegas, the  $N_2O$  production was most intense in the three upper layers. In these layers, nitrate reached zero at the same time  $N_2O$  mixing-ratios were peaking (at 4 h), indicating a shortage of nitrogen substrate for denitrification. If compared with nitrogen alone, the glucose treatment produced 3 to 30 times higher  $N_2O$  mixing-ratios. Glucose is thus clearly the main driver of nitrous oxide production

24

associated with these amendments. But glucose addition alone will run the system out of nitrate after only 4 hours of immobilization/denitrification.

**Flaminia** Nitrate-N + Glucose-C Treatment. The profile results for this treatment (Figure I.3.D) confirmed the expectation from the results of the carbon alone treatment that an additional supply of N substrate would increase the production and accumulation of  $N_2O$  in the soil. The peaks in soil mixing-ratios were equivalent in some layers, and much bigger in others, compared to those resulting from the Glucose-C treatment. The enhanced nitrous oxide peaks lasted much longer than in the glucose amendment. But even in this experiment, there seemed to have been some nitrate limitation, for at 10 cm, one very low nitrate concentration point coincided with a decrease in the nitrous oxide mixing ratio (and also coincided with an increase in ammonium concentration). It seems clear, as in the water treatment, that nitrate was leached out of the surface layers into lower ones after an intense rainfall. However, it is unclear why, between 2 and 8 h, there was a plateau in the measured nitrate for the upper two layers and in the N<sub>2</sub>O flux at the surface.

25

 $N_2O$  mixing ratios in the nitrate + glucose treatment are four to twenty five times larger than the ratios for the equivalent treatment at Vegas (Figure I.2.D). The enhanced peaks also lasted longer than at Vegas. In Flaminia, there was more soil moisture and that moisture was better distributed in the soil, but nitrate concentrations were similar. The key, we believe, were soil textural and structural differences (Table I.1). Larger bulk density (Flaminia pasture) with smaller porosity can influence infiltration and percolation rates, and very probably gas diffusivity rates (*Reiners* et al., 1993). The sandy Vegas soil had potentially much less space in micropores comparative to the clay soil in Flaminia. Consequently, the anaerobic fractional volume of the former could be much smaller.

As shown by *Burton* and *Beauchamp* (1994), the measurement of mixing-ratios gradients for these soil profiles proved useful in delineating the timing and location of gas production. The general close relationship between patterns of  $N_2O$  mixing-ratio dynamics and water infiltration with substrate amendment, suggested an overwhelming importance of episodic production in the upper soil layers, over production in deeper soil layers, in controlling the measured emissions.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

#### **Episodic Emission and Fluxes to the Atmosphere**

The cumulative curves (Figures I.4 and I.5), or running totals, are integrated summations of interpolated intervals of the minimum sampling period (30 min.) for the entire event period. The shape of the curves allows inferences about the importance of the irregularities in trace gas emission (episodic pulses, for instance) for the temporal accumulation of emissions. A straight line indicates that emissions are uniform over time, a condition where background flux monitoring suffices to making good estimates of real emissions. The higher the departure from a straight line, the worse the estimates of emissions based in background fluxes. In Vegas Water Event #1 (Figure I.4.A), the running total shows that the accumulation of emitted gas is progressive, and oscillating, well in accord with the fluctuation of the background fluxes. Even though a peak pulse can be identified soon after the simulated rain, its contribution to the progressive accumulation is small. In other situations, like the Vegas Water and Nitrate-N in Event #2 (Figure I.4.B), the peak is clearly distinguishable; but it is followed by a slight depression in the background flux making its contribution to the running total imperceptible, and consequently less important in the case of estimating real long term emissions. When the running total curve starts bulging upward, like Vegas Nitrate-N, Event #1 (Figure I.4.A), where 32 % of the total N<sub>2</sub>O emission over 9 days was emitted during 1 day (peak duration),

27

or in an extreme example in the same figure with Nitrate-N + Glucose-C where 96 % of all gas emitted occurs during the first day, then the emission regimen is very irregular.

Vegas. The effect of irrigation and amendment on the nitrous oxide production was most dramatic in the short term episodic peaks that followed additions. The simulated rainfall events always produced episodic emission pulses, as well as increased overall production of N<sub>2</sub>O. The effect of water alone could be seen in the water treatment at Vegas (Figures I.4.A to I.4.C). Twenty-five  $g N_2 O-N \cdot ha^{-1}$  (Figure I.4.C and Table I.4 Totals) was emitted [averaging 1.2 g  $N_2O-N \cdot ha^{-1} \cdot d^{-1}$ ], after three simulated rain events over a 22 day period. The dry Vegas control treatment emitted 14 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> [0.6 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>. d<sup>-1</sup>] over the same period. The episodic pulses of N<sub>2</sub>O associated with water additions contributed approximately 20% of the total flux. The approximately 20 g  $N_{2}O-N \cdot ha^{-1}$  attributable to background flux is still 1.4 times larger than the dry control background flux. This indicates that other nitrous oxide producing processes such as nitrification benefited from increased soil moisture. The emission pulses in this treatment,  $1 g N_2 O - N \cdot ha^{-1}$  for the first, and 2 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> for the last two were evidence that water additions cannot be related to  $N_2O$  emissions in a linear way.

The nitrate treatment, with a 50 kg N  $\cdot$  ha<sup>-1</sup> amendment, emitted 45 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> [2.0 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> d<sup>-1</sup>] in Vegas (Figures I.4.A to I.4.C) or 1.8 times the gas emitted by the Vegas water-alone treatment, after three simulated rain events over a 22 day period. That represented approximately 0.1% of the added nitrogen, or 4.7% if the system emitted at the same weekly rate during a full year. Episodic emissions accounted for 22% of the total flux in this treatment.

The treatment nitrate + glucose (Figures I.4.A to I.4.C) emitted  $303 g N_2 O-N \cdot ha^{-1} [13.7 g N_2 O-N \cdot ha^{-1} \cdot d^{-1}]$ . These results indicate a severe carbon limitation on denitrification in this soil, or, perhaps, that glucose can stimulate aerobes to consume most available soil oxygen which increases the anaerobic fractional volume in the soil stimulating denitrification (*Mosier* et al., 1986). Stoichiometric calculations showed that if glucose was totally respired aerobically, the amount added to the soil (250 kg of dissolved C  $\cdot$  ha<sup>-1</sup>) would have been enough to consume all of the atmospheric oxygen from the soil gas-phase down to almost 1 m deep, provided there was no diffusive replenishment from the atmosphere. The short time frame of intense reducing conditions here is the key to understanding why N<sub>2</sub>O emissions were so enhanced. This treatment emitted 0.6 % of the added N. In this treatment 91 % of the N<sub>2</sub>O was

produced during the episodic pulses, contrasting with the 22 % in Nitrate-N treatment (Table I.4).

**Flaminia Event #1**. The water treatment at Flaminia (Figure I.5.A) emitted  $116 g N_2 O - N \cdot ha^{-1}$  in 6 days. This was 17 times more  $N_2 O - N$  than the observed in the same treatment at Vegas. Considering that this kind of soil covers much larger areas and its use as pasture is much more common, these high emission numbers assume special significance (*Reiners* et al., 1993; *Keller* et al., 1993; *Luizão* et al., 1989).

The nitrate treatment (Figure I.5.A), with a 50 kg N  $\cdot$  ha<sup>-1</sup> amendment, emitted 374 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> [61 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>]; this represented 0.7 % of the added nitrogen. That emission is proportionally 30 times higher than the gas emitted at the Vegas nitrate treatment, and 3.2 times the gas produced at Flaminia water treatment. The level of N fertilization used in this experiment is relatively low compared to that used for agriculture in the area (e.g. banana plantations typically use 300 kg-N  $\cdot$  ha<sup>-1</sup>). Emissions associated with episodic fluxes increased from 15 % of total flux (Table I.5) in the water treatment, to 36 % in this treatment.

30

The glucose treatment at Flaminia (Figure I.5.A), emitted 1,273  $g N_2O-N \cdot ha^{-1} [208 g N_2O-N \cdot ha^{-1} \cdot d^{-1}]$ . This clay soil response to glucose was 11 times larger than the water treatment and 3.4 times larger than the nitrate treatment. The nitrate + glucose treatment in Flaminia (Figure I.5.A) emitted 3,336  $g N_2O-N \cdot ha^{-1} [545 g N_2O-N \cdot ha^{-1} \cdot d^{-1}]$ . This is 20 % less than would be predicted by a simple multiplication of the individual treatments. The emissions in this treatment were 38 times larger than the equivalent treatment in sandy Vegas soil. The episodic emission of nitrous oxide in the glucose treatment produced 91% of the measured emissions, while in the glucose + nitrate treatment the episodic emission was 39%.

**Flaminia Event #2** (Substrate search for  $N_2O$ -production). This series of tests cannot be directly compared with the ones in Event # 1 in Flaminia, because in Event #2 the experiments were protected from rainfall. These results were useful to show how a succession of simulated rain events with controlled drying periods can precisely define the temporal emission patterns of transient nitrous oxide pulses.

Because glucose is not a common amendment in fertilized soils, a mix of organic compounds extracted from decaying forest litter layer

[litter extract] was used as a source of carbon for experimentation. The results,  $121 g N_2 O-N \cdot ha^{-1} [20 g N_2 O-N \cdot ha^{-1} d^{-1}]$  (Figure I.5.C), is only marginally larger than the water treatment in Event #1 of Flaminia. The emission dynamics of this natural carbon treatment were significantly different from the water treatment; 72 % of N<sub>2</sub>O was emitted during the first episodic emission, compared with 15 % during the second episode.

Urea, a commonly used fertilizer, was also used as an experimental treatment. Urea produced a depression in emissions compared with the water treatment,  $101 g N_2 O - N \cdot ha^{-1} [17 g N_2 O - N \cdot ha^{-1} d^{-1}]$  (Figure I.5.B). The episodic emission of nitrous oxide accounted for 31 % of total emissions.

Litter extract combined with nitrate produced 296  $g N_2 O-N \cdot ha^{-1}$ [48  $g N_2 O-N \cdot ha^{-1} \cdot d^{-1}$ ] (Figure I.5.C), 2.4 times higher than litter extract alone. Litter extract with Urea-N produced 207  $g N_2 O-N \cdot ha^{-1}$  [34  $g N_2 O-N \cdot ha^{-1} \cdot d^{-1}$ ] (Figure I.5.C), 30 % less N<sub>2</sub>O than nitrate alone, which indicates that urea is not used as readily as nitrate as a substrate for denitrification. Urea applied with glucose, produced 539  $g N_2 O-N \cdot ha^{-1}$ [88  $g N_2 O-N \cdot ha^{-1} \cdot d^{-1}$ ] (Figure I.5.B), 1.8 times more than litter extract + nitrate. Dry urea (Figure I.5.B), sprinkled as a conventional fertilizer

over the soil, and watered one day after, produced results similar to the dissolved urea treatment. Finally, the Nitrate + 1/2 Glucose, could not meaningfully be compared with the Nitrate + Glucose of the Event #1 in Flaminia, due to the various rain events in Event #1. Noteworthy in this treatment was the sharp peak without the top plateau which occurred in Event #1. If the pulse was so brief, either soil moisture was diminishing quickly after the simulated rain event, or, as was the case for treatment Glucose in Event #1, the system was running out of nitrogen substrate, consequently shutting off denitrification.

#### **Importance of Episodic Nitrous Oxide Production**

The events in the experiments for both sites of this study lasted between 147 to 214 hours, or roughly one week, which is equivalent to the time period of recurrent sampling in typical long term trace gas emissions survey studies (e.g. *Keller* et al., 1993; *Weier* et al., 1991; *Luizão* et al., 1989). The hypothesis was that random or chronological periodic sampling might underestimate total N<sub>2</sub>O fluxes to the atmosphere from tropical soils if they miss the transient pulses associated with rain events, liquid amendment or irrigation.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

In order to assess the importance of peak magnitude with peak duration during the episodic emission of  $N_2O$ , we calculated a peak intensity parameter as follows:

$$\operatorname{Peak}_{i} = \frac{\operatorname{Peak}_{\operatorname{Pg}}}{\operatorname{Event}_{\operatorname{Pg}}} \cdot \frac{\operatorname{Event}_{\operatorname{Tp}}}{\operatorname{Peak}_{\operatorname{Tp}}}$$

where  $Peak_{pg}$  and  $Event_{pg}$  are the gas produced during the peak and during the whole event including the peak, respectively;  $Peak_{Tp}$  and  $Event_{Tp}$  are the time periods of the peak and the whole event, respectively. Peaks in this study were defined arbitrarily in the N<sub>2</sub>O flux time series as the part where fluxes depart abruptly from the background. This definition of peak could be made more objective and consistent using mathematical concepts of threshold and peak width limits borrowed from fields like chromatography.

Peak intensity is a dimensionless measure of how many times trace-gas emissions during the peak period are proportionally larger than emissions during the background period. Peak intensity also gives an inverse measure of probability for a random periodic sampling to catch those brief fluctuations [which in turn can also be random with respect to the sampling scheme]. Noting transient bursts of emissions with one, few

or many flux measurements (inadequate to define pulses), like those in the background of Flaminia's treatments for Event #1 (Figure I.5.A), intermingled with non-monitored rain events, contribute to increase the unexplainable scatter [error] in the data.

The higher the value of peak intensity, the worse the underestimate of emissions if only background non-peak emissions are sampled. The closer its value to the unity, the less important will be the contribution of the peak pulse to the average flux, which means closer to background, or broader the peak width. The critical realization is that the nature of the transient pulse sets apart the time-scale of this phenomenon, if compared with the long term background emissions. Moreover, those incompatible time hierarchies cannot be mixed without introducing big errors in the estimates.

When the right sampling strategy is devised, however, the flux data will reflect closely the real emission behavior of the soil system concerned. And as some of the results from this study suggest (Figures I.4.A, I.5.A, I.5.B & I.5.C; Tables I.4 & I.5), there can be a sizable if not overwhelming participation of transient bursts of emissions in the total 'real' emissions over few weeks. The realization of the importance of episodic emissions associated with rainfall is not new (e.g. *Bowman* et al.,

1993; *Davidson* et al., 1993; *Schimel* et al., 1988). However, to date, few long term studies have attempted to quantify the importance of episodic emissions in the total emissions.

# **Conclusions**

The series of experiments with the two volcanic tropical soils reported in this paper indicate that water additions and rainfall set the soil system to start emitting  $N_2O$  in intense pulses. The data in the soil profiles brought strong evidence of the connection between the movement of the wetting front into the soil and the change of  $N_2O$  mixing ratios at that level. Background  $N_2O$  emissions were found to respond differently depending on whether the treatment was dry, wet, fertilized, and with which kind of fertilizer. Soil extractable inorganic nitrogen showed remarkable and somewhat consistent patterns of oscillation associated with  $N_2O$  production and emission in transient pulses. The patterns associated with background also remained consistent with the conditions of the respective soil layer in many situations, even though the biogeochemical interpretation could not explain all the patterns observed.

36

The fact that both nitrogen and carbon produced intense responses suggests that these soils were limited in both substrates. However, in only one instance one of these substrates (nitrate) was observed to have been depleted as a result of supply of the other substrate (glucose). Another hypothesis, somewhat corroborated by the extraordinary response of these soils to glucose addition, is the limitation by environmental conditions on the use of these substrates, for example, redox potential. In such cases, the system can become limited in both substrates, provided the environmental conditions allow their use. In some situations, as during glucose addition, the carbon substrate itself became a source of change in the environment that then triggered further carbon usage, as well as use of other substrates optimally until exhaustion. Soil textures, apparently connected with pore size distribution, determined changes up to twenty fold in total gas emitted, which could mean that broader generalizations based on a few field measurements can be one order of magnitude wrong. Pulses of production can develop quite superficially in the soil, especially between 5 to 20 cm, and can develop to a maximum emission strength [which can be several orders of magnitude greater than the background level] within the range of 30 min. to 8 hours. The episodic part of the flux occurring in brief transient bursts of emissions, usually taking place within a day, can account for up to 98 % of total emissions produced in a week with one

moderate rain event. Those episodic pulses associated with rain, liquid amendment or both, varied greatly in intensity and duration among treatments.

If the frequency and distribution of rainfall and amendments to tropical soils is shown to generate pulses throughout the year as intense as the pulses measured in these experiments, then the global estimates of  $N_2O$  production will have to take into consideration this episodic production in order to account for the missing source.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Site	Depth	Bulk density	Textural Analysis (%)			pH	Minera (mg N Kg-	l N 1 soil)	Total N	Total C
	<u>(cm)</u>	(g.cm-3)	Sand	Silt	Clay	(H2O)	NO3-N	NH4+-N	(%)	(%)
1	2	0.7	66.5	26.5	7.0	6.4	19.6	12.6	0.4	3.9
	5	0.8	66.5	21.5	12.0	6.5	20.8	7.8	0.2	2.4
	10	0.9	69.5	18.5	12.0	6.6	5.8	1.4	0.2	2.0
	20	1.0	70.0	15.0	15.0	6.5	1.7	0.9	0.2	2.0
	40	1.0	66.5	23.5	10.0	6.4	0.5	0.2	0.1	0.7
2	2	1.4				4.6	12.1	20.3	0.4	3.7
	5	1.5				4.7	6.5	3.3	0.3	3.3
	10	1.5				4.8	8.1	4.6	0.3	2.8
	20	1.5				4.9	1.3	1.3	0.2	1.7
	40	1.4				4.9	0.5	1.8	0.1	1.3

 Table I.1.
 Some physical and chemical properties of the studied soils

1 Vegas 2 Flaminia

T

Table I.2. V	egas Site Treatments
--------------	----------------------

Treatment Plot	<b>Event #1</b> 22 mar 92	<b>Event #2</b> 2 apr 92	<b>Event #3</b> 9 apr 92
Control	none	none	none
Water	10 mm water	10 mm water	30 mm water
Nitrate-N	10 mm water + 50 Kg NaNO3-N/ha	10 mm water	30 mm water
Nitrate-N + Glucose-C	10 mm water + 50 Kg NaNO3-N/ha + 250 Kg Glucose-C/ha	10 mm water	30 mm water

Treatment	Event #1	Event #2		
Plot	1 may 92	25 may 92		
Water	10 mm water			
Nitrate-N	10 mm water + 50 Kg NaNO3-N/ha			
Glucose-C	10 mm water + 250 Kg Glucose-C/ha			
Nitrate-N + Glucose-C	10 mm water + 50 Kg NaNO3-N/ha + 250 Kg Glucose-C/ha			
Dry Urea-N		20 mm water + 100 Kg Urea-N/ha		
Urea-N		10 mm water + 50 Kg Urea-N/ha		
Extract of Litter-C		10 mm Aqueous Extract of Litter-C		
Nitrate-N + Extract of Litter-C		10 mm Aqueous Extract of Litter-C + 50 Kg NaNO3-N/ha		
Urea-N + Extract of Litter-C		10 mm Aqueous Extract of Litter-C + 50 Kg Urea-N/ha		
Nitrate-N + 1/2 Glucose		10 mm water + 50 Kg NaNO3-N/ha + 125 Kg Glucose-C/ha		
Urea-N + Glucose		10 mm water + 50 Kg Urea-N/ha + 250 Kg Glucose-C/ha		

 Table I.3.
 Flaminia Site Treatments

			nt		Peak			Background		
			Produced			Produced	N2O-N		Produced	N2O-N
[	TREATMENT	Period (hours)	N2O-N (g/ha)	Period (hours)	Intensity	(g/ha)	(%)	Period (hours)	(g/ha)	(%)
Event #1	Control	214.8	3.7					214.8	4	100
	Water]	214.8	6.6	11.2	2.4	1	13	203.5	6	87
	Nitrate-N	214.8	15	30.4	2.3	5	32	184.4	10	68
	Nitrate-N + Glucose-C	214.8	280	30.4	6.8	269	96	184.4	11	4
Event #2	Control	168.1	2					168.1	2	100
	Water	168.1	13	11.2	2.3	2	14	156.9	11	86
	Nitrate-N	168.1	19	11.2	1.7	2	10	156.9	17	90
	Nitrate-N + Glucose-C	168.1	13	11.2	4.6	4	27	156.9	9	73
Event #3	Control	148.5	9					148.5	9	100
	Water	148.5	8	11.2	3.1	2	24	137.3	6	76
	Nitrate-N	148.5	14	11.2	2.3	3	18	137.3	11	82
	Nitrate-N + Glucose-C	148.5	12	11.2	2.6	2	20	137.3	10	80
TOTALS	Control	531.4	13.9	······································				531.4	13.9	100
	Water	531.4	25.3	33.6	3.1	5	19.8	497.7	20.3	80.2
	Nitrate-N	531.4	45.2	52.8	2.2	10	22.1	478.6	35.2	77.9
-	Nitrate-N + Glucose-C	531.4	302.9	52.8	9.2	275	90.8	478.6	27.9	9.2

## Table I.4. Vegas episodic versus background N2O emissions

1

į

		Event		Peak		Backgrou	Background			
_			Produced			Produced	N2O-N		Produced	N2O-N
	TREATMENT	Period (hours)	N2O-N (g/ha)	Period (hours)	Intensity	(g/ha)	(%)	Period (hours)	(g/ha)	(%)
Event #1	Water	146.9	116	10.2	1.9	15	13	136.7	101	87
	Nitrate-N	146.9	374	10.2	2.5	64	17	136.7	310	83
	Glucose-C	146.9	1273	50.9	2.6	1158	91	96	115	9
	Nitrate-N + Glucose-C	146.9	4527	99	1.4	4165	92	47.8	362	8
Event #2	Dry Urea-N	146.9	193	10.2	10.8	145	75	136.7	48	25
	Urea-N	146.9	101	10.2	4.5	31	31	136.7	70	69
	Extract of Litter-C	146.9	539	26	5.1	485	90	120.8	54	10
	Nitrate-N + Extract of Litter-C	146.9	450	10.2	9.2	288	64	136.7	162	36
	Urea-N + Extract of Litter-C	146.9	121	10.2	10.3	87	72	136.7	34	28
	Nitrate-N + 1/2 Glucose-C	146.9	296	10.2	7.3	148	50	136.7	146	50
	Urea-N + Glucose-C	146.9	207	10.2	9.8	141	68	136.7	66	32

### Table I.5. Flaminia episodic versus background N2O emissions

43

.



**Figure I.1.** Horizontal layout of the field experiment at Vegas and for Event #1 at Flaminia. Components were symmetrical for all treatments. Tensiometers and soil gas-phase probes were distributed vertically at depths of 2, 5, 10, 20 and 40 cm. Soil in the soil sampling zone was sampled horizontally from within the soil pit. At each time step a set of soil samples was collected at the same depths used for tensiomenter and gas sampling. For each subsequent time step, soils samples were collected on a vertical line parallel to the preceding samples. See text for detailed explanations.



Figure I.2.A. Vegas soil time-series data for dry Control treatment. N<sub>2</sub>O exchange flux with the atmosphere is shown on top of the soil profile, associated with soil gas-phase N<sub>2</sub>O concentrations, soil extractable NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and soil water tensions. An event refers to the addition of substrate and/or water to the experiment, and includes the subsequent drying period until the next event or until the end of the experiment. The summits of the N<sub>2</sub>O peaks are labeled with exact flux or gas concentration values at that point in time (counted from the time of the addition event). Raingauge measured rainfall indicates total accumulated precipitation during measured interval.



Figure I.2.B. Vegas soil time-series data for Water treatment. Soil water tension represents average for all site-treatments which received water. Other features are the same as for figure I.2.A.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



Figure 1.2.C. Vegas soil time-series data for Nitrate-N treatment. Other features are the same as for figure 1.2.A.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



Figure 1.2.D. Vegas soil time-series data for Nitrate-N + Glucose-C treatment. Other features are the same as for figure I.2.A.



Figure I.3.A. Flaminia soil time-series data for Water treatment. Other features are the same as for figure I.2.A.



Figure I.3.B. Flaminia soil time-series data for Nitrate-N treatment. Other features are the same as for figure I.2.A.



Figure I.3.C. Flaminia soil time-series data for Glucose-C treatment. Other features are the same as for figure I.2.A.



Figure I.3.D. Flaminia soil time-series data for Nitrate-N + Glucose-C treatment. Other features are the same as for figure I.2.A.



Figure I.4.A. Vegas N<sub>2</sub>O emissions for the four treatments in Event #1. The cumulative curves, or running totals, are integrated summations of interpolated intervals of the minimum sampling period (30 min.) for the entire event period. P.P.G. means peak produced gas; E.P.G. means event produced gas; P.I. means peak intensity (see text).


Figure I.4.B. Vegas N<sub>2</sub>O emissions for the four treatments in Event #2. Other features are the same as for Figure I.4.A.



Figure I.4.C. Vegas N<sub>2</sub>O emissions for the four treatments in Event #3. Other features are the same as for Figure I.4.A.



Figure I.5.A. Flaminia N<sub>2</sub>O emissions for the four treatments in Event #1. Other features are the same as for Figure I.4.A.

56



Figure 1.5.B. Flaminia N<sub>2</sub>O emissions for first four treatments in Event #2. See text and Table 1.3 for definitions of treatments. Other features are the same as for Figure 1.4.A.



Figure I.5.C. Flaminia N<sub>2</sub>O emissions for last three treatments in Event #2. See text and Table 1.3 for definitions of treatments. Other features are the same as for Figure I.4.A.

# PART II

# EPISODIC NITROUS OXIDE SOIL EMISSIONS IN BRAZILIAN SAVANNA (CERRADO) FIRE-SCARS

# **Introduction**

Nitrous oxide  $(N_2O)$ , the third most important anthropogenic greenhouse trace-gas after carbon dioxide  $(CO_2)$  and methane  $(CH_4)$ , has been increasing in the global troposphere at a rate of close to 0.3 % per year (*Khalil* and *Rasmussen*, 1983; *Khalil* and *Rasmussen*, 1992; *Prinn*, *Cunnold* et al., 1990; *Weiss*, 1981). Unlike  $CO_2$  and  $CH_4$ , for which major global sources are reasonably well known, important atmospheric sources of  $N_2O$  are not yet quantified or even identified (*Kim* and *Craig*, 1993; *Robertson*, 1993). Of the presently known sources, soils are estimated to be the largest (e.g.*Robertson*, 1993 and references therein), with tropical soils expected to account for most of the emissions (e.g. *Griffiths* et al., 1993; *Keller* et al., 1983; *Matson* and *Vitousek*, 1987; *Robertson* and *Tiedje*, 1986; *Seiler* and *Conrad*, 1987)

60

The Brazilian savannas (sensu *Huntley* and *Walker*, 1982), known collectively as the cerrado biome, occupy 1.88 million km<sup>2</sup> (*Pereira*, 1982), second in area only to the Amazonian rainforest in South America. These frequently burned tropical expanses have become a potentialy important source for greenhouse trace-gas species. On a world wide basis, 1.8, 2.4 and 2.6 times more biomass is burned annually in savannas than burned in agriculture, forests, and as firewood, respectively (*Levine*, 1991). That volume of biomass could produce 3 to 4 times greater emissions of trace gases from direct fire than burning for deforestation in tropical rainforests (*Hao* et al., 1990).

On burned sites (fire-scars) post-fire soil processes, including trace-gas exchange with the atmosphere, can be considerably different from unburned sites (e.g.Andreae et al., 1988; Anderson and Domsch, 1989; Crutzen, 1985; Delmas, 1982; Fishman et al., 1986). The potential importance of post-fire change in emissions of nitrous oxide and other trace-gases was first identified by (Anderson et al., 1988) and (Levine et al., 1988), but prior to this work had not yet been studied for the cerrados in South America.

61

Because of good soil aeration, favorable temperatures, and comparatively more NH<sub>4</sub>-N than NO<sub>3</sub>-N availability, nitrification may be the most important pathway for N<sub>2</sub>O production in the cerrado soils, while denitrification would be rare due to high acidity and high permeability to atmospheric O<sub>2</sub> (Pereira, 1982; Robertson and Tiedje, 1987). Once vegetation is burned, depending on fire intensity, most of the nitrogen in various forms is released from the biomass (Tamm, 1991). Meteorological conditions during and after fire determine how much of the ammonia, nitrate and aerosols released by the fire will return to the system in dry and wet precipitation, and how much will be subject to long-range atmospheric transport (Andreae, 1992). Another important effect of fire on the ecosystem is the release of other basic nutrients in the ashes, which temporarily diminishes aluminum saturation and raises soil pH (Coutinho, 1990), consequently changing conditions for the nitrogen biogeochemistry in the soil. Additionally, following fire consumption of plant aerial parts, the short-term termination of plant nutrient uptake contributes to larger transient pools of  $NH_4^+$  and  $NO_3^-$  in the soil. Nitrate, however, is quickly leached from the cerrado soils (Suhet and Ritchey, 1981 cited in Pereira, 1982).

Studies of another tropical savanna in South America during the dry season suggested that production of N<sub>2</sub>O would be larger in the wet

62

season (*Hao* et al., 1988). Agricultural soils converted from cerrado vegetation are especially important for their significance as one of the most extensive land-use changes occurring on the planet. And the potential for increasing episodic emissions to become significant due to heavy nitrogen fertilization as these natural ecosystems are converted to agriculture or pasture has been widely recognized (e.g.*Vitousek* and *Matson*, 1993; *Duxbury* et al., 1993).

In this paper, we report on a study carried out on a range of savanna ecosystems after prescribed fire disturbance. The study was designed to measure the  $N_2O$  emissions in fire-scared cerrado ecosystems during the wet season. Additionally, nitrogen and carbon fertilization experiments were conducted in fire scars, and  $N_2O$  emissions were measured in three well established agricultural fields of corn, soybean and pasture. The study was carried out at a site with ongoing long term ecological fire disturbance studies (Instituto Brasileiro do Meio Ambiente / Projeto Fogo).

# **Methods**

#### **Study Site**

The Roncador reservation, a 1300 ha ecological station of the Intituto Brasileiro de Geografia e Estatistica (IBGE), lies 35 km to the south of Brasilia, the Brazilian capital, within the federal district  $(15^{\circ}56' 41" \text{ S}; 47^{\circ}53' 07" \text{ W}, \text{ from 1048 to 1150 m asl approx. elevation}), in the core zone of the central Brazilian pre-Cambrian shield. The terrain of the reserve is mostly developed on Tertiary detritic-lateritic sediments ($ *CODEPLAN*, 1984). The local climate, as for most of central Brazil, is seasonal, an*Aw*in the Köpen classification. The dry season extends roughly from May to September, and the variation in air temperature is moderate between seasons. Annual climatic means are: temperature, approximately 21°C, 1667 mm precipitation and 1200 mm potential evapotranspiration (*Pereira*et al., 1989).

The N<sub>2</sub>O flux measurements in the fire-scars (FScars) were conducted for four types of savanna vegetation (Table II.1) which encompassed the full range of physiognomic forms (Figure II.1) for the cerrado sensu lato (Coutinho, 1990). In spite of the great heterogeneity of vegetation, local climate and soils occurring over this South American biome (e.g., Coutinho, 1990; Dias, 1992; Santos, 1988), the cerrado physiognomic forms represented in the four sites chosen for this study can be found on approximately 78% of the Brazilian savannas (Dias, 1992). All sites except the campo limpo (savanna grassland) were located on the most extensive high plateaus. The dominant soil on these plateaus falls within the oxisol order in the USDA classification (USDA, 1975), and is

classified as a *latossolo vermelho-escuro álico*, clayey-distrophic, in the Brazilian classification (*Pereira* et al., 1989). This soil, representative of soils covering 43% of the cerrado biome (*Adámoli* et al., 1986), is very permeable, has low water retaining capacity and is very deep. The natural fertility on its superficial layer is very low, with high acidity and high exchangeable aluminum levels (Table II.2) (*Pereira*, 1982). The savanna grassland site was located on a lower slope formed from a broad alluvial Cenozoic plain. The soil was hydromorphic and not classified but possibly a *gley humic* in the Brazilian classification.

The savanna fertilization experiment (FertEx) was carried out on a plot of cerrado *sensu stricto* (wooded savanna) which had not been burned since 1989.

The agriculture/pasture experiments (APEx) were conducted on nearby commercial plantations within a radius of 36 km from the Roncador reservation. All three sites were located on plateau oxisols equivalent to those for the upland Roncador reservation, and had been under cultivation for at least 10 years.

# **Experimental Design**

The experimental plots used in this study are part of a longer term experiment carried out to study the effect of prescribed fire on diverse aspects of the cerrado vegetation and direct-fire emissions to the atmosphere (Projeto Fogo). The design has five 500 x 200 m plots for each system: tree\shrub savanna (Cs), wooded savanna (Ct) and savanna woodland (Cd), (see Table II.3), and two larger irregular plots for savanna grassland (Cl). Within one five-plot block the plots were organized as follows: one plot unburned for the last 18 years (control), one plot burned in 1991 (year) and three plots burned in 1992 (one in the early dry season, June, another in the mid dry season, August, and the last in the late dry season, September). The two plots for Cl were: one plot burned in 1989 and one plot burned in 1992 (late dry season, September). Only the plots burned in the late dry season of 1992 were chosen for the FScars episodic N,O emission experiments in this study.

Because  $N_2O$  production and consumption in soil are discontinuous over time (e.g.Brumme and Beese, 1992; Davidson et al., 1991; Grundmann and Rolston, 1987; Johnsson et al., 1991; Mosier et al., 1991; Sexstone et al., 1985; Terry et al., 1981) sampling in this study was designed to document episodic processes. For the episodic measurements in FScars, in FertEx and in APEx, each of the experimental sites had one

1.6 x 3.2 m plot subdivided into two 2.56 m<sup>2</sup> sub-plots (repetitions). Each sub-plot was 1.6m-sided square with two basic components or installations: one PVC ring or collar inserted approximately in the center of the square, and one array of stainless steel soil-gas-phase probes (except for year and control plots at the Cs site and agriculture/pasture sites) for sampling at various depths, installed to one side of the collar and extending under it.

The simulated rain events were water/solution additions applied using a garden watering can. The water or solutions were sprinkled evenly onto the sub-plots over a period of 15 minutes so that they would percolate into the soil without forming standing water. For each simulated rain event, measurements were done at time zero, which immediately preceded the additions, and then at 30 minutes, 2, 4, and 8 hours, one day after the additions, and daily thereafter until completion of the experiment. Each series of measurements associated with one simulated rain event is called here simply Event #x, x being just a sequence number. Single flux measurements did not have time-steps. The distribution of episodic measurements for each treatment as well as additions for FScars, FertEx and APEx during the wet season can be found in Tables II.3, II.4 and II.5 respectively.

In FertEx the treatment plots were contiguous and were contained within a radius of 10 m. All the nitrogen and carbon sources

were dissolved immediately before irrigation in local well-water. Event # 1 (Table II.4) occurred 2 days before the prescribed fire, with the original unburned vegetation in place. For this event only water was added and only for one plot (two repetitions). Due to frequent rain, the prescribed fire could occur only after the experimental area had been protected from rain for three weeks. The fire was set at noon time and burned guickly and well (white ash). The collars set up for Event # 1 (control) were removed before the fire, and reinstalled after the fire in the same positions. For Event # 2 (Table II.4), there were three fertilizer treatments and a control with water alone. The fertilizers were sodium nitrate (NaNO<sub>1</sub>) at a level of 50 kg N  $\cdot$  ha<sup>-1</sup> as the first fertilizer treatment, glucose (dextrose,  $\alpha$ -D(+) C<sub>6</sub>H<sub>1</sub>,O<sub>6</sub>) at a level of 250 kg C  $\cdot$  ha<sup>-1</sup> as the second treatment, and nitrate at 50 kg N  $\cdot$  ha<sup>-1</sup> plus glucose at 250 kg C  $\cdot$ ha<sup>-1</sup> as the third treatment. The 5:1 C:N ratio used to obtain denitrifying potential was similar to that used in soil core incubation studies (Parsons et al., 1993; Schuster and Conrad, 1992).

For APEx, all fields had received lime (CaCO<sub>3</sub>), corn had received nitrogen fertilizer prior to the experiment, and soybean seeds had been inoculated with *Rhizobium japonicum* nitrogen-fixing bacteria. At each agricultural site one collar was positioned between plants within a row, and the repetition was placed between rows. At the pasture site, one

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

collar went on the soil between grass clumps, and the other directly on a grass clump. The history of previous cropping and fertilization was not available, however, these sites represented well established agribusiness enterprises. The scope for each agriculture experiment was limited to two episodic measurements, the first done approximately one month after planting, and the second near harvest, approximately 100 days after planting (Table II.5). The scope for the pasture experiment was limited to one episodic measurement done at the beginning of the wet season, and then one single flux measurement done 100 days later (Table II.5).

# **Field Sampling**

The chamber enclosure technique used to quantify trace-gas exchange between soil and atmosphere has been widely used and is discussed at length by (*Hutchinson* and *Livingston*, 1993). The technique used was identical to the one used for the study discussed in Chapter 1. In this study, the two-part static vented-chambers consisted of a 25 cm internal diameter, 10 cm tall, polyvinylchloride (PVC) ring or collar and a molded acrylonitrile-butadiene-styrene (ABS) plastic top, 10 cm tall, with a gas sampling port, a pressure equilibration port, and a lip that fit over the PVC ring (*Matson* et al., 1990). The chamber top was well aerated before the beginning of each N<sub>2</sub>O flux measurement. The lip of the top was greased lightly with silicon grease (Apiezon) and the collar capped

69

tightly with it. Gas samples, withdrawn through an injection port at 1, 7, 14, 21 and 28 minutes after closure, were collected using 20 ml nylon syringes (S.E.S.I., VWR Scientific), each fitted with two butyl rubber o-rings (greased with Apiezon), and polypropylene stopcocks (Baxter Scientific). Each flux measurement consisted of a five syringe sample set (see Appendix A for detail in method), after which the chamber closure was opened. Air temperature was taken during the sampling. Nitrous oxide flux was calculated by regressing the linear change over time of the N<sub>2</sub>O mixing ratio in the chamber enclosure (*Keller* et al., 1986).

One week prior to the experiment the collar was inserted approximately 2 cm into the top soil. The reduced root mat coverage in the cerrado, compared with the Amazonian ecosystems, was similar to the La Selva sites, in that enhanced gas emissions with early insertion of rings into the soil was not a problem (see Part I and *Matson* et al., 1990). The sampling of soil-gas was carried out, similarly to the procedure used in La Selva, using horizontal probes made of stainless steel tubing (3.17 mm oD) formed into an L shape, installed adjacent to the PVC collar, at depths of 2, 5, 10, 20, and 40 cm (similar to those in Figure I.1). The drawing portion of the probe tubing, approximately 10 cm long, had 20 small holes drilled through the wall, distributed along its length. The upper part of the L ( 2 cm) was bonded (epoxy setting glue) to a capillary

70

stainless steel tubing (1.59 mm OD) leading upward outside the soil. On top, a cut-off hypodermic needle (1.59 mm OD) with a luer slip lock was hooked to the stainless steel tubing, tip to tip, using a short piece of polystyrene tubing. During the intervals between sampling, a plastic cap was used on the slip lock end to seal the probe from the atmosphere and from dirt.

#### Laboratory Analysis

Nitrous oxide was determined for one 2 ml sub-sample for each 20 ml field sample, using a Mini2 Shimadzu gas chromatograph fitted with stainless steel columns (3.2 mm od by 2 m), packed with 50-80 mesh HaySep (backflush column) and 50-80 mesh Porapaq Q (main column), and a <sup>63</sup>Ni electron capture detector. Operating conditions were: column temperature, 70° C; electron capture detector temperature, 300° C; P5 mixture (95% Ar with 5% CH<sub>4</sub>) carrier gas with a flow rate of 30 ml · min<sup>-1</sup>. The gases N<sub>2</sub>O and CO<sub>2</sub> were separated, but only N<sub>2</sub>O mixing ratios were quantified. Oxygen was removed from the carrier gas using an oxygen trap (Altech Oxy-Trap<sup>TM</sup>), and hydrocarbons, CFC's, etc. were removed with a mol-sieve purifier filter. Water vapor was removed from all samples with a pre-column of moisture absorbent (CaSO<sub>4</sub> - Dryrite<sup>TM</sup>). The standards used in the analysis were nitrous oxide in dinitrogen gas mixtures, at 338, 513 and 971 ppbv (Scott Specialty Gases), with the

71

lowest (338 ppbv) calibrated against NOAA (Nitrous Oxide and Halocarbons Division, Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado) secondary standards. The precision of this instrument was 1.9 % (standard deviation / mean). The minimum flux of N<sub>2</sub>O that could be detected with this system over a 28-min period at 25°C was 0.3 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>.

#### **Results and Discussion**

#### Savanna Fire-Scar Experiments (FScars)

Figures II.2 and II.3 show time series data on experimental results for soil-gas-phase N<sub>2</sub>O mixing ratios profiles and N<sub>2</sub>O fluxes.

Savanna Grassland (Cl) . At the Cl site,  $N_2O$  averaged fluxes were either negative or remained close to background levels throughout the measured period after fire (Figure II.2.A) . The single measurements made 15/Nov/92, 55 days after fire (d.a.f.), and 18/Feb/93, 150 d.a.f., showed that the  $N_2O$  mixing ratios to depths of 20 cm were either lower or indistinguishable from atmospheric mixing ratios (ambient, 310 ppb). The apparent difference between the two dates in the gas profile can be directly tied to soil moisture. The water table was very close to the surface, oscillating between 20 to 30 cm. In November, well into the wet season, the

soil column above the water table was so saturated that the sampling of soil-gas could not be done without unintentionally collecting soil water into the syringes. The mixing ratios reported here are those of the syringe headspace. There seemed to be a sink for  $N_2O$  at this date, given the somewhat strong downward gradient in the soil. Waterlogging induces anaerobiosis, which in turn promotes N<sub>2</sub>O reduction to N<sub>2</sub> (for a review of denitrification in subsurface environments see Rice and Rogers, 1993). In February of 1993 there had been a veranico (short dry spell in the wet season) during the time of the second measurement. On the second date, the soil sampling showed no N<sub>2</sub>O mixing ratio gradients in the profile, indicating neither production nor consumption with depth. Most likely this was due to the dryer conditions, but also due to vigorous growth of grass on the surface, indicating low nitrogen substrate availability for denitrification. The water addition two days after the second measurement of the flux and the gas profile made fluxes slightly negative. However, the magnitude of this change was not meaningful because it was below detection limit (BDL) for this study.

If one assumes that these few measurements are representative of fire-scar emission behavior, it is possible that during the wet season burned Cl savannas may be a net sink for tropospheric N<sub>2</sub>O. But with the highest measured sink-flux only 1 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup> it is unlikely that

this kind of savanna, which covers only 5.5 % of the cerrado (Table II.1), is of major importance in the overall cerrado N<sub>2</sub>O budget.

Tree/shrub savanna (Cs). Forty three days after fire (29/Oct/92) the N<sub>2</sub>O soil mixing ratio profile for Cs (Figure II.2.B) showed a consistent episodic pulse production after 20 mm of simulated rainfall. However, the N<sub>2</sub>O pulse is best expressed at 5 cm depth and does not translate into higher fluxes at the surface; with the exception of the flux which occurred two hours after simulated rain, all other fluxes for Event #1 fell below detection level. At time 0, immediately before the simulated rainfall, a weak gradient of N<sub>2</sub>O mixing ratios existed with depth, which could indicate increased background production with increasing depth. During pulse progression, a time lag occurred with greater mixing ratios with increasing depth (10, 20 and 40 cm), which indicated that the pulse for those depths resulted mostly from downward diffusion of  $N_2O$ . That can be a corroboration on the inference that  $N_2O$ is being produced primarily in the layer from 2 to 5 cm deep. Eight hours after simulated rainfall, the episodic pulse was over, and the mixing ratio gradient was reduced to virtually zero, a condition which remained unchanged until the end of the episodic measurement at 24h. An estimated integrated production of 0.2 g N<sub>2</sub>O-N · ha<sup>-1</sup> (·24h<sup>-1</sup>) fell BDL (Figure II.3.A; Table II.6).

74

For Event #2, 150 days after fire, there was a small background emission of 1 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup> before the simulated rainfall (Figure II.3.A). After 20 mm water addition most other flux measurements fell BDL. The soil N<sub>2</sub>O mixing ratio showed a much less intense pulse throughout the profile than observed during the pulse in Event #1, but indicated some brief disturbance associated with the water addition (Figure II.2.B). The Event #2 disturbance could be ascribed to physical displacement of soil atmosphere by percolating water, and to some momentary gas build up due to waterlogging of diffusional pathways from production microsites (or production in deeper layers) to the atmosphere. The estimated integrated production of 0.1 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup> in a one day episodic flux fell BDL (Table II.6).

The two other treatments with single measurements in the tree/shrub savanna, which is the control plot burned 18 years before the experiments, and the year plot burned in 1991(one year before the 92 prescribed fires), showed similar flux behavior (Figure II.3.A).

In conclusion, during the wet season the Cs savanna showed very weak or undetectable  $N_2O$  fluxes to the atmosphere, be it quasi-climax, 18 years after fire (a.f.), an imperceptible fire-scar (1 year + a.f.), or a still fresh fire-scar (less than two to more than five months a.f.). If this kind of vegetation, which occupies nearly 12 % of the cerrado biome (Table II.1), were to become of any potential importance as a net source of  $N_2O$ , it very likely would not be from emissions occurring during the main part of the wet season.

**Wooded Savanna (Ct)**. The  $N_2O$  soil gas profiles for Ct (Figure II.2.C) for 9/Nov and in 8/Dec/92, showed no episodic pulse associated with simulated rainfall for additions. For Event #1, the water addition lead to a progressive decrease in mixing ratios for up to 8 h from simulated rainfall. For Event #2, the water addition lead to a progressive increase in mixing ratios up to 4 h after the simulated rainfall. Throughout the profile time series for both events, a slight upward mixing ratio gradient was noticed, which should translate into some flux to the atmosphere on the surface. However, from the six flux measurements over the course of each event, only three in Event #1 and only two in Event #2 were slightly above detection limit.

The single measurement for 28/Feb/93, 166 d.a.f. (Figure II.2.C), shows a close similarity with the undisturbed condition in Event #2, 84 d.a.f.. The integrated gas production for both events showed that over one day the amount of gas

emitted/consumed fell BDL or slightly above, with 0.6 g  $N_2O-N \cdot ha^{-1}$  in Event #2 (Figure II.3.B; Table II.6).

During the wet season, a fire-scared Ct savanna (less than two, three and more than five months a.f.) showed very weak or undetectable  $N_2O$  episodic or background fluxes to the atmosphere. Thus, emissions during the main part of the wet season for this vegetation, which occupies 53 % of cerrado biome (Table II.1), probably will not become important as a net source of  $N_2O$ .

Savanna Woodland (Cd) . From the two events in the Cd savanna, only the second, 70 d.a.f., produced an episodic pulse, most intense at 2 h after simulated rainfall (Figure II.2.D). In the first event, 1/Nov/92, 40 d.a.f., water addition seemed to have slightly depressed soil  $N_2O$  mixing ratios. Nevertheless, for both events and for almost all time-steps, there was a weak upward gradient in soil-gas  $N_2O$  mixing ratios. Noteworthy here was the sizable difference in fluxes between repetitions, indicating a strong spatial heterogeneity. The integrated fluxes for both events showed either a non-detectable or a very low  $N_2O$ emission (Figure II.3.C; Table II.6).

The savanna woodland showed that despite weak upward soil  $N_2O$  gradients, and a detectable pulse in soil  $N_2O$  mixing ratios, fluxes at

the soil surface were less than 0.3 g  $N_2O-N \cdot ha^{-1} \cdot d^{-1}$ . With 8.3 % cover for the cerrado biome (Table II.1), during the wet season this kind of savanna is not likely to be of key importance for overall ecosystem  $N_2O$ emissions.

# Cerrado FScars Emissions in Comparison with Emissions in other Similar Ecosystems

Hao et al. (1988) measuring N<sub>2</sub>O emissions during the dry season from soils in Gran Sabana ecosystems, Venezuela, found a mean flux from undisturbed plots to be 0.5 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>. The fluxes were not significantly affected by burning the grass layer, but increased 5 fold upon water addition. *Matson* et al. (1991) studying sagebrush steppe ecosystems in Wyoming, USA, found annual mean N<sub>2</sub>O fluxes varying from 0.03 to 1 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup> with an area-average of 0.6 g N<sub>2</sub>O-N  $\cdot$ ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>. *Mosier* et al. (1991) studying two native grasslands in North America found fluxes of 1.8 and 3 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>.

The range of values found for  $N_2O$  emissions in the present study were similar. The fluxes for the Gran Sabana were the closest to the ones measured for the Brazilian cerrados (FScars), despite measurements in different seasons, suggesting that the nitrogen biogeochemistry for all tropical savannas in South America may be similar. The increase in flux after simulated rainfall in the dry season (*Hao* et al., 1988), and the lack of comparatively increased fluxes during the wet season, suggests that in the tropical savannas the main  $N_2O$ episodic emission should occur in the transition from the dry to the wet season, similarly to what was reported for a tropical deciduous forest in Mexico (*Garcia-Mendez* et al., 1991).

#### The Savanna Fertilization Experiment (FertEx)

In FertEx there are three important aspects that complement the information from FScars. The first is that the measurements made immediately before the fire event for Event #1 were made at the same site. The second aspect is water was added immediately following the fire. All the simulated rainfalls for FScars happened more than one month after fire, which missed the loss/gain of nitrogen substrates due to the fire itself, the immediate impact of ash input to the soil, and the temporary cessation of vegetative absorption of substrate from the soil. The third aspect of FerEx that complements FScars is that substrate/fertilizers were added in the former so that the differentiated  $N_2O$  emission response could provide clues to the biogeochemical limitations in the soil.

**Control Treatment**. For the control treatment, measurements taken both before and after the fire event showed clear responses to water addition (Figure II.4.A). The effect of fire on the water stimulated pulses was clear throughout the profile, but was most intense at depths of 5 and 10 cm. The briefness of these pulses indicated an intermediate transient pool of  $N_2O$  during nitrate reduction to  $N_2$ . The absence of lags in the pulses throughout the profile corroborates this interpretation, because  $N_2O$  was reduced before it had time to diffuse up and down.

In the pre-fire Event #1, the small episodic pulse was reflected on the soil surface with a small flux peak, which did not translate into positive emissions into the atmosphere (Figure II.5.A). For both events there were weak upward mixing ratio gradients. Integrated fluxes showed that Event #1, with plants present, produced no N<sub>2</sub>O in 24 h, while Event #2, with the ashes from the fire, produced 1.8 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> in 96 h (0.45 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>) (Figure II.5.A). This latter flux is only slightly above detection limit (Table II.7).

This control treatment in FertEx showed that immediately after fire, the behavior of  $N_2O$  episodic gas emission in a wooded savanna during the wet season is not substantially different than that of other similar systems, at one, two and five+ months after fire. However, these

experiments do not represent the soil biogeochemical state at the end of the dry season when substrate for denitrification has accumulated from decomposition and mineralization/nitrification. Most fires occur at the end of the dry season (August/September). So the prescribed fire in January for FertEx did not represent the soil conditions at the end of the dry season because a considerable volume of rain had percolated through the soil by that time, leaching substrates and stimulating biogeochemical processes to consume them. This prescribed fire was interesting insofar as it produced a sudden release of ashes on the previously protected and dry soil, and because it destroyed plants, ceasing plant nutrient absorption temporarily.

**Nitrate-N Treatment**. The Nitrate-N treatment clearly showed that nitrate is the most limiting substrate for N<sub>2</sub>O production in this soil (Figure II.4.B). First, the pulses for Event #2 were broader, indicating that the nitrous oxide formed into a transient pool was not quickly consumed, and had time to diffuse out into the atmosphere. The fluxes measured on the soil surface showed a clearly distinguishable pulse associated with the pulse inside the soil profile. Second, the overall production of 4.3 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> in 96 h (1.1 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>) was more than twice that of the control and glucose treatments (Figure II.5.B; Table II.7). However, this emission response was less than half of that for the equivalent treatment in a Costa Rican volcanic sandy soil (Vegas Nitrate-N, Part I), and one order of magnitude smaller than that for a volcanic clayey soil (Flaminia Nitrate-N, Part I).

**Glucose-C Treatment**. The profile results for Event #2 in the Glucose-C treatment showed a lack of extra response to water + glucose, if compared with water alone (Figure II.4.C). For comparison, the data plotted for Event #1 is the same as that for the control treatment. As in the control treatment, there were weak upward mixing ratio gradients, and the integrated production showed the same production as with water alone, that is 1.8 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> in 96 h (0.45 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>) (Figure II.5.C; Table II.7). The fact that glucose did not produce enhanced emissions here, as opposed to the increments in emissions observed in Costa Rica (Part I), is an indication that there are other limitations to denitrification in the Brazilian savanna, most likely a very low level of nitrate availability in the soil.

<u>Nitrate-N</u> + <u>Glucose-C Treatment</u>. A surprising result of this treatment was enhancements in  $N_2O$  mixing ratios for Event #2 throughout the period of observation, most intense at depths 10 and 20 cm (Figure II.4.D). Also striking were the differences between the two repetitions and the temporal extent of the enhancement. The gas production in the soil began with the addition of water + substrates, but it did not come back to the background level after the few hours as was common for most peaks in the other treatments. A synergistic effect between nitrate and glucose was evident. Glucose alone did not produce an effect, nitrate alone doubled emissions, and nitrate plus glucose quadrupled emissions; thus, compared with nitrate alone glucose helped the system to use up nitrate with doubled efficiency.

Total emission of 9.1 g  $N_2O-N \cdot ha^{-1}$  in 96 h (2.3 g  $N_2O-N \cdot ha^{-1} \cdot d^{-1}$ ) was about twenty times less than that of the equivalent treatment in the Costa Rican sandy Vegas soil, and one order of magnitude less than that of the equivalent treatment in clayey Flaminia soil (Part I) (Figure II.5.D; Table II.7).

# **Agriculture**/**Pasture Experiments** (APEx)

**Corn** (*Zea mayz*). In the Corn field, the emissions of Event #1 were the most striking and consistent of all APEx episodic measurements (Figure II.6.A). The highest emissions were found between rows, precisely where nitrogen fertilizer ( $(NH_4)_2SO_4$ ) was spread prior to the crop planting. Emissions within rows, where plant roots developed and supposedly absorbed most nutrients, were minimal. The total averaged emission of 3.7 g  $N_2O-N \cdot ha^{-1}$  in 24 h is equivalent to that of the Nitrate-N treatment of FertEx (Tables II.7 & II.8).

More than three months later, near the harvest, the emissions for Event #2 were minimal, with little difference between inter- or intra-row measurements. The total averaged emission of 0.6 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> in 24 h was six times smaller than the emissions in Event #1 and slightly above detection limit, indicating the possibility that the system was depleted of nitrogen substrate due to plant absorption, leaching and/or nitrification/denitrification gaseous losses (Table II.8).

In a review of N<sub>2</sub>O emissions from fertilized soils, *Eichner* (1990) listed four studies in temperate corn fields for which results ranged from 0.0 to 25.9 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>, and averaged of 12 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>. *Mosier* and *Hutchinson*, (1981) studying N<sub>2</sub>O emissions for the whole cycle of an irrigated corn plantation in northern Colorado, USA, found that on the average the system emitted 35.8 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup>  $\cdot$ d<sup>-1</sup>. They also found that approximately 30 % of the N<sub>2</sub>O was emitted during the first two weeks following fertilization, while NH<sub>3</sub> was being rapidly nitrified, and 59 % was emitted during the week following the first irrigation of the field, when restricted oxygen diffusion favored

denitrification. These facts suggest that the two episodic measurements in the present study might have missed the main emission periods soon after fertilization and soon after the first rainfalls.

In another similar study of  $N_2O$  plus  $N_2$  loss from denitrification on corn and barley fields in northern Colorado, *Mosier* et al. (1986) showed, that in the corn field, about 70 % of the total N gas emitted was  $N_2O$ . Based on this result, it was concluded that denitrification might play a smaller role in agricultural gaseous nitrogen loss than was traditionally believed. The present study agrees with that conclusion; the lack of episodic pulses following simulated rainfall suggests that denitrification is not a major pathway for  $N_2O$  production in this soil.

Soybean (*Glycinea\_max*). Unlike the corn field, emissions from the soybean field increased with time (Figure II.6.B), which can be an indication that *Rhizobium* fixed nitrogen was being liberated into the soil. With 1.29 g N<sub>2</sub>O-N  $\cdot$  ha<sup>-1</sup> in 24 h, 2.6 times more N<sub>2</sub>O was emitted, on average, for Event #2 than for Event #1 (Table II.8).

Here, similar to the corn field, water addition depressed emissions strongly. So in dry weather it is likely that emissions would be

many times larger than the totals registered in the two events here, as the flux measurements made before water additions indicate. Because atmospheric  $N_2$  fixed by *Rhizobium* first becomes  $NH_4$ , nitrification must proceed before nitrogen substrate is available for denitrification. The fact that water addition depressed  $N_2O$  emission, instead of enhancing it as in systems where denitrification is strong, suggests that nitrification is the main pathway for  $N_2O$  production in this agroecosystem.

Annual average  $N_2O$  emissions measured by *Bremner* et al. (1980), from soybeans fields on six different temperate soils, ranged from 0.9 to 5.4 g  $N_2O$ -N  $\cdot$  ha<sup>-1</sup>  $\cdot$  d<sup>-1</sup>. More than ten years ago, *Pereira* (1982) estimated that the approximate nitrogen input to the Brazilian cerrados via fixation in soybean crop fields would be  $0.15 \cdot 10^9$  Kg N  $\cdot$  yr<sup>-1</sup>, for a soybean production of about  $3 \cdot 10^9$  Kg  $\cdot$  yr<sup>-1</sup>. *Eichner* (1990) estimated total world wide N<sub>2</sub>O emissions from fields of cultivated legumes to be 23 to 315 Gg N<sub>2</sub>O-N in 1986. Soybean is one of the most important cash crops in the cerrado biome. Because soybean does not require nitrogen fertilization, it is generally planted in infertile soils, and after several growing seasons the harvest debris is turned under until the incorporated plant biomass renders the soils more fertile for other more demanding crops, like corn or wheat.

**Pasture** (*Paspalum* grass). Water addition in the pasture site strongly depressed emissions for a short while. The total production over Event #1 of  $0.5 g N_2 O - N \cdot ha^{-1}$  in 24 h (Figure II.6.C) was equivalent to Event #1 in the soybean field and Event #2 in the corn field (Table II.8). This production was also marginally larger than the minimum flux detection limit for the system used to measure it, and did not differ substantially from most events in the experiments of FScars upland plateaus. The differences in emissions from a grass clump to the sample between grass clumps indicated an effect of plant absorption on the overall availability of substrate for nitrification. Production in dry weather appeared to be greater than that with rain events. The single measurement made two months after the episodic measurement also did not show any extraordinary production. Pastures might be a relevant source of N<sub>2</sub>O only in those areas fertilized directly by animal urine and feces.

The magnitude of  $N_2O$  emissions found for this pasture was 5 to almost 300 times smaller than that found for pastures of varying ages after deforestation of Costa Rican rainforests (*Keller* et al., 1993), or 10 to 50 times smaller than a fertilized pasture in the Amazon (Luizão et al., 1989). Compared with emissions in temperate grasslands on sandy loam soils, for this study  $N_2O$  emissions still were 5 times smaller than the

unfertilized pasture and 12 times smaller than the fertilized pasture (*Mosier* et al., 1991).

Pastures are one of the most characteristic uses of the savannas of central Brazil because they somewhat resemble the original system. Extensive areas of savanna grassland and tree/shrub savanna are historically used for low intensity cattle ranching. Some areas are totally disturbed, with substitution of original grasses by exotic species and by liming and fertilization, in addition to cultural practices like the use of fire and decompaction (plowing) to periodically renew the grass. The pasture studied here was one under intensive management.

# Importance of the Conversion of Cerrado to High Input Agriculture

Large scale human interference in the nitrogen cycle is recognized as one of the most likely causes of the increasing  $N_2O$ atmospheric mixing ratio (*IPCC*, 1990). The land-use conversion rate for the last twenty years in the Brazilian cerrado has been alarming (*Dias*, 1992). By 1982, the area permanently cleared in savannas each year world-wide was half the area cleared in forests (*Lanly*, 1982). Despite edaphic and hydric limitations of the cerrado natural soils, factors like their excellent topography and texture for mechanized agriculture; together with liming, fertilization and irrigation techniques; low labor and land acquisition costs; extensive network of roads and proximity to major export corridors and consumer centers have rendered these ecosystems very attractive for high input cash-crop agribusiness enterprises, which are rapidly transforming this region into one of the largest grain belts in the world (*Dias*, 1992; *Pereira*, 1982).

Besides the attractions for agricultural frontier expansion, there are no provisions in the new Brazilian Constitution for the protection of savanna ecosystems (*Dias*, 1992) as there are for the Amazonian and Atlantic rainforests, and for other less extensive biomes under attack by encroaching development. Unless external factors change the dynamics of the present explosive frontier expansion, like fluctuations in cash-crop market prices, in time a total conversion of the Brazilian cerrados into high input agroecosystems will be almost unavoidable. Given this scenario, it is of paramount importance that the impact of this continental conversion of savanna ecosystems be better studied for its role as a potential additional source for radiatively active trace-gases.
#### **Conclusions**

The series of experiments with fire scared savanna soils, fertilization and fire effects and agriculture/pasture emissions of  $N_2O$ reported in this paper indicate that water additions do not stimulate intense pulses of  $N_2O$  emissions in this soil system.

The data in the  $N_2O$  mixing ratios profiles showed strong temporal coherence among the several layers, although the biogeochemical interpretation could not explain disagreement between the patterns observed in the soil and some of the associated patterns of emissions on the soil surface.

In the fertilization experiments,  $N_2O$  emissions were found to respond differently depending on which kind of fertilizer was used. The fact that nitrogen (but not carbon) produced a response, and that carbon could only enhance  $N_2O$  response when both substrates were applied together suggests that these soils were critically limited in nitrogen substrate. Small pulses of production could develop quite superficially in the soil, especially between 5 to 10 cm, and can develop to a maximum strength within the range of 30 min. to 2 hours. The episodic part of the flux occurring in brief transient oscillations in the background flux after a rain event could not differentiate the emission regimen. Those episodic faint pulses associated with liquid amendment varied slightly in intensity and duration among treatments. For the Fire-Scars and for the Agriculture/Pasture the depression in fluxes promoted by water addition suggested a lack of denitrification for these soils. The higher emission rate on dryer soil suggested that nitrification is the main biogeochemical N<sub>2</sub>O production pathway.

During the wet season the cerrado biome does not appear to be a major source of  $N_2O$  to the troposphere, even following fire events. However, the results of this study suggest that conversion of the cerrado to high input agriculture, with liming and fertilization, can increase  $N_2O$  emissions more than ten fold.

The cerrado biome as such, and during the wet season does not seem to be a major source of  $N_2O$  to the troposphere, not even after fire events. However, the results of this study have suggested that its conversion to high input agriculture, with liming and fertilization, can increase  $N_2O$  emissions more than ten times.

92

1

IDDIC II.I. ACACCACTON CAPCO AND ACHCEAT PRODUCTOR INC DAAMMAD IN CONCEAT DIA	Table II.1.	<b>I.1.</b> Vegetation ty	vpes and ge	eneral prope	erties for	the	savannas	in	central	Braz:	11
---	-------------	---------------------------	-------------	--------------	------------	-----	----------	----	---------	-------	----

Abbreviation - Type (portuguese name)	Area in 1000 km <sup>3</sup> (% of total for the biome)	Density trees/ha	Tree canopy cover
Cl - Savanna grassland (campo limpo)	112 (5.5)	0	0
<b>CS - Tree and/or shrub savanna</b> (campo sujo)	236 (11.6)	500	< 2
Ct - Wooded savanna (cerrado sensu stricto)	1080 (53.0)	1000	2 - 15
Cd - savanna woodland (cerrado denso ou Cerradão)	169 (s.3)	3000	15 - 40

\* from Sarmiento (1983) and Azevedo & Adámoli (1988)

Soil	Vegetation Type (portuguese name)								
Parameter	Ct - Savanna grassland (campo limpo)	Cs - Tree/shrub savanna (campo sujo)	Ct <b>- Wooded savanna</b> (cerrado sensu stricto)	Cd <b>- Savanna woodland</b> (cerrado denso)					
-1	22	26	24	20					
	33	36	34	32					
Silt (%)	20	16	15	16					
Sand (%)	46	18	51	53					
<b>pH</b> (H <sub>2</sub> O)	4.9	4.9	5.0	5.1					
Organic C (%)	2.2	2.3	2.4	2.3					
CEC (meq%)	1.1	1.2	1.4	1.8					
<b>Al<sub>3</sub></b> <sup>+</sup> (meq%)	0.7	0.6	0.7	0.6					
Al <sub>3</sub> <sup>+</sup> Sat. (%)	66	58	54	44					
Ca (meq%)	0.2	0.3	0.5	0.7					
Mg (meq%)	0.7	0.1	0.2	0.4					
K (meq%)	0.1	0.1	0.1	0.1					
P (ppm)	0.5	0.5	0.9	2.1					
<b>Zn</b> (ppm)	0.6	0.6	0.7	0.7					
Cu (ppm)	0.6	0.8	0.9	1.3					
Mn (ppm)	5.4	10.3	15.9	22.9					

**Table II.2.** Main superficial soil properties for the savannas in central Brazil<sup>\*</sup>

\* data from Lopes(1975, cited in Santos, 1988); average of 520 samples

Abbreviation - Type (portuguese name)	Site's Last Fire in	Episodic Event#1	Episodic Event#2	Single Measurements
<b>Cl- Savanna grassland</b> (campo limpo)	Sept/21/92	none	20mm water Feb/18/93 [150 d.a.f]	Nov/15/92 [55 d.a.f]
<b>Ct</b> - Wooded savanna (cerrado sensu stricto)	Sept/16/92	20mm water Nov/9/92 [55 d.a.f]	20mm water Dec/8/92 [84 d.a.f]	Feb/28/93 [166 d.a.f]
Cd - Savanna woodland (cerrado denso ou Cerradão)	Sept/23/92	20mm water Nov/1/92 [40 d.a.f]	20mm water Dec/1/92 [70 d.a.f]	Feb/28/93 [158 d.a.f]
CS - Tree and/or shrub savanna (campo sujo)	Sept/15/92	20mm water Oct/29/92 [44 d.a.f]	20mm water Feb/11/93 [150 d.a.f]	none
<b>CS - Tree and/or shrub savanna</b> (campo sujo) [Proj.Fogo's Year treatment]	1991	none	none	Oct/29/92 & Feb/11/93 [1 year a.f]
<b>CS - Tree and/or shrub savanna</b> (campo sujo) [Proj.Fogo's <i>Control</i> treatment]	1974	none	none	Oct/29/92 & Feb/11/93 [18 years a.f.]

Table II.3. Vegetation types and treatments for Savanna Fire-Scars Experiment (FScars)

d.a.f.= days after fire; Proj.Fogo = joint IBAMA/USForest-Service Project Fire

Treatment Plot	<b>Event#1**</b> Jan/10/93	Prescribed Fire Jan/12/93	<b>Event#2</b> Jan/12/93
Control	20mm water	burned well	20mm water
Nitrate-N	none	burned well	20mm water + 50 kg NaNO <sub>3</sub> - <b>N</b> /ha
Glucose-C	none	burned well	20mm water + 250 kg Glucose- <b>C</b> /ha
Glucose-C + trate-N	none	burned well	20mm water + 50 kg NaNO <sub>3</sub> - <b>N</b> /ha + 250 kg Glucose- <b>C</b> /ha

Table II.4. Treatments for the Savanna Fertilization Experiment (FertEx)

\* Fertilization experiment carried out on Ct - Wooded Savanna; \*\*Last burned before Event#1 in 1989

Crop	Site Planted in	Episodic Event#1	Episodic Event#2	Single Measurement
Corn (Zea mayz)	Nov/14/92	20mm water Dec/13/92 [29 d.a.p]	20mm water Feb/20/93 [98 d.a.p]	none
Soybean (Glycinea max)	Nov/14/92	20mm water Dec/20/92 [36 d.a.p]	20mm water Feb/21/93 [99 d.a.p]	none
Pasture (Paspalum grass)	Old	20mm water Dec/26/92	none	Feb/23/93

Table II.5.	Crop a	nd treatments	for th	e Agriculture/Pasture	Experiment	(APEx)

d.a.p.= days after planting

<b>Type</b> (portuguese name)	Episodic Event#1	Episodic Event#2		Sing Measure	le ments
	none	none	date :	L 0.? (	BDL)
(campo limpo)			date 2	2 0.? (	BDL)
<b>Ct</b> - Wooded savanna (cerrado sensu stricto)	-0.3	0.6		0.? (	BDL)
Cd - Savanna woodland (cerrado denso ou Cerradão)	0.7	0.3		0.? (	BDL)
CS - Tree and/or shrub savanna (campo sujo)	0.2 (BDL)	0.1 (BDL)		non	e
Cs - [Proj.Fogo's Year treatment]	none	none	date 1	0.? (	BDL)
			date 2	0.? (	BDL)
<b>Cs</b> - [Proj.Fogo's <i>Control</i> treatment]	none	none	date 1	0.? (	BDL)
			date 2	0.? (	(BDL)

### Table II.6. Mean $N_2O$ Flux Measurements (in g $\mathbf{N} \cdot ha^{-1} \cdot d^{-1}$ ) for FScars

BDL = below flux detection limit of analytical system and measurement technique,

which was 0.3 g  $N_2O-N \cdot ha^{-1} \cdot d^{-1}$ 

Treatment Plot	<b>Episodic</b> <b>Event#1</b> (Before Fire)	<b>Episodic</b> <b>Event#2</b> (After Fire)		
Control	0.? (BDL)	1.8		
Nitrate-N	none	4.3		
Glucose-C	none	1.8		
Glucose-C + trate-N	none	9.1		

Table II.7. Mean  $N_2O$  Flux Measurements (in g  $N \cdot ha^{-1} \cdot d^{-1}$ ) for FertEx

BDL = below flux detection limit of analytical system and measurement

technique, which was 0.3 g N<sub>2</sub>O-N·ha<sup>-1</sup>·d<sup>-1</sup>

Table	II.8.	Mean	N <sub>2</sub> O	Flux	Measurements	(in	g	$\mathbf{N} \cdot \mathbf{ha}^{-1} \cdot \mathbf{d}^{-1}$ )	for	APEx
-------	-------	------	------------------	------	--------------	-----	---	---	-----	------

Crop	Episodic Event#1	Episodic Event#2	Single Measurement
Corn (Zea mayz)	3.7	0.6	none
Soybean (Glycinea max)	0.5	1.3	none
Pasture (Paspalum grass)	0.5	none	0.? (BDL)

BDL = below flux detection limit of analytical system and measurement

technique, which was 0.3 g N<sub>2</sub>O-N·ha<sup>-1</sup>·d<sup>-1</sup>



Figure II.1. The forest-savanna-grassland ecocline in central Brazil. Modified from Countinho (1990).



## Savanna Grassland CI

Figure II.2.A. FScars soil time-series data for savanna grassland (Cl) site.  $N_2O$  exchange flux with the atmosphere is shown on top of the soil profile, associated with soil gas-phase  $N_2O$  concentrations. An event refers to the addition of water to the experiment, and includes the subsequent drying period until the next event or until the end of the experiment. The atm. lines indicate ambient  $N_2O$  mixing ratio (310 ppbv). There are two repetitions for each point/time (dashes). Averages are also shown (circles). Dates shown on the graph correspond to the beggining of the events. Points not connected by lines indicate single measurements for the given date.



Figure II.2.B. FScars soil time-series data for tree/shrub savanna (Cs) site. Other features are the same as for Figure II.2.A.



Figure II.2.C. FScars soil time-series data for wooded savanna (Ct) site. Other features are the same as for Figure II.2.A.



Figure II.2.D. FScars soil time-series data for savanna woodland (Cd) site. Other features are the same as for Figure II.2.A.



Figure II.3.A. FScars N<sub>2</sub>O emissions for tree/shrub savanna (Cs) site. The cumulative curves, or running totals, are integrated summations of interpolated intervals of the minimum sampling period (30 min.) for the entire event period. For a comparisson in this site, N<sub>2</sub>O fluxes from a control plot not burned since 18 years and other plot burned 1 year before are shown on the upper left corner. E.P.G. means event produced gas. Other features of the flux plots are the same as for Figure II.2.A.





Figure II.3.B. FScars N<sub>2</sub>O emissions for wooded savanna (Ct) site. Other features are the same as for Figure II.3.A.

### Savanna Woodland (flux) Cd



Figure II.3.C. FScars N<sub>2</sub>O emissions for savanna woodland (Cd) site. Other features are the same as for Figure II.3.A.



Figure II.4.A. FertEx soil time-series data for Control treatment. N<sub>2</sub>O exchange flux with the atmosphere is shown on top of the soil profile, associated with soil gas-phase N<sub>2</sub>O concentrations. An event refers to the addition of water to the experiment, and includes the subsequent drying period until the end of the experiment. The atmospheric lines indicate ambient N<sub>2</sub>O mixing ratio (310 ppbv). There are two repetitions for each point/time (dashes). Averages are also shown (circles). Event #1 was carried out on vegetation covered soil, and only for the control treatment.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



Figure II.4.B. FertEx soil time-series data for Nitrate-N treatment. Other features are the same as for Figure II.4.A.



Figure II.4.C. FertEx soil time-series data for Glucose-C treatment. Other features are the same as for Figure II.4.A.



Figure II.4.D. FertEx soil time-series data for Nitrate-N + Glucose-C treatment. Other features are the same as for Figure II.4.A.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

# Savanna Fertilization (flux) Control



Figure II.5.A. FertEx N<sub>2</sub>O emissions for Control treatment. The cumulative curves, or running totals, are integrated summations of interpolated intervals of the minimum sampling period (30 min.) for the entire event period. E.P.G. means event produced gas. Other features of the flux plots are the same as for Figure II.4.A.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

## Savanna Fertilization (flux) Nitrate-N



Figure II.5.B. FertEx N<sub>2</sub>O emissions for Nitrate-N treatment. Other features are the same as for Figure II.5.A.

## Savanna Fertilization (flux) Glucose-C



Figure II.5.C. FertEx N<sub>2</sub>O emissions for Glucose-C treatment. Other features are the same as for Figure II.5.A.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.





Figure II.5.D. FertEx N<sub>2</sub>O emissions for Nitrate-N + Glucose-C treatment. Other features are the same as for Figure II.5.A.

Agriculture (flux) Corn



Figure II.6.A. APEx N<sub>2</sub>O emissions for Corn (Zea mayz) plantation. The cumulative curves, or running totals, are integrated summations of interpolated intervals of the minimum sampling period (30 min.) for the entire event period. E.P.G. means event produced gas. Other features of the flux plots are the same as for Figure II.4.A.

Agriculture (flux) Soybean



Figure II.6.B. APEx N<sub>2</sub>O emissions for Soybean (Glycinea max) plantation. Other features are the same as for Figure II.6.A.

Agriculture (flux) Pasture



Figure II.6.C. APEx N<sub>2</sub>O emissions for Pasture (Paspalum grass). Other features are the same as for Figure II.6.A.

### **Bibliography**

- Adámoli, J., J. Macedo, L. G. Azevedo and J. Madeira Neto, Caracterização da região dos Cerrados, in Solos dos Cerrados: tecnologias e estrategias de manejo, vol. edited by W. J. Goedert, pp. Nobel, São Paulo, 1986.
- Anderson, I. C., J. S. Levine, M. A. Poth and P. J. Riggan, Enhanced biogenic emissions of nitric oxide and nitrous oxide following surface biomass burning, JGR, 93, 3893-3898, 1988.
- Anderson, T.-H. and K. H. Domsch, Ratios of microbial biomass carbon to total organic carbon in arable soils, *Soil Biol.Biochem.*, 21, 471-479, 1989.
- Andreae, G., M. O. Andreae, E. V. Browell, M. Garstang, G. L. Gregory, R. C. Harriss, G. F. Hill, D. J. Jacob, M. C. Pereira, G. W. Sachse, A. W. Setzer, P. L. Silva Dias, R. W. Talbot, A. L. Torres and S. C. Wofsy, Biomass-Burning Emissions and Associated Haze Layers Over Amazonia, J.Geophy. Res., 93, 1509-1527, 1988.
- Andreae, M. O., The Influence of Tropical Biomass Burning on Climate and the Atmospheric Environment, 1992
- Azevedo, L. G. and J. Adámoli, Avaliação agroecológica dos recursos naturais da região dos Cerrados, in *Simpósio sobre o Cerrado*, vol. 6, edited by pp. 729-761, EMBRAPA/CPAC, Brasilia, 1988.
- Bowman, A. F., I. Fung, E. Matthews and J. John, Global Analysis of the Potential for N2O Production in Natural Soils, *Global Biogeochemical Cycles*, 7, 557-597, 1993.
- Bremner, J. M., S. G. Robbins and A. M. Blackmer, Seasonal variability in emission of nitrous oxide from soil, *Geophys. Res. Lett.*, 7, 641-644, 1980.

119

- Brumme, R. and J. Beese, Effects of liming and nitrogen fertilization on emissions of CO2 and N2O from a temperate forest, *J Geophys Res*, 97, 12851-12858, 1992.
- Burton, D. L. and E. G. Beauchamp, Profile Nitrous Oxide and Carbon Dioxide Concentrations in a Soil Subject to Freezing, *Soil Sci.Soc.Am.J.*, 58, 115-122, 1994.
- Chapin, F. S., P. M. Vitousek and K. Van Clevel, The nature of nutrient limitation in plant communities, *Amer.Naturalist*, 127, 48-58, 1986.
- Cicerone, R. J., Science, 237, 35-41, 1987.
- CODEPLAN, Atlas do Distrito Federal, p. 79, Companhia de Desenvolvimento do Planalto Central, Brasilia, 1984.
- Coutinho, L. M., Fire in the ecology of the Brazilian cerrado, in *Fire in the Tropical Biota. Ecosystem Processes and Global Challenges*, vol. 84, edited by J. Goldammer, pp. 82-105, Springer-Verlag, Heidelberg, 1990.
- Crutzen, P. J., Tropospheric chemical composition measurements in Brazil during the dry season, J. Atmos. Chem., 2, 233-256, 1985.
- Davidson, E. A., Fluxes of Nitrous Oxide and Nitric Oxide from Terrestrial Ecosystems Ch. 12:, in Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes, vol. edited by J. E. Rogers and W. B. Whitman, pp. 219-235, American Society for Microbiology, Washington D.C., 1991.
- Davidson, E. A., Sources of nitric oxide and nitrous oxide following wetting of dry soil, *Soil Sci.Soc.Amer.J.*, 56, 95-102, 1992.
- Davidson, E. A., P. A. Matson, P. M. Vitousek, R. Riley, K. Dunkin, G. Garcia-Mendez and J. M. Maass, Processes Regulating Soil Emissions of NO and N2O in a Seasonally Dry Tropical Forest, *Ecology*, 74, 130-139, 1993.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

- Davidson, E. A., P. M. Vitousek, P. A. Matson, R. Riley, G. Garcia-Mendez and M. Maass, Soil Emissions of Nitric Oxide in a Seasonally Dry Tropical Forest of Mexico, *Journal of Geophysical Research*, 96, 15439-15445, 1991.
- Delmas, R., On the emission of carbon, nitrogen, and sulfur in the atmosphere during brushfires in intertropical savanna zones, *Geophys. Res. Lett.*, 9, 761-764, 1982.
- Dias, B. F. d. S., Manejo e Conservação dos Recursos Naturais Renováveis. Alternativas de desenvolvimento dos Cerrados., 97, 1992.
- Dickinson, R. E. and R. J. Cicerone, Review: Future global warming from atmospheric trace gases, *Nature*, 319, 109-115, 1986.
- Duxbury, J. M., L. A. Harper and A. R. Mosier, Contributions of Agroecosystems to Global Climate Change, in Agricultural Ecosystems Effects on Trace Gases and Global Climate Change, vol. 55, edited by pp. 1-18, American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 1993.
- Eichner, M. J., Nitrous Oxide Emissions from Fertilized Soils: Summary of Available Data, J. Environ. Qual., 19, 272-280, 1990.
- Fearnside, P. M., Spatial Concentration of Deforestation in the Brazilian Amazon, Ambio, 15, 74-81, 1986.
- Firestone, M. K. and E. A. Davidson, Microbial Basis of NO and N2O Production and Consumption in Soil, Dahlem Workshop on Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, 47, 1-5, 1989.
- Fishman, J., P. Minnis and H. G. J. Reichle, Use of satellite data to study tropospheric ozone in the tropics, J. Gephys. Res., 91, 14451-14465, 1986.

**121**<sup>°</sup>

- Garcia-Mendez, G., J. M. Maass, P. A. Matson and P. M. Vitousek, Nitrogen transformations and nitrous oxide flux in a tropical deciduous forest in Mexico, *Oecologia*, 88, 362-366, 1991.
- Goreau, T. J. and W. Z. Mello, Effects of deforestation on sources and sinks of atmospheric carbon dioxide, nitrous oxide, and methane from Central Amazonia soils and biota during the dry season: a preliminary study., Workshop on Biogeochemistry of Tropical Rain Forests: Problems for Research, 1987.
- Griffiths, R. P., B. A. Caldwell and P. Sollins, Effects of vegetation regime on denitrification potential in two tropical volcanic soils, *Biol. Fertil.* Soils, 16, 157-162, 1993.
- Grundmann, G. and D. Rolston, A water function approximation to degree of anaerobiosis associated with denitrification, *Soil Science*, 144, 437-441, 1987.
- Hahn, J. and P. J. Crutzen, Phil. Trans. R. Soc. Lond., B296, 521-541, 1982.
- Hao, W. M., D. Scharffe and P. J. Crutzen, Production of N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> from Soils in the Tropical Savanna During the Dry Season, J.Atmos.Chem., 7, 93-105, 1988.
- Hao, W. M., D. Scharffe, J. M. Lobert and P. J. Crutzen, Biomass Burning: An Inportant Source of Atmospheric CO, CO<sub>2</sub> and Hydrocarbons, Chapman Conference on Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications, 19-23, 1990.
- Hatshorn, G. S., Plants, in *Costa Rican Natural History*, vol. edited by D. H. Janzen, pp. 118-157, University of Chicago Press, Chicago, 1983.
- Huntley, B. J. and B. H. Walker, Ecology of Tropical Savannas, *Ecological Studies*, 42, 669, 1982.
- Hutchinson, G. L. and G. P. Livingston, Use of Chamber Systems to Measure Trace Gas Fluxes, in Agricultural Ecosystems Effects on Trace Gases and Global Climate Change, vol. 55, edited by pp. 63-78, American

#### 122

Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 1993.

- Hutchinson, G. L. and A. R. Mosier, Improved soil Cover Method for Field Measurement of Nitrous Oxide Fluxes, Soil Sci.Soc.Am.J., 45, 311-316, 1981.
  - IPCC, Climate Change The IPCC Scientific Assessment, Intergovernmental Panel on Climate Change, 1990.
- Johnsson, H., L. Klemedtsson, A. Nilsson and B. Svensson, Simulation of field scale denitrification losses from soils under grass ley and barley, *Plant Soil, 138, 287-302, 1991.*
- Keeney, D. R. and D. W. Nelson, Nitrogen Inorganic forms, in Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties, vol. edited by A. L. Page, R. H. Miller and D. R. Keeney, pp. 643-709, Agronomy Society of America, Madison, 1982.
- Keller, G., M. Keller, W. A. Kaplan, S. C. Wofsy and J. M. d. Costa, Emissions of N<sub>2</sub>O From Tropical Forest Soils: Response to Fertilization With NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>-3</sup>, J. Geophy. Res., 93, 1600-1604, 1988.
- Keller, M., T. J. Goreau, S. C. Wofsy, W. A. Kaplan and M. B. McElroy, Production of Nitrous oxide and consumption of methane by forest soils, *Geophy. Res. Let.*, 10, 1156-1159, 1983.
- Keller, M., W. A. Kaplan and S. C. Wofsy, Emissions of N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> from tropical forests soils, *J. Geophys. Res.*, 91, 11791-11802, 1986.
- Keller, M. and W. A. Reiners, Soil-Atmosphere exchange of Nitrous Oxide, Nitric Oxide and Methane under Secondary Succession of Pasture to Forest in the Atlantic Lowlands of Costa Rica., *Preliminary Draft*, 29, 1994.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

- 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.
- Khalil, M. A. K. and R. A. Rasmussen, Increase and seasonal cycles of nitrous oxide in the earth's atmosphere, *Tellus*, 35B, 161-169, 1983.
- Khalil, M. A. K. and R. A. Rasmussen, Nitrous Oxide: Trends and Global mass balance over the last 3000 years, *Annals of Glaciology*, 10, 9, 1988.
- Khalil, M. A. K. and R. A. Rasmussen, The Global Sources of Nitrous Oxide, J.Geophy.Res., 97, 14651-14660, 1992.
- Kim, K.-R. and H. Craig, Nitrogen-15 and Oxygen-18 Characteristics of Nitrous Oxide: A Global Perspective, *Science*, 262, 1855-1857, 1993.
- Lanly, J. P., Tropical Forest Resources, 1982.
- Levine, J. S., Introduction, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, vol. edited by J. S. Levine, pp. xxv-xxx, The MIT Press, Cambridge MA, 1991.
- Levine, J. S., W. R. CoferIII, E. L. Winstead, S. Sebacher and P. J. Boston, The effects of fire on biogenic soil emissions of nitric oxide and nitrous oxide, *Global Biogeoch.Cycles*, 2, 445-449, 1988.
- Li, C., S. Frolking and T. Frolking, A Model of Nitrous Oxide Evolution from Soil Driven by Rainfall Events: 1. Model Structure and Sensitivity, Journal of Geophysical Research, 97, 9759-9776, 1992a.
- Li, C., S. Frolking and T. Frolking, A Model of Nitrous Oxide Evolution from Soil Driven by Rainfall Events: 2. Model Applications, *Journal of Geophysical Research*, 97, 9777-9783, 1992b.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

- Livingston, G., G. P. Livingston, P. M. Vitousek and P. A. Matson, Nitrous Oxide Flux and Nitrogen Transformations Across a Landscape Gradient in Amazonia, J.Geophy. Res., 93, 1593-1599, 1988.
- Lopes, A. S., A survey of the fertility status of soil under "cerrado" vegetation in Brazil, M.S., North Caroline State University, Raleigh, NC, 1975.
- Luizão, F., P. Matson, G. Livingston, R. Luizão and P. Vitousek, Nitrous oxide flux following tropical land clearing, *Global Biogeoch. Cycles*, 3, 281-285, 1989.
- Matson, P. A. and P. M. Vitousek, Cross-system comparisons of soil nitrogen transformations and nitrous oxide flux in tropical forest ecosystems, *Global Biogeochemical cycles*, 1, 163-170, 1987.
- Matson, P. A., P. M. Vitousek, J. J. Ewel, M. J. Mazzarino and G. P. Robertson, Nitrogen transformations following tropical forest felling and burning on a volcanic soil, *Ecology*, 68, 491-502, 1987.
- Matson, P. A., P. M. Vitousek, G. P. Livingston and N. A. Swanberg, Sources of Variation in Nitrous Oxide flux from Amazonian Ecosystems, J.Geophy.Res., 95, 16,789-16798, 1990.
- Matson, P. A., C. Volkmann, K. Coppinger and W. A. Reiners, Annual nitrous oxide flux and soil nitrogen characteristics in sagebrush steppe ecosystems, *Biogeochemistry*, 14, 1-12, 1991.
- McElroy, M. B. and S. C. Wofsy, in *Tropical Rain Forests and the World* Atmosphere, vol. edited by G. T. Prance, pp. 36-60, 1986.
- Mosier, A. R., W. D. Guenzi and E. E. Schweizer, Soil Losses of Dinitrogen and Nitrous Oxide from Irrigated Crops in Northeastern Colorado, Soil Sci.Soc.Am.J., 50, 344-348, 1986.
- Mosier, A. R. and G. L. Hutchinson, Nitrous oxide emissions from cropped fields, J. Environ. Qual., 10, 169-173, 1981.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
- Mosier, A. R., D. Schimel, D. Valentine, K. Bronson and W. J. Parton, Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands, *Nature*, 350, 330-332, 1991.
- Instituto Meteorológico Nacional, Catastro de las series de precipitaciones medidas en Costa Rica, 1988.
- Nelson, D. W. and L. E. Sommers, Total Carbon, Organic Carbon, and Organic Matter, in *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*, vol. edited by A. L. Page, R. H. Miller and D. R. Keeney, pp. 539-579, Agronomy Society of America, Madison, 1982.
- Parsons, W. F. J., M. E. Mitre, M. Keller and W. A. Reiners, Nitrate limitation of N<sub>2</sub>O production and denitrification from tropical pasture and rain forest soils, *draft*, 20 plus figures, 1993.
- Pereira, B. A. d. S., P. P. Furtado, R. C. d. Mendonça and G. I. Rocha, Reserva Ecológica do IBGE (Brasilia - DF): Aspectos Históricos e Fisiográficos, B.FBCN, 24, 30-43, 1989.
- Pereira, J., Nitrogen Cycling in South American Savannas, Plant and Soil, 67, 293-304, 1982.
- Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford,
  P. Fraser and R. Rosen, Atmospheric Emissions and Trends of Nitrous
  Oxide Deduced from 10 Years of ALE-GAGE Data, J. Geophy. Res.,
  95, 18369-18385, 1990.
- Reiners, W. A., A. F. Bowman, W. F. J. Parsons and M. Keller, Tropical Rain Forest Conversion to Pasture: Changes in Vegetation and Soil Properties. Effects of Rain forest Convertion to Pasture, *draft*, 45 plus figures, 1993.
- Rice, W. and K. L. Rogers, Denitrification in Subsurface Environments: Potential Source for Atmospheric Nitrous Oxide, in Agricultural Ecosystems Effects on Trace Gases and Global Climate Change, vol. 55, edited by pp. 121-132, American Society of Agronomy, Crop

Science Society of America, and Soil Science Society of America, 1993.

Robertson, G. P., Fluxes of Nitrous Oxide and Other Nitrogen Trace Gases from Intensively Managed Landscapes: A Global Perspective, in Agricultural Ecosystems Effects on Trace Gases and Global Climate Change, vol. 55, edited by pp. 95-108, American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 1993.

Robertson, G. P. and J. M. Tiedje, 4th Int. Congr. Ecol., 1986.

- Robertson, G. P. and J. M. Tiedje, Nitrous Oxide Sources in Aerobic Soils: Nitrification, Denitrification and other biological processes, Soil.Biol.Biochem., 19, 187-193, 1987.
- Rudaz, A., E. A. Davidson and M. K. Firestone, Sources of Nitrous Oxide production following wetting of dry soil, *FEMS Microbiol. Ecol.*, 85, 117-124, 1991.
- Santos, J. R. d., Biomassa Aérea da Vegetação de Cerrado: Estimativa e Correlação com Dados do Sensor "Thematic Mapper" do Satélite LANDSAT, PhD thesis, Universidade Federal do Paraná, 1988.
- Sarmiento, G., The savannas of tropical America, in *Ecosystem of the World:* tropical savannas, vol. 13, edited by pp. 245-288, Elsevier, Amsterdam, 1983.
- Schimel, D. S., M. O. Andrea, D. Fowler, I. E. Galbally, R. C. Harriss, D. Ojima, H. Rodhe, T. Rosswall, B. H. Svensson and G. A. Zavarzin, Priorities for an International Research Program on Trace Gas Exchange, Dahlem Workshop on Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, 47, 321-331, 1989.
- Schimel, D. S., S. Simkins, T. Rosswall, A. R. Mosier and W. J. Parton, 10 Scale and the Measurement of Nitrogen-Gas Fluxes from Terrestrial Ecosystems, Workshop on Spatial and Temporal Variability of

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Biospheric and Geospheric Processes: Research Needed to determine Interactions with Global environmental Change, 35, 179-192, 1988.

- Schuster, M. and R. Conrad, Metabolism of nitric oxide and nitrous oxide during nitrification and denitrification in soil at different incubations conditions, *FEMS Microbiol. Ecol.*, 101, 133-143, 1992.
- Seiler, W. and R. Conrad, Cp 9: Contribution of Tropical Ecosystems to the Global Budgets of Trace Gases, Especially CH4, H2, CO, and N2O, The Geophysiology of Amazonia Vegetation and Climate interactions - International Conference on Climatic, Biotic, and Human interactions in the Humid Tropics, 133-162, 1987.
- Sexstone, A. J., T. B. Parkin and J. M. Tiedje, Temporal Response of Soil Denitrification Rates to Rainfall and Irrigation, Soil Sci.Soc.Am.J., 49, 99-103, 1985.
- Singh, H. B., Evir.Sci.Technol., 21, 320-327, 1987.
- Skole, D. L. and C. J. Tucker, Tropical deforestation, habitat fragmentation, and adversely affected habitat in the Brazilian Amazon, 1978-1988, Science, 1993.
- Smith, K. A. and J. R. M. Arah, Losses of nitrogen by denitrification and emissions of nitrogen oxides from soils, *The Fertilizer Society*, 299, 35, 1990.
- Sollins, P., F. Sancho, R. Mata and R. L. Sanford, Soils and Soils Research, in La Selva: Ecology and natural history of a neotropical rainforest, vol. edited by L. McDade, K. Bawa, H. Hespenheide and G. Hartshorn, pp. University of Chicago Press, Chicago, 1993.
- Suhet, A. R. and K. D. Ritchey, Nitrate Leaching in Cerrado Soil, 1981.
- Tamm, C. O., Nitrogen in Terrestrial Ecosystems. Questions of productivity, vegetational changes, and ecosystem stability, Ecological Studies, p. 116, Springer-Verlag, Berlin, 1991.

### *128*

- Terry, R. E., R. L. I. Tate and J. M. Duxbury, Nitrous Oxide Emissions from Drained, Cultivated Organic Soils of South Florida, J. of the Air Pollution Control Association, 31, 1173-1176, 1981.
- USDA, Soil Taxonomy. A basic system of soil classification for making and interpreting soil surveys, *Agriculture Handbook*, 436, 754, 1975.
- Vitousek, P. M. and P. A. Matson, Nitrogen tranformations in a range of tropical forest soils, Soil biol. Biochem., 20, 361-367, 1988.
- Vitousek, P. M. and P. A. Matson, Agriculture, the Global Nitrogen Cycle, and Trace Gas Flux, in *Biogeochemistry of Global Change*, vol. Tenth International Symposium on Environmental Biogeochemistry (ISEB), edited by R. S. Oremland, pp. 193-208, Chapman & Hall, San Francisco, 1993.
- Vitousek, P. M. and R. L. J. Sanford, Nutrient Cycling in Moist Tropical Forest, Ann. Rev. Ecol. Syst., 17, 137-167, 1986.
- Weier, K. L., I. C. Macrae and R. J. K. Myers, Seasonal Variation in Denitrification in a Clay Soil Under a Cultivated Crop and Permanent Pasture, Soil Biol. Biochem., 23, 629-635, 1991.
- Weiss, R. J., The Temporal and Spatial distribution of Tropospheric Nitrous Oxide, J Geophys Res, 86, 7185-7195, 1981.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

# **APPENDIX A**

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

- .....

### **CORRECTIONS FOR GAS LEAKS IN THE SAMPLING SYRINGES**

The body of the syringes used for sampling of gas, either for flux or for soil-gas-phase profile measurements, were made of nylon with butyl rubber O-ring seal on the working piston. Due to wear and scratching of the inner walls, mostly due to dust and other abrasive particles collecting there during field work, some diffusional leak of the samples stored in those syringes occurred in the Costa Rican study, from the time of sampling to the time of analysis. In order to correct the analyzed N<sub>2</sub>O concentrations to the original sampled concentration values, the diffusional leaks had to be assessed. The procedure described below was utilized to correct for this problem.

A complete series of leak tests was conducted on every syringe used in the experiments. The passive leak test consisted of washing the syringes three times with the known standard (800 ppbv  $N_2O$  in Nitrogen) before filling with the same standard and closing shut the syringe stopcock valve. These were then left on the bench for approximately 48h, a span twice as long as the average residence time for the real experiment samples, and then analyzed against the same standard. A first order exponential decay constant (k) for each syringe was then computed from the amount of  $N_2O$  lost over the period.

*131* 

The exponential diffusive leak function is

$$(C_1 - C_{atm}) = (C_0 \cdot e^{-kt} - C_{atm})$$

Where

- $C_0$  is the analyzed mixing ratio
- $C_1$  is the corrected mixing ratio
- k is the first order exponential decay constant
- *t* is the time between sampling (or filling in the leak tests) and analyzing
- $C_{atm}$  is the background mixing ratio of N<sub>2</sub>O in the troposphere in ppbv (310)

Once the time t was known, and k was determined for each syringe,  $C_1$  could be determined. Because for most samples the N<sub>2</sub>O mixing ratio differential to the atmosphere was high ( $C_0 >> C_{atm}$ ), the amount lost through diffusive leak ( $C_1 - C_0$ ) in the time before analysis (t) wasn't high enough to lose the signal (when  $C_0$  becomes = or indistinguishable from  $C_{atm}$ ; see Figures A.1 through A.4).

After diffusional leak corrections were made it turned out to be relatively easy to flag data points where the original sampled signal had been lost. This may be attributed to the nature of the data which had to fall on a linear fit for flux samples and also because there were many repetitions in spatial proximity for the soil-gas-phase samples. The syringes also had diverse k values and were used randomly in the sampling. Those points were then considered outliers and were cast out. For the study of the savannas in Brazil, all syringes were retrofitted with a second O-ring and greased (see Methods, Part II) so that no detectable diffusive leak occurred.



Figure A.1. Scatterplot showing distribution of diffusional syringe leaks for Vegas samples collected for flux measurement.



Figure A.2. Scatterplot showing distribution of diffusional syringe leaks for Vegas soil-gas-phase samples.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



Figure A.3. Scatterplot showing distribution of diffusional syringe leaks for Flaminia samples collected for flux measurement.





## APPENDIX B

#### FILE: THEDATA.WB1

V	CONT	ROL	FJ3	[ no wate	r odded							[ no fer	tilizer omm	endment									
E	Nominal	Real time	NITRATE	mg N/kg	soil	-		AMMONI	UM mg I	N/kg soi			GAS PR	OFILES	ppbv			FLUX	SOIL WA	TER TENS	SION mBa	<b>rs</b>	
G	Time	days	2cm	5cm	10 cm	20cm	40cm	2cm	5cm	10 cm	2000	40cm	2cm	5cm	10 cm	20cm	40cm	gN/ha.d	2 cm	5 cm	10 cm	20 cm	40 cm
A	0 h	0.0	16.68	44.14	4.06	2.11	0.45	6.98	17.45	1.13	1.06	0.20	371	375	401	423	468	2.10					
s	30 min	0.1																					
	2 h	0.2																					
	4 h	0.3																	-				
	8 h	0.5																					
	24 h	1.3	14.11	10.75	5.34	1.73	0.96	19.40	2.91	0.79	-0.26	0.45	340	421	405	512	573	5.70					
	60 h	3.0	2.28	11,20	6.55	1.66	0.51	0.89	5.16	1.92	3.11	0.29	326	364	391	439	473	4.00					
	144 h	5.9	05.54	~~~~			0.05	07.70	F 6F	4 50	4.00	0.07	322	343	358	395	442	-2.10					
	2-01	8.9	25.51	36.68	3.14	0.94	0.85	27.70	5.65	1.56	1.30	0.37	324	339	349	3/2	398	-0.90					
	2.30 mm	9.1											}				1		1				
	2-211 2.4h	0.2																					
	2-8h	9.4																					
	2 - 24 h	10.2		5.24	5.65	1.79	0.96		5.93	3.62	0.68	0.17	314	342	360	382	400	0.30					
	3-0h	16.0		15.20	9.33	41.55	2.76	Į	14.16	3.96	4.42	0.51	348	350	359	349	409	2.20	ļ				
	3 - 30 min	16.1																					
	3-2 h	16.2						1					i i										
	3 - 4 h	16.2																					
	3-8h	16.4		· <b>-</b>																			
	3-24 h	17.1	0.48	26.47	1.07	4.10	19.25	0.41	26.02	1.66	2.68	12.93	323	331	344	374	387	0.60					
	3-48 h	18.2											220	328	329	323	384	1.20					
	3-72 N 2 06 h	19.2											329	320	335	339	346	8.30	I				
	3 - 30 fi	20.2	21 70	12.44	4 63	1 73	0.14	20.66	2 20	1.60	0 33	0.05	350	3/0	302	351	407	0.20	1				
	3 - 144 h	22.1	21.79	12.44	4.63	1.73	0.14	29.66	2.39	1.60	0.33	0.05	359	368	391	351	423	1.40					

14/ 6 77	• <b>D</b>	15.11		11						10.05.												
WAIL	:H	FUL		10/10/	30mm wate	r odded 3	) min before	e times (	0.5/2-0.5	/3-0.5 h			I no fer	tilizer amm	endment							
Nominal	Real time	NITRATE	mg N/kg	soil			AMMON	IUM mg	N/kg soi	<u> </u>		GAS PR	OFILES	S ppbv		_	FLUX	SOIL WA	TER TEN	SION mB	ars (ave	rage)
Time	days	2cm	5cm	10 cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	gN/ha.d	2 cm	5 cm	10 cm	20 cm	40 cm
0 h	0.0	14.04	10.50	6.66	1.11	0.47	16.13	1.51	2.05	0.50	0.23	331	346	376	402	429	3.93	149	161	181	149	107
30 min	0.1	29.47	10.65	11.03	1.04	0.85	7.21	2.29	0.61	0.60	0.03	337	371	389	420	431	4.62	3	4	53	148	106
2 h	0.2	22.66	12.33	7.60	3.01	0.66	13.17	2.34	1.70	0.59	0.32	336	379	405	407	413	8.74	15	8	32	138	108
4 h	0.3	27.86	0.76	5.20	2.77	0.55	22.16	0.77	0.69	0.40	3.58	333	384	427	470	437	6.36	23	23	35	128	105
8 h	0.5	0.94	8.19	6.18	3.11	0.00	0.86	12.57	2.25	1.28	EAR	347	387	457	493	532	4.29	31	35	39	117	105
24 h	1.3	2.02	6.96	8.06	13.45	1.51	2.34	3.36	1.56	15.01	0.63	317	335	390	473	500	3.56	202	105	77	71	107
60 h	3.0	12.33	16.05	15.32	2.88	1.18	6.25	9.95	8.48	1,18	2.39	325	356	394	464	475	-2.78	188	227	180	129	104
144 h	5.9						ł					332	347	349	416	429	5.80	604	711	403	209	105
2-0h	8.9	17.78	11,84	9.62	11.78	1.28	11.70	4.04	2.27	3.39	0.77	320	336		370	391	0.72	322	590	437	216	96
2 - 30 mir	9.1	9.41	11.39	6.61	3.98		3.74	6.20	7.66	1.60		363	368	363	396	400	9.70	13	15	364	244	95
2 - 2 h	9.1		7.71	4.98	13.23	1.63		3.17	1.44	5.99	-1.03	356	362	389	418	406	9.06	45	47	334	231	112
2 - 4 h	9.2	29.46	14,27	6.96	2.80		8.01	1.07	3.46	2.29		340	349	358	396	409	4.80	77	86	288	241	116
2-8h	9.4	28.54	17.92	13.19	5.24		10.84	11.46	4.09	1,18		311	324	349	389	398	3.51	91	130	293	245	119
2 - 24 h	10.2	17.94	28.35	14.75	1.88		16.77	31.47	4.05	0.88		316	333	346	354	417	6.63	164	141	183	98	13
3-0h	16.0	28.32	21.33	13.05	2.10	0.89	32.27	11.07	1.57	2.32	0.34	337	336	358	378	390	3.85	153	108	367	328	103
3 - 30 mir	16.1	9.93	2.96	3.27	1.59		11.32	1.89	1.27	-0.09		356	382	388	423	379	6.86	7	6	245	161	93
3-2 h	16.2	12.39	11.96	6.84	1.59		10.03	6.10	3.46	1.38		384	421	491	313	379	11.62	14	14	6	14	74
3 - 4 h	16.2	28.42	9.98	5.23	1.86		7.39	6.79	1.93	1.93		359	506	592	520	456	5.49	37	34	19	19	71
3-8h	16.4	14.22	16.04	3.84	0.93		26.49	6.75	0.27	-0.14		323	351	386	466	458	2.50	49	41	27	26	67
3 - 24 h	17.1	1.59	1.69	7.97	23.79		0.19	0.96	7.76	35.20		325	338	376	424	422	0.89	124	60	37	37	54
3 - 48 h	18.2											319	330	353	364	396	3.35	210	97	109	54	53
3 - 72 h	19.2						1					327	328	362	316	411	7.60	187	89	117	65	56
3 - 96 h	20.2											333	347	366	403	402	1.94	136	134	110	74	25
3 - 144 h	22.1	17.30	7 55	2.32	33.98	0.34	41.04	4.02	1.46	29.22	1.11	1 338	368	388	371	465	3.58	34	32	40	68	23

Γ	F	WATE	R	FL1								[ no fert	ilizer amme	ndment									
	L	Nominal	Real time	NITRAT	E mg N/I	g soil		AMMONIU	M mg N/I	g soil			GAS PR	OFILES	ppbv			FLUX	SOIL W	ATER TEN	ISION mB	ars (aver	age)
	A	Time	days	2cm	5cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	gN/ha.d	2 cm	5 cm	10 cm	20 cm	40 cm
	M	0	0.0	15.81	8.85		1.14	44.90	2.51	8.56		5.21	682	947	1073	1526	1533	219.34	37.9	30.5	32.0	32.7	36.0
ł	1	0.5	0.1	16.56	11.60			16.69	2.21	1.83			1194	1758	1806	2288	2005	570.89	8.3	6.7	3.0	1.2	13.3
	N	2	0.2	18.58	9.65			15.22	3.23	2.65			1664	2683	3188	5607	3337	446.30	16.3	13.0	12.3	3.5	12.1
t	1	4	0.2	24.68	8.22			35.02	2.04	2.42			1208	1879	3053	4937	3184	399.83	22.9	24.2	23.0	11.8	9.8
L	A	8	0.4	11.38	4.96			44.39	3.06	2.47			747	1878	2269	3801	3051	142.84	32.5	31.1	27.0	16.6	16.5
		24	1.1	17.03	15.69	1.97		29.14	2.21	2.64	1.09		1256	3626	4152	7312	7034	330.98	78.4	48.6	39.8	28.9	28.5
		48	2.1	15.17	9.27	5.52		41.52	3.73	1.54	1.11		1154	3032	4007	7382	8414	138.11	150.6	66.7	52.7	38.1	36.5
		72	3.2	49.01	46.03	12.67		8.50	2.17	3.95	1.11		1303	2583	2972	4802	4796	-205.10	1				
		96	4.1	3.58	6.84	4.28		21.53	1.81	1.60	1.13		1253	3966	4636	6928	6832	250.17	19.4	20.8	19.5	7.9	8.1
		144	6.1	5.06	8.62	3.31		36.97	2.18	2.01	0.87		791	2171	2605	5271	6207	373.14	57.5	36.7	33.3	20.8	25.6



_						_																	
F	1	NITRO	DGEN	FL2							_	dissolv	ed fertilize	r ammendr	nent: 50Kg	/ha Nitroge	n equivalent	(NaNO3).					
L		Iominal	Real time	NITRAT	E mg N/I	g soil		AMMONIU	M mg N/k	g soll			GAS PF	OFILES	ppbv			FLUX	SOIL W	ATER TEN	ISION mB	ars (averi	age)
<b>A</b>		Time	days	2cm	5cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	2cm	_5cm	10 cm	20cm	40cm	gN/ha.d	2 cm	5 cm	10 cm	20 cm	40 cm
M		0	0.0	6.74	2.97	0.52	0.05	8.66	4.95	2.04	0.80	0.63	344	459	519	667	764	1269.62	37.9	30.5	32.0	32.7	36.0
1		0.5	0.1	49.43	22.82			11.94	4.41	3.41			1688	1766	1546	1097	1629	622.47	8.3	6.7	3.0	1.2	13.3
N	1	2	0.2	46.95	30.56			11.75	4.45	2.26			477	2079	2384	3401	3982	871.80	16.3	13.0	12.3	3.5	12.1
1		4	0.2	40.66	10.71			14.74	2.85	2.38			458	750		1281	1492	3228.81	22.9	24.2	23.0	11.8	9.8
A		8	0.4	47.71	29.22			9.07	2.92	1.82			1421	1924	3274	7951	9984	463.53	32.5	31.1	27.0	16.6	16.5
		24	1.1	33.63	46.50	23.18		3.33	7.24	34.46	1.28		441	702	949	1225	1296	4359.80	78.4	48.6	39.8	28.9	28.5
		48	2.1	47.36	29.52	11.97		15.17	3.80	2.41	1.00		1345	1777	2125	8813	10168	372.81	150.6	66.7	52.7	38.1	36.5
		72	3.2	11.41	16.05	0.80		46.65	3.06	1.49	0.93		1971	2399	2566	8331	9685	342.22	1				
		96	4.1	11.92	46.96	12.91		26.43	4.49	3.75	1.80		3662	4560	7473	16896	14663	817.22	19.4	20.8	19.5	7.9	8.1
		144	6.1	10.04	50.01	2.32		4.07	3.04	1.84	2.66		1465	3317	5416	6755	8522	653.10	57.5	36.7	33.3	20.8	25.6

F	CARE	ION	FL3								dissolv	ed fertilize	ammenda	nent: 250K	g/ha Carbo	n equivalent	(glucose).					
L	Nominal	Real time	NITRAT	E mg N/I	kg soil		AMMONIU	M mg N/k	ig soil			GAS PR	OFILES	ppbv			FLUX	SOIL WATER TENSION mBars (average			age)	
A	Time	days _	2cm	5cm	20cm	40cm	2ст	5cm	10 cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	gN/ha.d	2 cm	5 cm	10 cm	20 cm	40 cm
M	0	0.0	12.22	10.06	1.52	0.16	12.46	2.63	3.30	1.42	0.57	1263		1471	1891	2416	108.57	37.9	30.5	32.0	32.7	36.0
	0.5	0.1	8.40	4.59			2.36	3.07	2.43			20767	14591	11381	3881	2470	13416.61	8.3	6.7	3.0	1.2	13.3
N	2	0.2	4.00	3.53			12.26	4.60	2.29			13021	49882	48782	31986	4728	30797.29	16.3	13.0	12.3	3.5	12.1
	4	0.2	0.84	1.28			8.00	2.62	1.29			58895	69611	84593	57762	15545	15126.69	22.9	24.2	23.0	11.8	9.8
	8	0.4	3.55	4.04			25.56	4.04	2.15			22404	32606	43100	35778	22174	6266.03	32.5	31.1	27.0	16.6	16.5
	24	1.1	1.90	1.93	0.41		2.90	4.19	1.90	1.17		4644	11043	18642	26052	27608	0.00	78.4	48.6	39.8	28. <del>9</del>	28.5
	48	2.1	5.92	9.37	8.69		5.74	3.53	1.42	0.98		1486	3382	6234	10728	14775	371.01	150.6	66.7	52.7	38.1	36.5
	72	3.2	0.89	7.34	6.35		8.04	6.66	2.03	0.76		1590	3355	7035	9324	10360	209.67					
	96	4.1	2.07	4.85	1.88		40.51	6.09	2.66	1.09		2380	5875	8886	10850	10747	238.43	19.4	20.8	19.5	7.9	8.1
	144	6.1	17.17	4.89	4.00		0.63	2.45	1.33	0.83		_1024 _	1438	3104	1817	10819	401.47	57.5	36. <u>7</u>	33.3	20.8	25.6

-	
-	
<b>_</b>	

C + I	1	FL4								[dissolve	ed fertilizer	ommendm	ent: 250Kg	/ha Carbon	equivalent (	glucose) + 501	(g/ha Nitro	jen equivale	nt (NoNO3)		
Nominal	Real time	NITRAT	E mg N/i	kg soil		AMMONIU	M mg N/I	kg soil			GAS PF	OFILES	ppbv			FLUX	SOIL W	ars (aver	age)		
Time	days	2cm	5cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	2cm	5cm	10 cm	20cm	40cm	gN/ha.d	2 cm	5 cm	10 cm	20 cm	40 cm
0	0.0	13.76	4.15	1.78	0.74	15.15	3.11	4.52	1.79	0.78		1106	2028	1181	3271	315.62	37.9	30.5	32.0	32.7	36.0
0.5	0.1	51.52	25.72			12.34	3.50	4.08			14349	13181	7241	4018	3557	3904.64	8.3	6.7	3.0	1.2	13.3
2	0.2	8.78	42.48			5.75	7.29	1.80			34579	37519	32491	15115	4619	19249.85	16.3	13.0	12.3	3.5	12.1
4	0.2	41.27	29.28			18.18	7.39	1.99			1	72914	77678	55373	15709	19282.06	22.9	24.2	23.0	11.8	9.8
8	0.4	49.63	24.91			10.31	3.02	2.74			42144	76565	105449	44894	30943	19380.46	32.5	31.1	27.0	16.6	16.5
24	1.1	47.83	29.75	7.13		12.81	2.83	2.62	1.45		4038	22601	40506	55705	89408	1534.64	78.4	48.6	39.8	28.9	28.5
48	2.1	47.92	24.97	1.17		7.85	5.77	1.86	1.50		32090	40808	15379	39952	39291	9676.62	150.6	66.7	52.7	38.1	36.5
72	3.2	52.76	52.15	1.98		25.94	2.84	2.34	1.01		13821	26164	35520	31296	22345	4545.42					
96	4.1	3.30	10.00	9.76		47.01	4.47	3.23	1.08		8093	28914	73779	69663	32367	2423.18	19.4	20.8	19.5	7.9	8.1
144	6.1	20.14	43.55	12.20		9.08	2.95	1.21	0.77		2134	6547	8064	22054	23879	1226.09	57.5	36.7	33.3	20.8	25.6

I.